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Review Article

**CERIUM OXIDE NANOPARTICLES APPLICATIONS AND
TOXICOLOGY**

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Abstract:

Cerium is the most abundant of rare-earth metals found in the Earth's crust. Several Ce-carbonate, -phosphate, -silicate, and -(hydroxide minerals have been historically mined and processed for pharmaceutical uses and industrial applications. Of all Ce minerals, cerium dioxide has received much attention in the global nanotechnology market due to their useful applications for catalysts, fuel cells, and fuel additives. A recent mass flow modeling study predicted that a major source of CeO₂ nanoparticles from industrial processing plants (e.g., electronics and optics manufactures) is likely to reach the terrestrial environment such as landfills and soils. The environmental fate of CeO₂ nanoparticles is highly dependent on its physicochemical properties in low temperature geochemical environment. Though there are needs in improving the analytical method in detecting/quantifying CeO₂ nanoparticles in different environmental media, it is clear that aquatic and terrestrial organisms have been exposed to CeO₂ NPs, potentially yielding in negative impact on human and ecosystem health.

Keywords: *pharmaceutical, global nanotechnology, geochemical environment, analytical method*

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INTRODUCTION:

Cerium (Ce) is a member of the lanthanide series of metals on the periodic table. The discovery of Ce in an oxide form was first reported in 1803 by scientists in both Sweden and Germany [1-3]. This oxide was given the name “ceria” by discoverer Jons Jacob Berzelius in Sweden. Berzelius named the compound after the dwarf planet Ceres, which itself was named for the Roman goddess of agriculture. Cerium is the most abundant of the rare-earth metals found in the Earth's crust, where it comprises about 0.0046% by weight. Cerium and other lanthanide metals naturally occur in an array of minerals in the environment including carbonates (e.g., bastnäsite, (Ce,La)(CO₃)F), silicates (e.g., allanite, (Ca,Ce)(Al₂Fe²⁺)(Si₂O₇)(SiO₄)O(OH)), cerite (Ce,Ca)₉, (Fe,Mg)(SiO₄)₃(HSiO₄)₄(OH)₃, phosphates (e.g., monazite, (Ce,La,Nd,Th)(PO₄)), and oxides (e.g., euxenite, (Y,Ca,Ce,U,Th)(Nb,Ti,Ta)₂O₆). Of these minerals, however, only bastnäsite and monazite have been serving a major role for commercial uses. In the last several years, Ce-based compounds have received much attention because of their popular applications of CeO₂ nanoparticles (NPs) in industrial applications [4-5].

Cerium Chemistry

Aqueous Geochemistry Nearly 89% of naturally occurring Ce consists of four observationally stable isotopes (136Ce, 138Ce, 140Ce, 142Ce). With the exception of 140Ce (the most abundant isotope at 88.5% natural occurrence), these isotopes are expected to undergo double beta decay. Cerium (electronic configuration: [Xe] 4f¹ 5d¹ 6s²) exhibits a variable electronic structure which sets it apart from other lanthanides. The energy of the inner 4f level is nearly equal to the energy of outer or valence electrons. Since a very small amount of energy is necessary to change the relative occupancy (of these electronic levels), dual valence states of +3 and +4 occur in cerium [6-7]. In low temperature geochemical environments, cerium commonly exists in both the trivalent cerous state (Ce³⁺) and the tetravalent ceric state (Ce⁴⁺). Cerium exhibits a unique stability in the tetravalent state; other lanthanides are only stable in the trivalent state. Cerium oxide is most often noted for their catalytic ability, which is largely affected by redox behavior and is known to be directly dependent on cerium's redox state. The nanoparticles are often largely composed of Ce (III) (up to 60% in some cases) as well as Ce(IV); the more Ce(IV) in the nanoparticles, the stronger the catalase mimetic activity [8]. Another study has shown that a decrease in the 3+

/4+ ratios directly correlates with a loss of superoxide dismutase (SOD) mimetic activity [9]. Clearly, redox state plays a large role in determining the characteristics and behavior of cerium oxide nanoparticles.

