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RFP--5263

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PLUTONIUM SOLUTION STORAGE IN PLASTIC BOTTLES: OPERATIONAL EXPERIENCE AND SAFETY ISSUES

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RFP-5263
~~LSP-95-001~~

March 15, 1995

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EXECUTIVE SUMMARY

When plutonium operations at the Rocky Flats Environmental Technology Site were curtailed in December of 1989, a large number of plastic bottles containing plutonium solution were in storage. These bottles were being stored until the solutions could be processed. The bottles of plutonium solution were stored in gloveboxes and 55 gallon drums. The bottles stored in gloveboxes were vented, but the bottles stored in drums were sealed. When operations were curtained, there were over twenty 55 gallon drums containing plutonium solution stored in sealed plastic bottles.

The drums were stored for between 3 and 6 years before plans could be developed for safely opening the drums and sufficient glovebox space was available for storing the bottles. Most of the drums were opened in Building 771, but one drum was opened in Building 779. The drum opened in Building 779 contained 3 bottles of plutonium chloride solution and 2 of the bottles had failed and were leaking. The first 2 drums opened in Building 771 were opened to remove bottles containing >5 g/l plutonium solution. Some of the bottles removed from these 2 drums showed signs of having been pressurized. The bottles containing <5 g/l were left in these 2 drums until sufficient glovebox space was available for storing the bottles.

When sufficient glovebox space was available for storing the bottles contained in 55 gallon drums, a total of 23 drums were opened in Building 771 and the bottles were placed in gloveboxes and vented. When the drums were opened, 24 percent of the bottles were found to be pressurized. Of the 286 bottles removed from the drums opened in Building 771, 3 bottles showed signs of leakage and 3 of the bottles had definitely failed and leaked. Environmental stress cracking was identified as the failure mechanism for the three bottles that definitely failed and leaked.

Some of the vented bottles stored in gloveboxes degraded with time and the solutions from these degraded bottles were transferred to new bottles. These degraded bottles had been used to store strong nitric acid solutions. Examination of the bottles revealed that the bottle degradation was probably caused by the strong oxidizing acid. One vented polypropylene bottle failed while being moved inside of a glovebox. This bottle was very brittle and the bottle shattered when struck against the floor of the glovebox. Additional polypropylene bottle failures occurred in the Building 771 analytical laboratories. A vented polyethylene bottle failed while being moved inside a glovebox. This bottle contained 7 N nitric acid solution and the bottle failed in an area where the wall thickness was only half the normal wall thickness.

Several types of materials are used to manufacture bottles used to store plutonium solutions at Rocky Flats. These materials are low density polyethylene, high density polyethylene and polypropylene. Low density polyethylene appears to be the best material for bottles used to store plutonium solutions. Polypropylene does not appear to be a suitable material for bottles used to store plutonium solutions.

Pressurization of sealed bottles containing plutonium solution is caused by gas generated from radiolysis of the solution. Radiolysis of aqueous plutonium solutions will produce hydrogen and oxygen. Radiolysis of plutonium nitrate solutions will also produce nitrogen oxides. Most of the gas produced from aqueous plutonium solutions is generated from radiolysis of water in the solutions. The rate of gas generation from plutonium nitrate solutions decreases as the solution normality increases and the ratio of water to nitric acid decreases.

Computer spread sheet models were developed to gain a better understanding of the factors that lead to pressurization and failure of plastic bottles containing plutonium solutions. These models were developed using data obtained from the literature on gas generation rates for plutonium solutions. Leak rates from sealed plastic bottles were obtained from bottle leak tests conducted at Rocky Flats. Results from these bottle leak tests showed that narrow mouth four liter bottles will seal much better than wide mouth four liter bottles. The gas generation rate and leak rate data were used to develop models for predicting the rate of pressurization and maximum pressures expected in sealed bottles of plutonium solution containing various plutonium and acid concentrations.

The computer models were used to develop proposed time limits for storing or transporting plutonium solutions in sealed plastic bottles. For plutonium solutions containing <1.5 g/l, maximum safe storage times from 4 weeks to 12 months are proposed. The maximum safe storage times vary depending upon the plutonium concentration in the solution. Low concentration plutonium solutions can be stored safely for longer periods of time than high concentration plutonium solutions. For solutions containing >1.5 g/l plutonium, storage in sealed bottles should not be allowed. However, transportation of higher concentration plutonium solution in sealed bottles is required, and safe transportation times of 1 shift to 6 days are proposed.

Based upon the information contained in this report, the following recommendations are made.

1. Storage of plutonium solutions in sealed plastic bottles should not be encouraged as a routine practice.

2. If storage or transportation of plutonium solutions in sealed plastic bottles is required, the safe storage or transportation times proposed in this report should be followed.

3. Polypropylene bottles should not be used to store plutonium solutions.

4. Vented plastic bottles of plutonium solution stored in gloveboxes should be inspected periodically, because even vented bottles can eventually fail.

1.0 INTRODUCTION

When plutonium operations at the Rocky Flats Environmental Technology Site (the Site) were curtailed in December of 1989, a large number of plastic bottles containing plutonium solution were in storage. These bottles were being stored until the solutions could be processed. Some of these bottles were stored in gloveboxes, but there were over twenty 55 gallon drums containing plutonium solution stored in sealed bottles. Sufficient glovebox space was not available for storing all the bottles, and plans had to be developed to safely open the drums.

The drums were opened after being stored for 3 to 6 years and the bottles were removed, placed in gloveboxes, and vented. Some of these bottles were found to be pressurized and a few of the bottles had failed and were leaking. Solution from one of the failed bottles had leaked through both bags used to package the bottle, through the single drum liner bag and onto the rigid drum liner.

Vented plastic bottles containing plutonium solutions have been stored in gloveboxes at the Site for over 5 years. These bottles contain a variety of solutions, including strong nitric acid solutions. Some of these bottles have degraded and some of the bottles have failed.

Information on the pressurized bottles removed from 55 gallon drums has been assembled and analyzed. Information obtained from examination of the degraded and failed bottles has also been assembled and analyzed. Failure mechanisms were identified for the failed and degraded bottles. Mechanisms that result in bottle pressurization were identified and bottle leak rate tests were conducted to determine how well plastic bottles will seal. Leak rate tests were conducted on both narrow mouth and wide mouth plastic bottles.

Computer spread sheet models were developed to gain a better understanding of the factors that lead to bottle pressurization. Spread sheet models were developed to predict the rate of gas generation in plutonium solutions and to predict the leak rate from sealed plastic bottles. These spread sheet models were used to predict the rate of bottle pressurization and the maximum pressure expected in sealed bottles.

Storing plutonium solutions in sealed plastic bottles is not a good practice because of the potential for bottle pressurization and failure. However, there are circumstances that require the sealing of plastic bottles containing plutonium solution. The computer spread sheet models developed to predict gas generation and bottle pressurization rates were used to develop proposed safe storage and bottle transportation time limits.

2.0 OPERATIONAL EXPERIENCE

The 55 gallon drums containing stored bottles of solution were equipped with drum-vent filters assemblies, but the bottles were not vented. Most of these bottles contained solutions generated in the analytical laboratories, and these solutions are identified as Item Description Code (IDC) 541, Analytical Lab. Solution. A few of the bottles contained IDC 503 (Misc. Acid Waste, Plutonium) or IDC 508 (Acid Chloride Waste) solutions generated from research and development projects. Most of the bottles from the analytical laboratories contained plutonium in mixed nitric, hydrochloric acid solutions, but a few of the bottles contained uranium solution. All of these bottles contained approximately 4.2 liters of solution.

The 55 gallon drums containing sealed bottles of plutonium solution could not be opened until procedures were developed for opening the drums in a safe manner. The first drum was opened in Building 779 and this drum contained three 1-liter bottles of plutonium chloride solution. The plutonium concentrations in these solutions were 21.15, 17.16, and 27.55 g/l. These bottles were packaged with two plastic bags and the double bagged bottles were placed in "clam shell" containers. A clam shell is a seven-inch diameter by 14 inch tall polyethylene container with threads in the middle of the container. These bottles had been in storage for four years when the drum was opened in January 1992. One of these bottles was intact and there was no sign of leakage from this bottle. The second bottle had failed and solution had leaked into the second plastic bag surrounding the bottle. The third bottle had also failed and solution had leaked through both plastic bags, but the solution was contained by the clam shell. A crack was observed in one of the leaking bottles and the other leaking bottle was mushy on one side and rigid on the other side.

The next two drums were opened in Building 771 to remove bottles containing >5 g/l Pu solutions. The first drum opened, drum number D72507, contained four bottles of solution. Two bottles contained >5 g/l Pu solution and the other two bottles contained solutions that were 0.25 g/l Pu. This drum was not properly packaged and all four bottles of solution were laying on their sides.[1] The two bottles removed from drum D72507 contained 8.73 and 17.15 g/l Pu. Both bottles contained low normality (1.5 and 1.86 N H^+) solutions that were high in chloride ion (52.9 and 74.1 g/l Cl^-). Both bottles showed signs of having been pressurized, the bottoms of the bottles were rounded, and both bottles were hard and no longer pliable. The other two bottles in this drum did not show any signs of leaks or free liquid, but the outer containment bags on both bottles were contaminated.

The second drum, drum number D71529, did not contain any pressurized or leaking bottles, but information of interest was obtained when this drum was opened. During removal of the lids from these two drums, a Hydrogen Explosive Meter was used to determine the percentage of the Lower Explosive Level (LEL) of hydrogen inside the drums. The meter reading obtained when opening drum number D72507 was 0%. When drum number D71529 was opened, the meter indicated a reading of less than 2% of LEL. However, when the meter was placed further into the drum, a reading of 26% of LEL was recorded. After several bottles were removed from the drum, the meter reading dropped to less than 2% of LEL.

The readings obtained from the Hydrogen Explosive Meter were not quantitative since the hydrogen would diffuse rapidly out of the drum once the lid was removed. However, these readings can be used as a qualitative indication of the hydrogen content of the drums. The readings indicate that hydrogen is being produced in the bottles and is diffusing and/or leaking out of the bottles. However, the low hydrogen concentration readings indicate that the drum vents were working and not allowing hydrogen to accumulate in the drums.

When the two drums were opened in Building 771 to remove the >5 g/l Pu bottles, sufficient glovebox space was not available for storing all of the bottles. The bottles containing <5 g/l Pu were left in the drums until sufficient glovebox space was available for storing all of the bottles. However, the drums were renumbered and D72507 became D78741 and D71529 became D78727. When sufficient glovebox space was available for storing bottles, a total of 23 drums were opened in Building 771. The bottles were removed from the drums, placed in gloveboxes and vented. These 23 drums included the two drums which had been opened previously for removal of the >5 g/l Pu bottles.

