History of Prototype High Level Waste Canister SS-9 While in Air and Water Storage

by
D. J. Bradley

November 1977

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HISTORY OF PROTOTYPE
HIGH LEVEL WASTE CANISTER SS-9
WHILE IN AIR AND WATER STORAGE

by
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November 1977

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SUMMARY

Canister SS-9 was filled with high-level phosphate ceramic waste material in March 1969. Following 1.2 years water storage at 50°C, 3.5 years hot air storage at 400 to 500°C, and 10 months water storage at 50°C, the canister failed. The canister has three visible cracks, one of which is 13 in. long. It was concluded from metallography that failure was due to stress-assisted intergranular attack enhanced by metal sensitization during the hot air storage period, and a high chloride ion concentration in the canister storage water.

Cores were taken from Canister SS-9 and the leach rate of the material in deionized water was determined to be 5.1×10^{-4} g/cm²-day for the first day. Averaged over 90 days, the material leach rate was 3.1×10^{-5} g/cm²-day. Since it was known that the failure occurred sometime between quarterly canister storage water sampling periods, these leach rates were used to calculate an effective waste surface area presented by the canister cracks. Thus, the leach rates for the first day and the average for 90 days represent the extremes that could have occurred. The effective waste surface area contacted via the canister cracks was calculated to be between 1 and 20 m².

Based on the calculated effective surface area and the above leach rates of the phosphate ceramic material, 6.1 g of waste were dissolved per day. This is related to the activity of the canister as follows:

- Curies of ¹³⁷Cs in Canister SS-9 (corrected to May 1977) = 1.78×10^4
- Curies of ¹³⁷Cs leached in one day, based on above leach rates = 5.5×10^{-1}
Percent of total cesium in canister = 3.1×10^{-3}
- Curies of ¹³⁷Cs leached in one day based on averaged 90th day leach rate and total canister surface area of 1.35 m² = 1.41×10^{-2}
Percent of total cesium in canister = 7.9×10^{-5}

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HISTORY OF PROTOTYPE HIGH LEVEL
WASTE CANISTER SS-9
WHILE IN AIR AND WATER STORAGE

INTRODUCTION

This study investigates the history of a leak in a Waste Solidification Engineering Prototype (WSEP) high-level waste canister while in simulated water basin storage. The canister was a prototype fabricated of 310 stainless steel rather than the usual 304L stainless steel. The waste type was that of a phosphate ceramic material made as an early candidate for high level waste solidification. In this experimental program, the canister was subjected to a harsh storage history that would not be encountered in storage of full-scale high level waste canisters. The history of the canister (SS-9) is reviewed to give information on its filling and air and water storage conditions. The metallography of the canister failure is given, and the mechanism of containment breaching is postulated. The waste release from this failure is examined by means of data taken at the time of failure and recent leach test experiments on the waste material. The work discussed in this report was performed in the hot cell facilities of the 324 Building at the Pacific Northwest Laboratory.

CANISTER DESCRIPTION AND STORAGE HISTORY

During the week of March 22-27, 1969, a seamless 310 stainless steel canister (SS-9) was filled with a phosphate ceramic product containing 2×10^6 curies of radioactivity, as part of the Waste Solidification Engineering Prototypes program at the Pacific Northwest Laboratory (PNL).^(1,2)

Table 1 shows the run characteristics for this canister. Tables 2 and 3 show the compositions of the feed and glass products, respectively. Figure 1 outlines the spray solidification process used to make Canister SS-9. The PW-4m waste composition was designed to represent that derived from high burnup fuels reprocessed by "clean" techniques of the future (e.g., no metal salt additives). Because power reactor fuel wastes were not available, the waste used for Canister SS-9 was manufactured by combining:⁽¹⁾

<u>Constituent</u>	<u>Purpose</u>
1. Hanford Purex Plant High Level Waste specially prepared to have a low sulfate content. This is the acidic waste from the first extraction column.	Provide radioactive fission product spectrum, albeit at lower concentrations than in the nominal power reactor wastes, and typical non-radioactive Purex waste constituents, such as solvent degradation products.
2. Fission product rare earth concentrate, principally ^{144}Ce	Provide radionuclide decay heat equivalent to power reactor wastes.
3. Nonradioactive chemicals	Increase chemical composition as required to equal nominal WSEP waste compositions shown in Table 2.