Solubility and Chemical Properties of Ce Compounds

The solubility properties of Ce compounds. Solubility constants for Ce(III) and Ce(IV) bound to common ligands including hard bases like phosphate are listed in Table 1. Cerium phosphate readily precipitates out and is extremely insoluble. Cerium (IV) hydroxide exhibits similar properties. However, Ce (III) hydroxide is many orders of magnitude more soluble than cerium (IV) hydroxide. Among cerium species, even Ce(III) hydroxide is not regarded as particularly soluble. Among the most soluble species are Ce(III) chloride and cerium(III) nitrate. Cerium (III) selenite and cerium (III) sulfate are also relatively soluble. Since it is not possible to identify “true” analogues, instead comparisons must be made across systems with 3+ /2+ systems (such as that of europium) instead of cerium's 4+ /3+ system. Cerium has the notable characteristic of becoming more soluble as its coordination state becomes more reduced. Other lanthanides are only stable at 3+ with the exception of europium (Eu), which may be the only “good” analogue of Ce in the lanthanides. Europium usually assumes a trivalent oxidation state, but a divalent oxidation state is also very common. The solubility constant of Eu(III) hydroxide at 20 °C is 1.538 × 10⁻⁵, which is similar in magnitude but overall less soluble than Ce(III) hydroxide [10-11].

Geological

Occurrence Cerium is found in a variety of mineral classes, primarily including carbonates, phosphates, silicates, oxides and hydroxides. Main sources of industrial cerium include the carbonate mineral bastnäsite and the phosphate mineral monazite. These key cerium minerals and other lanthanide associated minerals are discussed in detail below.

Carbonates

Carbonates, the largest group of Ce-containing minerals, can be grouped in anhydrous, hydroxyl or halogen, and hydrated. Some of anhydrous carbonates are burbankite, carbocernaite, remondite, sahamalite, and tundrite. Carbonates with hydroxyl or halogen are bastnäsite, daqingshanite, huanghoite, hydroxylbastnäsite, parasite, rontgenite, and synchysite. Hydrate carbonates are ancyllit,

calcioancylite, lanthanit, rhabdophane, and thorbastnäsäsite.

As stated earlier, bastnäsäsite (Ce,La)(CO₃F) is one of two most important mineral sources of cerium and other rare-earth metals (such as Th). Bastnäsäsite is of particular importance to the discovery of Ce. An early mining of bastnäsäsite began at the Mountain Pass rare earth mine in San Bernardino, California with the discovery of a new class of rare earth deposit: a large carbonaceous mineral deposit containing significant amounts of bastnäsäsite. The major composition of bastnäsäsite consisted of approximately 49% cerium, 33% lanthanum, 12% neodymium with some praseodymium, samarium and gadolinium. Bastnäsäsite minerals also exhibited at least twice the Eu concentrations of a typical monazite. As more carbonatite deposits were discovered in Africa and China.

Phosphates

Though relatively few cerium phosphate minerals exist, they are very important to consider when identifying sources of cerium (Table 5). Until bastnäsäsite began to be processed around 1965, the phosphate mineral monazite, which usually forms small reddish-brown crystals, was the only significant commercial source of lanthanides such as cerium and thorium. Monazite is most often found in placer deposits, which are mineral accumulations often in the form of black sedimentary rocks. Monazite is fairly dense (about 4.6 to 5.7 g/cm³), a property consistent with that of most black sand minerals such as zircon and cassiterite. Placer deposits in India are particularly rich in monazite as well as deposits in Australia, Madagascar and South Africa [12-13]

