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STRONTIUM-90 HEAT SOURCES

Compiled and Edited by
Roberta Shor
Robert H. Lafferty, Jr.
P. S. Baker



A strontium-90 powered light buoy

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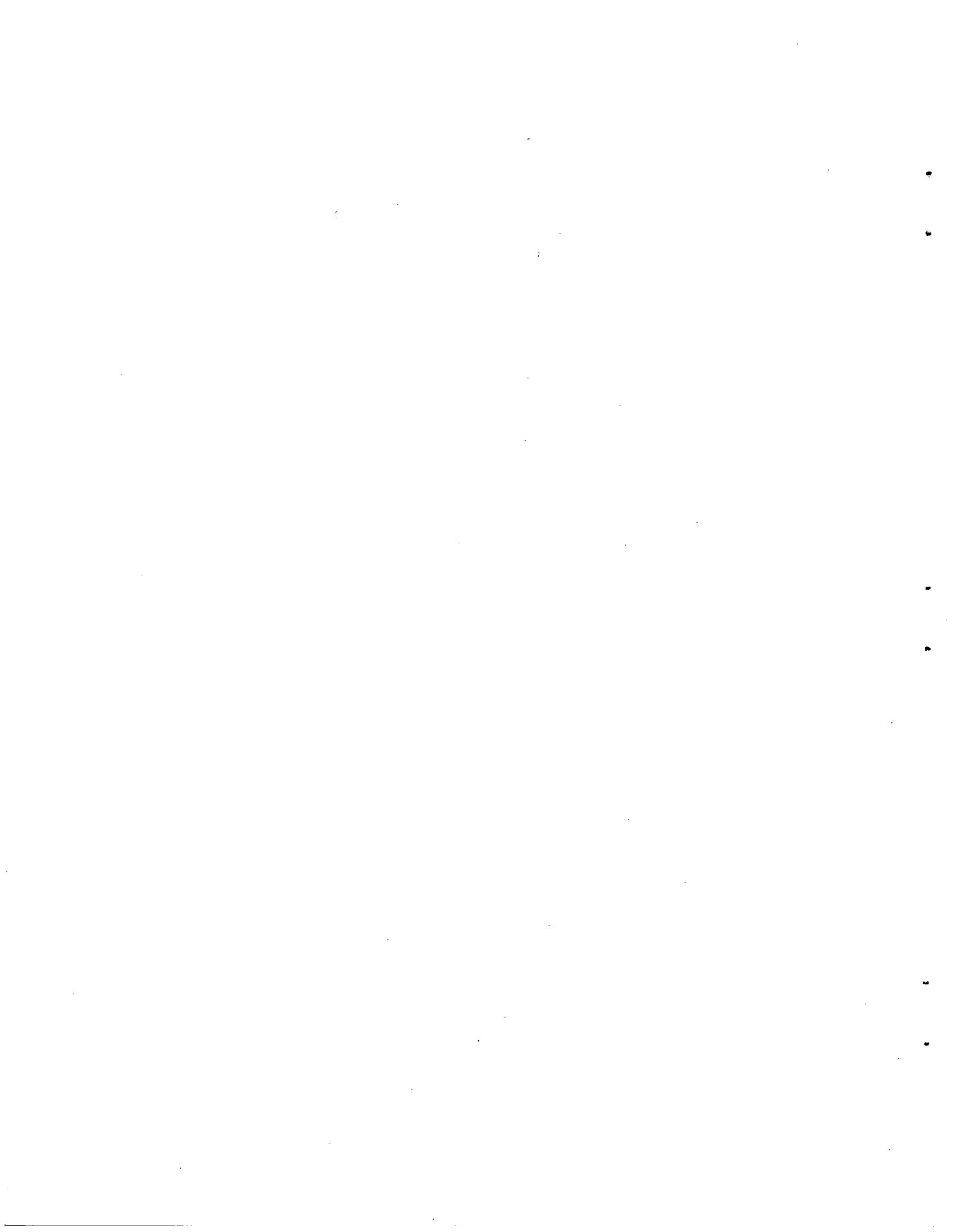
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STRONTIUM-90 HEAT SOURCES

Compiled and Edited by
Roberta Shor, Robert H. Lafferty, Jr., and P. S. Baker

MAY 1971

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee
operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION



FOREWORD

This report deals primarily with the large-scale production operations carried out from 1958 to July 1967 by Oak Ridge National Laboratory, the Hanford Works, and the Martin Company for the preparation of strontium-90 heat sources. Some work done between 1948 and 1958 is summarized very briefly to provide a background for these operations. Also—a few later developments (from July 1967 to May 1970) have been included where possible.

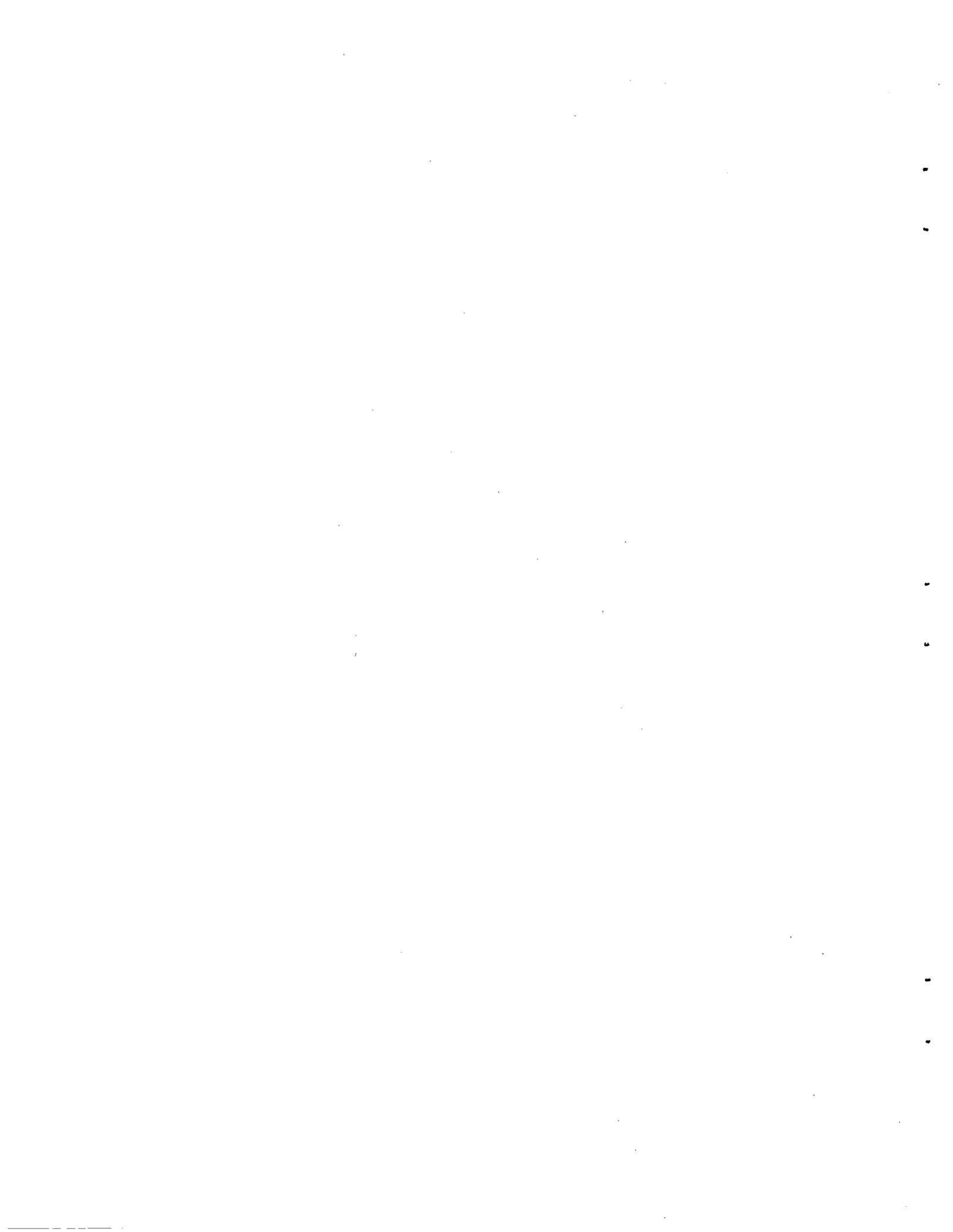
In writing this report, the editors have compiled summaries from experienced workers in the various phases of strontium fuel formation. We wish to acknowledge the original authors here. C. L. Ottinger wrote sections describing the Fission Products Development Laboratory building and facilities, the preparation of SrTiO_3 and SrO , the ^{85}Kr leak test of welded capsules, and the technique of cold-press and sinter formation of SrTiO_3 pellets.

D. E. Horner reviewed the strontium separation processes carried out at Oak Ridge National Laboratory and at the Hanford Works. The numerous original authors in Horner's review article are referred to in Chapter 2.

R. D. Seagren made many helpful suggestions about the section on transport of radioactive strontium and S. A. Reynolds summarized noncalorimetric analytical procedures. The calorimetric procedures are the work of J. C. Posey, T. A. Butler, P. S. Baker, and W. D. Box. R. E. McHenry contributed the major portion of the chapter on fuel fabrication including the development of the hot-press procedure. R. G. Donnelly wrote the section about capsule welding and E. E. Ketchen reported the measurement of thermal conductivity. Summaries from E. E. Pierce and E. Lamb describe the source examination. The properties of strontium fuel forms were compiled by S. J. Rimshaw and E. E. Ketchen.

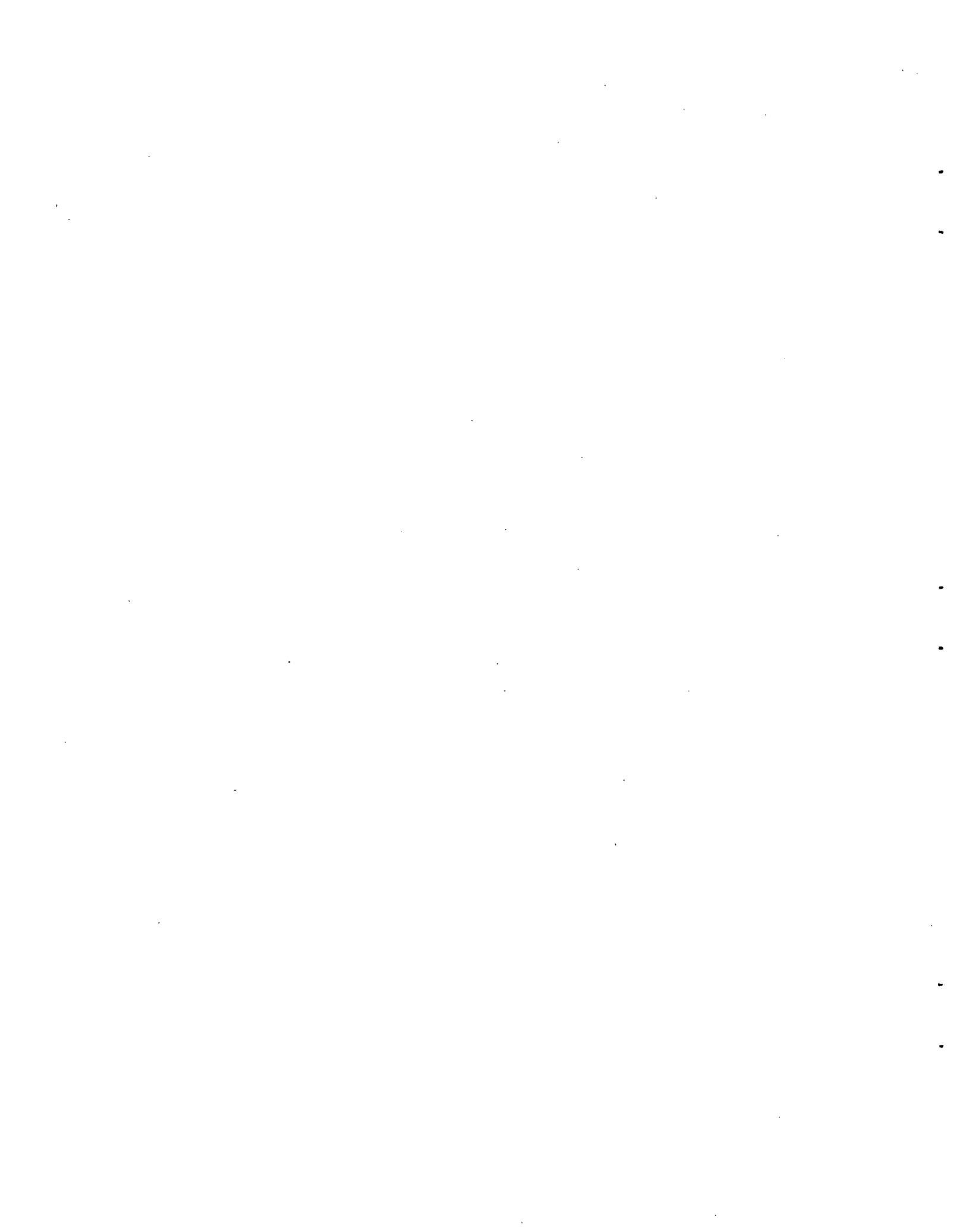
We thank the editors of *Chemical Engineering Progress Symposium Series* published by the American Institute of Chemical Engineers for permission to publish the material in Appendixes F and G.

We are also indebted to A. F. Rupp and J. H. Gillette of Oak Ridge National Laboratory; R. L. Moore and H. H. Van Tuyl of Battelle-Northwest; and W. G. Ruehle of Aerojet-General Corporation for reviewing sections of the report and giving us their helpful criticism.



GLOSSARY OF TERMS

AGN	Formerly Aerojet General Nucleonics Co.; now Aerojet Nuclear Systems Co.
BAMBP	4-sec-butyl-2(α -methylbenzyl)phenol
BNWL	Battelle Northwest Laboratories
Darex; Purex; Redox	Solvent extraction processes for recovery of U and Pu from spent reactor fuels
Decalso	Inorganic ion exchange resin
DOT	Department of Transportation
DOWEX 50W X 12	Organic ion exchange resin
DTPA	diethylenetriaminepentaacetic acid
D2EHPA	di(2-ethylhexyl)phosphoric acid
EDTA	ethylenediaminetetraacetic acid
FPDL	Fission Products Development Laboratory
FTW	formaldehyde treated waste
Hanford or HAPO	Hanford Atomic Products Operation, General Electric Co. (before 1965)
HAPO IA, HAPO II	Shipping casks
HDEHP = D2EHPA	di(2-ethylhexyl)phosphoric acid
HEDTA	(N-hydroxyethyl)ethylenediaminetriacetic acid
kCi	Kilocurie
LCG	Low Cost Generator (Martin Marietta Co. Nuclear Division)
Martin	Martin Marietta Co. Nuclear Division
MeV	Million electron volts
Mitsubishi	Mitsubishi Atomic Power Industries, Inc., Omiya, Japan
MPC	Maximum permissible concentration
NaD2EHP	sodium di(2-ethylhexyl)phosphate
Na ₅ DTPA	diethylenetriaminepentasodium acetate
NUMEC	Nuclear Materials and Equipment Corp., Apollo, Pa.
1WW	aqueous waste from solvent extraction uranium-plutonium recovery process that contains fission products
ORNL	Oak Ridge National Laboratory
PAW	Purex low-acid waste
RCA	Radio Corporation of America
RIPPLE	Radioisotope Powered Prolonged Life Equipment
RTG	Radioisotopic Thermoelectric Generator
Sentinel	Isotopes Inc. radioisotope thermoelectric generator
SNAP	Systems for Nuclear Auxiliary Power
STW	sugar treated waste
TBP	tributyl phosphate
TIG	Tungsten inert gas (welding method)
TRACS	Thermoelectric Radioisotope Conversion System
TZM	Refractory alloy; 99+% Mo, 0.5% Ti, 0.1% Zr
UKAEA	United Kingdom Atomic Energy Authority
URIPS	Underwater Radioisotope Power Source
W	Watt



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Strontium-90 Heat Sources

Compiled and Edited by

Roberta Shor, Robert H. Lafferty, Jr., and P. S. Baker

Abstract

Strontium-90 heat source production is described. This includes purification, transportation, preparation of fuel forms, analytical methods, densification, encapsulation, source testing, and examination of used sources. Details of source preparation, encapsulation, and testing are given.

1. INTRODUCTION

Compact electrical generators powered by heat from radioisotopes have been under development in the United States since the early 1950's for space, marine, and terrestrial uses. Essentially all the generators developed for marine and terrestrial uses have been powered by ^{90}Sr . This report summarizes the development work done by Oak Ridge National Laboratory (ORNL), Hanford Atomic Products Operation,* and Martin Company, Nuclear Division, which led to the production of ^{90}Sr heat sources for use in the generators.

Although the functions of the three contractors sometimes overlapped, work was generally divided as follows:

ORNL:developmental work on separation processes for ^{90}Sr and on preparation methods for radioactive compounds; preparation, fabrication, and encapsulation of the chosen chemical form of ^{90}Sr for the generator; and testing of the finished capsules.

Hanford:developmental work on separation methods for ^{90}Sr , scaling up the processes for production operation, and separating and purifying most of the ^{90}Sr used in the program.

Martin:design, construction, and testing of the generators for weather stations, buoys, lighthouses, and undersea beacons,^{1,2} and Quehanna pilot plant demonstration of fuel forming and encapsulation processes for the SNAP-7 series and for space applications.

The work that Martin did on generator development is outside the scope of this report but is described in the reports in the bibliography at the end of this chapter.

The report deals mainly with the large-scale production operations from 1958 to July 1967 but also summarizes very briefly work done from 1948 to 1958. Most of the material deals with work that was previously unreported or was described in reports having limited distribution. In the interest of continuity and coherence, however, certain portions are included which have been adequately reported elsewhere: for example, shipping, some aspects of the separation of fission products, and physical properties of the fuel forms. The development, present practices, and in some cases future possibilities of the steps involved in the preparation of strontium fuel forms for heat sources are discussed, including

1. separation of radiochemically pure ^{90}Sr from the reactor wastes in a chemical form suitable for further processing;
2. conversion of the separated ^{90}Sr to a chemical form that is suitable for a heat source,
3. fabrication of the separated chemical compound into pellets having a suitable density and purity for a heat source,
4. encapsulation of the pellets in a metal container that is resistant to corrosion by the source compound and by the environment in which it is to be used.

*The Hanford Atomic Products Operation of the General Electric Co. was divided in 1965 and 1966 among a number of contractors. For simplicity and convenience in this report, all the work done at Hanford is referred to as Hanford work. No effort has been made to identify the particular contractor responsible for the later work. However, the reports cited in the references and bibliographies are so identified.

Generator design is excluded, except as it relates to the properties of the fuel forms required in the generators.

The report also contains a brief history of the first large-scale production of ^{90}Sr for the Weather Bureau heat source, details of which are given in Appendixes F, G, H, and I

SELECTION OF ^{90}Sr AS HEAT SOURCE

Several qualities make ^{90}Sr attractive as a fuel for heat sources:

1. It is available in large amounts in the wastes resulting from the processing of spent reactor fuels.
2. Procedures for recovering ^{90}Sr of high radiochemical purity with low inert-contaminant levels have been developed.
3. Its half-life is 28.5 years.
4. Fuel forms can be made from fission-product (FP) wastes with adequate power density for applications in power-generator heat sources. Pure ^{90}Sr has a specific activity of 139 Ci/g and a specific power of 0.0067 W/Ci; however, fission-product strontium contains only 55 at. % ^{90}Sr . Achievable power densities are limited by the age of the FP ^{90}Sr , the amounts of inert contaminants present, and the deviations of the fuel material from theoretical physical density.

Several chemical forms of ^{90}Sr fuel were considered — SrTiO_3 , SrF_2 , SrO , Sr , and Sr_2TiO_4 . The properties that outweighed all others in the selection process were the power density, thermal stability, and solubility — particularly in sea water. The compound offering the most desirable combination of properties was SrTiO_3 , and it has been used in fabricating most of the ^{90}Sr heat sources to date.^{3,4} It is the least soluble in water and its power density is sufficient to meet generator design needs for present applications, being 0.7 to 0.9 W/cm^3 , depending on the method of preparation. The only other compound that has been used as a heat source is SrO . Its power density is $\sim 1.6 \text{ W}/\text{cm}^3$, but it is moderately soluble in water. Both compounds can be prepared by simple procedures adaptable to manipulator cell operations. Handling and storage problems are simpler for SrTiO_3 than for SrO , but decontamination of the cells where SrTiO_3 is handled is more difficult.

OPERATION OF RADIOISOTOPE-POWERED ELECTRICAL GENERATORS

Long life and minimum maintenance have been the major objectives of the development of radioisotopic

power sources for marine and terrestrial uses and for the United States space program. The power provided by suitable radioisotope sources can be as high as several watts per cubic centimeter of source material, with a useful source life of tens of years. The kinetic energy of the electromagnetic or charged-particle products of radioisotope decay either is transformed directly into electricity or is transformed indirectly through a preliminary conversion to heat. Most of the devices developed to date use a thermoelectric generator to convert the heat to electricity.

Radioisotope-powered thermoelectric conversion systems have demonstrated reliability and maintenance-free lives of $>40,000$ hr and power levels up to 100 W(e). Their initial capital cost per electrical watt is high, but their cost on a watt-hour basis compares favorably with that for other energy sources for applications in remote and inaccessible areas. Even in relatively accessible regions, the cost of transporting alternative energy supplies can be of considerable significance, and in inaccessible regions, such as the North or South Pole, desert, or jungle, the additional costs of transporting materials and of servicing the systems increase tremendously.

These thermoelectric devices convert heat from the decay of the radioisotope to electricity through the use of thermocouples or thermoelements. Modern thermoelectric generators employ semiconductor materials made into *n*- and *p*-type legs. The legs are cylinders bonded to hot and cold "shoes." The heat from the isotope source (^{90}Sr) flows into the hot shoe and moves up through each element to the cold shoe and into the cold reservoir. The difference in potential across the *p* and *n* elements is proportional to the difference in temperature between the hot and cold reservoirs. The maximum hot temperature and the efficiency of the generators depend on the material used for the thermoelements. The generators now in operation use lead telluride elements in an inert-gas atmosphere and operate at temperatures up to $\sim 530^\circ\text{C}$. The *p* and *n* elements are made from lead telluride having small differences in composition.¹ A 5% efficiency in converting heat to electrical energy is the highest achieved in the generators built in the SNAP-7 (Systems for Nuclear Auxiliary Power) program. The expected maximum efficiency for terrestrial application is 10% if GeSi and PbTe thermoelements in a cascade arrangement operate at 750°C with 130°C cold junctions.⁵

In August 1961 the first ^{90}Sr -powered automatic weather station was placed on Axel-Heiberg Island in Canada, 700 miles from the North Pole. The unmanned

Table 1.1. Status of ^{90}Sr -powered thermoelectric generators (1970)^{1,2,4,6,7,8}

Name	kCi	Power, W		Date installed	Buyer	Use	Place	Contractors	Comments
		Thermal	Electric						
Sentry (Weather Bureau)	17.5	110	5	1961	Weather Bureau	Weather station	Axel-Heiberg Island	Hanford, ORNL, Martin	Operated 3 yr; no ^{90}Sr failure
SNAP 7A	41	250	10	1962	U.S. Coast Guard	Buoy light	Curtis Bay, Md.	Hanford, ORNL, Martin	Gradual power loss greater than design predicted; disassembled April 1969
SNAP 7B	220	1400	60	1964	U.S. Coast Guard	Lighthouse	Baltimore, Md.	Hanford, Martin	Replaced 7F in 1965; still operating
SNAP 7C	41	250	10	1962	U.S. Navy	Weather station	Antarctic Mainland	Hanford, ORNL, Martin	Dismantled Nov. 1967
SNAP 7D	225	1400	60	1964	U.S. Navy	Barge weather station	Gulf of Mexico	Hanford, ORNL, Martin	Still operating
SNAP 7E	30	180	7.5	1964	U.S. Navy	Sonic beacon	Undersea near Fla.	Hanford, ORNL, Martin	Failure of pinger 1968
SNAP 7F	225	1400	60	1965	Phillips Petroleum and AEC	Buoy warning and control station	Gulf of Mexico	Hanford, Martin	Shield failed; sea water ruined thermoelements
URIPS (P1-1002) (P1-1001A)	7	45	1	1966	U.S. Navy	Deep sea	Port Hueneme, Calif.	Hanford, ORNL, AGN	Still operating at stated power
NUMEC (2)	30	200	7	1966	Israel	Undersea or surface		Hanford, ORNL, NUMEC	
U1-1001	7	45	1	1967	Jt. venture: AGN-BMI-Bendix	Geodetic bench mark	Pacific Ocean near Anacapa Island	Hanford, ORNL, AGN	First license for deep-ocean non-recovery use
NUMEC 100 MA (2) milli TRACS	2.7	2.2	0.1	1967	U.S. Navy	Deep sea	Port Hueneme, Calif.	Hanford, ORNL, NUMEC	
NUMEC TRACS-25A	118	440	20	1968	U.S. Navy	Tidal wave warning system	Bahamas	Hanford, ORNL, NUMEC	
RIPPLE III	4.6		0.7	1967	U.S. Navy (loan)	Undersea test	Port Hueneme, Calif.	Hanford, ORNL, UKAERE	
RIPPLE IV	15	100	2			Submarine cable repeater		Hanford, ORNL, UKAEA, and Submarine Cables Ltd.	
RIPPLE IX	30	200	4			Aircraft ground radio beacon		Hanford, ORNL, UKAEA, and Submarine Cables Ltd.	

Table 1.1 (continued)

Name	kCi	Power, W		Date installed	Buyer	Use	Place	Contractors	Comments
		Thermal	Electric						
MW-3000A	20		2.5	1967	U.S. Navy	Deep sea		Hanford, ORNL, Martin	
SNAP 21 (5 made)	40	200	10	1969	U.S. Navy	Undersea	Offshore San Clemente Is., Calif.	Hanford, ORNL, 3M	
LCG 25A	110	740	25	1966	U.S. Navy	Oceanographic instruments	Fairway Rock, Alaska	Hanford, ORNL, Martin	
LCG 25B	110	740	25	1967	U.S. Navy		Port Hueneme, Calif.		
SNAP 23A	200	1200	60	1969*	U.S. Navy	Terrestrial		Hanford, ORNL, Westinghouse	
Sentinel 25E (11,12,13)	106 each	700	25	Mar. 1969*	U.S. Navy	Oceanographic data stations		Hanford, ORNL, Isotopes, Inc.	
Sentinal 25D (8,9,10)	106 each	700	25	June 1969*	U.S. Navy	Terrestrial and to 1000 ft undersea buoys		Hanford, ORNL, Isotopes, Inc.	
LCG 25C1	110	740	25	1968	NASA	Interrogation, recording, and location system	Puerto Rico coast sub- surface buoy	Hanford, ORNL, Martin	Failure in auxil- iary equipment; reinstalled
P1-1003 -1004 -1005 -1006	8	53	1.2	1970	U.S. Navy	Deep ocean	Port Hueneme, Calif.	Hanford, ORNL, AGN	Qualified for 35- thousand-ft ocean depth

*Estimated date in late 1968.

station, designed to collect and relay data on temperature, wind velocity, and barometric pressure, was part of a joint project of the United States and Canadian weather bureaus. It operated successfully until August 1964 (Ref. 2).

The six generators of the SNAP-7 series (Table 1.1) were designed after demonstration of the Weather Bureau station and were similar to it and to each other in most respects. The sources for these generators were fabricated¹ by ORNL and Martin from ~1 MCi of ⁹⁰Sr that had been separated at Hanford in 1961.

The promising experience with the SNAP-7 series led to an expansion in AEC's plans for ⁹⁰Sr devices ranging in power from 0.1 to 10 kW(e). The technology developed in the earlier programs made it possible to design a more flexible generator system. The isotopic power program is now organized to provide power systems at a number of discrete power levels for applications of a more general nature than heretofore. For example, the SNAP-21 [10- to 20-W(e) systems] generator program may be used for various deep sea applications, navigational aids, seismological stations, oceanographic research, or hydrophone amplifiers. SNAP-23 [25- to 100-W(e)] is planned for surface applications, such as offshore navigational aids, unmanned seismological stations, microwave repeater stations, aircraft landing systems, and remote communications systems.^{2,6}

The United Kingdom Atomic Energy Authority (UKAEA) is designing and building thermoelectric generators using <100-W ⁹⁰SrTiO₃ for applications similar to those of the USAEC generators. Four to six devices have been completed in the RIPPLE (Radio-Isotope Powered Prolonged Life Equipment) program and several more are in various stages of design or construction (Table 1.1). Isotopes,* Aerojet-General, and NUMEC are now marketing commercial generators using ⁹⁰Sr heat sources, and the USAEC is supplying the sources for them as well as for the RIPPLE generators. Fuel forms are being fabricated at ORNL from about 8 MCi of ⁹⁰Sr that was separated by Hanford between 1961 and 1965 (Appendix A).

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*In 1968 the Martin Company sold its nuclear activities to Teledyne, Inc., whose subsidiary, Isotopes, Timonium, Maryland, is responsible for the Martin Company contracts and programs in this area.

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2. SEPARATION PROCESSES

Strontium-90 is one of five long-lived products formed in relatively high yield in reactors from the fission of uranium and recovered separately. The other abundant fission products having half-lives greater than 6 months are ^{99}Tc , ^{137}Cs , ^{144}Ce , and ^{147}Pm . An attractive goal, envisioned for many years, has been an integrated separations process that would separate each fission product in turn and result in a reduced amount of radioactive waste. The goal remains incompletely realized, but most of these fission products now can be purified in megacurie quantity.

At ORNL a small radioisotopes development group began separating fission products from reactor waste with an ion-exchange system¹ in 1948-50. Radiation degradation of the resins and high volume of wastes caused this method to be replaced with precipitation processes. At that time, ^{137}Cs purification received the primary emphasis because its long half-life and energetic gamma emission make it competitive with ^{60}Co . The process involving coprecipitation of cesium with ammonium alum was developed in the early 1950's and is one of the methods currently used for the production of ^{137}Cs .

The first flowsheets tested in 1957 for separation of multiple fission products consisted entirely of precipitation processes^{2,3} (See also Appendixes C, D, and E). The mainstream processes separated the fission products into four groups by a series of precipitation reactions at controlled pH and by the alum co-crystallization process for cesium: Fe, ^{106}Ru , and ^{99}Tc ; ^{90}Sr ; rare earths; and ^{137}Cs . Concentrated fractions were further purified by precipitations or crystallizations and by the chromatographic separation of the trivalent rare earths on ion-exchange columns after the major contributors of radiation energy, ^{144}Ce and ^{91}Y , had been removed.⁴ The completion of the Fission Products Development Laboratory (FPDL) in 1958 permitted the flexible processing of highly radioactive material.

At Hanford, fission-product separations work began in 1953. The processes being developed at that time were phosphotungstate⁵ and ferrocyanide⁶ precipitations for ^{137}Cs , and subsequently the PbSO_4 -carrier precipitation for ^{90}Sr and rare earths.⁷

The introduction of production-scale solvent extraction for plutonium and uranium recovery from reactor wastes suggested the application of similar techniques to fission product recovery. Ion-exchange and solvent-extraction methods were worked out in the late 1950's and early 1960's^{8,9,10, Appendix E} at FPDL. Solvent

extraction is used at Hanford now to recover in rough cuts the long-lived heat-producing fission products ^{90}Sr , ^{144}Ce , and ^{147}Pm . Cesium-137 is stored as alkaline supernatant of Purex 1WW (or other waste). In ^{137}Cs recovery the alkaline supernatant is absorbed on an inorganic ion-exchange medium at Hanford and shipped to ORNL for further purification with ammonium alum coprecipitation.

At the inception of the ^{90}Sr power program in 1958, Martin Co., Nuclear Division, was given responsibility for the selection of the strontium compound and encapsulation material to be used for thermoelement testing, and for generator design and construction.¹¹ ORNL worked on recovery of ^{90}Sr , preparation of strontium compound (SrTiO_3), pellet formation, encapsulation, and leak testing.

The first large-scale purification of ^{90}Sr , about 7 kCi, was carried out in the FPDL at ORNL in the summer of 1960. Production of ^{90}Sr was then transferred to Hanford, where there was developed a head-end precipitation process followed by an ion-exchange process^{12,13} for the purification of 75 kCi of ^{90}Sr in the period August 1960 to February 1961. From 1961 to 1964, over 8 MCi of ^{90}Sr was processed^{14,15,16} at Hanford by a solvent-extraction method very similar to one worked out on a laboratory scale by the ORNL Chemical Technology Division. The solvent extraction was preceded by the head-end PbSO_4 -carrier precipitation step. For the first 150 kCi of solvent-extracted ^{90}Sr , the ion-exchange process completed the purification.

The purification of ^{90}Sr for the SNAP-7 program may be summarized in the following way:

Date	Process	Amount	Site
1960	Precipitation	7 kCi	ORNL
1961	PbSO_4 carrier precipitation and ion exchange	75 kCi	Hanford
1961	PbSO_4 carrier precipitation, solvent extraction, and ion exchange	150 kCi	Hanford
1961 to 1964	PbSO_4 carrier precipitation and solvent extraction	8 MCi	Hanford

This chapter begins with a description of the requirements for ^{90}Sr purity in thermoelectric generators, and then the ^{90}Sr recovery and purification methods are discussed under headings of precipitation, ion exchange, and solvent-extraction processes.

PURITY REQUIREMENTS¹⁵

Because of design requirements for thermoelectric generators, stringent demands are made on the ⁹⁰Sr recovery process. Gamma emitters have to be removed to a level insignificant in comparison with the associated bremsstrahlung radiation in order to take advantage of the lower biological shielding requirements of ⁹⁰Sr-⁹⁰Y beta emitters. Thus, the specifications for the purified product require that each gram of ⁹⁰Sr contain less than 0.0015 Ci of gamma emitters with energies greater than 2 MeV, less than 0.015 Ci in the 1- to 2-MeV range, and less than 0.15 Ci in the 0.2- to 1-MeV range. This specification corresponds to separation factors of the order of 10⁴ to 10⁵ from ¹⁴⁴Ce, ⁹⁵Zr-⁹⁵Nb, ¹⁰⁶Ru, and most other gamma-emitting fission products.

A high degree of purification from inert contaminants is also required so that the specific heat-generating rate of ⁹⁰SrTiO₃ will equal or exceed the design criterion of the generators (0.5 W/cm³) in 1961, >0.85 W/cm³ since 1967. The contaminants have to be less than 25 wt % of the total cation weight, and the ⁹⁰Sr content has to be greater than 36% of the total cation weight.

The waste solutions resulting from the recovery of uranium from spent reactor fuel elements, which constituted the starting material for the recovery of fission products, were highly acidic and contained large quantities of inorganic ions such as sulfate, nitrate, iron(III), sodium, aluminum, and chromium (see Table 2.1 for the composition of Purex 1WW waste). Decontamination factors* of up to 2000 for iron, 700 for lead, 400 for aluminum and chromium, and 10 for calcium and barium were required at the time of the SNAP-7 program.

Strontium-90 is produced as a fission product during reactor operation along with ⁸⁹Sr, which has a half-life of 50.5 days, and other strontium isotopes (including the stable isotopes ⁸⁶Sr and ⁸⁸Sr). Yttrium-90, the decay daughter in secular equilibrium with ⁹⁰Sr, emits a very high energy beta particle. The intense high-energy beta activities of ⁸⁹Sr and ⁹⁰Y, as well as the softer beta activity of ⁹⁰Sr, result in high-energy bremsstrahlung radiation for which heavy shielding is required. Unless the strontium has aged sufficiently, the 50.5-day ⁸⁹Sr also contributes a substantial fraction of the heat of the isotopic mixture.

The radioisotopic properties of fission-product strontium are given in Table 2.2 (Ref. 17). A year of aging is necessary for a heat source with only a minor contribu-

*Ratio of initial to final weight of contaminant per gram of ⁹⁰Sr.

Table 2.1. Typical composition of Purex 1 WW waste

Component	Concentration, moles/liter	
	1961-65	October 1969*
H ⁺	4	6
SO ₄ ²⁻	1.0	0.6
NO ₃ ⁻	4.5	7.7
Na ⁺	0.6	0.7
Fe ³⁺	0.5	0.35
Al ³⁺	0.1	0.3
Cr ³⁺	0.01	0.035
Ni ²⁺	0.01	0.02
UO ₂ ²⁺	0.005	0.01
Sr ²⁺	0.002	0.0015
Cs ⁺	0.003	0.002
Sm ³⁺	0.006	0.006
Ce ³⁺	0.003	0.0025
Ru	0.003	0.002
Ca ²⁺	0.005	0.002
Zr		0.008
SiO ₂		0.1
PO ₄ ³⁻		0.015
Be ²⁺		0.05
Cu ²⁺		0.06
La ³⁺		0.0015
Li ⁺		0.001
Mg ²⁺		0.04
Mn		0.0065
Mo		0.0035
Ba ²⁺		0.0025
Nd ³⁺		0.0025
Solids	10%	10%

*Private communication, D. E. Larson, Atlantic Richfield Hanford Co., Richland, Washington.

Table 2.2. Radioisotopic properties of fission-product strontium

Isotope	Half-life	Beta energy, max MeV	Gamma energy, MeV
⁸⁹ Sr	50.5 d	1.463	0.91 (0.009%)
⁹⁰ Sr	28.5 y	0.546	None
⁹⁰ Y	64.0 hr	2.28	None

tion from ⁸⁹Sr; otherwise, the source will show a high initial decrease in heat output, characteristic of the short-lived ⁸⁹Sr. One curie of ⁸⁹Sr will contribute over 50% of the heat and 50% of the radiation produced by 1 Ci of ⁹⁰Sr in equilibrium with ⁹⁰Y. Removal of ⁸⁹Sr stabilizes the generator temperatures to match the narrow operating range of PbTe thermocouples.

Strontium, ingested or inhaled, concentrates in the bones of animals. Although less hazardous to man [i.e., characterized by a larger maximum permissible concentration (MPC)] than the alpha emitters, it is more dangerous than most other fission products.¹⁸

PRECIPITATION PROCESSES

ORNL Precipitation Process^{2,3, Appendix C,D}

This process was developed to use wastes from several reactor sites — ORNL, Hanford, and the National Reactor Testing Station — as feeds. The starting Purex waste is concentrated to half its initial volume; zirconium and niobium are removed by centrifugation; ruthenium, technetium, and iron are removed by centrifugation after the *pH* is adjusted to 2.5 with the controlled addition of ammonia gas; the rare earths are removed in the same manner at a *pH* of 8; and the strontium, calcium, and barium are precipitated with Na_2CO_3 . The alkaline earth carbonates are dissolved in HNO_3 , and barium is removed as BaCrO_4 at a *pH* 6. The mole ratio of calcium to strontium in the remaining solution is 10:1. A separation of these two cations with fuming HNO_3 gives less than satisfactory recovery of the strontium. However, in purifying the first 7 kCi of ^{90}Sr , the fuming HNO_3 precipitation was used when a mechanical failure occurred in the solvent extraction process¹⁰ for separation of calcium from strontium.

Hanford PbSO_4 -Carrier Precipitation Process

This precipitation process was developed and used at Hanford to recover megacurie amounts of crude ^{90}Sr for final purification.^{7,13, Appendix F} Initially, the process feed was concentrated Purex 1WW waste (Table 2.1), which contained essentially all the fission products and relatively large amounts of containment metals and sulfate in $\sim 4\text{ M HNO}_3$. Feed preparation with Purex acid waste (PAW*) includes a centrifugation step to remove solids (primarily silica and sulfates) which carry appreciable quantities of fission products.

A typical flowsheet of this recovery process, which has had several variations, is shown in Fig. 2.1. Cerium and other rare earths are precipitated as the sodium-rare-earth double sulfates, along with the strontium, by adjusting the sulfate concentration to $\sim 1\text{ M}$ and the *pH*

*PAW is similar to Purex 1WW but contains only about 1.0 M HNO_3 .

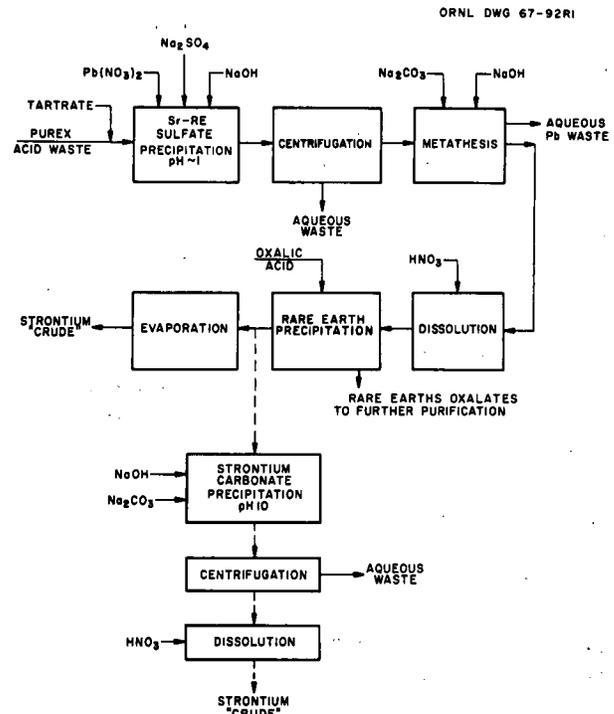


Fig. 2.1. Strontium and rare-earth recovery from Purex waste by PbSO_4 -carrier precipitation.⁷

of the solution to 1 to 2. Lead nitrate is added to carry strontium sulfate, and an iron complexing agent (such as tartrate or hydroxyacetic acid) is added to avoid precipitation of ferric sulfate. The precipitated sulfates are metathesized with a mixture of NaOH and Na_2CO_3 to remove lead (by conversion to soluble plumbite) and to convert the strontium, along with cerium and the other rare earths, to acid-soluble carbonates. These carbonates are dissolved in nitric acid and, after interim storage, cerium and the other rare earths are separated from strontium by precipitating them as the oxalates, leaving the strontium in solution. Strontium can be concentrated by evaporation or by precipitating strontium carbonate and dissolving it in nitric acid. The composition of a typical product solution is shown in Table 2.3. The crude solution is then ready for ion-exchange or solvent-extraction processing.

Subsequently the process was adapted for use in the Hanford Waste Management Program^{19,20} to separate strontium and rare earths from both acid Purex-sugar-treated waste and stored alkaline Purex and Redox wastes.²¹ No rare earth separation is achieved in this adaptation. Rare earths are separated instead by solvent extraction.

ION EXCHANGE PROCESSES

ORNL Ion-Exchange Process

An ion-exchange process was explored at ORNL with synthetic Purex 1WW. Strontium and rare earths are adsorbed on Dowex 50W-X8 resin; the complexing agent for other cations is citrate ion. Adsorbed strontium and rare earths are separated by elution with ammonium α -hydroxyisobutyrate. A preliminary precipitation step with $\text{Fe}_2(\text{SO}_4)_3$ to remove some of the rare earths and other impurities permits a higher loading of the resin, but with the higher loading, resin destruction increases by a factor of 10 to an unreasonable amount.^{2,2,3}

Hanford Ion-Exchange Process

An ion-exchange process developed at Hanford,^{1,2} similar in principle to those worked out for rare earth separations by F. H. Spedding and associates,^{2,4,25} was used successfully in seven production runs to purify 75 kCi of ^{90}Sr (Appendix G). Feed for the process was crude strontium (Table 2.3) from the PbSO_4 -carrier precipitation process.

Strontium is purified chromatographically in a series of six columns containing Dowex 50W-X12 cation-exchange resin. Feed solution, to which is added the complexing agent (N-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) and which is adjusted to pH 4 with ammonia, passes through the first three columns, which serve as sorption columns. These columns are washed with 0.1 M HEDTA at pH 4 and the strontium is eluted with ethylenediaminetetraacetic acid (EDTA), adjusted to pH 8-9, through columns 4 and 5. The elution proceeds in the order calcium, strontium, and barium. The strontium band moves onto column 6, which contains a "barrier" ion (copper, yttrium, or

neodymium), after all the calcium has been discarded from column 5. The barrier ion increases the efficiency of separation and sharpens the strontium band. The position of the strontium band is followed by observing the radiation glow. When the strontium is essentially all on column 6, this column is isolated and washed. Strontium is then eluted at an average concentration of ~ 40 g/liter with 5 M NH_4NO_3 . At the time of the production runs, 11 days of continuous operation were required to complete a run. (New resin was used for each of the seven runs; however, the resin discarded after each run was not excessively radioactive and did not appear to have suffered appreciable radiation degradation.) The final run of the series yielded 16.5 kCi of ^{90}Sr (83% recovery) contaminated with < 1 Ci each of ^{95}Zr – ^{95}Nb , and ^{144}Ce .

The method was adapted to serve for the final purification of ^{90}Sr product derived from a solvent-extraction recovery process. The solvent-extraction product solution, containing 0.03 M strontium and 1 M citrate at pH 2.3, is sorbed on the column, eluted with 3 M NaNO_3 , and separated from the solution by carbonate precipitation. In later production runs, this ion-exchange process was replaced by a two-cycle solvent-extraction process and then by one-cycle solvent-extraction process.^{15,26}

SOLVENT-EXTRACTION PROCESSES

ORNL Three-Cycle Solvent-Extraction Process

The recovery and purification of strontium and rare earths from waste solutions by solvent extraction with organic solutions of di(2-ethylhexyl)phosphoric acid (HDEHP) were proposed and developed at ORNL.²⁸⁻³⁰ A large number of extraction and stripping process variations are possible with this reagent; however, in the interest of time, emphasis was placed on a three-cycle process for treating Purex-type wastes as a demonstration of reagent utility. A key principle of this process (and similar processes developed later) is the use of an aqueous complexing agent such as tartrate or citrate to complex and hold in solution metals such as iron, which would ordinarily precipitate during adjustment of the feed pH. A stable feed is prepared by complexing Purex 1WW waste solution (Table 2.1) with ~ 2 moles of tartrate per mole of iron and adjusting the pH to ~ 5 with caustic, while diluting by a factor of 3. Strontium and mixed rare earths are coextracted in the first cycle with a solvent composed of 0.2 M HDEHP–0.1 M sodium di(2-ethylhexyl)phosphate (NaDEHP)–0.15 M tributyl phosphate (TBP) in a hydrocarbon diluent.

Table 2.3. Composition of strontium "CRUDE" product solution from PbSO_4 carrier precipitation

Component	m/l	Concentration	
		g/liter	curies/liter
Sr	0.0036	0.32	25.6
Ca	0.0025	0.1	
Ba	0.00036	0.05	
Fe	0.143	8.0	
Pb	0.027	5.6	
Na	0.425	10.0	
^{95}Zr – ^{95}Nb			70
^{144}Ce			750

They are stripped with 2 M HNO₃. Rare earths are separated from strontium in the second cycle by adjustment of the first-cycle raffinate to a pH of ~2.0. At this pH the mixed rare earths are extracted selectively. The strontium in the raffinate may then be concentrated and further decontaminated in a third extraction cycle at a pH of ~5; this cycle is essentially the same as the Hanford solvent-extraction process. The process was demonstrated successfully in miniature mixer-settler equipment in a hot cell with high-level Purex 1WW used as feed. About 98% of the strontium was recovered with overall decontamination factors of $\sim 3 \times 10^3$ from cesium, $\sim 10^4$ from ruthenium, $\sim 10^5$ from zirconium-niobium, $>1.5 \times 10^3$ from rare earths, and $>2 \times 10^4$ from iron.²⁷

Continued development has led to improvements or additions to the original flowsheet; e.g., appropriate adjustment of conditions in the second cycle now permits separation of strontium and calcium.³¹ The process can be applied to treatment of Purex wastes other than 1WW, such as sugar-treated waste (STW) and formaldehyde-treated waste (FTW), and can be modified to treat highly concentrated aluminum (e.g.; Redox) and stainless steel wastes (e.g., Darex).³²

Simplified ORNL Solvent-Extraction Process

A simplified tentative process has been outlined³³ for recovering strontium and mixed rare earths from Purex STW with NaDEHP; however, it has been tested only with synthetic cold feeds. The strontium and rare-earth products recovered by this process are less pure than those recovered by the earlier ORNL process described above, but the method requires less equipment and does not use large amounts of aqueous-phase complexing agents. In the first cycle, the rare earths, most of the iron, the ⁹⁵Zr–⁹⁵Nb, and most of the aluminum are extracted from unadjusted Purex STW in a single stage by NaDEHP in TBP with a hydrocarbon diluent as the solvent. The amount of NaDEHP fed to the system is regulated to provide a final extraction pH of 2 to 2.5. The rare earths are stripped selectively from the solvent with dilute nitric acid, and the solvent is prepared for recycle by a single-stage contact with dilute caustic at 40 to 50°C. In the second cycle a small amount of diethylenetriaminepentaacetate (Na₅DTPA) is added to the aqueous phase to complex nickel and chromium. Strontium is then extracted with NaDEHP in two or three stages at pH 4 to 5 and stripped with dilute nitric acid.

Hanford Solvent-Extraction Process

To a large extent this process was based on modifications and further development of the solvent-extraction technology developed at ORNL using HDEHP for recovery and purification of strontium and rare earths from Purex waste (see above). Many process variations and flowsheets have been devised at Hanford for different process objectives and for handling different waste compositions, but only the one used for production is described here.

The first Hanford solvent-extraction process for fission product separations^{13,14,15,Appendix H} was developed specifically for use in the Hot Semiworks Pilot Plant to purify ⁹⁰Sr for SNAP-7 program requirements. Feed is prepared from crude strontium product solution, recovered by the PbSO₄-carrier precipitation process (see above and Table 2.3), by addition of acetate for buffering, sodium hydroxide for adjusting acidity, a small amount of Na₂SO₄ for Ba removal, and diethylenetriaminepentaacetic acid (DTPA) for complexing the extraneous metals. This complexant suppresses extraction of iron, lead, and certain fission products such as zirconium–niobium and ruthenium. In the process flowsheet (Fig. 2.2), strontium, calcium, residual mixed rare earths, and some sodium are coextracted with 0.4 M HDEHP and 0.2 M TBP in hydrocarbon diluent.* A large portion of the extracted sodium is scrubbed from the solvent at pH 3.4 to 4.7 with sodium citrate–DTPA–sodium sulfate solution. Strontium is stripped selectively in a second contactor with 1 M citric acid at pH 1.5–2.1 to separate it from calcium and rare earths. The product is concentrated and the citrate is destroyed by oxidation with a boiling HNO₃–H₂O₂ solution. The product may be further purified by either an ion-exchange cycle or a second solvent-extraction cycle (Appendix H).

Improved Hanford Solvent-Extraction Process

Hanford has devised processes for direct treatment of low-acid Purex wastes by solvent extraction to recover strontium and rare earths.³⁴ This approach, which will not require the preliminary PbSO₄-carrier precipitation, was planned (1967) to be used in the new Waste Management Facility; a typical flowsheet²⁷ is shown in Fig. 2.3. The aqueous feed is complexed with citric acid and adjusted with NaOH to a pH of 4.5–5. Strontium

*Amsco, Shell spray base, or normal paraffin hydrocarbon (NPH).

