INSTITUTO DE ENERGIA ATÔMICA
SÃO PAULO

RADIOACTIVE WASTE MANAGEMENT

VOLUME ONE

R. E. Blanco,
W. E. Unger, A. R. Irvine, D. J. Crouse and C. D. Watson

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RADIATION EXPOSURE STANDARDS AND REGULATIONS FOR DISPOSAL AND CATEGORIZATION OF RADIOACTIVE WASTES*

R. E. Blanco

Radiation Exposure Standards

This lecture is divided into three parts: Radiation Standards, Regulations for Disposal of Wastes, and Waste Categorization. It is designed to acquaint the student with the basis for the derivation of the Regulations as well as some of the basic criteria for Radiation Standards. A detailed discussion of the development of Radiation Standards is beyond the scope of this course on waste disposal. A special course in Health Physics could be devoted to this topic. Similarly, the subjects of Site Selection and Environmental Monitoring warrant extensive study but will not be discussed in detail. Dr. E. G. Struxness, Associate Director of the ORNL Health Physics Division has prepared an introduction and an excerpt from ORNL-4101 which presents details on Radiation Safety Criteria. Extra copies of this material are available.

As I indicated in the first lecture, Site Selection and Environmental Monitoring are important surveys which must be made both before and after waste treatment and disposal operations are started. Copies of papers on these subjects presented at the IAEA conferences at Rio de Janeiro, Oxford, and Tokai Maru are available for loan in my office. In summary, the following items need detailed study in these two areas.

Site Selection

a) Geology, hydrology, meteorology, seismology
b) Effect of routine releases of radionuclides
c) Effect of accidental release of radionuclides

Environmental Monitoring

Details of the recommendations of the ICRP are given in publication Nº 7. Briefly these include:

a) Preoperational surveys
b) Routine operational surveys
c) Emergency surveys.

A principal objective of these surveys is to determine the critical nuclides, the critical population groups, and the critical pathways by which the nuclides can contact man.

Thus, the radiation exposure of man is the important value to be determined. The first part of this lecture is devoted to the determination of radiation safety criteria.

(*) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation. Notes for lectures on Nuclear Waste Treatment and Fuel Reprocessing presented at the Institute de Energia Atomica, Nuclear Engineering Division, Cidade Universitaria, Sao Paulo, Brazil, October-November, 1969.

SLIDE 1 Authorities Quoted on Radiation Safety (69-9262)

The ICRP was established in 1929 to organize standards for X-ray exposure. It is the oldest group and most of the standards and regulations in all countries are based on the ICRP recommendations. IAEA largely accepts the ICRP recommendations. The NCRP was organized in the USA in 1929 to survey the situation within the United States and make recommendations to the ICRP and later to the FRC and the U. S. government. The FRC is the official U. S. advisory committee that recommends rules and regulations for protection against radiation to the office of the president. These radiation guides are then published in the Federal Register and become a federal regulation. The FRC is composed of the secretaries of departments, such as Health, Education, and Welfare, and Labor; the Commissioner from the AEC, etc. The MRC, similarly advises the Ministry in the United Kingdom.

In addition, the AEC publishes a Manual for Standards for Radiological Protection to be used by government contractors.

SLIDE 2 Recommended Maximum Permissible Dose Equivalents for Occupational Workers (66-11360)

This slide shows the maximum permissible doses for occupational workers as recommended by the authoritative committees. All of the initial efforts of these committees was directed toward establishing limits for people working with radiation. More recently, they have also made recommendations for the members of the public. The occupational values for bone seeking radionuclides are based on experience over a 40-year period and the known effect of the incidence of cancer from the presence of 1 μg of ^{226}Ra in bone. This is the basic standard and is equivalent to approximately 30 rem/yr. The biological effect of 1 μg of ^{90}Sr or ^{239}Pu is approximately the same but appropriate calculations for decay energy, distribution in bone, etc., must be made for exact comparisons. Limits for bone marrow, body, head, gonads, eye lens, and trunk have been set a factor of 6 lower, i.e., 5 rem per year for the sum of both external and internal radiation. The formula for accumulated dose, 5 (N – 18), where N is the individual's age in years, is intended to provide some flexibility in occupational exposure situations when the need arises. Considering the 13-week permissible exposures (Column 2) where the formula applies, it is seen that 12 rems could be accumulated in one year. However, all five authorities emphasize that workers who have accumulated a dose higher than that permitted by the formula should not be exposed at a rate higher than 5 rems/year until the accumulated dose is lower than that permitted by the formula. In all cases, it is assumed that there is no "threshold" limit of risk – it assumes risk is proportional to dose at all radiation levels.

SLIDE 3 Annual Dose Levels for Members of the Public (66-11359)

This slide shows the recommended dose levels for the members of the public. First, we should note that it is a dose level – not a maximum limit as for the workers. It is assumed that strict controls can be applied to a worker but **not** the public. The dose level for the public is regarded as an average and can be exceeded by some individuals. Second, in general, the dose levels are about 1/10 that of the occupational limits, i.e., 0.5 rem/yr. Certain additional restrictions are applied for critical organs. Thus, they recommend that genetic dose not exceed 5 rem for the first 30 years of life, or 5/30 = 0.17 rem/yr for the general population. Thus, a dose of 0.5 rem in a year is acceptable, but the total for the first 30 years must not exceed 5 rem. Similarly, the dose for the thyroid is reduced to 0.5 rem/yr for average population groups (FRC) or to 1.5 rem/yr for children up to 16 yrs old (ICRP).

Thus, at present, there are two major groups, workers and members of the population. Distinction is also made for critical organs between$^{(1)}$ average (or total) population groups and$^{(2)}$ individuals of the public. Previous groupings of$^{(1)}$ general public and$^{(2)}$ public in the neighborhood of nuclear stations are eliminated.

SLIDE 4 Dose Rate from Natural Sources in Normal Areas (mrad/yr) (69-8610)

This slide shows the total natural radiation to be about 100 mrad/yr at sea level.

The cosmic radiation doubles for an approximate increase in elevation of 1500 meters. Thus, the levels of 170 mrad set by the ICRP and others for genetic dose control appear conservative.

The next two slides list the reasons that workers are permitted higher dose levels than the public.

SLIDE 5 Factors Affecting Radiation Limits for Workers (69-9261)

SLIDE 6 Factors Affecting Radiation Limits for Members of the Population (69-9260)

SLIDE 7 FRC Protective Action Guides for the Acute Contaminating Event (66-11575)

The FRC has prepared Protective Action Guides for use where an uncontrolled release of radionuclides occurs. In category I immediate action is required — dose is about equal to occupational. Category III is about equal to the general population level. II and III do not apply to ^{131}I, since it decays and disappears.

Other applications of dose limits and estimates of dose commitments (levels) where additional protective action is required are listed in the excerpt by Dr. Struxness from Report Nº ORNL-4101. The construction of a canal by nuclear explosives is used as an example.

SLIDE 8 Example of Maximum Permissible Body Burdens (MPBB) and Maximum Permissible Concentrations ($MPC_{A \text{ or } W}$) From ICRP, 1959 (69-9266)

This slide shows the ICRP recommendations for ^{137}Cs as an example. The ICRP has prepared extensive tables containing MPBB's and MPC's for all radioisotopes. These values are designed to limit the radiation dose of nuclear workers to the values listed in the previous slides. A standard man is defined as an average adult exposed occupationally and who drinks 2.2 liters of water per day (including food) and breaths 2×10^4 liters of air per day. Thus, if the concentrations of radionuclides in the air and water are controlled and external radiation is controlled by suitable monitoring machines the total dose can be limited to that specified by the ICRP (see Slide 1). The ICRP has developed precise methods for calculating dose to an individual from the concentrations of nuclides in air and water, including the following factors:

1) soluble or insoluble nuclides
2) residence time in body
3) half life of nuclide
4) standards for MPBB
5) organ or part of body affected

The values for 168-hr exposure are for continuous exposure and are reduced proportionally for 40-hr exposure (8 hr/day, 5-day week). The ICRP values generally form the basis for MPC's adopted for other countries.

Regulations for Disposal of Wastes

We now approach the difficult problem of preparing official regulations for the discharge and disposal of radioactive wastes. We have extensive knowledge on establishing limits of dose to man but very little knowledge in tracing the nuclides from the waste discharge point to man (pathways). Each river, ocean bay, or land area must be examined separately. Thus, most countries have based their waste discharge regulations on the ICRP dose recommendations with appropriate safety factors. Additional restrictions are imposed by licensing authorities as more information on pathways is obtained.

SLIDE 9 Liquid-Waste Discharge Limits (69-9264)

The U. S. discharge limits are set by the office of the president as recommended by the NRC. Generally the U. S. limits are about 1/10 of the ICRP values for the 168-hr week. If studies show that a population group would receive a dose in excess of this level, the discharge standard is reduced another factor of 3 to 1/30 of the ICRP. Thus, the U. S. discharge regulation roughly parallels the recommendations of the ICRP where the population dose levels are 1/10 or 1/30 of the occupational dose limits. The U. S. occupational limits (40-hr week) are about the same as the ICRP regulation.

This slide shows a comparison of the U. S., USSR, and ICRP limits but does not include the additional 1/3 reduction which can apply in the U. S. The USSR has arbitrarily used 1/100 of the ICRP limits.

The U. S. standards for protection against radiation are published in the Federal Register as Title 10 – Code of Federal Regulations – Part 20 (10 CFR-Part 20). This contains regulations for exposure and disposal of liquids and solids. The regulations for siting reactors is contained in (10 CFR-100). This regulation is also used for siting reprocessing plants but a new regulation is now being prepared for reprocessing plants.

The following annex is reproduced from **Radioactive Waste Categories** by E. Malasek presented at the IAEA Training Course at Rio de Janeiro, 1968, and from the U. S. Code of Regulations (10 CFR-20).

Application of the Lower Limit of the Activity of Radioactive Wastes in Some Countries ANNEX I

1 – Radioactivity Contamination Limits for Abandonment of Facilities and Equipment (Unofficial Material, Applied in the USA).

a) The maximum amount of fixed alpha radioactivity in disintegrations per minute per 100 square centimeters on buildings or equipment should not exceed 25,000.

b) The average amount of fixed alpha radioactivity in disintegrations per minute per 100 square centimeters on buildings or equipment should not exceed 5,000.

c) The maximum amount of removable (capable of being removed by wiping the surface with a filter paper or soft absorbent paper) alpha radioactivity in disintegrations per minute per 100 square centimeters on buildings or equipment should not exceed 1,000.

d) (i) The maximum level at one centimeter from the most highly contaminated surface of a building or piece of equipment measured with an open-window beta-gamma survey meter through a tissue equivalent absorber of not more than seven milligrams per square centimeter should not exceed one millirad per hour.

(ii) The average radiation level at one centimeter from the contaminated surface of the building or equipment measure, in the same manner should not exceed 0,2 millirad per hour.

e) The contamination limits for abandonment of facilities involving U-233 or plutonium should not exceed 1/10 of the limits in items a), b) and c) above.

Explanation:

These contamination limits were used for several very specific situations and under very specific conditions of control (administration), as follows:

The facilities had been used for storing, sampling and analysis of uranium and thorium ores and concentrates. There were also limited small scale chemical operations involved.

The facility that was involved in development and small scale manufacturing operations with natural and enriched uranium in mixed oxide fuel work. Portions of a small research reactor's service facilities were included in the decontamination operation (reference – AEC Public Document Room Record; Month, Day, Year; Page ?).

These values have also been used for the decontamination and release of a number of small scale unit operations systems that were involved in work with small quantities of U-233 and Plutonium.

2 – Rules and Regulations of the U. S. A. Part 20

Disposal by Release into Sanitary Sewage Systems (§ 20.303)

No licensee shall discharge licensed material into a sanitary sewerage system unless:

a) It is readily soluble or dispersible in water; and

b) The quantity of any licensed or other radioactive material released into the system by the licensee in any one day does not exceed the larger of subparagraphs (1) or (2) of this paragraph:

1) The quantity which, if diluted by the average daily quantity of sewage released into the sewer by the licensee, will result in an average concentration equal to the limits specified in Appendix B, Table I, Column 2, of this part; or

2) Ten times the quantity of such material specified in Appendix C of this part; and

c) The quantity of any licensed or other radioactive material released in any one month, if diluted by the average monthly quantity of water released by the licensee, will not result in an average concentration exceeding the limits specified in Appendix B, Table I, Column 2 of this part; and

d) The gross quantity of licensed and other radioactive material released into the sewerage system by the licensee does not exceed one curie per year.

Excreta from individuals undergoing medical diagnosis or therapy with radioactive material shall be exempt from any limitations contained in this section.

Disposal by Burial in Soil (§ 20.304)

No licensee shall dispose of licensed material by burial in soil unless:

a) The total quantity of licensed and other radioactive materials buried at any one location and time does not exceed, at the time of burial, 1000 times the amount specified in Appendix C of this part; and

b) Burial is at a minimum depth of four feet; and

c) Successive burials are separated by distances of at least six feet and not more than 12 burials are made in any year.

Appendix B, Table I, Column 2 contains the maximum permissible concentrations of individual radionuclides in water (μCi/ml) for professional workers.

APPENDIX B

CONCENTRATIONS IN AIR AND WATER ABOVE NATURAL BACKGROUND

[See notes at end of appendix]

Element (atomic number)	Isotope[1]		Table I Column 1 Air (μc/ml)	Table I Column 2 Water (μc/ml)	Table II Column 1 Air (μc/ml)	Table II Column 2 Water (μc/ml)
Actinium (89)	Ac 227	S	2×10⁻¹²	6×10⁻⁵	8×10⁻¹⁴	2×10⁻⁶
		I	3×10⁻¹¹	9×10⁻³	9×10⁻¹³	3×10⁻⁴
	Ac 228	S	8×10⁻⁸	3×10⁻³	3×10⁻⁹	9×10⁻⁵
		I	2×10⁻⁸	3×10⁻³	6×10⁻¹⁰	9×10⁻⁵
Americium (95)	Am 241	S	6×10⁻¹²	1×10⁻⁴	2×10⁻¹³	4×10⁻⁶
		I	1×10⁻¹⁰	8×10⁻⁴	4×10⁻¹²	2×10⁻⁵
	Am 243	S	6×10⁻¹²	1×10⁻⁴	2×10⁻¹³	4×10⁻⁶
		I	1×10⁻¹⁰	8×10⁻⁴	4×10⁻¹²	3×10⁻⁵
Antimony (51)	Sb 122	S	2×10⁻⁷	8×10⁻⁴	6×10⁻⁹	3×10⁻⁵
		I	1×10⁻⁷	8×10⁻⁴	5×10⁻⁹	3×10⁻⁵
	Sb 124	S	2×10⁻⁷	7×10⁻⁴	5×10⁻⁹	2×10⁻⁵
		I	2×10⁻⁸	7×10⁻⁴	7×10⁻¹⁰	2×10⁻⁵
	Sb 125	S	5×10⁻⁷	3×10⁻³	2×10⁻⁸	1×10⁻⁴
		I	3×10⁻⁸	3×10⁻³	9×10⁻¹⁰	1×10⁻⁴
Argon (18)	A 37	Sub[2]	6×10⁻³		1×10⁻⁴	
	A 41	Sub	2×10⁻⁶		4×10⁻⁸	
Arsenic (33)	As 73	S	2×10⁻⁶	1×10⁻²	7×10⁻⁸	5×10⁻⁴
		I	4×10⁻⁷	1×10⁻²	1×10⁻⁸	5×10⁻⁴
	As 74	S	3×10⁻⁷	2×10⁻³	1×10⁻⁸	5×10⁻⁵
		I	1×10⁻⁷	2×10⁻³	4×10⁻⁹	5×10⁻⁵
	As 76	S	1×10⁻⁷	6×10⁻⁴	4×10⁻⁹	2×10⁻⁵
		I	1×10⁻⁷	6×10⁻⁴	3×10⁻⁹	2×10⁻⁵
	As 77	S	5×10⁻⁷	2×10⁻³	2×10⁻⁸	8×10⁻⁵
		I	4×10⁻⁷	2×10⁻³	1×10⁻⁸	8×10⁻⁵
Astatine (85)	At 211	S	7×10⁻⁹	5×10⁻⁵	2×10⁻¹⁰	2×10⁻⁶
		I	3×10⁻⁸	2×10⁻³	1×10⁻⁹	7×10⁻⁵
Barium (56)	Ba 131	S	1×10⁻⁶	5×10⁻³	4×10⁻⁸	2×10⁻⁴
		I	4×10⁻⁷	5×10⁻³	1×10⁻⁸	2×10⁻⁴
	Ba 140	S	1×10⁻⁷	8×10⁻⁴	4×10⁻⁹	3×10⁻⁵
		I	4×10⁻⁸	7×10⁻⁴	1×10⁻⁹	2×10⁻⁵
Berkelium (97)	Bk 249	S	9×10⁻¹⁰	2×10⁻²	3×10⁻¹¹	6×10⁻⁴
		I	1×10⁻⁷	2×10⁻²	4×10⁻⁹	6×10⁻⁴
Beryllium (4)	Be 7	S	6×10⁻⁶	5×10⁻²	2×10⁻⁷	2×10⁻³
		I	1×10⁻⁶	5×10⁻²	4×10⁻⁸	2×10⁻³
Bismuth (83)	Bi 206	S	2×10⁻⁷	1×10⁻³	6×10⁻⁹	4×10⁻⁵
		I	1×10⁻⁷	1×10⁻³	5×10⁻⁹	4×10⁻⁵
	Bi 207	S	2×10⁻⁷	2×10⁻³	6×10⁻⁹	6×10⁻⁵
		I	1×10⁻⁸	2×10⁻³	5×10⁻¹⁰	6×10⁻⁵
	Bi 210	S	6×10⁻⁹	1×10⁻³	2×10⁻¹⁰	4×10⁻⁵
		I	6×10⁻⁹	1×10⁻³	2×10⁻¹⁰	4×10⁻⁵
	Bi 212	S	1×10⁻⁷	1×10⁻²	3×10⁻⁹	4×10⁻⁴
		I	2×10⁻⁷	1×10⁻²	7×10⁻⁹	4×10⁻⁴
Bromine (35)	Br 82	S	1×10⁻⁶	8×10⁻³	4×10⁻⁸	3×10⁻⁴
		I	2×10⁻⁷	1×10⁻³	6×10⁻⁹	4×10⁻⁵
Cadmium (48)	Cd 109	S	5×10⁻⁸	5×10⁻³	2×10⁻⁹	2×10⁻⁴
		I	7×10⁻⁸	5×10⁻³	3×10⁻⁹	2×10⁻⁴
	Cd 115m	S	4×10⁻⁸	7×10⁻⁴	1×10⁻⁹	3×10⁻⁵
		I	4×10⁻⁸	7×10⁻⁴	1×10⁻⁹	3×10⁻⁵
	Cd 115	S	2×10⁻⁷	1×10⁻³	8×10⁻⁹	3×10⁻⁵
		I	2×10⁻⁷	1×10⁻³	6×10⁻⁹	4×10⁻⁵
Calcium (20)	Ca 45	S	3×10⁻⁸	3×10⁻⁴	1×10⁻⁹	9×10⁻⁶
		I	1×10⁻⁷	5×10⁻³	4×10⁻⁹	2×10⁻⁴
	Ca 47	S	2×10⁻⁷	1×10⁻³	6×10⁻⁹	5×10⁻⁵
		I	2×10⁻⁷	1×10⁻³	6×10⁻⁹	3×10⁻⁵
Californium (98)	Cf 249	S	2×10⁻¹²	1×10⁻⁴	5×10⁻¹⁴	4×10⁻⁶
		I	1×10⁻¹⁰	7×10⁻⁴	3×10⁻¹²	2×10⁻⁵
	Cf 250	S	5×10⁻¹²	4×10⁻⁴	2×10⁻¹³	1×10⁻⁵
		I	1×10⁻¹⁰	7×10⁻⁴	3×10⁻¹²	3×10⁻⁵
	Cf 252	S	2×10⁻¹¹	7×10⁻⁴	7×10⁻¹³	2×10⁻⁵
		I	1×10⁻¹⁰	7×10⁻⁴	4×10⁻¹²	2×10⁻⁵
Carbon (6)	C 14 (CO₂)	S	4×10⁻⁶	2×10⁻²	1×10⁻⁷	8×10⁻⁴
		Sub	5×10⁻⁵		1×10⁻⁶	
Cerium (58)	Ce 141	S	4×10⁻⁷	3×10⁻³	2×10⁻⁸	9×10⁻⁵
		I	2×10⁻⁷	3×10⁻³	5×10⁻⁹	9×10⁻⁵
	Ce 143	S	3×10⁻⁷	1×10⁻³	9×10⁻⁹	4×10⁻⁵
		I	2×10⁻⁷	1×10⁻³	7×10⁻⁹	4×10⁻⁵
	Ce 144	S	1×10⁻⁸	3×10⁻⁴	3×10⁻¹⁰	1×10⁻⁵
		I	6×10⁻⁹	3×10⁻⁴	2×10⁻¹⁰	1×10⁻⁵

See footnotes at end of table.

APPENDIX B—Continued

CONCENTRATIONS IN AIR AND WATER ABOVE NATURAL BACKGROUND

[See notes at end of appendix]

Element (atomic number)	Isotope[1]		Table I Column 1 Air (μc/ml)	Table I Column 2 Water (μc/ml)	Table II Column 1 Air (μc/ml)	Table II Column 2 Water (μc/ml)
Cesium (55)	Cs 131	S	[illegible]	7×10⁻²	[illegible]	[illegible]
		I	[illegible]	3×10⁻²	[illegible]	[illegible]
	Cs 134m	S	[illegible]	2×10⁻¹	[illegible]	[illegible]
		I	[illegible]	3×10⁻²	[illegible]	[illegible]
	Cs 134	S	[illegible]	3×10⁻⁴	[illegible]	[illegible]
		I	[illegible]	1×10⁻³	[illegible]	[illegible]
	Cs 135	S	[illegible]	3×10⁻³	[illegible]	[illegible]
		I	[illegible]	7×10⁻³	[illegible]	[illegible]
	Cs 136	S	[illegible]	2×10⁻³	[illegible]	[illegible]
		I	[illegible]	2×10⁻³	[illegible]	[illegible]
	Cs 137	S	[illegible]	4×10⁻⁴	[illegible]	[illegible]
		I	[illegible]	1×10⁻³	[illegible]	[illegible]
Chlorine (17)	Cl 36	S	[illegible]	2×10⁻³	[illegible]	[illegible]
		I	[illegible]	2×10⁻³	[illegible]	[illegible]
	Cl 38	S	[illegible]	1×10⁻²	[illegible]	[illegible]
		I	[illegible]	1×10⁻²	[illegible]	[illegible]
Chromium (24)	Cr 51	S	[illegible]	5×10⁻²	[illegible]	[illegible]
		I	[illegible]	5×10⁻²	[illegible]	[illegible]
Cobalt (27)	Co 57	S	[illegible]	2×10⁻²	[illegible]	[illegible]
		I	[illegible]	1×10⁻²	[illegible]	[illegible]
	Co 58m	S	[illegible]	8×10⁻²	[illegible]	[illegible]
		I	[illegible]	6×10⁻²	[illegible]	[illegible]
	Co 58	S	[illegible]	4×10⁻³	[illegible]	[illegible]
		I	[illegible]	3×10⁻³	[illegible]	[illegible]
	Co 60	S	[illegible]	1×10⁻³	[illegible]	[illegible]
		I	[illegible]	1×10⁻³	[illegible]	[illegible]
Copper (29)	Cu 64	S	[illegible]	1×10⁻²	[illegible]	[illegible]
		I	[illegible]	6×10⁻³	[illegible]	[illegible]
Curium (96)	Cm 242	S	[illegible]	7×10⁻⁴	[illegible]	[illegible]
		I	[illegible]	7×10⁻⁴	[illegible]	[illegible]
	Cm 243	S	[illegible]	1×10⁻⁴	[illegible]	[illegible]
		I	[illegible]	7×10⁻⁴	[illegible]	[illegible]
	Cm 244	S	[illegible]	2×10⁻⁴	[illegible]	[illegible]
		I	[illegible]	8×10⁻⁴	[illegible]	[illegible]
	Cm 245	S	[illegible]	1×10⁻⁴	[illegible]	[illegible]
		I	[illegible]	8×10⁻⁴	[illegible]	[illegible]
	Cm 246	S	[illegible]	1×10⁻⁴	[illegible]	[illegible]
		I	[illegible]	8×10⁻⁴	[illegible]	[illegible]
Dysprosium (66)	Dy 165	S	[illegible]	1×10⁻²	[illegible]	[illegible]
		I	[illegible]	1×10⁻²	[illegible]	[illegible]
	Dy 166	S	[illegible]	1×10⁻³	[illegible]	[illegible]
		I	[illegible]	1×10⁻³	[illegible]	[illegible]
Erbium (68)	Er 169	S	[illegible]	3×10⁻³	[illegible]	[illegible]
		I	[illegible]	3×10⁻³	[illegible]	[illegible]
	Er 171	S	[illegible]	3×10⁻³	[illegible]	[illegible]
		I	[illegible]	3×10⁻³	[illegible]	[illegible]
Europium (63)	Eu 152 (T/2=9.2 hrs)	S	[illegible]	2×10⁻³	[illegible]	[illegible]
		I	[illegible]	2×10⁻³	[illegible]	[illegible]
	Eu 152 (T/2=13 yrs)	S	[illegible]	2×10⁻³	[illegible]	[illegible]
		I	[illegible]	2×10⁻³	[illegible]	[illegible]
	Eu 154	S	[illegible]	6×10⁻⁴	[illegible]	[illegible]
		I	[illegible]	6×10⁻⁴	[illegible]	[illegible]
	Eu 155	S	[illegible]	6×10⁻³	[illegible]	[illegible]
		I	[illegible]	6×10⁻³	[illegible]	[illegible]
Fluorine (9)	F 18	S	[illegible]	2×10⁻²	[illegible]	[illegible]
		I	[illegible]	1×10⁻²	[illegible]	[illegible]
Gadolinium (64)	Gd 153	S	[illegible]	6×10⁻³	[illegible]	[illegible]
		I	[illegible]	6×10⁻³	[illegible]	[illegible]
	Gd 159	S	[illegible]	2×10⁻³	[illegible]	[illegible]
		I	[illegible]	2×10⁻³	[illegible]	[illegible]
Gallium (31)	Ga 72	S	[illegible]	1×10⁻³	[illegible]	[illegible]
		I	[illegible]	1×10⁻³	[illegible]	[illegible]
Germanium (32)	Ge 71	S	[illegible]	5×10⁻²	[illegible]	[illegible]
		I	[illegible]	5×10⁻²	[illegible]	[illegible]
Gold (79)	Au 196	S	[illegible]	5×10⁻³	[illegible]	[illegible]
		I	[illegible]	4×10⁻³	[illegible]	[illegible]
	Au 198	S	[illegible]	2×10⁻³	[illegible]	[illegible]
		I	[illegible]	1×10⁻³	[illegible]	[illegible]
	Au 199	S	[illegible]	5×10⁻³	[illegible]	[illegible]
		I	[illegible]	4×10⁻³	[illegible]	[illegible]

See footnotes at end of table.

Appendix C

(from U. S. Federal Code of Regulations — Part 20)

Material	Micro-curies	Material	Micro-curies	Material	Micro-curies
Ag-105	1	Ir-192	10	Sc-46	1
Ag-111	10	K-42	10	Sm-153	10
As-76, As-77	10	La-140	10	Sn-113	10
Au-198	10	Mn-52	1	Sr-89	1
Au-199	10	Mn-56	50	Sr-90 + Y-90	0.1
Ba-140 + La-140	1	Mo-99	10	Ta-182	10
Be-7	50	Na-22	10	Tc-96	1
C-14	50	Na-24	10	Tc-99	1
Ca-45	10	Nb-95	10	Te-127	10
Cd-109 + Ag-109	10	Ni-59	1	Te-129	1
Ce-144 + Pr-144	1	Ni-63	1	Th (natural)	50
Cl-36	1	P-32	10	Tl-204	50
Co-60	1	Pd-103 + Rh-103	50	—	—
Cr-51	50	Pd-109	10	U (natural)	50
Cs-137 + Ba-137	1	Pm-147	10	U-233	1
Cu-64	50	Po-210	0.1	U-234, U-235	50
Eu-154	1	Pr-143	10	V-48	1
F-18	50	Pu-239	1	W-185	10
Fe-55	50	Ra-226	0.1	Y-90	1
Fe-59	1	Rb-86	10	Y-91	1
Ga-72	10	Re-186	10	Zn-65	10
Ge-71	50	Rh-105	10	Unidentified	—
H-3 (HTO or	—	—	—	radioactive materials	—
HO-32	250	Ru-106 + Rh-106	1	or any of the	—
I-131	10	S-35	50	above in unknown	—
In-114	1	Sb-124	1	mixtures	0.1

NOTE: For purposes of § § 20.203 and 20.304, where there is involved a combination of isotopes in known amounts the limit for the combination should be derived as follows: Determine, for each isotope in the combination, the ratio between the quantity present in the combination and the limit otherwise established for the specific isotope when not in combination. The sum of such ratios for all isotopes in the combination may not exceed "1" (i.e. "unity").

Example: For purposes of § 20.304, if a particular batch contains 2,000 μCi of Au-198 and 25,000 μC of C-14, it may also include not more than 3,000 μC of I-131. This limit was determined as follows:

$$\frac{2{,}000\,\mu C\ \text{Au-198}}{10{,}000\mu C} + \frac{25{,}000\,\mu C\ \text{C-14}}{50{,}000\mu C} + \frac{3{,}000\,\mu C\ \text{I-131}}{10{,}000\mu C} = 1$$

The denominator in each of the above ratios was obtained by multiplying the figure in the table by 1,000 as provided in § 20.304.

3 — United Kingdom (unofficial material)

For small disposals of beta gamma emitting radioactive waste, permissible levels can be calculated from broad general considerations of the dispersal of the waste and the habits of the general public. Tentative conservative levels have been suggested for the disposal of liquid radioactive wastes to sewers and rivers, and for disposal of solid radioactive waste by tipping.

These levels and the reasoning behind them are contained in a paper by A. W. Kenny "The degree of treatment required for low and intermediate level radioactive wastes to prevent the hazardous pollution of the environment" given at a IAEA Symposium in Vienna, 6-10 December 1965.

The title of the Symposium was "Practices in the treatment of low and intermediate level radioactive wastes".

The levels, which are approximate guides, are summarized below, but for complete accuracy the Symposium report, in which the paper appears, should be referred to.

Solid Liquid Waste

To sewers $< 10^{-4}$ μCi/ml ($\geqslant$ 10 times dilution)
To rivers $< 10^{-5}$ μCi/ml.

Solid Waste to Refuse Tips

Maximum activity per article, 1 μCi.
With tenfold dilution with inactive refuse
Maximum activity permitted — 10^{-4} μCi/g with not more than 10 μCi per article.

4 — Radioactive Substances Act, 1960 (United Kingdom)

Natural elements exempted from the provisions of the Act (i.e. are not considered radioactive under the Act) are summarized at the Third Schedule:

Element	Microcuries per gramme		
	solid	liquid	gas or vapour
Actinium	1×10^{-5}	2×10^{-4}	7×10^{-11}
Lead	2×10^{-5}	1×10^{-7}	3×10^{-9}
Polonium	1×10^{-5}	7×10^{-7}	6×10^{-9}
Protoactinium	1×10^{-5}	9×10^{-7}	3×10^{-11}
Radium	1×10^{-5}	1×10^{-8}	1×10^{-9}
Radon	—	—	1×10^{-6}
Thorium	7×10^{-5}	1×10^{-6}	6×10^{-10}
Uranium	3×10^{-4}	2×10^{-5}	2×10^{-9}

5 — Radiation Protection Law, 25 April 1963 (Czechoslovakia)

Radionuclides exempted from the provisions of the Law (i.e. are not considered radioactive under the Law) are defined in § 2:

Class of Radionuclides	specific activity (μCi/g)	total activity (μCi)
A	0.002	0.1
B	0.02	1
C	0.2	10
D	2	100

The classification of radionuclides into individual classes is given in the Annex II of the Law:

Class A — particularly toxic: Sr-90 + Y-90, Pb-210 + Bi-210, At-211 products of decay, Ra-228, Ac-227, U-238, transuranium elements.

Class B — highly toxic: Ca-45, Fe-59, Sr-90, Y-91, Ru-106 + Rh-106, I-126, I-129, I-131, Cs-134, Ba-140 + La-140, Ce-144 + Pr-144, Sm-151, Eu-152, Eu-154, Tu-170, Bi-207, Ra-223, Ra-224, Ac-228, Th-227, Th-228, Th-230, Th-232, Th-234, Pa-230, Pa-231, Pa-234, U-230 — U-237.

Class C — medium toxic: C-14, N-16, Na-22, Si-31, P-32, S-35, Cl-36, K-42, Ca-47, Sc-46, Sc-47, Sc-48, V-48, Mn-52, Mn-56, Fe-55, Co-58, Co-60, Ni-59, Ni-63, Ni-65, Cu-64, Zn-65, Ga-72, As-73, As-74, As-76, As-77, Se-75, Br-82, Kr-87, Kr-88, Rb-86, Rb-88, Sr-85, Sr-89, Sr-91, Sr-92, Y-91, Y-92, Y-93, Zr-93 + Nb-93, Zr-95 + Nb-95, Mo-99, Tc-96, Tc-97, Tc-99, Ru-105, Pd-103 + Rh-103, Pd-109, Ag-105, Ag-111, Cd-109 + Ag-109, Cd-115, Sn-113, Sb-122, Sb-124, Sb-125, Te-127, Te-129, Te-132, I-132, I-133, I-134, I-135, Cs-135, Cs-137 + Ba-137, Ba-131, Ce-141, Ce-143, Pr-142, Pr-143, Nd-147, Nd-149, Pm-147, Pm-149, Sm-153, Eu-155, Gd-153, Gd-159, Tb-160, Dy-166, Ho-166, Er-169, Tu-171, Yb-175, Hf-181, Ta-182, W-185, W-187, Re-183, Re-186, Re-188, Os-191, Os-193, Ir-190, Ir-192, Ir-194, Pt-191, Pt-193, Pt-197, Au-196, Au-198, Au-199, Hg-197, Hg-203, Te-200, Te-202, Te-204, Pb-203, Pb-212, Bi-206, Th-131, Pa-233, U-240.

Class D — low toxic: H-3, Be-7, N-13, N-17, F-18, Ce-38, Ar-37, Ar-41, Cr-51, Zn-69, Ge-71, Kr-77, Kr-85, Rb-87, Nb-97, Ru-97, In-115, Sb-129, Te-132, Xe-133, Xe-135, Cs-131, Ba-139, La-141, La-142, Ce-145, Pr-145, Nd-144, Sm-147, Dy-165, Re-187, Tl-201, natural uranium, natural thorium.

Categorization of Radioactive Wastes

Various establishments adopt somewhat empirical standards by which they divide wastes into appropriate categories. The categories chosen may well fit the needs of the individual establishment but they are rarely identical to those used elsewhere. The terms "low-level", "intermediate-level" and "high-level" radioactive wastes are widely used to describe diferent concentrations of radioactive materials in wastes. Unfortunately, these terms do not have quantitative definitions and in this way confusion arises when reference is made simply to "high", "low" or "medium-level" wastes undefined by concentration or radioactivity level.

Only very few countries, in their legal regulations, have defined the categories of wastes. The terminology is not precise and this may result in a misunderstanding between waste management staff and health and safety inspection as far as interpretation of such regulations is concerned.

A panel of experts was convened at IAEA in 1967 to recommend an international standard for categorization. E. Malasek summarized the information and conclusions from the panel in an excellent paper presented at the IAEA training conference in Rio de Janeiro in 1968. Much of this lecture is excerpted from this paper.

Slides 10 and 11 illustrate the present methods of categorizing wastes.

SLIDE 10

There are no countries that have the same classification system and even within one country it may be different, which is illustrated in the case of France in this slide.

Japan has a semi-official classification of radioactive wastes that was recommended by a special scientific group of the Atomic Energy Commission. The classification of liquid effluents is based on treatment, possibilities of discharge into the environment and ICRP standards. The classification of gaseous effluents is based on MPC levels. The classification of solid wastes is based on preconditioning and transportation standards.

The USA does not have an official classification set by the government. However, a definition of categories of wastes has been accepted as a standard by the United States of America Standards Institute (USASI) which is sponsored by many scientific societies and manufacturers. This standard is based on the MPC's as set by the ICRP. We will discuss this more later.

SLIDE 11

Liquid Wastes – This slide shows a comparison of classifications used in various installations. At present, in most countries the classification of liquid wastes into three basic groups is in use. The limits are defined by activity, by decontamination factor which is necessary to reach before discharge or by the multiplication factor to MPC.

The upper limit of low active liquid wastes is between 10^{-4} μCi/cm^3 and 10^{-1} μCi/cm^3, the lower limit of high active liquid wastes between 10^{-1} μCi/cm^3 and 10^3 μCi/cm^3. Thus, "high active" wastes in Poland are "low active" in the United Kingdom and Norway and "intermediate active" in all other countries.

Solid Wastes – The general opinion of the IAEA panel was that solid wastes should be classified according to the radiation dose on the surface of wastes rather than in correspondence with activity per volume. Special attention must be given to solid wastes containing alpha-emitters. In the USASI standard both radionuclide content and surface radiation are considered.

Gaseous Wastes – At most installations, gaseous wastes are not categorized but are merely defined by the total activity content per volume.

Need for Categorization

Categorization of wastes is necessary for the efficient operation of nuclear installations. A standard universal system is desirable to improve communications between workers at different installations.

Several approaches to standardization are possible. Categories can be proposed on the basis of health and safety requirements, in accordance with practical experience at waste treatment plants, or according to the regulations for the safe transport of radioactive materials. On an international scale, the differences between legal regulations are very considerable especially as far as interpretation of MPC's is concerned.

Definition of Categories

The USASI adopted the MPC's as defined by IAEA as the basis for categorization. However, the IAEA panel pointed out a number of objections to this procedure as follows:

a) Maximum permissible concentrations are a secondary standard, the primary standard is dose and more specifically the dose equivalent. Therefore, the original formulation of MPC – the activity in Ci/ml has been changed recently and in IAEA Safety Series nº 9, "Basic Safety Standards for Radiation Protection – 1967 Edition", expressed in the values of the annual intake by ingestion and inhalation.

b) MPC cannot be used completely as a guide in terms of what an intake can be to the individual in the population. They use the standard man, but in fact the weight of people is different in different countries.

c) MPC does not consider the process and hazard arising from handling, transportation, and discharge of radioactive wastes into the environment. Thus, the MPC values for individual members of the public in drinking water are unimportant, because the source of exposure is not drinking water, but as a result of concentration factors of 10^4 – 10^5 in sea-weed, fish, lobster, or shrimp.

d) The values of MPC are based on the present experience and are changed within relatively short intervals.

e) The MPC recommended by the Agency in the "Basic Safety Standards for Radiation Protection" are not accepted in all countries. It has been shown that between MPC included in laws and regulations of different countries there are significant differences.

f) MPC cannot be applied for discharge of liquid effluents into the open sea. In this case it is better to use another standard – for example MPC-sea recommended by the United States National Academy of Sciences.

g) The thorough application of MPC requires an exact knowledge of all radioisotopes present in the waste together with their chemical form (for example solubility in water) and activity level. For such type of analysis very complicated and expensive monitoring equipment together with skilled staff are required, what is often not available especially for small users and developing countries and it increases significantly the costs of waste management.

It appears to me, that these objections are largely a listing of problems in using MPC's for any purpose, i.e., complex formulae, complex analyses, and changing values. It is particularly difficult to relate the discharge concentrations to the dose to be received by man. The dose to man is actually the purpose for which MPC's were derived. However, in spite of all of these problems, most countries have adopted waste discharge regulations based on the MPC's or factors of the MPC's. Therefore, it appears appropriate to me to use the MPC's as a fundamental unit as in the USASI standard.

I will show several slides to compare the proposed IAEA standards with the USASI standards.

SLIDE 12 Proposed Categories of Liquid Radioactive Wastes (IAEA) (69-9267)

Category 1: includes liquid wastes whose radionuclides concentration is equal or below 10^{-6} μCi/ml. Liquid effluents are not normally treated but discharged directly into the environment.

Category 2: includes liquid wastes whose radionuclides concentration is higher than 10^{-6} μCi/ml and equal or lower than $10^{-3}$$\mu$Ci/ml. Liquid effluents are normally treated by usual methods – chemical treatment, ion-exchange or evaporation and shielding of equipment is not necessary.

Category 3: includes liquid wastes whose radionuclides concentration is higher than 10^{-3} μCi/ml and equal or lower than 10^{-1} μCi/ml. Liquid effluents are treated by usual methods and shielding of some parts of equipment is possible.

Category 4: includes liquid wastes whose radionuclides concentration is higher than 10^{-1} μCi/ml, and equal or lower than 10^{4} μCi/ml. Liquid effluents are treated by usual methods and shielding of equipment is necessary.

Category 5: includes liquid wastes whose radionuclides concentration is higher than 10^{4} μCi/ml. Liquid effluents are stored and cooling is necessary.

SLIDE 13 Proposed Categories of Solid Radioactive Wastes (IAEA) (69-9269)

Category 1: includes solid radioactive wastes with beta, gamma-emitters, and a negligible amount of alpha-emitters whose radiation dose on the surface is not higher than 0,2 R/h. Such solid wastes can be handled and transported without any special precautions.

Category 2: includes solid radioactive wastes with beta-, gamma-emitters, and a negligible amount of alpha-emitters whose radiation dose on the surface is higher than 0.2 R/h and equal or lower than 2 R/h. Such solid waste can be transported in simple containers shielded with a thin layer of concrete or lead.

Category 3: includes solid radioactive wastes with beta-, gamma-emitters, and a negligible amount of alpha-emitters whose radiation dose on the surface is higher than 2 R/h. Such solid wastes can be handled and transported only if special precautions are taken.

Category 4: includes solid radiactive wastes with alpha-emitters and a negligible amount of beta-, gamma-emitters which are not suspected from the point of view of criticality. The activity should be expressed in Ci/m^{3}.

SLIDE 14 Proposed Categories of Gaseous Radioactive Wastes (IAEA) (69-9268)

Category 1: includes gaseous effluents whose radionuclides concentration is lower than 10^{-10} Ci/m^{3}. Those gaseous effluents are usually not treated but discharged directly into the air.

Category 2: includes gaseous effluents whose radionuclides concentration is higher than 10^{-10} Ci/m^{3} and equal or lower than 10^{-6} Ci/m^{3}. The radioactivity is connected mainly with particles and gaseous effluents are usually treated by simple filtration.

Category 3: includes gaseous effluents whose radioactivity concentration is higher than 10^{-6} Ci/m^{3}. The radioactivity is connected mainly with gases and gaseous effluent are usually treated with filtration in connection with other methods.

SLIDE 15 Categories of Radioactive Wastes for Unidentified Radionuclides (69-9270)

This data are taken from the standard published by USASI and an abbreviated version published in Nuclear Safety, Vol.9, Nº 6, November-December 1968. I have reproduced the Table I. This slide shows the values that would be used in conjunction with Table I for determining the waste classification for unidentified radionuclides. The values are based on ^{90}Sr. At most atomic installations ^{226}Ra, ^{228}Ra, and ^{210}Pb are known to be absent, and hence unknown activity is assumed to be ^{90}Sr, and the next most limiting radionuclide. If ^{226}Ra, ^{228}Ra, and ^{210}Pb could be present the following values must be decreased by a factor of approximately 30.

In summary, the categories listed in this slide (USASI) are similar in some cases to those proposed by the IAEA. The USASI categories can be used as pure numbers as are the IAEA values. However, the USASI values are calculated on a precise basis as defined by the ICRP and consequently reflect a reasonable degree of relative hazard.

Table I

Radioactive Waste Categorization
(Not Intended For Regulatory Use)

Class A (population level)	
Liquid and gas	$\leq$ maximum permissible concentration (MPC)* for members of the population at large (including persons living in the neighborhood of controlled areas)
Solid	$\leq$ maximum permissible quarterly intake (MPQI) for members of the population at large (including persons living in the neighborhood of controlled areas)/kg. solid
Surface radiation ‡	$\leq$ maximum permissible whole body exposure (MPE)*for members of the population at large † (including persons living in the neighborhood of controlled areas)
Class B (occupational level)	
Liquid and gas	$>$ Class A but $\leq$ (MPC)*occupational exposure (40-hr. wk)
Solid	$>$ Class A but $\leq$ (MPQI)**for occupational exposure/kg. solid
Surface radiation ‡	$>$ Class A but $\leq$ (MPE) ¶.for occupational exposure † (40-hr. wk)
Class C (low level)	
Liquid and gas	$>$ Class B but $\leq$ 10^4 x Class B
Solid	$>$ Class B but $\leq$ 10^4 x Class B
Surface radiation	
Class C-1	$\leq$ (MPE) ¶ (occupational) at surface †
Class C-2	$>$ (MPE) ¶ (occupational) at surface †
Class D (intermediate level)	
Liquid, gas, or solid	$>$ Class C but $\leq$ 10^4 x Class C
Solid	$>$ Class C but $\leq$ 10^4 x Class C
Surface radiation	
Class D-1	$\leq$ (MPE) ¶ (occupational) at surface †
Class D-2	$>$ (MPE) ¶ (occupational) at surface †
Class E (high level)	
Liquid, gas or solid	$>$ Class D
Surface radiation ‡	
Class E-1	$\leq$ (MPE) ¶ (occupational) at surface †
Class E-2	$>$ (MPE) ¶ (occupational) at surface †

* "ICRP Publication 6, Recommendations of the International Commission on Radiological Protection, as Amended 1959 and Revised 1962," (1964), Pergamon Press (also references 2 and 3).

† In the 1958 report of ICRP Committee II (3,7) the recommended MPE to the gonads or the whole body is 5 rem./yr. for occupational exposure. For the population at large, it is assumed to be 1/100 of 5, or 0.05; for whole body genetic effect.

‡ Applies to surface of container, object, or pool of liquid.

** MPQI = (MPC_W for 168-hr. occupational exposure) (2,200 ml. day) 91 days/quarter)
= MPC_W) (2×10^5); MPC_W applies to water.

¶ Section C of "Radiation Protection – Recommendations of the International Commission on Radiological Protection" (adopted Sept. 9, 1958), Pergamon Press, London (1959) (ICRP, Publ. 1).

REFERENCES AND EXCERPTS FROM:

Radiation Exposure Standards

1. K. E. Cowser, S. V. Kaye, P. S. Rohwer, W. S. Snyder, E. G. Struxness, *Dose Estimation Studies Related to Proposed Construction of an Atlantic-Pacific Interoceanic Canal with Nuclear Explosives: Phase I,* ORNL-4101 (March 1967).

2. "Recommendations of the International Commission on Radiological Protection (Adopted September 17, 1965)," ICPR Publication 9, Pergamon Press.

3. "Principles of Environmental Monitoring Related to the Handling of Radioactive Materials," ICRP Publication 7, a report by Committee 4 of the International Commission on Radiological Protection, (Adopted by the Commission on Sept. 13, 1965), Pergamon Press.

4. "Recommendations of the International Commission on Radiological Protection," ICRP Publication 2, Report of Committee II on Permissible Dose for Internal Radiation, Pergamon Press (1959).

Regulations for Disposal of Wastes

1. E. Malasek, "Radioactive Waste Categories," IAEA Regional Training Course on Radioactive Waste Management, Rio de Janeiro, Brazil, October 14-25, 1968.

2. United States Code of Federal Regulations – Title 10, Part 20.

3. United States Code of Federal Regulations – Title 10, Part 100.

Categorization of Radioactive Wastes

1. E. Malasek, "Radioactive Waste Categories," IAEA Regional Training Course on Radioactive Waste Management, Rio de Janeiro, Brazil, October 14-25, 1968.

2. R. E. Blanco, "Proposed Definition of Radioactive Waste Categories* A Summary of a USASI Standard," Nuclear Safety **9**(6), 515-18 (December 1968).

3. *Proposed Definition of Radioactive Waste Categories,* United States of America Standards Institute, American Institute of Chemical Engineers, 345 East 47th St., New York, N. Y., USA. (Approved June 7, 1967).

ORNL DWG. 69-9262

AUTHORITIES QUOTED ON RADIATION SAFETY

1. International Commission on Radiological Protection (ICRP)
2. International Atomic Energy Agency (IAEA)
3. Federal Radiation Council (FRC)
4. National Council on Radiation Protection and Measurements (NCRP)
5. British Medical Research Council (MRC)

ORNL-DWG 66-11360

RECOMMENDED MAXIMUM PERMISSIBLE DOSE EQUIVALENTS FOR OCCUPATIONAL WORKERS

Organ	Maximum Dose Equivalent (rem) in 13 Weeks	Maximum Permissible Dose Equivalent (rem) in 1 Year	Accumulated Dose Equivalent (rem)
Red Bone Marrow	3 — I,A,N,F	5 — I, A,N	5(N-18) — I,A,N,F
Total Body	3 — I,A,N,F	5 — I,A,N	5(N-18) — I,A N,F
Head and Trunk	3 — N,F	5 — N	5(N-18) — N,F
Gonads	3 — I,A,N,F	5 — I,A,N	5(N-18) — I,A,N,F
Lenses of Eyes	3 — A,N,F 8 — I	5 — A,N,F 15 — I	5(N-18) — I,A,N,F
Skin	8 — A,N 10 — F 15 — I	30 — I,N,F, 32 — A*	
Thyroid	8 — A,N 10 — F 15— I	30 — I,N,F 32 — A*	
Bone	8 — A 10 — F* 15 — I	30 — I,N 32 — A*	
Hands, Forearms Feet and Ankles	20 — A,N 25 — F 38 — I	75 — I,N,F 80 — A*	
All Other Organs	4 — A 5 — F 8 — I	15 — I,N,F 16 — A*	

I = ICRP

A = IAEA

N = NCRP

F = FRC

* = Implied

ORNL-DWG 66-11359

Table 4

ANNUAL DOSE LEVELS FOR MEMBERS OF THE PUBLIC

Organ or Tissue	NCRP[a]	FRC[b]	ICRP	IAEA
Gonads, Red Bone Marrow	0.5 rem	0.5 rem[c]	0.5 rem	0.5 rem
Total Body	0.5 rem	0.5 rem[c]	0.5 rem	0.5 rem
Lenses of the Eyes	0.5 rem		0.5 rem	0.5 rem
Other Single Organs	1.5 rems		1.5 rems	1.5 rems
Skin, Bone, Thyroid	3 rems	1.5 rems[d]	3 rems[e]	3 rems
Hands, Forearms, Feet, Ankles	7.5 rems		7.5 rems	7.5 rems

[a] These levels are based on NCRP's simple recommendation that the permissible dose to members of the population at large be reduced to not more than 1/10 of the occupational values.

[b] The FRC dose not recommend Radiation Protection Guides for individual organ doses to the population other than gonads and whole body.

[c] The FRC specifies that the RPG for gonads shall be 5 rems in 30 years for average population groups on the assumption that the majority of individuals do not vary from the average by a factor greater than 3; thus, the permissible annual dose to gonads and whole body for average population groups would be 0.17 rems.

[d] The FRC recommends RPG's for the thyroid of 1.5 rems/yr for individual and 0.5 rem/yr to be applied to the average of suitable samples of an exposed group in the population.

[e] The ICRP recommends 1.5 rems/yr to the thyroid of children up to 16 years of age.

ORNL DWG. 69-8610

DOSE RATES FROM NATURAL SOURCES IN "NORMAL" AREAS (mrad/y)

	IRRADIATION SOURCE	GONADS	CELLS LINING BONE SURFACES	BONE MARROW
External	Cosmic rays			
	Ionizing component	28	28	28
	Neutrons	0.7	0.7	0.7
	Terrestrial (including air)	50	50	50
Internal	K^{40}	20	15	15
	Rb^{87}	0.3	< 0.3	< 0.3
	C^{14}	0.7	1.6	1.6
	Ra^{226}	-	0.6	0.03
	Ra^{228}	-	0.7	0.03
	Po^{210}	0.3	2.1	0.3
	Rn^{222} (dissolved in tissues)	0.3	0.3	0.3
	Total	100	99	96

United Nations Supplement No. 14 (A/6314), August 1966

ORNL DWG. 69-9261

FACTORS AFFECTING RADIATION LIMITS FOR WORKERS

1. Represents an homogeneous, adult population.

2. Is exposed during a 5-day, 40-hour work week, 50 weeks per year for working lifetime of 50 years.

3. Is protected by personal monitoring, radiation protection, and special health surveillance programs.

4. Receives direct benefits of his employment.

ORNL DWG. 69-9260

FACTORS AFFECTING RADIATION LIMITS FOR MEMBERS OF THE POPULATION

1. Heterogeneous population, including foetuses and children.
2. Constitutes overwhelming proportion of the population's genetic pool.
3. Exposures may be continuous for an average lifetime of 70 years.
4. Exposures are not monitored and no special health surveillance is provided.
5. Benefits are limited.

ORNL-DWG 66-11575

Table 5

FRC PROTECTIVE ACTION GUIDES FOR THE ACUTE CONTAMINATING EVENT

Radionuclide	PAG's for Category I[a]	PAG's for Category II[b]	PAC's for Category III[c]
^{137}Cs	10 rads in first year to bone marrow or whole body of individual; 3 rads to average of suitable sample; total dose must not exceed 15 rads.	5 rads in first year to bone marrow or whole body of individual; 2 rads to average of suitable sample.	0.5 rads in first year to bone marrow of individual; 0.2 rads to average of suitable sample.
^{89}Sr	Same as above	Same as above	Same as above
^{90}Sr	Same as above	Same as above	Same as above
^{131}I	30 rads in first year to thyroid of individual; 10 rads to average of suitable sample (considered to consist of children of 1 year of age).	None specified	None specified

[a] Category I is concerned with immediate transmission of radionuclides through the pasture-cow-milk-man pathway. PAG is stated in terms of a projected dose that might otherwise be received if protective action is not taken. Protective action must be initiated in about 1 week to be effective in averting most of the potential intake.

[b] Category II is concerned with the transmission of radionuclides to man through dietary pathways other than that specified in Category I during the first year following an acute contaminating event. Immediate protective action to reduce the potential intake will not usually be required because of the normal delay in the use of food crops or animal feed crops.

[c] Category III is primarily concerned with the long-term transmission of ^{90}Sr through soil into plants in the years following a contaminating event. Any protective action that may be taken must be based on the long-term reduction of radionuclide concentrations in products grown in the contaminated area.

ORNL DWG. 69-9266

EXAMPLE OF MAXIMUM PERMISSIBLE BODY BURDENS (MPBB) AND MAXIMUM PERMISSIBLE CONCENTRATIONS ($MPC_{A \text{ or } W}$) FROM ICRP, 1959

Radionuclide and Type of Decay		Organ of Reference (critical organ)	Maximum Permissible Body Burden q (μc)	Maximum Permissible Concentrations			
				For 40-hr Week		For 168-hr Week	
				(MPC) ($\mu c/cm^3$)	(MPC) ($\mu c/cm^3$)	(MPC) ($\mu c/cm^3$)	(MPC) ($\mu c/cm^3$)
$_{55}Cs^{137}$	(sol.)	Total body	30	4×10^{-4}	6×10^{-8}	2×10^{-4}	2×10^{-8}
β^-, γ, e^-		Liver	40	5×10^{-4}	8×10^{-8}	2×10^{-4}	3×10^{-8}
		Spleen	50	6×10^{-4}	9×10^{-8}	2×10^{-4}	3×10^{-8}
		Muscle	50	7×10^{-4}	10^{-7}	2×10^{-4}	4×10^{-8}
		Bone	100	10^{-3}	2×10^{-7}	5×10^{-4}	7×10^{-8}
		Kidney	100	10^{-3}	2×10^{-7}	5×10^{-4}	8×10^{-8}
		Lung	300	5×10^{-3}	6×10^{-7}	2×10^{-3}	2×10^{-7}
		GI (SI)		0.02	5×10^{-6}	8×10^{-3}	2×10^{-6}
	(insol.)	Lung			10^{-8}		5×10^{-9}
		GI (LLI)		10^{-3}	2×10^{-7}	4×10^{-4}	8×10^{-8}

ORNL DWG. 69-9264

LIQUID-WASTE DISCHARGE LIMITS

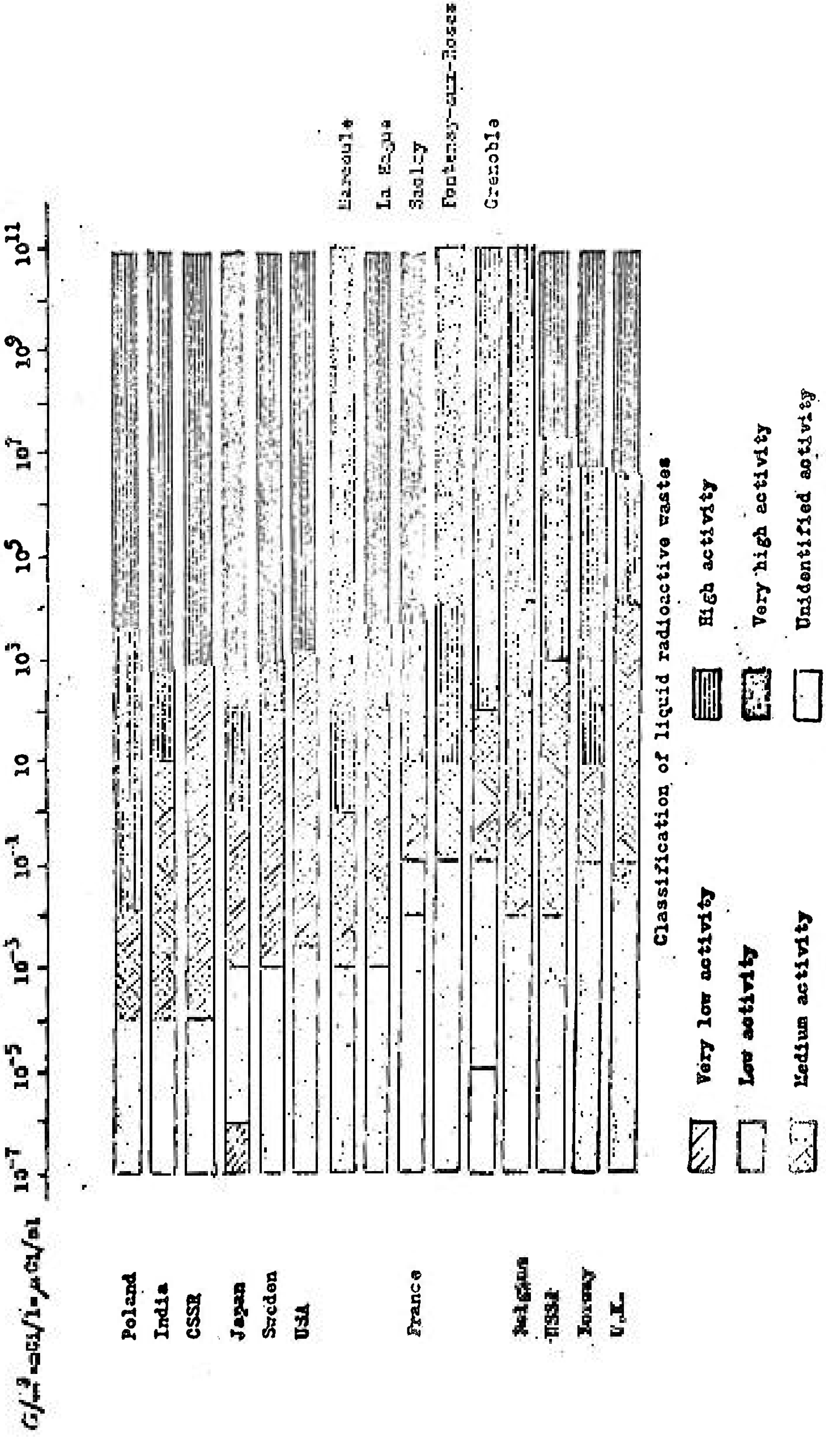
	Activity, $\mu c/cm^3$		
Isotope	USA	USSR	ICRP (168-hr)
^{3}H	3×10^{-3}	3×10^{-4}	5×10^{-2}
^{32}P	2×10^{-5}	5×10^{-6}	2×10^{-4}
^{60}Co	3×10^{-5}	1×10^{-5}	3×10^{-4}
^{90}Sr	3×10^{-7}	3×10^{-8}	4×10^{-6}
^{95}Zr	6×10^{-5}	2×10^{-5}	6×10^{-4}
^{95}Nb	1×10^{-4}	3×10^{-5}	1×10^{-3}
^{103}Ru	8×10^{-5}	2×10^{-5}	8×10^{-4}
^{106}Ru	1×10^{-5}	3×10^{-6}	1×10^{-4}
^{131}I	3×10^{-7}	6×10^{-7}	2×10^{-5}
^{137}Cs	2×10^{-5}	1×10^{-6}	2×10^{-4}
^{144}Ce	1×10^{-5}	3×10^{-6}	1×10^{-4}

Classification of liquid effluents in France

Categories	Nuclear Centres					
	Saclay	Fontenay-aux-Roses	Grenoble	Cadarache	Marcoule	La Hague
Very high active	$> 10^4$ Ci/m^3	$> 10^4$ Ci/m^3	-	(1)	> 100 Ci/m^3	> 100 Ci/m^3
High active	10^2-10^4 Ci/m^3	> 10 Ci/m^3	$> 10^2$ Ci/m^3		1-25 Ci/m^3	10^{-3}-50 Ci/m^3
Medium active	1-10 Ci/m^3	< 10 Ci/m^3	10^{-1}-10^2 Ci/m^3		10^{-3}-1 Ci/m^3	
Low active	10^{-2}-10^{-1} Ci/m^3	< 0.1 Ci/m^3	10^{-5}-10^{-1} Ci/m^3		$< 10^{-3}$ Ci/m^3	$< 10^{-3}$ Ci/m^3

(1) At the Cadarache Nuclear Research Centre the classification of liquid effluents is based on their content of salts rather then on their activity; a distinction is made between:

- effluents with a low content of salts whose activity may reach 10 Ci/m^3; these are treated by evaporation;
- effluents with a high content of salts with possible presence of solvents and detergents; their activity is less than 0.5 Ci/m^3; they are treated by co-precipitation.


G/m³ = Ci/l = µCi/ml
10^{-7}
10^{-5}
10^{-3}
10^{-1}
10
10^{3}
10^{5}
10^{7}
10^{9}
10^{11}
Poland
India
CSSR
Japan
Sweden
USA
France
Marcoule
La Hague
Saclay
Fontenay-aux-Roses
Grenoble
Belgium
USSR
Norway
U.K.
Classification of liquid radioactive wastes
Very low activity
Low activity
Medium activity
High activity
Very high activity
Unidentified activity

ORNL DWG. 69-9267

PROPOSED CATEGORIES OF LIQUID RADIOACTIVE WASTES (IAEA)

Category	Activity Level A (μCi/ml)	Remarks	
1	$A \leq 10^{-6}$		
2	$10^{-6} < A \leq 10^{-3}$		treatment by usual metho
3	$10^{-3} < A \leq 10^{-1}$	Shielding possible	
4	$10^{-1} < A \leq 10^{4}$	Shielding necessary	
5	$10^{4} < A$	Cooling necessary	

ORNL DWG. 69-9269

PROPOSED CATEGORIES OF SOLID RADIOACTIVE WASTES (IAEA)

Category	Radiation Dose D on the Surface of Wastes	Remarks
1	$D \leq 0.2$ R/h	
2	0.2 R/h $< D \leq 2$ R/h	β, γ activity, α-emitters negligible
3	2 R/H $< D$	
4	α-activity expressed in Ci/m^3	α-emitters, β, γ emitters negligible - not suspected from the point-of-view of criticality

ORNL DWG. 69-9268

PROPOSED CATEGORIES OF GASEOUS RADIOACTIVE WASTES (IAEA)

Category	Activity Level A (Ci/m^3)	Remarks
1	$A \leq 10^{-10}$	Usually not treated effluents
2	$10^{-10} < A \leq 10^{-6}$	Effluents usually treated by filtration
3	$10^{-6} < A$	Effluents usually treated by other methods

ORNL DWG. 69-9278

CATEGORIES OF RADIOACTIVE WASTES FOR UNIDENTIFIED RADIONUCLIDES

Class		μCi/cc Air MPC	μCi/cc Liq. MPC	μCi/kg MPQ	rem/yr MPE
A	Population at large	1×10^{-11}	1×10^{-7}	0.02	0.05
B	Occupational (40 hr)	1×10^{-9}	1×10^{-5}	0.7	5
C	Low Level	1×10^{-5}	1×10^{-1} (0.1 mCi/l)	0.7×10^{4}	5
D	Intermediate Level	0.1	1×10^{3} (1 Ci/l)	0.7×10^{8} (70 Ci/kg)	5
E	High Level	0.1	$>1 \times 10^{3}$ >(1 Ci/l)	$>0.7 \times 10^{8}$ (70 Ci/kg)	5

INTRODUCTION TO WASTE MANAGEMENT AND FUEL REPROCESSING

R. E. Blanco

The objective of this course is to present the more important aspects of waste management and fuel reprocessing. It will not be possible to cover all of the subjects in detail, but the student will receive a broad picture of the status and problems along with literature references. This should provide him with the basic knowledge required before entering work in these areas.

The principal emphasis will be placed on waste management. The lectures on waste management are based on documents published by the International Atomic Energy Agency (IAEA), lectures presented at IAEA training courses in Japan, United Kingdom, and Brazil (Rio, October 1968), and documents published in the U. S. and other countries. The lectures on fuel reprocessing are largely based on documents published in the U. S.

The IAEA is an agency located in Vienna and supported by the United Nations. The Division of Health, Safety and Waste Disposal and other divisions have prepared two series of publications to assist countries in planning nuclear operations. These are the Nuclear Safety Series and the Technical Reports Series.

SLIDE 1 IAEA Waste Management Programme, Principal Aspects (69-8606)

SLIDE 2 Steps in Waste Management (69-7899)

a) Preoperational site surveys and continuing research and development are required.

Waste management can be defined as the treatment of wastes to retain the radionuclides and discharge the purified bulk liquids, gases, and solids to the environment. The discharge streams must meet certain specified limits on radionuclide concentration to protect man's environment.

SLIDE 3 Philosophies of Waste Management (69-7896)

The IAEA has issued a report in the Safety Series (Nº 24) which presents the basic factors in treatment and disposal of radioactive wastes.

SLIDE 4 Typical Waste Management Flow Sheet (69-9627)

SLIDE 5 General Breakdown of Waste Management System (69-9223)

SLIDE 6 General Factors in the Selection of a Waste Management System (69-8607)

How are the limits for discharge determined? Each country makes its own regulations, but all of them are based on the maximum permissible concentrations (MPC) as established by the International Committee on Radiological Protection (ICRP). We will look at the regulations in detail later and also at the basis for determining discharge limits.

SLIDE 7 Definitions of Terms (69-9168)

SLIDE 8 Definitions of Terms (continued) (69-9169)

SLIDE 9 Maximum Permissible Concentration of Unidentified Radionuclides in Water (69-7898)

a) This shows limits for unidentified nuclides.

b) Other tables are available for use with identified nuclides.

SLIDE 10 Maximum Permissible Concentration of Unidentified Radionuclides in Air (69.7897)

ORIGIN OF WASTES

SLIDE 11 Radioactive Wastes from the Fuel Cycle (69-83)

Mining — ^{222}Rn is the greatest hazard. A charge of air in the mine is required every 4 minutes. The total amount of Ra discharged is small compared to that discharged from earth surface.

Milling — Radium is by far the most important radioactive contaminant from uranium mills. Analyses of samples from clarified tailings-pond water from several mills in the U. S. from 1957-59 showed that the permissible radium specification for drinking water was exceeded in all cases. Radium can be removed from tailings by coprecipitation when the tailings are neutralized or by adsorption with natural barium sulfate.

Refining — Amount of ^{226}Ra is very low.

Fuel Fabrication — Careful control must be maintained for Th and any recycle fuel containing traces of plutonium. Varying amounts of uranium-bearing wastes are produced in the form of alloy scrap, liquids, contaminated metal pieces, paper, rags, and airbone dust. One of the main hazards is fire, as uranium dust or shavings can ignite spontaneously when exposed to air.

Reactor Fuel Chemical Processing — Contains more than 99.9% of all radionuclides in wastes produced by nuclear industry.

OTHER WASTE SOURCES

Radioisotopes — More than 100 different radioisotopes are now produced for use in research and industry. The estimated total activity shipped from U. S. AEC installations to private users of radioisotopes in the U. S. since 1946 is well over 2 million curies.

Research Establishments — Because of the wide diversity of operations, general statements about volumes and activity levels of wastes from research establishments are not very meaningful. Such wastes are not of proportions comparable to those from fuel reprocessing plants, but large research centers such as Harwell and Oak Ridge produce enough radioactive waste to demand its segregation and treatments according to levels of radioactivity. The higher-activity wastes are usually put through a concentration process (evaporation or precipitation); the concentrate is stored in tanks as a liquid or disposed of as a solid by burial or dumping into the sea; the condensate or effluent is usually discharged to a surface stream or treated as low-level waste.

At some nuclear research establishments in the U. S. it can be seen that the volumes vary from 0.4 to 680 million liters per year and the activity discharged varies from 0.006 to 200 curies per year. These low-level wastes arise from process cooling water, decontamination of laboratories and equipment, low-activity experiments, laundries, and effluents from the treatment of higher-level wastes.

Hospitals and Industry – Radionuclides are widely used in medical and biological research, diagnosis, and therapy. The nature of hospital wastes would present a difficult disposal problem were it not for the fact that the amount of radioactive material used as "unsealed sources" is quite small. Another factor that makes for ease of handling is the limited number of radionuclides thus used, most of which have short half-lives. Iodine-131, phosphorus-32, iron-59, chromium-51, sodium-24, carbon-14, and gold-198 are the main radionuclides used directly and not as sealed sources. The excreta of patients receiving large doses of radioactive material are collected with special precautions but usually can be put safely into domestic sewers.

SLIDE 12 Origin of Radioactive Wastes (66-680)

a) This illustrates the fuel cycle of which fuel processing is an important step. The unused Th, Pu, and U must be separated from the fission products and recovered for reuse.

SLIDE 13 Origin of Wastes from Fuel Processing (65-915)

All fuel processing plants in the world use solvent extraction as the processing method.

Spent fuel elements removed from reactors have to be processed to recover the depleted uranium, to remove the so-called fission products resulting from the breakdown of the uranium nucleus and to obtain the plutonium which is also formed. In terms of radioactive content, the wastes arising from processing plants represent more than 99.9% of the total waste produced by the nuclear energy industry.

