RADIUM DISPOSITION OPTIONS FOR THE DEPARTMENT OF ENERGY

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ABSTRACT

The Department of Energy (DOE) has developed plans to disposition its excess nuclear materials, including radium-containing materials. Within DOE, there is no significant demand for radium at this time. However, DOE is exploring reuse options, including uses that may not exist at this time.

The Nonactinide Isotopes and Sealed Sources Management Group (NISSMG) has identified 654 radium-containing items, and concluded that there are no remaining radium items that do not have a pathway to disposition. Unfortunately, most of these pathways end with disposal, whereas reuse would be preferable.

DOE has a number of closure sites that must remove the radium at their sites as part of their closure activities. NISSMG suggests preserving the larger radium sources that can easily be manufactured into targets for future reuse, and disposing the other items.

As alternatives to disposal, there exist reuse options for radium, especially in nuclear medicine. These options were identified by NISSMG. The NISSMG recommends that DOE set up receiver sites to store these radium materials until reuse options become available.

The NISSMG recommends two pathways for dispositioning radium sources, depending on the activity and volume of material. Low activity radium sources can be managed as low level radioactive waste per DOE Order 5820.2A. Higher activity radium sources are more appropriate for reuse in nuclear medicine applications and other applications.

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Radium (Ra) is a natural decay product of uranium and thorium and is primarily recovered from uranium minerals as a byproduct. About five to seven tons of processed uranium minerals will produce about one gram of radium. Although radium may qualify for disposal at low-level radioactive waste (LLW) disposal sites, good-quality (high activity) radium is rather expensive and highly valuable. The amount of separated radium at Department of Energy (DOE) closure sites that has been identified so far by the Nonactinide Isotopes and Sealed Sources Management Group (NISSMG) is not very large. However, the closure sites must find ways to disposition this radium, as part of their closure activities. Although disposal as LLW is an option, the NISSMG is reviewing other disposition options for the radium, such as beneficial reuse or classification as a national resource material.

GENERAL BACKGROUND

Radium is one of those radioactive elements found in nature because it is the daughter product of naturally occurring radioactive elements. Ra-244 results from thorium-232 (Th-232) decay; Ra-226 results from uranium-238 (U-238) decay; and Ra-223 results from U-235 decay. Radium isotopes range from Ra-205 to Ra-234. Other than Ra-226, all are short-lived and uncommon.

Madam Curie discovered radium in 1898 in the pitchblende or uraninite of North Bohemia, where it occurs. There is about one gram of radium in seven tons of pitchblende. Radium is present in all uranium minerals, and could be extracted, if desired, from the extensive wastes of uranium processing. Large uranium deposits are located in Ontario, Canada, New Mexico, Utah, Australia, and elsewhere.

Radium emits alpha, beta, and gamma rays, and, when mixed with beryllium, produces neutrons. One gram of Ra-226 undergoes 3.7×10^{10} disintegrations per second. The curie (Ci) is defined as that amount of radioactivity that has the same disintegration rate as one gram of Ra-226. Twenty-five isotopes are now known; Ra-226, the common isotope, has a half-life of 1599 years. Radium loses about one percent of its activity in 25 years, being transformed into elements of lower atomic weight. Lead is a final product of disintegration.

Health concerns for the public center on radium in water and radon gas, a daughter product. One gram of radium produces about 0.0001 milliliters (at standard temperature and pressure) of radon gas per day. Occurrence and treatment of radium-containing soil and water is well documented (1).

Radium is also a concern when the naturally occurring radioactive material accumulates when the production of oil and natural gas from underground reservoirs carries small quantities of radium to the surface. Over time, radium, usually ^{226}Ra but also ^{228}Ra, concentrates in the sulfate pipe scale and sludge deposits, eventually contaminating equipment and soil. If naturally occurring radioactive material is present above regulatory levels, the waste requires disposal with limited and costly options (2).

Health benefits have been attributed to natural radium. Notable radium "cures" and spas, particularly in the United States and Europe date from the Roman times (3).

Within the DOE complex, radium is found wherever uranium or thorium is found. The largest quantities are found in the byproduct from recovery of uranium from ore. Useful forms—liquids, salts, metals, compounds and alloys—have been applied to measurement and calibration, particularly as calibration sources.

INVENTORY

NISSMG inventoried 654 radium containing items totaling 22.5 Ci at 22 sites, and they believe that this accounts for the entire inventory of radium items within the DOE Office of Environmental Management purview. There are no known significant quantities of radium in the complex other than sources, standards, samples, and by-product material. Since these materials either have a disposition path or are to be dispositioned with other materials, no orphan materials are known at this time.

