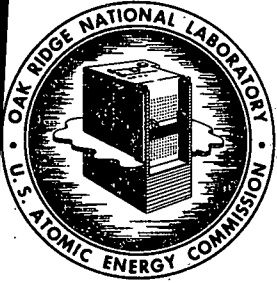


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NATURE OF RADIOACTIVE WASTES

by
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for the
U. S. Atomic Energy Commission

Radioactive materials in waste streams from the many processing steps in the nuclear energy industry present a new problem in environmental pollution control. New techniques and standards for the handling and disposing of liquid, solid, and gaseous wastes have been developed within the past fifteen years to meet the difficult control problems presented by these radioactive wastes. During this period, technological foundations have been established for a nuclear power industry which will surely develop into a major contributor to the energy production of the United States and the world.

Although the exact nature of the reactors and fuels to produce economic nuclear power has yet to be determined, the fuel cycle and the resulting radioactive wastes are predictable, based on our present knowledge.

The many integrated processes of a nuclear industry must be considered to define the nature of wastes that are being and will be produced.

All of the processes for the recovery and preparation of uranium and thorium as fuel produce wastes containing radioactive materials in more concentrated form than exists in nature so that problems of confinement or dispersal are introduced. New radioactive species are produced by the fission process, or by the capture of neutrons which result from fission by elements in a fission reactor.

The radioactive materials that must be considered are produced from:

Naturally Occurring Feed Materials

- (1) U^{238} and its natural decay chain. 99.28% of natural uranium, decaying with a half-life of 4.51×10^9 years. In nature it can be considered to be in equilibrium with its decay daughters. (3) Important isotopes to be considered in wastes are U^{238} ; Th^{234} (24.5 days)- Pa^{234} (6.7 hrs); Th^{230} (8.3×10^4 yrs); Ra^{226} (1590 yrs); Rd (3.8 days); possibly Po^{210} (140 days).
- (2) U^{235} and its natural decay chain. 0.71% of natural uranium, decaying with a half-life of 7.07×10^8 years. Not a significant contributor of hazardous radioactive species because of low concentration.
- (3) U^{234} and its decay daughters. 0.005% of natural uranium. Decay products are not significant because of low concentration in natural uranium.
- (4) Th^{232} and its decay chain. 100% abundant in nature. Decays with a half-life of 1.39×10^{10} years. Important decay daughters are Ra^{228} (6.7 yrs); Th^{228} (1.9 yrs); Ra^{224} (3.64 days)- $Thoron^{220}$ (54.5 sec); Bi^{212} (60.5 min); Po^{212} (very short); Tl^{208} (3.1 min). The decay chain of thorium contains isotopes which emit particles and photons of much greater energy than uranium; it is, therefore, more hazardous than uranium.

Fission Products of U^{235} , U^{233} , or Pu^{239} Fission

The fission products resulting from any of the three fissionable isotopes are generally similar in their distribution between the elements starting with atomic number thirty (Zn^{72}), and atomic number sixty-six (Dy^{161}). From the standpoint of waste disposal, those of most interest possess long half-lives and/or have high hazard potential for man as defined by their allowable concentrations in the human body.

Those most significant, classified by half-life and yield, are:

	Half-life	Approximate % of Total FP Activity after Decay		
		100 days	3 years	30 years
Cs ¹³⁷	26.6 yrs	≈2	15	~49
Sr ⁹⁰	28.0 yrs	≈2	15	~49
Pm ¹⁴⁷	2.6 yrs	3	15	≈1
Ce ¹⁴⁴ -Pr ¹⁴⁴	290 days	45	50	-
Kr ⁸⁵ (gas)	10.3 yrs	≈1	1	≈1
I ¹³¹ (gas)	8.1 day	≈1	-	-
Zr ⁹⁵ -Nb ⁹⁵	63 days	33	-	-
Ba ¹⁴⁰ -La ¹⁴⁰	12.8 days	≈1	-	-
Ru ¹⁰³ -Rh ¹⁰³	41.0 days	5	-	-
Ru ¹⁰⁶ -Rh ¹⁰⁶	1.0 yr	2	3	-
Sr ⁸⁹	54 days	7	-	-
Xe ¹³³ (gas)	5.27 days	≈1	-	-

Note: Irradiation basis is exposure for one year to 3×10^{13} thermal neutron flux.

The fission products are the major new radioactive materials produced by the fission process; they appear in small concentrations in many waste streams in the fuel cycle but to the greatest extent in the waste streams from fission reactor fuel reprocessing plant wastes. For the long periods over which we must consider storing radioactive wastes, it is apparent that the fission products cesium-137 and strontium-90, along with the noble gas, krypton-85, are of most importance.

The energy released by fissioning of uranium or plutonium amounts to approximately 201 Mev per atom fissioned, or approximately 24,000 kw (1 megawatt day, if fissioned at the rate of 1 g/day) of heat per gram of material fissioned. The major portion of this - over 80 per cent - appears as heat generated by fast moving fission fragments. Part of the remaining 20 per cent - approximately 6 per cent - of the energy is released slowly by the decay of radioactive fission products. The fission products decay with emissions of beta particles and gamma rays. The rate of energy emission decreases rapidly at first, more slowly later as shown by the following, taken for long irradiation (350 days) at a neutron flux of 3×10^{13} n/cm²/sec:

- (1) A total fission product power of 38.5 watts/gram of U²³⁵ originally is available at time of shut-down.