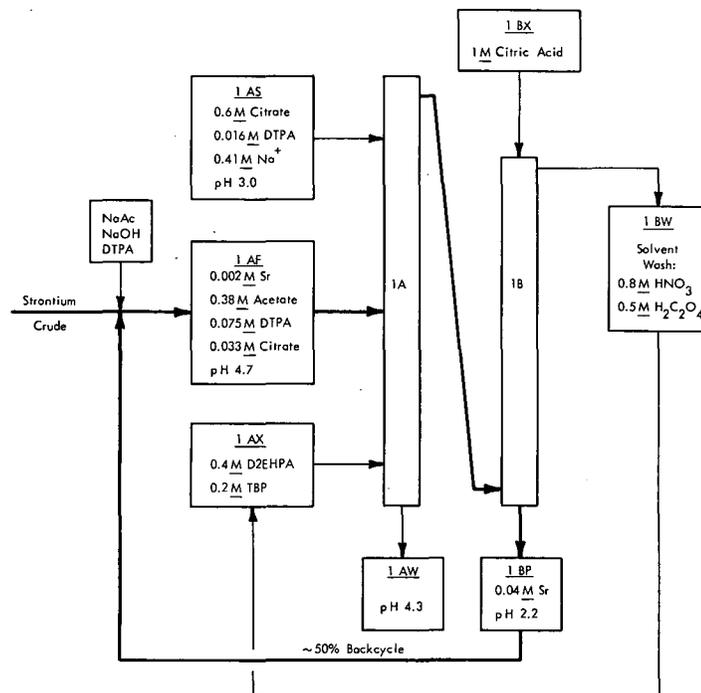


Fig. 2.2. Strontium recovery using one cycle of solvent extraction.¹⁵

and rare earths are coextracted at 40-50°C with HDEHP (partially in the sodium salt form) and TBP in a hydrocarbon diluent, and the solvent is scrubbed with hydroxyacetic - hydroxyethylethylenediamine tri-sodium acetate solution to decrease the sodium concentration. Strontium is stripped selectively from the extract with 0.03 M HNO₃, the rare earths with 2.5 M HNO₃, and the waste metals with 1.8 M NaOH-0.075 M Na tartrate solution at ~50°C. The NaDEHP is then partially converted to the hydrogen form before it is recycled to the extractor.

Another process³⁶ for direct treatment of low-acid wastes was considered for use in the Waste Management Program. In this process, HDEHP combined with the substituted phenol, 4-sec-butyl-2(α-methylbenzyl)-phenol (BAMBP), is used to coextract cesium along with strontium and rare earths at pH 4. The process was dropped from consideration despite its promising aspects because BAMBP is highly susceptible to degradation by nitrous acid under the conditions outlined in the proposed flowsheet.

The Hanford Waste Management Program (1965-1970) uses a solvent-extraction process with HDEHP to

concentrate and purify ⁹⁰Sr from Purex wastes for storage.³⁵ A typical product solution for storage is shown in Table 2.4.

Table 2.4. Crude strontium composition

Constituent	Concentration	
	Molarity	g/l
H ⁺	2.85	2.8
Sr ²⁺	0.096	8.4
Na ⁺	0.51	11.7
Ca ²⁺	0.158	6.3
Mg ²⁺	0.183	4.5
Ba ²⁺	0.0016	0.22
Mn ²⁺	0.201	11.0
Ni ²⁺	0.0024	0.14
Al ³⁺	0.041	1.1
Cr ³⁺	0.0055	0.29
Fe ³⁺	0.011	0.61
Pb ²⁺	0.010	2.1
¹⁴⁴ Ce-Pr ³⁺		(232 Ci/l)
⁹⁰ Sr ²⁺		(705 Ci/l)

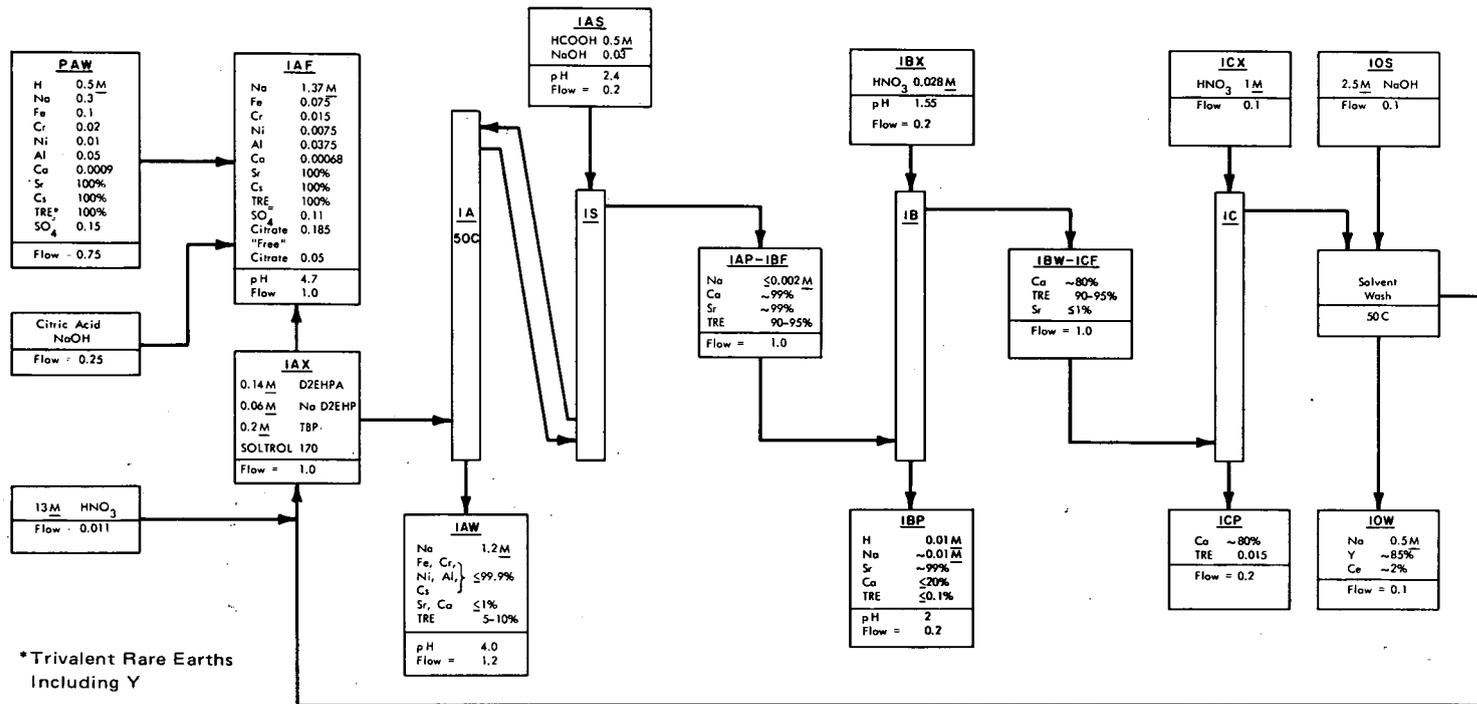


Fig. 2.3. Recovery of strontium and rare earths from Purex PAW. [Shows the composition of waste expected at Hanford if the ferrous sulfamate reduction method for partitioning plutonium is replaced by reduction with U(IV); the waste is relatively low in iron and sulfate concentration.]³⁴

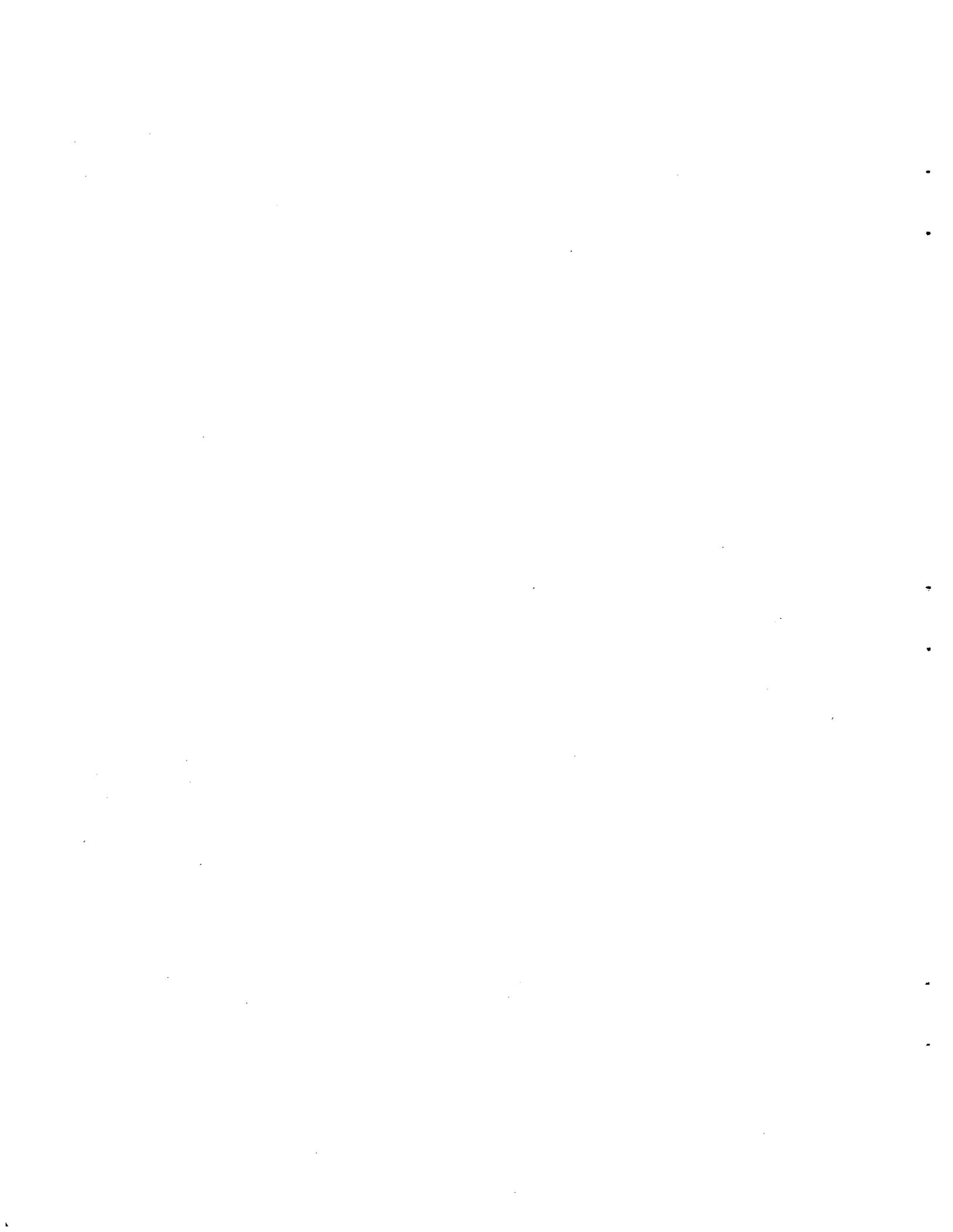
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3. TRANSPORTATION AND BUILDING FACILITIES

The purified ^{90}Sr from Hanford is shipped to other sites for conversion to a chemical form suitable for use as heat sources. The shipping procedure and the facilities to handle the ^{90}Sr at the Fission Products Development Laboratory (FPDL) at ORNL are described in this section.

SHIPMENT OF RADIOACTIVE MATERIAL

Development of Shipping Container

Standards of transport safety for radioactive materials have evolved over a twenty-year period. The first transcontinental shipment¹ of the purified ^{90}Sr from Hanford to Oak Ridge, Tennessee, constituted the largest-scale shipment of radioactive isotopes up to that time (1961). This undertaking, having no clear precedent, required the establishment of a number of "ground" rules somewhat analogous to nuclear reactor hazards standards but further complicated by the uncertainties concomitant with transportation by rail. (Other means of transport, such as motor truck, water, and air, were excluded for various reasons.) Considerable engineering and development effort was devoted to ensuring safety in container filling, transport, and unloading. The maximum conceivable incidents in transcontinental rail shipment were first evaluated. These hypothetical incidents were developed in cooperation with the Bureau of Explosives of the American Railroad Association and the USAEC Divisions of Materials Licensing and Operational Safety. The maximum incidents judged credible at that time were:

1. Impact of the strontium container system equivalent to a free fall of 30 ft onto an unyielding surface.
2. Direct adiabatic burial (that is, engulfment in a landslide) for a period up to 48 hr.
3. Direct oil flame impingement for up to 2 hr as might conceivably occur in a railroad fire.

Combinations of these credible incidents were also considered, such as impact followed by fire or impact followed by burial, and other potentialities such as impalement by structural members. Engineering data from the railroad and missile fields were employed in design. These design and development efforts have been documented by Smith and McLenegan.^{2,3,4}

HAPO-IA and HAPO-II Casks

Two types of shipping casks, described in Table 3.1, were devised.¹ Cask HAPO-IA was used for shipping the ion-exchange-purified ^{90}Sr product and involved the use of granular synthetic sodium aluminosilicate, Decalso (Permutit Co.), as the ion-exchange medium. The use of Decalso had been developed at ORNL for shipping of aqueous ^{137}Cs in their Shielded Transfer Tank (STT).⁵ Approximately 30 kCi were loaded on 11 gal of the medium contained in an annular bed in a lead shielded cask. The strontium was eluted at ORNL with NH_4NO_3 solution from the exchange medium.

HAPO-II incorporated major improvements in the cask for the shipment of ^{90}Sr . The weight was reduced to one half that of HAPO-IA by transporting the strontium as a solid, SrCO_3 , instead of as a liquid absorbed on an ion-exchange medium. Strontium carbonate is collected in the form of an annular filter cake, which is geometrically restricted to $\frac{5}{8}$ in. thickness, so as not to exceed the temperature limitation. This HAPO-II cask has been used for shipment both to ORNL and to the Martin Co., Quehanna, Pennsylvania, sites. The filter (Fig. 3.1) is constructed of type 321 stainless steel and fits inside the cask. The SrCO_3 precipitate is collected by a fine-mesh composite stainless steel wire-cloth filter in an annular space $\frac{5}{8}$ -in. thick, 9- $\frac{1}{2}$ in. in diameter, and about 18 in. high as the slurry is transferred through the cask during loading. The precipitate is then thermally stabilized by heating to about 260°C and purging with helium. At the receiving site the fission products are removed from the container by dissolution.

Figure 3.2 shows the assembled filter cask. The cask is an externally finned, hollow cylinder with lead shielding between a 1-in.-thick outer shell and a $\frac{1}{2}$ -in.-thick inner shell. The assembled cask is about 3- $\frac{1}{2}$ ft in diameter, 4- $\frac{1}{2}$ ft high, and weighs ~9 tons. The low-melting alloy, Wood's metal, is used to transfer the heat from the filter container to the cask inner wall. Two banks of expansion relief tubes are provided within the cask well to protect the cooling coils and the filter container from possible deformation caused by the expansion of Wood's metal following solidification. Shipment of solvent-extraction-purified strontium in this cask was in ~120 kCi lots.

Table 3.1. Shipping cask design specifications

	HAPO IA	HAPO II
Type insert	Inorganic ion exchange	Slurry filter
Weight: cask	20 T	9 T
buffer	17.5 T	11.5 T
Size: diameter and height		
cask	4 ft 4 in. X 5 ft 11 in.	3 ft 4 in. X 4 ft 8 in.
buffer	10 X 14 ft	8 X 12 ft
Date available	March 1961	June 1961
Number available	1	2
Heat-transfer medium	Wood's metal (MP = 71°C)	Wood's metal (MP = 71°C)
Lead thickness	8.75 in.	6.5 in.
Emergency design conditions	Impact at 44 fps Total engulfment for 48 hr Flame impingement for 2 hr	Impact at 44 fps Total engulfment for 48 hr Flame impingement for 2 hr
Design pressure	300 psig	200 psig
Design temperature	200°C	550°C
Maximum allowable shipping pressure	100 psig	100 psig
Rated maximum heat generated	5000 Btu/hr	11,600 Btu/hr
Proposed shipment		
Desired isotope	^{90}Sr	^{90}Sr
Amount	80 kCi	Up to 170 kCi
Normal decay heat generated	4100 Btu/hr	8600 Btu/hr
Chemical composition	Sr^{++} absorbed on exchange material	SrCO_3
Physical state	Absorbed cation in demineralized water	Dried salt
Radioactive impurities	^{89}Sr	^{89}Sr

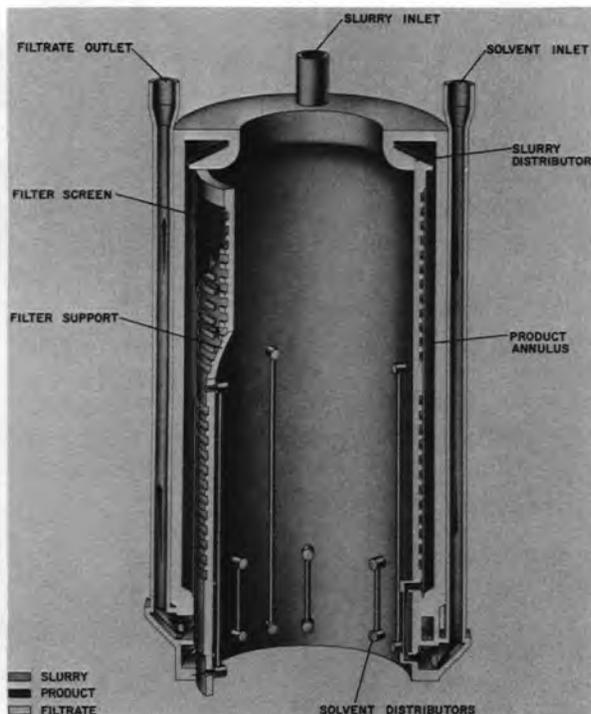


Fig. 3.1. HAPO-II filter-container.

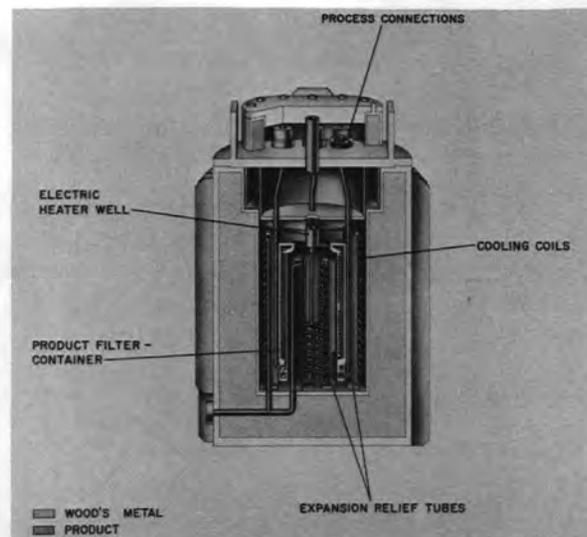


Fig. 3.2. HAPO-II filter-cask.

Returning briefly again to the protective devices developed, Fig. 3.3 shows the installation of a shipping cask within a protective buffer designed to withstand the shock, engulfment, and fire conditions established as maximum credible incidents. The buffer consists of four coaxial cylindrical steel shells separated by rubber cushions for energy absorption on impact. Air-cooling passages are designed to be sufficient for dissipation of

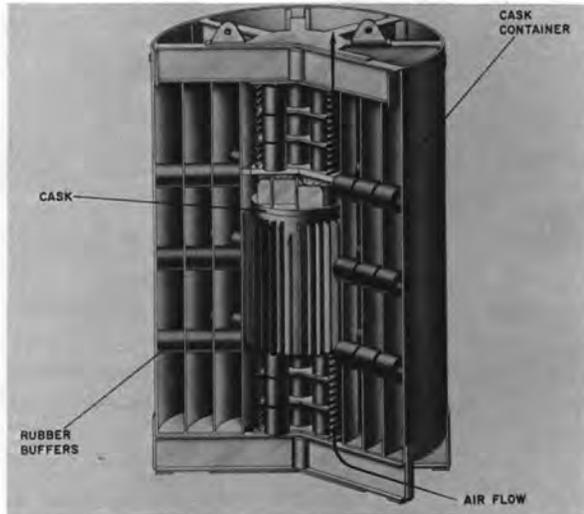


Fig. 3.3. HAPO-II filter-cask in container.

heat of self-absorption and yet limit flame impingement on the cask proper in case of fire.

Figure 3.4 shows the completed shipping system (common to all casks) as attached to a railroad car.

Shipment of Encapsulated Strontium-90

Shipment of the ^{90}Sr in its encapsulated form, when it is ready to be placed in a thermoelectric generator, may be made in the generator itself. The generators, designed for long life in hostile environments, usually are also constructed to satisfy safety requirements of shipping.

Other containers may be used, of course, such as ORNL uranium-shielded casks for quantities up to 400 kCi. A Department of Transportation (DOT) special permit is shown in Appendix J for this cask. Figure 3.5 shows a picture of the Weather Bureau generator being loaded on a truck at ORNL.

Current Regulations

Since 1967 the DOT has assumed duties relating to the safety of carriers, formerly exercised by the Interstate Commerce Commission (ICC) and other agencies. In particular the Hazardous Materials Regulations Board of the DOT regulates radioisotope shipments and issues the special permits required for large shipments of radioactive materials. The USAEC serves as an expert adviser.



Fig. 3.4. HAPO II loaded on railroad flat car.



Fig. 3.5. Weather Bureau source being loaded on transport truck.

In 1966 the USAEC issued a formal set of regulations governing the shipping of radioactive material by its contractors and licensees, entitled "Safety Standards for the Packaging of Radioactive Materials," which are included in AEC Manual Chapter 0529 and Part 71 of Title 10 of the Code of Federal Regulations. The DOT issued new regulations, complementing and supplementing the AEC regulations, which bring the US regulations in harmony with those of the International Atomic Energy Agency (IAEA). The revisions became effective in January 1969.

In accordance with the philosophy on which international shipping regulations are based, DOT has divided radioactive material into seven groups, depending on the radiotoxicity of the isotope concerned, and has divided shipping packages into Types A and B. Smaller amounts of more toxic material and larger amounts of less toxic material may be shipped in the same type of package. Type A packages are limited to small amounts of radioactive material which, if released in the event that a package is destroyed, would not have cata-

strophic consequences. Type B packages are for shipments of somewhat larger amounts of radioactive material and are designed to contain the radioactive material under conditions of hypothetical shipping accidents. Quantities of radioactive material larger than those specified for Type B packages (greater than 20 curies of ^{90}Sr in normal form, or 5000 curies of ^{90}Sr in special form) must be shipped in packages specially approved by the AEC and the DOT. Limits are set on permissible external radiation and temperature, as well as proximity to passengers or explosives or other hazardous material.

FISSION PRODUCTS DEVELOPMENT LABORATORY

Overall Facilities

The ORNL FPDL building (Fig. 3.6a) is a tri-level structure enclosing 7,700 ft² of floor space and containing 376 thousand ft³ of free space. The first two levels consist of operating and service areas built around a cell block and constructed of standard concrete-block siding. The third level consists of an aluminum-sided crane bay that encloses the area over the top of the cell block.

The main cell block contains nine chemical processing cells and six manipulator cells constructed of massive concrete walls (Fig. 3.6b). Three additional manipulator cells are connected to the cell blocks, and four concrete cells are located underground on the north side of the building. Additional low-level cells are available for off-gas scrubbers, services, and decontamination. As indicated in Fig. 3.7 the cells form the primary containment and the building walls are sealed to form the secondary containment barrier. All entrances to the building are air-locked.

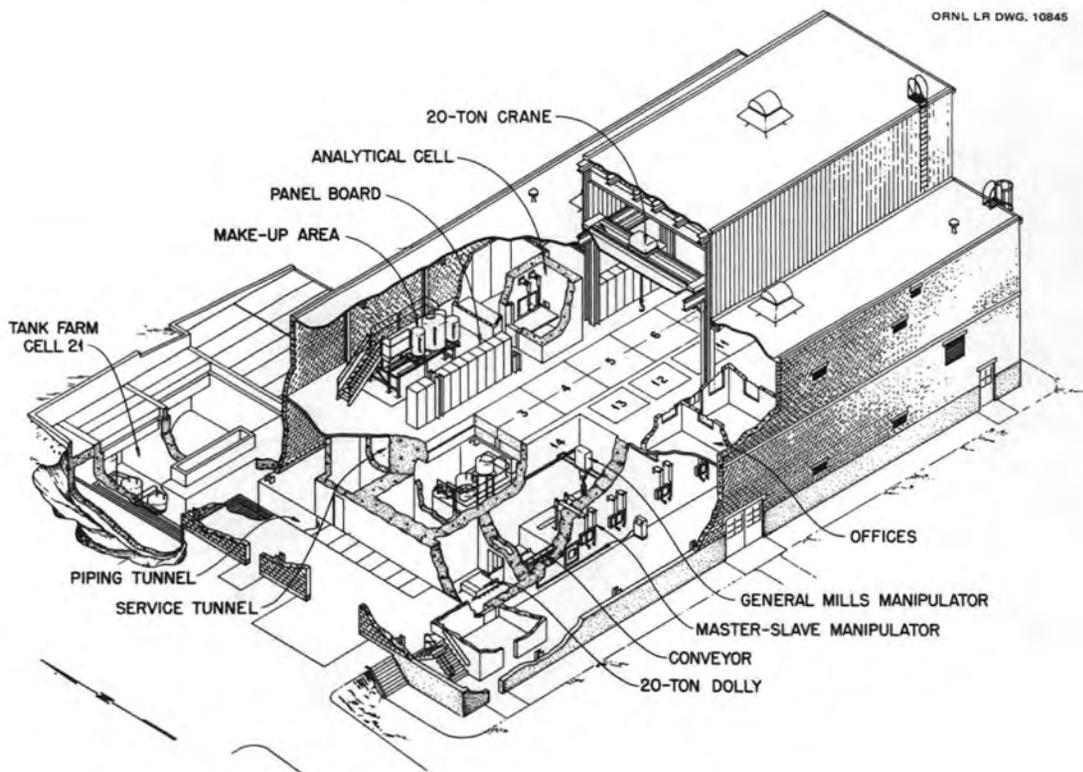
Shielding and operating procedures provide protection for the operating personnel at a level of <50% of the allowable tolerances. The shielding permits the processing of fission products that have been aged as little as six months.

Process equipment is operated from graphic panelboards. The panelboard controls send pneumatic or electrical signals to secondary pneumatic relays located in the service tunnel or in service cubicles. The secondary relay system operates the in-cell devices. Temperatures, pressures, liquid levels, specific gravities, noise, and motor speeds are indicated on the panelboards. Low cell ventilation, off-gas, steam pressure, and water pressure are indicated by an air-horn alarm, as are high building radiation, high radiation in the cell ventilation system, and high process-waste activities.



PHOTO 62847

Fig. 3.6a. Fission Product Development Laboratory building.



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Fig. 3.6b. Fission Product Development Laboratory building – cutaway drawing.

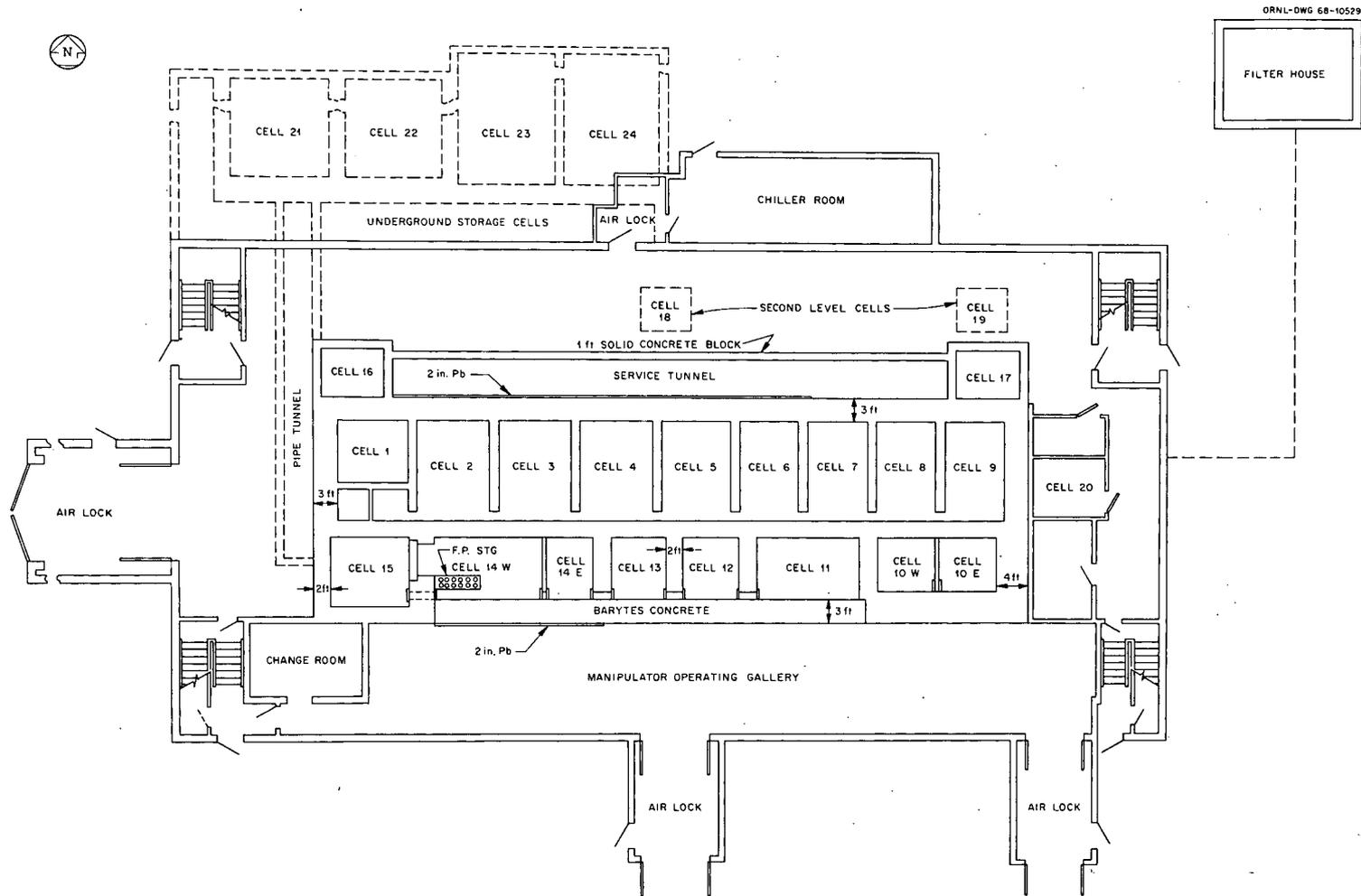


Fig. 3.7. Fission Product Development Laboratory, first floor plan.

Liquid radioactive waste from process vessels and cell drains is collected in tanks at the FPDL tank-farm cells, where it is sampled for radiochemical analysis before transfer to the ORNL liquid-waste system. The process cooling water system is a closed recirculation loop, and the process heat is removed by refrigeration equipment. The process steam condensate is condensed, monitored, and collected in a surge tank for disposal to the hot-waste system or the process-waste system. The operating area floor and sink drains are drained by gravity to the process-waste system.

The FPDL has gas-handling systems for radioactive off-gas, cell-ventilation air, and building-ventilation air. The radioactive off-gas system handles the gases and vapors from each process vessel and maintains the vessels at a negative pressure with respect to the cells. The individual lines are manifolded to form a single header which discharges through a scrubber system consisting of two packed-column-type scrubbers operated in series. The usual scrubber sequence consists of using chilled 0.67 M H_3PO_4 solution followed by chilled 4 M NaOH. Other combinations of scrubber solutions can be used if necessary to control the gases produced by certain reactions. The scrubber solutions are recirculated through the scrubbers and are changed routinely; the used scrubber solutions are discharged to hot-waste system. The gases pass from the second scrubber through a heater, a stainless steel roughing filter, and an absolute filter; they are monitored as they are discharged to the ORNL gaseous-waste system. This system has a maximum capacity of 1000 cfm and operates normally at 400 cfm.

The cell-ventilation system maintains the cells at a negative pressure with respect to the building. Individual ducts from each cell are manifolded and combined at the underground filter pit. The gas passes through stainless steel roughing filters and absolute filters and is monitored as it is discharged into the ORNL gaseous-waste system. The capacity of this system is 12 thousand cfm and the normal throughput is 6 thousand cfm.

The building-ventilation system provides air for personnel and air for the cell-ventilation system. Air is pulled into the building through roughing filters and absolute filters. The quantity of air is regulated to equal the air being removed by the cell-ventilation system. If the building air becomes contaminated, a supplementary inlet connecting the building to the cell-ventilation system opens automatically and rapidly exhausts the building air to the ORNL gaseous-waste system.

The FPDL equipment for controlling the release of radioactive materials to the environment is designed for an absolute minimum discharge under normal operating conditions. In the event of an uncontrolled release of either gaseous or liquid activity, the activity will be contained within the building.

Strontium-90 Processing Facilities and Equipment

All ^{90}Sr processing at ORNL is done in the contained shielded cells at the FPDL. Operations such as feed-cask unloading, bulk-solution storage and sampling, and mixing of feed solutions are done in remotely operated stainless steel equipment. Conversion of the ^{90}Sr to $^{90}SrTiO_3$ or ^{90}SrO and powder handling operations are carried out in manipulator cells. Source encapsulation, testing, and loading for shipment are done either in FPDL manipulator cells or in similar cells in other Isotopes Development Center facilities.

Three process cells are used for ^{90}Sr feed handling and storage. One cell is provided with equipment for the unloading and testing of ^{90}Sr shipping casks. This equipment consists of flexible lines adapted for semi-remote connection to the cask, a cask-cooling and -heating system, instrumentation for measuring cask temperature and pressure, and a closed-circuit television system for observation during unloading operations. All process line connections to a cask are made by means of 15-ft-long tools operated through small ports in the top of the cell. The cell is sealed before unloading operations begin and is not opened until the cask is emptied and rinsed.

The ^{90}Sr solution storage system consists of six 250-gal stainless steel tanks, located in two adjacent cells. These vessels are equipped with cooling systems and standard remote instrumentation. In each three-tank cell, one tank has an agitator, sampling lines, and a system for controlled evaporation. The six tanks are interconnected for flexibility of transfers among them, and an overflow system prevents the overfilling of any tank. All solution transfers within the process equipment are done by steam-jet vacuum or gravity flow.

Two manipulator cells at the FPDL are routinely used for fuel preparation and pelletization. One of them contains a 150-liter stainless steel precipitator and its associated equipment plus a furnace for calcination and sintering. The other cell is equipped for pelletization, and contains a hot press, a small hydraulic press, and the required powder-handling equipment such as blenders, balances, and die-loading equipment.

All major fixed equipment in the cells, except for the furnaces, is of welded stainless steel construction. The

cells are lined with stainless steel for ease of decontamination and are equipped with standard cell services such as controlled ventilation, electrical power, water, and instrumentation. Master-slave Model-8 manipulators with side cants, motion locks, and, in some cases, power grips are used. The cells are isolated from the other FPDL manipulator cells by a system of airlocks. This system provides for control of cell ventilation as well as for minimizing cross-contamination of the ^{90}Sr by different radioisotopes being handled in other cells.

Encapsulation of $^{90}\text{SrTiO}_3$ sources can be done in other manipulator cells at the FPDL; more commonly, however, the fuel is transferred to similar cells operated by the Isotopes Division. In both cases the encapsulation equipment is identical and consists of source loading tools, welder, testing equipment of various types, and decontamination equipment.

Since the cells at the FPDL are directly maintained, every effort is made to make the equipment reliable, simple, and adaptable to maintenance by manipulators. The airlocks in the cell system limit the size of items that may be inserted to a maximum of about 1 ft in any dimension. Installation of large equipment in a cell may require a complete decontamination for personnel entry. Contamination in certain cells is kept low enough to permit entries for the installation of equipment for final source assembly since contamination of the finished sources and shipping containers must be kept very low.

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4. PREPARATION OF STRONTIUM TITANATE

Purified ^{90}Sr is converted to SrTiO_3^* in the next step of making a ^{90}Sr heat source. The preparation of SrTiO_3 , a brief account of development work on other processes, and the analytical methods associated with the process are discussed in this chapter.

The process developed at the ORNL Fission Products Development Laboratory (FPDL) has been used to prepare most of the heat sources now in service throughout the world, including those of the SNAP-7 Program, as shown in Table 1.1. A schematic outline of the process steps for converting purified SrCO_3 to encapsulated SrTiO_3 is shown in Fig. 4.1.

SNAP 7-B and -F heat sources were prepared by Martin Co., Nuclear Division in their Quehanna Pilot

Plant by procedures very similar to those worked out at ORNL.¹⁻³

The phase diagram of the $\text{SrO}-\text{TiO}_2$ system shows the existence of two compounds, Sr_2TiO_4 and SrTiO_3 .⁴ The less water-soluble of the two, SrTiO_3 , has been used in nearly all of the applications (Table 1.1). Current best values of the physical properties of strontium compounds are compiled in Chapter 8.

Work on a satisfactory method for the preparation of SrTiO_3 at ORNL began in the fall of 1958. Wet ball milling or dry powder mixing, which were being developed by Martin Co., were rejected at the outset by ORNL as unsuitable for hot-cell operation. Processes using organic materials did not appear promising because of probable radiolysis. Several methods were explored in the effort to make a SrTiO_3 product with reproducible chemical composition and physical properties. The best method was one of the first attempted. A slurry of TiO_2 in a solution of NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ is mixed with $\text{Sr}(\text{NO}_3)_2$ solution to form a mixture of SrCO_3 and TiO_2 solids. (The solids are filtered off and calcined to form SrTiO_3 .) This method has been used to prepare all of the SrTiO_3 powder produced at FPDL. The use of Na_2CO_3 instead of $(\text{NH}_4)_2\text{CO}_3$ was the only variation in the production method of Martin Co., Nuclear Division.

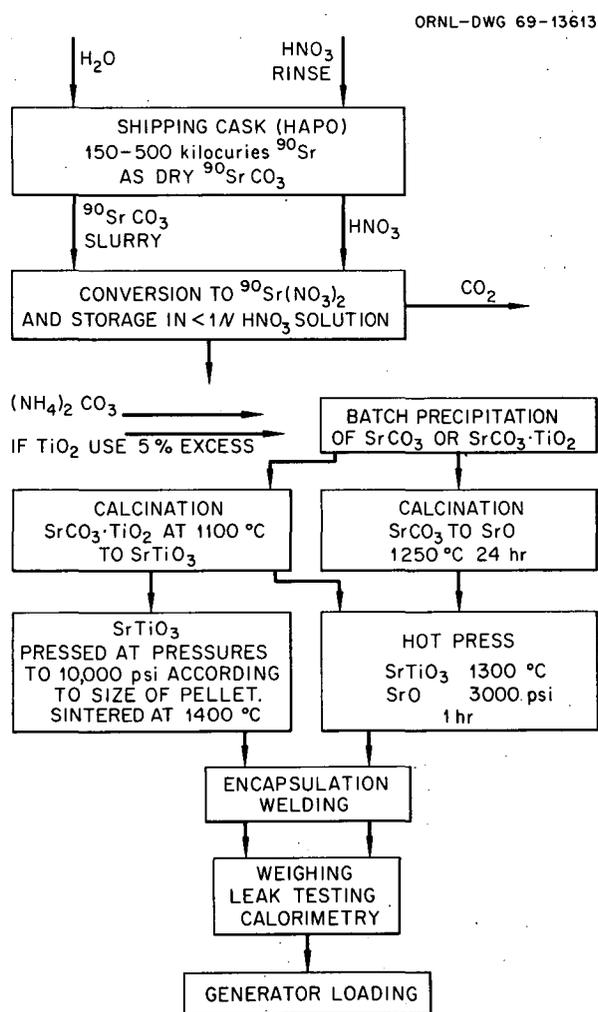


Fig. 4.1. Schematic outline of process steps for converting purified SrCO_3 to encapsulated SrTiO_3 or SrO .

PRESENT PROCEDURES FOR COMPOUND PREPARATION

Feed Material

The first step in preparing the feed material is the unloading of the HAPO-II casks by drawing water through the cask under steam-jet vacuum and slurring the $^{90}\text{SrCO}_3$ into a collection tank. After most of the $^{90}\text{SrCO}_3$ is removed from the cask, the cask is rinsed with 2 M nitric acid; the acid is added to the collection tank to convert the $^{90}\text{SrCO}_3$ slurry to $^{90}\text{Sr}(\text{NO}_3)_2$ solution. The amount of acid used is calculated so as to yield a final solution $\sim 1 M$ in HNO_3 for storage. The cask is dried, sealed, leak-tested, decontaminated and then shipped back to Hanford.

The $^{90}\text{Sr}(\text{NO}_3)_2$ solution is sampled and stored at the FPDL in stainless steel water-cooled tanks, which can hold 6 MCi of $^{90}\text{Sr}(\text{NO}_3)_2$ feed solution. The radiochemical purity of this material is $>99.9\%$ (exclusive of

*Except for sources made of SrO .

Table 4.1. Feed composition*
Range of composition, wt %

Cation	Maximum	Minimum
Sr	97	92
Ca	5	2
Ba	2	0.5
Mg	2	0

*One gram of ^{90}Sr will produce 0.0232 g of ^{90}Zr after one year's decay.

^{89}Sr , the amount of which is dependent on the age of the material); its major inert contaminant is calcium. Table 4.1 shows a typical feed analysis.

Strontium Titanate

Batches of ~ 40 kCi of $^{90}\text{Sr}(\text{NO}_3)_2$ solution are transferred from storage into a 150-liter stainless steel precipitation vessel (Fig. 4.2). This vessel is equipped with an agitator, a heating-cooling jacket, and a bottom-discharge line, as well as the standard instrumentation, sampling and off-gas lines, and other services. The solution is sampled; then it is adjusted, by evaporation and addition of ammonium hydroxide, to a ^{90}Sr concentration of ~ 10 g/liter (~ 750 Ci/liter) at pH 3 to 5. Based on the total ^{90}Sr content in the batch and the elemental analysis of the feed solution, the amount of TiO_2 required to form the titanates of the alkaline

earths present is calculated. This amount of TiO_2 plus a 5% excess is slurried into an ammoniacal $(\text{NH}_4)_2\text{CO}_3$ solution of sufficient concentration to yield a final precipitation solution 0.7 M in $(\text{NH}_4)_2\text{CO}_3$. The $^{90}\text{Sr}(\text{NO}_3)_2$ solution is heated to 70°C ; then the $(\text{NH}_4)_2\text{CO}_3\text{-TiO}_2$ slurry is added. The slurry is digested, cooled, and filtered through porous Al_2O_3 filter thimbles. No difficulty is experienced in the filtration. The $^{90}\text{SrCO}_3\text{-TiO}_2$ mixture on the filter is washed with dilute $(\text{NH}_4)_2\text{CO}_3$ solution; then it is dried by drawing air through the filter. The Al_2O_3 filter thimbles have a total volume of ~ 1800 ml, and the volume of 40 kCi of dried precipitate is ~ 1500 ml.

After the filter thimble is removed from the system, the heat generated by the ^{90}Sr dries the precipitate completely. Since a normal batch has a thermal output of ~ 250 W, careful handling of the material is necessary to prevent damage to manipulator boots and other materials in the cell. When the precipitate is dry, it is stirred to break up any lumps; then the filter thimble is inserted into a furnace (Fig. 4.3). The furnace temperature is increased at a rate of 100°C/hr to a final temperature of 1100°C . This temperature is maintained for 4 hr; then, after the furnace is cooled at a rate of 100°C/hr to $<400^\circ\text{C}$, the thimble is removed.

Batches of ~ 10 kCi each of the calcined $^{90}\text{SrTiO}_3$ are ground in a stainless steel blender to produce a uniform power. The $^{90}\text{SrTiO}_3$ product, which is usually light brown in color, can be handled, weighed, and transferred using standard laboratory size equipment



Fig. 4.2. Top view of reaction vessel.



Fig. 4.3. Filter thimble being placed in furnace.

adapted for manipulator cell use. The product is assayed calorimetrically for ^{90}Sr content. An aliquot of the powder is weighed into a brass cup and the heat output is measured by means of a differential temperature calorimeter as described later in this chapter. Several calorimetric determinations are run on each powder batch to ensure product uniformity.^{5,6} The powder has the approximate composition given in Table 4.2.

After a batch of product is assayed, the powder can be formed into pellets immediately; it may be packaged for shipment as powder; or it may be stored. Temporary storage is done in stainless steel screw-top cans, which are loaded with up to 7-kCi lots of powder and stored in dry water-cooled tubes in an in-cell storage facility at the FPDL. This storage system has a capacity of approximately 2 MCi of $^{90}\text{SrTiO}_3$ powder. For long-term storage, welded stainless steel containers are used, each of which holds 3.3 kCi of powder. These containers also serve as shipping cans for large amounts of $^{90}\text{SrTiO}_3$; larger or smaller shipments can be made in similar welded containers of various sizes. A circumferential groove is provided in these containers so that they can be opened with a tube cutter.

Experience has shown that the best grade of $^{90}\text{SrTiO}_3$ powder for the formation of dense pellets by the press-and-sinter method (see Chapter 5) is one which contains 5 to 10% excess TiO_2 over that calculated to be required to form the titanates of the alkaline earths present. Density of pressed and sintered

Table 4.2. Typical SrTiO_3 composition

Component	Wt %
Strontium	36 (~30 Ci of ^{90}Sr per g of powder)
Titanium	28
Calcium	3
Zirconium	5
Barium	0.5
Magnesium	0.5
Oxygen	26
Iron, lead, carbon	Traces (<1% total)

pellets averages 3.5 g/cm^3 . From the feed analysis, the ratio of ^{90}Sr to total Sr, Ca, Ba, and Mg is calculated, and from these data the heat output of a particular batch can be related to its chemical composition. When the composition of a product is outside the range desired, the powder may be blended mechanically with other products, which vary in the other direction, to produce products of the desired grade. Several product batches of varying compositions may be combined in one blending operation. Standard blending practices are carried out in a stainless steel blender. Successful blendings have been made by using powders in which the TiO_2 was deficient by as much as 30% or was 40% in excess of the stoichiometric amount, but most powders are much closer in composition. When one of the powders is deficient in TiO_2 , the blended material is recalced. No differences have been found in the

pellet-forming characteristics of powders that were prepared from the same feed solution, even when one powder batch was the result of a blending operation and the other was a single batch that did not require blending. Hot-pressed pellets may be made with TiO₂-to-SrO ratios that vary from TiO₂ in 30% excess of stoichiometric to pure SrO by changing the amount of TiO₂ in the slurry.

Strontium Oxide

The chemical processing operations for the preparation of ⁹⁰SrO are very similar to those for ⁹⁰SrTiO₃. The precipitation procedures simply eliminate the TiO₂ addition. Calcination of the dried ⁹⁰SrCO₃ to ⁹⁰SrO is carried out at 1250°C for 24 hr. The ⁹⁰SrO products are converted to pellets immediately after calcination. During the short period between calcination and pelletization (while samples are being assayed, dies are being loaded, etc.), the bulk ⁹⁰SrO is kept at ~550°C to minimize combination reactions with atmospheric water and carbon dioxide. The possibility of these adverse reactions eliminates ⁹⁰SrO as an inventory form for storage.

Strontium Fluoride

Two satisfactory methods of preparing SrF₂ have been tested at ORNL with nonradioactive strontium. In the first, solid SrCO₃ is heated in a nickel crucible with solid NH₄HF₂. Gaseous products are expelled leaving pure SrF₂ powder. In the second method, a solution of Sr(NO₃)₂, HNO₃, NH₄F, and urea is heated at 95°C for 8 to 10 hr. The SrF₂ precipitates at a pH 5-6; the increase in pH occurs slowly by the hydrolysis of the urea. The dried solid can be formed easily into pellets by the cold press and sinter technique. At Hanford, SrF₂ is precipitated from a neutralized Sr solution with the addition of NaF.

OTHER METHODS OF PREPARING SrTiO₃

Other ways of preparing SrTiO₃ were developed, but none was as successful as the original slurry precipitation method. Ammonium oxalate was substituted for (NH₄)₂CO₃ in one development method. The oxalate precipitation was abandoned when Sr(C₂O₄) was found to be soluble in 4 M NH₄NO₃. (NH₄NO₃ was used to elute strontium from the Decalso ion exchanger in HAPO-IA shipping cask.)

More effort was devoted to finding a form of soluble titanium that would make possible the simultaneous precipitation of strontium and titanium. Gray and

Samos^{7,8} Martin Co., Nuclear Division, report a method that caused the titanium to be hydrolyzed in the presence of Sr(OH)₂ by adding isopropyltriethanolamine titanate (DuPont Tyzor TE) to the alkaline mixture of NaOH and Sr(OH)₂. This method was not tested with radioactive strontium.

Some "soluble" titanium preparations tested at FPDL failed to give reproducible strontium-to-titanium ratios when precipitated with (NH₄)₂C₂O₄. These "soluble" forms of titanium were prepared by adding concentrated NaOH or NH₄OH and H₂O₂ to TiO₂.

Attempts to extract nickel ions from solid nickel titanium oxalate with NH₄OH and simultaneously to substitute strontium ions from Sr(NO₃)₂ solution gave an impure product.

R. F. Maness⁹ reports a process in which titanium nitrate in the presence of Sr(NO₃)₂ is hydrolyzed by boiling at a pH 0.5 and the strontium precipitated at a pH 11 with NaOH. It was not used with ⁹⁰Sr.

ANALYTICAL METHODS

Conventional Methods

Most of the methods used to analyze process solutions and solid SrTiO₃ products are conventional now in laboratories like the Oak Ridge facility¹⁰ which are equipped to analyze samples producing high levels of radiation. The methods are summarized in Table 4.3. An analytical cell in the FPDL building is shown in Fig. 4.4.

Calorimetry

Process control depends largely on calorimeters for the analysis of ⁹⁰Sr. Calorimetric methods are dependable and accurate for massive, concentrated radioactive

Table 4.3. Analytical methods used in Sr processing

Quantity to be found	Method	References
SrTiO ₃	Fusion and dissolution	11
⁹⁰ Sr	Gross β by proportional counters	12-a, 13-a, 15
⁸⁹ Sr	Yttrium removal with HDEHP, then Sr absorption study	12-b, 13-b
Other fission products	Gamma spectrometry	14, 16
Mass analysis	Mass spectrometry	12-d, 12-e
Ca, Ba, Sr	Flame spectrophotometry	12-c, 17
Ti, Zr, Mg, Fe, Pb	Emission spectroscopy	13-c, 18



Fig. 4.4. Analytical cell in Fission Product Development Laboratory building.

samples. Calorimeters measure heat produced by radioactive decay. The instruments used at FPDL were designed and constructed to measure the rate of heat production by radioactive materials.

Solids Calorimeter — For solid samples of ^{90}Sr , the calorimeter used in the FPDL measures the temperature gradient produced by the conduction of heat through a path of known properties.^{5,6} It occupies a minimum of hot-cell space and is easily operated, is resistant to damage, and is low in cost. The basic design of such a calorimeter is shown in Fig. 4.5. The upper part is a metal cup mounted on a metal shaft, at the base of which is a heat sink cooled by a stream of water at constant temperature. The heat produced by radioactive decay of the source is absorbed by the cup and conducted down the shaft to the heat sink. At steady state, the temperature difference between the top and the base of the shaft is nearly proportional to the rate at which heat is produced by the radioactive source. Extraneous heat loss is minimized by enclosing the cup and the shaft in an inverted Dewar flask.

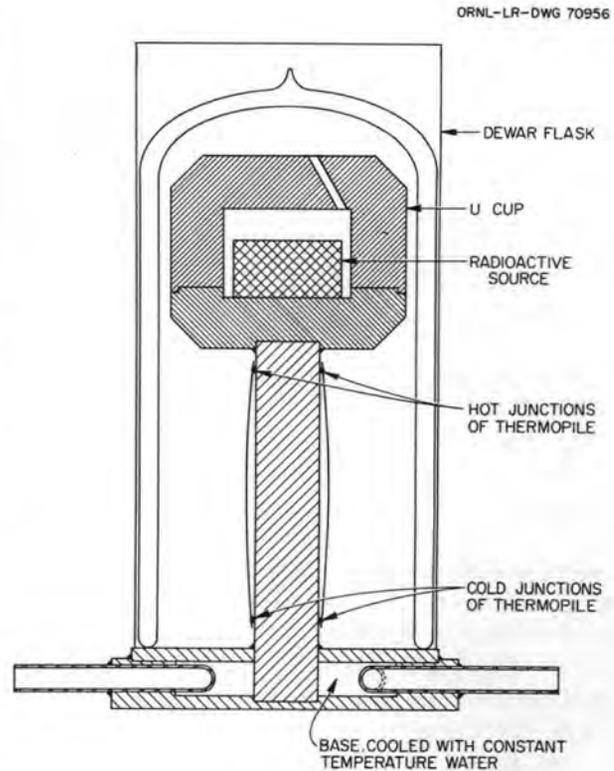


Fig. 4.5. Calorimeter for solid samples of Sr-90.