Reprocessing normally consists of the decladding of the fuel by mechanical or chemical means followed by dissolution of the residue in nitric acid. During this stage, volatile fission products, notably krypton, xenon, and iodine, are released. The acid fumes are removed by scrubbing, which also removes some iodine, and the purified gas discharged through tall stacks to the atmosphere.

Solvent extraction of the acid solutions is next employed to remove the uranium and plutonium leaving the fission products in the aqueous phase. More than 99% of the crude products are separated in this first stage of the process, and this fission product solution comprises the highest level waste arising in the industry.

Fission product mixtures contain about 35 chemical elements in the form of about 90 primary fission product isotopes. They also include more than 120 additional isotopes arising from the radioactive decay of primary fission products.

SLIDE 14 Principle Fission Products of Interest in Waste Disposal (69-8599)

This slide lists the more important fission products in the wastes from power reactors and fuel processing plants. The principle factors in determining the relative importance are the half lives and the degree of retention in the body. The latter is reflected in the MPC listings. The half life also determines the number of years that a high-level waste will produce significant amounts of heat. Heat production is a very important item in designing high-level waste management systems.

From the waste treatment and disposal aspects, it is those fission products which have half-lives between several days and 30 years, which are of importance. This slide lists these isotopes and shows that the isotopes Sr-90 and Cs-137 may contribute less than 4% of the total activity after 100 days; approximately 30% after 3 years and about 98% after 30 years.

REFERENCES AND EXCERPTS FROM:

1 – Advanced Training Seminar in Radioactive Waste Management – Japan 1965

a) ______Keher, "Introduction to Waste Management"
b) F. N. Browder, "Origin of Nature of Waste"
c) F. N. Browder, "Philosophies in Waste Management"

2 – *Basic Safety Standards for Radiation Protection,* 1967 Edition, IAEA Safety Series No. 9 (July 1967).

3 – *Economics in Managing Radioactive Wastes,* IAEA, Technical Reports Series No. 83 (April 1968).

4 – R. H. Burns, "Origin and Nature of Wastes," Advanced Training Seminar in Waste Management – Oxford, 1967.

ORNL DWG. 69-8696

IAEA WASTE MANAGEMENT PROGRAM
PRINCIPAL ASPECTS

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1. Special technical services
2. Abstracts of research and development, international scope
3. Publications: operational procedures, guidebooks, reports
4. Meetings: symposia, panels, meetings
5. Training courses
6. Research contracts

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STEPS IN WASTE MANAGEMENT

(a) Collection
(b) Transport
(c) Monitoring before treatment
(d) Treatment
(e) Conditioning of concentrated radioactive component before storage or disposal
(f) Storage or final disposal of concentrated radioactive component
(g) Monitoring of treated waste before disposal
(h) Disposal of treated waste
(i) Environmental monitoring

ORNL DWG. 69-7896

PHILOSOPHIES OF WASTE MANAGEMENT

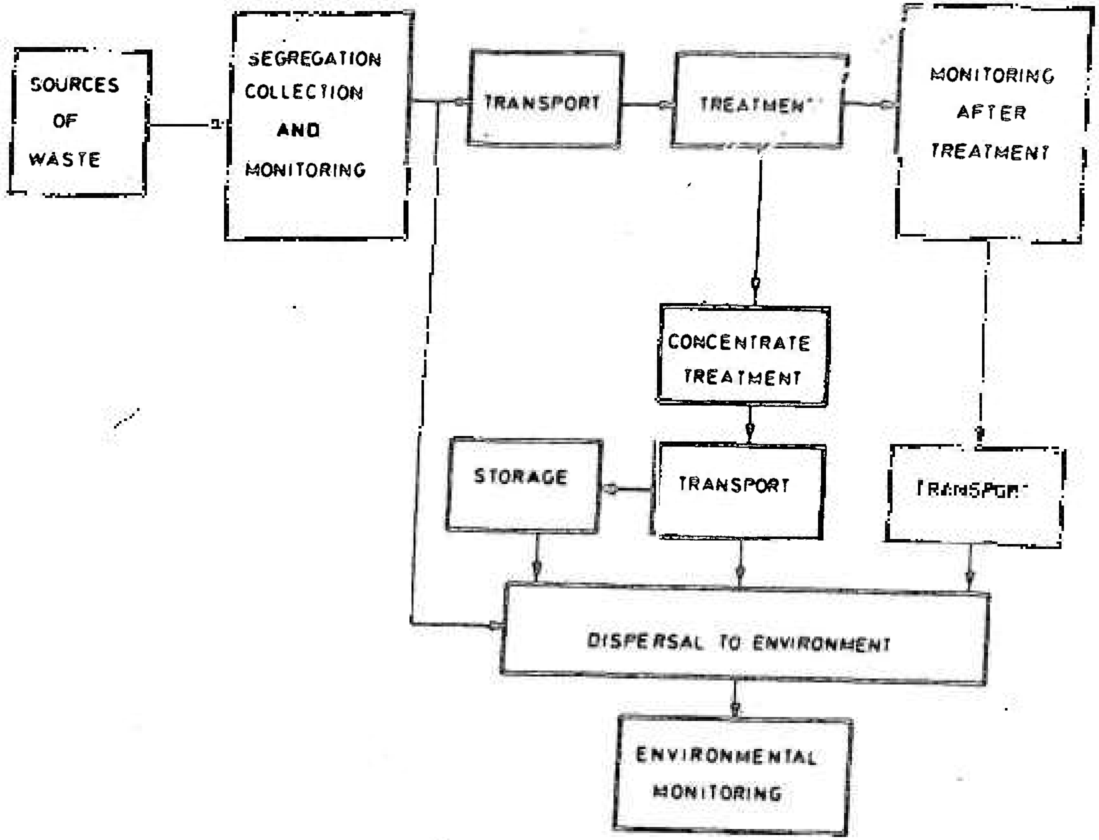
1. Concentrate and Contain
   Example: Evaporation

2. Dilute and Disperse
   Example: Discharge to a River

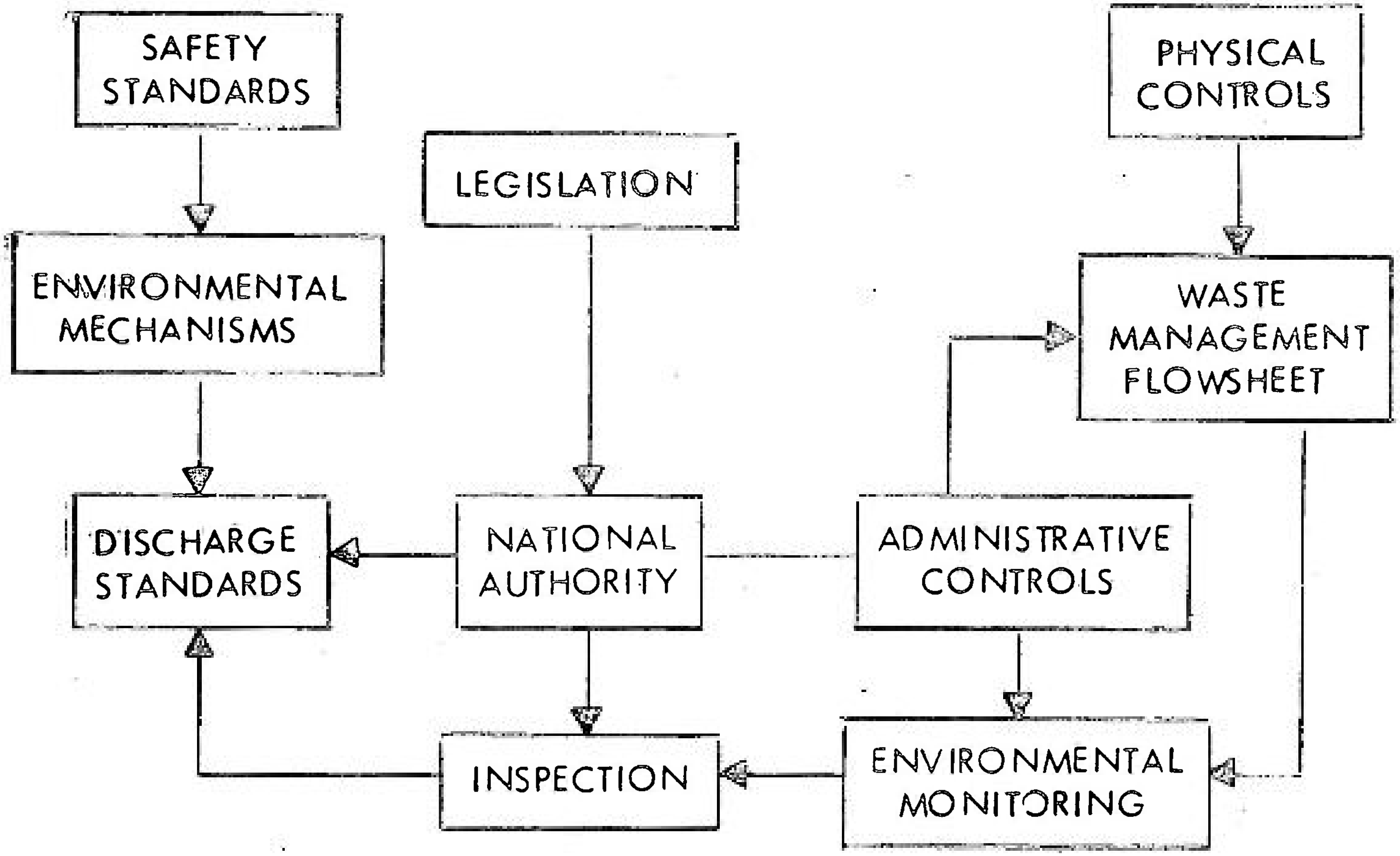
3. Partial Containment
   Example: Discharge to Natural Zeolitic Formation

4. Delay and Decay
   Example: Hold in Tanks Until Short-Lived Radionuclides Decay

ORNL-DWG 69-9627



TYPICAL WASTE MANAGEMENT FLOW SHEET



GENERAL BREAKDOWN OF WASTE MANAGEMENT SYSTEM

ORNL DWG. 69-

GENERAL FACTORS IN THE SELECTION OF A WASTE MANAGEMENT SYSTEM

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1. Dispersal to the environment - Discharge limits determine by authorities and regulations.
2. Public relations - Public accepts X rays but objects to ne operations.
3. Economics - Compromise between costs and safety.
4. Types of waste.
5. Determine waste collection, treatment, and storage metho
6. Define monitoring and waste records.

ORNL DWG. 69-9168

Part 1

DEFINITIONS OF TERMS

Curie (Ci)	Quantity of radionuclide in which the number of disintegrations are 3.7×10^{10}/sec
Roentgen (R)	Quantity of radiation/0.001293 g of air producing 1 esu of ions ≈ to absorption of 83.8 ergs of energy/g of air.
RAD	Radiation absorbed dose, 100 ergs of absorbed energy/g of absorbing material
REM	Radiation equivalent man, amount of radiation that produces same biological effect in man as one R

ORNL DWG. 69-9169

Part 2

DEFINITIONS OF TERMS

MPD	Maximum permissible dose which may be received by persons working with radiation
$MPC_{(A \text{ or } W)}$	Maximum permissible concentration in air or water which will produce a MPD
Decontamination Factor (DF)	Concentration of radionuclides in the original stream divided by the concentration in the treated stream

ORNL DWG. 69-7898

MAXIMUM PERMISSIBLE CONCENTRATION OF UNIDENTIFIED RADIONUCLIDES IN WATER

[$(MPCU)_w$ VALUES] FOR CONTINUOUS OCCUPATIONAL EXPOSURE

LIMITATIONS	$\mu c/cm^3$ of water
If no one of the radionuclides Sr^{90}, I^{126}, I^{129}, I^{131}, Pb^{210}, Po^{210}, At^{211}, Ra^{223}, Ra^{224}, Ra^{226}, Ra^{228}, Ac^{227}, Th^{230}, Pa^{231}, Th^{232}, and Th-nat is present, then the $(MPCU)_w$ is	3×10^{-5}
If no one of the radionuclides Sr^{90}, I^{129}, Pb^{210}, Po^{210}, Ra^{223}, Ra^{226}, Pa^{231}, and Th-nat is present, then the $(MPCU)_w$ is	2×10^{-5}
If no one of the radionuclides Sr^{90}, I^{129}, Pb^{210}, Ra^{226}, and Ra^{228} is present, then the $(MPCU)_w$ is	7×10^{-6}
If neither Ra^{226} nor Ra^{229} is present, then the $(MPCU)_w$ is	10^{-6}
If no analysis of the water is made, then the $(MPCU)_w$ is	10^{-7}

ORNL DWG. 69-7897

MAXIMUM PERMISSIBLE CONCENTRATION OF UNIDENTIFIED RADIONUCLIDES IN AIR

(MPCU)$_a$ VALUES FOR CONTINUOUS OCCUPATIONAL EXPOSURE

LIMITATIONS	$\mu c/cm^3$ of air
If there are no α-emitting radionuclides and if no one of the β-emitting radionuclides Sr^{90}, I^{129}, Pb^{210}, Ac^{227}, Ra^{228}, Pa^{230}, Pu^{241}, and Bk^{249} is present, then the (MPCU)$_a$ is	10^{-9}
If there are no α-emitting radionuclides and if no one of the β-emitting radionuclides Pb^{210}, Ac^{227}, Ra^{228}, and Pu^{241} is present, then the (MPCU)$_a$ is	10^{-10}
If there are no α-emitting radionuclides and if the β-emitting radionuclide Ac^{227} is not present, then the (MPCU)$_a$ is	10^{-11}
If no one of the radionuclides Ac^{227}, Th^{230}, Pa^{231}, Th^{232}, Th-nat, Pu^{238}, Pu^{239}, Pu^{240}, Pu^{242}, and Cf^{249} is present, then the (MPCU)$_a$ is	10^{-12}
If no one of the radionuclides Pa^{231}, Th-nat, Pu^{239}, Pu^{240}, Pu^{242}, and Cf^{249} is present, then the (MPCU)$_a$ is	7×10^{-13}
If no analysis of the air is made, then the (MPCU)$_a$ is	4×10^{-13}

ORNL DWG 69-83 R1

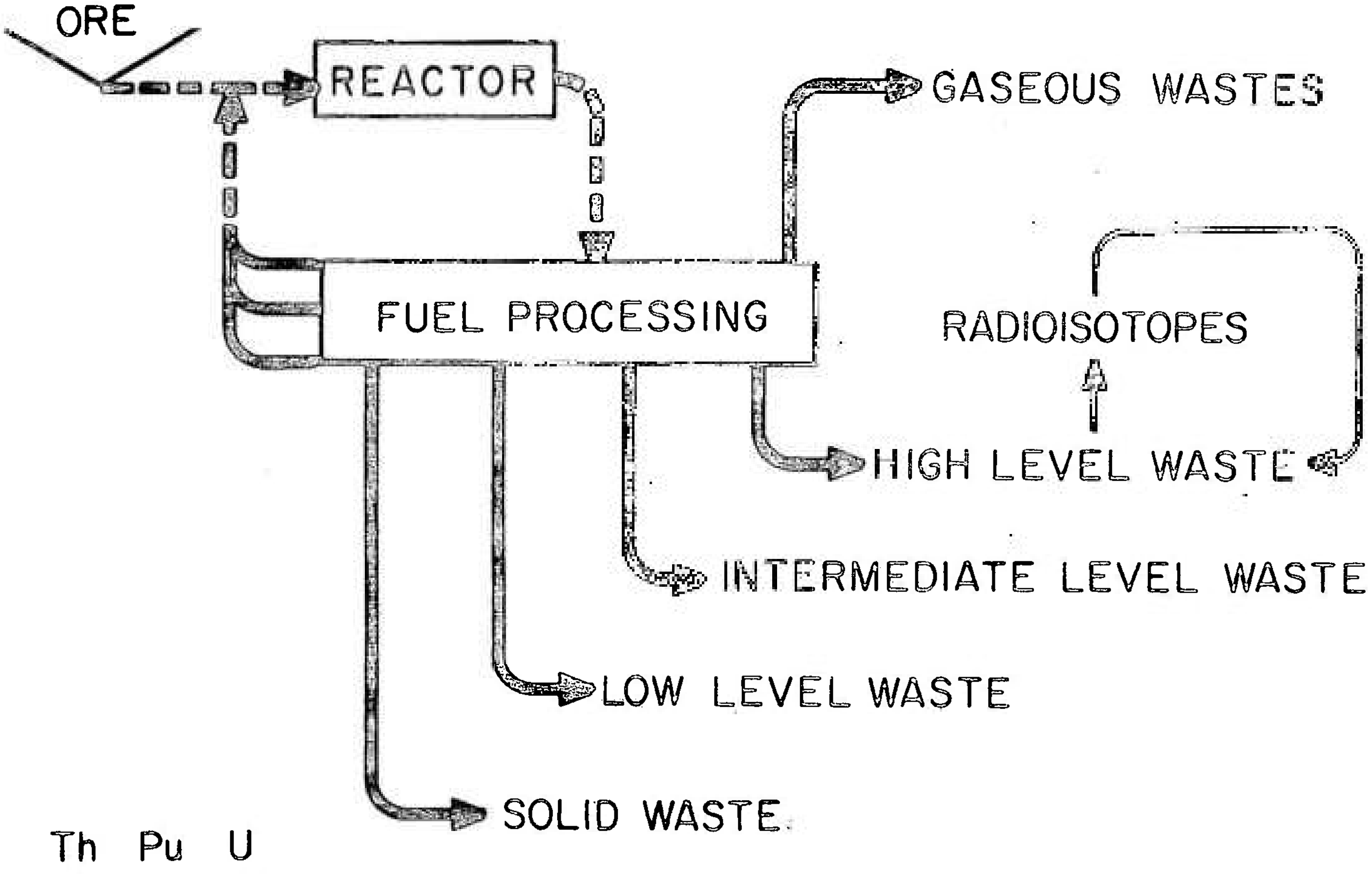
RADIOACTIVE WASTES FROM THE FUEL CYCLE

	Types of Wastes and Principal Constituents		Approximate Radioactivity Level (Ci/ton U)
Mining and Milling	Gaseous:	^{222}Rn, ^{218}Po, ^{214}Bi, ^{214}Po	10^{-4} - 10^{-3}
	Liquid, Solid:	U, ^{226}Ra, ^{230}Th, ^{210}Pb	0.5 - 1
Refining	Liquid:	^{238}U, ^{234}Th, ^{234}Pa, ^{226}Ra	10^{-4} - 10^{-3}
Fuel Fabrication	Liquid, Solid:	U, Pu, Th	10^{-4} - 10^{-3}
Reactor Operation	Gaseous:	^{13}N, ^{41}A, ^{89}Kr, ^{87}Kr, ^{138}Xe, ^{135}Xe	10 - 100[a]
	Liquid, Solid:	^{58}Co, ^{60}Co, ^{59}Fe, ^{51}Cr, ^{3}H	50 - 100[a]
Chemical Processing	Gaseous:	^{85}Kr, ^{133}Xe, ^{131}I	7000[b]
	Liquid, Solid:	Fission Products, Pu, Am, Cm	6,000,000[b]

[a] At time of waste discharge or shipment based on fuel exposure of 20,000 Mwd/ton of U.

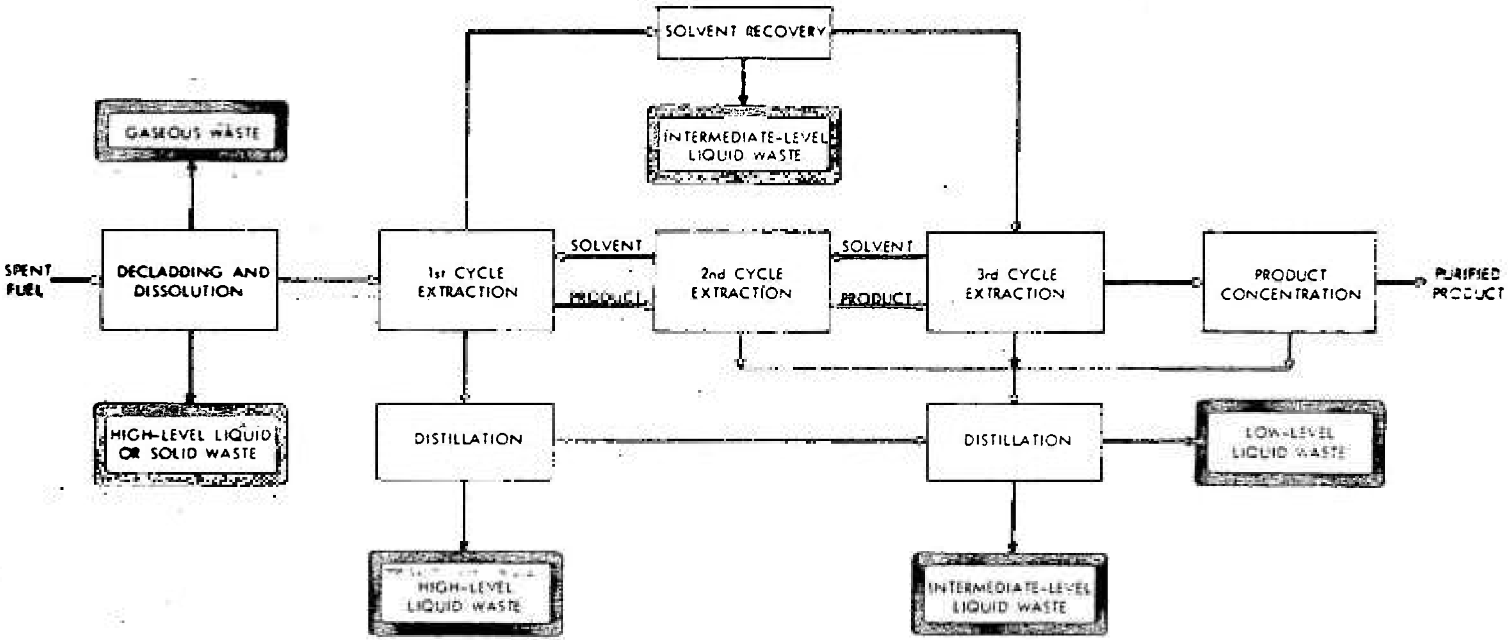
[b] Waste from fuel at 20,000 Mwd/ton, 120 days cooled.

ORNL-DWG 66-680



ORIGIN OF RADIOACTIVE WASTES

ORNL DWG 65-915



Origin of Fuel Processing Wastes.

ORNL DWG. 69-4599

PRINCIPAL FISSION PRODUCTS OF INTEREST IN WASTE DISPOSAL

Radionuclide	Half-Life	Percent of Total After Decay Indicated		
		100 days	3 years	30 years
Strontium-90	28 years	<2	15	49
Cesium-137	30 years	<2	15	49
Promethium-147	2.65 years	3	15	<1
Cerium-144	284 days	45	50	--
Krypton-85	10.6 years	<1	1	<1
Iodine-131	8.05 days	<1	--	--
Zirconium-95	65 days	33	--	--
Barium-140	12.8 days	<1	--	--
Ruthenium-103	40 days	5	--	--
Ruthenium-10~~3~~6	1.0 year	2	5	--

AQUEOUS METHODS FOR REPROCESSING LWR AND HTGR FUELS

R. E. Blanco

The lecture for today will cover a review of aqueous methods for processing nuclear fuels and represents the work of many people in the Chemical Technology Division of Oak Ridge National Laboratory and other US-AEC laboratories. I will start with the basic concepts and review the progress over the past 20 years. Finally, I will describe the methods used today and the estimated reprocessing costs. The methods being developed for future LMFBR fuel will be discussed in subsequent lectures.

SLIDE 1 Important Reactor Fuel Types in the U. S. (67-5489)

This slide shows the important fuel types. Today I will describe the aqueous processing methods for the plutonium production and thermal power reactor fuels.

SLIDE 2 Typical Fuel Assemblies (Photo 83597)

This slide shows typical fuel assemblies. (a) Zr-2-clad Dresden, (b) stainless steel-clad-ThO_2-UO_2 Elk River, and (c) stainless steel-clad-UO_2. The length containing active materials is about 3 meters and the tube diameter is about 1.2 cm. Note the massive end assemblies that are removed by abrasive disc sawing prior to processing.

SLIDE 3 Experimental Graphite Fuel (Photo 85576)

This shows a section of an experimental graphite fuel block for the Public Service of Colorado reactor. The holes would be filled with $\sim 100\,\mu$ diam particles of ThC and UC imbedded in a resin binder. The present form of graphite fuel for the Peach Bottom Reactor has the particles imbedded in the massive graphite. The actual fuel may be hexagonal (14 in. across the flat faces). The Peach Bottom fuel is 3-in.-diam rods 90-in.-long with Th/U carbide particles imbedded in the graphite.

SLIDE 4 Steps in Reactor Fuel Processing (67-5196)

All reactor fuels require some form of mechanical disassembly such as sawing off the end boxes and some form of dissolution to convert them to the physical form required for the separation step. Pure Pu, Th, and U are produced in the separation step and a waste stream containing fission product poisons and valuable radioisotopes. The products U, Pu, and Th are refabricated into new fuels. If essentially all of the radioactive fission products have been removed, they generally can be handled directly without hazards. If large amounts of fission products remain, the fuel must be refabricated remotely behind massive shielding.

SLIDE 5 Principal Separation Methods (67-5488)

Solvent extraction is the primary separation method used at all processing plants in the world today. A high decontamination factor is obtained and thus, the U product can be handled directly during fuel refabrication without hazard. The plutonium can also be refabricated directly into fuels for a few cycles. Ion exchange also achieves high decontamination and it is generally used as a final cleanup step after solvent extraction in the processing plants. The volatility process also achieves high decontamination factors but further pilot plant tests are required to demonstrate its feasibility. Pyrochemical processes are being developed by Argonne National Laboratory. These processes achieve low decontamination factors and are designed for fast recycle of fuels and remote fuel fabrication. Precipitation is not used as a primary separation method. It is relatively expensive, since it is not a continuous process, such as solvent extraction. The decontamination factors are generally very low and losses of valuable materials are high. Recovery of greater than 99% and preferably 99.9% of the U, Pu, and Th are required because of their value, \$12/g ^{235}U and \$10/g Pu, and \$20/kg natural U and \$10 kg Th.

SLIDE 6 Definition of Terms (67-5223)

SLIDE 7 Types of Solvents Used (67-5224)

The principal solvent used in all processing plants is TBP in a hydrocarbon diluent. Normal dodecane is the best diluent because of its stability to radiation and acid degradation. Hexone is still used at one plant in the U. S. and the United Kingodm used an ether, Butex ($C_4H_9 \cdot O(C_2H_4 \cdot O)_2 \cdot C_4H_9$) in addition to TBP.

SLIDE 8 Distribution Coefficients in the Purex Process (64-6175)

This slide illustrates the principal of the Purex process for the separation of Pu and U from fission products. When the Pu is in the Pu^{+4} state it extracts with the U, i.e., a high distribution coefficient. Thus, U and Pu are separated from the fission products which have low distribution coefficients. In the next step the Pu is reduced to Pu^{+3} (a low distribution coefficient) with ferrous sulfamate ($Fe(SO_3NH_2)_2$) and the Pu is separated from the uranium.

SLIDE 9 Solvent Saturation in the Purex Process (10452)

This illustrates the increase in separation of the U and Pu from the rare earths as the saturation of the solvent with uranium increases. This is controlled by the rate of flow of the organic and aqueous streams.

SLIDE 10 Purex Process Flowsheet (67-6342R)

All fuel reprocessing plants in the world use this process or versions of this process. This also illustrates the Thorex process by substituting Th for Pu; $Fe(SO_3NH_2)_2$ would not be used.

SLIDE 11 Purification of Plutonium by Cation Exchange (67-5194)

Plutonium is maintained in the Pu^{+3} state with hydroxyl amine. The plutonium is adsorbed and some of the U and FP's pass through the column. The remaining uranium and fission products are removed by the sulfuric acid wash. The plutonium product is then recovered by elution with nitric acid. The sulfamic acid is present to prevent oxidation of the plutonium by the HNO_3 and the formation of oxide gases in the resin bed.

SLIDE 12 Purification of Plutonium by Anion Exchange (67-5195)

Pu^{+4} is converted to an anion in concentrated (7 M) HNO_3 and is sorbed on the anionic resin. The uranium and fission products remain as cations and pass through the column, thus providing an excellent separation from plutonium. The plutonium is removed from the resin with dilute HNO_3 (0.6 M) which converts the Pu to the cationic Pu^{+4} form. The plutonium is also concentrated from about 0.6 g/liter to 50 g/liter in the product.

All of the fuel processing plants in the world use solvent extraction and ion exchange processes similar to those that I have shown. Basic developments of these processes was completed by 1955 but new improvements have been made continually since that time. The major development effort since then has been to develop head-end fuel dissolution methods for the new fuel types which have stainless steel and zirconium cladding or consist of massive graphite. The older fuels had aluminum cladding which was easily dissolved in caustic. The next three slides illustrate the decladding processes that were developed in the period 1955-1960. Similar processes are now used at the Eurochemic plant at Mol, Belgium.

SLIDE 13 (No title) (Lr 55537)

This slide illustrates the use of NaOH containing $NaNO_3$ to dissolve the aluminum cladding. The presence of $NaNO_3$ prevents the formation of hazardous hydrogen and the products are ammonia and nitrogen. The caustic-aluminum solution is sent to an underground waste tank for storage. The UO_2 or U metal core is not soluble and the loss of U and Pu to the decladding solution is $< 0.1\%$. The core is then dissolved in nitric acid.

SLIDE 14 Sulfex Process for Dejacketing Stainless Steel Jacketed Fuels with Dilute Sulfuric Acid (LR 31144)

In this case, 6 M H_2SO_4 is used to dissolve the stainless steel cladding. The hydrogen formed must be diluted to a non-explosive concentration. The loss of U to the decladding solution is less than 0.01% for non-irradiated fuel. A special high nickel stainless steel alloy, Carpenter 20 or Ni-o-nel, must be used as a material of construction.

SLIDE 15 Zirflex Process for Dejacketing Zircaloy-2 Jacketed Fuels with Ammonium Fluoride (LR 31143)

In this case, a mixture of NH_4F and NH_4NO_3 is used to dissolve Zircaloy cladding. The gaseous product is ammonia. The high nickel alloy Ni-o-nel is a satisfactory material of construction. The losses of U was $< 0.02\%$ for unirradiated fuel.

SLIDE 16 Sulfex Decladding of Irradiated SS-UO_2 Fuel Pins (LR 69211)

The next three slides illustrate the type of experiments that are performed to develop fuel processing methods. In this case we are determining the effect of lenght of irradiation time on the loss of U and Pu to the decladding solutions and on the dissolution rate. Here, we see that the loss of U and Pu did not increase significantly and the dissolution rate of UO_2 in HNO_3 was about the same.

SLIDE 17 Zirflex Decladding of Irradiated Zr-2-UO_2 Fuel Pins (LR 69212)

Here again we see no significant increase in U and Pu loss.

SLIDE 18 Sulfex Decladding of Irradiated ThO_2 - UO_2 Fuel Pins (LR 61539)

Here we see that the loss of U and Th increased with irradiation level so that we suspect that sulfex decladding may not be satisfactory for ThO_2-UO_2 fuels. Normally ThO_2-UO_2 dissolves relatively slowly in 13 M HNO_3--0.05 M HNO_3--0.05 M Al but the dissolution rate was 5 to 6 times faster for highly irradiated fuels. Generally, for ThO_2-UO_2 and PuO_2-UO_2 fuels, we have found a faster dissolution rate at higher irradiation levels than at zero irradiation. However, conversely for UC fuels, we found that unirradiated carbides were soluble in nitric acid but that they became passive after irradiation. All of this serves to illustrate the need for tests on irradiated fuels to establish precise process conditions.

SLIDE 19 Fast Oxide Breeder Processing (64-7520)

These results show that the losses of U and Pu are excessively high in the sulfex process for highly irradiated fast reactor oxide fuels. In addition, we found that the radioactive ^{137}Cs migrated to the surface and appeared in the sulfex solution creating a waste storage problem.

Thus, in summary for the aqueous decladding processes, the Sulfex and Zirflex processes are satisfactory in terms of Pu and U losses for the thermal power reactor fuels containing UO_2 but are probably not acceptable for ThO_2-UO_2 fuels or for fast reactor UO_2-PuO_2 fuels. In addition, the large volumes of aqueous declading wastes constituted an expensive storage problem.

In the last 10 yr a mechanical shear leach process has been developed to cut the fuels into short pieces from which the cores can be leached with acids. Thus, the Sulfex and Zirflex processes have never been used in the U. S. Our production plants use caustic to dissolve the aluminum cladding but our first commercial processing plant, the Nuclear Fuel Services Plant, uses the shear-leach process. The second plant, to be built by General Electric, will also use this process.

SLIDE 20 Shear-Leach Cycle (63-2800R)

In this process the cladding remains in the metallic form and is buried in the earth or stored in a concrete vault. Published reports claim that the shear-leach process costs 20 to 30 times less than the aqueous Sulfex and Zirflex processes for the removal and storage of the cladding material.

SLIDE 21 (No title) (Photo 62615)

You will see this 250 ton shear in a movie to be shown at a later lecture session.

SLIDE 22 (No title) (Photo 55391)

SLIDE 23 (No title) (Photo 55395)

SLIDE 24 (No title) (Photo 55398)

SLIDE 25 (No title) (Photo 55390)

SLIDE 26 Typical Product Resulting from Intact Shearing (1-in. lengths) of Porcelain Filled Consolidated Edison Core B Fuel Assembly (Photo 66439)

The presence of grids in advanced fuels causes the product to jam up in the discharge tube.

SLIDE 27 Consolidated Edison Core B Multi-Tube Withdrawal Mechanism (647235)

Machine is designed to push the tubes from the assembly so that they can be sheared in bundles free from the basket grids.

SLIDE 28 Perforated Baskets Evaluated in Bench Scale Leaching Studies (Photo 63947R1)

Shows different types of basket receivers tested. A simple triangular array of holes with 5% of total surface as openings was best.

SLIDE 29 Engineering Scale Batch Leacher (64-4184 R1)

Thermo cyclic leacher; 9-in.-ID x 10-ft-high. Fines are flushed from bottom. Liquid comes through sides of basket. The dissolution rate is about 0.5 ton of U/day, with about 2 hr for each batch of fuel. Zircaloy and stainless steel fines do not accumulate in the leacher. They collected in the effluent. Large amounts of zircaloy fines are not allowed to accumulate to eliminate the hazard of fire. They are dissolved in HF-HNO_3.

SLIDE 30 Inclined Drum Leacher for Countercurrent Nitric Acid Leaching of UO_2 from Sheared Pieces of Metal Clad UO_2 (LR 38945)

The leacher is an Archimedes screw which raises the solids countercurrent to the acid flowing downwards (20-in.-diam x 6-ft-long, semi-continuous turning). This unit could dissolve about 1 ton/day of UO_2 but was not very successful because the UO_2 and ThO_2-UO_2 settled as a sludge which was not contacted efficiently by the acid.

SLIDE 31 Neutron Activation Apparatus and Leached-Hull Monitor (Photo 86939R)

This monitor is used to determine the amount of U or Pu remaining in the cladding pieces prior to discharge. A 150 kv Cockcroft-Walton accelerator generated neutrons (3-5 x 10^{10} neut/sec) to activate residual fuel. Delayed neutrons emitted by the fuel are counted. As little as 0.01 g of ^{235}U can be detected in an 8-in x 8-in. section in the presence of 831 R/hr of ^{60}Co gamma radiation.

SLIDE 32 Typical Shear-Leach Data (64-7770)

SLIDE 33 Burn-Leach Process for HTGR Fuels (68-12733)

At present, the Peach Bottom Reactor near Delta, Pennsylvania, is the only HTGR in operation in the United States. This reactor currently uses hot-pressed graphite fuel compacts containing pyrolytic-carbon-coated (Th, U)C_2 particles rather than the improved fuels planned for future HTGR's. The second HTGR, the Fort St. Vrain Reactor, is expected to be completed in 1972. This 330-Mw HTGR prototype will contain hexagonally shaped graphite fuel elements (or blocks) that are about 31 in. long and 14 in. across the flats. (These fuel elements are similar to those planned by Gulf General Atomic for future HTGR's.) The fuel will consist of coated particles that are held in vertical holes of the hexagonal fuel block by means of a carbonized resin binder. Three basic types of particles will be used — a ThC_2 fertile particle, a $^{235}UC_2$ fuel particle, and a ThO_2-$^{233}UO_2$ recycle particle. All of these particles will be triplex-coated, with a buffer coating and an outer coating of pyrolytic carbon and an intermediate coating of silicon carbide. A fuel burnup of about 80,000 Mwd/ton is anticipated.

Methods for processing HTGR fuels are being developed. The objectives are to recover the ^{233}U and the thorium from the fertile and recycle particles and to separate the highly burned ^{235}U particles. The high ^{236}U content of the latter makes the ^{235}U undesirable for recycle to this reactor. The burn-leach process has been selected as the preferred reprocessing method as opposed to the grind-leach process. The major factor in this choise is the necessity of physically separating the particles.

The principal processing problems encountered in the burn-leach method are: (1) mechanical operations prior to burning, (2) control of the fluidized-bed burner, (3) removal of radioactive particles and gases from the off-gas, and (4) separation of the ^{233}U-containing particles from the ^{235}U particles. This slide shows the tentative flowsheet for processing HTGR fuel, studied at ORNL. The fuel block is sawed and crushed prior to burning in a fluidized bed of alumina. Initial sawing, crushing, and burning tests of full-size unirradiated fuel were successful. Hot-cell tests, using 1-1/2-and 3-in.diam burners and long-cooled, Peach Bottom type fuel samples that had been irradiated up to 41,500 Mwd/ton were also successful. The gas leaving the cooled sintered stainless steel filters was clean enough to be discharged without further treatment. However, additional safety can be ensured by passage of the gas through absolute filters and subsequent dilution in the discharge stack. Preliminary tests indicate that screening would be an effective method for separating the ^{233}U, ^{235}U, and alumina particles. A roll grinder could be used to crush the silicon carbide coating to expose the core to the Thorex leach solution (13 M HNO_3, 0.05 M Al^{3+}, 0.05 M F^-). Burning the residue carbon before leaching may be required, if losses of uranium and thorium to the inner graphite coating are significant. Finally, the thorium and uranium will be separated from the fission products and from each other by the Thorex solvent extraction process.

A conventional processing plant designed for LWR reactor fuel would require a separate head-end system to burn and leach HTGR fuel; however, the Thorex process could, undoubtedly, be adapted for use in the existing solvent extraction equipment.

SLIDE 34 Hot Cell Burner (69-9489)

Fluidized bed of 60-120 mesh alumina.

This illustrates the type of experimental equipment used to develop the burn-leach process. The principal problem in the burn-leach process is the feasibility of preventing the loss of radioactive dusts in the off-gas. Approximately 30 tests with radioactive fuels have just been completed and we believe that the sintered metal filter, with the coating of graphite dust that collects on it, will give decontamination factors of at least 10^6 for Ru, Cs, and gross gamma activity. This combined with back-up filters will provide adequate off-gas decontamination. The uranium and thorium is easily recovered from the ashes by leaching.

SLIDE 35 Effect of Filter Temperature on Fission Product Removal (67-5229)

This data shows that the decontamination factor decreases as the temperature increases but that completely satisfactory fission product removal was obtained at temperatures below 300°C. The activity of the gas leaving the carbon coated sintered metal filter was predominantly ^{137}Cs, with a specific activity of 1.3×10^{-11} μc/cc at 100°C. This is lower than the MPC for the population at large for continual exposure of 2×10^{-9} μc/cc. An additional dilution of the off-gas by a factor of at least 10^6 would be required in any event for diluting ^{85}Kr when processing 85,000 Mwd/ton fuel. Thus, you can see that off-gas dilution to control krypton is added insurance, even if we did not use absolute off-gas filters to back up the sintered metal filter. We have demonstred that absolute filters will remove residual particulate material. We think this conclusively demonstrates a satisfactory and simple off-gas cleanup system.

The small amount of particles that pass through the sintered filter appears to be an aerosol of Ru-Cs with a particle size of less than 0.2 μ. Essentially all of this material was retained on the first 5 fiberglass filter packs and none could be detected after the 5th pack. The final gas contained $<$ 100 counts/min/ml.

SLIDE 36 Leaching the Alumina-Ash Residue from Burning Graphite Fuels (67-5228)

These results show that satisfactory recovery of uranium and thorium were achieved and that relatively small amounts of radioactivity, about 6% of the gross gamma, remains with the alumina. Since the alumina will probably be recycled, this residual activity should not be a major problem. It appears that the alumina must be stored as a high-level waste in any event. A flow-sheet was developed where the amount of alumina to be leached was reduced by 20-40%. In this case, the ash residue is sieved to separate most of the 40-μ-diam ThO_2-U_3O_8 from the 200-μ-diam alumina particles. Only the former is leached and the latter is recycled.

SLIDE 37 Roll Grinder (66-149R)

Graphite fuel is first broken to about -6 mesh in a hammer mill and then passed into the 4-in.-wide x 12-in.-diam rolls. This roller could crush about 0.25 metric ton of (U + Th) Peach Bottom fuel per day. Uranium recovery by acid leaching was about 99% when the UC_2 fuel particles were 75μ in diameter and 99.8% when they were 150 μ. With highly irradiated fuels (8850 to 41,500 Mwd/ton) the uranium and thorium losses are 1-5% and 2.5-7%, respectively and 20-30% of the fission products (Ru, Cs, and Ce) remain in the graphite. Thus, at present, the grind-leach process does not appear to be satisfactory for U/Th carbide in graphite fuels.

SLIDE 38 Flowsheet Nomenclature (LR 40141)

Originally the solvent extraction flowsheet names had specific meanings – they now apply only to types. Purex refers to the extraction of depleated, natural, or slightly enriched uranium and plutonium with TBP solutions in a diluent($\sim$1 M TBP $\approx$30%). Thorex refers to the extraction of Th and ^{233}U with TBP solutions (generally 1 M or greater). Interim 23 (Int.23) refers to the extraction of ^{233}U using dilute TBP solutions leaving the Th with the fission products.

SLIDE 39 Acid Thorex Flowsheet (LR 74020R1)

The flowsheet presently used to recover thorium and uranium-233 from irradiated thorium is designated the "Acid Thorex Flowsheet." This name indicates that nitric acid rather than aluminum nitrate is used as the salting agent. The feed solution contains less than a stoichiometric amount of nitrate; that is, it is "acid deficient". This "acid deficient" feed results in the conversion of protactinium, zirconium, and niobium to hydroxynitrates which are very insoluble in the solvent. This provides greatly increased separation from these radionuclides. Acid deficient feeds cannot be used in Purex flowsheets due to the formation of inextractable plutonium polymers at these low acid conditions.

The salting acid necessary for complete thorium extraction is added below the feed plate. If acid were added at the feed plate, the solubility of the thorium-TBP complex in the kerosene type diluent would be decreased so much that two organic phases would be formed (third phase formation).

The use of HNO_3 rather than $Al(NO_3)_3$ results in a great decrease in the salt content and volume of the aqueous waste from thorium processing plants without loss of decontamination from fission products.

SLIDE 40 Interim-23 For Recovery of Uranium-233 (Dwg. 74020-RI)

The Interim-23 flowsheet was developed for the recovery of the uranium-233 from irradiated thorium while allowing the thorium to remain in the aqueous waste with the fission products. This separation is accomplished by using dilute solvent which is highly saturated with the uranium and therefore prevents thorium extraction.

This slide shows a later modification of the flowsheet where di-sec-butyl phosphonate is used instead of TBP. This solvent gave better separation of U from Th.

SLIDE 41 Effect of Thorium Loading on Fission Product Decontamination (LR-Dwg. 21059)

Satisfactory separation of the desired metals from fission products can be obtained only by using favorable operating conditions. If more solvent is used than is necessary to extract the desired metal, additional fission products will be extracted thereby decreasing the decontamination factor. However, if insufficient solvent is used, the losses of the desired products become excessive. This slide shows this principle using thorium extraction as an example. The more highly saturated the solvent becomes in the solvent, the greater the decontamination from fission products.

From this slide, it would appear that zirconium-niobium and ruthenium are more easily separated from thorium than are the rare earth elements. The reverse is true. A small amount of the zirconium-niobium and ruthenium is highly extractable and accompanies the thorium through the extraction because several different kinds of complexes occur.

SLIDE 42 Effect of Acidity of Scrub on Decontamination (LR-Dwg. 40136)

This slide illustrates the effect of scrub acidity on the decontamination of thorium from zirconium-niobium and ruthenium. Note that at low acidities, the separation of zirconium-niobium is greatest, whereas that of ruthenium is least. At high acidities, the reverse is true. The choise of acidity, therefore depends upon the history of the fuel to be processed, i.e. cooling time, dissolution conditions, etc.

SLIDE 43 Estimated Total U. S. Nuclear Electric Capacity (66-166 R4)

The recent growth of the nuclear industry in the U. S. has been unexpectedly fast. About 50% of the new steam electric plants are nuclear in 1967 to 1969 as compared to 26% in 1965. The predicted growth of the nuclear industry is shown is Slide 43, i.e., to about 150,000 Mw(e) in 1980, 280,000 Mw(e) in 1985, and 734,000 by the year 2000. Actually, the long-range estimates are uncertain and range from 130,000 to 170,000 Mw(e) in 1980 and 675,000 to 734,000 Mw(e) in the year 2000. Thus, we would need to process about 8 to 14 metric tons of uranium per day in the year 1980, and 25 to 50 tons per day in the year 2000. This would require 25 to 50 one-ton-per-day plants and, consequently, we at ORNL tend to favor the use of larger 6- to 10-ton-per-day plants where the predicted unit processing costs are lower.

One private U. S. company, the Nuclear Fuels Services Company (NFS), is in operation at the present time and the General Electric (G. E), Allied Chemical, and Atlantic Richfield Companies have announced their intention of entering the field. The NFS and G. E. plants have capacities of 1 or possibly 2 tons of fuel per day for the present reactor types and Allied (and probably Atlantic Richfield) 5 tons per day. The present power reactors are slightly enriched uranium dioxide clad in Zircaloy-2 or stainless steel and are pressurized water or boiling water reactors.

SLIDE 44 Approximate Nuclear and Coal Power Costs (mills/kwh) (67-5200)

This slide shows the cost factors in producing nuclear energy. The cost of the reactor is relatively large and the total cost of fuel processing and the disposal of radioactive wastes is about 4.2% of the total. With private financing, nuclear power costs about 4.0 vs 4.33 for a coal plant. Private financing includes a fixed charge rate of 12% for the reactor and 22% for the processing plant compared to 7 and 7.7 for public financing. Public financing does not include taxes and the return on investment is 4-5% vs 6-12% for the private case.

SLIDE 45 Importance of Size in Fuel Processing (67-5199)

This slide shows the effect of size of the processing plant on fuel processing costs. For an increase in processing rate by a factor of 5 the capital cost only doubles and the unit cost decreases from 0.17 to 0.07 mills/kwh. The cost of money and plant depreciation is a big fraction of the cost (~ 58%). Therefore, we favor larger chemical plants.

SLIDE 46 Projected Costs of LWR Fuel: Processing, (68-12231) Waste Management, and Shipping

To demonstrate the trend that we expect to observe in reprocessing costs, we have projected the costs of fuel processing, waste management, and shipping. Assuming that the installed nuclear-generated electrical capacity will increase from 12,000 Mw(e) of LWR's in 1970 to about 50,000 in 1975 and about 200,000 (plus ~30,000 of LMFBR's) in 1985, the fuel processing rate will increase from less than 1 ton/day in 1970 to approximately 5 tons/day in 1975 and approximately 30 tons/day in 1985.

The predicted costs, which are based on present-day dollars, with no allowance for escalation, and a constant LWR fuel burnup of 20,000 Mwd/ton, reflect, primarily, the effect of plant size. Presently, the combined processing-waste management cost for LWR fuels irradiated to a burnup of 20,000 Mwd/ton is about 0.2 mill/kwhr(e), as set by the NFS price schedule. By 1975, assuming the existence of one or more plants of 3- to 5-tons/day capacity, this cost should decrease to about 0.18 mill/kwhr(e). By 1985, assuming several plants of 5- to 10-tons/day capacity to be on-stream, the cost should decline still further to approximately 0.11 mill/kwhr(e). The cost for processing LMFBR fuel is estimated to be about twice that for LWR fuel on a weight basis; however, on a mill/kwhr(e) basis, it should be about equal to that for LWR fuel because of the higher burnup and thermal efficiency of the former. The expected lower cost in the future results from the lower unit costs that are anticipated for the larger-sized plants assumed. If future fuel burnups exceed 20,000 Mwd/ton, a further reduction in processing costs should be realized; however, this would not change the waste management costs.

CONCLUSION:

In conclusion, I would like to outline aqueous fuel processing problems to be studied in the future. These include: (1) Developing better head-end methods; (2) Perfecting processes for the graphite fuels; and (3) Adapting the present head-end and solvent extraction methods to the processing of fast reactor fuels.

REFERENCES AND EXCERPTS FROM:

1. Don E. Ferguson and R. E. Blanco, "General Survey of Reprocessing of Thermal Reactor Fuels," presented at the 1968 American Nuclear Society International Meeting in Washington, D. C., November 10-15, 1968; to be published in the *Proceedings.*

2. *Chem. Technol. Div. Ann. Prog. Rept. May 31, 1967*, ORNL-4145 (Oct. 1967).

3. *Chem. Technol. Div. Ann. Prog. Rept. May 31, 1968*, ORNL-4272 (Sept. 1968).

4. *Chem. Technol. Div. Ann. Prog. Rept. May 31, 1969*, ORNL-4422 (in press)

5. V. C. A. Vaughen, J. H. Goode, J. R. Flanary, H. O. G. Witte, *Hot-Cell Evaluation of the Burn-Leach Method for Reprocessing Irradiated Graphite-Base HTGR Fuels*, ORNL-4120 (to be published).

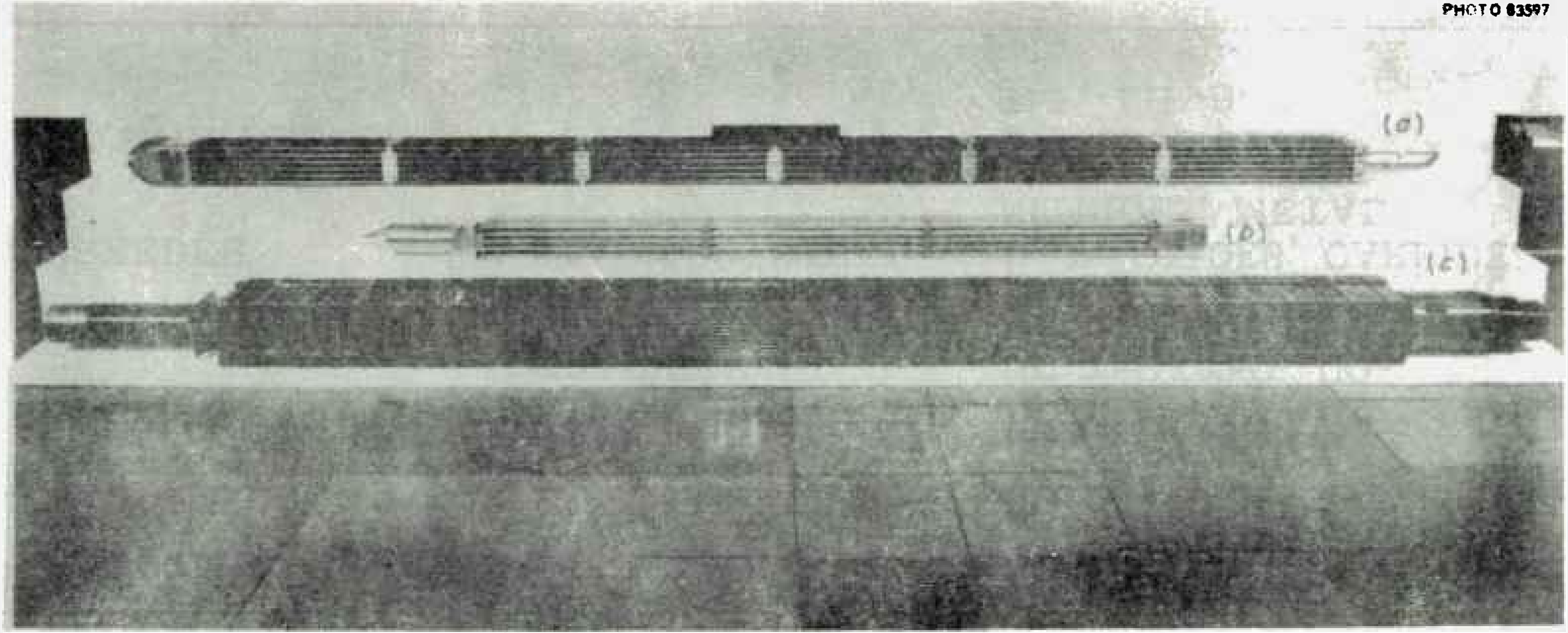
6. F. L. Culler and R. E. Blanco, "Dissolution and Feed Preparation for Aqueous Radiochemical Separation Processes," Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Vol. 17, United Nations, Sept. 1 – Sept. 13, 1958, P/ 1930.

7. F. L. Culler, Jr., and R. E. Blanco, "Advances in Aqueous Processing of Power Reactor Fuels," Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy, Vol. 10, United Nations, August 31 – Sept. 9, 1964, P/249.

IMPORTANT REACTOR FUEL TYPES IN THE U.S.

	CLAD	CORE
Pu PRODUCTION	ALUMINUM	U METAL
THERMAL POWER	ZIRCALOY-2	UO_2
	STAINLESS STEEL	UO_2
	GRAPHITE	UC-ThC, ThO_2-UO_2 (~ 100 μ spheres)
FAST BREEDER	STAINLESS STEEL	U, Pu OXIDES, CARBIDES, NITRIDES, METAL
MOLTEN SALT BREEDER	--------	LiF-BeF_2-UF_4 ThF_4-LiF-BeF_2

PHOTO 83597

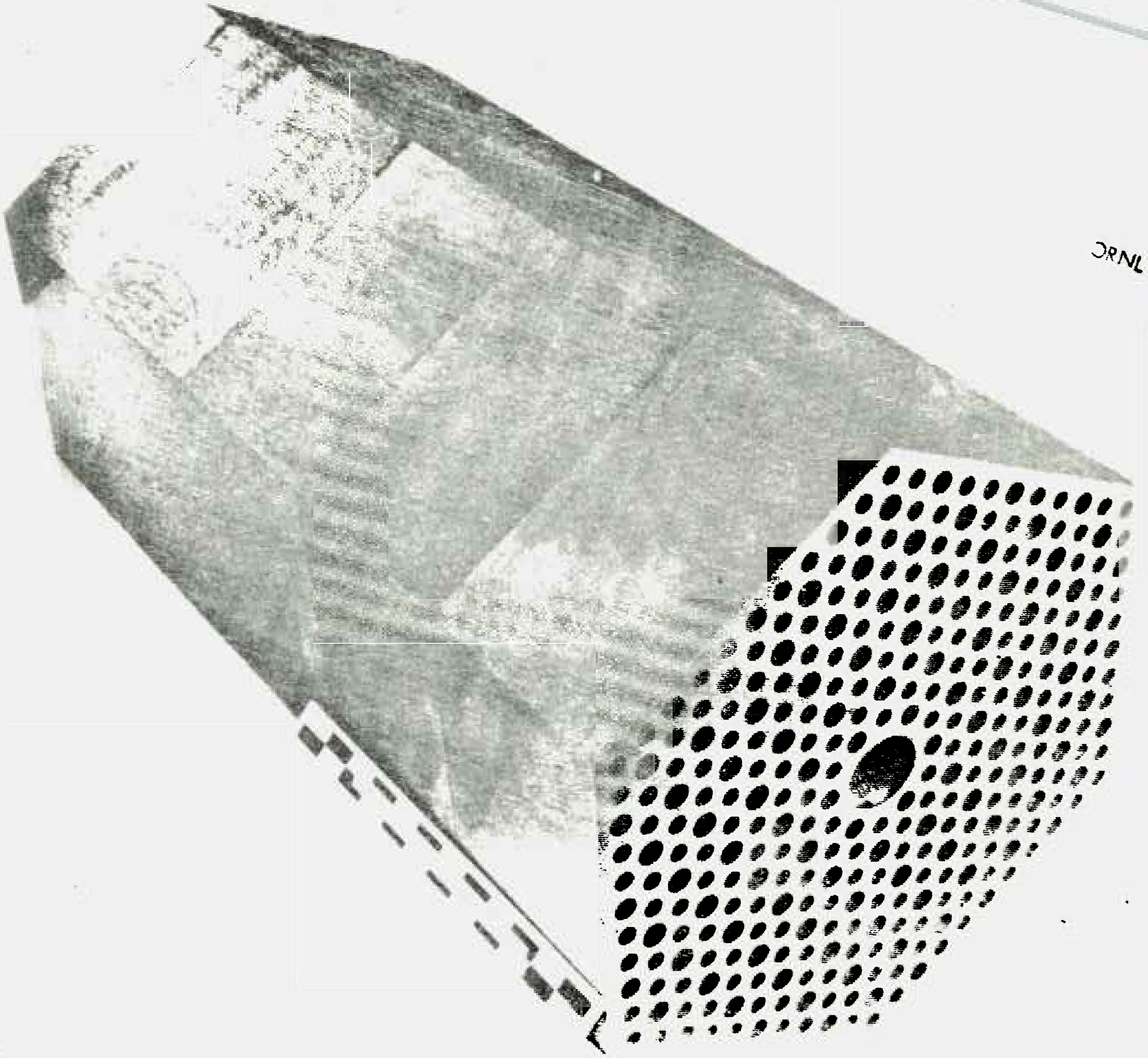


FUEL ASSEMBLIES

a. DRESDEN - Zr-2 - UO_2

b. ELECTRIC POWER - SS - UO_2 - ThO_2

c. CON EDISON - SS - UO_2



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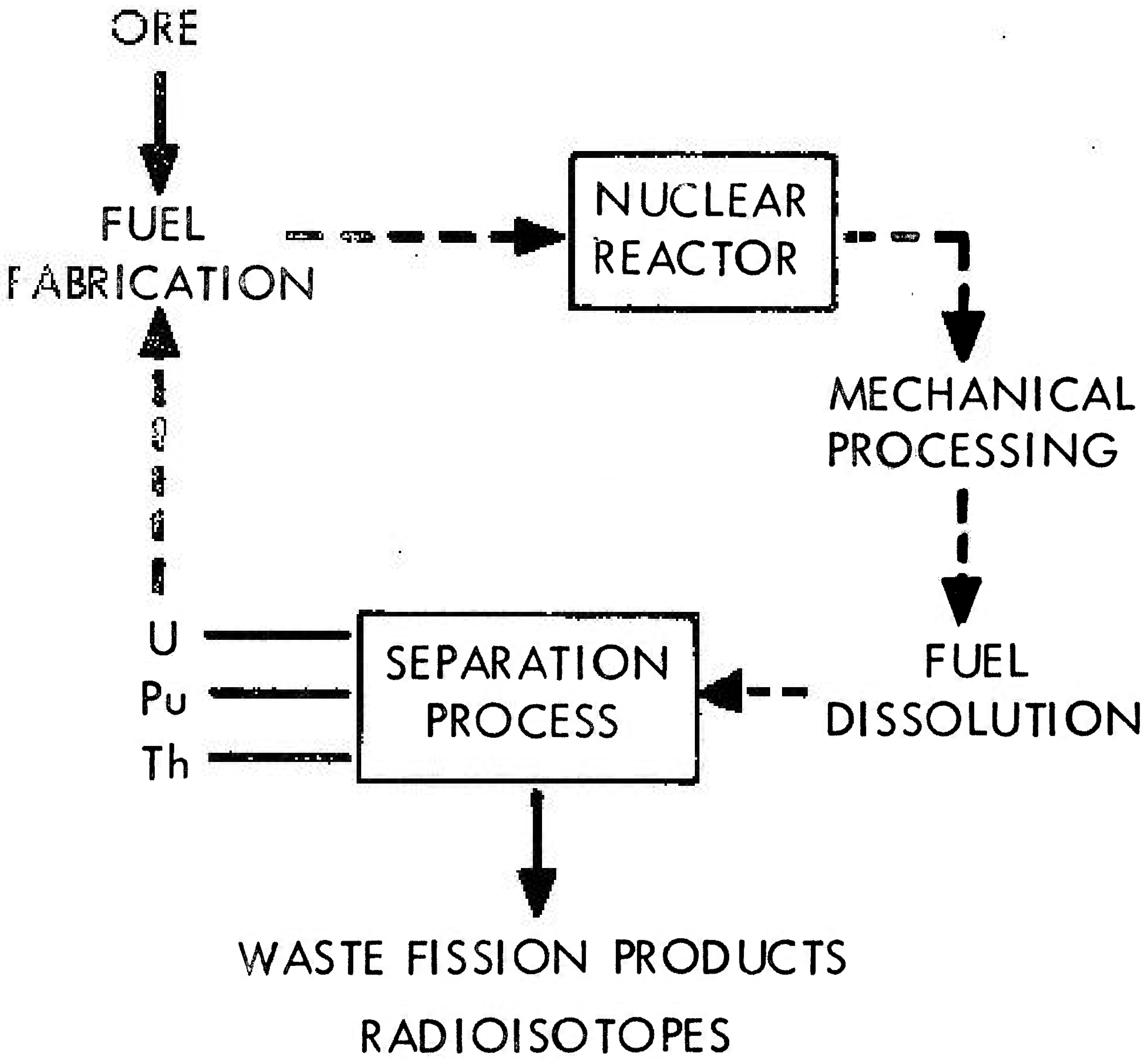
ORNL Dwg. 67-5196

STEPS IN REACTOR FUEL PROCESSING



ORNL DWG. 67-5488

PRINCIPAL SEPARATION METHODS	DECONTAMINATION FACTOR	FUEL FABRICATION	STATUS
SOLVENT EXTRACTION	HIGH (10^6-10^8)	DIRECT	PRODUCTION PLANTS
ION EXCHANGE	HIGH (10^6-10^8)	DIRECT	PRODUCTION PLANTS
FLUORIDE VOLATILITY	HIGH (10^6-10^8)	DIRECT	PILOT PLANT
METAL MELT REFINING	LOW (3)	REMOTE	PILOT PLANT
PYROCHEMICAL	MEDIUM (10^2-10^4)	REMOTE	LABORATORY
(PRECIPITATION)	(LOW 1 to 20)		(PRODUCTION PLANT)

ORNL DWG 67-5223

DEFINITION OF TERMS

Distribution Coefficient	U,DC_a^o	$\frac{\text{U Conc. in Organic Phase}}{\text{U Conc. in Aqueous Phase}}$
Separation Factor for U/Th	SF_{Th}^{U}	$\frac{U,DC_a^o}{Th,DC_a^o}$
Decontamination Factor for Ru	Ru, DF	$\frac{\text{Original, Cts Ru min}^{-1}\text{ (gU)}^{-1}}{\text{Product, Cts Ru min}^{-1}\text{ (gU)}^{-1}}$

ORNL DWG 67-5224

SOLVENTS AND DILUENTS USED IN THE UNITED STATES

Solvent	Aqueous Phase	Separation Process
Tri-n-butyl Phosphate (TBP)	HNO_3	Purex Thorex
Methyl-iso-butyl (Hexone) Ketone	$Al(NO_3)_3$	Redox
Di-butyl-carbitol (Carbitol)	$Al(NO_3)_3$	U Recovery
Diluents		
Normal-dodecane (NDD)		
Amsco	50% Naphthenes (C_5-C_6), 45% branched paraffins, 5% n-paraffins	
Ultrasene	57% Naphthenes and branched paraffins, 40% n-paraffins	

ORNL DWG. 64-6175

DISTRIBUTION COEFFICIENTS BETWEEN 3 M HNO_3 AND 30% TBP (80% SATURATION WITH URANIUM)

Ion	DC
U VI	8
Th IV	2
Pu VI	0.8
Pu IV	2
Pu III	1×10^{-3}
Cs I	$< 10^{4}$
TRE III	4×10^{-4}
Ce III	1×10^{-2}
Zr	1×10^{-3}
Ru (variable with complex)	1×10^{-3} to 2

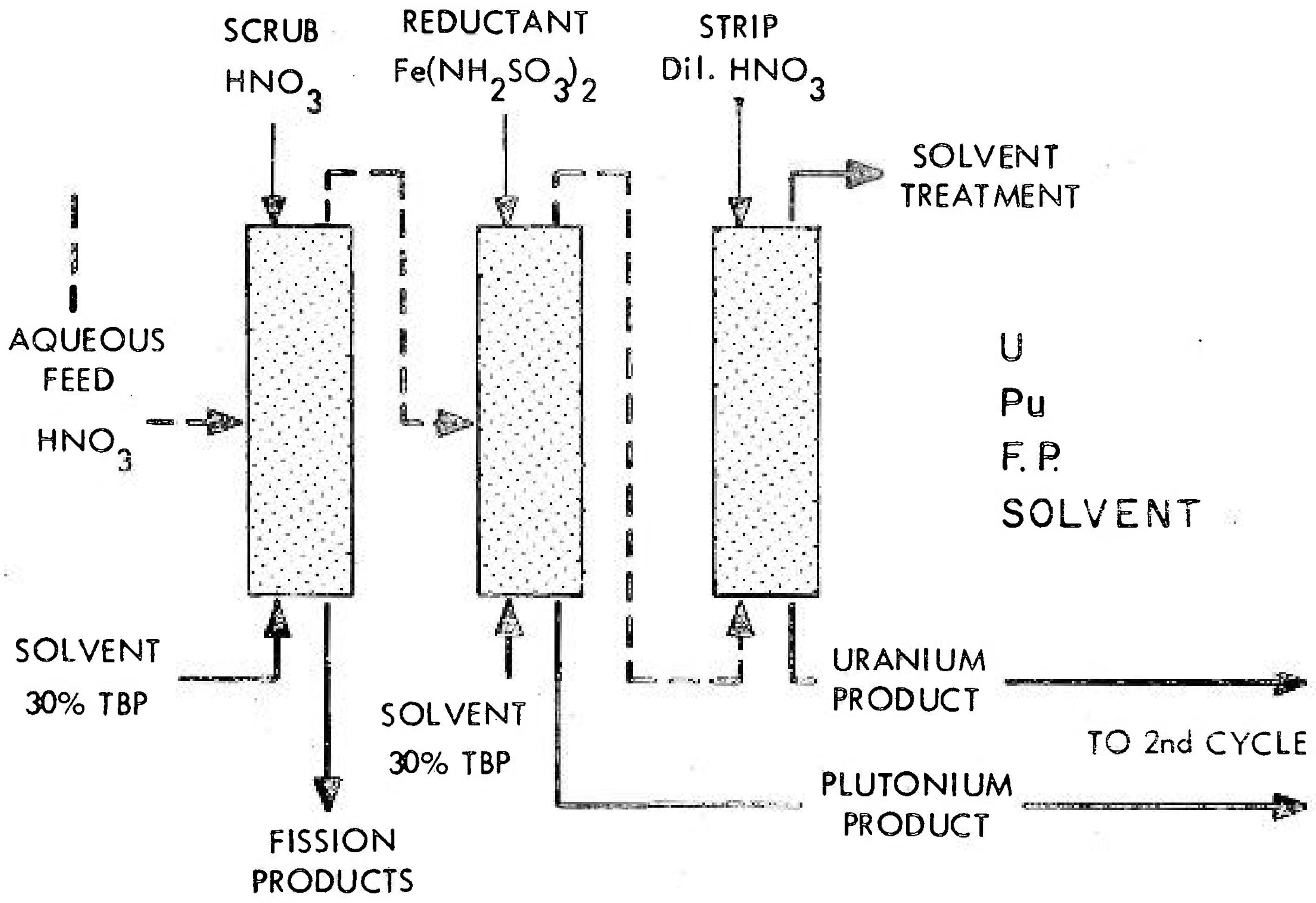
ORNL-LR-DWG. 10452

DISTRIBUTION OF URANIUM, PLUTONIUM, AND FISSION PRODUCTS AS A FUNCTION OF PERCENTAGE URANIUM SATURATION OF SOLVENT

AQUEOUS: **NITRIC ACID SOLUTION OF U, Pu, AND MIXED FISSION PRODUCTS**
SOLVENT: **30% TBP IN AMSCO 123-15**

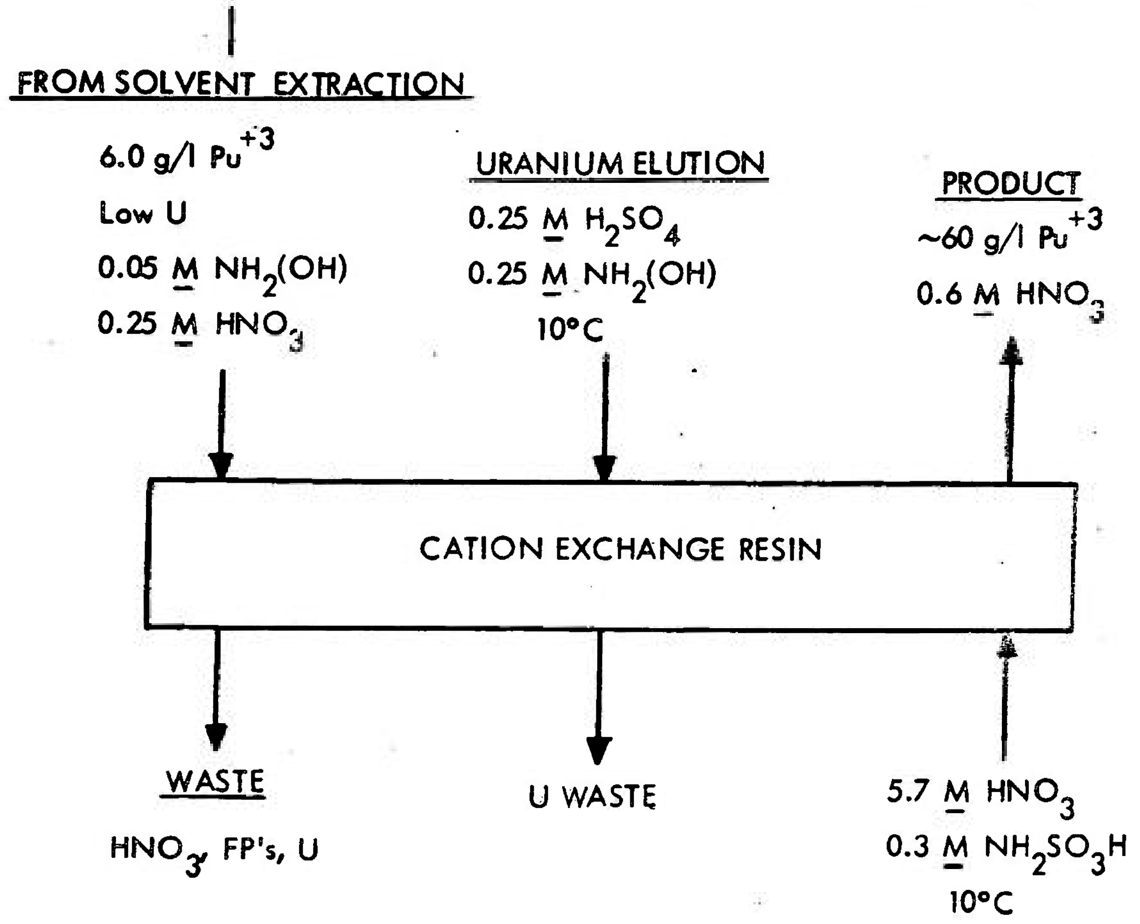
URANIUM SATURATION OF SOLVENT (%)	DISTRIBUTION COEFFICIENT (O/A)			
	U	Pu(IV)	GROSS β	TOTAL RARE EARTHS
37.0	13.7	3.7	0.011	0.0073
54.9	10.2	1.3	0.005	0.0032
70.2	6.4	1.3	0.0025	0.0014
77.2	4.5	1.0	0.0015	0.0007
86.8	2.3	0.57	0.0007	0.0002