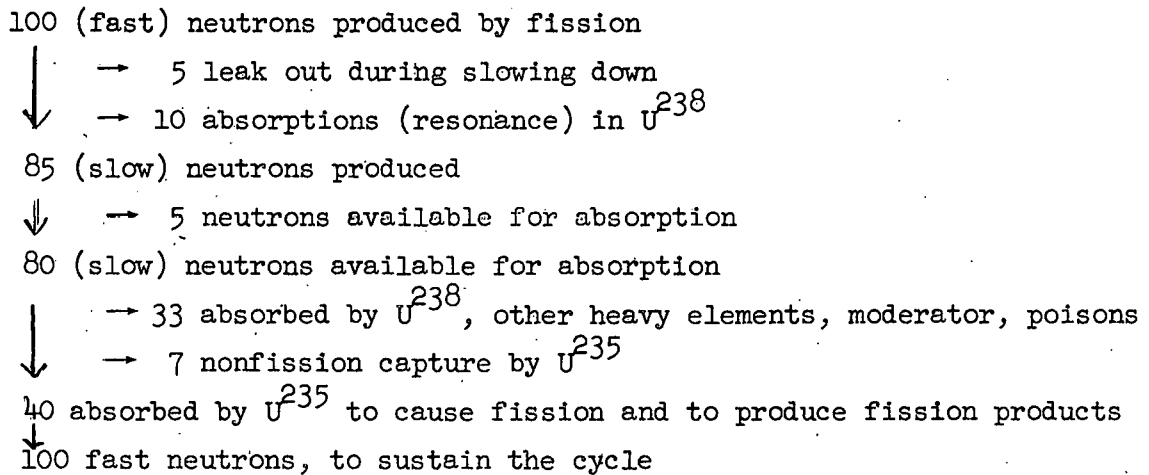
- (2) Decay reduces this rate by a factor of 10 in three hours to 3.85 watts/g U^{235} originally
- (3) There is a factor of 100 reduction in heat release in 58 days; a factor of 1000 in 520 days; a factor of 10,000 in 4050 days.

Radioactive Elements Produced by Parasitic Neutron Capture

Neutrons produced during the fission process interact with and ultimately are captured by the surrounding atoms in a reactor. The four main processes in which neutrons (produced on the average of 2.5 fast neutrons per fission for U^{235} -3.0 per fission for Pu^{239}) take part are:

- (1) Complete loss of neutrons from the system; this loss is kept to a minimum by efficient reactor design.
- (2) Nonfission capture by fissionable and fertile nuclei like U-235, U-238, Th-232 or Pu-239.
- (3) Nonfission capture - referred to as parasitic capture - by the moderator, coolants, structural materials, fission products, and impurities in the fuel moderator and coolants.
- (4) Fission capture of neutrons of various energy levels by fissionable materials and of fast neutrons by U-238 and Th-232 if they are present.

For a typical thermal reactor, using natural or slightly enriched uranium, the neutrons would be directed by design into the following approximate distribution: (4)



The neutrons absorbed by nonfission processes produce in part, other radioactive nuclei which must be considered as contributors to the radioactivity of wastes from the fission-fuel cycle. The most important of these parasitic captures from the waste disposal standpoint are those which:

- (1) Activate the circulating coolants and coolant impurities in a reactor
- (2) Activate the structural materials of the reactor and fuel elements, and corrosion products which circulate in the coolant to the neutron field
- (3) Are absorbed by nonfission capture in fissionable and fertile isotopes to produce new heavy elements that have long half-lives and will appear in some very small but significant amounts in the fuel recycle and in the waste streams from radiochemical separations plants.

Obviously, the neutrons that are absorbed by fission capture in U^{235} , U^{233} or Pu^{239} (or fast fission for U^{238} and Th^{232}), produce the major radioactive constituents in wastes, the fission products.

Description of Wastes from the Nuclear Power-Feed Preparation-Fuel Recycle

There are many separate operations which are necessary to prepare fissionable and fertile materials as satisfactory reactor fuels; there are several general classes of materials which must be brought together in proper balance to operate a self-sustaining, heat-producing reactor; and there are many steps required to recycle and recover fissionable and fertile material from irradiated fuel. Each of these produces solid, liquid, and gaseous wastes in which the concentration, half-lives, and relative hazards of contained radioactive materials varies. A general flowsheet, with notations concerning the type of waste, for the nuclear fuel cycle complex is given in Figure 1.

Discussions of Wastes from Raw Materials Production Operations

(Data taken from references (5)(6)(7)(8) which are to be part of the published record of these hearings)

Uranium is recovered from the product of many mines and 26 mills in the western United States, plus very small operations in the Florida leach zone area. The western mills range in size from 50 to 3500 tons of ore per day, with a total daily mill feed capacity of approximately 21,000 tons of ore per day. For all mills the average uranium content is approximately 0.25% expressed as U_3O_8 (multiply by 0.85 to get elemental uranium). Thus, the daily production is approximately 50 tons of U_3O_8 concentrates per day as impure oxides. This production is approximately 35 per cent of the total non-Communist bloc product of uranium.

The waste products of uranium mines are not significant from the general waste disposal picture. The principal problems are radon gas, protection of miners from

radioactive dust, and a decay product of uranium which is released by the uranium-bearing minerals, mostly carnotite or autunite. Harmful concentrations of these airborne radioactive materials are prevented by sufficient ventilation. The air exhausted from the mines does not present a problem of general atmospheric contamination.

The problem of handling slightly radioactive water from most of the mines is non-existent because most of the mines are dry. In the few areas where mine water pumping is required, such as the Ambrosia Lake, New Mexico area, the water which is removed presents no disposal problem.

The uranium mills produce several types of wastes which must be disposed of to the environment. The most significant problem for the area immediately adjacent to the mills is that associated with the large volumes of process raffines which are produced. The production rate of contaminated water from milling operations is approximately 865 gallons per ton of ore treated, or 285 gallons of liquid waste per pound of uranium (not as U_3O_8) produced, for a total daily production of 18 million gallons. This quantity of water, minus about 60 gallons per ton which remains with solid tailings, is disposed of by overflowing large retention ponds to a stream, if available, or allowed to percolate into the ground.

The total quantity of radioactive material in the uranium ore as delivered to the mills is less than 100 curies per day. Most of this appears in the liquid tailings which contain large quantities of chemicals, some of which also present problems in disposal. The following Table 1 summarizes preliminary studies on radioactive contamination of the mill wastes:

Table 1

<u>Isotope</u>	<u>Selected Measurements of Activity micro curies/ml</u>	<u>Permissible concentration for unrestricted areas(2) micro curies/ml</u>	<u>Fraction of Permissible Level</u>
1. U natural	3×10^{-5} to 9×10^{-8}	7×10^{-6}	max. 40
2. Radium-226	2.7×10^{-6} to 8×10^{-8}	4×10^{-9}	all over
3. Thorium-230	3.9×10^{-5} to 2.8×10^{-8}	not given	
4. Thorium-234 plus Pa ²³⁴	1.2×10^{-4} to 1.8×10^{-7}	3×10^{-1}	all under
5. Po ²¹⁰	not reported	3×10^{-6}	
6. Radium-222	not reported	2×10^{-7}	

Note: Two measurements out of six are slightly high. These can be controlled easily in recovery process by adjusting acid strength in tailings effluent.

