67.
1-19-78

BNL 50733

Dr. 1751

TRITIUM STORAGE DEVELOPMENT

PROGRESS REPORT NO. 12
APRIL-JUNE 1977

MASTER

Prepared for the
NUCLEAR FUEL CYCLE AND PRODUCTION DIVISION
UNITED STATES DEPARTMENT OF ENERGY
WASHINGTON, D.C. 20545

eB

DEPARTMENT OF NUCLEAR ENERGY

BROOKHAVEN NATIONAL LABORATORY
ASSOCIATED UNIVERSITIES, INC.
UNDER CONTRACT NO. EY-76-C-02-0016 WITH THE
UNITED STATES DEPARTMENT OF ENERGY

DISCLAIMER

BNL 50733
UC-70
(Nuclear Waste Management - TID-4500

TRITIUM STORAGE DEVELOPMENT

PROGRESS REPORT NO. 12
APRIL-JUNE 1977

PETER COLOMBO, Project Head

Contributors:
P. Colombo
R. Johnson
R. Neilson, Jr.

DEPARTMENT OF NUCLEAR ENERGY

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

NOTICE

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
Price: Printed Copy $4.50; Microfiche $3.00

November 1977 400 copies

Table of Contents

List of Figures

List of Figures (Continued)

List of Tables

List of Tables (Continued)

SUMMARY

Laboratory work was continued on hydriding of zirconium sponge and rod under varying conditions of temperature (400-900°C) and pressure (0-1000 torr) to determine optimum conditions for the formation of hydrides with desirable mechanical properties. Titanium sponge and rod were also hydrided for comparison. Zirconium and titanium samples containing tritium were prepared and initial leach data were obtained. Leach rates for zirconium in distilled water ranged from 1.1×10^{-6} to 4.8×10^{-6} cm/day under static conditions and from 2.1×10^{-6} to 1.1×10^{-5} cm/day under dynamic conditions. The leach rates for titanium sponge and rod under static conditions ranged from 2.2×10^{-7} to 1.7×10^{-6} cm/day. Construction of the engineering scale equipment has been completed and testing has been started prior to operation.

Lysimeter testing of polymer impregnated tritiated concrete (PITC) specimens at the Savannah River Plant (SRP) has continued. After sixty-two weeks, the average of the four test specimens indicates a linear rate of release with a slope of 5.23×10^{-2} cm/yr beginning after 250 days. A duplicate PITC static leach specimen in distilled water after 386 days indicates a linear rate of release with a slope of 3.18×10^{-2} cm/yr. Developmental work is continuing on the injector technique for PITC. Nontritiated prototype specimens, as well as tritiated specimens for static leach testing in distilled water, were prepared.

I. TRITIUM STORAGE IN METAL HYDRIDE

A program has been initiated to demonstrate a safe and economical process for the fixation of tritium as a tritide in a metal hydride. For tritium absorption and retention purposes, zirconium appears to be most desirable although alternatives such as Ti, Hf, V, Nb and certain alloys of these can also be used. The choice of zirconium as the leading candidate metal for this study is based on its known properties and on chemical and physical properties of the hydride. The process can be reversed, if desired, by heating the hydride above its decomposition temperature (defined as the temperature at which the hydride dissociation pressure is above 1 atm) and collecting the evolved gas. While the fixation process will be developed for long term storage or disposal by burial, retrievability of the tritium will be considered for future needs such as for use in controlled thermonuclear reactors.

A. Hydrogen-Metal Reaction Studies

Hydriding was carried out in metal or glass tubes connected to a manifold which gave access to gas reservoirs, pressure gauges, and a vacuum line (see Figures 1 and 2). All volumes were calibrated, so that the progress of reaction could be followed by pressure measurements. The reaction vessel was kept at a controlled temperature by a tube furnace. In a typical experiment, a 2.5 g metal specimen was outgassed while being heated from room temperature to a chosen reaction temperature. Hydrogen was then admitted by opening the valve to one of the hydrogen reservoirs, previously filled to a known pressure. The pressure during hydriding thus varied from an initial high to a final low point which was often close to zero. Hydriding was usually rapid; and, since the reaction is exothermic to the extent of about 39 kcal per mole H_2 reacted, the temperature sometimes rose as much as 50°C above the control point. Hydrided samples were cooled, weighed to provide a check on the hydrogen uptake as deduced from pressure readings, and examined visually to determine whether cracking or signs of physical degradation were present.

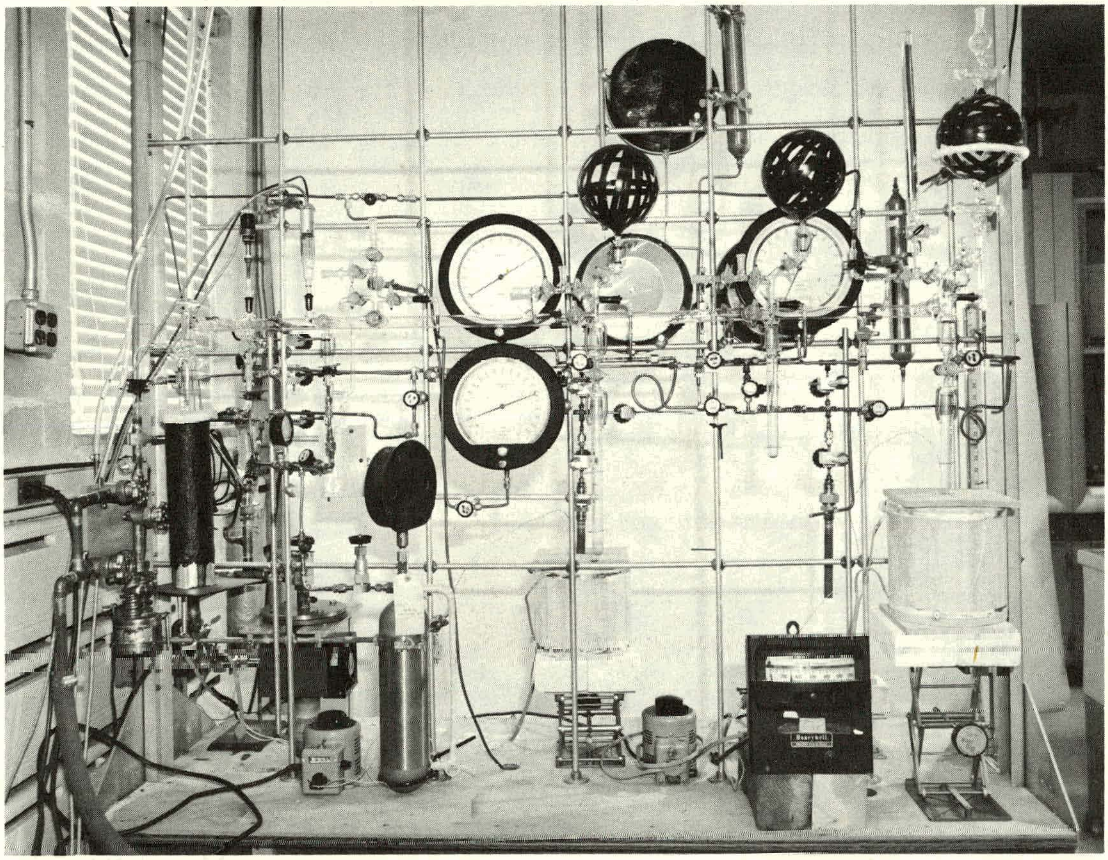


Figure 1. Low-Pressure glass system for hydriding studies.