The temperature difference between the ends of the shaft (ΔT) is measured by an iron-Constantan thermopile with the junctions attached to the upper and lower extremities of the shaft. The junctions of the thermopile are evenly distributed about the circumference of the shaft at either end. A single layer of plastic-impregnated glass tape provides electrical insulation from the shaft; a second layer holds the junctions in place. Copper lead wires are connected to the thermopile at the hot-junction end of the shaft. One of the iron-Constantan junctions is replaced by an iron-copper and a Constantan-copper junction. The lead wires pass under the edge of the Dewar flask through a channel machined in the base of the calorimeter.

The construction materials were selected to maintain nearly exact proportionality between the thermopile output and the thermal power of the source. Iron-Constantan couples were chosen for the thermopile because their sensitivity ($\text{mV}/^\circ\text{C}$) varies only slightly within the range of temperatures measured. Copper was selected for the shaft because its thermal conductivity is relatively constant. The departures from constancy of thermopile sensitivity and thermal conductivity which do occur are opposite in effect to the small loss of heat through the Dewar flask.

Table 4.4. Calibration data obtained with calorimeter

Thermal power, W	Thermopile output, mV	Calibration constant, W/mV
24.18	6.594	3.667
24.32	6.626	3.671
18.38	5.005	3.673
18.08	4.929	3.669
12.27	3.339	3.674
12.32	3.354	3.675
6.17	1.682	3.676
		av 3.672

The calorimeters are calibrated before use by an electric heater placed in the cup as a substitute for the radioactive source. The voltage drop across the heater, the heater current, and the thermopile output are measured with precision commercial electrical equipment. The electrical measurements during calibration and those during use are the only instances when a high degree of precision must be attained. Comparatively loose tolerances are permissible in fabrication.

The calorimeter was designed for measuring the thermal powers of ^{90}Sr samples of 5 to 50 W. The difference in temperature between the ends of the shaft (ΔT) is $\sim 1.5^\circ\text{C/W}$.

The reproducibility of results obtained with this calorimeter is illustrated by the calibration data given in Table 4.4. No individual value of the calibration

constant differs from the average by more than 0.13%. If deviations from the average are treated as random errors, the 95% confidence limit of a single determination is 0.2%.

The performance of the calorimeter is only moderately sensitive to the rate of flow or to the temperature of the cooling water provided that both are constant during any given determination. Variation of the flow rate from 1.1 to 8 liters/min produced a change of only 0.4% in the calibration constant. A change in the cooling-water temperature from 10 to 27°C lowered the constant by 1.4%. A lowering of 1.56% was calculated from the known change of the iron-Constantan thermopile and the copper shaft with temperature. The agreement is within experimental error.

The heat output from the SrTiO_3 powder is measured after the calcination step. The powder is then stored until the fuel is to be fabricated into pellets. Pressed pellets as well as encapsulated pellets are also assayed calorimetrically. A capsule being placed in the calorimeter is shown in Fig. 4.6.

Calorimetry of Solutions — A calorimeter suitable for solutions has been designed, constructed, and tested.¹⁹ The solution of $\text{Sr}(\text{NO}_3)_2$ resulting from the removal of ^{90}Sr from HAPO-II casks is assayed immediately and stored until the next step in the fuel preparation process. These stored solutions evaporate rapidly from the ^{90}Sr heat of disintegration, making it necessary to obtain an additional analysis immediately before the



Fig. 4.6. Calorimeter for solid samples.

$\text{SrCO}_3\text{-TiO}_2$ precipitation step. The change in the strontium concentration of evaporated solutions can be determined quickly (10 min) by a solution calorimeter at this stage in the process.

The calorimeter (Fig. 4.7) is of the Tian-Calvert type in which the heat input is balanced by an equal amount of cooling provided by a Peltier device. It consists of a 5-cm³ cell constructed entirely of silver for optimum heat transfer. The cell contains nine silver rods protruding into the solution to act as heat paths. All inside surfaces are gold-plated to reduce attack by corrosive agents. The cell is insulated on all four sides and at the top with 3 in. of urethane foam to minimize heat loss in these directions.

The bottom of the cell is bonded to the cold face of the thermoelectric element with electrically insulating, heat-conductive epoxy. The hot face of the module is bonded with the same epoxy to a copper heat sink. The heat sink is immersed in a constant temperature bath that encloses the entire calorimeter. The bath temperature is held to $\pm 0.05^\circ\text{C}$ by means of a mercury regulator controlling the amount of heat added to the bath. Heat is withdrawn at a constant rate by circulating water through a coil in the liquid.

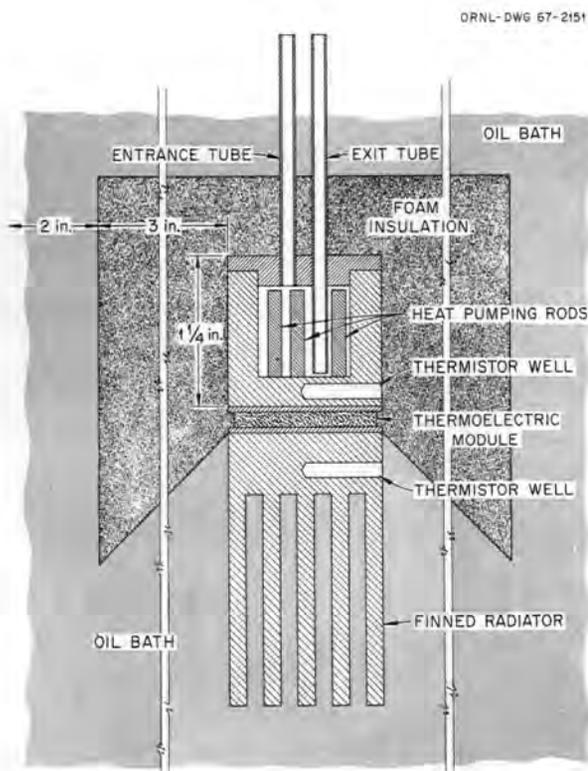


Fig. 4.7. Calorimeter for solutions of Sr-90.

In normal operation, the cell is filled with a solution of a radiochemical by either vacuum or pressure transfer, and the heat generated by the activity is sensed by a thermistor in the base plate of the cell. The change in resistance of this thermistor causes an imbalance in a Wheatstone bridge located in the detector circuit. This imbalance is then noted in a summing junction that limits the amount of power available to the thermoelectric module through an operational amplifier. The amplifier is designed to operate with reset and proportional control to supply the exact current necessary to balance the heat input from the solution. A measure of this current is directly related to the amount of heat in the solution. The relationship between the current supplied to the thermoelectric module and the watts of power in the solution is determined by calibration using electrical resistors.

The calorimeter was calibrated by placing three 0.5-W resistors in series inside the silver cell between the heat-pumping rods. These resistors were then connected to a dc power supply by Teflon-covered lead wires. Voltage to the resistors was measured by a vacuum-tube voltmeter accurate to $\pm 2\%$ full scale. The current was measured with an accuracy of $\pm 1\%$ full scale.

By varying the voltage and amperage supplied to these resistors, a calibration of the cell was obtained over the following activity:

Isotope	Activity range, Ci/ml
⁹⁰ Sr	0.5 to 150
¹³⁷ Cs	0.8 to 200
¹⁴⁴ Ce	0.5 to 125
²³⁸ Pu	0.1 to 30
²⁴⁴ Cm	0.1 to 38

The reproducibility of the determination of a known amount of power was determined to be $\pm 1\%$ over the useful range of the instrument. This calorimeter enables users to determine quickly and accurately the isotopic power content of a solution without completely removing a sample from the processing facility. The sample can then be returned directly to the main solution for further processing.

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5. FABRICATION OF FUELS

This chapter describes the ORNL experience at the Fission Products Development Laboratory (FPDL) in converting powdered SrTiO_3 or SrO into pellets suitable for encapsulation. Design of the source, shield, and generator requires reproducible physical properties, especially accurate dimensions, in the pellets. Ideal physical characteristics of a source include high density, high thermal conductivity, high melting point, high thermal stability, and good mechanical properties.

Several methods for fabricating materials (especially polycrystalline ceramics) into dense pellets are described in the literature.¹⁻⁴ In general all these methods consist in the application of heat and/or pressure over a period of time. The heat and pressure may be applied simultaneously or in sequence. Forming methods can be divided into three groups:

1. **Cold-forming**, which usually consists of the application of pressure to the material. Cold-forming methods include slip casting; extrusion; injection molding; die pressing; isostatic pressing; vibratory compaction. The compacts produced by pressing may be subsequently heated to yield higher densities.
2. **Hot-forming**, which consists in the simultaneous application of heat and pressure; the hot-forming methods are hot-pressing by uniaxial pressure, biaxial pressure, isostatic pressure with gas or liquid medium or with semifluid "sand," and hot swaging.
3. **Melt-casting**, which consists of the application of heat, but with no pressure applied.

The application of pressure in any hot- or cold-forming method sometimes involves a high energy-rate procedure such as pneumatic impaction, explosion, or electrical discharge.

All the methods of cold-forming, hot-forming, and melt-casting were evaluated for use with strontium fuel forms. The following methods were tested experimentally: die pressing — heat treating; isostatic pressing — heat treating; uniaxial hot pressing; biaxial hot-pressing; melt-casting. The methods of isostatic hot-pressing and pneumatic impaction at high temperatures were evaluated by visiting and consulting with other workers, and other methods were evaluated by a literature search.

From this study, several general conclusions were drawn with reference to forming of strontium fuels. With the exception of isostatic pressing (followed by firing) which requires expensive and complicated equip-

ment, the cold-forming methods have two primary advantages over the hot-pressing methods for SrTiO_3 : they are simple to carry out in a hot cell and they are inexpensive. However, the densities achieved with cold-pressing are low, and the reproducibility and dimensional control are poor. These factors are difficult to regulate even with closely controlled and reproducible powders. In the case of strontium fuels, the control of particle size (a critical parameter in cold-forming methods) is not feasible. In the case of isostatically pressed samples, if the pressure exceeds the strength of the particles, high unfired (green) densities can be obtained. The small additional shrinkage on firing allows good control of dimensions.

The hot-forming method (except isostatic hot-pressing) has two distinct advantages over the cold-forming or melt-casting methods: improved dimensional accuracy of the compact formed and adaptability of the method to a wide variety of materials. The hot-forming method also has the advantage that two materials can be allowed to react to produce the desired compound as the compact is being formed (reactive hot-pressing). Isostatic hot-pressing gives poor dimensional control unless the powder is prepressed to densities greater than 85% of theoretical; this is not possible with the ^{90}Sr power fuels investigated. In addition, isostatic hot-pressing is difficult and expensive for hot-cell operation.

Uniaxial or biaxial hot-pressing can be accomplished readily in a hot cell with moderate equipment costs.

Melt-casting methods are more applicable to materials that melt below 1200°C than with current strontium fuels having high melting points (Sr_2TiO_4 , 1860°C ; SrTiO_3 , 2040°C ; and SrO , $\sim 2400^\circ\text{C}$). The melt-casting method was not considered competitive with hot-pressing. In general the densities obtained by casting are low due to high void volumes and to formation of casting "pipes."

In this chapter, cold-forming techniques are discussed first; this is followed by a description of hot-pressing techniques that were developed; the chapter concludes with a brief section on melt-casting.

COLD-PRESSING AND SINTERING

Strontium-90 titanate pellets processed before 1966 were formed by the cold-pressing and sintering method. The procedure has been used successfully for a number of multikilocure fuels.⁵ Fuels fabricated since 1966 have been made by other methods.

Strontium Titanate

Pellets of $^{90}\text{SrTiO}_3$ are formed by pressing calcined $^{90}\text{SrTiO}_3$ powder in tool-steel dies and then sintering the pellets at 1400°C to improve the density. Most pellets are made in the form of cylinders with diameter-to-height ratios of 2:1 or greater. The pellet form of $^{90}\text{SrTiO}_3$ is by far the most commonly used. Pellets with diameters as small as 0.4 cm and as large as 8.8 cm have been prepared. Also, pellets of shapes other than cylindrical can be formed. Rectangular blocks of $^{90}\text{SrTiO}_3$ with dimensions of $2.5 \times 2.5 \times 0.5$ cm have been made successfully. Certain applications make use of powdered, sintered $^{90}\text{SrTiO}_3$ or of $^{90}\text{SrTiO}_3$ blended with other materials. It is preferable from a scheduling and economic standpoint to fabricate a large number of identical pellets during a continuous operation since the size of the necessary equipment such as handling tools and dies will be different for different size pellets.

Variations in the chemical composition of the $^{90}\text{SrTiO}_3$ used to form pellets have a marked effect on the final results achieved. Of the several variables that affect the quality of the finished pellets (such as calcination time, powder handling history, and storage life) the chemical composition has the largest influence, yet is the most difficult to control. Relatively small amounts of impurities change the physical density of the pellets, in addition to their effect in diluting the $^{90}\text{SrTiO}_3$. The extent of this change relative to concentrations of various impurities is not known. Both the effect of impurities and the analytical procedures necessary for their control have yet to be determined. Although there are analytical techniques capable of quite rigid characterization of a particular ^{90}Sr system, these are time-consuming, elaborate, and expensive; such techniques are not adaptable to large-scale continuous operations.

Dimensional control is not as exact in the press-and-sinter techniques as in the hot-press method; nevertheless, adequate power density and required diameter must be ensured. The problem of diameter control is important in the case of those sources that require the minimum practical clearance between the pellets and the capsule wall. Since it is impossible to predict the final pellet density accurately from the normally available powder-composition data, empirical methods are used to effect process control of pellet quality. As has been pointed out, the chemical composition of the powder has the major role in defining the final pellet characteristics. Although the true chemical composition may be known only approximately, different batches of product can be shown to have essentially identical

compositions by means of calorimetry. The precision of the calorimeter used for ^{90}Sr heat output determination is better than 1%, compared with 5% for routine ^{90}Sr determination by radiochemical methods. Thus, if a series of batches of $^{90}\text{SrTiO}_3$ powder were all prepared from the same original feed, they could be blended to produce a uniform material as measured by calorimetry. Experience has shown repeatedly that the densities of pellets made from powders characterized in this manner are reproducible.

When a series of pellets is to be made, the first operation is to prepare the necessary amount of $^{90}\text{SrTiO}_3$ powder of a uniform composition; or, if the supply of a particular feed is not sufficient, a limited number of such $^{90}\text{SrTiO}_3$ powder increments are prepared. A test die is fabricated with a diameter comparable with that expected to be required to produce finished pellets of the proper diameter. Several test pellets are pressed from each of the prepared powder increments. The pellets are then sintered and measured. Based on the results of the test pellets, the production dies are fabricated, with their diameter sized to produce pellets of the proper dimensions.

The $^{90}\text{SrTiO}_3$ powder for each pellet may be weighed individually, or a known amount of powder may be placed in a vessel and powder increments dispersed from the vessel by volume until the powder supply is exhausted. The technique chosen will depend on the desired reproducibility of pellets. In many cases the total power requirement is the only significant consideration, and pellet weights may vary considerably without harm. At times, however, the proposed arrangement of pellets within the capsule dictates close control of pellet weights.

Dies and punches are lubricated with a solution of stearic acid in acetone. A bottom punch and an unlubricated tool-steel shim are placed in the die. The measured $^{90}\text{SrTiO}_3$ powder increment is added to the die through a funnel, and another shim is placed on the powder. The top punch is then placed in the die, and the assembly is centered on the movable base plate of the hydraulic press. The exposed flat surfaces of both punches are provided with depressions which fit corresponding protrusions in the base plate and extension punches. These serve to align the assembly and provide the necessary clearances for extrusion of the pellet.

Pellets with diameters of <1 cm are pressed in a single stage, with the press being raised to impose the proper pressure and then lowered to release the pressure and allow extrusion of the pellet. For larger pellets, a double pressing is required since it had been found that the larger pellets formed by a single pressing procedure cracked in the sintering process. For this procedure, the

die and punch assembly is mounted on a hanger assembly by side arms before pressing is done. The press is raised to impose the initial pressure, which is maintained for 5 min. The press is then lowered, the extension punches are removed, and the die body is inverted. Extension punches are reinserted, and the press is raised to impose the final pressure, which is again maintained for 5 min. The pressures used vary with the sizes of the pellets. For pellets of 2- to 10-cm diameter, the initial and final pressures are ~ 5 thousand and ~ 10 thousand psi.

After the pressing, the extension punch arrangement is changed so that the die body is positioned in the center of the column formed by the extension punches, shims, and pellet. The hanger assembly is removed, leaving the die body held only by friction. A slight pressure is held on the punch column to maintain the alignment of the system. A manipulator-operated hydraulic jack is then used to slide the die body down the column and expose the pellet. The pressure on the punch column is relieved and the top punches and shim are removed. The pellet and the bottom shim are then slid off onto a handling tray. From the tray the pellet is slid onto a bed of zirconia granules (to prevent the pellets from sticking to the tray) in an alumina sintering tray. The "green" pellet is rather fragile and cannot be handled or picked up directly with manipulator tools. It is moved by sliding it onto flat surfaces by means of a

semicircular push tool having a radius slightly larger than the pellet. Figure 5.1 shows a typical press, and unfired pellets from the press are shown in Fig. 5.2.

Several pellets may be placed on one sintering tray. When a full furnace load of green pellets has been prepared, the sintering trays are loaded into the furnace. The furnace temperature is increased at 100°C/hr to a final temperature of 1400°C . This temperature is maintained for 8 hr; then the furnace is cooled at 100°C/hr to $<400^\circ\text{C}$. The finished pellets are removed from the furnace, inspected, measured, and stored in the cell on zirconia beds.

The finished pellets are usually hard, dense, very dark brown or black, and are not easily broken. Normal techniques are used in weighing, measuring, and handling these pellets. The power density of finished pellets will vary from batch to batch, with the average being $\sim 75 \text{ W/cm}^3$.

Pellet breakage generally is not a serious problem. Of the approximately 250 pellets made for use in the SNAP-7 program, only three pellets were broken. Some breakage has been experienced during fabrication of large pellets (8.8 cm, 100 W) by the cold-press and sintering procedure, and during fabrication of smaller, higher-density pellets by the hot-press technique when sheaths were not used. Strontium titanate is rather sensitive to thermal shock; hence, the changing environments of the pellets (from insulating to noninsulating)

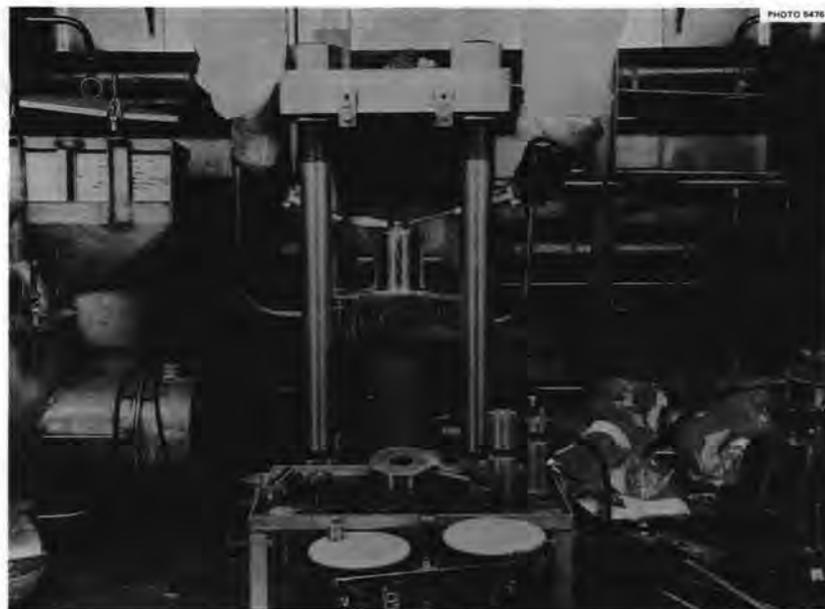


Fig. 5.1. Pellet cold-pressing equipment.



Fig. 5.2. Pellets before sintering.

together with the internal heating of the pellets probably account for the observed breakage. Resistance to thermal shock decreases with increasing density.

Strontium Oxide

Other chemical forms of strontium having a greater power density than the titanate may be used in future thermoelectric generator applications. One of these forms, SrO, was prepared for use by Nuclear Materials and Equipment Corp. (NUMEC). The cold-press and sinter technique was not successful in forming pellets of SrO. However, a brief account of the developmental work leading to this conclusion is given here.

Strontium oxide powder was prepared by calcining SrCO_3 at 1200°C in air for 4 hr. Pellets were prepared by pressing in steel dies at pressures of from 30 to 100 thousand psi. The densities of the unfired pellets increased with forming pressure. The highest density, 4.0 g/cm^3 (theoretical density = 4.5 to 5.1 g/cm^3 *), was obtained at the highest pressure. The pellets pressed under various conditions were subjected to temperatures of 1400 to 2100°C in air for 4 hr. No increase in density was observed as a result of heating to any of the temperatures investigated. The strength of the pellet, however, increased in all cases, the pellet being strongest when fired at 1500°C . At the highest temperature, a pronounced increase in grain size was also noted.

*The theoretical density varies with different proportions of impurities.

Strontium oxide tends to absorb water at temperatures $<500^\circ\text{C}$. While satisfactory sources can be made by using a dry atmosphere or only short exposure of the calcined SrO powder or pellet to air, methods of reducing the sensitivity of SrO to moisture were investigated. A lower-melting, continuous phase showing low sensitivity to moisture was sought. Solid solutions of SrO with other minor components were studied by the addition of up to 20% by weight of MgO, NiO, Al_2O_3 , SiO_2 , BeO, SrF_2 , Fe_2O_3 , and talc. Some reduction in sensitivity to moisture was demonstrated by each of the additives, but none was sufficiently effective. None of the additives had any measurable effect in promoting the densification of SrO during sintering.

Higher densities in unfired compacts are generally related to increased grain size. Prolonged calcining of SrO was used to increase the grain size, and pellets were prepared from SrO that had been calcined at 1400°C for 40 hr. The hard cake produced during the calcining step was crushed, and then pellets were formed, at pressures of 30 to 120 thousand psi. The densities obtained are given below:

Pellet formation pressure, psi	Density, g/cm^3	
	Unfired	After firing at 1400°C
30,000	3.8	3.8
120,000	4.4	4.5

During prolonged sintering of SrO, a significant loss in weight of material was noted. Further tests indicated that 2 to 4% of the SrO is lost during a 24-hr calcining cycle at 1450°C in air. The mechanism for volatilization was not determined but was believed to be due to vaporization of Sr(OH)₂ produced by reaction of the SrO with moist air.

HOT PRESSING

The densification of powdered materials by hot pressing can be described as a function of time, temperature, and pressure by assuming a plastic-flow model.¹⁻⁶ Several workers^{2,3,7} have used this model to explain the experimental data. Only a qualitative review of the kinetics of hot pressing is given here.

If pressure is applied to a material at any given temperature, the density of the material will increase as a reciprocal log function of time and will approach a relative value of density asymptotically, which is usually referred to as the end-point density for that particular pressure and temperature.

Above a critical yield-point pressure, the fraction of the end-point density achieved at a given temperature is proportional to the pressure applied.

$$kP = 1 - (1 - D)^{2/3} \ln \frac{1}{1 - D}$$

P = pressure

D = fraction of end-point density at one temperature

k = a constant at one temperature, a function of the critical yield point having the dimensions of inverse pressure at constant temperature

An increase in temperature will also increase the end-point density. A complex function for the effect of temperature on the end-point density has been given by McClelland and Smith⁸ for BeO and Al₂O₃. They conclude that at sufficiently high temperatures, where the yield point of the material is small compared to the pressure applied, the end-point density rapidly approaches the theoretical density. Experience with strontium fuel compounds has indicated in all cases tested that 4 thousand psi and 1400°C are sufficient to assure that the yield point is small compared to the pressure applied.

Typical curves showing the effect of time, temperature, and pressure (McClelland and Smith⁸) with BeO and Al₂O₃ are given in Figs. 5.3 and 5.4; strontium fuel forms showed similar behavior.

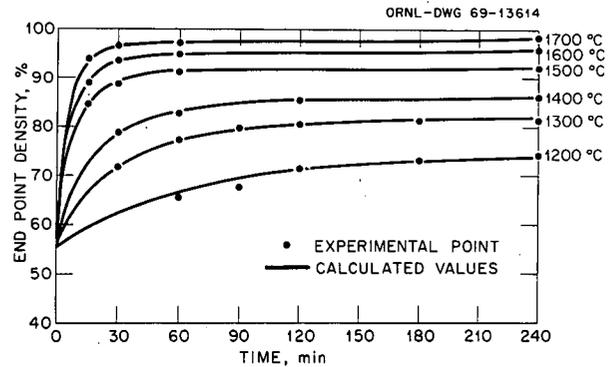


Fig. 5.3. Time-temperature dependence of density of BeO.

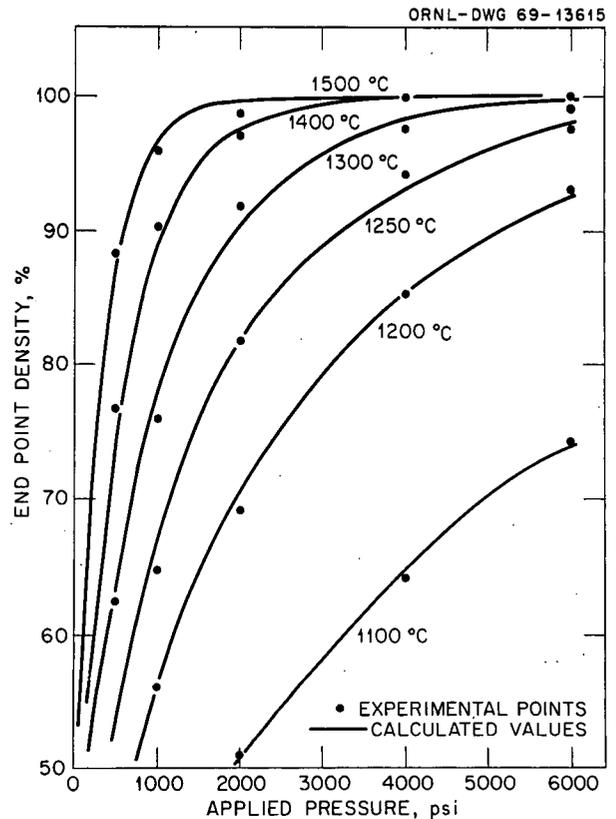


Fig. 5.4. Effect of pressure on the end-point density of Al₂O₃.

The failure of the cold-pressing and sintering method in forming SrO pellets was only one factor leading to the investigation of alternative compacting methods. However, most of the hot-pressing development work was done with SrO; consequently, discussion of hot-pressing of different chemical forms will begin with SrO.

Strontium Oxide

The development effort on the hot-press fabrication of strontium fuel was begun in November 1964. The first investigation was done jointly with the Development Division of the Y-12 Plant.

By hot-pressing SrO powder at 1375°C for 2 hr at 1800 psi, a SrO cylinder 2 in. high by 2 in. in diameter was formed, with a density of 4.75 to 4.81 g/cm³ and very high strength. (The theoretical density of SrO is 4.5 to 5.1 g/cm³). Pressure was applied to the SrO powder and the temperature then increased over the 2-hr period to 1375°C. The hot-press graphite die was lined with a molybdenum sleeve to prevent reaction of the SrO with the graphite, and the pressing was carried out in an argon atmosphere. The diameter of the completed pellet was within 0.002 in. of the desired 2.000 in.

An additional experiment was run using SrO with impurities that are typical of available ⁹⁰Sr products. The composition and theoretical density of this material are shown below; the mixture had a calculated theoretical density of 4.57 g/cm³.

Element	Composition, % (as metals)	Theoretical density of oxide, g/cm ³
Strontium	92.3	4.70
Calcium	3.7	2.62
Barium	3.7	5.72
Magnesium	0.3	3.65

The material was formed into a 2-in.-diam by 2-in.-high pellet by pressing at 1800 psig at ~1100°C, using a platinum liner in the graphite die. The platinum liner was retained as a cladding for the pellet to reduce contact of the SrO with the atmosphere. The density of the pressed oxide was 4.54 g/cm³.

Following the success of hot-pressing at Y-12, a hot press for radioactive material in a hot cell was designed and fabricated⁹ for use at FPD. Subsequent development and production of strontium fuels were accomplished with this press. In addition, a small hot press for laboratory or glove-box operation was designed and fabricated⁹ (Figs. 5.5 and 5.6).

Three 202-W ⁹⁰SrO heat sources were prepared by hot pressing. Four batches of ~35 kCi of ⁹⁰SrCO₃ each were prepared, and the dried ⁹⁰SrCO₃ powder was calcined in air at 1200°C for a minimum of 24 hr. The resulting products were assayed for ⁹⁰Sr by weighing increments of the powder and determining the heat output. Small samples of powder were dissolved in nitric acid and analyzed spectrographically for inert

contaminants; these solutions were also analyzed for radioisotope contamination. Mass analysis indicated 53.3 ± 0.5% ⁹⁰Sr. Analysis of strontium oxide is shown below.

Component	Total cations, wt %	
	Feed (SrCO ₃)	Product (SrO)
Sr	87.6	87.3
Ca	8.8	11.0
Ba	1.7	1.0
Mg	0.9	0.2
Fe	0.0	0.2
Si	0.1	0.1
Al	0.9	0.2

The fuel pellets were prepared by pressing the SrO (202 W) in a platinum-lined graphite die. The platinum liner remained with the SrO pellet to protect it from the atmosphere. The temperature of the hot press was

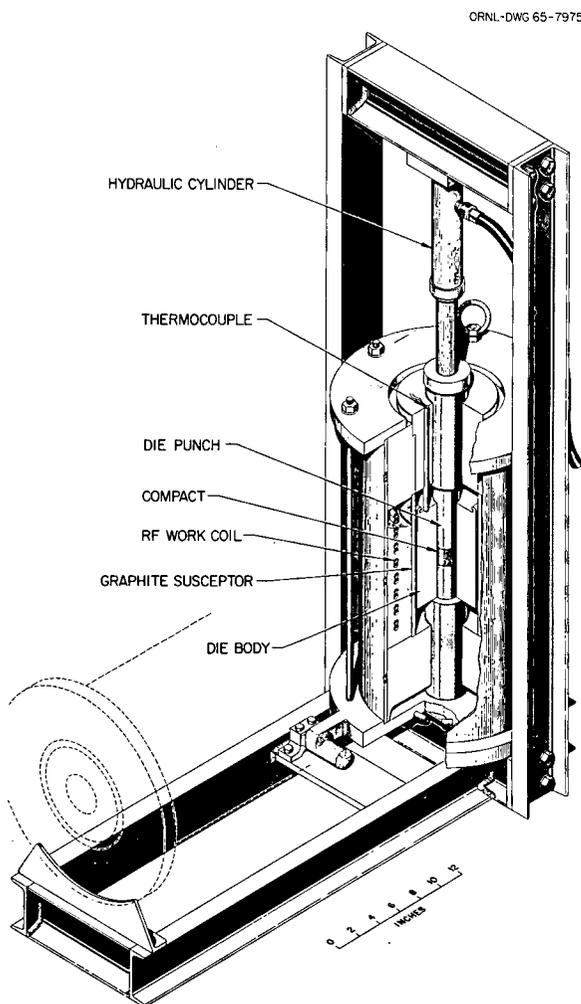


Fig. 5.5. Hot press for remote operation.

increased from ambient to 1200°C. At this temperature the pressure was raised to 3700 psi at a rate of 800 psi/min and maintained at 3700 psi for 1 hr.

The pellets were of excellent appearance with no change in appearance or dimensions after 10 days. Table 5.1 gives a description of the three pellets.

The SrO pellets were encapsulated in an inner liner of Hastelloy alloy X of 0.030-in. wall thickness. The outer capsule was 0.060-in.-thick Hastelloy alloy C. Prior to use, the capsules were tested by ultrasonic, dye-penetrant, and helium leak testing. Following the welding of both the inner and outer capsules, the welds were leak-tested with ^{85}Kr .

The completed sources were tested by thermal cycling 10 times from 500 to 700°C. Following the thermal

cycling, the sources were again leak checked and smeared for external activity. The results of the leak test are shown in Table 5.2.

Experience indicated that most of the densification occurs at less than 800°C. Tests were made with full pressure applied to the die punch, beginning at room temperature and increasing to 1200°C. If the temperature is increased at a rate of 100°C/hr from 750 to 850°C, full densification is attained at 850°C. However, if the temperature is raised to above 1200°C before pressure is applied, the density does not exceed 4.4 g/cm³ even if the temperature is increased to 1600°C. The above experiments were done in a vacuum hot press with a capacity for up to 1-in.-diam pellets (see Fig. 5.7). The results of the above experiments suggest that either a large change occurs in the surface energy of the powder at about 850°C or a sintering aid which exists as an impurity in the SrO powder is destroyed at that temperature. The latter is believed to be more

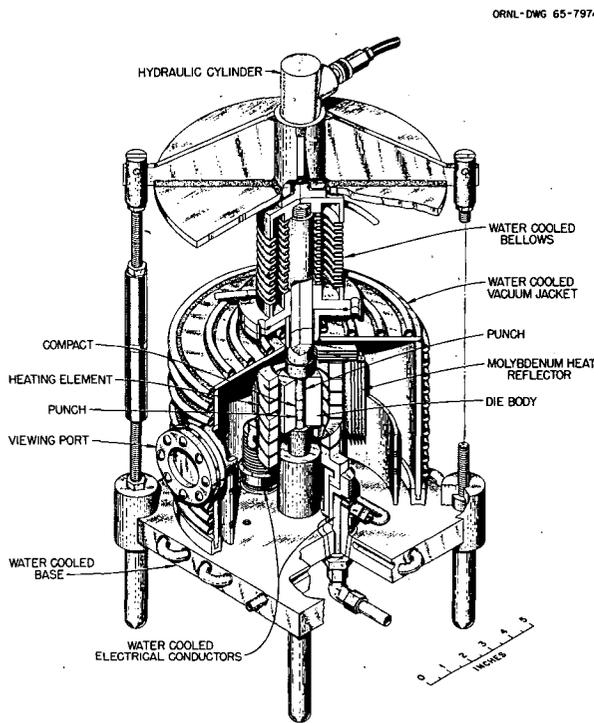


Fig. 5.6. Miniature hot press.

Table 5.1. Composition and size of hot-pressed ^{90}SrO pellets
Diameter: 5.56 cm

	Pellet Number		
	1	2	3
Height, cm	5.46	5.41	5.11
Weight, g			
SrO	527	531	525
Platinum	105	87	100
Total	632	618	625
Volume, cm ³			
SrO	127	127	120
Platinum	5	4	5
Total	132	131	125
Density, g/cm ³			
SrO	4.2	4.2	4.4
Pellet	4.8	4.7	5.0
Power density, W/cm ³	1.52	1.53	1.61

Table 5.2. ^{90}SrO source leak test results

Source number	Leak rate cm ³ /sec			Maximum smear count d/min	
	Inner capsule	Outer capsule		Before heat cycle	After heat cycle
		After welding	After heat cycle		
1	$<3 \times 10^{-8}$	$<1.5 \times 10^{-8}$			
2	$<6 \times 10^{-9}$	$<2 \times 10^{-9}$	$<3 \times 10^{-8}$	130	770
3	$<2 \times 10^{-9}$	$<2 \times 10^{-9}$	$<3 \times 10^{-8}$	80	90

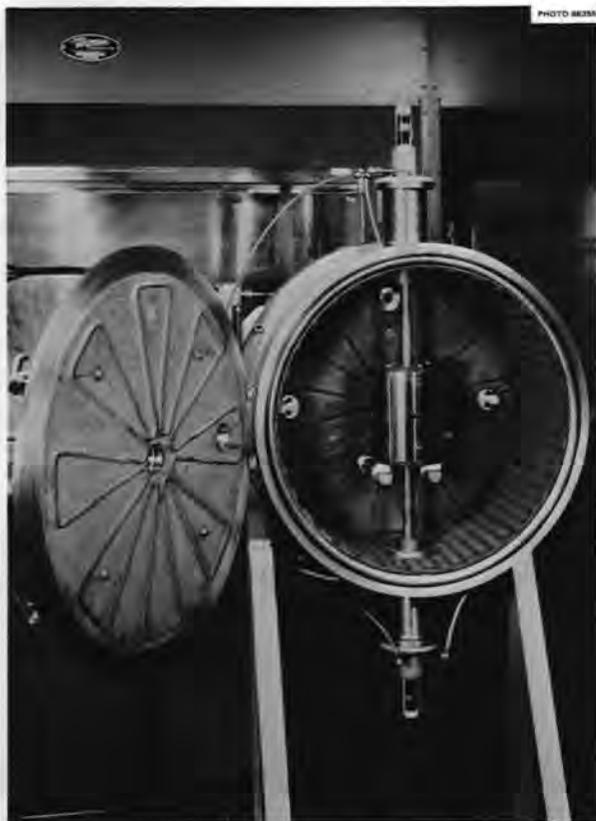


Fig. 5.7. Vacuum hot-press equipment.

likely. Small amounts of either $\text{Sr}(\text{OH})_2$ or SrCO_3 could be present and account for the low-temperature sintering. As a matter of precaution, the pellets are heated to 1200°C following densification to calcine any $\text{Sr}(\text{OH})_2$ or SrCO_3 that might be present.

Estimates from thermodynamic data predict that SrO will not react with carbon to produce strontium carbide at temperatures of less than $\sim 1500^\circ\text{C}$. Since the final procedure does not require a temperature in excess of 1200°C , tests were made on hot pressing SrO directly in graphite dies instead of molybdenum-lined dies. The SrO pellets were analyzed for strontium carbide and none was found. No problems of sticking of the SrO to the graphite die and punch material were encountered. The only need for a platinum liner is to provide protection from moisture when pellets are fabricated in air.

When pellets are formed by hot-pressing in an inert atmosphere, small bubbles of the gas at the pressing pressure can be trapped in the pellet. The gas may subsequently diffuse into the void volume and cause an increase in the pressure inside the capsule. With vacuum hot-pressing, this possibility is avoided, and the pellets have a higher density.

Strontium Titanate

The initial hot-pressing tests on SrTiO_3 were done on nonradioactive titanate in equipment at the Y-12 Plant Development Division. These tests indicated that essentially theoretical densities could be obtained on 2-in.-diam compacts by hot-pressing at 1300°C for 30 min with a pressure of 2500 psi. The densities obtained were 5.00 g/cm^3 (calculated density = 5.05). The SrTiO_3 was freshly precipitated and calcined powder. Full pressure was applied to the press at the start of the heating cycle.

Subsequent tests over a wide range of conditions and with various powders led to several conclusions. The factors that control the densification are discussed separately.

While a hot-pressing procedure is relatively insensitive to the history of the powder, it has been observed that slightly higher densities for given pressing conditions can be obtained with freshly prepared powder. The next highest densities are obtained with aged SrTiO_3 powder, and the lowest with highly sintered or previously hot-pressed and crushed material.

In general the higher the temperature at which the pellet is pressed the higher the density (up to 100% of theoretical) or the shorter the time and the lower the pressure to obtain a given density. The temperature should never exceed 1450°C . At this temperature the pellet rapidly decreases in density with extensive fragmentation. This is presumed to be due to a solid-solid phase transition at that temperature. At 1350°C , densification of all powders tested was sufficiently rapid for pressing times of less than 1 hr to be required.

The pressure that can be applied to a die is limited by the die geometry and the strength of the graphite. A pressure of 4 thousand psi is adequate for a pressing time of less than 1 hr. Die designs for 4 thousand psi on 4-in.-diam compacts are considered practicable. Pressures in excess of 4 thousand psi, when strength considerations permit, will reduce the pressing time required. Sintering of SrTiO_3 powder occurs at an appreciable rate at 900 to 1000°C . For this reason the pressing should be started at 900°C .

Strontium titanate pellets of 2-in. diameter were hot-pressed to essentially theoretical density under the following conditions:

Maximum temperature	1200°C
Pressure	1000 psi at 1000°C , increasing to 4000 psi at 1200°C
Time at maximum temperature	1 hr

The theoretical density of pure SrTiO_3 is 5.11 g/cm^3 . The calculated density of fission-product $^{90}\text{SrTiO}_3$ with the Mg, Ca, and Ba impurities is 5.05 g/cm^3 .

Future application of SrTiO_3 may require sources with diameters of up to 5 in. Strontium titanate treated at high temperatures (1200 to 1400°C , the temperatures for hot-pressing) in a neutral or reducing atmosphere undergoes a reduction in the oxygen stoichiometry. Under reducing conditions, SrTiO_3 has the composition $\text{SrTiO}_{2.99}$ (Ref. 10). Pellets of reduced SrTiO_3 are jet black. If the pellets are of high density and reduced, they are severely strained and subject to cracking. Annealing cannot be accomplished at $<2000^\circ\text{C}$. Pellets of SrTiO_3 3-in. in diameter have been hot-pressed from both active and inactive SrTiO_3 . All 3-in.-diam radioactive pellets have exhibited extensive cracking due to thermal gradients. Pellets of inactive SrTiO_3 are highly sensitive to thermal shock, and also frequently crack. To help maintain the integrity of the pellets, several conditions of the preparation and fabrication procedure were studied in order to determine their influence on cracking. The only significant

result is the observation that low-density pellets ($<4.0 \text{ g/cm}^3$) are much less likely to crack.

Two methods were tested successfully on 1-in.-diam pellets. These were (1) inclusion of randomly oriented 5-mil wire, $\frac{1}{4}$ -in. long, in the pellets, and (2) jacketing the pellet with platinum wire gauze. The wire gauze is mechanically held in the surface of the pellet. A later technique was developed, using nickel wire screens incorporated in the horizontal plane. This has been used on pellets as large as 4 in. diam (300 W) with good success. The cost savings relative to platinum are significant.

A series of photographs taken at various stages in the fabrication of the SrTiO_3 encapsulated pellets comprising the three Aerojet General Nucleonics (AGN) 45-W sources (Tables 1.1 and 6.5) describe the hot-pressing procedure in detail. Figure 5.8 shows a hot press in its open, horizontal, loading position. The powder is first pre-pressed. In Fig. 5.9 the pellet charge is added incrementally to the die body holding the bottom punch. After the addition of each 20% increment, nickel screen is added, and the powder is pressed at



Fig. 5.8. Hot press in loading position (horizontal).

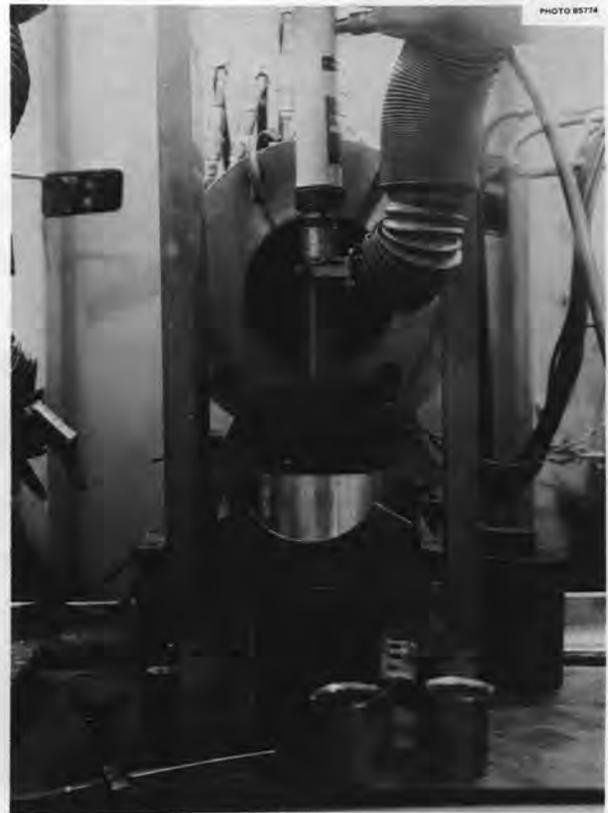


Fig. 5.9. Pre-pressing, addition of powdered charge.



Fig. 5.10. Die body insertion in hot press.



Fig. 5.11. Hot press in pressing position (vertical).

2000 psi with a stainless steel punch. After all the charge and screens have been added, the top punch is inserted.

The loaded die body is removed from the pre-pressing assembly and inserted into the hot press (Fig. 5.10); the guide collar and drive punch (shown at right) are then inserted on top of the die body to align the system. Thermocouples are inserted through penetrations in the guide collar so that they contact the die body. The hot press is then raised to the vertical position and a set of brass shims and mica insulators is placed between the graphite drive punch and the hydraulic press ram. The hot press is heated by means of a radio-frequency motor generator to 1100°C , then a pressure of 3000 psi is imposed. While the pressure is still on the system, the hot press temperature is raised to 1300°C and the pressure and temperature are maintained for $\frac{1}{2}$ hr. The pressure is then relieved and the hot press is cooled to approximately 300°C . During all periods in which the hot press is above 300°C , a flow of inert gas is maintained through the hot press cavity. In some cases an inert atmosphere is maintained in the entire cell.

Alternate furnaces use resistance as well as rf heaters. The hot press in the pressing position (vertical) may be seen in Fig. 5.11. Also shown is a die body with punches and a guide collar.

The die body is removed from the hot press and placed into the pre-pressing assembly. A steel drive punch is used to extrude the punches and pellet, which are allowed to drop into a handling tray. The completed pellets are weighed and measured. A ring gage with I.D. identical to the capsule is used to check diameter and roundness of the pellet (Fig. 5.12).

Pellets for AGN sources No. 1, 2, and 3 are shown numbered from the left in Fig. 5.13.

A typical capsule, fabricated by AGN and fueled at ORNL, is shown in Fig. 5.14. The capsules are degreased and the capsules and caps are wrapped in plastic for insertion into the cell. Pellets are inserted into the capsules and the press-fit lid is fitted. In Fig. 5.15, source No. 1 is on the left with cap in place; pellet No. 2 is being inserted into its capsule; pellet No. 3 is on the ceramic tray. In Fig. 5.16, the cap is first aligned on the capsule; then a strike plate is held in contact

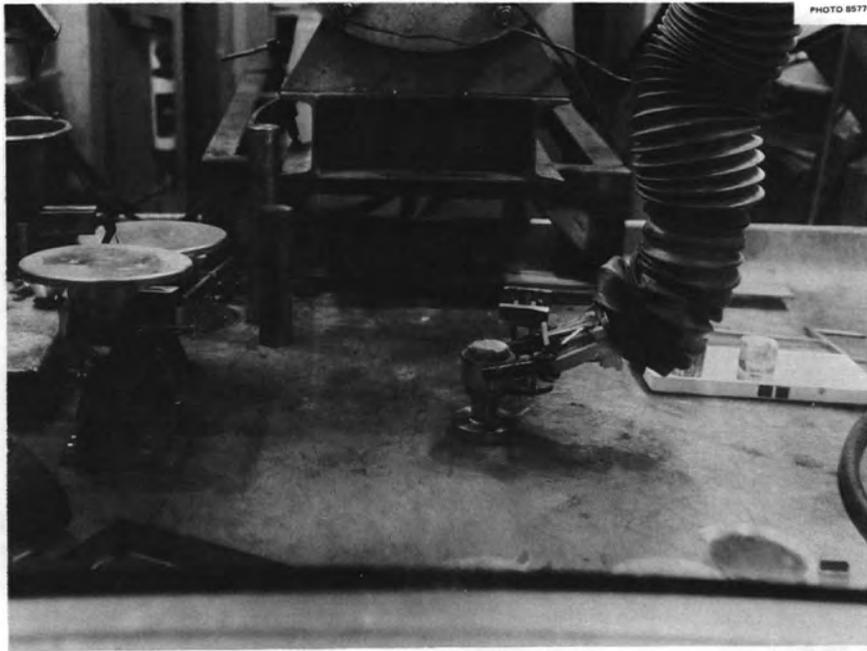


Fig. 5.12. Measuring pellet with ring gage.

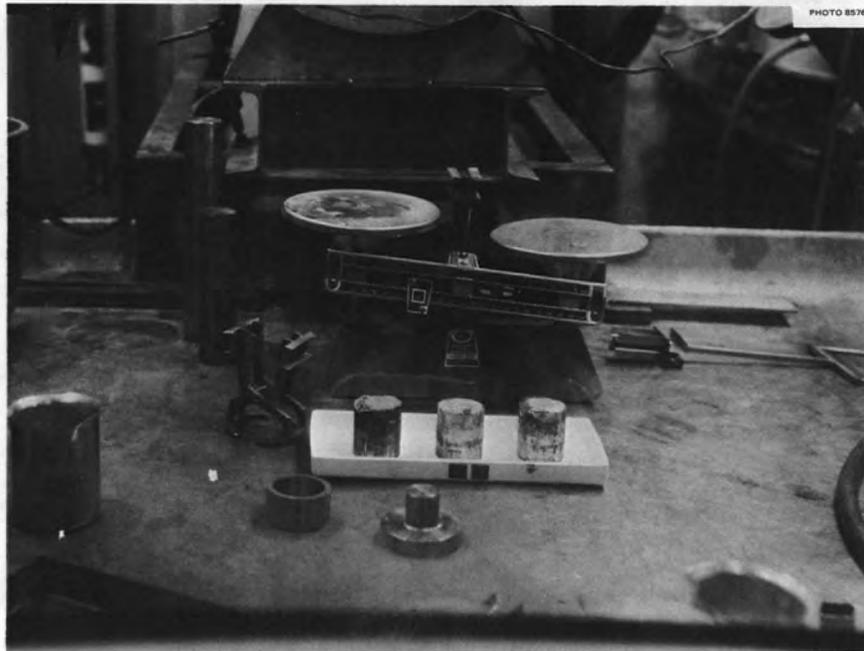


Fig. 5.13. Pellets for AGN source, 15.3 W(thermal) each.

with the cap and is tapped to insert the cap. The flat plate and the tapping on the cap serve to force the cap evenly into the capsule, thus forming an even weld area. The loaded capsules are finally welded, leak tested, and assayed calorimetrically. Welding and leak testing are discussed in Chapter 6 and calorimetry in Chapter 4.

Handling tools used in the cell are made of stainless steel. During pellet fabrication and capsule loading, no

water is used in the cell and no organic materials are allowed to contact the fuel. Since the die bodies are made of graphite, some graphite will adhere to the surfaces of the pellets; this can be seen as discoloration on the pellets. Pellets are brushed with stainless steel brushes, but no other cleaning is done on them. Completed pellets are stored on aluminum oxide trays and pellets and capsules are handled with stainless steel tools. During welding, the capsules are held in a brass chill block. Cotton swabs are used to clean weld areas and paper smears are used to detect contamination. Decontamination solutions used for final capsule cleaning are detergents, weak nitric acid, and water.

Strontium Orthotitanate

The preparation of Sr_2TiO_4 powder is identical to that of SrTiO_3 but only one-half as much TiO_2 is required. The hot-pressing characteristics of Sr_2TiO_4 are very similar to those of SrTiO_3 except that slightly higher temperatures are used. The calculated density of fission-product $^{90}\text{Sr}_2\text{TiO}_4$ is 4.93 g/cm^3 . The conditions for hot pressing Sr_2TiO_4 are the following:

Temperature	1400°C
Pressure	1000 psi applied at 800°C; pressure and temperature increased to 4000 psi at 1400°C
Time at maximum temperature	30 min



Fig. 5.14. Capsule for AGN source.