The procedures developed for safely opening the 23 drums contained forms for recording observations on the condition of the plastic bottles. The forms from these procedures were collected and the information compiled and analyzed. The information recorded on the forms was based upon visual observations and, therefore, is qualitative in nature. However, analysis of the information has resulted in some valuable conclusions.

The first 10 drums of bottles were opened in September and October of 1992 and these drums had been in storage for 3 to 4 years. The last 13 drums were opened during December 1993 through March 1994. These drums had been in storage for 5 to 6 years. During removal of the lids from the drums, a Hydrogen Explosive Meter was again used to determine the percentage of the LEL of hydrogen inside the drum. The meter readings obtained when opening the first ten drums varied from 0 to 7 percent and the readings obtained when opening the last 13 drums varied from 0 to 22 percent.

Some of the bottles removed from these 23 drums were identified as being pressurized by the personnel opening the drums and a few of the bottles had failed and/or leaked. A listing of the drums is given in Table 1. The number of pressurized and leaking bottles is noted in the table. As the data in Table 1 show, 12 of the drums contained pressurized bottles, and 6 of the drums contained bottles which definitely had leaked or showed signs of possible leakage. Of the 286 bottles contained in these 23 drums, 68 of the bottles (24 percent) were identified as being pressurized.

2.1 PRESSURIZED BOTTLES

Bottles were noted as being pressurized if the bottom of the bottle was visibly deformed. The bottoms of pressurized bottles were bowed from 1/4 to 3/8 inch. Since identification of pressurized bottles relied upon visual observation of bottle deformation, bottles not identified as being pressurized could have contained some pressure, but the pressure was not sufficient to cause visible deformation of the bottle. A listing of the bottles identified as being pressurized is given in Table 2.

Table 1

Listing of Drums Opened

DRUM NUMBER	ORIGIN OF DRUM	NUMBER OF PRESSURIZED BOTTLES	NUMBER OF LEAKING BOTTLES
D729212905082	BUILDING 559	0	0
D653802904566	BUILDING 559	0	0
D728152905084	BUILDING 559	0	0
D539332904826	BUILDING 559	8	0
D729142905087	BUILDING 559	2	0
D710462904835	BUILDING 559	7	0
D715302904999	BUILDING 559	8	0
D710402905259	BUILDING 559	4	1
D787272904933	BUILDING 559	6	0
D722562905264	BUILDING 559	0	0
D647572904460	BUILDING 559	0	0
D663162904677	BUILDING 559	5	0
D670882904641	BUILDING 559	5	1
D679352905027	BUILDING 559	0	0
D680972904825	BUILDING 559	9	1
D704662904824	BUILDING 559	0	0
D715252905269	BUILDING 559	0	0
D722462905090	BUILDING 559	0	1
D730772905258	BUILDING 559	6	1
D733112905268	BUILDING 559	5	0
D775380261942	BUILDING 771 (1)	1	1
D7737502	BUILDING 771 (1)	0	0
D7874101	BUILDING 771 (1)	0	0

(1) The bottles in these drums contained IDC 508 and IDC 503 solutions.

Table 2

Pressurized Bottle Information

DRUM NUMBER	BOTTLE NUMBER	GENERATION POINT	WASTE TYPE	H+	CHLORIDE g/l	Pu g/l	DATE GENERATED
D539332904826	49185	C-12	Ga WASTE	0.325	11.70	1.25	8/02/89
	49212	C-12	Ga WASTE	0.375	10.20	1.12	8/14/89
	49208	C-13	Pu ASSAY WASTE	1.80	6.73	1.10	8/10/89
	49184	C-13	Pu ASSAY WASTE	1.85	6.73	1.12	8/01/89
	49193	C-13	Pu ASSAY WASTE	1.70	6.02	1.05	8/03/89
	49195	C-08	Ga WASTE	0.35	14.50	0.899	8/04/89
	49181	C-13	Pu ASSAY WASTE	1.75	5.60	1.05	7/28/89
	49188	C-13	Pu ASSAY WASTE	1.75	6.30	0.885	8/2/89
D729142905087	60947	C-13	Pu ASSAY WASTE	1.83	7.45	1.33	10/19/89
	60946	C-13	Pu ASSAY WASTE	1.65	6.03	1.27	10/18/89
D710462904835	49269	C-13	Pu ASSAY WASTE	1.75	15.20	1.14	8/28/89
	49285	C-13	Pu ASSAY WASTE	1.90	6.74	1.25	9/06/89
	49287	C-13	Pu ASSAY WASTE	2.00	7.45	1.19	9/06/89
	49286	C-13	Pu ASSAY WASTE	1.80	6.38	1.38	9/06/89
	49257	C-08	Ga WASTE	0.40	5.32	2.29	8/23/89
	49274	C-13	Pu ASSAY WASTE	1.90	6.38	1.23	8/31/89
	49280	C-13	Pu ASSAY WASTE	1.60	6.03	1.11	9/01/89

Table 2 (Continued)

Pressurized Bottle Information

DRUM NUMBER	BOTTLE NUMBER	GENERATION POINT	WASTE TYPE	H+	CHLORIDE g/l	Pu g/l	DATE GENERATED
D715302904999	51610	C-13	Pu ASSAY WASTE	2.10	7.44	1.38	9/20/89
	51607	C-12	Ga WASTE	0.40	12.80	1.42	9/16/89
	51608	C-13	Pu ASSAY WASTE	1.97	7.44	1.30	9/19/89
	49300	C-13	Pu ASSAY WASTE	2.02	7.09	1.30	9/15/89
	49294	C-13	Pu ASSAY WASTE	1.90	7.09	1.23	9/12/89
	49297	C-13	Pu ASSAY WASTE	2.10	7.80	1.44	9/14/89
	49292	C-13	Pu ASSAY WASTE	1.93	7.09	1.18	9/11/89
	49290	C-13	Pu ASSAY WASTE	1.88	6.73	1.20	9/7/89
D710402905259	49218	C-13	Pu ASSAY WASTE	1.90	5.60	1.17	8/15/89
	49227	C-13	Pu ASSAY WASTE	1.95	7.09	1.21	8/18/89
	49223	C-13	Pu ASSAY WASTE	2.02	8.15	1.29	8/17/89
D787272904933	49293	C-12	Ga WASTE	0.28	14.20	1.11	9/12/89
	49296	C-12	Ga WASTE	0.35	15.60	1.24	9/13/89
	60919	C-08	Ga WASTE	0.28	8.15	1.29	10/9/89
	60942	C-08	Ga WASTE	0.375	17.40	1.11	8/18/89
	60904	C-12	Ga WASTE	0.30	8.51	1.33	9/20/89
	60937	C-08	Ga WASTE	0.30	12.80	1.26	10/17/89

Table 2 (Continued)

Pressurized Bottle Information

DRUM NUMBER	BOTTLE NUMBER	GENERATION POINT	WASTE TYPE	H+	CHLORIDE g/l	Pu g/l	DATE GENERATED
D663162904677	58727	C-12	Ga WASTE	0.27	15.80	1.27	1/12/89
	58794	C-08	Ga WASTE	0.35	7.09	1.47	2/7/89
	6010	C-08	Ga WASTE	0.30	11.35	1.54	2/13/89
	6013	C-17	U ASSAY WASTE	2.15	10.00	0.609	2/15/89
	6015	C-08	Ga WASTE	0.36	12.94	1.34	2/15/89
D670882904641	58790	C-13	Pu ASSAY WASTE	1.65	6.74	1.40	2/2/89
	6007	C-13	Pu ASSAY WASTE	1.60	7.45	0.993	2/13/89
	6008	C-13	Pu ASSAY WASTE	1.63	6.30	1.23	2/13/89
	6009	C-13	Pu ASSAY WASTE	1.73	6.56	1.02	2/13/89
	6014	C-13	Pu ASSAY WASTE	1.65	6.03	0.979	2/15/89
D680972904825	49113	C-40	SPECIAL PROJECTS	1.63	2.90	0.206	6/21/89
	49139	C-12	Ga WASTE	0.28	14.18	1.11	6/23/89
	49164	C-08	Ga WASTE	0.43	16.66	1.42	7/19/89
	49173	C-08	Ga WASTE	0.55	25.80	1.32	7/24/89
	49178	C-08	Ga WASTE	0.38	16.60	0.959	7/27/89
	49180	C-40	SPECIAL PROJECTS	1.65	5.15	1.98	7/28/89

Table 2 (Continued)

Pressurized Bottle Information

DRUM NUMBER	BOTTLE NUMBER	GENERATION POINT	WASTE TYPE	H+	CHLORIDE g/l	Pu g/l	DATE GENERATED
D680972904825	49187	C-08	Ga WASTE	0.42	11.70	1.17	8/2/89
	51968	C-40	SPECIAL PROJECT	2.05	12.00	0.796	4/12/89
D730772905258	60964	M-20	X-RAY FLUORESCENCE	N/A	27.60	0.292	10/23/89
	63403	C-13	Pu ASSAY WASTE	0.80	8.51	1.00	11/30/89
	63404	C-13	Pu ASSAY WASTE	0.93	9.57	1.29	11/30/89
	63433	C-13	Pu ASSAY WASTE	0.90	7.09	1.06	12/02/89
	63436	C-13	Pu ASSAY WASTE	0.85	6.74	1.33	12/02/89
	63449	C-13	Pu ASSAY WASTE	0.83	6.74	0.960	12/04/89
D733112905268	60945	C-13	Pu ASSAY WASTE	2.08	7.80	1.30	10/18/89
	62862	C-12	Ga WASTE	0.20	12.40	1.486	11/20/89
	62882	C-12	Ga WASTE	0.20	18.40	1.31	11/27/89
	62891	C-12	Ga WASTE	0.23	19.50	1.20	11/29/89
	63429	C-12	Ga WASTE	0.15	14.70	1.46	12/1/89

An analysis was conducted to determine if any differences could be identified between pressurized and non-pressurized bottles. The bottles which leaked were included with the pressurized bottles. The factors that were evaluated were plutonium concentration, hydrogen ion concentration, chloride ion concentration and the point of origin. The results of this analysis are given in Table 3, and they show that, for the factors that were evaluated, the only significant differences between the bottles that were pressurized and the bottles that were not pressurized were plutonium concentration and point of origin. The average plutonium concentration in the pressurized bottles was 1.26 g/l. The average plutonium concentration in the non-pressurized bottles was 1.06 g/l and the average plutonium concentration in all the bottles was 1.11 g/l.

Of the bottles that were pressurized, 19.1 percent were generated in glovebox C-08 in Building 559, whereas only 9.6 percent of the non-pressurized bottles and 11.9 percent of all the bottles were generated in box C-08. Additional analysis of the data showed that 38.2 percent of the bottles generated in glovebox C-08 were pressurized. A summary of the percent of pressurized bottles by point of origin is given in Table 4.