The problems of disposal of wastes from milling operation at the moment present severe local problems which affect water supplies in an area where water is in short supply. The concentration of radioactive material in the effluent surely can be reduced to tolerance levels at additional costs to the product uranium. Here for the first time, we have an example of one of the most difficult of the general waste problems, that of handling large volumes of wastes containing very small, but above tolerance, concentration quantities of radioactive material.

Radioactive wastes in the mining and milling of thorium ores are of a similar nature to those for uranium, but the radioactivity of the wastes is a more serious problem because of the presence of the more energetic decay products of thorium and their lower biological tolerances. Most of the thorium produced to date has been recovered from monazite sand which is primarily from India, Brazil, Australia, and to a very limited extent, from North Carolina and Florida stream beds. If appreciable quantities of thorium are recovered in the United States from imported or domestic ores, the control of wastes from these operations will require close attention. Sizeable production of rare earths, which occur along with thorium in the weathered pegmatite as part of the primary mineral, monazite, also produce wastes of a similar nature. Thoron gas is more radioactive than its counterpart, radon, in the uranium decay series because of its shorter half-life and its slightly more energetic alpha particle.

Since thorium has not yet become a major fuel material, the problems peculiar to its recovery from ore will not be discussed further.

Feed Materials Operations

Ore concentrates containing on the average of 70 per cent U_3O_8 are further chemically purified to produce uranium salts that are fed to the gaseous diffusion cascades for the separation of U^{235} from U^{238} ; reduced with Ca or Mg to uranium metal; or converted to uranium compounds such as uranium dioxide to be used as power reactor feed material. The refining of ore concentrates, both domestic and foreign, is accomplished by solvent extraction processes (with the exception of the new fluoride volatility plant of the General Chemicals Company) in integrated centers by Mallinckrodt of St. Louis and Weldon Springs; and by The National Lead Company of Ohio at Fernald, Ohio. Purified uranium is produced as a nitric acid solution which is converted through a series of chemical steps to uranium tetra-

fluoride. This salt is then converted to uranium metal for power reactor or plutonium production reactor use.

The radiochemical nature of the liquid wastes from the processing of ore concentrates is similar to that of the mill raffinates, containing natural uranium and its decay daughters. For each ton of uranium processed, approximately 1000 gallons of solvent extraction raffinates are produced; if recycled uranium from within the feed materials complex is added to this, the volume of purification cycle raffinates may be on the order of 1500 gallons for each ton of fresh concentrate introduced. Because this waste is low in salt content it is volume-reduced and stored; only condensate below acceptable tolerance is discharged.

Additional volumes of liquid wastes containing only minor quantities of radioactivity result from operations leading to UF_4 product. Gases from the reduction and hydrofluorination of UF_4 must be scrubbed to remove chemical fumes and entrained uranium. Scrubber effluents are monitored for activity level and discharged to streams or rivers at below tolerance levels.

Waste materials from uranium metal production are leached to remove contained uranium; the leach liquors are treated by the solvent extraction purification cycle or by ion exchange. Raffinates from these operations are discharged at safe levels to the environment. The solid reduction bomb liner - MgF and fused dolomite - after leaching, is sufficiently free of uranium and radioactive materials to be marketed as a possible raw material for Mg production.

Diffusion plant feed can be prepared from two sources of uranium:

(1) concentrates from milling; and (2) recycled uranium from production reactors, such as those at Hanford and Savannah River, or the Idaho Chemical Processing Plant. The uranium product from large radiochemical separations plants has been allowed to decay for sufficient time to permit the decay of parasitically-produced U^{237} , which is a beta-gamma emitter with a 6.7 day half-life resulting from a double neutron capture by U^{235} . The uranium recycled from the reactors is separated from Pu so that there are only 10 parts of Pu per billion parts of U. Normally, the fission products are removed completely, as well as the decay daughters of uranium itself. Wastes from the gaseous diffusion complex are carefully treated, monitored, and discharged at below tolerance levels.

Estimating the volume of slightly contaminated water which is discharged from a feed materials plant is difficult; it has not been possible to relate volume to the number of tons of uranium processed. During 1955, it has been reported that approximately 95,000,000 gallons of treated water was discharged to the surface at the Feed Materials Center, Fernald, Ohio.⁽⁹⁾

As is the case with the liquid wastes from milling of uranium ore, the feed material liquid wastes are characterized by large volumes of liquid containing below tolerance concentrations of radioactive materials.

Solid wastes, such as uranium-contaminated ore drums; used equipment and piping; filter cakes from scrap and MgF_2 and dolomite liners for metal reduction; solid residues from various operations; are easily disposed of by burial in protected areas.

Radioactive Wastes from Operating Reactors

Radioactive materials, other than those occurring in nature, are generated in a nuclear reactor. The nonfission capture of neutrons by coolants, impurities in coolants, structural materials, and corrosion products produces radioactive material which must ultimately be discharged from the reactor. Fission products can be released from ruptured fuel elements either as a single burst or gradually, depending upon the nature of the rupture. Fission products and new heavy elements, produced by fission and fertile or heavy element absorption of neutrons, usually remain sealed in fuel elements until they are dissolved in radiochemical processing plants; radiochemical processing will be discussed in a later

Active Material in Water Cooled Reactor Cooling Circuits

In water cooled reactors the radioactive nuclides produced by the irradiation of water - not considering impurities and corrosion products - produce radioactive nuclei of short half-life, but of sufficient radioactive intensity to control the thickness of shield which protect the cooling circuit pumps and piping. From water, the following are produced by (n, γ) or (n, p) reactions: nitrogen-16 (half-life: 7.4 sec); nitrogen-17 (half-life: 4.14 sec); oxygen-19 (half-life: 29 sec). Additional nitrogen-16 and nitrogen-17 can be produced from dissolved oxygen and nitrogen in water; most pressurized water reactors, therefore, use deaerated water. The minor amount of argon present in air, which can be dissolved in cooling water will capture a neutron to produce argon-41 (half-life: 1.82 hrs). These gases have short half-lives and although of importance

in the design of reactor facilities, they are of no consequence for waste disposal consideration except where once-through cooling is employed, a practice that is uneconomic for power producing reactors.