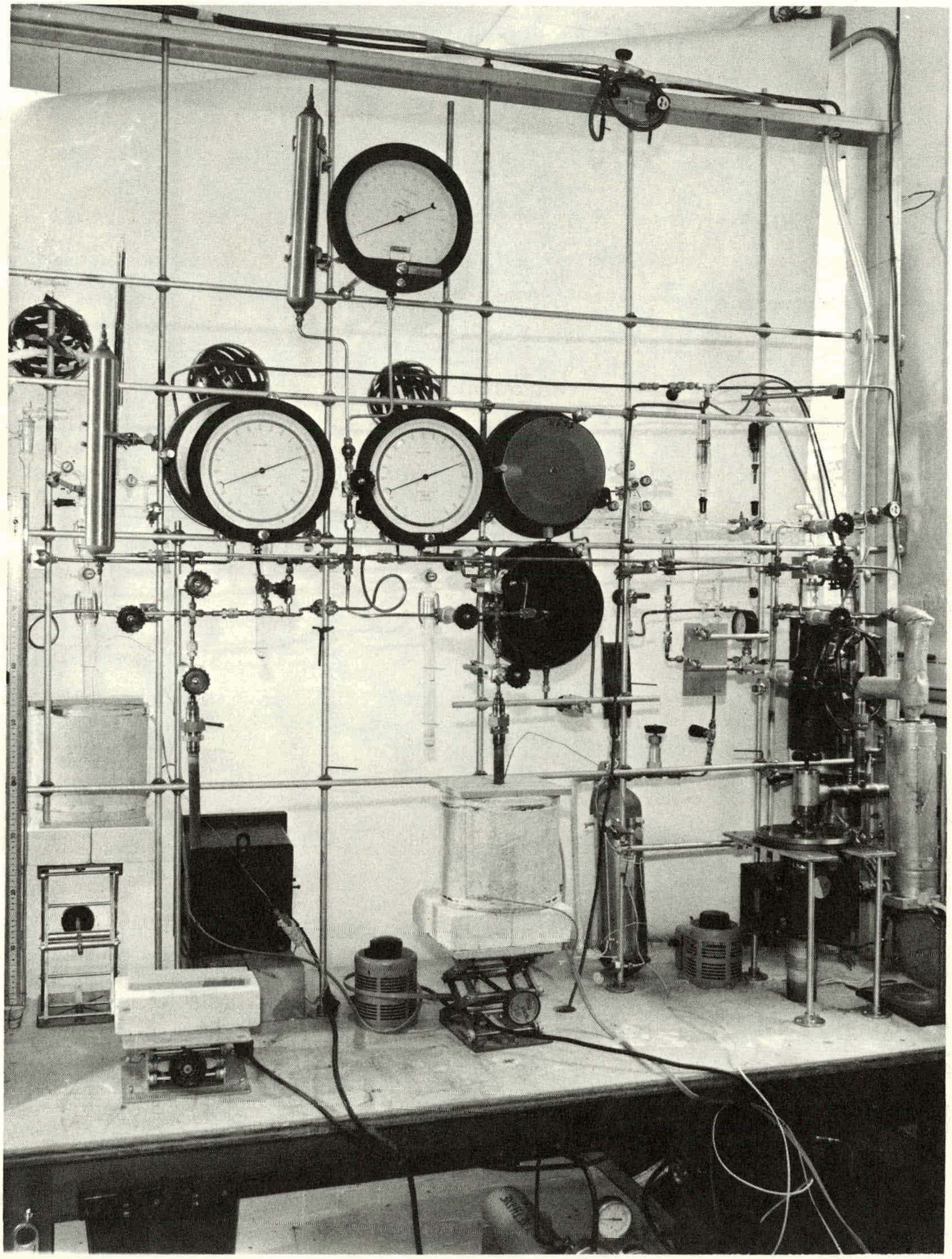


Figure 2. High-Pressure metal system for hydriding studies.

The experimental results for zirconium sponge and rod are given in Tables 1 and 2. In Figures 3 and 4 are shown sponge and rod specimens, respectively, with the experimental conditions for their preparation given in Tables 3 and 4, respectively. The results may be summarized as follows:

1. Zirconium sponge is much more readily hydrided than rod. Sponge was hydrided to a H/Zr atom ratio of approximately 1 in one minute at 450°C (samples 30a-30d), and to H/Zr atom ratios of 1.77 and 1.92 in five minutes at 500°C (samples 34e and 34f). These ratios for sponge can be compared with rod, which required 60 minutes at 600°C for a H/Zr atom ratio of approximately 1 (sample 29a) and 15 minutes at 650°C for a H/Zr atom ratio of 1.15 (sample 33b).
2. Sponge can absorb more hydrogen than rod before cracking occurs. H/Zr atom ratios approaching 2 were attained with sponge (samples 30f, 32c, and 34f) at 450-625°C. Rod invariably cracked at H/Zr atom ratios above 1 unless a higher hydriding temperature was used (900°C, sample 31d).
3. With both sponge and rod, control of pressure was important. Cracking tended to occur when the reaction vessel was opened to reservoirs containing hydrogen at 900 torr and the final pressure after hydriding was also high. This effect was more pronounced at lower temperature and higher H/Zr atom ratio.

The physical integrity of the hydride product is dependent on a number of factors. Higher temperature, lower pressure, and lower H/Zr atom ratio, in general, appear to cause less physical degradation. In addition, the form and size of the reaction metal have an effect. Solid metal apparently is less able to undergo the changes in crystalline structure and density that occur during hydride formation and heating and cooling compared with a porous material that is better able to absorb the stresses. The larger, more massive pieces are also subject to greater degradation. Scheele and Burger[1] conclude that tubing

Experimental Hydriding of Zirconium Sponge

Sample No.	Weight, g	Hydriding temp., °C	Hydriding press., torr		H/Zr atom ratio (a)	Time, min	Notes
			Initial	Final			
29c	2.5685	600	460	2	1.07	15	No change
29d	2.6845	600	460	1	0.83	20	No change
29e	2.6365	600	460	8	1.07	3	No change
30a	3.7932	450	700	0	1.06	1	No change
30b	3.0606	450	528	0	1.01	1	No change
30c	3.0505	450	507	0	0.91	1	No change
30d	2.9086	450	506	0	1.03	1	No change
30e	3.0946	450	986	56	1.54	26	No change
30f	2.8868	450	984	20	1.82	24	No change
31e	2.2418	900	985	590	1.04	34	No change
31f	2.3808	900	985	342	1.52	44	No change
32a	1.7207	625	928	390	1.76	107	Brittle, fragments
32b	1.7182	625	926	338	1.86	110	Brittle, fragments
32c	1.6200	625	977	414	1.95	43	Some chips
32d	2.2268	625	974	290	1.42	43	Some chips
34e	1.5159	500	510	8	1.77	5	No change
34f	1.4527	500	510	2	1.92	5	No change

(a) Atom ratio determined by weight gain.

TABLE 2

Experimental Hydriding of ¼ Inch Zirconium Rod

Sample No.	Weight, g	Hydriding temp., °C	Hydriding press., torr Initial	Hydriding press., torr Final	H/Zr atom ratio [(a)]	Time, min	Notes
29a	2.8898	600	475	10	0.98	60	Fine cracks
29b	2.8935	700	475	10	0.91	65	Fine cracks
31a	2.9139	900	968	488	0.89	11	No cracks
31b	2.8779	900	968	297	1.29	13	No cracks
31c	3.1783	900	991	463	0.94	50	No cracks
31d	2.9700	900	991	246	1.44	45	No cracks
33a	2.6324	650	524	1	0.93	105	Cracks
33b	2.5296	650	524	85	1.15	15	Cracks
33c	2.2353	800	404	60	0.85	75	No cracks
33d	2.5255	800	467	39	1.00	35	No cracks
34a	2.3120	850	501	0	1.27	74	Cracks
34b	1.8514	850	325	92	0.76	30	No cracks
34c	2.6234	900	362	100	0.59	32	No cracks
34d	2.6060	900	362	40	0.71	34	No cracks

(a) Atom ratio determined by weight gain.

TABLE 3

Experimental Conditions for Sponge Samples in Figure 3

Sample No.	Weight, g	Hydriding temp., °C	Hydriding press., torr Initial	Hydriding press., torr Final	H/Zr atom ratio[a]	Time, min
a	Not hydrided					
16b	1.7833	500	229	63	1.96	28
32b	1.7182	625	926	338	1.86	110
31e	2.2418	900	985	590	1.04	34
28k	3.6274	425	617	0	1.13	--
28c	1.2077	450	71	0	1.97	20
30d	2.9086	450	506	0	1.03	1
15e	2.0952	600	190	19	1.75	46

(a)Atom ratio determined by weight gain.

TABLE 4

Experimental Conditions for Rod Samples in Figure 4

Sample No.	Form	Weight, g	Hydriding temp., °C	Hydriding press., torr Initial	Hydriding press., torr Final	H/Zr atom ratio (a)	Time, min
b	¼" Rod	Not hydrided					
23b	¼" Rod	2.7693	200-475	410	60	0.79	95
23d	¼" Rod	2.7530	400-640	170	61	0.76	240
23g	¼" Rod	2.7296	750	344	33	1.74	200
26b	¼" Rod	2.8016	400-600	692	55	1.28	215
33d	¼" Rod	2.5255	800	467	39	1.00	35
25a	Zircaloy	1.8329	600	374	230	1.74	160
25b	Zircaloy	2.3689	800	140	46	0.79	145

(a) Atom ratio determined by weight gain.