Glovebox C-08 in Building 559 was used for determining the gallium content of plutonium metal. The analysis was performed by dissolving plutonium metal in hydrochloric acid (HCl). A reagent solution mixture containing aqueous sodium acetate, aqueous citric acid, and oxine dissolved in methanol was added to the HCl solution. The oxine complexed any gallium present and the gallium/oxine complex was extracted from the solution using chloroform. The methanol used as a solvent for oxine would remain in the aqueous solution. The radiolytic gas yield from methanol is higher than the radiolytic gas yield from water. Therefore, for bottles with the same plutonium content, the gas generation rate in bottles of solution from box C-08 would be higher than the gas generation rate in bottles of solution from other sources. This higher gas generation rate could explain why a higher percentage of bottles from box C-08 were pressurized.

Glovebox C-12 in Building 559 was also used for gallium analysis. A review of the data in Table 3 shows that 17.7 percent of the pressurized bottles were from box C-12, where as, 19.3 percent of the non-pressurized bottles and 18.9 percent of all bottles were generated in box C-12. Additional analysis of the data (see Table 4) showed that 22.2 percent of the bottles from box C-12 were pressurized. A reason for the difference in percent of pressurized bottles from boxes C-08 and C-12 could not be determined.

The other point of origin that showed a high percentage of pressurized bottles was glovebox C-17 in Building 559. Only 4 bottles of solution were generated from box C-17, but 100 percent of these bottles were either pressurized or the bottles had failed. A more complete discussion of the bottles generated in box C-17 is presented in the next section.

Table 3

Comparison of Pressurized and Non-Pressurized Bottles

CHARACTERISTIC EVALUATED		PRESSURIZED BOTTLES (1)	NON-PRESSURIZED BOTTLES	ALL BOTTLES
GENERATION POINT	C-08	19.12%	9.63%	11.89%
	C-12	17.65%	19.27%	18.88%
	C-13	50.00%	50.92%	50.70%
	C-17	5.88%	0.00%	1.40%
	OTHER	7.35%	20.18%	17.13%
PLUTONIUM CONCENTRATION, g/l	MINIMUM	0.0043	0.00	0.00
	MAXIMUM	4.86	1.99	4.86
	AVERAGE	1.26	1.06	1.11
SOLUTION NORMALITY	MINIMUM	0.15	0.0001	0.0001
	MAXIMUM	7.4	9.0	9.0
	AVERAGE	1.31	1.25	1.26
CHLORIDE CONCENTRATION, g/l	MINIMUM	2.90	0	0
	MAXIMUM	281	191	281
	AVERAGE	14.33	15.37	15.12

(1) Includes bottles which failed

Table 4

SUMMARY OF BOTTLE POINT OF ORIGIN AND PRESSURIZATION

POINT OF ORIGIN	PERCENT OF BOTTLES PRESSURIZED (1)
C-08	38.24
C-12	22.22
C-13	23.45
C-17	100.00
OTHER	17.13

(1) Includes bottles which failed

2.2 LEAKING AND FAILED BOTTLES

Of the 286 bottles that were removed from the 23 drums, two bottles showed signs of leakage, one bottle had a hole in the lid of the bottle, and three of the bottles had definitely failed. Information on the leaking and failed bottles is given in Table 5. One bottle which showed signs of leakage was bottle number 5142 from drum number D77538. The exact origin of this solution is unknown, but the solution is categorized as IDC 508. The bottle was observed to be pressurized when it was removed from the drum, and moisture was observed in the bags used to package the bottle.

The other bottle which showed signs of leakage was bottle number 49141 from drum number D68097. This bottle contained IDC 541 solution, and the bottle was generated in box C-17 in Building 559. This bottle, and two of the other bottles in this drum, had been over filled. The solution in this bottle was up into the threaded portion of the neck. Therefore, there was almost no free volume in this bottle. The bottom of this bottle was observed to be slightly bulged, and moisture was observed in the plastic bags used to package the bottle. The lid on this bottle was noted as being loose, which appears to be in direct contradiction to the observation that the bottom of the bottle was bulged. However, a conversation with D. J. Pretty, 771/774 Operations, revealed that the bottom of the bottle was definitely bulged, because the bottom of the bottle relaxed and became flat after the bottle was vented. The drum that contained this bottle had the highest hydrogen concentration of any of the 23 drums opened (22 % of LEL), and 9 of the 14 bottles in this drum were pressurized. The lids on two of the other bottles in this drum were observed to be loose, and the tape used to tape the lids to the bottles had deteriorated on all of the bottles. All of the bags used to package the bottles in this drum were contaminated, and the rigid liner was contaminated.

Bottle number 63402 from drum number D73077 was generated in box C-13 in Building 559. A small quantity of solution was observed in the bagout bag containing this bottle. The lid on this bottle had a small (~1/8 inch diameter) hole in the center of the lid. The solution observed in the bagout bag probably leaked out of the hole in the lid during drum movement operations.

The first bottle observed to have definitely failed was bottle number 49225 in drum number D71040. This bottle was generated in box C-08 in Building 559. The bottle was found to be leaking, and approximately 1/3 of the contents of the bottle had leaked into the plastic bag containing the bottle. The bag was pressurized, but no liquid had escaped from the bag. This bottle was bagged into a glovebox and the solution in the bag and bottle transferred into a new bottle. The failed bottle was examined by Tom Hergert and Dick Saiki of the Materials and Surface Technologies (MST) group.[2] The examination revealed that the bottle had a crack approximately 1.5 inches long, located near the intersection of the mold parting line and the bottom rim of the bottle. The crack was longer on the inside surface of the bottle, and it was originally concluded that the bottle had been mechanically damaged at some point in time. However, this conclusion was changed after additional failed bottles were examined by MST personnel. Examination of additional failed bottles revealed

Table 5

Leaking Bottle Information

DRUM NUMBER	BOTTLE NUMBER	GENERATION POINT	WASTE TYPE	H+	CHLORIDE g/l	Pu g/l	DATE GENERATED
D710402905259	49225	C-08	Ga WASTE	1.70	34.70	0.736	8/17/89
D670882904641	58755	C-17	U ASSAY WASTE	1.50	14.37	4.17	1/13/89
D680972904825	49141	C-17	U ASSAY WASTE	1.95	6.26	4.86	6/23/89
D722462905090	51606	C-17	U ASSAY WASTE	2.50	8.46	0.534 (1)	9/15/89
D730772905258	63402	C-13	Pu ASSAY WASTE	0.80	6.74	0.90 (2)	11/30/89
D775380261942	5142	UNK	IDC 508	7.40	281	0.004 (3)	9/30/88

(1) Re-analysis of this solution showed a Pu concentration of 4.04 g/l.
(2) Bottle had small hole in lid.
(3) This bottle contains 5.75 g/l U.

that they had failed due to environmental stress cracking.[3] The intersection of the mold parting line and the bottom rim of a plastic bottle is an area of high stress. Chemical attack on this high stress area could have occurred, but the extent of chemical attack, if any, could not be determined. The bottle could have become pressurized and the pressure could have contributed to failure of the bottle. In any case, the MST personnel concluded that the bottle failed due to environmental stress cracking instead of mechanical damage as originally thought.

The second bottle that was observed to have definitely failed was bottle number 58755 from drum number D67088. This bottle was generated in box C-17 in Building 559. Approximately half of the contents of this bottle had leaked into the bags used to package the bottle, and a few drops of solution had leaked from the outer bag onto the cardboard spacer used to support the top layer of bottles. Examination of this bottle revealed that the bottle contained a gel type precipitate in the bottom of the bottle. An examination of the physical condition of this bottle was conducted by MST personnel.[3] This examination revealed a thin crack approximately 1/8 to 1/4 of an inch from the bottom of the bottle, parallel to the bottom rim and perpendicular to the mold parting line. This crack was discolored (brownish tint) and approximately 3-4 inches long. The crack started on the inside of the bottle and progressed to the outside of the bottle, with actual penetration of the outside wall occurring only in the middle of the crack. The MST personnel concluded that the bottle failure occurred primarily as a result of environmental stress cracking.

The third bottle that was observed to have definitely failed was bottle number 51606 from drum number D72246. This bottle was also generated in box C-17 in Building 559. Analysis of the original sample from this bottle indicated that the solution contained 0.534 g/l Pu. An orange colored, gelatinous precipitate was present in the bottom of the bottle, and reanalysis of the bottle contents showed that the plutonium content was much higher than the 0.534 g/l Pu originally reported. When the new sample was mixed to suspend the solids in the solution, a Pu concentration of 4.04 g/l Pu was obtained by X-ray analysis. When the sample was allowed to sit over night and only the supernatant liquid was sampled, a Pu concentration of 1.05 g/l was obtained by X-ray. All of the solution in this bottle had leaked out of the bottle, through both bags used to package the bottle, through the single drum liner bag and onto the rigid liner. Some of the solution also permeated the outer bags on two of the other bottles in the drum. These two other bottles were originally thought to have leaked, until it was discovered that the solution was only in the outer bags and no solution was present in the inner bags. Examination of the failed bottle by MST personnel revealed that this bottle had a crack in approximately the same location as the crack observed in bottle number 58755.[3] The failure mechanism for this bottle was probably the same as the failure mechanism identified for bottle number 58755.

Two of the bottles that definitely failed and one of the bottles that showed signs of leakage were generated in box C-17 in Building 559. Box C-17 was used for analysis of uranium in plutonium solutions, oxide, and metal. Box C-17 was also used for analysis of uranium in oils, sludges and other organics. The samples were prepared for analysis using various techniques, but in all cases, the uranium was extracted using a mixture of tributyl phosphate and isooctane to separate the uranium from plutonium prior to analysis using a laser fluorometer. It is possible that solutions generated in box C-17 contained small quantities of organic materials. However, these three bottles all contained high plutonium concentrations (>4 g/l), and the solutions were fairly low in hydrogen ion concentration (<2.5 N).

The gas generation rate in plutonium solutions is known to increase as the plutonium concentration increases and the hydrogen ion concentration decreases. The high gas generation rate from the solutions generated in box C-17 is the most probable cause for failure of these bottles. However, the fourth bottle of solution generated in box C-17 was pressurized, and this bottle was reported to contain only 0.6 g/l Pu. Other bottles of low plutonium concentration solution were also reported to be pressurized, but it is interesting that all of the bottles generated in box C-17 were either pressurized or had failed.