The long-lived activity in water cooling systems results primarily from the activation of structural or fuel components in-core with subsequent release to the coolant; or from corrosion products which are swept into the neutron field by the coolant. Some of the irradiated products are deposited in the external cooling systems of the reactor as indicated by the heat exchanger radiation levels in the S-1-W reactor⁽¹⁰⁾, which were 600 mr/hr at full reactor power and 350-400 mr/hr at 10 per cent full power. The principal constituents contributing to this activity were measured after 93 full-power hours of operation; similar measurements were made with the Army Package Power Reactor coolant after 700 full-power hours. The nuclides identified in solids for the S-1-W, and in solids plus circulating water for the APPR-1 were:⁽¹⁰⁾

<u>Nuclide</u>	<u>Half-life</u>	<u>S-1-W (Zirconium) % of Total</u>	<u>APPR-1 (Stainless Steel) % of Total</u>
Co ⁶⁰	5.2 years	19.5	55.4
Co ⁵⁸	71 days	5.5	-
Cr ⁵¹	27 days	1.1	0.4
Zr ⁹⁵	65 days	0.7	-
Fe ⁵⁹	45 days	0.7	7.3
Hf ¹⁸¹ (175)		53.3*	-
Mn ⁵⁶	2.6 hours	in solution	14.2
% Identified		80.8	77.3

*from abrasion of hafnium control rod

Other nuclides of importance that might be present in water coolants are:

Na ²⁴	15 hours	produce from Al ²⁷ in systems utilizing aluminum
Fe ⁵⁵	2.9 years	produced from Fe ⁵⁴

From the standpoint of waste disposal the most significant nuclides are Co⁶⁰ and Fe⁵⁵ because of their longer half-lives. For reactors used for plutonium production, water is pumped once through only; the resulting activated water and

water impurities are allowed to decay for a period of hours, which reduces most of the activity to tolerable discharge levels.

Circulating water systems are purified using ion exchange resins and associated filters on side streams.

Little quantitative data exists to relate radioactive material discharge with discharge coolant volumes and reactor operating power. Experience at Argonne National Laboratory with the Experimental Boiling Water Reactor (20 Mw thermal power) for one year of operation is summarized: ⁽¹¹⁾

EBWR - 127 cu. ft. solid waste containing average of 90 millicuries/cu. ft.

- 200,000 gallons of water with an average specific activity of 2×10^{-4} millicuries/gallon, for a total of 11.4 and 40 curies, respectively.

In addition to liquid wastes and solid wastes, radioactive gases are released. In many reactors shielding, instrument tubes, and other auxiliaries are cooled by air. Argon-40, present as an impurity in air, captures a neutron to become Argon-41 (half-life: 1.8 hrs), which presents no waste disposal problem because of its short half-life.

To summarize, induced activity in cooling water circuits provides another source of large volume low activity wastes. The radionuclides can be removed by ion exchange and filtration.

Activity in Other Coolants

The induced activity in liquid metal reactors is very high because of the production of Na^{24} . However, sodium is not removed from the reactor coolant system so that the activity is contained or can be allowed to decay before discharge.

Organic cooled and moderated reactors produce reasonably large quantities of organic residues and gas as a result of the radiation decomposition of organic coolants such as the di- or terphenyls. Based on limited experience with the Organic Moderated Reactor Experiment, a 100-Mw reactor might produce 300 cubic feet of nonradioactive gas (except for fission gas leaks from ruptured fuel), and 3600 pounds of essentially nonradioactive solid sludge. ⁽¹²⁾

Origin of Concentrated Fission Product Wastes (Prepared by J. O. Blomeke, et al (13)
Oak Ridge National Laboratory

Irradiated reactor fuels are chemically processed to reclaim the unburned nuclear fuel and recover the transmutation products, such as Pu²³⁹ or U²³³, from mixtures of the fission products and inert components of the fuel. At the present time, these are separated by solvent extraction. While the processing details vary with the fuel being processed and the plant performing the operation, the basic principles are the same. Solid fuels, which have been stored 90-120 days following removal from the reactor (to permit decay of short-lived fission product activities), are dissolved in nitric acid, and the solution is fed to the mid-section of an extraction column where it is contacted with an immiscible organic solvent that enters at the bottom. The solvent selectively extracts the uranium and plutonium; and an aqueous salt solution, added to the top of the column, scrubs the traces of fission products from the organic extract before it leaves the top of the column. The waste, containing more than 99.9% of the dissolved fission products, and inerts in the feed and scrub solutions, leaves at the bottom of the column. The uranium and plutonium are separated from each other and decontaminated further from fission products by additional treatment; but the waste from these steps contains very small amounts of activity and, in some cases, is recycled to the process.

Several processes in current use for processing irradiated fuels are shown in following table. It should be noted that the volumes given refer to the wastes as they come from the extraction column. In current practice, the wastes are evaporated to smaller volumes and are frequently neutralized before being stored in underground steel and concrete tanks.

Characteristics of Solvent Extraction Processes

<u>Process</u>	<u>Application</u>	<u>Solvent</u>	<u>Salting Agent</u>	<u>Approx. Vol. Untreated High-activity Waste</u>
Purex	{ Pu-natural Uranium	TBP in hydrocarbon	HNO ₃	990 gal/metric ton U
Redox		Hexone	Al(NO ₃) ₃	1000 gal/metric ton U
Hexone-25	{ Enriched U-Al alloys	Hexone	Al(NO ₃) ₃	700 liters/kg enriched U
TBP-25		TBP in hydrocarbon	HNO ₃ + al(NO ₃) ₃	670 liters/kg enriched U
Thorex	Th-U ²³³	TBP in hydrocarbon	Al(NO ₃) ₃	1360 gal/metric ton Th

Characteristics of Present Wastes

Three types of irradiated fuels are currently being processed: (1) natural uranium, where plutonium and uranium are separated from fission products and from each other; (2) uranium-235 - aluminum alloys where uranium-235 is recovered and separated from fission products; and (3) thorium, where uranium-233 and thorium are separated from fission products and each other. In each process the fuel is dissolved with nitric acid solutions, in preparation for the subsequent liquid-liquid extraction step. The solvents used for extraction are tributyl phosphate (TBP) or methyl isobutyl (hexone). When TBP is used, it is diluted with a paraffinic hydrocarbon in order to obtain more favorable physical characteristics, and nitric acid is usually used as the salting agent in the aqueous scrub. This yields a waste (see below) that can be evaporated to much smaller volumes than is possible when aluminum nitrate is used as a salting agent, as in hexone extractions.