ORNL-DWG 67-6342

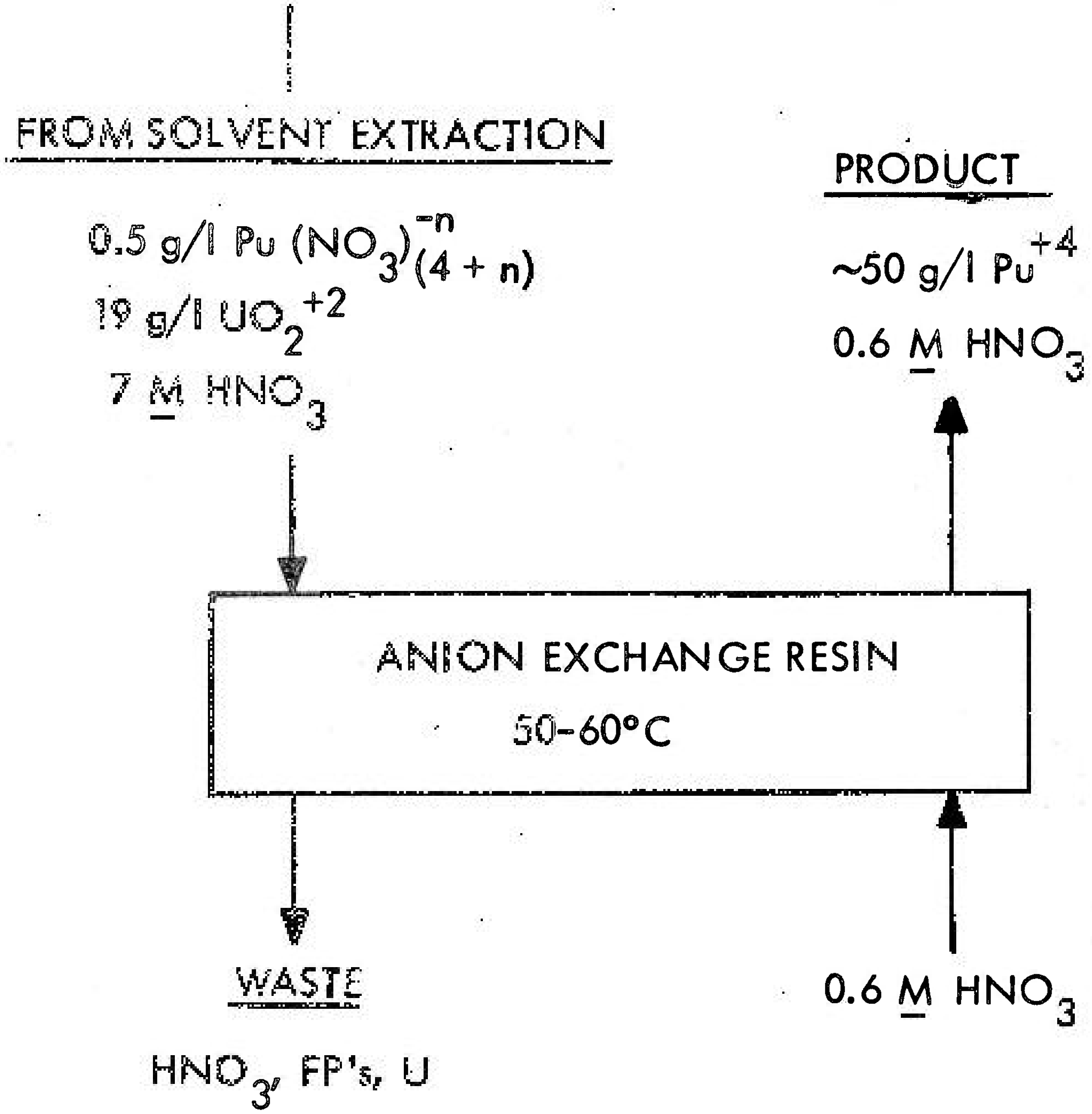


FIRST CYCLE SOLVENT EXTRACTION "PUREX PROCESS"

ORNL Dwg. 67-5194

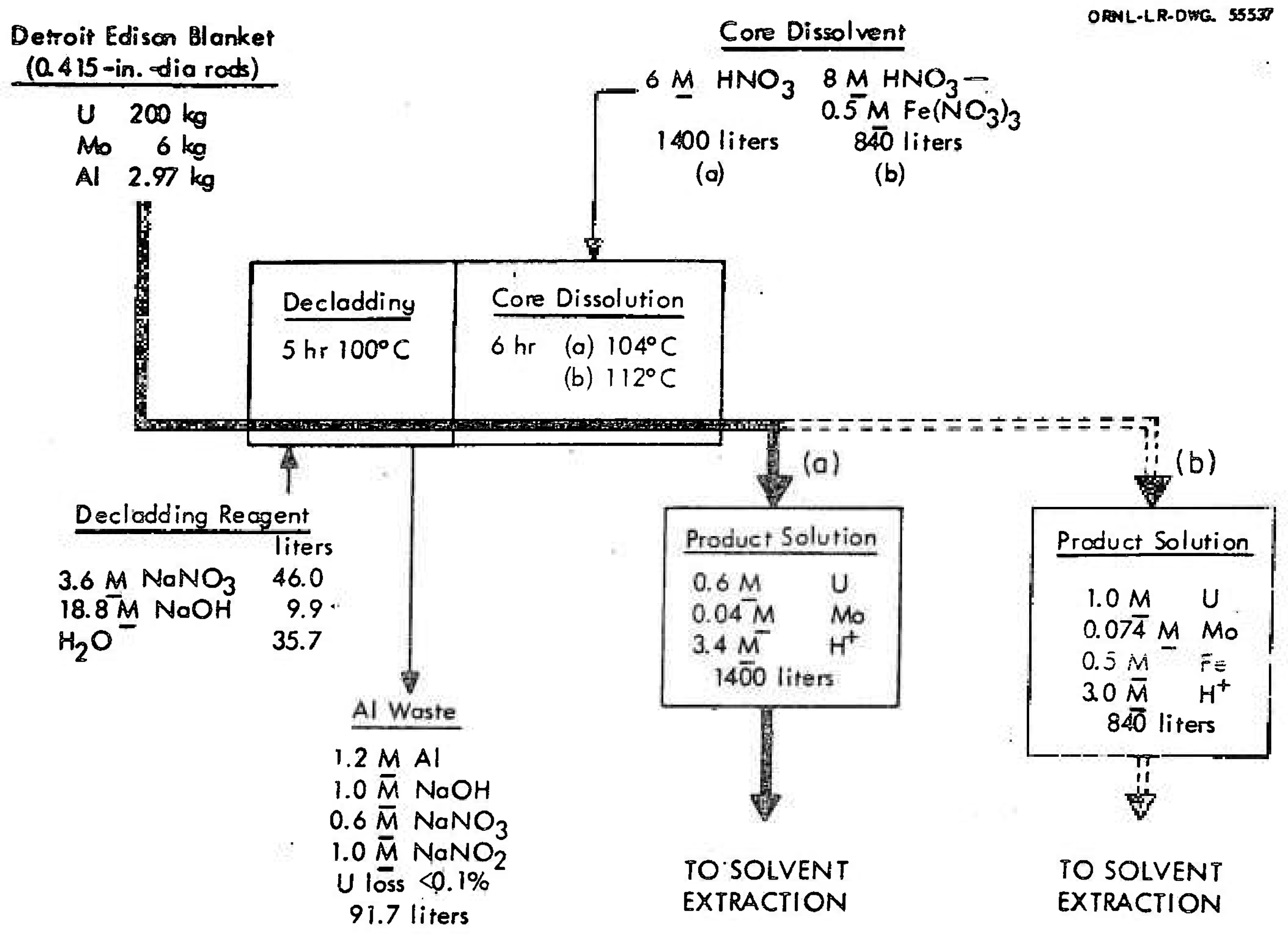


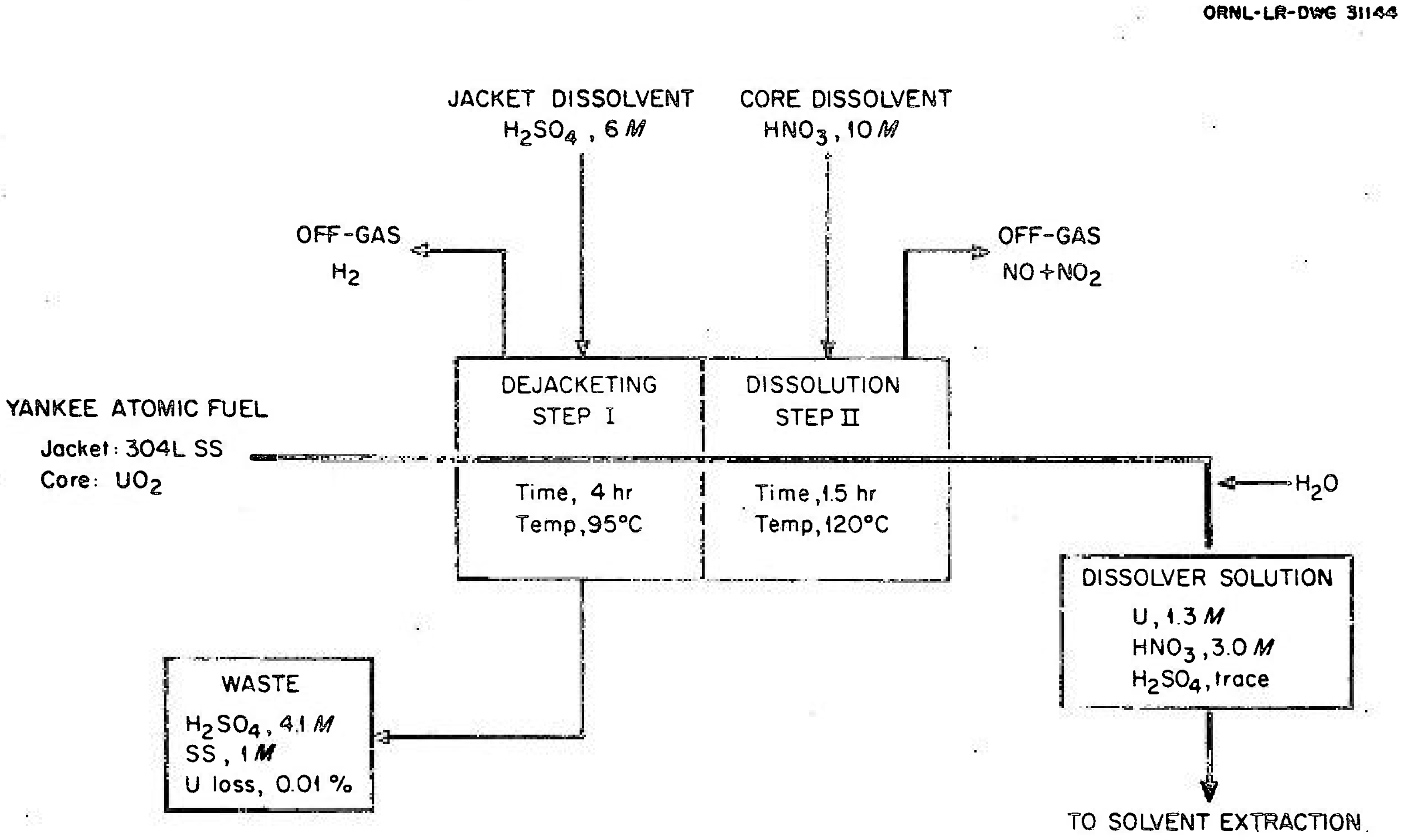
PURIFICATION OF PLUTONIUM BY CATION EXCHANGE



ORNL Dwg. 67-5195

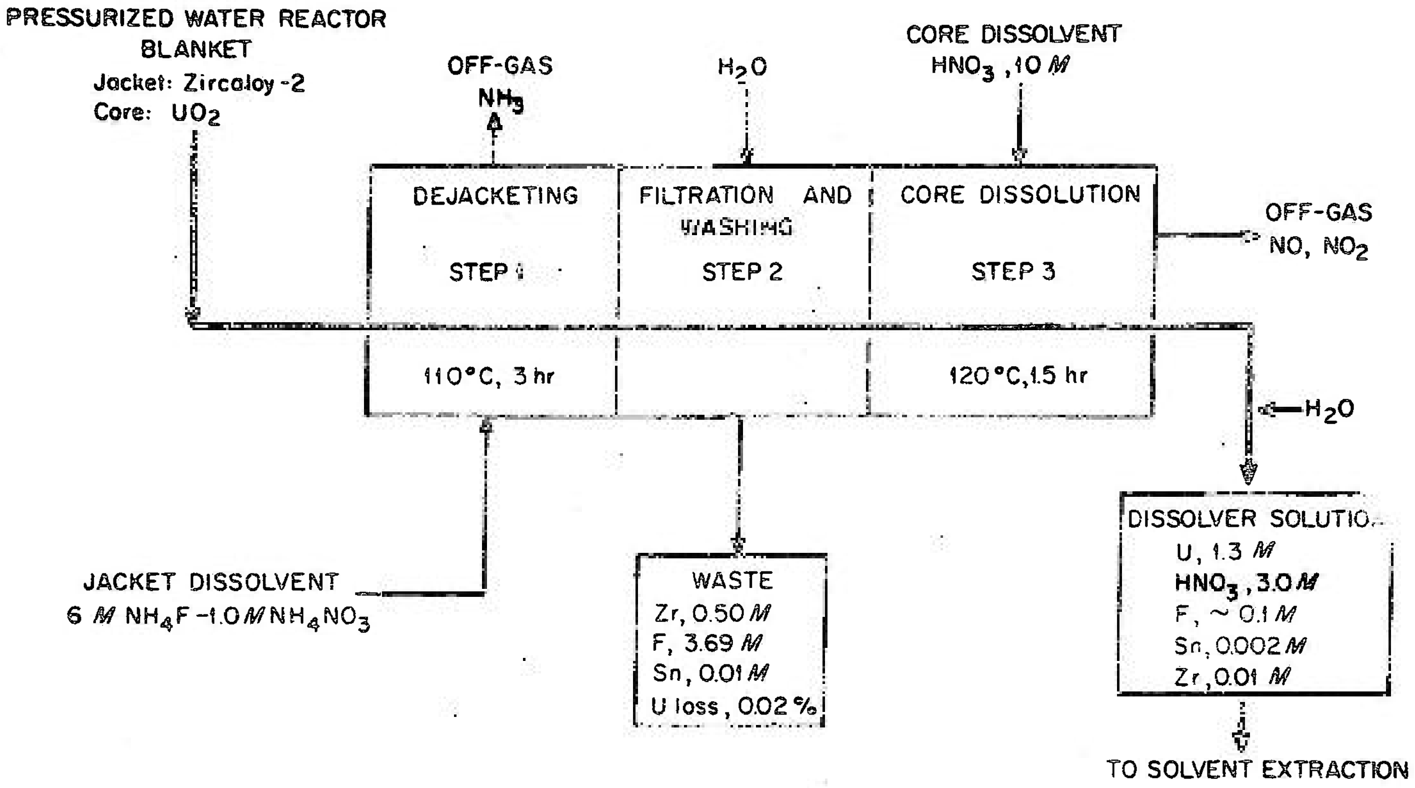
PURIFICATION OF PLUTONIUM BY ANION EXCHANGE


ORNL-LR-DWG. 55537
Detroit Edison Blanket
(0.415-in.-dia rods)
U 200 kg
Mo 6 kg
Al 2.97 kg
Core Dissolvent
6 M HNO3
1400 liters
(a)
8 M HNO3 — 0.5 M Fe(NO3)3
840 liters
(b)
Decladding
5 hr 100°C
Core Dissolution
6 hr (a) 104°C
(b) 112°C
Decladding Reagent
liters
3.6 M NaNO3 46.0
18.8 M NaOH 9.9
H2O 35.7
Al Waste
1.2 M Al
1.0 M NaOH
0.6 M NaNO3
1.0 M NaNO2
U loss <0.1%
91.7 liters
(a)
Product Solution
0.6 M U
0.04 M Mo
3.4 M H+
1400 liters
TO SOLVENT EXTRACTION
(b)
Product Solution
1.0 M U
0.074 M Mo
0.5 M Fe
3.0 M H+
840 liters
TO SOLVENT EXTRACTION



SULFEX PROCESS FOR DEJACKETING STAINLESS STEEL JACKETED FUELS WITH DILUTE SULFURIC ACID.

ORNL-LR-DWG 31143



ZIRFLEX PROCESS FOR DEJACKETING ZIRCALOY-2 JACKETED FUELS WITH AMMONIUM FLUORIDE.

ORNL-LR-DWG. 69211

SULFEX DECLADDING OF IRRADIATED SS-UO_2 FUEL PINS

REAGENT: 4-6 M H_2SO_4; 2-5 hr

BURNUP Mwd/TU	IRRAD. RATE Mw/TU	UO_2 DENSITY % THEORETICAL	LOSSES, %		PELLET CONDITION
			U	Pu	
0	0	93 ± 1.5 (YANKEE)	0.005	--	INTACT
800	25	93 ± 1.5 (YANKEE)	0.005	0.02	FRAGMENTED
9,700	17	93-95 (PWR)	0.03	0.03	FRAGMENTED[a]
20,000	28	93-95 (PWR)	0.10	0.17	FRAGMENTED
25,000	50	96 (SPECIAL)	0.06	0.03	FRACTURED[b]

[a] LESS THAN 0.5% FINER THAN 10 MESH.

[b] LESS THAN 0.1% FINER THAN 10 MESH.

ORNL-LR-DWG. 69212

ZIRFLEX DECLADDING OF IRRADIATED Zr2-UO_2 FUEL PINS

REAGENT: BOILING 6 M NH_4F-1 M NH_4NO_3; 1-3 hr

BURNUP Mwd/TU	IRRAD. RATE Mw/TU	UO_2 DENSITY % THEORETICAL	LOSSES, %		PELLET CONDITION
			U	Pu	
0	0	93-95 (PWR)	0.01	--	INTACT
182	5.0	93-95 (PWR)	0.01	0.01	FRAGMENTED[a]
13,700	24	93-95 (PWR)	0.11	0.08	FRAGMENTED
17,700	45	93 (SPECIAL)	0.05	0.02	FRACTURED[b]

[a] LESS THAN 0.5% FINER THAN 10 MESH.

[b] LESS THAN 0.1% FINER THAN 10 MESH; FRACTURED BUT IN ONE PIECE.

ORNL-LR-DWG. 61539

SULFEX DECLADDING OF IRRADIATED ThO_2-UO_2 FUEL PINS

Reagent: 4–6 *M* H_2SO_4; Pellet density 9.1–9.5 g/cc

PIN NO.	UO_2 (%)	Mwd/TON OF CORE	DECLADDING TIME (hr)	LOSSES (%)	
				U	Th
1	9.1	0	3	0.008	0.006
			16	0.008	0.01
2	9.1*	740	1	0.07	0.11
3	6.5*	12,000	3	0.3	0.29
4	4.2*	19,600	3	0.09	0.02

*PELLETS SEVERELY SHATTERED (8–20 MESH).

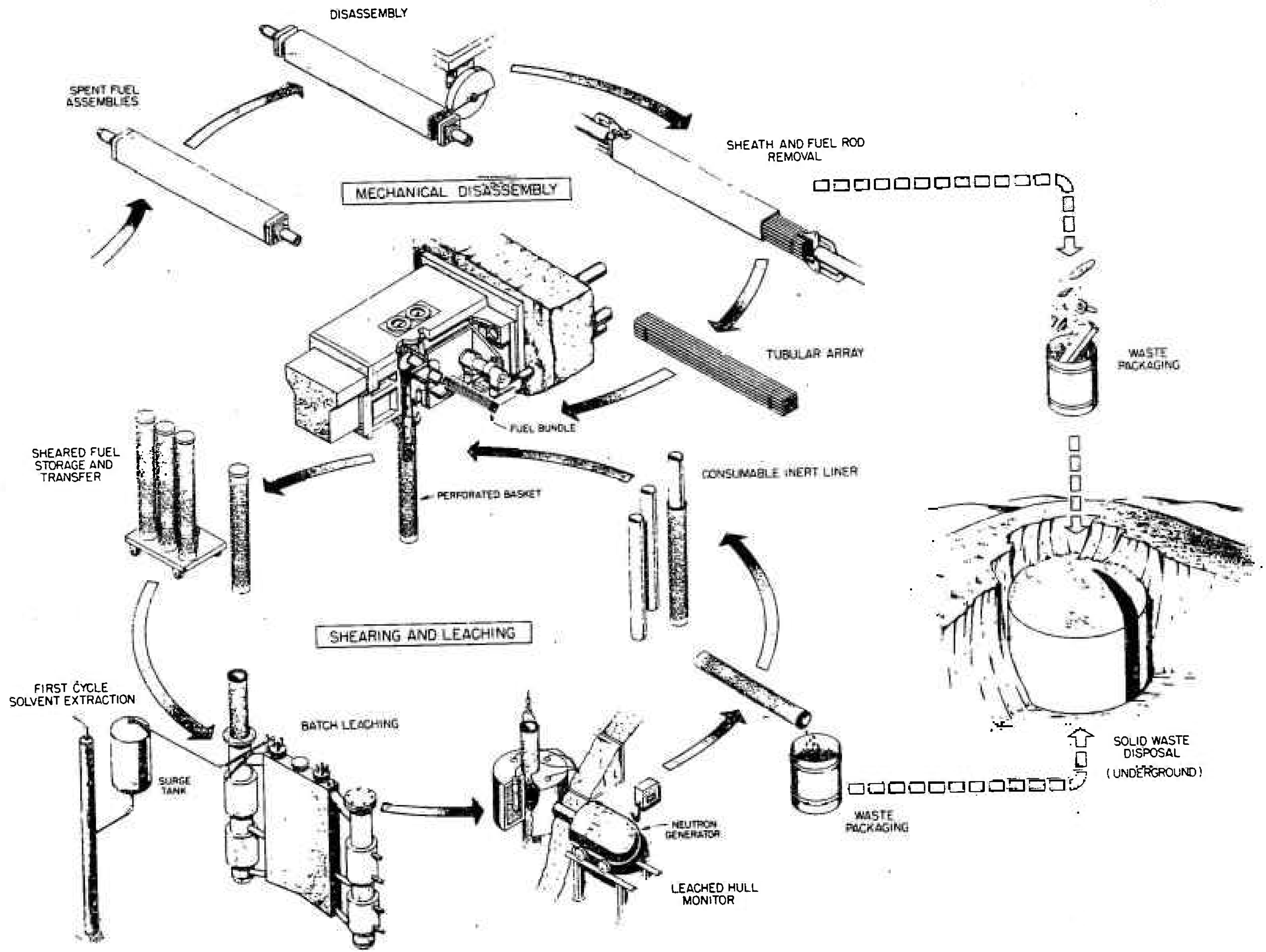
ORNL DWG. 64-7520

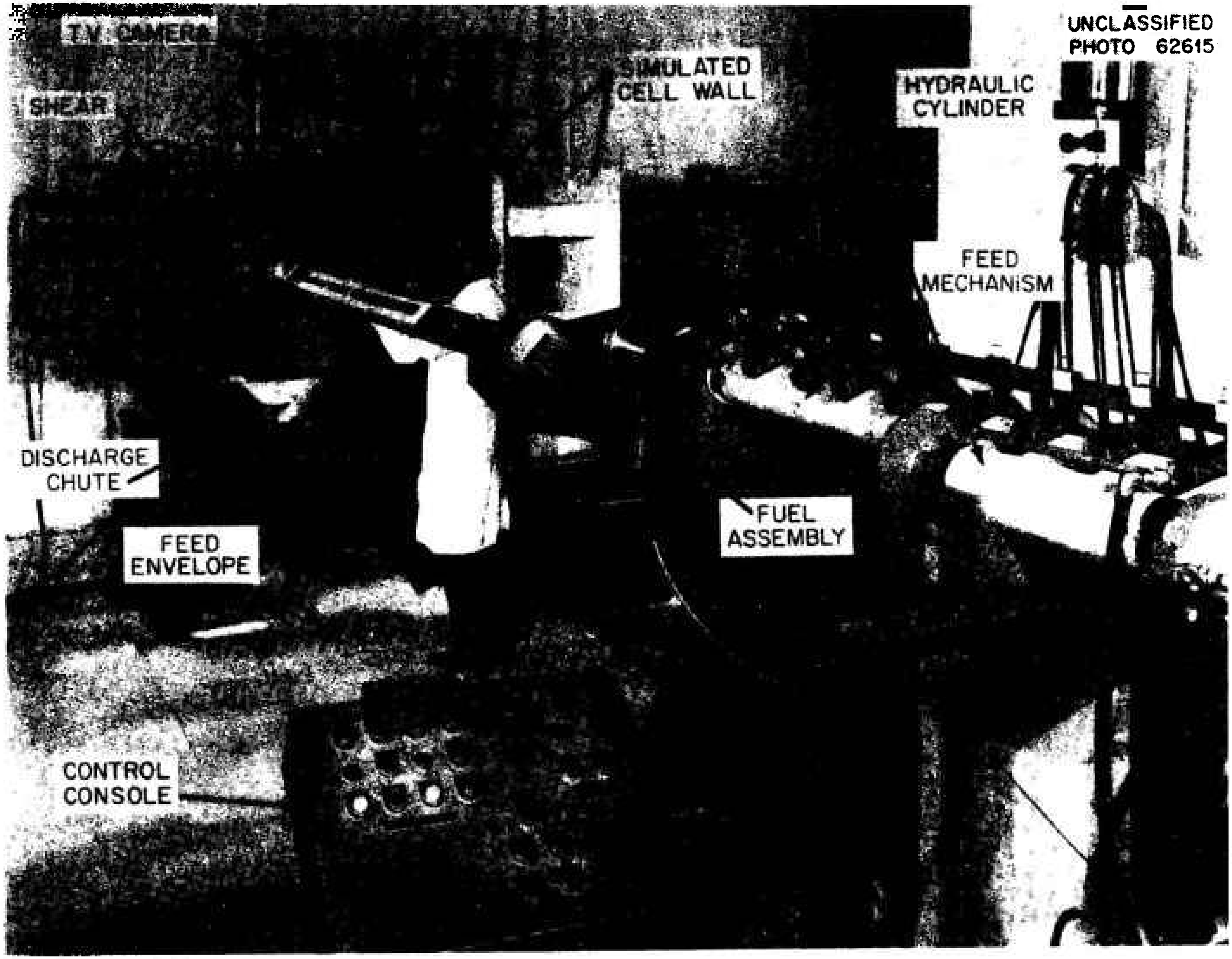
FAST OXIDE BREEDER PROCESSING

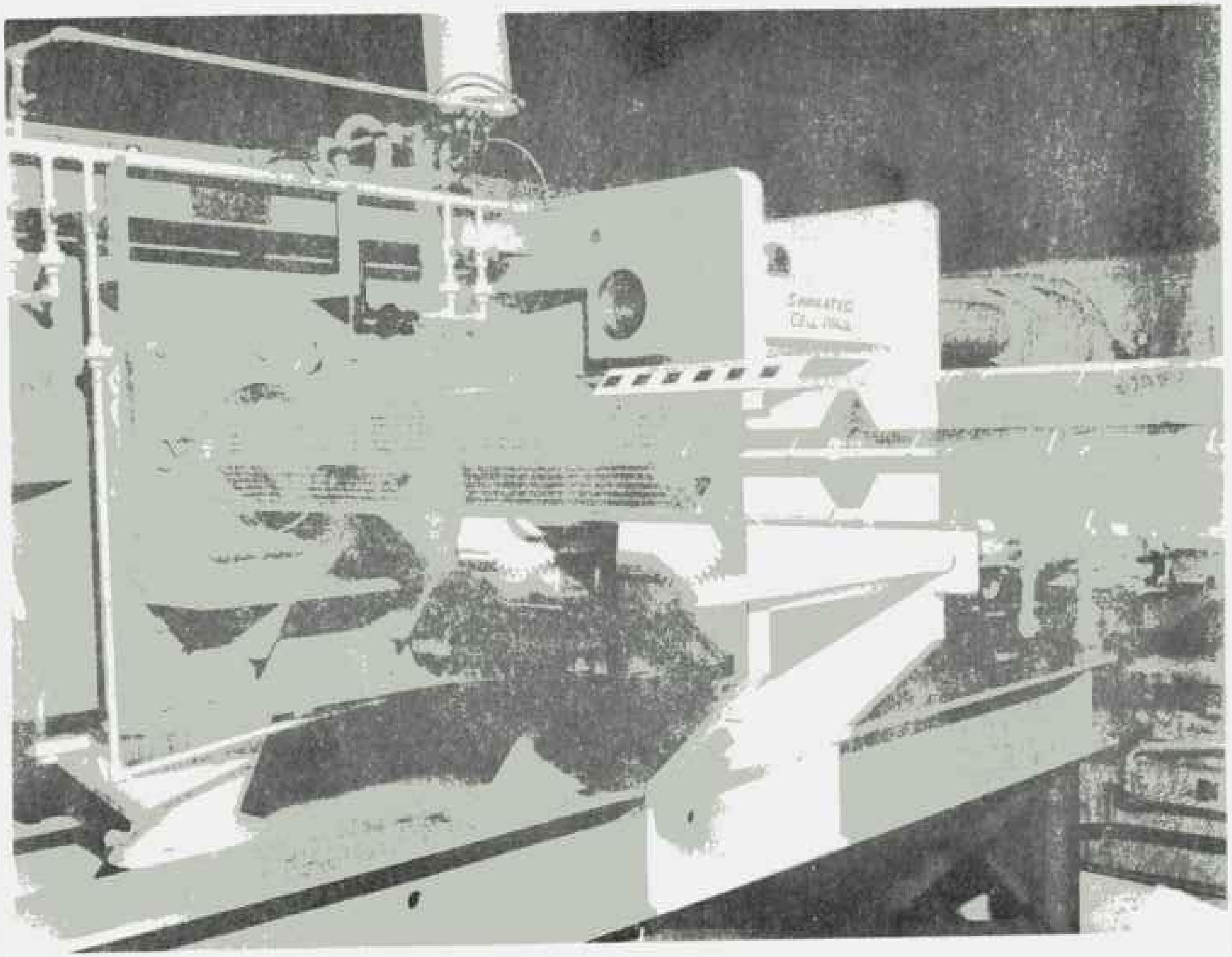
Soluble Losses to $6\underline{M}$ H_2SO_4 Decladding Solutions

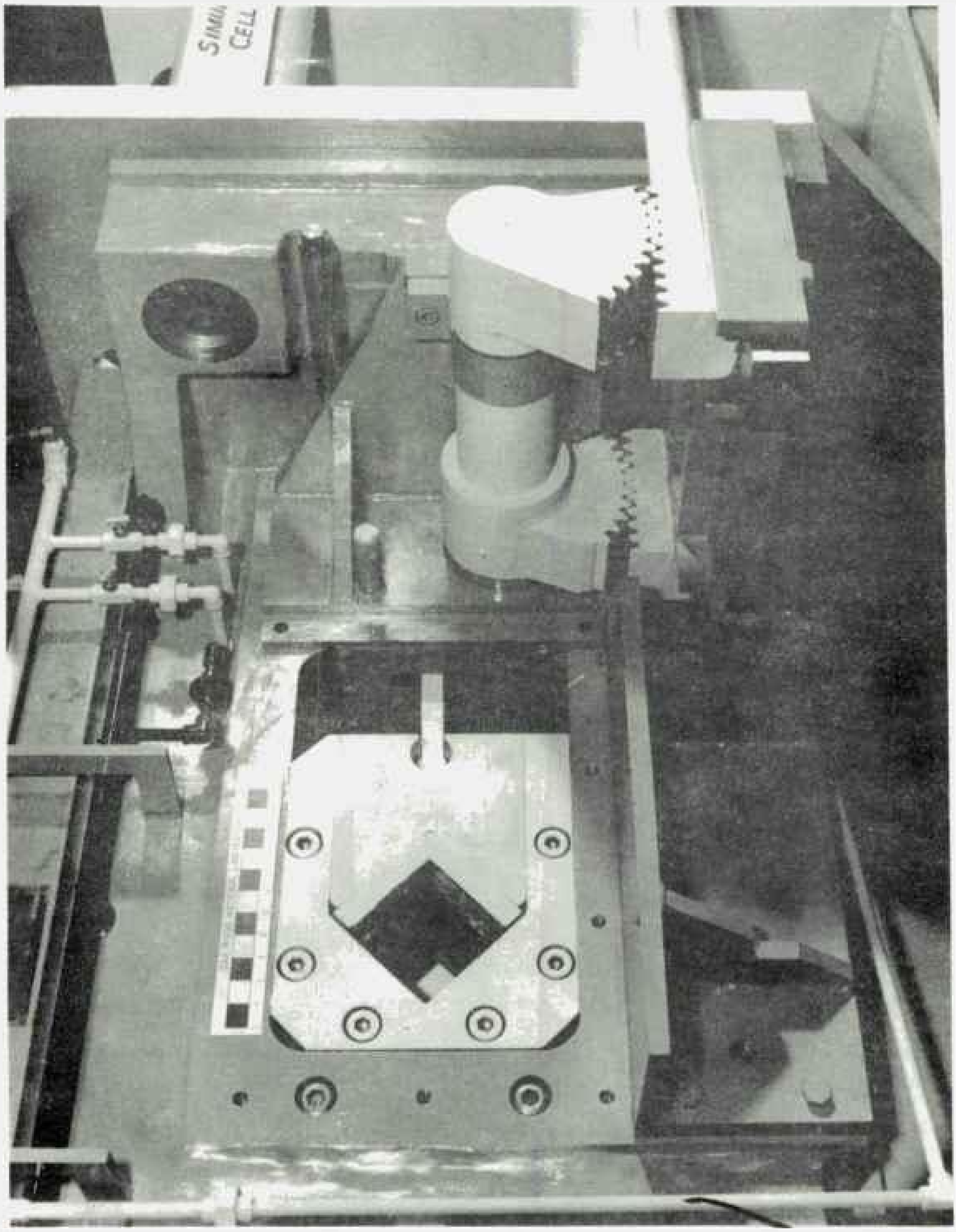
SPECIMEN NUMBER	BURNUP Mwd/tonne	SOLUBLE LOSS PERCENT OF TOTAL		
		U	Pu	Cs γ
X-1-S	36,300	1.18	1.86	47.2
V-4-S	42,700	0.61	0.67	73.1
V-3-P	54,400	1.36	2.35	62.0
VI-1-S	69,100	1.79	1.68	93.7
V-2-P	77,400	3.09	4.50	68.0
AVERAGE		1.55	1.54	59.49

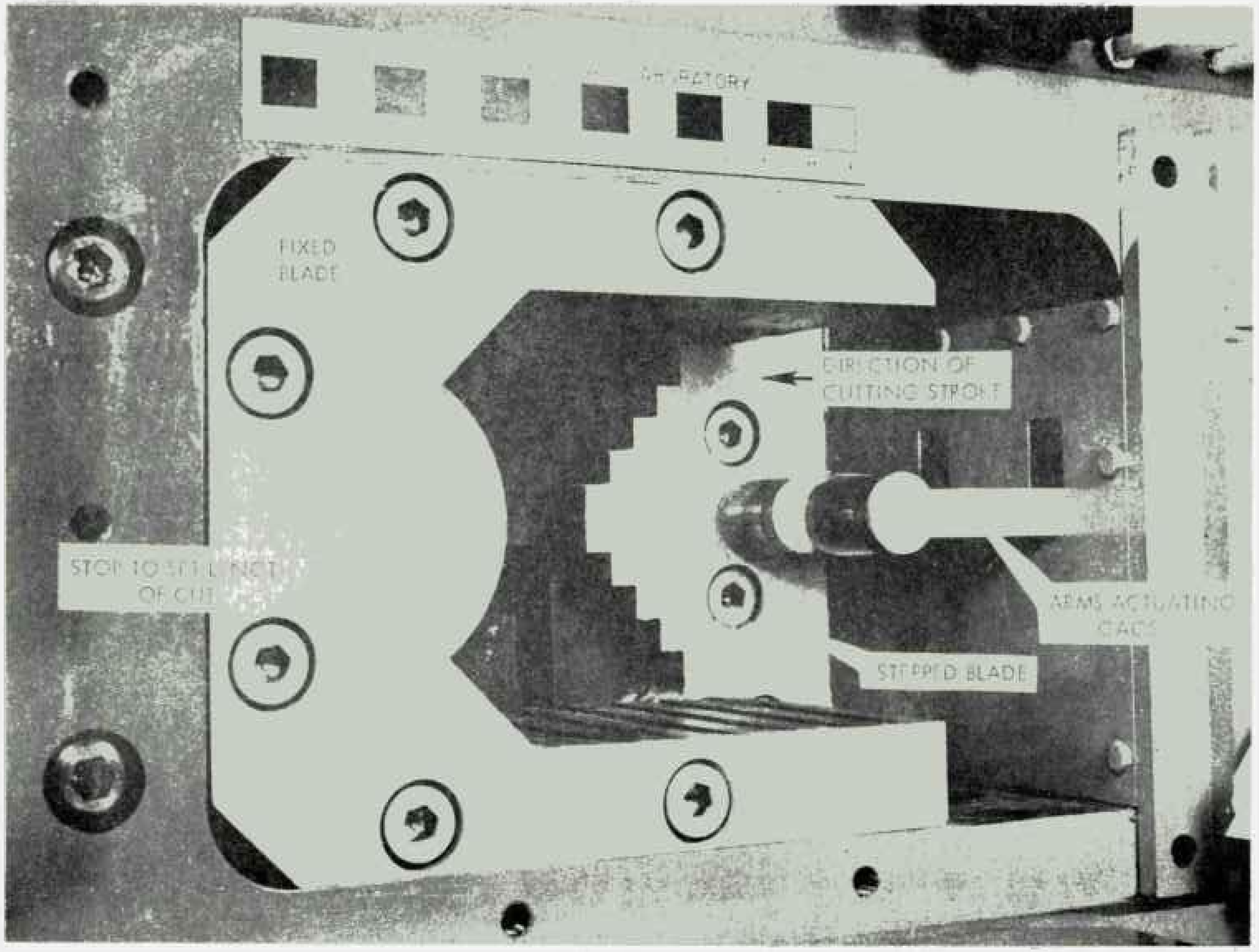
ORNL-DWG 63-2800P

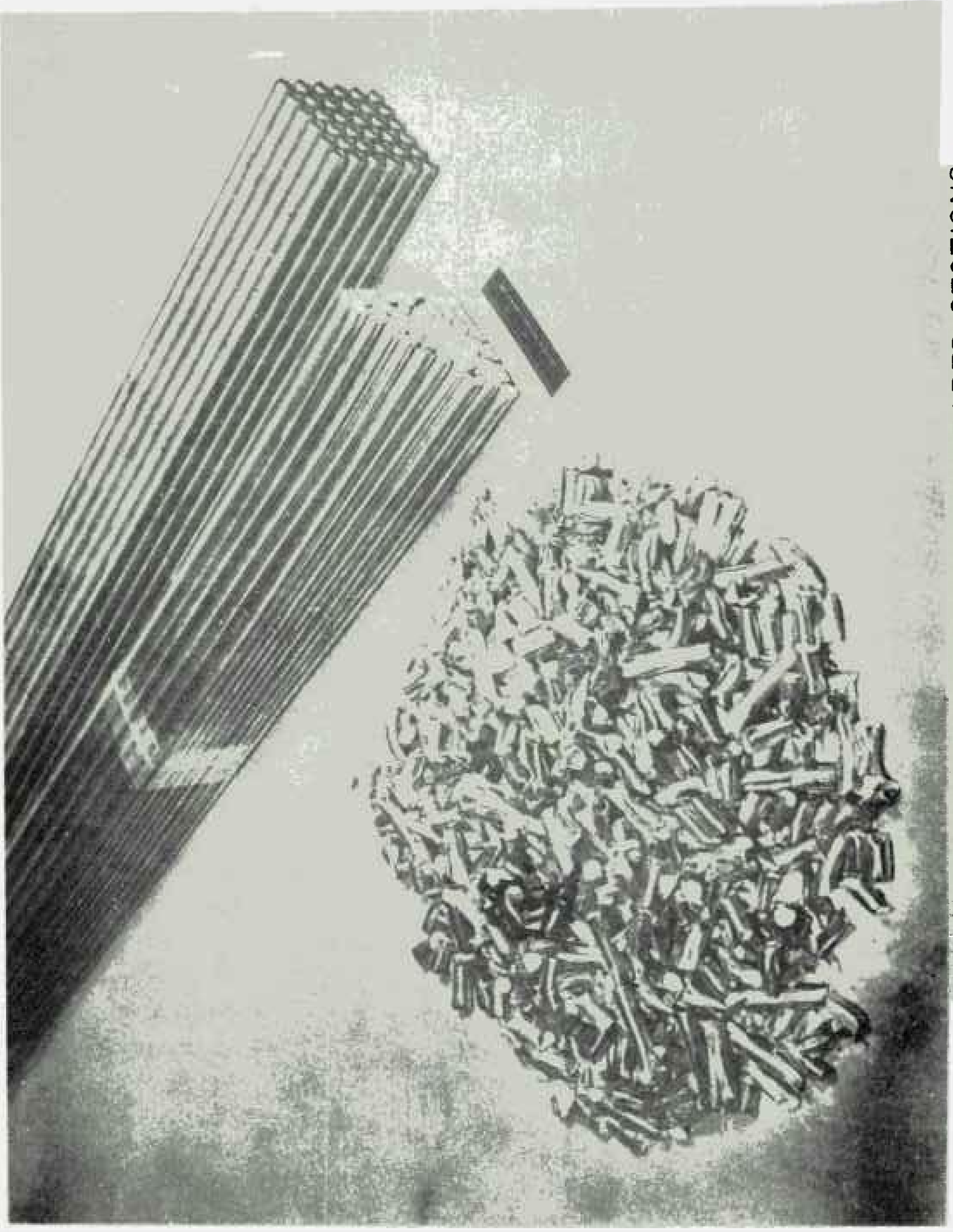



UNCLASSIFIED
PHOTO 62615
T.V. CAMERA
SHEAR
SIMULATED CELL WALL
HYDRAULIC CYLINDER
FEED MECHANISM
DISCHARGE CHUTE
FEED ENVELOPE
FUEL ASSEMBLY
CONTROL CONSOLE



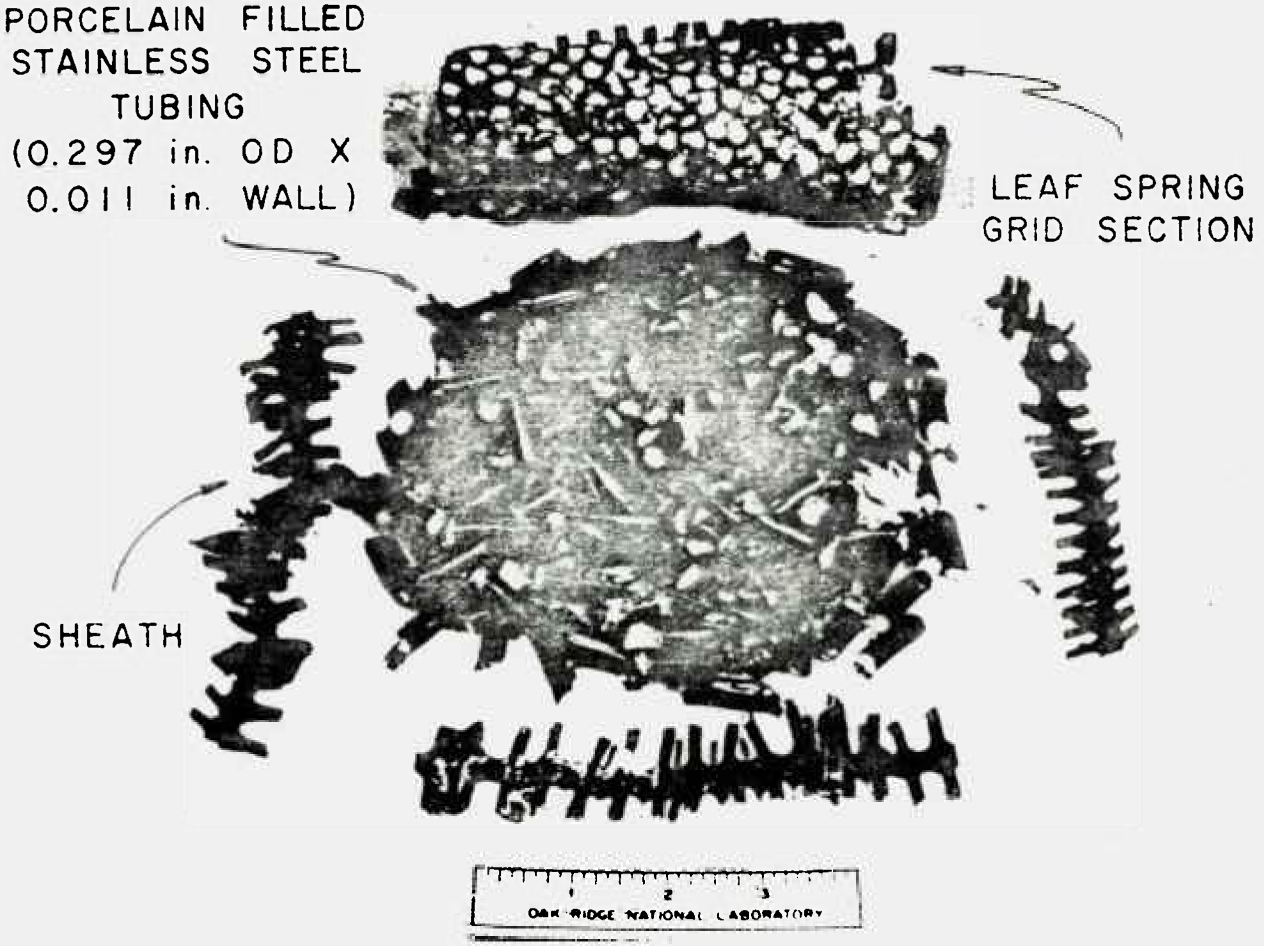

SIMU
CELL


VIBRATORY
FIXED BLADE
DIRECTION OF CUTTING STROKE
STOP TO SET LENGTH OF CUT
ARMS ACTUATING GAGE
STEPPED BLADE

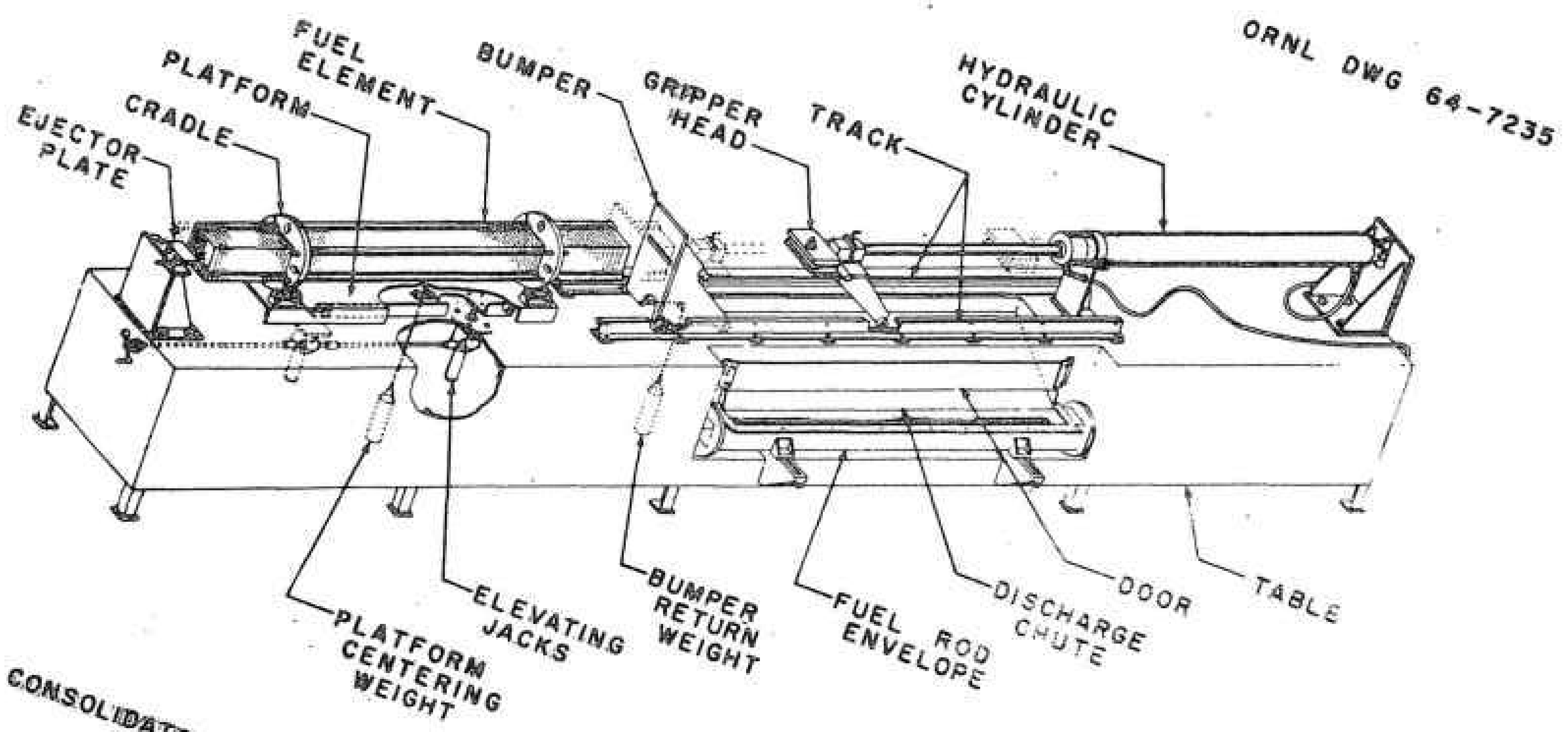


PROTOTYPE FUEL BUNDLE AND SHEARED SECTIONS

ORNL-PHOTO 66439

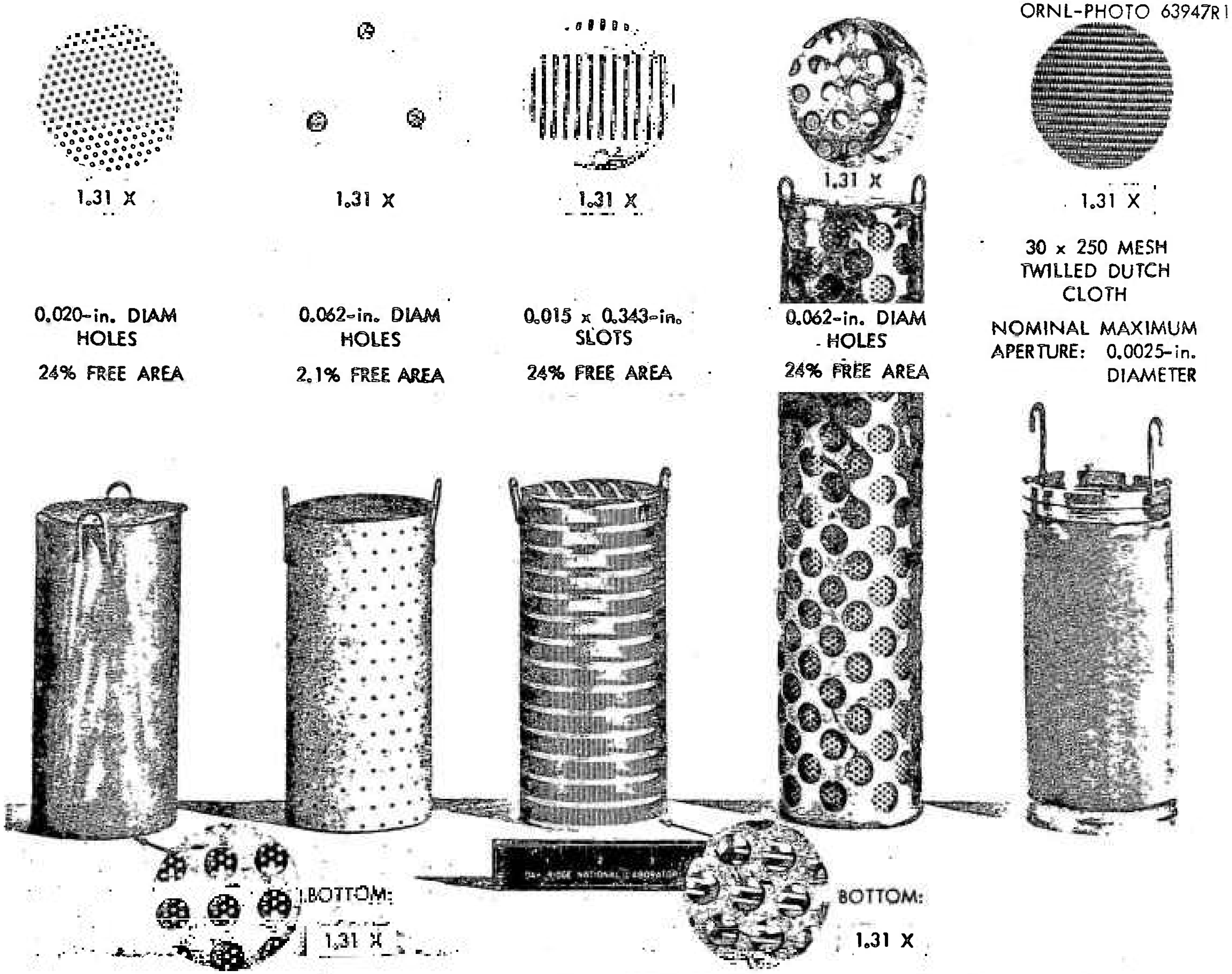


TYPICAL PRODUCT RESULTING FROM INTACT SHEARING (1-INCH LENGTHS) OF PORCELAIN FILLED CONSOLIDATED EDISON CORE B FUEL ASSEMBLY



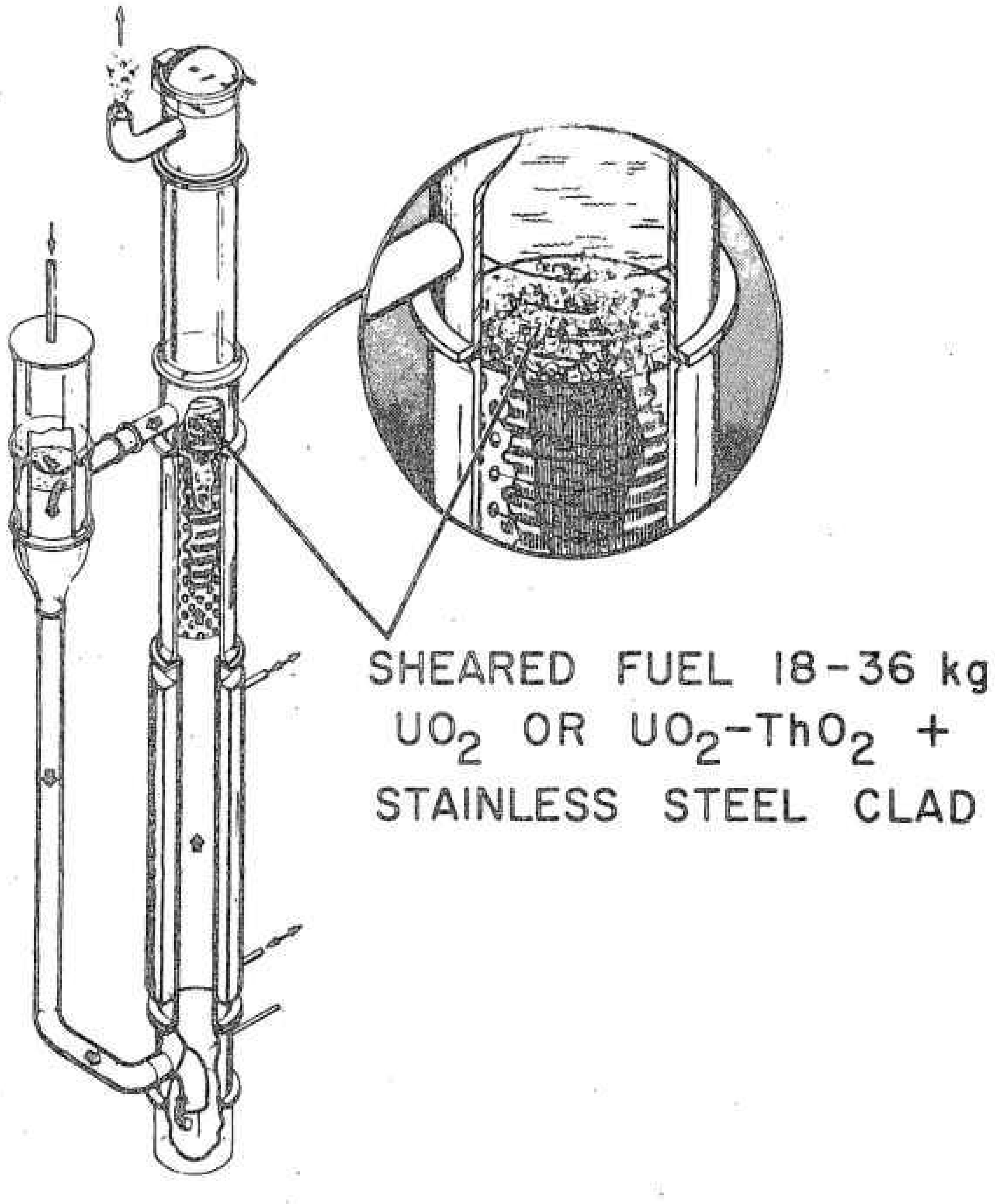
CONSOLIDATED EDISON CORE B MULTI-TUBE WITHDRAWAL MECHANISM

ORNL-PHOTO 63947R1

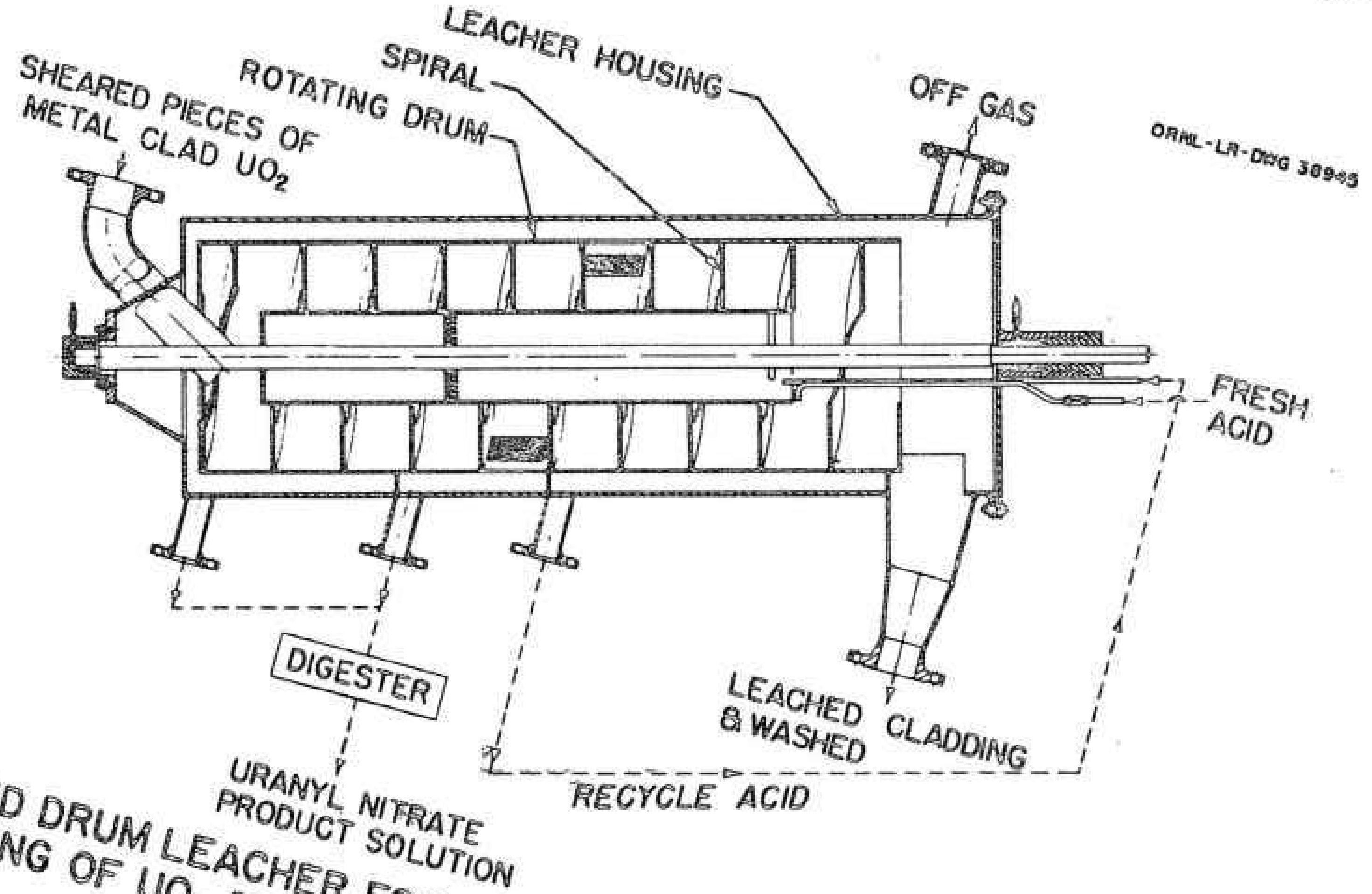


PERFORATED BASKETS EVALUATED IN BENCH SCALE LEACHING STUDIES. ALL BASKETS 3-in. O.D. X 6-in. HIGH EXCEPT NUMBER 4 WHICH IS 3-in. O.D. X 12-in. HIGH

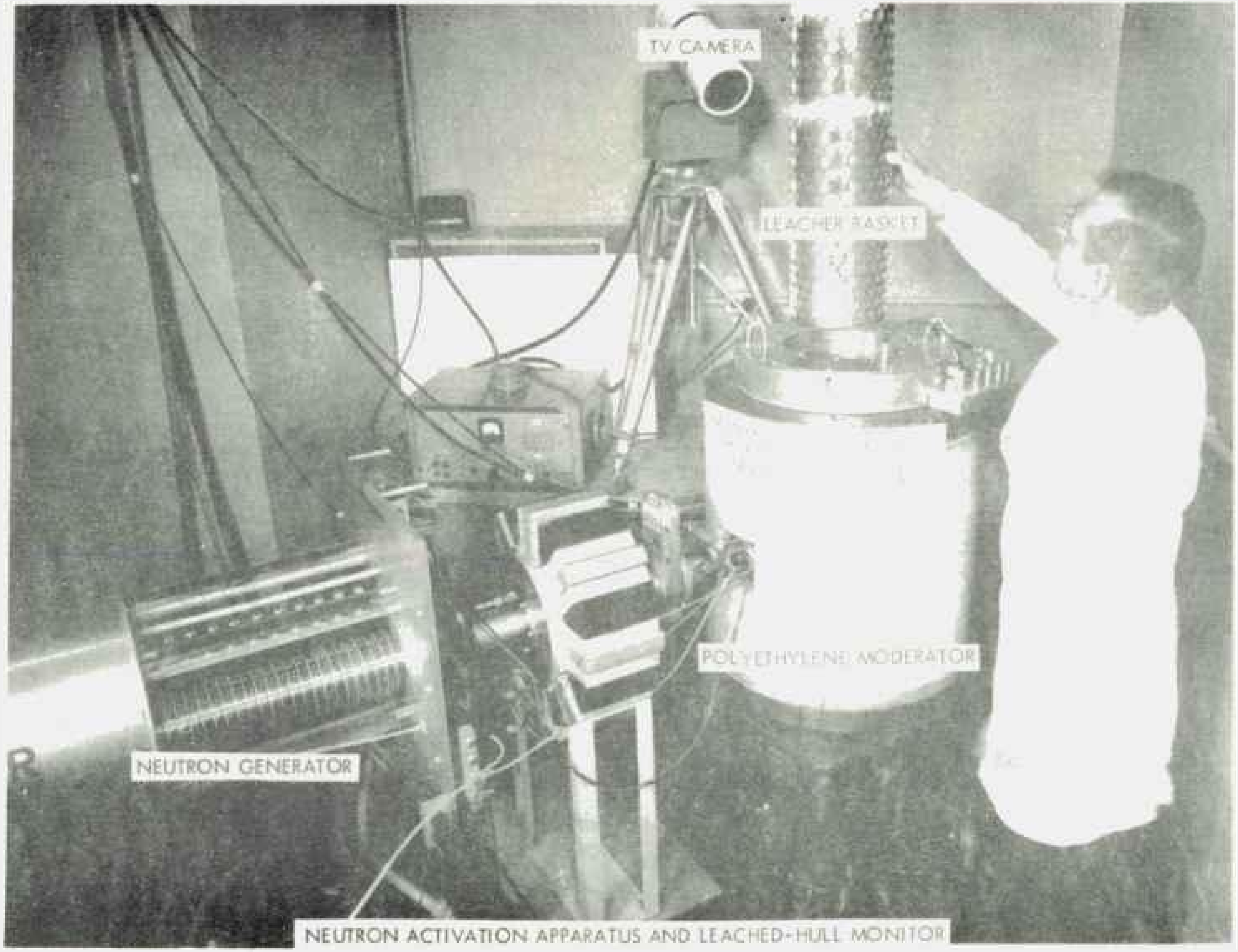
ORNL-DWG 64-4184R1



ENGINEERING SCALE BATCH LEACHER



INCLINED DRUM LEACHER FOR COUNTERCURRENT NITRIC ACID LEACHING OF UO_2 FROM SHEARED PIECES OF METAL CLAD UO_2



NEUTRON ACTIVATION APPARATUS AND LEACHED-HULL MONITOR

ORNL DWG. 64-7770

TYPICAL SHEAR-LEACH DATA

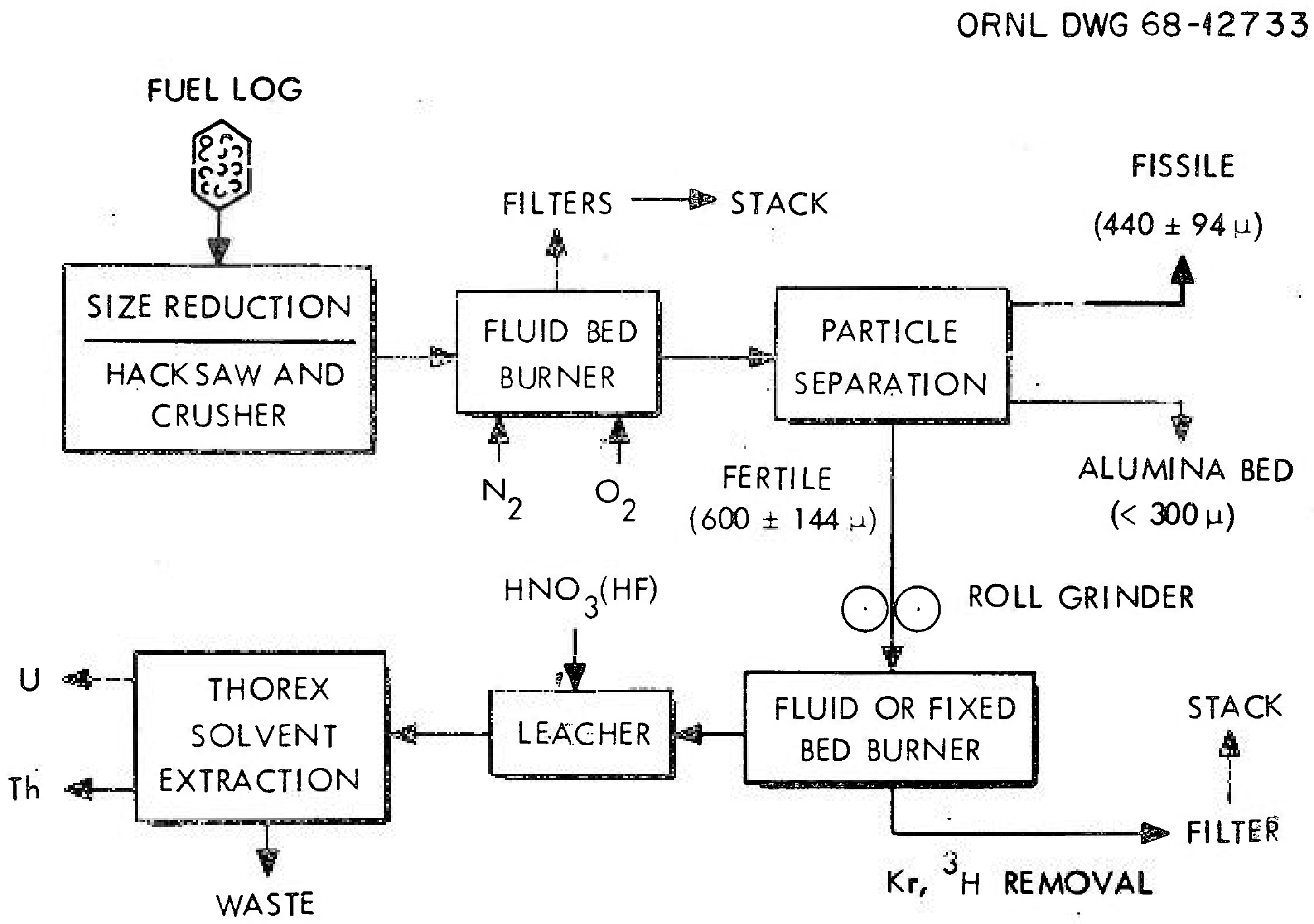
(WITH STEPPED BLADE, MOVING 1.22 in./sec, 4.5 cuts/min.)