Silicates

Silicates comprise the most abundant group of minerals in the earth's crust. Silicates play an extremely important role in soil minerals (Table 6). A significant amount of Ce is found in the silicate mineral allanite, (Ca,Ce,Y)²(AlFe³⁺)₃(SiO₄)₃(OH), Cerite-(Ce), (Ce,Ca)₉, (Fe,Mg)(SiO₄)₃(HSiO₄)₄(OH)₃, gadolinite-(Ce) (Ce,La,Nd,Y)₂, Fe²⁺Be₂Si₂O₁₀ and Joaquinite-(Ce), NaBa₂Ce₂FeTi₂[Si₄O₁₂]₂O₂(OH,F)·H₂O. Like bastnäsäsite and monazite, allanite can be broken down into three further classifications: allanite-(Ce) ((CaCe)(Al₂Fe²⁺)(Si₂O₇)(SiO₄)O(OH)), allanite-(La), and allanite-(Y). Allanite is a useful source of rare earth elements because it can contain up to 20% rare earths by composition. The high concentrations of thorium and other radioactive elements in the mineral lead to radiative degradation and structure disruption of allanite and surrounding minerals.

Oxides and Hydroxides

Cerium (hydr)oxide minerals are least common of all Ce minerals such as aeschynite-(Ce) (Ce,Ca,Fe,Th)(Ti,Nb)₂(O,OH)₆, euxenite-(Y) (Y,Ca,Ce,U,Th)(Nb,Ti,Ta)₂O₆, and perovskite CaTiO₃ with Ce varieties. Of the few oxides and hydroxides that contribute to commercial cerium sources, euxenite is the most significant oxide phase despite its low composition percent of cerium (~4%). Unlike allanite, monazite and bastnäsäsite, euxenite exists almost entirely in the euxenite-(Y) form, featuring yttrium as its major component instead of cerium. Like allanite, euxenite also exhibits radiation damage to itself and nearby minerals due to high radioactive content. With hardness values varying between 5.5 and 6.5 Mohs, euxenite features a hardness comparable to slightly higher hardness than its other cerium-containing counterparts, allanite, monazite, and bastnäsäsite. Euxenite occurs along with monazite in black sands as well as in granite pegmatites.

Drugs and Pharmaceuticals

Cerium compounds have recorded uses in drugs and pharmaceuticals as early as the mid nineteenth century. In 1854, cerium nitrate was first reported to relieve vomiting. Cerium(III) oxalate was administered for many following decades for anti-vomiting effects in cases of sea sickness, gastrointestinal and neurological disorders, and especially in pregnant women. Cerium (III) oxalate was used as an antiemetic until the mid-1950s when it was replaced by the antihistamine meclizine which is still in use today. Trivalent cerium exhibits similar size and bonding properties to Ca²⁺, an extremely biologically important cation. Ce³⁺ can replace Ca²⁺ in biomolecules due to their similar ionic radius, thus Ce³⁺ compounds strongly exhibit the ability to act as anticoagulant, or anti-clotting, agents. Several of the lanthanides, including cerium, are well-known for their anticoagulant properties and have been employed as antithrombic drugs [14-15].

Mischmetal

While commercial applications of Ce are numerous, it is most commonly used in the form of mischmetal for metallurgical purposes. Mischmetal is an alloy of rare earth metals in various naturally occurring proportions; a typical composition includes approximately 50% Ce and 25% lanthanum, as well as small amounts of Nd and Pr. Mischmetal reacts with impurities found in metals to form solid compounds, thereby reducing the effect of these impurities on the properties of the metal. Mischmetal is used in steel manufacturing to improve shape control, reduce hot shortness, and increase heat and oxidation resistance [16-17].

Organic Synthesis Starting Materials

Cerous chloride (CeCl_3) is used as a catalyst in Friedel-Crafts alkylation reactions as well as a starting material for the preparation of other Ce salts. Anhydrous cerous chloride is generally prepared via thermal treatment of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$. This hygroscopic solid is important in organic syntheses such as Luche reduction and alkylation of ketones for which organolithium reagents cannot be used [18-19].