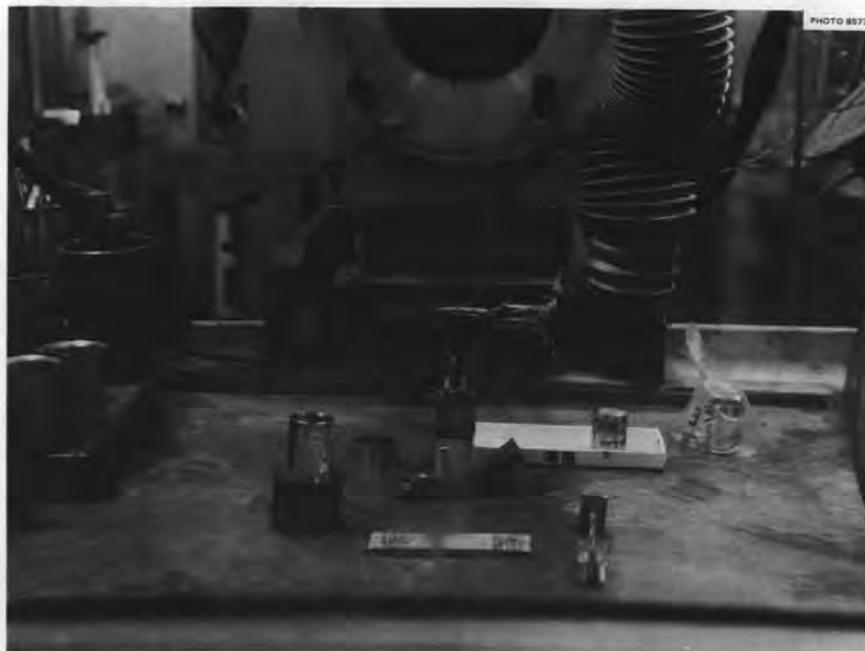


Fig. 5.15. Pellets being inserted in capsules.



Fig. 5.16. Pressing the cap on a capsule.

The average density of 24 pellets made under the above conditions is 4.94 g/cm^3 .

Strontium Fluoride

Strontium fluoride pellets were hot-pressed at 1100°C for 15 min and 2000 psi to produce compacts with 93% theoretical density (theoretical density = 4.24 g/cm^3). These pellets were pressed in an argon atmosphere. It is expected that higher density can be obtained in a vacuum hot press.

MELT-CASTING

Strontium Titanate

Melt-casting experiments were conducted on SrTiO_3 . Samples of SrTiO_3 melted at 2000°C in argon at 1 atm contained pores of up to $\frac{1}{2}$ -in. diameter. In an attempt to reduce the porosity, a sample of SrTiO_3 was melted in vacuum. The resulting material had a highly porous foam-like structure. From the results it is thought that SrTiO_3 decomposes at its melting point (2040°C) to yield a material of composition $\text{SrO} \cdot \text{TiO}_{2-x}$ where x may vary from a small value up to 0.5. The results also indicate that the decomposition pressure of SrTiO_3 at its melting point is >1 atm.

A correlation and extrapolation of composition-pressure-temperature data of Moser, Blumenthal, and

Whitmore¹⁰ gave decomposition pressure of >50 atm at 2000°C for TiO_2 . These experiments and the literature data indicate that SrTiO_3 cannot be melted and cast using conventional methods.

Strontium Fluoride

Strontium fluoride can be readily melted at about 1400°C . Attempts to cast SrF_2 have been limited to melting and solidifying in the same crucible (molybdenum crucibles were used and no interaction was observed). When melted in argon, the SrF_2 solid exhibited bubble inclusion from outgassing. When melted in vacuum, extensive vaporization occurred. The results to date are quite promising and further development could result in perfection of the melt-casting method for fabrication of SrF_2 sources.

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6. SOURCE ENCAPSULATION AND TESTING

The final step in the preparation of a heat source is to encapsulate the pellets in a suitable metal to hold the pellets in the desired location and to prevent absolutely the spread of radioactive material to the environment. The resulting capsules must be leak free, thermally and structurally stable, and capable of delivering the designed quantity of heat to the generator elements. They also must be resistant to chemical attack by the radioactive fuel and by the environments encountered during source fabrication and normal use, and in credible accidents after source fabrication.

Source fabrication studies at ORNL include consideration of the heat flow and the temperature distribution within the source. The designers of a generator generally require that a specified heat flux be delivered at a given temperature. These requirements must be met without creating excessive temperature anywhere in the source. High temperature reduces the strength of structural materials and increases corrosion rates. It can also cause melting or movement of the radioactive fuel by volatilization. Extremely high temperatures could occur in heat sources of poor design.

Large temperature drops may develop at interfaces between layers of encapsulating material and at the interface between the fuel and the capsule. The number of interfaces should be minimized, and calculations must show that the maximum possible temperature is not exceeded.

Large temperature differences may exist between the surface and the interior of the radioactive fuel (with or without a diluent or matrix material) in heat sources. These gradients are created by the flow of heat, which is generated throughout the radioactive material, to the surface. Very high internal temperatures can result.

At the present state of generator development, the maximum temperature designated for the surface of the

strontium titanate capsules is $<1000^{\circ}\text{C}$. In SNAP-7 generators it is $\sim 500^{\circ}\text{C}$. The maximum internal temperature can be lowered by the configuration of the capsule, by dilution with a good conductor (cermets), or by the introduction of metallic inclusions into the SrTiO_3 .

The welding and testing of capsules are discussed in this chapter.

WELDING OF ^{90}Sr CONTAINERS

Inert-Gas, Tungsten-Arc Welding

The primary fuel container for present-day ^{90}Sr sources is a Hastelloy alloy C capsule, welded by the inert-gas tungsten-arc process. The main reasons for the choice of Hastelloy alloy C as the primary container are its excellent seawater corrosion resistance and satisfactory weldability. However, in one case, a source prepared for a Si-Ge thermoelectric converter was encapsulated in a TZM (99% Mo, 0.5% Ti, 0.1% Zr) inner capsule and Hastelloy alloy X outer container. Other than for the common choice of Hastelloy alloy C as an encapsulating material, there has been no standardization in capsule-weld design. The joint design and the weld penetration requirements have been set largely by the particular application rather than by limitations in source fabrication technology.

Since ^{90}Sr is not an alpha-emitter, no gas builds up in the capsule and a full-penetration, pressure-vessel type of weld is not generally required. Thus, the characteristic of $^{90}\text{SrTiO}_3$ containers has been a partial penetration weld produced by the inert-gas tungsten-arc process. In most cases the weld-joint design has been some modification of the edge-type of "trepanned" design (Fig. 6.1). This design is employed for several

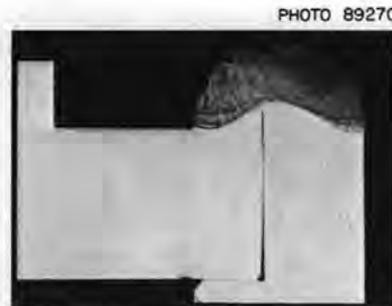
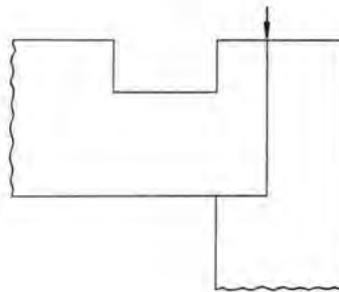


Fig. 6.1. Edge-type weld joint.

reasons. First, it is a relatively low-restraint joint which minimizes any tendency toward cracking due to shrinkage as the weld cools. This is particularly important if the cap and capsule body are fairly massive. In this case, a partial penetration weld in a plain butt-type joint would almost invariably crack due to the restraining effect of the relatively cool and therefore strong material surrounding the weak weld metal as it attempts to contract during cooling. This tendency is aggravated by the presence of the unwelded portion of the joint which acts as a built-in crack starter at the root of the weld.

The second reason for use of this joint design is that the shape of the weld bead can be observed easily. From this, the experienced welder can judge the amount of weld penetration being obtained, which in turn allows him to control the process during the operation.

The third reason for preference of the edge-type weld joint design is that no filler metal is required. Compared with a flat butt-type joint, the edge-type joint can be thought of as providing its own filler metal. Open groove-type joints which require filler metal are not generally desirable for this application because the added complexity of the wire feeding equipment and wire handling adds to the difficulty of welding in a hot cell and requires additional space. The chief reason for considering such a weld would be the need for

additional weld metal penetration. However, if a weld of great depth is to be obtained by one of these methods, the weld must also be quite wide. Thus, a tremendous amount of weld metal would be required on a comparatively small weldment (the capsule) and the result would likely be an unacceptable distortion.

When the welding gas must be of known composition, purity, and pressure, a closed-chamber welder is used, which has provisions for evacuating the system, introducing the gas, measuring the temperature and pressure, remotely positioning the electrode, viewing the welding operations, and cooling the source. (A typical assembly is shown in Fig. 6.2.)

If the welding atmosphere need not be closely controlled, open tungsten - inert-gas (TIG) welding can be used. (Figure 6.3 shows a typical open welder used for cylindrical sources.) Most remote welding techniques employ a fixed electrode with the source being rotated in a chuck. Sources with very low radiation and many alpha emitters can be welded with a hand-held torch in a glove box.

In welding these sources by the conventional inert-gas tungsten-arc process, it has been found useful to have the welder maintain complete control over the welding current. This is very desirable if, for some reason, an inaccurate estimate were made of the preheating effect of the fuel pellets. However, as greater assurances of weld penetration and overall quality are required



Fig. 6.2. Closed chamber welder.



Fig. 6.3. Open remote welding assembly.



Fig. 6.4. Operator using remote semiautomatic welding equipment.

because of a developed welding procedure which adequately takes into account the effect of capsule preheat, operator "control" can become an uncontrolled variable. Thus, the trend is toward a welding procedure developed and carried out semiautomatically on a program-controlled welding power supply. By this method, a greater assurance of weld quality can be obtained. Figure 6.4 is a photograph of such a piece of equipment in use, and a sample of such a welding procedure is given below.

Degrease capsule body and cap and place both in hot cell
 Insert capsule body into chuck
 Insert fuel into capsule
 Position cap
 Position electrode
 Set programmed welder controls as indicated

Sequence timer No. 1	5 sec
No. 2	51 sec
No. 3	5 sec
Up time	2 sec

Down time	4 sec
Initial current	75 amp
Weld current	170 amp
Finish current	10 amp

Set argon shield gas at 25 cfh

Rotate chuck at 48.6 sec/revolution

Turn power on

Push weld sequence start button

When cycle is completed, stop rotating chuck

In addition to the leak-testing procedures described in the next section, other inspection procedures are used to better assure the quality of the welded capsule. These include the inspection of "quality assurance samples," one of which is welded immediately prior to the fueled capsule or capsules and another immediately after. These sample capsule welds are normally of the same joint configuration as the actual capsule, but do not always mock up the fueled capsule completely. For instance, the sample might not be of full height or be completely machined.



Fig. 6.5. Electron-beam welding equipment.

The examination of these samples usually includes dye or fluorescent penetrant inspection of the weld area for cracks or pits, and a leak test. They are subsequently sectioned for metallographic examination of the welds. This is done to verify the weld penetration and quality at either two sections of weld 180° apart or four sections 90° apart. This procedure can give reasonable assurance of the fueled capsule weld quality if the sample welding adequately mocks up the fueled capsule.

Electron-Beam Welding

If welds are needed with penetration significantly greater than that which can be obtained by the techniques described above, electron-beam welding is adaptable to hot-cell use. Electron-beam welding is preferred over adding filler wire to conventional welds because of the drawbacks cited above for filler-wire additions and because the electron-beam process is very amenable to remote operations. Figure 6.5 is a photograph of the electron-beam welding equipment; the chamber, vacuum system, and electron-beam gun (left side of picture) would be positioned in-cell and the control console and power supply would be positioned out-of-cell. A typical weld on a Hastelloy alloy C capsule is shown in Fig. 6.6 joining a 0.300-in.-thick cap to a 0.250-in.-thick walled capsule.

The depth and continuity of the electron beam weld are inspected by a pulse-echo ultrasonic method. The

method shows defects in the weld of the order of the size of the reflected sound wavelength. The calibration recordings are shown in Fig. 6.7. Data are recorded as a plane view of the capsule weld area. Each continuous line represents one circumferential path around the capsule, and the spacing between lines represents a 0.006-in. index along the capsule axis. The lines are skewed so that a vertical deflection of a pen (caused by discontinuity indications) can be detected. This chart represents data obtained from an ultrasonic reference standard made to simulate a SNAP-21 capsule.

Holes with differing diameters were placed in the mockup capsule at a depth to simulate flaws at the weld joint position. The primary reference is the 0.015-in.-diam electrodischarge-machined (EDM) hole in line with the series of holes. It is evident from Fig. 6.7 that the primary EDM hole is easily detected on three successive circumferential paths. Also detected is the 0.015-in.-diam EDM hole near the top surface of the capsule mockup (hole center line ~ 0.012 in. from the top edge). This indicates that gross discontinuities in the top 0.020 in. of a weld would be detected. The response in this area would be reduced, however, as is evident from the indications obtained from the top-edge EDM hole. This loss in sensitivity results from only a portion of the ultrasonic energy being introduced into the capsule; the remainder is lost over the top of the capsule. A fueled capsule weld recording is shown in Fig. 6.8.

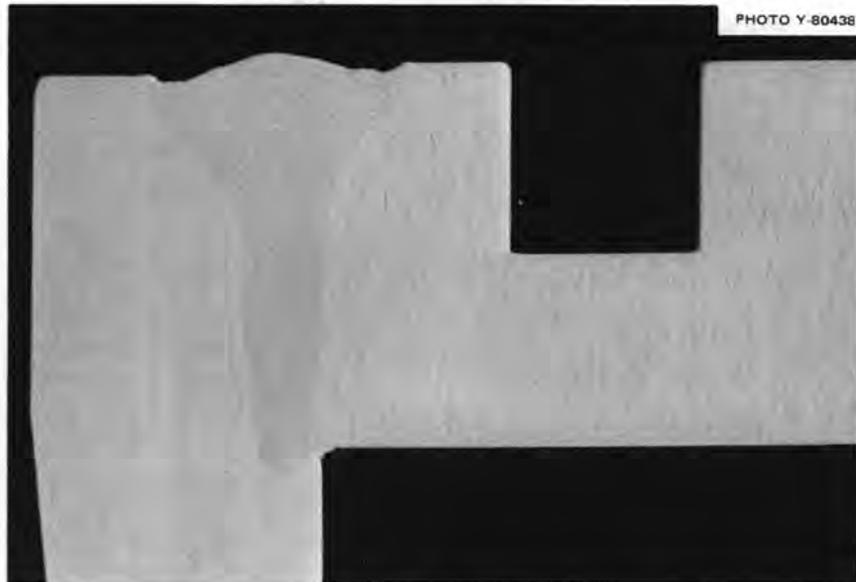


Fig. 6.6. Electron-beam weld Hastelloy Alloy-C capsule.

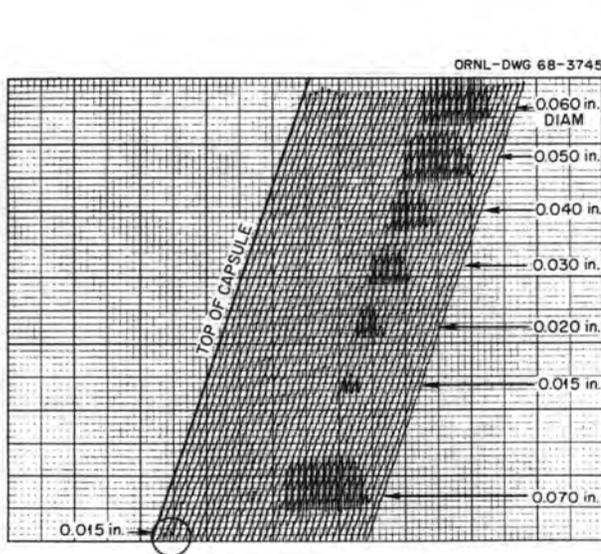


Fig. 6.7. Recording of ultrasonic response from SNAP-21 capsule calibration standard with various hole sizes.

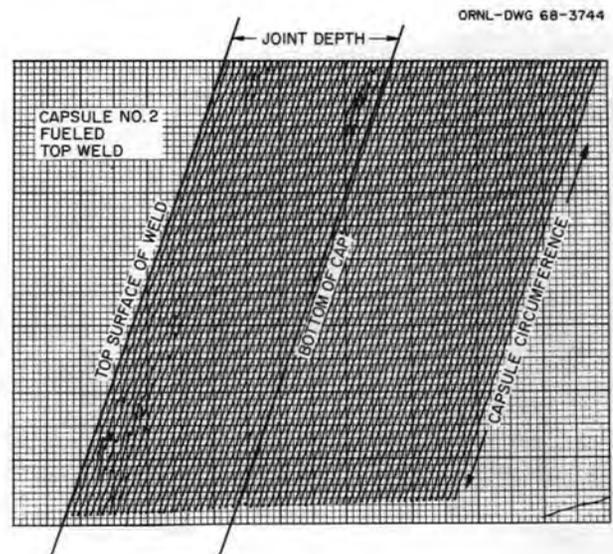


Fig. 6.8. Results of ultrasonic inspection of the top electron-beam weld of a fueled SNAP-21 capsule.

LEAK TESTING

Radioactive materials for use as radiation or heat sources must be encapsulated in a manner which will prevent the release of radioactivity during normal operations or under potential accident conditions. Most sources are encapsulated in welded metal containers and an important requirement is a demonstration that the welded closure is free from significant leaks. Methods of

leak testing at FPD are usually limited to those procedures which can be performed by remote means using manipulator-operated equipment. These methods involve immersion in some type of liquid; however, in cases where immersion methods are unsuitable because the source has a high thermal output or the encapsulating method is incompatible with the test liquid, a ^{85}Kr leak-test procedure is used.

Visual Examination

The value of a thorough visual examination should not be discounted, for in many instances examination of seal areas under moderate magnification (5 to 20X) clearly reveals porosity.

Vacuum Leak Test

The source to be leak-tested is immersed in ethylene glycol or isopropyl alcohol, and the pressure above the liquid is reduced to about 125 mm Hg absolute; a leak is indicated by a stream of bubbles rising through the liquid. The sensitivity of the test was determined by preparing a number of calibrated leaks, measuring the hole sizes microscopically, and measuring the leak rates. Under the test conditions described above, leak rates as small as 3×10^{-6} cm³/sec can be readily detected, and leaks of 1×10^{-7} cm³/sec have been detected by subjecting the capsule to a higher gas pressure immediately before the test. The relationship between the leak diameter (D), surface tension of the immersion liquid (T), and pressure differential required to initiate bubbling (ΔP) can be expressed by the empirical equation, $\Delta P = 4T/D$. Either isopropyl alcohol or ethylene glycol can be used as the immersion liquid because of their relatively low vapor pressures and surface tensions.

The vacuum leak test can be used only if the free volume in the capsule is adequate to support a stream

of air bubbles in the event of a leak. The test has been used successfully on samples having free volumes as small as 0.1 cm³; however, this is the minimum volume for which it should be used. This test may fail if there is a large leak. The observer can easily miss the one or two large bubbles which escape.

Immersion Test

When the free space in the capsule is insufficient for the vacuum leak test, an alternative test can be used. This test involves adding a small amount of an easily soluble salt such as lithium chloride to the nonradioactive source compound in the prototype capsule being tested and submerging the source in water in a vessel which is alternately evacuated and vented to atmospheric pressure for 20 min. The water is then analyzed by a flame photometric technique capable of detecting lithium concentrations as low as 0.003 $\mu\text{g}/\text{cm}^3$. A soluble radioactive tracer (²⁴NaCl) can be substituted for the nonradioactive tracer and standard counting methods can be used for analysis. If SrO is the source material, the activity can be counted directly. SrTiO₃ is too insoluble to indicate a leak (sic). An IAEA test for "special form material" and a British test for sealed sources is an immersion test of this kind.



Fig. 6.9. Hot-water bubble leak test.

Hot-Water Bubble Test

The source at room temperature is quickly immersed in water that is just below the boiling point ($\sim 90^{\circ}\text{C}$). If a stream of bubbles emanates from the source due to the expansion of air in the source, a leak is indicated. The sensitivity of this test is estimated to be $\sim 10^{-4}$ cm^3/sec . Figure 6.9 illustrates the test.

Air-Pressure Bubble Test

This test is a variation of the hot-water bubble test. The source is placed in a pressure vessel at ~ 7 atmospheres air pressure for 15 min and then is quickly transferred to the hot water. A leak is present if a stream of bubbles is observed.

Weight-Gain Test

In this test, the source is weighed and placed in a water-filled pressure vessel. The water pressure is then increased to the desired value and held for a predetermined length of time, after which the source is air-dried and weighed. A gain in weight indicates that water has entered the capsule through a leak. There are many variations of this test, particularly in the pressure used and the length of the test. A typical set of conditions used is a water pressure of 300 psig for a period of 1 hr.

The weight-gain test may be unreliable where there is extraneous material on the source capsule that can be dislodged by the water. The internal void volume should be large enough so that water will enter the capsule through a leak under the test conditions. The weight of the water entering a leak should be at least five times the sensitivity of the weighing equipment and the time allotted for the test must be sufficient to reach this weight of water at the test pressure. Clean, distilled water should be used so that particulate matter will not plug the leak hole. In the case of very large leak holes and small internal void volumes, the water may be lost in the drying step and the leak will not be found. The water pressure should not be so high as to deform the source capsule. For small leaks an evacuation step immediately preceding the pressurization may remove air from the void space and provide additional space for water which may enter through a leak.

Smear Test

All accessible surfaces of the source are wiped with an absorbent paper disk, 25 mm in diameter. No attempt is made to scrub the source vigorously, but it is thoroughly wiped, using moderate pressure on the paper.

Both wet and dry smear papers are used, and the wet smears consistently pick up a higher count than the dry smears. In all cases in which a wet smear shows a leak, however, the corresponding dry smear also shows a leak. The smear test does not always indicate a leaking capsule.

Alternative Procedure — ^{85}Kr Leak Testing

When none of the above methods can be used because the sources have high thermal output or are incompatible with the test liquid, an alternative leak-test procedure is used. Krypton-85 is introduced into the capsule atmosphere during or after welding; then test conditions are established which will allow the ^{85}Kr to pass through any leaks into a controlled atmosphere, where the amount of ^{85}Kr can be determined by counting and the leak rate can be calculated. The size, shape, quantity of radioactive material, temperature, or fabrication material of the source do not influence this ^{85}Kr test procedure except as they relate to handling procedures. Leak tests can be made in environments simulating expected operating environments or accident conditions, and long-term shelf-life tests with periodic leak-rate measurements can be made. The procedure is simple and easily adaptable to remote operation. A leak rate sensitivity of 10^{-8} cm^3/sec is adequate for testing most sources, and leaks of this size can be detected by direct measurement techniques using the ^{85}Kr test procedure.

The ^{85}Kr leak-test method has been used at the ORNL Isotopes Development Center since 1959 (Ref. 3). It was first used to check sealed radioactive gas shipping cylinders for leaks; later it was also used routinely to show that glass ampules containing radioactive gases were properly sealed before they were shipped. The ^{85}Kr method for leak testing welded sources has been in use since 1961 and was used to test all the SrTiO_3 encapsulated sources. The method is easily adaptable for routine testing of large numbers of capsules.^{4,5}

Apparatus and Equipment — A shielded gas cylinder⁶ is used to introduce the ^{85}Kr into the atmosphere of the welder chamber or pressurization chamber. The ^{85}Kr is loaded into the transfer cylinder from a stock cylinder of purified ^{85}Kr , and a valved connector is used to attach the transfer cylinder to the chamber.

The leak-test chamber provides a sealed environment in which to collect the ^{85}Kr during the test. In its simplest form this chamber is a cylindrical vessel with a gasketed top. Penetrations for introducing the gas, discharging the gas to vent or vacuum, measuring the pressure, and sampling are through the removable top.

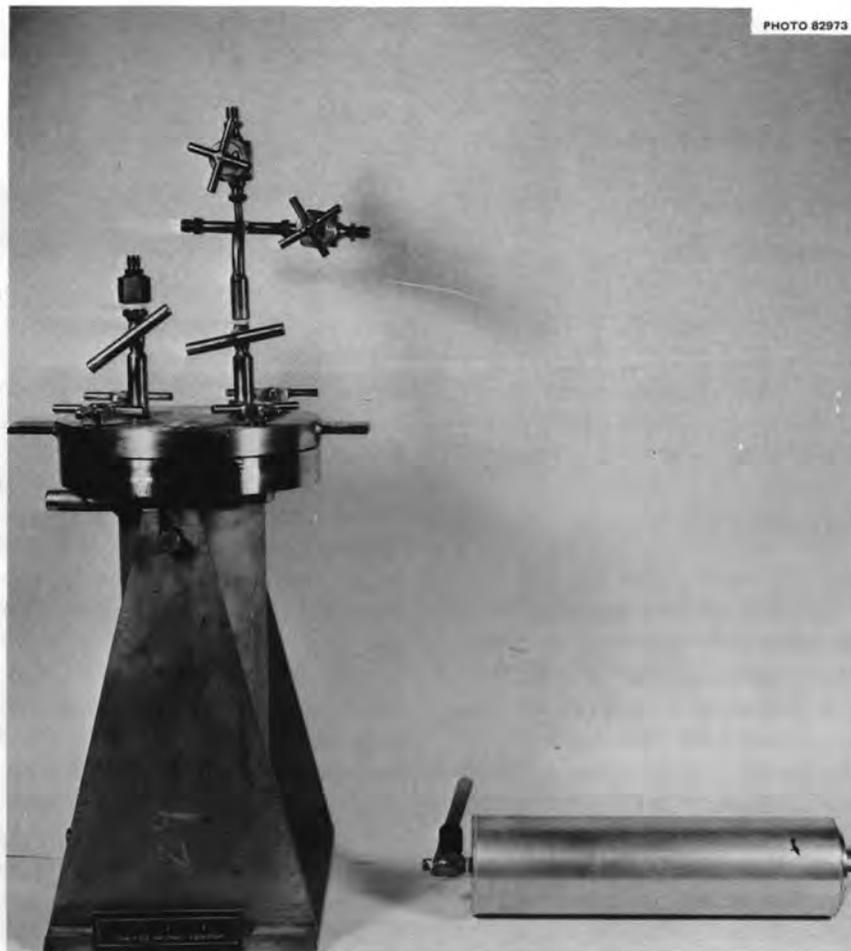


Fig. 6.10. Leak test chamber (R) and sampling cylinder (L).

Other designs incorporate cooling systems, temperature-measuring devices, viewing windows, and other special attachments.

The sampling cylinder is a specially constructed gas cylinder containing a Geiger-Mueller (GM) tube. (A typical leak test chamber and sampling cylinder are shown in Fig. 6.10.) On one end of the cylinder is a valved connector for attaching the cylinder to the nipple of the leak-test chamber; the instrument connector for the GM tube projects from the other end of the cylinder.

A radioactive gas counter specifically calibrated for ^{85}Kr is used to detect the ^{85}Kr in the sampling cylinder. The GM tube of the cylinder connects to the counter so that the sampling cylinder becomes the detection chamber of the counter.

A pressurization chamber is used when the ^{85}Kr is introduced into the capsule after welding. This chamber is similar in design to the leak-test chamber, and

sometimes the leak-test chamber is used for this operation.

Purified krypton gas containing $\sim 5\%$ ^{85}Kr is a standard product of the Isotopes Development Center and is routinely available in large amounts. This fission-product gas is recovered during the processing of nuclear fuel, and purification is effected by a chromatographic process.⁷ Both the chemical and radiochemical purities of the standard material are $>99\%$. Krypton-85 has a half-life of 10.3 yr, is essentially a pure beta emitter ($>99\%$ 0.695-MeV beta; 0.65% 0.15-MeV beta; and 0.54-MeV gamma), and is one of the least biologically hazardous radioisotopes [relative hazard value* of 2.47×10^{-5} (Ref. 8)]. Since only a very small quantity of ^{85}Kr is actually introduced into the capsule, the radiation from the ^{85}Kr is negligible.

*Ratio of the average $\mu\text{Ci}/\text{cm}^3$ inhaled under defined conditions to the maximum permissible concentration for occupational exposure (relative hazard value for $^{226}\text{Ra} = 1$).

Krypton-85 Introduction — When the closed chamber welder is used, the source is loaded and capped before being inserted into the welder. Provisions must be made to ensure that the ^{85}Kr will be introduced into the capsule before welding, and this is usually done by cutting small vertical grooves in the edge of the capsule cap. These grooves are welded closed as the weld is made. Another method is to provide a vent nipple in the cap and close the vent with a separate spot weld after the major weld is made. After the capsule has been positioned in the welder, the welder chamber is sealed. The welding atmosphere is established by alternately evacuating the chamber and back-filling it with welding gas. (This may be done several times, depending on the welding requirement.) While the chamber is under vacuum on the last cycle, the radioactive gas transfer cylinder containing a known amount of ^{85}Kr is attached to the chamber, and the ^{85}Kr is admitted. The chamber is then filled with welding gas at the required pressure and the capsule is welded. No special venting of the capsule is required when open welding is used since the ^{85}Kr is introduced after the weld is made. The capsule is frequently loaded and capped in the same assembly used for the welding.

After a visual inspection and preliminary leak test, the capsule is placed in the pressurization chamber. The chamber is evacuated, a known amount of ^{85}Kr is introduced into the chamber, and the chamber is pressurized with inert gas. The system is then allowed to stand for a specified period. The amount of ^{85}Kr used, the pressure, and the pressurization time will be determined by the required leak-test sensitivity and the operational status. The ^{85}Kr is removed from the chamber either by returning it to storage or discharging it into the radioactive gas disposal system.

Leak-Testing Procedure — Handling techniques and test procedures vary with the capsule characteristics. Size, shape, capsule material, radioactive material content, and final use for the capsule must all be considered. Many capsules have high thermal output and require cooling during handling or during the test period. In some cases, it is necessary to ensure that the capsule temperature does not go below a certain value; some tests may need to be performed at high temperatures to simulate operating conditions. Evaluation of the required time, amount of ^{85}Kr needed, and other handling aspects must be made on an individual basis.

In general, the preintroduction of ^{85}Kr is the preferred method from a leak test standpoint. This procedure requires less ^{85}Kr , is simpler, and is more accurate, since the postintroduction method requires calculation of capsule void volume and internal pres-

sure. The closed-chamber welding procedure is, however, the more expensive method.

All essential equipment must be calibrated before the tests are started, and such items as the volume occupied by the capsule and its chill block, the capsule void volume, and the capsule internal pressure must be measured or calculated in order to define the proper procedure. Other operations that may be required include measurement of heat output and radiation, dimensional checks, heat cycling, and pressure-vacuum cycling. Capsules are decontaminated to a low level before being tested, and preliminary leak tests, such as the liquid immersion-gas bubble test, are usually made at this point. The capsule and the leak-test equipment must be as clean as possible, since ^{85}Kr can be trapped on organic materials or other impurities, thereby resulting in erroneous values. When several tests are being made in series, the leak-test chamber is flushed thoroughly with inert gas between tests to remove residual ^{85}Kr . Capsules are usually tested individually, but groups of capsules may be checked qualitatively. Ideally, a capsule will be tested under conditions approximating those expected during the use of the source. When this cannot be done, the leak-test results can be used to extrapolate to the expected conditions.

The procedure for collecting and counting the ^{85}Kr consists in inserting the capsule into the leak-test chamber, sealing the chamber, and alternately evacuating and back-filling with inert gas several times.

The chamber is filled with inert gas at a predetermined pressure, and other necessary test conditions, such as capsule temperature, are established. The system is allowed to stand for the required collection period, the length of which depends on the desired limit of detection, with longer collection periods resulting in increased sensitivity.

The sampling cylinder is evacuated, a ^{85}Kr background count is made, and the cylinder is attached to the nipple on the leak-test chamber. The valves between the leak-test chamber and the sampling cylinder are opened for sampling of the chamber; then the cylinder is sealed and removed. The sampling cylinder is attached to the radioactive gas counter and the ^{85}Kr is counted.

A given capsule may be tested several times under different conditions. Frequently a shelf-life test is made, in which the capsule is retested at the end of a certain period of time or at intervals during a specified length of time.

Calculations — The required sensitivity for leak-rate determination varies with the type of source being

tested. In the leak-rate range between 10^{-4} and 10^{-8} $\text{cm}^3/\text{sec.}$, certain assumptions can be made to simplify calculations. Since there is no migration of gas by chemical methods, the gas-transfer mechanism can be considered to be 100% by viscous flow. The viscosities of gases normally used (air, H_2 , He, Ar, Kr) are similar, and no diffusion phenomena are involved. Therefore, the exiting gas can be assumed to be of the same composition as the contained gas.

In the calculations to be described, it is assumed that $P_c > P_t$ and in the postintroduction method that $P_p - P_c = P_c - P_t$, where

P_c = pressure in the capsule,

P_t = pressure in the test chamber,

P_p = pressure in the pressurization chamber.

Although the leak rate is usually quoted in cm^3/sec under the test conditions, rather than being related to any standard conditions, corrections can be applied if a closer estimate is needed of the leak rate in situations which differ from the test conditions. Cases where such corrections might be required include those in which the capsule operating environment would be significantly different from the test environment and in which a very sensitive leak test was required or in which the pressure conditions varied significantly from those established for the test. A special case involves sources

containing alpha emitters, since decay of the radioactive material evolves as gas.

Estimates of leak cross sections can be made by using the results of the ^{85}Kr leak test and known characteristics of the source. The ^{85}Kr leak test is adequate for small leaks, but for relatively large leaks the loss of test gas during evacuations will cause erratic results. This action can sometimes result in a negative leak test, when actually there is a large leak. The ^{85}Kr test is most effectively used in conjunction with other less sensitive tests to prevent misinterpretation of results. Decontamination of the capsule to the low levels required for testing indicates the absence of gross leaks.

The data required for the leak-rate calculations and the nomenclature used in the equations to be presented are given in Table 6.1.

The calculation of the leak rate differs between the two techniques of ^{85}Kr introduction only in the method for calculating the activity concentration of ^{85}Kr in the capsule atmosphere. With closed-chamber welding and preintroduction of ^{85}Kr , the activity concentration of ^{85}Kr in the capsule atmosphere is the same as that in the welding gas. This value is given by

$$S = \frac{A_w}{V_w} \quad (1)$$

When the method of open welding, postintroduction of ^{85}Kr is used, the value of S can be expressed by

$$S = \frac{A_p t_p L}{V_c V_p} \quad (1a)$$

For a capsule containing an atmosphere of activity concentration S, the amount of ^{85}Kr passing through the leak in time t_c is given by

$$A_c = S t_c L \quad (2)$$

The leaked gas is collected in a closed system of volume V_t , which is then sampled by means of a sampling cylinder of volume V_s ; so the amount of ^{85}Kr in the sampling cylinder is

$$A_s = \frac{A_c V_s}{V_t + V_s} \quad (3)$$

For a count rate of C and a counter efficiency of e, A_s is given by

$$A_s = \frac{C}{2.22 \times 10^6 e} \quad (4)$$

Table 6.1. Nomenclature for leak rate calculations

Symbol	Definition	Units
V_w	Free volume of welder chamber ^a	cm^3
V_p	Free volume of pressurization chamber ^b	cm^3
V_s	Volume of sampling cylinder	cm^3
V_t	Free volume of leak test chamber	cm^3
V_c	Free volume in capsule ^b	cm^3
t_p	Pressurization time ^b	sec
t_c	Collection time	sec
A_p	^{85}Kr added to pressurization chamber ^b	μCi
A_w	^{85}Kr added to welder chamber ^c	μCi
A_c	^{85}Kr collected in test chamber	μCi
A_s	^{85}Kr collected in sampling cylinder	μCi
S	Activity concentration of ^{85}Kr in capsule atmosphere	$\mu\text{Ci}/\text{cm}^3$
C	Count rate of ^{85}Kr in sampling cylinder	counts/min
e	Efficiency of counter	counts/dis
L	Leak rate under test conditions	cm^3/sec

^aIncluding volume of gas transfer cylinder.

^bRequired for postintroduction method only.

^cRequired for preintroduction method only.

Combining Eqs. (3) and (4) and solving for A_c gives

$$A_c = \frac{C(V_t + V_s)}{2.22 \times 10^6 e V_s t_c S} \quad (5)$$

By substituting for A_c in Eq. (2) and solving for L , the leak rate can be expressed as

$$L = \frac{C(V_t + V_s)}{2.22 \times 10^6 e V_s t_c S} \quad (6)$$

Substitution of the two expressions for S given in Eqs. (1) and (1a) yields

$$L = \frac{C(V_t + V_s) V_w}{2.22 \times 10^6 e V_s t_c A_w} \quad (7)$$

for the preintroduction method and

$$L = \sqrt{\frac{C(V_t + V_s) V_c V_p}{2.22 \times 10^6 e V_s t_c A_p t_p}} \quad (7a)$$

for the postintroduction method.

All the volumes shown above except the capsule free volume can be determined during equipment calibration. Where required, these values are corrected to account for the space occupied by the capsule, chill block, etc., during the test. The capsule free volume is calculated from the known dimensions of the capsule and the in-cell measured volume of the radioactive material put into the capsule. The amount of ^{85}Kr added to the system and the counter efficiency factor are also premeasured. Other data are either taken during the test or calculated.

To illustrate the technique of selecting leak test parameters, the following example is assumed:

1. A capsule is to be leak tested with a sensitivity of $1 \times 10^{-7} \text{ cm}^3/\text{sec}$.
2. The expected capsule free volume is 5 cm^3 .
3. The size of the capsule is such that the volumes during test conditions would be

$$V_w = 10,000 \text{ cm}^3$$

$$V_p = 100 \text{ cm}^3$$

$$V_s = 500 \text{ cm}^3$$

$$V_t = 100 \text{ cm}^3$$

4. The fabrication schedule will permit a 10-hr pressurization time and a 5-hr collection time.
5. The counter efficiency has been determined to be 0.01 count/dis, with a background variance of ± 25 counts/min.

6. The capsule material may be welded by either open- or closed-chamber techniques.

Since the counter background can vary over a range of 50 counts/min from high to low, any count rate of < 50 counts would represent an uncertain leak. Therefore the leak test must be such that a $10^{-7} \text{ cm}^3/\text{sec}$ leak would give a count rate that is significantly higher than 50 counts/min. To calculate the amount of ^{85}Kr required if the preintroduction method were used, the values of C and L are taken as 500 counts/min and $1 \times 10^{-7} \text{ cm}^3/\text{sec}$, respectively, and Eq. (7) is solved for A_w , giving $2.7 \times 10^5 \mu\text{Ci}$, or 0.27 Ci. The amount of ^{85}Kr required if the postintroduction method were used is calculated by solving Eq. (7a) for A_p , using the same values for L and C . This calculation gives $2.1 \times 10^6 \mu\text{Ci}$ or 2.1 Ci.

Similar calculations can be made to arrive at the optimum conditions for any case. Many adjustments can be made — shorter collection times can be balanced by the use of larger amounts of ^{85}Kr , longer pressurization times require less ^{85}Kr , etc.

Summary — The gas-leak rates of welded capsules containing radioactive materials can be determined with a high degree of sensitivity using relatively simple equipment by means of the ^{85}Kr leak test. This test is particularly useful when the capsule must be tested under controlled conditions, since the precision of the test is essentially independent of the test environment. Radiation from the ^{85}Kr introduced into the capsule is negligible compared with that from the capsule contents, and no chemical compatibility problems are involved. The method is easily adaptable for routine testing of large numbers of capsules. When combined with other standard leak-test methods, the ^{85}Kr leak test provides for determination of leak rates over a wide range of sensitivities. Practical limitations on the use of this test method are only those which would also limit the fabrication of capsules in manipulator cells.

HEAT TRANSFER AND THERMAL CONDUCTIVITY

Source fabrication studies at ORNL include a consideration of the heat transfer and temperature distribution from the center of the encapsulated source to the surfaces from which the heat will be drawn to operate the generators. Designers of the generator apparatus set the limits for the minimum temperature and heat flux to be delivered to these surfaces.^{9,10}

Design calculations show the need for good thermal conductivity values. High-temperature thermal conductivity data are lacking for most of the source materials.

Furthermore, thermal conductivities are affected to an appreciable degree by impurities and porosity; thus nominally identical samples may differ in conductivity. An example is the second-generation ^{90}Sr power generators such as SNAP-23 which requires an isotopic heat source of 10-cm diameter, delivering 1200 W of thermal power. An accurate knowledge of the thermal conductivity of these large sources will be needed in calculation of thermal gradients and the consequent change in physical properties.

Conventional methods for thermal conductivity measurements require large, well-instrumented samples. But radioactive samples are often small and always difficult to instrument. The large thermal gradients present in high power-density isotopic fuels may limit the sample size. An example is a sample of SrO having a difference in temperature of 50° across 1 cm at 800°C , the heat flow being in one direction only. Scarcity of radioactive material also limits the size of the sample in some cases.

A procedure for measuring the thermal conductivity of radioactive sources has been tested with inactive SrO, SrTiO₃, and Sr₂TiO₄ and with radioactive SrTiO₃ (Ref. 11). The thermal conductivities are measured in a thermal comparator apparatus which was modified to measure $\frac{1}{2}$ -in.-high by 1-in.-diam disk-shaped samples without thermocouples in the sample. The data obtained from several materials demonstrate that systematic errors can be corrected by using empirical calibration constants and that the random error is small. The apparatus (a modified 3M Company Tc-200)¹¹ is shown in Fig. 6.11 and 6.12.

The apparatus is a thermal comparator in which a heat flow (Q) supplied by a heater (a) flows in sequence through a specimen of known thermal conductivity (the standard), a specimen of unknown thermal conductivity (the sample), and another standard, to a heat sink (b). The first standard, the sample, and the lower standard are referred to as S₁, S₂, and S₃, respectively. Thermocouples are placed in positions represented by numbers. The assembly is referred to as the "thermal conductivity stack." The temperature at which the thermal conductivity is measured is controlled by a heater in the heat sink. The heat (Q) flowing through the standards (S₁ and S₃) can be calculated from the equation

$$Q = \frac{kA\Delta T}{\Delta h}$$

where

k = thermal conductivity of the standard,

A = cross sectional area of the standard,

ΔT = temperature drop in the standard over a distance Δh .

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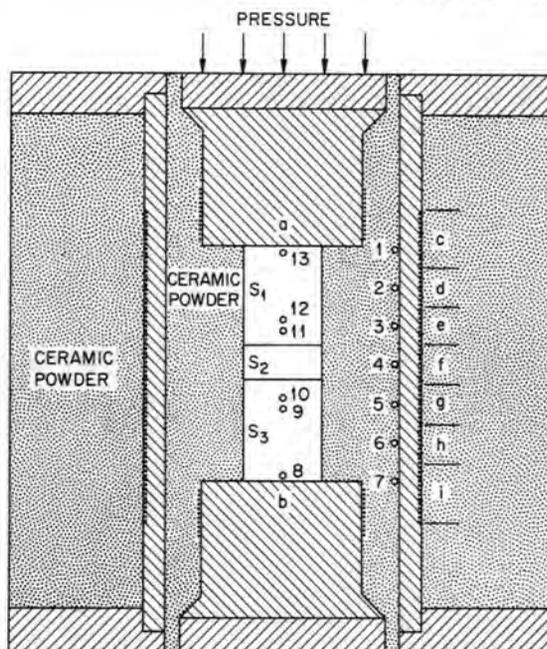


Fig. 6.11. Cross section of the thermal conductivity apparatus.



Fig. 6.12. Thermal conductivity apparatus.

The temperatures of the lower end of standard S_1 and the upper end of standard S_3 are obtained by extrapolating (using the above equation) the temperatures measured at point 10 and 11 to the ends of the standards S_3 and S_1 , respectively.

The thermal conductivity stack is surrounded by a series of individually controlled guard heaters represented by letters in Fig. 6.11. Low-density ZrO_2 (bubble zirconia) is used as an insulating medium between the guard-heater wall and the thermal conductivity stack. The guard-heater wall is held within $\pm 1^\circ C$ of the adjacent stack to ensure a minimum of radial heat loss or gain from the thermal conductivity stack.

The thermal conductivity of the radioactive fuel is measured using the same apparatus with the same type of sample. However, with radioactive samples, the method is absolute rather than comparative. The heat flow, Q , is supplied by the sample and is accurately determined by calorimetric methods. The top heater, which is not required, serves as a guard heater. The standard, S_1 , is replaced by a temperature monitor of low thermal conductivity. The top guard is adjusted to give zero ΔT (and zero heat flow) for the two thermocouples in the temperature monitor. The temperature of the monitor is the same as the temperature at the top of the sample. The temperature at the bottom of the sample is measured by the bottom monitor (which replaces the bottom standard). The bottom monitor measures the heat flow from the sample and indicates the correctness of the adjustment of the guard heaters. The sample height for several radioactive fuels for a ΔT of $50^\circ C$ is given below:

Radioactive fuel	Sample height, cm
^{90}SrO	1.02
$^{90}Sr_2TiO_4$	1.40
$^{90}SrTiO_3$	1.72
$^{170}Tm_2O_3$	0.51
$^{244}Cm_2O_3$	0.35

A major source of error in the thermal-conductivity measurements results from the variation of the conductivity of the bottom interface. Radioactive samples are rougher in surface but only one interface is used.

Large thermal-conductivity differences were found between radioactive and inactive samples of $SrTiO_3$. Differences are believed to be caused by several factors: differences in density and in amounts of impurities and crystal-lattice defects resulting from radiation damage of the radioactive samples. The average thermal con-

ductivity of 3 hot-pressed pellets of $^{90}SrTiO_3$ is shown by the equation

$$1/k = 0.0268T + 19.754$$

where T is in degrees Kelvin and k is in $W/^\circ C \cdot cm$.

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7. EXAMINATION OF USED SOURCES

Three sources have been examined at ORNL after high-temperature endurance tests: a source primarily intended for use in an RCA generator test; a source used in development work for the hot-press process; and a SNAP-7A source disassembled after 5-1/2 years of service. The results of these examinations are included here.

RCA TEST SOURCE

In June 1963 the Astro-Electronics Division of the Radio Corporation of America requested and was granted the use of ~83.5 kCi of ^{90}Sr from the USAEC Division of Isotopes Development for testing a thermoelectric space-power generator of 20-W electric capability. RCA directed the generator test at ORNL using FPD facilities. The fuel, $^{90}\text{SrTiO}_3$ pellets encapsulated first in a thin stainless steel capped cup, then in a TZM (99.4% Mo; 0.5% Ti; 0.1% Zr) welded primary capsule, and finally in a Hastelloy alloy X welded secondary capsule, was prepared by ORNL. The RCA test determined the generator conversion efficiency and compatibility of the generator materials with the encapsulated source. At the conclusion of the generator test, an experiment was conducted to estimate the extent of high-temperature corrosion of the outer surfaces of the source capsule.

The corrosion test was run for 142 days at approximately 1000°C. The capsule was placed in an insulated container with an argon purge of 120 cfm. The insulated container was placed in a shielded cask to protect the cell viewing window and personnel entering the adjoining cells from excessive radiation exposure. All the heat involved was generated by the intense radioactivity from the five $^{90}\text{SrTiO}_3$ pellets.

After the source capsule was loaded into the insulated container, the temperature rose to 600°C in 1-1/4 hr. The temperature of the source capsule leveled off at 1015 to 1025°C, and the temperature measured between the outer wall of the insulated container and the inner wall of the cask was 55 to 60°C. Simplytrol* indicators with Chromel-Alumel* thermocouples were used to obtain the measurements. The accuracy of the thermocouple and indicator was checked with a potentiometer with the following results: Simplytrol, 965°C; potentiometer, 951°C. Four days after the experiment was started, the temperature had increased to 1035°C. The flow of argon was increased to approximately 240 cfm; however, the temperature continued to increase to 1050°C.

The source capsule was removed from the insulated container after 18 days of operation at a temperature of 1015 to 1050°C, and was placed in a stainless steel beaker with argon purge for cooling. During the RCA experiment the source capsule was wrapped with thin rhodium foil, which became tightly attached to some areas of the surface. Visual examination revealed that areas of the capsule free of rhodium foil were slightly cleaner than when the experiment began.

The capsule was replaced in the insulated container which contained less insulation than originally in the top area in order to maintain a temperature of <1000°C. The temperature leveled off at ~970°C.

After 55 days of operation at elevated temperatures, the capsule was again cooled and examined. No significant changes were observed. Photographs were made of the capsule with a Questar* telephoto assembly. Figure 7.1 shows a cutaway of the capsule and the Rokide-A* coating. A photograph of the assembly and the insulation demonstrates the glow caused by the heat of the capsule (Fig. 7.2). The capsule with rhodium coating is shown in Fig. 7.3.

The capsule was replaced in the assembly under the same conditions (995°C, argon flow 240 cfm) and left for 142 days. The source capsule was not examined internally. The outside of the capsule after 142 days at elevated temperatures still showed no significant changes.

SrO SOURCES

In a second compatibility experiment, a 32-kCi (202-W) SrO source clad in platinum and contained in an inner capsule of Hastelloy alloy X and an outer capsule of Hastelloy alloy C was exposed to 780°C for 90 days. Visual examination of the source capsule at the end of 90 days revealed a slight bulge in the bottom of the capsule. The compatibility test was terminated for destructive examination of the source. The platinum-clad fuel (Fig. 7.4) was easily slipped out of the inner capsule and was intact. The groove near the bottom of the fuel piece (Fig. 7.4) was caused by the cutting tool penetrating too deeply through the inner capsule wall. No effects of the high-temperature exposure were evident other than a recrystallization of the platinum metal. Some surface marks which had the

*Trademark.

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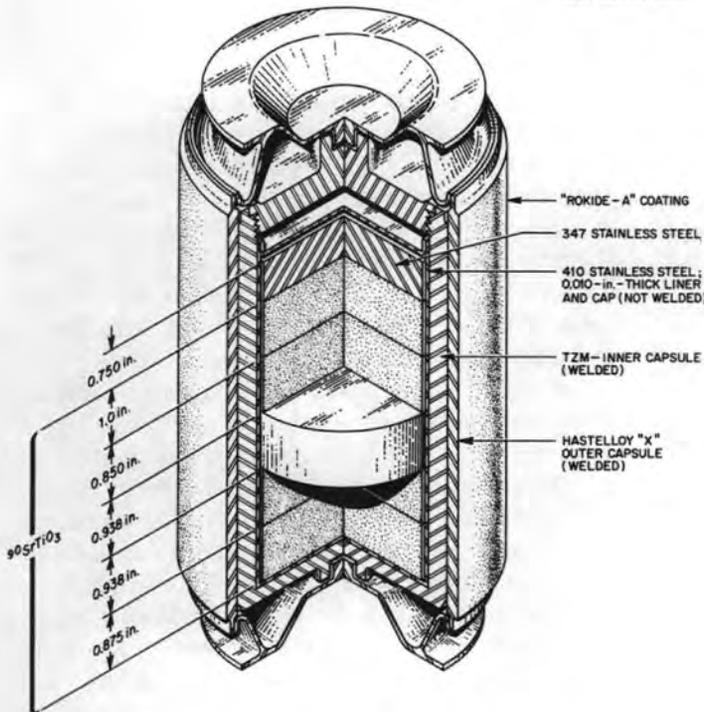


Fig. 7.1. RCA source and capsule.

appearance of cracks were observed but they had not caused significant dimensional changes in the fuel piece. No visible corrosion or interaction with the fuel piece was evident on the wall of the inner capsule.

The components of the source capsule were metallographically examined. The overall dimensions of the assembly were 2.4 in. diam and 2.6 in. height. Measurements showed that the bottom of the inner and outer capsules had bulged 0.016 and 0.054 in., respectively. Examination of the components, with the aid of a stereomicroscope, disclosed no obvious defects in either the inner or outer capsules. One suspicious region in the closure weld of the inner capsule was noted; however, a metallographic section through this region showed no evidence of a leak path.

