PROCESSES AND CHARACTERISTICS

OF MAJOR ISOTOPES

HANDLED AT

MOUND

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* attached: PRS Status Map (drawing # FSE-960150)

HISTORY OF KEY PROJECTS AT MOUND: WASTE GENERATION

Mound, originally called Mound Laboratory, has been a research, development, and production facility since its beginnings in the late-1940s. As an integral part of the DOE (originally the AEC, and briefly, the ERDA), Mound has performed work in support of weapons and nonweapons energy programs with emphasis on explosives and nuclear technology. Historical projects have included research and production of polonium-210 and plutonium-238, thorium and protactinium-231, radium-226 and actinium-227, and stable isotopes of noble gases such as helium, argon, neon, krypton, and xenon. Tritium recovery has been a large part of plant operations since the 1950s.

The following subsections summarize the salient features of the major programs at Mound. Each subsection includes an overview of the project activity, the general scale of the project, dates, process descriptions associated with the project, wastes generated by the project, and the disposition of the wastes, if known. The ideal program cycle includes research, pilot plant, production, and then D&D phases. Not all programs followed the entire ideal cycle. Locations referred to in the following subsections are shown on Figure 2.1.

POLONIUM PROJECT

In the summer of 1942, the COE organized the Manhattan Engineer District. The purpose of the District's Manhattan Project was to build an atomic bomb. Polonium-210 was vital to this program, because it was to be used in a neutron source that would ensure initiation of a chain reaction. The polonium project was undertaken by MCC at the company's Central Research Department in Dayton, Ohio, in September 1943 (Gilbert 1969), and became known as the Dayton Project. Subsequently, polonium-based neutron sources were produced for other industrial and research applications.

In 1954, the Mound began a program using polonium-210 to convert nuclear energy to useable electric energy. This application of nuclear energy, using a thermoelectric principle, was demonstrated that same year, and in February, Mound received a directive to fabricate a polonium-powered model steam-electric plant (Roberson 1954). A model was built and demonstrated in 1954 (Olt et al. .1954). In 1956, a conceptual design to produce a mercury boiler fueled with polonium was described (Hittman 1956). By 1958, an RTG powered by polonium-210 was built.

The power density of polonium is unique and made it attractive as a power source. One pound of polonium-210 occupies a volume of approximately 3 cubic inches and produces heat at the rate of 3.6 x 108 British Thermal Units (BTUs) per minute or about 64 kilowatts of electric power. With a thermal energy output of 120 watts per g, polonium-210 was selected initially for use in the RTG.

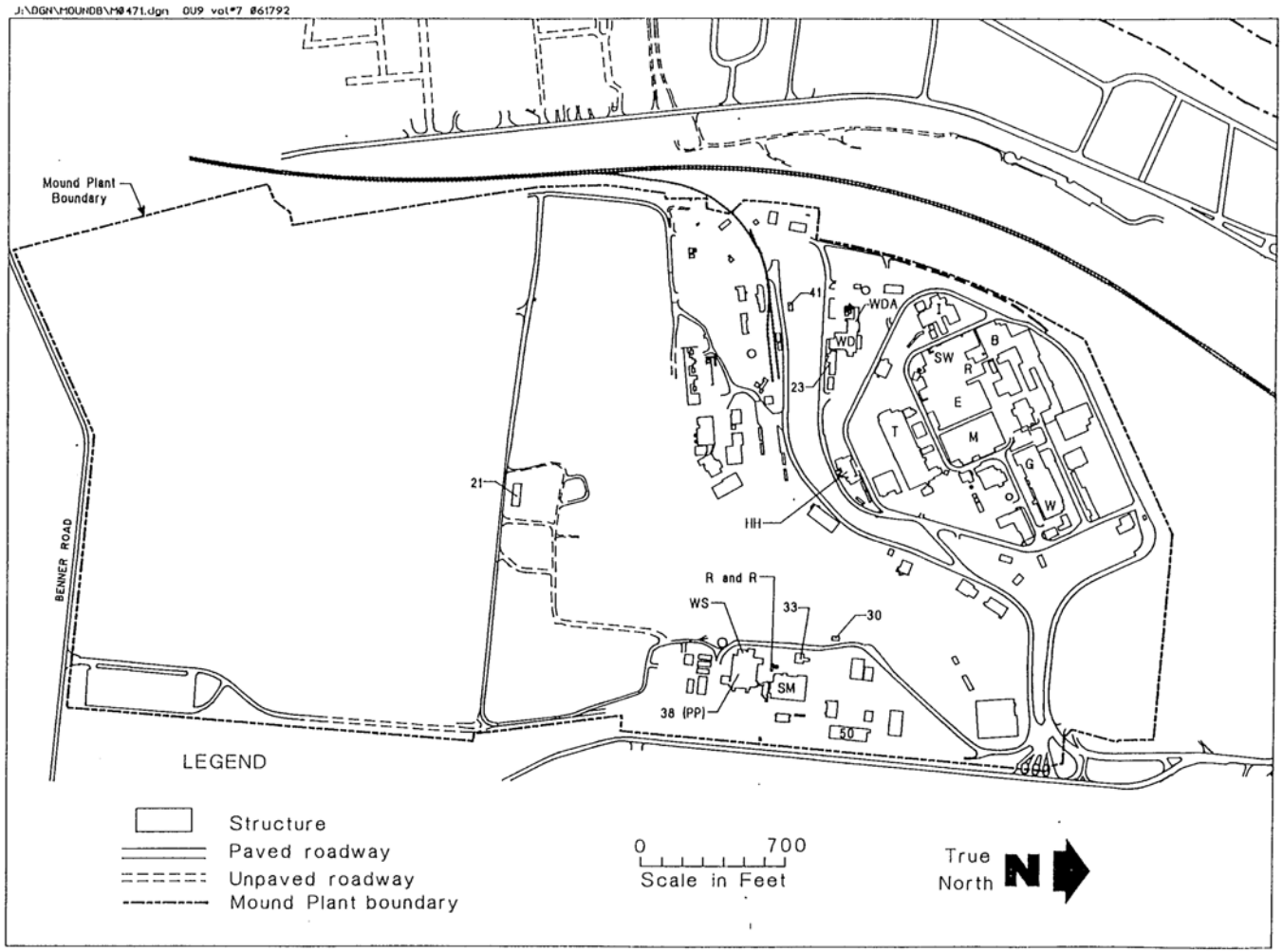


Figure 2.1. Mound building locations.

Known as SNAP, these generators convert the thermal energy generated by radioactive decay to electrical energy. The first SNAP-3A, fueled with polonium-210, provided power to a satellite radio transmitter. The use of satellites powered by SNAP for global communication was first demonstrated under President Eisenhower in 1961, at which time the President's peace message was broadcast via a satellite containing a radio transmitter powered by the SNAP-3A RTG.

Because polonium-210 has a short half-life (138 days), its usefulness was limited for application on long duration satellite and space probe missions. Polonium research and production at Mound were eventually phased out in 1971.

Project Description

Prior to 1944, polonium had not been isolated in pure form or in any appreciable quantity. Therefore, any program involving the recovery, purification, and fabrication of polonium metal from a variety of sources required an understanding of the chemical and physical properties and the metallurgy of polonium-210. The Dayton Project's goal was to develop an understanding of the properties of polonium and its metallurgy (Gilbert 1969).

Initially, the recovery of polonium was attempted from naturally occurring sources such as lead-containing wastes from uranium, vanadium, and radium refining operations. Upon investigation, it became apparent that sufficient quantities of polonium could not be recovered from these sources without processing prohibitively large amounts of material. To obtain polonium in the quantities needed, other approaches to its production were investigated, and the transmutation of bismuth metal to polonium-210 by neutron irradiation was selected for production scale operations.

Process Description

In February 1949, the polonium operations were transferred from Dayton to Mound (Moyer 1956). At this time, the process for producing polonium-210 had been decided upon. Polonium-210 would be produced by the transmutation of bismuth by neutron bombardment. The reaction proceeds as shown in the equation

$$_{83}\text{Bi-209} + n \rightarrow {}_{83}\text{Bi-210} \rightarrow {}_{84}\text{Po-210} + \text{beta}$$

with the $_{83}$Bi-210 decaying to polonium-210 in 5.4 days. All polonium processing activities at Mound involving irradiated bismuth were conducted on the first and second floors of T Building. Initially, bismuth, in the form of 12-inch by 3-3/4-inch by 3-3/4-inch bricks weighing 58 pounds, was irradiated in the Clinton reactor at Oak Ridge, Tennessee. Subsequently, bismuth metal was cast into slugs and inserted into 2S aluminum cans. Aluminum covers were welded to the cans, sealing in the bismuth metal.

This operation and the neutron irradiation were performed at the Hanford operations facility in Richland, Washington, where a higher neutron flux was achievable.

After irradiation, the aluminum cans containing bismuth were shipped to Mound in lead casks that provided radiation shielding. Upon arriving at Mound, the aluminum cans were removed from the casks and stored in a pool of water that provided further shielding until they were removed for use in the polonium recovery process. The pool was located on the second floor of T Building. The lead casks were surveyed for radiation and, if necessary, were rinsed with water to remove surface contamination. They were then shipped back to the Hanford facility for reuse. Numerous approaches to decanning were investigated including mechanical cutting, chemical dissolution, and melting the bismuth in a furnace and pouring it out of the can. In those instances where the aluminum can was separated from the bismuth slug, the aluminum can was shipped to Oak Ridge for burial.

In the polonium production process, the separation of the bismuth slug from the aluminum can was accomplished by chemical dissolution. This occurred on the second floor of T Building where the can was dissolved in a 17 percent hydrochloric acid bath. The bismuth slug did not react with hydrochloric acid and was removed from the bath and washed with water to prepare it for dissolution. The aluminum used in fabricating the can and the bismuth contained impurities such as iron, silicon, cobalt, lead, tin, zinc, silver, chromium, vanadium, and gallium. Upon irradiation, these impurities produced gamma-emitting isotopes that, at the time of bismuth processing, created a radiation health hazard.

The processing techniques for bismuth and polonium varied depending on the required form and purity and because of the research and development nature of this program. Most bismuth research and development was performed in the R Building. As the knowledge of physical and chemical properties grew, it was applied to production techniques to meet and improve product purity requirements.

Chemical Separation of Polonium from Irradiated Bismuth

The separation of polonium-210 from bismuth took place on the second floor of the T Building. This chemical separation process is shown in Figure 2.2. The process is generally described by Huddleston et al. (1963). The process began with the dissolution of the bismuth metal slug in a mixture of nitric and hydrochloric acids (Lonadier and Huddleston 1964). During this step, gaseous nitric acid, nitrogen dioxide, and hydrogen gas were generated. These gases were passed through a caustic scrubber, and the acidic components were neutralized before being exhausted through the high efficiency particulate air (HEPA) filter bank to the building's stack. After the bismuth slug was completely dissolved, the resulting solution was denitrated by the addition of formic acid and heating the solution to 100°C.

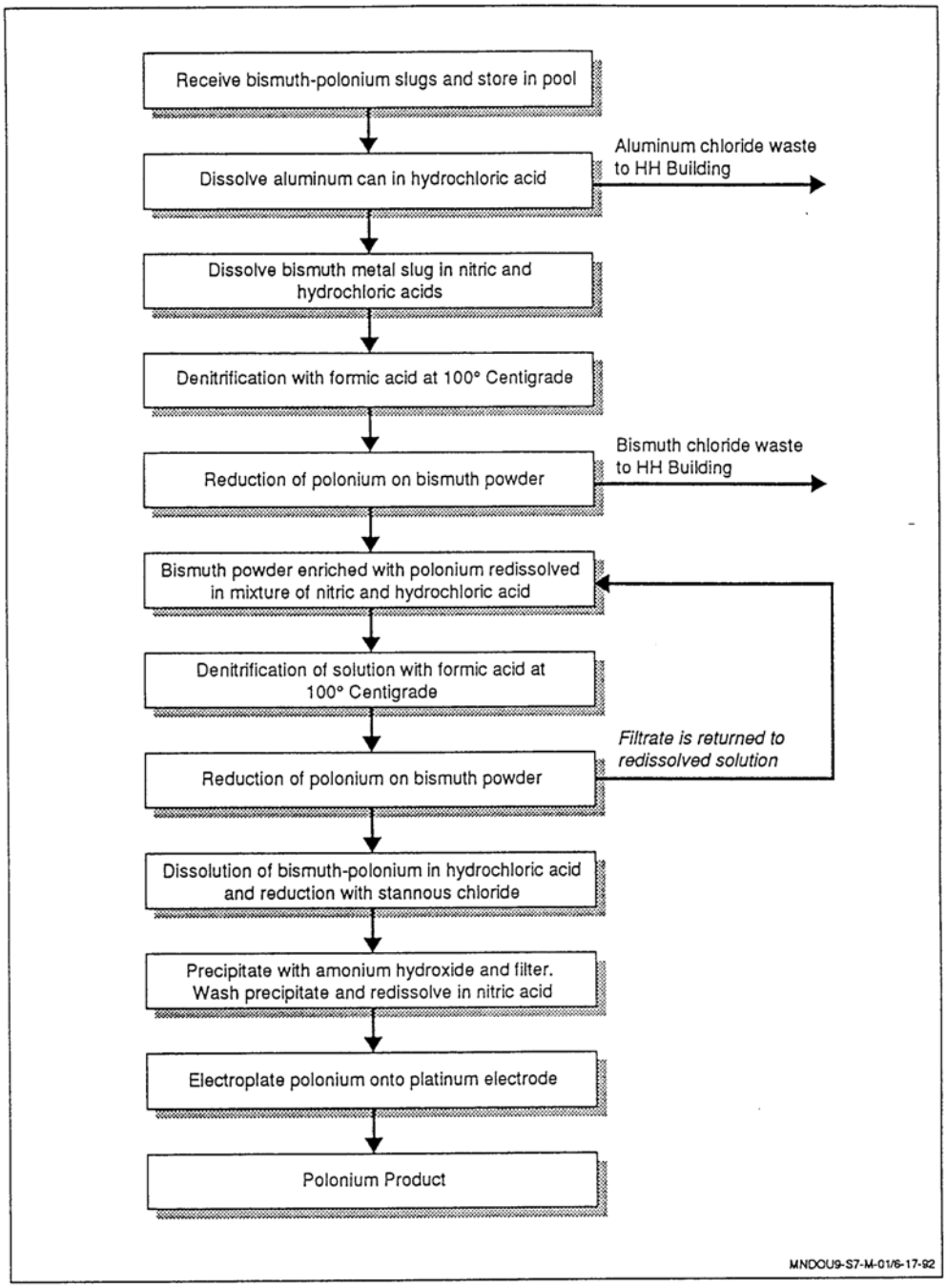


Figure 2.2. Bismuth-polonium separation process.

The next step in the process involved the separation of polonium from the polonium-bismuth solution. The polonium was recovered from the mixture by passing the solution over a bed of 140- to 200-mesh bismuth metal powder. The polonium was deposited on the bismuth powder and the filtrate was sent to the HH Building where it was processed as a waste**.** The aluminum chloride and bismuth chloride wastes were processed in the HH Building until other commitments for space required moving the waste treatment facility to the T Building in 1959. The polonium waste treatment facility was set up on the first floor of T Building, but the waste continued to be referred to as HH sludge.