Nanoparticles: Catalysts, Glass Additives and Fuel Additives

Cerium in its nanoparticulate form is especially important when considering applications of Ce. Nanoparticles are substances that are less than 100 nm in all three dimensions. Although the applications of compounds such as CeCl_3 and CeBr_3 discussed above are important, Ce compounds are best known for their uses in catalysts, fuel cells, glass (de)pigmentations, and fuel additives. All of these applications are based on the same compound: cerium dioxide (CeO_2), or ceria. Ceria, which can be in the form of a white, pale-yellow, or brownish powder depending on its purity, is by far the most widely commercially used cerium compound. Ceria exhibits cubic crystal structure akin to a fluorite type structure. The fluorite structure of CeO_2 allows for rapid diffusion of oxygen as a function of the number of oxygen vacancies since the oxygen atoms in the crystal are all in plane with one another. As the number of vacancies increases, the oxygen is more easily able to move around in the crystal, allowing reduction and oxidation of molecules or cocatalysts on the crystal's surface. It is used as a co-catalyst in a number of reactions, including the water-gas shift and steam reforming of ethanol or diesel fuel into hydrogen gas and carbon dioxide. It is useful in the Fischer-Tropsch reactions and in selected oxidations [20].

Gadolinium, samarium, or platinum doped CeO_2 is a useful material for solid oxide fuel cells due to its relatively high oxygen ion conductivity at intermediate temperatures [21]. Substituting a fraction of the CeO_2 with these elements is a way to increase ionic conductivity and create a better electrolyte since this introduces oxygen vacancies in the crystal without adding electronic charge carriers. A large amount of oxygen vacancies within the electrolyte will form on the anode (reducing) side of the fuel cell. Some of the ceric oxide is reduced to cerous oxide under these conditions; this transformation increases the electronic conductivity of the material. The lattice constant of CeO_2 increases under reducing conditions as well as with decreasing nanocrystal size as a result of this reduction of the cerium cation from Ce(IV) to Ce(III). This increase

compensates for the formation of oxygen vacancies, resulting in an increase in the fuel cell efficiency. Nanoparticulate CeO_2 has a particularly high oxygen storage capacity which, when coupled with its ease of transition between trivalent and tetravalent states and its high natural abundance, makes it an excellent choice as a catalyst. Nanoparticulate CeO_2 is most often used in catalytic converters in automobiles due to its non-stoichiometric ability to give up oxygen without decomposing. Ceria can release or take in oxygen in the exhaust stream of a combustion engine depending on its ambient partial pressure of oxygen. Through this mechanism, NO_x emissions are reduced and carbon monoxide is converted to carbon dioxide. Ceria is relatively inexpensive but its addition has been shown to provide substantial reductions in the amount of platinum catalyst needed for complete oxidation of NO_x and other harmful incomplete combustion products [22]. Fuel burns more cleanly upon addition of CeO_2 , resulting in less air pollution. It has also been characterized as a useful catalyst in systems including oxidation of volatile organic carbon [23] and toluene [24], ozonation of organic compounds [25], and water-gas shift reactions [26].

Potential Future Applications of Cerium (III) Oxides: the Ceria Cycle for Hydrogen Production and Catalysts

While CeO_2 exhibits a particularly large wide variety of uses, another useful oxide of cerium must be mentioned as well: Ce(III) oxide. Cerium dioxide and Ce(III) oxide (or cerous oxide) are combined in an extremely useful process known as the ceria cycle. The ceria cycle serves as a pathway of great interest for hydrogen production. This thermochemical process splits water into hydrogen and oxygen and is carried out in two steps: the endothermic dissolution of CeO_2 followed by the exothermic hydrolysis of Ce_2O_3 . The high reactivity of Ce_2O_3 with steam draws the main interest in this cycle; however, a major drawback lies in the partial vaporization of CeO_2 during the reduction step at reduced pressure. Water is the only material input to the ceria cycle and heat is the only energy input, making the ceria thermochemical cycle "a promising process for hydrogen production." The ceria cycle is also sometimes referred to as the cerium oxide cycle.