Table I gives the characteristics of the high-activity wastes produced by these processes. It should be emphasized that the numbers given are all approximations, the actual values depending on the operating characteristics of the particular chemical plant and the details of the chemical flowsheet being used. In addition to the concentrations of inert chemicals given here, all the wastes contain fission products and lesser amounts of uranium, plutonium, and other heavy elements. The presence of these heavy elements is attributable mainly to process losses which usually approximate 0.1%.

Purex-type wastes are mainly solutions of fission products in nitric acid and their physical properties are essentially those of about 1 M HNO_3 . Trace constituents are iron, nickel, and chromium, present in varying amounts as products of corrosion of the stainless steel process equipment. Because of their low solids content, these wastes can be concentrated by evaporation to relatively small volumes and much of the nitric acid distilled and recovered for reuse in the process. Purex-type waste can be concentrated to about 8 M HNO_3 , at which point oxidation of the fission product ruthenium to the volatile RuO_4 begins. The waste is then neutralized by addition of 50% NaOH solution and evaporated to near the solubility limit of the dissolved salts. Recent work at Hanford has reduced the fission product raffinate volumes to about 80 gallon per ton of U.

Table 1

CHARACTERIZATION OF FIRST CYCLE HIGH LEVEL AQUEOUS WASTES FROM SELECTED SOLVENT EXTRACTION PROCESSES

Process	Chemical Properties, Constituents (M), Approximate, Exclusive of Fission Products and Heavy Elements														Waste Volume gal/g U ²³⁵ Consumed	Approximate Specific Gravity	Approximate Concentration of U in Feed g/liter	Waste Activity ⁽²⁾						
	H	Al	Fe	Cr	Ni	Zr	Na	NH ₄	NH ₃	Sn	Mn	Mg	Hg	NO ₃				F	SO ₄	PO ₄	Cl	curies/gal	Total watts/gal ⁽³⁾	BTU/hr/gal
Redox	-0.2	1.2	*	*	*		0.46							4.1					0.27	1.18	450	1720	8.6	29.4
Purex	2.5 to 7.0		*	*	*		*							2.5 to 7.0		*			0.34	1.07	300	1320	6.7	22.7
Thorex	-0.1	0.5	*	*	*		*						0.01	1.4	0.05		*		0.34	1.12	350 (Th)	81	0.4	1.37
Hexone-"25"	-0.2	1.5	*	*	*			0.5					0.01	4.5					0.31 to 0.13	1.23	2-5	1620 to 3940	8.1 to 20.2	27.7 to 69.0
TBP-"25"	0.5	1.6	*	*	*								0.01	5.5		0.02	*		0.22 to 0.11	1.29	3-6	2580 to 5160	12.9 to 26.0	44.1 to 88.6
Zirconium-HF for enriched U	0.8 to 2.0	.8		0.1		0.5			0.02					2.3	3.0				~1.50	~1.1	0.3	350	1.75	6.0
Stainless Steel-H ₂ SO ₄ for enriched U-235	2.6	0.25	0.05	0.01	0.03		*			0.001				2.4		0.30			~0.35	~1.3	2-3	1500	7.5	25.0

Notes: (1) Wastes are untreated; they are essentially as they leave the solvent extraction plant and are subject to further treatment such as evaporation, neutralization, chemical treatment for fission product removal, etc.

(2) Basis for activity numbers: Irradiation period 4000 Mwd/t for natural uranium
 5×10^{13} n/(cm)²(sec)
 4000 grams U²³³ chain per ton of thorium
 53% burn-up for U²³⁵ in enriched fuel elements
 100 days decay cooling from time of reactor discharge

(3) After 100 days' decay, the distribution of energy is approximately 50% γ and 50% β .

(4) Waste volume per gram U²³⁵ consumed is an inverse function of burnup; i.e., for hexone-25 at 20% burnup, the gal/g U²³⁵ = $(\frac{53}{20})(0.14)$.

(5) Waste activity varies approximately as the (irradiation level)^{0.2}

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The wastes from the rest of the processes considered here contain significant amounts of aluminum. In the Redox process, aluminum is added as a salting agent. In the processes for enriched uranium, it is present in the feed solution since it is a major component of the original fuel. In the Thorex process, it is used to provide what is known as an "acid deficient" condition, i.e., one in which the aluminum partially hydrolyzes to the monobasic or dibasic nitrates. The acid deficient solution is also used in the Redox and Hezone-25 processes.

The Redox waste contains some sodium, which is added in adjusting the feed solution to an acid deficient condition, and some dichromate, which is used to oxidize the plutonium to an extractable valence state. Ammonia is used to adjust for acid deficiency in the TBP-25 process.

The Hexone-25 and TBP-25 wastes have mercury, and the Thorex waste has both mercury and fluoride, which are added as catalysts in dissolving the fuel.

Ferrous sulfamate is added in the TBP-25 process scrub solution to reduce plutonium to a nonextractable valence state, thus effecting its separation with the fission products from uranium.

The trace constituents in these wastes include iron, nickel, and chromium as products of stainless steel corrosion, and, in some cases, small amounts of silicon and other impurities originally present in the fabricated fuel. Phosphate and sulfate are used in the Thorex process to increase the decontamination of specific fission products and remove interfering ions.

The aluminum-bearing wastes are normally evaporated until the aluminum concentration reaches 2.2 M. If neutralization is desired, the pH is adjusted to about 13 by addition of 50% NaOH solution, 25-30% in excess of the stoichiometric amount required to form sodium aluminate.