The bismuth-polonium powder was redissolved in a mixture of nitric and hydrochloric acid, and the resulting solution was denitrated with formic acid. The denitrated solution was again passed over bismuth powder and polonium was reduced on the surface of the bismuth powder. The supernatant solution, containing some polonium, was returned for recycling to the previous concentration step in the process. When a polonium concentration of approximately 15,000 parts per million (ppm) was reached, the polonium-bismuth powder was dissolved in hydrochloric acid catalyzed by hydrogen peroxide. The polonium in this solution was reduced using stannous chloride, and the polonium was filtered from the solution and washed with stannous chloride and a dilute hydrazide hydrogen chloride solution. After the polonium metal was washed, it was redissolved using hydrochloric acid and hydrogen peroxide. This solution was then treated with ammonium hydroxide, and the polonium was precipitated as the hydroxide. The hydroxide was filtered and washed to prepare it for the final step of polonium purification. The polonium hydroxide was redissolved in nitric acid, and the polonium was electroplated onto a platinum gauze electrode. The polonium metal was then ready for fabrication.

Other processes have been developed at Mound to separate polonium-210 from bismuth. Two additional processes, the silver process and the tellurium process, were actually employed on a production scale. Both processes could be used with the denitrated solution of the bismuth slugs. In the case of the silver process, the polonium spontaneously deposited onto the silver surface as polonium metal. Bismuth was not reduced by silver and therefore remained in solution. Next, the silver containing polonium was dissolved in nitric acid. This solution was treated with ammonium hydroxide, which precipitated the polonium. The silver remained in solution as a silver ammonium ion.

The tellurium process was used following the first step of polonium concentration using bismuth powder. Telluric acid and stannous chloride were added to a denitrated solution of polonium and bismuth, and the solution was heated. The tellurium precipitated and coagulated, and the polonium co-precipitated with the tellurium. This process resulted in the precipitation of some bismuth, which was eliminated by repeating the process. After the second precipitation step, the washed precipitate was dissolved in aqua regia, and the polonium recovery proceeded as in the bismuth process.

Bismuth Metal Recovery

At the beginning of the polonium program, the bismuth oxychloride sludge produced in the HH Building was stored at Mound for possible recovery of the bismuth and re-irradiation at the Hanford facility (McEwen 1952b). In 1948, an electrolytic process was developed that successfully recovered bismuth, and in March 1950, seven bismuth slugs were produced from recovered metal. These were sent to Hanford for neutron irradiation. In 1952, Mound constructed a bismuth metal recovery facility in the HH Building, with the capacity to produce 17,000 pounds of bismuth annually, that would process the accumulated drums of bismuth sludge (Belcher 1952b). The amount of sludge being stored at Mound in 1952 was equivalent to 62,000 pounds of bismuth. This amount of sludge represented approximately 200 55-gallon drums, which were reportedly stored inside of T Building (Grasso 1991 b). In 1953, a large quantity of high purity bismuth was located at the Brookhaven National Laboratory. This material, amounting to 64 tons, was made available to Mound and was sufficient to satisfy requirements for several years. This eliminated the need for the recovery facility and the recommendation was made that it be dismantled (Anson et al. 1953).

Separation of Polonium from Bismuth by Distillation

A major element of the polonium program was to develop improved processes for the separation of polonium from bismuth. During the period from 1949 to 1952, Mound conducted experimental work on the separation of polonium by distillation (Endebrock and Engle 1953). This work turned into a materials research program; however, as of 1953, no satisfactory alloys had been found that remained inert to bismuth and polonium under the conditions required for distillation.

PLUTONIUM PROJECT

Plutonium-238 research and development activity began at Mound in the mid-1950s. Initial research concerning plutonium-238 was transferred to Mound from Lawrence Livermore National Laboratory in 1959. The first reduction of metallic plutonium-238 was achieved at Mound in the spring of 1960. Research and development relating to the application of plutonium-238 as a radioisotopic heat source material followed the initial work. These research and development activities included materials research, the development of processes for the production of heat source materials, and development of fabrication and metallurgical technology that would ensure the containment and stability of heat source materials in RTG systems. Research and development activities were also conducted on the design of RTG systems for the various applications of this technology. During that time, Mound produced well over 500 RTG units.

The RTG systems were used in a variety of applications including electric power generators for satellites, life support systems, spacecraft, pacemakers, and an artificial heart. Table 11.3 is a list of some of the RTG units manufactured at Mound. Between 1961 and the end of 1982, 34 RTGs were employed in 19 space systems; most of these were manufactured at Mound. The first SNAP was launched to provide 2.6 watts of power to the TRANSIT navigation satellite (Morse 1963). Metallic plutonium was used in the SNAP units during the early 1960s, because the heat sources were designed to disintegrate and burn up completely upon reentry from orbit. The heat sources were encapsulated in exotic metals, such as iridium, to isolate the plutonium, prevent chemical reactivity, and provide containment in the event of an accident during launch. This philosophy was changed in the mid-1960s, and the SNAP units were redesigned to retain integrity under all circumstances rather than to burn up upon reentry. Metallic plutonium was abandoned in favor of plutonium oxide. The plutonium oxide heat sources were not as susceptible to fire or other accidental processes of oxidation.

A major technological development from the reactor fuels research conducted at Mound contributed to the heat source program as well. Chemically and thermally stable microspheres produced in an inductively coupled plasma torch exhibited a remarkable freedom from loose contamination. This eliminated many of the hazards normally associated with the handling of plutonium oxide and made previously unattractive applications feasible.

From the early 1960s to the late-1970s, Mound processed plutonium-238 for use in heat sources within the RTG and manufactured the RTG units themselves (Luthy 1991). Processing of plutonium metal and plutonium oxide from materials supplied from the SRP was conducted in the SM and PP (later known as Building 38) buildings constructed in 1960 and 1967, respectively. Other work was performed in R Building and in Building 50. The fabrication of heat sources from plutonium metal was terminated in the mid-1960s, although the oxide processes continued into the late-1970s.

Table II.3. Radioisotope Fueled Thermoelectric Generator Program

Program	Year	Fuel Form	Watts/Unit
SNAP 3A	1958	Polonium-210	96
SNAP 3B	1961	Plutonium-238	52
SNAP 15B	1963-64	Plutonium-238	1
SNAP 15A	1964	Plutonium-238	1.6
Heat Pipe	1964	Plutonium-238	104
Poodle	1964	Gadolinium polonide	250
SNAP 3C	1965	Plutonium zirconium	58
SNAP 19	1965	Plutonium-238	102
SNAP 27	1965-71	Plutonium dioxide (microspheres)	1480
Life Support	1966	Plutonium dioxide (shards)	70
SNAP 19B	1966-67	Plutonium dioxide (microspheres)	570
SNAP 19B Intact Reentry Heat Source	1966-67	Plutonium dioxide (microspheres)	570
Artificial Heart	1967	Plutonium-238	25
Swimsuit Heater	1967	Plutonium zirconium	105
Dart I	1967	Plutonium dioxide (microspheres)	157
Pacemaker	1967	Plutonium-238	0.134
SNAP 19B Intact Reentry Heat Source	1968	Plutonium dioxide (microspheres)	620
Dart II	1968	Plutonium dioxide (microspheres)	155
Apollo Lunar Radioisotope Heater	1968	Plutonium dioxide (microspheres)	15
Pacemaker	1968-69	Plutonium-238	0.238
Life Support II	1969	Plutonium dioxide (microspheres)	105
Life Support II	1969	Plutonium dioxide (microspheres)	50
Pacemaker	1969-72	Plutonium-238	0.238
Pioneer	1970-72	Plutonium metal cermet	650
Pioneer Radioisotope Heater Unit	1970-72	Plutonium metal cermet	1
Rite I	1971	Plutonium dioxide (microspheres)	420
Milliwatt Generator	1971—	Plutonium dioxide (shards)	4.5

Table II.3. (page 2 of 2)

Program	Year	Fuel Form	Watts/Unit
Artificial Heart	1972	Plutonium dioxide (microspheres)	33
Transit	1972	Plutonium metal cermet	850
Rite II	1972	Plutonium metal cermet	825
X-Ray	1972	Plutonium dioxide	0.6
X-Ray	1972	Plutonium dioxide	1.8
Army Corps	1972	Plutonium dioxide (shards)	6
Pacemaker	1972-73	Plutonium dioxide (shards)	0.226
Viking	1972-73	Plutonium metal cermet	685
Multi-Hundred Watt (Lincoln Experimental Satellite 8/9)	1972-76	Plutonium dioxide	2400
NAVY	1975	Plutonium dioxide (shards)	18
Voyager Radioisotope Heater Unit	1976-77	Plutonium dioxide	1
Multi-Hundred Watt (Voyager)	1977	Plutonium dioxide	2400
Five-Watt RTG (heat source)	1983	Plutonium dioxide	125
Light Weight Radioisotope Heater Unit	1985	Plutonium dioxide	1
General Purpose Heat Source[a]; Galileo and Ulysses	1984-86	Plutonium dioxide	4500
Five-Watt RTG[a]	1987	Plutonium dioxide	125
High Performance Generator MOD-3[a]	(pending)	Plutonium dioxide	2400

[a]RTG programs include RTG assembly and testing in addition to heat source hardware fabrication.
RTG - radioisotopic thermoelectric generator

Encapsulation of the processed plutonium heat sources with exotic metals was also performed at Mound until the late-1970s. After that, the encapsulated plutonium oxide heat sources were supplied by the SRP. Since early 1979, Mound has not handled unencapsulated plutonium-238. Throughout the history of the plutonium-238 processing program, a plutonium recovery process was included as part of the total material control and recycling effort. Some of the recovery processes were transferred to the SRP in 1975. Limited operations continued at Mound until 1982 in support of the D&D activities of the former plutonium processing facilities.

Process Descriptions

Plutonium-238 used in RTG systems was shipped to Mound from the SRP. Initially, the plutonium was received as an oxalate or a nitrate and subsequently as an oxide. These materials were stored in vaults in Buildings 50, SM, and T. The plutonium was taken from storage and entered into any one of the following processes for the production of heat source materials: pressed plutonium oxide (PPO), plutonium-molybdenum cermet (PMC), or plutonium metal (Luthy 1991).

In order to control and contain plutonium during processing and fabrication and to protect the process operators and other building personnel, operations were performed in alpha glove boxes. These glove boxes were identified by glove box number and glove box line. Buildings SM, 50, R, and 38, which housed plutonium operations, were designed to control emissions to the atmosphere. The buildings operated under a slight negative pressure to the atmosphere, and the glove box line's atmosphere and building air were filtered through a double HEPA filter system before venting to the atmosphere via a stack. Table 11.4 shows a summary of the amounts of plutonium released through stack emissions during the period of plutonium processing and subsequent D&D of the facilities.

Pressed Plutonium Oxide (PPO) Fabrication Sphere Process

The PPO process for the production of RTG heat sources was the longest lived plutonium heat source program at Mound. The PPO process was used at Mound from the mid-1960s to the late-1970s and thereafter at other RTG heat source facilities. RTG units with PPO heat sources were used in equipment for the lunar Apollo program, numerous types of life support equipment, the Lincoln Experimental Satellite, and the Voyager spacecraft. The Milliwatt Generator still uses this technology.

Table **11.4.** Summary of **Mound Plutonium Effluents**

Year	Plutonium	
	Air *(μCi)*	Water *(μCi)*
1960	250,125	
1961	160	
1962	140	
1963	108	
1964	252	
1965	5,803	
1966	30,442	
1967	54,347	24,900
1968	5,720	243,800
1969	10,544	109,700
1970	4,342	7,420
1971	401	15,234
1972	74	60,586
1973	84	16,043
1974	28	19,755
1975	23	17, 862
1976	15	2,973
1977	12	3,584
1978	14	4,947
1979	12	3,157
1980	15	773
1981	8	1,110
1982	21	1,207
1983	4	1,003
1984	7	1,342
1985	5	991
1986	6	691
1987	5	472
1988	5	997
1989	4	1,419
1990	18	670
1999*	**.003**	**3.6**

Note: Data from Mound Environmental Monitoring Reports (EG&G 1989a) and unpublished data

*Most recent data available (taken from Annual Site Environmental Report for Calendar Year 1999)

The PPO process shown in Figure 2.3 involved either a microsphere or shard process for which all but a few steps were identical. The process began by transferring plutonium-238 dioxide into the glove box. The oxide was unloaded from its container and dissolved in a mixture of nitric-hydrofluoric acids. After dissolution was completed, the resulting plutonium nitrate solution was adjusted with nitric acid to provide a 2.0 to 2.5 normal (N) hydrogen ion concentration. If necessary, a valence adjustment was made, and the resulting solution was treated with ammonium hydroxide to precipitate a plutonium hydroxide. The solution was filtered, and the plutonium precipitate was washed with dilute ammonium hydroxide solution. The washed precipitate was then vacuum dried for 1 to 2 hours and air dried overnight. The dried plutonium precipitate was crushed to produce a fine powder. The ratio of isotopes in the final production was 80% plutonium-238, 16% plutonium-239, 3% plutonium-240, 0.8% plutonium-241, and 0.2% plutonium-242.

In the microsphere process, the powder was fed through a plasma torch, producing microspheres of uniform size that went directly to the hot press facility. In the shard process, the powder was sieved for size and placed in a controlled atmosphere furnace at an atmosphere of oxygen-16. The material was heated to 1,600°C for 2 to 4 hours. This step produced a sintered plutonium-238/oxygen-16. The sintered oxide was then transferred to the hot press facility where a sphere was fabricated. The die body was sprayed with colloidal graphite and then charged with plutonium dioxide particles. The die was loaded into the press, and the hot press chamber was evacuated. With a force of 2,500 pounds per inch and a temperature of 1,480°C, a sphere of plutonium dioxide was formed. The plutonium dioxide sphere was removed from the die, weighed, and gauged. The sphere was placed in a controlled atmosphere furnace and treated with oxygen-16 at 700°C for 1 hour. Next, the sphere was placed in a vacuum furnace and was allowed to outgas for 30 minutes at a temperature of 1,200°C and a vacuum of 1 x 10^-5. The sphere at this point underwent calorimetry for specification testing. Now ready for encapsulation, the sphere was transferred to the R Building. Encapsulation involved welding a machined metal cover over the sphere. Encapsulation materials included iridium, graphite, tantalum, titanium, and hastelloy (an alloy of cobalt, molybdenum, chrome, tungsten, and iron).

Plutonium-Molybdenum Cermet (PMC) Production Process

The PMC process used as a heat source, a cermet consisting of a sintered granular plutonium dioxide coated with molybdenum. The cermet is processed to produce a solid material that can be machined to required dimensions and assembled into the heat source capsules. The PMC process is shown in Figure 2.4 (MRC 1974c).

RTGs employing PMC heat sources were widely used in many applications, including the National Aeronautics and Space Administration Pioneer F spacecraft launched in March 1972. This was the first spacecraft to rely entirely on an RTG system for electric power. The Pioneer spacecraft was also fitted with 12 1-watt radioisotopic heater units fabricated from PMC heat source material. These units provided the thermal energy required to prevent damage to sensitive instrumentation. The U.S. Navy also used cermet RTG systems in their TRANSIT satellite, which was part of a world-wide navigational system. The Viking I and II Mars mission spacecraft launched in the early 1970s used PMC heat sources in their RTGs. The PMC process for RTG heat sources was used at Mound until 1973 when it was discontinued in favor of the PPO process.