Toxicity of Cerium: Nanoparticle Toxicity

Nanoparticle toxicity is only well-understood for a small range of nanomaterials since the field is relatively new. Nanoparticles tend to sorb more than their bulk counterparts and exhibit multiple exposure routes for biological organisms including ingestion, inhalation, absorption /adsorption onto surfaces, uptake across epithelia, and multiple other pathways.

Several toxicity mechanisms have been suggested for a variety of NPs.

In general, two major considerations for NP toxicity are (1) size relative to their bulk counterparts; and (2) mechanisms often associated with capping agents. Nanoparticle toxicity characteristically exhibits size-dependent effects since their high surface to volume ratio due to the fact that a high percentage of atoms are located at the surface.

For a large variety of NPs including species such as NP silver, silicon dioxide, and titanium dioxide it has been demonstrated that smaller sizes (and thus greater reactivities) lead to heightened toxicity effects across biological systems. Nanoparticles tend to exhibit much higher toxicities than their bulk counterparts; this tendency is especially exaggerated in bacteria due to the NP's higher affinity for attachment to bacterial cell walls that could potentially perturb the electron transfer reaction and respiration[27]. As mentioned previously, NPs have much larger surface areas than their bulk counterparts and thus they also often exhibit much greater reactivity and ability to interact with biological systems. Several toxicity mechanisms have been postulated: (1) the production of ROS; (2) the release of reaction products (e.g., ionic metal(loid)s via (non)reductive dissolution); (3) photocatalytic behavior; and (4) phase transformation (e.g., sulfidation in the case of Ag(0)). A primary mechanism of NP toxicity is thought to be the ability to generate ROS such as free radicals. Reactive oxygen species contain unpaired valence electrons which yield extremely high chemical reactivity and the ability to induce severe damage to cells, including DNA and RNA damage, oxidations of lipids and proteins, and enzyme (cytochrome P) deactivation. A wide array of NPs has been found to induce ROS production; among these are carbon nanotubes (CNTs), fullerenes (C60), and titanium dioxide NPs (TiO2). The release of metal ions from quantum dots (e.g., CdSe) and nanosilver can be highly toxic to bacterial cells [35–37] as well as organic coatings of NPs [38]. Furthermore, surface charges arising from coating/capping agents of NPs affect homo- and hetero- aggregation behavior. This could facilitate the NP interactions with cells, resulting in the oxidative stress and consequences. In general, polymers are popular capping agents along with other organic materials (e.g., citric- and oleic-acid) although the quality of capping agents is varied in different NPs [28-29]

CONCLUSION:

A cerium compound of particular interest is nanoparticulate ceria, also known as cerium oxide (CeO2). By far, CeO2 NPs are the most widely

commercially used cerium compound for electronics, automotive, and solar panels for energy. As the production of CeO2 NP increases, so does the usage in the industry and consumer markets. The recent study by Keller and Lazareva (2013) predicted more than 60%–86% of engineered NPs including CeO2 NPs will end up in landfills and soils, and the pathway of WWTP effluent and biosolids to the soil-water environment is fairly limited [49]. The estimated concentrations of CeO2 NPs in WWTP in the San Francisco Bay (SFB) area are 10–2 to 1 µg/L in effluent and 1 to 10 µg/kg in dry biosolids. In other study by Gottschalk et al. (2013) [89], even much smaller concentration of CeO2 NPs in WWTP effluent and biosolid are reported (0.5×10^{-4} µg/L and 10–6 mg/kg, respectively). While there are needs in improving the detection and quantification of CeO2 NPs in different environmental media, it is imminent that organisms in ecosystem will be exposed to these low concentrations (micro gram per liter or kilogram)

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