This waste, although not actual high exposure power reactor fuel waste, was considered to have been a good approximation for the study of solidification processing and interim storage for periods up to at least 10 years. The chemical stand-ins (Table 2) used for some of the more expensive fission products did not amount to more than 5.9 mole % of the content of the final

TABLE 1. Spray Solidifier Feed and Run Data⁽²⁾

Solidified Run Number	SS-9
Date of Run	3/22-27/69
Canister Size, ID, cm	20.3
Type	PW-4m
Feed Volume, liters/tonne	630
Feed Temperature, °C	30
Feed Consumed, liters	792
Total Feed Time, hr	52
Total Feed Time Off, hr	7.0
Average Feed Rate, liter/hr	15.2
Bulk Density, g/cm ³	2.9
Volume of Product, liters	68.4
Fill Height, cm	210.8
Centerline	
Temperature in Air, °C	594
Wall Temperature in Air, °C	352
Mass of Solidified Product, kg	198.3
<u>Radioactivity</u>	
Total Radioactivity in Feed to Calclner,(a) kCi	2030
Total Radioactivity in Canister, kCi	2025
Radioruthenium in Feed to Calclner, kCi	10.2
Feed Heat Rate Density, W/liter	8.0
Fission Product Heat to Canister, W	7200
Ruthenium Volatilized, %	57
¹⁴⁴ CePr Entrainment from Solidifier,(b)%	0.023
<u>Equivalent Spent Fuel Waste</u>	
Waste to Canister, tonne U equivalent	1.26
Average Processing Rate, Tonne/day	0.58
Equivalent Age of Waste, yr	2.3

(a) Radioactivity was predominately ¹⁴⁴CePr.

(b) Based on heat generation rate in pod
and ISOGEN program.

TABLE 2. Chemical Compositions of High-Level Liquid Wastes for WSEP Demonstrations(1)

	Constituent	Concentration, Molarity at 378 liters/tonne PW-4m(a)
Nonfission Products	H	0.50
	Fe	0.050
	Cr	0.012
	Ni	0.008
	Al	0.001
	Na	0.10
	U	0.010
	Hg	<0.001
	NO ₃	2.4
	PO ₄	0.003
	SiO ₃	0.010
	F	<0.001
Fission Products (b)	Mo	0.130
	Tc(Mo)	0.031
	Sr	0.036
	Ba	0.041
	Cs(K)	0.078
	Rb(K)	0.014
	Y+RE	0.27
	Zr	0.14
	Ru	0.0082
	Ru(Fe)	0.0738
	Rh(Co)	0.013
	Pd(Ni)	0.043
	Ag(Cu)	0.0016
	Cd(Cu)	0.0025
	⁹⁰ Sr	0.0018
	¹⁰⁶ Ru	0.00003
	¹³⁷ Cs	0.0039
	¹⁴⁴ Ce	0.0053
Oxide Weight, kg/tonne		
Nonradioactive Chemicals		4.6
Fission Products		49.0
Total		53.6

(a) Fission product content corresponds to thermal reactor fuel exposures of 45,000 MWd/tonne at 30 MW/tonne, tonne = 1000 kg UO₂.

(b) Elements in parentheses were used as stand-ins for the more expensive fission products.