The initial steps of the PMC process are identical to the PPO process. Plutonium dioxide received from the SRP and Mound plutonium recovery underwent dissolution with nitric acid and hydrofluoric acid followed by a hydrogen ion concentration and valance adjustment using nitric acid. Precipitation took place using ammonium hydroxide, and the plutonium precipitate was separated from the supernatant liquid by filtration. The precipitate was washed with dilute ammonium hydroxide and then dried. The dried precipitate was sized and then sintered in a furnace at 1,200°C. Sintering took place in an atmosphere of oxygen-16. The isotopic composition was similar to the products of the PPO process. If the sintered material met acceptance criteria, it continued to the next step of the process, which resulted in a molybdenum coating of the plutonium dioxide. After molybdenum coating, the material was pressed into discs using a hot die press. This cermet material was capable of being machined and was processed to produce discs of 2.1 inches in diameter and 0.2 inch in height. The discs were then assembled into the heat source capsules. The assembly of the machined cermet elements into containment capsules involved tungsten inert gas and electron beam welding of metal and metal alloy containers and internal components. Materials used in fabrication included inconel, tantalum, platinum rhodium, yttrium, and iridium.

Plutonium Metal Production Process

In the early 1960s, the production of plutonium metal began with the plutonium nitrate solution received from the SRP. The process was housed in a dry air glove box line in R Building. The process was transferred to the SM Building in 1963 and remained there until the use of plutonium-238 metal gave way to PPO, microsphere, and cermet as heat source materials. The plutonium nitrate solution was received into the glove box line in R Building, where the plutonium was precipitated with oxalic acid. The plutonium oxalate was filtered, and the filtrate was returned to plutonium recovery. The plutonium oxalate precipitate was washed and dried. The oxalate was placed in a platinum crucible and converted to plutonium tetrafluoride using hydrogen fluoride gas. The plutonium tetrafluoride was transferred to a magnesium crucible, and finely divided calcium metal and iodine were added. The

crucible was placed in a steel reduction bomb, and the assembly was purged thoroughly with argon gas and then sealed with a bolt-on cover. The bomb assembly was placed in an induction furnace and heated. When the material in the crucible reached a temperature of 300°C, the reduction process began and continued as the exothermic reaction proceeded and the temperature reached approximately 1,600°C. After the bomb was allowed to cool to room temperature, it was opened, the plutonium-238 metal was broken away from the slag, and the metal was cleaned with a brush to remove adherent slag and calcium metal. The clean plutonium metal then went to the foundry. The nitric acid wash solution and the slag from the reduction process was sent to plutonium recovery. The crucible went through a leaching process to recover the residual plutonium-238. The solution went to plutonium recovery and the crucibles were packed and shipped for burial as high-risk waste, because they were a line-generated material.

The plutonium metal "button" was placed in a crucible, and, in an inert atmosphere, the metal was melted and poured into a mold that had the shape of a truncated cone. After the metal cooled, it was removed from the mold and was ready to be encapsulated. All solid materials coming in contact with plutonium in this process were treated to recover plutonium. Ash and leach solutions went to plutonium recovery for processing.

Plutonium-238 metal was used for RTG heat sources from the late-1950s to the mid-1960s. The metallic heat sources were first used in SNAP-3B and SNAP-9A and were among the first to be launched into space. Many of the TRANSIT series navigational satellites in the early 1960s were powered by metallic plutonium heat sources. Mound Plant stopped producing metallic RTG heat sources in the mid- to late-1960s in favor of the PPO and PMC processes.

Plutonium-238 Recovery Process

Plutonium production activities resulted in line-generated byproducts and waste materials that were evaluated for appropriate treatment, recovery, and disposition. The recovery of plutonium-238 from production activities represented a significant element of the plutonium program. The processes of plutonium recovery evolved over time. In 1959 and 1960, all wastes from the research and development activities in R Building were drummed for offsite recovery. In the first few years of SM operations, plutonium recovery consisted of processing all high-risk aqueous wastes. In late 1962, the processing of high-risk wastes was curtailed and Mound began to distinguish between disposable and recoverable high-risk wastes. The disposable high-risk wastes were processed for offsite disposal. The recoverable aqueous process streams were initially processed by simple evaporation and ion exchange. In 1963, no facilities were available for the dissolution and processing of solid materials (Brown 1963). Most solid materials were saved for future processing. The processes of dissolution,

fluorination, incineration, and pyrosulfate fusion were added over the next several years (McMannon 1963-1966; Geichman 1992). In 1967, the recovery processes were moved to Building 38. The discussions that follow provide details of these processes.

Wastes and byproducts from the production processes were characterized on the basis of their plutonium content and were classified as recoverable, high-, or low-risk waste. Solid or liquid wastes that had a plutonium content exceeding the economic discard limit would be classified as recoverable wastes, and the materials were sent to the plutonium recovery process in SM Building. The economic discard limit was established by comparing the cost involved in recovering the plutonium-238 contained in a specific type of waste to the cost of obtaining the same quantity of plutonium-238 from normal production of the radionuclide (Vallee 1967). When the cost to recover the plutonium-238 from a waste material was less than the cost to produce the same quantity of plutonium from materials obtained from the SRP, then that waste material contained plutonium in excess of the discard limit. Recoverable materials contained plutonium in excess of the discard limit were recycled through the recovery processes. Waste materials that contained plutonium below the discard limit were defined as high- or low-risk wastes. Figure 2.5 identifies the in-line plutonium process wastes and their disposition as they had developed by 1973.

During the first years of SM operation, plutonium-bearing acidic solutions were accumulated in holding tanks in SM-1 . These solutions were processed in a steam evaporator, and the evaporator condensate was processed by an ion exchange column. The effluent from the ion exchange column was treated as low-risk waste. This system was taken out of service in 1962. Plutonium recovery of aqueous wastes was moved out of the waste treatment area into the process area. From 1963 to 1968, the plutonium recovery process for aqueous wastes consisted of two ion exchange columns, 6 inches in diameter by 2 ft in length. Approximately 100 gallons of waste, containing 1 to 200 g of plutonium, would be processed every other day. The effluent from the ion exchange columns was sent to an in line glove box evaporator. The evaporator condensate went to SM-1 as a low-risk waste. The solid residue from the evaporator went back for plutonium recovery if it exceeded the discard limit, or was designated as a high- or low-risk waste.

Within the production lines, the recovery processes for a given plutonium waste depended on the form and composition of the waste and whether it had a low or high plutonium concentration. The major steps in this process included physical and chemical processing elements. The physical process included ultrasonic wash, evaporation, and filtration. Simple washing and leaching of glove box material occurred in the process since the beginning of the program. Chemical processing elements included dissolution, precipitation, fusion, incineration, ion exchange, and fluorination. The chemical processing of solids began in 1964. Incineration did not become part of the operations until 1965.

The plutonium recovery processes are shown in Figure 2.6 as they had developed by 1973. In glove boxes, solid objects contaminated with plutonium would be washed or leached in water or acid solutions with the aid of ultrasonic cleaning equipment. Following this step, the objects would be gamma scanned or wiped and counted. They were then returned to their original use or, based on the activity, they were declared high- or low-risk waste. The wash water and leachate were sent to plutonium recovery. High temperature-fired plutonium oxide and ceramic RTG materials, not meeting product specifications, were dissolved in a mixture of nitric and hydrofluoric acid or underwent fusion with pyrosulfate. Glass fiber filters were dissolved in a hydrofluorinator-pressurized vessel, and the volatile silicon tetrafluoride generated in the process was removed via a caustic scrubber. The highly acidic solutions containing plutonium were sent to the plutonium recovery process. The caustic scrubber solutions were designated as recoverable, high-risk or low-risk waste, based on the discard limit, and either sent to recovery or waste treatment. Other solid materials containing recoverable plutonium or off-specification RTG material that resisted efforts at dissolution would undergo pyrosulfate fusion followed by dissolution.

Combustible wastes generated in the glove box line were processed in one of two ways: During production, if paper towels or rags accumulated significant quantities of plutonium-238, the thermal energy released by the plutonium would cause the towel or rag to start smoldering. The glove box operator would put the towels and rags in an open-topped metal can and allow the process to continue. Since the glove box had an inert atmosphere, there was no open flame. After a period of time, the can contained a carbonized ash that contained plutonium oxide. The process is analogous to pyrolysis and low-temperature ashing. The volatile pyrolysis products were swept from the glove box and, after HEPA filtration, were discharged to the atmosphere via the building's stack (Geichman 1992). All other combustible wastes including paper, wood, leaded neoprene gloves, and in-line glove box HEPA filters were treated in an incinerator installed in a glove box. The incinerator consisted of a large steel tub that was heated by means of a natural gas burner. The atmosphere in the glove box and incinerator chamber was deplete of oxygen; therefore, the process was identical to that described earlier except for the fact this pyrolysis process took place at a very high temperature. The gaseous pyrolysate from the incinerator was scrubbed using a sodium hydroxide solution (Geichman 1992). The pyrolysate, after scrubbing and glass fiber/asbestos filtration, was discharged to the atmosphere via the building stack. The ash residue from the incinerator was sent back for dissolution and leaching.

In the early 1960s, nearly all potentially recoverable solid materials were stored for future plutonium recovery. Solid process wastes, such as the slag from the metal reduction of plutonium, could not be processed until the recovery methods were developed. Large items could not be processed by washing and leaching operations. These potentially recoverable materials were packaged in 30-gallon drums and stored in the SM drum storage area. In time, some drums corroded and began to leak.

When leaking drums were discovered, a major effort was undertaken to correct the problem by overpacking the drums into 55-gallon drums. In August 1964, a small facility was constructed in which drummed recoverable wastes could be sorted and redrummed or sent to plutonium recovery (Bowser 1992). The facility, known as the R and R Building (Figure 2.1), contained a special glove box facility in which the 55-gallon drums were opened. The contents of the inner 30 gallon drums were sorted by plutonium concentration. Recoverable materials above the discard limit were returned to the plutonium recovery process, liquids were sent to the wastewater treatment, and other solids below the discard limit were drummed for offsite disposal.

TRITIUM PROCESSES

The start up of tritium-related operations at Mound began in the mid-1950s (Meyer 1957d, 1958b). Tritium processing activities included production, disassembly, analysis, and development of nuclear components that contained tritium. In support of these activities, Mound has been involved in development of tritium enrichment and recovery process technology and the processing and containment of tritium-contaminated wastes. At the present time, Mound has the facilities for the recovery and purification of tritium from all types of materials and wastes generated by other DOE sites. This recovery and purification system is known as the tritium recycle and enrichment system.

In the early 1970s, a major effort was undertaken at Mound to reduce the fugitive emissions of tritium. As much as 80% of the total annual release of tritium to the atmosphere could be attributed to diffusion of tritium out of glove box operations and other containment areas to the room ventilation systems (Bixel et al. 1975). In January 1972, a tritium effluent control project was undertaken with the goal of reducing fugitive tritium emissions to less than 10% of the RCG for hydrogen/tritium (HT) and hydrogen/tritium oxide (HTO). Table 11.6 shows the history of tritium effluents from 1959 to 1989.

Tritium is also processed at Mound to recover helium-3. Small amounts of tritium from this recovery process were vented to the atmosphere via the HH stack. After 1970, the tritium gas from this process was collected in cylinders and transported to the SW Building and fed to the effluent removal system (ERS). The use of cylinders was discontinued after the installation of a pipeline between the HH and the SW Buildings to transfer tritium from the helium-3 process to ERS (MRC 1984b).

Process Description

Tritium processing activities take place in the T, SW, R, and HH Buildings (Phipps 1991). Processes associated with tritium are performed in inert atmosphere glove boxes, in analytical glove boxes, and in systems that are enclosed in high velocity fume hoods. Gaseous effluents from glove boxes, pass boxes, vacuum pumps, and process lines are processed to remove tritium and tritium oxide before these gaseous effluents are released to the atmosphere. Mound refers to this process as the tritium recycle and enrichment system.

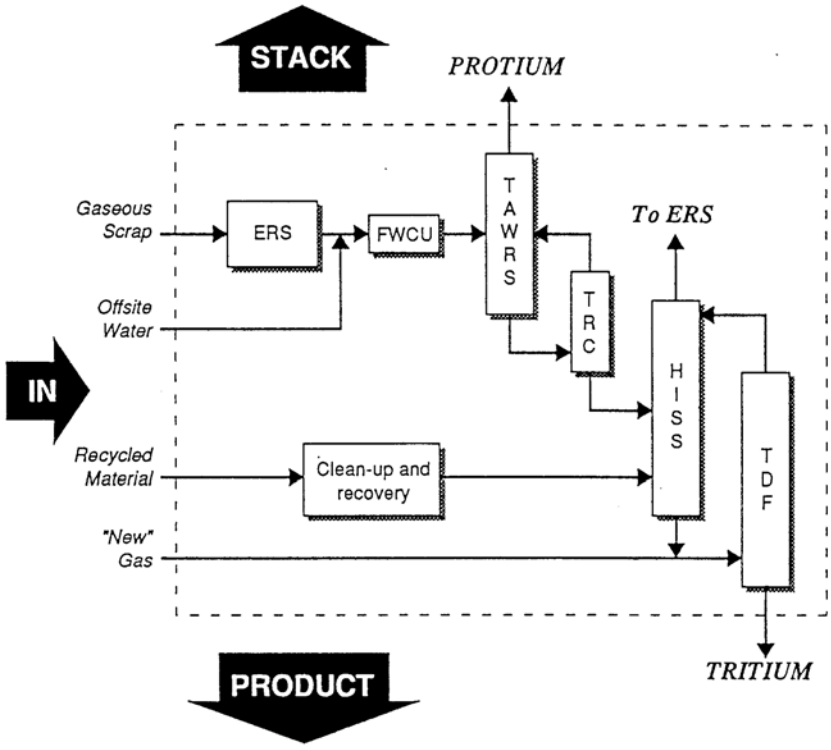
Various tritium-containing scrap materials are processed for the recovery of tritium. These tritium-containing materials include gaseous scrap, offsite tritiated water, recycled material, and new gas. Scrap material containing tritium is processed in the isotope recovery system, and the tritium gas is transferred to the tritium recycle and enrichment system. Tritium gas and tritiated water enter into the recovery process based on the concentration of tritium in the gas feedstock. In the isotope recovery system, the tritium is absorbed onto a molecular sieve column that is cooled with liquid nitrogen. Gases such as nitrogen, argon, helium, and methane are separated from tritium by this process and are exhausted to the atmosphere via the stack in SW Building. The tritium is desorbed from the molecular sieve column and is enriched by the thermal diffusion process. The tritium product is stored for future use, and the waste gas from the thermal diffusion column goes to the ERS for further recovery of tritium.

Tritium Recycle and Enrichment System

In the late 1980s, Mound began operating an integrated tritium recovery and purification system that is referred to today as the tritium recycle and enrichment system (Hedley 1991). This system evolved over the years and began with the ERS. Other components of the recycle and enrichment system are: the tritium aqueous waste recovery system (TAWRS); the tritium recovery column (TRC); the hydrogen isotope separation system (HISS); and the thermal diffusion facility (TDF). This system produces tritium of better than 99% purity. The process flow sheet for the tritium recycle and enrichment system is shown in Figure 2.7.