2.3 FAILED AND DEGRADED VENTED BOTTLES

As discussed previously, a few of the sealed plastic bottles removed from drums were found to have failed. Some vented plastic bottles stored in gloveboxes have also failed. One vented bottle failure occurred in September 1994 in Building 771. Low concentration (~0.2 g/l) plutonium nitrate solution was drained from tank number 467 and placed into 4 liter bottles inside a glovebox. During movement of one of the bottles, a large crack developed around the bottom portion of the bottle and the entire contents of the bottle emptied onto the floor of the glovebox.[4] During the inspection of the failed bottle, the bottle was struck against the floor of the glovebox and shattered into several pieces. Inspection of the failed bottle revealed that the bottle material was polypropylene. Conversations with Building 771 Analytical Laboratory personnel revealed that they had experienced similar failures with wide mouth, four liter polypropylene bottles.

Failure of another vented bottle also occurred in Building 771. The bottle (number 42048) contained low plutonium concentration (0.12 g/l), high normality (7 N) nitric acid solution. The solution was generated from experiments involving plutonium recovery from incinerator ash. The ash was dissolved in strong nitric acid and the dissolution filtrates were processed through an anion exchange column. The bottle had been in storage over 4 years. The bottle failed while being moved in a glovebox and most of the bottle contents spilled onto the glovebox floor. Examination of the bottle by MST personnel revealed a longitudinal crack at the bottom of the bottle extending approximately 4-5 inches.[3] The wall thickness in the failed area was only 0.040 to 0.050 inches. The wall thickness of a typical 4 liter, narrow mouth, polyethylene bottle is 0.080 to 0.110 inches. Environmental stress cracking was identified as the failure mechanism for this bottle. Chemical attack by the strong nitric acid on the thin area of the bottle may have contributed to the failure.

In addition to failed bottles, degraded bottles have also been found during routine inspection of bottles stored in gloveboxes. One of these bottles (number 44693) was observed in Building 771. This was a low density polyethylene bottle with a polypropylene lid. The bottle contained 4 liters of 1.91 g/l plutonium solution with a hydrogen ion concentration of 6.7 N and a chloride ion concentration of 7.54 N. This bottle had been in storage since October 1988. Examination of the bottle revealed multiple vertical surface cracks on one side of the bottle ranging in length from 1.5 to 6 inches.[5] The other side of the bottle showed no signs of degradation or cracking. The interior surface of the bottle above the liquid level showed severe blistering and the blisters contained free liquid. The MST personnel who inspected the bottle concluded that the damaged side of the bottle had probably been exposed to some sort of heat source.

Additional degraded bottles were also discovered in Building 771. These bottles were 2 liter wide mouth plastic bottles. An inspection of these six bottles was conducted by MST personnel.[6] Three of the bottles were manufactured from polypropylene, and two of these bottles were degraded. The first degraded polypropylene bottle, number 42070, contained 2.78 g/l plutonium solution with an acid concentration of 10.30 N and a chloride ion concentration of 0.50 g/l. This bottle had been stored for 5 years. The bottle was embrittled and multiple crack striations and "star" cracks were created when the bottle was flexed. The bottle lid was also embrittled and the lid cracked when flexed. The second bottle, number 42071, had also been stored for 5 years. This bottle contained 3.72 g/l plutonium solution with an acid concentration of 10.50 N and a chloride ion concentration of 0.35 g/l. Cracks were observed all the way through the bottle and the bottle lid was also embrittled. The third bottle, number 43863, had only been in service for a little over one year. This bottle was only moderately stiff and flexing of the bottle did not produce any cracks.

Of the other three bottles that were inspected, one bottle was high density polyethylene (HDPE) and the material of manufacture could not be determined for the other two bottles. The HDPE bottle, number 43830, contained 2.78 g/l plutonium in a 9.2 N nitric acid solution. This bottle had been in storage for 6 years, and both the inside of the bottle and bottle lid were embrittled. The bottle was very stiff and cracked during flexing, but none of the cracks penetrated completely through the wall of the bottle.

The first bottle of unknown material composition, number 43872, had been in storage for 5 years and contained 2.0 g/l plutonium solution. The bottle was very brittle and "star" cracks occurred when the bottle was flexed. The second bottle of unknown material composition, number 43924, contained 3.07 g/l plutonium solution with an acid concentration of 10.80 N and a chloride ion concentration of 1.06 g/l. This bottle had been in storage for 5 years and was relatively flexible. Only one area of this bottle showed signs of embrittlement after heavy flexing. However, the coating on the inside of the bottle lid had failed through delamination.

All six of these bottles contained strong nitric acid solution, and the five bottles that were embrittled had been in storage for 5 years. Both polyethylene and polypropylene are attacked by strong oxidizing acid like nitric acid. The plutonium concentrations in these solutions were relatively low. Therefore, radiolytic degradation of the plastic was probably not a significant factor in the deterioration of these bottles.

3.0 BOTTLE LEAK TESTS

Data obtained from opening drums containing sealed bottles of plutonium solution revealed that some of the bottles were pressurized. However, other bottles with similar chemical compositions were not visibly pressurized. All of the bottles removed from the drums were narrow mouth four liter plastic bottles. However, some degraded wide mouth plastic bottles stored in gloveboxes have also been found. In order to gain a better understanding of how well plastic bottles could be sealed, MST personnel were requested to perform leak rate tests on plastic bottles.[7] Tests were conducted using both wide mouth and narrow mouth four liter polyethylene bottles.

The wide mouth polyethylene bottle tests were all conducted using empty bottles. Tests were conducted with the lids tightened finger tight, and with lids tightened to 5 and 10 ft-lbs of torque. A torque of 5 ft-lbs was determined to be equal to the amount of torque an operator would use to tighten a lid prior to removing a bottle from a glovebox. At 10 ft-lbs torque, some distortion of the bottle threads occurred. The bottles were pressurized using helium gas, and the helium supply was then turned off. The pressure in the bottles was monitored to determine the rate of pressure decrease. An initial, or charged, pressure of 5 psig was used for the finger tight and 5 ft-lb torque tests, and a charged pressure of 25 psig was used for the 10 ft-lb torque tests. During pressurization of the bottles, MST personnel noted that the bottom of the bottles started to deform when the pressure reached 3 psig. At this pressure, the bottle bottoms bulged and assumed a convex shape. Between 3 and 5 psig, this deformation was measured at approximately 5/16 to 3/8 inch.

Test results revealed that wide mouth bottles with finger tight lids would not hold pressure. All of the pressure was relieved within a few seconds. Bottles with lids tightened to 5 ft-lbs torque held pressure for a longer period of time, but all the pressure was relieved after 48 hours. Some of the bottles tested with lids tightened to 10 ft-lbs torque still held some pressure after 48 hours, but the leak rate was still very rapid.

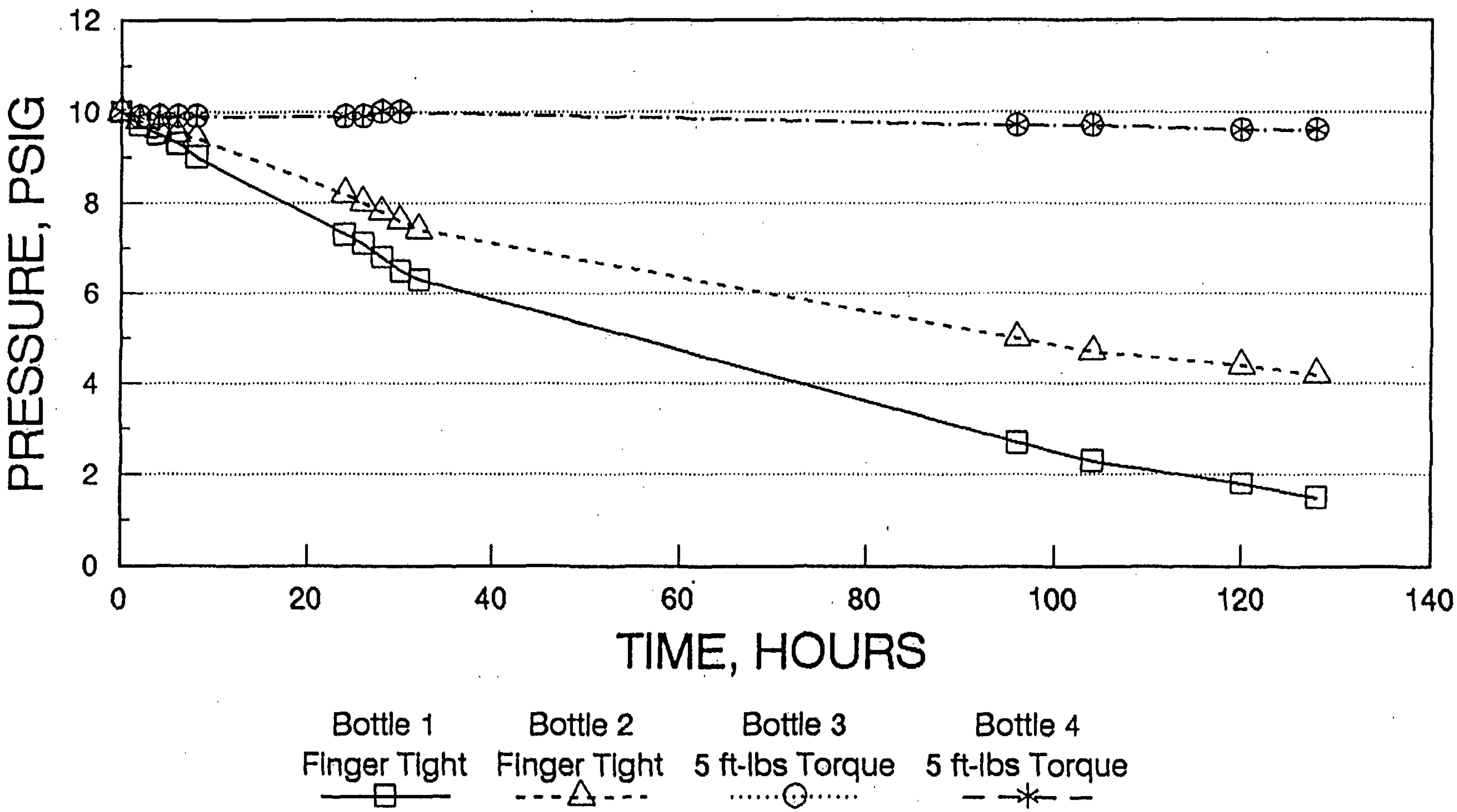
Tests with narrow mouth four liter bottles were conducted using empty bottles and bottles containing various quantities of water. All of the tests with narrow mouth four liter bottles were conducted using helium gas with a charged pressure of 10 psig. During bottle pressurization, MST personnel again noted the bottle deformation that was observed with the wide mouth bottles. The bottoms of the narrow mouth bottles bulged from 3/8 to 1/2 inch at pressures between 3 and 5 psig. Tests with empty bottles were conducted with finger tight lids (bottles number 1 and 2) and with lids tightened to 5 ft-lbs torque (bottles number 3 and 4).