Metallographic examination of sections from the inner and outer capsules revealed that the inner surface of the inner capsule (Hastelloy alloy X) had experienced a general oxidation type of attack to a depth of ~ 1 mil. Also, on regions of the inner surface of the inner capsule a localized reaction had resulted in clusters of fine metallic crystals. Some of the clusters were as much as 0.060 in. across and as high as 0.020 in. The capsule wall had been affected to a depth of 0.003 in. in these areas. An attempt was made to identify the clusters by x-ray diffraction. Positive identification could not be made, since this particular compound had never been cataloged, but there is strong



Fig. 7.2. RCA source capsule in insulated container.



Fig. 7.3. RCA capsule showing Rh foil.



Fig. 7.4. Pt-clad SrO pellet magnified.

evidence that the clusters were complex platinum intermetallics that had resulted from localized reactions between the platinum liner and the Hastelloy alloy X container. Metallographic examination of a portion of the platinum liner revealed severe intergranular penetration by a nonmetallic compound and loss of material from both the inner and outer surfaces. In one region examined, the unaffected wall thickness was only 0.002 in.

SNAP-7A GENERATOR

The SNAP-7A generator fueled with $^{90}\text{SrTiO}_3$ was received in 1967 for defueling and inspection from the U.S. Coast Guard Station at Curtis Bay, Maryland, where it had been in operation since December 1961 in a navigational buoy. The outer case appeared to be in good shape, with only a thin film of rust deposited evenly over the surface. Figure 7.5 shows the generator before it was dismantled. Radiation readings of 20 mr/hr beta-gamma were measured at 5 in. from the top of the shielding case. The maximum power output measured was 4.2 W(e) as of April 20, 1967. The internal pressure of the generator as determined during periodic servicing was 18.5 psia in April 1967, compared with 15.9 psia in March 1964. Two samples of the generator fill gas were analyzed by mass spectrometry. The results of the analysis are given in Table 7.1.

Table 7.1. Mass spectrometric analysis of SNAP-7A generator fill gas

Compound	Amount, vol %	
	Sample 1	Sample 2
Hydrogen	0.04	0.02
Helium	74.5	75.3
Methane	0.14	0.01
Water	1.45	1.17
Hydrocarbons	<0.01	<0.02
Nitrogen and carbon monoxide	0.51	0.42
Oxygen	0.28	0.16
Argon	23.1	22.9
Carbon dioxide	<0.004	0.02

The weld on the generator casing cover was ground off, and the generator casing was separated from the biological shield, which was a large uranium cup completely encased in $\frac{1}{4}$ -in.-thick Hastelloy alloy C plate. The generator with the casing was lifted out of the shield and examined. There was no visible evidence that the Hastelloy alloy C generator casing had been amalgamated by the mercury heat-transfer medium in which the casing had floated for 5 years. A sample of



Fig. 7.5. SNAP-7A generator before dismantling.

the mercury was examined spectrographically, with the results given below:

Element	Amount, wt %
Silver	$\sim 6 \times 10^{-5}$
Cobalt	$< 3 \times 10^{-5}$
Chromium	$< 6 \times 10^{-6}$
Copper	3.3×10^{-5}
Iron	$< 1 \times 10^{-5}$
Manganese	$< 6 \times 10^{-6}$
Molybdenum	$< 2 \times 10^{-5}$
Sodium	$< 2 \times 10^{-4}$
Niobium	$\sim 3 \times 10^{-4}$
Nickel	7.7×10^{-6}
Lead	2.2×10^{-4}
Uranium	$< 6 \times 10^{-4}$
Vanadium	$< 1 \times 10^{-5}$
Tungsten	$< 6 \times 10^{-5}$

The mercury was removed from inside the biological shield and the Hastelloy alloy C shield liner was examined visually. There was no evidence of amalgamation.

The generator was defueled in one of the FPDL cells on April 25, 1967, and the fuel capsules were inspected. The insulation block was found to be broken, but no other physical damage to the generator was noted. No radioactive contamination was detected during the removal of the top plate. The maximum radiation reading at the top of the biological shield was 750 mr/hr. When the defueled generator was removed from the cell, a smear test of the outside lip read 1200 dis/min, and all inside smears read < 500 dis/min. No ^{90}Sr was detected on any of the smears.

The thermoelectric module section of the SNAP-7A generator assembly was shipped to the Naval Ships Research and Development center at Annapolis, Maryland, for further examination and testing.

A core section of the biological shield was examined microscopically. It was found that the solder (50% Pb – 50% Sn) which had been used to bond the uranium and Hastelloy alloy C to form a heat-transfer path had only ~ 1 -mil penetration on the side exposed to mercury and on the side exposed to the marine atmosphere. The solder was well bonded to the uranium, but there was no bond to the Hastelloy alloy C.

Table 7.2. Summary of SNAP-7A pellet data

Capsule and position number	Batch and pellet number	Weight, g		Diameter, cm		Height, cm		Pellet condition
		Initial	Final	Initial	Final	Initial	Final	
I-S	18-4	43.8	44.0	3.7	3.6	1.2	1.3	Good
I-P	19-2	49.3	49.8	3.5		1.2		Broken
I-L	18-T	47.7	47.1	3.7	3.8	1.4	1.4	Good
I-H	17-1	46.9	47.4	3.8	3.8	1.4	1.3	Good
I-E	19-1	49.6	49.4	3.5	3.5	1.2	1.2	Good
I-B	18-3	43.3	44.2	3.8	3.5	1.3	1.2	Good
II-S	18-6	43.5	43.1	3.7	3.7	1.3	1.2	Good
II-P	19-4	49.5	49.1	3.5	3.5	1.2	1.2	Cracked
II-L	19-T	49.7	49.6	3.3	3.3	1.3	1.4	Good
II-H	17-2	46.7	46.7	3.8	3.8	1.3	1.5	Good
II-E	19-3	49.4	49.2	3.5	3.5	1.2	1.1	Cracked
II-B	18-5	43.5	43.5	3.7	3.6	1.2	1.3	Good
III-S	18-8	44.1	43.4	3.7	3.6	1.3	1.2	Cracked
III-P	19-6	49.2	49.5	3.5	3.4	1.2	1.2	Cracked
III-L	18-1	47.6	46.8	3.8	3.7	1.4	1.3	Cracked
III-H	17-3	46.7	47.7	3.7	3.7	1.4	1.3	Chipped
III-E	19-5	49.2	49.4	3.5	3.5	1.2	1.2	Cracked
III-B	18-7	43.8	43.8	3.7	3.6	1.3	1.2	Good
IV-S	18-10	43.6	43.2	3.7	3.8	1.3	1.3	Good
IV-P	19-8	49.6	49.6	3.5	3.5	1.2	1.1	Good
IV-L	18-2	47.6	46.8	3.8	3.8	1.4	1.6	Good
IV-H	17-4	47.0	47.7	3.8	3.7	1.3	1.6	Good
IV-E	19-7	49.1	49.1	3.5	3.5	1.2	1.1	Cracked
IV-B	18-9	43.6	43.2	3.7	3.8	1.3	1.3	Good

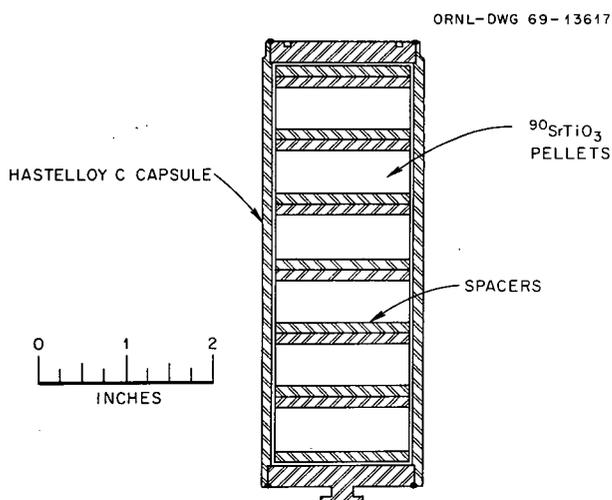


Fig. 7.6. Typical SNAP-7A capsule.

The nickel-plated uranium top plug of the biological shield was subjected to a standard AEC water-vapor corrosion test. The test consists of exposing the plated plug to saturated water vapor at 92.5°C for 20 hr. The test was performed five times for a total exposure of 100 hr. There was no evidence of corrosion or penetration of the nickel plate.

Each SNAP-7A fuel capsule contained six $^{90}\text{SrTiO}_3$ pellets and a number of Hastelloy alloy C spacers encapsulated in a welded Hastelloy alloy C capsule. The capsules were essentially identical in fuel content (Table 7.2) and arrangement (Fig. 7.6). All the $^{90}\text{SrTiO}_3$ used in these sources was prepared during August 1961 from the same $^{90}\text{Sr}(\text{NO}_3)_2$ feed material. Portions of three batches of $^{90}\text{SrTiO}_3$ with power concentrations of 0.231, 0.233, and 0.219 W/g were used. The calculated compositions of these fuel batches, based on the original feed analysis and decay to August 1967, are given in Table 7.3. All the pellets used in the SNAP-7A sources were made by the cold-pressing and sintering method. Two $^{90}\text{SrTiO}_3$ batches which were deficient in titanium dioxide yielded pellets with an average power density of 0.73 W/cm³; the 7% excess TiO₂ material yielded pellets with an average power density of 0.92

W/cm³. All pellets were intact when loaded into the capsules.

Capsule Inspection

Each of the four capsules was removed from the generator and given a smear test; no significant contamination was detected. All the capsules appeared to be in excellent condition; all were discolored to a dull gray. No defects in the weld areas could be detected by visual inspection. The diameter of the capsules was measured by passing them through 1.900 in. (original 1.872 in.) ID ring gages (1 and 4 in. long). The maximum height measured 5.21 in. (original 5.198 in.).

Leak Tests

The capsules were individually leak tested by the hot-water air-bubble method; no leaks were detected. Two capsules at a time were leak tested with ^{85}Kr . The ^{85}Kr leak tests revealed no leaks (limit of detection, 1×10^{-7} cm³/sec). The capsules had originally been welded in helium at 30 psig.

Heat Output

The water-jacketed calorimeter was used to determine the heat outputs of the four capsules. The calorimeter was electrically calibrated in the 50- to 60-W range immediately before the capsules were assayed, and a calorimeter factor of 6.8 W/mV at 55-W output was determined. The calculated heat contents (based on original loading data and corrected for decay from September 1961) are compared below with those experimentally determined (on April 27, 1967):

Calculated heat output, W	Experimental heat output, W
54.9	56.6
54.6	56.6
55.0	56.7
54.8	56.6
219.3	226.5

Table 7.3. Calculated composition of $^{90}\text{SrTiO}_3$ fuel

Batch No.	Constituent, wt %						Power concentration, W/g	Ratio	
	Sr	Ca	Ba	Zr	Ti	O		SrO:TiO ₂	^{90}Sr :Sr
17	38.1	2.9	0.2	6.0	26.2	26.6	0.199	0.95	0.47
18	38.5	2.9	0.2	6.0	25.9	26.5	0.201	0.93	0.47
19	36.1	2.7	0.2	5.7	27.9	27.4	0.189	1.07	0.47

The 3% difference in total heat output is probably due to overcorrection for ^{89}Sr contribution. This correction amounted to 15.5% of the initial gross heat, based on a radiochemically determined $^{89}\text{Sr}/^{90}\text{Sr}$ curie ratio of 0.35. The observed heat output difference could be due to a ^{89}Sr determination that was 15% too high; this is of the same order as the variations in ^{89}Sr determinations by the methods used at that time. Since the original loading data were based on several incremental pellet heat output measurements, the measurements of the full capsules are probably more precise.

The surface temperatures of the capsules at equilibrium when suspended in air were measured with a contact thermocouple. These temperatures ranged from 95 to 120°C. The calculated temperature is in the range of 140 to 150°C based on a metallic surface and still air. However, the dark surface of the capsule, the movement of air, and the use of a single point contact thermocouple can contribute to a lower observed temperature than that calculated.

Inside Capsule and Pellet Examination

Figure 7.7 shows the unopened capsules with the weld made in the hot cell. Equipment for cutting and measuring capsules and pellets is shown in Fig. 7.8. Each capsule was opened by cutting through the wall at a point 1 cm below the end welded in the hot cell. The capsule was inverted and the capsule body was lifted off

to expose the spacers and the fuel. Spacers and pellets were identified as they were removed from the capsule.

After the pellets and spacers were removed, the capsules were brushed to remove any loose material. A 2-cm-high ring section was cut from the center of the capsule body. The other (shop) weld was cut off the capsule 1 cm from the end. The two weld sections, center section, and selected spacers from each capsule were packaged for transfer to the High Radiation Level Examination Laboratory (HRLEL) for metallurgical inspection.

There was no visible evidence of mechanical damage or chemical attack on the inside capsule surfaces or on the spacers. The fuel pellets and spacers were easily removed from the capsules. No residual fuel could be seen on the disassembled capsule parts. The maximum radiation reading on the package, with specimens shielded only by the thin metal walls of the package, was 300 mr/hr; this reading indicates that relatively little ^{90}Sr was retained in the specimens.

Of the 24 pellets (Fig. 7.9), 15 were completely intact, 7 were cracked across the diameter, 1 was slightly chipped, and 1 was broken into several pieces. One half of the broken pellet was intact and the other half was broken up (this pellet had initially cracked diametrically like the 7 other pellets). There was no detectable change in the color of the pellets.



Fig. 7.7. SNAP-7A capsules showing hot cell welds.

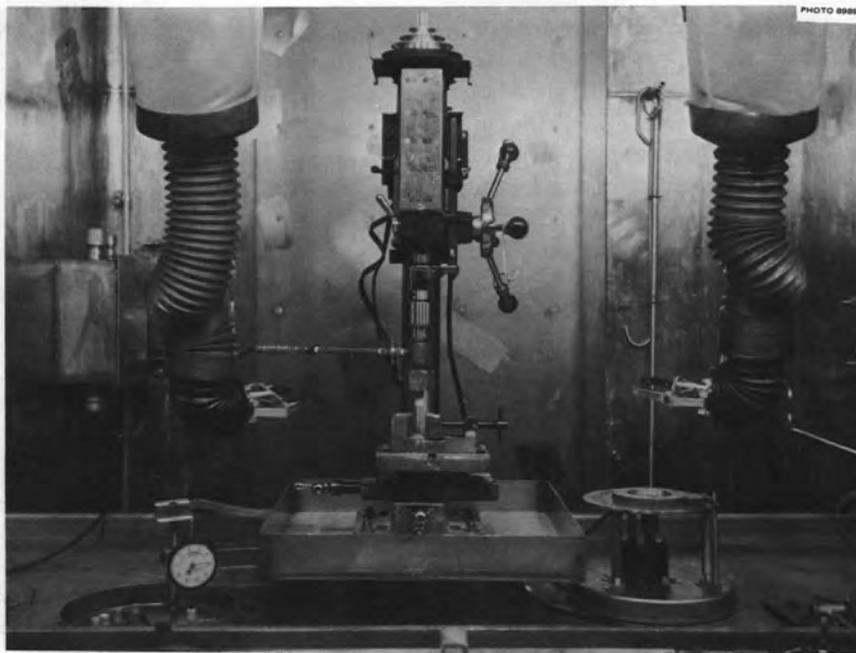


Fig. 7.8. Equipment for cutting, grinding, and measuring cylindrical pellets of $^{90}\text{SrTiO}_3$.

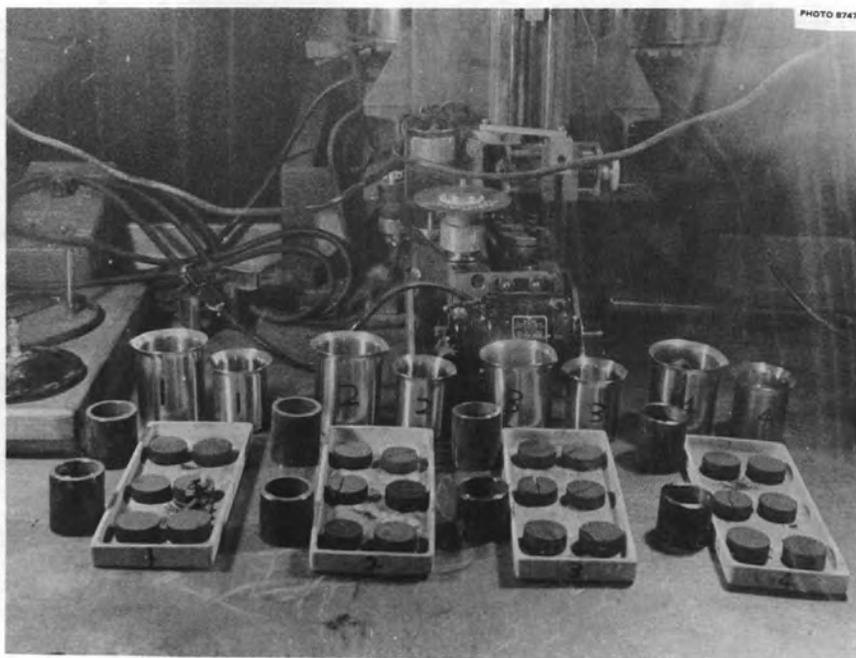


Fig. 7.9. SNAP-7A pellets after opening.



Fig. 7.10. Appearance of a suspect defect region from the closure weld of SNAP-7A capsule No. 4 (30X magnification). Reduced 55%.

The pellets were weighed and measured (Table 7.2), but no significant dimensional changes were noted. The total weight of fuel material recovered was 1127 g, of which 1123 g was as pellets (or individual pieces) and 4 g as loose powder, as compared with 1124 g original loading.

Metallurgical Examination of Capsules

The four disassembled SNAP-7A capsules were transferred to the HRLEL for visual and metallographic examination. Visual examination of the components (with the aid of a remote stereomicroscope) disclosed no evidence of gross incompatibility or weld defects. However, the closure weld on one capsule (No. 4) did contain a small region that was suspicious (Fig. 7.10).

The components of capsule No. 4 were selected for metallographic examination, which included a typical section through the bottom and upper closure welds, as well as a section through the suspect region mentioned above. In addition, a section was taken through the wall of the capsule at about midlength, and through several spacers that had been placed between the $^{90}\text{SrTiO}_3$ pellets (Figs. 7.11 and 7.12).

Examination of the closure weld revealed a minimum penetration of 0.085 in. The suspicious region in this weld was found to be the result of small interdendritic discontinuous shrinkage voids. Successive regrinding and repolishing showed that these voids were confined

to a region less than 0.005 in. around the weld. The presence of these voids should not have affected the integrity of the weld. A minimum penetration of 0.180 in. was measured on the bottom weld and there was no evidence of any microstructural defects.

Metallographic examination of the capsule wall disclosed no evidence of incompatibility; the inner and outer surface regions appeared to be identical. Examination of the spacers yielded similar results.

Summary

There was no serious deterioration of these sources during their 5- $\frac{1}{2}$ -yr life. The distribution of the broken pellets according to fuel batch is interesting: 6 of the 9 high-density, titanate-excess pellets broke, while only 2 of the 15 low-density, titanate-deficient pellets broke (neglecting the pellet that was only chipped). Similar effects have been noted previously, both with cold-pressed, sintered pellets and, more markedly, with hot-pressed pellets.

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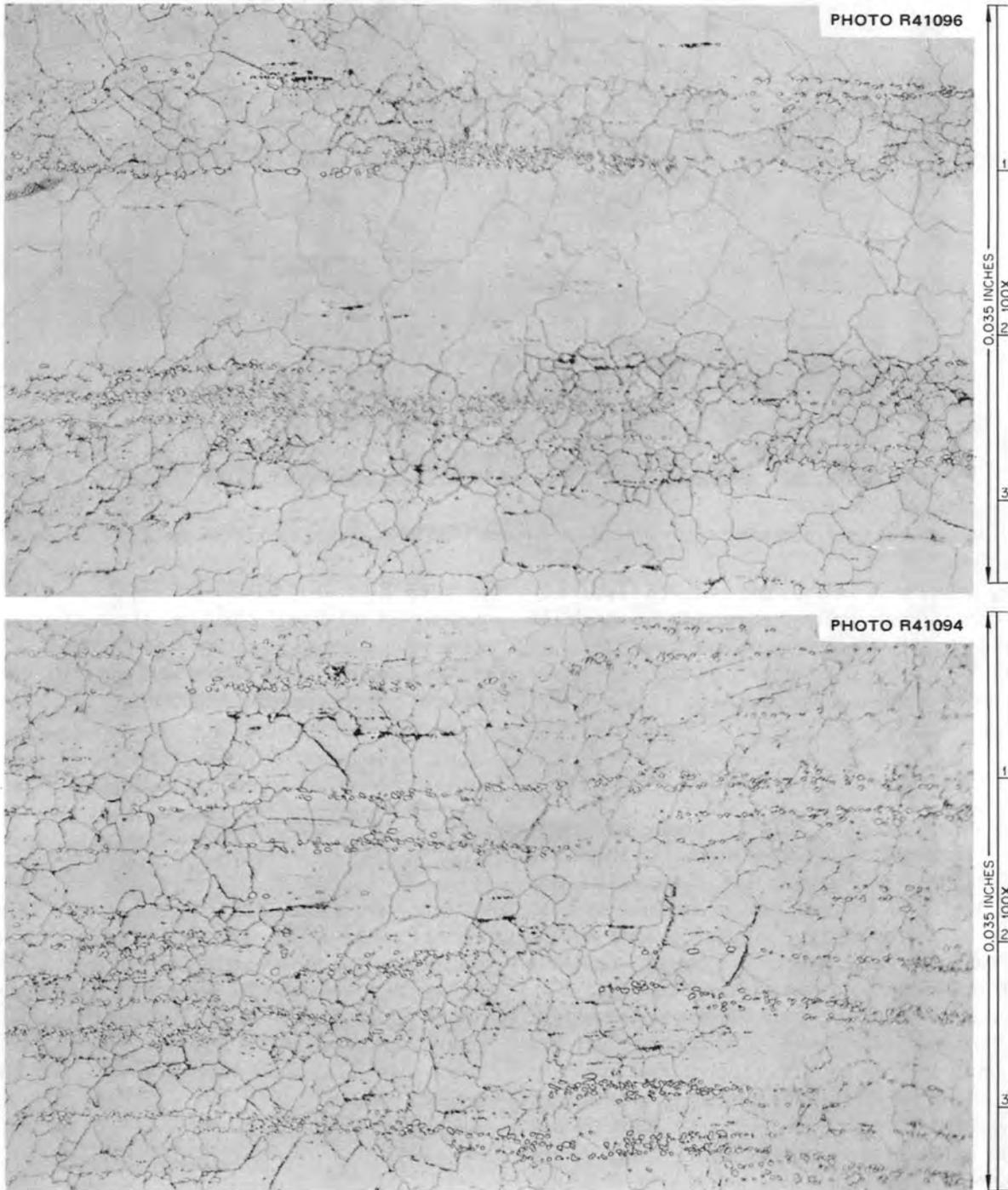


Fig. 7.11. Appearance of typical areas from the inner (upper) and outer (lower) surface regions of the container material near midlength of capsule No. 4, SNAP-7A (etched).

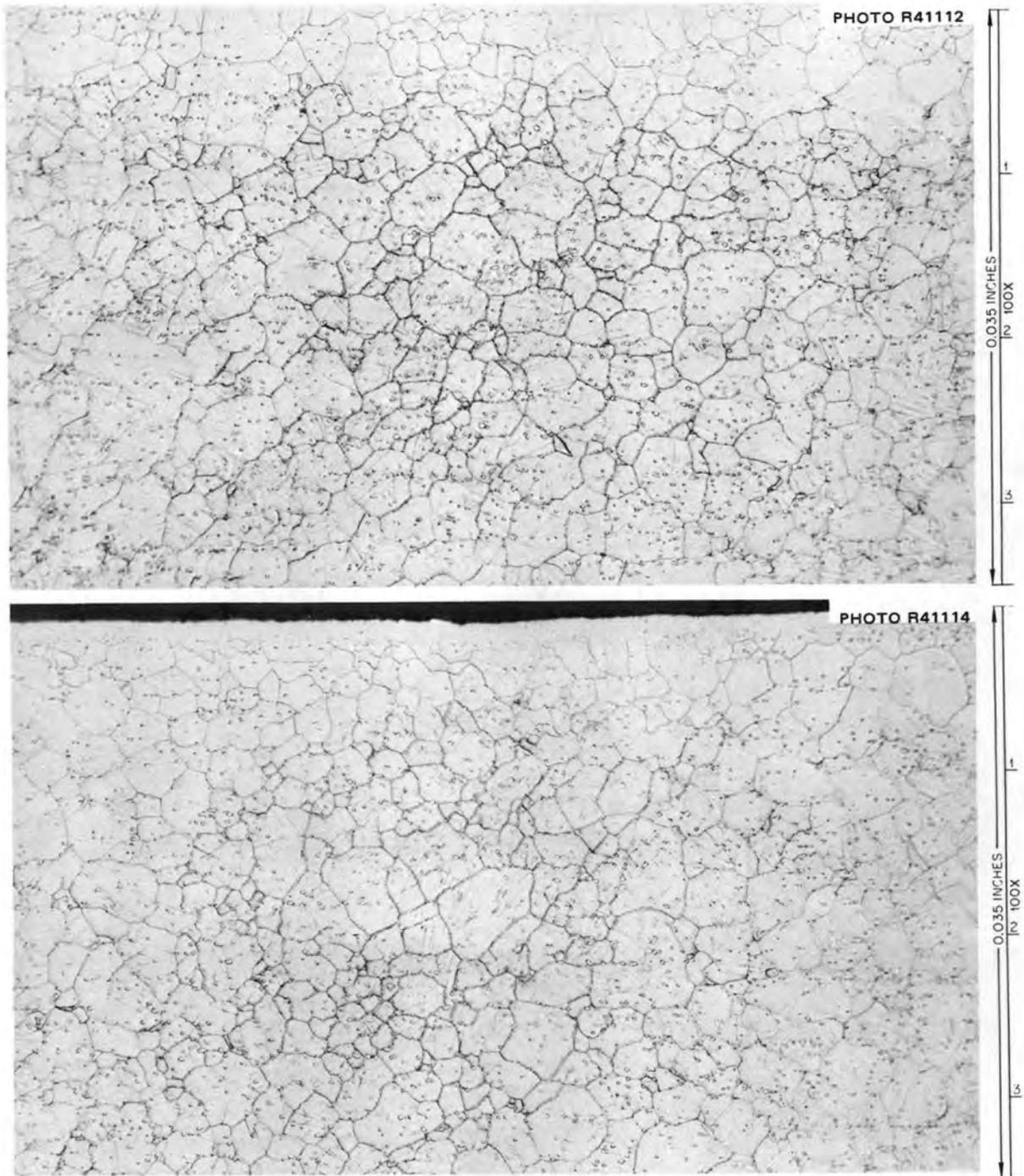
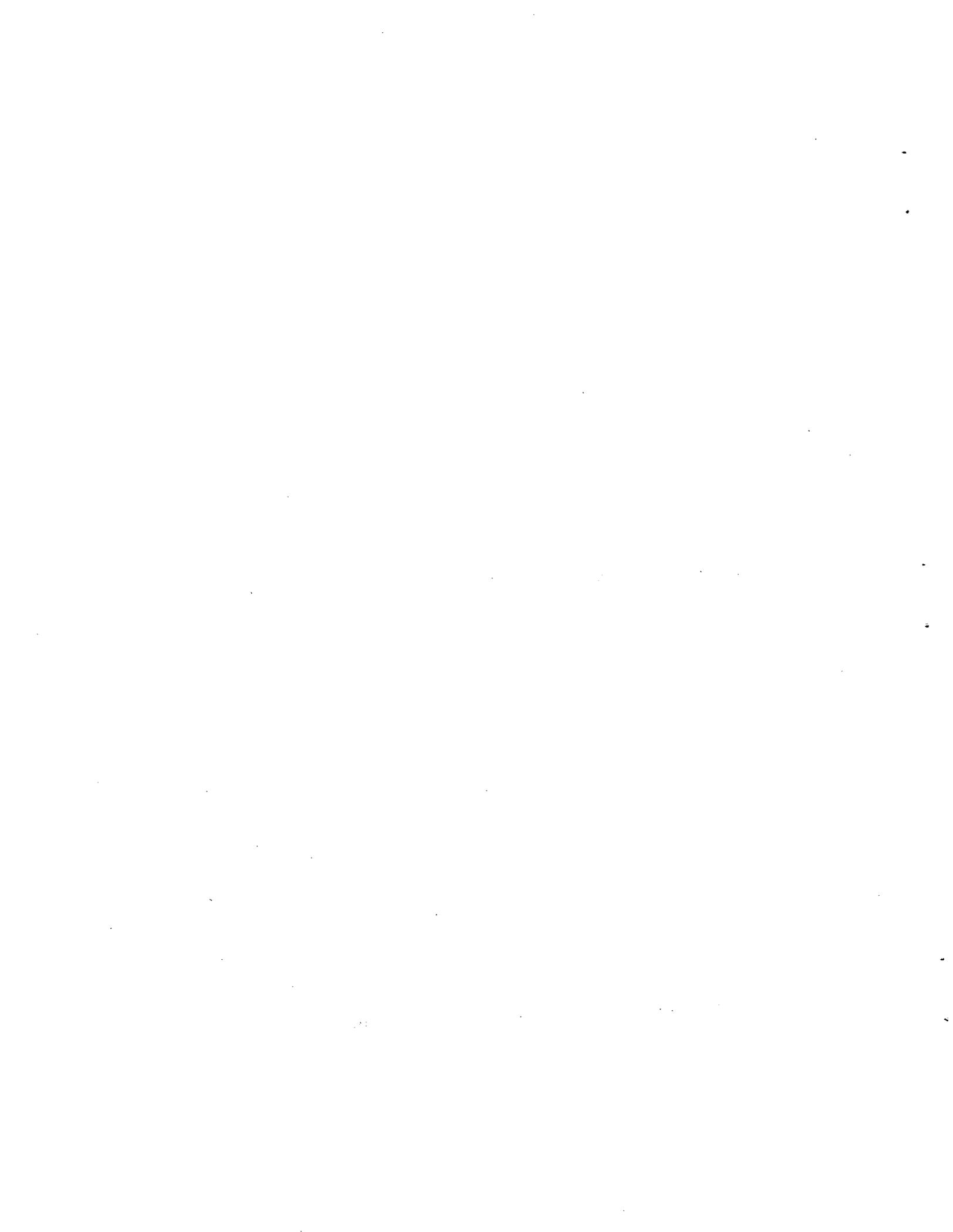


Fig. 7.12. Typical appearance of the spacer (upper) and fuel side (lower) of spacer from capsule No. 4, SNAP-7A (etched).



8. PROPERTIES OF STRONTIUM FUEL FORMS

EXPLANATION OF TABLES

This compilation represents the best values available for each property and fuel form.¹ Substitution of a substance similar to the fuel form is made in some cases. The substitute substance is indicated by a parenthetical superscript. If no value is given, none has been found.

COMPOSITION

Nuclidic abundance
Average MW 89.08 (Ref. 1, 2, 3, 4, 5)

Isotope	% Abundance	Half-life
⁹⁰ Sr	55.0	28.5 years
⁸⁸ Sr	43.9	Stable
⁸⁶ Sr	1.1	Stable
⁸⁹ Sr	*	50.5 days

*Abundance depends on the cooling. ⁸⁹Sr: ⁹⁰Sr will decrease by a factor of ~2 for each 50 days of cooling.⁵ Strontium-90 fission yield is 5.8% of total fissions.

Chemical Composition of HAPO Feed Received by FPD

Range of composition		
Cation	Maximum, wt %	Minimum, wt %
Sr	97	92
Ca	5	2
Ba	2	0.5
Mg	2	0

One gram of ⁹⁰Sr will produce 0.0232 g of ⁹⁰Zr after one year's decay.

Average chemical composition

Cation	Metal, wt %	Metal, atom %
Sr	95	96.69
Ca	3.5	1.60
Ba	1.0	1.57
Mg	0.5	0.14

The ¹⁴⁴Ce constitutes 0.03% of the radioactivity at a maximum. Cesium-137 has been found to be as high as 0.003% of the total activity. Ruthenium-106 has not been found in the strontium feed.

RADIATION^{2,5,6}

Beta

Nuclide	Max E, MeV	Avg E, MeV	Abundance, %	W/kCi	Particles per W·sec
⁹⁰ Sr	0.546	0.1936	100	1.164	5.51 × 10 ¹²
⁹⁰ Y	2.284	0.9365	100	5.551	5.51 × 10 ¹²
Total power				6.715	

No alpha, gamma, neutron, or fission.

Bremsstrahlung

The high-energy bremsstrahlung photons from ⁹⁰Sr and ⁹⁰Y in matrices of SrO and SrTiO₃ are given in the following tabulations. Sources of ⁹⁰Sr-⁹⁰Y activities require slightly more shielding than sources of ¹³⁷Cs-¹³⁷Ba activities because of the high energy of some of the bremsstrahlung radiation from ⁹⁰Y which emits a 2.27-MeV beta particle. Dose rates as a function of shielding are given in Figs. 8.1 to 8.8.

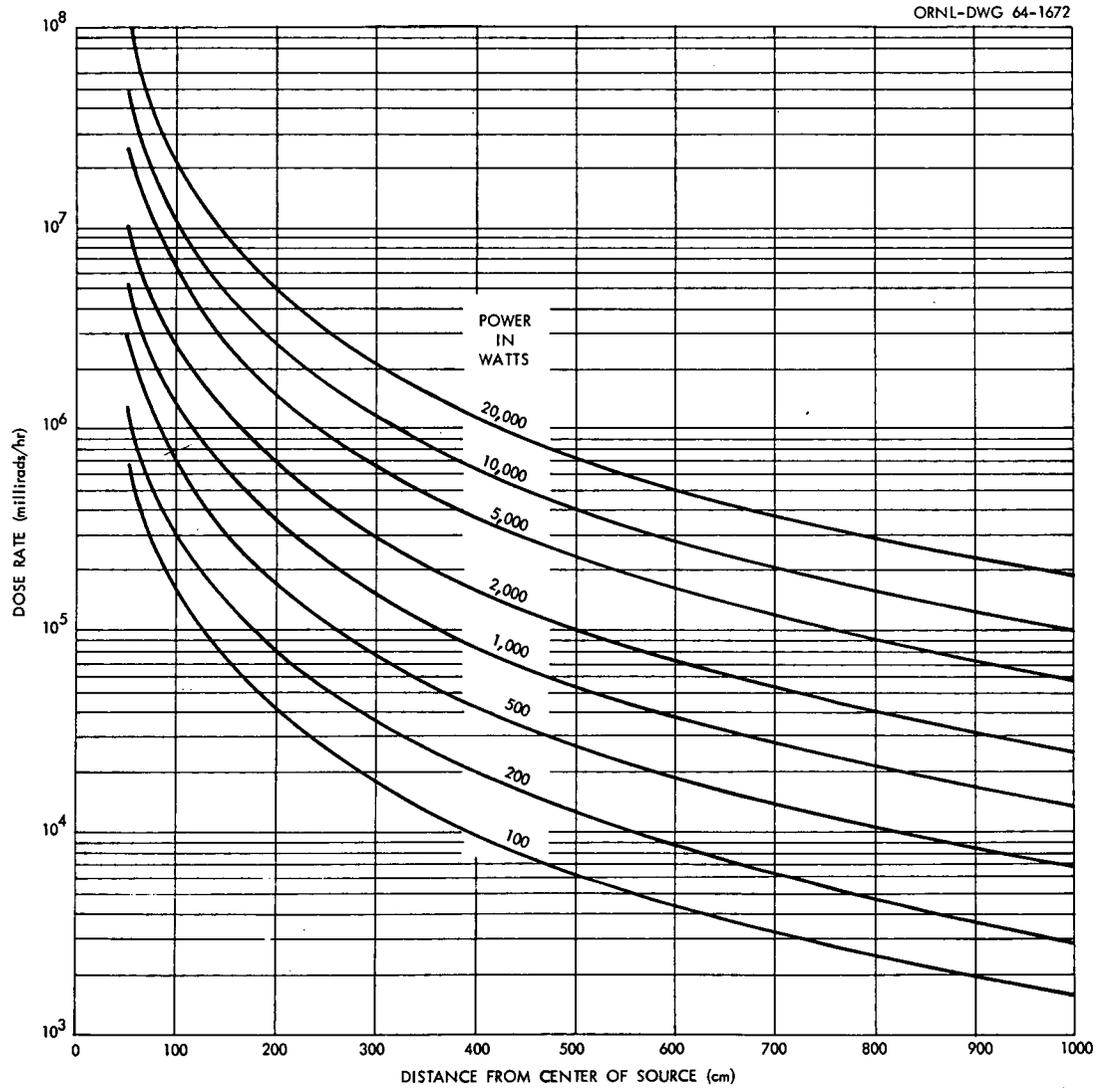


Fig. 8.1. Bremsstrahlung dose rates⁵ from unshielded isotopic power sources of ^{90}Sr (SrTiO_3) as a function of distance from center of source.

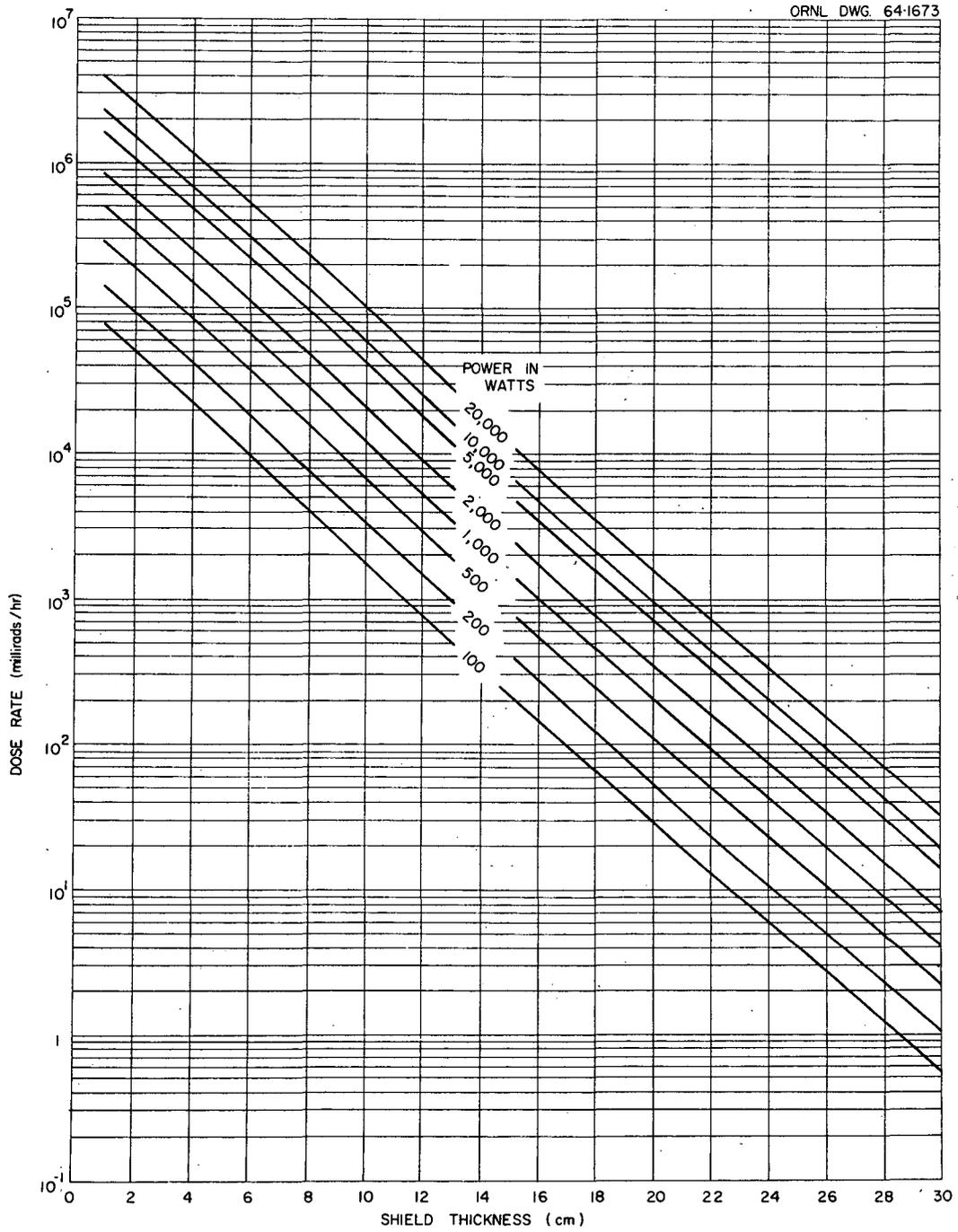


Fig. 8.2. Bremsstrahlung dose rates⁵ from iron-shielded isotopic power sources of ^{90}Sr (SrTiO_3). Center of source to dose point separation distance = 100 cm.

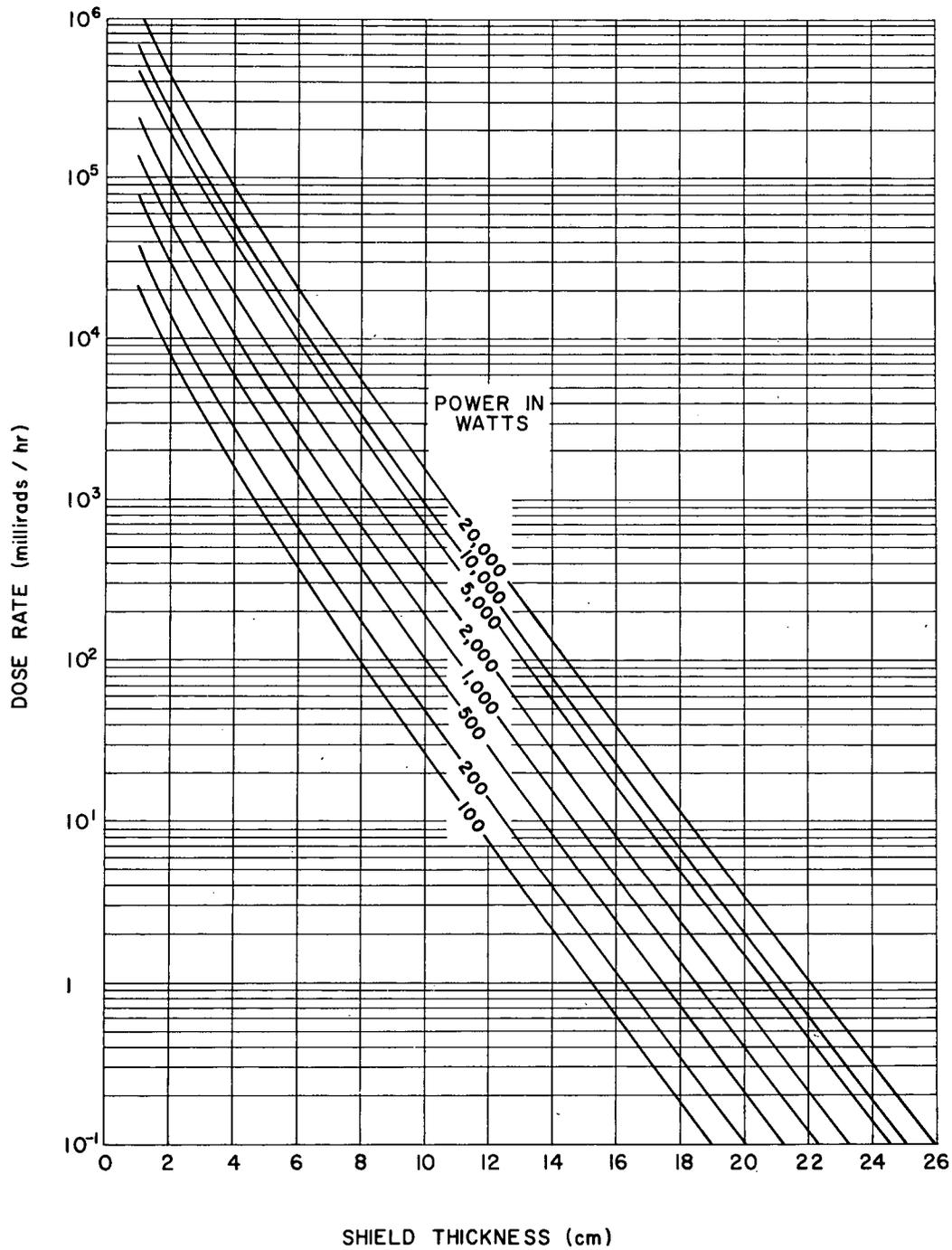


Fig. 8.3. Bremsstrahlung dose rates⁵ from lead-shielded isotopic power sources of ⁹⁰Sr (SrTiO₃). Center of source to dose point separation distance = 100 cm.

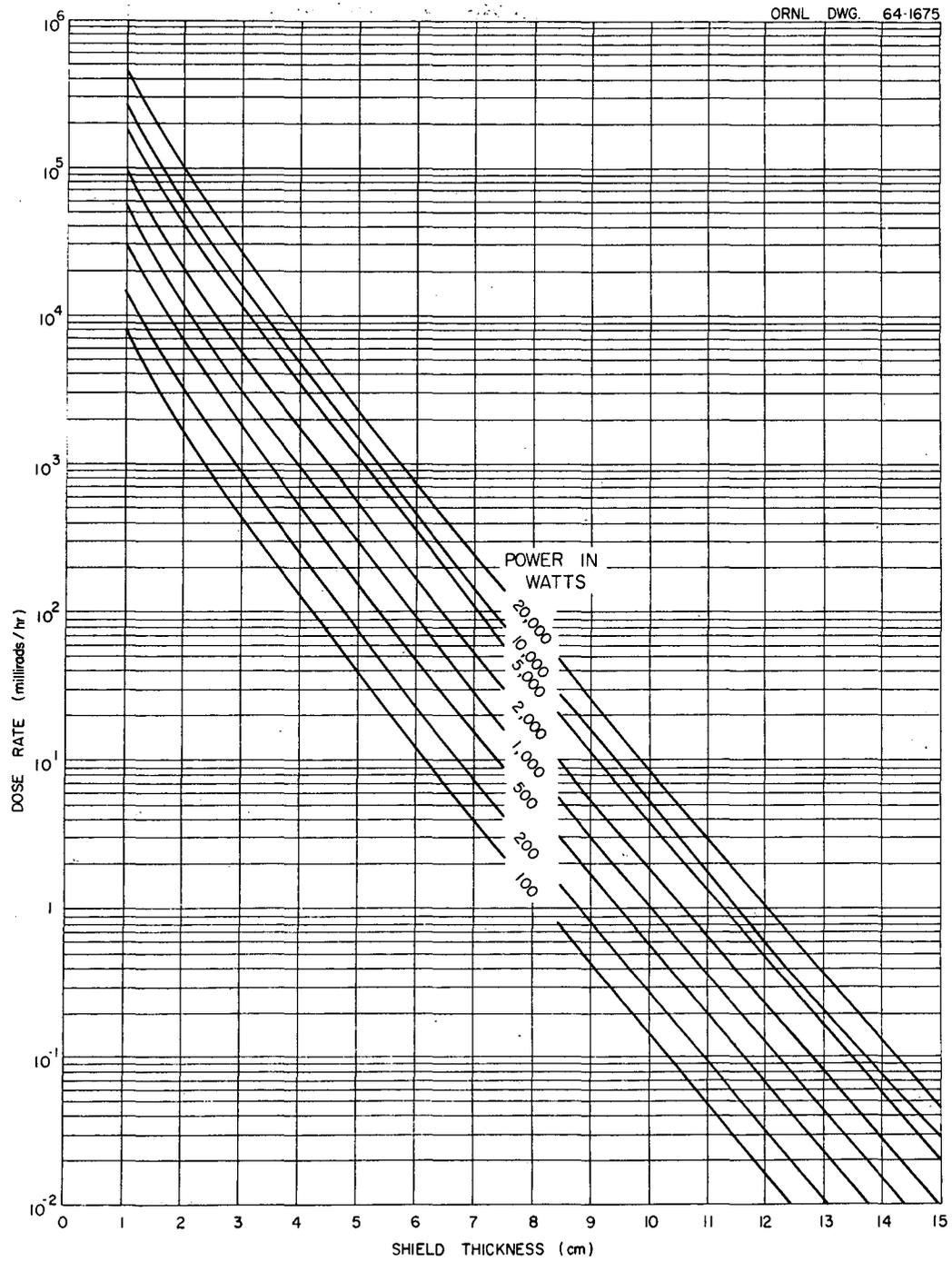


Fig. 8.4. Bremsstrahlung dose rates⁵ from uranium-shielded isotopic power sources of ^{90}Sr (SrTiO_3). Center of source to dose point separation distance = 100 cm.

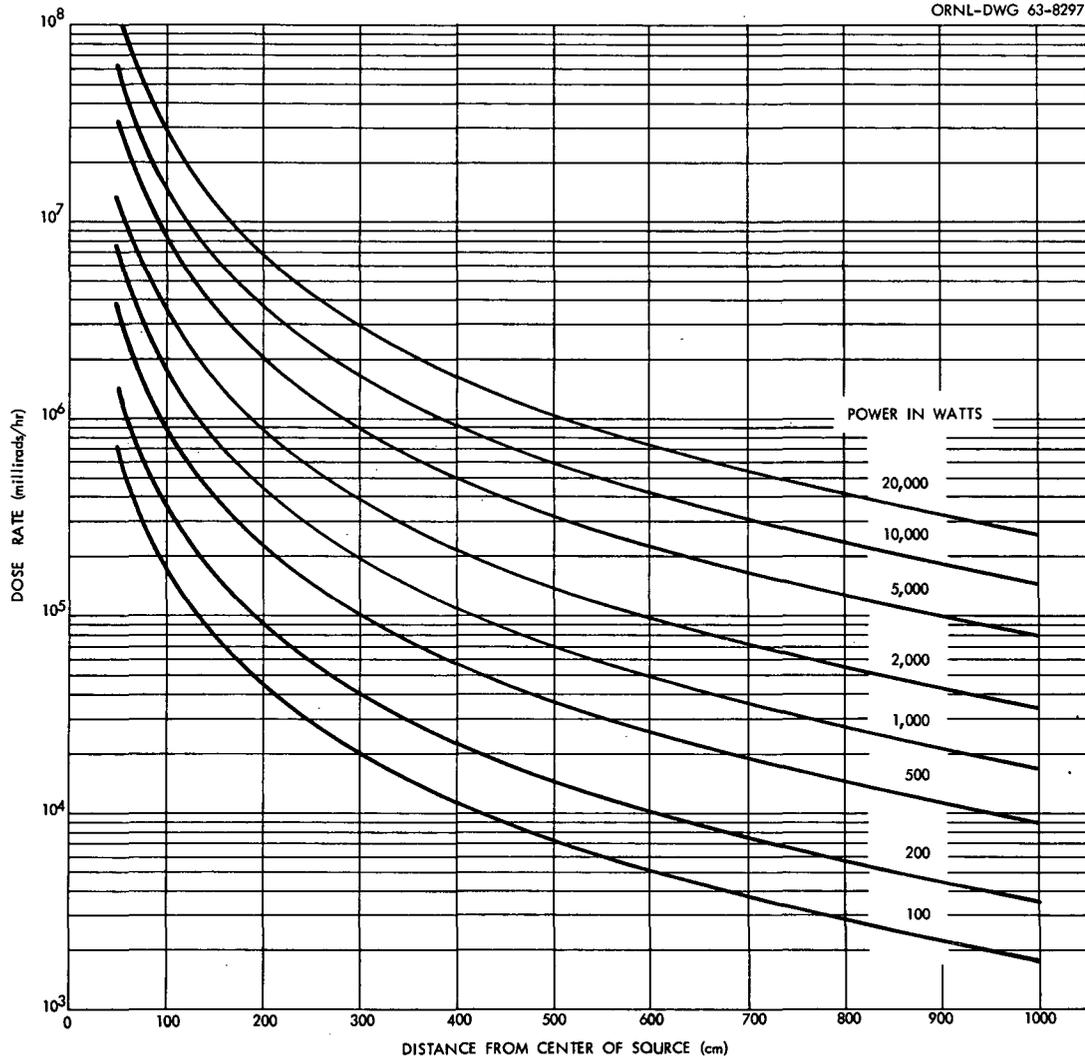


Fig. 8.5. Bremsstrahlung dose rates⁵ from unshielded isotopic power sources of ⁹⁰Sr (SrO) as a function of distance from center of source.