Effluent Removal System

The ERS is a detritification system used to process tritium-contaminated gases generated at Mound. It serves primarily to process gases from vacuum pump exhausts, pass boxes, and glove box lines. The ERS has also proven useful in processing gaseous atmospheres associated with maintenance and decontamination-related activities. The ERS receives tritium-containing gas at a volumetric flow rate of up to 40 cubic ft per minute; at higher volume flows, an emergency tank can be used to divert high peak flows to prevent system overload (MRC 1977a). A process flow diagram of the ERS is shown in Figure 2.8. The tritium-containing gas stream enters the ERS refrigerated filter system, which separates water, organic solvents, and vacuum pump oil from tritium and other fixed gases. The gaseous stream passes through two additional beds of molecular sieve to remove traces of water and organic vapor. The tritium-containing gas stream is heated to a temperature ranging from 500° to 700°C and then passes over a bed of hopcolite (copper oxide and magnesium dioxide) and a second bed containing a platinum catalyst. Tritium is converted to the oxide, and tritiated organics are oxidized to carbon dioxide and tritium oxide. The tritium oxide is removed from the process stream



ERS – effluent removal system

FWCU – feed water cleanup system

TAWRS – tritium aqueous waste recovery system

TRC – tritium recovery column

HISS – hydrogen isotope separation system

TDF – thermal diffusion facility

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Figure 2.7. Tritium recycle and enrichment system (EG&G n.d.).

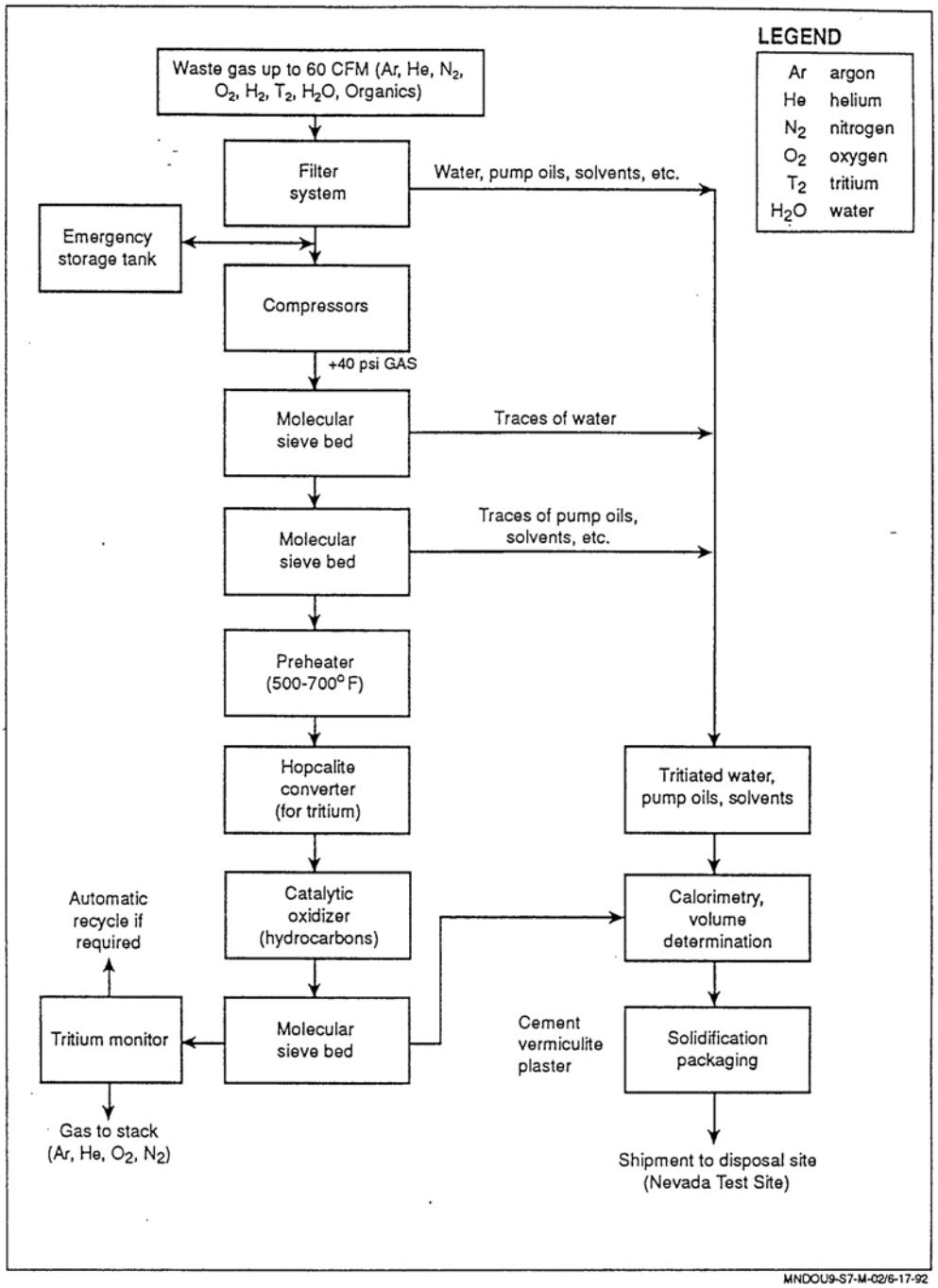

Figure 2.8. Flow diagram of effluent removal system (MRC 1979).

with a 13 X molecular sieve bed downstream of the oxidation catalyst beds. The absorbed HTO is recovered from the dryers and the tritiated hydrogen and tritium are recovered in the TAWRS. The gas stream is monitored and analyzed for tritiated hydrogen and HTO. If the processed gas stream meets discharge criteria, it is vented to the atmosphere via the SW Building stack.
If it does not meet discharge criteria, the gas can be recycled through the ERS process.

Tritium Effluent Control

The tritium effluent control project was initiated at Mound in 1972 in order to develop the state-of-the art tritium control technology necessary to achieve reduction of tritium in effluents to 10% of the RCG values (MRC 1976a). The glove box atmosphere detritiation system (GADS) was an outgrowth of this program. The GADS was a significant development for reducing fugitive emissions from glove box operations. As mentioned earlier, 80% of the annual fugitive emissions of tritium resulted in diffusion of tritium into the room and building atmosphere from glove box operations. The GADS consists of a recirculating helium purification unit that removes tritium along with other gases such as nitrogen, oxygen, and water vapor from the glove box inerting atmosphere. The GADS operates on the principle of catalytic oxidation and adsorption of these gases at liquid nitrogen temperatures, on a bed of 5A molecular sieve.

In 1976, the tritium effluent control laboratory was near completion. This laboratory was responsible for developing separation and tritium-enrichment technology for both gaseous and liquid effluents. Two support systems were operational relative to tritium developmental activities. These support systems were known as the emergency containment system (ECS) and the air detritiation system (ADS). In the event a tritium-containing system failed during testing in the environmental test laboratory, the ECS swept the tritium-contaminated atmosphere in the test laboratory to an evacuation tank. The ADS consisted of a platinum catalyst bed that converted tritium in the effluent to an oxide. A drier bed removed the oxide from the gas stream, and a blower recirculated the air in the glove box line until the tritium level was low enough to permit discharge to the atmosphere via the building stack. In the event there was a glove box line breach, the ventilation system in the laboratory was isolated and the entire room air was recirculated through a large platinum catalyst reactor and a drier or oxide removal system until tritium levels returned to normal values.

Tritium Aqueous Waste Recovery System (TAWRS)

In the 1980s, the TAWRS became operational to process tritium oxide coming from SW and T Buildings. High-level tritium oxide was dissociated by electrolysis, and the hydrogen/tritium gas mixture was sent to a cryogenic distillation/palladium chromatography processing unit. The tritium

from this process was transferred to the HISS; the hydrogen gas, containing on the order of 10 tritium, was sent to the intermediate level of the TAWRS for tritium recovery or was discharged to the atmosphere via the stack. The tritium-rich gas stream from the high-level side of TAWRS was further purified by the TRC and the HISS. The tritium product went into storage prior to shipment to the SRP or was used in Mound tritium programs. The less pure tritium stream from the TDF was returned to the high-level TAWRS.

The TRC is a single column cryogenic distillation system that receives the low concentration tritium stream produced by the TAWRS. The distillate from the TRC is returned to the TAWRS, and the still bottom is the feedstock to the HISS. There is no waste stream generated by the TRC system.

The HISS is a tritium recovery and enrichment system that employs low-temperature distillation as the separation process. The HISS receives recycled tritium-containing material and tritium-containing gaseous material from the TAWRS and the TRC. The HISS enriches the tritium via a three-stage cryogenic distillation process and is capable of producing tritium enrichments greater than 90%. The process flow sheet is shown in Figure 2.9. The tritium-enriched stream is transferred to the TDF, and the distillable is returned to the ERS. No waste stream is generated by the HISS.

The TDF employs gaseous phase thermal diffusion technology to process the still bottom from the cryogenic distillation system in the HISS. The TDF produces gaseous tritium of better than 99% purity. The low tritium side of the TDF is returned to the HISS for recycling. No waste stream is generated by this process.

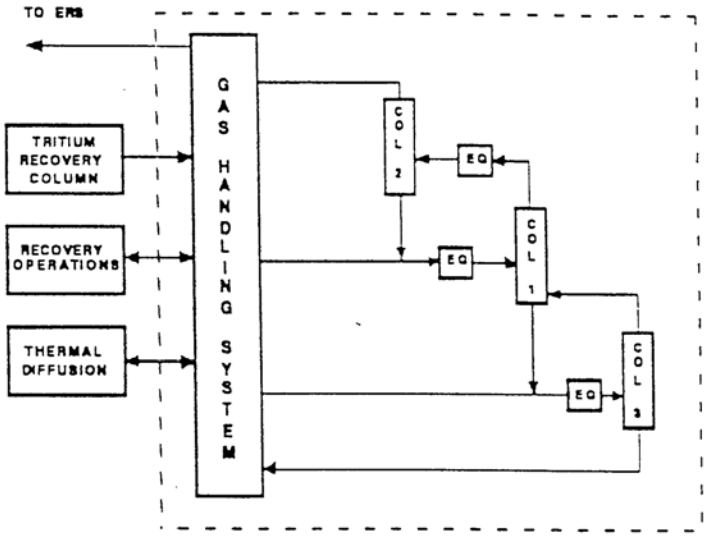

Figure 2.9. Hydrogen isotope separation system (HISS) (EG&G n.d.).

Table **11.6.** Summary of Mound Tritium Effluents

Year	Tritium	
	Air (Ci)	Water (Ci)
1959	31,527	
1960	102,427	
1961	240,644	
1962	244,455	
1963	313,932	
1964	262,638	
1965	206,750	
1966	199,561	
1967	364, 685	169
1968	275, 856	202
1969	315,252	2,332
1970	179,468	250
1971	73,503	399
1972	30,483	244
1973	15,331	149
1974	10,031	105
1975	8,859	58
1976	6,206	46
1977	4,896	57
1978	7,346	32
1979	3,831	34
1980	3,795	26
1981	4,285	22
1982	4,283	14
1983	4,293	8
1984	3,430	8
1985	4,795	6
1986	3,555	6
1987	3, 863	6
1988	3,204	4
1989	41,534	6
1999*	**804**	**2.4**

Note: Ci - curies Records we have gathered stand in '59 and '67

* Most recent data available (taken from Annual Site Environmental Report for Calendar Year 1999)

RADIUM-226 AND ACTINIUM-227 PROGRAMS

Because of the short half-life of polonium-210, a search for other alpha-emitting isotopes, with a specific activity and neutron-generating efficiency comparable to polonium-210, was undertaken in the 1940s, as part of the substitution materials program. Actinium-227, being an alpha-emitter with a half-life of 21 years, was selected as a possible replacement for polonium-210 in the production of initiators. There were several problems with using actinium-277 in weapons components. Actinium-227 is not present in sufficient quantities in natural source materials; but, like polonium-210, it could be produced by neutron irradiation of a target material. In the case of actinium-227, radium-226 was the target material.

Radium-226 occurs with uranium in pitchblende ores at about 1 part in 3 million. The actinium must be separated from the radium after irradiation, a considerable effort since the workers must be shielded from the high-gamma radiation. The actinium must then be purified and reduced to its metallic state. Only then can the actual weapons initiator be fabricated. All of these processes went through the research and development stage at Mound (MCC 1950a,b). The actinium work generally lagged behind the radium work because large quantities of actinium were needed. The program grew rapidly from 1951 to 1952; but, by July 1953, the program was de-emphasized (MCC 1953a,b). A few initiators were produced at Mound that were probably never used by the AEC.

In support of the actinium program, a decision was made to develop a radium recovery process and a radium processing plant at Mound. Sources for radium were researched in the late 1940s and were identified in the United States, Canada, and Belgium. In the process of recovering uranium from the Belgian Congo pitchblende ore at the Mallinckrodt Chemical Works, St. Louis, Missouri, a residue containing radium, known as K-65 residue, was produced (MCC 1951). In September 1949, Mound requested 200 pounds of the K-65 (Miller 1949; Haring 1949a). In December of that year, Mound workers toured the Mallinckrodt plant to observe the processing operations of the pitchblende ore. Mound had received the K-65 residue in October and was using it to develop the process chemistry that would be used to recover radium from K-65. This research effort, performed in R Building, included studies on radium separation chemistry, concentration of radium from barium, coprecipitation of lead and radium, and separation of barium and radium by ion exchange and fractional crystallization (Salutsky et al. 1953). At the same time the research work was taking place, preliminary engineering studies concluded that the pilot plant at Mound should be able to process 300 pounds of K-65, or about 100 mg of radium, per day (Rauscher 1950). It is unclear from the available records how much actual processing of K-65 residue took place, but it appears that the pilot plant was never built. The actual yield of radium from the K-65 residue is unknown, but it appears to have been small.

Radium from other AEC sources was directed to Mound to expedite the program. In February 1950, 30 g of radium were being prepared for irradiation at the Hanford reactor, with costs incurred and accountability assigned to Mound (Bobbitt 1950). The source of this radium was Argonne National Laboratory (ANL). In November 1950, Mound was assigned the responsibility of processing the 30 g of radium that were then still in the Hanford reactor. Plans were also made to re-irradiate radium that was purified through processing.

In February 1950, Mound personnel visited ANL to observe the separation and purification of actinium from irradiated radium (Engle 1950). The radium-actinium technology developed at ANL was essentially transferred to Mound. To conduct this program, a new general purpose (GP) Building was planned that later became known as the SW Building. In June 1951, a special shielded process facility, which is generally referred to as the old cave, was constructed in a room on the east side of the building.

The cave design was duplicated from one in use at ANL. The cave was approximately 20 ft by 5 ft by 12 ft high and was placed approximately in the center of the room. The front had a shielded portion about 6 ft high, constructed of concrete and steel, with four large plate glass window tanks. The working surface inside the cave was about 3 ft high with lead access doors along the back and sides. A 1 ton traveling crane served the entire cave room and facilitated moving the heavy casks. The area in front of the cave was considered the low-risk side; the area around the ends and back, where feed materials and supplies were stored, was the high-risk area. All entry into the cave was controlled (Engle 1950). Drainage in the building was provided by a series of lateral channels in the floor. Within the cave area, these channels were lined with concrete and drained to enclosed sumps: one in the high-risk area and one in the low-risk area.