FUEL	CLAD	FORCE (tons)	CORE DISLODGED (%)	CLAD DISLODGED (%)	99.9% LEACH TIME (h)
UO_2 (PELLETS)	STAINLESS STEEL OR ZIRCALOY-2	50–90	36[a]	2	1-1/2
			28[b]	2-1/2	2
UO_2-ThO_2 (PELLETS)	STAINLESS STEEL	50–75	85[c]	8	8
			36[a]	2	12

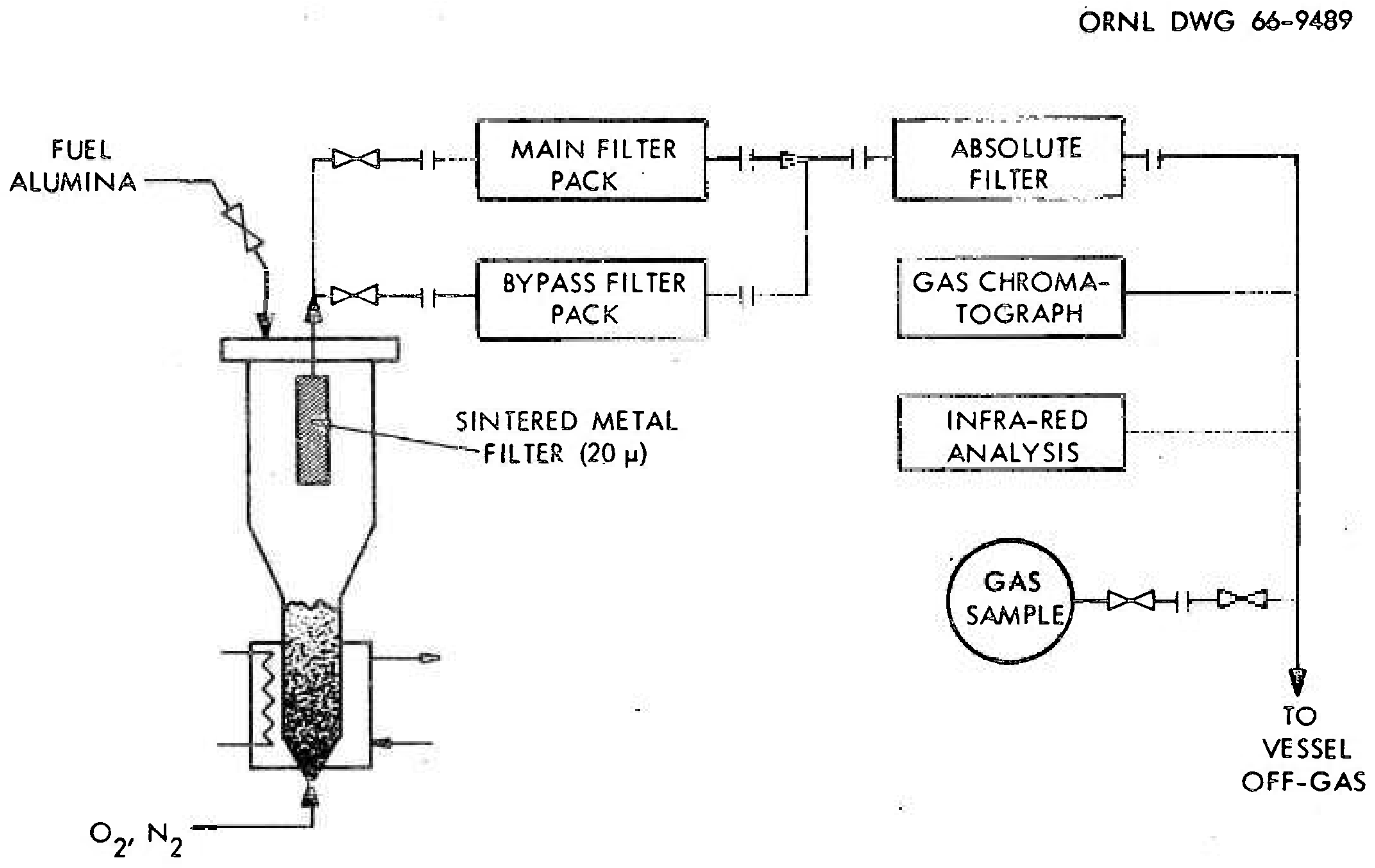
[a] 1 in. SHEARED LENGTH.

[b] 1-1/2 in. SHEARED LENGTH.

[c] 1/2 in. SHEARED LENGTH.



BURN LEACH PROCESS FOR HTGR FUELS


ORNL DWG 66-9489
FUEL
ALUMINA
MAIN FILTER PACK
BYPASS FILTER PACK
ABSOLUTE FILTER
GAS CHROMATOGRAPH
INFRA-RED ANALYSIS
SINTERED METAL FILTER (20 μ)
GAS SAMPLE
TO VESSEL OFF-GAS
O_2, N_2

ORNL DWG 67-5229

EFFECT OF FILTER[*] TEMPERATURE ON FISSION PRODUCT REMOVAL

Filter Temp., (°C)	Decontamination Factors for Filtered Off-Gas				
	Gr γ	^{106}Ru	^{125}Sb	^{137}Cs	^{144}Ce
100	2.7×10^7	5.8×10^7	3.6×10^6	2.1×10^7	5.7×10^7
160	8.1×10^6	1.3×10^6	---	8.7×10^6	9.3×10^5
285	7.2×10^6	1.8×10^7	1.1×10^7	9.5×10^6	6.1×10^6
500	8.1×10^2	$\geq 1.5 \times 10^4$	$>7.2 \times 10^3$	8.4×10^3	$\geq 9.7 \times 10^4$

[*] Sintered metal filter only.

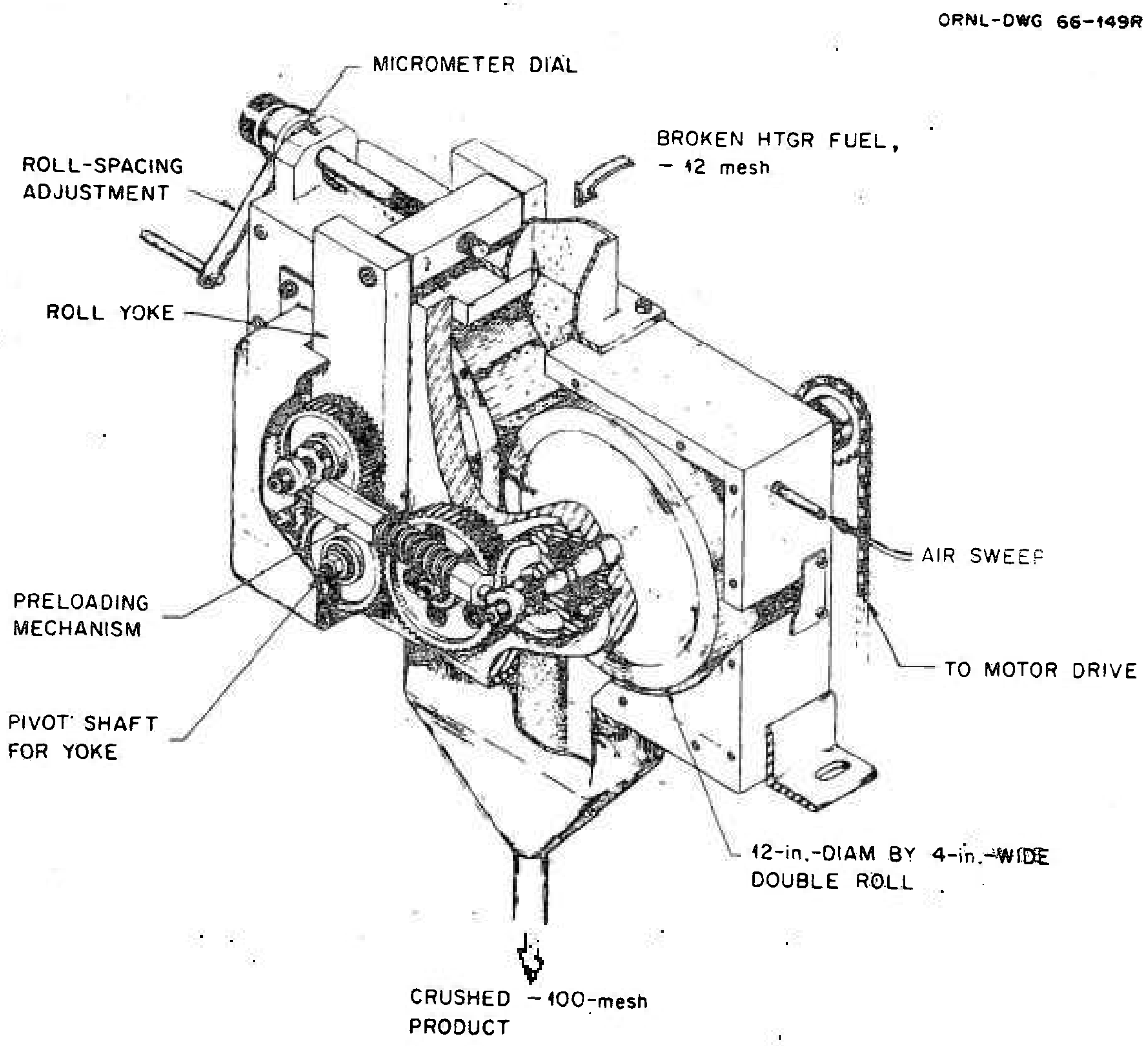
ORNL DWG 67-5228

LEACHING THE ALUMINA-ASH RESIDUE FROM BURNING GRAPHITE FUELS

General Atomic Gail III A; III B fuel: 8,000 and 41,500 Mwd/ton;
Leach: 13 $\underline{M}$ HNO_3--0.05 $\underline{M}$ HF--0.01 $\underline{M}$ $Al(NO_3)_3$

	Recovered by Leaching[a] (%)	Held by Alumina[a] (%)
Th	99.33 ± 0.44	0.71 ± 0.36
U	99.82 ± 0.15	0.07 ± 0.07
Gr γ	94.43 ± 4.80	4.98 ± 2.74
^{106}Ru	82.96 ± 14.9	16.94 ± 16.1
^{125}Sb	90.07 ± 16.4	9.69 ± 16.4
^{136}Cs	96.82 ± 2.78	5.90 ± 1.95
^{144}Ce	96.45 ± 3.40	3.12 ± 2.78

[a] Within 95% confidence level.


ORNL-DWG 66-149R
MICROMETER DIAL
BROKEN HTGR FUEL, − 12 mesh
ROLL-SPACING ADJUSTMENT
ROLL YOKE
AIR SWEEP
PRELOADING MECHANISM
TO MOTOR DRIVE
PIVOT SHAFT FOR YOKE
12-in.-DIAM BY 4-in.-WIDE DOUBLE ROLL
CRUSHED PRODUCT −100-mesh

ORNL-LR-DWG. 40141

FLOWSHEET NOMENCLATURE

THE FOLLOWING FLOWSHEET NAMES, WHICH ORIGINALLY WERE GIVEN TO SPECIFIC SOLVENT EXTRACTION FLOWSHEETS, HAVE NOW BEEN APPLIED TO FLOWSHEET TYPES.

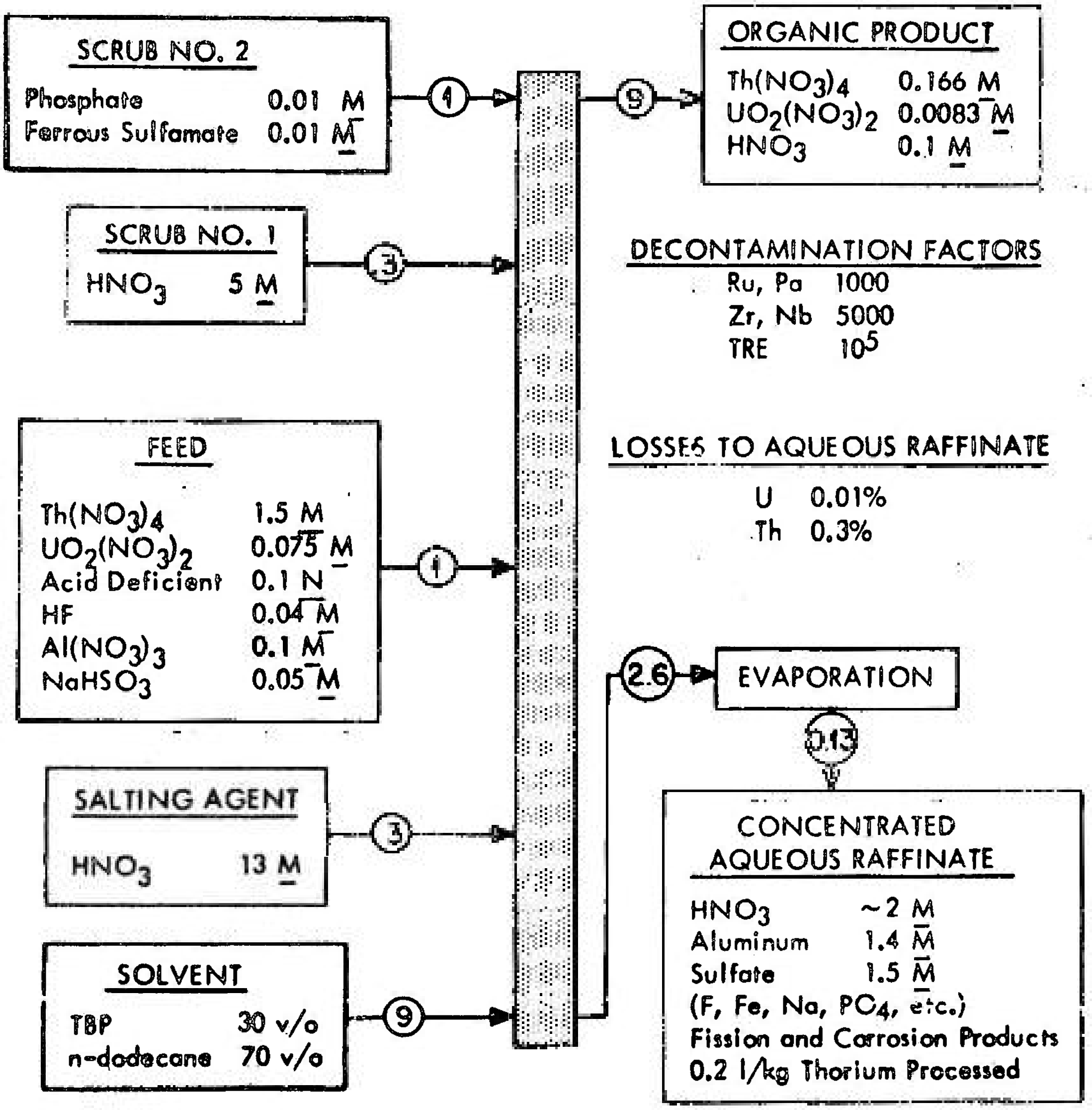
"PUREX" – EXTRACTION OF NATURAL OR SLIGHTLY ENRICHED URANIUM FROM HNO_3 SALTED SOLUTION BY 20–40% TBP.

"25-TBP" – EXTRACTION OF ENRICHED URANIUM, U^{233} OR Pu WITH 2 TO 20% TBP OR "25 PROCESS"

"THOREX" – EXTRACTION OF THORIUM AND URANIUM WITH 30–45% TBP.

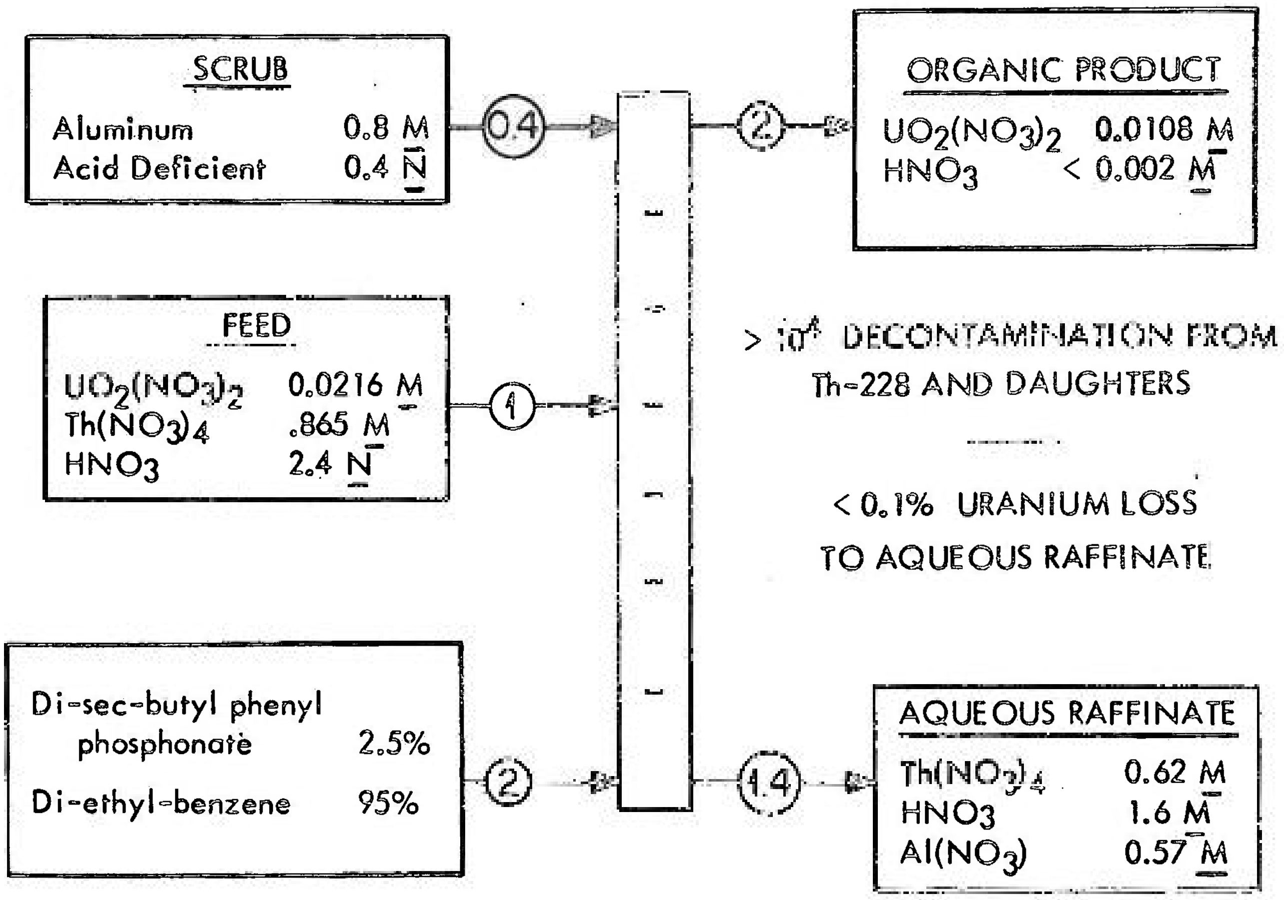
"INT-23" – EXTRACTION OF URANIUM FROM AN IRRADIATED THORIUM SOLUTION WITH 1 TO 10% TBP.

ORNL-LR-DWG. 74838



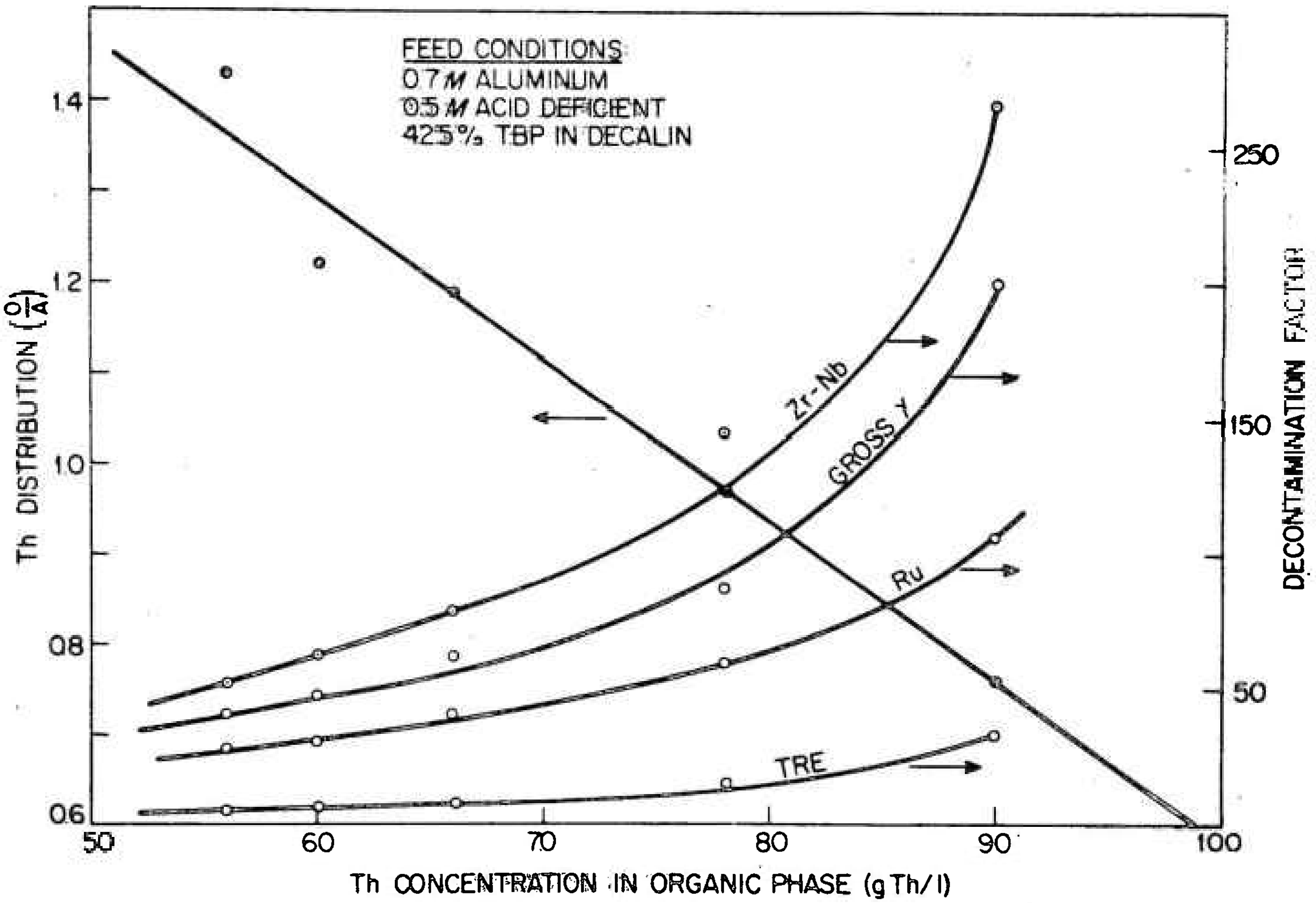
ACID THOREX PROCESS FOR CO-EXTRACTION OF URANIUM AND THORIUM

UNCLASSIFIED
ORNL-LR-DWG. 74020R1

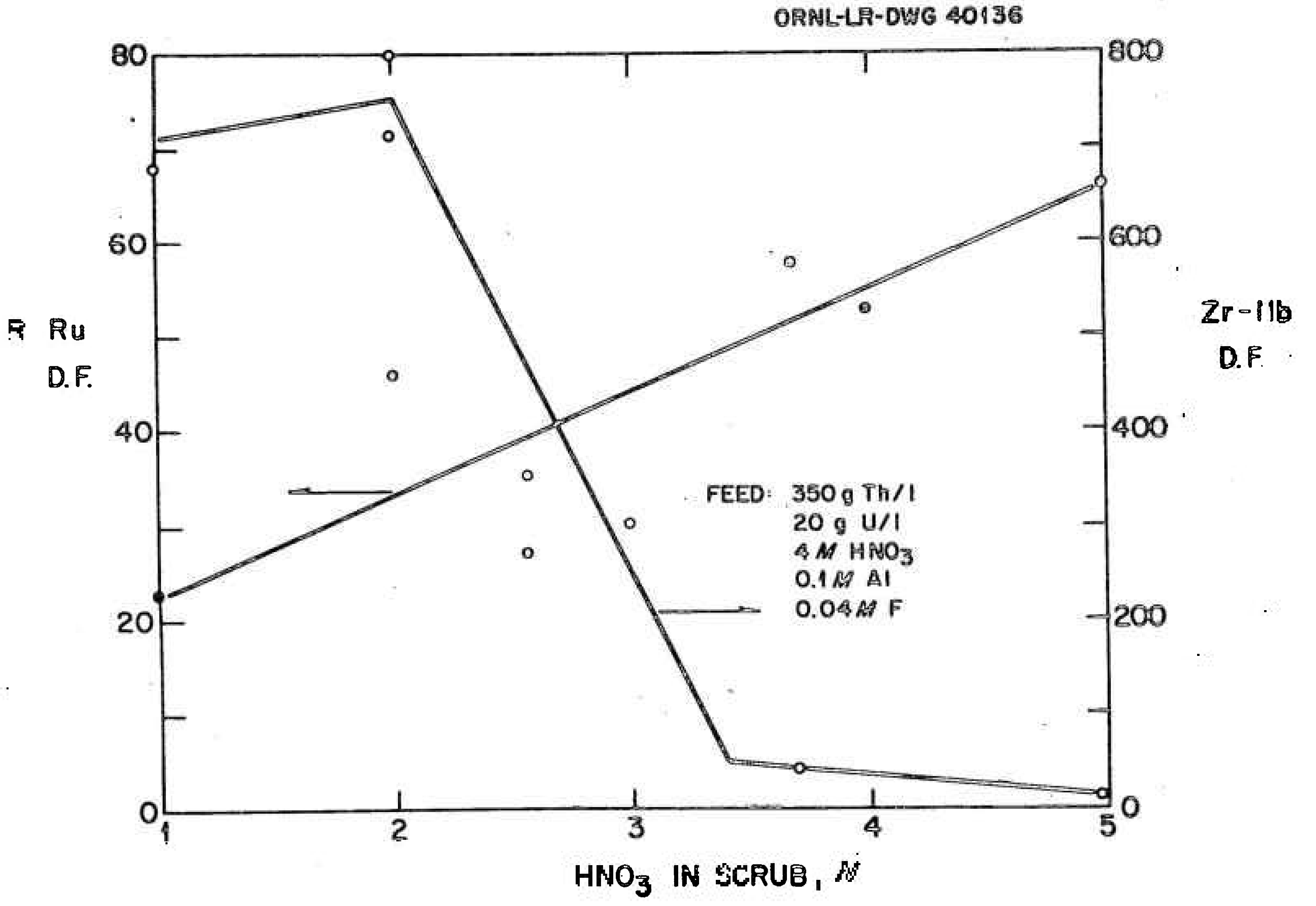


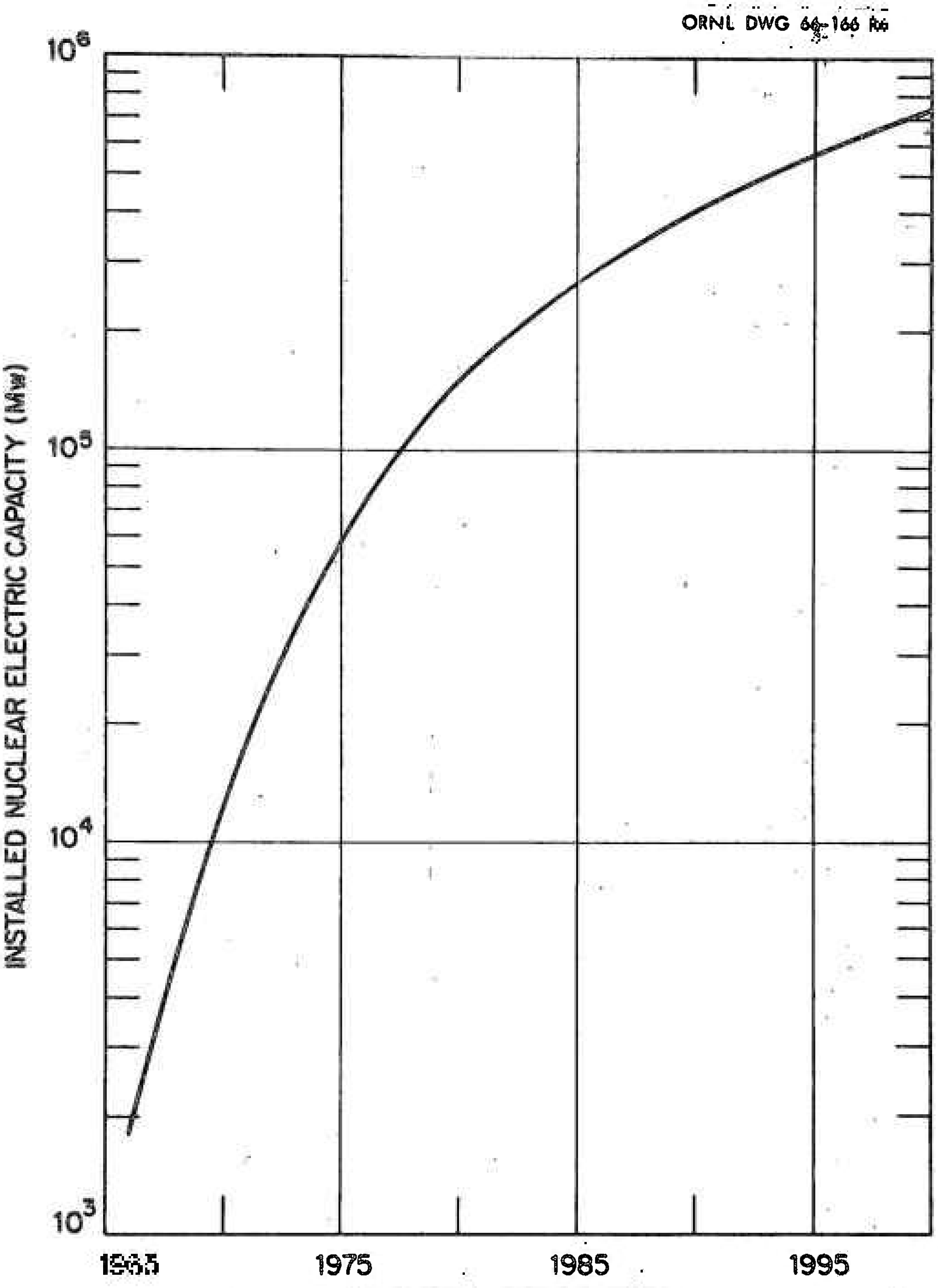
EXTRACTION OF U-233 FROM DAUGHTERS OF U-232

ORNL-LR-DWG 21059



D. C. $\left(\frac{O}{A}\right)$ VS Th CONCENTRATION IN ORGANIC PHASE


ORNL-LR-DWG 40136
Ru
D.F.
Zr-Nb
D.F.
80
60
40
20
0
800
600
400
200
0
1
2
3
4
5
HNO$_3$ IN SCRUB, N
FEED: 350 g Th/l
20 g U/l
4 M HNO$_3$
0.1 M Al
0.04 M F



PROJECTED U.S. NUCLEAR ELECTRIC CAPACITY (AEC-1967)

ORNL Dwg. 67-5200

APPROXIMATE NUCLEAR AND COAL POWER COSTS (mills/kwh)

Nuclear	Private	Public
Reactor Capital Cost	1.90	
Reactor Operating Cost	0.45	
Fuel:		
Ore production	0.37	
Conversion: U_3O_8 to UF_6	0.07	
Enriching	0.48	
Pu credit	-0.25	
Fuel inventory	0.25	
Fabrication	0.56	
Processing & waste (0.017)	0.17	
TOTAL	4.00	2.4
Coal Plant	4.33	2.9

ORNL Dwg. 67-5199

IMPORTANCE OF SIZE IN FUEL PROCESSING

	Plant Size (MT/day)	
	2	10
Spent-Fuel Reprocessing[a]		
Capital Investment, $\$10^6$	37	64
Annual Operating Cost, $\$10^6$	3.2	6.7
Annual Waste Disposal Charges, $\$10^6$	2.3	6.0
Unit Capital Cost at 22% FCR,[b] \$/kg	15.7	5.4
Unit Operating and Waste Costs, \$/kg	10.6	4.9
Unit Total Cost, \$/kg UO_2	26.3	10.3
Unit Total Cost, mills/kwh(e)	0.18	0.07

---

[a] 20,000 Mwd/MT, 30% efficiency.

[b] Fixed charge rate (depreciation, ROI, taxes, insurance).

ORNL DWG 68-12231

Projected Costs of LWR Fuel:
Processing, Waste Management, and Shipping

	Year		
	1970	1975	1985
Nuclear capacity, 10^3 Mw(e)	12	50	230
Processing rate, tons/day	0.6	5	30
Costs, mill/kwhr(e)[a]			
Processing	0.18	0.16	0.093
Waste	0.021	0.019	0.016
Fuel shipping	0.033	0.030	0.025

---

[a] Burnup, 20,000 Mwd/ton. Thermal efficiency, 0.325.

AQUEOUS METHODS FOR REPROCESSING LMFBR ELEMENTS

R. E. Blanco

The development of aqueous processing methods for LMFBR fuels is a major program in the Chemical Technology Division of ORNL at the present time. Much of the aqueous processing technology described in the previous lecture can be applied to reprocessing Liquid Metal Cooled Fast Breeder Reactors (LMFBR). However, a number of new, difficult problems occur in reprocessing LMFBR fuels. These problems and our current proposed solutions to the problems are the subject of this lecture. Briefly, the major problems in reprocessing LMFBR fuels arise from the heat generated and the radioactive gases volatilized from short-cooled high burnup fuel. The high plutonium concentration in the fuel also causes criticality problems, and the complicated fuel element design causes mechanical handling problems. The problem of removing radionuclides from off-gases will be discussed in a subsequent lecture.

Early fast breeders are now in existence in the U. S., EBR I, EBR II, and SEFOR; and a large AEC Fast Flux Test Facility (FFTF) will start up in about 1973. Other demonstration reactors are planned in the late 1970's, and commercial reactors are expected in the early 1980's. Thus, present day fuel reprocessing plants must be revised so they can handle the reprocessing load until enough fuel is available to support a reprocessing facility specially designed for LMFBR reprocessing. Thus, our reprocessing development program has two main objectives. An initial objective is to modify existing aqueous processing methods and combine them with new head-end processing steps to permit interim processing of LMFBR fuels in plants which will be constructed during the next 10 years. The longer-term objective is to develop aqueous processes for more efficient treatment of the advanced fuels in either multipurpose or single-purpose central plants.

I have attached a reprint of a recent paper on reprocessing LMFBR prepared by members of the Chemical Technology Division of ORNL. This paper and the references given in the paper serve as a basis for this lecture.

SLIDE 1 A I Reference Oxide Fuel Core and Axial Blanket (68-9502) (see attached paper)

LMFBR FUELS

It is expected that oxide fuels sheathed in stainless steel will be a characteristic of the early LMFBR reactors, and, for this reason, oxide fuels have been adopted as the reference fuel for initial processing studies. Advanced fuels, such as the carbides and nitrides, have attractive properties and may be of future interest. From early scouting experiments, it appears that carbides and nitrides are easily converted to oxides by heating in an oxidizing atmosphere.

The oxide core fuel element has three zones: the center section is the core containing uranium oxide plus about 20% plutonium oxide as the fissionable material, and the two end sections contain depleted uranium oxide that form the axial blanket of the reactor. While it is practicable to separate the core from the two end blanket sections and process them separately, there is no apparent advantage in doing so, and it has been assumed that they will be processed together. Elements of depleted uranium oxide that form the radial blanket surround the core section of the reactor.

SLIDE 2 Fuel Comparison: Light Water Reactors and Future Fast Breeders (69-8442)

Burnup — Fast breeder reactor fuels will differ from light water fuels currently being processing in the U. S. Fast reactors will suffer much higher specific burnup to minimize fuel cycle costs; but since the core and blanket are likely to be integral in the same fuel element, it is likely that they will be processed together and their average burnup will be not too much different from that currently planned for the more advanced LWR fuels.

Specific Power — Fast breeders will strive for the highest specific power possible to minimize reactor inventory cost.

Decay Heat — The combination of the increased burnup and specific power in fast breeders leads to higher decay heats in the fuel elements after discharge from the reactor, aggravating shipping and head-end handling problems. Heat dissipation is the primary problem in shipping short-cooled fuels, as we shall see when we discuss shipping problems.

Dissolver Insolubles — While normally not troublesome, fast breeder fuels will contain approximately four or five times the concentration of insoluble fission products, molybdenum, zirconium, niobium, rhodium, and palladium.

Retention of Radioactive Gases — Retention of I, Xe, and Kr is the second primary problem in processing short-cooled fuels.

The problem of removing iodine from the off-gas will be discussed in a subsequent lecture. In addition to 10^5 curies, about 2.5 kg of various isotopes of iodine would be released each day from a 5 ton/day reprocessing plant.

Plutonium Content — Fast breeder fuels will contain ten times more plutonium, which will aggravate criticality considerations in plant design, but more importantly, the value of the plutonium supplies the economic inducement for processing at as short a decay time as tolerable.

FUEL SHIPPING

SLIDE 3 Typical Carrier for Shipping LWR Fuels (Photo 93592)

This slide shows a typical cask used for the transport of irradiated fuel elements from light water reactors. Casks typically range in weight from 20 to 100 tons. The Navy presently has a number of casks that weigh 125 tons. The normal shielding material is lead, although steel and even depleted uranium can be used to advantage occasionally. The fuel assemblies are held in racks in an air atmosphere. The trend is to larger casks which will tend to improve the payload to cask weight ratio. Only 2 to 5% of the loaded cask weight is payload, and this upper limit is achieved only in the heavier casks. Many casks are designed to dissipate the fuels heat load from their finned outer surface. In this way the possibility of overheating is minimized since there are no mechanical parts to fail.

Casks are required to meet certain government regulations before they can be approved or licensed. The most stringent of the regulations requires the cask system (which can include an energy absorbing buffer) to be capable of withstanding a 30-ft free fall onto a solid unyielding surface, a 1475°F fire for 30 minutes, a 40-in. drop onto a 6-in.-diam piston (to resist puncture) and submergence in water.

SLIDE 4 Westinghouse Carrier (Photo 97030)

This slide shows the special railroad car for transporting a 75-ton cask designed for Westinghouse. This cask will carry 10 Yankee fuel elements (reactor at Rowe, Massachusetts), and is capable of dissipating 80 Kw of heat. It has two forced (water) circulation coolant systems, one as backup for the other.

Considerable shipping experience has been accumulated in shipping both isotopes and irradiated fuel elements. Accidents have occurred, but because of the foresight of the regulatory bodies, the care taken by the designer, and the responsibility assumed by the cask operators, no major release of activity has been recorded.

SLIDE 5 Projected Costs of LWR Fuels: Processing, Waste Management, and Shipping (68-12231)

This slide shows a recent cost estimate which illustrates the effect of size of processing plant on reprocessing costs and fuel shipping costs. The present-day spent fuel shipping cost is ~0.033 mill/kwhr(e) for an estimated average shipping distance of 1000 miles. This cost is expected to decrease as shipping distances decrease and cask utilization increases, but probably by no more than about 25% by 1985. The cost for shipping short-cooled LMFBR fuels is estimated to be higher by about a factor of 2 to 3.

SLIDE 6 Fast Reactor Fuel Shipping Cost (67-3707)

This slide depicts the probable cost of fuel shipment 1000 miles from the reactor station to a central processing plant, as a function of decay of that fuel before shipment. However, this comparison is only valid if the amount of fuel is constant. Actually the lower curve should decrease because more fuel could be shipped in a given carrier after a longer cooling period.

Because of the high investment in fissile material for the LMFBR [about \$20/kW(e) at \$10/g fissile Pu], the fissile inventory charge is quite significant, i.e., about 0.3 mill/kWh(e) for the period (~500 days) the fuel is in actual service in the reactor. For each additional day in which a fuel charge is withheld from service, the inventory cost will increase by ~0.0006 mill/kWh(e). This is to be compared with an increase in inventory cost for LWR fuel of ~0.0001 mill/kWh(e). Hence, the incentive to recover spent fuel at short decay time is greater in the case of the LMFBR than the LWR.

SLIDE 7 LMFBR Shipping Carrier (68-9921) (see attached paper)

The shipment of LMFBR fuels after short cooling periods is one of the most challenging and difficult problems in the development program. The primary considerations are to provide for the dissipation of the decay heat of the fuel and to maintain cask integrity under accident conditions. A very rugged cask that is believed to provide for safe shipment of short-decayed LMFBR fuel has proceeded through preliminary design, prototype development, and shock testing at ORNL. The full-size cask, which is 7 ft in diameter and 24 ft long and weighs 150 tons, is intended for shipment of 2 tons of core LMFBR fuel at 20 days cooling or 36 subassembly core elements generating about 200 kw of thermal power.

This cask uses a primary coolant of sodium, which provides efficient heat transfer from the surface of the fuel element to the steel cask wall. The use of steel (instead of lead), which has a high melting point, and sodium, which has a low vapor pressure, will permit a temperature of 1300°F (the nominal reactor temperature) as the operating limit for the cask interior. The high temperature alone increases the efficiency of this design by a factor of approximately 8 over previous designs. The secondary coolant system is an integral part of the 18- to 22-in.-thick steel shielding vessel. The steel vessel is, in turn, contained in an energy-absorbing steel crash shield that is designed to limit the maximum impact conditions on the cask to 50 g. The temperature of 20-day-cooled fuel elements will not exceed 1300°F even if accidental loss of the external coolant occurs.

We believe this can be accomplished by use of the following: (1) an exceptionally rugged containment system; (2) energy-absorbing members to protect the cask from heavy impact loads; (3) steel as the biological shield; (4) sodium as primary coolant; and (5) the arrangement of multiple fuel elements in close array inside a single fuel cavity.

FUEL RECEIVING

SLIDE 8 Receiving and Handling (68-12294) (see attached paper)

The receiving facilities must be designed to withdraw the subassemblies from their sodium-filled container(s) into an inert atmosphere (see Fig(s). 5 and 6). Storage of the fuel will be in sodium, or, if it is to be cleaned before shearing, in inert gas with forced cooling. The possibility of failed, sodium-logged pins makes storage in water unattractive. LMFBR fuels will be immersed in molten sodium during their irradiation, and probably during transit to the processing facility. There may be sodium inside the fuel pins, either as the result of failure of the tubes or by design (sodium bonding for heat transfer). The presence, or the threat of the presence, of sodium in the fuel pins will influence the method of handling and storage of LMFBR fuel at the reprocessing plant.

Head-End

The preparation of the fuel element for subsequent chemical steps is complicated because of the need for efficient dissipation of large amounts of heat while performing remote operations. A core fuel element will exceed the maximum allowable temperature of 1300°F in about 20 minutes if not cooled.

SLIDE 9 Central Reprocessing Point for Spent LMFBR Fuel. (Conceptual Fuel Receiving, Unloading, Cleaning and Storage Facility (68-14055) (see attached paper)

SLIDE 10 ORNL Semicontinuous Prototype Shear (5 x 5 in. Tube Bundle) (68-2079AR) (see attached paper)

If it is practical to disassemble the fuel element into individual rods or small clusters, the heat dissipation problem is ameliorated and the mechanical shear can be small, relatively inexpensive, and easily maintained. Disassembly involves trimming the end fittings with an abrasive saw and slitting the shroud with a milling slitter. The wire-wrapped pins can then be handled and fed to the shear in arrays of about 25 without exceeding the maximum temperature of 1300°F. If spring clip spacers are used in place of wire wrapping, an additional removal step to free the rods will be required. This shear is capable of shearing 2.5 tons of fuel per day when handling arrays of 25 pins.

SLIDE 11 Flowsheet for Reprocessing LMFBR Fuel by Aqueous Solvent Extraction (68-11074)

A modified flowsheet is being developed which is broadly similar to that used in present plants, such as Nuclear Fuel Services, the first private plant in the U. S. However, significant modifications are required.

High Speed Shear - (Described in previous slide.)

Fuel Oxidizer

The removal of radioactive gases from the off-gas is a major problem in processing 30- to 60-day-cooled LMFBR fuel. We are studying a pre-treatment method that would release these gases in a concentrated stream to facilitate treatment and/or isolation. This method involves treatment of the sheared fuel with oxygen at 450 to 700°C to oxidize UO_2 to U_3O_8 and to release the interstitially trapped volatile fission products. Greater than 90% of the tritium, 20 to 98% of the Kr, and about 75% of the iodine were removed in initial small scale tests at ORNL.

Dissolver

Both batch and continuous dissolvers are being studied.

Solvent Extraction

A modified purex process is being developed. With LMFBR fuels, complete decontamination of the uranium will probably not be required in the near future. Indeed, studies indicate that it would be more economical to store the partially decontaminated uranium and use new uranium in the recycle fuels. Modifications of the flowsheet under consideration include: (1) the use of 15% TBP instead of 30% TBP, and the limitation of the fissile plutonium concentration in the feed to 5 g/liter to assist in criticality control, (2) the use of ferrous nitrate-hydrazine or uranous nitrate-hydrazine instead of ferrous sulfamate as the reductant in the partitioning column, and (3) the use of co-extraction and stripping in the first cycle and elimination of the partitioning column. The plutonium could be separated in a second cycle, using a secondary amine, such as di(tridecyl)amine, from which the plutonium is easily stripped with dilute nitric acid. Further purification of the plutonium would require additional cycles of solvent extraction with TBP or amines. Conventional ion exchange systems could also be used as the final purification step.

SLIDE 12 Actual and Projected Solvent Dose with Thermal and Fast Reactor Fuels (67-6964)

Aqueous solvent extraction uses a solvent, usually TBP in a hydrocarbon diluent. Radiation damage to the solvent, if excessive, can result in anaomalous behavior, stripping difficulties, emulsion formation, precipitation with cumulative plugging of the contactor equipment, and some impairment of the decontamination factor. These problems, which are annoying and should be ameliorated if possible, are usually exaggerated in the literature. Actually, most of the literature data was obtained in experiments performed on separate phases and not with mixed phases under comparable process conditions. Therefore, it is difficult and frequently misleading to use some of the existing solvent exposure data as bases for predicting solvent performance in fast reactor fuel processing.

This slide shows exposures which can be reported with some certainty for four processes, and these are compared with some calculations which have been made for future fast reactor fuel processing. The predicted doses of 0.03 whr/liter/cycle for the pulse column at 150 days cooling and 0.07 for 30 days cooled are comparable to present operating experience.

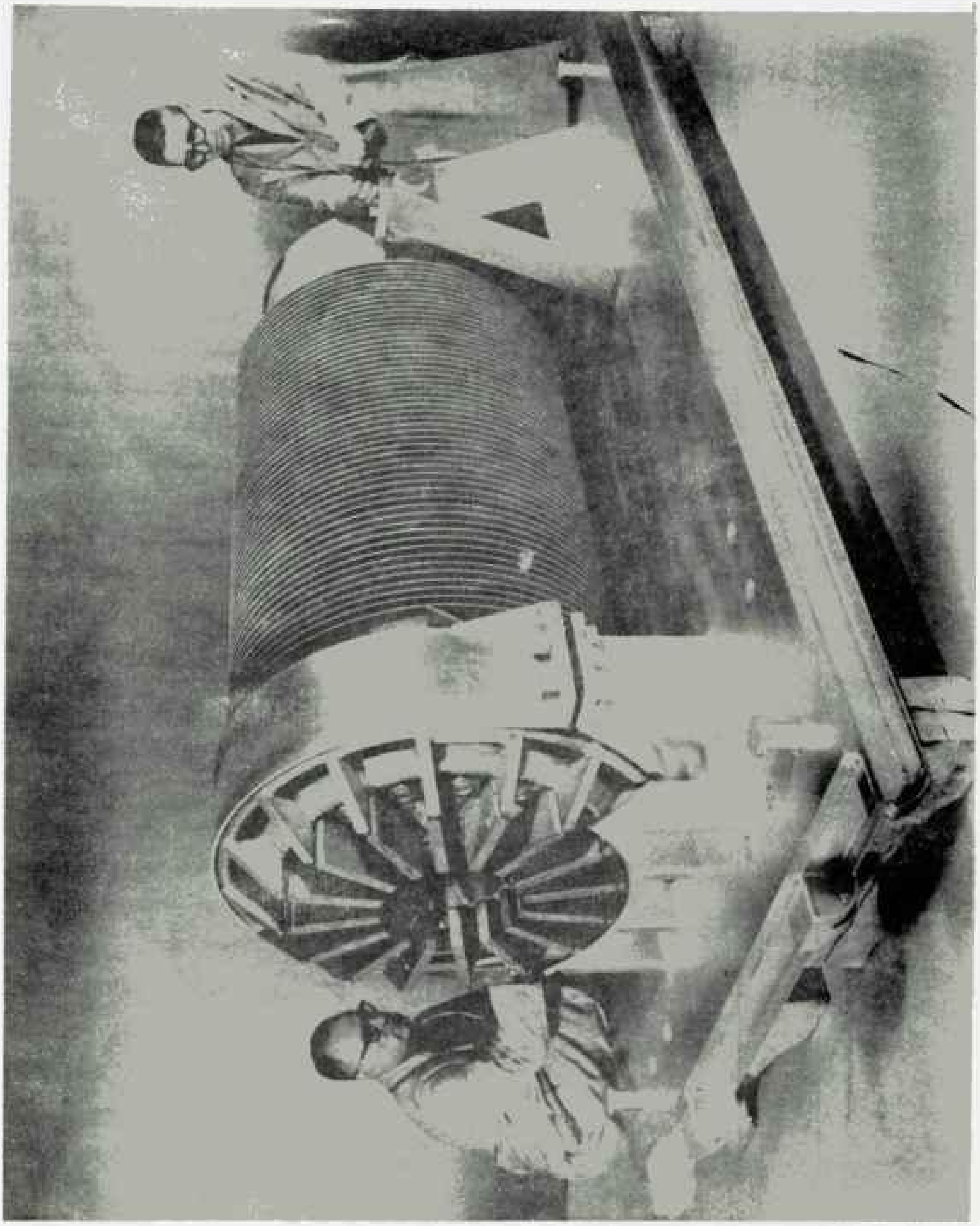
The problem of solvent damage by radiation has been evaluated by surveying the operating experience in existing fuel processing plants and in experiments at ORNL. The latter, employing fuel irradiated to a burnup of 33,000 Mwd/ton and cooled 30 days, were designed to exceed the proposed LMFBR processing conditions. It was concluded that radiation damage is not an overriding problem. Production plants have operated successfully with high total radiation doses to the solvent. Laboratory scale tests of the LMFBR-TBP flowsheet showed no decrease in solvent decontamination efficiency or other observable effects after three cycles of extraction and solvent washing in which the solvent received a radiation dose up to 2.0 whr per liter per cycle. A radiation dose of about 0.1 whr per liter per cycle is expected in a pulse column system; however, doses should be lower, by at least a factor of 10, if fast contactors such as the Savannah River centrifugal contactor or the ORNL stacked-clone contactor are used.

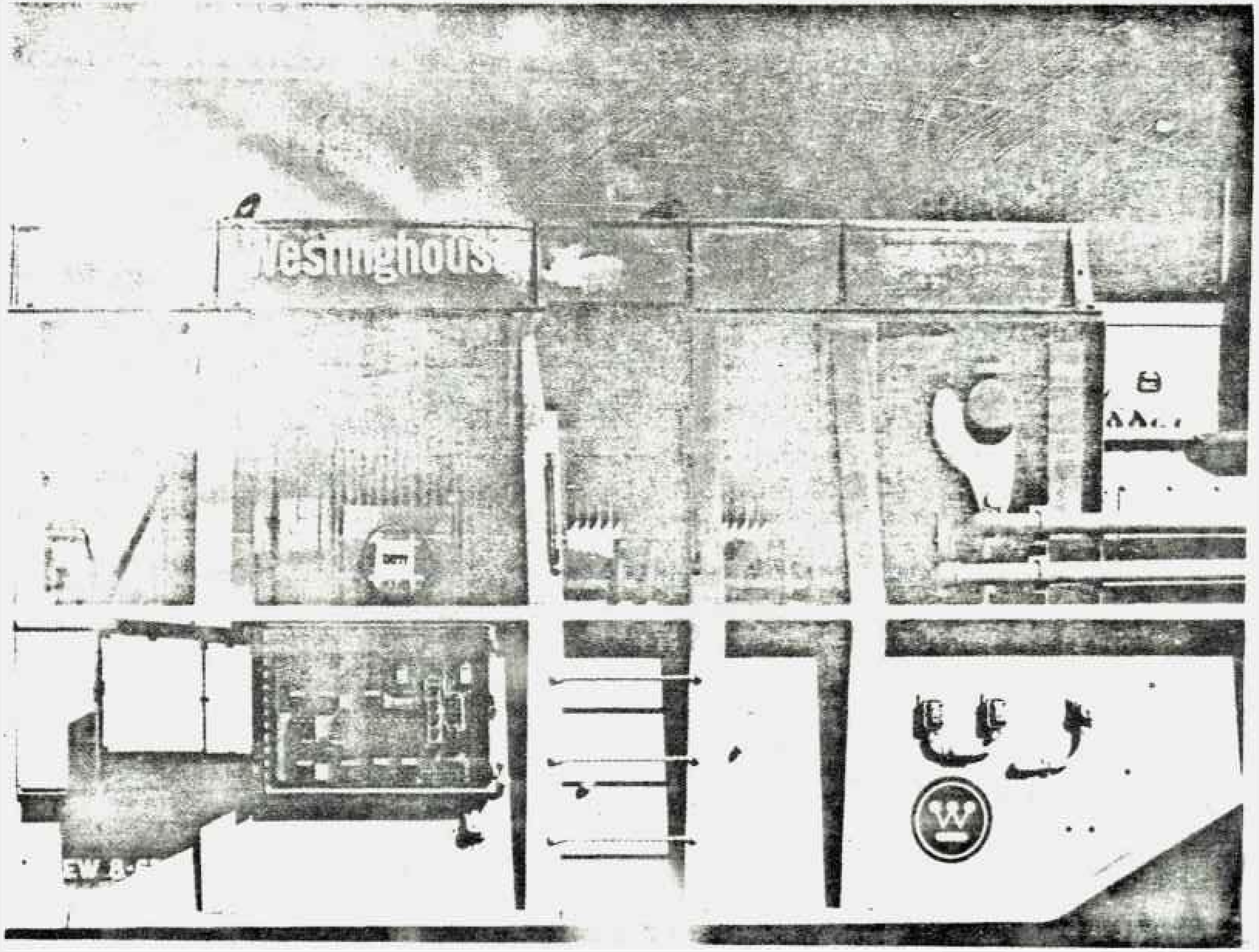
In conclusion, we believe we are making excellent progress on the total problem of reprocessing LMFBR fuel and particularly on the difficult problems of shipping and receiving where heat evaluation is controlling and on retension of volatile fission products, where ^{131}I is the principal problem.

ORNL DWG 69-8442

FUEL COMPARISON: LIGHT-WATER REACTORS AND FUTURE FAST BREEDERS

	TYPICAL FAST FUEL		TYPICAL LWR WITH ENRICHED UO_2
BURNUP, Mwd/METRIC TON			
CORE	80,000		20,000
CORE AND BLANKET, AVERAGE	33,000		
SPECIFIC POWER, kw/kg FUEL IN CORE	150		30–40
DECAY HEAT, w/kg FUEL			
30-DAY DECAY:			
CORE	200		47
(CORE AND BLANKET)	(80)		
150-DAY DECAY:			
CORE	(76)		17
(CORE AND BLANKET)	(30)		
PLUTONIUM CONTENT, g/kg FUEL			
CORE	240		8
(CORE AND BLANKET, 72% Pu IS FISSILE)	(100)		
IODINE, CURIES/TON	30-DAY	150-DAY	150-DAY
CORE	4×10^5	12	3
CORE AND BLANKET	2×10^5	5	
PROCESS CONTAINMENT FACTOR FOR 1-TON/DAY CAPACITY	$\sim 10^8$	$\sim 10^3$	$\sim 10^2$




Westinghous
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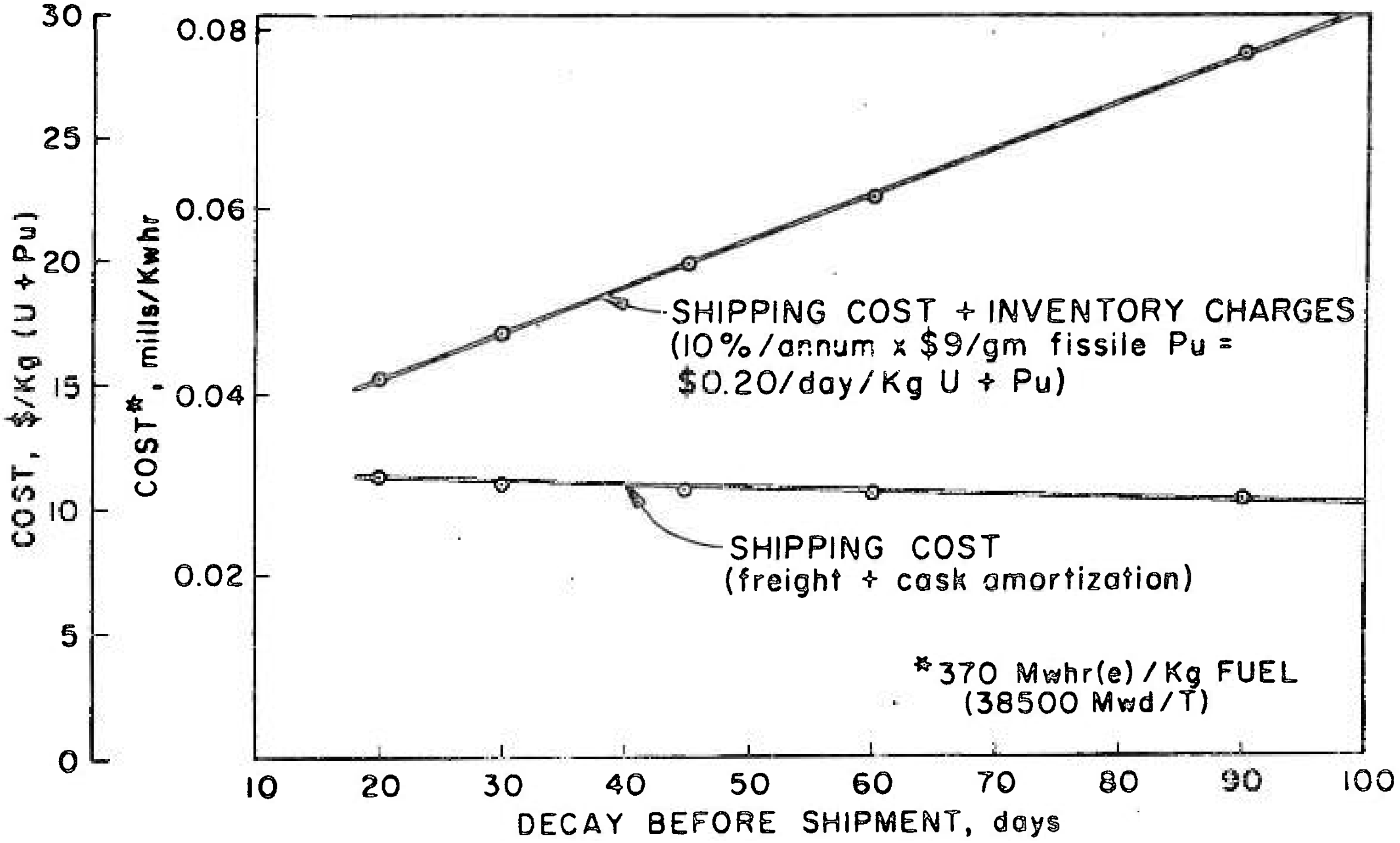
ORNL DWG 69-12231

Projected Costs of LWR Fuel: Processing, Waste Management, and Shipping

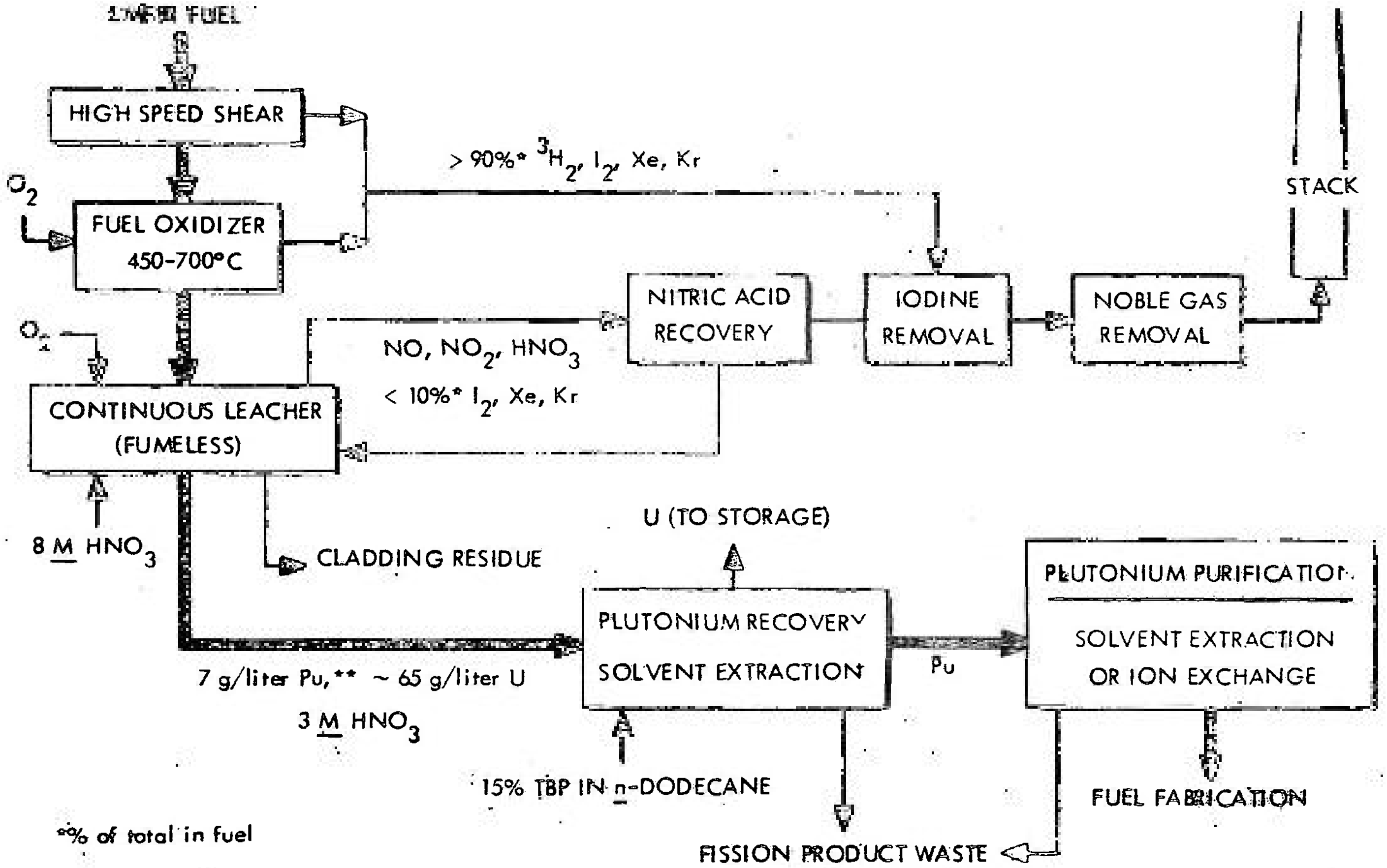
	Year		
	1970	1975	1985
Nuclear capacity, 10^3 Mw(e)	12	50	230
Processing rate, tons/day	0.6	5	30
Costs, mill/kwhr(e)[a]			
Processing	0.18	0.16	0.093
Waste	0.021	0.019	0.016
Fuel shipping	0.033	0.030	0.025

[a] Burnup, 20,000 Mwd/ton. Thermal efficiency, 0.325.

ORNL DWG 67-3707



ORNL DWG 68-11074



*% of total in fuel

**5 g/liter fissionable Pu

FLOWSHEET FOR REPROCESSING LMFBR FUEL BY AQUEOUS SOLVENT EXTRACTION

ORNL DWG 67-6964

ACTUAL AND PROJECTED SOLVENT DOSE WITH THERMAL AND FAST REACTOR FUELS

Process	Contactor	Feed (watts/liter)	Dose, w-hr/liter Per Cycle	Dose, w-hr/liter Total
Actual				
Savannah River Purex	Mixer-Settler	--	--	10-200
Windscale	Mixer-Settler	--	0.04	--
Short-Decay Thorex	Pulsed-Column	10	0.12	--
Dounreay Fast Reactors	Mixer-Settler	$\sim$3	$\sim$0.3	1.5
Projected for Fast Reactors				
ORNL	Pulsed-Column	2[a]	0.03	--
		6	0.07	
Karlsruhe	Mixer-Settler	7	1	--
KAPL	Mixer-Settler	120	1.7	--

[a] 38,000 Mwd/ton, 75 g fuel/liter; 150 day cooled - 2 watts/liter; 30 day cooled - 6 watts/l.

APPLICATION OF AQUEOUS REPROCESSING TO LIQUID METAL FAST BREEDER REACTOR FUEL *

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ABSTRACT

The low-priced power that is one of the incentives for the development of the Liquid Metal Fast Breeder Reactor (LMFBR) depends in part on economic processing of spent fuel. Some form of the Purex Aqueous Solvent Extraction process is used by nearly every major fuel processing facility in existence, and it will be desirable to extend its application to include the processing of the LMFBR fuels. These fuels are inherently more difficult to process than present light-water reactor (LWR) fuels, owing to the fact that LMFBR fuels will operate at higher specific powers and for greater burnup and will contain more plutonium than the corresponding LWR fuels. The higher specific power and burnup produce heat dissipation problems during handling and transport of the spent fuel. The high plutonium content makes short cooling a significant economic incentive, and development work will be aimed at improving our technique for accommodating short-lived fission products to make short-cooled processing feasible.

INTRODUCTION

This paper presents a description of the problems involved in the application of aqueous chemical processing technology to the reprocessing of spent Liquid Metal Fast Breeder Reactor (LMFBR) fuels. The present status of technology is also presented, based on the development program in progress at Oak Ridge National Laboratory and on technology available from private and AEC reprocessing installations. The objectives of the ORNL development program are; first, to reduce, with time, the uncertainties that exist in applying present aqueous processing technology to future LMFBR fuels; second, to provide the technology necessary to adapt LWR fuel processing plants to the processing of LMFBR fuels in the interim period before the LMFBR fuel load increases to the point that it can support a separate processing plant; and to provide the technology necessary for eventual commercial LMFBR fuel reprocessing plants. The latter, long-term approach is reserved for those problems that are occasioned by the economic incentive for short-decay processing and which are of such technical complexity as to require an extensive development period.

The first fuels to be reprocessed will be produced in the Fast Flux Test Reactor (FFTR) and the demonstration reactors now being proposed. The Atomic International Reference Oxide Reactor (NAA-SR-Memo-12604), has been selected as the reference reactor for the initial reprocessing development program, since it is representative of many of the new problems in reprocessing, which are not present or are not as significant with light water reactors (LWR) fuels. These problems are derived from four factors: (1) the desire to minimize inventory costs and reprocess the fuel as soon after discharges as possible, which causes higher thermal power, radiation level, and concentrations of important volatile fission products; (2) a high concentration of plutonium, which requires special consideration for criticality control; (3) the presence of liquid sodium on, or in, the fuel rods, and (4) the dimensions and method of fabrication of the fuel assemblies, which present problems in preparing, or disassembling, the fuel prior to reprocessing.

(*) Presented at the Symposium on Reprocessing of Nuclear Fuels, Ames, Iowa, August 25-27, 1969. **Nuclear Metallurgy,** Vol. 15, CONF-690801.

The present intention is to modify the current technology for shipping and reprocessing LWR fuels to the extent required for LMFBR fuels. The Purex solvent extraction process is used in all major fuel reprocessing facilities in existence and its important favorable features also apply to the processing of LMFBR fuels. The unexcelled separation efficiency, the process versatility, the ease of adaptation of the process to continuous high-capacity equipment, and the vast operating experience available from major processing facilities make the aqueous solvent extraction process on obvious choice for adaptation to reprocessing of LMFBR fuel.

PUREX PROCESS

The Purex process, as applied to LWR oxide fuels (see Fig. 1) consists of fuel shearing to rupture the corrosion-resistant sheath and expose the fuel, dissolution in nitric acid, solvent extraction, and conversion of the uranium and plutonium nitrate product to oxides for refabrication into fuel elements. The spent fuel is transported from the reactor to the chemical processing plant in shielded casks, which are unloaded in a water-filled pool or canal. The fuel elements are transferred to a head-end cell, sheared into approximately 1/2 in. lengths and the product leached with nitric acid in batch dissolvers. The residual sheared, leached hulls are disposed of as solid waste. The nitric acid solution of the fuel, containing uranium, plutonium, and nearly all of the fission products, is the feed solution for the solvent extraction process.

The solvent for the Purex process in an organic complexing compound tributyl phosphate (TBP), in an inert hydrocarbon kerosene-like diluent such as dodecane. The solvent is brought into intimate countercurrent contact with the aqueous feed solution where the TBP extracts the uranium and plutonium into the organic phase, leaving the fission and corrosion products in the aqueous solution. The latter is stored as high-level radioactive waste. The organic solution is selectivity stripped of plutonium with dilute nitric acid by reducing the plutonium valence from +4 to +3. The uranium is then stripped in a third contactor. The plutonium is further purified by additional extraction cycles or by ion exchange.

The uranium and plutonium may be precipitated from their dilute nitric acid solution and converted to oxides by thermal decomposition, or they may be directly converted to oxides by the sol-gel process, in which the nitric acid is removed from aqueous solutions of plutonium or uranium by extraction with an amine or heavy alcohol. In the sol-gel process the uranium or plutonium, as the acid extraction proceeds, gradually forms into a colloidal suspension or sol. This can be handled like a true solution. Progressive removal of water by evaporation or by extraction with a hygroscopic solvent converts the sol to a plastic gel. Sols of plutonium and uranium can be combined and gelled togheter to form an oxide in which the two elements are homogeneously dispersed. The gel when fired to ~1200°C approaches theoretical density and is suitable for fabrication into reactor elements(1,2). The sol-gel process is designed to couple easily with the Purex process for preparing plutonium for recycle. However, uranium from LMFBR fuels has little value and will probably be stored. Makeup uranium will be supplied from diffusion plant tailings for many decades.

