Dried Plutonium Nitrate Decontamination Using HNO₃ or Freon 113

by

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INTER-OFFICE MEMORANDUM

SAVANNAH RIVER PLANT

DPSPU-88-272-16

February 4, 1988

Key Words

Decontamination
Plutonium
Nitrate
Glass
Gloves
Nitric Acid
Freon®

TO: E. N. MOORE, 704-F

INFORMATION ONLYFROM: H. P. HOLCOMB, 772-F *HPH*DRIED PLUTONIUM NITRATE DECONTAMINATION USING HNO₃ OR FREON® 113INTRODUCTION AND SUMMARY

In your memorandum of Dec. 8, 1987, you requested the Separations Technology Laboratory to perform tests to determine the relative effectiveness of Freon® 113 and 18% (3.15M) nitric acid on removing dried plutonium nitrate from Hypalon® gloves destined for use in F B-Line.

Experiments have been designed and conducted to test removal of dried plutonium nitrate from either the gloves or from Pyrex® glass using Freon® 113 or 18% HNO₃. For either case, Freon® 113 was very inefficient for removing dried plutonium nitrate under conditions of moderate agitation of the liquid in contact with the dried compound. Nitric acid, 3.15M, proved to be an excellent agent for decontaminating purposes for both the gloves and for the glass. In tests conducted on the glass or on the gloves on which dried plutonium nitrate had not been removed by Freon® 113, followup with nitric acid efficiently removed the residual plutonium nitrate.

Plutonium nitrate is only one of the many forms of plutonium that can exist as contamination on process waste materials. We chose it for these initial comparative tests because of its availability in solution with known composition and activity, its chemical stability in the experiments conducted, and its relatively high solubility in one of the test agents, nitric acid.

Solubility of the dried plutonium nitrate in 3M HNO₃ is the reason for its success vis-a-vis the failure of Freon® 113 to remove the dried material under identical test conditions. Solubility of plutonium nitrate in Freon® 113 is extremely low and any such aqueous-soluble plutonium material associated with the organic can be removed from the organic by its contact with nitric acid. Success in decontaminating dried plutonium nitrate with nitric acid lent credence to the efficacy of our experimental designs.

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Tests were also conducted to give some measure of the resistance of the Hypalon® glove to continuous contact with 18% HNO₃ or with Freon® 113. Following two weeks' immersion, there was little physical difference noted from the starting material, except the glove piece immersed in the Freon® underwent an 8% weight gain.

These tests do not address the effectiveness of the removal of other plutonium compounds from waste materials using acid or Freon®. Other decontaminating means, such as high pressure spray cleaning with Freon® or other agents, should be evaluated under proper test conditions that are not available in the Separations Technology Laboratory.

EXPERIMENTAL - MATERIALS

Glove Tested

The glove provided for testing was a "North Asymmetrical Glove, 8YLY30 (3-87)" with the number "B3550" imprinted on the outer cuff.

Pieces of the glove, roughly circular and 1½" in diameter, were cut from near the palm area. After placing each test piece on an individual Kimfill® board, 200 µL of a stock Pu(NO₃)₄ solution, described following, was deposited near the center of the glove piece. Small portions of 3M HNO₃, used to rinse each pipette, were also deposited on the glove. Each test piece was then dried under an infrared heat lamp until there was no liquid remaining. A Polaroid photo of the resulting test piece is attached as Figure 1.

Stock Solution of Plutonium Nitrate

A stock solution of Pu(NO₃)₄ was prepared so that a 200-µL aliquot would contain approximately 1×10^8 alpha d/m. This was done by adding 1 mL of a C-7 solution to 10 mL of 1M HNO₃. The resulting gross alpha analysis of the 11 mL was 6.026×10^8 d/m/mL. On alpha pulse height analysis, 92.13% of the alphas were from Pu²³⁹⁻⁴⁰. Therefore, a 200-µL aliquot of this solution would contain 1.20×10^8 d/m alpha, 1.10×10^8 of which were Pu²³⁹⁻⁴⁰.

Reagent Solutions

Freon® 113 liquid was provided by you. A sufficient quantity of 3.15M (18%) HNO₃, for use in all tests, was prepared by dilution of 15.7M with deionized water.

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EXPERIMENTAL - INITIAL TESTS USING DRIED PLUTONIUM NITRATE ON GLASS

Distribution of Plutonium Nitrate Between Freon® 113 and 3.15M Nitric Acid

One initial concern was to how to determine the plutonium content of the Freon® 113 since it is organic and somewhat difficult to prepare alpha mounts of. We decided to try a stripping technique in which 200 μ L of the plutonium nitrate stock solution was added to a centrifuge cone containing 10 mL of 3.15M HNO_3 (top phase) and 10 mL of Freon® 113 (bottom phase). The resulting mixture was vortex mixed for 2 minutes and then centrifuged to ensure effective separation of phases. Following the contact, duplicate alpha mounts showed the nitric acid phase to contain 1.12×10^8 d/m and 1.21×10^8 d/m, respectively, indicating, from the average, that better than 97% of the plutonium nitrate was contained in the acid phase.