The wastes generated in the cave could not be treated by the waste treatment process in the WD Building. A separate processing facility was constructed in room 1-B, adjacent to the cave in room 1-A. An evaporation treatment system was chosen (Jackson 1953, McEwen 1951). The system consisted of the evaporator and three waste storage tanks: one with a capacity of 1,000 gallons and the other two with capacities of 500 gallons each. This process equipment was installed and cold test runs were completed in early 1952 (Mead 1952). Hot test runs were made using wastes generated from research activities in the R Building. The 1,000-gallon tank and evaporator were also used for the Purex pilot plant in late 1952 and early 1953.

By March 1952, three radium-actinium separation runs had been completed in the cave. The first run contained 0.6 g of radium, the second and third contained 5 g each. By June 1952, 7.751 Ci of actinium had been separated from irradiated radium.

Four additional irradiated slugs were due in from Hanford in August 1952. The radium that resulted from the separation was to undergo additional irradiation. A can designed to hold radium was approved for use in the materials test reactor (MTR) in Idaho, and the first charging of radium at the MTR was scheduled for November 1952. About 60 g of radium were actually in storage (Schauer 1953).

The research and development work on actinium was actually conducted on lanthanum until a source of actinium became available in 1951. Experiments focused on the separation of lanthanum from barium using an ion exchange process. Dowex-50 was the typical exchange resin used. Reduction of lanthanum fluoride with lithium suggested yields up to 100% (Mead 1952). In October 1952, Mound was directed to construct a laboratory and pilot plant for actinium initiators. Equipment needed for housing the actinium purification and fluoride preparations was installed in the R Building. By July 1953, however, the actinium pilot plant was de-emphasized by the AEC (Schauer 1953).

By July 1952, an assessment of the cave area indicated high levels of contamination that represented a serious radiological hazard to personnel working in the area (Bradley 1952d). The health physics surveys indicated surface and airborne contamination so high that instrument readings could not be evaluated. All work in the cave area stopped until decontamination and modifications were made (Mead 1953, Bradley 1952g). These were not finished until nearly spring of 1954. During this hiatus, research on the separation methods was continued.

On June 1, 1954, work was resumed on the separation and purification of radium-226, actinium-227, and thorium-228 from neutron-irradiated radium-226. By October 1954, almost 48 g of radium had been processed and canned (MCC 1954). As a result of this work, 47.5 Ci of radium, 14.9 Ci of actinium-227, and 24.6 Ci of thorium-228 were purified by the end of that year (McCarthy 1955).

By December 1954, plans for final cleanup of the cave were being made (Mead 1954). D&D of the cave was performed over the next few years, as budget permitted. A shipment of 47 g of radium was returned to the AEC of Canada, Ltd., in Ottawa, in December 1957 (Meyer 1958a).

Process Description

The production of actinium at Mound involved both the separation of radium from the K-65 residues and separation and purification of radium and actinium from irradiated radium. Radium separated from the K-65 residues and radium obtained from other sources was shipped to the Hanford reactor facility where it was irradiated with neutrons in accordance with the following reaction:

$$_{88}\text{Ra-226} + {}_{0}\text{n-1} \rightarrow {}_{88}\text{Ra-227} \rightarrow {}_{87}\text{Ac-227} + \beta$$

After irradiation, the material was returned to Mound for the separation and subsequent purification of actinium-227. The radium was also recovered and stored.

K-65 Residue Pilot Plant

Mallinckrodt Chemical Works, St. Louis, Missouri, had been processing Belgian Congo pitchblende ore to recover uranium. As a result of the process, the radium that occurs in pitchblende ore remained in the gangue when the ore was extracted with nitric acid. The gangue was neutralized with sodium carbonate and bicarbonate and stored for eventual recovery of radium. This neutralized gangue was referred to as K-65 residue. This material was caustic and had a 30% moisture content (Rawlings 1951). The acidic liquid containing the concentrated uranium nitrate underwent a solvent extraction procedure with diethyl ether, and the aqueous phase was again treated with sodium hydroxide; this resulted in the formation of a caustic sludge referred to as the St. Louis Residue or the Cotter Concentrate. Mound also processed Cotter Concentrate to recover protactinium-231 and thorium-230. No analytical data are available that characterize the K-65 residue. However, there are analytical data available for the Cotter Concentrate. The metals found in the Cotter Concentrate can be expected to be present in the K-65 residue as well, but not necessarily in the same concentrations. The constituents found in K-65 residues are presented in Table 11.7 (Rawlings 1951).

Table 11.7. Composition of K-65 Residue (Rawlings 1951)

Constituent	Concentration Weight %
Water	30
Lead oxide	19
Barium sulfate *	7
Silicon dioxide	35
Metals **	9

*375 mg of radium contained with the barium.

** Metals that may be found in the K-65 are similar to those identified in Cotter Concentrate. See subsection 2.9 for a discussion of those metals

In October 1949, 200 pounds of the K-65 residue were shipped from Mallinckrodt in a single 55-gallon steel drum and stored in the old explosives bunker at Mound (Garner 1991). The radium recovery process began with the transfer of an aliquot sample to the SW Building. The process developed at Mound for extracting radium from the K-65 residue is a modification of the method used by Madame Curie and her co-workers. Whereas the Curie process separated the radium as a bromide, the Mound process separated it as a chromate. The processing of the residue began with leaching the material with water to extract soluble salts. The residue was then treated with a mixture of sulfuric and hydrofluoric acid to remove silica. The residue was then treated with sodium carbonate solution to convert radium and barium sulfates to carbonates. The traditional Curie process used fractional crystallization to separate the radium from the barium, but this was slow and difficult.

Experiments were performed using ion exchange as a substitute, but it is not clear that any technique was ever used to produce any quantity of radium. There is no evidence that Mound ever received additional shipments of the K-65 residues after the initial 200 pounds. Sources of refined radium were identified in Canada and Belgium to satisfy the radium-actinium program.

Radium-Actinium Separation Process

The process of separation of actinium from radium developed by ANL used solvent exchange. The irradiated radium bromide was dissolved in water and the actinium was extracted in a solution of thenoyltrifluoracefone. The thenoyltrifluoracetone was found to polymerize and turn gummy upon standing, and the process was modified to include benzyl acetone. Eventually, an oxalate precipitation method was developed.

The oxalate precipitation method used for separation and purification of actinium began with the dissolution of the irradiated radium in 90% nitric acid and the formation of an insoluble radium nitrate. The radium nitrate was redissolved and then precipitated as a carbonate. The radium carbonate was recovered by filtration and placed in a platinum container for future neutron irradiation. The filtrates from the dissolution and precipitation steps described above contained actinium-227 and thorium-228 and were combined. Thorium was precipitated as the iodate. The filtrate containing actinium was treated with dimethyl oxalate, and the actinium was precipitated as the oxalate. Additional purification may have taken place within ion exchange columns, but this process is not well documented.

Metallic actinium was prepared by igniting the oxalate to form an oxide. The oxide was dissolved in nitric acid and precipitated as a fluoride by addition of hydrofluoric acid. The actinium fluoride was then treated with lithium to reduce the actinium to the metal.

THORIUM-232 REFINERY PROGRAM

In the mid-1950s, Mound was directed to conduct research toward the development and operation of a process for extraction of thorium from Brazilian Monazite sludge and other AEC waste materials. The goals were to develop a large-scale process for the recovery of thorium from a variety of thorium bearing ores and other thorium-containing feed materials and to construct a refinery to produce thorium in quantities required by the AEC. The refinery was to provide a thorium salt suitable for the preparation of metallic thorium of high purity for the thorium fuel cycle planned for the breeder reactor. Pilot-scale studies in preparation for a large-scale thorium refinery were conducted at Mound to refine the techniques that had been developed elsewhere. The process developmental work done at Mound is known as the Monex process (MRC 1973a). The Monex pilot plant was assembled in room 1 B of the SW Building in the spring of 1955. At the same time, construction began on the thorium refinery that was to be built in the west side of the SW Building.

Extensive remodeling of the WD Building was also planned, but never implemented. Wastewater processing was to be focused on reduction of trace radium contaminants (Huddleston 1955). The project hardly got started before it was cancelled. The actual directive to construct the facility was issued March 11, 1955 (Wende 1955), but construction was canceled May 9, 1955 (MCC 1955d). The roof that had been removed for construction was replaced and sealed. All the foundations, footings, and piers had been poured inside the building. All the extensive interior excavations were backfilled with gravel and soil. Research work on the pilot plant was continued after the construction was halted and was completed by July 1955 (McCarthy 1955).

In anticipation of the completion of the thorium refinery, Mound received at least 1,650 tons of thorium-containing sludge from United Lead Company between December 1954 and June 1955 (McCarthey 1955). These shipments included Brazilian Monazite sludge, thorium oxalate, and sulfate sludge residues (Weisler 1955). The Brazilian Monazite sands are treated with caustic to recover the phosphates as sodium phosphate. The residual Monazite sand is then treated with hydrochloric acid to dissolve the rare earths. These are removed in the supernate. The remaining residue was known as Brazilian Monazite sludge (Mead et al. 1955). The sludge was extremely corrosive, being basic or acidic depending on the pretreatment it received, and contained approximately 55% water. The analysis of this sludge showed a wide range of thorium and rare earth components. Estimates of the original quantities of sludge materials are given in Table 11.8. Table 11.9 provides a typical elemental analysis of Brazilian Monazite sludge (Mead et al. 1955). These results are based on the sample being dried at 110°C. This drying results in the removal of water. When the sample is heated to elevated temperatures, metal hydroxides and chlorides are converted to the oxides. The typical sludge lost additional weight amounting to 14% due to an oxidation at an elevated temperature referred to as ignition. These materials were contained in over 6,000 55-gallon drums and were delivered to Mound by railcar. Many of the drums were in deteriorated condition. One shipment was received by truck in April 1955 in particularly poor condition, indicating that significant spillage had occurred enroute (Scott 1955b). Some thorium metal scrap, machine turnings, and oxide were also received from Nuclear Metals, Inc. The thorium metal scrap consisted of thorium metal chips, a variety of alloys, and aluminum-clad thorium metal. Thorium alloys also contained uranium, aluminum, and iron. Thorium with aluminum and copper cladding was also part of the metal scrap inventory (Nuclear Metals, Inc. 1955). One shipment in January 1955 consisted of 45 kg of oxide and 25 kg of turnings (Waldfogle 1955). The drums shipped by railcar were unloaded in the old Warehouse 9.

The drums were stored in many areas of the plant, including Warehouse 15, the Quonset hut, W Building, G Building (Scott 1955a), and many open areas (Figure 2.10).

Although the thorium refinery project was terminated, the drums of thorium residues continued to be stored at Mound. Because of the corrosive nature of these sludges, the drums leaked and frequent repacking was necessary. Typically, 20 to 40% of the drums were repacked annually. Initially, repacking of leaking drums took place in Warehouse 15, but the elevated radiation levels (radon?) forced the work outside to Area 3 and later to Area 9 (Figure 2.10). In 1961, a new bulk storage facility was proposed for containment of the sludge. This facility, known as Building 21, was completed in 1964, and most of the contents of the drums were transferred into the building at that time. By 1973, at least 117 55-gallon drums of thorium residue were still stored outside the building but were to be moved inside (Storey 1973a). Building 21 originally did not have any doors or windows and was referred to as a silo. The sectioned roof allowed the materials to be loaded. The oxalate sludge was stored in a separate room from the hydroxide sludges. By this time, the sludges had lost a significant amount of moisture; and, during the dumping of the material into the bin through a roof opening, significant emission of fugitive dust occurred, contaminating the surrounding area. The thorium sludges remained in storage in Building 21 until a decision was made to dispose of the material. General Atomic Company purchased the sludge and began packaging the material in 55-gallon drums and shipping it to its facilities in October 1974, completing the task in July 1975. Once the silo building was clean, it was used to store the drums of Cotter Concentrate.

Process Description

The preliminary design for the thorium refining process, the starting point for the developmental studies at Mound, was based upon pilot plant studies conducted at the National Lead Company of Fernald, Ohio, and the ORNL, where a thorium extraction process known as the Thorex process was developed. The background work conducted at these two facilities formed the basis for laboratory and pilot development studies for the Monex process conducted at Mound. The Monex process development work at Mound took place in the R Building in 1954 and 1955. The Monex pulse column pilot plant was installed in room 1-B of the SW Building. The pilot plant was constructed of laboratory glassware and 2-inch glass columns. A berm constructed around the pilot plant served the purpose of containing any spills. The process itself was designed to use the Brazilian Monazite sludge that had been produced by treating Monazite sand with caustic to crack the insoluble phosphate ore. The soluble sodium phosphate supernatant was removed, and the slurry was treated with hydrochloric acid to solubilize certain rare earth-elements. The solids that remained after the rare earth elements were removed were called Brazilian Monazite sludge.

Table II.8. Quantities of Thorium Sludges and Thorium-Bearing Materials Stored at Mound as Feedstocks for the Monex Process

Monex Feedstocks	Material Weight (lbs)	Thorium Content (kg)	Thorium Content (% dry weight)
Brazilian hydroxide sludge	2,700,000	270,013	>40
Brazilian oxalate sludge	286,000	36,876	~30
Domestic oxalate sludge	309,000	22,291	~20
Other material, miscellaneous	33,000		
Metal scrap	24,000		
Oxides and grinder sludge	78,000		
Indian nitrate	72,000		
Thorium, aluminum, and copper alloys	1543	656	43

Data from Nuclear Metals, Inc. 1955; MCC 1955b; McCarthy 1955

Table II.9. Typical Elemental Analyses of Brazilian Sludge

Element	Concentration (Weight %)	Element	Concentration (Weight %)
Aluminum	0.01 - 0.1	Lead	0.01 - 1.0
Calcium	0.1 - 1.0	Praseodymium	1.0 - 10.0
Cerium	<10.0	Selenium	Not Detected
Copper	0.001 - 0.01	Silicon	1.0 - 10.0
Erbium	Not Detected	Samarium	1.0 - 10.0
Gadolinium	1. - 10.	Terbium	Not Detected
Holmium	Not Detected	Titanium	7.0
Lanthanum	<10.	Thulium	0.1 - 1.0
Lutetium	Not Detected	Yttrium	1.0 - 10.0
Magnesium	0.01 - 0.1	Ytterbium	0.1 - 1.0
Neodymium	1.0 - 10.0	Radium-228	Not Analyzed
Thorium oxide[a]	45	Radium-224	Not Analyzed
Rare earth oxide[a]	15	Zirconium oxide[a]	1.4
Silicon dioxide[a]	4.4	Phosphorous oxide[a]	5.3
Titanium oxide[a]	7.0	Uranium oxide[a]	
Iron oxide[a]	4.3	Chloride[a]	1.0
Loss on ignition[a]	14		1.4

Data from Mead et al. 1955
[a]Percentages on dry basis at 110°C; MRC 1973a,d.