High level wastes now in storage at the major processing plants are given in the following⁽¹⁵⁾

	<u>Total</u>
Wastes in storage (10^6 gallons)	72.7
Total tank capacity (10^6 gallons)	103.8
Total number of tanks	170

Fission Product Levels

Although the fission products are the source of most of the radiation hazard, they do not greatly influence the chemical properties of the wastes because they are present in such low concentrations. For every mega-watt-day of irradiation, about 1.1 g of fission products--both radioactive and stable--is formed. On this basis, it can be seen that most of the untreated wastes contain of the order of 1 g/liter of total fission products, consisting of isotopes of some 37 elements lying between zinc and dysprosium in the periodic table. While the total number of fission product atoms does not change after irradiation, the concentration of specific fission products does change with time, and for any given fuel is a function of the reactor power level during irradiation, the length of time the fuel has been irradiated, and the time elapsed since discharge from the reactor. The estimate of individual fission product levels and the nuclear properties of fission product mixtures is beyond the scope of this paper, but an extensive correlation of such information for thermal fission of U^{235} has been published. (14)

The contribution to the total beta activity by fission products of ten different mass numbers is presented in Figure 2. For the purposes of this illustration, natural uranium irradiated in a thermal neutron flux of 3×10^{13} n/cm²/sec for one year was chosen as a basis. At a decay time of 10 days, 63 d Zr⁹⁵ and its daughter, 35 d Nb⁹⁵, account for 20 percent of the total beta activity. They are followed in order of decreasing significance by 12.8 d Ba¹⁴⁰ and 40 h La¹⁴⁰ and by 290 d Ce¹⁴⁴ and its 17.5 m Pr daughter. In the range of 100 to 1000 days decay, 290 d Ce¹⁴⁴ - 17.5 m Pr¹⁴⁴ represent 40 to 60 percent of the total activity. After this time, Sr⁹⁰ and Cs¹³⁷ and their daughters begin to assume an increasingly dominant role. In all, the isotopes considered here represent about 63 percent of the total activity after 10 days decay, 87 percent after 100 days decay, and greater than 98 percent at 1000 days and thereafter.

One of the properties of fission product mixtures of most interest to waste disposal is their heat emission. In any disposal scheme, provision must be made to dissipate the heat evolved as a consequence of radioactive decay if elevated temperatures which can lead to chemical instability, corrosion, and entrainment during storage are to be avoided. A typical curve of the fission

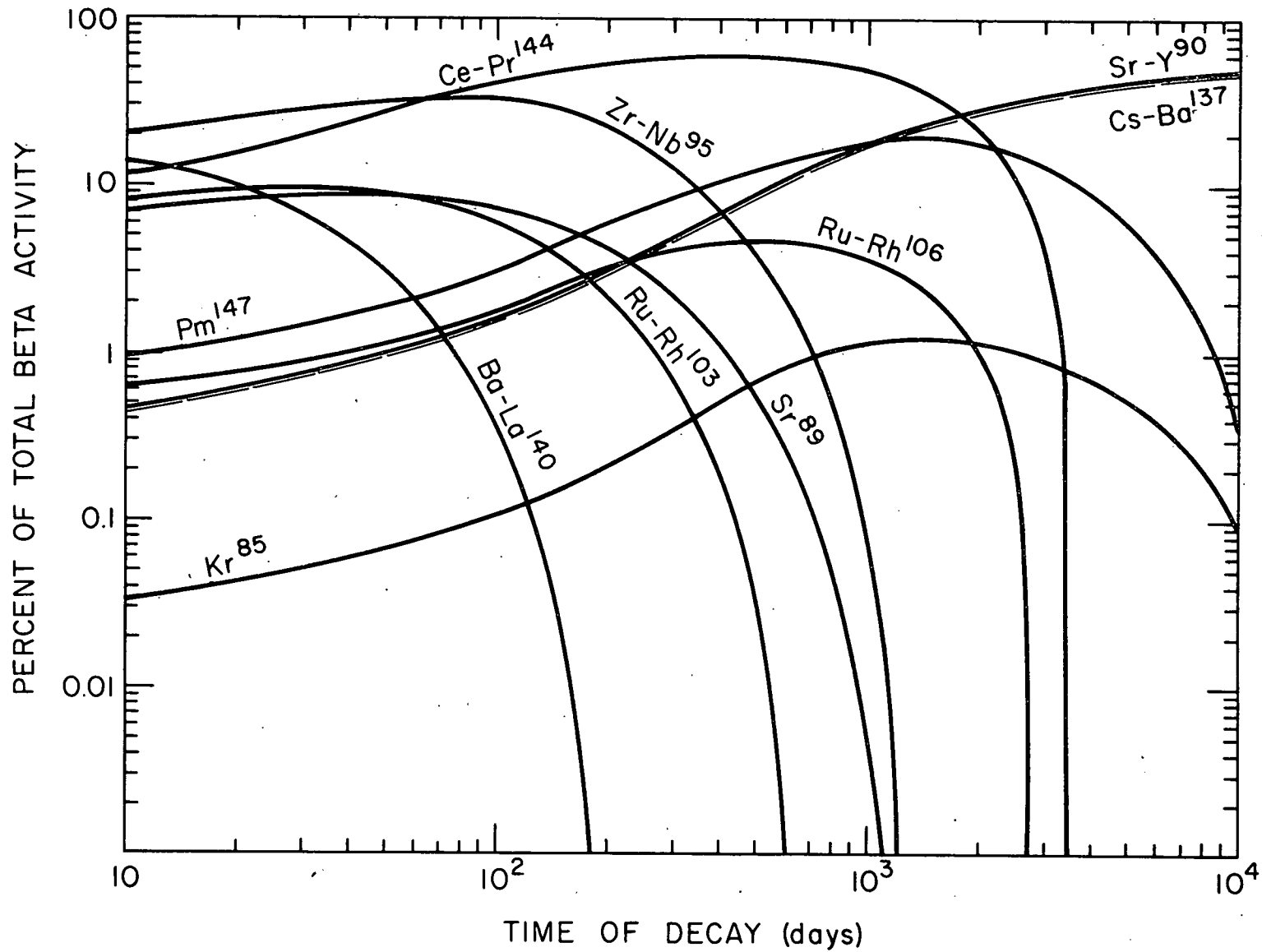


FIGURE 2 DISTRIBUTION OF FISSION PRODUCT ACTIVITY AS A FUNCTION OF DECAY TIME. BASIS: IRRADIATION AT THERMAL FLUX OF 3×10^{13} n/cm²/sec FOR 1 YR.

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product power expected in wastes from processing a fuel of high burnup is given in Figure 3. In this figure the specific-fission product power (in watts/gal of waste) is plotted against the time of decay. If it is assumed that 800 gal of waste has been produced from processing 1 metric ton of natural uranium, irradiated to 10,000 Mwd/ton at a specific power of 33 Mw/ton, besides the total power, the contributions are noted for the rare gas fission products (normally separated when the fuel is dissolved), the rare earths, which are the major heat producers, and the long-lived hazards, Cs^{137} and Sr^{90} . After one day's decay, the fission power is rather formidable, 1700 watts/gal; but after a 100 days' decay, a reasonable time to allow before processing this fuel, the power has dropped to about 200 watts/gal. The power emission continues to fall until a decay time of about 3300 days, or nine years, the rare earths have begun to drop to a level where strontium and cesium and their daughters constitute the main source of power evolved in the waste. At this point the total power amounts to about 0.5 watt/gal and decreases according to the 27 to 28-year half-life of Sr^{90} and Cs^{137} .