TABLE 3. Nominal Composition of Phosphate Ceramic Solidified Wastes, (a) Canister SS-9(1)

<u>Component</u>	<u>wt%</u>
P ₂ O ₅	45.0
SiO ₂	0.1
Na ₂ O	7.5
K ₂ O	1.0
Li ₂ O	2.5
Fe ₂ O ₃	18.2
Al ₂ O ₃ (b)	2.0
Cr ₂ O ₃	0.2
NiO	0.9
U ₃ O ₈	0.6
Re ₂ O ₃	9.9
ZrO ₂	3.9
MoO ₃	5.1
RuO ₂	0.2
Co ₃ O ₄	0.2
CuO	0.1
SrO	0.8
BaO	1.4
⁹⁰ SrO	0.046
¹⁰⁶ RuO ₂	0.0009
¹³⁷ Cs ₂ O	0.13
¹⁴⁴ CeO ₂	0.22
Theoretical wt% Fission Product Oxides (c)	28.3
Bulk Specific Gravity	3.0

(a) Chemical stand-ins were used for some fission products. See Table 2.

(b) Representative Al₂O₃ concentrations in the radioactive products are shown in parentheses. The Al₂O₃, nontypical of power reactor wastes, resulted from the small and variable amounts of aluminum unavoidably present in the Hanford Purex plant HLW used in preparing the WSEP wastes. In preparing the wastes for the WSEP radioactive runs the iron concentration was reduced in proportion to the aluminum present.

(c) Calculated on a no-substitution basis.

FIGURE 1. Outline of WSEP Waste Solidification Process for Canister SS-9

melt-formed solidified product. No effects attributable to the use of the chemical stand-ins were found in laboratory tests.

Table 4 shows an analysis of the major radioactive isotopes in a solidified waste sample taken from the SS-9 canister run in March 1969. This table also shows their decay corrected levels as of May 1977, when the last leach samples were analyzed. The predominant isotope in the SS-9 canister for the first 4.6 years was ^{144}Ce . After this time, ^{137}Cs , because of its much longer half-life, became the major radiation source.

As shown in Table 5, radiation effects on the phosphate ceramic waste due to fission product decay should become apparent within 10 years because a very significant fraction of the total fission products present will decay in this period. The primary objective of the SS-9 run was to determine short-term decay effects, since no actinides were present in the waste.

TABLE 4. Major Radioisotope Content of Canister SS-9

	Per Gram Phosphate Ceramic		Total Canister	
	March 1969	May 1977	March 1969	May 1977
Cs^{137}				
d/min	2.43×10^{11}	2.00×10^{11}	4.82×10^{16}	3.97×10^{16}
grams	1.27×10^{-3}	1.05×10^{-3}	2.52×10^2	2.08×10^2
curies	1.09×10^{-1}	8.99×10^{-2}	2.16×10^4	1.78×10^4
Ce^{144}				
d/min	1.29×10^{13}	7.23×10^9	2.56×10^{18}	1.43×10^{15}
grams	1.82×10^{-3}	1.02×10^{-6}	3.61×10^2	2.02×10^{-1}
curies	5.81×10^0	3.25×10^{-3}	1.15×10^6	6.45×10^2
Ru^{106}				
d/min	4.91×10^{10}	1.51×10^8	9.73×10^{15}	2.99×10^{13}
grams	6.61×10^{-6}	2.03×10^{-8}	1.31×10^0	4.02×10^{-3}
curies	2.21×10^{-2}	6.78×10^{-5}	4.38×10^3	1.34×10^1

TABLE 5. Comparison of Canister SS-9 and Commercial Reactor Wastes

	Canister SS-9, (a)	Commercial (b)(3) Reactor Waste,
	Curies	Curies
Ru^{106}	4.4×10^3	1.3×10^5
Cs^{137}	2.2×10^4	1.3×10^5
Ce^{144}	1.2×10^6	1.6×10^5
Total Fission Products at 2 yr	1.23×10^6	1.25×10^6
Total Fission Products at 10 yr	1.8×10^4	3.06×10^5

(a) For 1.26 MTU equivalent at 2 yr age.

(b) For 1.26 MTU reprocessed, 33,000 MWD/MTU at 2 yr age.