Results from these tests are shown in Figure 1. As was expected, bottles with finger tight lids lost pressure much more rapidly than bottles with lids tightened to 5 ft-lbs torque. However, the narrow mouth bottles with both finger tight lids and lids tightened to 5 ft-lbs torque lost pressure at a much slower rate than was the case with wide mouth four liter bottles. Pressure in the narrow mouth bottles with lids tightened to 5 ft-lbs torque exceeded 9.5 psig five days after the test was started.

Figure 1

PRESSURE TEST RESULTS

EMPTY 4 LITER NARROW MOUTH BOTTLES



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Additional tests were conducted with four liter bottles containing 3.9 and 3.75 liters of water. These tests were all conducted with the bottle lids tightened to 5 ft-lbs torque, and the tests were run for longer time periods than those used for previous tests. Results from tests using bottles containing 3.9 liters of water are shown in Figure 2, and test results from bottles containing 3.75 liters of water are shown in Figure 3. The test results shown in Figures 2 and 3 show that there was a wide variation in leak rate from bottle to bottle. However, even the bottle with the highest leak rate (bottle number 8) contained over 3 psig pressure 20 days after the test was started.

4.0 DISCUSSION

Information obtained from opening 55 gallon drums containing sealed bottles of plutonium solution shows that sealed, narrow mouth 4 liter plastic bottles will become pressurized if they are stored for a sufficient period of time. This information also shows that some bottles will fail if the storage time is too long. Data obtained from the leak test experiments show that both narrow mouth and wide mouth four liter bottles will hold pressure. However, the leak rate for wide mouth bottles is much faster than the leak rate from narrow mouth four liter bottles. Information obtained from inspection of bottles in gloveboxes shows that even vented plastic bottles will fail eventually if the bottles are used to store strong oxidizing acid solutions.

Plastic bottles manufactured from three types of polyolefin resin are used at Rocky Flats; low density polyethylene, high density polyethylene and polypropylene. Experience with polypropylene bottles has not been good and polypropylene does not appear to be a suitable material for storing acidic plutonium solutions. Low density polyethylene appears to be the most suitable material for storing acidic plutonium solutions.

Plastic bottles have been used at Rocky Flats for over 30 years to store plutonium and uranium nitrate and chloride solutions. However, until operations were curtailed in December 1989, solutions were only stored in plastic bottles for relative short periods of time (up to 1 year). Since plastic bottles are now being used to store solutions for longer periods of time, some method for predicting safe storage times for solutions in plastic bottles is required. A computer spread sheet model was developed to predict gas generation rates from various types of solution. Models have also been developed to predict the rate of pressure increase in plastic bottles and the expected maximum pressure for various types of solution.

4.1 BOTTLE PRESSURIZATION MODEL DEVELOPMENT

Gas generation from plutonium nitrate solutions is caused by radiolysis of the solution and most of the gas is generated from radiolysis of water in the solutions.[8] Measurements of the rate of gas generation from plutonium nitrate solutions were performed at Hanford.[9] These measurements showed that the rate of gas generation from a plutonium nitrate solution decreased as the normality of the solution increased and the ratio of water to nitric acid decreased. The gas generation rates measured in the Hanford study are given in Table 6.

Figure 2

PRESSURE TEST RESULTS

NARROW MOUTH 4 LITER BOTTLES WITH 3.9 L WATER

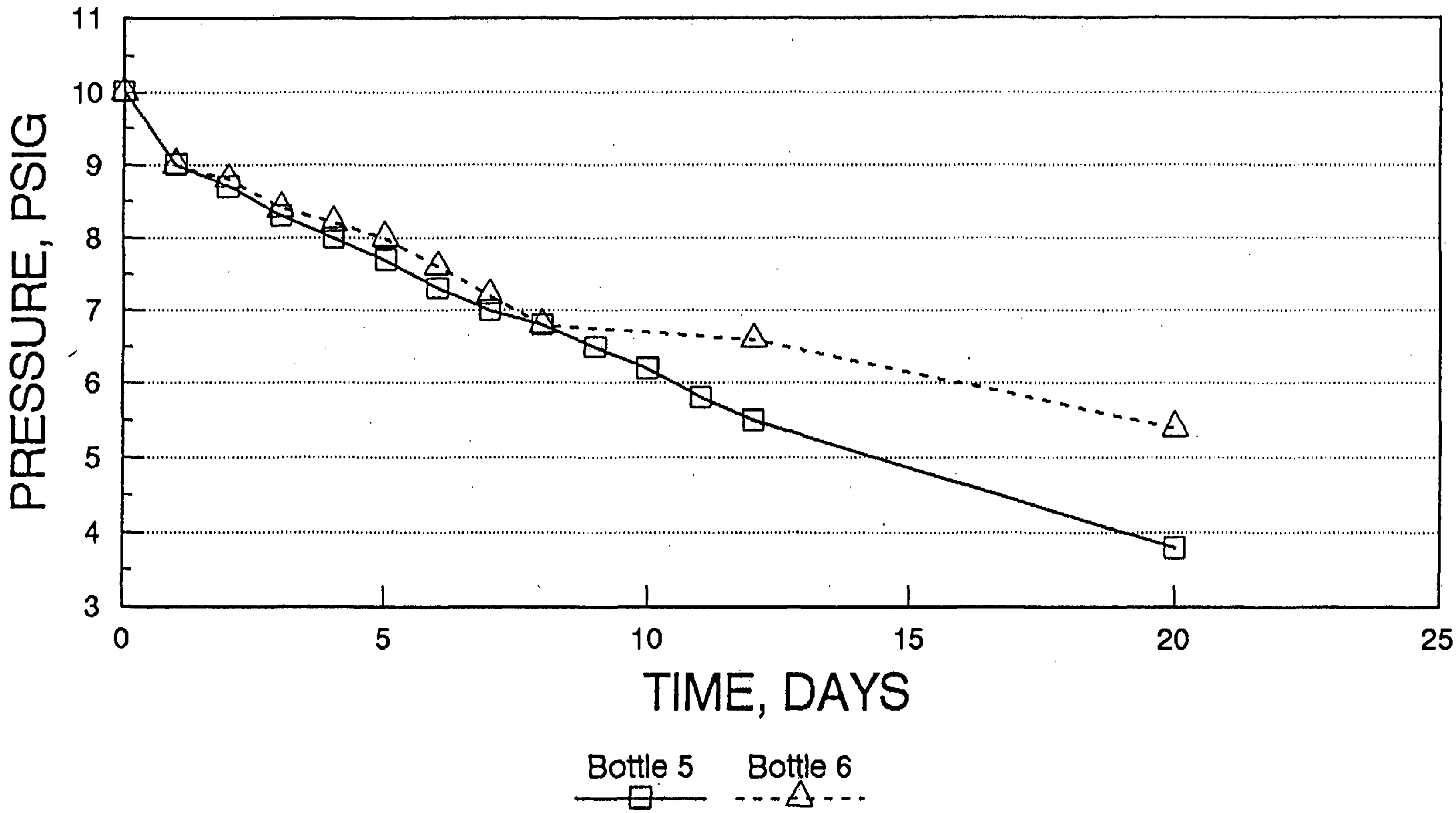

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Figure 3

PRESSURE TEST RESULTS

NARROW MOUTH 4 L BOTTLES WITH 3.75 L WATER

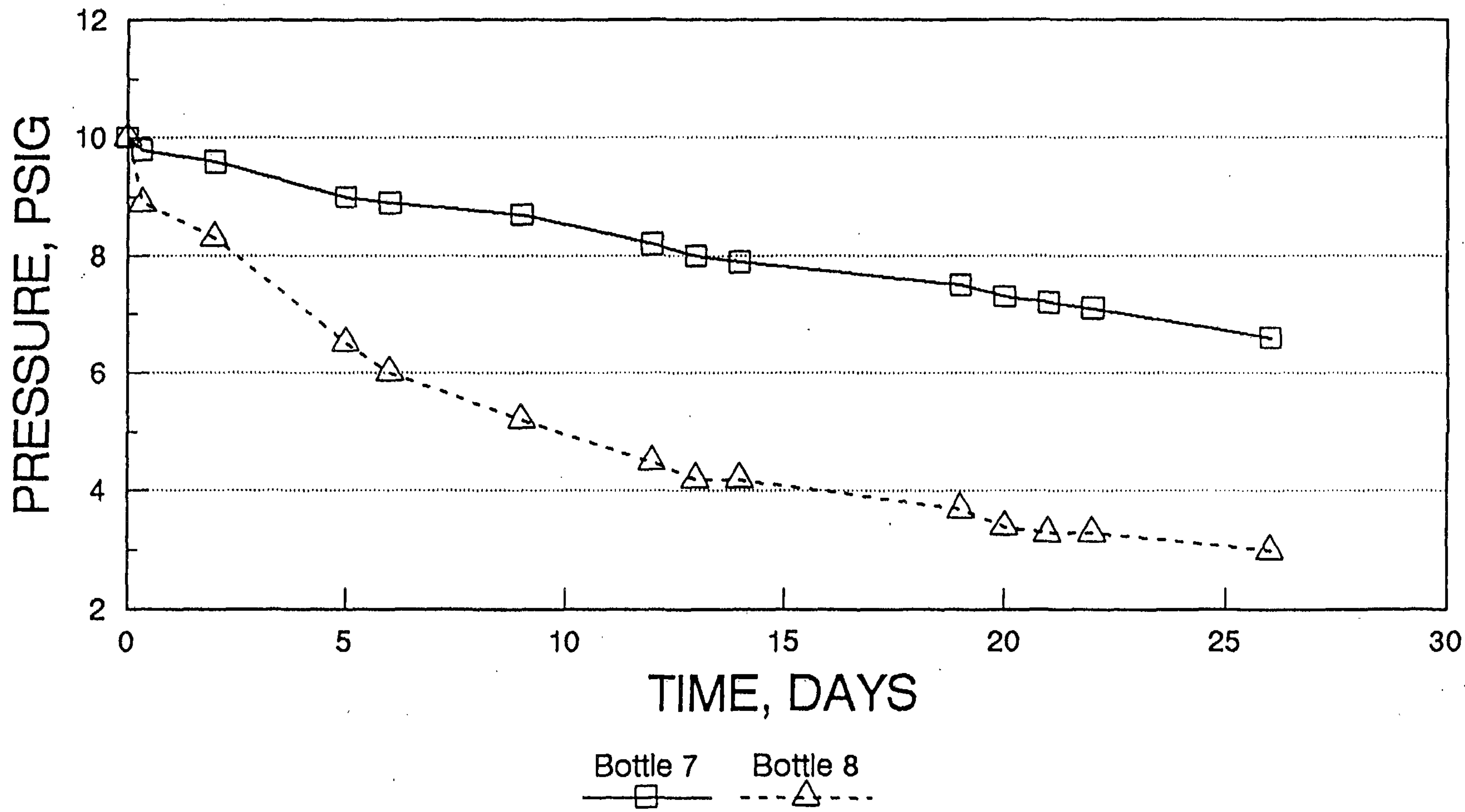

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Table 6

GAS GENERATION RATES FOR PLUTONIUM NITRATE SOLUTIONS, CC/DAY

Pu CONCENTRATION g/l	SOLUTION NORMALITY									
	1	2	3	4	5	6	7	8	9	10
1	0.25	0.14	0.09	0.065	0.058	0.035	0.025	0.018	0.012	0.009
2	0.5	0.28	0.18	0.13	0.116	0.07	0.05	0.036	0.024	0.018
5	1.25	0.7	0.45	0.325	0.29	0.175	0.125	0.09	0.06	0.045
10	2.5	1.4	0.9	0.65	0.58	0.35	0.25	0.12	0.12	0.09

The primary products of the radiolysis of a plutonium nitrate solution are hydrogen and oxygen. Some oxides of nitrogen are also produced, but the quantity of nitrogen oxides is small compared to hydrogen and oxygen in solutions containing <5 M nitric acid.[10] However, a study performed at Pacific Northwest Laboratory (PNL) showed that the presence of polyethylene will alter the composition of radiolytic produced gases.[11] The PNL study showed that the oxygen content of the radiolytic produced gases was decreased by polyethylene, and hydrogen was the primary radiolytic produced gas identified when polyethylene was present.