Glass Beaker Tests - Components

Several preliminary tests were conducted using 50-mL beakers in which 200 μ L of the plutonium nitrate stock solution had been deposited on the beaker inner bottom, with pipette rinse acid added. The beakers plus liquid, containing plutonium nitrate, were dried under heat lamps just until no liquid was visibly present.

Solutions employed were the stock Freon® 113 and the stock 3.15M HNO_3 . Agitation of the solution in contact with the dried plutonium nitrate was by a 3/4" X 5/16" Spinbar® powered by a Variac-controlled magnetic stirrer, always used at the same power setting when mixing.

For each test, a new, separately-dried, Pu-containing beaker and new Spinbar® were employed to minimize cross-contamination. Every test was done in duplicate.

Glass Test #1 - Pu Nitrate Dried In Beaker Mixed with 18% HNO_3

To the prepared beaker was added 20 mL of 3.15M HNO_3 plus a new Spinbar®. The beaker and its contents were magnetically mixed so that a good liquid vortex was produced for 30 minutes. The Spinbar® rotated on the bottom of the beaker where the deposited $\text{Pu}(\text{NO}_3)_4$ remained following drying.

Following mixing, the liquid contents was removed. The beaker and Spinbar® were gently rinsed with 5 mL additional acid that was combined with the original wash acid. Alpha mounts of the acid were prepared and counted.

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Results were:

	<u>Duplicate #1</u>	<u>Duplicate #2</u>
Total alpha d/m re-covered in the 25 mL of 3.15M HNO ₃	1.21 X 10 ⁸	1.18 X 10 ⁸
% recovery of total alpha originally dried in beaker	101	98

Therefore, the 3.15M HNO₃ was quite effective in removing the dried plutonium nitrate from the bottom of the beaker.

Glass Test #2 - Pu Nitrate Dried in Beaker Mixed with Freon® 113

This test was conducted exactly like Glass Test #1 except 20 mL of Freon® 113 was used as the liquid in the 50-mL beaker containing 1.2 X 10⁸ alpha d/m dried on the bottom. Mixing, with a new Spinbar®, was conducted in the same manner.

However, to check the alpha content of the Freon® 113 after mixing, a 5 mL aliquot of it was equilibrated with 5 mL of 3.15M HNO₃. An alpha mount of the acid phase was mounted and counted and assumed, because of the acid-Freon® equilibration test previously conducted, to be equivalent to the alpha removed and thus contained in the Freon® 113 phase.

Results were:

	<u>Duplicate #1</u>	<u>Duplicate #2</u>
d/m alpha associated with Freon® phase	1.73 X 10 ⁵	1.34 X 10 ⁵
% recovery by Freon® of initially dried Pu nitrate alphas	0.14%	0.11%

So, Freon® 113 was inefficient in removing the dried plutonium nitrate in the beaker bottom, even with the Spinbar® in almost direct contact with the dried material while mixing.

Glass Test #3 - Pu Nitrate Dried in Beaker Mixed with Freon® 113 Followed by Filtration of Freon® Through 1.2-μ Membrane Filter

For this test, conducted similarly to Glass Test #2, the Freon® 113, following mixing, was filtered through a 1.2 μ-rated membrane

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filter to see if possibly some plutonium particulates were being retained by the Freon®. Following filtration of the wash and rinses, the filters were placed in a clean beaker with 10 mL of 3.15M HNO₃ and mixed for 30 minutes to remove any Pu solubles from the filters. The acid was alpha mounted and counted.

Results were:

	<u>Duplicate #1</u>	<u>Duplicate #2</u>
d/m alpha associated with 1.2-μ filter removed by the acid	1.15 X 10 ⁵	6.01 X 10 ⁴
% of original alpha dried in beaker captured on filter and removed by acid	0.1	0.05

There were very few acid-soluble Pu particulates that were retained by the 1.2-μ membrane filter on filtration of the Freon® that had been mixed with the dried Pu nitrate.

Glass Test #4 - Flush of Beakers Used in Glass Test #3 With HNO₃

The beakers from Glass Test #3, following mixing with Freon® 113, were employed in a test to see what residual dried Pu nitrate, not removed by Freon®, could be removed by 3.15M HNO₃. So, to each beaker was added 10 mL of the acid together with a new Spinbar®. Each was mixed for 30 minutes. Following the mixing, an aliquot of the acid was alpha mounted and counted.