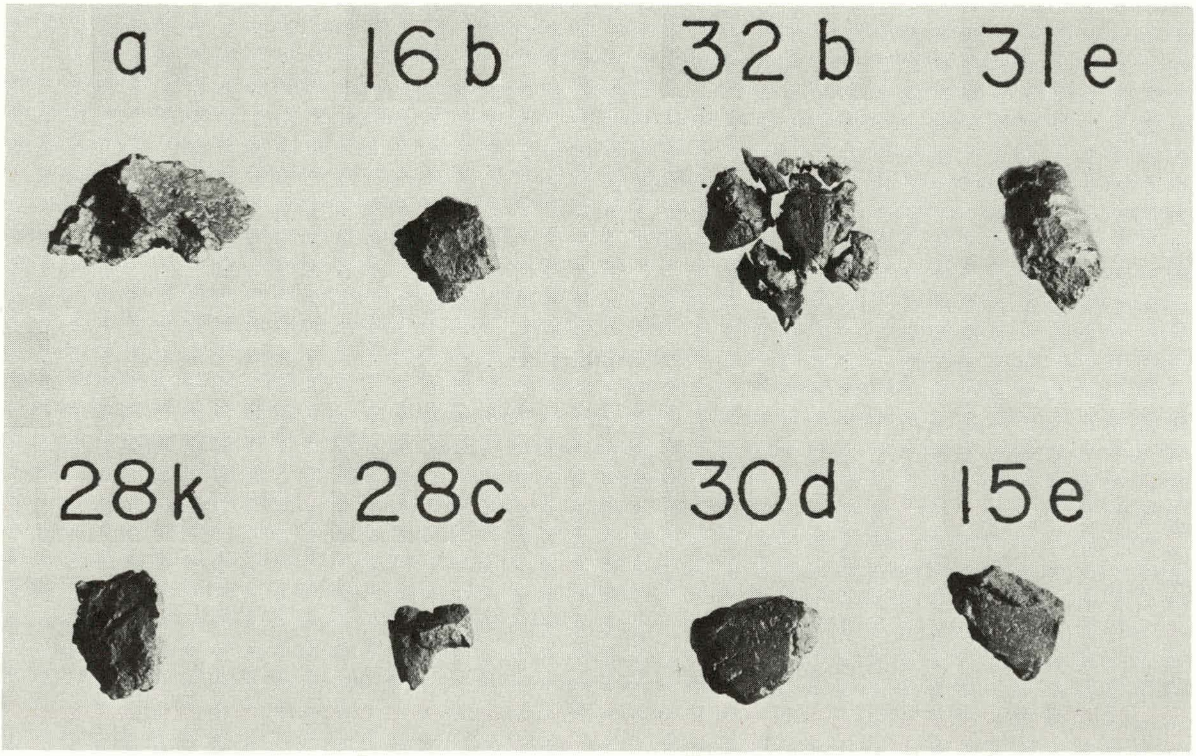


Figure 3. Zirconium sponge and hydrides.

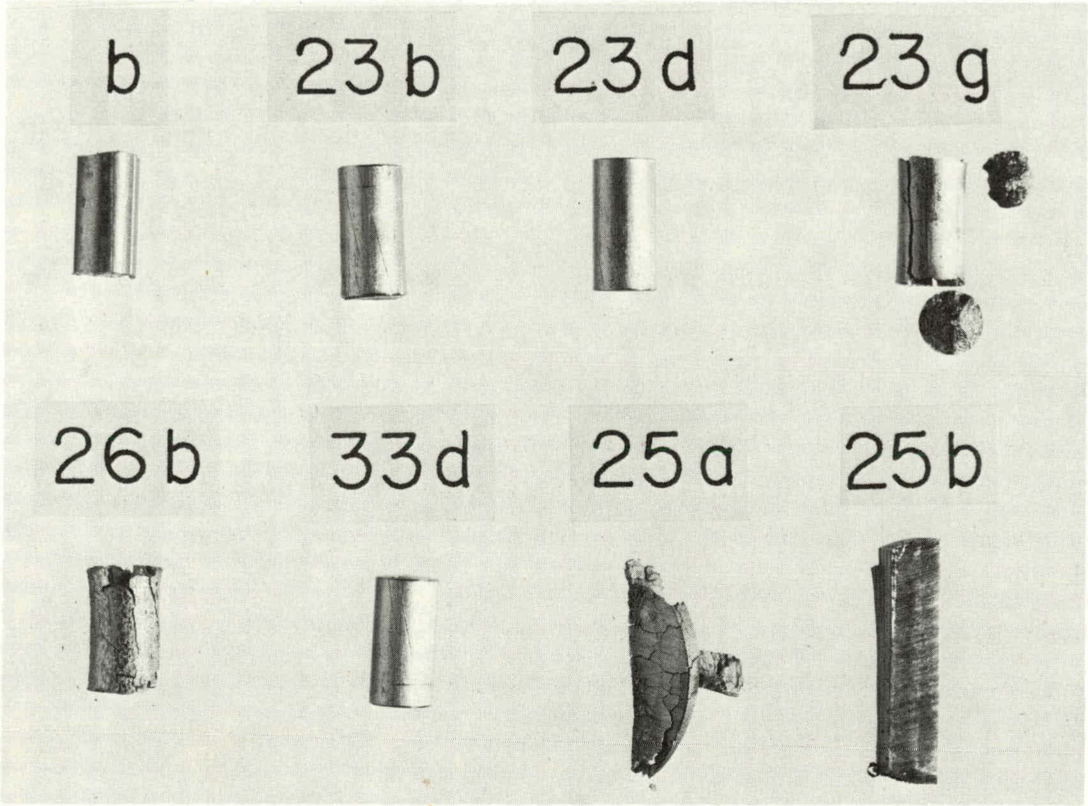


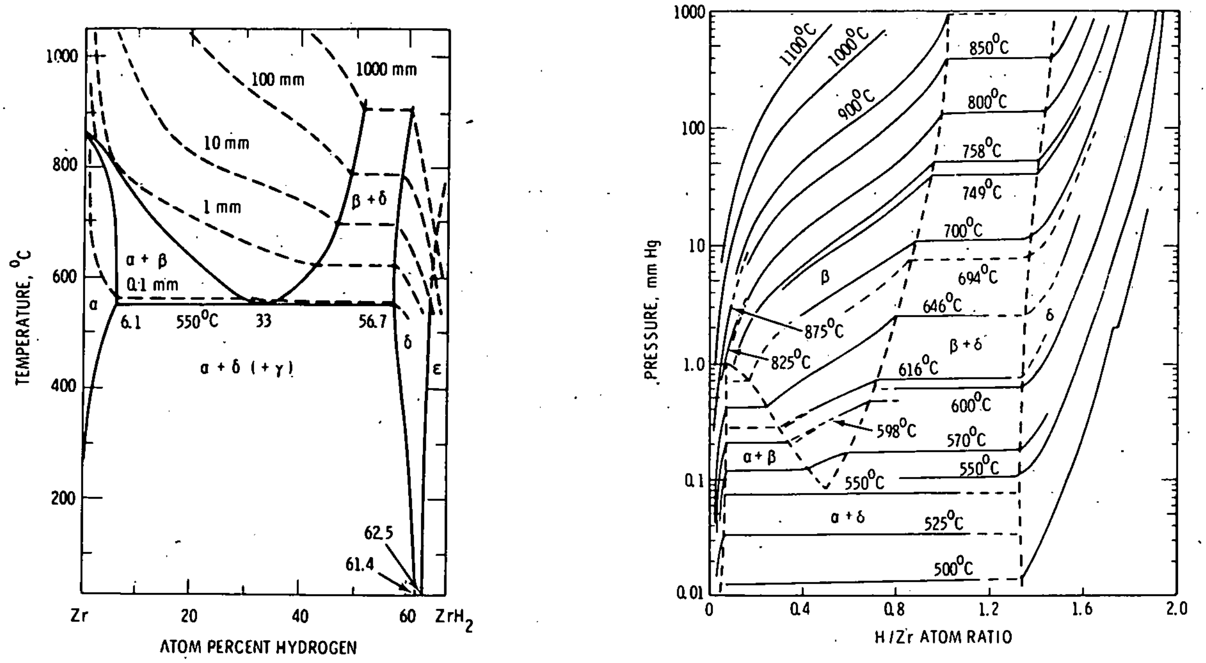
Figure 4. Zirconium rod and hydrides.

accepted hydrogen with less destruction of physical integrity.

The zirconium-hydrogen system has been investigated by Beck and Mueller,[2] and the pressure, temperature, composition relationships correlated by them are shown in Figure 5. The alpha and beta zirconium phases, as well as the delta and epsilon hydride phases, are indicated in these diagrams. Changes in physical and chemical properties can occur during hydriding and heating and cooling, especially during phase change, and thus lead to physical instability of the product. Beck and Mueller have determined and correlated a number of physical properties of the zirconium-hydrogen system and have observed a "brittle range" between 60.0 and 62.5 atom % hydrogen, which is in the all-delta region.

The work of Gulbransen and Andrew[3] shows that the hydride reaction at 300°C obeys the square root of pressure law, and that therefore the rate determining step is diffusion of hydrogen monatomically into the zirconium lattice. If diffusion is assumed to be controlling in the temperature range of our investigation, nonhomogeneity in hydrogen concentration during reaction would be expected. Because of differences in the physical properties (density, yield strength, coefficient of expansion, etc.) as related to hydrogen concentration, stresses induced in the metal during hydriding and heating and cooling can lead to physical breakdown of the product. Scheele and Burger,[1] however, examined the interior and exterior of a rod sample for uniformity of hydriding and found the hydrogen content to be the same. This does not preclude the existence of nonhomogeneity during reaction.

Reaction at higher temperature appears to cause less physical degradation and may be due to stress relieving as suggested by Scheele and Burger.[1] In addition, the equilibrium hydrogen pressure is significantly increased at the higher temperature, especially at the higher H/Zr atom ratios, and would lead to suppression of higher H/Zr atom ratio product formation at the surface. The diffusion and initial reaction in the interior of the metal on the other hand should be



Zirconium-Hydrogen Phase Diagram

Pressure-Composition Isotherms (Composite Data)

Figure 5. Phase diagram and pressure composition isotherms for the zirconium-hydrogen system.(2)

enhanced at the higher temperature. Thus, the overall effect would be a more uniform formation of hydride and less induced stress. With sponge the diffusion distance in the metal is greatly reduced and there is therefore less of such an effect.

B. Rehydriding of Zirconium Sponge

Two sponge samples were hydrided, dehydrided and then rehydrided several times to a H/Zr atom ratio of approximately 1.9. Sample 15b lost 9 mg of the original 2.3648 g after five cycles and some air darkening and brittleness was observed. Sample 17a had no significant weight change after four cycles and broke into several pieces.