LMFBR FUELS

It is expected that oxide fuels sheathed in stainless steel will be a characteristic of the early LMFBR reactors, and, for this reason, oxide fuels have been adopted as the reference fuel for initial processing studies. Advanced fuels, such as the carbides and nitrides, have attractive properties and may be of future interest. From early scouting experiments, it appears that carbides and nitrides are easily converted to oxides by heating in an oxidizing atmosphere.

The oxide core fuel element has three zones: the center section is the core containing uranium oxide plus about 20% plutonium oxide as the fissionable material, and the two end sections contain depleted uranium oxide that form the axial blanket of the reactor (Fig. 2). While it is practicable to separate the core from the two end blanket sections and process them separately, there is no apparent advantage in doing so, and it has been assumed they will be processed together. Elements of depleted uranium oxide that form the radial blanket surround the core section of the reactor.

The average burnup of the fast breeder fuel is expected to be approximately 80,000 Mwd/metric ton for the core, and about 33,000 Mwd/metric ton for the core and blanket mixture (see Table I). This average burnup is about that expected for LWR fuels. Fast-breeder reactors will have a high fissionable plutonium inventory and the specific power will be about 150 kw/kg of fuel in the core compared to 35 for LWR's. This combination of high burnup and high specific power makes the decay heat of discharged core fuel from fast-breeder reactors about a factor of 5 higher than that of thermal reactors. There will also be a higher concentration of long-lived fission products in the LMFBR core fuel, roughly in proportion to the higher burnup. Fast-breeder fuels have a higher plutonium content than light-water fuels by about a factor of 10, which complicates the control of criticality, emphasizes the importance of plutonium chemistry, and may occasion the need for shielding for plutonium product handling operations to attenuate the neutrons generated by α-n reactions and spontaneous fissions. The value of the plutonium content of LMFBR fuel results in an economic incentive for minimizing the decay period before reprocessing.

INTERIM PROCESSING

During the interim period, before facilities designed specifically for short-cooled fast-breeder fuel are available, it should be possible to process the fuel from early fast-breeder reactors, the FFTR and demonstration reactors, in existing LWR processing facilities modified for this purpose. Such fuel could be cooled until shipment is possible (not necessarily optimum for commercial fast-breeder fuel but economically torelable during the interim period) and then processed at about half normal capacity in an existing LWR plant altered to accommodate the greater length of the FFTR elements, deal with sodium contamination, and provide capacity for the higher plutonium content.

A preliminary evaluation was made of the capacity of the NFS plant for the processing of LMFBR fuel. Assuming a mixed core and blanket feed of 180 days decay, a throughput of 1/2 ton/day of LMFBR fuel was found to be compatible with existing licensing agreements at NFS. Modifications in the front end receiving and mechanical head-end facilities, and in the plutonium tail-end ion-exchange equipment would be required. A flowsheet based on 15% TBP and subcritical feed concentrations would be dictated by the geometrically unrestricted equipment at NFS. A plant operating time of 40 days should accommodate the 20 tons of fuel discharged per year from a 1000-Mw(e) LMFBR reactor. It was assumed that the capital modifications required would cost $5 million, the annual charges of which would be borne by the LMFBR fuel processed, in addition to the plant operating cost of $31,300 per process day. On this basis the LMFBR fuel reprocessing cost would be on the order of 0.4 mill/kwhr(e).(3)

PROCESS ADAPTATION

The long-range economic success of the LMFBR concept is dependent upon a relatively cheap fuel cycle and it is necessary to establish chemical processing feasibility and acceptable processing costs if the LMFBR concept is to be attractive to commercial interests. The high plutonium content of LMFBR fuel represents a high dollar value, and the inventory penalty while the fuel is not producing power can become an appreciable fraction of the processing cost. At 12% per annum, a month's storage is the economic equivalent of a 1% process plutonium loss; and a 6 month preprocessing decay, required under present technology for the decay of fission product iodine, would constitute an inventory penalty approximately equal to the processing cost. The optimum preprocessing decay period cannot now be established, but the incentive for minimizing it is readily apparent. The problems of heat dissipation, radioactivity, and volatile fission product retention are an exponential function of the decay period.

Shipping and Receiving:

LWR fuel has been shipped in casks safely over a number of years using only air as the primary coolant. Shipping LMFBR fuel in air-filled casks is not feasible at cooling time of less than one year. For this reason we are proposing that a liquid metal be used as the primary coolant. Sodium is an obvious choise, assuming that its loss during accident conditions can be prevented. All shipments of spent fuel are subject to the Department of Transportation (DOT) regulations which state that a cask must survive a 30 ft drop and a 1475°F fire of 30 min duration without excessive release of radioactive materials or reduction in shielding.(4) Mechanically reliable closures are commercially available that can probably be adapted to survive any of the postulated impact conditions of a major accident. We have made a conceptual design of a cask that uses steel for shielding. Approximately 20 in. of steel will be required and the cask can be so rugged that its rupture during any postulated impact, particularly if fitted with an energy-absorbing exterior frame as shown in Fig. 3, is virtually not conceivable. The illustrated model survived the 30 ft fall and impact on an unyielding surface, with only superficial damage to the cask proper and no leakage of the seal.

The postulated fire test would not produce excessive temperatures in the fuel cavity owing to the heat capacity of the massive steel shield. This will require that the cask be at near-ambient temperature prior to the initiation of the fire, and a secondary coolant system is envisioned (see Fig. 4).

The conceptual design illustrated would accommodate 18 fuel elements, although a 36-element cask may be technically attainable. The major parameters were varied as a function of the ratio of weight of the cask to weight of fuel, W_s/W_f (see Table II). The cask design has not been optimized, but one restraint was the arbitrary acceptable maximum fuel-pin cladding temperature of 1300°F, its maximum operating temperature in the reactor. Graded shielding refers to the tapering of the ends of the carrier to the minimum required shielding to economize on weight.(5) Shortening the fuel by cropping the inactive fuel element ends (gas plenum and end fittings) is attractive from the shipping standpoint, in reducing the carrier size and weight, but the investment in cropping equipment at the reactor station for less than a 5000 Mw(e) station has been estimated to offset the saving in shipping cost.(6)

LMFBR fuels will be immersed in molten sodium during their irradiation, and probably during transit to the processing facility. There may be sodium inside the fuel pins, either as the result of failure of the tubes or by design (sodium bonding for heat transfer). The presence, or the threat of the presence, of sodium in the fuel pins will influence the method of handling and storage of LMFBR fuel at the reprocessing plant. The receiving facilities must be designed to withdraw the subassemblies from their sodium-filled container(s) into an inert atmosphere (see Fig(s). 5 and 6). Storage of the fuel will be in sodium, or, if it is to be cleaned before shearing, in inert gas with forced cooling. The possibility of failed, sodium-logged pins makes storage in water unattractive.

Head-End

The preparation of the fuel element for subsequent chemical steps is complicated because of the need for efficient dissipation of large amounts of heat while performing remote operations. A core fuel element will exceed the maximum allowable temperature of 1300°F in about 20 minutes if not cooled.

The most attractive and versatile head-end step at present is the mechanical shearing of the fuel into short lenghts. Melting of the cladding or dissolution of the cladding in molten metals such as zinc or antimony-copper alloy are interesting alternatives for some possible cladding materials, but both require the physical separation and recovery of the fuel oxides, a difficult step.

If it is practical to disassemble the fuel element into individual rods or small clusters, the heat dissipation problem is ameliorated and the mechanical shear can be small, relatively inexpensive, and easily maintained (see Fig. 7). Disassembly involves trimming the end fittings with an abrasive saw and slitting the shroud with a milling slitter. The wire-wrapped pins can then be handled in arrays of about 25 without exceeding the maximum temperature of 1300°F. If spring clip spacers are used in place of wire wrapping, an additional removal step to free the rods will be required.

The problem of the retention of ^{131}I, encountered even in the processing of LWR fuels of 150 days decay, is an important problem with LMFBR fuels. Iodine retention factors are required that are in the range of 10^3 for 150-day-cooled FFTR fuel (near the range of present practice) to 10^8 for future LMFBR fuel processed after 30 days decay. The chemistry of iodine is complex and much more knowledge is needed of the behavior of iodine in the various conditions encountered in a fuel processing plant before a treatment system can be designed with the reliability required for LMFBR fuels. As an exemple, the presence of organic vapors and organic iodides in the off-gas system reduces the efficiency of iodine removal steps. Early studies indicate that the organic materials can be eliminated from the off-gas by conversion to CO_2, H_2O, and I_2 in a catalytic oxidizer using Hopcalite catalyst (oxides of copper and manganese) at 150 to 500°C. A catalytic-oxidizer-charcoal-adsorber system was tested in the Transuranium Processing Plant (TRU) at Oak Ridge National Laboratory and an iodine retention factor of about 10^6 was demonstrated.

It has been found that fission gases interstitially trapped in oxide fuels can be volatilized and collected in a relatively small volume when oxide fuels are heated in oxygen at temperatures greater than ~400°C. Similar volatilization is expected on oxidation of carbide or nitride fuels. Early studies show that nearly quantitative removal of noble gases and $> 90\%$ removal of iodine and tritium is obtained on conversion of UO_2 to U_3O_8. The release of gases is more difficult when the fuel contains a high percentage of PuO_2 (~20%). However, $> 90\%$ of the tritium and 20-98% of the krypton have been removed from highly irradiated 20% PuO_2-UO_2. The removal of iodine from PuO_2-UO_2 remains to be demonstrated.

The efficiency of iodine removal from off-gases should be much higher if it is contained in a small volume of gas after the fuel is sheared but before it reaches the dissolver. This should greatly reduce the problems attributed to removing iodine from dissolver off-gases in current processing experience. The oxidative heat treatment may have other advantages as well. Sodium contamination (failed fuel rods) would be deactivated, and the oxidation of UO_2 to U_3O_8 involves a phase change which tends to break the oxide into a fine granular form, making the physical separation of the oxides from the stainless steel cladding a possibility and providing for a faster dissolution of the fuel in nitric acid. This improvement is probable but whether it applies also to the mixed oxide is yet to be determined. The oxidation of uranium oxide before dissolution also decreases the evolution of nitrous oxides in the dissolver off-gas. The oxidation step may also be a useful means of converting the carbide and nitride advanced fuels to oxides.(7,8)

Dissolution:

The dissolution of solid solutions of $(Pu,U)O_2$ proceeds quite readily in nitric acid and the use of fluoride as a catalyst does not appear to be required. LMFBR fuel samples irradiated to 100,000 Mwd/metric ton have been successfully dissolved in hot-cell tests at ORNL in 8 M HNO_3 in 4 to 8 hours.(9,10) Residues contained $< 0.2\%$ plutonium and consist mainly of ruthenium and rhodium and insoluble stainless steel corrosion products.

Irradiated fuels prepared by the sol-gel, co-precipitation, and mechanical blending processes have been successfully dissolved. However, if a true solid solution has not been formed, the PuO_2 may dissolve too slowly in nitric acid. The sol-gel and co-precipitation processes inherently produce intimate mixtures of PuO_2 and UO_2. Care must be exercised to assure homogeneous blending of oxides if a solid solution is to be produced.

Elemental iodine is evolved rapidly from the hot nitric acid dissolving solution. Iodine present as the iodide oxidizes rapidly to elemental iodine, and that present as the iodate is reduced to elemental iodine by the nitrous acid formed during dissolution of UO_2. In small-scale tests at ORNL, > 99% of the iodine has been removed during dissolution by a proper arrangement of the condenser system (to avoid refluxing iodine back to the dissolver) and by adding iodide and nitrite to the system at the end of the dissolving period. It is desirable to remove iodine before extraction because of the difficulty of containing iodine in the subsequent processing steps.

Extraction:

Solvent extraction processes require organic extraction media, and organics are susceptible to radiation damage. However, radiation damage to the solvent, in spite of the high specific activity of the LMFBR fuels, should not be a significant problem.

The estimated total single-cycle dose to the solvent in pulsed column operation is about 0.11 watt-hr/liter for the 15% TBP flowsheet and about 0.25 watt-hr/liter for the 50% TBP flowsheet. These doses include an allowance of 20% of the β-γ dose obtained in the extraction-scrub section to cover alpha irradiation and irradiation from ^{131}I (which may have accumulated in the solvent). The estimates are for columns operating in the organic-phase-continuous mode at 80% of flooding with an efficiency corresponding to an HETS of 2.5 ft.(9) The British have demonstrated sustained solvent extraction where the single-cycle dose was about 1.4 watt-hr/liter.(11) By using high-speed contactors, such as the centrifugal contactors in use at Savannah River,(12) the extent of solvent exposure to radiation can be held far below the limits that have already proved satisfactory in plant practice.(13) These contactors also have high capacity and quick response and are applicable over a wide range of scale. On the basis of laboratory and hot-cell tests, we have concluded further that pulse columns, such as are currently used in many fuel processing plants, are adequate for LMFBR fuel processing.

Separation of plutonium from uranium is accomplished in the Purex process by reducing the plutonium to the three-valent state to selectively strip it from the solvent. Ferrous sulfamate is used as the reductant in U. S. processing plants. However, LMFBR reactor fuels have a much higher plutonium content and, consequently, the use of ferrous sulfamate could contribute relatively large amounts of iron sulfate to the waste. The sulfate also would interfere severely with plutonium extraction in the second TBP cycle.

The use of ferrous nitrate, stabilized with a small concentration of a holding reductant such as hydrazine, has shown promise in small-scale cold tests.(14) Its use has the advantage of eliminating sulfate, although it still contributes iron to the waste (about as much iron as there is total weight of fission products). By appropriate control of the acid concentration, the partitioning can be accomplished using as little as 25% of the stoichiometric amount of iron otherwise needed, reducing the iron contributed to the waste to about 20% of the weight of the fission products.

Uranium(IV) has been studied extensively as a reductant by many investigators and is used on a production basis in France. It has the advantage of not adding metal contaminants to the waste. The U(IV) nitrate can be prepared by electrolytic reduction, by reduction with H_2 in the presence of platinum catalyst, or by photoactivated reduction with formaldehyde. The reaction rate for reduction with U(IV) is slower than for Fe(II), which may be of importance if short-residence contactors are used.

Final purification of plutonium by extraction using secondary amines is an attractive alternative to anion exchange, the process used in present processing plants. A continuous countercurrent extraction process has obvious advantages over the batch ion exchange process, particularly where criticality considerations may be limiting and where the equipment must be remotely operated and maintained. Shielding will probably be required, because of the α-n reactions and spontaneous fissions from the plutonium. In addition, extraction processes will couple readily to the preparation of reactor-grade oxides by the sol-gel process.

SUMMARY

The economic advantage of large-scale processing plants is so prominent that central processing facilities of capacities in the order of 5 tons/day or greater throughput are generally to be preferred to a proliferation of small (< 1 ton/day) facilities. The continued expansion of the power economy and the increasing technology of power transmission makes large central power parks, in the order of 20,000 Mw, a plausible concept. An on-site processing facility to serve this power park (~1 ton/day) begins to acquire favorable economics due to savings in fuel shipping and inventory costs. The essential processing problems are similar except for fuel transport.

It is expected that plant design trend will be in the direction of high-capacity, small-volume equipment; this is equivalent to minimizing the plant inventory of both reactor fuel and process reagents. Continuous equipment (as opposed to the batch operations characterizing the industry in the past), and perhaps parallel lines to ensure operational continuity, will be easier to maintain and cheaper to operate. Minimizing the in-process inventory will serve both safety and economy considerations.

Fuel casks are expensive but are most economical in large sizes (about 120 tons). Casks will be designed to ensure containment of the enclosed fuel throughout the postulated accidents that might occur during shipment. The cask seals will be designed to permit the carrier to be readily loaded and unloaded at the processing plant to minimize carrier turnaround time.

Present mechanical shears are designed to accept entire subassemblies, denuded only of their hardware. Were the fuel elements designed to be readily disassembled, preshipment disassembly might prove economical by decreasing the cask size and facilitating heat dissipation during shipment. Small, inexpensive, easily maintained, high-capacity shears will be especially attractive if the fuel is easily disassembled.

The most noxious problem facing processing plants of the future is that of the volatile fission products, especially ^{131}I. The volatile fission products, iodine, the noble gases, xenon and krypton, and tritium, perhaps can be volatilized from oxide fuel at moderate temperatures (450 to 750°C). If dilution by the cell atmosphere is minimized, the fission product gases can be very concentrated, making their capture and reduction to solid form efficient and reliable.

The advantages of continuous leachers have always been recognized, but the simpler batch dissolvers were not only adequate but even preferred for small plants, particularly where process control relied upon chemical analysis. Continuous leachers are presently under active development, in response to the obvious advantages of their small physical volume from the standpoint of criticality control.

Countercurrent solvent extraction has been carried out in a variety of contactors: mixer-settlers and pulse columns and more recently in fast centrifugal contactors. The latter reduces radiation and chemical damage to the solvent, and reduces the solvent inventory (and therefore the fire hazards associated with the organics are also reduced). Centrifugal contactors are so responsive that automatic control can be used to simplify operation.

The cell ventilation and vessel off-gas systems are primary sources of routine and accidental radioactivity release. Recycle of cell off-gas is feasible and will minimize the volume of off-gas needing routine treatment. Recycle will probably be quite economical and the use of an inert cell atmosphere (necessary for the sodium-contaminated LMFBR fuel) will become practical. The use of inert cell atmosphere throughout the plant will practically eliminate the hazard of solvent fires.

In many cases the aqueous high-level radioactive wastes will continue to be stored for interim periods in tanks. However, the trend is toward solidification and immobilization of these wastes as soon as possible, as dictated by safety and economics. The technology of solidification of wastes is now in the final stages of development.(15,16)

REFERENCES

1. *Chem. Technol. Div. Ann. Progr. Rept. May 31, 1968,* ORNL-4272.
2. *Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969,* ORNL-4422.
3. E. L. Nicholson, *Preliminary Investigation of Processing Fast-Reactor Fuel in an Existing Plant,* ORNL TM-1784 (May 1967).
4. Code of Federal Regulations, Title 10, Part 71, as published in the Federal Register, Vol. 31, Nº 141, July 22, 1966.
5. A. R. Irvine, "Shipping Cask Design Considerations for Fast-Breeder-Reactor Fuel," *Proceedings of the 16th Conference on Remote Systems Technology, Idaho Falls, Idaho, March 11-13, 1969.*
6. B. C. Finney, R. S. Lowrie, and C. D. Watson, *A Conceptual Design and Cost Estimate of an On-Site Facility for Cleaning, Disassembling, and Canning Short-Cooled LMFBR Fuel in Preparation for Shipment to a Central Reprocessing Plant,* ORNL TM-2050 (May 1968).
7. J. R. Flanary *et al., Nucl. Appl. 1,* 219 (1965).
8. C. Moreau and J. Phillipot, *Compt. Rend. 256,* 5366 (1963).
9. W. E. Unger *et al., Aqueous Processing of LMFBR Fuels Progress Report, March 1969, Nº 1,* ORNL TM-2552 (April 1969).
10. W. E. Unger *et al., Aqueous Processing of LMFBR Fuels Progress Report, April 1969, Nº 2,* ORNL TM-2585 (May 1969).
11. R. H. Alardice, "Reprocessing of Fast Reactor Fuels by Aqueous Methods, Part 2. Second and Third Generation Fast Reactors," presented at Institutt for Atomenergi, Kjeller Research Establishment, Norway, August 1967.
12. A. A. Kishbaugh, *Performance of Multistage Centrifugal Contactor,* DP-841 (October 1963).
13. C. A. Blake, Jr., *Solvent Stability in Nuclear Fuel Processing: Evaluation of the Literature, Calculation of Radiation Dose, and Effects of Iodine and Plutonium,* ORNL-4212 (March 1968).
14. D. E. Horner, *The Use of Ferrous Nitrate as a Plutonium Reductant for Partitioning Plutonium and Uranium in Purex Processes,* ORNL-4383 (February 7, 1969).
15. J. O. Blomeke *et al.,* "Estimated Costs of High-Level Waste Management," *Proceedings of the Symposium on the Solidification and Long-Term Storage of Highly Radioactive Wastes,* February 14-18, 1966, Richland, Washington, CONF-660208, pp. 830-43.
16. K. J. Schneider, *Status of Technology in the United States for Solidification of Highly Radioactive Liquid Wastes* BNWL-820 (October 1968).

LIST OF FIGURES

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ORNL DWG 68-10616

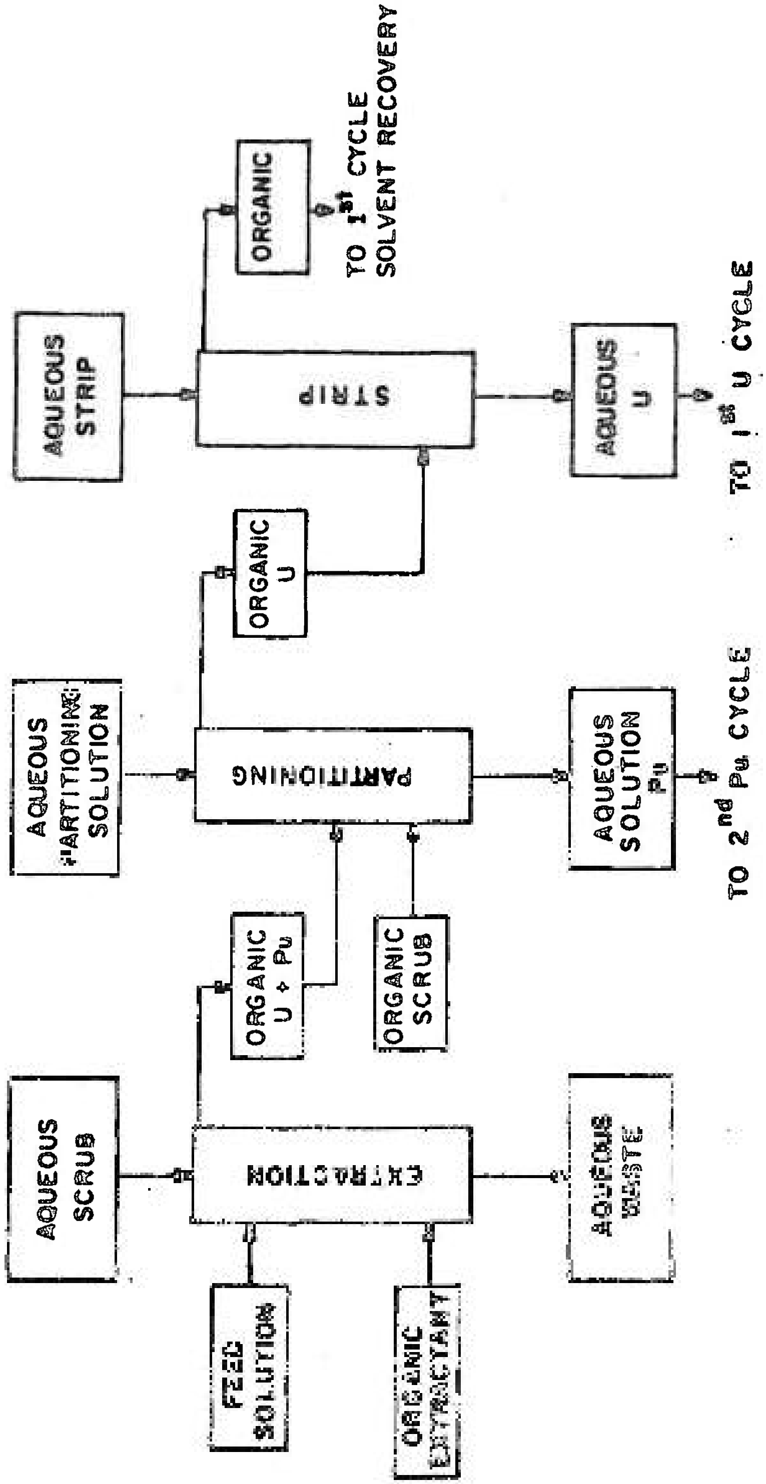
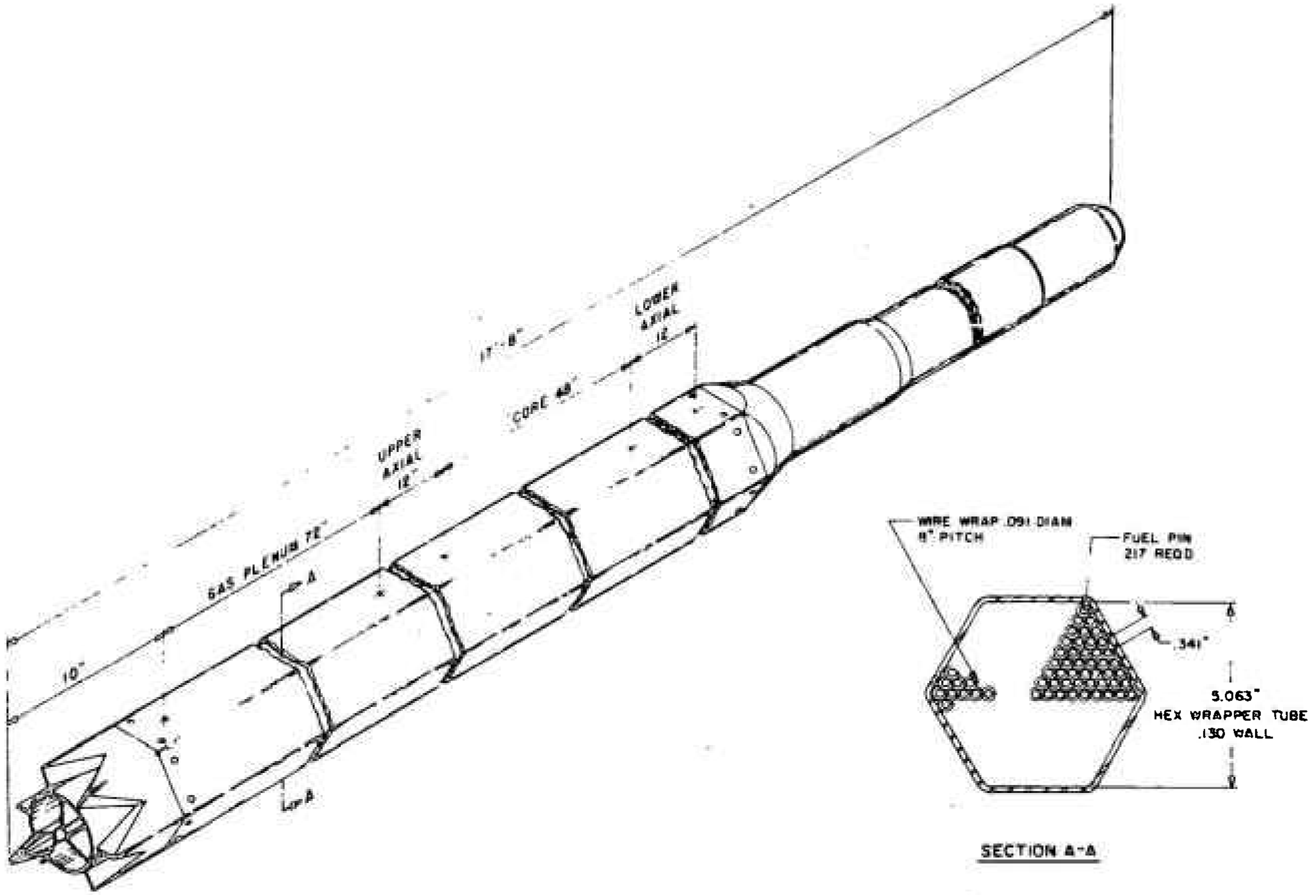


Table 1. Fuel Comparison: Light-Water Reactors and Future Fast Breeders

	Typical Fast Fuel		Typical LWR With Pu Recycle	Typical LWR With Enriched UO_2
Burnup, Mwd/metric ton				
Core	80,000		34,000	20,000
Core and blanket, average	33,000			
Specific power, kw/kg fuel in core	150		30-40	30-40
Decay heat, w/kg fuel				
30-Day decay:				
Core	200		50	47
(Core and blanket)	(80)			
150-Day decay:				
Core	(76)		22	17
(Core and blanket)	(30)			
Plutonium content, g/kg fuel				
Core	240		27	8
(Core and blanket, 72% Pu is fissile)	(100)			
Iodine, curies/ton	30-Day	150-Day	150-Day	150-Day
Core	4×10^5	12	3	3
Core and blanket	2×10^5	5		
Process containment factor for 1-ton/day capacity	$\sim 10^8$	$\sim 10^3$	$\sim 10^2$	$\sim 10^2$

ORNL DWG 68-9502



AI REFERENCE OXIDE FUEL CORE AND AXIAL BLANKET

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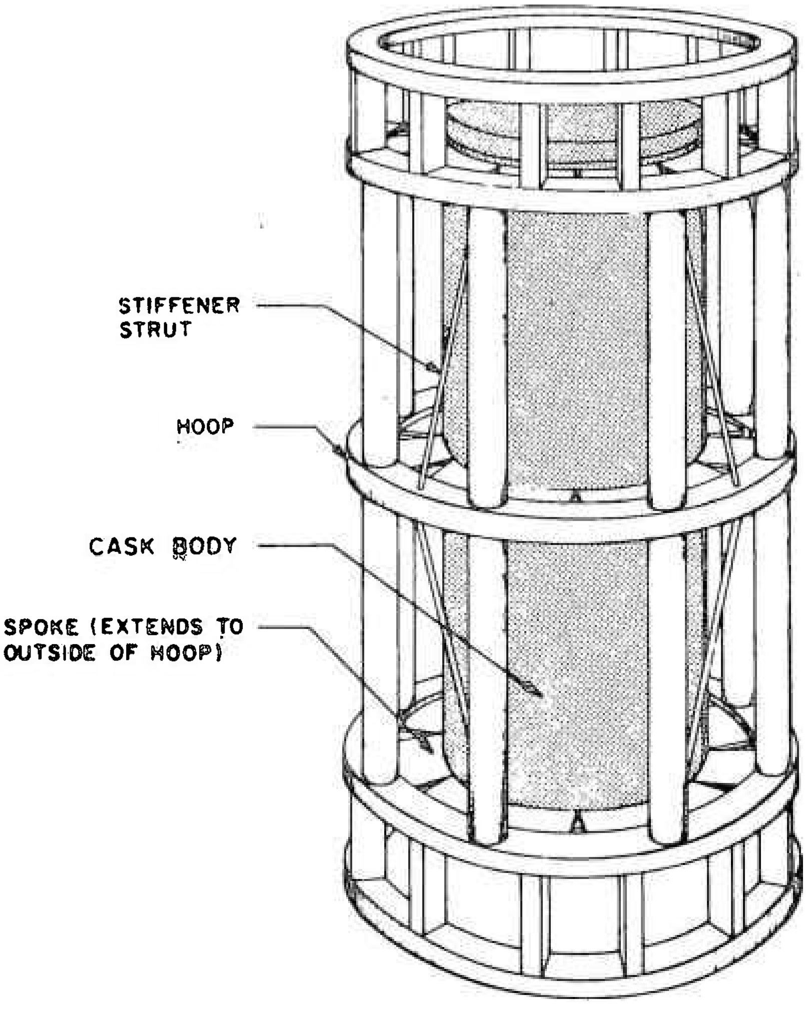
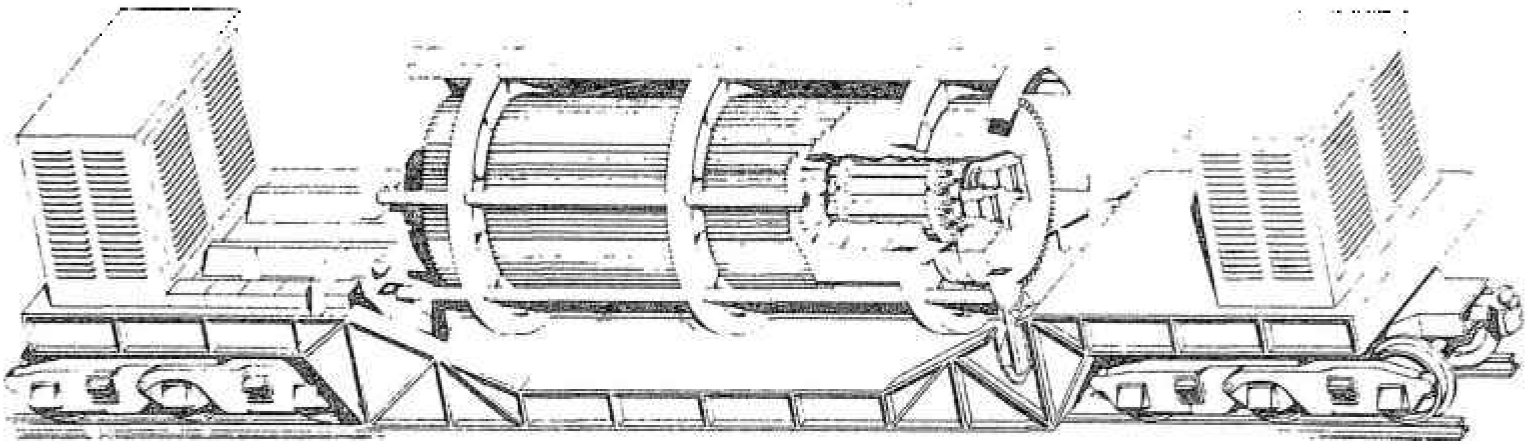


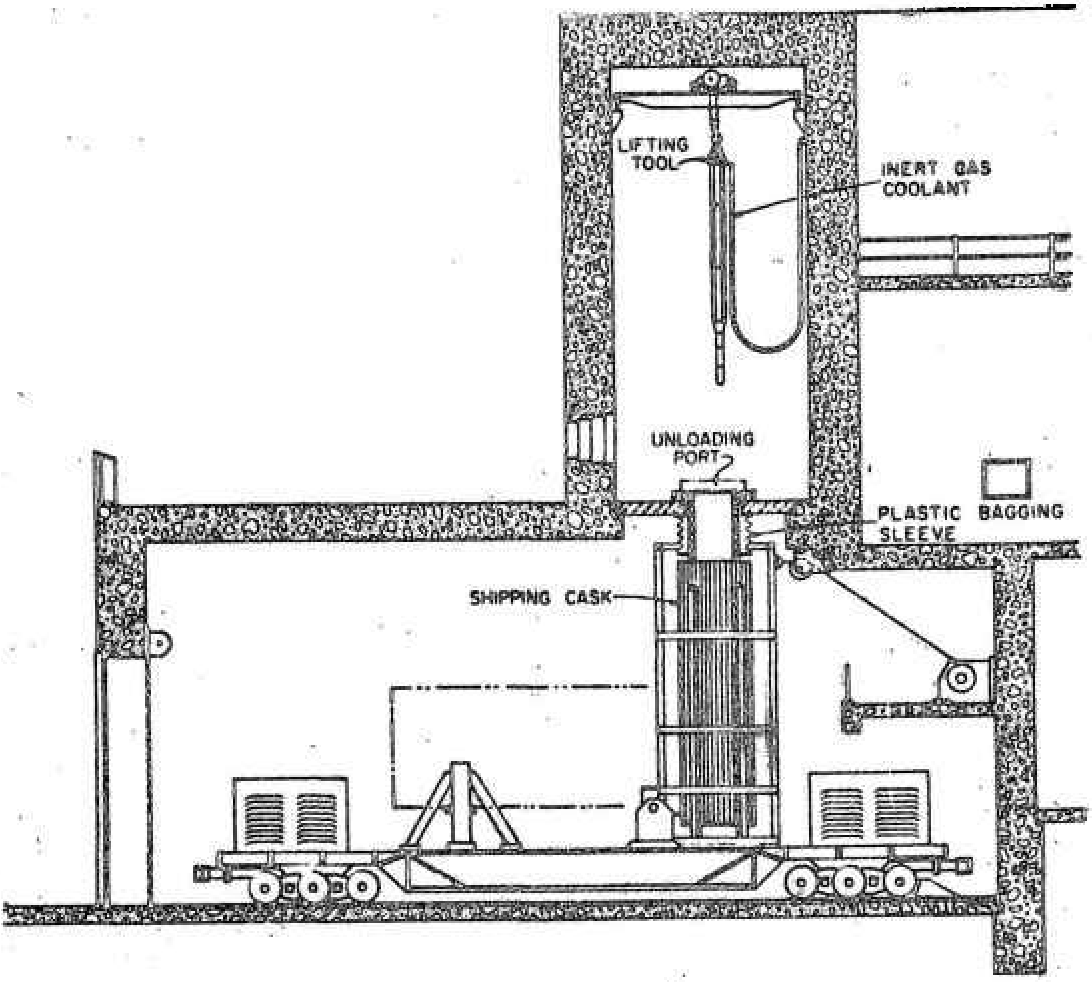
CASK WITH CRASH FRAME

ORNL-DWG 68-9921

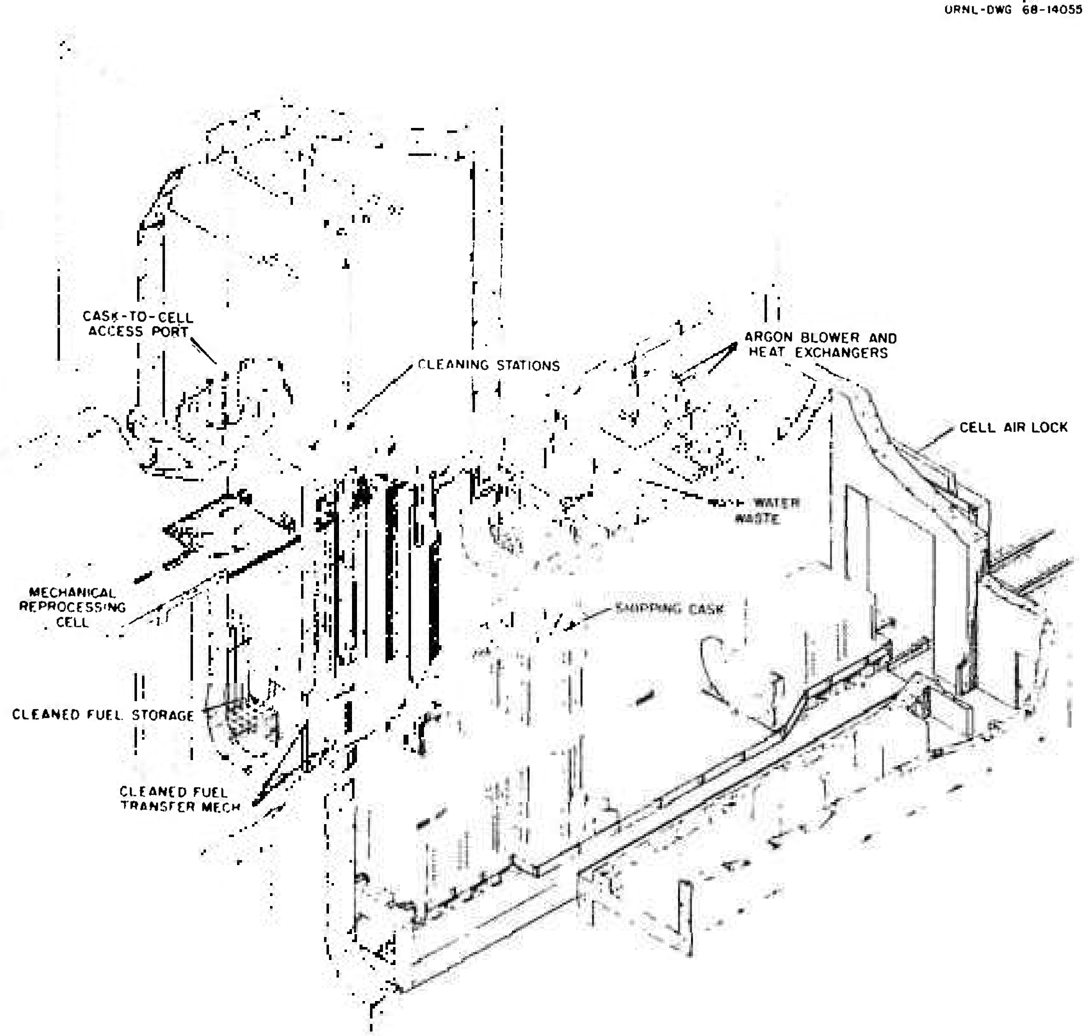


LMFBR SPENT FUEL SHIPPING CASK (18 ASSEMBLIES)

ORNL DWG-68-12250



RECEIVING & HANDLING

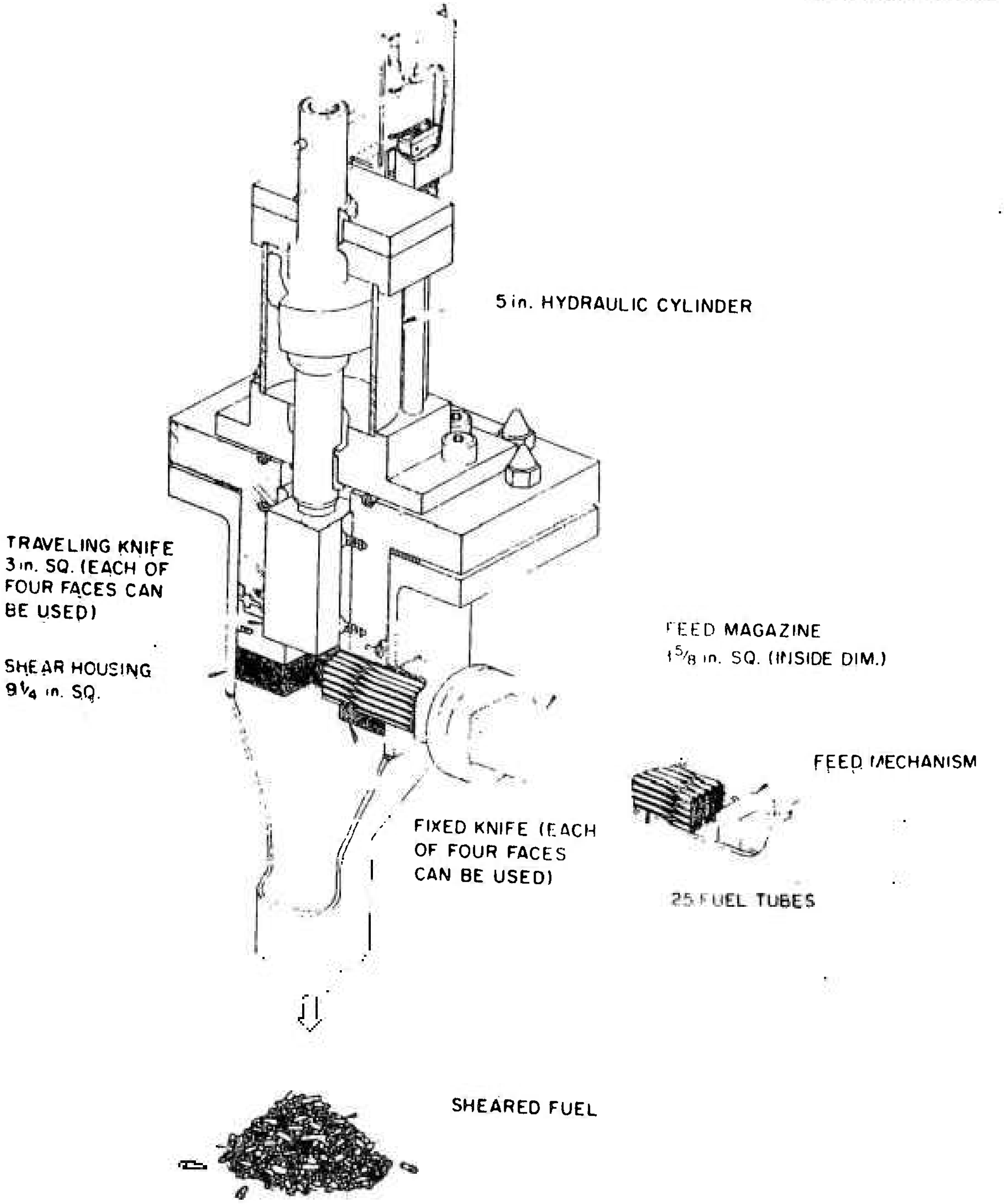


Central Reprocessing Plant for Spent LMFBR Fuel.
(Conceptual Fuel Receiving, Unloading, Cleaning and Storage Facility)

Table 2. Effect of Parameter Variation on Fuel Shipping

Variable	Basis for Comparison	Condition	Temperatures (°F) After Fire Accident: Outside Skin	Temperatures (°F) After Fire Accident: Max. Pin	Shielding-to-Fuel Ratio (W_s/W_f)
Decay time	36 subassemblies	20-day-cooled	710	1155	40
		90-day-cooled	510	805	28
Excess hardware	18 subassemblies, 20-day-cooled	Full length (17 ft 8 in.)	555	895	56
		Cropped (7 ft 8 in.)	800	1291	49
Shipment quantity	20-day-cooled	6 subassemblies	400	610	106
		18 subassemblies	555	895	56
		36 subassemblies	710	1155	40
Shielding design	18 subassemblies, 20-day-cooled	Uniform shielding	520	872	83
		Graded shielding	555	895	56

Note: Unless otherwise noted, all shielding is graded and fuel subassemblies are shipped with all hardware intact.



ORNL Semicontinuous Prototype Shear (5×5 in. Tube Bundle).

NON-AQUEOUS METHODS FOR REPROCESSING MSR FUEL

R. E. Blanco

For about the past 10 years ORNL has been evaluating the feasibility of a molten-salt breeder reactor. The first phase of the program was the operation (for about 3 years) of the MSRE a 7-MW single fluid experimental reactor. The carrier salt for this reactor is $LiF-BeF_2-ZrF_4$ (64-31-5 mole %). The containment vessel is fabricated of Hastelloy N. The reactor is moderated with graphite. The reactor was initially fueled with ^{235}U, but last year this uranium was removed from the salt by fluorination and replaced with ^{233}U. The reactor has operated about 6 months now with ^{233}U as the fuel. At present, small additions of plutonium to the reactor are being made, so that the reactor can be operated with both ^{233}U and ^{239}Pu present. If all goes well (technically and financially), the reactor will ultimately be fueled solely with ^{239}Pu.

The success of the MSRE has prompted the acceleration of the development of breeders. Regardless of the reactor design, an MSR will not breed unless protactinium is isolated from the neutron flux on a rather short cycle (3 to 5 days), and fission products are continuously removed from the salt (30 to 60 day cycle). These are the major chemical separations that must be made if an economical MSBR is to be a reality.

First I will describe the older two region reactor two fluid MSBR and the proposed fuel processing method. The objective is to make the student familiar with all variations in fuel processing. Later I will describe the present one-region reactor and the fuel processing method we are studying at the present time.

SLIDE 1 Two-Region Molten Salt Breeder (64-6959R)

This shows early concept evaluated at ORNL. The core salt consists of BeF_2, LiF, and UF_4, and the blanket of $ThF_4-LiF-BeF_2$. The core temperature is 705°C (inlet 538°C) and the blanket is 677°C (inlet 622°C). The neutrons from the core convert thorium into ^{233}Pa, which is removed from the blanket and allowed to decay to ^{233}U. Actually, more uranium is formed than is burned up, making this a breeder reactor. This design uses graphite tubes to carry the core salt. Hastelloy N is the material of construction (77% Ni, 12% Mo, 7% Cr, 4%Fe).

SLIDE 2 Possible Methods for Purifying MSBR Fuel Salt (67-5191)

This shows possible methods for processing the core salt to recover the ^{233}U and eliminate the fission products.

SLIDE 3 Possible Methods for Recovering Pa from MSBR Blanket Salt (67-5190)

Methods for processing the blanket salt to recover the Pa. Must remove the Pa continuously to have breeder. Also reduces the inventory since all of the salt will not have to be retained for decay of ^{233}Pa in an external tank.

$$\begin{tikzcd}
{}^{232}\mathrm{Th}\ (n,\gamma) \arrow[r] & {}^{233}\mathrm{Th} \arrow[r, "\beta", "23\ \mathrm{M}"'] \arrow[d, "(n,\gamma)"] & {}^{233}\mathrm{Pa} \arrow[r, "\beta", "27\ \mathrm{d}"'] & {}^{233}\mathrm{U} \\
 & {}^{234}\mathrm{Th} \arrow[r, "\beta", "24\ \mathrm{d}"'] & {}^{234}\mathrm{Pa} \arrow[r, "\beta", "6.7\ \mathrm{h}"'] & {}^{234}\mathrm{U}
\end{tikzcd}$$

SLIDE 4 MSBR Fuel Stream (66-8387)

This slide describes the fuel salt for a 2-fluid MSBR. This stream consists of essentially 2 moles LiF per mole BeF_2 and contains 0.22 mole % ^{233}U as UF_4. This stream will be processed for fission product removal at the rate of 14.5 ft^3/day which represents a cycle time of 47 days.

SLIDE 5 MSBR Fertile Stream (66-8388)

The next slide describes the fertile stream of a 2-fluid MSBR consisting of LiF and ThF_4 and a minor amount of BeF_2. The stream would contain 0.005 mole % ^{233}U as UF_4 which results from decay of ^{233}Pa if ^{233}Pa is not removed from the stream. The stream would be processed for uranium removal at a rate of 144 ft^3/day which represents a cycle time of 23 days. When ^{233}Pa is removed from the stream, the concentration of ^{233}U may be as low as 0.005 mole %.

SLIDE 6 MSBR Fuel and Fertile Stream Processing (67-6344 R)

The processing facility will be located on-site and will be an integral part of the reactor complex. The process flowsheet is shown in the next slide. In processing the fuel stream, uranium is first removed from the carrier salt by fluorination. Fission products which follow the uranium at this point are separated by selective absorption on beds of NaF and MgF_2. The UF_6 is collected in a cold trap for return to the fuel stream. After fluorination, the barren carrier salt contains most of the fission products, and, particularly, the rare earths. Next, most of the LiF-BeF_2 carrier salt is distilled from less volatile fission product fluorides. The distillation is carried out at 1000°C and a pressure of about 1 mm Hg. Distillation concentrates the important neutron poisons in the LiF-rich still-pot bottoms. The carrier salt and the UF_6 will then be recombined by absorbing the UF_6 in recirculating, reconstituted fuel salt and reducing with hydrogen.

For the process shown, the fertile stream consisting of ThF_4 and BeF_2 will be processed for the removal of U only. Part of the uranium will be used to replace that consumed in the fuel stream, and the remainder will be sold. Since only 1.3% of the fissions occur in the fertile stream, fission products accumulate slowly and can be removed economically by discarding fertile salt on a 30-yr cycle. An important process improvement is based on the removal of ^{233}Pa from the fertile stream. Development of a Pa-removal scheme could lead to a fuel doubling time of 13 yr rather than the 21 yr doubling time for the process shown.

SLIDE 7 Relative Volatilities of Rare Earth Fluorides vs Lithium Fluoride at 1000°C (67-9318)

Relative volatilities (alpha) measured in the laboratory are given in the next slide. The rare earth fluoride concentrations in the salt, LiF-BeF_2 (90-10 mole %) were 3-5 mole %. The distillate was LiF-BeF_2 (66-34 mole %). With the exception of PrF_3, the relative volatilities of the rare earths are of the order of 3×10^{-4} and are low enough to allow a great deal of latitute in still design. The relative volatility of BeF_2 with respect to LiF was 4.7.

SLIDE 8 Schematic of Still Used at MSRE (69-10952 SI)

During the past year, about 11 liters of irradiated MSRE fuel salt was distillated at 1000°C and 0.04 to 0.08 mm Hg using apparatus like that shown in this slide. The surface of the salt in the still-pot was quiescent, to avoid excessive boil up and entrainment. The condenser is of large diameter to provide lots of surface for heat removal. The condenser is not force-cooled. Heat is dissipated by natural convection and by radiation from the surface. The still was fabricated of Hastelloy N. The still pot was 14 inches O. D. and about 24-30 inches high. The condenser was 10-inch ID by 51 inches long. The condensate tank was about 16 inches OD by 24 inches high.

With the irradiated fuel, relative volatilities of BeF_2 and ZrF_4 were about the same as those obtained in cold laboratory studies. Relative volatilities for rare earths were only about 10^{-2} compared with about 10^{-4} in the lab work. Entrainment probably accounts for the apparent discrepancy in the results.

Distillation is not applicable to the primary separations required in the processing of 2-fluid MSBR's. Distillation will be useful only for the recovery of lithium and beryllium from waste streams.

SLIDE 9 MSBR Vessel (69-6003)

This slide shows the current concept of a single-fluid, 2-region MSBR. Salt is passed through an array of graphite tubes so spaced that a core-blanket effect is achieved.

SLIDE 10 Single-Fluid MSBR (69-9246)

The reference single-fluid, 2-region MSBR contains about 1500 cubic feet of salt having the composition 71.7 mole % LiF, 16 mole % BeF_2, 12 mole % ThF_4, and about 0.3 mole % $^{233}UF_4$. The reactor system would be fabricated of Hastelloy N, and would use graphite as the moderator. In order to have efficient operation and to maintain a breeding ratio of greater than 1, neutron absorbers such as fission products (mainly xenon and rare earths) and ^{233}Pa (which is formed from ^{232}Th) must be continually removed from the salt. Protactinium-233 must be removed from the neutron flux on a short time cycle (3 to 5 days), and the rare earths should be removed on a cycle of 30 to 60 days. The chemical processing system for effecting these separations must be close-coupled to the reactor in order to minimize fuel inventory.

SLIDE 11 Single Fuid MSBR Processing by Reductive Extraction (68-814)

The processing method presently being studied involves reductive extraction using bismuth under reducing conditions to isolate the protactinium and fission products from the fuel salt. Salt from the reactor flows into the bottom of an extraction column where it meets a countercurrent stream of bismuth that contains thorium and lithium. Operation of this system is based on the fact that Pa is intermediate in nobility to U and Th. As the salt stream passes up the column, uranium is preferentially reduced and transferred to the downflowing metal stream and is carried out of the column. Protactinium accumulates in the center of the column in a decay tank, which is actually an enlarged stage in the column. Salt leaving the column is practically free of uranium and protactinium, but contains the rare earths. A portion of this stream is sent to another reductive extraction system for the rare-earth-thorium separation.

SLIDE 12 Protactinium Isolation for a Single Fluid MSBR (68-9438)

This slide gives a closer look at the protactinium isolation system. Salt enters the bottom of the column at a rate of 2.5 gal/min; the countercurrent bismuth flow is 5.3 gal/min. The salt flow rate represents a 3-day Pa processing cycle. The extraction column has 4 theoretical stages below and 3 stages above the Pa decay tank, which has a volume of 200 cubic feet. The ^{233}Pa contained in this tank generates about 5 MW of heat that must be removed.

The electrolytic cell atop the column serves two purposes: (1) Uranium is oxidized at the anode from the recirculating bismuth stream into the salt that returns to the reactor. (2) At the cathode, thorium and lithium are reduced into the bismuth stream that enters the column. These elements are the reductants used to selectively reduce and extract the Pa and U. The thorium and lithium concentration in the bismuth entering the column are about 1600 and 40 ppm, respectively.

A portion of the salt stream (which contains a controlled amount of U) entering the Pa decay tank (Point 1 on the slide) is diverted to a fluorinator in which uranium is removed as UF_6. Fluorination serves 3 purposes: (1) Monitoring the UF_6 provides a method for controlling the flow rates in the sistem. (2) The ^{233}U decay product is removed from the system. Excess UF_6 is removed for sale; the remainder is reacted with hydrogen in the salt that returns to the reactor to complete reconstitution of the salt. (3) Fluorination removed iodine, bromine, and oxygen from the salt.

A point 2 in the slide, a side stream of the metal phase is diverted to a hydrofluorinator where all metals in the bismuth are oxidized into a salt that is ultimately discarded to waste. This treatment provides for the removal of corrosion products (Fe, Ni, Cr) and certain fission products (Zr, Zn, Cd, etc.) from the system. Since some uranium is present in this salt, it must be recovered by fluorination before the salt is discarded.

SLIDE 13 Rare Earth Removal System (68-9443)

This slide provides a closer look at the system in which rare earths are separated from thorium. Rare earth and thorium distribution coefficients are low (0.01 to 0.04); also, separation factors are low (1 to 3.5). Consequently, a high flow rate and many stages are required in the contactor if a separation is to be effected. Salt flowing at 0.25 gal/min enters the column at an intermediate point. This flow rate corresponds to a 30-day processing cycle. The metal-to-salt flow ratios are about 34 in the upper column and about 85 in the lower. Under proper operating conditions, rare earths are concentrated in the salt phase, part of which is discarded. The electrolytic cell operates in a manner similar to that in the protactinium isolation system.

SLIDE 14 Fission Product Disposition (68-7755)

Not all fission products are removed by reductive extraction. Xenon, krypton, and tritium will be removed from the reactor itself on a 1-minute cycle by a helium purge. Iodine, bromine, and oxygen are removed by fluorination. Hydrofluorination of bismuth removes Zr, Zn, Sn, etc. Strontium, Cs, Rb, and Ba are removed by salt discard. Noble metals exist in the reactor as a smoke, or are plated on the surfaces within the reactor. Those in the smoke will deposit in the reactor off-gas system. A good method for periodically removing them will have to be devised.

SLIDE 15. Equilibrium Expression (69-9235)

Distribution of a solute between a salt phase and a liquid bismuth phase can be expressed as the general reaction shown. From the equilibrium constant, it can be shown that a plot of log D vs. the lithium distribution coefficient (or lithium concentration in the metal phase) should be linear with a slope equal to the valence of the species in the salt phase. The distribution coefficient is defined as the concentration in the metal phase divided by the concentration in the salt phase.

SLIDE 16 Reaction Vessel (69-1241)

This is a schematic diagram of the laboratory-scale apparatus used in the determination of distribution coefficients. The reductant concentration in the bismuth phase was gradually increased by addition of thorium or lithium. Samples of both phases are taken with time; analyses of these samples provide the distribution coefficient data as a function of the reductant concentration in the metal phase. The argon cover gas had to be made ultra pure to avoid oxidation of reductant from the metal phase. Both Mo and mild steel levers have been used. Hydrofluorination cannot be done in mild steel.

SLIDE 17 Laboratory Apparatus (Photo 91146)

Shows assembled reaction vessel, Ni liner, and mild steel crucible. Along side are a copper gasket and 3 stainless steel samplers.

SLIDE 18 Distribution Coefficients for U, Pa, and Th with L_2B (69-1240)

Distribution coefficients for U, Pa, and Th obtained at 600°C using LiF-BeF_2 (66-34 mole %) as the salt phase. Uranium is trivalent, but both Pa and Th are tetravalent. Linear increase of log D with increasing log D_{Li} was expected from the theory.

SLIDE 19 Rare Earth Distribution Coefficients (69-7889)

Shows behavior of 3 rare earths in different salts. Note low distribution coefficients, and the fact that Eu is divalent compared with the trivalency of the other rare earths. Distribution coefficients change by a factor of up to two with salt composition and decrease by about 50% as the temperature changes from 550° to 750°C.

SLIDE 20 Summary of Distribution Coefficients (69-1255)

Line graphs summarizing distribution coefficient data for several elements. Under expected operating conditions, D_U is about 1, and the U-Pa separation factor is about 100. The Pa-rare earth separation factor is about 800. Rare-earth--thorium separation factors are only in the range of 1 to 3.5. Variation of the salt composition and/or the temperature has some effect on the extractability of the various components, but not enough to markedly improve the situation in the rare earth removal system.

SLIDE 21 Solubilities in Liquid Bismuth (68-11057)

Using the apparatus shown earlier, we measured the solubility of thorium in bismuth. The value obtained at 600°C is about 2000 ppm. Using the reductive extraction technique, we got an estimated value of the protactinium solubility of 1100 ppm at 500°C. The temperature dependence of the solubilities for the actinide metals is about the same. This allows estimate of a value of 4500 ppm for the Pa solubility at 600°C.

SLIDE 22 Hg-H_2O Studies in Baffled Column (Photo 93524)

First engineering studies dealt with contactors. Before actually working with salt and bismuth, engineers made some studies in baffled columns using mercury and water to learn about axial mixing, holdup, stage heights, etc., with high-density-difference liquids.

The experimental work with salt and bismuth is just now beginning.

SLIDE 23 Schematic of Eletrolytic Cell (69-10582)

Development of electrolytic cells is just starting. This slide illustrates one possible cell concept. Salt flows across two chambers filled with bismuth; one chamber is the anode, the other the cathode. Bismuth flows perpendicularly to the plane of the slide. The two troughs of Bi are separated and are insulated by a layer of frozen salt.

Development of a workable cell is one of the key requirements for a successful reductive extraction process.

The theoretical current requirement for the cell in the Pa isolation system is 10,000 amperes. Current efficiencies of at least 50% at a current density of 5000 amps/ft^2 might be achieved so that about 4 ft^2 of surface would be required for each electrode. The rare earth removal system will require a cell about 3 times this size. The cell design must allow the electrodes to be placed in close proximity because the resistivity of the salt is fairly high (0.5 ohm-cm). A long current path would cause intolerable electrical losses and accentuate the heat removal problem. Consideration is being given to providing corrosion protection, as well as electrical insulation, of anodic surfaces other than the bismuth surface by freezing a layer of salt on the surfaces. Ample internal heat from radioactive decay and electrical losses is available to support the required thermal gradient for maintaining the protective frozen wall.

Preliminary experiments have been carried out in static cells. Work with flow cells is just now starting.

SLIDE 24 Engineering Problems (69-9265)

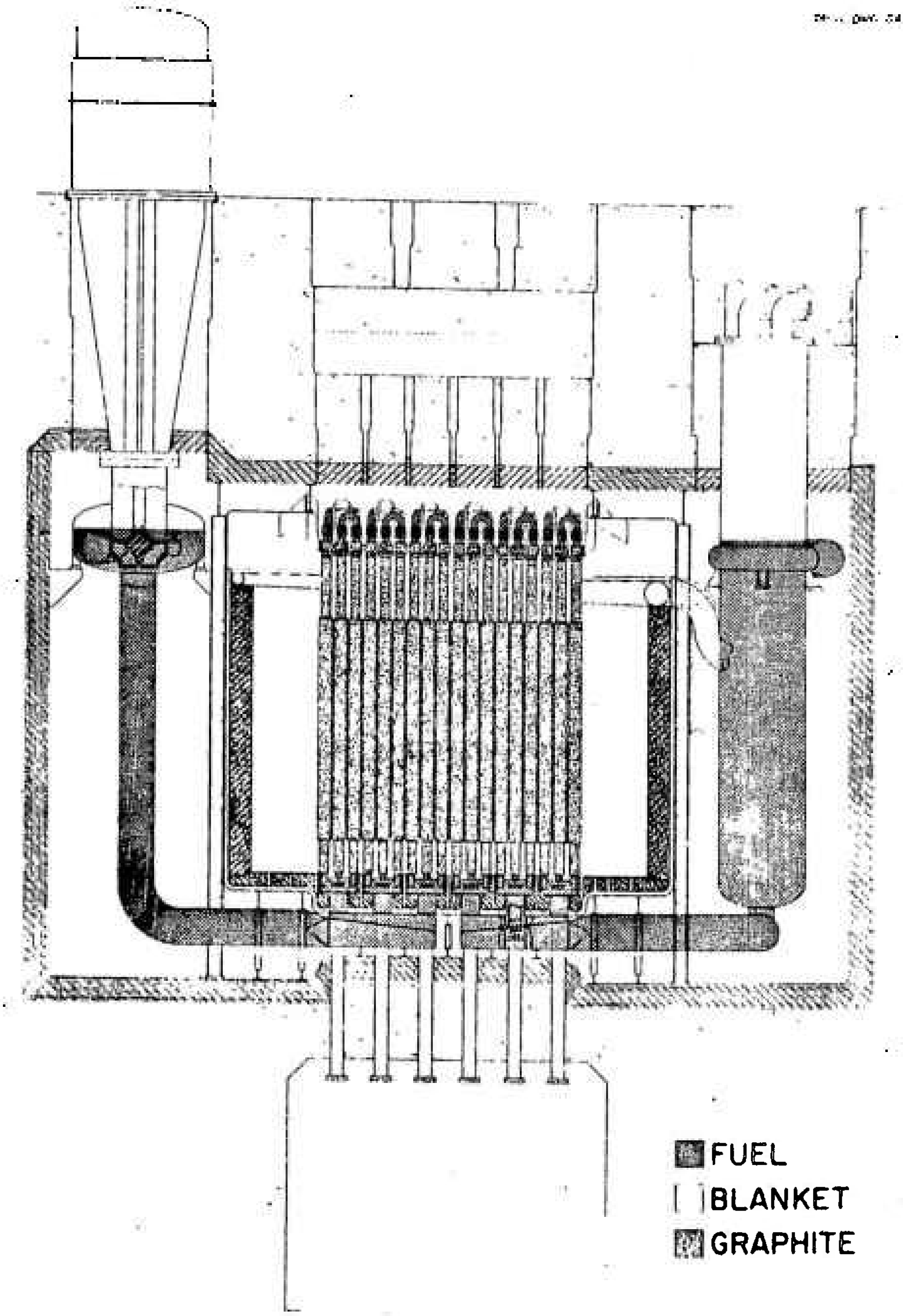
Engineering development of the reductive extraction process is just entering the hardware stage. Development is required in four major areas: (1) contactors, (2) electrolytic cells, (3) materials of construction, and (4) inline instrumentation for process control. The contactor development has, so far, been conducted mostly with mercury and water to simulate bismuth and salt to permit estimation of flooding rates, pressure drops, and holdup with high-density-difference fluids. Axial mixing, which could be serious at high metal-to-salt flow ratios, is also being studied. Only simple electrolytic cells have been tested. Materials that might be suitable for containment of salt-bismuth systems are graphite, refractory metals (such as Mo), and a modified low-carbon steel. Since graphite and the refractory metals are not too attractive for use in large, complicated equipment, the development effort is centered on use of refractory-metal-coated steel and on testing of new special iron-base alloys.

Ultimately, alternative methods for processing MSBR fuels must be developed.

SLIDE 25 Fuel Cycle Cost, Conversion Ratio and Salt Discard Rate (69-10581)

This slide shows effect of no processing, or just uranium removal, on conversion ratio and fuel cycle cost. This is for a single-fluid reactor, with a salt composition of ^{7}LiF-BeF$_2$-ThF$_4$ (72-16-12 mole %). The estimated fuel cycle cost for a breeder (CR = 1.06) with complete reductive extraction processing is about 0.3 mill/kwhe.

Average conversion ratio is about 0.8 with either no processing or with periodic uranium recovery by fluorination. Fuel cycle cost decreases with increasing salt replacement interval. After about 6 years, curves flatten out. If uranium is recovered every 6 years and salt is thrown away, fuel cycle cost is about 0.6 mill/kwhe. If both uranium and salt are discarded, fuel cycle cost is about 0.9 mill/kwhe. Even though salt discard does not produce highly unfavorable economic picture, the LiF, BeF$_2$, and ThF$_4$ could be recovered and reused. With 6-year recycle of uranium and carrier salt, would have a good converter that would produce reasonably low-cost power, even by U. S. standards. Power cost is about 3 mills/kwhe regardless of whether the reactor is a breeder or a converter.



TWO REGION MOLTEN SALT BREEDER

ORNL Dwg. 67-5191

POSSIBLE METHODS FOR PURIFYING MSBR FUEL SALT

A.

(1) Fluorinate to recover uranium from salt as UF_6.

(2) Distill LiF-BeF_2 at 1000°C and 0.5 mm pressure, leaving fission product fluorides in still-pot bottoms. DF about 10^2

B.

(1) Fluorinate to recover uranium from salt as UF_6.

(2) Reductively extract rare-earth fission products:

$$REF_{(salt)} + Li_{(Bi)} \xrightarrow{\sim 600°C} LiF_{(salt)} + RE_{(Bi)}$$

ORNL Dwg. 67-5190

POSSIBLE METHODS FOR RECOVERING Pa FROM MSBR BLANKET SALT

1. Precipitation with Oxides:

$$PaF_{4(salt)} + MO_x \xrightarrow{\sim 600^\circ C} Pa_2O_5 + MF_{2x}$$

M can be Be, Ca, Zr, or Th.