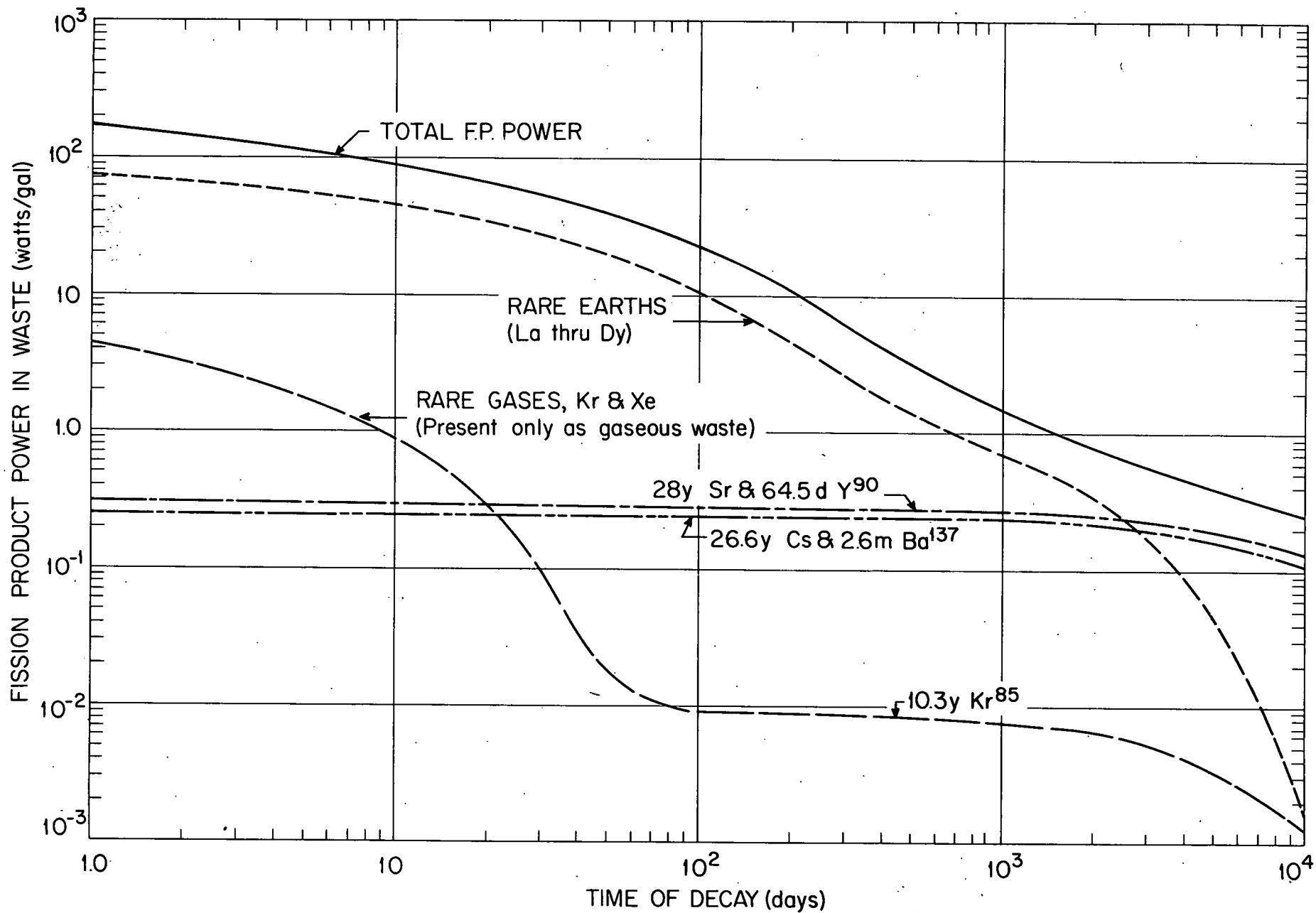


FIGURE 3 FISSION PRODUCT POWER IN WASTE AS A FUNCTION OF DECAY TIME. BASIS: 800 GAL WASTE PER METRIC TON U, IRRADIATED 10,000 Mwd/ton At 33 Mw/ton SPECIFIC POWER.

Comments on High-Level Wastes from Possible
Processes other than Solvent Extraction

At the present time, and probably for some time to come, all radiochemical fuel reprocessing is being done by organic solvent extraction; the existing solvents will be used to recover fissionable and fertile material from feed solutions prepared by a variety of aqueous feed preparation methods, each adapted to a specific type of power reactor fuel. The solvent extraction processes are likely to remain major techniques because of their versatility and economy. It is probable that a single reprocessing plant will serve many power reactors; if 12,000 Mwd/metric ton (heat) burn-up can be achieved, reprocessing costs in such a centralized processing plant with a capacity of 6 tons/day will probably be about 0.3 mil/kwhr (electricity). Such a central plant would process the fuel output of possibly ten large power reactors.

New processes are being developed. For reactors of high fuel and fertile material content, such as the fast breeder, where inventory charges are high, processes which give partial fission product decontamination are being studied. The pyrometallurgical processes being studied at Argonne for EBR-II are examples of this type of process. Wastes from the fuel melting slagging, or salt washing, will be produced principally in solid form. The exact nature of wastes from this kind of process are not yet known.

Another process techniques which has been operated successfully on a large pilot plant scale (as yet, still at low activity levels) at Oak Ridge National Laboratory, and on a smaller scale at Argonne is the fluoride volatility process. Fuel elements will be dissolved in a fused fluoride salt mixture with hydrofluoric acid gas at temperatures of approximately 650°C. The uranium can then be removed from the fused salts and most of the fission products with fluorine gas, which converts UF_4 in the fused salt to volatile UF_6 gas. The few fission products that follow the uranium can be removed by absorption on sodium fluoride or by distillation. The fission products would be discharged as a component of the solidified salt mixture. This process has yet to be demonstrated on an engineering scale. It also now is limited in application to fully enriched U^{235} fuels only.