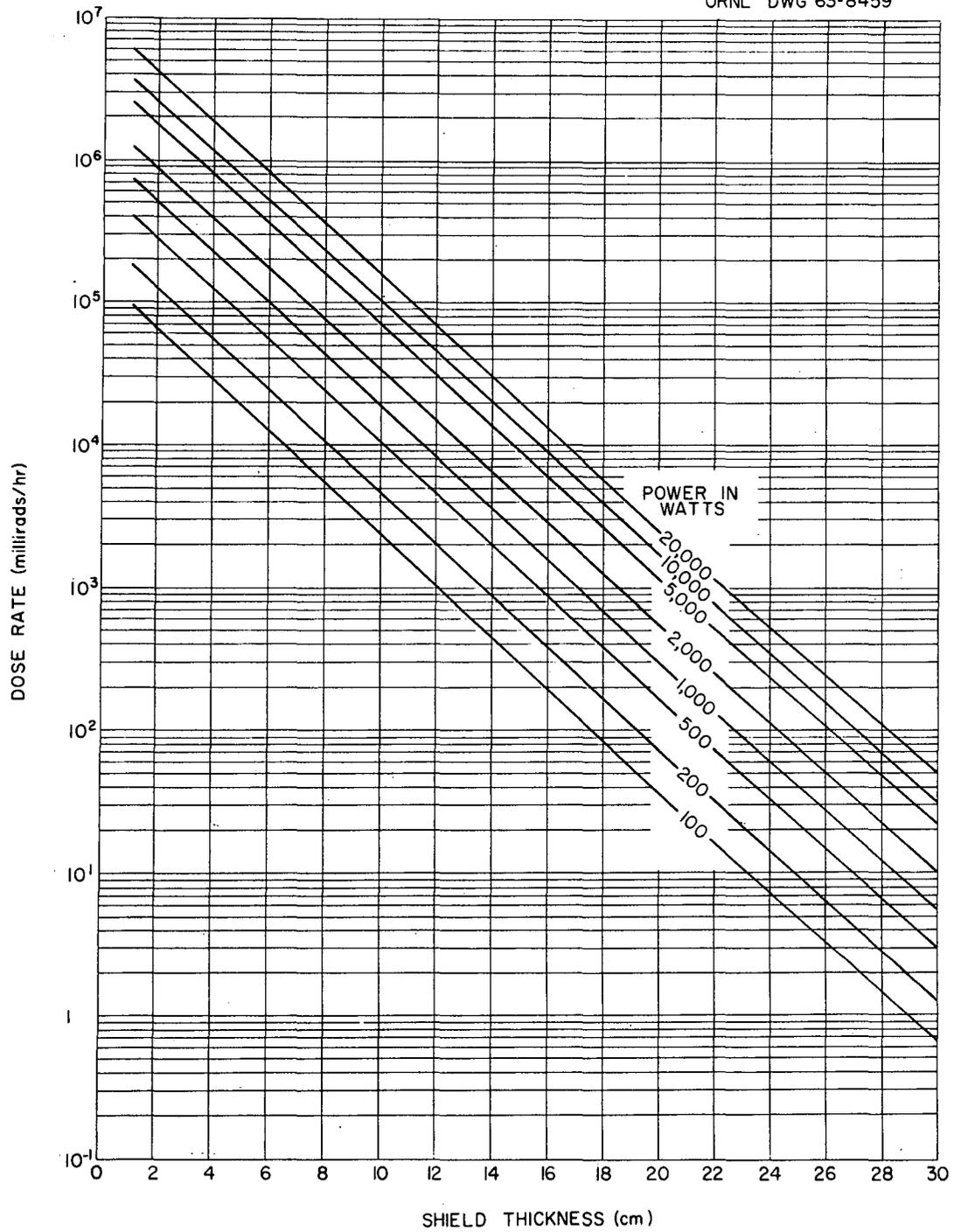


Fig. 8.6. Bremsstrahlung dose rates⁵ from iron-shielded isotopic power sources of ^{90}Sr (SrO). Center of source to dose point separation distance = 100 cm.

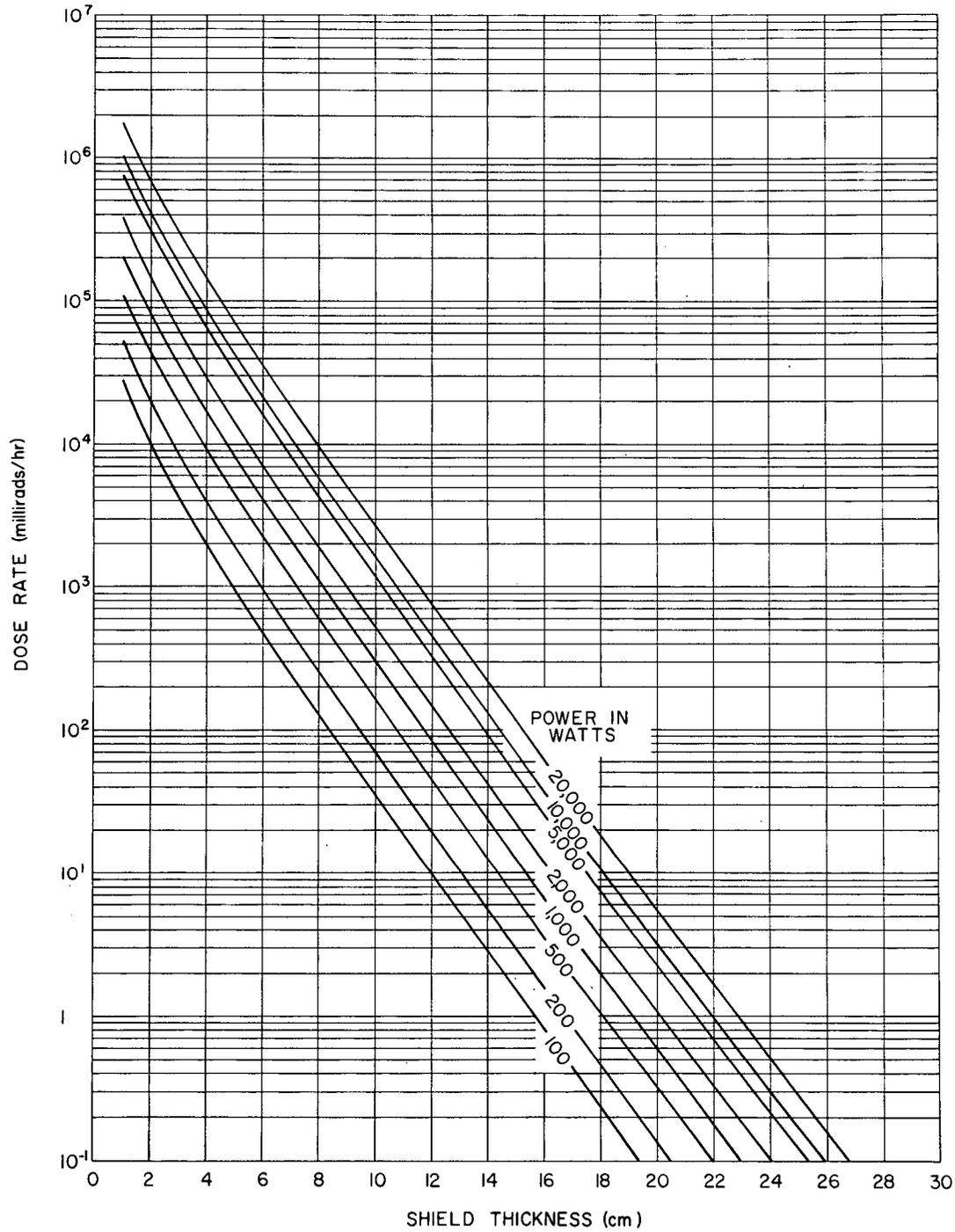


Fig. 8.7. Bremsstrahlung dose rates⁵ from lead-shielded isotopic power sources of ^{90}Sr (SrO). Center of source to dose point separation distance = 100 cm.

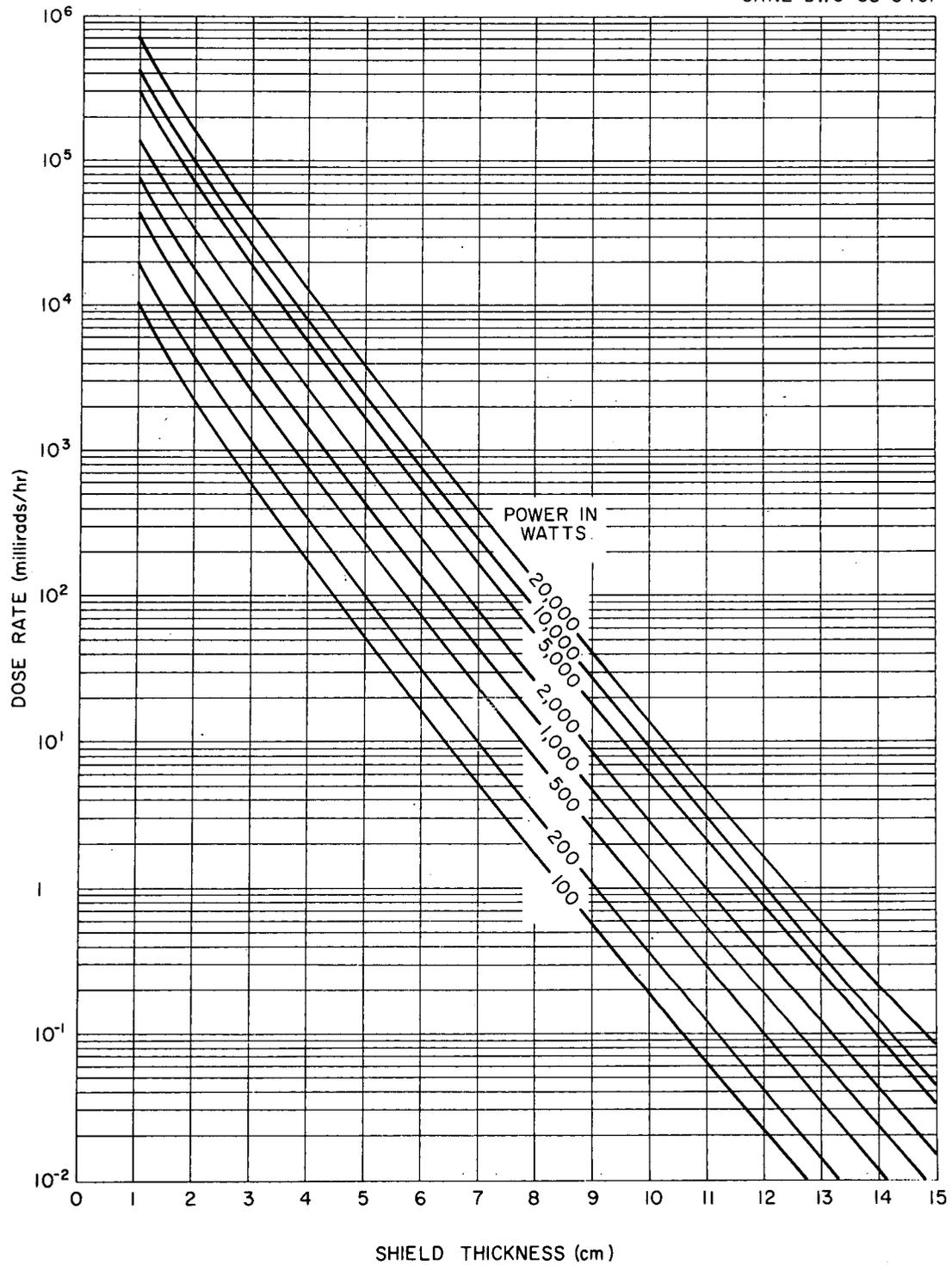


Fig. 8.8. Bremsstrahlung dose rates⁵ from uranium-shielded isotopic power source of ^{90}Sr (SrO). Center of source to dose point separation distance = 100 cm.

Production of bremsstrahlung photons
from strontium-90 beta in strontium oxide
matrix (Ref. 5)

Maximum beta-particle energy	0.545 MeV
Average beta-particle energy	0.201 MeV

Bremsstrahlung energy group, MeV	Within ΔE energy group	
	Photons per beta particle	Photons/W-sec
0.020 \pm 0.01	1.378×10^{-2}	7.58×10^{10}
0.040 \pm 0.01	5.523×10^{-3}	3.04×10^{10}
0.060 \pm 0.01	2.998×10^{-3}	1.65×10^{10}
0.080 \pm 0.01	1.841×10^{-3}	1.01×10^{10}
0.100 \pm 0.01	1.208×10^{-3}	0.66×10^{10}
0.120 \pm 0.01	8.239×10^{-4}	0.45×10^{10}
0.140 \pm 0.01	5.759×10^{-4}	3.17×10^9
0.160 \pm 0.01	4.086×10^{-4}	2.25×10^9
0.180 \pm 0.01	2.923×10^{-4}	1.61×10^9
0.200 \pm 0.01	2.099×10^{-4}	1.15×10^9
0.220 \pm 0.01	1.505×10^{-4}	0.83×10^9
0.240 \pm 0.01	1.074×10^{-4}	0.59×10^9
0.260 \pm 0.01	7.604×10^{-5}	0.42×10^9
0.280 \pm 0.01	5.315×10^{-5}	2.92×10^8
0.300 \pm 0.01	3.654×10^{-5}	2.01×10^8
0.320 \pm 0.01	2.458×10^{-5}	1.35×10^8
0.340 \pm 0.01	1.609×10^{-5}	0.88×10^8
0.360 \pm 0.01	1.016×10^{-5}	0.56×10^8
0.380 \pm 0.01	6.135×10^{-6}	3.37×10^7
0.400 \pm 0.01	3.491×10^{-6}	1.92×10^7
0.420 \pm 0.01	1.835×10^{-6}	1.01×10^7
0.440 \pm 0.01	8.638×10^{-7}	0.48×10^7
0.460 \pm 0.01	3.456×10^{-7}	1.90×10^6
0.480 \pm 0.01	1.065×10^{-7}	5.86×10^5
0.500 \pm 0.01	2.007×10^{-8}	1.10×10^5
0.520 \pm 0.01	1.000×10^{-9}	5.50×10^3
0.540 \pm 0.01	0.000	
Total bremsstrahlung energy, MeV/beta particle		1.411×10^{-3}

Production of bremsstrahlung photons from yttrium-90
beta in strontium oxide matrix (Ref. 5)

Maximum beta-particle energy	2.27 MeV
Average beta-particle energy	0.944 MeV

Bremsstrahlung energy group, MeV	Within ΔE energy group	
	Photons per beta particle	Photons/W-sec
0.100 \pm 0.05	6.152×10^{-2}	3.38×10^{11}
0.200 \pm 0.05	2.415×10^{-2}	1.33×10^{11}
0.300 \pm 0.05	1.281×10^{-2}	0.70×10^{11}
0.400 \pm 0.05	7.674×10^{-3}	4.22×10^{10}
0.500 \pm 0.05	4.894×10^{-3}	1.69×10^{10}
0.600 \pm 0.05	3.234×10^{-3}	1.78×10^{10}
0.700 \pm 0.05	2.181×10^{-3}	1.20×10^{10}
0.800 \pm 0.05	1.485×10^{-3}	8.17×10^9
0.900 \pm 0.05	1.014×10^{-3}	5.58×10^9
1.000 \pm 0.05	6.887×10^{-4}	3.79×10^9
1.100 \pm 0.05	4.630×10^{-4}	2.55×10^9
1.200 \pm 0.05	3.00×10^{-4}	1.65×10^9
1.300 \pm 0.05	1.973×10^{-4}	1.09×10^9
1.400 \pm 0.05	1.231×10^{-4}	0.68×10^9
1.500 \pm 0.05	7.337×10^{-5}	4.04×10^8
1.600 \pm 0.05	4.117×10^{-5}	2.26×10^8
1.700 \pm 0.05	2.125×10^{-5}	1.17×10^8
1.800 \pm 0.05	9.740×10^{-6}	5.36×10^7
1.900 \pm 0.05	3.728×10^{-6}	2.05×10^7
2.000 \pm 0.05	1.058×10^{-6}	5.82×10^6
2.100 \pm 0.05	1.670×10^{-7}	9.19×10^5
2.200 \pm 0.05	4.768×10^{-9}	2.62×10^4
Total bremsstrahlung energy, MeV/beta particle		2.814×10^{-2}

Production of bremsstrahlung photons from stontium-90
beta in strontium titanate Matrix (Ref. 5)

Maximum beta-particle energy	0.545 MeV
Average beta-particle energy	0.201 MeV

Bremsstrahlung energy group, MeV	Within ΔE energy group	
	Photons per beta particle	Photons/W·sec
0.020 \pm 0.01	1.009×10^{-2}	5.55×10^{10}
0.040 \pm 0.01	4.044×10^{-3}	2.22×10^{10}
0.060 \pm 0.01	2.195×10^{-3}	1.21×10^{10}
0.080 \pm 0.01	1.348×10^{-3}	7.41×10^9
0.100 \pm 0.01	8.845×10^{-4}	4.86×10^9
0.120 \pm 0.01	6.034×10^{-4}	3.32×10^9
0.140 \pm 0.01	4.217×10^{-4}	2.32×10^9
0.160 \pm 0.01	2.993×10^{-4}	1.65×10^9
0.180 \pm 0.01	2.141×10^{-4}	1.18×10^9
0.200 \pm 0.01	1.537×10^{-4}	8.45×10^8
0.220 \pm 0.01	1.103×10^{-4}	6.07×10^8
0.240 \pm 0.01	7.871×10^{-5}	4.33×10^8
0.260 \pm 0.01	5.571×10^{-5}	3.06×10^8
0.280 \pm 0.01	3.895×10^{-5}	2.14×10^8
0.300 \pm 0.01	2.678×10^{-5}	1.47×10^8
0.320 \pm 0.01	1.801×10^{-5}	0.99×10^8
0.340 \pm 0.01	1.179×10^{-5}	6.48×10^7
0.360 \pm 0.01	7.448×10^{-6}	4.10×10^7
0.380 \pm 0.01	4.497×10^{-6}	2.47×10^7
0.400 \pm 0.01	2.559×10^{-6}	1.41×10^7
0.420 \pm 0.01	1.345×10^{-6}	0.74×10^7
0.440 \pm 0.01	6.333×10^{-7}	3.48×10^6
0.460 \pm 0.01	2.534×10^{-7}	1.39×10^6
0.480 \pm 0.01	7.807×10^{-8}	4.29×10^5
0.500 \pm 0.01	1.472×10^{-8}	8.10×10^4
0.520 \pm 0.01	7.336×10^{-10}	4.03×10^3
0.540 \pm 0.01	0.000	
Total bremsstrahlung energy, MeV/beta particle	9.924×10^{-4}	

Production of bremsstrahlung photons from yttrium-90
beta in strontium titanate matrix (Ref. 5)

Maximum beta-particle energy	2.27 MeV
Average beta-particle energy	0.944 MeV

Bremsstrahlung energy group, MeV	Within ΔE energy group	
	Photons per beta particle	Photons/W·sec
0.100 \pm 0.05	4.537×10^{-2}	2.50×10^{11}
0.200 \pm 0.05	1.782×10^{-2}	0.98×10^{11}
0.300 \pm 0.05	9.456×10^{-3}	5.20×10^{10}
0.400 \pm 0.05	5.665×10^{-3}	3.12×10^{10}
0.500 \pm 0.05	3.613×10^{-3}	1.99×10^{10}
0.600 \pm 0.05	2.389×10^{-3}	1.31×10^{10}
0.700 \pm 0.05	1.611×10^{-3}	0.89×10^{10}
0.800 \pm 0.05	1.098×10^{-3}	6.04×10^9
0.900 \pm 0.05	7.493×10^{-4}	4.12×10^9
1.000 \pm 0.05	5.092×10^{-4}	2.80×10^9
1.100 \pm 0.05	3.425×10^{-4}	1.88×10^9
1.200 \pm 0.05	2.264×10^{-4}	1.25×10^9
1.300 \pm 0.05	1.460×10^{-4}	8.03×10^8
1.400 \pm 0.05	9.110×10^{-5}	5.01×10^8
1.500 \pm 0.05	5.434×10^{-5}	3.00×10^8
1.600 \pm 0.05	3.050×10^{-5}	1.68×10^8
1.700 \pm 0.05	1.576×10^{-5}	8.67×10^7
1.800 \pm 0.05	7.220×10^{-6}	3.97×10^7
1.900 \pm 0.05	2.764×10^{-6}	1.52×10^7
2.000 \pm 0.05	7.850×10^{-7}	4.32×10^6
2.100 \pm 0.05	1.239×10^{-7}	6.81×10^5
2.200 \pm 0.05	3.540×10^{-9}	1.95×10^4
Total bremsstrahlung energy, MeV/beta particle	2.078×10^{-2}	

Biological Tolerances for ^{90}Sr

Maximum permissible body burdens and maximum permissible concentrations for radionuclides in air and in water for occupational exposure⁷

Organ of reference (critical organ underscored)	Max. permissible burden in total body, q(μCi)	Maximum permissible concentrations, $\mu\text{Ci}/\text{cm}^3$			
		For 40-hr week		For 168-hr week	
		Water	Air	Water	Air
(Sol) { <u>Bone</u>	20	4×10^{-6}	3×10^{-10}	10^{-6}	10^{-10}
		10^{-5}	9×10^{-10}	4×10^{-6}	3×10^{-10}
		10^{-3}	3×10^{-7}	5×10^{-4}	10^{-7}
(Insol) { <u>Lung</u>	20	10^{-3}	5×10^{-9}	4×10^{-4}	2×10^{-9}
			2×10^{-7}		6×10^{-8}

*Abbreviations GI and LLI refer to the gastrointestinal tract and lower large intestine, respectively.

SPECIFIC POWER

Assume

148.9 Ci/W(thermal), 139.0 Ci/g or 0.933 W/g (100%

^{90}Sr)^{1,2,5,8}

	Sr metal	SrTiO ₃	SrO	SrF ₂	Sr ₂ TiO ₄
100% Sr (55%) ^{90}Sr					
W/g	0.513	0.247	0.435	0.360	0.315
Ci/g	76.5	36.8	64.8	53.7	47.0
95% Sr & 5% Ca, Mg, Ba					
W/g	0.487	0.235	0.411	0.336	0.294
Ci/g	72.7	34.1	61.2	50.0	43.8

PHYSICAL AND CHEMICAL PROPERTIES

	Sr metal	SrTiO ₃	SrO	SrF ₂	Sr ₂ TiO ₄
Density g/cm ³					
100% Sr	2.6(9)*	5.11(13)*	4.975(58)*	4.29(14)*	4.99(15)*
95% Sr	2.5	5.03	4.63	4.20	4.93
Liquid Sr, $\rho = 2.648 - 2.62 \times 10^{-4}T$ (°K)(1225–1580°K)(53)*					
Surface tension			(MgO)		
at MP dynes/cm	165(17,18)*		1200(21)*	184(22)*	
$\sigma = 392 - 0.085 T$ (°K) (1152–1602°K)(53)*					
Melting Point, °C	772(10)*	2040(23)*	2457(24)*	1463(25)*	1860(27)*
Boiling Point, °C	1372(10)*	2500- 3000(52)*	3227(24)*	2477(26)*	2500- 3000(52)*
ΔH , kcal/mole	$\alpha \rightarrow \beta$	Phase change occurs(23)*			$\alpha \rightarrow \beta$ (23)*
Phase transition	0.2(11)* at 589°C	1400 and 1640°C			1600°
ΔH Fusion, kcal/mole	2.4(11)*		16.7(26)*	4.3(26)*	
ΔH Vaporization, kcal/mole	33.2(12)*	71†(10)*		71†(26)*	71†(10)*
ΔH Formation, kcal/mole	0	-399(28,29)	-141.0(29)* -144.2(59)* -140.5(60)*	-290(29)*	-545.6(28,30)*
ΔG Formation, kcal/mole	0	-379(28,30)*	-133.8(29)*	-277.2(29)*	-518.2(28,30)*
S_{298} , cal/mole·°K	12.5(19)*	26.0(31)*	13.0(29)*	20.5(26)*	38.0 ± .3(37)*
Hardness	(Cu)(20)* 16-18 Brinell		3.5(32)* Mohs		
Crush Strength, lbs/in ²		(CaTiO ₃)(33)* 19,100			
Bend Strength, lbs/in ²		43(34)*			
Viscosity, Centipoise					
SrF ₂	$\log \eta = 0.781 + \frac{436}{T}$		(T in °K)		(16)*
Coefficient of thermal expansion/°C					
Sr metal	2.0×10^{-5} (25°C)				(10)*
SrTiO ₃	12.1×10^{-6} (0-1400°C)				(56)*
SrO	11.3×10^{-6} (0-1400°C)				(56)*
SrF ₂	$15.72 \times 10^{-6} - 0.62 \times 10^{-8}T + 1.17 \times 10^{-10}T^2$ (28 to 284°C) T = °C				(56)*
Sr ₂ TiO ₄	11.7×10^{-6} (average of SrO and SrTiO ₃)				
Specific heat cal/g·°C					(T in °K)
Sr metal	0.0719 (25°C)				(12)*
SrTiO ₃	$0.154 + 0.96 \times 10^{-5}T - 2.54 \times 10^3 T^{-2}$				(37)*
SrO	$0.117 + 1.22 \times 10^{-5}T - 1.50 \times 10^3 T^{-2}$				(11)*
SrF ₂	$0.125 + 5.51 \times 10^{-5}T$				(26)*
Sr ₂ TiO ₄	$0.134 + (1.34 \times 10^{-5}T) - (1.63 \times 10^3 T^{-2})$ (300-1800°K)				(38)*
Enthalpy $H_T - H_{298}$ in cal/mole					(T in °K)
Sr metal	$5.13 T + 1.66 \times 10^{-3} T^2 - 1731$ (298 to 862°K)				(11)*
SrTiO ₃	$9.12 T - 3582$ (862 to 1043°K)				(11)*
SrO	$12.13 T + 0.063 \times 10^{-3} T^2 + 1.55 \times 10^3 T^{-1} - 4192$				(11)*
SrF ₂	$15.7 T + 3.5 \times 10^{-3} T^2 - 4980$				(26)*
Sr ₂ TiO ₄	$38.45 T + 1.92 \times 10^{-3} T^2 + 4.67 \times 10^5 T^{-1} - 13,207$ (300-1800°K)				(38)*
SrTiO ₃	$28.23 T + 0.88 \times 10^{-3} T^2 + 4.66 \times 10^5 T^{-1} - 10,058$				(38)*

*References

†From Trouton's Rule

The following equations are derived from above data by a method of least mean squares. The data covered the range 350 to 900°C. Useful range of equation is 200 to 1400°C.

$$\text{SrO} \quad 1/k = 109.51 + 0.0916T, k = \text{cal/cm}\cdot\text{sec}\cdot^\circ\text{C} \\ (T \text{ in } ^\circ\text{K})$$

$$\text{SrTiO}_3 \quad 1/k = 55.76 + 0.0673T$$

$$\text{Sr}_2\text{TiO}_4 \quad 1/k = 110.26 + 0.0268T$$

Composition of material simulating freshly prepared Hanford product from which thermal conductivities were measured

	wt, %		
	SrTiO ₃	SrO	Sr ₂ TiO ₄
SrO	51.03	91.69	65.56
BaO	1.92	3.46	2.47
CaO	2.42	4.34	3.10
MgO	0.28	0.51	0.37
TiO ₂	44.35		28.50

Thermal conductivity of various SrO-TiO₂ compositions.

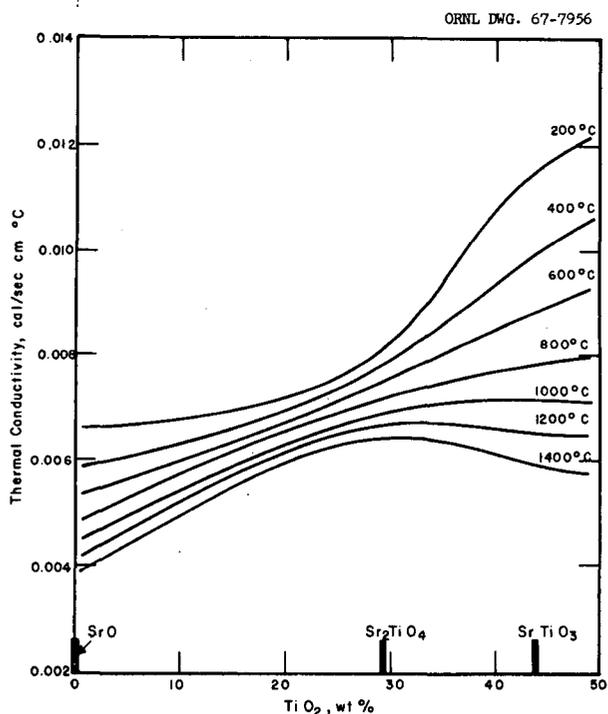


Fig. 8.9. Thermal conductivity of various SrO-TiO₂ compositions.

The curves in Fig. 8.9 were obtained by interpolating the data for the stoichiometric SrO, Sr₂TiO₄, SrTiO₃, and TiO₂. (Ref. 47, 48)

Thermal conductivity of radioactive strontium titanate.^{54,55}

Data were obtained on three hot-pressed pellets having 92, 92, and 98% theoretical densities with TiO₂/alkaline-earth oxide mole ratios of 0.86, 0.95, and 1.25. The ages of the SrTiO₃ in the pellets were 0.5, 3.5, and 4.25 years. It was found that the age of SrTiO₃ and the variation in pellet composition and theoretical density did not have an effect on the results within the limit of experimental error. A single equation for the thermal conductivity as a function of temperature was derived from the data by the method of least mean squares:

$$1/k = 82.65 + 0.112T (^\circ\text{K})$$

where k is the thermal conductivity in cal/cm·sec·°C. The data were measured over a range of 350 to 850°C and are considered usable from 200 to 1400°C. Values of k as a function of temperature are given below at the 95% confidence level.

Thermal conductivity cal/cm·sec·°C × 10 ³	Temperature, °C
7.37 ± 0.90	200
6.32 ± 0.25	400
5.54 ± 0.15	600
4.93 ± 0.16	800
4.44 ± 0.23	1000
4.03 ± 0.28	1200
3.70 ± 0.31	1400

Thermal Diffusivity, cm²/sec

These values were obtained by dividing the thermal conductivity by the product of the specific heat and the density.

°C	Sr (Ref. 20)	SrF ₂ (Ref. 50)	SrTiO ₃ (Ref. 47)	SrO (Ref. 47)	Sr ₂ TiO ₄ (Ref. 47)
20	1.64	0.0219			
200			0.0151	0.0122	0.0124
300		0.0091			
400			0.0124	0.0103	0.0114
600			0.0107	0.0091	0.0106
725		0.0043			
800			0.0093	0.0080	0.0099
1000			0.0083	0.0072	0.0094
1200			0.0075	0.0065	0.0089
1400			0.0068	0.0060	0.0085

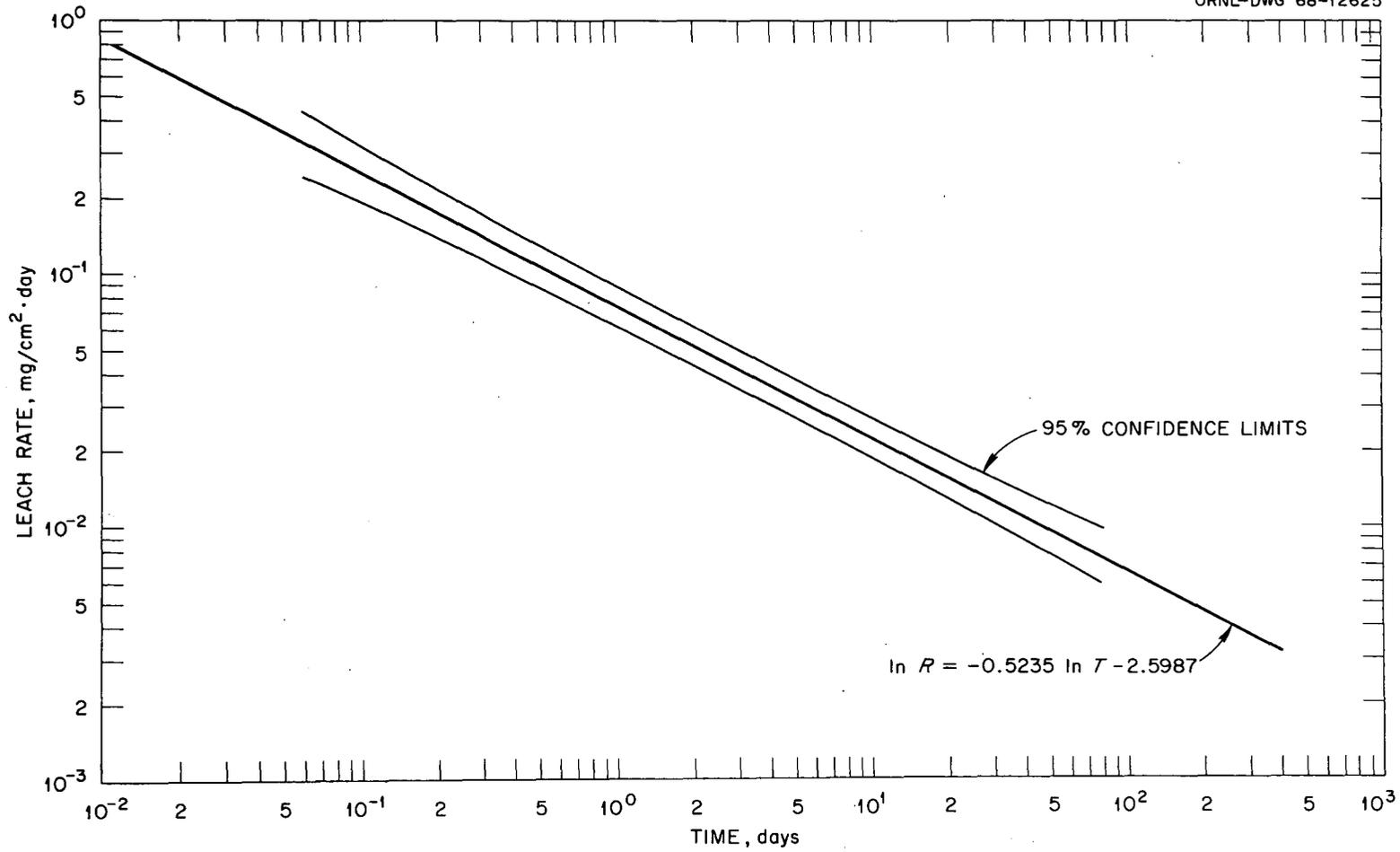


Fig. 8.10. Leach rate of $^{90}\text{SrTiO}_3$ as a function of time (distilled water).

**Thermal diffusivity of radioactive strontium titanate
(94.7% of theoretical density)**

Thermal diffusivity, ^a cm ² /sec	Temperature, °C
0.01068	200
0.00869	400
0.00739	600
0.00645	800
0.00574	1000
0.00511	1200
0.00461	1400

^aThese values were calculated by dividing the thermal conductivity by the product of the specific heat and the density.

Solubility

- (1) Sr metal reacts vigorously with H₂O (Ref. 39).
- (2) SrF₂ 0.9 × 10⁻³ M 18°C (Ref. 39).
- (3) Sr₂TiO₄ (Ref. 50)

°C	m/l × 10 ⁴			
	H ₂ O	Natural seawater	Synthetic seawater	0.1 M HCl
25	1.7	1.7	1.8	1.7
65	1.7	2.4	2.9	2.7

- (4) SrO hot pressed pellets d = 4.54 g/cm³ Rate of dissolution in H₂O at 4.4 cm/min 1.49 g/cm²·day (Ref. 55)
- (5) SrTiO₃ (Ref. 55)

Leach rates were determined on five ⁹⁰SrTiO₃ fuels having densities ranging from 62 to 92% of theoretical. The low density samples were recovered from SNAP-7A fuel capsules after seven years of operation. The high density samples were prepared by hot pressing. The samples were intact after an immersion of 76 days in distilled water. The data were fitted to a single equation by a method of least squares and are presented in Fig. 8.10 with the 95% confidence limits. A single equation

to represent the data is as follows:

$$\ln R = -0.5235 \ln T - 2.5987$$

where

R = leach rate, mg/cm²·day

T = time, days.

**COMPATIBILITY WITH
CONTAINMENT MATERIALS**

**Oxidation and corrosion resistance of hastelloy
alloy C (HC), inconel 600 (I),
and platinum (P) samples**

Capsules exposed to air at 1100°C

Sample No.	Time in furnace, months	Weight, g			
		Before	After	Loss	Loss, %
HC-8	4	4.6446	2.3919	2.2527	48.5
I-8	4	4.2403	3.8670	0.3733	8.8
P-8	4	2.1740	2.1735	0.0005	0.023
HC-9	5	4.7473	2.2394	2.5079	52.83
I-9	5	4.4367	3.8044	0.6323	14.25
P-9	5	2.1435	2.1430	0.0005	0.023
HC-10	6	4.7237	1.1604	3.5633	75.4
I-10	6	4.3377	2.8739	1.3538	32.0
P-10	6	2.0898	2.0859	0.0039	0.12
HC-11	7	4.7537	1.4191	3.3346	70.15
HC-16	12	4.8058	0.6172	4.1886	87.2
I-11	7	4.4127	3.8271	0.5856	13.3
I-16	12	4.4103	3.2946	1.1157	25.3
P-11	7	2.2027	2.2020	0.0007	0.03
P-16	12	2.4130	2.3393	0.0737	3.05
HC-1*	3	4.7003	4.4276	0.2727	5.8
I-1*	3	4.3887	4.2291	0.1596	3.64
P-1*	3	2.0524	2.0518	0.0006	0.03
HC-2*	6	4.7326	2.4655	2.2671	47.9
HC-4*	11	4.5738	1.3691	3.2047	70.1
I-2*	6	4.3861	3.6248	0.7613	17.36
I-4*	11	4.2683	3.5832	0.6851	16.1
P-2*	6	2.1696	2.1686	0.0010	0.05
P-4*	11	2.0899	2.0895	0.0004	0.02

*Samples after exposure to soil (East Tennessee red clay) at 1100°C

Compatibilities of inactive strontium compound with container materials

Source material and exposure	Container material								
	Superalloys				Refractory metals				
	Hastelloy alloy X	Haynes alloy No. 25	Ni-o-nel	N-155	Mo	Nb	Ta	W	TZM
Strontium metal (Sr)									
1000°C, 1000 hr	SR	NR	SR	MR	NR		SR	NR	NR
1000°C, 5000 hr		MR		MR			SR	NR	
1000°C, 10,000 hr		MR	MR	MR	NR		SR	SR	
Strontium oxide (SrO)									
1000°C, 1000 hr	SR		SR	SR	NR	NR	SR	SR	
1850°C, 168 hr					SR	MR	SR	SR	
Strontium-9% beryllium oxide (SrO-9% BeO)									
1000°C, 1000 hr		MR	MR	SR	NR			NR	NR
Strontium fluoride (SrF ₂)									
1000°C, 1000 hr	SR	SR	SR	SR	NR		SR	SR	
Strontium disilicide (SrSi ₂)									
1000°C, 168 hr	DR	DR	DR	DR	DR		DR	DR	DR
Strontium titanate (SrTiO ₃)									
1000°C, 1000 hr	SR	SR	SR	SR	NR		NR	NR	NR
1850°C, 1000 hr					NR	SR	SR	NR	MR

Legend: NR – Negligible or no reaction (compatible) SR – Slight reaction
 DR – Destructive reaction (incompatible) MR – Major reaction

A number of reactions were dependent on time and temperature; for example, Haynes alloy No. 25 with strontium metal showed no attack at 1000°C up to 1000 hr but fell into the major reaction classification after 5000 and 10,000 hr at 1000°C. This indicates that Haynes alloy No. 25 should probably not be considered for use with strontium metal at temperatures >1000°C and times >5000 hr.

After exposure of 2036 hr at 925°C to inactive liquid strontium metal, it was found that molybdenum and stainless steel 321 showed good compatibility with liquid strontium metal; that wrought iron and Haynes alloy No. 25 were worthy of further study; and that Hastelloy C, Hastelloy alloy N, Hastelloy alloy X, and titanium had dissolved and were incompatible with strontium metal.

Comparison of chemical analysis of compatibility test materials before and after exposure for 1000 hr at 1100°C

Material analyzed	Material contacted	Concentration, ppm						Concentration, %			
		Carbon		Oxygen		Strontium		Chromium		Manganese	
		Before	After	Before	After	Before	After	Before	After	Before	After
Haynes alloy No. 25	SrTiO ₃	960	230	10	60	<50	<200	20.5	20.4	0.8	0.5
	Sr ₂ TiO ₄	960	1070	10	80	<50	700	20.5	21	0.8	0.7
	SrO	960	1210	10	490	<50	<200	20	19	0.8	0.8
Hastelloy alloy C	SrTiO ₃	490	60	15	60	<50	<300	16.1	16.4	0.45	0.6
	Sr ₂ TiO ₄	490	510	15	110	<50	700	16.1	16.1	0.45	0.7
	SrO	490	670	15	1500	<50	<200	16.1	16.0	0.45	0.5
316 stainless steel	SrTiO ₃	430	230	160	190	<50	<200	17.7	17.7	2.1	2.5
	Sr ₂ TiO ₄	430	500	160	210	<50	500	17.7	17.9	2.1	2.0
	SrO	430	950	160	620	<50	100	17.4	17.0	2.1	1.8
SrTiO ₃	Haynes alloy No. 25	270	600					0.004	0.4	0.0004	0.1
	Hastelloy alloy C	270	150					0.004	1.3	0.0004	0.4
	316 stainless steel	270	560					0.004	4.0	0.0004	0.4
Sr ₂ TiO ₄	Haynes alloy No. 25	50	520					0.004	0.004	0.001	0.001
	Hastelloy alloy C	50	940					0.004	0.04	0.001	0.010
	316 stainless steel	50	270					0.004	0.002	0.001	0.001

Chemical reaction

References		Oxygen	Nitrogen	Inorganic acids	H ₂ O
20	Sr	Fast	No at RT reacts elevated T	Reacts	Reacts
43	SrTiO ₃	No	No	Slightly soluble	No
46	SrO	No	No	Soluble	Sr(OH) ₂
46	SrF ₂	No	No	Insoluble	Slightly soluble
43	Sr ₂ TiO ₄	No	No	Soluble	Slight

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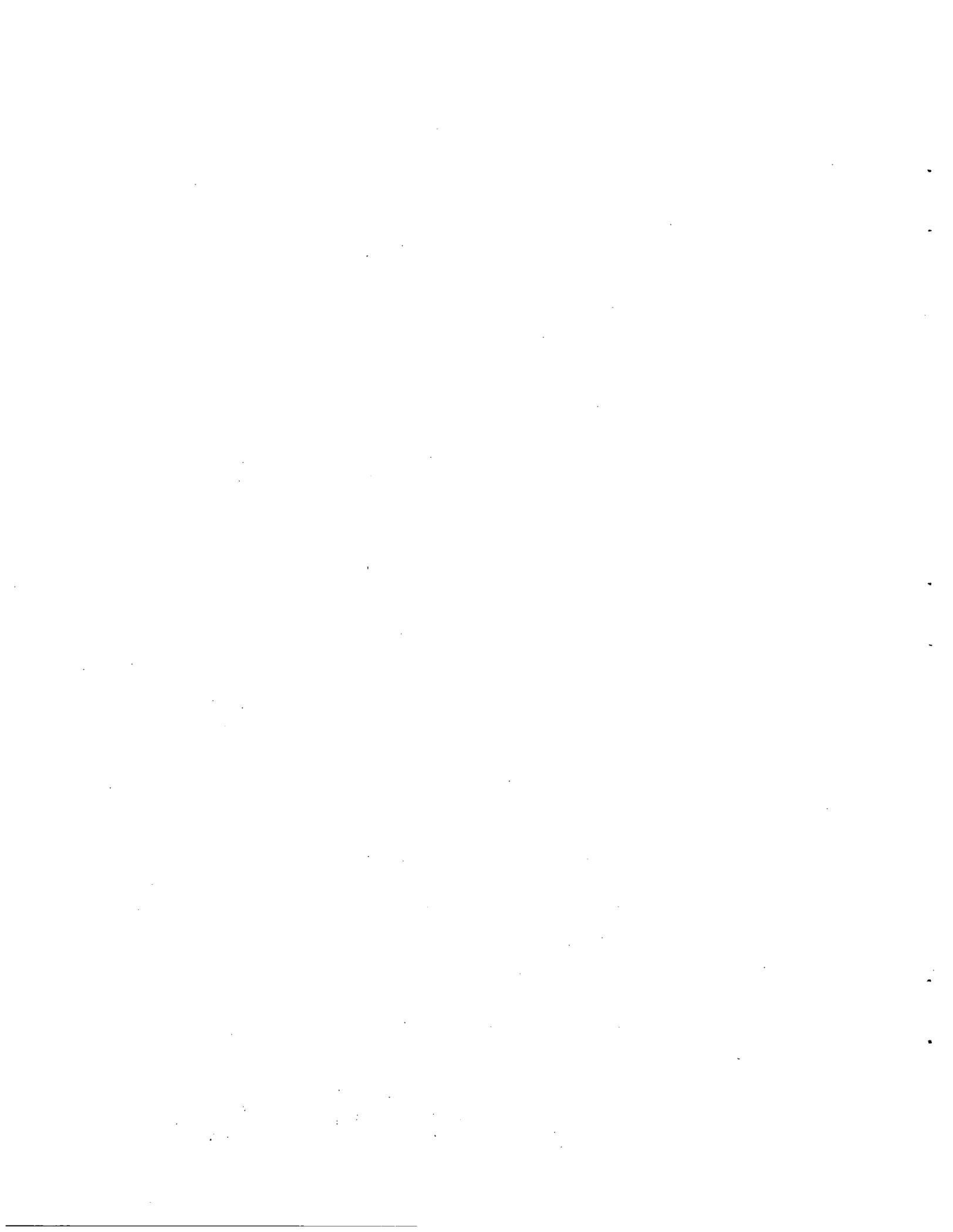
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Sr-90 Heat sources produced at ORNL

Source name or buyer	Date completed	Weight SrTiO ₃ (or SrO) g	Density of pellet g/cm ³	Thermal power W	Activity kCi	Specific activity Ci/g	Pellet power density W/cm ³	Number of units†	Number capsules per unit	Number pellets per capsule	Capsule volume cm ³	Capsule dimensions		Pressing technique		Specific power W/g	Capsule power density W/cm ³
												diameter	height	Cold press sinter	Hot press		
Weather Bureau	5/16	763	4.5	110	17.5	22.9	0.650	1	1	11	354	<u>6.34</u>	✓		0.144	0.311	
SNAP-7A	9/61	1124	3.6	255	40.5	36.0	0.817	1	4	6	243	<u>13.0</u> <u>4.75</u>	✓		0.227	0.263	
SNAP-7C	8/61	1280	3.5	250	39.8	31.1	0.686	1	4	7	243	<u>13.7</u> <u>4.75</u>	✓		0.196	0.264	
SNAP-7D	5/62	6738	3.5	1411	224	33.3	0.735	1	13	14	390	<u>13.7</u> <u>4.75</u>	✓		0.210	0.254	
SNAP-7E	3/62	850	3.0	195	30.9	36.3	0.690	1	4	6	243	<u>21.9</u> <u>4.75</u>	✓		0.230	0.201	
RCA test	7/64	2541	3.9	526	83.5	32.8	0.806	1	1	5	1710	<u>13.7</u> <u>10.5</u> <u>19.6</u>	✓		0.207	0.308	
NUMEC-SrO	2/66	625	4.8	202	32.0	51.2	1.55	3	1	1	130	<u>5.56</u> <u>5.33</u>		✓	0.383	1.04	
AGN	12/66	283	4.9	45	7.2	25.3	0.79	3	1	1	77	<u>4.28</u> <u>4.6</u>		✓	0.182	0.585	
SNAP-23	12/68	6018	4.3	1127	165.7	27.5	0.80	1	1	4	2590	<u>12.7</u> <u>20.4</u>	✓		0.187	0.435	
RIPPLE A IV, 1&2	8/67	554	4.5	100	15.3	27	0.82	2	1	1	116	<u>5.08</u> <u>3.2</u>	✓		0.181	0.45	
RIPPLE A IX, 1&2	8/67	1087	4.5	200	30	27	0.84	2	1	1	206	<u>5.08</u> <u>6.2</u>	✓		0.185	0.49	
Mitsubishi SrO	8/67	180	4.2	62	9.1	50.6	1.35	1	1	1	92	<u>4.14</u> <u>3.41</u>	✓		0.344	0.675	
Sentinel 8 Isotopes, Inc.	11/68	1214	4.4	254	37.4	30.8	0.92	1	1	1	896	<u>9.5</u> <u>12.5</u>	✓		0.209	0.28	
LCG Sentinel-25	1967											<u>9.5</u> <u>26.0</u>		✓			
Martin Co.*	1969	3850	4.3	720	106.0	27.5	0.80	10	1	3	1850			✓	0.187	0.39	
SNAP-21 3M/ORNL	1968	1100	4.7	205	30.2	27.4	0.88	6	1	1	435	<u>8.1</u> <u>8.4</u>	✓		0.186	0.47	
NUMEC	6/67	90	4.6	16.6	2.45	27.2	0.86	3	1	3	41	<u>2.5</u> <u>8.3</u>	✓		0.185	0.41	
TRACS-25 NUMEC	2/68	3717	4.8	800	117.7	31.6	1.04	1	1	3	1610	<u>8.4</u> <u>19</u>	✓		0.215	0.495	

*Martin Co. nuclear operations were taken over by Isotopes, Inc., while order was in progress.

