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STUDY OF POLYETHYLENE BOTTLES

AS

CONTAINERS FOR PLUTONIUM NITRATE

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June, 1968

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STUDY OF POLYETHYLENE BOTTLES AS CONTAINERS FOR PLUTONIUM NITRATE

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ABSTRACT

High density polyethylene bottles have been used for the past two years as primary containers for plutonium nitrate solutions under both transport and storage conditions. During the first six months of use, some concern was evidenced because of leaks at the bottle seal, malfunction of the bottle vents, and stress cracks in the bottles. The results of an R & D program conducted by the Atlantic Richfield Hanford Company for correcting these problem areas is reported.

INTRODUCTION

Power reactor development, non-defense government and commercial program plutonium needs are supplied from the plutonium nitrate inventories accumulated at Hanford. These inventories are currently composed of plutonium manufactured in Hanford reactors and in commercial power reactors. The power reactor plutonium is converted to nitrate by Nuclear Fuels Services' New York plant and purchased by the United States Atomic Energy Commission (USAEC) under its "Buy Back Agreement" with the utilities who own the power reactors.

Plutonium nitrate is shipped from its point of origin to the customer in specially designed 10 liter shipping containers licensed by the United States Department of Transportation, (DOT) Hazardous Materials Regulations Board, Figure 1.¹ At Hanford, the plutonium nitrate is placed in the Hanford 10 liter storage container, Figure 2, until it is needed.

Since 1966, approximately 1400 kg of plutonium in 6900 liters of plutonium nitrate representing 700 individual 10 liter packages have been transported.

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In the earlier shipments, small quantities of plutonium nitrate leaked from some of the polyethylene bottles and contaminated the inside of the pressure vessel. None of the plutonium escaped from the shipping containers in these instances; the public safety was not compromised. Most of the leaks were found to be faulty seals between the cap and the bottle, with a few others traceable to the slit vent in the bottle cap. Decontamination of the inside of the pressure vessel was an expensive undesirable nuisance, but it had to be done to keep the shipments moving.

Material in inventory that had been in polyethylene bottles for three to four months presented another problem of potentially serious proportions. As much as a liter of plutonium nitrate leaked through cracks in the bottom of the polyethylene bottle into the inner chamber of the storage container.

A research and development program was initiated in May, 1967, to:

1. Characterize the environment to which the polyethylene bottle is exposed when it is filled with plutonium nitrate solution;
2. Characterize the material used in the bottles;
3. Develop improved bottle cap seals and vents; and
4. Evaluate alternate materials from which bottles could be fabricated.

The experiments required to define the environment and to evaluate the polyethylene bottles were conducted in the laboratory facilities of the Atlantic Richfield Hanford Company, (ARHCO), and the Pacific Northwest Laboratory (PNL). The development and testing of seals, venting devices, and alternate bottle materials were performed by ARHCO.

ENVIRONMENT

The studies of the environment to which the bottles are exposed in both the shipping and storage situations may be described as one in which:

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1. Significant volumes of gas are evolved from the plutonium nitrate solution by both radiolytic means and valence reduction of the plutonium VI present to plutonium IV; and
2. Nitric acid in concentrations of two molar (2M) to ten molar (10M) is present.

The environmental studies demonstrated that significant volumes of gases evolve from the plutonium nitrate-nitric acid solutions $(\text{Pu}(\text{NO}_3)_4)^{2,3}$. These gases are presumed to be evolved by alpha radiolysis of water and the reduction of the plutonium VI present in the solution to the more stable plutonium IV. The former reaction generates oxygen and hydrogen, and the latter oxygen. The alpha radiolysis of water appears to be the beginning of a chain of chemical reactions which ultimately result in the generation of the gaseous end products. The amount of gas formed should be directly proportional to the radiation dose, or the energy absorbed by the system. The alpha particles emitted by the plutonium present are the source of this energy. The gases evolved by radiolysis were found to be constant over the test period. Neither the rate of evolution nor the composition of the gas was affected by changes in temperature of the test solutions. It was noted that the gas evolution rate decreased as the nitric acid concentration increased. The gas generation rate per gram of ^{239}Pu per day for $\text{Pu}(\text{NO}_3)_4$ solutions having 2M to 10M nitric acid concentration is shown in Figure 3.