The most dominant bulk material containing radium, estimated at 4.4 kilograms of radium in 8,890 cubic yards of material, is contained in Silos 1 and 2 at the Fernald Environmental Management Project (FEMP). The material is classified as by-product material resulting from the processing of uranium ore concentrates. It is specifically exempt from regulation as solid waste under the Resource Conservation and Recovery Act (RCRA) and is handled under Comprehensive Environmental Response and Liability Act (CERCLA) requirements. The path forward is clear and the task of disposing the material at the Nevada Test Site has begun. It will however take years to complete.

The only other radium materials are associated with sources, standards and samples. One third of the items consist of sources. Although over 600 items were identified near the end of 1998, only 18 items contained more than about 0.5 gram of radium at that time. A summary of the larger sources (4), prepared in 1998, is shown in Table I. These could be potential candidates for future use/reuse

Table I Large Beryllium Sources

Facility	Material	Activity, Ci (980930)
Brookhaven National Laboratory	Ra-226-Be	2.963
Brookhaven National Laboratory	Ra-226-Be	2.963
Los Alamos National Laboratory	Ra-226	2.484
Argonne National Laboratory - West	Ra-226	1.500

Facility	Material	Activity, Ci (980930)
Argonne National Laboratory - East	Ra-226-Be	1.095
Brookhaven National Laboratory	Ra-226-Be	1.006
Brookhaven National Laboratory	Ra-226	0.982
Argonne National Laboratory - East	Ra-226	0.980
Argonne National Laboratory - East	Ra-226-Be	0.976
Los Alamos National Laboratory	Ra-226	0.974
Oak Ridge National Laboratory	Ra-226	0.916
Lawrence Berkeley National Laboratory	Ra-226	0.885
Oak Ridge National Laboratory	Ra-226	0.545
Rocky Flats	Ra-226	0.500
Los Alamos National Laboratory	Ra-226	0.497
Argonne National Laboratory - East	Ra-226-Be	0.490
Los Alamos National Laboratory	Ra-226	0.487
Argonne National Laboratory - East	Ra-226-Be	0.485

BENEFICAL USES

Because of other useful and more practical sources, the need for radium sources and materials have declined. As such, there is no significant demand, particularly in the DOE complex. The most promising new development has been the attention given radium, particularly Ra-233, for cancer therapy applications. Some recent DOE-sponsored research (5) has been very encouraging, but there remains little ongoing work. Radon gas recovered from radium sources is used in cancer therapy. Radium-226 can be irradiated in a neutron flux to produce thorium-228 (Th-228), Th-229, and actinium-227 (Ac-227), which are useful in nuclear medicine. Other isotopes of radium, especially Ra-223, Ra-224, Ra-225, and Ra-228 are useful in many applications such as in luminous paints, and in neutron and gamma-ray sources. There is some promising cancer research using bismuth-213 (45 minute half-life) which can be manufactured Ac-225 produced from radiuom targets in a reactor such as the Advanced Test Reactor at the Idaho National Engineering and Environmental Laboratory. With this in mind, the NISSMG suggests preserving the larger radium sources that can easily be manufactured into targets for future reuse. Because of the small volume of these materials, they can be managed in any existing nuclear material storage facility.

Use in Treatment of Cancer

Of more recent interest is use of Ra-223 in radioimmunotherapy of cancer (5). "Ra-223 can be complexed and linked to protein delivery molecules for specific tumor-cell targeting. It decays through a cascade of short-lived alpha- and beta-emitting daughters with emission of about 28 MeV (million electron volts) of energy through complete decay. The first three alpha particles are essentially instantaneous. Photons associated with Ra-223 and progeny provide the means for tumor and normal-organ imaging and dosimetry. Two beta particles provide additional therapeutic value. Ra-223 may be produced economically and in sufficient amounts for wide scale application. Many aspects of the chemistry of carrier-free isotope preparation, complexation, and linkage to the

antibody have been developed and are being tested. The radiation dosimetry of a Ra-223-labeled antibody shows favorable tumor to normal tissue dose ratios for therapy. The 11.4-day half-life of Ra-223 allows sufficient time for immunoconjugate preparation, administration, and tumor localization by carrier antibodies before significant radiological decay takes place. If 0.01 percent of a 37 million bequerele (MBq) (one mCi) injection deposits in a one-gram tumor mass, and if the activity is retained with a typical effective half-time (75 hours), the absorbed dose will be 163 mGy MBq-1 (600 rad mCi-1) administered."

Several characteristics of a radionuclide determine whether it has potential applications in medicine. The choice of suitable radionuclides is limited by practical considerations involving physical half-life, radiation emissions (energies and abundances), availability, cost and difficulty of production, decay products, and chemistry of complexation, linkage to monoclonal antibodies or other cell-directed delivery systems, and suitability to specific applications. Alpha-emitting radionuclides currently considered for systemic radiotherapy include astatine-211 (At-211) (7.2 hours), bismuth-212 (Bi-212) (60 minutes), bismuth-213 (46 minutes), actinium-225 (10 days), terbium-149 (4.15 hours) and Ra-223 (11.4 days). It is well known that alpha particles provide a more effective radiation than beta particles for tumor cell-killing in radioimmunotherapy of cancer. Alpha emitters such as Bi-213 and At-211 will soon be used in the United States and elsewhere for systemic therapy of cancer.

