

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

Cesium is the rarest of the naturally occurring alkali metals, ranking 40th in elemental abundance. Although it is widely distributed in the earth's crust, cesium is found at relatively low concentrations. Granites contain cesium at about 1 ppm of cesium and sedimentary rocks contain approximately 4 ppm of cesium. Cesium is found in muscovite, beryl, spodumene, potassium feldspars, leucite, petalite, and other related minerals. The most common commercial source of cesium is pollucite, which contains between 5 and 32% Cs₂O (Burt 1993). There are three basic methods of converting pollucite ore to cesium metal or related compounds: direct reduction with metals; decomposition with bases; and acid digestion. In each method, grinding of the mined ore to approximately 75 µm sized particles precedes chemical conversion.

Direct Reduction With Metals. Pollucite is directly reduced by heating the ore in the presence of calcium to 950 °C in vacuum, or in the presence of either sodium or potassium to 750 °C in an inert atmosphere (Burt 1993). Excessive amounts of reducing metal are required, and the resultant cesium metal is impure, requiring further distillation and purification.

Decomposition With Bases. Alkaline decomposition is carried out by roasting the pollucite ore with either a calcium carbonate-calcium chloride mix at 800–900 °C or with a sodium carbonate-sodium chloride mix at 600–800 °C followed by a water leach of the roasted mass. The resultant cesium chloride solution is separated from the gangue by filtration (Burt 1993).

Acid Digestion. Acid digestion of pollucite is the preferred commercial process for producing pure cesium. Hydrofluoric, hydrobromic, hydrochloric, and sulfuric acid may be employed in this method. Hydrofluoric and hydrobromic acid digestion yield the greatest cesium recovery, but the inherent difficulties of safely handling these acids limit their use. Digestion with hydrochloric acid takes place at elevated temperatures and produces a solution of mixed cesium chlorides, aluminum, and other alkali metals separated from the siliceous residue by filtration. The impure cesium chloride can be purified as cesium chloride double salts that are then recrystallized. The purified double salts are decomposed to cesium chloride by hydrolysis or precipitated with hydrogen sulfide (Burt 1993).

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Sulfuric acid digestion is performed at 110 °C with a 35–40% solution of sulfuric acid, followed by a hot water wash and vacuum filtration. Cesium alum is crystallized from the leach filtrate by stage cooling to 50 °C and then to 20 °C and roasted in the presence of 4% carbon. The residue is leached to produce cesium sulfate solution, which can be converted to cesium chloride (Burt 1993).

Radioactive isotopes of cesium such as ^{134}Cs and ^{137}Cs are produced by nuclear fission in fuel rods in nuclear power plants and in fallout from nuclear weapons. Radiocesium can be recovered from fission products by digestion with nitric acid. After filtration to remove the waste, the radioactive cesium phosphotungstate is precipitated using phosphotungstic acid (Burt 1993). Other processes for the removal of ^{134}Cs and ^{137}Cs from radioactive waste involve solvent extraction using macrocyclic polyethers, or crown ethers and coprecipitation with sodium tetraphenylboron (Burt 1993).

5.2 IMPORT/EXPORT

The United States is 100% import-reliant for elemental cesium. No economic data, such as production volume, consumption, or import/export volumes of cesium, are available. Although there is no information regarding the countries shipping cesium or cesium compounds to the United States, it is believed that Canada is the major foreign source of cesium (USGS 1999). Other possible sources of cesium-bearing material include Germany and the United Kingdom.

5.3 USE

There are relatively few commercial uses for cesium metal and its compounds. Cesium is used as a getter (combines chemically with residual gas in partial vacuum to increase the vacuum) for residual gas impurities in vacuum tubes and as a coating to reduce the work function of the tungsten filaments or cathodes of the tubes. Crystalline cesium iodide and cesium fluoride are used in scintillation counters, which convert energy from ionizing radiation into pulses of visible light (Burt 1993). Cesium is also used in magnetohydrodynamic power generators as a plasma seeding agent (Lewis 1997). Recently, cesium compounds have been employed as catalysts in organic synthesis, replacing sodium or potassium salts. One of the most interesting uses of cesium is in the production of highly accurate atomic clocks. When exposed to microwave radiation, the natural vibration of cesium atoms occurs at a frequency of 9,192,631,770 Hz, and 1 second in time is defined as the duration of 9,192,631,770 periods of radiation absorbed or emitted by the transition of ^{133}Cs atoms in two hyperfine levels of their ground state. Radioactive ^{137}Cs has been approved as the gamma ray source for the sterilization of wheat, flour,

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potatoes, surgical equipment and other medical supplies, and sewage sludge, and is also used as a calibration source in gamma ray spectroscopy (Lewis 1997). ^{137}Cs is also used in industrial radiography and for imaging of transport containers at border crossings. ^{131}Cs was recently approved by the U.S. FDA as an active source in radioactive seeds used to treat prostate cancer (FDA 2003).