2. Reductive Extraction:

$$PaF_{4(salt)} + Th_{(Bi)} \xrightarrow{\sim 600^\circ C} Pa_{(Bi)} + ThF_{4(salt)}$$

3. "Brillo" Process:

$$Pa^{o} + \text{steel wool} \xrightarrow{\sim 600^\circ C} \text{Pa sorbed on steel wool}$$

ORNL DWG 66-8387

MSBR FUEL STREAM

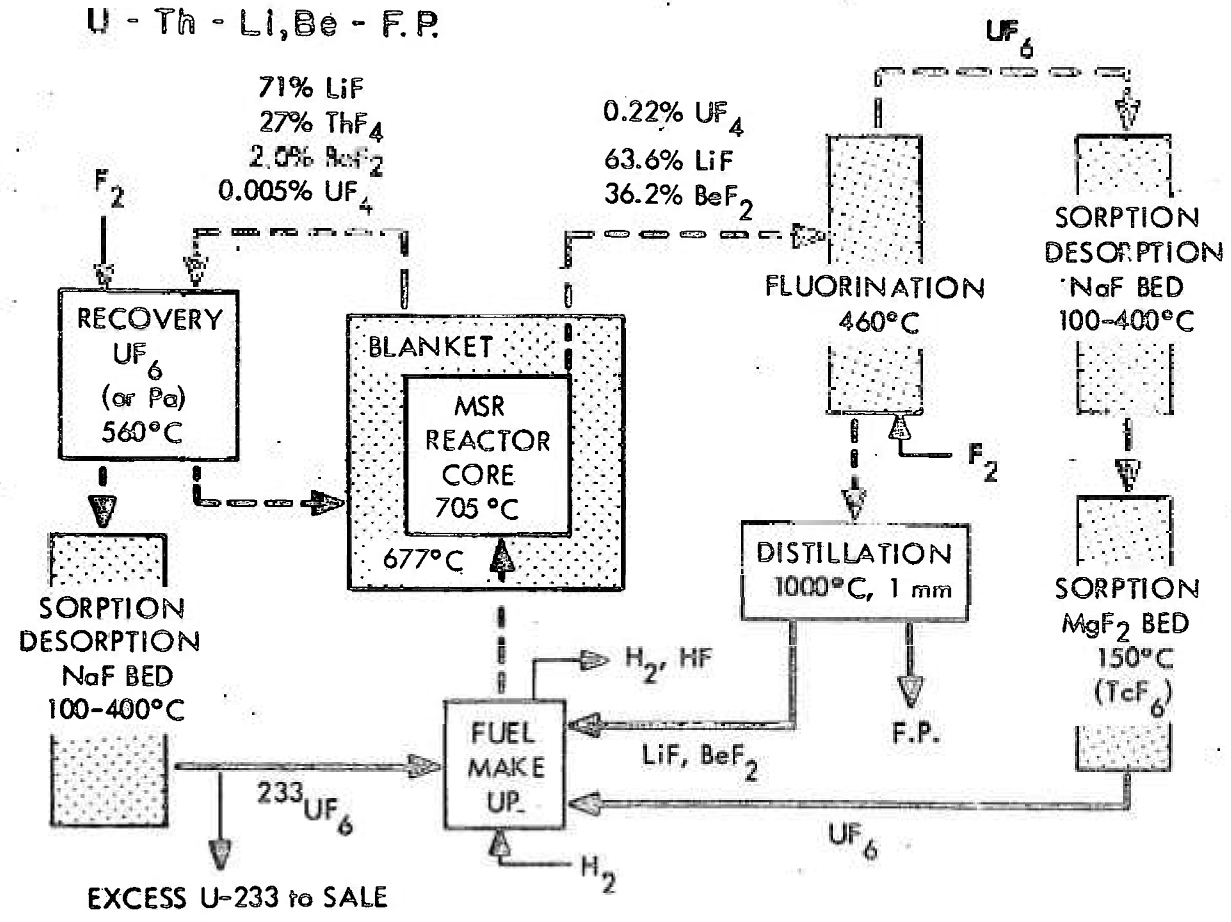
COMPOSITION, MOLE %	
LiF (99.995 at. % ^{7}Li)	63.6
BeF_2	36.2
UF_4 (FISSILE)	0.22
LIQUIDUS TEMPERATURE, °C	~460
PROCESSING RATE, ft^3/DAY	14.5
CYCLE TIME, DAYS	47

ORNL DWG 66-8388

MSBR FERTILE STREAM

COMPOSITION, MOLE %	
LiF (99.995 at. % ^{7}Li)	71
ThF_4	27
BeF_2	2
$^{233}UF_4$	0.005
LIQUIDUS TEMPERATURE, °C	~565
PROCESSING RATE, ft^3/DAY	144
CYCLE TIME, DAYS	23

ORNL Dwg. 67-6344 R



PROCESSING MOLTEN SALT REACTOR FUEL AND BLANKET

ORNL-Dwg. 67-9318

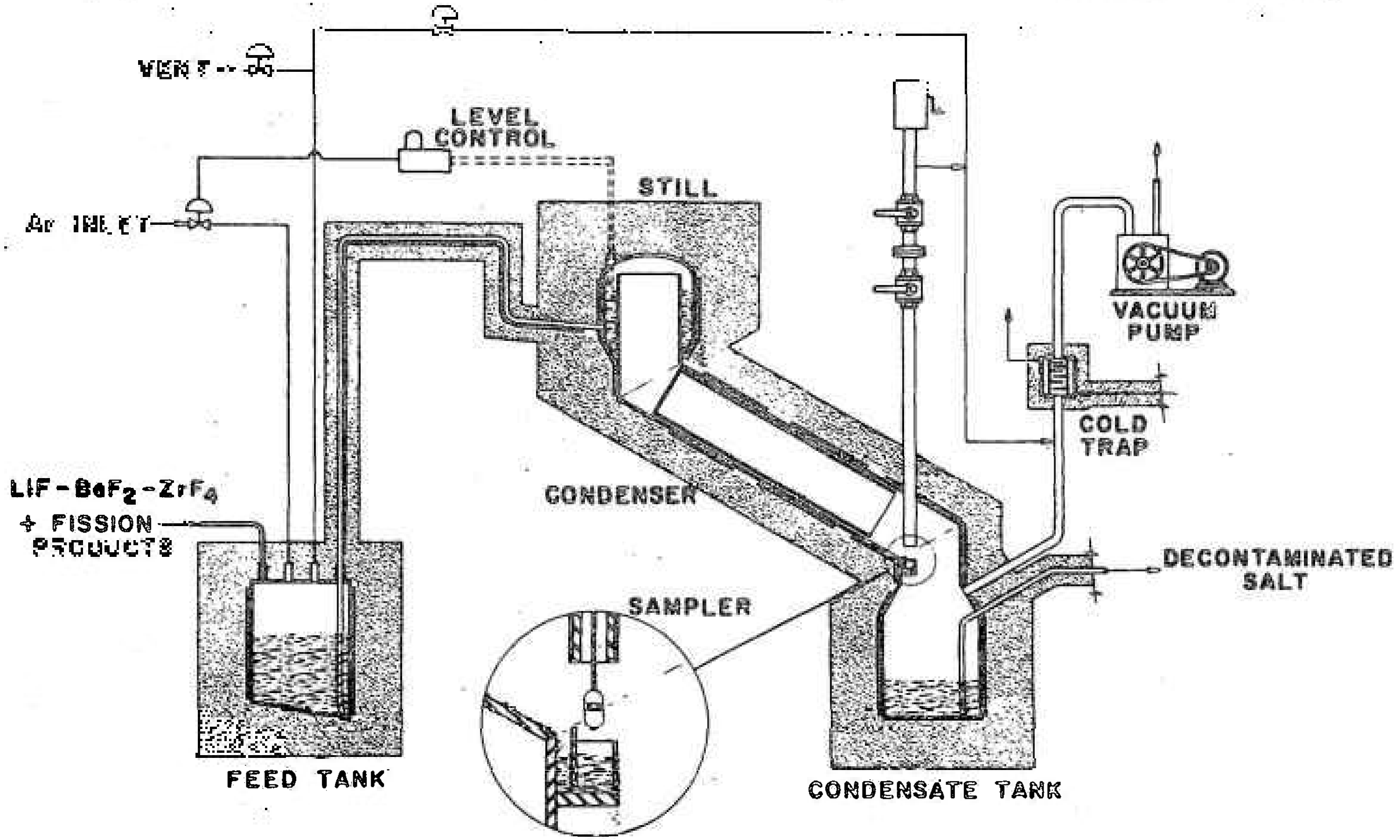
RELATIVE VOLATILITY (ALPHA) OF RARE EARTH FLUORIDES VERSUS LITHIUM FLUORIDE AT 1000°C*

Component	Rel. Vol. (α)	Component	Rel. Vol. (α)
LaF_3	1.4×10^{-4}	YF_3	3.3×10^{-5}
CeF_3	3.3×10^{-4}	BaF_2	2.0×10^{-4}
PrF_3	1.9×10^{-3}	SrF_2	1.1×10^{-4}
NdF_3	$<3 \times 10^{-4}$	BeF_2	4.7
SmF_3	$<3 \times 10^{-4}$	LiF	1.0

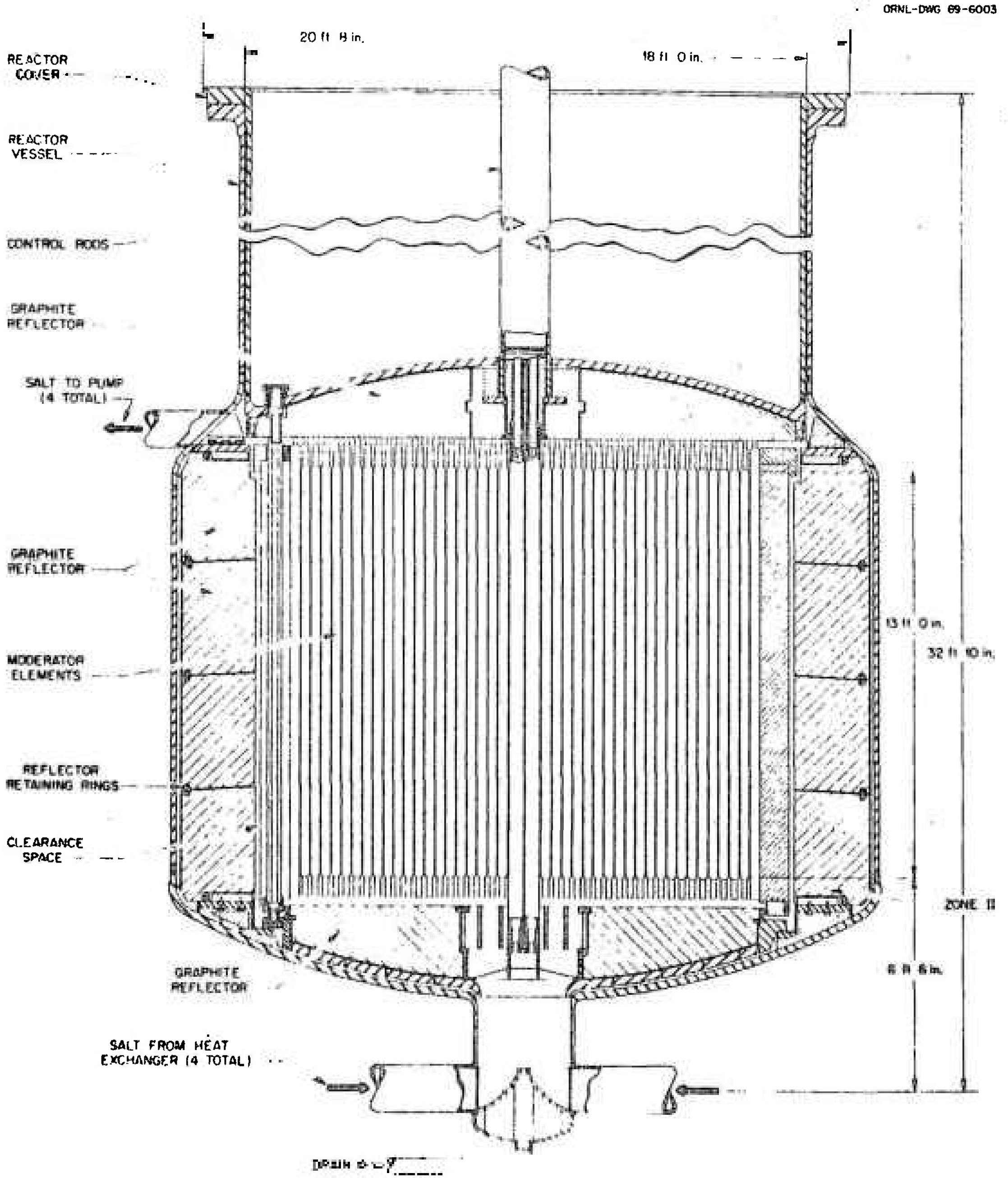
---

*3-5 mole % of component in a mixture of 8.5 mole Li/mole BeF_2.

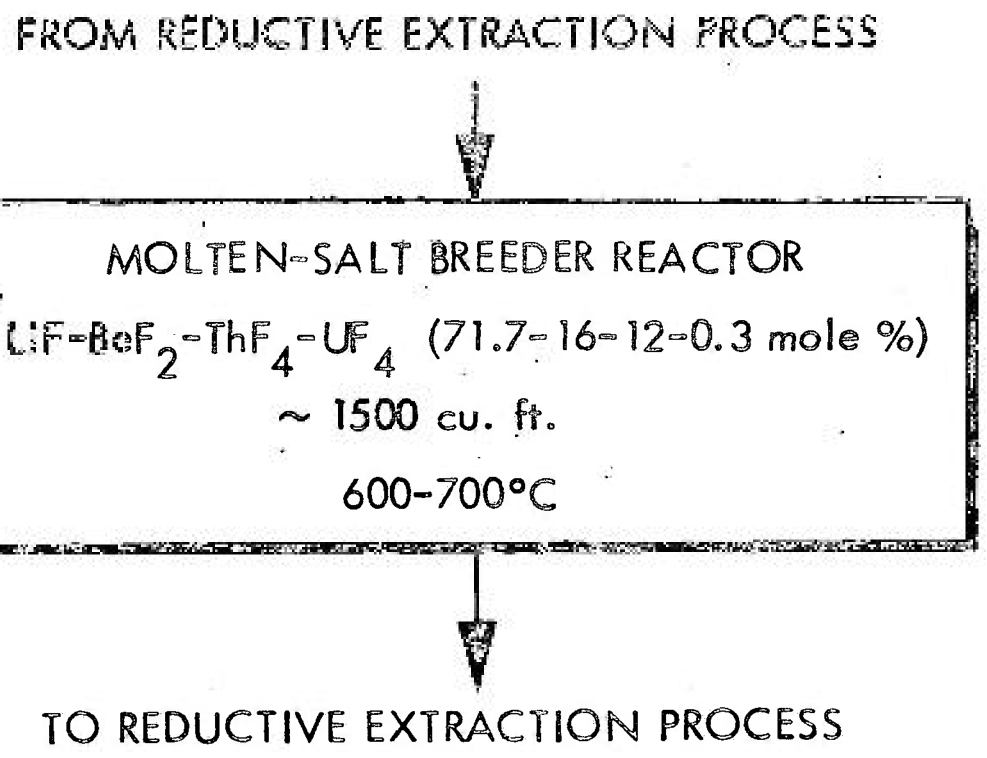
ORNL DWG 66-10952 S1



VACUUM DISTILLATION OF LiF-BeF_2-ZrF_4


ORNL-DWG 69-6003
REACTOR COVER
REACTOR VESSEL
CONTROL RODS
GRAPHITE REFLECTOR
SALT TO PUMP (4 TOTAL)
GRAPHITE REFLECTOR
MODERATOR ELEMENTS
REFLECTOR RETAINING RINGS
CLEARANCE SPACE
GRAPHITE REFLECTOR
SALT FROM HEAT EXCHANGER (4 TOTAL)
DRAIN
20 ft 8 in.
18 ft 0 in.
13 ft 0 in.
32 ft 10 in.
ZONE II
6 ft 6 in.

ORNL DWG. 69-9246



FROM REDUCTIVE EXTRACTION PROCESS

MOLTEN-SALT BREEDER REACTOR

^{7}LiF-BeF$_2$-ThF$_4$-UF$_4$ (71.7-16-12-0.3 mole %)

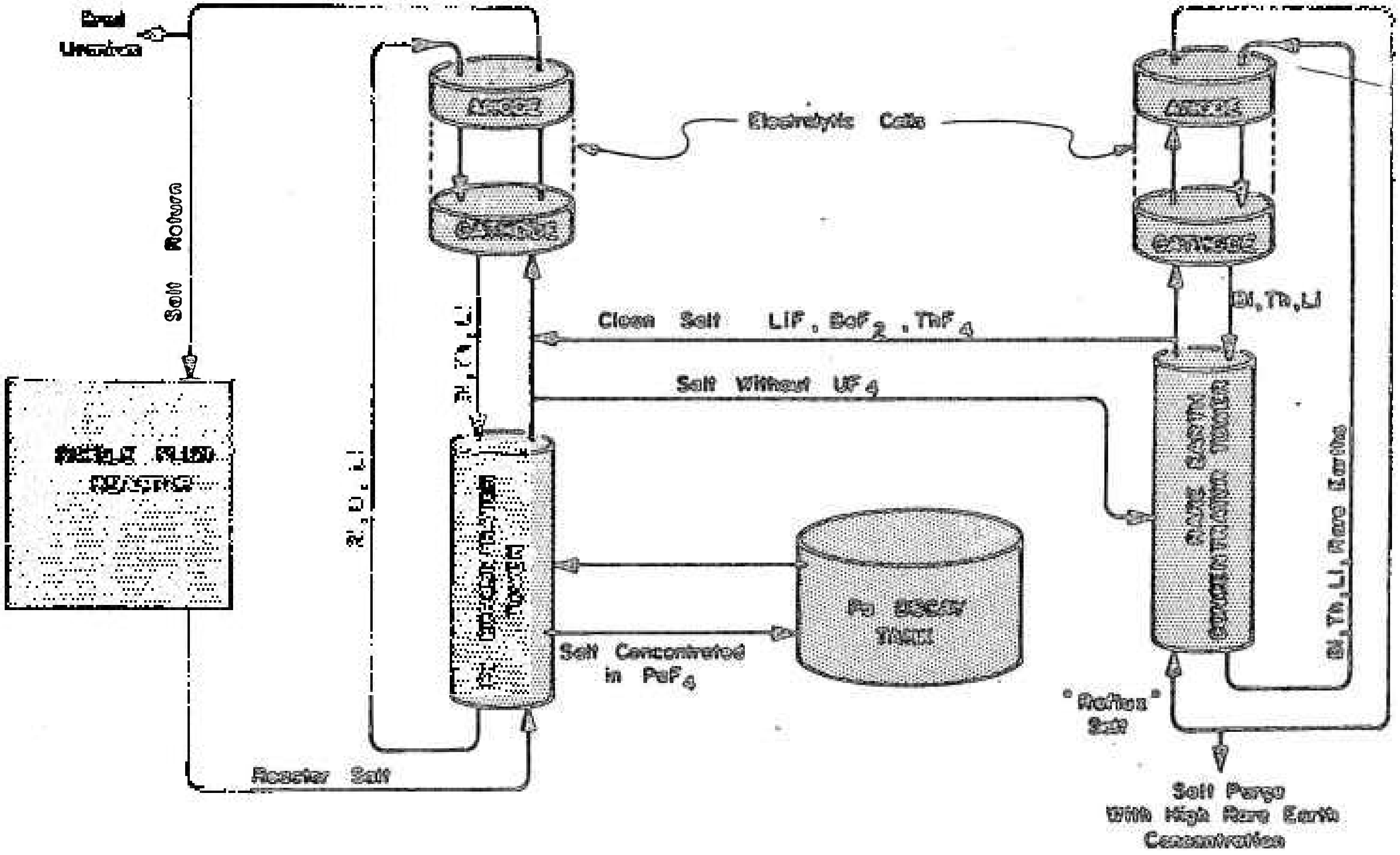
~ 1500 cu. ft.

600-700°C

TO REDUCTIVE EXTRACTION PROCESS

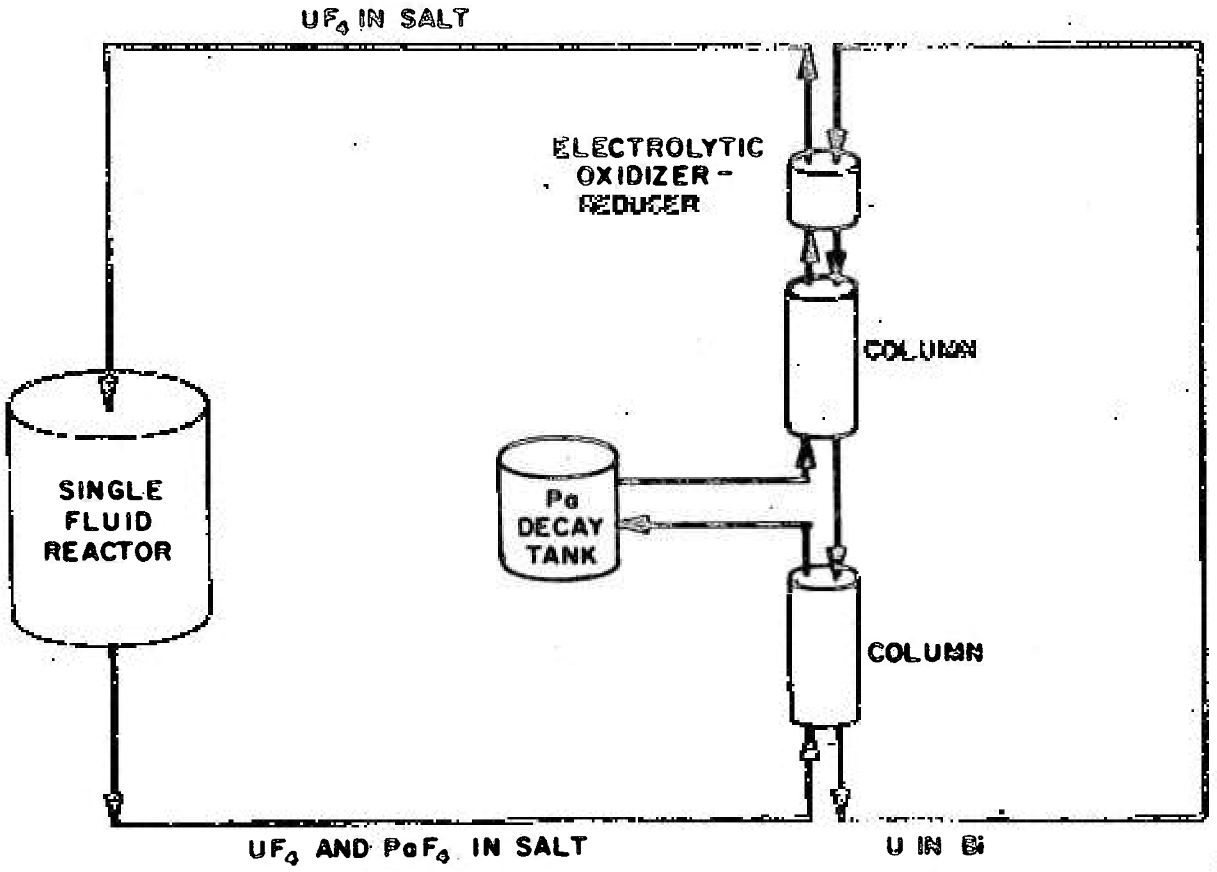
SINGLE-FLUID MOLTEN-SALT BREEDER REACTOR

ORNL DWG. 68-214



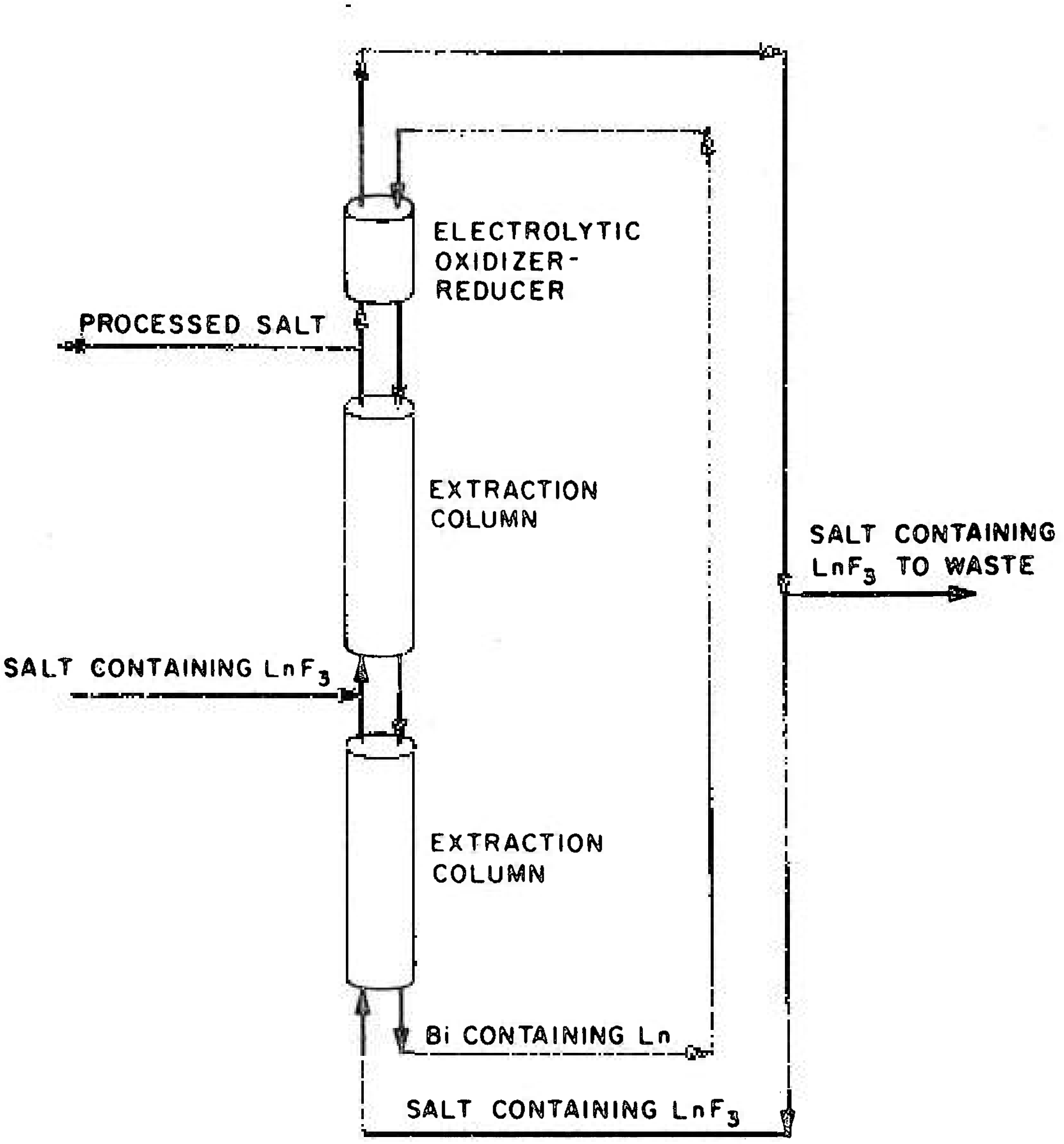
SINGLE FLUID MSBR PROCESSING BY REDUCTIVE EXTRACTION

ORNL DWG 68-9438



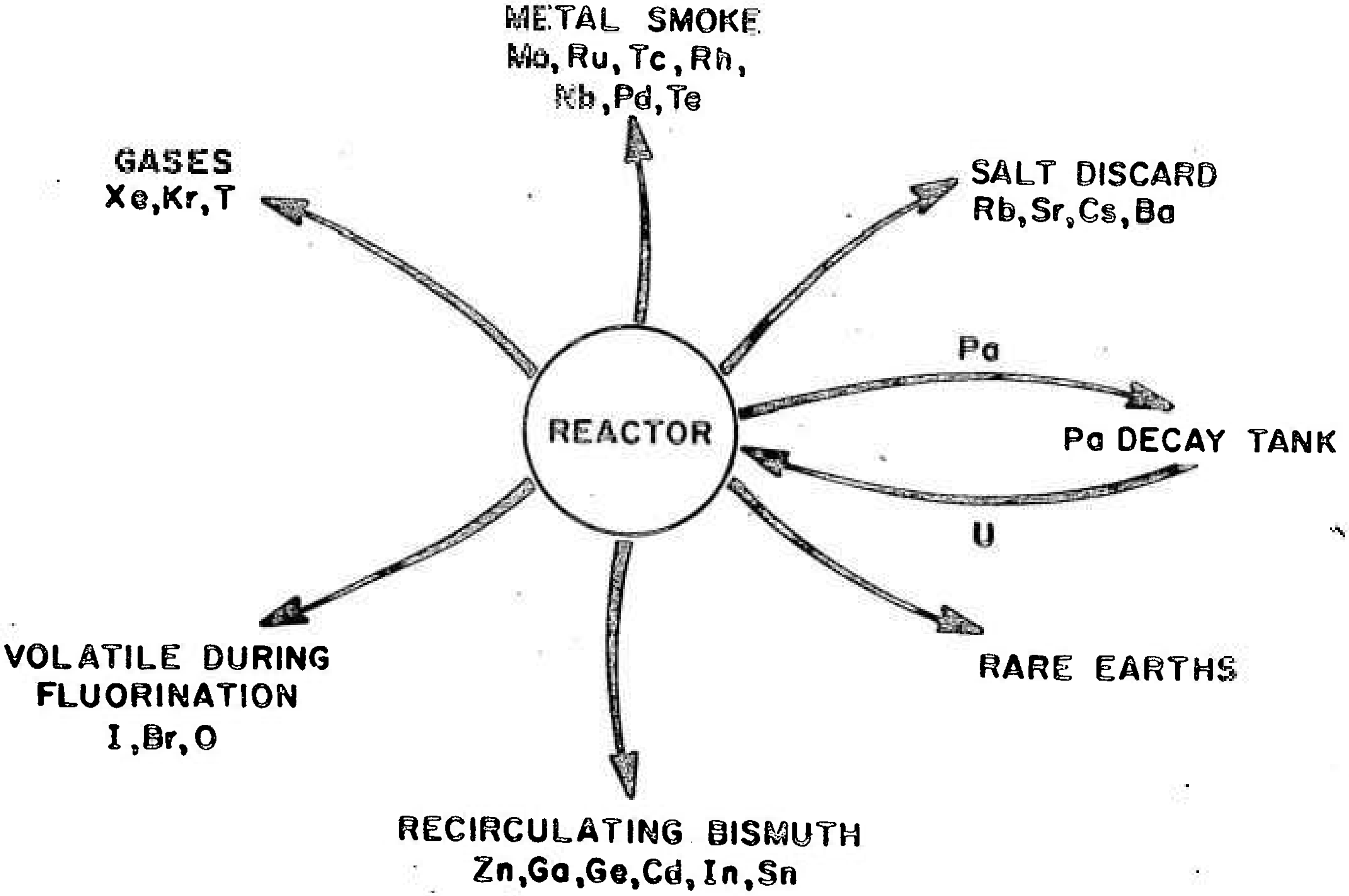
PROTACTINIUM ISOLATION FOR A SINGLE FLUID MSBR

ORNL DWG 68 9443



RARE EARTH REMOVAL FROM A SINGLE FLUID REACTOR BY REDUCTIVE EXTRACTION

ORNL DWG 68-7755 R1

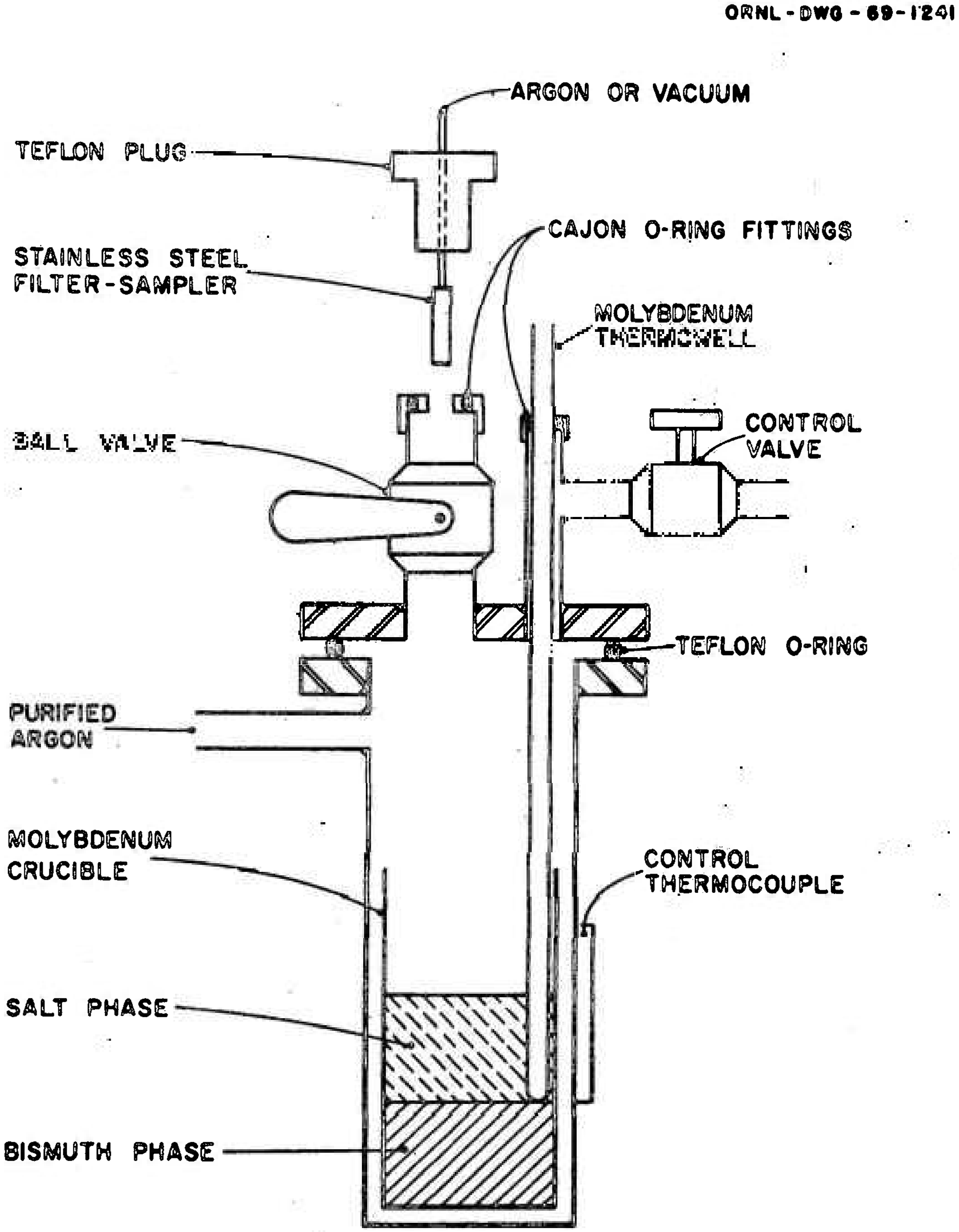


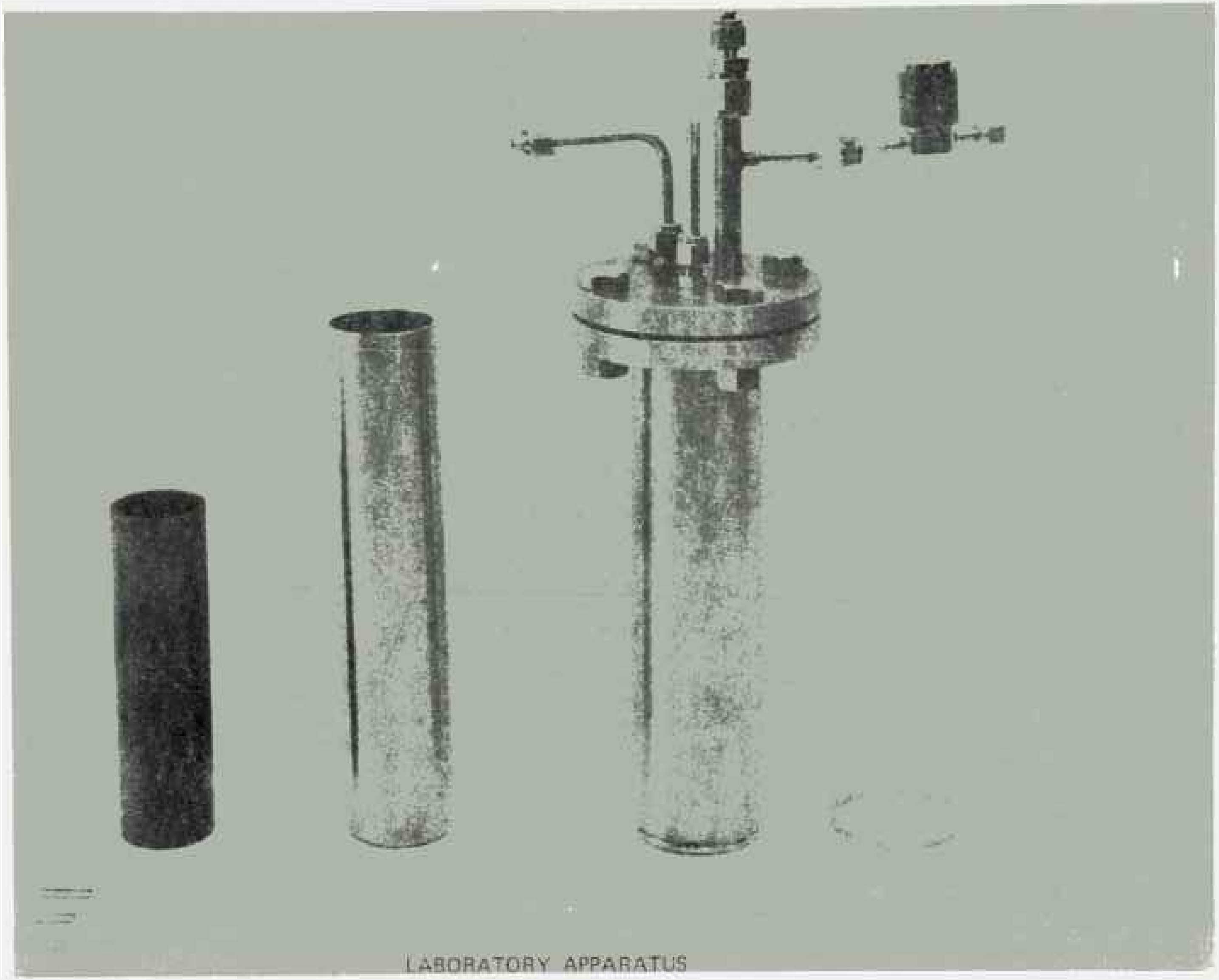
ORNL DWG. 69-9235

$$MF_{n(salt)} + n\ Li_{(Bi)} = M_{(Bi)} + n\ LiF_{(salt)}$$

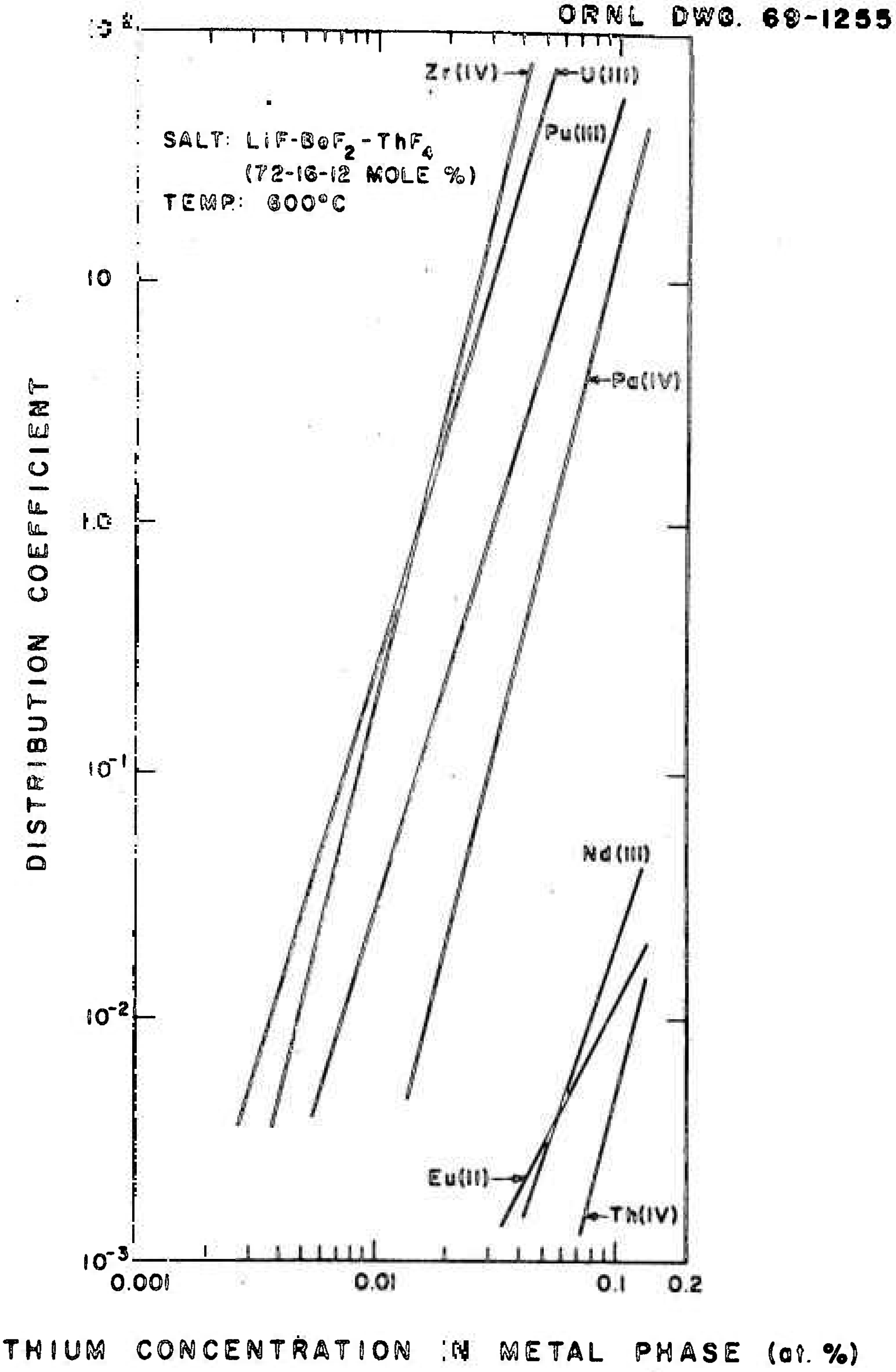
$$\log D_M = n \log D_{Li} + \log K'$$

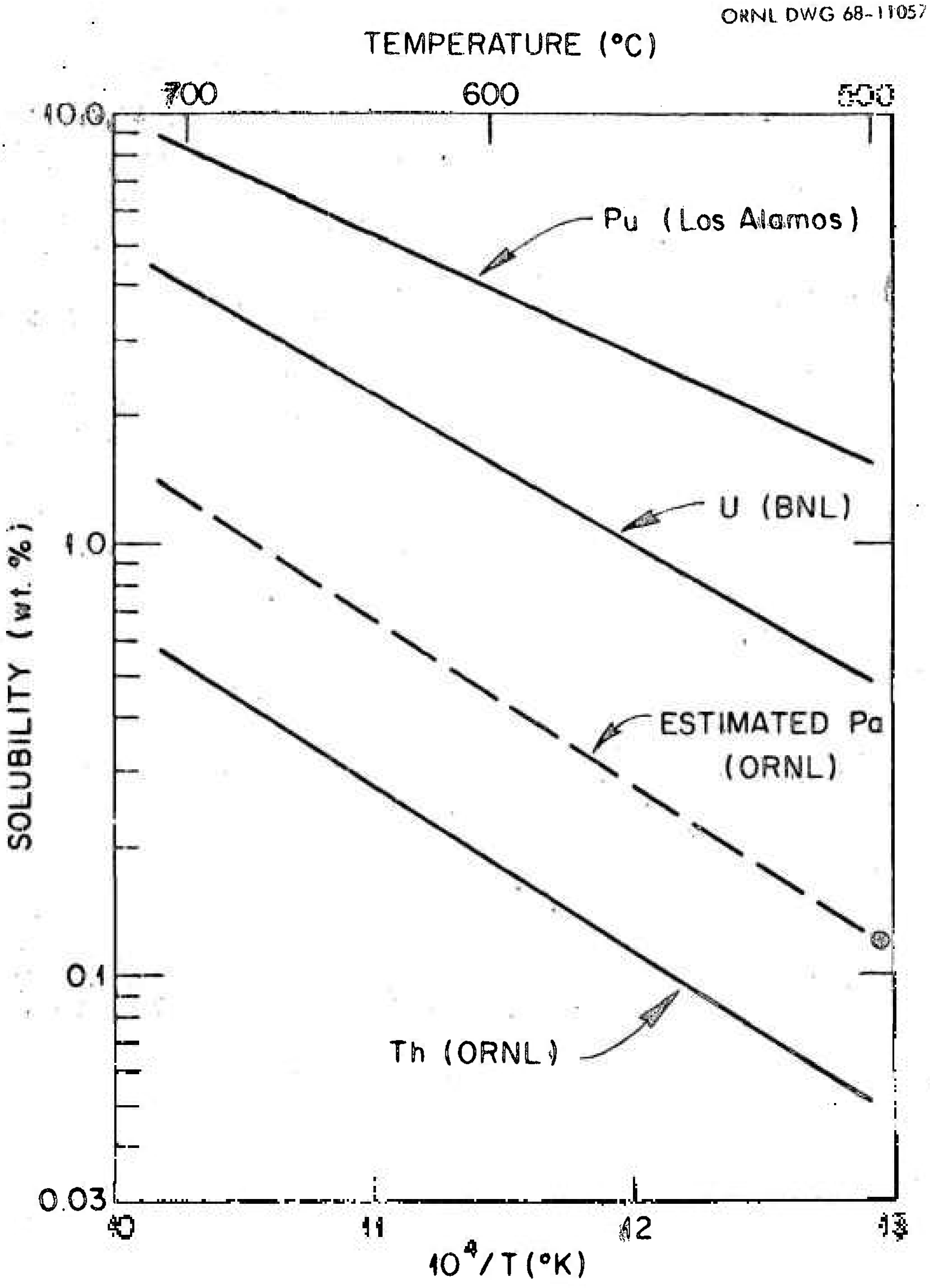
$$D_M = \frac{\text{mole fraction of component } M \text{ in Bi phase}}{\text{mole fraction of component } MF_n \text{ in salt phase}}$$


ORNL-DWG-69-1241
ARGON OR VACUUM
TEFLON PLUG
CAJON O-RING FITTINGS
STAINLESS STEEL FILTER-SAMPLER
MOLYBDENUM THERMOWELL
BALL VALVE
CONTROL VALVE
TEFLON O-RING
PURIFIED ARGON
MOLYBDENUM CRUCIBLE
CONTROL THERMOCOUPLE
SALT PHASE
BISMUTH PHASE

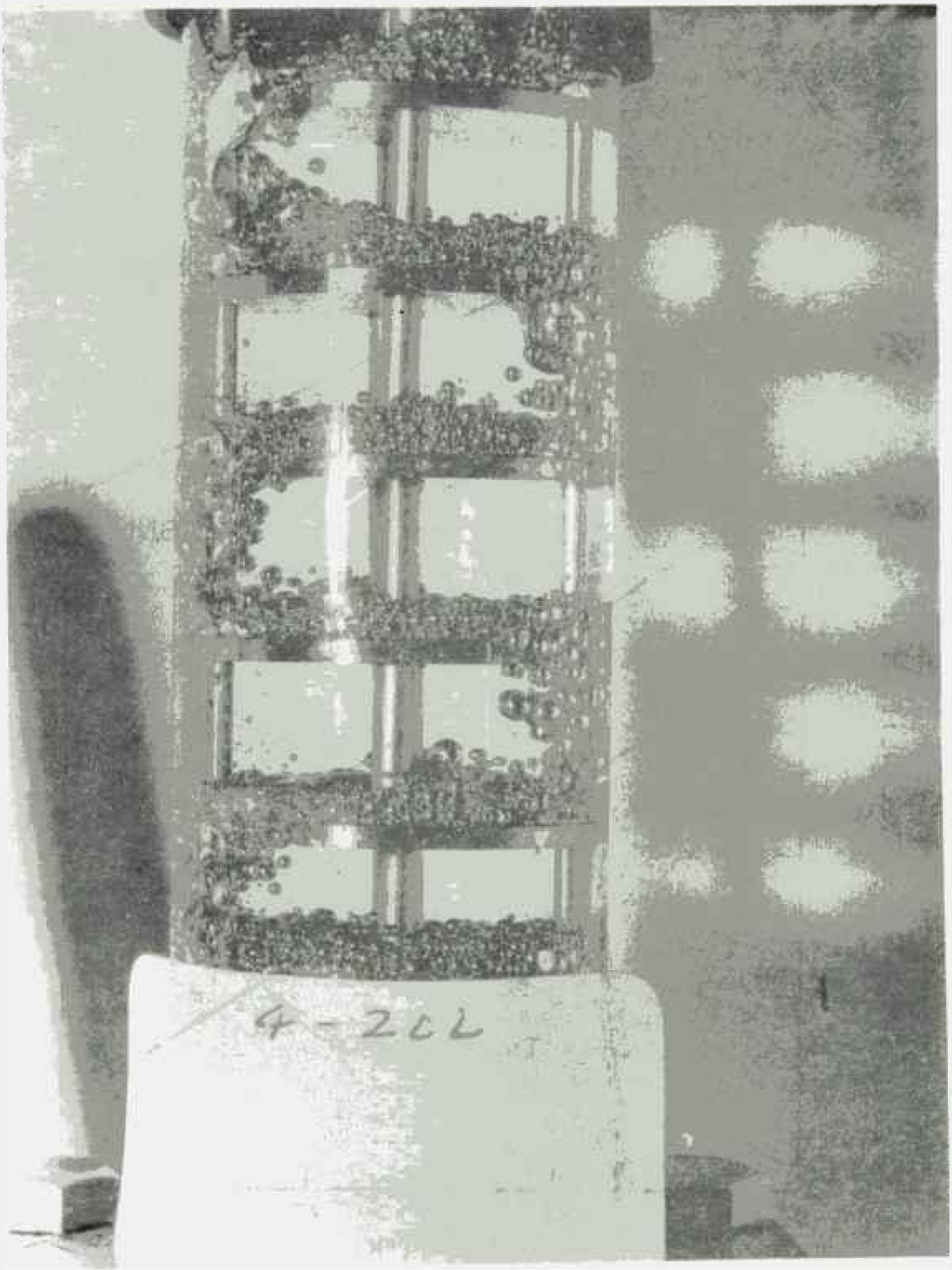


LABORATORY APPARATUS


ORNL DWG. 69-1255
SALT: LiF-BeF$_2$-ThF$_4$
(72-16-12 MOLE %)
TEMP: 600°C
Zr(IV)
U(III)
Pu(III)
Pa(IV)
Nd(III)
Eu(II)
Th(IV)
10^2
10
1.0
10^{-1}
10^{-2}
10^{-3}
0.001
0.01
0.1
0.2
DISTRIBUTION COEFFICIENT
LITHIUM CONCENTRATION IN METAL PHASE (at. %)

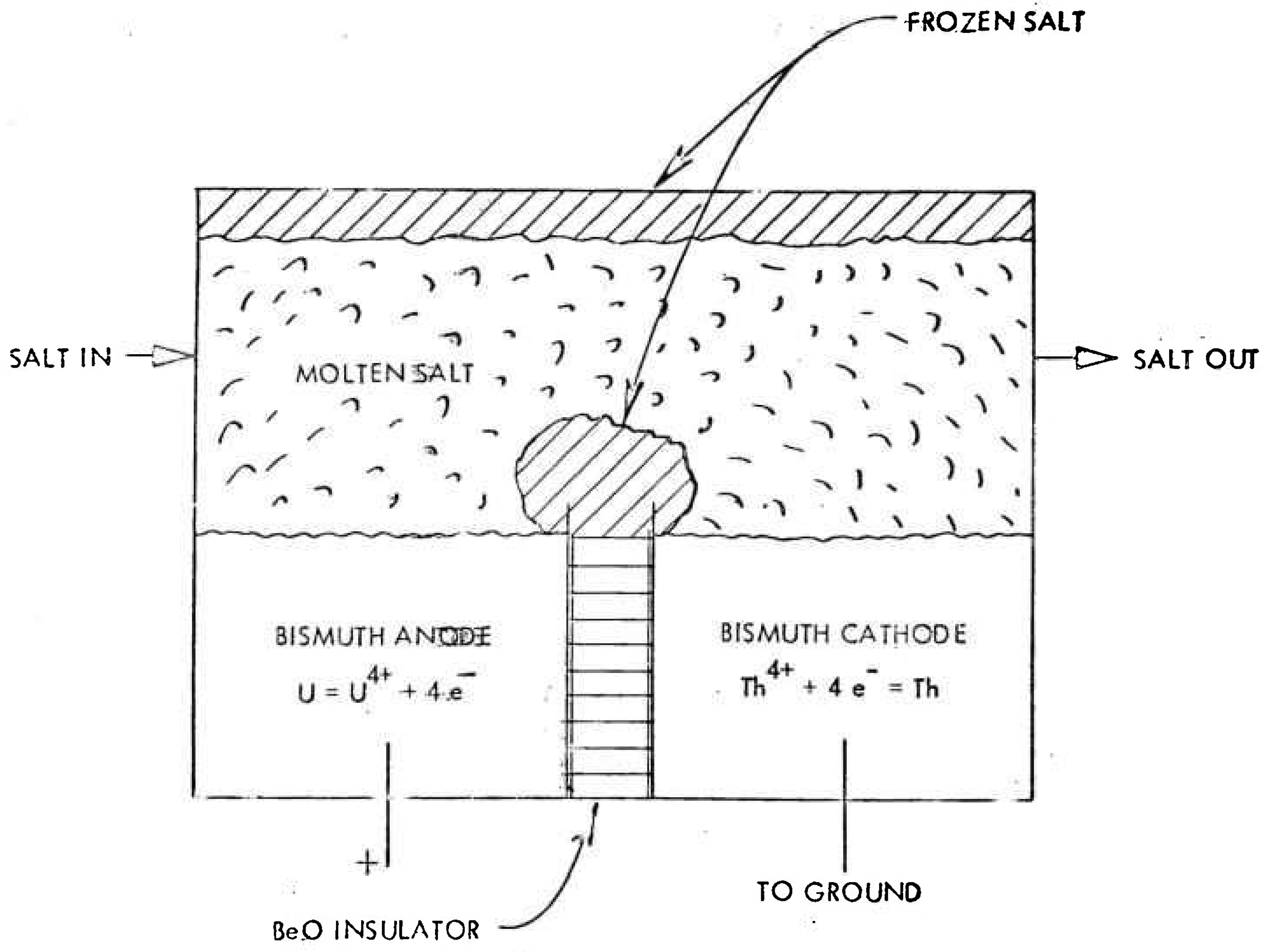


SOLUBILITIES IN LIQUID BISMUTH



Hg-H$_2$O STUDIES IN BAFFLED COLUMN

ORNL DWG. 69-10582



FLOW-THROUGH ELECTROLYTIC CELL

ORNL DWG. 69-9265

MAJOR ENGINEERING PROBLEMS IN REDUCTIVE EXTRACTION PROCESS

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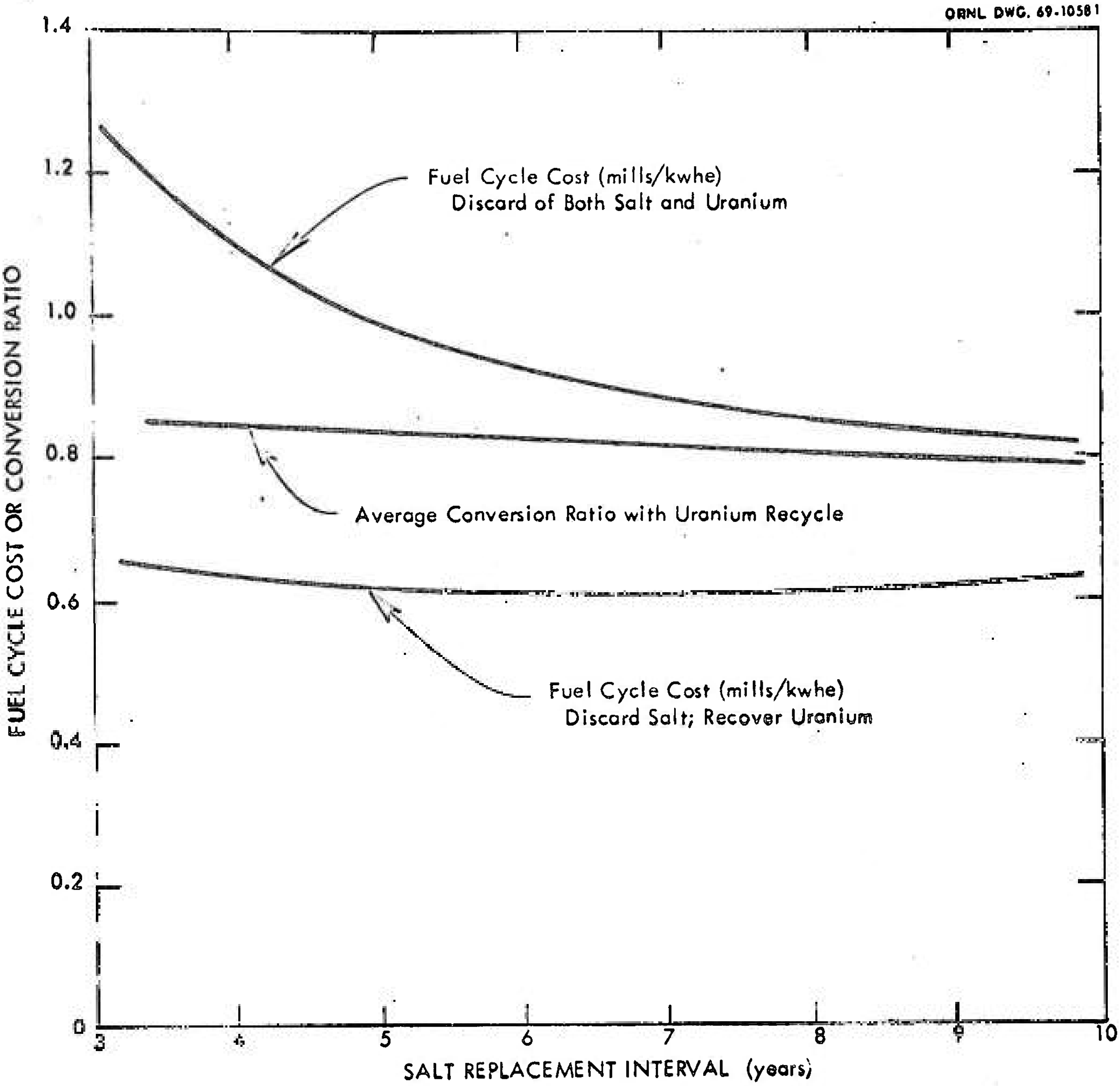
1. Contactor development.
2. Development of Electrolytic cells.
3. Materials of Construction.
4. Inline instrumentation for process control.
5. Frozen-wall protection of fluorinators and electrolytic cells.


ORNL DWG. 69-10581
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
FUEL CYCLE COST OR CONVERSION RATIO
3
4
5
6
7
8
9
10
SALT REPLACEMENT INTERVAL (years)
Fuel Cycle Cost (mills/kwhe)
Discard of Both Salt and Uranium
Average Conversion Ratio with Uranium Recycle
Fuel Cycle Cost (mills/kwhe)
Discard Salt; Recover Uranium

NONAQUEOUS METHODS FOR REPROCESSING LWR AND LMFBR FUEL

R. E. Blanco

In this lecture, I will discuss nonaqueous methods for reprocessing fuels. The fluoride volatility process has been studied for many years in the U. S. at Brookhaven Laboratory (BNL), Argonne National Laboratory (ANL), the Oak Ridge Gaseous Diffusion Plant (ORGDP), and the Oak Ridge National Laboratory (ORNL). A large pilot plant was scheduled for construction at ORNL but construction was cancelled about two years ago. Since then the process variables have been studied at ANL. A pyrochemical method, the salt transport process, is also being studied at ANL. The volatility process is also being studied in France and Belgium and pyrochemical processes in Belgium and Italy. Some work is also active in the U. S. S. R. on these processes, but the extent is not known. In the U. S., the main development effort is being applied to developing the aqueous method for processing LMFBR fuels, and volatility and pyrochemical methods receive much less effort. They are considering supporting methods to be used if their development is successful and if they should be needed for special purposes. For exemple, volatility processing is an important step in processing molten salt reactor fuel.

VOLATILITY PROCESSES

SLIDE 1 Potential Advantages of the Fluoride Volatility Process (67-5806)

This slide shows several potential advantages of the fluoride volatility process. This is the type of data which must be confirmed in the pilot plant tests.

SLIDE 2 Boiling Points of Fission Product Fluorides (67-5803)

This slide illustrates the basis for all fluoride volatility processes. It is seen that both PuF_6 and UF_6 have relatively low boiling points compared to most of the fission products. Normally, iodine is not a problem since it has a half life of 8 days and has mostly disappeared after 120 days of cooling. Thus, the basis for the process is to treat fuels with fluoride to selectively volatilize uranium and plutonium while the fission products do not volatilize.

SLIDE 3 Problems in the Fluoride Volatility Processes (67-5807)

Research and development on fluoride volatility processes has occurred since 1950. This slide lists some of the processing problems that have occurred and the solutions to these problems.

It was found that the heat of reaction of fuel elements with fluorine could be adequately controlled by either using a fluidized bed of alumina or a molten salt to transfer the heat to the vessel wall. The molten salt method was used in an earlier pilot plant at Oak Ridge National Laboratory. Previous attempts to use liquid fluorinating agents were insuccessful because the rate of reaction could not be controlled. Satisfactory methods have been developed for removal of the fuel claddings as I will show later. Generally, nickel has proved to be a satisfactory material of construction for the gaseous fluorine system. The corrosion rate is high but acceptable in the fused salt system.

The principal remaining chemical problem in the volatility system is the volatilization and purification of plutonium. The rate of fluorination of PuF_4 or PuO_2 to form PuF_6 is much slower than for uranium but at temperatures higher than 300°C, the rate is adequate. However, PuF_6 is thermodynamically unstable, and a large excess of elemental fluorine must be maintained to prevent decomposition to PuF_4 and losses of this solid on equipment surfaces. A completely satisfactory method for final purification of PuF_6 by a non-aqueous method has not been developed as yet. I will show several processing alternatives later. As we shall se later, the low chemical processing rates contribute to high processing costs.

SLIDE 4 General Procedure for Processing Uranium Alloy Nuclear Fuels by Fused Salt Volatility Methods (63-6167 R)

This slide illustrates the fused salt volatility process which was developed and pilot planted at ORNL. It is principally designed for use with enriched uranium fuels that contain only ^{235}U and do not contain significant amounts of plutonium after irradiation. Hence, plutonium recovery is not required. The Zr-U alloy fuel is rapidly dissolved in the fused salt with HF and then F_2. The fused salt carries away the heat of reaction. The uranium is purified by passage through a bed of NaF at 400°C where impurities adsorb. The UF_6 passes through and is sorbed on the 100°C bed. Many impurities pass on through. This bed is then heated to 400°C to volatilize the UF_6. Many impurities remain on the sodium fluoride. This method is the principle technique used for purifying enriched uranium where small amounts of uranium are present. Fractional distillation of the fluorides would probably be preferable where tonnage amounts of the uranium must be purified. A fluidized bed of alumina could be substituted for the fused salt step and the Zr-U fuel could be processed with HCl to remove the Zr as $ZrCl_4$ and the uranium as UF_6 with F_2.

SLIDE 5 Schematic of ORNL Volatility Pilot Plant (Dwg. 59438)

This slide shows simplified version of the molten salt fluoride volatility pilot plant at ORNL (for enriched uranium fuels), shows separate vessels for dissolution in HF, and fluorination with F_2. The lower part of the movable bed NaF absorber is first maintained at 100°C and impurities pass through. The temperature is then raised to 400°C and the UF_6 moves out of the top of the bed and is retained in a cold trap. After each test part of the NaF is discharged into the fluorinator where it dissolves and forms part of the fused salt for the next batch. This process achieved excellent recovery and purification of the uranium (DF's of 10^7 to 10^9).

SLIDE 6 Movable Bed Temperature Zoned Adsorber (Dwg. 50451R)

SLIDE 7 NaF Absorption-Desorption Process (Dwg. 61850)

This slide shows the details of the NaF purification process. The remaining Np and Tc are removed on a bed of MgF_2 in a later step. IF_7 and TeF_6 are not sorbed at 100°C. The following are irreversibly filtered or sorbed at 400°C ZrF_4, NbF_5, CrF_4, CrF_5, PuF_6, RuF_5 and fluorides of Cs, Sr, and REs.

Now I will discuss the present process for processing power reactor fuels where both uranium and plutonium must be recovered. This process is being installed in the ORNL pilot plant.

SLIDE 8 Equations for Fluidized-Bed Volatility Process for Zr-Clad UO_2 (66-9521)

SLIDE 9 Equations for Fluidized-Bed Volatility Process for Zr-Clad UO_2 (66-9523)

SLIDE 10 Equations for Fluidized-Bed Volatility Process for Stainless Steel Clad-UO_2 (67-5805)

SLIDE 11 Flowsheet for Fluidized-Bed Volatility Pilot Plant as of Nov. 30, 1966 (67-6345 R)

This is the general flowsheet for the pilot plant which had been planned for ORNL. The pilot plant is designed to process about 40 kg of UO_2/batch (per week) in an 8-in. by 12-ft high fluidized bed. The full size fuel element or the sheared pieces of fuel could be put into the fluid bed unit. The bed contains 58 kg of 48 to 100 mesh alumina at a weight ratio of fuel to alumina of about 1 (44.58). The alumina acts as a heat transfer media. The Zircaloy-2 cladding is removed as $ZrCl_4$ with HCl gas at 450°C in 4 hr and hydrolyzed with steam at 450°C and collected as zirconium oxide. The uranium is converted to U_3O_8 with oxygen at 450°C in 1 hr and then volatilized as UF_6 with bromine pentafluoride at 300°C. Plutonium and most of the FP's do not volatilize with BrF_5. Much of the activity in this stream will be removed by the 400°C NaF trap, then the UF_6 and BrF_5 is condensed and further purified by fractional distillation in 3-4 hr. The plutonium is volatilized with F_2 at 300-550°C over a period of 10-15 hr. Some of the remaining Mo, Ru (3.7%), Nb (1.3%), and 0.8% of the gross beta and gamma will also be volatilized with the PuF_6 but the fluorides of Cs, Sr, and the RE's are not volatile.

SLIDE 12 Possible Methods for Purification of Plutonium in Volatility Processes (67-5804)

This shows possible methods for purifying plutonium which have been or are now being evaluated.

1) Slow selective sublimation and thermal decompositon at 300°C; expected decontamination factors are 100.

2) Sublimation with chemical reduction at 300°C with BrF_5; expected decontamination factors are 100.

3) Washing with BrF_5; expected decontamination factors are 100.

4) This illustrates the difference between the UF_6-NaF system and the PuF_6-LiF system. In this case, PuF_6 is reduced to PuF_4 and must be revolatilized. Kinetics of sorption reaction and revolatilization are too slow.

5) Sorb on NaF and dissolve in liquid HF; 80 to 90% of the ruthenium and less than 98% of the niobium removed.

The best system at present is to dissolve in aqueous nitric acid and use anion exchange.

Construction of the pilot plant was halted. At this time, it does not appear that there is sufficient incentive for large expenditures for further development of fluidized-bed volatility. Allied Chemical studied the economics of the volatility process and dropped volatility from consideration for the processing plant they are planning and decided to build an aqueous plant. In making their evaluation, Allied adopted the conservative approach of comparing volatility with aqueous processing on the basis of known technology. On this basis, volatility could not compete with established aqueous methods. The volatility process had not been fully developed and demonstrated in a "hot" pilot plant at the time this cost estimate was made, so presumably many conservative assumptions were made in designing the volatility plant. One of the principal technical problems was the lack of a satisfactory process for decontaminating PuF_6 after it is volatilized out of the primary reactor.

Other operating parameters which undoubtedly added to the capital cost include: 1) a processing time of 48 hr in the primary 8-in.-diam fluid bed. Thus, only one metric ton of fuel could be processed in two days and two parallel reactors would be required to achieve a processing rate of one ton per day; and (2) a poorly defined criticality problem. Typical plutonium contents of 6 to 10 kg per metric ton are expected for fuels with nominal burnups of 25,000 Mwd/metric ton. The minimum critical mass of dry PuO_2 is 16 kg as a dense sphere. Conservative design assumptions must assume, however, that the plutonium may not remain homogeneously dispersed in the fluid bed and may, in fact, become concentrated in one zone. The critical mass for the fluid bed reactor was assumed to be 30 kg. Since the operator does not know precisely the amount of plutonium entering the system and probably cannot sample the residual fluid bed with great accuracy and certainty, he cannot determine the precise amount of plutonium in the bed after reusing the bed several times. Discard of the bed after one or a few uses becomes a significant cost item. Thus, the volatility process must be developed as a continuous process to overcome some of these disadvantages.

SLIDE 13 Fluoride Volatility Process for Fast Reactor Fuels (68-10626)

Argonne National Laboratory has started the development of a continuous volatility process to overcome some of the disadvantages of the batch process. This slide shows conceptual flowsheet. The fuel is mechanically separated from the stainless steel cladding and converted to a homogeneous powder that can be sampled for input accountability and fuel burnup determinations. The oxide powder is then fed continuously to fluidized-bed fluorinators, where uranium and plutonium are converted to hexafluorides by reaction with fluorine gas. The nonvolatile fission product fluorides of Groups I, II, III, and IV are discharged from the fluorinators along with the alumina powder that is used as the bed material. The mixed hexafluoride gases and fluorine are cooled in a partial condenser to about 15°C in order to condense the bulk of the volatile ruthenium and niobium pentafluorides. After condensation in refrigerated traps, the uranium and plutonium hexafluorides are separated from each other by thermal decomposition of the PuF_6 to the nonvolatile tetrafluoride at about 350°C; the PuF_4 is then refluorinated to PuF_6. Next, the UF_6 gas from the thermal decomposer is purified by fractional distillation to separate the remaining fission products. Finally, the hexafluorides of uranium and plutonium are mixed in the desired ratio and converted to oxides by gas-phase reaction with steam and hydrogen.

SLIDE 14 Continuous Fluorination Step (68-12212)

The fluorination concept is that of a continuous operation employing two fluorinatiors in series. The first fluorinatior would receive fuel and alumina in power form and convert the uranium and a small fraction of the plutonium to the hexafluorides by reaction with a fluorine-oxygen mixture at 350°C. The alumina bed containing PuF_4 and fission products would overflow from this reactor into the second fluorinator, where fluorination of the PuF_4 would be completed by reaction with concentrated fluorine gas at 550°C. To permit the discharge of the waste alumina bed and fission products and yet maintain very low plutonium losses, the second fluorinator would have to contain at least two fluid-bed stages arranged in countercurrent flow with the fluorine gas.

The rate of the fluorination of plutonium is limited by the thermodynamic equilibrium of the fluorination reaction; therefore, a large flow rate of recycled fluorine must be employed. Plutonium fluorination decrease as the plutonium is depleted from the bed. Therefore, continuous fluorination is considered to be desirable in order to maintain a high fluorination rate.

The fluorination reactors represent the point of largest accumulation of fissible material, and hence present stringent requirements for safety from the standpoint of criticality. For geometrical control, the fluorinators are visualized as approximately rectangular slabs 10 cm thick, 1.2 m wide, and 3 m high.

The gas streams leaving the two fluorination vessels are handled separately to facilitate the recycle of the reagent gases. Oxygen is a product of the fluorination of the fuel oxides in the first fluorinator, and the recycle of this gas produces a mixture of fluorine and oxygen. The second fluorinator operates with a recycle of virtually pure fluorine.

The next few slides show equipment pieces constructed for the ORNL volatility pilot plant.

SLIDE 15 Fluid Bed Unit (Photo 66-1237)

This 8 in. x 12-ft-high fluid-bed unit was constructed for the pilot plant. Heaters and cooling coils have been bonded to the surface by spraying with copper for heat transfer and then with stainless steel for oxidation resistance.

SLIDE 16 Primary Reactor Proposed for FBVPP (65-8199)

SLIDE 17 Main Filter for Primary Reactor (65-8200)

This filter is composed of nickel fibers with a 10 μ nominal pour size.

SLIDE 18 Picture of a Condenser (Photo 84787-R)

25 cm diam x 3 meters long

SLIDE 19 Interior View of a Condenser (Photo 84943)

PYROCHEMICAL SALT TRANSPORT PROCESS

Unlike aqueous and fluoride volatility processes, pyrochemical processes have been oriented toward fast breeder reactor fuels from the outset. The melt refining process, which was developed to recover the enriched uranium fuel alloy used in the core of EBR-II, is a simple oxidative slagging procedure. This on-site, fully remote process, together with the other steps of the fuel cycle, has been in routine operation for about four years.