These results suggest that zirconium sponge be considered as a candidate material for retrievable tritium storage, despite some evidence of physical degradation.

C. Hydriding of Titanium

Titanium sponge and rod samples were hydrided and the results are given in Table 5. Longer reaction times were required in comparison with zirconium to achieve comparable hydrogen-to-metal (H/M) atom ratios. For sponge at 500°C, a 29 minute reaction time was required for a H/M ratio of 1.40 (sample 35a), and 77 minutes for a H/M atom ratio of 1.79 (sample 35d). At a higher temperature (550°C), a longer, rather than shorter, reaction time was required probably because of the high equilibrium hydrogen pressure at that temperature. Titanium rod required 445 minutes at 600°C for ratios of 1.44 and 1.16, probably for the reason just given, as well as because of its form. In general, the specimens remained intact and less brittleness was observed when compared with zirconium.

D. Leach Testing

Leach tests were begun on tritiated zirconium and titanium hydrides under both static and dynamic conditions. Specimens were placed in 10-25 ml of distilled water in glass containers. Magnetic stirring bars were used to determine leach rates under dynamic conditions. In

TABLE 5

Experimental Hydriding of Titanium Sponge and Rod

Sample No.	Weight, g	Hydriding temp., °C	Hydriding press., torr Initial	Final	H/Ti atom ratio[(a)]	Time, min	Notes
			Sponge				
35a	1.0019	500	500	20	1.40	29	
35b	1.0064	500	500	18	1.44	30	
35c	1.0287	500	802	250	1.72	77	
35d	1.0144	500	801	202	1.79	77	
35e	1.0136	550	608	97	1.64	65	Tritiated
35f	1.0365	550	607	29	1.80	230	Tritiated
35g	1.0079	550	567	53	1.39	155	Tritiated
35h	1.0097	550	663	70	1.42	145	Tritiated
			Rod				
35i	1.2061	600	670	86	1.44	445	Tritiated
35j	1.0807	600	627	176	1.16	445	Tritiated
35k	1.1961	550	599	--	1.09	--	Tritiated
351	1.1966	550	605	--	0.86	--	Tritiated

(a) Atom ratio determined by weight gain.

both cases, 1 or 2 ml aliquots of leachant were removed at the end of the test period for sampling, filtering, and counting in a liquid scintillation counter. The leachant was not changed.

Leach rates for zirconium under static and dynamic conditions are given in Tables 6 and 7, respectively. The leach rates expressed as (cumulative fraction tritium release per day) x (V/S) ranged from 1.1 x 10^{-6} to 4.8 x 10^{-6} cm/day under static conditions and from 2.1 x 10^{-6} to 1.1 x 10^{-5} cm/day under dynamic conditions. The factor (V/S), where V is the specimen volume and S is its geometric surface area, is included so that the tritium release as expressed is independent of sample geometry and size. Zirconium sponge is irregularly shaped and quite porous and its (V/S) was conservatively estimated to be equivalent to a geometric cylinder of equal weight with a diameter of one half its length.

The total tritium activity in the zirconium hydride specimens used for static testing ranged from 10^4 to 10^5 counts per minute, and the total tritium activity was approximately ten times greater for the dynamic specimens, which, however, were leach tested for much shorter periods of time. The leachant tritium activity for both static and dynamic tests was barely above detectible limits and therefore a quantitative comparison and interpretation is difficult. Nevertheless, the data indicated that long term storage of tritium in zirconium in either solid or sponge form appears to be feasible.

Leach rates for titanium in distilled water under static conditions are given in Table 8. The (cumulative fraction tritium release per day) x (V/S) ranged from 2.2 x 10^{-7} to 1.7 x 10^{-6} cm/day, with two samples below the detectible limit and the remainder barely above the detectible limit. The titanium sponge is also irregularly shaped and porous and its (V/S) factor was conservatively estimated to be equivalent to that of a 1/16 inch cube-shaped geometric solid. The leach rates for titanium appear to be at least as good as they are for zirconium.

E. Engineering Scale Studies

An engineering-scale study of the storage of waste tritium as a

TABLE 6

Static Leach Testing Zirconium in Distilled Water(a)

Sample No.	Form	H/Zr atom ratio	Cumulative fraction tritium release rate, day^{-1}	V/S, cm	(Cumulative fraction tritium release rate) x (V/S), cm/day
20b	Sponge	1.99	3.1×10^{-5}	0.095(b)	2.9×10^{-6}
20e	Sponge	1.98	2.5×10^{-5}	0.095(b)	2.4×10^{-6}
20m	Sponge	1.65	4.8×10^{-5}	0.099(b)	4.8×10^{-6}
20n	Sponge	1.99	2.2×10^{-5}	0.113(b)	2.5×10^{-6}
28e	Sponge	1.54	1.3×10^{-5}	0.132(b)	1.7×10^{-6}
24c	¼" Rod	0.81	0.9×10^{-5}	0.127	1.1×10^{-6}
24e	½" Rod	0.84	1.6×10^{-5}	0.104	1.6×10^{-6}

(a) Leach time period of 74-116 days.

(b) V/S for sponge estimated to be equivalent to a geometric cylinder of diameter one half the length and of equal weight.

TABLE 7

Dynamic Leach Testing of Zirconium in Distilled Water[a]

Sample No.	Form	H/Zr atom ratio	Cumulative fraction tritium release rate, day^{-1}	V/S, cm	(Cumulative fraction tritium release rate) x (V/S), cm/day
30a	Sponge	1.06	1.8×10^{-5}	0.144[b]	2.5×10^{-6}
30b	Sponge	1.01	1.4×10^{-5}	0.134[b]	1.9×10^{-6}
30c	Sponge	0.91	1.6×10^{-5}	0.134[b]	2.1×10^{-6}
30d	Sponge	1.03	2.5×10^{-5}	0.132[b]	3.3×10^{-6}
33a	¼" Rod	0.93	4.7×10^{-5}	0.127	6.0×10^{-6}
33b	½" Rod	1.15	7.8×10^{-5}	0.126	9.8×10^{-6}
33c	¼" Rod	0.85	8.1×10^{-5}	0.123	1.0×10^{-5}
33d	¼" Rod	1.00	9.0×10^{-5}	0.126	1.1×10^{-5}

---

[a] Leach time period of 15-17 days.

[b] V/S for sponge estimated to be equivalent to a geometric cylinder of diameter one half the length and of equal weight.

TABLE 8

Static Leach Testing of Titanium in Distilled Water[a]

Sample No.	Form	H/Zr atom ratio	Cumulative fraction tritium release rate, day^{-1}	V/S, cm	(Cumulative fraction tritium release rate) x (V/S), cm/day
35e	Sponge	1.64	8.4×10^{-6}	0.026[b]	2.2×10^{-7}
35f	Sponge	1.80	5.2×10^{-5}	0.026[b]	1.4×10^{-6}
35g	Sponge	1.39	1.7×10^{-5}	0.026[b]	4.4×10^{-7}
35h	Sponge	1.42	(c)	0.026[b]	(c)
35i	Rod	1.44	1.5×10^{-5}	0.111	1.7×10^{-6}
35j	Rod	1.16	9.5×10^{-6}	0.106	1.0×10^{-6}
35k	Rod	1.09	9.6×10^{-6}	0.104	1.0×10^{-6}
35l	Rod	0.86	(c)	0.110	(c)

(a) Leach time period of 26 days.

(b) V/S for sponge estimated to be equivalent to a 1/16 inch geometric cube.

(c) Below detectable limits.

tritide in a metal hydride is underway. In this process, concentrated tritium effluent, such as from the Mound Laboratory isotope exchanger, is reacted with metal such as zirconium to form a stable tritide-hydride compound suitable for disposal at burial sites or for storage in a retrievable form for use such as in controlled thermonuclear reactors. The developmental work at BNL, however, will be limited to operation with tracer quantities of tritium.

In the engineering scale flowsheet (see Figure 6), a feed stream of H_2 or HT is regulated by a flow rate controller provided with a flow integrator. The pressure is monitored by gauges and pressure transducers (maximum design pressure: 100 psig). A vacuum system consisting of a cold trap, diffusion pump, and mechanical pump capable of producing a vacuum level of 10^{-4} to 10^{-5} torr is provided for outgassing the reaction metal and removal of trace quantities of oxygen, which has an inhibiting effect on the tritide-hydride reaction. The reaction vessel (see Figure 7) is approximately 3 inches in diameter and 19 inches high and is provided with a porous metal filter to prevent discharge of reaction product fines. An electric heater clamped externally to the vessel is used to provide an operating temperature up to 600°C. Temperatures in the reactor are monitored externally and also internally with a centerline thermowell. The reaction metal will be placed in a wire mesh basket inside the reactor to permit optimum positioning for temperature control and measurement, and also to avoid expansion problems that can result from hydride formation. The vessel can be charged with one individual rod or sponge specimen up to its maximum capacity of approximately 5 kg of metal.

Construction of the engineering scale equipment has been completed and testing has been started prior to operation.