Oxygen is released during the reduction of the Pu VI to Pu IV. The reaction is essentially complete three weeks after the final separation of the plutonium. This source of gas is easily eliminated from the shipping problem: the $\text{Pu}(\text{NO}_3)_4$ is held for three weeks before shipment is made.

The other environmental element which was considered is the presence of an oxidative media in the form of nitric acid. Tests performed by PNL⁴ show that the attack by nitric acid on the 10 liter polyethylene bottle is of no significance when there is little or no stress applied to the bottle. Since the Rocky Flats type L-10 container has come into

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fairly widespread use in the United States, the test data have been put into a form which can be used with this container, Figure 4. The Hanford shipping bottle when loaded with 10 liters of plutonium nitrate has 800 cc of free volume. When the bottle is sealed in the pressure vessel of the type L-10 shipping container, Figure 5, there is a total of 3200 cc of void space in the vessel, (800 cc in the bottle, and 2400 cc around the bottle).

Applying these data to a normal shipment of plutonium nitrate, it can be shown that appreciable pressures can be built up in an unvented bottle, while they would be negligible if permitted to escape from the bottle into the pressure vessel. For example, let us assume that a shipment of 2500 grams of plutonium, in a 4M nitric acid solution, is to be shipped across country in a type L-10 container. Let us also assume that the container will be sealed for 14 days from the time it is closed by the consignor until it is opened by the consignee. Using the data in Figure 4, the pressure build-up in a sealed bottle is calculated to be 3 psi per day, or in 14 days will be 42 psig. A pressure of this magnitude precludes the use of a sealed polyethylene bottle. If the bottle is provided with a venting device which will release the gas from the bottle when the pressure reaches, say, 5 psig, then we find that there is a build-up rate of less than 1 psig/day and in 14 days there is only 10 psig in the pressure vessel. This pressure is not significant when compared to the strength of the pressure vessel.

BOTTLE MATERIAL

The original selection of high density polyethylene bottles provided the industry with a relatively inexpensive, single trip container. The cost of decontamination and return of the container was eliminated and each shipment could be made in a clean container.

The PNL work⁴ showed that the bottles used for transport and storage of $\text{Pu}(\text{NO}_3)_4$ were blow molded of high density polyethylene. The polyethylene in these bottles had a density of 0.946 grams/cc and a melt index ranging from 0.233 to 0.244.

The PNL work also showed that the cracks found in the bottles which failed in storage were environmental stress cracks resulting from exposure of the bottles to elevated pressures. The pressures resulted from the gases generated by radiolysis being contained in the bottle when the bottle vent failed to function.

The bottle failures under storage conditions were duplicated by placing a 10 weight percent Igepal CD630* solution, a surfactant, in the bottle and raising the temperature to 50°C. Tests were conducted on Hanford 10 liter bottles at 15, 20, and 25 psig. Failure occurred after 40 hours at 25 psig, 176 hours at 20 psig, and 2516 hours at 15 psig. One bottle was tested at atmospheric pressure and ambient temperature, (20°C). After 750 hours there was no evidence of incipient failure. The temperature was then raised to 50°C, and the test continued for an additional 1500 hours. There was still no evidence of failure. The test was discontinued at this point. This test has been verified in actual experience. Twenty-four vented 10 liter polyethylene bottles loaded with plutonium nitrate and 2M to 5M nitric acid have been stored at an ambient temperature of 20-25°C for 8 to 12 months without a failure.

BOTTLE CAP SEAL

Contamination of the pressure vessel of the shipping container has been caused mainly by leakage of $\text{Pu}(\text{NO}_3)_4$ through the bottle cap seal.

*Igepal is an alkyl aryl polyethylene glycol ether produced by the General Aniline and Film Corporation.

The original seal, shown in Figure 6, required a very careful assembly to be leak tight.

The new seal, Figure 7, uses a standard Viton V-494-7*, O ring gasket having nominal dimensions 2 3/4 inch I.D. x 3 1/8 inch O.D. x 3/16 inch W. The O ring gasket is placed in the cap, a standard 83 millimeter carboy closure, and the cap is sealed using 15 foot pounds of torque. Under test conditions, Viton showed a slight tendency to swell after two to three months exposure to nitric acid.⁵ This characteristic of Viton is not detrimental in this application. The seal has been in use for the last ten months and no leakage has been observed from any of the bottles shipped using this seal.