SLIDE 20 Salt Transport Process for LMFBR Fuel (68-10627)

The Salt Transport Process, now under development at Argonne National Laboratory, uses extractions between liquid metal and salt solvents to accomplish the separation of uranium, plutonium, and fission products. The fuel is declad by dissolving away the stainless steel with liquid zinc, which does not attack uranium and plutonium oxides. The solubility of "stainless steel" in zinc at 800°C is about 10 wt %. The zinc decladding should not be affected by sodium-logged fuel pins, and prior removal of external sodium is not required.

In the plutonium-uranium oxide reduction step, the uranium, plutonium, and fission product oxides are suspended in a molten $CaCl_2$-CaF_2 salt, which is stirred with a liquid Cu--33 wt % Mg alloy containing about 5 wt % calcium. The metallic uranium, with a solubility of about 50 ppm, is precipitated, and the plutonium metal remains in solution with the Cu-Mg alloy. The gaseous fission products (FP-1) from the decladding and reduction steps are collected in the argon cover gas. In the reduction step, the alkali and alkaline earth fission products and most of the iodine (FP-2) and the CaO (formed as a byproduct) remain in the salt, wich is a waste stream. The other fission products appear in the Cu-Mg alloy. Laboratory and bench-scale engineering studies have shown that, with both high-fired UO_2 pellets and mixed UO_2-PuO_2, greater than 99% reduction can be obtained under these conditions. One interesting observation in this connection is that PuO_2 is reduced considerably faster than UO_2.

At this point, the Cu-Mg alloy contains the plutonium in solution, and the uranium in the form of precipitated metal. This alloy also contains the rare earth fission products--FP-3--and the noble and refractory metal fission products--FP-4. The supernatant liquid metal, which contains the plutonium, is processed through a rare earth removal step in which the rare earth fission products are extracted from the Cu-Mg-Pu solution by a molten salt.

The separation of rare earths from plutonium is a key step in this process since it is the limiting factor for the overall decontamination of plutonium. The Cu-Mg system was selected as a solvent metal for this step, primarily because it provides a plutonium-rare earth separation factor of about 1000. The composition of the molten salt in this step is 67 mole % $MgCl_2$--18 mole %NaCl--12 mole % KCl--3 mole % MgF_2. The large $MgCl_2$ content is required in order to obtain suitably high distribution coefficients for a practical separation; the addition of NaCl and KCl serves to decrease the melting point below the desired operating temperature of 600°C; the small amount of fluoride facilitates disengagement of the liquid salt and metal phases. With this salt-metal combination, a multistage extraction should provide a plutonium decontamination factor of about 100 for each stage. At present, a four-stage extraction is being considered.

The only fission products remaining in the Cu-Mg-Pu alloy after the rare earth extraction step are those designated FP-4. In the next step (i.e., the salt transport step), the plutonium is transferred selectively from the Cu-Mg alloy to a Zn--14 wt % Mg alloy by cycling a molten salt between the two alloys. This salt can be of the same composition as the one used for rare earth extraction. In this step the FP-4 fission products remain in the Cu-Mg alloy. An intermediate stage is provided between the Cu-Mg and Zn-Mg alloys to remove any entrained Cu-Mg alloy and to provide further separation of the FP-4 fission products. In this intermediate stage the salt is contacted with a Cd--18 wt % Mg alloy.

A portion of the Cu-Mg alloy, which now contains only the FP-4 group of fission products, is discarded as waste. The remainder, after appropriate additions of makeup calcium and fresh Cu-Mg, is used in the reduction step for the next batch of fuel.

Laboratory studies and engineering experiments involving 200-g batches of plutonium have shown that this operation can be performed successfully with essentially complete ($>$ 99.8%) plutonium recovery. A large quantity of chemical data concerning the solubilities and distribution coefficients of plutonium in this system has been generated.

Metallic plutonium is recovered from the Zn-Mg-Pu alloy by vacuum distillation of the zinc and magnesium. Small-scale engineering studies with 200-g batches of plutonium are currently in progress.

It is questionable whether the value of uranium justifies its decontamination and immediate recovery. It might prove more economical, for example, to add a small amount of iron to form a molten alloy that can be transferred from the vessel. Recovery of this material in a large, central plant should be relatively inexpensive.

SLIDE 21 (68-12214)

According to the current concept, the decladding and reduction steps are performed in the same vessel, which will probably be constructed of tungsten-coated graphite. A one-metric-ton-per-day plant will require two of these vessels and that three subassemblies will be handled at a time in each vessel. Following the decladding, the reduction step and the transfers of liquid metal solutions of uranium and plutonium from this vessel are carried out as indicated earlier. This vessel will be about 2 m tall and 45 cm in diameter.

A seven-stage mixer-settler is planned for the rare earth extraction and plutonium salt transport separations. In the first four stages, rare earths are extracted from the Cu-Mg-Pu alloy. In the fifth stage, the plutonium is extracted from the Cu-Mg donor alloy by the salt, and in the seventh stage it is re-extracted into the Zn-Mg acceptor alloy. The sixth stage is included primarily as a precautionary measure whereby any entrained Cu-Mg alloy is removed from the salt by liquid cadmium or zinc, which does not extract plutonium. This stage also provides additional removal of any refractory or noble metal fission products. The metal phase in this stage will require only very infrequent replacement. For the conceptual one-metric-ton-per-day plant, this seven-stage unit is expected to be about 1.8 m long by perhaps 50 by 60 cm. A preliminary design for a mixer-settler that can be fabricated from a refractory metal such as tantalum or molybdenum-tungsten alloy is complete, and a single-stage unit for testing is being built.

The vacuum distillation equipment for plutonium probably will be of slab geometry to ensure criticality control. About three such units will be required, each one being about 50 by 75 cm long and 3.75 cm thick.

Additional development effort is needed on: (1) the design of a practical, high-temperature, ultistage mixer-settler, (2) the design of the head-end and zinc decladding equipment, mainly in the mechanical aspects of fuel handling, and (3) the design of process equipment that is capable of fully remote operation.

The apparent advantages of pyrochemical processes are (1) their applicability to handle short-cool high-burnup fuel, (2) the small compact equipment which can be used, (3) the production of solid low-volume wastes, (4) their abatement of critical mass restrictions because of the lack of water in the process, and (5) the processes are suitable to close cycle on-site processing. Materials of construction are a problem and the life of a process vessel must be determined. Actual tests of pyrochemical processes in large-scale pilot plants with radioactive fuels will be required to determine the relative economic position of pyrochemical processing.

REFERENCES AND EXCERPTS FROM:

General

1. D. E. Ferguson and R. E. Blanco, "*General Survey* of Reprocessing of Thermal Reactor Fuels," presented at the 1968 American Nuclear Society, International Meeting in Washington, D. C., November 10-15, 1968; to be published in the *Proceedings.*

2. E. L. Youngblood and F. W. Miles, Hazards Evaluation for the Fuidized Bed Volatility Pilot Plant, ORNL-TM-2092, July 1968.

3. Chem. Tech. Div. Ann. Progr. Rept. May 31, 1965, ORNL-3830, pp. 69-95.

4. Chem. Tech. Div. Ann. Progr. Rept. May 31, 1964, ORNL-3627, pp. 29-72.

5. W. H. Carr, S. Mann, and E. C. Moncrief, "Urania-Zirconia Alloy Fuel Processing ORNL-Volatility Pilot Plant," Chem. Eng. Progr. Symp. Series Vol. 60, 47, 1964.

6. P. Chiotti, editor, *Nuclear Mettalurgy,* Vol. 15, Symposium on Reprocessing of Nuclear Fuels, August 25-27, 1969, Ames, Ill. (The following papers are in this symposium volume.)

   a. **Melt Refining**

   D. E. Hampson *et al.*, "Melt Refining of EBR-II Fuel," p.57.

M. J. Feldman, *et al.*, "Remote Refabrication of EBR-II Fuels," p.77.

b. Salt Transport Process

R. K. Steunenberg *et al.*, "Status of the Salt Transport Process for Fast Breeder Reactor Fuel," p. 325.

J. B. Knighton *et al.*, "Uranium and Plutonium Purification for the Salt Transport Method," p. 337.

R. D. Pierce *et al.*, "Multi-Stage Contactors for Liquid Metal-Salt Extraction," p. 511.

c. Fluoride Volatility Process

M. J. Steindler *et al.*, "Laboratory Development of the Fluoride Volatility Process for Oxidic Nuclear Fuels," p. 177.

N. M. Levitz *et al.*, "Plutonium-Bearing Fuel Materials," p. 211.

A. A Jonke *et al.*, "The Potential of the Fluoride Volatility Process for Fast Breeder Reactor Fuels," p. 231.

ORNL DWG. 67-5806

POTENTIAL ADVANTAGES OF THE FLUORIDE-VOLATILITY PROCESS

(1) No degradation of reactants by radiation. Highly irradiated fuels can be processed.

(2) Reduce fuel inventory costs. Long time periods for radioactive decay not required to reduce radiation level.

(3) Lower processing costs. Absence of neutron moderator (water) should permit larger equipment and higher concentrations of chemicals.

(4) Solid waste products. Radioactive wastes are produced as solids suitable for permanent storage.

ORNL DWG. 67-5803

BOILING POINTS OF FISSION PRODUCT FLUORIDES

Fluoride	B.P. (°C)
TeF_6	-39
IF_7	4
MoF_6	35
BrF_5	41
TcF_6	52
UF_6	55.2
NpF_6	56.4
PuF_6	62
IF_5	100
SbF_5	150
NbF_5	229
RuF_5	313
ZrF_4	903
R.E. F's	> 1000

ORNL DWG. 67-5807

PROBLEMS IN THE FLUORIDE VOLATILITY PROCESSES

(1) Control heat of reaction with gaseous fluorine.
  a. Fluidized bed of alumina
  b. Fused fluoride salt

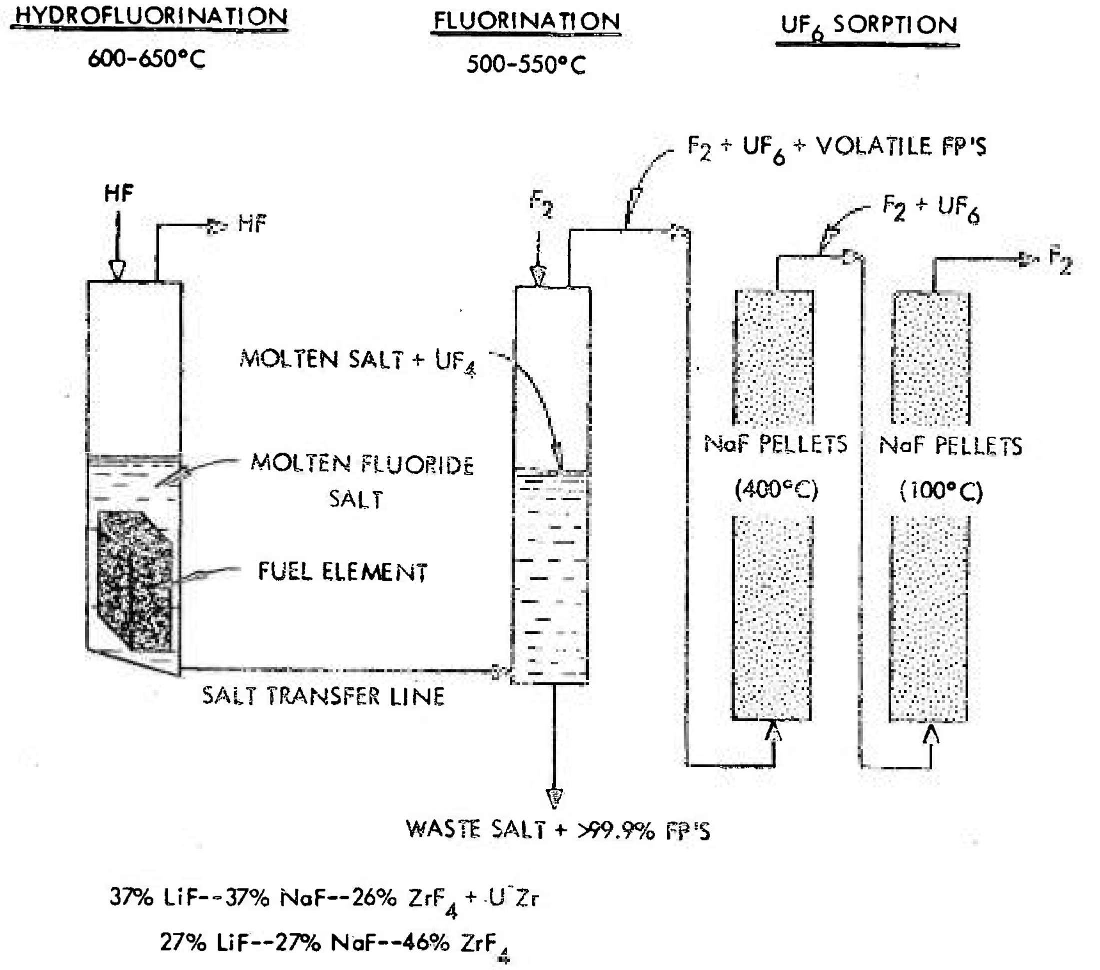
(2) Control rate of reaction with liquid CF_3 or BrF_3

(3) Removal of the fuel cladding material.
  a. Hydrochlorination for zirconium
  b. Oxidation for graphite
  c. Oxidation-hydrofluorination for stainless steel

(4) Corrosion – Ni material of construction.

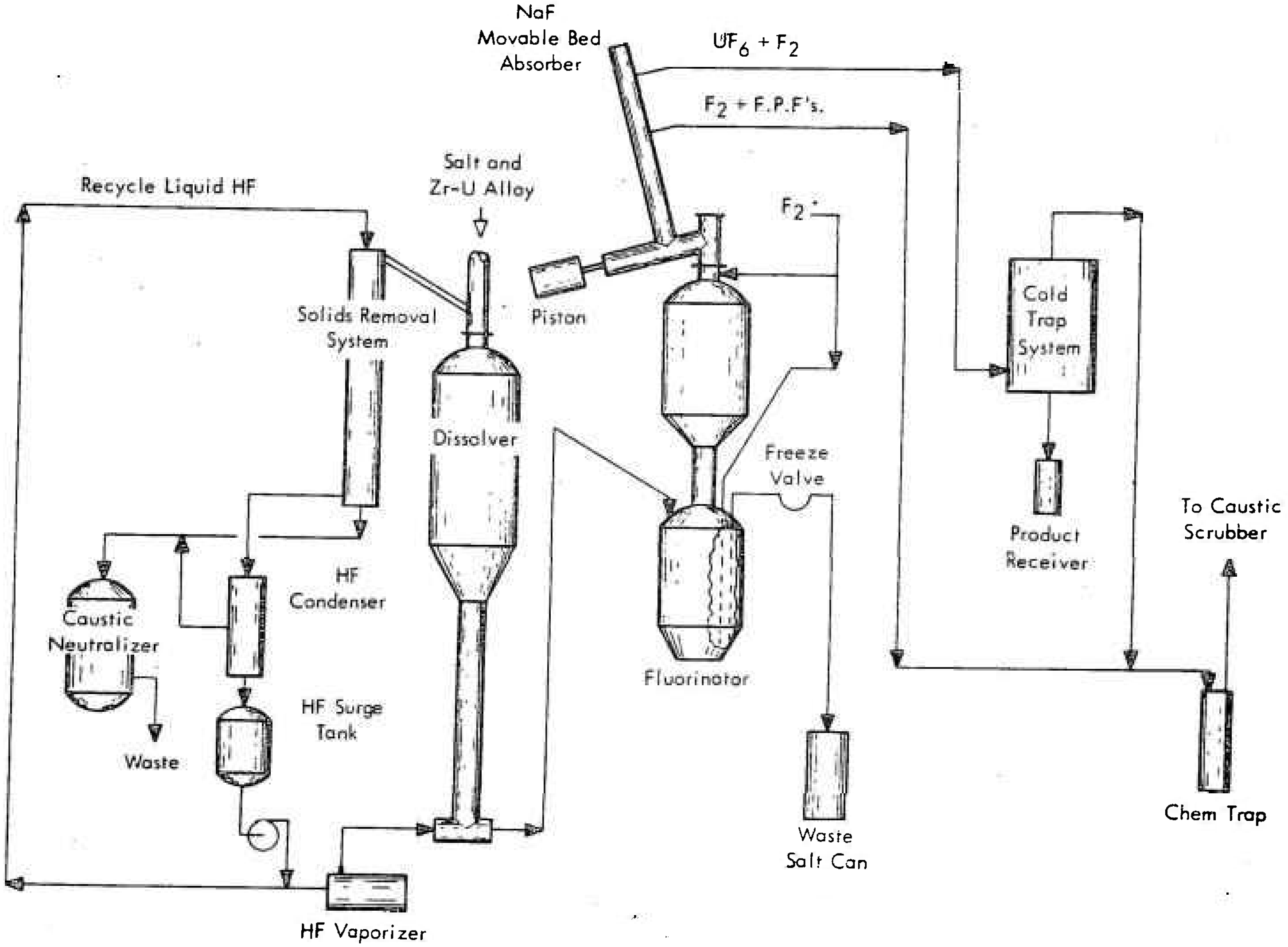
(5) Volatilization and purification of plutonium.

ORNL Dwg. 63-6167 R



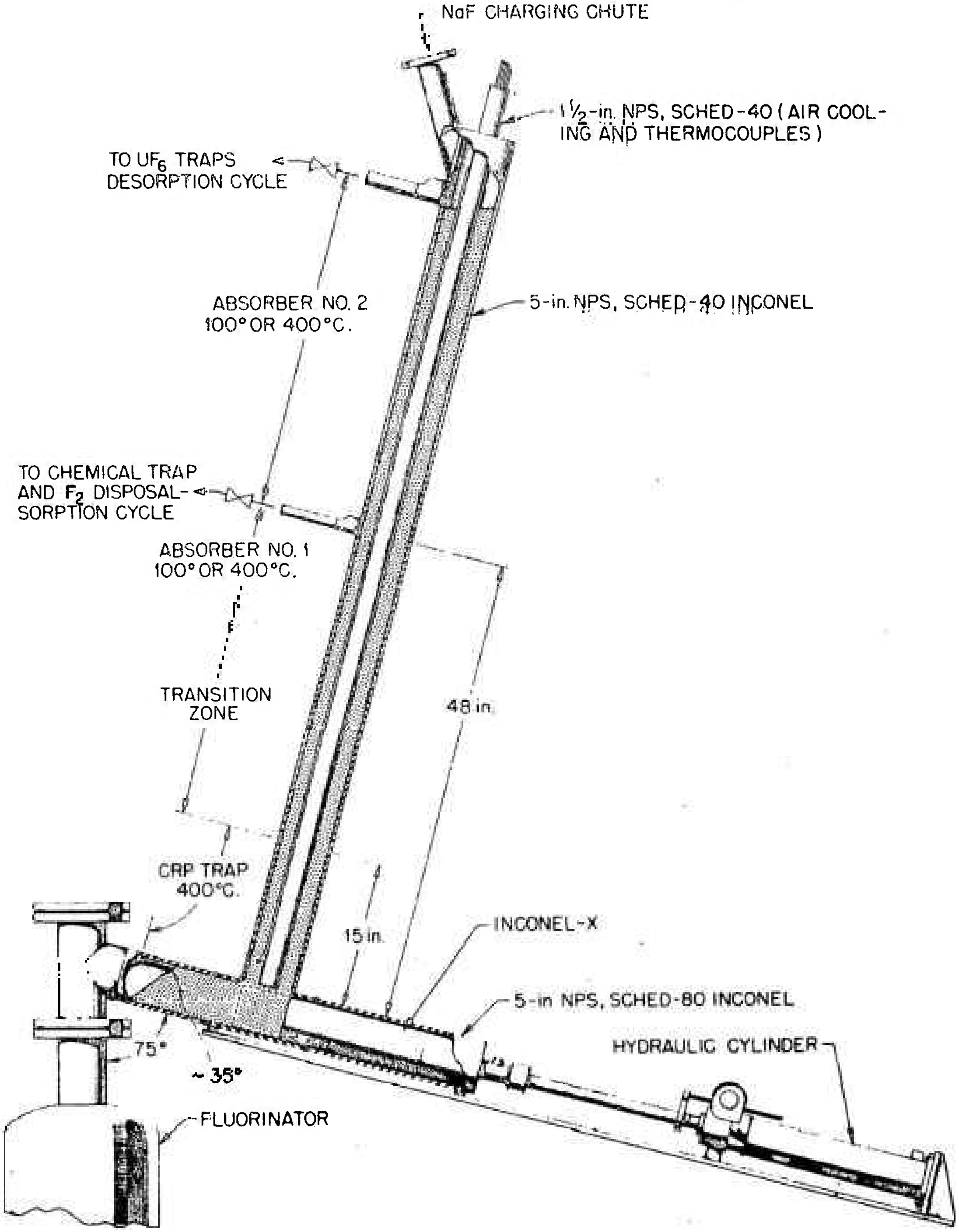
GENERAL PROCESSES FOR PROCESSING URANIUM ALLOY NUCLEAR FUELS BY FUSED-SALT VOLATILITY METHODS

ORNL-LR-DWG. 59426

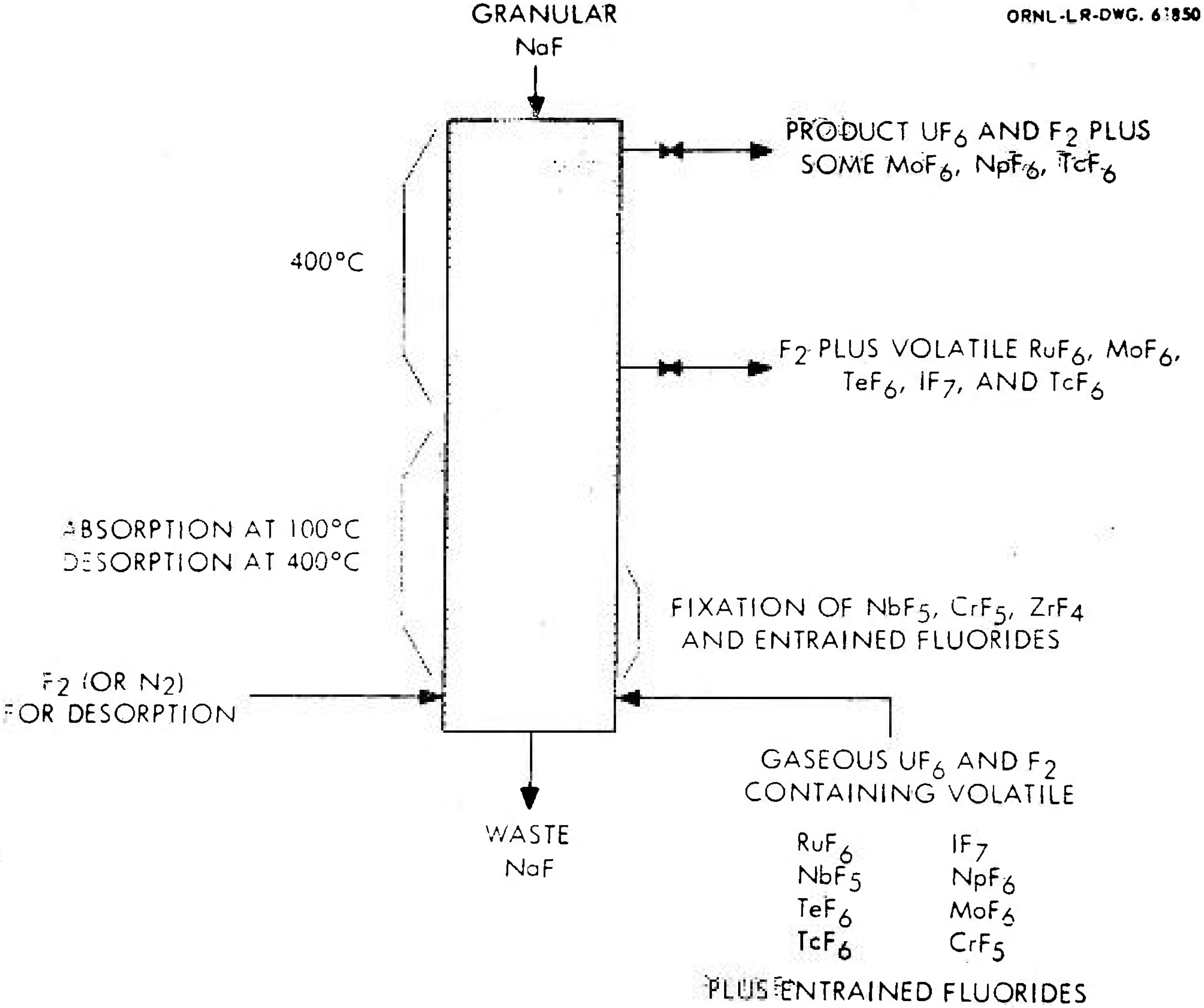


SCHEMATIC OF ORNL VOLATILITY PILOT PLANT

ORNL-LR-DWG 50451R



Movable Bed Temperature-Zoned Absorber



NaF ABSORPTION-DESORPTION PROCESS

ORNL DWG 66-9521

FLUIDIZED-BED VOLATILITY PROCESS FOR Zr-CLAD UO_2

DECLADDING

$$Zr + HCl \xrightarrow{400°C} ZrCl_4 + H_2$$

PYROHYDROLYSIS

$$ZrCl_4 + 2\,H_2O \xrightarrow{350°C} ZrO_2 + 4\,HCl$$

OXIDATION

$$3\,UO_2 + O_2 \xrightarrow{450°C} U_3O_8$$

ORNL DWG 66-9523

FLUIDIZED-BED VOLATILITY PROCESS FOR Zr-CLAD UO_2 (Cont'd)

FLUORINATION

$$U_3O_8 + 9\ F_2 \xrightarrow{450°C} 3\ UF_6 + 4\ O_2$$

OR

$$U_3O_8 + 18/5\ BrF_5 \xrightarrow{300°C} 3\ UF_6 + 9/5\ Br_2 + 4\ O_2$$

$$PuF_4 + F_2 \xrightarrow{300-550°C} PuF_6$$

SEPARATION AND PURIFICATION

ORNL DWG. 67-5805

FLUIDIZED-BED VOLATILITY PROCESS FOR STAINLESS STEEL CLAD UO_2

Decladding

$$\mathrm{Fe,\ Ni,\ Cr} + 60\%\ \mathrm{O_2}\text{—}40\%\ \mathrm{HF} \xrightarrow{600°\mathrm{C}} \mathrm{F_2O_3} + \mathrm{NiO} + \mathrm{Cr_2O_3} + \text{some fluorides}$$

Oxidation

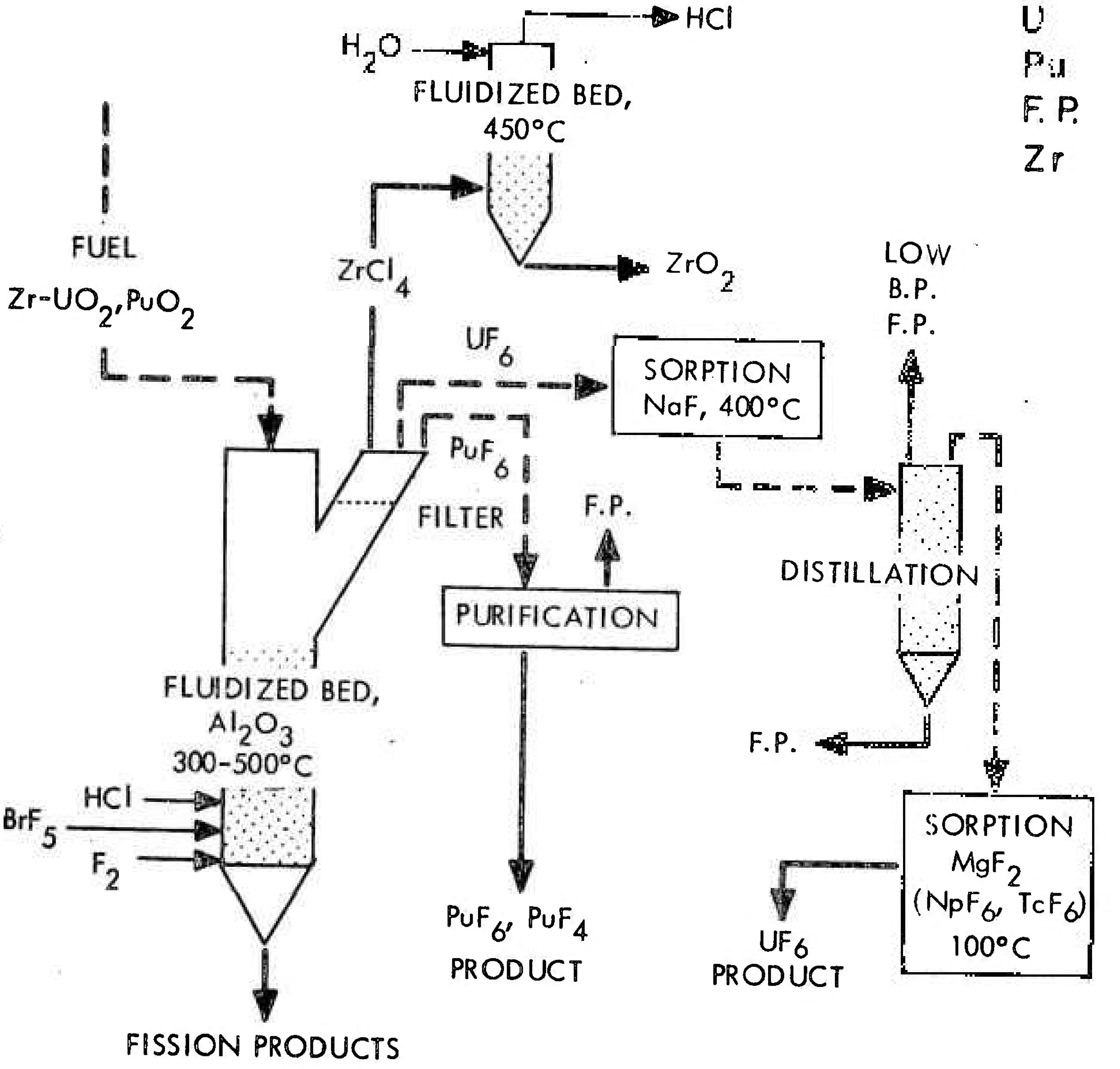
$$\mathrm{UO_2} + 60\%\ \mathrm{O_2}\text{—}40\%\ \mathrm{HF} \xrightarrow{600°\mathrm{C}} \mathrm{UF_4} + \mathrm{UO_2F_2}$$

Fluorination

$$\mathrm{Fe_2O_3} + \mathrm{NiO} + \mathrm{Cr_2O_3} + \mathrm{F_2} \xrightarrow{500°\mathrm{C}} \mathrm{FeF_3} + \mathrm{NaF_2} + \mathrm{CrF_x}$$

$$\mathrm{UF_4} + \mathrm{UO_2F_2} + \mathrm{F_2} \xrightarrow{500°\mathrm{C}} \mathrm{UF_6}$$

ORNL Dwg. 67-6345 R



FLUIDIZED BED FLUORIDE VOLATILITY PROCESSES

ORNL DWG. 67-5804

POSSIBLE METHODS FOR PURIFICATION OF PLUTONIUM IN VOLATILITY PROCESSES

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(1) Sublimation of $PuF_6 \xrightarrow[\text{decomposition}]{\text{thermal, °C}} PuF_4$

(2) Sublimation of $PuF_6 \xrightarrow[\text{reduction}]{\text{selective, } BrF_3\text{, 300°C}} PuF_4$

(3) $PuF_4 \xrightarrow[\text{gas or liquid}]{\text{washing with } BrF_5\text{-}BrF_3} PuF_4$

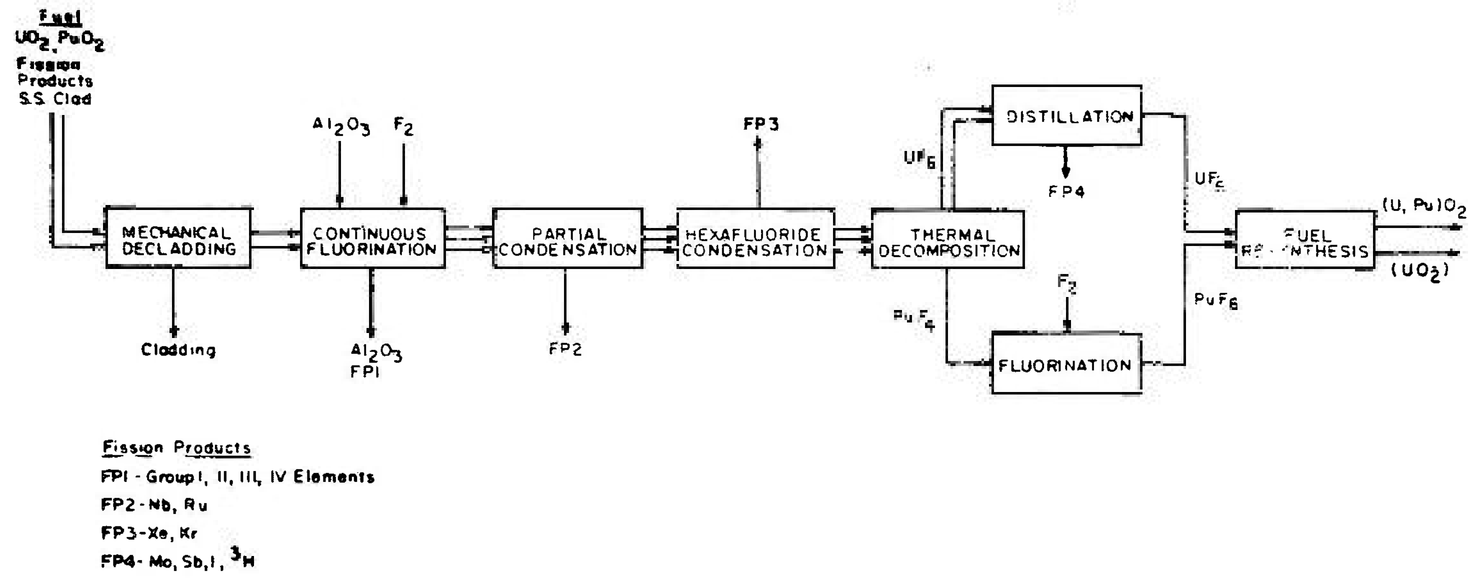
(4) $PuF_6 + LiF \xrightarrow{\text{sorb-desorb}} PuF_4 \cdot 4LiF + F_2$

(5) $PuF_6 + NaF \longrightarrow PuF_4 \cdot xNaF$

Dissolve NaF in liquid HF $\longrightarrow PuF_4$

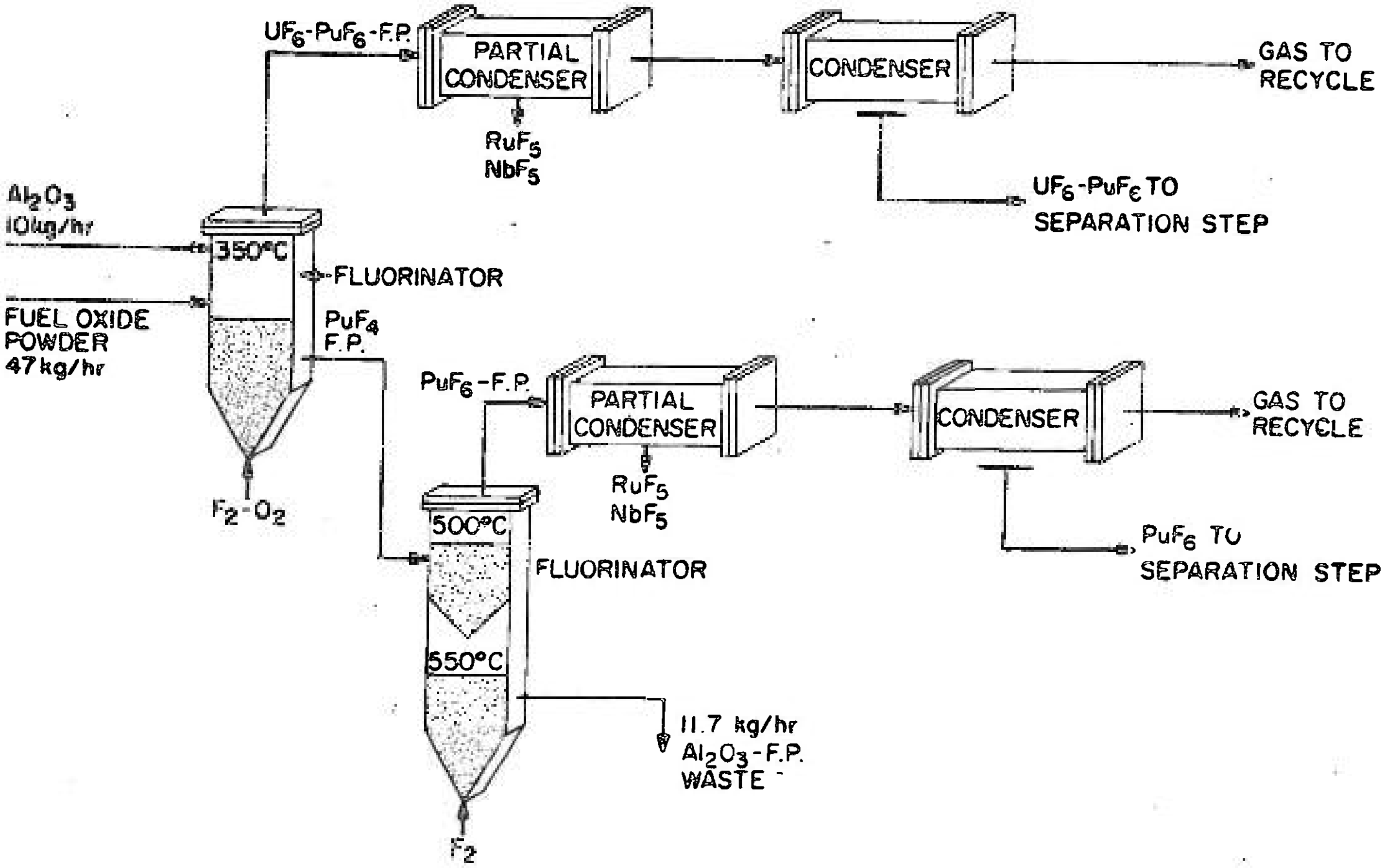
Dissolve in aqueous $HNO_3 \longrightarrow$ anion exchange $\longrightarrow Pu(NO_3)_2$

ORNL DWG. 68-10626

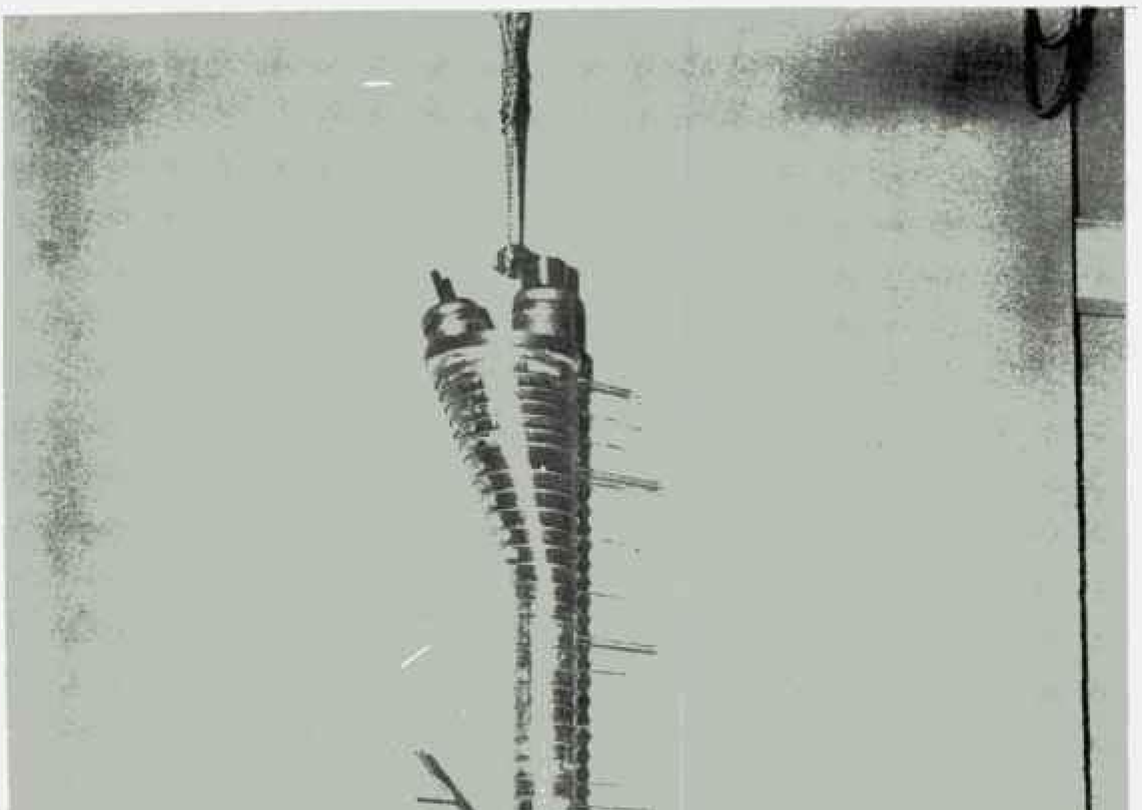


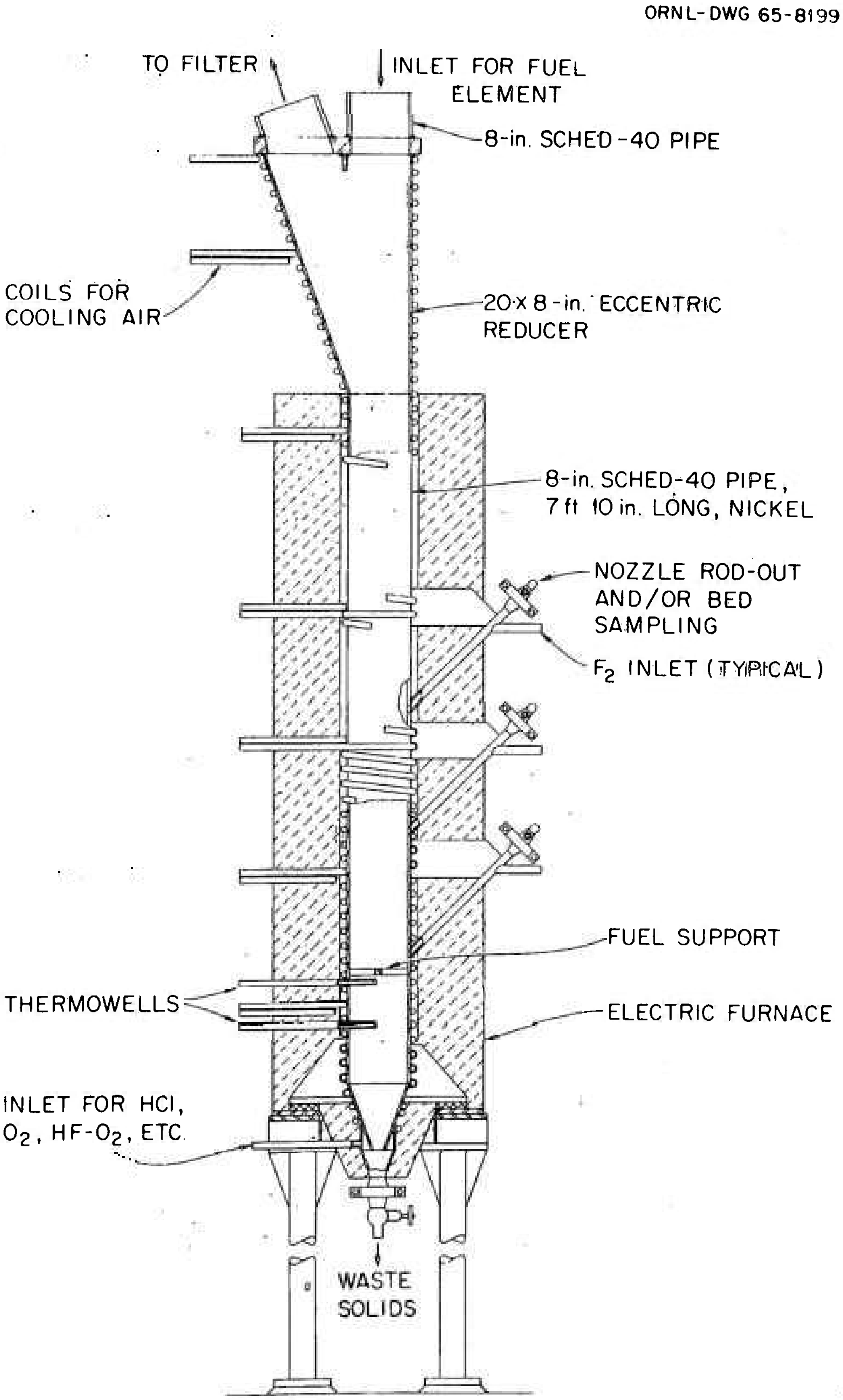
FLUORIDE VOLATILITY PROCESS FOR FAST REACTOR FUELS

ORNL DWG 68-12212

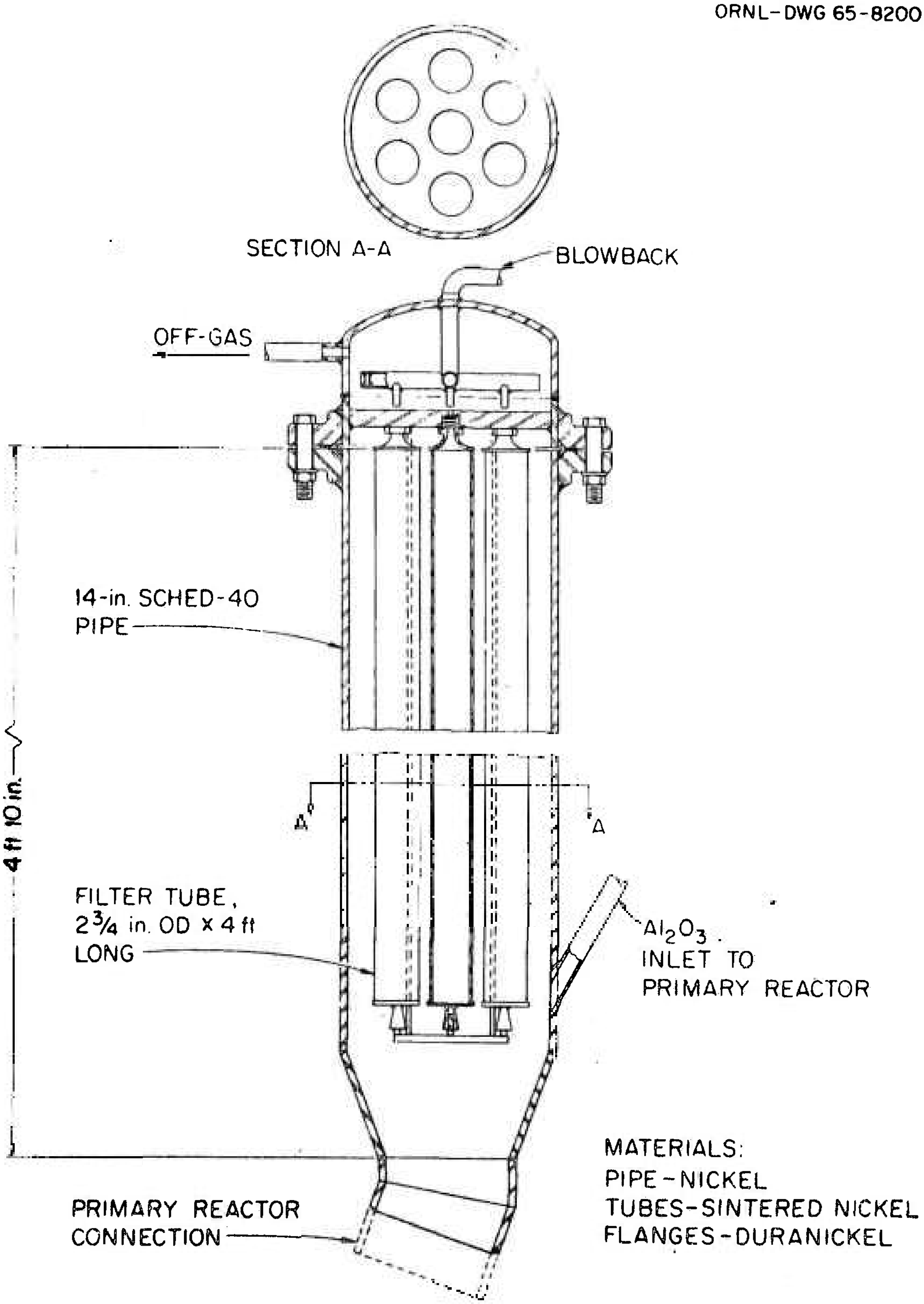


CONTINUOUS FLUORINATION STEP





Primary Reactor Proposed for FBVPP.



Main Filter for Primary Reactor.

PHOTO 84787-R

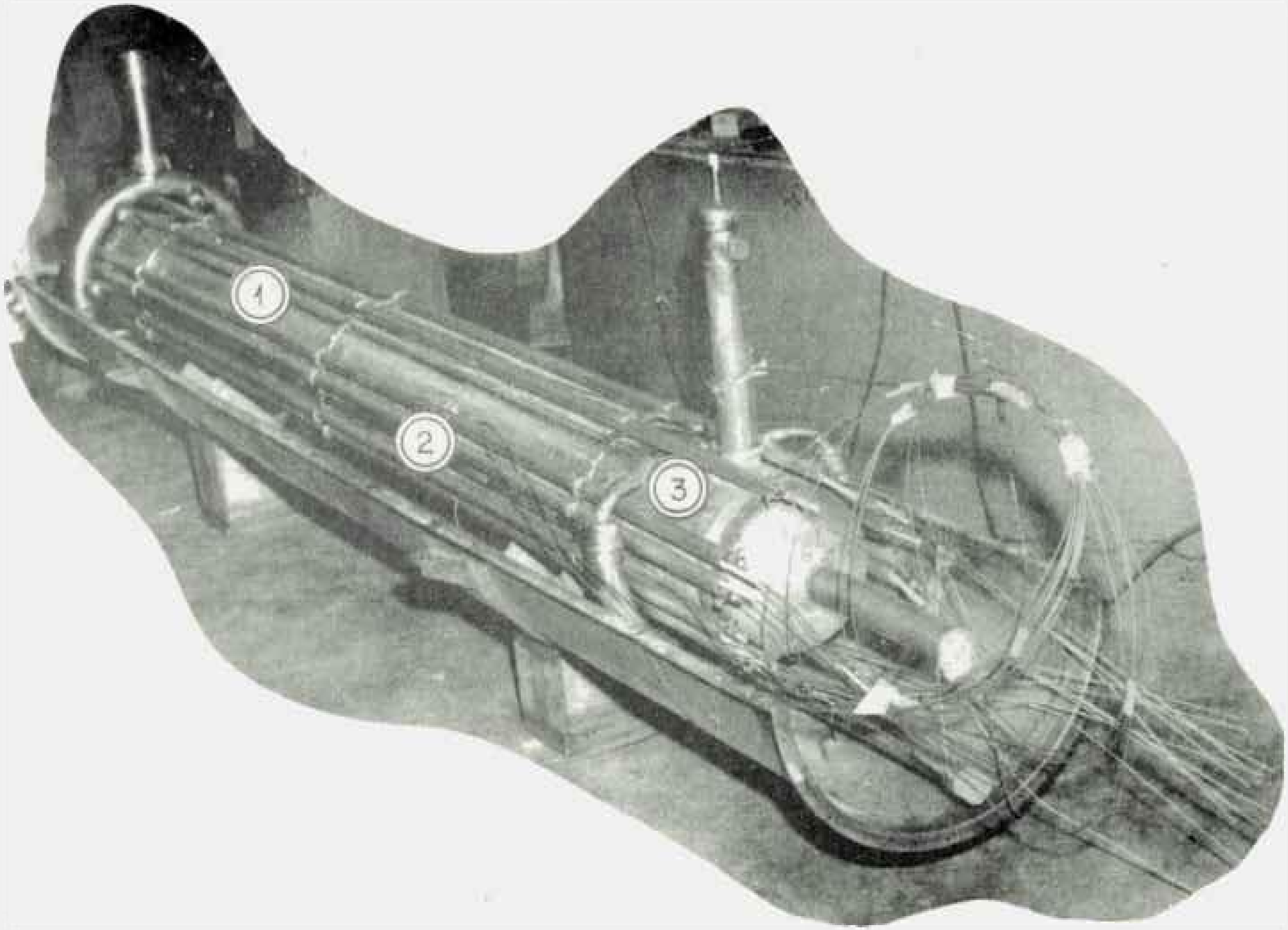
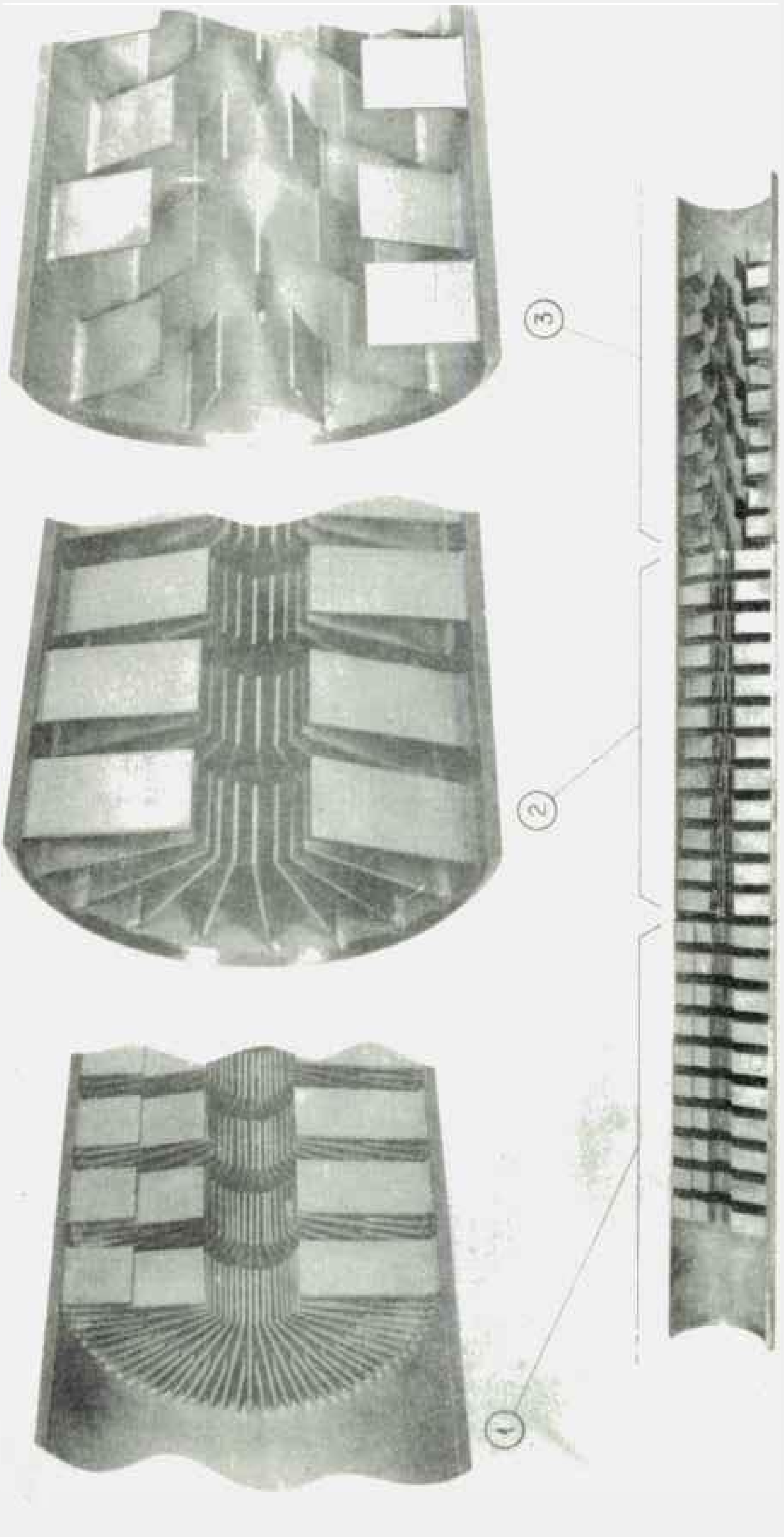
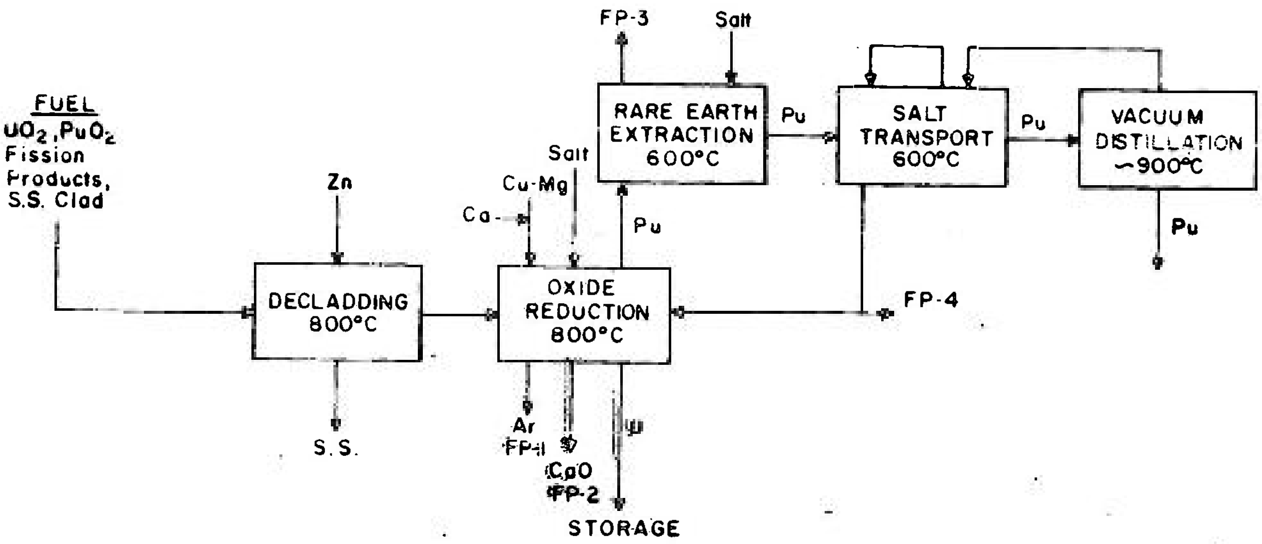


PHOTO 84943

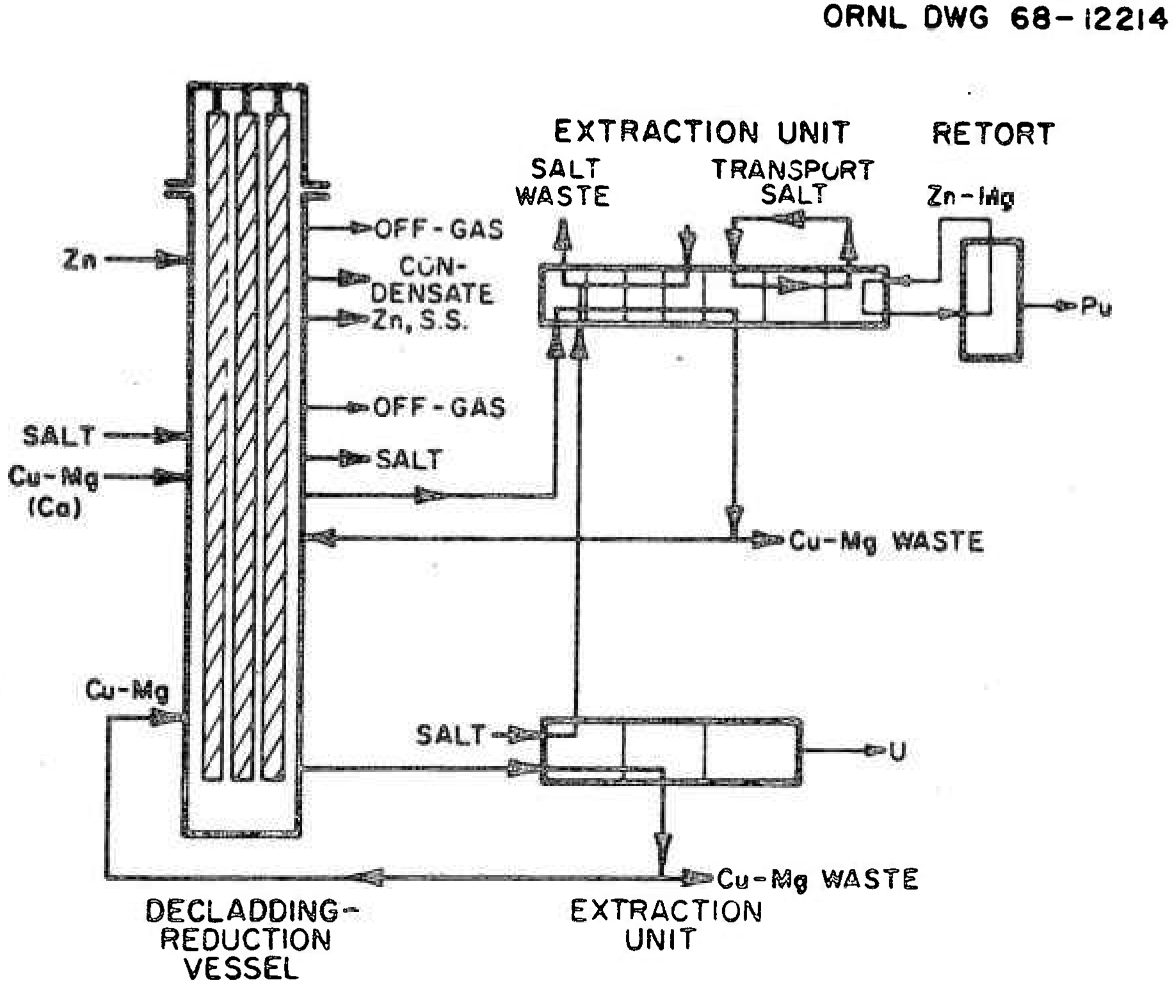


ORNL DWG. 68-10627



FP-1 Kr, Xe, ^3H
FP-2 Rb, Cs, Sr, Ba, Sm, I
FP-3 Y, Rare Earths
FP-4 Zr, Nb, Mo, Tc, Ru...

SALT TRANSPORT PROCESS FOR LMFBR FUEL



MAJOR EQUIPMENT ITEMS FOR SALT TRANSPORT PROCESS

REMOVAL OF IODINE AND NOBLE GASES FROM OFFGAS FROM FUEL REPROCESSING PLANTS

R. E. Blanco

INTRODUCTION

The routine discharge of radioactive gases and effluents is one of the major problems facing the reprocessing industry today. This problem will become more acute as we progress to higher burnups, larger plants, and, perhaps, shorter-cooled fuels. Development of iodine removal systems for fuel processing plants has only proceeded as far as that required for early LWR fuels. Present technology does not provide the degree of decontamination or the positive control that would be required in processing LMFBR fuels cooled less than 150 days. The principal method for controlling iodine emissions today is by cooling for decay of 8-day ^{131}I. All existing processing plants cool fuel at least about 130 days. The first fuels processed at Nuclear Fuel Services (NFS) plant were cooled 2.5 years and required a retention or decontamination factor of about 17 for processing 1 ton/day. Later, fuels will have higher burnups and require decontamination factors of about 600/ton processed.

Extensive cooling is probably not practical for LMFBR fuels because of the large inventory charges. ORNL is studying the problems in processing at cooling times as low as 30 days after discharge. Somewhere between 30 and 60 days is probably a practical assumption.

MAGNITUDE OF THE PROBLEM

The first three slides illustrate the magnitude of the problem with LMFBR fuels.

SLIDE 1 Concentrations of Volatile Fission Products in Spent Reactor Fuel (68-10555-A)

a) An advanced LWR is compared with a reference LMFBR.

b) Core and blankets are mixed for processing LMFBR fuels.

c) At 30 days cooling for the LMFBR vs 150 days for the LWR, an extra decontamination factor of 149,000/1.95 = ~8 x 10^4 is required.

SLIDE 2 Decontamination Factors Required for Gases from Fuel Processing Plants. Site boundary distance of 2 to 3 km from 100-meter stack. (68-10554-A)

a) A 5 ton/day plant at 30 days cooling requires a DF of 4 x 10^7 for iodine.

b) At 150 days cooling, the DF required drops to ~500 which is similar to that for LWR fuels.

c) About 10^8 is the target for the ORNL program.

d) For reference purposes, the discharge limit at the Nuclear Fuel Services reprocessing plant is 3.2 curies per year or 0.01 Ci/day for a 300-day year.

SLIDE 3 The Effect of Downwind Distance on the Average Annual Downwind Ground Concentration Per Unit Emission Rate From a 100-Meter-Tall Stack. (69-9244)

The discharge limits shown in the previous slide were based on limiting the concentration of volatile fission products at a distance of 2-3 km from the stack (site boundary) to those concentrations listed in the U. S. federal regulations (i.e., 1/3 of Appendix B in 10 CFR-20 – see lectures on Regulations). This slide shows examples of curves that are used to estimate dilution factors. In this case the average annual downwind concentration per unit of emission rate was 3 x 10^{-7} (curie/m^3/curie/sec) for meteorological conditions in the ORNL area.

SLIDE 4 Curies and Weights of Iodine Produced in a 5 ton/day Reprocessing Plant (69-4139)

a) The mass of iodine must be considered in addition to the curies.

b) About 2.5 kg of iodine is produced per day in a 5 ton/day processing plant of which 1.8 kg is 1.7 x 10^6 yr. ^{129}I and the remainder stable ^{127}I.

c) This mass of iodine must be retained, stored, and processed as a long-lived hazardous waste for ultimate shipment to a federal final waste disposal area (salt mine).

STATUS OF PRESENT IODINE REMOVAL METHODS

Valuable practical information is available from units in present fuel processing plants, but it largely consists of overall decontamination factors rather than analysis of performance by species of iodine. Thus, complete and accurate kinetic evaluation of treatment systems is not practical and scale-up and projection for new systems is impossible without further detailed data. Valuable information is also available from the nuclear safety program. However, much of this is difficult to interpret for use in fuel reprocessing plants. The Nuclear Safety Program (sprays, foams, silver surfaces, graphite, etc.) is not always applicable to reprocessing plants. The latter in some cases requires continuous treatment methods which can remove kilograms of iodine per day.

SLIDE 5 Hanford Dissolver – Off-Gas System (68-5349)

a) Processing plants in the United States use silver reactors followed by acid scrubbers.

b) Silver reactors give DF's of 10^2 to 10^3 and cooled nitric acid scrubbers give about 150 for two scrubbers in series.

c) NFS is now converting to a caustic scrubber plus some form of polishing treatment silver zeolites or charcoal because of the high cost of silver when is used in a primary unit to retain kg's of iodine per day.

d) Most European plants have installed caustic scrubbers followed by charcoal but they have no experience with iodine because iodine is removed by decay.

e) One campaign at Dounreay with 90-day-cooled fast-reactor fuel showed iodine DF's of ~200 with a $Hg(NO_3)_2$–HNO_3 scrubber.

f) Caustic scrubbers have shown DF's of $10^2 - 10^4$ in various hot-cell and plant applications.

g) We think that one of the principal limitations in present equipment is the low efficiencies of many of the methods for removing organic iodides.

SLIDE 6 Flowsheet for Reprocessing LMFBR Fuel by Aqueous Solvent Extraction (68-11074)

For LMFBR fuels, ORNL is developing methods for removing volatile gases in a non-aqueous head-end step. Thus, the gases are more concentrated and tritium is not diluted with water. The volatilization-oxidation step is called voloxidation.

SLIDE 7 Methods for Removal of Iodine from Off-Gas Streams (69-4141)

A literature survey showed a large variation in the reported efficiency of these methods. DF's ranged as follows: NaOH scrubber, 10^3-10^5; Hg--HNO_3 scrubber, 10^2-10^3; cooled HNO_3 scrubber, 10^2-10^4; Hg tower, 10^2-10^3; charcoal absorber, 10^4-10^5; silver zeolites, 10^4-10^5.

There is not sufficient knowledge of the chemical behavior of iodine under the various conditions encountered in a fuel processing plant to design an off-gas system. We know that iodine exists in at least three oxidation states and forms a variety of compounds with various impurities, some of which are volatile. A systematic study of the chemistry of iodine in shearing, the voloxidizer, dissolution, acid and caustic scrubbing, charcoal traps, and silver beds under a range of variables of temperature, off-gas composition, and oxidation-reduction conditions is in progress at ORNL. Only after such studies have been made can processes be chosen to remove and positively retain iodine to the degree required for short-cooled LMFBR fuel processing. In addition, it will be necessary to do engineering-scale tests of equipment and process design and finally hot-cell and hot pilot plant-scale tests to prove the reliability of the iodine retention system.

The next three slides show logic diagram flowsheets which we are using to guide our development program. All promising removal methods are being evaluated and additional chemical and engineering data developed where necessary.

SLIDE 8 Voloxidizer Off-Gas Treatment System (69-2256-A)

a) The bulk of iodine, tritium, and noble gases would be volatilized from the voloxidizer and shear in a limited amount of carrier gas and retained by the methods shown. These methods were selected on the basis of suitability for removal and storage of large masses of active and inactive iodine.

b) Waste storage and disposal studies for kg's of ^{129}I in caustic or other media are also starting.

SLIDE 9 Dissolver Off-Gas Treatment System (69-2254-A)

a) Any remaining iodine is volatilized from the dissolver and retained in a separate primary treatment system.

b) Caustic scrubbers will be studied to determine species and efficiency of removal.

c) $Hg(NO_3)_2$-HNO_3 are being actively studied to determine types of HgI complex, rates of absorption, capacity, etc. Studies show that this system can give DF's of at least 10^3 for methyl iodide.

SLIDE 10 Secondary Treatment System (69-2255–A)

a) The secondary system is designed to remove traces of iodine or iodine-bearing impurities (organics, particles, etc.). A catalytic oxidizer could eliminate all organic materials or, alternatively, organic iodides could be removed directly by appropriate methods.

b) We believe that the positive removal of organic materials (conversion to H_2O, CO_2, and I_2) is an important safety feature, since I_2 is easily absorbed with DF's up to 10^5 on charcoal or silver zeolites.