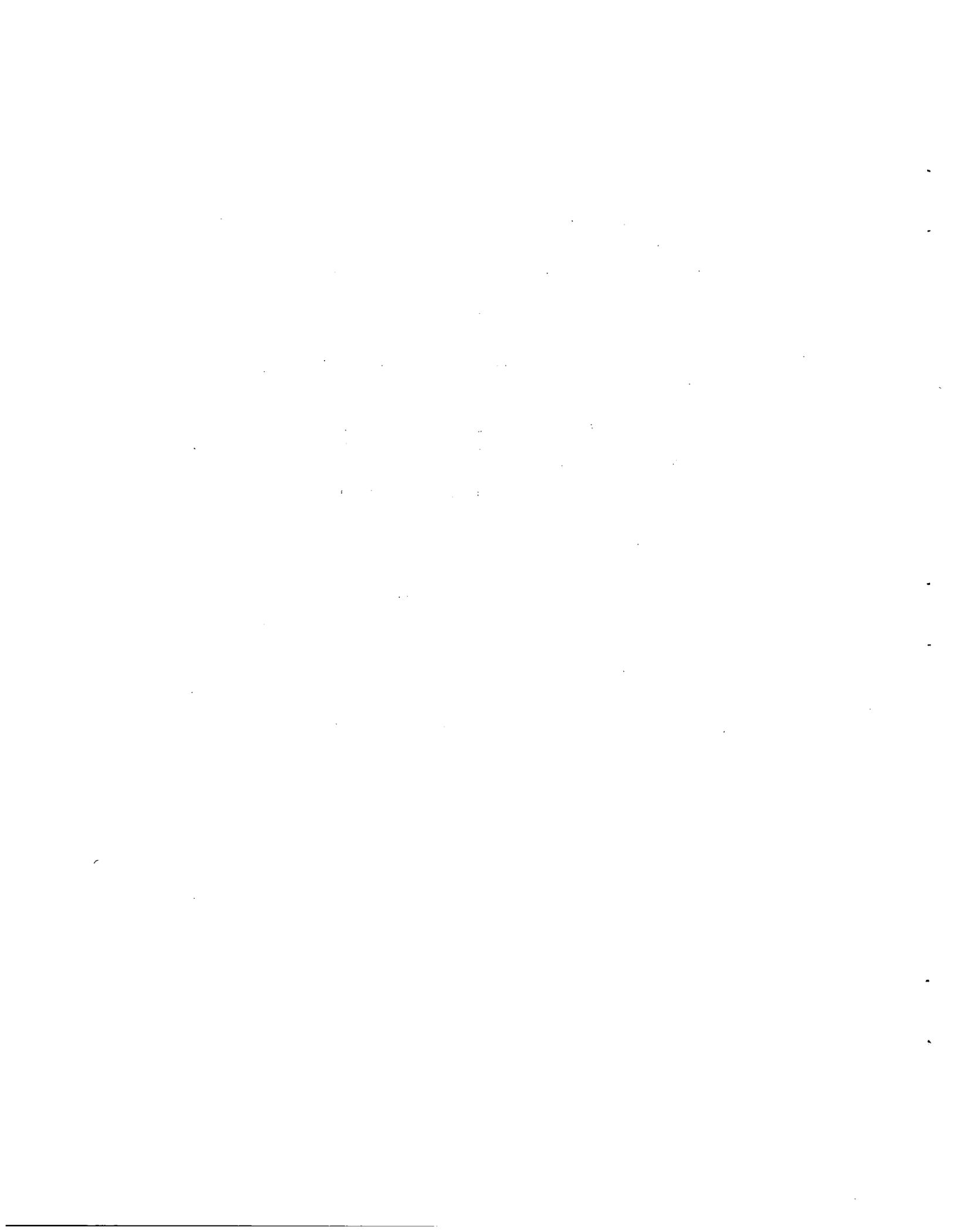
†Quantities, weight, activity, power, and dimensions are averages of the units if more than one unit was made.



APPENDIX B

CHRONOLOGY, SOURCE DEVELOPMENT

- 1948-54 Cesium co-precipitation with alum from acidic or basic waste solutions, ORNL. Purification of kCi quantities of ^{137}Cs .
- 1957-62 Development and laboratory scale testing of D2EHPA solvent extraction process for strontium purification, ORNL.
- 1958 Use of Decalso ion exchange medium for Cs, ORNL. Completion of Fission Products Development Laboratory. Beginning of strontium power program.
- 1958-60 Selection of strontium compound, solubility tests, capsule material selection, generator design and thermoelectric element tests, Martin Co. Nuclear Division.
- 1960 First 7 kCi of ^{90}Sr purified by precipitation methods, ORNL. Solvent extraction separation of Ca-Sr with D2EHPA, ORNL. SrTiO_3 preparation. Pellet formation and encapsulation, ORNL. Development PbSO_4 carrier precipitation process for Sr head-end purification, pilot plant scale, HAPO. Ion exchange purification of Sr pilot plant scale, HAPO.
- 1961 75 kCi Sr purified by PbSO_4 precipitation and ion exchange, HAPO.
- 1960-1964 Quehanna plant operation, Martin Company Nuclear Division. Preparation of SrTiO_3 powder, pellet fabrication and encapsulation.
- Mar. 1961 HAPO-I A cask shipment.
- 1960-61 HAPO purification, 1 MCi ^{90}Sr . Pilot plant scale.
- Summer 1961 Weather station installed at Axel-Heiberg near North Pole. First radioactive thermoelectric application.
- May 1961 HAPO-II cask shipment of ^{90}Sr .
- 1961-1964 8 MCi ^{90}Sr purified at HAPO by PbSO_4 carrier precipitation and solvent extraction, D2EHPA.
- 1966 Hot pressed fuel $^{90}\text{SrTiO}_3$, ^{90}SrO . Precipitation of tetraoxalate as a finishing process for Cs purification.



APPENDIX C

Excerpt from: A. F. Rupp, Large Scale Production of Radioisotopes, in Proc. Intern. Conf. Peaceful Uses At. Energy, Geneva, 1955, Vol. 14, pp. 68-84, United Nations, New York, 1956.

Long-Lived Fission Products

Cobalt-60 is an extremely good source of radiation, having two gamma rays per disintegration (1.17 MeV and 1.33 MeV), and it can be obtained in extremely high specific activity (a maximum of 70 curies per gram obtained up to this time). However, the only moderately long half-life of 5.3 years and the fact that it is not a true by-product of the nuclear reactor suggest that it may eventually become of secondary importance, especially as a source of industrial gamma radiation as compared with fission-product cesium-137. Cesium-137 has a half-life of 33 years, gamma radiation of 0.67 MeV from its short-lived barium-137 daughter, and is a true by-product, being a fission product which occurs in relatively high yield (6%). Therefore, much attention has been devoted to the separation of large quantities of cesium-137 from reactor wastes. Other fission products in the reactor wastes can be separated at the same time if there is a market for these materials. Other long-lived radioisotopes in wastes which are of greatest interest are strontium-90, cerium-144, ruthenium-106, europium-155, promethium-147, and technetium-99.

In 1948, work was started on the development of industrial-type processes for economically removing these important fission products from reactor wastes and fabricating the radioactive material into suitable sources. The processes have been taken through the laboratory and semi-works stages, during which 1000-curie quantities of ^{137}Cs and 100-curie quantities of ^{90}Sr , ^{144}Ce , and ^{106}Ru have been produced. Most emphasis has been placed on the cesium separation and purification process, since it was deemed most valuable of all the fission products. During the development period, many types of processes were tried for the separation of cesium. Since cesium has relatively few insoluble compounds, the first methods tried were all based upon isolating cesium by removing all the other elements in the solution by ion exchange or precipitation. However, many of the reactor wastes are contaminated to a very great extent with Group I elements, such as sodium and potassium. Therefore, a more direct means of isolating cesium was necessary. Various precipitants were tried, such as silico-tungstic acid, phospho-tungstic acid, ferrocyanides, and other compounds of this type which have been long known and

used for analytical purposes. However, most of these were not well-adapted to industrial type processes and the most promising process appeared to be the one in which advantage is taken of the co-crystallization of the relatively insoluble cesium alum with potassium or ammonium alum.^{1,3} By saturating the solution with the potassium alum (or as now used, ammonium alum) at approximately 80–90°C, and then cooling to bring down a crop of alum crystals, it was found that the cesium was quite selectively co-crystallized with the batch of crystals that was brought down, more than 99% of cesium being removed from the solution.^{1,4} By decanting off the supernatant liquor, another batch of material containing cesium could be put into the crystallizers and the previous crystals redissolved. More ammonium alum was added to saturate the solution at 80°C, and a new crop of crystals grown, this time including all the cesium that has been brought down during the first step plus the newly added cesium. Successive crystallizations of this type are made, and the crop of crystals grown after each crystallization becomes progressively richer in cesium. This procedure can be followed until cesium losses in the supernatant liquor become higher than desired. In the semiworks equipment designed for this process, a number of crystallizers are used, some of which handle the supernatant liquor for recrystallization and recovery of small amounts that have been passed into the supernatant liquor; others are used to concentrate the cesium by dissolving the alum crystals in pure water and then growing smaller batches of crystals to get the cesium into progressively smaller volumes of liquid. If enough cesium is accumulated, it is possible to precipitate pure cesium-ammonium alum. Cesium-137 in the process comes down almost radiochemically pure (>99%) after one crystallization. Only insignificant amounts of cerium and ruthenium-106 superficially contaminate the first batches of crystals. However, some inactive fission products, such as rubidium, accompany the cesium and must be removed by selective, controlled crystallizations near the end of the process; by these successive crystallizations, one can enrich certain fractions in cesium and others in rubidium. At all stages of the process, the various fractions can be recycled to an appropriate previous point in the crystallization cycle and, in this way, losses can be easily kept to a minimum.

The crystallization process is also well adapted to removing cesium, either before or after the other fission products are removed from a fission product mixture. However, in most cases it is probably desirable to remove the other constituents, such as alkaline earths, ruthenium, and rare earths, before the cesium is removed.

Because of its complex chemistry, ruthenium-106 has always been one of the most difficult of the fission products to cope with in fission mixtures. The procedure developed for separating ruthenium from fission product waste consists of controlled homogeneous precipitation of iron at a pH of 2.0 by the hydrolysis of urea, or the controlled addition of very small quantities of ammonia gas into the mixture with high-speed agitation, producing a granular precipitate of hydrated iron oxide which coprecipitates over 90% of the ruthenium and technetium in the solution. This fraction is then removed for storage and combining with other similar fractions from succeeding batches passing through the plant.

All second-stage processing is done by combining portions of similar fractions going through the plant until a large enough quantity is accumulated to process in the later steps in the process, thereby giving a more economical operation.

The effluent from the ruthenium-technetium-iron hydroxide precipitation contains cesium, alkaline earths, and rare earths. The next step is to remove the rare earths as the hydroxides by precipitation from a carbonate-free solution, thus allowing the alkaline earths to pass into the filtrate. The rare earth precipitation is made by passing airborne ammonia gas into the solution with high-speed agitation. The rare earth group precipitates quite completely, there being a plentiful supply of inactive neodymium, lanthanum, and other rare earths to carry down all of the cerium, promethium, and europium that are present. It may be well to remark at this point that with procedures of this kind, where one is dealing with large quantities of fission products, classical methods are usually quite satisfactory, since high enough concentrations of the fission products are present for ordinary precipitations. This is in contrast to the early radiochemical work where only minute concentrations of fission products were available.

After removal of the rare earth group as the hydroxides,* the filtrate containing cesium and the alkaline earths is treated with sodium carbonate to precipitate

*Or, the hydroxide and carbonate groups may be brought down together for later separation.

the alkaline earths, mostly inactive barium and radioactive strontium-90. After this precipitation, there remains only cesium in the effluent for removal by the previously described alum crystallization process.

The constituents of the main groups are further separated and purified in the following manner. The iron-technetium-ruthenium precipitate is dissolved and the technetium is selectively precipitated as the tetraphenyl arsonium (TPA) pertechnetate.¹⁵ The effluent containing iron-ruthenium is re-precipitated as $\text{Fe}(\text{OH})_3$ and is dissolved in concentrated sulfuric acid, treated with potassium permanganate and the ruthenium is distilled, as ruthenium tetroxide, into hydrochloric acid or nitric acid containing sufficient quantities of hydrogen peroxide to reduce the ruthenium to the Ru^{+3} state. The ruthenium chloride solution is then used for the preparation of large sources.

Ruthenium is one of the few fission products that can be easily prepared in metallic form as an electroplated metallic source. The ruthenium chloride (or nitrate) solution is treated with red fuming nitric acid and/or hydrochloric acid, depending upon the starting solution, to produce ruthenium nitroso-chloride. Very satisfactory ruthenium electroplating can be done from a bath of ruthenium nitroso-chloride, producing smooth metallic surfaces. Sources have been made by electroplating ruthenium-106 having a specific activity of approximately 40 curies/g onto copper surfaces, in sufficient thickness to indicate that 10,000 curies could probably be plated onto an area of one square foot. Immediately after electroplating the radioactive ruthenium, the plated source is transferred to a wash solution of sulfurous acid and then placed in a ruthenium nitroso-chloride bath, where a flash covering of inactive metallic ruthenium is placed over the active ruthenium. The plate is then rewashed and placed in a silver cyanide electroplating bath and plated with a thin coating of silver. The plate is finally slipped into an envelope made of thin stainless steel and sealed by welding. The stainless steel envelope has handling projections for placing the source in carriers and inserting it into radiation devices.

The technetium precipitate of phenyl arsonium pertechnetate is further purified by several re-precipitations as the pertechnetate and then as the technetium sulfide, followed by dissolution in ammonia and hydrogen peroxide to produce ammonium pertechnetate solution as a final product.

The rare earth group contains three main constituents, cerium-144, promethium-147, and europium-155. Of these constituents, cerium-144 is present in by far the largest quantity. Since it provides most of the

Table C.1. Characteristics of separated fission products

	^{137}Cs	^{90}Sr	$^{144}\text{Ce}^*$	$^{106}\text{Ru}^*$	^{147}Pm	^{155}Eu	$^{60}\text{Co}^\dagger$
Stable nuclides also present	^{133}Cs ^{135}Cs	^{88}Sr	^{140}Ce (^{142}Ce)	^{99}Ru ^{101}Ru (^{102}Ru) (^{104}Ru)	None	^{153}Eu	^{59}Co
Active nuclide, weight/kCi	12.7 g	5.1 g	0.31 g	0.3 g	1.07 g	0.87 g	0.88 g
Active + stable, weight/kCi	31.7 g	9.5 g	~2 g	~26 g	1.07 g	~5 g	20 g
Weight/kCi compound	40.0 g (CsCl)	11.2 g (SrO)	~2.5 g (CeO ₂)	26 g (Metal)	1.25 g (Pm ₂ O ₃)	~64 g (Eu ₂ O ₃)	20 g (Metal)
Weight/kCi obtained experimentally	39.8 g (CsCl)	~70 g (SrO)	2.6 g (CeO ₂)	30 g (Metal)	~7 g (Pm ₂ O ₃)	—	20 g (Metal)
Practical volume/kCi	15 cm ³ (CsCl)	~23 cm ³ (SrO)	1.3 cm ³ (CeO ₂)	2.5 cm ³ (Metal)	~1 cm ³ (Pm ₂ O ₃)	—	2.25 cm ³ (Metal)

*After one year of decay.

†For comparison purposes, using 50 curie/g material.

radiation in moderately old fission product mixtures, it is important to separate it from promethium and europium so they can be further purified in lightly shielded equipment. Several methods are available for removing cerium-144: namely, selective extraction from concentrated nitric acid into tributyl phosphate solutions, or a carefully controlled precipitation of ceric phosphate in acid solution. Cerium may also be separated from the other rare earths as a ceric iodate; however, this process produces a relatively large quantity of the very voluminous ceric iodate precipitate in which large losses of europium-155 occur. Furthermore, the conversion of the iodate to more usable forms of cerium oxide or hydroxide is very difficult because of the large quantity of iodine to be removed. However, by close pH control, cerium can be removed with about 90% efficiency by precipitating as the ceric phosphate. If the cerium is then reduced to the Ce⁺³ state, it can be re-precipitated as the hydroxide and thus separated from phosphate. The next step after dissolving the cerium hydroxide is to re-precipitate cerium as the oxalate, in which form it can be ignited to ceric oxide. Ceric oxide can either be packed by vibration into thin stainless steel tubes which are sealed by welding, or combined with silica and other ceramic ingredients and fused into thin layers on iron plates, which are then encapsulated within thin stainless steel jackets and sealed by welding. Experiments are still in progress to determine the best way of fabricating cerium sources. However, it appears that it will be necessary in any case to fabricate the cerium in fairly thin layers to prevent self-absorption of the radiation, since only a fraction of the ^{144}Ce radiation is hard gamma radiation.

The fractions of rare earths containing promethium and europium are purified by taking up on a steam-heated cation exchange column and selectively eluting with ammonium citrate solution, as previously noted. Radioactivity "peaks" are obtained indicating which fractions are rich in europium and promethium; after separation, these fractions are again fractionated on ion exchange columns to produce products of the desired purity. Europium may be further purified by reducing to the Eu⁺² state by electrolytic reduction or passage through a zinc metal reductor, followed by coprecipitation with barium sulfate, or direct precipitation if the quantity of Eu is large enough. By oxidation of the europium to Eu⁺³, it can be separated from barium carrier and sulfate. Further purification may be made by reduction with sodium amalgam and re-extraction from the amalgam as the hydroxide, finally precipitating as the oxalate.

The characteristics of the fission product preparations are shown in Table C-1.

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APPENDIX D

Excerpt from: E. Lamb, H. E. Seagren, and E. E. Beauchamp, Fission Product Pilot Plant and other Developments in the Radioisotope Program at the Oak Ridge National Laboratory, in Proc. Intern. Conf. Peaceful Uses At. Energy, 2nd Geneva, 1958, Vol. 20, pp. 38-43, United Nations, Geneva, 1958.

Since the first radioisotope shipment from the Oak Ridge National Laboratory in 1946, research and development in its radioisotope program has been directed toward increased production efficiency and the production of a greater number of radioisotope products. The number of radioisotope products offered for sale has grown from two, ^{14}C and ^{131}I , to over 100 at present. The annual sales and shipments have grown steadily.

The processes used to separate and purify radioisotopes encompass such diverse methods as ion-exchange chromatography, extraction, chelation, distillation, cryogenics, electrochemistry, adsorption and gas-phase chromatography. Chemical process development is directed at first to the selection of standard chemical reactions applicable without modification to the small-scale production of a radioisotope. As production requirements increase, refinements to the process are developed to allow for radiation effects, for limitations imposed by remote handling, and for scale-up effects resulting from larger batch sizes. In general, more latitude in the selection of chemical reactions is possible during the initial, lower production phase because processing is done in laboratory-scale glass vessels. However, as production increases, the process is usually transferred to stainless steel equipment in which the chemical system must be limited to one not corrosive to stainless steel.

As the chemical procedure used to process a radioisotope evolves, a similar evolution must follow in equipment development. Much production may be done initially in temporary experimental glassware shielded by lead-brick barricades. As radiation levels rise with increased production, a permanent installation of glass equipment is made in a lead or concrete cubicle. Transfers of process liquids in such an installation are made by vacuum and are controlled by valves or glass cocks operated by handles extending through the shield. A further increase in volumes to be processed often requires that the processing be done in stainless steel equipment ranging from a volume of 10 to 2000 gallons. In this kind of equipment, standard components are used as much as possible for economy, but restrictions are imposed by the effect of radiation on organic materials such as plastic gaskets and lubricants.

Liquid transfers are made by steam jets, mixing operations are done by motor-driven agitators, and precipitates are separated from solution in centrifuges. Intensely radioactive solids, such as ^{60}Co or powdered ^{137}Cs , are handled, in thick-walled concrete cells equipped with master-slave and power-operated manipulators and viewing windows filled with lead glass or zinc bromide solution.¹

Fission Product Pilot Plant

An excellent example of process evolution and equipment development is presented by the processing of long-lived fission products. At first produced in curie amounts in glassware by ion-exchange methods, and then in hundred-curie quantities in liter-size stainless steel equipment, the fission products, ^{137}Cs , ^{144}Ce , ^{147}Pm , ^{106}Ru , ^{90}Sr , and ^{99}Tc , are now processed in quantities of hundreds of kilocuries annually in the Fission Product Pilot Plant (F3P).

The historical development and status of the chemical processes and plant construction of the F3P were reported by A. F. Rupp at the 1955 Geneva Conference.² Since that presentation, many refinements have been made in the process chemistry, resulting in the simplification of equipment and greater recovery efficiencies. These improvements are shown in the flow sheet in Fig. D-1.

The recovery of fission products from the waste streams of the two commonly used metal-recovery processes is being demonstrated during the first phase of operation of the F3P. The Redox process for metal recovery results in a waste stream which is high in aluminum and mercury content and neutralized by the addition of NH_4OH . The Purex process produces wastes containing nitric acid as the major constituent.

Certain chemical reactions are common to the processing of both types of waste, although the sequence in which they are used differs. Cesium alum is co-crystallized with ammonium alum by cooling to 15°C the solution which has been saturated with ammonium alum at 80°C .³ In the case of Redox waste the crystallization operation is performed first to remove the major portion of the aluminum prior to further processing. Since both ammonium and aluminum ions are present in the waste solution, the alum is formed by

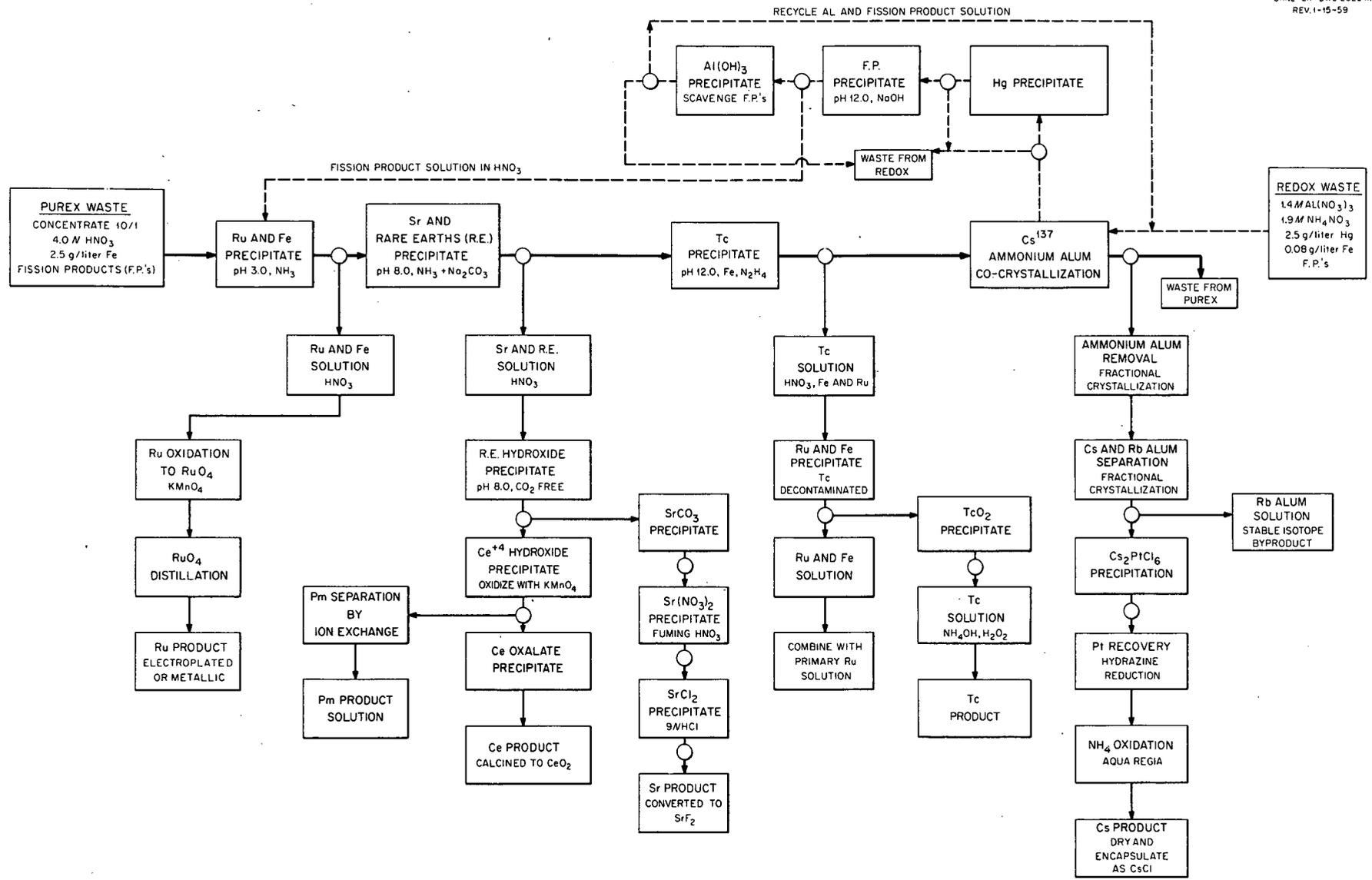


Fig. D.1. Separation of fission products from reactor waste.

the addition of Na_2SO_4 . After the removal of mercury from the solution which has been decanted from the crystals, ruthenium, strontium, and the rare earths are precipitated from a caustic solution in which the aluminum remains soluble as sodium aluminate. The nitric acid solution of this precipitate is treated the same as the acid Purex waste to separate ruthenium, strontium, and the rare earths by successive precipitations in which gaseous ammonia is metered into the solution to adjust the pH. Technetium is coprecipitated from both waste streams with hydrated ferric oxide in a solution made 0.1 M in hydrazine hydrate at pH 3.0. In the case of Purex waste, cesium is precipitated by the addition of ammonium alum to the solution to form crystals after all other fission products are removed.

The precipitates obtained in the first-stage processing according to either flowsheet are dissolved in nitric acid and are processed further to obtain purified fission products as described by Rupp.² In the case of ^{137}Cs a notable advance has been made in the purification method in the past three years. The process for the recovery of ^{137}Cs previously included a precipitation of aluminum from the cesium alum and an ion-exchange metathesis of Cs_2SO_4 to CsOH , which was converted to CsCl . Although this method has been proved feasible by the production of kilocurie amounts of ^{137}Cs , the organic contaminants resulting from the radiation damage to the anion exchange resin are undesirable in that additional processing is required to remove them. A reaction in which ^{137}Cs is precipitated as cesium chloroplatinate directly from the cesium alum solution has replaced the ion-exchange step with a resultant improvement in product quality and simplification of equipment.

The cesium is first concentrated in the alum crystals by performing successive ammonium alum crystallizations from fission product solutions. Then the ammonium alum is removed by two or three crystallizations from water solutions of the alum. The alum remaining contains about 15% by weight of stable fission product rubidium which must be removed if a cesium product of high specific activity is desired. This removal is accomplished by fractional crystallizations from the concentrated alum solution with the loss of less than 0.5% of the cesium.

After the removal of the rubidium alum, cesium is precipitated as cesium chloroplatinate from a slurry of alum in 1.0 N HCl with a recovery of ^{137}Cs exceeding 99.9%. The platinum is recovered and the cesium is converted to a soluble form by treating a water slurry of the cesium chloroplatinate with an excess of hydrazine hydrate. The excess N_2H_4 is destroyed by boiling

the solution and the platinum is dissolved in aqua regia for reuse in the process with an overall loss per cycle of about 0.1%.

The filtrate from the platinum reduction step, containing CsCl , NH_4Cl , and HCl , is concentrated by evaporation, and the ammonium ion and any residual hydrazine are destroyed by successive additions of aqua regia. The excess nitrate ion is removed by the addition of HCl , with boiling. The HCl is finally removed by evaporation to a low volume with successive additions of water. The purified solution is then evaporated to yield dry CsCl , which is incorporated in welded stainless steel source units.

This process was tested on a semi-plant scale by processing 8870 curies of ^{137}Cs . The purified product solution contained 8760 curies of ^{137}Cs accounting for an over-all process efficiency of 98.8%.⁴ The solution was evaporated to dryness to obtain the powder. The specific activity (curies per gram of $^{137}\text{CsCl}$) was determined as 22.0 curies per gram. The only significant impurities detected in the product were sodium, rubidium, and iron chlorides, which averaged approximately 1% each by weight.

The dry CsCl is readily compressed into pellets. These pellets are then encapsulated in two concentric stainless steel capsules, each of which is sealed by inert-gas-shielded arc welding.

The processes for the separation of ^{144}Ce and ^{147}Pm from the rare-earth solution contain refinements resulting from recent developments. The recovery of cerium is improved by precipitating ceric oxalate from the rare-earth solution instead of ceric phosphate as shown in the original flowsheet. After the removal of cerium, the solution containing promethium, europium, and americium is removed from the F3P to be separated on steam-heated ion-exchange columns.

When the ^{147}Pm is to be used to activate phosphors it must contain less than 200 alpha counts per min per millicurie of ^{147}Pm . The method developed for the purification of large quantities of ^{147}Pm involves the precipitation of promethium fluoride from a solution made 3.0 M in H_2SiF_6 .⁵ The fluoride precipitate, which contains about 7% of the original americium, is dissolved in a solution of boric acid and nitric acid. The fluoride precipitation is repeated until an acceptable alpha decontamination is obtained.

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APPENDIX E

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Strontium-90 Process

The alkaline-earth separation process is outlined in App. D, Fig. D-1. Subsequent ^{90}Sr -purification processes have been modified. Barium is a normal fission-product contaminant of ^{90}Sr and is present in approximately equal weight ratio to the strontium isotopes. Calcium is introduced as a contaminant by reagent additions in the F3P chemical processes and from process water, which contains small amounts of calcium.

Barium is separated by the classical chromate precipitation method. A suitable precipitation process for the separation of large amounts of calcium from the remaining ^{90}Sr is not yet available. A liquid-liquid extraction process was developed which will separate calcium from a mixture containing calcium and strontium in a 20 to 1 weight ratio.⁹

Laboratory experiments showed that the distribution coefficients of calcium ions between D2EHPA and aqueous solutions in the pH range 1 to 5 were several times greater than those of strontium ions. The data suggested that excellent separations might be achieved in a mixer-settler countercurrent solvent-extraction system. The flowsheet development was directed toward the utilization of a 20-stage mixer-settler unit.

The use of an ion-exchange-type organic such as D2EHPA in a solvent-extraction cascade introduces certain unusual problems. When metallic ions pass from one phase to the other, an equivalent number of

hydrogen ions pass in the opposite direction. Thus, in a separation process which is sensitive to pH conditions, such as the one in question, a method of buffering must be used to control large potential variations in the distribution coefficients within the stages of the cascade.

The hydrogen ion concentration is controlled by converting the strontium and calcium to acetates and adjusting the aqueous solution to 0.1 M in acetic acid, which results in a self-buffering system with a pH value of approximately 2.5.

In this process, essentially all the calcium concentrates in the D2EHPA organic phase and the strontium in the aqueous phase. The variation in the distribution coefficients, caused by the variation in organic "loading" and consequent reflux, produces a buildup of materials near the feed point and subsequently results in a highly unstable system. The control of excessive variation of the distribution coefficients in the cascade is effected by the addition of 2-ethylhexanol to the D2EHPA-Amsco organic phase. The alcohol reduces the distribution coefficients under conditions of low organic-phase loading but causes only a small reduction at high loading. This effect is probably due to an association compound formed between the alcohol and the D2EHPA which acts in a manner analogous to that of a weak acid when titrated by a strong base. At low organic-phase loading, a small amount of free D2EHPA is present; however, as the free D2EHPA is complexed by reaction with metallic ions, it is replaced by

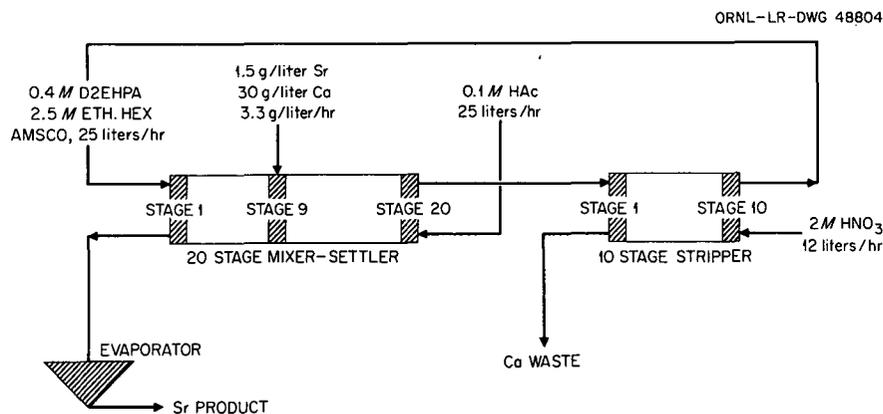


Fig. E.1. Ca-Sr flowsheet.

dissociation of the D2EHPA–alcohol compound. As a result, the free D2EHPA concentration – and consequently the distribution coefficients – are only moderately sensitive to organic-phase loading.

A flowsheet, shown in Fig. E-1, was developed which uses 0.4 M D2EHPA in Amsco, modified by 2-ethylhexanol so as to be 2.5 M with respect to the alcohol. This flowsheet, within the limits of analytical error, gives a nearly quantitative separation of calcium from strontium without loss of the strontium product.

Strontium-90 sources which are intended for use as heat sources are prepared as strontium titanate in the form of sintered pellets. Strontium titanate powder is prepared by precipitating a strontium–titanium oxalate compound which is converted to SrTiO_3 by calcining at 1200°C. Pellets are formed from the powder in dies under 50,000 lb/in² hydraulic pressure and then sintered at 1450°C to a density of about 4.7 g/cm³.

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APPENDIX F

Excerpt from: R. E. Burns, R. L. Moore, A. M. Platt, and W. H. Swift, Recovery and Purification of Megacurie Quantities of Strontium-90, *Chem. Eng. Prog. Symp. Series*, 60(47): 1-8 (1964).

PbSO₄ Carrier Precipitation

Background and objectives of the recent Hanford campaign for the recovery and purification of strontium-90 from separations plant waste for the Atomic Energy Commission's (A.E.C.) SNAP (Systems for Nuclear Auxiliary Power) program have been described.¹ The Hanford program consisted of four parts: (1) recovery of a crude strontium concentrate from Purex waste, (2) purification of a portion of this material by ion exchange in the shielded, manipulator-equipped, high-level chemistry cells, (3) processing of the remainder (and larger part) in an idle solvent-extraction pilot plant known as the *Hot Semiworks*, and (4) design and fabrication of shipping casks for the product. At the time that the Hanford strontium project began, laboratory development had fortunately already been in progress for some time on the first portion of the program and large-scale tests had been initiated at the Purex plant (in the head-end centrifuge cell and associated equipment, which are no longer used for Purex feed clarification). This work was aimed at developing precipitation technology for the recovery of fission-product concentrates, technology which could be used in one of the idle Hanford precipitation canyons (bismuth phosphate plants) if a multimegacurie demand for fission products should develop. A load-out station for "crude" had also been constructed at the Purex plant. The processing of Purex waste was accordingly able to start almost at once, by use of a lead carrier precipitation process, and a megacurie of strontium-90 was recovered in a period of about six months. The recovered concentrate was stored in two available 15,000-gal stainless steel tanks (both equipped with agitators and cooling coils) to age for strontium-89 decay. The Purex strontium concentrate was well purified from most of the major components of the Purex waste but still required additional decontamination from cerium-ruthenium and zirconium-niobium-95, as well as purification from the other alkaline earths (calcium and barium). The technology for solvent extraction and ion exchange purification was much less advanced and required extensive development in a short time.

When the strontium commitment was received, modest-sized research equipment had been installed in a hot cell to prove out an ion exchange process for the

recovery of highly purified promethium-147. Larger tanks and columns were fabricated and installed and the flowsheet was modified for strontium purification and used to purify the first 60,000 Ci of strontium, which made possible completion on schedule of the Weather Bureau unit and its shipment to the Arctic before the shipping lanes froze. SNAP-7-A and SNAP-7-B were fabricated from a blend of hot-cell and semiworks strontium. During the hot-cell strontium campaigns, the hot semiworks was taken out of mothball status and extensively re-equipped to purify strontium by a di-2-ethylhexyl phosphoric acid (HDEHP) solvent-extraction process, initial development of which was carried out at Oak Ridge. The solvent-extraction process was further developed in the laboratory, scaled up in a pulse-column-equipped cold Hanford pilot plant, and finally demonstrated in a series of hot-cell runs. When the high-capacity semiworks process went on stream, the hot-cell equipment used for ion exchange purification reverted to research use. The Hanford program was completed and over 1 million Ci of strontium recovered and purified within about a year from A.E.C. authorization to proceed. The Hanford purified strontium was shipped to Oak Ridge and to Martin Company for conversion to titanate and loading into the heat sources. The hot-cell strontium was shipped on Decalso, an inorganic ion exchange medium, and eluted with ammonium nitrate at Oak Ridge; the semiworks product was shipped both to Oak Ridge and Martin as dried strontium carbonate in a special filter cask.

Details of the precipitation concentration of strontium from Purex waste are described in the following section. The ion exchange purification process which was used for purifying the first 60,000 Ci is discussed in detail elsewhere.¹

Isolation of Crude Strontium Concentrate From Purex Waste

The Hanford Purex plant, operated by the Chemical Processing Department of General Electric and previously described by Irish,³ is one of the largest radiochemical processing plants in the United States. The plant employs a tributyl phosphate solvent-extraction flowsheet for the processing of plutonium-production reactor fuels, producing purified plutonium and uranium as the primary end streams. A major by-product

of the operation is a highly concentrated aqueous raffinate stream containing essentially all the fission products initially associated with the reactor fuels. This acidic waste stream, termed 1WW, is normally made alkaline with caustic prior to storage in underground waste tanks. The stream can, however, be processed for the recovery of a number of valuable fission products, of which strontium-90 is the one of greatest current interest.

Since the start-up of the Hanford Purex plant in 1956, aggressive programs directed at plant and chemical flowsheet improvements have resulted in process simplification and the freeing of a number of costly equipment pieces and their auxiliaries, forming the nucleus for a large-scale fission-product recovery system. This equipment has been isolated from the rest of the Purex plant and is available for pilot plant testing of fission-product recovery processes and for interim production use. Thus, Hanford, having installed equipment available and a ready source of fission products, has become the major U.S. supplier of semirefined fission-product fractions.

Table 2.1 in Chapter 2 shows the approximate composition of Purex 1WW, the starting material for recovery of fission products. As can be seen, 1WW is an aqueous solution of predominantly nitric and sulfuric acids with comparatively large quantities of metallic ions such as iron and sodium. The fission-product, and particularly strontium, content on a weight basis is, of course, extremely low compared to the inert constituents. The radioactive material content is, however, sufficiently high that self-heating of the solution by radioactive decay energy is one of its principal characteristics.

The chemical processing equipment, made available for fission-product recovery by improvements in the main Purex plant operation, consists essentially of three stainless steel tanks servicing two 48-in.-diameter solid-bowl centrifuges in parallel. These machines perform the separative function. Auxiliary solution make-up vessels and other normal services are also provided. All equipment is remotely installed and operated behind massive shielding and containment structures.

With the advent of the strontium-90 program, chemical flowsheets were extensively evaluated in laboratory and plant tests to find optimum conditions matching the raw material (the 1WW raffinate) to the equipment available for processing. The main process function was to achieve a gross strontium separation from nonradioactive materials as well as from other fission products such as the rare earths, cerium-144, ruthenium-103 and 106, zirconium-niobium-95, and cesium-137. Additional strontium concentration was also desired.

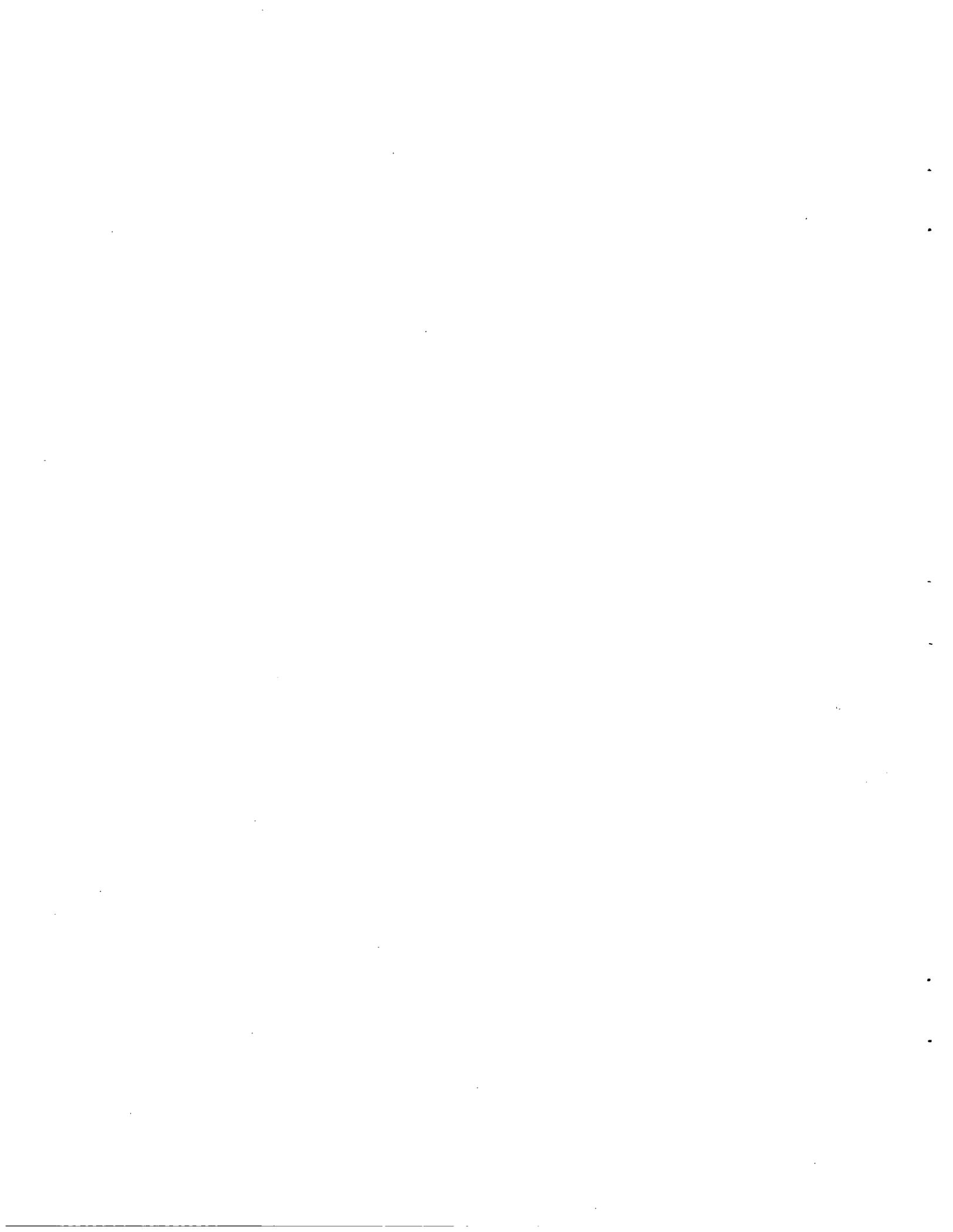
Figure 2.1 in Chapter 2 outlines the chemical process flowsheet as it finally evolved. Strontium, and incidentally a large portion of the rare earths, is initially coprecipitated with lead sulfate at a pH of 1 to 2. Tartrate ion is added prior to pH adjustment to complex and prevent precipitation of the relatively large quantities of iron present in the 1WW. Following a one-hour digestion period at $90^{\circ}C$, this material is centrifuged and the centrifugate (containing the great majority of the zirconium-niobium, ruthenium, and cesium) discarded along with the gross inert impurities such as iron and sodium. As no special cooling provisions were made in the centrifuges, the batch size employed in this step is limited primarily by the ability of the centrifuge to dissipate the very sizable amount of radioactive decay heat.

Following centrifugation, the lead sulfate carrier is essentially leached from the centrifuge bowl by a metathesis reaction employing a sodium hydroxide-sodium carbonate solution. This dissolves most of the lead and converts the strontium and rare earths to insoluble hydroxides and carbonates. In the leaching step the centrifuge is operated in a manner similar to a household washing machine; that is, reagents are added and the centrifuge is alternately started and braked to "slosh" the contents around. At the end of this operation the solids remaining in the bowl are the strontium and rare earth carbonates. Dissolution of these is accomplished with nitric acid prior to the next step.

Following nitric acid dissolution of the carbonates, a fairly classical oxalate precipitation of the undesirable rare earths and cerium is accomplished by addition of oxalic acid followed by adjustment to 0.5 to 1.0 M nitric acid in the precipitator tank. After centrifugation for removal of the oxalates, the centrifugate is further neutralized to a pH of 10, and carbonate added to a concentration of 0.2 M , to achieve concentration by coprecipitation of remaining traces of iron and strontium. This final precipitate, when centrifuged and dissolved, constitutes the so-called Purex "Crude" and, after storage for initial strontium-89 decay (50-day half-life), served as feed material to the two refining processes described below. Performance of the strontium crude recovery process is represented by an overall recovery to 50 to 60% with some loss due to the equipment limitations. Radioactive decontamination factors ranged from 5 to 10 for cerium-144 and zirconium-niobium-95 and greater than 50 for ruthenium-103 and 106 and cesium-137. All waste streams were neutralized with sodium hydroxide and routed to the underground waste-storage tanks associated with the Purex plant.

References

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APPENDIX G

Excerpts from: L. A. Bray, L. F. Lust, R. L. Moore, F. P. Roberts, F. M. Smith, H. H. Van Tuyl, and E. J. Wheelwright, Recovery and Purification of Multikilocurie Quantities of Fission-Product Strontium by Cation Exchange, Chem. Eng. Prog. Sym. Series, 60(47): 9-19 (1964).

Fission Product Chemistry Operation was given the two-fold responsibility of (a) devising the necessary precipitation-type flowsheet by which a strontium crude concentrate might be isolated from the Purex 1WW waste and (b) developing a final purification ion exchange process and then, with Purex strontium crude as feed solution, producing 60,000 curies of highly purified fission-product strontium-90. Chemical Development Operation was given the task of developing a solvent-extraction flowsheet and processing the major part of the Purex strontium concentrate in an idle solvent-extraction pilot plant known as the *Hot Semi-works*. The two approaches were taken to give an added margin of success and to meet the tight time schedule for the Weather Bureau unit. This document reports the work performed by the Fission Product Chemistry Operation.

Because of operational and new equipment difficulties, the PbSO_4 carrier precipitation flowsheet was not successfully used until late November 1960, and so the composition of the Purex strontium crude was not known until early December. The approximate composition was as follows:

Sr = 0.32 g/liter (25.6 curies/liter)

Ca = 0.1 g/liter

Ba = 0.05 g/liter

Fe = 8.0 g/liter

Pb = 5.6 g/liter

Na = 10.0 g/liter

Zr-Nb-95 = 70 curies/liter

Ce-Pr-144 = 750 curies/liter

At the time the strontium purification program was initiated, A-Cell of the 325A facility contained a six-column ion exchange processing unit. The unit had been designed for testing a process for the separation of promethium-147 from the adjacent rare earths, and three successful "cold" runs had been completed in the equipment. Because of the availability of in-cell equipment and a preliminary flowsheet, ion exchange was used for the final strontium purification to be done in the 325A facility. Consequently, the five-month period beginning in August 1960, was devoted to "cold"

flowsheet demonstration runs, in-cell equipment changes, and associated laboratory work leading to the final flowsheet. The research conducted during this period was severely handicapped because the composition of the feed solution could only be guessed and was not known until December, just prior to the first full-scale "hot" run.

Hot-Cell Ion Exchange Equipment

A-Cell of the 325A Building High Level Facility is a stainless-steel-lined cubicle 15 ft wide, 8 ft deep, and 11 ft high (from the floor up to the General Mills' track). The cell is equipped with three large lead-glass viewing windows, two sets of Model-8 manipulators, a through-the-wall periscope, and a sufficient number of through-the-wall services. The six-column ion exchange unit shown in the piping schematic of Figure 1 (not shown) was installed in the cell. The columns were mounted on two racks toward the rear of the cell and the stainless steel tanks 1, 1A, 3, 4, and 7 were placed under the windows at the front of the cell. A heavy 4 by 6 ft stainless steel tray was placed over tanks 1A, 3, and 7 immediately in front of one of the two operating windows. Tanks 5 and 6 (calibrated 5-gal Pyrex glass carboys used to collect, sample, and measure the volume of effluent solution from the columns) were placed on one corner of the stainless steel tray. The columns were so placed that by use of all three windows they could be viewed over their entire length. All valves not operated by air pistons were placed to be operated by the Model-8 manipulators. The air-operated valves are $\frac{1}{4}$ -in. Durimet 20 screwed-end type-F plug valves. All other valves are Hoke stainless steel needle valves or Dahl stainless steel demidiaphragm valves. The last two kinds of valves were modified with extended handles, so that they might be easily operated by the Model-8 manipulators. All solution lines within the cell are stainless steel tubing (type 304, 304L, or 347) and the fittings are stainless steel Crawford Swagelok.

One piece of equipment that proved to be invaluable to the success of this project, was a four-position lead-shielded sample holder placed at the front of the cell in such a position that slits in the sample holder lined up with two through-the-front-face step ports.

Thus, with scintillation crystals in the two ports, connected to a 400-channel pulse height analyzer, it is possible to determine the gamma spectrum of analytical samples without removing them from the cell.⁸

Resin is slurried into the columns from the front face of the cell through the resin-addition line (wall 115) by applying a 10- to 15-lb air pressure to a 6-gal polyethylene bottle containing a slurry of resin in water. The resin-addition line extends into the resin and terminates at a point near the bottom of the bottle. Resin is removed from the columns by pumping water upflow through the columns and backwashing the resin out the top of the columns, then diverting the resin through the resin line (wall 257) to a shielded resin-disposal cask. No difficulty has been encountered in adding resin to the columns. A water backwash is sufficient to remove resin from 1-in. and 2-in.-diam. columns but not sufficient to remove all of the resin from 4-in.-diam. columns. The remaining resin is removed from the 4-in.-diam. columns by floating it out on a dense solution of aluminum nitrate.

The vacuum-vent-pressure system for each column is used to adjust the liquid level height in the column, for column degassing, and for a variety of other uses during column operation.

The pump is a remote-head, stainless-steel, double-diaphragm, Lapp Pulsafeeder Model CPS2. The reagent head with one diaphragm is located in the cell and a second diaphragm is mounted near the pump, external to the cell. A 1-in.-diam. line, hydraulically connecting the two diaphragms contains water.

Raw feed solution is transferred to feed tanks 1 or 1A from B-Cell or directly from a shielded transfer cask by vacuum transfer. After feed adjustments, the prepared feed is pumped through one or more of columns 1, 2, or 3 in series and to tanks 5 or 6, where it is measured and sampled. The feed-effluent solution is then transferred by vacuum to waste tanks 3 or 4. The column piping is such that the columns may be used singly or with two or more of them in series.

On the initial installation, columns 1, 2, and 3 were 2-in.-diam. Pyrex glass pipe 6 ft. long with stainless steel end fittings. These columns were jacketed with 3-in.-diam. Pyrex glass pipe through which thermostated water circulated for temperature control. Columns 4, 5, and 6 were 1-in.-diam. Pyrex glass pipe, 6 ft long, jacketed with 2-in.-diam. Pyrex pipe for temperature control. This system of six columns was used successfully for the three "cold" rare earth runs and for the first three "cold" strontium runs. The columns were then removed and replaced by larger columns when it became evident that a production effort would be

made. On revision, columns 1, 2, and 3 are 4-in.-diam. Pyrex glass pipe 9 ft long jacketed with a 6-in.-diam. Pyrex glass pipe. Columns 4, 5, and 6 are 2-in.-diam. Pyrex glass pipe 9 ft long jacketed with a 3-in.-diam. Pyrex glass pipe. The end fittings are of stainless steel.

Summary of Full-Level Production Runs and Results Obtained

Since the operational procedure was similar for each of the runs, a brief description will be given prior to a more detailed description of each run. The strontium crude was transported from the Purex Chemical Separations Plant to the 325A Building in 200-gal shielded casks. Once in the 325A Building, a loaded cask was placed in a special enclosed loading station and connected via $\frac{1}{2}$ -in. polyethylene tubing to a shielded $\frac{1}{2}$ -in. stainless steel line leading directly to one or more in-cell storage tanks. Fresh resin was used for each run. The resin placed in the elution columns was completely saturated with barrier ion X by passing a nitrate solution of ion X through the columns, followed with a water flush.

A stock solution of (N-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) was prepared by dissolving the organic acid in water and ammonium hydroxide followed by a final volume and pH adjustment to give a solution of 2.3 M HEDTA at pH 4.0. Because of the large volume of feed solution required per run and the relatively small size of feed tanks 1 and 1A, it was necessary to make up more than one batch per run. Raw feed solution was measured into either tank 1 or 1A, a given volume of HEDTA was added, and then ammonium hydroxide was added to give a pH of 3.9 to 4.2. The usual practice was to add 40% excess HEDTA beyond that required to complex the iron and lead (in order to assure that an excess was indeed present and that all the cerium would be complexed).