Following the end of the SS-9 run, the canister was stored in water at 50°C for 1.2 years, then transferred to an environmental test pod for hot air storage for 3.5 years. During this time, the wall temperature ranged between 400 and 500°C. Figure 2 shows a cutaway view of the environmental test pod. In January 1974, the canister was placed in water storage at about 50°C, also in an environmental test pod.

During October 1974, it became apparent that Canister SS-9 was leaking significantly. The evidence was seen as a sharp increase in the pod water activity, which is sampled on a quarterly basis. Representative pod water analyses prior to the leak are shown in Table 6. Normally the pod water sample bottles read 1 mr/hr. However, when the samples were taken on October 3, 1974, the water from the pod containing SS-9 read 250 mr/hr.

TABLE 6. Canister SS-9 Storage Pod Water Analysis

<u>Sampled</u>	<u>pH</u>	<u>Cl⁻¹</u> <u>ppm</u>	<u>Cr⁺⁶</u> <u>g/l</u>	<u>¹³⁷Cs</u> <u>d/min-ml</u>
3/28/74	7.6	9	0.209	4.02x10 ⁵
6/24/74	7.4	12.7	0.518	4.00x10 ⁵

Several tests were run to verify the high water activity before the canister was removed from the pod. The pod was emptied and refilled with 416 ml of water. The water activity, as determined by a CP held next to 100 ml of water in a glass sample bottle, increased steadily:

- After 18 hr 18 mr/hr
- After 70 hr 70 mr/hr
- After 120 hr 240 mr/hr.

The general location of the leak was determined by incremental addition of water to the pod. This revealed the leak to be within the bottom 2 ft of the canister. Following these tests the canister was removed from the pod and hung in the air for examination and drying.

FIGURE 2. Environmental Test Pod for Nuclear Waste Containers

DESCRIPTION AND CAUSE OF CANISTER FAILURE

Upon visual examination, the canister was seen to have three apparent cracks. Figure 3 shows the canister and the three areas that proved to be cracks. Figure 4 shows a close-up of the largest crack before and after cleaning by wire brush. The before-cleaning sequence follows the residue trail down below the bottom of the crack. Figure 5 shows the remaining two cracks. Figure 6 shows the canister with the locations of the cracks, and Table 7 gives data on the cracks.

TABLE 7. Measurements Taken on Canister SS-9 Cracks

	<u>Large Crack</u>	<u>Medium Crack</u>	<u>Small Crack</u>
Radial Angle ^(a)			
Location, degrees	100-107	190	155
Distance from Bottom of Canister to Start of Crack, inches	4 1/2	3 1/2	3 1/2
Length of Crack, inches	13	1 1/2	1/2

(a) Indexed to thermocouple arm, see Figure 6.

A sample was then core drilled from the canister for Huey testing (ASTM A-262, five 48-hr exposures to boiling 65% HNO₃),⁽⁴⁾ a standard test for sensitization of stainless steel. Since most of the canisters in the WSEP program were 304L, it was of interest to compare a 304L sample taken from a canister stored in air for 2 years at 400°C after 1 year storage in water.⁽⁵⁾ The results, given in Table 8, show that both canisters were severely sensitized.

Five samples were then core drilled from canister SS-9 for metallographic purposes. Table 9 gives the locations of these samples.

FIGURE 3. Canister SS-9 After Failure

FIGURE 4. Canister SS-9 Major Crack Before and After Cleaning

2ND CRACK

2ND CRACK CLEANED

3RD CRACK

FIGURE 5. Canister SS-9 Second and Third Cracks

FIGURE 6. Location of Failure Areas

TABLE 8. Huey Test Data

Material	Corrosion Rate (mils/month) ^(a)					
	48-hr Periods					
	1	2	3	4	5	Avg
304L Stainless Steel	57	155	170	168	154	141
310 Stainless Steel	45	180	207	222	209	173

(a) The maximum rate for acceptable material is usually 2 mils/mo (avg).