SLIDE 11 **Volatilization of Fission Products from LMFBR Fuel (1800 – 100,000 Mwd/ton) by Oxidation (69-4140)**

Heating UO_2 in an air stream at 750°C removed 90-99% of the iodine. The amount removed from PuO_2-UO_2 remains to be determined.

a) The Transuranium Processing Plant (TRU) is an important testing area for our developmental methods. A special rack is being installed for our use in the June compaign. The first tests on the new rack will concern:

1) Factors governing complete removal of iodine from the dissolver solution,
2) $Hg(NO_3)_2$-HNO_3 scrubbing,
3) Caustic scrubbing, and
4) Catalytic oxidation using a Hopcalite trap at 900 to 1000°F.

b) A campaign to process six HFIR targets in the TRU facility, for the recovery of transcurium elements, was carried out in mid-February, 1968. New iodine removal equipment was installed on the off-gas stream from the dissolver and evaporator with the purpose of eliminating iodine release from TRU and to hopefully demonstrate iodine DF's in excess of 10^4 on an operating plant. The iodine removal system consisted of a caustic scrubber for removal of acid vapor, a heater to raise the air temperature to 650°F, a catalytic oxidizer (Hopcalite bed) to destroy organic vapors and convert all iodine forms to I_2, a cooler, and finally a charcoal bed to trap iodine.

Of the 400 curies of iodine that were present in the targets at the start of the run, a total of 2.4×10^{-3} curies were released through the iodine removal system during the ensuing five weeks. Iodine decontamination factors across the iodine removal system averaged 2×10^4 during the first few days of the run, up to the time organics were introduced to the process. After organics were introduced, decontamination factors average $\sim 1 \times 10^3$ during the following four weeks. The average release rate of ^{131}I through the removal system was 1×10^{-4} curies/day with a maximum release rate of 2.5×10^{-4} curies/day.

The Hopcalite bed was operated at a nominal temperature of 650°F whith the inlet to the charcoal bed maintained at 120°F. During periods when tanks containing organics were sparged, the Hopcalite bed temperatures reached temperatures as high as 900°F for short periods of time, from heat of combustion of organics.

High organic concentrations in the gas stream to the Hopcalite bed lead to a reduction in I_2 DF's across the system by a factor of 10 or more with Hopcalite bed temperatures of 650°F. In a series of experiments to study the effect of Hopcalite bed temperature on DF, iodine was sparged from an organic waste storage tank while operating the Hopcalite bed at either 550-665°F or 850-950°F. Iodine DF's averaged 250 at the lower temperature (consistent with experience during the run) and ~8000 at the higher temperature. It appears that total organic destruction and conversion of all iodine to I_2 were not accomplished, particularly at the lower Hopcalite temperature.

More work is needed to characterize the combustion products and iodine forms coming from a Hopcalite bed at various temperatures when burning high molecular weight organics. Also the capacity of the oxidation unit must be determined. The lowering of DF's at high bed temperatures, probably indicates that the burning capacity had been exceeded.

The overall results from operating the new iodine removal system at the TRU facility are encouraging. The decontamination factors that were demonstrated are completely adequate for the TRU facility and preliminary plans are under way for a similar system to be installed on the total vessel and cubicle off-gas system (400 cfm) later this year. Decontamination factors in the range of 10^3 to 10^4 were demonstrated across the Hopcalite bed, charcoal-bed systems. Organic concentrations were at times much higher in the feed to the Hopcalite bed than would be observed in a larger system, and this high organic concentration appeared to be detrimental to iodine decontamination. Probably the capacity of the unit was exceeded in these tests.

In more recent tests with a caustic scrubber followed by the Hopcalite-charcoal system, DF's up to 10^6 were obtained.

STATUS OF PRESENT NOBLE GAS REMOVAL METHODS

SLIDE 12 Processes for Removal of ^{85}Kr from Off-Gas at a Fuel Reprocessing Plant (68-12090)

1. All will probably meet required removal limits.
2. All require removal of other gases such as NO, NO_2, N_2O, H_2O, H_2.
3. Room temperature charcoal at 3 ton/day, ~42 cfm. Cost about \$$10^6$ including gas clean-up system and 90% recovery of Kr. Could have higher Kr recovery. N_2O, O_2 removed by H_2 reduction on Pd catalyst. Smaller beds are an advantage. Demonstrated on Homogeneous Reactor.
4. Low-temperature charcoal – Needs better removal of condensible gases; smaller charcoal beds; line plugging occurred from leakage of moist air. Too many impurities in product. Pilot plant at Idaho Chemical Processing Plant (ICPP).
5. Cryogenic distillation – Lower capital and operating costs than low – temperature charcoal; 30 atm; B. P. (°C); N_2 – 195; O_2 – 182, Kr – 151; Xe – 109; N_2O – 88. Lines plug from condensation of H_2O, N_2O. Pilot plant at ICPP.
6. Liquid extraction – Now being developed at the Oak Ridge Gaseous Diffusion Plant at Oak Ridge. Good radiation resistance; water removal required; no burning hazard. Pilot plant now operating at ~6 scfm at ORGDP.
7. Permselective membranes – Now being developed at ORNL. No burning hazard; room temperature operation; water removal not required; small equipment – laboratory scale at present, 10 yd^2 single-stage; unit constructed but not tested; chemical and radiation resistance unknown.
8. Clathrate separation. Hydro quinones; stable at room temperature and pressure and 10^8 rads; crystallization from aqueous solution at 150 atm; requires high pressures, slow crystallization rate, poor removal from dilute streams.
9. Perhaps the biggest two advantages of the liquid extraction and permselective membrane processes are the (a) lack of fire hazard and (b) they are true continuous engineering processes rather than batch processes.

ABSORPTION IN FLUOROCARBON SOLVENTS

This process is being investigated in a nonradioactive pilot plant at the Oak Ridge Gaseous Diffusion Plant (ORGDP).

SLIDE 13 Solubility of Krypton in Various Liquids (G-68-533)

1. Many solvents studied here and at other laboratories, such as BNL.
2. UCON-12 or Freon-12 type solvents appear best based on high solubilities, low fire hazard, high radiation stability.
3. UCON-12 or Freon-12 is shown here but Freon-11 (CCl_3F) is also promising because it can operate at higher temperatures and needs less refrigeration.
4. One objective of pilot plant tests is to determine which is best.

SLIDE 14 Relative Solubilities of Gases in Refrigerant-12 (G-67-350)

1. Note better separations at low temperatures.

SLIDE 15 Krypton-Xenon Absorption Process Pilot Plant Schematic Flow Diagram (G-68-520)

1. Water is removed by molecular sieves.
2. Air is compressed and passed through desicant.
3. Gases are sorbed at low temperature and high pressure in first column.
4. Higher temperatures and lower pressures in fractionator and stripper.
5. O_2, N_2, and some noble gases removed in fractionator and recycles.
6. Noble gases removed in final stripper. (Conditions shown on next slide.)

SLIDE 16 Preliminary Absorption Data from Pilot Plant Shakedown Tests (G-68-534)

1. Flexible pilot plant – designed to operate over a range of –100°F to –15°F with Freon 12 and –15°F to 70°F with Freon 11.
2. Demonstrated 98% Kr removal.
3. Kr conc. in product 7%.
4. O_2 conc. in product 50%.
5. Conclusions
   a) Preliminary pilot plant tests every encouraging.
   b) No apparent large problems.
   c) Development people at ORGDP think that corrosion from Cl_2 or F_2 radiation degradation products will not be significant in dry systems.
   d) Calculate $\sim$0.25 lb of solvent decomposed/10^6 curies of Kr or Xe.
   e) So about 0.02 lb/day for 10 ton/day. 150-day-cooling or 0.2 lb/day for 30-day cooled.

PERMSELECTIVE MEMBRANES

This process is being developed at ORNL.

SLIDE 17 **Comparison of Porous and Permselective Membranes**

1. We use the G. E, methyl, phenyl, silicone rubber membrane.
2. Porous do not separate.
3. Permselective does.
4. Permeability = solubility x diffusion rate.
5. Proposed pressure is ΔP of ~12 atm.
6. Plastic fiber mat and screen for support on low-pressure side.
7. New membranes eliminate mat on high-pressure side which gives 40% higher than all values shown on today's slides.

SLIDE 18 **Definition of Permselective (68-12-88)**

SLIDE 19 **Separation Factors of Krypton from Oxygen (68-8793-R)**

1. Oxygen is the limiting contaminant. Kr and Xe diffuse faster than A and O_2; A diffusion same as O_2; N_2 diffuses 50% of O_2; N_2O is unknown; NO, NO_2, F_2 must be removed; H_2O and CO_2 diffuse faster and must be removed physically.
2. Operate with 30% of the gas passing through membrane so α is about 2.0 at 12 atm or 150 lb/in.^{2} for separation of Kr from O_2, A.

SLIDE 20 **Flowsheet for Standard Cascade (68-10564)**

1. Design for about 150 lb/in.^{2} on high-pressure side.

SLIDE 21 **Removal of Kr and Xe from Off-Gas from 1000 Mwe Vented Reactor (68-3577-R21)**

1. Either exhaust to atmosphere or recycle.
2. Could also use liquid extraction process.

SLIDE 22 **Permselective Membranes for Separating Noble Gas from Cover Gas of a 1000 Mwe Reactor (68-12092)**

1. Total volume with compressors is 15 ft x 15 ft x 15 ft. Quite small.
2. DF of 10^3.

SLIDE 23 **Cost of Noble Gas Separation Processes (69-9256)**

1. Capital costs for equipment only; costs are not accurate or optimized yet.
2. Function of processing rate.
3. The three lines represent removal of Kr in a permselective membrane plant.

4. The three black circles represent removal of Kr by absorption in a fluorocarbon plant.

   At 100 cfm, the Freon Plant:

   \$104 for DF 100 conc. factor 60 (point 3)

   \$258 for DF 314 conc. factor 30 (point 2)

   \$832 for DF $> 10^3$ conc. factor 1574 (point 1)

   where feed gas is 1000 ppm of noble gas (actually 90% cold Xe and 10% ^{85}Kr and cold Kr)

   At 100 cfm, for Membrane Plant:

   \$280 for DF 10 conc. factor 100

   \$420 for DF 100 conc. factor 100

   \$600 for DF 1000 conc. factor 100

   Costs of much higher decontamination factor plants are little more than low decontamination plants.

CONCLUSION

In any event, the incremental cost of treating the Kr-85 waste by any one of the above methods should not add more than \$200 per tonne to the cost of reprocessing fuel, which is approximately 1.0% of the total reprocessing cost.

REFERENCES AND EXCERPTS FROM:

1. D. E. Ferguson and R. E. Blanco, "General Survey of Reprocessing of Thermal Reactor Fuels," presented at the 1968 American Nuclear Society International Meeting in Washington, D. C., November 10-15 1968; to be published in the *Proceedings.*

2. Syril M. Slansky, Henry K. Peterson, and Vernon G. Johnson, "Nuclear Power Growth Spurs Interest in Fuel Plant Wastes," *Environmental Science & Technology* **3**(5), pp. 446-51, May 1969.

3. R. H. Rainey, W. L. Carter, S. Blumkin, D. E. Fain, "Separation of Radioactive Xenon and Krypton from Other Gases by Use of Permselective Membranes," Operating and Developmental Experience in the Treatment of Airbone Radiactive Wastes, (SM-110/27) International Atomic Energy Agency, New York, August 26-30, 1968.

4. J. R. Merriman, J. H. Pashley, K. E. Habiger, M. J. Stephenson, and L. W. Anderson, "Concentration and Collection of Krypton and Xenon by Selective Absorption in Fluorocarbon Solvents," Operating and Developmental Experience in the Treatment of Airbone Radioactive Wastes, (SM-110/25) International Atomic Energy Agency, New York, August 26-30, 1968.

5. *Chem. Technol. Div. Ann. Progr. Rept. May 31, 1968,* ORNL 4272.

6. *Chem. Technol. Div. Ann. Progr. Rept. May 31, 1969,* ORNL 4422.

7. Walton A. Roger and Stanton L. Reese, "The Removal of Iodine from Reprocessing-Plant Effluents," *Reactor and Fuel-Processing Technology* **12**(2), Spring 1969, pp. 173-80.

ORNL-DWG-68-10555-A

CONCENTRATIONS OF VOLATILE FISSION PRODUCTS IN SPENT REACTOR FUEL

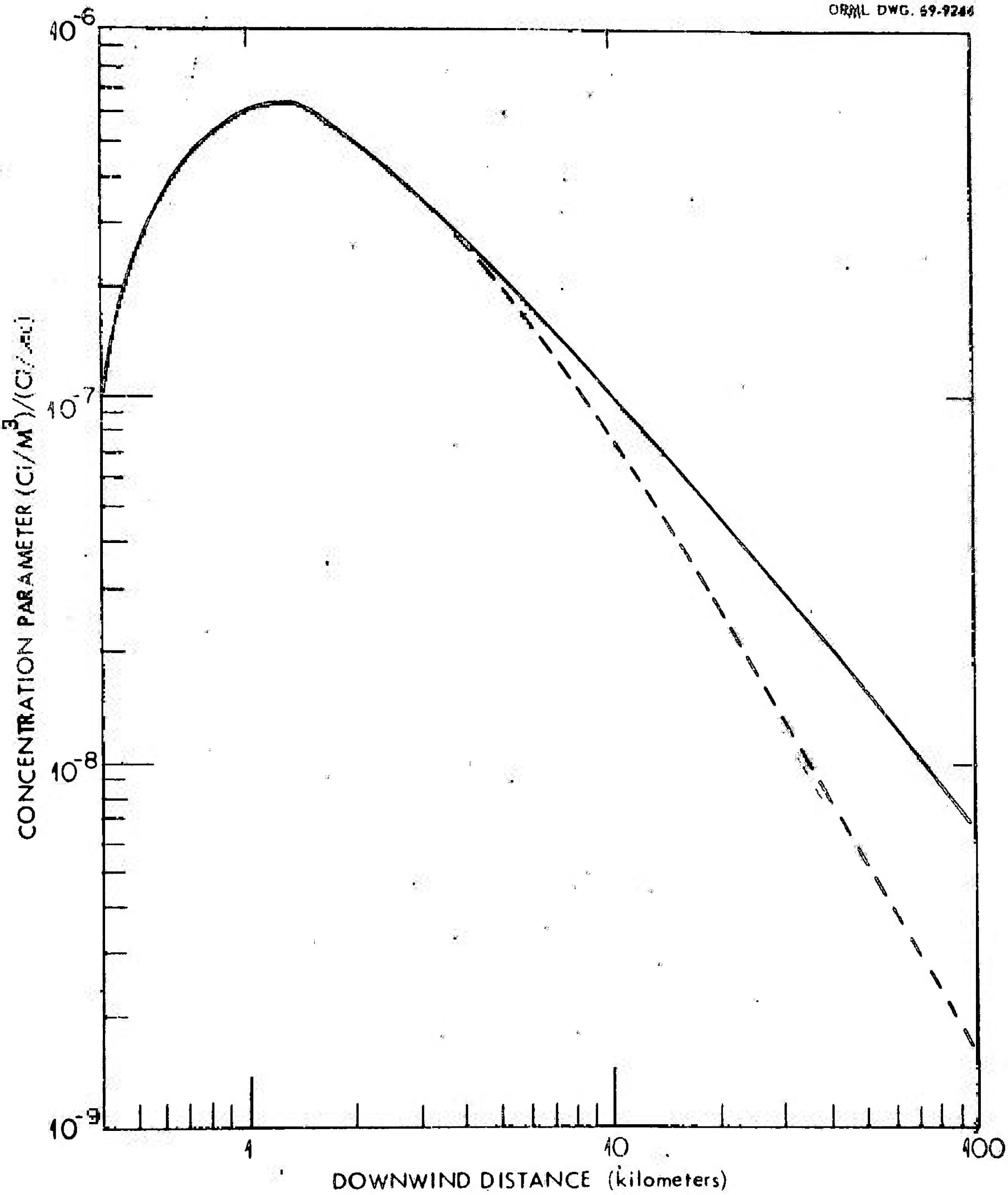
	Reactor	LWR	LMFBR (Core + Blanket)		
Fuel	Burnup (Mwd/t)	33,000	33,000		
	Sp. Power (Mw/t)	30	58		
	Decay (days)	150	30	60	150
Concentration (Ci/t)					
	^{85}Kr	11,200	10,300	10,200	10,000
	^{135}Xe	0.0053	74,400	1430	0.010
	^{3}H	688	932	928	915
	^{131}I	2.16	139,000	10,500	4.52
	^{129}I	0.038	0.0528	0.0533	0.0537

ORNL-DWG-68-10554-A

DECONTAMINATION FACTORS REQUIRED FOR GASES FROM FUEL PROCESSING PLANTS. SITE BOUNDARY DISTANCES OF 2 TO 3 km FROM 100-METER STACK.

Type of Effluent	Decay (days)	Required DF's for Plant Capacity (t/d) of:			
		1	5	10	40
Noble gas	30[a]	2	10	20	90
	≧ 60[a,b]	-	1.3	2.6	10
Tritium	≧ 1[a]	-	-	-	1.4
Iodine	30[b]	7×10^6	4×10^7	7×10^7	3×10^8
	60[b]	6×10^5	3×10^6	6×10^6	2×10^7
	150[b]	2×10^2	1×10^3	2×10^3	9×10^3
	150[c]	1×10^2	5×10^2	1×10^3	4×10^3

[a] Burnup = 33,000 Mwd/t; [b] Specific power = 58 Mw/t; [c] Sp. power = 30 Mw/t.



THE EFFECT OF DOWNWIND DISTANCE ON THE AVERAGE ANNUAL DOWNWIND GROUND CONCENTRATION PER UNIT EMISSION RATE FROM A 100-METER-TALL STACK

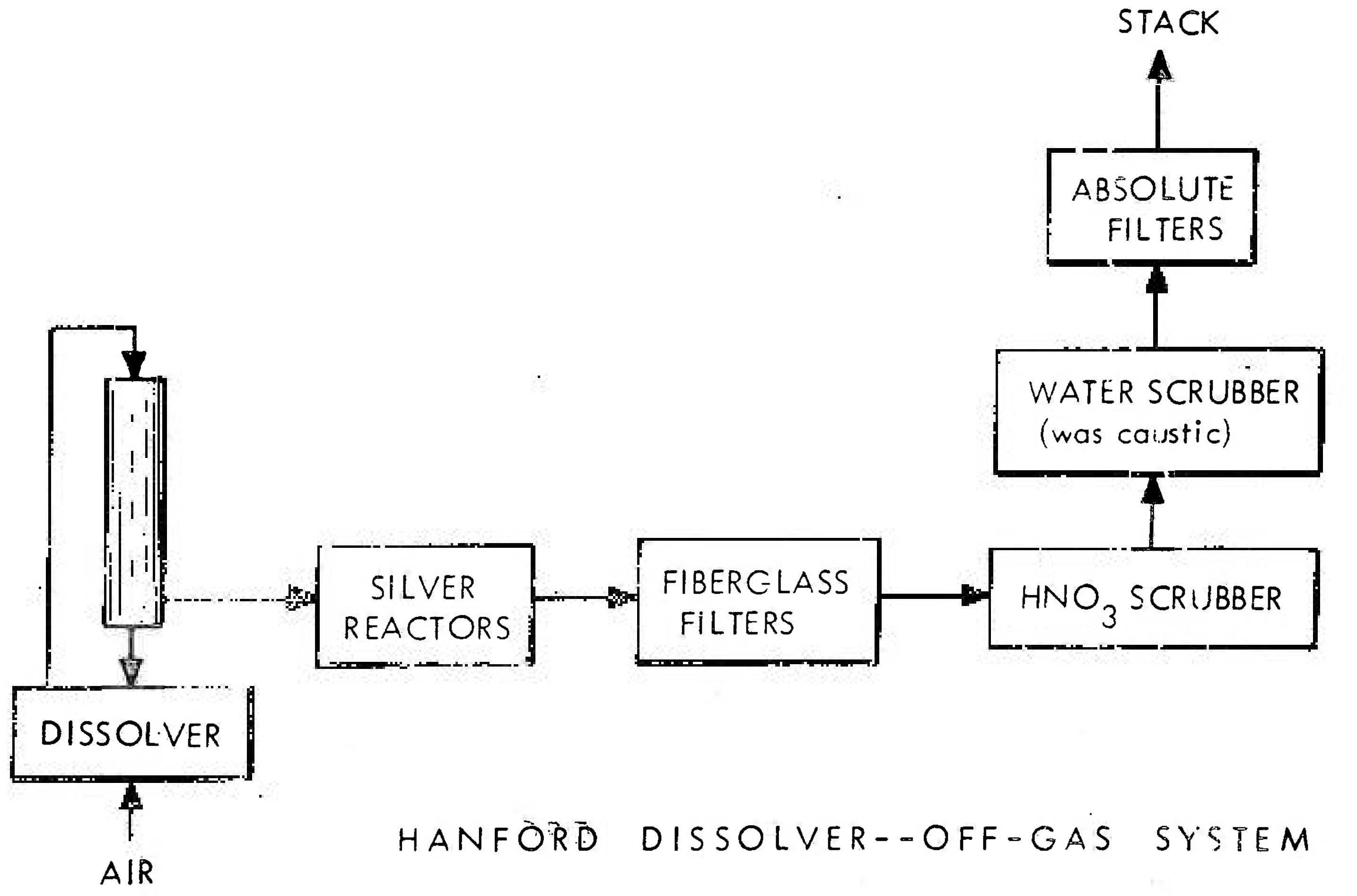
ORNL DWG-69-4139

CURIES AND WEIGHTS OF IODINE PRODUCED IN A 5 TON/DAY REPROCESSING PLANT

LMFBR (core and blankets):	33,000 Mwd/ton	69 Mw/ton
LWR:	33,000 Mwd/ton	24.5 Mw/ton

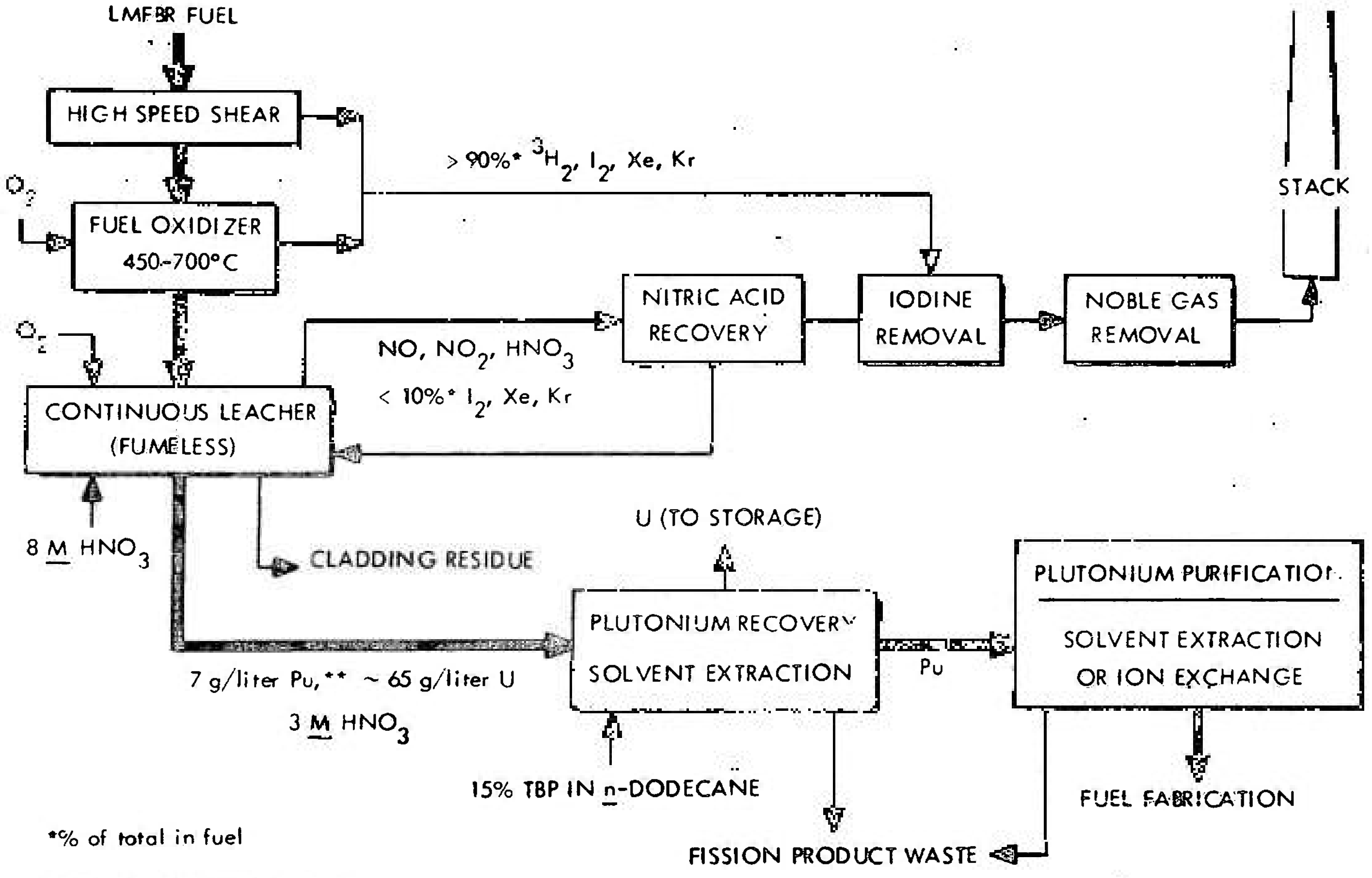
	LMFBR				Advanced LWR	
Cooling time (days)	30		60		150	
	Ci	g	Ci	g	Ci	g
^{127}I (stable)	0.	695.	0.	700.	0.	295
^{129}I (1.6 x 10^7 yr)	0.32	1840.	0.32	1860.	0.16	940
^{131}I (8.05 days)	7.7 x 10^5	6.2	5.8 x 10^4	0.47	9.6	7.7 x 10^{-5}
^{132}I (2.3 hr)	2.4 x 10^4	0.002	40.	3.8 x 10^{-6}	7.0 x 10^{-8}	6.8 x 10^{-1}
Total	8.0 x 10^5	2540	5.8 x 10^4	2560	9.7	1230

ORNL DWG 68-5349



HANFORD DISSOLVER--OFF-GAS SYSTEM

ORNL DWG 68-11074



*% of total in fuel

**5 g/liter fissionable Pu

FLOWSHEET FOR REPROCESSING LMFBR FUEL BY AQUEOUS SOLVENT EXTRACTION

ORNL DWG-69-4141

METHODS FOR REMOVAL OF IODINE FROM OFF-GAS STREAMS

a. Caustic solution with additives (thiosulfate for reduction or amines for fixation)

b. Dilute nitric acid

c. Mercuric nitrate-nitric acid

d. Activated charcoal

e. Impregnated charcoal (KI)

f. Impregnated charcoal (triethylene diamine)

g. Silver reactors (135°C)

h. Hydrous zirconium oxide (saturated with iodine)

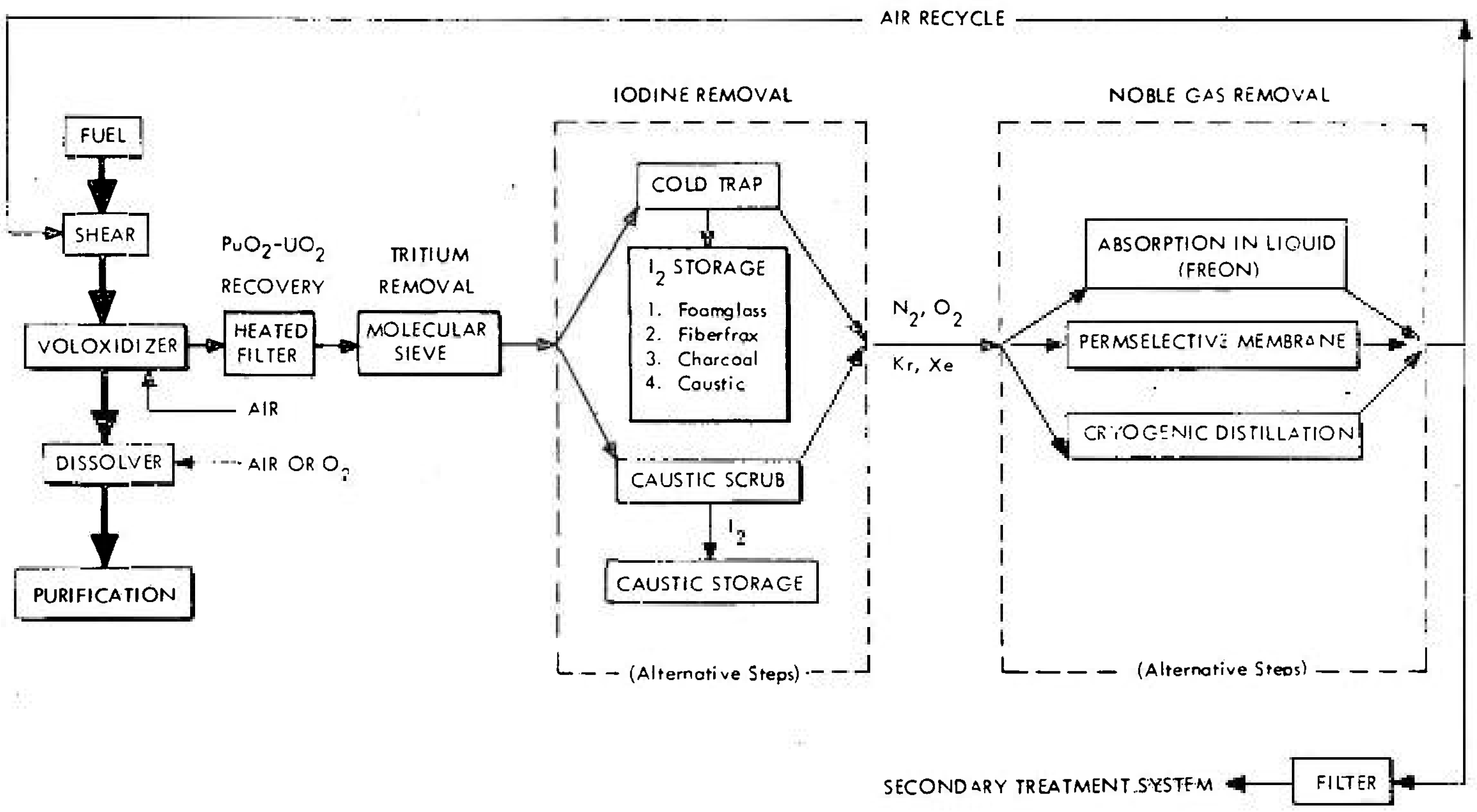
i. Impregnated zeolite (silver)

j. Ion-exchange resins

k. Catalytic oxidizer (Hopcalite catalyst, O_2, 150-500°C, charcoal bed)

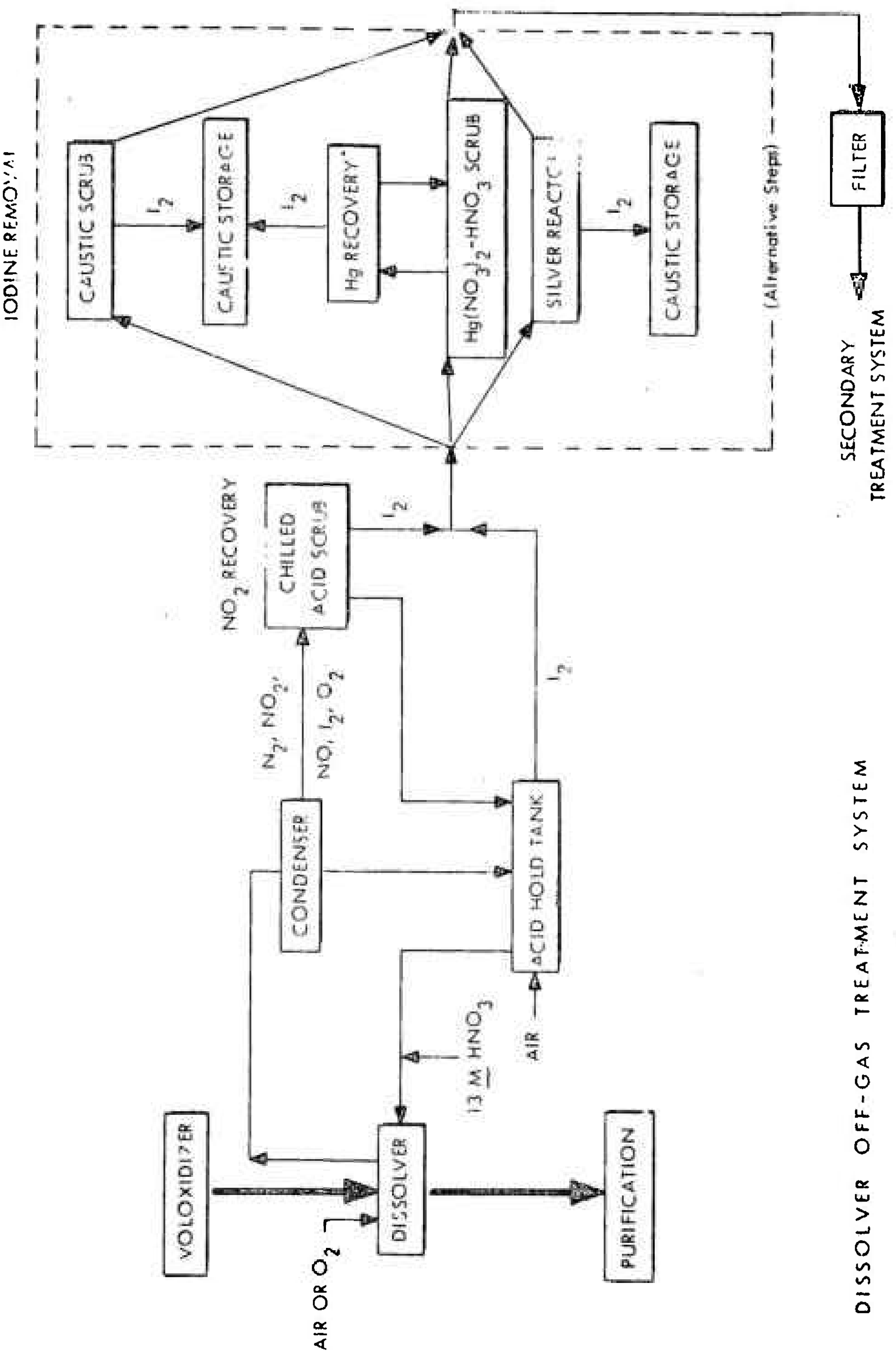
l. Cold trapping

ORNL Dwg 692256-A



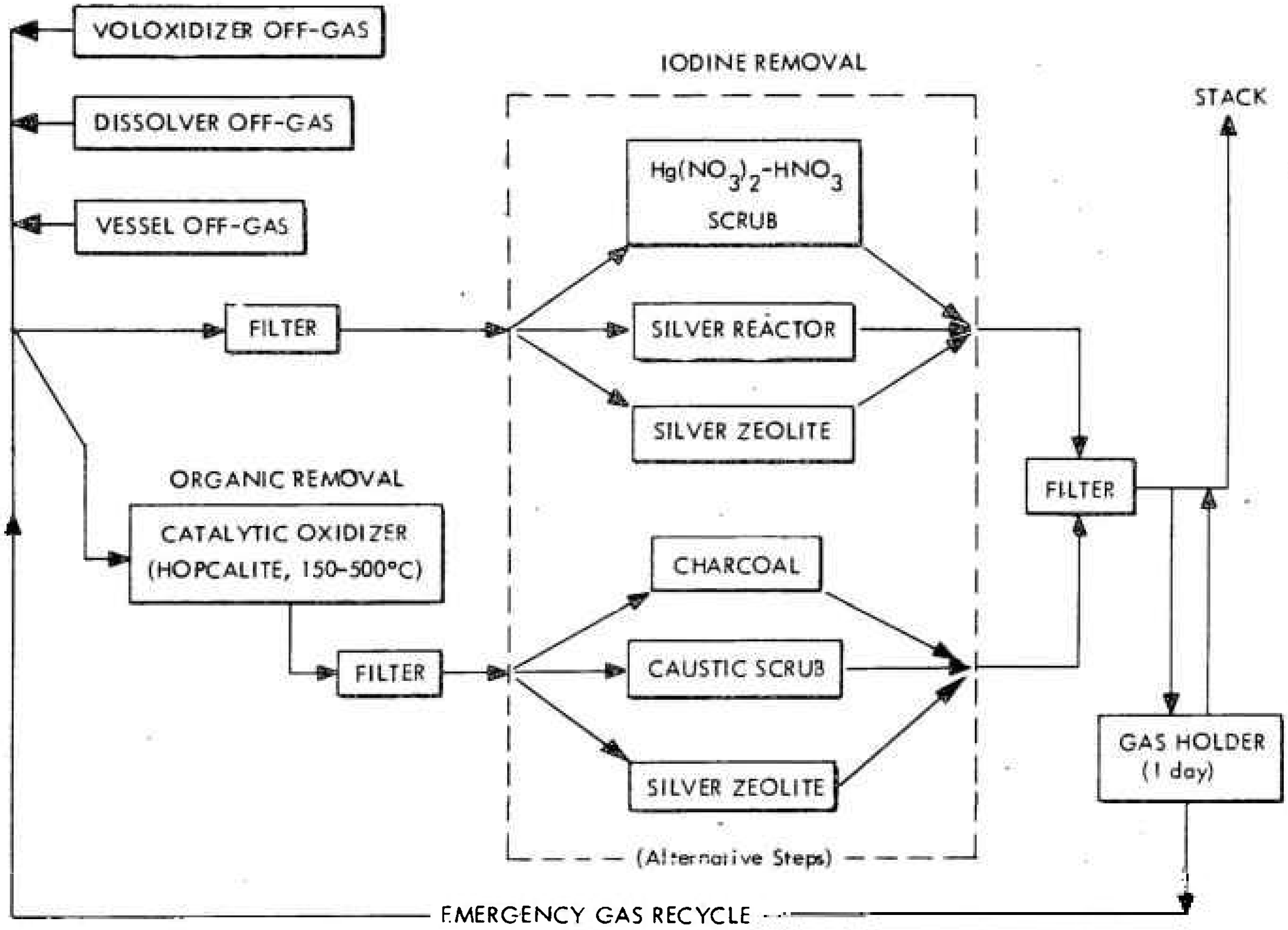
VOLOXIDIZER OFF-GAS TREATMENT SYSTEM

ORNL Dwg 69-2254-A



DISSOLVER OFF-GAS TREATMENT SYSTEM

ORNL Dwg 69-2255-A



SECONDARY TREATMENT SYSTEM

ORNL DWG-69-4140

VOLATILIZATION OF FISSION PRODUCTS FROM LMFBR FUEL (1800 - 100,000 Mwd/ton) BY OXIDATION WITH AIR

Fission Product	Percent Volatilized			
	450°C	750°C	800°C	850°C
Xe[a]-Kr	6[a] - 36[b]	11[a] - 99[b]	87[b]	79[b]
$^3H_2$	94 - 99	94 - 99	n.d.	n.d.
I_2[c]	8 - 98	90 - 99	n.d.	n.d.
Cs	n.d.	n.d.	~ 10	~ 70

[a] 1800 Mwd/ton.

[b] 100,000 Mwd/ton.

[c] With short-decay UO_2; short decay $(U,Pu)O_2$ tests in June 1969.

ORNL-DWG 68-12090

PROCESSES FOR REMOVAL OF ^{85}Kr FROM OFF-GAS AT A FUEL REPROCESSING PLANT[a]

Process	% Kr[b] Removed	Development Status	Comments
Room Temperature Charcoal Beds or Molecular Sieves	99	Large scale with reactors	Simple operation, charcoal ignites.
Low Temperature Charcoal Beds or Silica Gel	99	Large scale with reprocessing plant	Small bed volumes; charcoal ignites.
Cryogenic Distillation	99	Large scale with reprocessing plant	Small equipment; ozone explosion hazard.
Liquid Extraction	99	Pilot plant tests	Small equipment; no fire hazard.
Permselective Membranes	99	Laboratory studies; large-scale single unit constructed	Small equipment; no fire hazard.
Clathrate Precipitation	Unknown	Laboratory studies	^{85}Kr collected as solid; degraded by radiation; slow ppt'n; 150 atm.

---

[a] Varying gas pretreatments required.

[b] Minimum design values.

G-68-533

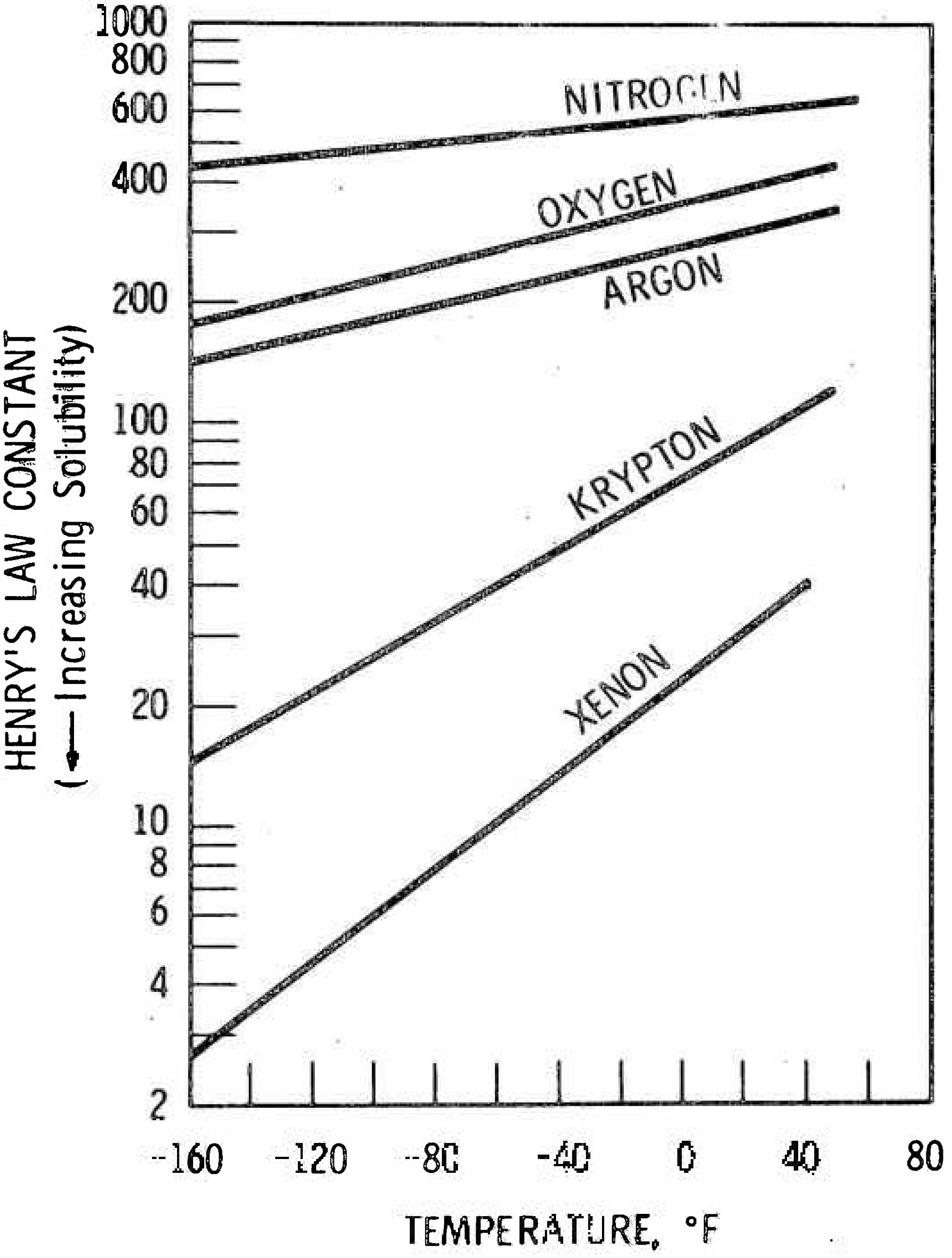
SOLUBILITY OF KRYPTON IN VARIOUS LIQUIDS

SOLVENT	MELTING POINT, °F	BOILING POINT, °F	SOLUBILITY DATA TEMPERATURE, °F	SOLUBILITY, vol/vol[a]
Water	32	212	86	0.05
Mesitylene	- 62.9	328.5	77.9	0.63
p-Xylene	55.8	280.4	86	0.72
n-Hexane	- 139	154.4	77	1.05
n-Heptane	- 131.8	209.1	77.4	1.16
n-Dodecane	14.7	421.3	77	0.82
Amsco 123-15			77	0.56
			- 67	1.50
Ultrasene			73.4	0.58
Terphenyl	186.8	784.4 (exp)	77	0.30
CCl_4	- 9.4	170.2		ca. 1.3
N_2O	- 131.4	- 127.3	77	ca. 1.3 (extrapolated)
			- 112	8.5
CCl_2F_2	- 252.4	- 21.6	77	ca. 1.7 (extrapolated)
			- 112	12.6

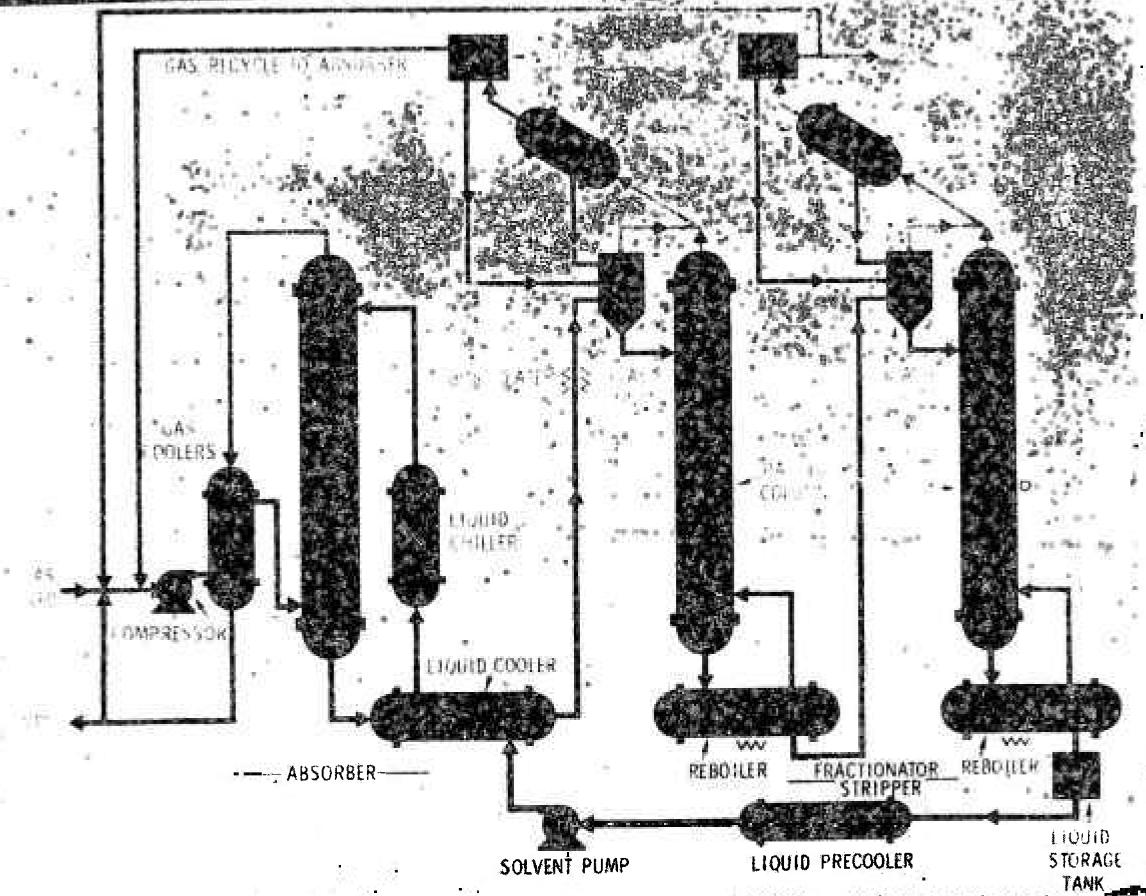
[a] Volume of gas (corrected to 59°F and 1 atmosphere) absorbed under total system pressure of 1 atmosphere per unit volume (corrected to 59°F) of solvent.

G-67-350

RELATIVE SOLUBILITIES OF GASES IN REFRIGERANT-12 (FROM BNL - 542)



KRYPTON-XENON ABSORPTION PROCESS
PILOT PLANT SCHEMATIC FLOW DIAGRAM

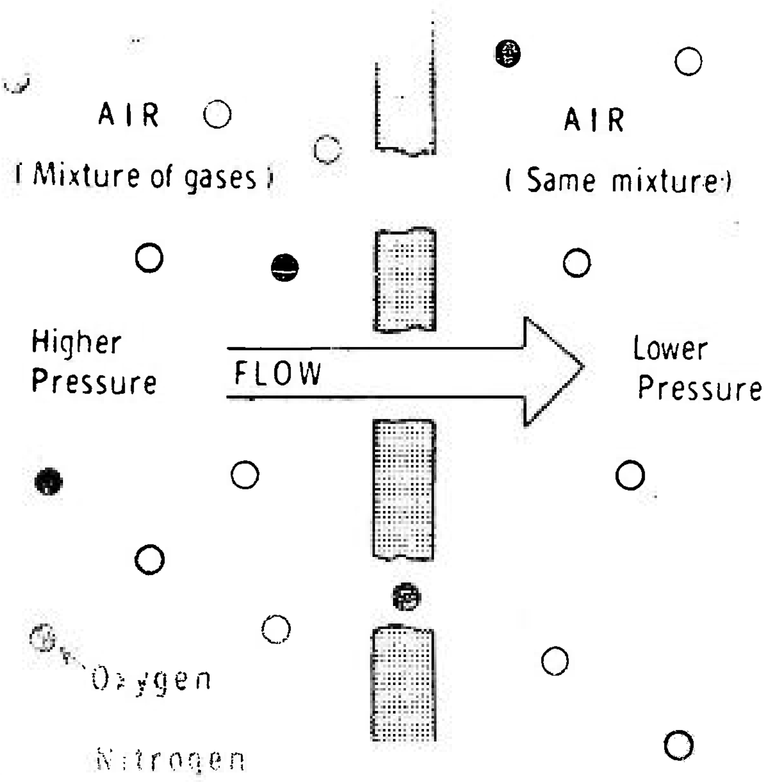


G-68-534

PRELIMINARY ABSORPTION DATA FROM PILOT PLANT SHAKEDOWN TESTS

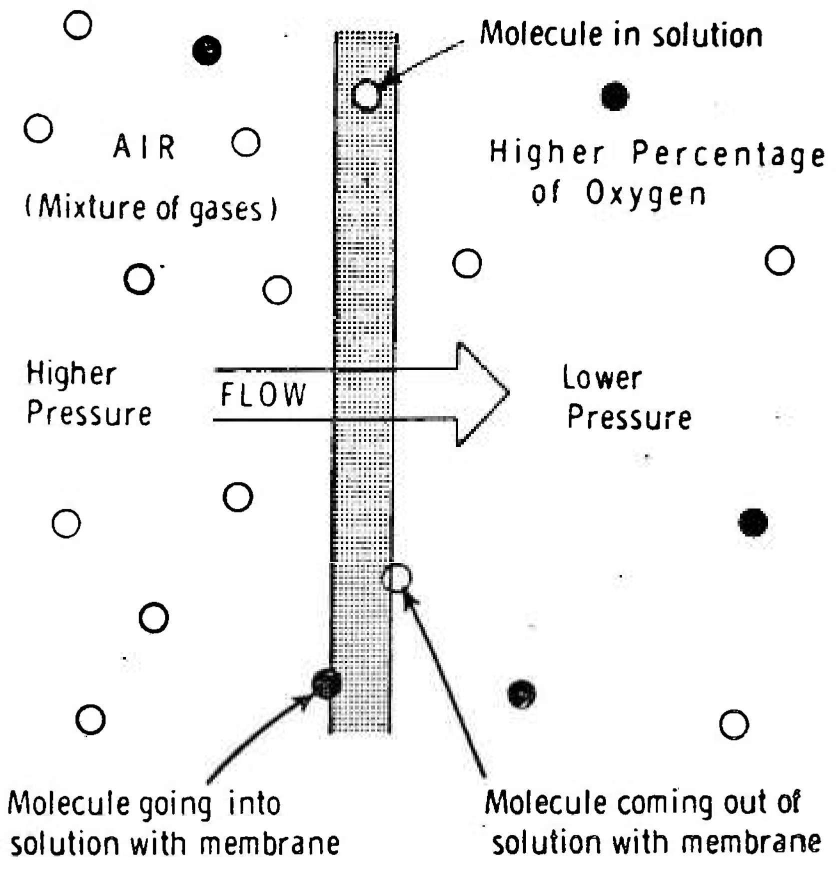
Solvent	Refrigerant-11
Temperatures and Pressures:	
Absorber	39-42°F; 27-28 atmospheres
Fractionator	118-137°F; 2.6-3.3 atmospheres
Stripper	78-96°F; 1.1-1.5 atmospheres
Liquid Feed Rate to Absorber	1.0-1.1 gpm
Gas Feed Rate to Absorber	5.1-6.6 scfm
Absorber L/G Ratio	28-48 (weight basis)
Absorber Feed Krypton Concentration	470-2740 ppm
Krypton Removal in Absorber	85-98% (approximate range)
Stripper Product Flow Rate	0.01-0.06 scfm
Krypton Concentration in Stripper Product	1.2-7.2%
Oxygen Concentration in Stripper Product	49-65%
Overall Process Krypton Concentration Factor:	
Normal	11-100
Oxygen Free	22-270

S MEMBRANE



s pass through openings

PERMSELECTIVE MEMBRANE

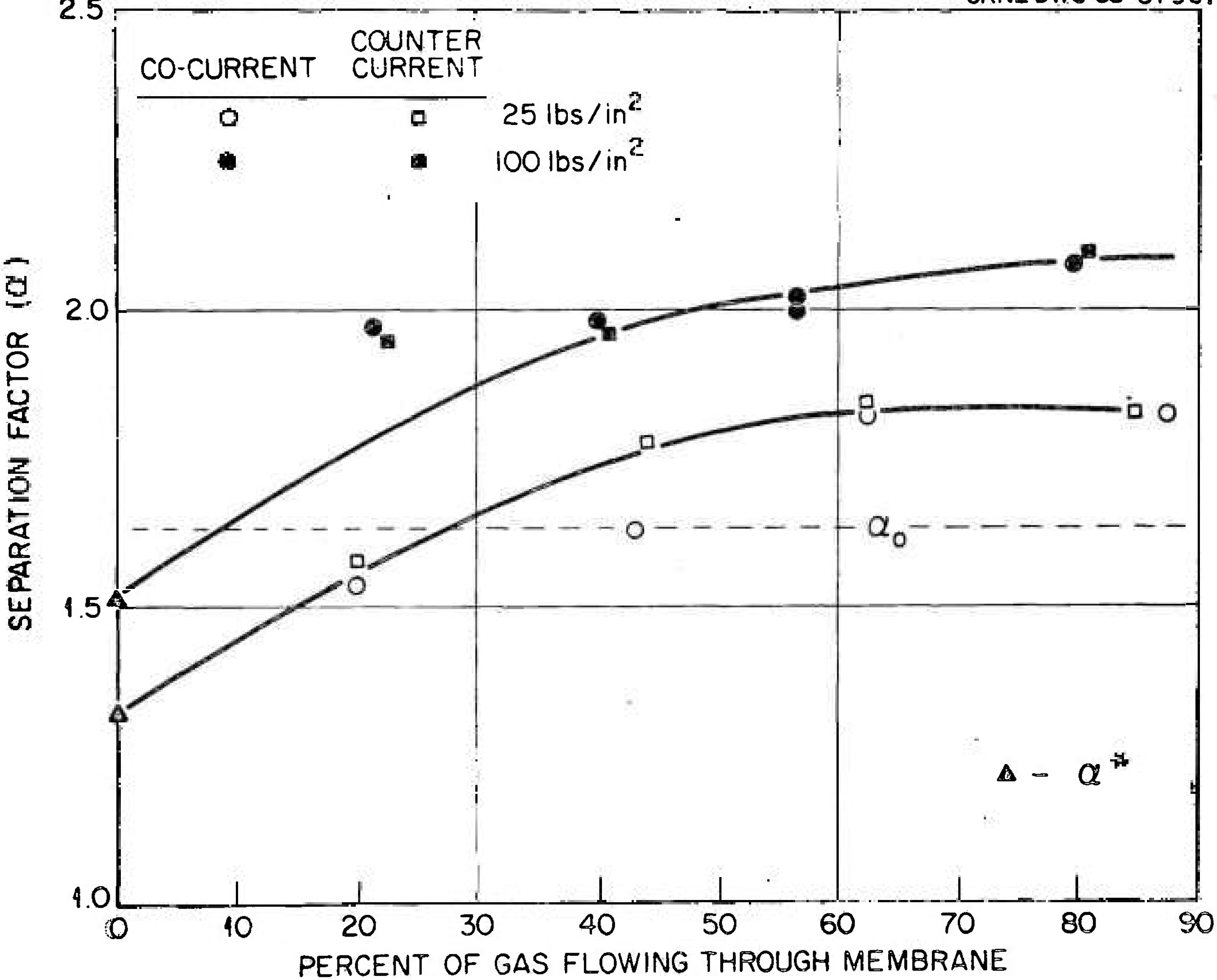


Permeability = (Solubility) x (Rate of Diffusion)

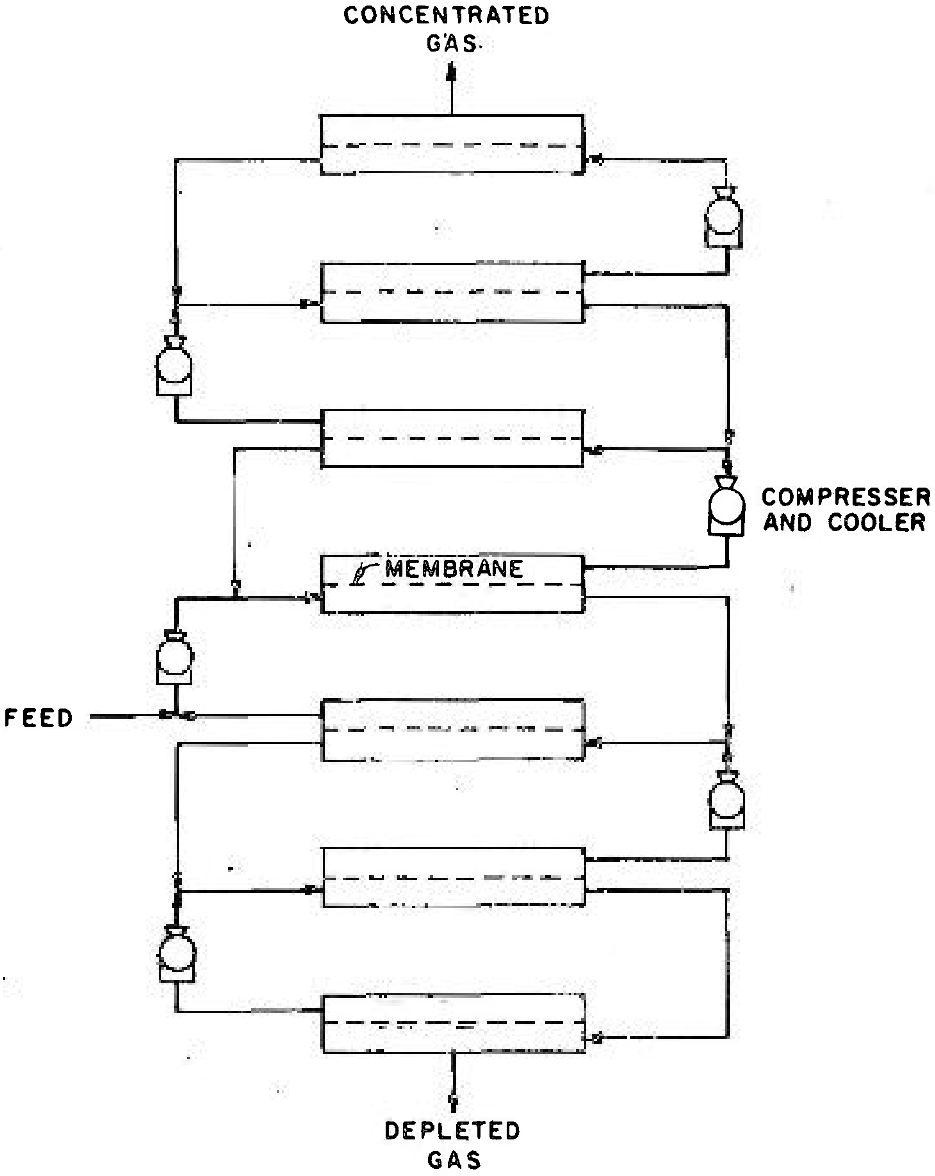
ORNL-DWG 68-12088

$$\text{PERMEABILITY} = \frac{\text{FLOW (ml/sec) X THICKNESS (cm)}}{\text{AREA (cm}^2\text{) X PRESSURE DROP (cm Hg)}}$$

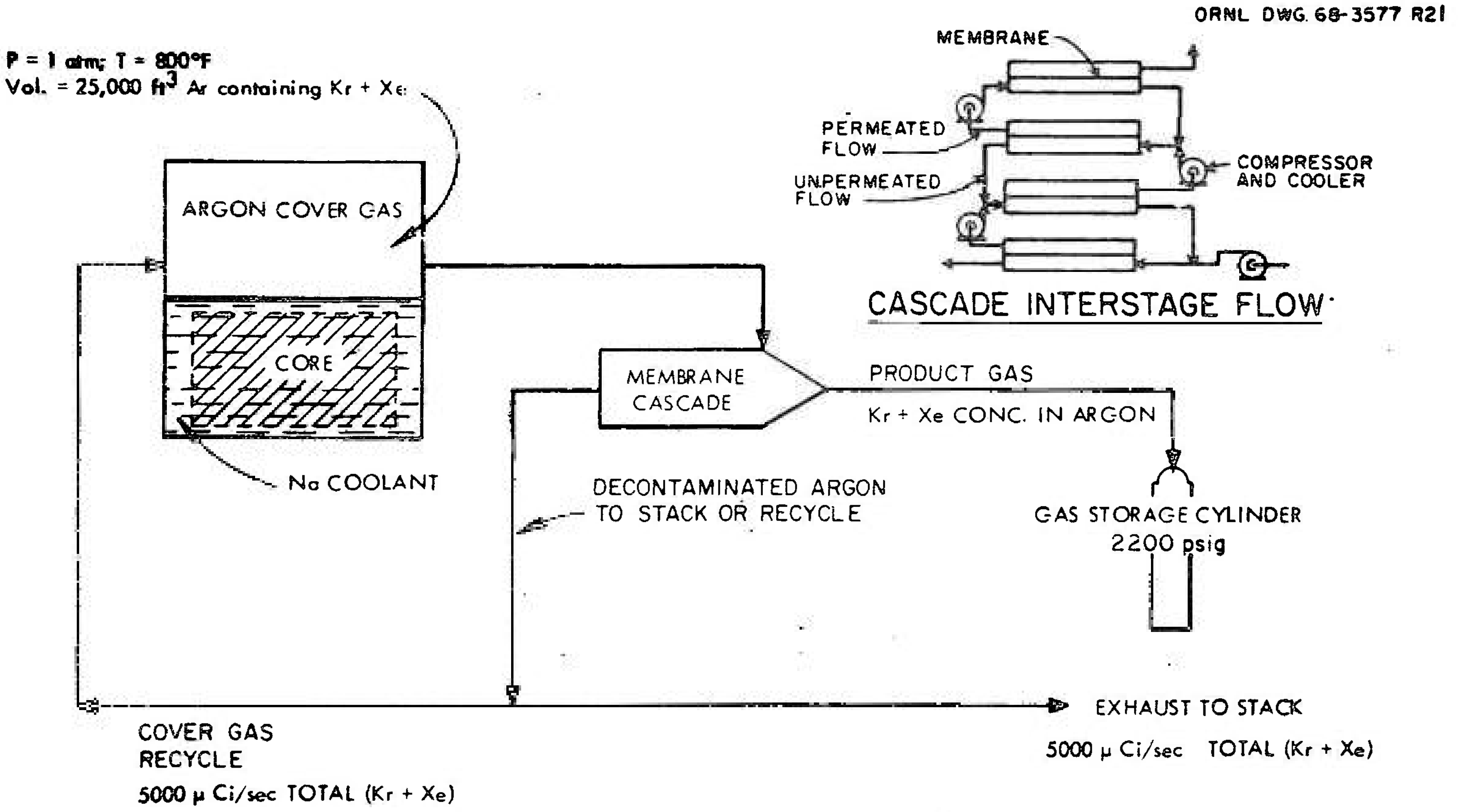
ORNL DWG 68-8793R



ORNL DWG 68-10564



STAGEWISE OPERATION OF MEMBRANE PLANT


ORNL DWG. 68-3577 R21
P = 1 atm; T = 800°F
Vol. = 25,000 ft^3 Ar containing Kr + Xe
ARGON COVER GAS
CORE
Na COOLANT
MEMBRANE
CASCADE
PRODUCT GAS
Kr + Xe CONC. IN ARGON
GAS STORAGE CYLINDER
2200 psig
DECONTAMINATED ARGON
TO STACK OR RECYCLE
COVER GAS
RECYCLE
5000 μ Ci/sec TOTAL (Kr + Xe)
EXHAUST TO STACK
5000 μ Ci/sec TOTAL (Kr + Xe)
MEMBRANE
PERMEATED
FLOW
UNPERMEATED
FLOW
COMPRESSOR
AND COOLER
CASCADE INTERSTAGE FLOW

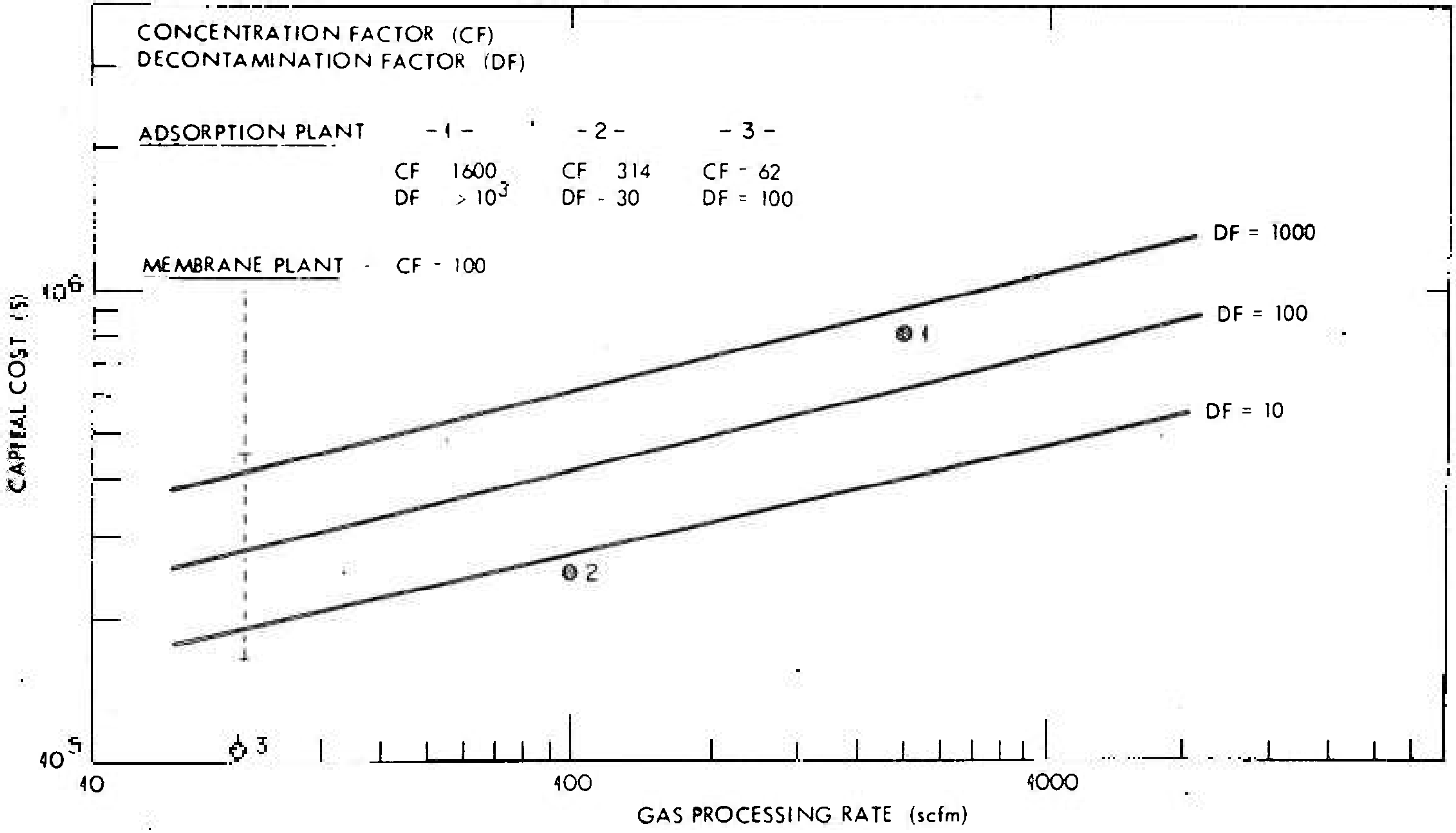
ORNL-DWG 68-12092

PERMSELECTIVE MEMBRANES FOR SEPARATING NOBLE GAS FROM COVER GAS OF A 1000 MW(e) REACTOR

GAS PROCESSING RATE, SCFM	10
DECONTAMINATION FACTOR	
Kr	10^3
Xe	10^9
CASCADE	
NUMBER ENRICHING STAGES	15
NUMBER STRIPPING STAGES	23
MEMBRANE AREA, YD^2	5020
CASCADE VOLUME, FT^3 (15' x 15' x 15')	3400
HIGH-PRESSURE SIDE, PSIG	150
LOW-PRESSURE SIDE, PSIG	0
PRODUCT GAS (TO BE STORED)	
Kr CONCENTRATION, AT. %	0.4
Xe CONCENTRATION, AT. %	14
CONCENTRATION FACTOR, PRODUCT/FEED	100
NUMBER STORAGE CYLINDERS PER WEEK[a]	5
INSTALLED COST, DOLLARS	342,000

[a] STANDARD N_2 CYLINDERS AT A PRESSURE OF 2200 $LB/IN.^2$

ORNL DWG. 69-9256



ESTIMATED CAPITAL COST FOR REMOVING NOBLE GAS FROM FUEL REPROCESSING PLANT OFF-GAS

(ESTIMATED RATE: ~ 100 scfm 5 tons fuel/day)