BOTTLE VENT

A reliable bottle vent is a vital part of the $\text{Pu}(\text{NO}_3)_4$ shipping systems. It was mentioned above that the gases evolved from plutonium nitrate solutions could create destructive stresses in unvented polyethylene bottles.

It was decided that an optimum bottle vent for transport and storage of $\text{Pu}(\text{NO}_3)_4$ would:

1. Not leak when inverted for short periods of time or when dropped in the inverted position;
2. Release gas, when the internal pressure reaches the five to ten psig range, at a rate of 350 cc per day; and
3. Resist attack by the environment described above for the bottle.

In the course of the program, a number of designs of pressure relief devices, using a variety of materials reported to be resistant to nitric

*A fluorelastomer manufactured by E. I. DuPont de Nemours Co.

acid attack, were built and tested. The designs evaluated included variations of the original "top hat" design with slit vent, filters, membranes, traps, check valves, and several commercial pressure relieving devices. A pressure relief device which satisfies the above requirements has been developed, using a modified version of a standard vessel (drum) vent, Figure 8, patented and manufactured by the Duo-Vent Vacuum Closure Company of Philadelphia, Pennsylvania. Figure 9 shows one version of this modified vent mounted in a bottle cap. The vent assembly consists of:

1. A Duo-Vent valve made of ethylene propylene rubber;
2. A polyethylene valve seat, and;
3. A polyethylene valve cover.

The valve is mounted in the closure adaptor which is then centered over a one-eighth inch diameter hole in the center of the bottle cap, and heat sealed to the inner surface of the cap. The vent cover is centered over this vent and also heat sealed to the cap. In use, when the pressure inside the bottle has reached three psi above the external pressure, the gases pass through the 1/32-inch diameter hole in the vent cover, up through the Duo-Vent valve and the one-eighth inch diameter hole in the bottle cap. The vent cover protects the vent from acid splashes and acts as a surge chamber to prevent the escape of liquid if the vessel is dropped upside down. When the bottle is dropped in an inverted position, a small amount of liquid may be forced through the small hole in the vent cover by the pressure surge caused by the impact. During the inverted drop tests, no liquid passed the vent. If the bottle stays in the inverted position until sufficient gas is evolved to raise the bottle pressure and open the vent, liquid will be forced through the vent. This is an unusual situation which would occur only through careless handling, or an accident in transit. Should this situation occur, the plutonium solution would leak into the pressure vessel of the shipping container and be contained there.

"Slit vents" made from 1/8- and 3/32-inch thick teflon and polyethylene discs were tested.⁵ These discs were recessed on the pressure side to a thickness of 0.040 inches on a 1/4-inch diameter. Various sized slits were made in the recessed area; the practical minimum being 0.004 inches wide by 0.050 inches long. It was very difficult to make a slit small enough to prevent leakage when the bottle is inverted.

Observations of shipments made over the last ten months in which the original "top hat" vent was modified by adding a second slit, a perpendicular bisector of the original slit, Figure 10, have shown no leakage from the bottle into the pressure vessel. However, this type vent will leak if the vessel is inverted. This experience leads to the observation that inversion of the shipping container is not a normal condition of transport and that a slit type vent in a disc of teflon or polyethylene might be considered acceptable.

ALTERNATE BOTTLE MATERIALS

Another part of this program was the evaluation of alternate materials for the fabrication of primary containers for plutonium nitrate. Polyvinyl chloride (PVC), polycarbonate, low density polyethylene, and stainless steel were evaluated.

A 10 liter bottle was fabricated using PVC pipe and fittings. Testing PVC in nitric acid showed some leaching of chloride occurred. A question was raised concerning the possibility of chloride contamination of the plutonium solution contained in a PVC bottle. The question was not satisfactorily answered in the experiments conducted.² It was considered not practical to carry this investigation further.

A Lexan* bottle showed promise, but no fabricators were found who had molded this material into bottles this size. It was decided to stop further work on this material at the present time.

Low density polyethylene bottles were tested and found inadequate for the service.

Two stainless steel bottles were designed and fabricated. One design has a valved vent, and is intended to be sealed during shipment and vented upon arrival at destination, and vented periodically during storage. The other design is of lighter construction and includes a vent assembly intended to prevent escape of liquid and prevent pressurization during normal shipment or storage. Estimates of the cost of these bottles vary from \$95 for the vented bottle to \$133 for the sealed bottle.