TABLE 9. Locations of Metallographic Samples

Location Number	Distance from Bottom of Canister, in.	Angle, ^(a) in Degrees	Comments
1	13 1/2	100	Section containing top of large crack.
2	4 1/2	107	Section near bottom of large crack.
3	4	190	Contains part of small crack and bottom cap weld.
4	3 1/2	255	From a bottom section of the cap weld.
5	10	300	From opposite side of large crack.

(a) Indexed to thermocouple arm, see Figure 6.

Figure 7 shows these five samples after they were core drilled from the canister. Both the internal steel surface and its adjoining ceramic surface (external ceramic surface) are shown. These samples were then polished for metallographic examination of the longitudinal cross sections. Prior to viewing, the samples were electrolytically etched in oxalic acid.

INTERNAL CANISTER SURFACE

EXTERNAL GLASS SURFACE

1

1

2

2

CLEANED CANISTER SURFACE

3

3

4

4

5

5

FIGURE 7. Core Samples Taken from Canister SS-9

Figures 8 through 12 show the micrographs of Samples 1 through 5, respectively. Figures 8 and 10, containing crack areas, show gross intergranular attack. Figures 9 and 12 show good areas of the canister, and Figure 11 shows the bottom cap weld. This sample had some micro-cracking extending through the weld and into the canister wall. All the polished areas examined were free of transgranular cracking, a stress corrosion cracking indicator. Samples taken from areas free of macro-cracks, samples 2 and 5, were also free of mini-cracks.⁽⁶⁾

After all examinations were completed the lower portion of Canister SS-9 was covered with an overpack before being returned to pod storage. The overpack was TIG welded with a manipulator, while the canister was suspended vertically. The 3/8-in. thick 304L stainless steel overpack was tack welded and then sequence welded. Some undercutting of the canister metal was observed during welding. The canister was vacuum dried; the overpack was then helium leak-checked. The canister was returned to the water test pod and high activity in the storage water has not been seen.⁽⁷⁾

Canister SS-9 was in a stressed condition after being filled with phosphate ceramic product. The coefficients of thermal expansion for the phosphate glass and 310 steel canister are $6 \times 10^{-6} \frac{\text{in.}}{\text{in.}^\circ\text{C}}$ ⁽⁸⁾ and $14.4 \times 10^{-6} \frac{\text{in.}}{\text{in.}^\circ\text{C}}$ ⁽⁹⁾ respectively. Thus as the canister cooled upon completion of the run, it became highly stressed since the glass prevented its normal contraction. The storage period in hot air was ideal for sensitization, causing carbon and chrome migration to the grain boundaries and formation of chrome carbide intergranularly. This made the canister very susceptible to intergranular attack. During water storage, a significant chloride concentration of 13 ppm was found, which was conducive to stress corrosion.

In conclusion, it can be seen from this evaluation that 310 stainless steel becomes highly sensitized after prolonged air storage at elevated temperatures and should not be subsequently stored in water. The failure of the canister appears to have been caused by stress-assisted intergranular attack enhanced by the high chloride concentration in the pod storage water.

INTERNAL SURFACE EDGE 75X

EXTERNAL SURFACE EDGE 75X

INTERNAL SURFACE EDGE 225X

EXTERNAL SURFACE EDGE 225X

FIGURE 8. Photomicrographs of Canister Wall Section from WSEP Canister SS-9 - Sample Area #1 (Oxalic Acid Electrolytic Etch)

INTERNAL SURFACE EDGE 75X

EXTERNAL SURFACE EDGE 75X

INTERNAL SURFACE EDGE 225X

EXTERNAL SURFACE EDGE 225X

FIGURE 9. Photomicrographs of Canister Wall Section from WSEP Canister SS-9 - Sample Area #2 (Oxalic Acid Electrolytic Etch)