Several assumptions were required for development of the bottle pressurization model. Plutonium solutions containing nitric acid, hydrochloric acid and mixed nitric and hydrochloric acids are stored in plastic bottles at Rocky Flats. However, since water is the major source of radiolytic produced gas, the gas generation rates measured at Hanford for plutonium nitrate solutions were assumed to be valid for hydrochloric acid and mixed nitric acid-hydrochloric acid solutions. Both polyethylene and polypropylene bottles are used at Rocky Flats to store solutions. However, most of the bottles being used are polyethylene, and polyethylene bottles were assumed for the model. Based upon the results of the PNL study, the gas produced from radiolysis of plutonium solutions in polyethylene bottles was assumed to be hydrogen. Another assumption was that the hydrogen would collect in the head space above the solution, and the bottle surface available for hydrogen permeation would be the surface above the liquid level in the bottle.

Regression analysis was performed on the data given in Table 6 and this analysis showed that a very good fit was obtained for the exponential expression given in Equation 1 below.

$$Y = ae^{bx} \qquad \text{Equation 1}$$

where Y = gas generation rate, cc/day/g Pu
x = acid normality
0-4 N $a = 0.3669$
$b = -0.4483$
4-10 N $a = 0.3005$
$b = -0.3548$

If the data from Table 6 are plotted, the shape of the curve changes at 4 N nitric acid. Analysis of the data above and below 4 N nitric acid showed that a better fit was obtained using different "a" and "b" constants for solutions below and above 4 N nitric acid.

The rate of pressure increase in a polyethylene bottle containing plutonium nitrate solution is controlled by the rate of gas generation from the solution and the rate of gas loss from the bottle. The rate of gas generation varies depending on the plutonium concentration and solution normality. Gas is lost from a sealed polyethylene bottle by permeation of the gas through the walls of the bottle and leakage through the threads of the bottle lid.

The rate of permeation of hydrogen through polyethylene can be calculated using a form of Henry's law, which is shown by Equation 2 below.[12]

$$N = P(p_1 - p_2)/L \qquad \text{Equation 2}$$

where N = permeation rate, cc/s-cm^2
P = permeability, cc-mm/cm^2-s-mm Hg
p_1 = partial pressure of gas inside bottle, mm Hg
p_2 = partial pressure of gas outside bottle, mm Hg
L = thickness of bottle, mm

The hydrogen permeability constant used for Equation 2 is given below.

$$P_{H2} = 8.6 \times 10^{-10}, \text{ cc-mm/cm}^2\text{-s-mm Hg}$$

The partial pressure of hydrogen outside of a bottle (p_2) was assumed to be zero. The overall rate of permeation for hydrogen is the product of the permeation rate (N) and the surface area (A) of the bottle available for permeation.

$$\text{Hydrogen Permeation Rate} = N \times A \qquad \text{Equation 3}$$

Thickness measurements were made at various locations on a polyethylene bottle and the thickness was found to vary depending upon where the measurements were taken. The thickness measurement data were used to calculate the average thickness of the portion of bottles above the solution level for bottles containing various quantities of solution. The surface area available for permeation of hydrogen also varies depending upon the quantity of solution in a bottle. Surface area calculations were performed for bottles containing various quantities of solution. The results of these thickness and surface area calculations are given in Table 7.

Regression analysis was performed on the pressure versus time data obtained from the MST leak rate tests (Figures 1 through 3). The amount of torque a person would apply when tightening a bottle lid prior to removal of the bottle from a glovebox was determined to be 5 ft-lbs. Therefore, only the data from tests conducted using this amount of torque to tighten the bottle lid were analyzed. The data obtained for bottles number 3 and 4 were identical and, therefore, only data from the test with bottle number 3 were analyzed. This analysis showed that a good fit was obtained for the exponential expression given in Equation 4 below.

$$Y = ae^{bx} \qquad \text{Equation 4}$$

where Y = pressure, psig
x = time, days

The "a" and "b" constants for Equation 4 varied from bottle to bottle, and these constants are given in Table 8.

Equation 4 was then used to calculate the leak rate from the test bottles at various pressures. The leak rate was calculated as cc/day and this leak rate

Table 7

CALCULATED AVERAGE THICKNESS AND SURFACE AREA FOR POLYETHYLENE BOTTLES

SOLUTION VOLUME, LITERS	AVERAGE THICKNESS, mm	SURFACE AREA, cm^2
3.0	3.35	539
3.5	3.5	403
3.75	3.6	336
3.9	3.6	293
4.0	3.7	267
4.2	3.6	67

Table 8

CONSTANTS FOR PRESSURE VERSUS TIME EQUATION

BOTTLE NUMBER	SOLUTION VOLUME, l	CONSTANTS	
		a	b
3	0	10.0108	-0.00787
5	3.9	9.6798	-0.04628
6	3.9	9.2366	-0.02906
7	3.75	9.8539	-0.01513
8	3.75	8.5128	-0.04531

was then divided by the surface area to obtained a leak rate corrected for surface area. A plot of the data obtained from these calculations is shown in Figure 4. As the data in Figure 4 show, the leak rate for bottles 3 and 7 were almost identical when expressed as cc/day/sq cm. Bottle 8 had the highest leak rate.

Regression analysis was performed on the data shown in Figure 4 and an extremely good fit was obtained for the liner expression given in Equation 5 below.

$$Y = a + bx \qquad \text{Equation 5}$$

where Y = leak rate, cc/day/sq cm
x = pressure, psig

Again, the "a" and "b" constants varied from bottle to bottle and these constants are given in Table 9. As the data in Table 9 show, the "a" constants are all essentially zero, and Equation 5 becomes Y = bx.

Equation 5 was used to calculate the total leak rate from the test bottles at various pressures. Equation 3 was used to calculate the portion of the leak rate that occurred due to permeation of gas through the polyethylene. Subtracting the permeation leak rate from the total leak rate gave the leak rate through the bottle lid threads. The results of these calculations for the bottles with the lowest leak rate (bottle number 7) and the highest leak rate (bottle number 8) are given in Table 10. As the data in Table 10 show, the permeation leak rate for bottle 7 was greater than the leak rate through the bottle lid threads. For bottle 8, the leak rate through the bottle lid threads was much greater than the permeation leak rate. Since bottles 7 and 8 both contained 3.75 liters of water and the surface available for gas permeation was the same, the permeation leak rate was the same for both bottles.

Separation of the leak rate determined for the test bottles into the leak rate due to permeation and the leak rate due to thread leakage allow for the calculation of leak rates for bottles containing 4.2 liters of solution. This calculation was performed so that the pressures that should have existed in the sealed bottles removed from 55 gallon drums could be calculated. The calculated leak rates for bottles containing 4.2 liters of solution are shown in Figure 5. The leak rates shown in Figure 5 are based upon the leak rates from test bottles number 7 and 8, the bottles with the lowest and highest leak rates. The leak rate equation developed from the data shown in Figure 5 is given below.