5.4 DISPOSAL

Because of its high reactivity, special precautions are required for the handling and disposal of pure cesium metal. Cesium metal is usually stored and transported in stainless steel containers, which are contained in outer packing, to ensure that the metal remains in a dry, oxygen-free environment.

Most nonradioactive cesium minerals, compounds, and materials do not require special disposal and handling requirements. However, some chemical forms may be classified as hazardous materials if the compound is chemically reactive, flammable, or toxic. Care should be taken to read and understand all of the hazards, precautions, and safety procedures for each specific chemical form. In addition, all federal, state, and local laws and regulations should be investigated and subsequently followed with regard to disposal and handling of the specific chemical form of the cesium mineral, compound, or material.

Radioactive cesium requires special disposal and handling requirements. Radioactive waste containing ^{134}Cs and ^{137}Cs is usually grouped into four categories: low-level waste (LLW), high-level waste (HLW), mixed waste, and spent nuclear fuel.

Low-level waste is all radioactive waste that cannot be classified as either HLW, spent fuel, or mixed waste. Low-level does not necessarily mean low radioactivity or low environmental hazard. Low-level waste types that may be contaminated with ^{134}Cs and ^{137}Cs include both wet and dry wastes. Examples of the physical form of LLW are: spent ion exchange resins, filter sludges, filter cartridges, evaporator bottoms, compactible trash, noncompactible trash, irradiated components, ashes produced from the incineration of combustible material, contaminated detergents or solvents, organic liquids, and discarded contaminated equipment or tools. Of the LLW generated today, approximately 64% of the volume and 70% of the radioactivity is generated as a result of nuclear power plant activities or supporting fuel cycle operations. Other sources of LLW are commercial, academic, and government research laboratories and medical facilities. Radiocesium contamination accounts for only a small fraction of the activity of LLW. Nearly all of the ^{134}Cs and ^{137}Cs produced as a result of fission events remains trapped within the spent nuclear fuel rods (DOE 1996b). Low-level waste from Department of Energy (DOE) sources is currently

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disposed of at several DOE facilities across the United States. Only two sites accept non-DOE LLW: Barnwell, South Carolina and Richland, Washington (DOE 1996a). As required by the Federal Low Level Radioactive Waste (LLRW) Policy Act in 1980 and the 1985 amendments, states are required to build facilities to contain LLW generated from sources within its boundaries. The law encourages states to cooperate together in coordinating LLW disposal facilities. Many states have formed “compacts” to collaborate on construction of these LLW facilities. However, other than Barnwell, South Carolina and Richland, Washington, no other facility in the United States is accepting LLW from non-DOE sources (Eisenbud 1987). Over half of the LLW in the eastern United States is disposed of at the Barnwell site (Eisenbud 1987). The method of disposal for LLW has been to package the material in drums or boxes and bury the material in shallow pits and trenches. Approximately 3 million cubic meters of LLW generated has been disposed of in this way (DOE 1996a).

As defined by the Nuclear Waste Policy Act, HLW is “the highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentration...” (42 USC 100). Most HLW has been generated from the production of plutonium. A smaller fraction is related to the recovery of enriched uranium from naval reactor fuel. This waste typically contains highly concentrated solutions of relatively long-lived fission by-products such as ^{90}Sr and ^{137}Cs , hazardous chemicals, and toxic heavy metals. Liquid HLW is typically stored in large underground tanks of either stainless steel or carbon steel depending on whether they are acid or alkaline solutions. Approximately 100 million gallons of liquid HLW is stored in underground tanks in Washington, South Carolina, Idaho, and New York. These tanks contain a variety of radioactive liquids, solids, and sludges. Some of the liquid waste has been solidified into glass, ceramic slag, salt cake, and sludge. High-level waste in solid form is stored in underground bins (DOE 1996a).

Mixed waste contains both radioactive and chemically hazardous materials. All HLW is managed as mixed waste and some LLW is classified as mixed waste. Certain hazardous mixed wastes that contain radioactive isotopes have been incinerated in Oak Ridge, Tennessee (DOE 1996a). Spent nuclear fuel, such as fuel elements and irradiated targets used in nuclear reactors, are currently stored at the commercial nuclear power plants and DOE facilities where they were produced. Spent fuel is highly radioactive, due to the large concentration of fission products, and must be stored in special water-cooled pools that shield and cool the material. Nearly all of the DOE spent fuel, about 3,000 metric tons, is stored at four sites: Hanford, Savannah River, Idaho National Environmental and Engineering

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Laboratory, and West Valley. Commercial reactors have generated >30,000 metric tons of spent fuel. The spent fuel from these facilities is located at >100 commercial nuclear reactor sites around the country.

The establishment of a HLW and spent fuel repository for both DOE and commercial waste is currently under evaluation at Yucca Flats, Nevada. This commercial waste storage facility will not be ready to accept spent fuel before 2010.