Problems of Active Gaseous Wastes from Radiochemical Plants

The fission product gases which remain after the normal cooling period of approximately 100 days are primarily Kr⁸⁵, a noble gas with a 10.27 years' half-life; and I¹³¹ in small quantities because of its relatively short half-life of 8.0 days. If processing reactor fuel elements is started with a shorter decay period than 100 days, iodine-131 becomes a controlling isotope in the gases which are released during dissolution operations. Xe¹³³, a noble gas with a half-life of 5.27 days, will also be present in significant concentration in dissolver off-gas streams.

Iodine must be removed completely from the off-gas streams; processes exist that are 99.99% efficient for I₂ removal which have been operated for many years. Dissolver gases contain, along with the fission gases and air, gaseous oxides of nitrogen and possibly other acid gases. Iodine is removed from the waste gas by passing it over a bed of silver nitrate coated ceramic packing at elevated temperature. The oxides of nitrogen are removed by scrubbing with sodium hydroxide; krypton and xenon, if present, may be diluted with air and discharged through tall stacks to the atmosphere. Both xenon and krypton can be removed by adsorption on charcoal at low temperatures; by liquefaction; or by other methods currently under investigation.

If natural uranium is irradiated in an average flux of 3×10^{13} n/cm²/sec for a year, there will be the following concentrations of the above isotopes:

Isotope	Half-life	curies/g U ²³⁵ .	curies/g U ²³⁵
		consumed at 20 days decay	consumed at 100 days decay
Kr ⁸⁵	10.27 years	0.358	0.354
I ¹³¹	8.0 days	10.3	0.0109
Xe ¹³³	5.27 days	11.8	0.00110

Small particles which contain radioactive elements present very serious problems. From the radiochemical plant it is possible to release aerosols of high specific activity; many operations in the chemical process produce mists or entrained solids, such as solution transfer by steam jet, evaporation, and mixing with air sparging. All chemical plants must be provided with filters of exceptional efficiency. Particles containing highly alpha-active materials, such

as mixtures of the plutonium isotopes, thorium and uranium-233, protactinium-233, and the heavy element produced by parasitic neutron capture by fissionable and fertile isotopes.

The one additional fission product that has appeared in very high concentrations from certain steps of the solvent extraction processes is ruthenium. Under the strongly oxidizing conditions required for a scavenge precipitation step to remove ruthenium, zirconium, and niobium as solids on manganese dioxide, part of the ruthenium oxidizes to the volatile RuO_4 , which then plates out as a solid scale on vent lines and other equipment, or passes through the equipment and filters to condense later as very fine particles of high specific activity. The loosely attached films containing ruthenium flakes off, and appear as highly active particles; this is a particularly difficult problem during maintenance periods when equipment and piping are changed. If this problem is experienced in a process, there are known conditions to prevent or correct it for the distillation of ruthenium oxide.

Low and Intermediate-Level Liquid Wastes
(Excerpt from reference (15))

Low-level or intermediate liquid wastes result from fuel processing operations also, usually from second and third cycle separations and from fuel dejacketing. In addition, low-level liquids derive from reactor cooling systems, laboratory operations and laundry operations. In proper environmental situations, these wastes are susceptible to either direct dispersal to the environment or discharge following treatment. Because of their large volume, millions of gallons per day, total costs of treatment, where required, tend to be substantial. To minimize these costs, yet keeping within strict bounds of safety, maximum possible use is made of nature's dilution capacity. Site selection for nuclear facilities plays a very important role in this regard.

The major operation of this kind is at Hanford and is related directly to the environmental situation existing there. Hanford Atomic Products Operation discharges approximately 50,000 curies/month and expects to continue discharging about the same amount in the future. Sr and Cs have been scavenged from this activity so that it essentially consists of short-lived material when discharged. Nitrate ion and ruthenium, and more recently cobalt 60, have been detected in monitoring wells associated with these operations but not as health-significant levels to date.

Some liquid wastes at the smaller sites are concentrated to relatively small volumes, packaged and then shipped to the larger sites for land burial or to the oceans for burial at sea. The following table, far from accurate and complete, provides a rough estimate of volumes of low-level liquid wastes:

Low-Level Liquid Waste Discharge Data

<u>Site</u>	<u>Type of Maximum Treatment</u>	<u>Approximate Volume Discharged Per Year</u> (10 ⁶ gals)	<u>Total Curies Discharged</u> (x 10 ³)
ANL	Depends on specific waste	47	
BNL	Evaporation	120	(2-3) ⁽¹⁾
FMPC	Calcination	90	
HAP0	Decay Storage	7,668 ⁽³⁾	2,096 (since 1944)
KAPL	Evaporation	126	
LASL	Co-ppt	14	
NRTS	Decay Storage	420	1.7 (1955 and 1956)
ORNL	Soda-lime treatment	159	75 (since 1948)
Rocky Flats	Evaporation	40	
SRP	Decay Storage	20	0.8 (since 1955 and 1956)
WAPD	Evaporation	137 ⁽²⁾	(1)
Total		8,841	2,173.5

*Activity discharged without further control

- (1) To sea burial in packages
- (2) Includes infiltrated storm water
- (3) Includes condenser cooling water not normally radioactive

Other More General Sources of Radioactive Wastes

The wastes described in the previous sections are all produced as more or less undesirable by-products of a major process; they are collected into large packages, reduced in volume, and stored with as little dispersal as possible. However, many of the radioactive isotopes, produced either from fission or by neutron capture, have use in small quantities as industrial and medical radioisotopes, and are sold in millicurie to curie quantities to thousands of users under licenses issued by the AEC. The benefits of the radioisotope program have been great; the expansion of this program, number of users, and the use of much more energetic sources is foreseen. All these sources, unfortunately, must at some point, become waste materials.

Control of these widely distributed sources and their disposal has been established under the licensing plan. The AEC Division of Inspection is responsible for maintaining good practice in the handling and disposal of the sources. Another control, more absolute in the sense that it can limit the total quantity of radioactive material "in circulation", is the one that can be exercised in limiting the quantities in use at the source of supply. It is an inherent feature of limitations already established by law that a general contamination problem affecting a large segment of the population cannot develop from the profitable use of radioactive sources and tracers.

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