$$Y = a + bx \qquad \text{Equation 6}$$

where Y = leak rate, cc/day
x = pressure, psig

Bottle 7
a = 0.0030398
b = 0.347556

Bottle 8
a = 0.00165
b = 1.63957

Figure 4
LEAK RATE FOR NARROW MOUTH 4 LITER BOTTLES

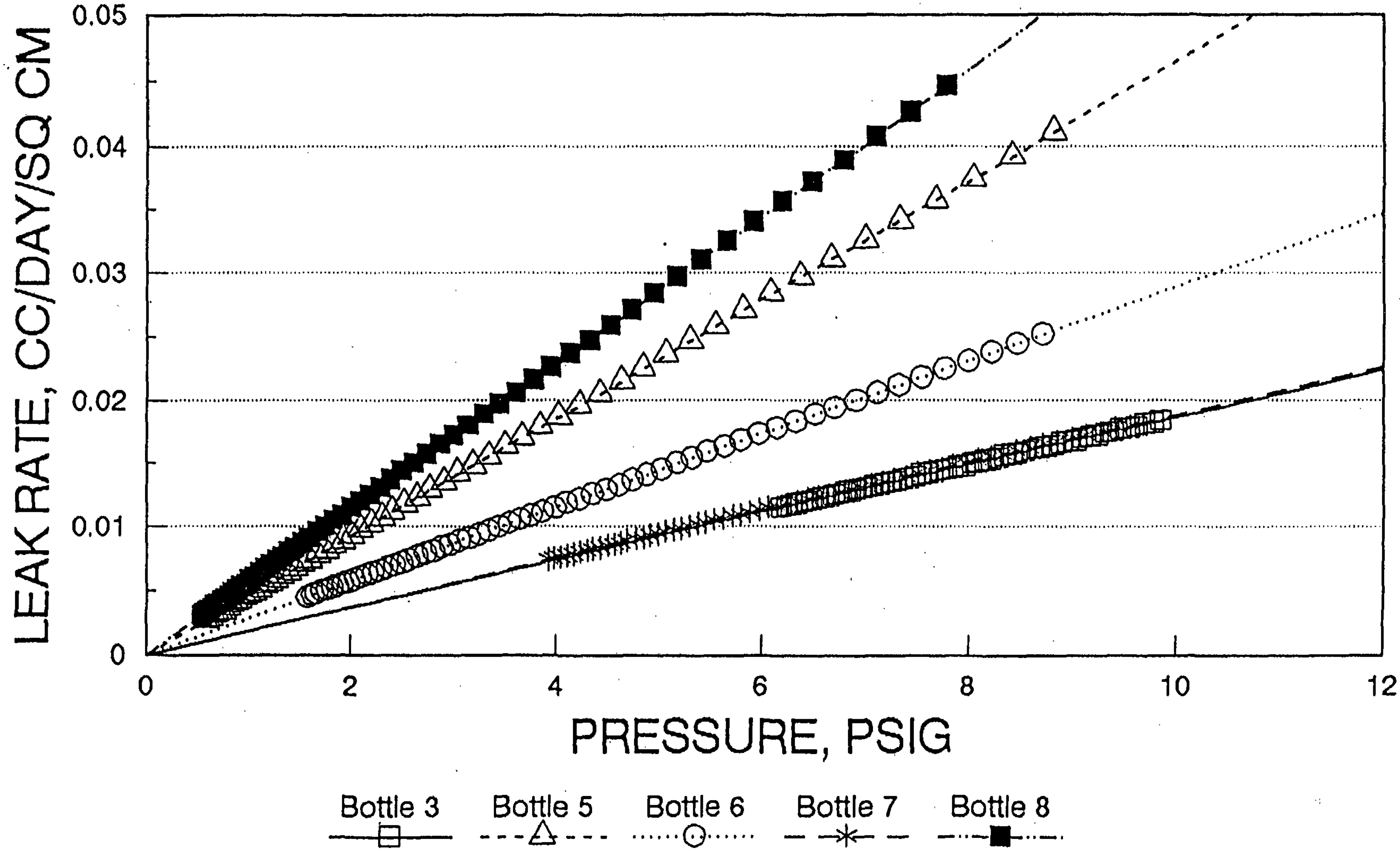

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Table 9

CONSTANTS FOR LEAK RATE VERSUS PRESSURE EQUATION

BOTTLE NUMBER	SOLUTION VOLUME, l	CONSTANTS	
		a	b
3	0	-0.000002	0.0018636
5	3.9	0.0	0.0046548
6	3.9	0.0000107	0.0028933
7	3.75	0.0000106	0.0018846
8	3.75	0.0000049	0.0057352

Table 10

PERMEATION AND THREAD LEAK RATES FOR LOWEST AND HIGHEST LEAK RATE BOTTLES

BOTTLE NUMBER 7

PRESSURE, PSIG	LEAK RATE			
	CC/DAY/SQ CM	CC/DAY	PERMEATION CC/DAY	THREADS CC/DAY
9	0.01697	5.6951	3.2086	2.4865
8	0.01509	5.0627	2.8521	2.2106
7	0.01320	4.4302	2.4956	1.9346
6	0.01132	3.7978	2.1391	1.6587
5	0.00943	3.1653	1.7826	1.3828
4	0.00755	2.5329	1.4260	1.1068
3	0.00566	1.9004	1.0695	0.8309
2	0.00378	1.2680	0.7130	0.5549
1	0.00189	0.6355	0.3565	0.2790

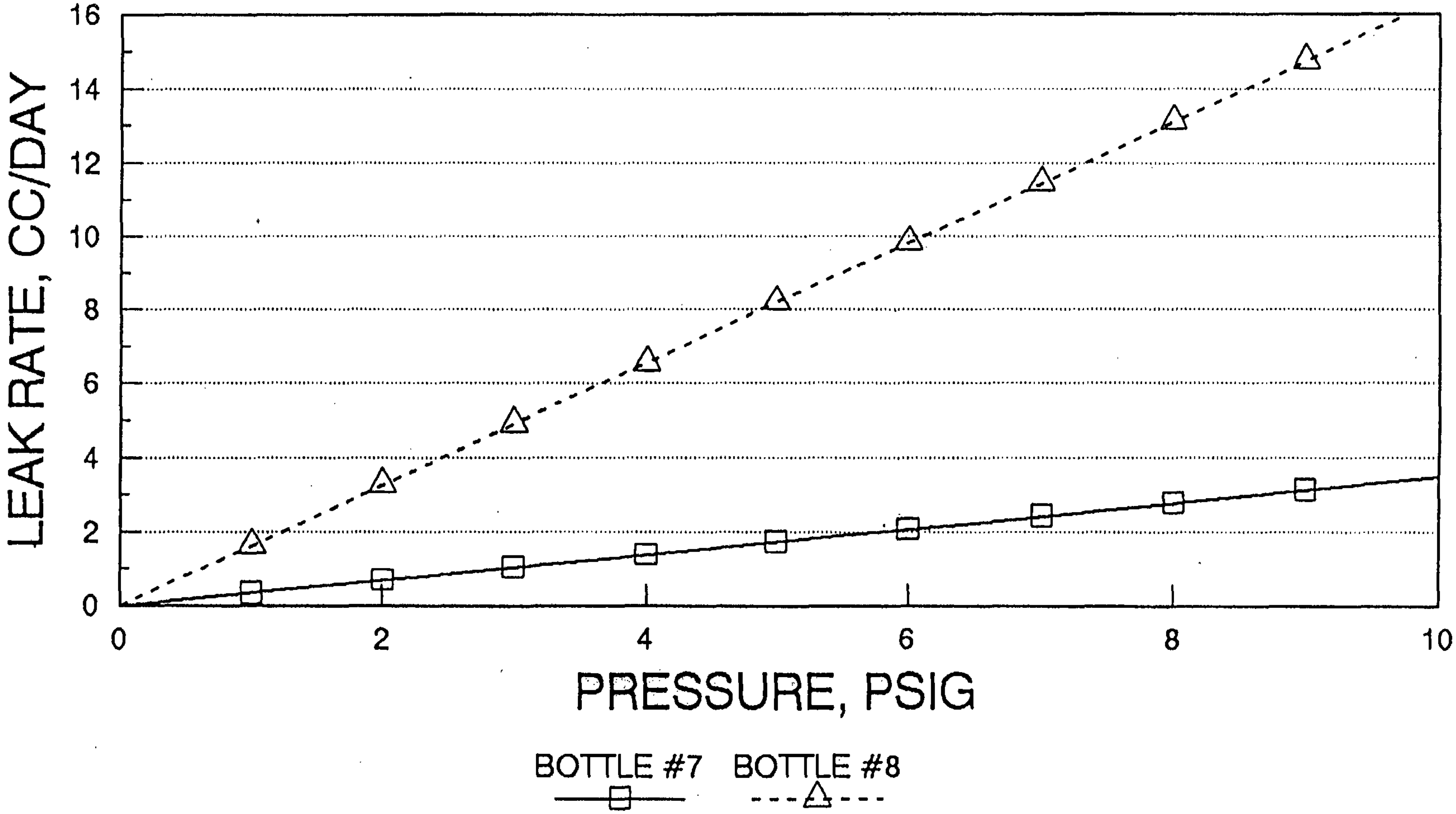
BOTTLE NUMBER 8

PRESSURE, PSIG	LEAK RATE			
	CC/DAY/SQ CM	CC/DAY	PERMEATION CC/DAY	THREADS CC/DAY
9	0.05162	17.3219	3.2086	14.1133
8	0.04589	15.3974	2.8521	12.5453
7	0.04015	13.4730	2.4956	10.9774
6	0.03442	11.5485	2.1391	9.4094
5	0.02868	9.6240	1.7826	7.8415
4	0.02295	7.6995	1.4260	6.2735
3	0.01721	5.7751	1.0695	4.7055
2	0.01148	3.8506	0.7130	3.1376
1	0.00574	1.9261	0.3565	1.5696

Figure 5

LEAK RATE FOR FOUR LITER BOTTLE

CONTAINING 4.2 LITERS SOLUTION



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4.2 ACTUAL BOTTLE PRESSURE CALCULATIONS

The bottle leak tests performed by MST were conducted using helium and bottles of plutonium solution are expected to contain hydrogen. However, the helium and hydrogen permeability constants are similar for polyethylene. The hydrogen permeability constant is 8.6×10^{-10}, cc-mm/cm^2-s-mm Hg and the permeability constant for helium is 7.4×10^{-10}, cc-mm/cm^2-s-mm Hg.[12] Therefore, the leak rate data obtained using helium should be applicable for bottles containing hydrogen gas.

Equilibrium pressures were calculated for sealed bottles of plutonium solution removed from drums containing pressurized bottles. The equilibrium pressure was assumed to be the pressure at which the gas generation rate is equal to the leak rate. These bottles had all been stored for over 3 years and calculations for the rate of pressure increase in these bottles indicated that the pressure in all of the bottles should have reached equilibrium. Gas generation rates were calculated using Equation 1 from Section 4.1 and leak rates were calculated using Equation 6. Equilibrium pressures were calculated for pressurized and non-pressurized bottles using leaks rates based upon the leak rates obtained from bottle number 7 and from bottle number 8.

A summary of the results of the equilibrium pressure calculations is presented in Table 11. As the date in Table 11 show, there was very little difference between the calculated equilibrium pressure for bottles observed to be pressurized as compared to bottles observed not to be pressurized. Based upon the bottle number 7 leak rate, over 90 percent of the bottles observed to be pressurized should have contained over 2 psig pressure. However, the same is true for the non-pressurized bottles.

During the MST bottle leak tests, bulging of the bottle bottom was observed to occur at a pressure of approximately 3 psig. Calculated equilibrium pressures based on the bottle number 7 leak rate are less than 3 psig for over half of the bottles observed to be pressurized. However, the bottles used for the bottle leak tests were new bottles and the old bottles removed from the 55 gallon drums may have shown indications of pressurization at lower pressures. Only 6 of the 62 bottles observed to be pressurized should have contained pressures less than 2 psig and the calculated pressures for 2 of these 6 bottles were over 1.9 psig.

If the bottles noted as being pressurized had leaked at the same rate as bottle number 8, then none of the equilibrium pressures would have exceeded 1.8 psig. Results from the MST leak tests showed a wide variation in leak rate from bottle to bottle. Results from the equilibrium pressure calculations also indicate that wide variations in leak rate existed for the actual bottles of plutonium solution. The computer spread sheet models described in this report appear to be useful for predicting the combinations of plutonium concentration and acid normality with the potential for causing pressurization of sealed bottles. However, for a bottle containing solution with a given plutonium concentration and acid normality, the most important factor for determining whether the bottle will become pressurized if it is sealed would appear to be how well the bottle seals.