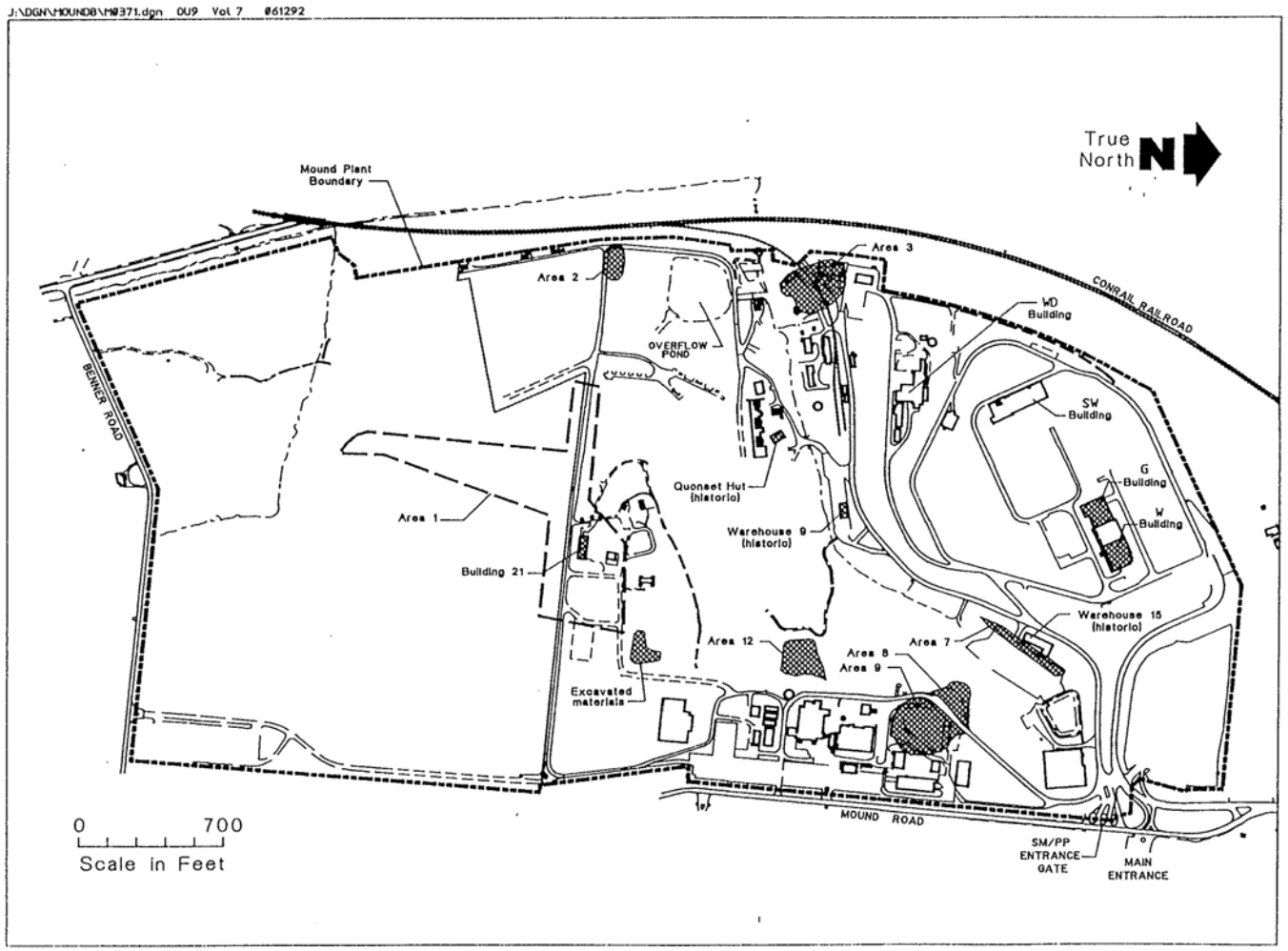

Figure 2.10. Thorium ore storage, disposal, and redrumming areas.

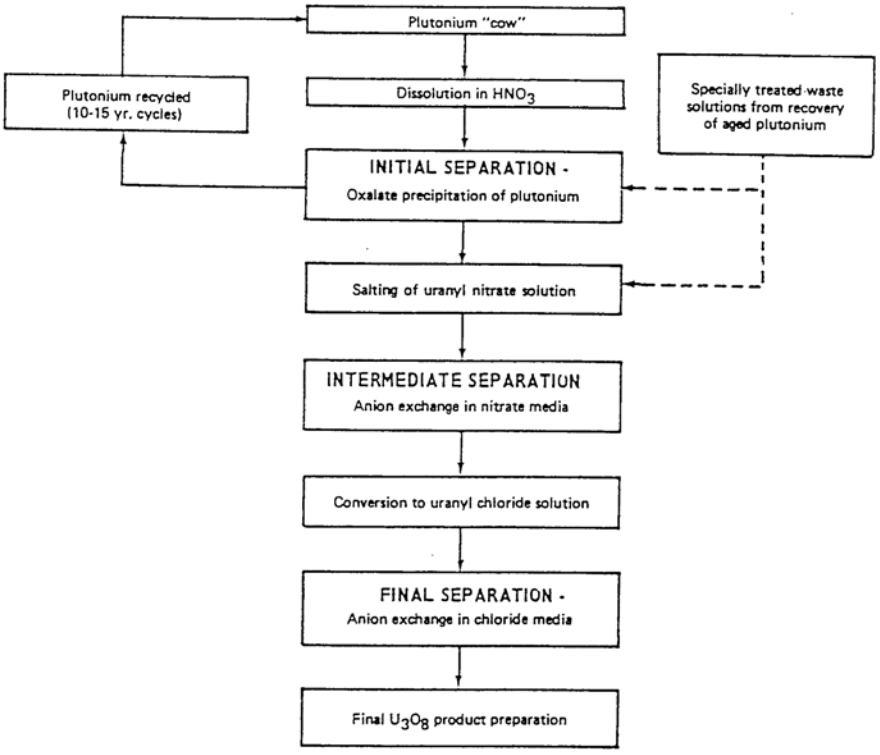

Figure 2.11. Chemical separation steps for recovery and purification of uranium-234 from plutonium-238 (Keister et al. 1978).

The Monex process was a solvent extraction process that relied on the stripping of thorium into an aqueous nitric acid phase. The first step was the efficient extraction of thorium from the thorium containing sludges into a solution that was suitable as a feedstock to the process. Batch and continuous nitric acid digestions were studied in the laboratory to develop data and obtain feed solutions for batch countercurrent and pulsed column extractions. The extraction steps employed tributyl phosphate as a solvent. The countercurrent experiments used a kerosene-based diluent, and the pulsed columns used an oleum-treated Amsco, an aromatic hydrocarbon. From these studies, the normality of nitric acid in batch digestion solutions was determined.

The pilot plant actually used a pulsed column configuration. The feed solution was prepared in 100-gallon vessels. The feedstock was dissolved in nitric acid, the thorium and uranium were extracted in the tributyl phosphate, and the thorium was partitioned from uranium by stripping with nitric acid. The latter two steps were called a cycle, and two cycles were considered sufficient for purification (Mead et al. 1955). No information was given on the volumes of the pilot plant runs, although the available data suggest that a few pounds of sludge were probably all that were processed.

The feedstock preparation research included experimentation with all the thorium sludges on hand, including hydroxide, oxalate, and some sulfide. The countercurrent studies used a clarified feed, whereas the pulsed columns used a slurry. Recycled thorium metal, consisting of machine turnings and scrap, was also digested as feed. Most of the metal had a coating of machine oil that was removed. Trichloroethylene was typically used. Less than 100 g of metal appear to have been used in the experiments (Mead et al. 1955).

THORIUM-230 (IONIUM) PROGRAMS

Ionium is an alpha-active thorium isotope with a half-life of 8.05 x 10^4 years. Ionium and thorium-230 are names that have been used interchangeably to identify this isotope. The interest in ionium goes back to 1946 (Peppard 1949), when a survey was conducted to identify sources of ionium. This survey looked at various fractions obtained from processing uranium and its ores to identify sources of ionium and protactinium-231 (Bruehlman 1947). In 1949, the ionium program reached a second milestone when a pilot plant was constructed at ANL to process 3,600 gallons of Mallinckrodt sparged turbid liquor from a material referred to as the airport cake, a raffinate produced by the diethyl ether solvent extraction of uranium (Peppard 1949). The material containing ionium was being produced at the Mallinckrodt Chemical Works uranium refinery in St. Louis, Missouri (Fariss 1955; Eichelberger and Scott 1956a).

In July 1955, Mound submitted a proposal to the AEC to design and install a facility that would be used for process chemistry development. The work would isolate ionium from raffinates produced at Mallinckrodt (McCarthy 1955). In November 1955, Mound received a directive to proceed with the design and construction of this facility, with a target completion date of February 1956 (Johnson 1955). The process chemistry research and development took place in the R Building. The larger columns required for production separation also were assembled in the R Building. Ionium was to be used as a tracer element in the Redwing test program, and kilogram quantities of ionium were needed for weapons diagnostic tests. Between April 6 and May 18, 1956, five shipments of a total of 400 g of ionium were made to the AEC (Haubach 1956a, 1956b, 1956c, 1956d).

In July 1956, Mound was directed to produce an additional 500 g of ionium for the ORNL research stockpile and to refine the process chemistry for use in a future large-scale production program (Ager 1956). This required an additional supply of the Mallinckrodt feed solution, a delivery that was apparently never made. By November 1956, the remaining 73 L of feed had been processed to produce about 70 g of ionium (Eichelberger and Scott 1956c). Unfortunately, all of the undesirable impurities contained in the original feed solution were concentrated in the remaining solution. Forty nine grams of the remaining ionium were shipped to the University of California Radiation Laboratory in December 1956 (Eichelberger and Scott 1957).

The ionium program was closely tied by chemistry and process development to the protactinium-231 program. In the late 1950s, capsules containing about 250 g of thorium oxide and apparently containing the remaining 22 g of ionium were sent to the MTR in Idaho for irradiation.

This process was designed to produce protactinium-231 and protactinium-233 by neutron absorption by thorium-230 and thorium-232, respectively (Schuman 1960, 1961; Kirby 1960). The capsules were stored for at least a year in the reactor canal to allow the protactinium-233 to decay to a safe handling level. The capsules were returned to Mound, but it is not known if they were ever processed. They may remain in storage as research materials.

In the early 1960s, Mound conducted a search of ionium sources. Forty-nine samples from 17 uranium mills or processing sites were received and analyzed. Several samples of airport cake from the Mallinckrodt Chemical Works were used for comparison. Analysis of the samples by neutron activation analysis at ORNL indicated that the airport cake was the best source of ionium available (Eichelberger 1961 b). These research efforts led to the procurement of additional quantities of airport cake some years later. The airport cake was also known as Cotter Concentrate and was processed for thorium 230 and protactinium-231 in the 1970s.

Process Description

Mallinckrodt raffinates that have been partially processed at the St. Louis uranium refinery were shipped to Mound in 55-gallon steel drums. This feedstock consisted of a caustic-neutralized fluoride slurry containing ionium, thorium-232, rare earths, scandium, uranium, and traces of protactinium.

The process equipment associated with separation and purification of ionium includes stainless steel storage tanks, mixers and mixing vessels, Pyrex glass contractors, mixer settlers, centrifuges, pulse columns, stainless steel process waste tanks, evaporator equipment, and Pyrex lines and valves for transfer of reagents and process liquids. The recovery of ionium began with the acidification of the Mallinckrodt material with nitric acid followed by centrifugation to remove solids. The supernatant liquid was treated with aluminum nitrate to form a slurry that was removed in a mixer settler vessel. The supernatant liquid underwent a series of solvent extractions followed by aqueous scrubs. The solvent-solvent extraction steps used diethyl ether and pentaether (dibutoxytetraglycol). Aqueous scrub solutions contained nitric acid, ammonium nitrate, and ammonium hydroxide. The ionium was recovered from the process as the nitrate.

PROTACTINIUM-231

The need for protactinium-231 was generated in the early 1950s, when it was selected as a surrogate for protactinium-233 in the study of the physical and chemical properties of this element. Protactinium-233, an isotope with a half-life of 27 days, was to be created in the thorium-232 $\rightarrow$ protactinium-233 $\rightarrow$ uranium-233 sequence, in the thorium breeder blankets of the breeder reactor program.

Programs at Mound involving the recovery and purification of protactinium-231 began in the early 1950s and continued intermittently to September 1979, at which time the demand for protactinium and thorium was significantly reduced. During this period, a number of separate programs were identified that separated and purified protactinium from a variety of source materials. Material processed came from the Mallinckrodt Chemical Works in St. Louis, Missouri; the AEC, Fernald Plant, Ohio; and the Cotter Corporation, Cannon City, Colorado. An attempt was made in the early 1960s to produce protactinium from irradiated thorium-230, but the materials were apparently never processed at Mound.

The first of the protactinium programs was initiated in 1954 at Mound at the request of the ORNL. The goal of the program was to isolate and purify 1 g of protactinium-231 from residues from previous uranium processing. The process chemistry research phase for this program took place in room 167 of the R Building.

By October 1954, the procedures for separating the protactinium from the residues, sometimes referred to as raffinates, had been developed on a laboratory scale (Martin 1955). Some of the experimental work may have been done on residues supplied from Fernald Plant, Ohio. Equipment was then installed in room 145 of the R Building to process raffinate residues supplied by Mallinckrodt (MCC 1955 c,e). Batches weighing 5 kg each were run with a goal to separate milligram quantities of protactinium-231 and provide data for a small process plant. The pilot plant for this program was installed in the HH Building and completed in July 1955. Operations in HH Building were suspended in March of 1956 and moved to the SW Building. Equipment salvaged from the Monex thorium refinery pilot plant was adapted to the protactinium program (Meyer 1956c).

Approximately 80 drums, containing a total of about 20,000 pounds of residue, were shipped to Mound for processing. This feed material was referred to as the Sperry cake, Sperry filter cake, or Sperry press cake. This cake contained 0.1 to 0.2 ppm of protactinium in a matrix of iron, aluminum, calcium, magnesium, cobalt, and copper. When received, it appeared very inhomogeneous, and spectrographic analysis indicated that it was significantly different in composition from samples used during research phases. No two drums were alike. Since only about half of the quantity of the material was needed for 1 g of protactinium-231, individual batches were selected from the lot.

The first drum, containing 288 pounds of material, was processed in August 1955 (McCarthy 1955f). The extractions were very time-consuming because of the analytical procedures required for each step of the process. By August 1956, 700 mg of protactinium-231 had been recovered from 43 drums of raffinate. Fifty gallons of residual solids contained another 200 mg of protactinium-231 (Eichelberger and Scott 1956b):

After the first gram was successfully separated, work proceeded on the extraction of a second gram from the balance of the raffinate residues on hand. The gram of protactinium-231 had been requested in December 1954 by the AEC, Division of Research (Walker 1954). In researching the extraction process for the remaining, less desirable supply of the Sperry cake, it was found that the original sodium chloride process could be modified (Eichelberger and Scott 1956c). Experimental 1-inch columns were set up in room 1 B of the SW Building for studying flow rates, extraction efficiencies, and other column parameters. The full-scale pilot plant was assembled in the HH Building, using 6-inch glass pipe columns. The plant was to be ready for operation by February 1957 (Eichelberger and Scott 1957), but general problems plagued the protactinium recovery and the fate of this program is not clearly known. Approximately 240 mg of protactinium-231 are known to have been recovered from the raffinates, residues, and analytical samples during the second attempt. The product was stored in approximately 140 mL of 50% diisobutyl carbinol in benzene (Eichelberger 1961 a).

In the late 1950s, Mound submitted about 22 g of thorium-230, referred to as ionium, to the MTR in Idaho for transmutation to protactinium-231 by neutron irradiation. As of March 15, 1960, the ionium underwent neutron irradiation and was stored in the MTR canal, allowing the decay of protactinium 233 (from the irradiated thorium-232 [Schuman 1960, 1961; Kirby 1960]). The ionium remained in storage for over one year before it was shipped to Mound in lead casks. Some of the capsules swelled during either irradiation or storage and were probably never opened or processed. Although this program is no longer active at Mound, 10 or 1 1 lead capsules containing irradiated ionium have been stored as resource materials.