INTERNAL SURFACE EDGE 75X

EXTERNAL SURFACE EDGE 75X

INTERNAL SURFACE EDGE 225X

EXTERNAL SURFACE EDGE 225X

FIGURE 10. Photomicrographs of Canister Wall Section from WSEP Canister SS-9 - Sample Area #3 (Oxalic Acid Electrolytic Etch)

1/2 in.
= 170 μ

170 μ

INTERNAL SURFACE EDGE 75X

EXTERNAL SURFACE EDGE 75X

1/2 in.
= 56 μ

56 μ

INTERNAL SURFACE EDGE 225X

EXTERNAL SURFACE EDGE 225X

FIGURE 11. Photomicrographs of Canister Wall Section from WSEP Canister SS-9 - Sample Area #4 (Oxalic Acid Electrolytic Etch)

INTERNAL SURFACE EDGE 75 X

EXTERNAL SURFACE EDGE 75 X

INTERNAL SURFACE EDGE 225 X

EXTERNAL SURFACE EDGE 225 X

FIGURE 12. Photomicrographs of Canister Wall Section from WSEP Canister SS-9 - Sample Area #5 (Oxalic Acid Electrolytic Etch)

IMPLICATIONS OF CANISTER FAILURE AND SUBSEQUENT LEACHING
IN A WATER STORAGE BASIN

In August 1976, Canister SS-9 was core drilled to remove phosphate ceramic material for leach testing. Three cores 1.91 cm in diameter were taken; their location and characteristics are given in Table 10.

TABLE 10. Canister SS-9 Core Sample Measurements

Sample Number	Distance from Bottom of Canister, cm	Radial Location, degrees	Sample Weight, g	Geometric Sample Surface Area, cm ²	Sample Volume, cm ³
SS-9-1	186.4	180	17.880	29.4	11.0
SS-9-2	110.2	180	16.803	32.3	9.8
SS-9-3	54.3	180	28.942	58.1	14.8

Figure 13 shows photographs of the three cores used for leaching. The cores were then placed in a Paige leaching apparatus, as shown in Figure 14, for contact with deionized water. In the Paige test, the sample is contacted with the recirculating leachant at ambient temperatures. The effects of the small change in surface area during leaching were not considered in this study.

The solutions were sampled and changed according to the time schedule given in Table 11.

TABLE 11. Leaching Schedule

Sample Series Number	Cumulative Leach Time, days	Sample Leach Time, days	Date Sampled
1	1	1	08-24-76
2	2	1	08-25-76
3	3	1	08-26-76
4	4	1	08-27-76
5	7	3	08-30-76
6	15	8	09-07-76
7	21	6	09-13-76
8	28	7	09-20-76
9	58	30	10-20-76
10	84	26	11-15-76
11	113	29	12-13-76
12	145	32	01-14-77
13	173	28	02-11-77
14	199	26	03-08-77

SS-9-1

SS-9-2

SS-9-3

FIGURE 13. Core Samples for Leaching Experiments

FIGURE 14. Paige Leaching Apparatus

The leach solutions were analyzed by gamma spectroscopy for ^{137}Cs . Leach rates were then calculated according to the formula

$$R = \frac{a_o}{A_o S \Delta T}$$

where R = leach rate in g/cm^2 per day

a_o = disintegration/min for total leach solution

A_o = disintegration/min for total sample

S = sample surface area, cm^2

ΔT = leach time, days.

Table 12 shows the results of the leach rate calculations for samples SS-9-1 through SS-9-3. Figure 15 shows these results plotted together. The leaching studies were done to obtain a leach rate for the phosphate

ceramic material so that a correlation could be made back to the measurements taken when the canister failed. Knowing the leachate activity at the time of failure in mr/hr, (see Page 9) the conversion factor between mr/hr and disintegrations per minute for the leach solution, and the leach rate of the material allows calculation of the effective surface area of waste contacted as a result of the canister failure.