Table 11

SUMMARY OF EQUILIBRIUM PRESSURE CALCULATION RESULTS

PRESSURE RANGE, PSIG	PRESSURIZED BOTTLES, PERCENT OF ALL PRESSURIZED BOTTLES		NON-PRESSURIZED BOTTLES, PERCENT OF ALL NON-PRESSURIZED BOTTLES	
	#7 LEAK RATE	#8 LEAK RATE	#7 LEAK RATE	#8 LEAK RATE
0 TO 1	1.61	80.65	2.53	78.48
1 TO 2	8.06	19.35	5.06	21.52
2 TO 3	46.77	0	44.30	0
3 TO 4	12.90	0	15.19	0
4 TO 5	16.13	0	18.99	0
>5	14.52	0	13.92	0

4.3 SEALED BOTTLE SAFE STORAGE TIMES

Storage of plutonium solutions in sealed plastic bottles is not a practice which should be encouraged, because of the potential for pressurization and bottle failure. As discussed previously in this report, gas generation rate experiments have shown that the gas generation rate in plutonium solutions increases as the solution normality decreases. Therefore, plastic bottles containing low normality plutonium solutions will tend to pressurize faster than bottles containing high normality solutions. Even though the gas generation rate decreases in high normality solutions, the rate of chemical attack on polyethylene increases as the normality increases in nitric acid solutions. As the plutonium concentration increases, the rate of radiolytic damage to the plastic increases. Therefore, bottle failure mechanisms exist for both low and high normality acid solutions. However, there are situations which necessitate the sealing of plastic bottles containing plutonium solutions. Since these situations do exist, guidelines are required to allow for the safe storage or transportation of these solutions.

The computer spread sheet models discussed in this report have been used to develop proposed guidelines for safe storage of plutonium solutions in sealed bottles. As stated previously, MST personnel observed that the bottom of a polyethylene bottle will deform at a pressure of approximately 3 psig. Equilibrium pressure calculations for bottles of actual plutonium solutions observed to be pressurized indicate that bottle deformation may occur at pressures as low as 2 psig. Therefore, a pressure of 1 psig was established as the maximum safe pressure for the proposed sealed bottle storage guidelines. This pressure is the pressure at which some action will be required to vent the bottle, and the time at which the pressure in a sealed bottle is expected to reach 1 psig is defined as the action time. Since some planning will probably be required before the bottle can actually be vented, and delays in implementing a plan often occur, a shorter time is defined as the alert time. The alert time is the time at which the pressure in a sealed bottle is expected to reach one half the action pressure, or 0.5 psig. The alert time is the time when planning for venting of sealed bottles must begin.

Calculations were performed to determine the alert and action times for solutions with a variety of plutonium and acid concentrations. These calculations were performed assuming a four liter polyethylene bottle containing 3.75 liters of solution. The 3.75 liter number was chosen because this is the maximum volume that will be allowed in the next revision of the Rocky Flats On-Site Transportation Manual. The leak rate measured for bottle number 7 was used for these calculations since this was the slowest leak rate measured during the MST bottle leak tests. The results of these calculations are given in Table 12, which shows the expected time for the pressure in a sealed bottle to reach 0.5, 1 and 3 psig.

The information given in Table 12 was used to develop alert and action times for storage or transportation of sealed bottles of plutonium solution. In order to keep the safe storage time guidelines relatively simple, alert and action times were developed based upon the lowest solution normality for a given plutonium concentration where the plutonium can reasonably be expected to remain in solution without plutonium polymer formation.

Table 12

MATRIX OF TIMES TO REACH 0.5, 1 AND 3 PSIG IN 4 LITER BOTTLES

Pu, g/l	ACID NORMALITY																				
	0.1			0.2			0.3			0.4			0.5			1			2		
	TIME IN DAYS REQUIRED TO REACH PRESSURE SHOWN (PRESSURE IN PSIG)																				
	0.5	1	3	0.5	1	3	0.5	1	3	0.5	1	3	0.5	1	3	0.5	1	3	0.5	1	3
0.1	N/A																				
0.2	N/A																				
0.25	212	N/A																			
0.3	105	N/A	N/A	123	N/A	N/A	136	N/A	N/A	162	N/A	N/A	207	N/A	N/A	N/A					
0.4	60	N/A	N/A	65	N/A	N/A	70	N/A	N/A	76	N/A	N/A	83	N/A	N/A	150	N/A	N/A	N/A		
0.5	43	212	N/A	46	404	N/A	49	N/A	N/A	52	N/A	N/A	56	N/A	N/A	83	N/A	N/A	N/A		
0.6	33	105	N/A	36	119	N/A	38	136	N/A	40	162	N/A	43	207	N/A	60	N/A	N/A	182	N/A	N/A
0.7	27	76	N/A	29	83	N/A	31	91	N/A	33	101	N/A	35	113	N/A	47	N/A	N/A	106	N/A	N/A
0.8	23	60	N/A	25	65	N/A	26	70	N/A	28	76	N/A	29	83	N/A	39	150	N/A	79	N/A	N/A
0.9	20	50	N/A	22	53	N/A	23	57	N/A	24	62	N/A	25	67	N/A	33	105	N/A	64	N/A	N/A
1	18	43	N/A	19	46	N/A	20	49	N/A	21	52	N/A	22	56	N/A	29	83	N/A	54	N/A	N/A
1.5	11	25	213	12	27	N/A	12.5	28	N/A	13	30	N/A	14	31	N/A	18	43	N/A	31	91	N/A
2	8	18	84	9	19	92	9.5	20	102	10	21	114	10.5	22	130	13	29	N/A	21.5	54	N/A
3	5	12	43	5.5	12	45.5	6	12.5	49	6.5	13	52	7	12.5	56	8.5	18	83	14	31	N/A
4	4	8	29	4.5	8.5	31	4.5	9	33	4.5	9.5	35	5	10	37	6	13	51	10	21.5	122
5				3.5	7	24	3.5	7.5	24.5	3.5	7.5	26	3.75	8	28	5	10	37	8	17	74
6				3	6	19							3.5	7	22	4	8	29	6.5	13.5	54
10				1.5	3.5	11							2	4	12	2	5	16	4	8	27
15				1	2	7							1	2.5	8	1.5	3	10	2.5	5	17
20													1	2	6	1	2.5	7.5	2	4	12

N/A-Equilibrium pressure is less than pressure shown

Table 12 (Continued)

MATRIX OF TIMES TO REACH 0.5, 1 AND 3 PSIG IN 4 LITER BOTTLES

Pu, g/l	ACID NORMALITY																				
	3			4			5			6			7			8			9		
	TIME IN DAYS REQUIRED TO REACH PRESSURE SHOWN (PRESSURE IN PSIG)																				
	0.5	1	3	0.5	1	3	0.5	1	3	0.5	1	3	0.5	1	3	0.5	1	3	0.5	1	3
0.6	N/A																				
0.7	N/A																				
0.8	N/A																				
0.9	254	N/A	N/A	N/A																	
1	139	N/A	N/A	N/A																	
1.5	58	N/A	N/A	N/A																	
2	38	139	N/A	76	N/A	N/A	N/A														
3	23	58	N/A	40	165	N/A	83	N/A	N/A	N/A											
4	16	38	N/A	28	77	N/A	35	114	N/A	58	N/A	N/A	119	N/A	N/A	N/A					
5	13	28.5	N/A	21	52	N/A	26	71	N/A	42	187	N/A	73	N/A	N/A	207	N/A	N/A	N/A		
6	10.5	23	140	17	40	N/A	21	52	N/A	33	101	N/A	54	N/A	N/A	104	N/A	N/A	N/A		
10	6	13	50	10	21	115	12	26	315	17	42	N/A	27	73	N/A	43	207	N/A	75	N/A	N/A
15	4	8	29	6	14	53	7.5	16	71	11	25	187	17	39	N/A	25	67	N/A	40	158	N/A
20	3	6	20	5	10	35	6	12	45	8	18	80	12	27	N/A	18	43	N/A	28	75	N/A

N/A-Equilibrium pressure is less than pressure shown

The alert and action times are given in Table 13. For solutions containing >1.5 g/l plutonium, the gas generation rate is rapid enough that storage of these solutions in sealed bottles should not be allowed. The alert times given in Table 13 for bottles containing >1.5 g/l plutonium are the time periods during which transportation of seal bottles should be completed. The action times are the maximum time periods that these higher plutonium concentration solutions can be sealed. As the proposed alert and action times in Table 13 show, careful planning will be required for transportation of >1.5 g/l plutonium solutions, because the time periods during which these bottles can be sealed are fairly short.

Table 13

PROPOSED SAFE STORAGE OR TRANSPORTATION TIMES

MODE	PLUTONIUM, g/l	ALERT TIME	ACTION TIME
STORAGE	<0.25	6 MONTHS	12 MONTHS
	0.25 TO <0.5	2 MONTHS	4 MONTHS
	0.5 TO <1	3 WEEKS	6 WEEKS
	1 TO <1.5	2 WEEKS	4 WEEKS
TRANSPORTATION	1.5 TO <6	3 DAYS	6 DAYS
	6 TO 15	1 DAY	2 DAYS
	>15	1 SHIFT	1 DAY

5.0 CONCLUSIONS AND RECOMMENDATIONS

There are several conclusions that can be drawn from the information presented in this report. Gas generation occurs in plutonium solutions due to radiolysis of the solution. The gas generation rate is higher for low normality solutions than for high normality solutions, and a sealed bottle containing low normality solution will pressurize faster than a sealed bottle containing high normality solution. However, the rate of chemical attack on plastic bottles is faster for high normality solutions of oxidizing acids, such as nitric acid. Since gas generation from plutonium solutions is due to radiolysis, the rate of gas generation is directly proportional to the plutonium concentration for solutions with the same acid concentration.

Hydrogen, oxygen and nitrogen oxides are produced as a result of radiolysis of plutonium solutions, with hydrogen and oxygen being the primary gases produced in low normality solutions. Due to a reaction between oxygen and polyethylene that has not been identified, the primary gas which accumulates in polyethylene bottles containing low normality plutonium solution is hydrogen. If bottles of plutonium solution are sealed for sufficient periods of time, the bottles will become pressurized and a few of the bottles may fail. The equilibrium pressure will be determined by the acid normality, plutonium concentration, and how well the bottles seal. For a given acid normality and plutonium concentration, the equilibrium pressure will be determined by how well the bottles seal.

Several types of materials are used to manufacture bottles used to store plutonium solutions at Rocky Flats. These materials are low density polyethylene, high density polyethylene and polypropylene. Low density polyethylene appears to be the best material for bottles used to store plutonium solutions. Polypropylene does not appear to be a suitable material for bottles used to store plutonium solutions.

Based upon the information contained in this report, the following recommendations are made.

1. Storage of plutonium solutions in sealed plastic bottles should not be encouraged as a routine practice.

2. If storage of plutonium solutions in sealed plastic bottles is required, the alert and action times given in Table 13 of this report should be followed, and the bottles should be vented before the end of the action time.

3. Polypropylene bottles should not be used to store plutonium solutions.

4. Vented plastic bottles of plutonium solution stored in gloveboxes should be inspected periodically, because even vented bottles can eventually fail.

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