II. POLYMER IMPREGNATED TRITIATED CONCRETE (PITC)

A. Lysimeter Testing of PITC Specimens

The Savannah River Plant (SRP) suggested that specimens containing one to ten curies of tritium would provide adequate detectibility in

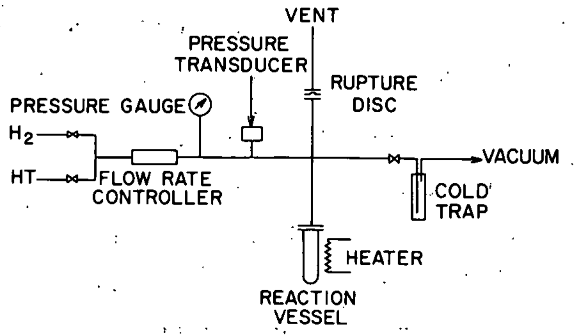


Figure 6. Tritium storage in metal hydride - engineering scale flowsheet.

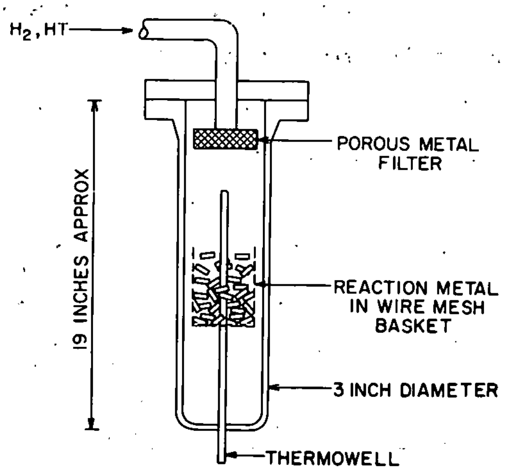


Figure 7. Metal hydride reaction vessel.

lysimeter testing and that a specimen size of one cubic foot would be convenient. Because of the low rate of tritium release expected in the lysimeter testing of PITC, ten curies of tritium were added to each specimen. The specimens were prepared in five gallon (0.67 ft^3) screw-top polyethylene carboys. The containers represented a standard size that was easily obtainable; this size was acceptable to SRP.

The size of the specimen and its container were not compatible with the end-over-end drum tumbling technique[4] being developed for large scale PITC composites. It was determined that a conventional dough type mixer (Blakeslee model B-20) when used with a water to cement ratio of 0.22 produced a product of similar density as that obtained by end-over-end tumbling with the same water to cement ratio. Since the resultant polymer loading in a homogeneous cement casting using soak impregnation is dependent upon the initial density, the PITC specimens produced by this method are representative of the product produced by end-over-end tumbling.

The amount of water necessary to give a water to cement ratio of 0.22 for each cement casting was determined. Two milliliters of tritiated water with a specific activity of 5 Ci/ml were added to this water to provide a tritium content of ten curies for each specimen. The water was added to portland type III cement and mixed until a uniform consistency was obtained. The cement mix was transferred to a five gallon polyethylene carboy which was vibrated to provide proper packing of the mix. The carboy was sealed and placed in an oven for five days at 40°C to ensure complete curing of the cement.

After removal from the oven, the casting was allowed to equilibrate to room temperature before polymer impregnation. The soak impregnation technique developed at BNL was employed, in which sufficient monomer is introduced into the void space above the specimen in its container and allowed to soak into the concrete. The specimen was impregnated with styrene monomer containing 0.5 wt.% AIBN (2, 2' - [Azobis-2-methylpropionitrile]) as a polymerization catalyst. After addition of the monomer, the carboy was sealed and the monomer allowed to soak into the concrete overnight. The carboy containing the tritiated concrete was then placed into an oven at 65°C over the weekend for polymerization of the monomer. Subsequent to the equilibration of the PITC to room temperature, the polyethylene carboy was sliced away. Four polymer impregnated tritiated concrete specimens were prepared by this technique.

Table 9 lists the formulational data for the four PITC specimens sent to SRP for lysimeter testing. Each specimen contained ten curies of tritium. The specimen geometry is cylindrical with approximate dimensions of 27 cm diameter x 28 cm for a composite volume of 0.566 ft^3. The tritiated concrete had a density of 91.5 ± 0.3 lb/ft^3. Impregnation produced PITC specimens with a density of 106.6 ± 0.2 lb/ft^3 and a polymer loading of 16.5 ± 0.3%.

The four PITC specimens shipped to SRP were buried without containers in individual lysimeters as shown in Figure 8. Each lysimeter consists of a steel tank 1.83 m in diameter and 3.05 m deep which was buried in the ground with its open top approximately 15 cm above the soil surface. The PITC specimen was buried 1.5 m below the soil surface and approximately 1.2 m above the bottom of the lysimeter using SRP soil excavated during placement of the steel tank. Rain falling on the exposed soil at the lysimeter surface permeates the soil, contacts the PITC specimen, and accumulates in a gravel layer on the sloping bottom of the lysimeter. A pump is used to collect the percolate water. After the initial time required for soil saturation, percolate water was collected weekly with volume and tritium concentration data compiled.

The tritium concentration in the air above the lysimeter was also measured periodically. This required the placement of a cover on the open top of the lysimeter for approximately 24 hours. Figure 9 shows the lysimeter with the top cover in place. Air was collected and passed first through a Linde* 4A molecular sieve trap to retain tritium oxide (HTO) and then through palladium coated Linde 4A molecular sieve to collect elemental tritium (HT) that passed through the first trap.

---

* Union Carbide Corporation, New York

TABLE 9

Formulational Data for PITC Specimens for Lysimeter Testing at SRP

Specimen Number	Formulation, Wt.% Cement	Formulation, Wt.% Water	HTO Content ℓ/ft^3	Initial Mass, kg	Impregnated Mass, kg	Polymer Load, %
121-1	82.0	18.0	7.44	23.4	27.3	16.7
121-2	82.0	18.0	7.47	23.5	27.4	16.6
121-3	82.0	18.0	7.47	23.5	27.3	16.2
121-4	82.0	18.0	7.47	23.5	27.4	16.6

Each specimen contains ten (10) curies of tritium.

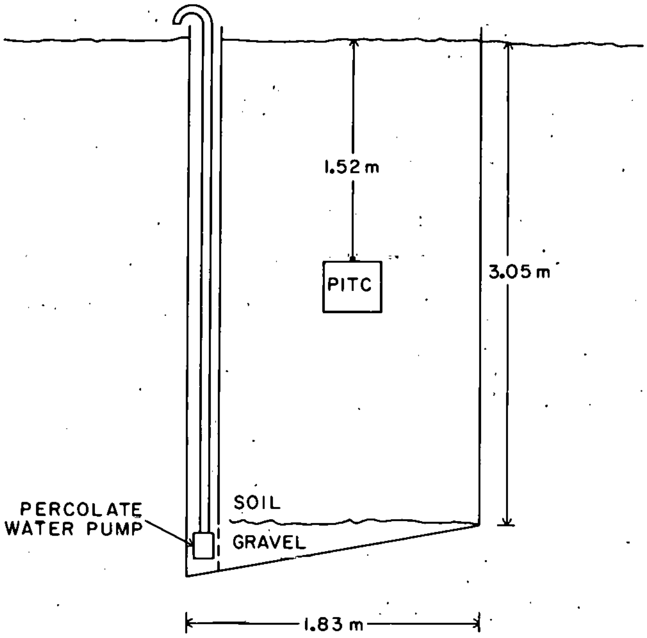


Figure 8. SRP test lysimeter for measurement of the rate of tritium release from polymer impregnated tritiated concrete (PITC).