Advantages and Disadvantages of Ra-223

Ra-223 can be produced relatively inexpensively (compared to other proposed alpha emitters) and in relatively large amounts by chemical extraction from a generator system containing Th-227 or Ac-227. These starting materials are obtained by neutron irradiation of common Ra-226. The main challenge in applying Ra-223 to therapy of cancer is the difficulty of complexing radium, which is highly electropositive and averse to forming complexes with most ligands.

The principal advantages of Ra-223 over other candidate alpha emitters are: relative ease of production in amounts needed; relatively low cost of production; suitable half-life for many applications; potential for commercial distribution as a generator-supplied carrier-free radionuclide; photons for imaging and dosimetry; and high energy per decay for effective cell killing.

The principal disadvantages of Ra-223 are: the difficulty of complexation and linkage to protein delivery systems; long decay chain; and relatively long third daughter (Pb-211, half-life = 36 minutes)." The individual concerns sometimes associated with potential use of Ra-223 are examined in the citation.

Proposed Method of Production

The parent of Ra-223, Ac-227, can be produced efficiently in both thermal and fast reactors by neutron irradiation of Ra-226, which is commonly used in well-logging sources, neutron starters, and radium needles. After irradiation, the Ac-227 can be chemically separated from the target irradiation product mixture. Ac-227 can then be purified to remove silica solids, any actinide contaminants (uranium or plutonium) that may be present, and elemental iron. The Ac-227 in equilibrium with decay products is then transferred to an anion exchange column and is eluted with 0.35 molar nitric acid. The Th-227 remains alone on the column. Actinium-227 and Ra-223 are recycled back into the original container for later use. Ten days later, the anion exchange column is eluted again with 0.35 molar nitric acid to obtain pure Ra-223. The resulting solution is boiled down with hydrochloric acid to form the final product Ra-223-chloride. (5)

Separation of Radium from Other Materials

Early in the operations at Fernald, 1950-1951, a research project was undertaken to recover the "rare metal" radium from the by-product material by a technique other than the classical Curie procedure and its modifications (6). A complete laboratory process using Versene was substantially reached.

Since then, studies on separation of radium have focused around environmental concerns with a few studies on extraction. The role of barium sulfate in extraction of Ra-226 has been studied in the context of naturally occurring radioactive material associated with produced brine waters and areas associated with oil production and processing

(7). These results would be informative and potentially applicable if radium recovery processing were to be undertaken. Studies more closely related have been conducted in Canada where radium refining by Eldorado Gold Mines Limited began in Port Hope, Ontario, in 1933 (8). (A summary of recovery and separation techniques, mostly recent, included in the paper is very informative.) The interesting conclusion, for dilute initial concentrations of 850 pico curies per gram (pCi/g) of Ra-226 in contaminated soils neutralized by limestone, was that all attempts to reduce the Ra-226 concentration to less than 100 pCi/g were unsuccessful with generally less than 50 percent removal.

Recent work has applied new separation techniques to measurement and removal of Ra-223 from water and environmental samples (9).

Of most direct relevance is the recent work in Syria on the successful separation of radium from uranium and thorium series materials.

DISPOSAL

Disposal as Low Level Radioactive Waste

Radium contained in sealed sources may be classified as source or byproduct materials under the Atomic Energy Act (AEA), or it may fall outside of the AEA and be defined as naturally occurring or accelerator-produced radioactive materials (NOARM). Department of Energy (DOE) Order 5820.2A defines NOARM as any radioactive material that can be considered naturally occurring and is not source, special nuclear, or byproduct material, or any radioactive material that is produced in a charged particle accelerator. The vast majority of radium contained in sealed sources is source material and thus falls under the AEA 11(e)(1) classification of byproduct material. The issue is whether NOARM radionuclides (specifically radium) contained in sealed sources qualify as "small amounts" acceptable for management at the Nevada Test Site (NTS) or Hanford under DOE Order 5820.2A.

DOE Order 5820.2A specifies that, generally, NOARM materials are to be managed in accordance with volume 40 of the Code of Federal Regulations (CFR), section 192 residual radioactive material guidelines, but that small amounts of NOARM may be managed as LLW. This provision ensures that DOE low-level waste disposal capacity is not consumed by large quantities of low activity NOARM wastes. The exception provides a mechanism for the proper management of waste streams such as sealed sources, which are much smaller in quantity and generally higher in activity than ordinary NOARM and hence warrant management as LLW.