The last protactinium program carried out at Mound took place in the 1970s. The plan was to recover protactinium from the Cotter Concentrate and is described in a companion section of this report.

Process Description

The process used at Mound for the recovery of protactinium-231 was referred to as the sodium chloride process (NAS n.d.). The recovery of protactinium began with the dissolution of the raffinate in 2 N hydrochloric acid solution that was saturated with sodium chloride and contained titanium trichloride. The solution was boiled, resulting in the formation of a precipitate that contained protactinium. The precipitate was separated from the supernatant liquid by filtration and was then digested with sodium hydroxide. The residue from the alkaline digestion step was treated with sodium hydroxide and 6 N hydrochloric acid. The resulting slurry was extracted with diisobutyl carbinal (DIBC) in Amsco kerosene. The protactinium was contained in the DIBC phase. In the next step, the DIBC phase was stripped with water containing hydrochloric acid and sulfuric acid. The protactinium was stripped from the acidic aqueous phase with DIBC. At this point in the process, the protactinium contained a solution of iron, niobium, and other metal impurities. These metals were removed in the protactinium purification step of the process.

Experiments continued on the efficiency of the protactinium-231 recovery process. After the initial project goals were achieved, the separation of the remaining raffinates posed a more difficult problem, because they had been highgraded and the remaining materials had lower protactinium concentration and higher quantities of impurities. Dissolution in nitric acid was tried, and it was found that nitric acid alone could not solubilize the protactinium; therefore, sulfuric acid was of prime importance. Efforts were taken to dissolve the raffinates directly and extract the resulting slurry. The pilot plant that was to have been assembled in the HH Building would have greatly decreased the time and labor involved with the extractions. Only the experimental column assembly in SW Building is known to have been used. In these experiments, sulfuric acid was made up with hydrochloric acid, and the raffinate was digested at fuming temperatures (about 230°C).

Several extraction steps were apparently required, because the protactinium did not always come out in the first extraction, depending on the particular composition of the raffinate. The high iron content of the raffinates posed the most difficulty. It is not known whether this process was ever fully developed and used to process the remaining 43 drums of raffinate, but it does not appear so.

RARE ISOTOPE PROGRAMS

An important research and development program at Mound involved the production, separation, and purification of rare radioactive isotopes. This program, currently known as the Rare Isotope Program, has also been known as the Separation and Purification of Special Heavy Element Isotopes and Separations Technology. The isotopes that were processed included plutonium-238, protactinium-231, thorium-229, thorium-230, thorium-228, uranium-233, uranium-234, actinium-227, polonium-209, and radium-226. This work began at Mound in the mid-1950s (Miller 1955) and continued until 1985 (Figgins 1991). The separation processes were generally carried out in the SW, SM, and R buildings.

The Rare Isotope Program can be characterized as having numerous projects that are linked to the preparation of specific isotopes. The projects were started at different times during the 25-year period that the program was active, and they varied in size and duration. The source materials for the recovery of rare isotopes also differed.

Protactinium-231 and thorium-230 were obtained from uranium-bearing ores or sludges. Uranium-234, a daughter product that "grows" as the plutonium-238 ages, was obtained from "milking" plutonium-238. Thorium-229 was obtained from milking uranium-233. The latter was produced by irradiation of thorium-232 to produce protactinium-233; the protactinium-233 then decays to uranium-233. An aged source was also needed to obtain uranium-233. Other isotopes were produced by irradiation of an appropriate target element.

Thorium-230, also known as ionium, was irradiated at the MTR in Idaho in an attempt to produce protactinium-231. These processes involved the use of only gram or milligram quantities of these isotopes each year.

The chemical processes for separating the desired isotope from its matrix were dependent on the isotope's chemical and physical properties. The chemical procedures used in processing rare isotopes included dissolution in strong acids, precipitation or coprecipitation, ion exchange, and solvent-solvent extraction. Each isotope presented a different degree of radiation hazard that, in turn, affected the scale of the process; the use of hot cells; the disposal and treatment of waste generated; and the disposal, storage, or treatment of starting or source materials.

To support laboratory- and pilot-scale isotope separation processes, analytical services such as x-ray diffraction, calorimetry, mass spectrometry, and wet chemical analysis, were performed to monitor and control the separation processes and to define the isotope purity in the finished product. The samples and sample solutions were, in most cases, returned to the isotope separation process for isotope recovery. After purification, the isotopes were shipped to the ORNL's Isotope Pool and were then sold to various clients for research purposes.

The larger and more extensive programs for plutonium, protactinium, thorium, and polonium are described in other subsections of this report. The following subsections provide summaries of the smaller programs.

Uranium-234

Plutonium-238, with a half-life of 87 years, decays by alpha emission to uranium-234. The uranium-234 was chemically separated from aged plutonium-238 at Mound over a 10-year period that began in 1962. Uranium-234 was used in conjunction with uranium-235 in fission chambers (detectors) for neutron flux measurements. The uranium-234 produced was shipped as the oxide to ORNL.

The production of uranium-234 took place in the R Building, and a satellite operation referred to as the solvent extraction system was housed in Room 1 of the SM Building. In the R Building, 13 alpha glove boxes were dedicated to the production of approximately 10 g of uranium-234 annually. The solvent extraction system continued to operate into the early 1 970s.

Process Description

The recovery process of uranium-234 from plutonium-238 (Keister et al. 1978) was divided into three major chemical separation steps (Figure 2.1 1), and each step of the process was performed in a separate glove box line. The initial step removed the bulk of the plutonium by precipitation as the oxalate. The plutonium from returned heat source materials was dissolved in nitric acid followed by precipitation with dimethyloxalate. The plutonium oxalate was calcined at 450°C and returned to storage for future processing. The filtrate containing uranium-234 was concentrated by evaporation, and nitric acid was added with continued heating to decompose the oxalate. The resulting uranyl nitrate was ready to enter the intermediate step of the process. With the addition of aluminum nitrate to the uranyl nitrate and a pH adjustment, the resulting solution was transferred to an anion exchange column and the uranium-234 was eluted first with 7 N nitric acid. Next, the plutonium was eluted with 0.35 molar nitric acid. The uranium-234 went to the final separation step and the plutonium-containing fraction was sent to plutonium recovery. In the final separation of the process, the uranyl nitrate was converted to the chloride, and the resulting solution was transferred to a Dowex anion exchange column. Uranium was separated from plutonium and neptunium by elution with varying molar concentrations of hydrochloric acid. The uranyl chloride eluent from the resin column was treated with ammonium hydroxide to form a precipitate that was filtered, washed, and dried. It was then converted to uranium oxalate. The plutonium and neptunium elements were sent to respective recovery operations (Keister et al. 1978).

In SM-1, raffinate solutions generated by ion exchange column in the plutonium recovery operations were processed by the solvent extraction system. The uranium-containing fraction was sent to R Building for recovery and purification of uranium-234, and the waste was returned to plutonium recovery operations. The uranium-234, containing eluent from the ion exchange column, was extracted with tri-n-octylphosphine oxide (TOPO). The aqueous phase was returned to plutonium recovery, and plutonium contained in the TOPO was stripped with a carbonate solution and sent to R Building for processing and uranium-234 recovery. The TOPO remained in SM-1 and was reused in the solvent extraction process.

Thorium-229

The interest in thorium-229 was as a source material for the production of francium-221, astatine-217, and other members of the 4n + 1 decay series. These isotopes were not readily available from other sources. Thorium-229 is the natural decay product of the uranium-233 that was produced via the thorium fuel cycle by the neutron irradiation of thorium-232. A kilogram of uranium-233 was received at Mound from Los Alamos National Laboratory in 1958 (Meyer 1958d). The uranium-233/thorium 229 project was initiated at Mound in 1966, and the work was performed in the hot cell facility in the SW Building. The project was initiated on a laboratory scale. During the course of this program, 1.5 kg of aged uranium-233 were processed to obtain 30 mg of thorium-229. This program was shut down temporarily for more than one year and then restarted with minor changes in process equipment and no change in process materials. This program was concluded in the mid 1970s.

Process Description

The process of separating and purifying thorium-229 from uranium-233 was based on laboratory-scale process development (Hertz et al. 1975). A small-scale separation was fully operational in the new hot cell facility of the SW Building. The processing of uranium-233 was conducted in two type A glove boxes and a fume hood interconnected on the north wall of SW-22. Additional laboratory equipment associated with this process was located on the laboratory benchtop in SW-140 and in the fume hoods in SW-132. The process began by dissolving the uranium-233 in nitric acid. The next step of the process involved the liquid-liquid extraction of the nitric acid solution with di-sec-butylphenyl phosphorate and TOPO in diethylbenzene. The thorium was then stripped from the organic phase with 0.5 molar oxalic acid followed by a second strip of the organic phase with 8 molar nitric acid. A 50 to 75-g batch averaged 20- to 30-hr separation time (Hertz et al. 1975).

COTTER CONCENTRATE

In the processing of pitchblende ore to recover uranium, a residue was produced that was determined to contain significant quantities of protactinium-231 and thorium-230. This residue became known as Cotter Concentrate. The project to recover these isotopes from the Cotter Concentrate was undertaken in the early 1970s and was terminated in the late-1970s. It was generally part of the rare isotopes programs. The residue was known by a number of different names including Cotter Concentrate, St. Louis airport cake, or simply airport cake. The resounding usefulness of this material had been established many years earlier during the ionium (thorium-230) program. In the 1940s, the Mallinckrodt Chemical Works of St. Louis, Missouri, processed a Belgian Congo pitchblende ore for the recovery of uranium. This process involved dissolution with nitric acid followed by solvent extraction using diethyl ether. The raffinate from this process was limed, and the limed cake was then stored and became known as the St. Louis residues. The residue was then purchased by a St. Louis investment group that was going to further process the residue. This group went bankrupt, and the lending institution took over ownership of the material.

In 1968, the bank sold the residue to the Cotter Corporation of Canon City, Colorado. Cotter processed the St. Louis residue to recover additional quantities of uranium and strategic metals such as cobalt, nickel, and copper. The Cotter process involved dissolution in sulfuric acid, followed by solvent extraction with di-2-ethyhexylphosphoric acid. From November 1972 until August 1973, Cotter added an additional step to the process at the request of Mound. This step involved a pH adjustment of the solvent extraction strip solution followed by filtration. This process change enhanced the concentrations of isotopes of interest to Mound (Hertz et al. 1983). This residue from the filtration process contained thorium-230, protactinium-231, and uranium. At the end of the processing of the St. Louis residues by Cotter, 1,251 drums of material were collected and remained at the Cotter mill site. In 1975, the material was redrummed and shipped to the Mound. This material became known as the Cotter Concentrate.

The Cotter Concentrate consisted of a moist solid, with a water content as high as 50% by weight. The major constituents were thorium, uranium, and iron (Draper 1987). The concentrations of thorium 232 and uranium-238 were 10,000 ppm and 60,000 ppm, respectively. Thorium-230 and protactinium-231 were present at levels of 300 ppm and 0.5 ppm, respectively. Other elements present in the Cotter Concentrate included sodium, silicon, vanadium, lead, beryllium, magnesium, and silver (Watrous 1973). Rare earth elements may have been present, but no analytical data were available regarding speciation and concentrations. In 1985, five drums of the Cotter Concentrate were sampled and analyzed for EP Toxicity metals (Marple 1985). Selium was found to be present at concentrations ranging from 0.33 to 30.0 mg/L. The general composition of the Cotter Concentrate is shown in Table 11.10. The composition varied from drum to drum.

The Cotter Concentrate was shipped to Mound in 1,251 55-gallon drums. The objectives of this program were to develop methods for the recovery of thorium-230 and protactinium-231 from the Cotter material and to design and construct a pilot plant facility that would process this material and furnish small quantities of these isotopes to the heavy elements isotopes pool at the ORNL. The concentrate acquisition, analysis, laboratory development, and pilot plant construction took place from 1970 to 1974. The pilot plant operation in SW Building ran from 1974 to 1979. During this period, 22 drums of Cotter Concentrate were processed to recover and purify 339 g of thorium-230 and 890 mg of protactinium. The purified radioisotopes protactinium-231 and thorium-230 were shipped to ORNL for sale. The drums of Cotter Concentrate were stored in Building 21, which had previously served as the silo for the thorium ores and sludges. To facilitate drum storage, the building was modified after the sludges were removed in 1975. In 1987, the entire lot of Cotter Concentrate was shipped from Mound to the NTS where it is stored as a resource material (MRC 1987).

Process Description

Three to four drums of the Cotter Concentrate were brought to the pilot plant facility located in the west section of the SW Building. Actual processing took place within the "hot cell" or "cave" that had been built to shield workers from penetrating gamma radiation. The drum contents were transferred to the acid digesters as the first step in the process. A flow sheet of the protactinium recovery process is shown in Figure 2.12 (Hertz et al. 1983). The process begins with the Cotter Concentrate being dissolved in concentrated nitric acid at 100°C, followed by dilution with water to 2 to 3 molar acidity and continued digestion**.** The solution was filtered, and the filtrate underwent a solvent-solvent extraction with di-sec-butylphenyl phosphonate (DSBPP) in carbon tetrachloride to recover uranium. The uranium was recovered from the organic phase by precipitation with ammonium hydroxide. The aqueous phase underwent a second solvent-solvent extraction with TOPO dissolved in carbon tetrachloride. Thorium was extracted from the TOPO solution into the organic phase and subsequently recovered with a 0.5 molar sulfuric acid solution. The thorium was then recovered from the sulfuric acid solution by precipitation with oxalic acid. The thorium precipitate was washed and calcined to obtain thorium oxide, which was then set aside. The protactinium was recovered from the TOPO solution with a 0.5 molar solution of oxalic acid. This oxalic acid solution containing protactinium was concentrated by evaporation in a still, and then the protactinium was precipitated as the phosphate by the addition of phosphoric acid. The protactinium-231 was then purified by treatment with a TOPO and di-2-ethylhexyl-phosphoric acid (DEHPA) mixture in a solvent extraction followed by DIBC extraction. The protactinium was stripped from the DIBC with oxalic acid and then recrystallized with sulfuric acid. Some uranium-233 was recovered from the DSBPP solvent extraction step. The residue was redrummed and returned to storage for future processing.