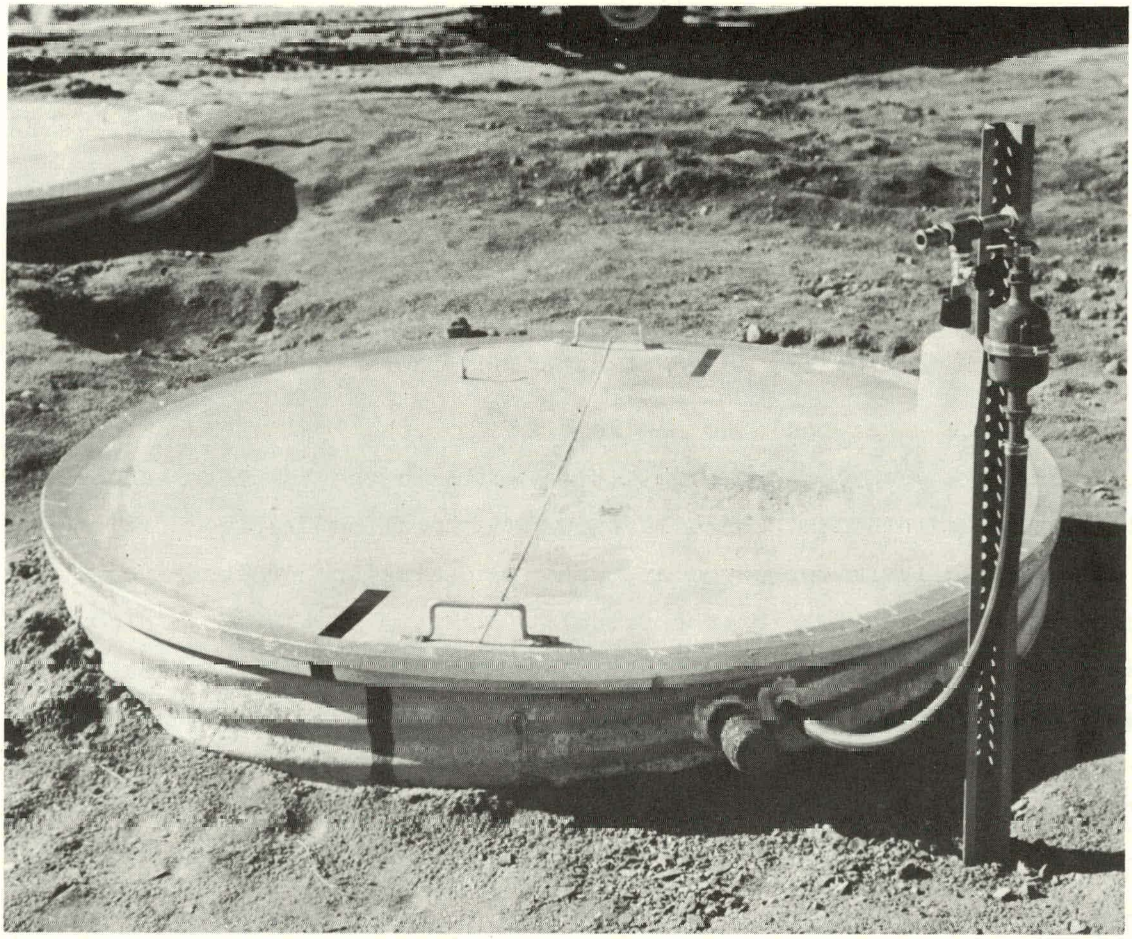


Figure 9. Lysimeter with top cover in place for air sampling.

The four test lysimeters are denoted NE, SE, SW, and NW according to their compass position and contain respectively specimens 121-1, 121-2, 121-4, and 121-3. The specimens were each set in a nylon sling, wrapped in a polyethylene bag, and placed into a 30 gallon drum for shipment to SRP. Vermiculite was poured into the space between the drum and the polyethylene bag containing the sample. An air sampling valve and pressure gauge were mounted on the drum head, however, no pressurization occurred. Figure 10 shows one of the PITC specimens being lowered into its lysimeter. After it was placed in the lysimeter, the nylon sling was removed, and the specimen was then covered with soil. Additional soil is added if settling occurs in the lysimeter.

Percolate water could not be removed from the lysimeters before the fourteenth week; prior to this time, soil in the lysimeter absorbed all incident rainfall. Figure 11 shows the total cumulative tritium release in the lysimeter percolate water for sixty two weeks since burial after correction for the percolate tritium content from a control lysimeter. The cumulative rainfall after the first fourteen weeks is also shown in this figure. No tritium content in the air was noted for either the specimen or control lysimeters and as such, subsequent references to tritium release are understood to refer to tritium in the percolate water. The initial tritium releases are seen to be very low. This may be partially an artifact due to channeling of water down the sides of the lysimeter which otherwise might have been absorbed in the soil.

The tritium releases from the lysimeters have been averaged in Figure 12 and expressed as (cumulative fraction tritium release) x (V/S) where V is the specimen volume and S is its geometric surface area. The factor (V/S) is included so that the tritium release as expressed is independent of sample geometry and size for leach times which are short relative to total tritium release. The lysimeter test specimens exhibit a (V/S) ratio of 4.545 cm; for comparison,

Figure 10. PITC specimen being lowered into lysimeter.

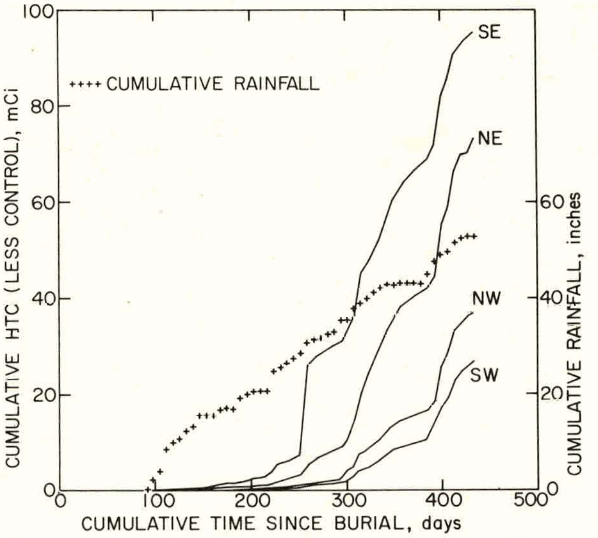


Figure 11. Cumulative tritium release and rainfall for the SRP lysimeters.

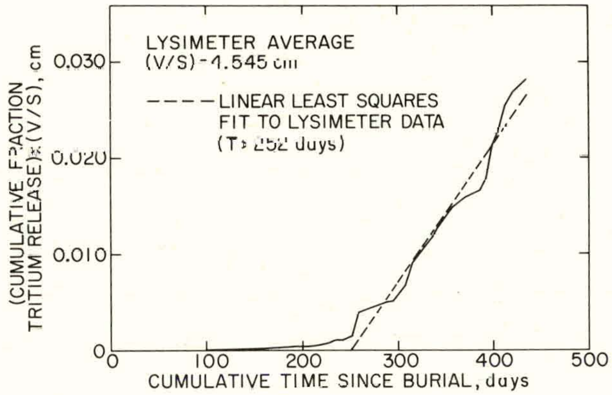


Figure 12. (Cumulative fraction tritium release) x (V/S) versus time since burial, lysimeter average.

(V/S) for a thirty gallon drum is approximately 9.0 cm. Regression analysis of the average data obtained after the thirty sixth week provides a linear least squares fit with a slope of 1.43×10^{-4} cm/day corresponding to a daily fraction tritium release rate of 3.5×10^{-5}. In Figure 13, this least squares fit is expressed as:

$$(\Sigma a_n/A_o)\ (V/S) = 5.23\text{x}10^{-2}\ t\ (yr) - 3.58\text{x}10^{-2},\ \text{cm}$$

thus giving a slope expressed as cm/yr while the second term implies that this rate of release began after 250 days and no prior tritium release occurred. This projects a complete tritium release after 87.6 years. When this release is corrected for decay, it is seen that the maximum fraction of the initial contained tritium which appears in the environment is 7.2% after 17.7 years from the beginning of the initial tritium release.

The tritium releases projected have been for the lysimeter average with 0.566 ft^3 specimens (V/S = 4.545 cm) with no container. Figure 14 projects the cumulative tritium release corrected for decay for 30 gallon drum size waste forms (V/S = 9.0 cm) as a function of container lifetime. A fraction tritium release rate of $5.23\ \text{x}10^{-2}$ cm/yr is assumed. The maximum quantity of tritium present in the environment appears 17.7 years after container failure. This fraction of the initially contained tritium is 2.15×10^{-2}, 1.22×10^{-2}, 2.24×10^{-3}, and 1.33×10^{-4} for container lifetimes of 10, 20, 50, and 100 years.

B. Static Leach Testing of the Lysimeter Duplicate Specimen

A PITC specimen (without container) of the same dimensions and formulation as those in lysimeter testing at SRP is in static leaching in distilled water at BNL. This specimen which also contains ten curies of tritium had a density of 95.4 lbs/ft^3 prior to impregnation and 107.7 lbs/ft^3 afterwards for a polymer loading of 12.9%. The lower polymer loading in this specimen as compared to the lysimeter test specimens results from the higher initial density of the concrete (due to more vibratory tamping) and a minimization of polymer on the upper surface of the composite. Leach testing was performed by immersing the specimen

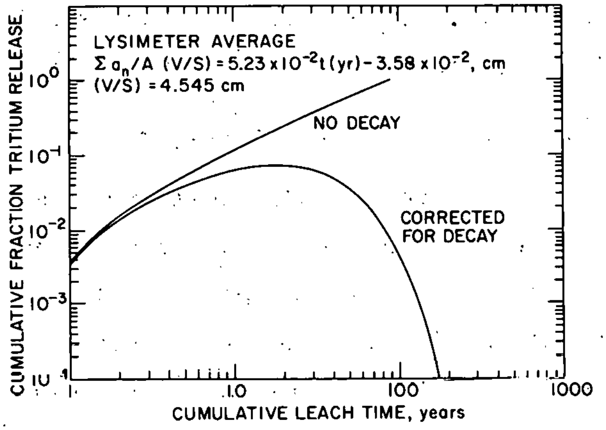


Figure 13. Projected cumulative fraction tritium release with time, based on the test lysimeter average rate of release.

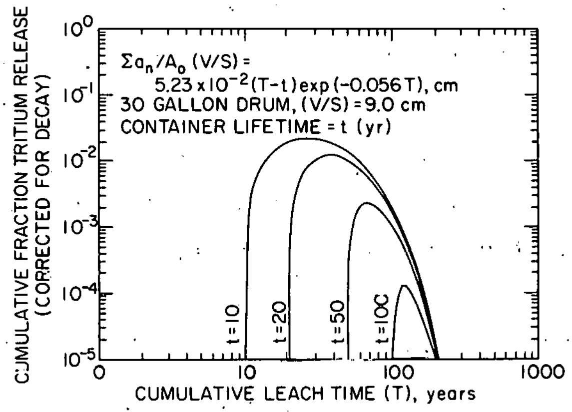


Figure 14. Projected cumulative fraction tritium release for PITC in containers with finite lifetimes.

without a container in 40 liters of distilled water such that all surfaces were exposed to the leachant. The leachant was not changed; one cm^3 was taken during sampling for analysis by liquid scintillation counting. The results after 386 days of leaching are shown in Figure 15. The rate of release is approximately linear with a slope of 3.18×10^{-2} cm/yr. A complete release after 143 years is projected as indicated in Figure 16. When corrected for decay, it becomes apparent that the maximum fraction of the initially contained tritium appearing in the environment is 4.55×10^{-2} after 17.7 years.