The prepared feed was then pumped through the feed absorption columns (column 1, 2, or 3) until an appreciable strontium breakthrough occurred. At that point the feed cycle was terminated and the columns were washed free of excess feed solution with a wash solution, 0.1 M HEDTA adjusted to pH 4.0 with ammonium hydroxide. The wash caused little or no movement of strontium.

Following the washing cycle, the absorption columns were connected in series with column 4 and the system was eluted with a 0.030 M solution of ethylenediaminetetraacetic acid (EDTA) adjusted to pH 8.40 to 8.82 with ammonium hydroxide. All operations were at ambient cell temperature (30° to 35°C). As the elution

progressed, the strontium banded between the calcium and the barium. The position of the strontium could be determined visually by turning off all cell lights and observing the radiation glow produced by the strontium. Column 5 was valved into the system when needed.

By the time the strontium band moved to the bottom of column 5, the band was relatively free of calcium, barium, or any other extraneous impurity. Elution was continued with the column effluent solution going to waste until all the calcium was removed from column 5 and the strontium appeared in the effluent. At this point column 6 was valved into the system and the strontium band eluted onto the resin in column 6. When the strontium was entirely on column 6, a valve manipulation isolated column 6 from column 5, thus separating the strontium from the trailing barium band. The barrier ion X on column 6 served to confine the strontium on column 6. Thus, at the end of the elution cycle, the purified strontium was absorbed in a compact band on the top portion of column 6 with the barrier ion occupying the resin bed below the strontium band.

During the several runs, copper, yttrium, and neodymium were used as the barrier ion on column 6. Each forms a much more stable complex with HEDTA than does strontium and could therefore be removed from column 6 by pumping a 0.1 M solution of HEDTA (adjusted to pH 4.0 with ammonium hydroxide) through the column without significant movement of the strontium band. A wash of water removed the complexing agent from the column and the purified strontium was then removed from the column by one of several desorbing agents. A 0.10 M solution of HEDTA adjusted to pH 9.0 with ammonium hydroxide quickly and completely removed the strontium at an average concentration of 9 g/liter. A 5 M solution of ammonium nitrate will effectively remove the strontium at an average concentration in excess of 40 g/liter. Four- to six-molar nitric acid is also a very effective eluting agent.

Run 1

Dowex 50W, X-12 (50-80 mesh) resin was placed in each column. The resin in columns 1 and 2 (used as adsorption columns) was in the ammonium cycle. Columns 3, 4, 5, and 6 were used as elution columns and contained resin in a mixed hydrogen-copper cycle. The feed-cycle flow rate averaged 10 ml/(min)(sq. cm). The absorption and elution cycles were performed at ambient cell temperature. Following the removal of copper from column 6 and a subsequent water flush, the strontium was removed with 6 M HNO₃. The results of the run are given in Table G-1.

The greatest difficulties encountered in the run were the presence of excessive solids in the Purex crude feed and the unexpected reduction of some of the copper to metal on the resin. This reduction is accomplished by the intense radioactive field in the presence of EDTA. No reduction takes place in the absence of EDTA. These results were duplicated in cobalt source experiments. In addition, an unexpectedly low resin-adsorption capacity resulted from the very high monovalent ion concentration in the feed solution (ammonium ion from neutralization of excess acid in the Purex feed). Several thousand curies of strontium-90 passed through the adsorption columns and to waste because the analytical results on the feed effluent samples were slow coming from the analytical laboratory.

Run 2

Columns 2 and 3 were filled with ammonium cycle Dowex 50W, X-12 (50-80 mesh) resin and were used as adsorption columns. Columns 4, 5, and 6 were filled with the same resin. The resin in columns 4 and 5 was then converted to the calcium cycle by passage of a calcium nitrate solution through them and the resin in column 6 was saturated with copper and hydrogen from a solution of 0.5M CuSO₄, 0.5M H₂SO₄. The use of calcium as the barrier ion on columns 4 and 5 served to restrain the strontium while permitting cerium as well as the strontium-90 daughter, yttrium-90, to pass through and on to waste and avoided the partial column plugging caused by reduction of cupric ion to metallic copper. The strontium was removed from column 6 with 3 M HNO₃. Flow rates and temperature were similar to those of run 1. The results are shown in Table G-1. A considerable quantity of cerium-144 was inadvertently loaded onto column 2 from one batch of prepared feed because of an error in the HEDTA addition. The resin darkened and exhibited a higher pressure drop in a matter of 2 to 3 hr. The cerium was selectively removed by washing the resin with 0.1 M HEDTA buffered to pH 4.0 with ammonium hydroxide and loading then continued.

Run 3

At the start of run 3, columns 2 and 3 were filled with ammonium cycle Dowex 50W, X-12 (50-80 mesh) resin and were used as adsorption columns. Columns 4 and 5 contained the same resin but in the calcium cycle and column 6 contained the same resin in the copper-hydrogen cycle.

The first portion of the prepared feed contained an unusually large amount of solids and column 2 plugged after a very short feed cycle. The feed was then diverted

Table G.1. Fission-product strontium recovery and purification

	Run 1	Run 2	Run 3	Run 4	Run 5		Run 6		Run 7
					A	B	A	B	
Feed solution									
Purex crude									
Volume, l	673	250	435	617	537	345	558	211	762
Sr 90, Ci	15,000	9,250	11,300	10,200	7,700	8,100	14,800	5,200	19,800
Zr-Nb-95, Ci	4.0×10^4	1.7×10^4	4.3×10^5	1.4×10^4	6,800	5,700	6,300	3,500	8,700
Ce-Pr-144, Ci	4.6×10^5	1.8×10^5	2.7×10^5	2.1×10^5	1.7×10^5	1.5×10^5	2.5×10^5	9.1×10^4	3.4×10^5
Fe, g/l	8.0	8.1	9.0	4.47	4.5	7.8	10.9	7.8	7.8
Pb, g/l	4.5	5.7	4.0	3.9	3.9	2.7	2.6	2.7	2.6
Na, g/l	7.8	7.8	9.1	5.0	5.0	29.0	32	29	29
HNO ₃ , g/l	0.6	0.6	0.6	56	60	62	63	62	63
Prepared feed									
Volume, l	763	287	506	710	1,150	1,442	2,460	929	3,398
Dilution factor	1.14	1.15	1.17	1.15	2.14	4.24	4.4	4.4	4.46
Rework of Waste from Previous Runs									
Volume, l				816	30				
Sr 90, Ci				3,800	1,500				
Product									
Sr 90 in product, Ci	5,100	8,350	9,500	12,400	13,600		11,200		16,500
Sr 90 in rework, Ci	1,600	200	500	1,500					
Product purity									
Sr, g	62	102	97	156	166		137		201
Ca, g.	2	2	2	3.8	3.2		<1		<1
Ba, g.	3	2	2	1.8	1.8		<1		<1
Ce-Pr-144, Ci	<1	<1	<1	0.04	0.07		3.4		<1
Zr-Nb-95, Ci	<0.05	<0.05	<0.05	0.03	0.01		0.47		<1

to column 3 and column 1 was filled with Dowex 50W, X-12 (20-50 mesh) resin in the ammonium cycle. After column 3 had been loaded to a high breakthrough and the resin water washed, the feed was diverted to column 1. The larger-mesh resin in column 1 permitted a higher feed flow rate and allowed most of the solids to pass through. Following the complete loading of column 1, the resin was water washed and an attempt was made to load more feed through column 2 with only limited success. The loading cycle was therefore discontinued and the elution cycle initiated. The solution flow rates and temperature were approximately the same as in the first two runs.

Following the removal of the copper barrier from column 6 with an HEDTA wash, the strontium was removed with 0.1 *M* HEDTA adjusted to pH 8.8 with ammonium hydroxide. The eluted strontium was collected in 4-liter Pyrex glass jugs. The strontium-90 concentration in the eluate was approximately 8 g/liter. The results of the run are given in Table G-1. Acidification of the strontium-HEDTA solution to pH 2.0 permitted direct adsorption of the strontium in the Decalso shipping cask and gave higher Decalso-loading capacities than can be obtained in the presence of competing sodium, ammonium, or hydrogen ions.⁹ Consequently HEDTA elution was favored, when the shipping cask was available for loading. At other times it was necessary to elute with ammonium nitrate or nitric acid, since the HEDTA underwent radiolysis on prolonged storage.

Run 4.

Columns 1, 2, and 3 were filled with Dowex 50W, X-12 (20-50 mesh) resin in the ammonium cycle and were used as adsorption columns. Columns 4 and 5 were filled with Dowex 50W, X-12 (50-80 mesh) resin in the calcium cycle. Column 6 contained Dowex 50W, X-12 (50-80 mesh) resin in the yttrium cycle. Except for occasional loading of some cerium due to insufficient HEDTA addition to the feed, the feed adsorption and elution cycles were quite uneventful. The feed solution flow rate, elution flow rate, and temperature were the same as for the other runs. The Purex crude feed for this run and all subsequent runs was clarified by centrifugation at the Purex plant and was relatively free of solids. Use of the coarser resin and centrifuged feed effectively eliminated difficulty with column plugging.

Prior to charging of freshly prepared feed to the absorption columns, 816 liters of rework material from the previous runs were passed through the adsorption columns. The results of run 4 are given in Table G-1.

The strontium was removed from column 6 by elution with a 5 *M* ammonium nitrate solution adjusted to pH 1.0 with nitric acid. All the strontium was eluted in 8 liters with over 11,000 curies being eluted in only 4 liters.

Run 5

Once again columns 1, 2, and 3 were filled with ammonium-cycle Dowex 50W, X-12 (20-50 mesh) resin, columns 4 and 5 with Dowex 50W, X-12 (50-80 mesh) resin in the calcium cycle, and column 6 with yttrium-cycle Dowex 50W, X-12 (50-80 mesh) resin. In an attempt to increase the resin capacity for strontium, the feed solution was diluted with water by a factor of 2.14 during the preparation step. This does not change the ratio of divalent to monovalent ion concentration in the feed, but the dilution does increase divalent ion distribution factor relative to that of the monovalent ion. A second type of raw feed in which the sodium concentration was very high was used as part (column B, Table G-1) of the run 5 feed. This material was diluted by a factor of 4.24 during the feed preparation step.

The flow rates, temperature, and elution sequences were the same as in run 4. The results are given in Table G-1. The higher yield of strontium from a much less desirable feed indicates the success of the feed dilution step.

Run 6

Column and resin conditions at the start of run 6 were the same as those for run 5 except that neodymium was used as the barrier ion on column 6 in place of yttrium. Two different feed solutions were used in the feed preparation step (columns A and B, Table G-1), but the dilution factor of 4.4 was kept constant throughout the loading steps. In an attempt to increase the yield of strontium per run, the three absorption columns were loaded twice. Feed solution was passed through columns 1, 2, and then 3 — each column was added to the series when needed — until a 25% breakthrough from column 3 was experienced. The columns were then washed free of feed solution with 0.1 *M* HEDTA at pH 4.0 and then water. The three columns were then connected together in series with column 4 and the strontium eluted from columns 1, 2, and 3 onto 4 with 0.03 *M* EDTA (adjusted to pH 8.4 with ammonium hydroxide). Following a water wash of column 4 to remove the EDTA, columns 1, 2, and 3 were then reloaded. The reloaded columns were then washed first with the HEDTA solution and then water.

Columns 1, 2, 3, and 4 were then connected together in series and the elution commenced again.

The strontium band on column 6 was more than 200 cm long. The strontium was removed from column 6 with 5 M ammonium nitrate at pH 1.0. Unfortunately, a valve leak in the product removal line permitted a loss of approximately one third of the strontium so the product yield was less than run 5. The results are shown in Table G-1.

Run 7

This run was a duplicate of run 6 except that a rerouting of the product prevented any losses via the defective valve. Nearly 15,000 curies of strontium-90 were collected in one 4-liter product fraction, and all the strontium was collected in 8 liters. The results are given in Table G-1.

Resin Radiolysis

At no time during the seven runs was the resin damaged sufficiently to affect the run adversely. The resin was discarded after each run and was not excessively "hot." No quantitative determination of residual resin activity was made. Following the completion of run 7, the resin in columns 1 and 4 was loaded to breakthrough with copper from a copper sulfate solution. The capacity of the resin was found to be not altered significantly, indicating little damage to cross-linkage. The resin in column 1 had received a dosage of approximately 2×10^8 r.

Process Applications

During the adsorption cycle of the first strontium production run, the capacity of the resin in the adsorption column was limited to approximately 3 g Sr/liter of resin. The low strontium capacity was a direct result of the high mole ratio of monovalent ions (sodium and ammonium) to strontium ions. The ratio in the prepared feed solution was 500. In both run 1 and run 2 nitric acid was added to the low-acid Purex crude in unsuccessful attempts to dissolve the precipitate. This acid caused an increase in the final ammonium ion concentration when neutralized by ammonium hydroxide during the feed pH adjustment step.

Laboratory runs using synthetic feed solutions indicate the existence of a direct relationship between feed dilution and strontium adsorption on the resin. Without dilution, feed containing 0.4 g Sr/liter and an ammonium-to-strontium mole ratio of 167 gave a loading of 12 g Sr/liter of resin. In a second experiment a feed

Table G.2. Effect of feed dilution on strontium adsorption capacity of Dowex 50W, X-12 resin

	Run 1	Run 2	Run 3	Run 4
Sr (g/l)	0.4	0.4	0.2	0.1
Ca (g/l)	0.15	0.15	0.077	0.038
Pb (g/l)	1.62	1.62	0.81	0.40
Fe (g/l)	8.34	8.34	4.2	2.1
NH ₄ (g/l)	13.7	30	15	7.5
HEDTA (g/l)	50	50	25	12.5
Dilution factor	1	1	2	4
Feed pH	4.0	4.0		
Resin capacity at 10% breakthrough (g. Sr/l of resin)	12.0	2.8	6.4	11.7

containing 0.4 g Sr/liter and an ammonium-to-strontium ratio of 364 gave a loading of 2.8 g Sr/liter of resin. A twofold dilution of the feed used in the second experiment yielded a loading of 6.4 g Sr/liter of resin and a fourfold dilution gave a loading of 11.7 g Sr/liter of resin. The results of the four runs are summarized in Table G-2.

These results indicate that a reduction of the monovalent ion concentration in the feed, combined with a dilution of the feed during the final feed preparation step, would yield a substantial increase in the resin adsorption capacity of future production runs. Since the resin capacity for strontium during the feed cycle is the limiting factor on the amount of pure strontium produced per run, the strontium production per run would be substantially increased.

In future Purex production runs, if the carbonate concentration step is used, if the strontium crude feed is clarified by centrifugation, and if advantage is taken of the feed-dilution technique, it would be possible to load 12 g of Sr/liter of resin. This would allow the recovery and purification of 58,000 curies of strontium-90 in a single loading cycle run in the High Level Cell ion exchange equipment. If a double-feed-cycle technique like that in production run 7 were used, the production of pure strontium would be increased to a little over 100,000 curies/run.

In a new production facility designed for this process, a three-column system would be satisfactory. One 8-in. diam adsorption column containing a 10-ft resin bed would contain 98.6 liters of resin and thus would have a one-cycle adsorption capacity of 95,000 curies of strontium-90. Two 4-in.-diam elution columns of the same length would be adequate to yield a product purity comparable to that of production run 7.

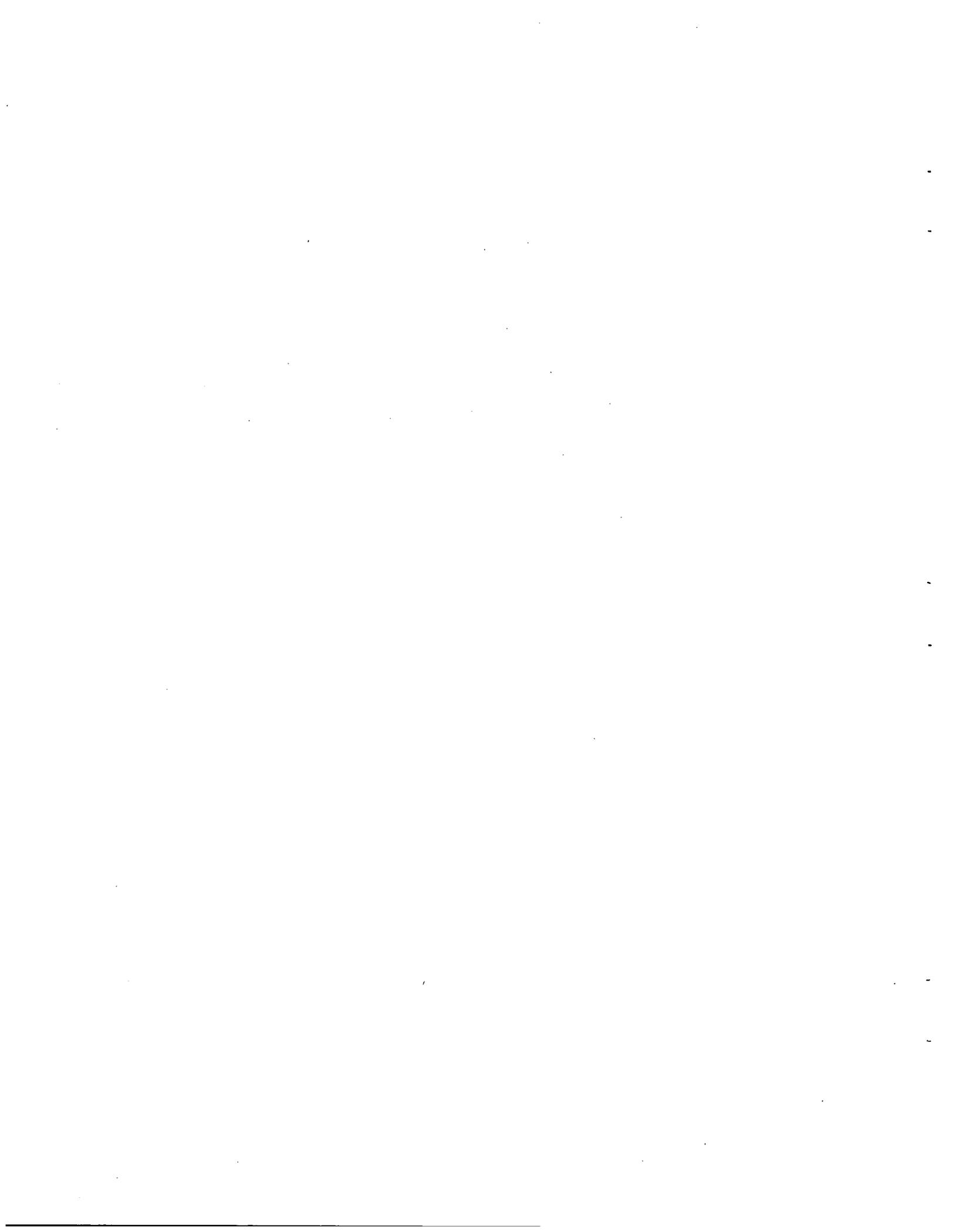
Summary and Conclusions

In seven production runs, 75,000 curies of ^{90}Sr was isolated and purified in the ion-exchange equipment of Hanford Laboratories High Level Cells.³ The production goal (60,000 curies of purified ^{90}Sr) and the time schedule were met or exceeded, and the product exceeded the customer's purity requirements. The hot-cell-purified strontium made possible the completion on time of the Weather Bureau power source and the Martin 10-W SNAP 7-A and 7-C units. The isotopic purity of the strontium product was 56% ^{90}Sr . The chemical purity was greater than 95% strontium. The zirconium-niobium-95 contamination of the product was less than 5×10^{-5} curies/curie of ^{90}Sr , and the cerium-praseodymium-144 contamination was less than 1×10^{-5} curies/curie of ^{90}Sr .

The final run yielded 16,500 curies of ^{90}Sr in an eight-liter product solution. The product was >98% strontium and contained less than one curie of zirconium-niobium-95 or cerium-praseodymium-144. Eleven days of continuous operation was required to complete the run.

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APPENDIX H

Excerpt from: Members of the Chemical Development Operations Hot Semiworks Strontium-90 Recovery Program, USAEC Report HW-72666, Hanford Atomic Products Operation, General Electric Co., 1963.

SECTION 5. HOT SEMIWORKS STUDIES

C. R. Cooley and G. L. Richardson

Introduction and Summary

In 1960, the idle *Hot Semiworks Pilot Plant* at Hanford was selected for the strontium program. Previously the contact maintained Semiworks had been used for development work on the Redox and the Purex processes which required similar solvent extraction equipment. In September 1960, design, construction modifications, and testing started concurrently and continued through to March 1961.

Principal modifications to the facility included provisions for a cross country feed line, product load-out cell, and modifications to increase reliability, i.e., duplication of services, adoption of long shaft pulser design, all welded piping and alternate routings to provide multiple cycles of solvent extraction through the same equipment.

Actual hot processing for strontium was initiated in early May and was completed in October of 1961. The process used in the *Hot Semiworks* was developed by the *Cold Semiworks* and laboratory studies. Essentially, this process consisted of extracting strontium from a buffered, complexed feed with a D2EHPA solvent, followed by preferential stripping of the strontium from the solvent with 1 M citric acid. Additional cycles of solvent extraction or ion exchange were used as needed to provide the necessary product purity.

Approximately 744 kilocuries of ^{90}Sr meeting customer purity specifications were produced for shipment from an input of 1184 kilocuries of Purex crude feed. In addition, 169 kilocuries requiring further purification were isolated awaiting product storage space. The total recovery of ^{90}Sr , including the impure fraction, was 1044 kilocuries, or 88% of that entering the process. This total includes 131 kilocuries of purified strontium which were lost or otherwise unaccounted for during between-run operations. Four runs comprised the recovery program.

The run flowsheets were based on the *Cold Semiworks* flowsheet; however, during the runs, several important modifications were made. These resulted eventually in the demonstration of a satisfactory one-cycle process for producing a specification stron-

tium product and a multicycle process for producing both a strontium and a cerium product. Significant stages in the evolution were:

1. A twofold concentration of the strontium product was achieved with no adverse effects by backcycling about 50% of the first cycle solvent extraction product to the feed. The back-cycle concept doubled the amount of product that could be accumulated during a run (without boildown) and, theoretically, provided a twofold improvement in the cerium DF (decontamination factor).
2. Although the ion exchange cycle produced a very high purity product, it was batch-size limited to about 200 kilocuries of ^{90}Sr and was replaced by solvent extraction methods after the first run.
3. Two cycles of solvent extraction using ethylenediaminetetraacetic acid (EDTA) as the complexing agent would provide acceptable cerium DF's only if both cycles used citric acid as the stripping agent. Typical cerium DF's in the extraction (A) columns were only 3 to 10, compared with 40 to 100 in the citrate-stripped partition (B) columns.
4. A one-cycle process was attained by substituting ethylenetriaminepentaacetic acid (DTPA) for EDTA in the feed. The substitution improved the first cycle cerium DF about tenfold without significantly increasing the chemical cost of the process.
5. Over 50% of the cerium and promethium in the feed could be extracted along with the strontium by substituting citric acid for most of the EDTA or DTPA in the feed. However, poor material balances leave some uncertainty about the extent to which rare earths can be routinely extracted from complexed Purex wastes.

One product loadout was made during the program using a bicarbonate precipitation procedure. Inability to slurry all of the precipitate into the filter cask prevented loading more than 120 kilocuries of ^{90}Sr out of 150 kilocuries precipitated.

The plant and process as a whole performed exceedingly well. The process fully demonstrated the feasibility of using solvent extraction on a large scale for removing strontium from Purex-treated wastes and tentatively the feasibility of coextracting cerium and

other rare earths. For the short-term program the contact-maintained plant was operable about 70% of the time through the addition of all-welded piping, duplication of services, and the use of long vertical-shaft pulsers.

Description of the Facility

The *Hot Semiworks* is a miniature processing plant consisting of four basic components: 1) a three-cell arrangement of concrete shielding to serve as the hot processing building using contact maintenance, 2) a cold processing building serving as a remote operation center and auxiliary source of services to the hot processing portion, 3) a ventilation and off-gas handling building to treat and discharge effluent gases through a 200 foot stack, and 4) general miscellaneous service buildings, i.e., offices, shops, storage, etc., to house supporting personnel and auxiliary functions.

The functions of the three cells were subdivided into: the high-level feed, waste and product handling in A Cell (a 22 by 40 foot cell 20 feet high, containing 13 processing tanks with a total of 3500 gallons of storage); the solvent extraction and ion exchange processing in B Cell (a 20 by 38 foot cell 50 feet high); and the solvent treatment and storage plus the condensate storage in C Cell (identical to A Cell but containing 14 processing tanks with a total capacity of 4900 gallons of storage).

An example of the flowsheet for the *Hot Semiworks* processing is shown in Figure 2.2 in Chapter 2. The crude feed from the Purex plant separations was stored in two 15,000 gallon tanks at C Tank Farm vault. For a run period, the feed was pumped through a 2-inch underground transport line to A Cell in about 500 gallon batches. After feed preparation, it was pumped to B Cell and through the two solvent extraction pulse columns using D2EHPA solvent extraction as described in other portions of this report. Once started, a run would continue until the capacity of the receiver tanks or of the ion exchange column was reached. The product was collected in A Cell and stored to await loadout in a slurry filter cask¹⁶ as the carbonate for transcontinental shipment to ORNL or Martin Company. The wastes were concentrated about threefold in A Cell and discharged to C-Farm waste tanks through an existing waste effluent line. Condensates were accumulated in C Cell and periodically discharged. The organic was collected and batch washed in C Cell for recycle. The spent organic was discharged to a specific organic retention crib at the end of the program.

Only two solvent extraction pulse columns and one fixed-bed ion exchange column were installed in this

program. This provided equipment simplicity and permitted duplication of services such as feed and waste routes. Considerable operating flexibility and additional reliability were thus attained. Successive passes through the same equipment could be made if additional strontium purification was required for product strontium. In flowsheets describing the runs, the 1A, 2A, and 3A columns are the same columns but refer to the first, second, and third passes.

The compound extraction, or A column, was 4 inches in diameter with a 10-ft extraction section and a 15-ft scrub section. Both disengaging sections were 8 inches in diameter and 5 feet long. The top disengaging section contained a temperature element, interface-specific gravity dip tubes, and a rate indicating overflow orifice. The bottom disengaging section contained an interface jet line, a remote-indicating interface float, a temperature element, a differential pressure cell to indicate column loading (flooding), and the pulse transmission lines from the long vertical shaft piston pulser, as described later. Bottom interface control was used exclusively in the A column to give an organic-continuous column.

The 4-in.-diam stripping, or B column, was 16 feet tall and was operated exclusively aqueous continuous. The disengaging sections were 8 inches in diameter. The top section was 3 feet long and contained dip tubes for interface detection. The bottom section was 5 feet long and contained a temperature element, an interface float (used to detect floods), a differential pressure cell, and the pulse transmission line.

The cartridge assembly for the columns as developed in Cold Semiwork studies (Section 4, not shown) is given below:

	Nozzle plate cartridges		
	Column		
	1A Extraction	1A Scrub*	1B Strip
Cartridge height, ft	10	15	16
Plate spacing, in.	4	4	4
Hole diameter, in.	0.188	0.125	0.125
Plate free area, %	23	10	10
Nozzle depth, in.	0.05	0.05	0.05
Nozzle orientation	Down	Down	Up

*19% free area louver-type redistributor plates inserted at 3-foot intervals.

Flow control to all columns was maintained through remotely operated valves and indicating-controlling rotameters. Cold streams were fed by gravity flow; the feed and solvent streams were pumped with modified

canned rotor-type pumps, described later under equipment performance.

The ion exchange column was a single fixed-bed unit containing 100 liters of 50-100 mesh Dowex 50W X 12 cation exchange resin. The 8 in. diam, 15-ft-high column was serviced by a temperature element, a water-cooling jacket, and numerous remotely operated valves. Spent resin was jetted into a filter container for burial.

In addition to the normal cell radiation detection units, three collimated ion chambers were installed on several of the process streams to indicate relative activity readings. A beta and gamma monitor was installed on the effluent line of the ion exchange column to detect ^{90}Sr and ^{144}Ce breakthrough.

Run Results

A total of seven runs was made in the *Hot Semiworks*. The first three runs, using cold and traced feeds, were intended primarily for training and plant shakedown. They satisfactorily demonstrated the operability of the equipment and the *Cold Semiworks* flowsheet and are not discussed further.

The final four runs, designated Sr-4, -5, -6, and -7 were designed not only to recover ^{90}Sr but also to obtain data applicable to the development of improved processes for use in the Waste Management Program at Hanford. The flowsheet for each run contained significant variations from the flowsheets tested in the laboratory and *Cold Semiworks*. For example, Run Sr-4 demonstrated the feasibility of recycling a portion of the solvent extraction product to the feed stream. Run Sr-5 demonstrated the replacement of the tail-end ion exchange column with a second cycle of solvent extraction. Run Sr-6 demonstrated the use of DTPA in place of EDTA with the elimination of a tail-end cycle. Run Sr-7 attempted the recovery of cerium and promethium together with strontium using a citrate-complexed feed.

The feeds were prepared Purex crude, derived from Purex concentrated waste by the procedure of Bray and Van Tuyl.² The results of Run Sr-6 are discussed below.

Run Sr-6

The flowsheet for Sr-6 is presented in Figure 2.2 in Chapter 2. Significant differences from the flowsheet for Sr-4 were the substitution of DTPA for EDTA and the use of only one purification cycle. About 90 liters of 1BP were backcycled to each 2000-liter feed batch. In addition, the solvent (used in the earlier runs) was continuously washed with a mixture of nitric and oxalic acids and recycled.

This run provided the first valid comparison of DTPA as a complexing agent. Before its use in the HSW, only a few laboratory experiments had been made showing its effect on distribution ratios. These data indicated that a mole per mole replacement of EDTA with DTPA would affect the strontium distribution very little but would depress the cerium distribution ratio about 100-fold at the optimum 4.7 pH. As shown in the run summary, definite improvement in cerium DF was obtained.

First, and most significantly, the product from this one-cycle DTPA process was within specifications with respect to all impurities. Second, the strontium losses, though about threefold higher than normal, were not excessive. This performance was achieved despite the use of reused solvent (part of it had received a radiation dose of over 300 watt-hours/liter) and operation at rates 10 to 20% above the rates used in previous runs.

The 1A column efficiency should have given lower strontium losses if flowsheet conditions were optimum. Conceivably the oxalic acid-nitric acid mixture used to wash the solvent during the run may have been entrained to some extent with the 1AX and perhaps contributed to the 1A strontium loss through formation of a strontium oxalate precipitate.

Sr-6 Run summary

Sr^{90} Input: 363 kCi
 Sr^{90} Product: 305 kCi

	Column		Overall
	1A	1B	
Strontium loss, %	13	3	16
Strontium product DF's:			
Ce ¹⁴⁴	~24	~100	2400
ZrNb ⁹⁵	>510		>1800
Ru ¹⁰⁶	>30		>90
Calcium		40	40
Barium	9.4		9.4

Product purity

Element	Ci/Ci Sr ⁹⁰		Grams/grams Sr total	
	Actual	Specification	Actual	Specification
Ce ¹⁴⁴	1.1×10^{-3}	$\leq 10^{-3}$		
ZrNb ⁹⁵	$< 3.5 \times 10^{-5}$	$\leq 8 \times 10^{-4}$		
Ru ¹⁰⁶	$< 7 \times 10^{-5}$	$\leq 6 \times 10^{-4}$		
Calcium			0.020	
Barium			0.020	<0.33

At the end of the run, the citric acid product solution was concentrated twofold and allowed to sit undisturbed for about one month. During this period, radiation (which averaged 6.7 watts/liter) was expected

to destroy over 99% of the citrate. However, at the end of this period, most of the strontium had precipitated and the system was highly buffered. Eventually, about 1200 gram-moles of nitric acid was added to ensure dissolution of the precipitate (indicated by solution pH less than 3). This represented about one mole of nitric acid per mole initial citrate, or nearly four moles per equivalent of metal ion.

References

1. Smith C. W., *Strontium-90 Shipping Cask – Design Criteria and Hazards Evaluation*, HW-68081, Jan. 13, 1961.
2. Bray, L. A. and H. H. Van Tuyl, *Laboratory Development of a Carrier-Precipitation Process for the Recovery of Strontium from Purex Wastes*, HW-69534, May 9, 1961.

APPENDIX I

FUELING WEATHER BUREAU GENERATOR

Monthly Report for May 1961, E. E. Pierce to R. A. Robinson (Oak Ridge National Laboratory)

The 5 watt (Electric) Weather Bureau Generator was successfully fueled with SrTiO₃ pellets and welded. The following is a summary of the completion of the project:

⁹⁰SrTiO₃ Processing and Pelletizing

1. Precipitate (Batch 1, Sr11*). Two filters were used in series in Cell 11 to assure that all of the precipitate was collected. An Al₂O₃ filter assembly was placed down stream from the stainless steel filter. Inspection of the Al₂O₃ filter revealed a trace of white precipitate on the lower one-third of the unit which was estimated to be less than three grams. The precipitate was removed from the stainless steel filter and placed in the Al₂O₃ filter for calcining.

A period of nine hours elapsed between the filtration and the precipitate removal. The precipitate was dry and caked on the stainless steel filter. Considerable scraping was required to remove the precipitate.

2. Calcining. The Al₂O₃ filter containing the strontium titanyl oxalate precipitate was placed in the furnace in Cell 11. The furnace temperature was raised at 100°C per hour to 1200°C, held for four hours and lowered at 100°C per hour to 200°C. The SrTiO₃ was transferred from the Al₂O₃ filter to a porcelain vessel. Total weight of the powder was 172.4 grams.

Batch 2, Sr11 was handled in a similar manner and contained 210.5 grams.

3. Blending. Each batch of the powder was blended thoroughly in a stainless steel Waring Blendor vessel. Both batches of powder were then blended together. A plastic cover was placed over the stainless steel cover to minimize the loss of powder during the blending operation. The weight of the blended powder was 382.5 grams. The loss during the total blending operation was 0.4 grams.

4. Pelletizing. Six pellets were fabricated from the above powder, three containing 65 grams each and three containing 56 grams each. A pellet was also pressed from a previous batch of powder containing 69.67 grams.

5. Sintering. Seven pellets were sintered in the furnace in Cell 11. The pellets were placed on Al₂O₃ trays containing a layer of zirconium oxide granules approximately one-eighth in. thick. The temperature was raised at 100°C per hour to 1400°C, held at 1400°C for 8 hours, and then lowered at 100°C per hour. The zirconium oxide granules stuck slightly on the bottom of each pellet but were easily removed with a spatula.

6. Cutting Oversized Pellet. A pellet fabricated with the 2.52 inch diam die failed to shrink to the required diameter of 2-¹/₁₆ inches. The pellet was made from Batch 2 containing 90 grams of powder. The diameter of the pellet was 2-³/₈ inches.

A device was assembled consisting of a rotating brass cylinder 2-¹/₁₆ inches I.D. and a holder for the pellet mounted in a machinist vise. The rotating cylinder was mounted on a guide that permitted limited vertical travel. A slurry of 320-mesh silicon carbide and water was used with the brass cylinder to provide a cutting surface. Approximately 8 hours were required to complete the operation. The pellet weighed 69.58 grams, and pieces from the pellet weighing 9.80 grams were recovered.

7. Pellet Summary. The following table contains a description of the pellets as assembled for insertion into the fuel capsule.

Pellet No.	Batch No.	Weight, g	Density g/cm ³	Remarks
1	1	65	3.5 (est)	Pellet broken. Placed in Pt cup
2	1	65	3.5 (est)	Pellet broken. Placed in Pt cup
3	1	100	3.5 (est)	Pellet broken. Placed in Pt cup
4	2	69.57	3.0	Pellet intact
5*	1-2, Sr11	64.65	4.49	
6*	1-2, Sr11	64.94	4.56	
7	1-2, Sr11	65.05	4.52	Pellet intact
8	1-2, Sr11	56.07	4.40	Pellet intact
9	1-2, Sr11	55.85	4.46	Pellet intact
10	1-2, Sr11	56.60	4.39	Pellet intact
11	2	69.67	3.50	Pellet intact

*A total of 20.24 grams of powder from Batch 1 was sintered in two platinum cups. Also added to the cups were pieces of the residue from cutting pellet No. 4 totaling 9.80 grams and the two pellets as listed in the above table.

*Refers to SrTiO₃ powder history.

The following table shows the total amount of powder used from each batch and the thermal output of the powder as determined by calorimetry.

Batch No.	Weight, g	Specific power total power	
		W/g	W
1	250.24	0.10	25.02
2	149.04	0.103	15.35
1-2, Sr11	363.16	0.192	69.72
			110.09

Fuel Capsule Loading

The eleven SrTiO₃ pellets were placed in a special holder to permit the loading of the Hastelloy alloy C capsule without disturbing the pieces in the platinum cups. The pellets were alternated as to specific activity in order to get an even distribution of heat. The capsule was placed on top of the holder and the assembly was inverted thus transferring all of the pellets into the fuel capsule. The free space above the pellets was approximately $\frac{3}{16}$ of an inch. The fuel capsule was then transferred to Cell 14 for the welding operation.

Fuel Capsule Welding

The capsule cover was installed with a vacuum tool to prevent contacting the area to be welded. A special tool with three contact points was used to place the capsule in the welder.

The fuel capsule was welded in a helium and ⁸⁵Kr atmosphere at 30 psig. Approximately 0.2% of the inert-gas atmosphere was fission-product gas containing 100 millicuries/cm³ of ⁸⁵Kr.

The welder was purged by evacuating to 26 inches of Hg vacuum and pressurizing to 30 psig with helium. This was repeated nine times. During the ninth evacuation 35 cc of fission-product gas was introduced and the welder was pressurized with helium prior to the welding operation.

The first welding attempt was not successful. Expanding gas inside the capsule raised the cover slightly at the beginning of the welding operation. The capsule was removed from the welder and the cover was pressed back in place. The capsule was replaced in the welder and the complete purge operation repeated. The welded closure was completed successfully.

Fuel Capsule Leak Test

After the welding operation was completed, the capsule was transferred to a water cooled pressure

vessel. The vessel was evacuated to 26 inches of Hg vacuum and held for 20 minutes. The pressure was raised to atmospheric and a gas sample was obtained in an evacuated counting chamber. The results were 621 c/min with a background of 658 c/min. After five hours another sample showed 636 c/min with a background of 528 c/min. The samples were counted for a total of five minutes.

Assuming a leak rate of 1.0 cm³/year or 3.15×10^{-7} cm³/sec., 0.2% fission product gas, 1 cm³ of fission product gas = 100 millicurie of ⁸⁵Kr, and one hour accumulation, the sample would register 5×10^3 cpm. This is based on calibration data of 2.2×10^3 cpm/ 1×10^{-1} microcuries of ⁸⁵Kr for the counting chamber.

Fuel Capsule Smear Results

The fuel capsule was decontaminated by scrubbing with a brush in a detergent solution, rubbing with stainless steel scouring pads, and cleaning finally with wet wipes.

Paper smears with an area of 4.25 cm and attached to wooden handles were used to check the fuel capsule for surface contamination. Six smears were made on the capsule with the following results.

Smear No.	Location on capsule	Approx. area covered, cm ²	Results, d/m
1	Top (ORNL weld)	20	280
2	Bottom (Martin weld)	20	850
3	Side (~90° apart)	30	1410
4	Side (~90° apart)	30	280
5	Side (~90° apart)	30	250
6	Side (~90° apart)	30	870

Moderate pressure was used and the smears were obtained by contacting the fuel capsule and removing the smear papers several times. This was necessary to prevent charring of the papers by the hot surface of the capsule. All smears were removed from the cell in plastic bags to prevent contamination from handling.

Generator Loading

The generator was mounted on the special welding and handling fixtures. During the examination and tests it was found that the outside diameter of the generator was not uniform. A weld bead caused a bulge on the side that interfered with the performance of the welder and with the leak detector cover. The leak detector cover was enlarged in order to fit down over the top but it was impossible to get a seal. It was decided that the ⁸⁵Kr could be pressured into the space inside the cover

and would be pulled into the evacuated generator if a leak existed. The welder would be adjusted after the first pass if necessary.

The generator was assembled with the fuel capsule, retaining plate, snap ring, insulation, and cover plate. The weld bead pulled to the outside on the first pass due to the bulge on the generator. The position of the electrode was adjusted and a second pass was made. Visual inspection indicated that the weld was satisfactory.

Generator Leak Test

The generator was tested by placing the leak test cover over the weld area and introducing a mixture of approximately 2% fission product gas and 98% argon. The generator was evacuated to 1000 microns and held for 10 minutes. A mixture of 95% argon and 5% hydrogen was used to return the generator to atmospheric pressure. A sample was obtained from the generator in the ^{85}Kr counting chamber. The results were 684 c/min with a background of 635 c/min. Tests of longer duration were not made because of the rapid temperature rise of the unit. The internal temperature was 355°C prior to installing the generator in the shielded cask.

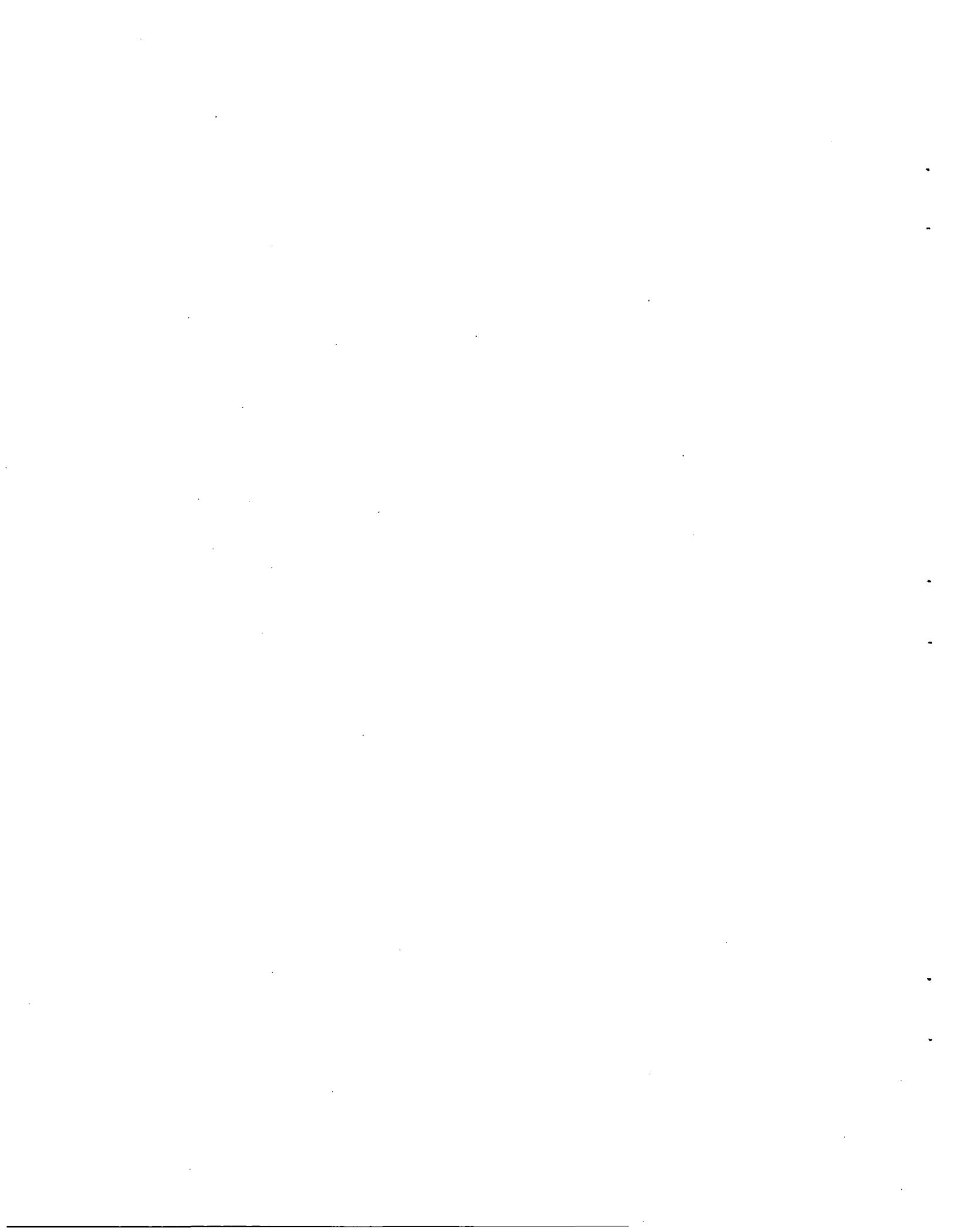
Generator Smear Test

Five smears were made on the sealed generator as follows.

Smear No.	Location on Generator	Approx. area covered, cm ²	Results, d/m
1	Top	100	240
2	Side	75	90
3	Side	75	50
4	Side	75	90
5	Plug and flange	100	150

Transferring Generator into Shielded Cask

The special welding and handling device was lifted and the generator was rotated 180°. This oriented it to a position for lowering it into the shielded cask. Fourteen pounds of Hg in the cask provided a thermal bond between the generator and the cask. The generator was lowered into the cask and disconnected from the welding and handling fixture. It was then secured in place and removed from the cell.



APPENDIX J

ORNL DWG. 68-2170

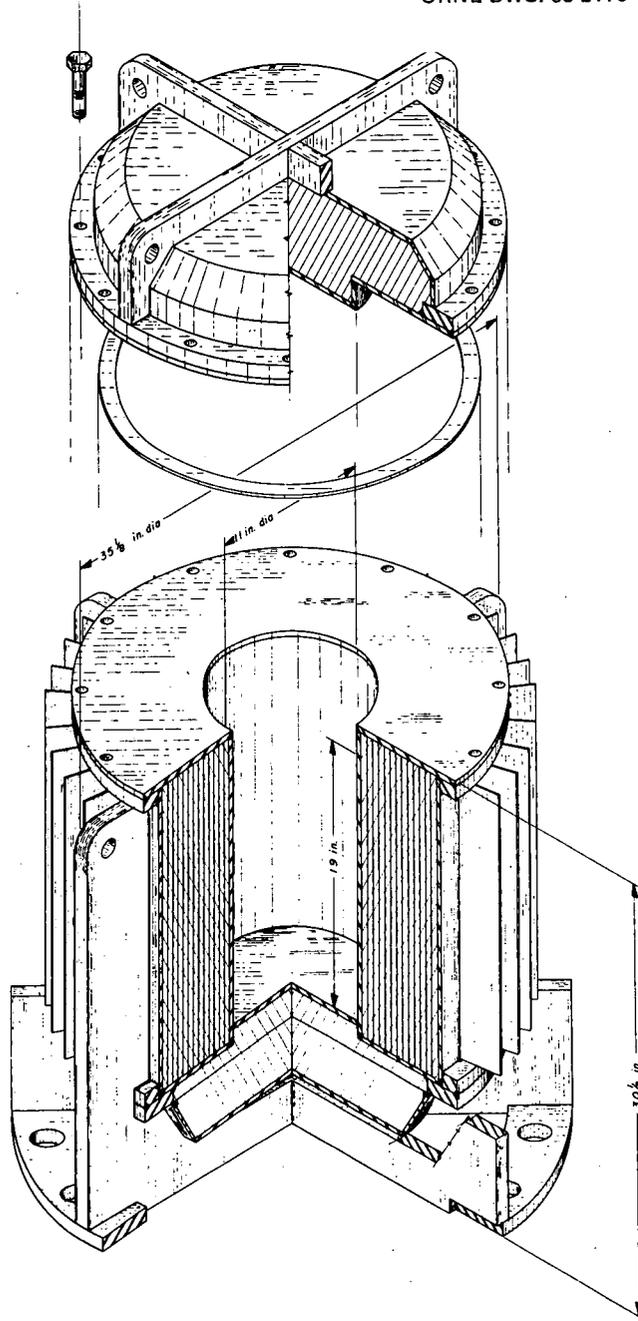


Fig. J.1. Oak Ridge National Laboratory uranium shielded cask.



DEPARTMENT OF TRANSPORTATION
 HAZARDOUS MATERIALS REGULATIONS BOARD
 WASHINGTON, D.C. 20590

SPECIAL PERMIT NO. 5595

This special permit is issued pursuant to the authority of 46 CFR 146.05-4 of the U. S. Coast Guard Dangerous Cargo Regulations, and 49 CFR 173.22(a)(1), Department of Transportation (DOT) Hazardous Materials Regulations, as amended.

1. The OAK RIDGE NATIONAL LABORATORY, is hereby authorized to ship radioactive material, n.o.s., further described as encapsulated non-fissile radionuclides under the provisions of 46 CFR 146.25-30 and 146.25-400 of the U. S. Coast Guard Dangerous Cargo Regulations, and 49 CFR 173.393(f)(9) of the U. S. Atomic Energy Commission (USAEC), Oak Ridge Operations Office, approval dated January 19, 1968, and as further provided for herein.
2. The authorized packaging shall consist of a DOT Specification 55 uranium shielded cask, approximately 25 1/2 inch O.D. by 43 inches long, with cooling fins with 35 5/8 inch O.D. All radioactive material will be either singly or doubly encapsulated, or contained in DOT Spec. 2R inner containers. The package is identified as Model Nos. "L" or "M", and is described on Paducah Plant, Union Carbide's drawing numbers E-M-12176-A, -B, -C, -D, and -E; and E-M-11920-D, -E, and -F.
3. The closure device must have affixed to it a tamperproof lock wire and seal, or equivalent, adequate to prevent inadvertent opening of the container, and of a type that must be broken if the package is opened.
4. The authorized contents of each package shall consist of not more than 400,000 curies of any non-fissile solid radionuclide, having a heat load not to exceed 6130 watts in Model L or 4000 watts in Model M.
5. The maximum temperature at any accessible point on the external surface of the package shall not exceed 150° F., under normal conditions of transportation.

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6. The authorized package meets the criteria of the International Atomic Energy Agency for Type B packaging for large quantity radioactive materials.

7. Prior to each shipment authorized by this permit, the consignee shall be notified of the dates of shipment and expected arrival.

8. The outside of each package shall be plainly and durably marked "DOT SP 5595" and "RADIOACTIVE MATERIAL", in connection with and in addition to the other markings and labels prescribed by the DOT regulations. Each shipping paper issued in connection with shipments made under this permit must bear the notation "DOT SPECIAL PERMIT NO. 5595" in connection with the commodity description thereon. In accordance with 49 CFR 173.9(c) of the DOT regulations, the special permit identification may be either tag or label securely affixed to each package. For export shipments, the outside of each package shall be also marked "TYPE B".

9. The permit does not relieve the shipper from compliance with any requirement of the DOT regulations, including 46 CFR Parts 146 to 149 of the U. S. Coast Guard Regulations, except as specifically provided for herein.

10. Shipments are authorized only by cargo vessel, motor vehicle, rail freight, and rail express. For shipments by water, stowage shall be "on deck in open", or "on deck protected" in such a manner as not to impede air circulation.

11. For shipments by water, the shipper or agent shall notify the U. S. Coast Guard Captain of the Port in the port area through which the shipment is to be made, of the name of the vessel on which the shipment is to be made, and of the time, date, and place of loading. When the initial notification is given in a port area, it shall be accompanied by a copy of this permit, addressed to the attention of that Captain of the Port.

12. The shipper must furnish a record of experience to the Board if any extension or amendment to the permit is requested. This report must include the approximate number of packages shipped and the number of packages involved in any loss of contents. The modes of transportation used for these shipments must also be shown.

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13. This permit shall expire April 30, 1970.

Issued at Washington, D.C., this 8th day of April 1968.


E. G. Grundy, Capt.
For the Commandant
U. S. Coast Guard


W. R. Fiste
For the Administrator
Federal Highway Administration


H. E. Longhurst
For the Administrator
Federal Railroad Administration

Address all inquiries to: Secretary, Hazardous Materials
Regulations Board, U.S. Department of Transportation,
Washington, D.C. 20590. Attention: Special Permits.