Table 11.10. **General Composition of Cotter Concentrate**

Element	**Concentration (Weight %)**
Sodium	> 0.1
Iron	> 0.1
Silicon	> 0.1
Vanadium	> 0.1
Molybdenum	> 0.1
Aluminum	0.05
Titanium	0.04
Copper	0.02
Zirconium	0.02
Nickel	0.03
Beryllium	< 0.005
Manganese	0.007
Magnesium	< 0.005
Silver	<0.005
Uranium oxide	21,740 g/drum
Thorium-232	99.9 g/drum
Protactinium-231	0.060 g/drum
Thorium-230	11.1 g/drum
Average moisture content	47% (wt/wt)

Data from Watrous 1973; Rawlings 1951

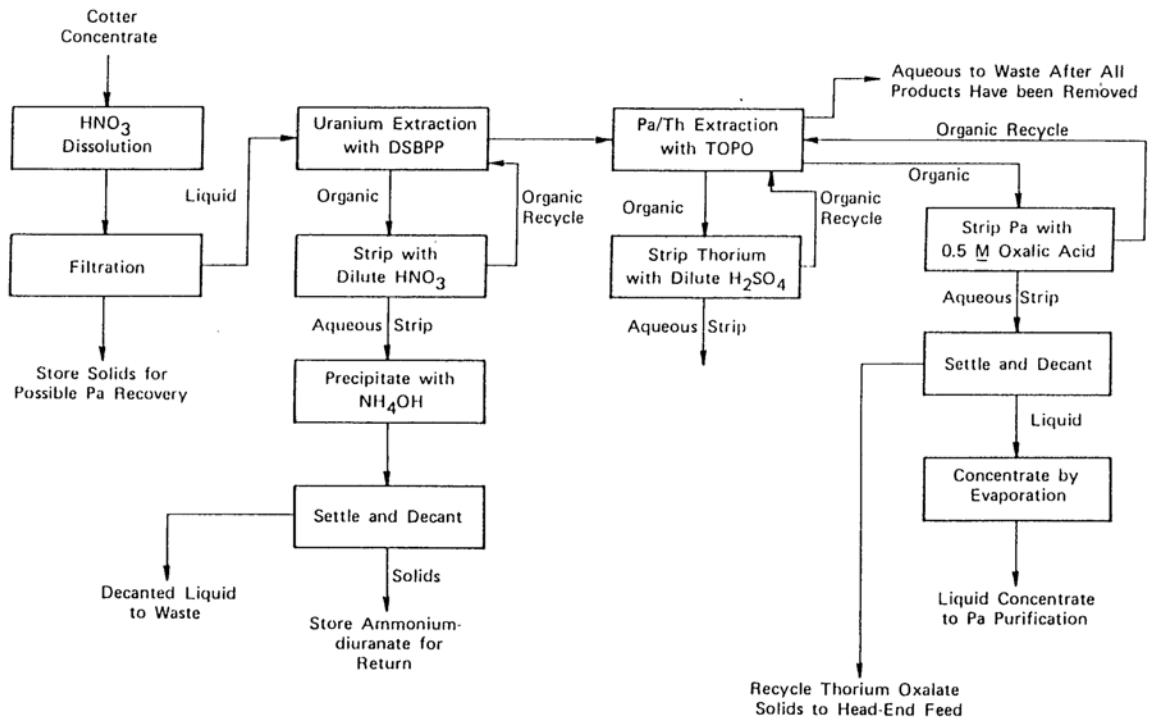

Figure 2.12. Recovery of protactinium-231 and thorium-230 from Cotter Concentrate (Hertz et al. 1983).

Appendix A
Physical Characterizations

Plutonium-238

Half-Life:
Physical: 87.7 years.
Biological: Bone, 100 years; liver, 40 years.
Sources: Minor constituent of nuclear weapons fallout *(*3.5% Pu-239/240 by activity). Produced for power sources (SNAP) by Np-237 (n, β) Pu-238.
Principal Modes and Energies of Decay (MeV): α 5.50 (71%), 5.46 (29%); γ 0.039 (11%).
Special Chemical Characteristics: Generally forms insoluble fluorides, hydroxides, and oxides. Solubility in water dependent on redox, pH, and organic ligands present.
Biological Characteristics: Deposits mainly on endosteal surfaces of mineral bone.
Principal Human Metabolic and Dosimetric Parameters:
*f*1 = 1 x 10^-4 (compounds other than oxides and hydroxides), *f* 1= 1 x 10^-5 (oxides and hydroxides).
ALI *(μCi)* = 8.1 (oral, *f1* = 10^-4*),*
= 8.1 *x* 10^1 (oral, *f*1 = 10^-5),
= 5.4 *x* 10^-3 (inhalation, IC-W, *f*1 = 10^-4*),*

Inhalation Class (IC): Y (oxides and hydroxides), W (all other compounds).
DAC (μCi/cm3) = 2.4 x 10^-12 (IC-W)
= 8.1 x 10-12 (IC-Y).
Systemic Transfer Fractions: Skeleton *(0.45)* and liver *(0.45).*
Additional Dosimetric Considerations (rem/μCi): Bone surfaces *(6.7* oral *f1 =* 10^-4; *6.7 x* 10^-1 oral *fl* = 10^-5; *8.1 x* 10^3 inhalation, IC-W; *3.1 x* 10^3 inhalation, IC-Y); liver *(1.5* oral f1 = 10^-4; *1.5 x* 10^-1 oral *f1 = 10^-5; 1.8 x* 10^3 inhalation, *IC-W; 6.7 x* 10^2 inhalation, IC-Y); lungs (1.2 x 10^3 inhalation, IC-Y).

Plutonium-239

Half-Life:
Physical: 2.41 x 10^4 years.
Biological: See Pu-238.
Sources: Produced in thermal reactors by neutron irradiation of U-238. Used in nuclear weapons and as fuel for fast reactors. Approximately *325* kCi of Pu-239/240 have been distributed worldwide from nuclear weapons testing (Hardy *et al., 1973).*
Principal Modes and Energies of Decay (MeV): a 5.10 (11%), 5.14 (15%), 5.15 (73%); Lα x-ray 0.014 (1.5%), x-ray 0.014 (10%), Lβ 0.018 (0.1%).
Special Chemical Characteristics and Biological Characteristics: See Pu-238.
Principal Human Metabolic and Dosimetric Parameters:
*f*1 = 1 x 10^-4 (compounds other than oxides.and hydroxides).
f1 = 1 x 10^-5 (oxides and hydroxides).
ALI *(μCi) = 5.4* (oral, *f1 = 10^-4),*
= *5.4 x* 10^1 (oral, f1 = 10^-*5),*
= *5.4 x* 10^-3 (inhalation, IC-W, *f*1 = 10^-*4,*
= *1.3 x* 10^-2 (inhalation, IC-Y, *f*1 = *10^-5).*
Inhalation Class (IC): Y (oxides and hydroxides),
W (all other compounds).
DAC (μCi/cm3) = 2.2 x 10^-12 (IC-W)
= 5.4 x 10-12 (IC-Y).
Systemic Retention Fractions: See Pu-238.
Additional Dosimetric Considerations (rem/μCi): Bone surfaces *(7.8* oral *f1* = 10^-4; 7.8 *x* 10^-1 oral *f1* = 10^-5; 9.3 *x* 10^3 inhalation, IC-W; *3.5 x* 10^3 inhalation, IC-Y); liver *(*1.6 oral, f1 = 10^-4; 1.6 *x* 10^-1 oral, *f*1 =10^-5; 2.0 *x* 10^3
inhalation, IC-W; *7.8 x* 10^-2 inhalation, IC-Y); lungs (1.2 x 10^3 inhalation, IC-Y).

Polonium-210

Half-Life:
Physical: 138.4 days.
Biological: Whole body, 50 days.
Sources: Naturally occurring from uranium decay chain and 209Bi(n, γ)210Bi beta minus 210Po
Principal Modes and Energies of Decay (MeV): α 5.3 (100%).
Special Chemical Characteristics: Tendency for radiocolloid formation.
Range of Normal Intake: 1-5 pCi/day.
Average Natural Tissue and/or Body Burden: 160-800 pCi, mean 360 pCi
Principal Human Metabolic and Dosimetric Parameters:
f_l = *0.1.*
ALI (μCi) = 2.7 (oral),
= 5.4 x 10^-1 (inhalation, IC-D or W)

Inhalation Class (IC): W (oxides, hydroxides, and nitrates),
D (all other compounds).
DAC (μCi/m3) = 2.7 *x* 10^-10 (IC-D or -W).
Systemic Transfer Fractions: Liver (0.1), kidney (0.1), spleen (0.1), and all other tissues and organs *(0.7).*
Retention in the body given by the expression *R(t)* = exp(- *0.693t/50),* where *t* is in days.
Additional Dosimetric Considerations (rem/μCi): Kidneys *(9.3* oral; 4.4 x 10^1 inhalation, IC-D; 1.4 x 10^1 inhalation, IC-W); spleen *(*1.6 *x* 10^1 oral; 8.1 *x* 10^1 inhalation, IC-D; 2.5 *x* 10^1 inhalation, IC-W). Dose rate from natural body burden is 50 mrem/year to bone surfaces (assumes equilibrium with Pb-210). Builds in from Pb-210, especially in mineral bone.
Special Ecological Aspects: Air → lichen → reindeer → human pathway results in abnormally high body burdens, as do high fish and shellfish diets; also present in tobacco smoke.

Radium-226

Half-Life:
Physical: 1599 years.
Biological: Whole-body retention is best represented by a complex exponential plus power function equation (see ICRP, 1973a).
Sources: Naturally occurring from 238U decay chain.
Principal Modes and Energies of Decay (MeV): a 4.78 (94.4%), 4.60 (5.6%); y 0.186 (3.3%).
Biological Characteristics: Deposits in bone with nonuniform distribution. Following decay of 226Ra in bone, ~70% of 222Rn diffuses to the blood and is exhaled.
Normal Intake: 2.3 x 10^-12 g/day (2.3 pCi 226Ra/day).
Average Natural Tissue and/or Body Burden: 3.1 x 10^-11 g (~31 pCi).
Principal Human Metabolic and Dosimetric Parameters:
f_l = 0.2.
ALI (μ Ci) = 1.9 (oral, for limiting nonstochastic effects to bone surfaces),
= 5.4 x 10^-1 (inhalation, see above limitations).
Inhalation Class (IC): W.
DAC (μ Ci/cm3) = 2.7 x 10^-10.
Systemic Transfer Fractions and Retention Expressions: See ICRP (1973a).
Additional Dosimetric Considerations (rem/ μ Ci): Bone surfaces (2.5 x 10^1 oral, 2.8 x 10^1 inhalation), lungs (5.9 x 10^1 inhalation). (Dose commitments based on 226Ra + daughters assuming ~30% 222Rn retention.)

Radium-228

Half-Life
Physical: 5.8 years.
Biological: See 226Ra.
Sources: Occurs naturally as a decay product of '-'-aTh.
Biological Characteristics: See 226Ra. No loss of 220Rn occurs because of its short half-life (56 sec).
Normal Intake: No systematic measurements. Believed to be ¼ to ½ that of 226Ra
Normal Body Burden: Believed to be ¼ to ½ that of 226Ra.
Principal Metabolic Parameters: See 226Ra.

Thorium-230

Half-Life:
Physical: 8.0 x 10^4 years.
Biological: See Th-232.

Specific Activity: 0.154 Ci/g natTh.
Sources: Naturally occurring member of the U-238 series.
Principal Modes and Energies of Decay (MeV): a 4.688 (76. 3%), 4.621 (23.4%), γ Ra L X-rays.
Special Chemical Characteristics: See Th-232.
Biological Characteristics: See Th-232.

Average Natural Tissue and/or Body Burden: ~ 3 pCi total body (Wrenn *et al.,* 1981).

Principal Human Metabolic and Dosimetric Parameters:
f_1 = 2 x 10^-4.
ALI (μCi) = 2.7 (oral, for limiting nonstochastic effects to bone surfaces),
= 5.4 x 10-3 (inhalation, IC-W, see above limitation),
= 1.6 x 10^-2 (inhalation, IC-Y, see above limitation).
Inhalation Class (IC): Y (oxides and hydroxides),
W (all other compounds).
DAC (μCi/Cm3) = 2.7 x 10^-12 (IC-W),
= 5.4 x 10^-12 (IC-Y).
Systemic Transfer Fractions: See Th-232.
Additional Dosimetric Considerations (rem/μCi): Bone surfaces (1.3 x 10^1 oral, 3.2 x 10^3 inhalation, IC-Y); lungs (1.1 x 10^3 inhalation, IC-Y).
Special Ecological Aspects: Th-230 is found in elevated concentrations in uranium mill tailings and in certain phosphate fertilizers.

Thorium-232

Half-Life:
Physical: 1.41 x 10^10 years.
Biological: Bone, 8 x 10^3days; liver and remaining tissues, 700 days.
Specific Activity: 1.1 *x* 10^5 pCi/g Th.
Sources: Naturally occurring.
Principal Modes and Energies of Decay (MeV): α 4.01 (77%), 3.96 (23%), γ Ra L X-rays.
Special Chemical Characteristics: Hydroxides and oxides are insoluble; nitrates, sulfates, chlorides, and perchloride salts are readily soluble.
Biological Characteristics: Tendency to concentrate on bone surfaces.
Normal Intake: ~ 5 x 10^-7 g/day (Linsalata *et al.,* 1986b).
Average Natural Tissue and/or Body Burden: ~ 12 μg or 1.3 pCi, total body (Wrenn *et al.,* 1981).

Principal Human Metabolic and Dosimetric Parameters:
f_1 = 2 x 10^-4.
ALI (μCi) = 8.1 x 10^-1 (oral, for limiting nonstochastic effects to bone surfaces),
= 1.1 x 10^-3 (inhalation; IC-W, see above limitation),
= 2.7 x 10^-3 (inhalation, IC-Y, see above limitation).
Inhalation Class (IC): Y (oxides and hydroxides);
W (all other compounds).

DAC (μCi/Cm3) = 5.4 x 10^-13 (IC-W);
= 1.1 x 10^-12 (IC-Y).
Systemic Transfer Fractions: Bone (0.7), liver (0.04), and all other tissues and organs (0.16).
Additional Dosimetric Considerations (rem/ μCi): Bone surfaces (7.0 x 10^1 oral, 1.9 x 10^4 inhalation, IC-Y); lungs (3.5 x 10^3 inhalation, IC-Y).
Special Ecological Aspects: Thorium-bearing minerals result in anomalously high natural radiation levels in certain areas in Brazil and India. Depending on the type of rock, the concentration of Th-232 in the earth's crust is 2-20 μg/g and about 10 μg/g in normal soils.

Tritium (3H)

Half-Life:
Physical: 12.3 years.
Biological: ~10 days (range: 4-18) total body for HTO.
Natural Levels: 6-24 pCi/liter of H2O in surface prior to advent of bomb testing.
Sources: Cosmic-ray interactions with N and 0; ternary fission; spallation from cosmic rays, Li-6 (n,α) H-3. World inventory of naturally produced tritium is approximately 26 MCi. Approximately 3600 MCi have been added to the Northern Hemisphere from weapons testing.
Principal Modes and Energies of Decay (MeV): β - 0.018.
Special Chemical and Biological Characteristics: Not selectively concentrated in any organ. Metabolized as H20.
Principal Organ: Total body.
Amount of Element in Body: 7 x 10^3 g.
Principal Human Metabolic anal Dosimetric Parameters:
*f*1 = 1.0.
ALI (μCi) = 8.1 x 10^4 (HTO)
DAC (μCi/cm3) = 2.2 x 10^-7 (HTO).
Retention in body described by single exponential function: R(t) = exp(-0.693t/10), where t is the elapsed time in days.
Additional Dosimetric Considerations (rem/μCi): Total body (6.3 x 10^-5 oral or inhalation). Annual dose equivalent rate from natural H-3 ~ 10^-3 mrem/year and ~ 1.9 mrem/year from fallout H-3 (Northern Hemisphere).
Other: Production rates, 6.6 MCi/megaton of thermonuclear bombs; in light-water reactors, produced primarily by ternary fission and secondarily by neutron interactions with light elements. 5-10 Ci/MWe year for PWR; 0.3-0.9 CI/Mwe year for BWR.