The cost of the stainless steel bottle is considerably higher than polyethylene bottle. It could not be considered a "one trip" container because of the investment involved. To keep track of the container, an accounting system would have to be put in place. Each consignee would have to empty the bottles into his process vessels or provide other storage vessels in a reasonable time so the bottle could be returned to shipping service. This is sufficient nuisance without considering the problems of accountability, cross-contamination of shipments, decontamination, etc. to reject these bottles.

CONCLUSIONS

Based on laboratory tests and experience with the shipping and storage of plutonium nitrate in polyethylene bottles, it is concluded that vented, high density (0.955 ± 0.005 gm/cc) polyethylene bottles, containing plutonium nitrate solutions having up to 250 grams of plutonium per liter

*G. E. Co. trade name for polycarbonate.

with nitric acid concentration of up to 10M, can be shipped or stored at 20°-30°C for at least one year without failure of the bottle.

The bottles should be blow molded of polyethylene having a density $0.955 \pm .005$ grams/cc. The bottles should be 4.5 inches maximum outside diameter by 50 1/4 inches long and have a minimum wall thickness of 0.100 inches. The bottle capacity should be approximately 10.8 liters.

A Viton O ring gasket is recommended for the seal between the bottle and cap. The cap should be tightened to a torque of 15 foot pounds.

The EPR Duo-Vent valve assembly shown in Figure 9, meets the criteria established as the basis for evaluating vent devices and is the first choice for a bottle vent.

The slit vent in teflon or polyethylene discs meet all the criteria, except that it leaks when the bottle is inverted. It is the second best choice for a bottle vent.

Should further investigation show that cost of the EPR Duo-Vent assembly is excessively high and that the inverted container during transport is not a normal condition, the slit vent is an excellent second choice.

The recommendations for loading and handling of the bottles are:

1. Plutonium nitrate solutions should not be loaded for shipment until at least 90 percent of the plutonium is in the quadrivalent state.
2. Bottles of plutonium nitrate which are to be stored for extended periods should be checked periodically to assure that the vent is functioning properly and that the bottle has not become pressurized.
3. Each component of the bottle assembly should be checked for defects by the user prior to being put into service. The bottle should be checked for leaks, the vent checked for operation at the proper pressure, and the seal tightened and checked for leakage.

4. Until the new vent is available, the presently approved "top hat" vent with the modified vent slit, Figure 10, should be incorporated in the cap assembly.

FIGURE LIST

1. Type L-10 Shipping Container
2. 10 Liter Storage Container
3. Radiolytic Gas Generation Rates for Plutonium Nitrate Solutions
4. Pressure Build-Up in Plutonium Nitrate Solution Shipping Containers by Radiolysis
5. L-10 Pressure Vessel
6. Vent Cap Without O Ring
7. Vent Cap With O Ring
8. EPR Duo-Vent Valve Assembly
9. Cap With EPR Duo-Vent Valve Assembly
10. Vent Cap "Modified Slit" for Polyethylene Shipping Bottle

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TYPE L-10
SHIPPING CONTAINER
(DOT-SP-5060)

FIGURE 1

HANFORD STORAGE CONTAINER

FIGURE 2

FIGURE 3
Gas Generation Rate cc/gram Pu²³⁹/day

PRESSURE BUILD-UP IN PLUTONIUM NITRATE
SOLUTION SHIPPING CONTAINERS BY RADIOLYSIS

- Bottle pressure (not vented)
- + Pressure vessel (bottle vented)
- 10 liters of 250 grams Pu/liter
2500 grams Pu.
- Normal ARHCO $\text{Pu}(\text{NO}_3)_4$

L-10 PRESSURE VESSEL

FIGURE 5

VENT CAP WITHOUT O RING

FIGURE 6

VENT CAP WITH O RING

FIGURE 7

EPR DUO-VENT VALVE
ASSEMBLY

FIGURE 8

CAP WITH EPR DUO-VENT
VALVE ASSEMBLY

FIGURE 9

VENT CAP "MODIFIED SLIT"
FOR POLYETHYLENE
SHIPPING BOTTLE

SECTION "A-A"

MATERIAL: POLYETHYLENE

FIGURE 10