The NTS Waste Acceptance Criteria (WAC) Working Group estimates the total quantity of sealed sources (not just radium) currently in inventory is 500 cubic feet, when prepared for final disposal. Based on an estimated average NTS waste generation volume of 500,000 cubic feet per year, this represents 0.1 percent, assuming all the sealed sources are disposed in the same year (the radium sources are a very small fraction of this amount). This demonstrates that the radium sources that are destined for management as LLW can be considered a small amount in accordance with DOE Order 5820.2A.

Disposal of Radium at DOE Closure Sites

The Mound Site successfully disposed of two sources containing 100 nanocuries (nCi) (1E-7 curies) of Ra-226 through private sector procurement. The sources were solidified by ATG at a cost of $3,000 plus transportation costs and disposed at United States (U.S.) Ecology as naturally occurring radioactive materials. The original plan was to dispose of the sources at the Nevada Test Site (NTS), however, this would have required the NTS WAC to be modified

Rocky Flats Environmental Technology Site (RFETS) has six sources containing 0.613 Ci of Ra-226 and 26 sources with 0.001 Ci of Ra-226. NISSMG recommends that the same disposal option be exercised for the smaller sources, and recommends that the larger sources be considered for reuse, if they are in a form that can easily be made into targets.

The Fernald Site has 52 Ra-226 sources, of which 50 contain a total of 0.005 Ci of activity. These 50 sources should be disposed in the same manner as the Mound Site sources. The two remaining sources have about 0.01 Ci of activity and could be considered for reuse.

Disposal of By-Product Material at Fernald

During its 37 years of operation, the Fernald Site's primary mission was to process uranium into metallic "feed" materials which were shipped, or "fed," to other DOE facilities for use in the nation's atomic weapons program. The principal products were variously sized, highly purified uranium metal forms of assorted standard isotopic assays. The production process at the Fernald Site began with the purification of uranium contained in materials that were recycled from production and that were received from other sites. Scrap metals generated on site or received from other sources were also refined for production. The materials were then heated in a furnace, which upgraded them to chemical processing requirements.

Within Operable Unit 4, silos 1 and 2, known as the K-65 Silos, contain the residues generated from the processing of high-grade uranium ores. This processing was performed to extract the uranium compounds from the natural ores. These ores, commonly pitchblende, were shipped to the United States from a mine in the former Belgian Congo. The K-65 residues contain high activity concentrations of radionuclides, including radium and thorium, and are classified as by-product materials, consistent with Section 1l(e)2 of the AEA, generated consequential to the processing of natural uranium ores.

Silos 1 and 2 contain residues and bentonite clay. The bentonite clay layer was added in 1991 within the K-65 Silos to reduce radon emanation. Radionuclides at significant activity levels within these silos are actinium, radium, thorium, polonium, and a radioactive isotope of lead-210. Each of these radionuclides are naturally occurring elements found in the original ores processed at the Fernald Site and Mallinckrodt. It is estimated that the silos contain approximately 27 metric tons (30 tons) of uranium.

Non-radiological constituents detected in significant concentrations in Silos 1 and 2 residues include sodium, magnesium, molybdenum, nickel, barium, lead, calcium, iron, polychlorinated biphenols (PCBs), and tributyl phosphate (a solvent used in the former uranium extraction process).

Following an initial plan (10) and final Record of Decision (11) in December 1994, the selected remedy consisted of the removal of the contents of Silos 1, 2, and 3; remediation by vitrification and off-site disposal of the treated material at the Nevada Test Site; and the demolition, removal and final disposition of the contaminated concrete, debris, and soils. DOE/FEMP then initiated the Vitrification Pilot Plant Treatability Study Program. The purpose of the pilot-scale program was to collect performance data to support full-scale application of the joule-heated vitrification technology to the silos material. Technical and operational difficulties encountered during the implementation of the program resulted in documented schedule delays and cost increases. In September 1996, DOE formally requested extension of enforceable milestones associated with the project.

On July 22, 1997, the DOE/FEMP and the EPA formally entered into an agreement resolving disputes concerning the schedule and path forward for the remediation of the Silos 1, 2 and 3 materials.

A remedial feasibility study was then prepared (12). Subsequently, a final record of decision (13) was issued. The selected option was complete removal of contents of Silos 1 and 2 followed by treatment using chemical stabilization to stabilize characteristic metals to meet RCRA requirements, as amended, toxicity characteristic limits and attain the NTS WAC. Packaging and transportation of treated Silos 1 and 2 materials will be subject to regulations under the U.S. Department of Transportation (DOT) 49 CFR Subtitle B, Chapter I, Subchapter C, Hazardous Materials Regulations.

FEMP has embarked on a multi-year program to execute the decision. With a path forward now approved, FEMP would prefer to have no changes to the plan. Only if some radium were to become national resource materials, would it be appropriate to consider an option to make it available.

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