C. Preparation of PITC by the Injector Technique

While the end-over-end drum tumbling method has been pursued to date and developed to a workable form, it is desirable to produce PITC by a technique which is more directly compatible with the glove box operations in use with high level tritiated aqueous waste. Such a technique using an injector to distribute the aqueous tritiated waste in dry cement is in development.

A schematic diagram of the injector technique is shown in Figure 17. In this process, the cement casting container is filled with dry cement and compacted by vibration. The injector, which is simply a hollow tube containing several orifices along its length through which the aqueous waste is dispersed, is inserted into the dry cement. Tritiated aqueous waste is then introduced into the cement through the injector. Aqueous waste is added to the cement until the waste reaches the external surfaces of the cement as evidenced by dampness. The injector is withdrawn and the cement casting is allowed to cure. After the casting has cured, catalyzed styrene monomer is introduced into the casting container and allowed to soak through the composite. After the casting has been completely permeated by the monomer, the monomer is thermally polymerized. Subsequent to the waste injection, this process is the same as the previously developed end-over-end drum tumbling method.

As shown in Figure 18, this process does not produce a homogeneous composite. Rather the aqueous waste content is higher near the centerline

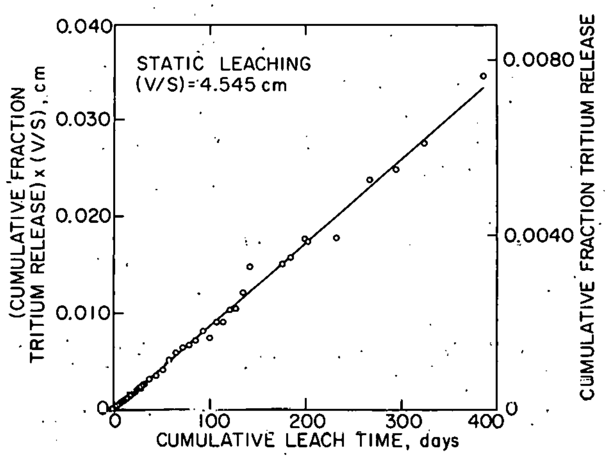


Figure 15. (Cumulative fraction tritium release) x (V/S) versus leach time for static leaching of the lysimeter test duplicate specimen.

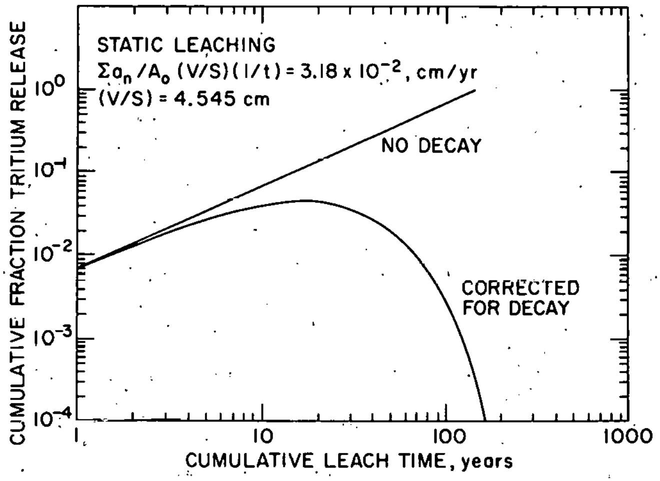


Figure 16. Projected cumulative fraction tritium release with time for static leaching of the lysimeter test duplicate specimen.

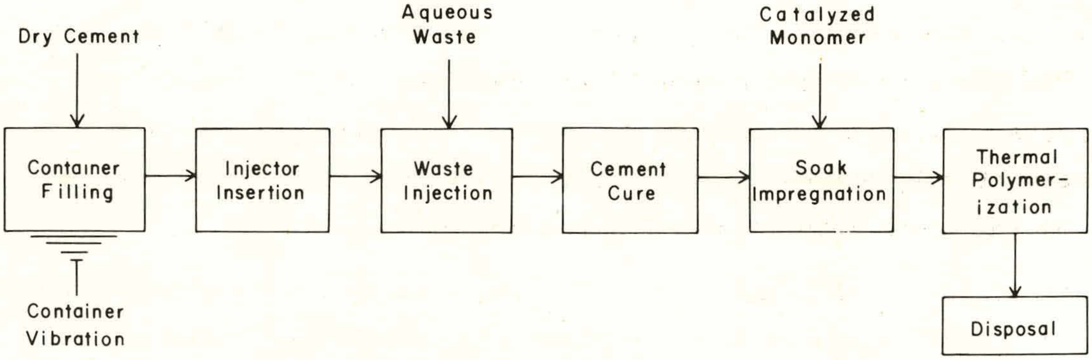
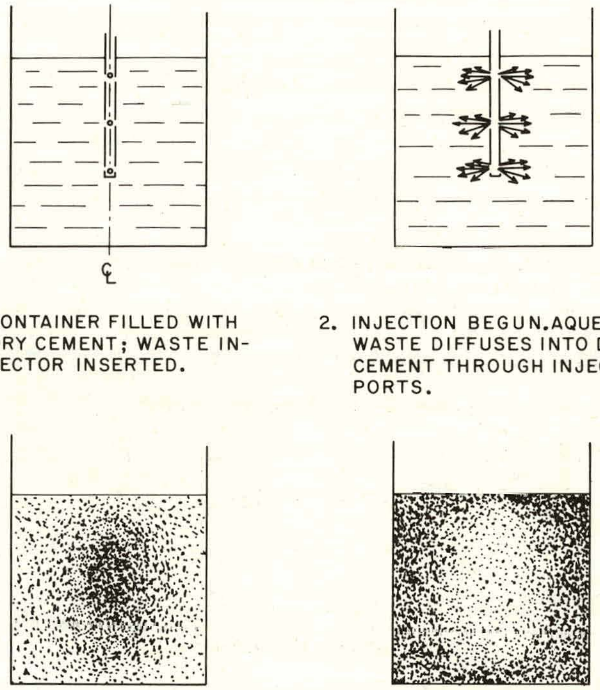


Figure 17. Conceptual fixation of aqueous waste in polymer impregnated concrete by the injector technique.



1. CONTAINER FILLED WITH DRY CEMENT; WASTE INJECTOR INSERTED.

2. INJECTION BEGUN. AQUEOUS WASTE DIFFUSES INTO DRY CEMENT THROUGH INJECTOR PORTS.

3. AQUEOUS WASTE DIFFUSES THROUGH THE CEMENT. THE WASTE CONTENT IN THE CEMENT DECREASES AS THE CASTING SURFACES ARE APPROACHED.

4. AFTER IMPREGNATION, THE POLYMER LOADING OF THE COMPOSITE IS HIGHEST AT THE CASTING SURFACES, EFFECTIVELY ENCAPSULATING THE WASTE. POLYMER IS PRESENT THROUGHOUT THE COMPOSITE.

Figure 18. Fixation of aqueous waste in polymer impregnated concrete by the injector technique.

of the composite coincident with the injector and decreases as the surface is approached. The polymer loading, however, is highest near the surfaces of the composite and decreases as the centerline is approached, although polymer is present throughout the composite. This effectively encapsulates the waste. An apparatus for producing PITC by this technique is shown in Figure 19.

Prior to the preparation of PITC specimens by the injector technique for leach testing in distilled water and leach testing at SRP two specimens were made with nontritiated water to establish a procedure.

The "cold" prototype specimens were cast in five gallon screw top autoclavable polypropylene carboys similar to the carboys used previously for preparation of specimens for lysimeter testing at SRP. For each of the two specimens, 19.2 kg of dry portland type III cement was compacted for ten minutes with a vibrator. Water was fed into the center of the cement through a vertical glass injector tube (1.2 cm I.D.) with the end fused down to a 1/16 inch diameter opening and positioned five inches from the bottom of the carboy. In addition, two sets of four 1/16 inch diameter openings equidistant about the circumference were located one inch apart with the lower set one inch above the bottom of the tube. A total of 4.23 kg of water in each specimen to give a water to cement ratio of 0.22 was fed in at a rate of approximately 44 ml/min. After completion of water injection, the injector was withdrawn and the cement was cured over a five day period in an oven set at 40^{o}C. The specimens were then cooled to room temperature and impregnated with styrene monomer catalyzed with AIBN (2,2' - [azobis-2 methylpropionitrile]) by overnight soaking. Polymerization then took place in an oven set at 65^{o}C. Specimen I was catalyzed with 0.5 wt.% AIBN for comparison with specimen 2, for which 1.0 wt.% AIBN was used.