TABLE 12. Leach Rates of Canister SS-9
Phosphate Ceramic Based on ^{137}Cs

Sample Series Number	Sample Leach Time, days	Leach Rate g/cm ² - day		
		SS-9-1	SS-9-2	SS-9-3
1	1	8.3×10^{-4}	2.7×10^{-4}	4.2×10^{-4}
2	1	3.8×10^{-4}	1.1×10^{-4}	2.2×10^{-4}
3	1	1.8×10^{-4}	5.4×10^{-5}	1.4×10^{-4}
4	1	1.0×10^{-4}	4.5×10^{-5}	1.4×10^{-4}
5	3	5.5×10^{-5}	3.1×10^{-5}	7.8×10^{-5}
6	8	3.0×10^{-5}	1.8×10^{-5}	4.7×10^{-5}
7	6	3.1×10^{-5}	1.9×10^{-5}	3.9×10^{-5}
8	7	3.1×10^{-5}	1.8×10^{-5}	2.9×10^{-5}
9	30	1.9×10^{-5}	8.5×10^{-6}	1.1×10^{-5}
10	26	1.9×10^{-5}	7.4×10^{-6}	8.5×10^{-6}
11	29	1.7×10^{-5}	6.4×10^{-6}	8.2×10^{-6}
12	32	1.4×10^{-5}	6.6×10^{-6}	6.7×10^{-6}
13	28	1.3×10^{-5}	5.5×10^{-6}	6.9×10^{-6}
14	26	1.6×10^{-5}	7.0×10^{-6}	8.0×10^{-6}

The average leach rate for the three samples tested was calculated for the first day and a period of the first 90 days to be 5.1×10^{-4} g/cm²-day and 3.1×10^{-5} g/cm²-day, respectively. Because the actual time of failure occurrence was unknown, these average leach rates represent upper and lower boundaries as the failure had to occur sometime during the quarterly sampling period for the canister storage pods.

FIGURE 15. Leach Rates of Canister SS-9 Phosphate Ceramic Waste

The conversion factor between $\frac{\text{disintegrations}}{\text{minute}}$ and $\frac{\text{mrem}}{\text{hr}}$ for the SS-9 leach solution was found by experiment to be

$$1 \frac{\text{mrem}}{\text{hr}} = 9.8 \times 10^6 \frac{\text{disintegrations}}{\text{minute}}$$

based on ^{137}Cs .

The effective waste surface area seen by the leach solution due to the cracks was calculated using the following equation:

$$\text{Effective Surface Area} = \frac{\left(\begin{array}{c} \text{Averaged} \\ \text{Dose Rate} \\ \text{of Storage Pod} \\ \text{Water} \end{array} \right) \left(\begin{array}{c} \text{Conversion Factor} \\ \text{Between Dose Rate} \\ \text{and Activity} \end{array} \right) \left(\begin{array}{c} \text{Water Volume} \\ \text{in Storage Pod} \end{array} \right)}{\left(\begin{array}{c} \text{Activity of } ^{137}\text{Cs in} \\ \text{Phosphate Ceramic, Decay} \\ \text{Corrected to Time of} \\ \text{Failure} \end{array} \right) \left(\begin{array}{c} \text{Leaching} \\ \text{Time} \end{array} \right) \left(\begin{array}{c} \text{Leach Rate of} \\ \text{Phosphate Ceramic} \\ \text{Based on } ^{137}\text{Cs} \end{array} \right)}$$

The effective surface areas were calculated to be 1.2 m² based on averaged first day leach rate, and 19.9 m² based on averaged leach rate over 90 days. Because of the frequency of pod water sampling, the failure had to occur sometime between 1 and 90 days. The surface area of 1.2 m² assumes a failure on the day before the storage water was analyzed. The surface area of 19.9 m² corresponds to a failure one day after the previous pod water sampling. Thus, these numbers represent the extremes of the surface areas that could have been contacted. Although the surface area may seem large, this does not necessarily imply deep penetration due to the probable size of the waste particles encountered. Table 13 shows the amounts of various-sized particles needed to yield the surface areas given above. The table also shows data on Canister SS-9.