On initial visual inspection after removal from the carboy container, the external polymer surface of specimen 2 appeared to be less opaque and slightly harder (see Figure 20). Examination eight weeks later indicates that no cracking has occurred on either

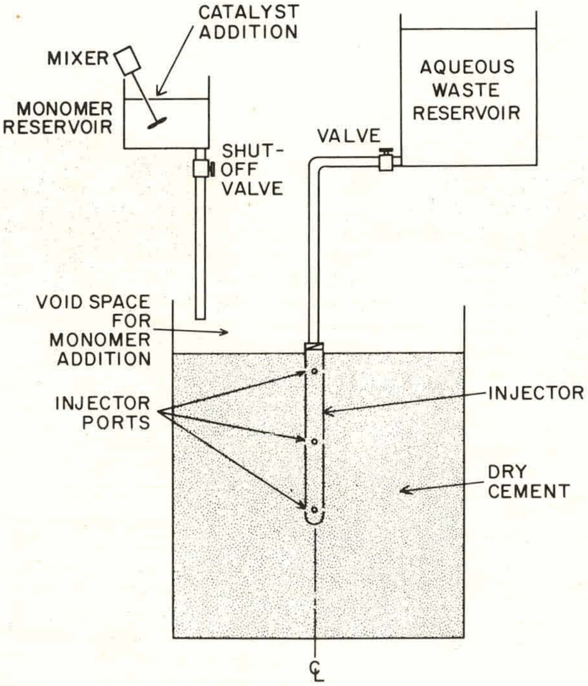


Figure 19. Injector technique for the fixation of aqueous wastes in polymer impregnated concrete.

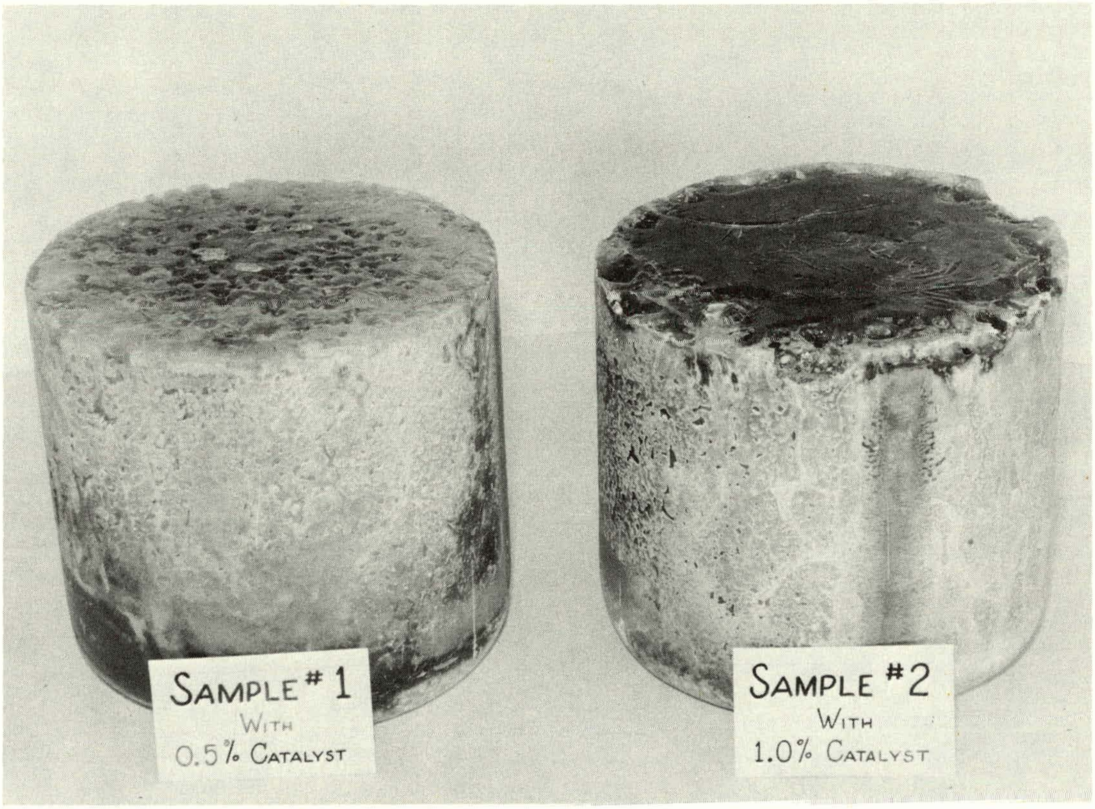


Figure 20. Prototype specimens for leach testing prepared with 0.5% and 1.0% AIBN Catalyst.

specimen. Both specimens measured 28 cm in diameter with an average height of 26.3 cm, representing a volume of 0.572 ft^3 each. The composite densities for specimens 1 and 2 were both 90.4 lb/ft^3 prior to impregnation and 112.5 and 112.4 lb/ft^3, respectively, after impregnation, corresponding to polymer loadings of 24.5% and 24.3%, respectively. These polymer loadings do not represent optimum values, since excess polymer was present on top of both castings.

Two specimens for leach testing in distilled water were prepared with tritium labeled water that provided an activity level of 4.6 Ci for each specimen. The procedure described previously was used to prepare specimens T1 and T2 that were impregnated with polystyrene containing 0.5 and 1.0 wt.% AIBN, respectively, having densities after impregnation of 110.7 and 111.9 lb/ft^3, respectively, corresponding to polymer loadings of 22.5 and 23.8%, respectively. The composite measurements and densities prior to impregnation were identical to the previous two specimens. Static leach testing in distilled water will be initiated.

References

1. R. D. Scheele and L. L. Burger, "Zirconium Hydride as a Storage Medium for Tritium", BNWL-2083, July 1976.

2. R. L. Beck and W. M. Mueller, "Zirconium Hydrides and Hafnium Hydrides", in Metal Hydrides, edited by W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, Academic Press, pp 241-335, 1968.

3. E. A. Gulbransen and K. F. Andrew, "Kinetics of the Reactions of Zirconium with O_2, N_2 and H_2", Metals Transactions, Vol. 185, pp 515-525, 1949.

4. Colombo, P., et al., The Fixation of Aqueous Tritiated Waste in Polymer Impregnated Concrete and in Polyacetylene, BNL 20898, Brookhaven National Laboratory, Upton, New York, October 1975.

DISTRIBUTION LIST

B.C. Musgrave
Allied Chemical Corporation
550 Second Street
Idaho Falls, Idaho 83401

A.K. Williams
Allied General Nuclear Services
Barnwell, South Carolina 29812

Martin Steindler
Argonne National Laboratory
9700 South Cass Avenue, Bldg. 205
Argonne, Illinois 60439

L.E. Trevorrow
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

R.I. Newman, Vice President
Barnwell Nuclear Fuels Plant
Allied-Gulf Nuclear Services
P.O. Box 847
Barnwell, South Carolina 29812

L.L. Burger
Battelle Northwest Laboratories
325 Building
Richland, Washington 99352

Victor Benaroya, Chief
Effluent Treatment Systems Branch
Directorate of Licensing
Department of Energy
Washington, D.C. 20545

F.E. Coffman
Division of Operational Safety
Department of Energy
Washington, D.C. 20545

John C. Dempsey
Development Branch
Division of Nuclear Fuel Cycle and Prod.
Department of Energy
Washington, D.C. 20545

W.H. McVey, Chief
Fuel Cycle Branch
Division of Reactor Research
and Development
Department of Energy
Washington, D.C. 20545

N. Thomasson
Environmental Protection Agency
401 M Street, S.W., Room 910
Washington, D.C. 20460

L.T. Lakey
Exxon Nuclear Company
2101 Horn Rapids Road
Richland, Washington 99352

G. Winsor
Manager Safety and Analytical Ser.
Midwest Fuels Recovery Plant
Morris, Illinois 60450

M. Barbier
Mitre Corporation
1820 Dolly Madison Avenue
McLean, Virginia 22101

George Abell
Monsanto Research Corporation
Mound Laboratory
Miamisburg, Ohio 45352

C.J. Kershner
Monsanto Research Corporation
Mound Laboratory
Miamisburg, Ohio 45352

Emil Mershad
Monsanto Research Corporation
Mound Laboratory
Miamisburg, Ohio 45352

C.A. Burchsted
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, Tennessee 37830

DISTRIBUTION LIST (Continued)

Herschel W. Godbee
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, Tennessee 37830

E.H. Kobish
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, Tennessee 37830

K.H. Lin
Oak Ridge National Laboratory
P.O. Box X
Oak Ridge, Tennessee 37830

E.C. Choi
Ontario Hydro
700 University Avenue
Toronto, Ontario
M5G1X6 Canada

R.H. Hawkins
Savannah River Laboratory
Bldg. 735A, Room B123
Aiken, South Carolina 29801

D.A. Orth
Savannah River Laboratory
Bldg. 773-A, Room 117
Aiken, South Carolina 29801

D.T. Pence
Science Applications, Inc.
1200 Prospect Street
P.O. Box 2361
La Jolla, California 92038

J.J. Cohen
University of California, Lawrence
P.O. Box 808
Livermore, California 94550

BROOKHAVEN NATIONAL LABORATORY DISTRIBUTION

B. Manowitz
M. Steinberg
P. Colombo
R. Johnson
R. Neilson, Jr.
W. Becker
L. Belkin - DOE
D. Schweller - DOE