TABLE 13. Particle Parameters Needed to Yield Effective Surface Areas

Mesh No.	Sphere Radius, cm	Particles Needed Based On:		Volume Needed, cm ³ Based On:		Grams Glass Needed Based On:	
		1 day	90 days	1 day	90 days	1 day	90 days
10	1.0x10 ⁻¹	9.5x10 ⁴	1.6x10 ⁶	400	6630	1200	19900
100	7.49x10 ⁻³	1.7x10 ⁷	2.8x10 ⁸	30	497	90	1490
325	5.86x10 ⁻⁵	2.8x10 ¹¹	4.6x10 ¹²	0.24	3.9	0.72	11.7

Note:

- Surface Area Canister SS-9 = 1.35 m²
- Volume of Canister SS-9 = 68,400 cm³
- Mass of Phosphate Ceramic in Canister SS-9 = 198,300 g.

Based on the calculated effective surface area and the leach rate of the phosphate ceramic material, 6.1 g of waste were dissolved per day. This is related to the activity of the canister as follows:

- Curies of ^{137}Cs in Canister SS-9
(corrected to May 1977) $= 1.78 \times 10^4$
- Curies of ^{137}Cs leached in one day $= 0.55$ curies
Percent of total canister $= 0.0031$
- Curies of ^{137}Cs leached in 90 days $= 49.4$ curies
Percent of total canister $= 0.28$

Assuming a failed canister of the same magnitude as Canister SS-9, an idea of its effect on a water storage basin can be shown. Consider the following assumptions:

- Storage basin is 36 ft long, 19 ft wide, and 38 ft deep.
- Water volume, after subtracting five hundred 1 ft diameter x 10 ft long canisters, is 6.25×10^5 liters.
- Released radioactivity is homogeneously distributed throughout the storage basin.
- Fractional release of ^{137}Cs as given above for one leaking canister in the storage basin.

Given these assumptions, Table 14 shows the expected activity in the storage basin for a 1-day and a 90-day release.

TABLE 14. Water Storage Basin Activity from One Failed Canister
Based on ^{137}Cs

Release Time	Activity of Water		
	$\mu\text{C}/\ell$	$\frac{\text{dis}}{\text{min}-\ell}$	$\frac{\text{mrem}}{\text{hr}-\ell}$
1 day	0.88	1.96×10^6	0.20
90 days	79	1.76×10^8	18

The activities given in Table 14 do not consider the use of ion exchange systems, which are an integral part of water storage basins.

REFERENCES

1. J. E. Mendel and J. L. McElroy, Waste Solidification Program, Vol. 10, Evaluation of Solidified Waste Products. BNWL-1666, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, July 1972.
2. J. L. McElroy et al., Waste Solidification Program Summary Report, Vol. 11, Evaluation of WSEP High Level Waste Solidification Processes. BNWL-1667, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, July 1972.
3. M. J. Bell, ORIGEN - The ORNL Isotope Generation and Depletion Code. ORNL-4628, Oak Ridge National Laboratory, Oak Ridge, TN, May 1973.
4. M. G. Fontana and N. D. Greene, Corrosion Engineering. McGraw-Hill Book Co., New York, NY, 1967.
5. J. L. McElroy, ed., Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, 9/74 to 12/74. BNWL-1893, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, February 1975.
6. J. L. McElroy, ed., Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, 4/75 to 6/75. BNWL-1932, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, September 1975.
7. J. L. McElroy, ed., Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, 1/75 to 3/75. BNWL-1908, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, June 1975.
8. R. J. Thompson, J. E. Mendel, and J. H. Klempeter, Waste Solidification Demonstration Program: Characterization of Nonradioactive Samples of Solidified High-Level Waste. BNWL-1393, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, June 1970.
9. R. H. Perry, C. H. Chilton, and S. D. Kirkpatrick, Chemical Engineers' Handbook. 4th ed., McGraw-Hill Book Co., New York, NY, 1963.

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