Results were:

	<u>Duplicate #1</u>	<u>Duplicate #2</u>
Total alpha d/m recovered in acid	1.0 X 10 ⁸	9.0 X 10 ⁷
% recovery in the acid of the original Pu alphas dried in the beaker	83	75

This fourth glass test shows that a minimum of 75% of the original Pu nitrate dried in the beaker bottom remained there even following contact by Freon® 113 for 30 minutes with Spinbar® agitation near the deposit. Most of the residual Pu nitrate was recovered in the acid wash.

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EXPERIMENTAL - TESTS USING FREON® 113 OR 3.15M HNO₃ TO REMOVE
DRIED PLUTONIUM NITRATE FROM HYPALON GLOVE PIECES

Procedure

For each of these tests, 100 mL beakers were used in which the glove piece containing the dried plutonium nitrate was folded and placed into the beaker so that the resulting semiconical glove piece had the deposited plutonium facing upwards. Quantities of liquid, 80 mL, were used so that the entire glove piece was submerged. A Spinbar® was used for agitation and could move freely without contact with the submerged glove piece. This experimental setup, used for all of the glove tests, is shown in the attached Polaroid photo labeled Figure 2. Mixing was constantly controlled via the same Variac setting for the magnetic stirrer. A slight vortex was present at the top portion of the liquid. New Spinbars® and beakers were used for each test to prevent cross contamination. Again, every test was conducted in duplicate.

Glove Test #1 - Mixing with Freon® 113

After mixing for 30 minutes with 80 mL of Freon® 113, the liquid was transferred to a 250-mL Erlenmeyer flask. The beaker and its contents were gently rinsed with 40 mL of incrementally-added Freon®, which was combined with the original 80 mL in the flask. The 120 mL of Freon® was equilibrated with 40 mL of 3.15 M HNO₃ to remove any plutonium associated with the Freon® phase. An aliquot of the acid phase was alpha mounted and counted.

Results were:

	<u>Duplicate #1</u>	<u>Duplicate #2</u>
Total alpha d/m associated with Freon® phase	9.0 X 10 ⁴	3.6 X 10 ⁵
% of original alpha deposited on glove removed by Freon®	0.08	0.3

A Polaroid photo, Figure 3, is attached showing the appearance of the glove piece used in Duplicate #1 following contact with the Freon®. The dark character of the dried plutonium nitrate is still quite apparent and, as the data indicate, very little dried plutonium nitrate was removed by the Freon® wash.

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Glove Test #2 - Washing Freon®-Treated Gloves With Acid

Each of Freon®-washed glove pieces from Glove Test #1 was placed into a clean 100-mL beaker. 80 mL of 3.15M HNO₃ was added, and a new Spinbar® inserted. Mixing was again for 30 minutes. After mixing, the acid was emptied into individual, clean 125 mL Erlenmeyer flasks. The beakers, Spinbars®, and test pieces were washed with portions of 40 mL of 3.15M HNO₃. The washes were added to the respective flasks, and their contents mixed well. Aliquots were alpha mounted and counted.

Results were:

	<u>Duplicate #1</u>	<u>Duplicate #2</u>
Total alpha d/m recovered in acid	1.26 X 10 ⁸	1.34 X 10 ⁸
% of initially dried Pu nitrate recovered by acid washing following initial Freon® wash	105	112

These data, combined with those from the previous test, indicate that the Freon® 113 removed very little of the dried plutonium nitrate from the glove pieces. The residual Pu was readily recoverable by acid washing.

Glove Test #3 - Removing Dried Pu Nitrate From Glove Pieces
With 3.15M HNO₃

New glove pieces with 200 µL of dried plutonium nitrate stock solution on them were placed into new beakers. Into each was added 80 mL of 3.15M (18%) HNO₃ and a new Spinbar®. Mixing was for 30 minutes at the same spin rate as the previous experiments. Following the mixing period, the liquid was drained from the beakers into clean, individual 125-mL Erlenmeyer flasks. Each beaker was rinsed with portions of a total of 40 mL of 3.15M HNO₃ with the rinses being added to the initial washes. Following thorough mixing, alpha mounts were prepared and counted.

Results were:

	<u>Duplicate #1</u>	<u>Duplicate #2</u>
Total alpha d/m recovered in acid washes & rinses	1.30 X 10 ⁸	1.07 X 10 ⁸
% of initial alpha d/m dried in beaker recovered in acid	108	89

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A Polaroid photo, shown as Figure 4, is a picture of the glove piece from Duplicate #1 following the acid washing. Its appearance is very similar to those of the pieces resulting from acid washing of the initially-Freon®-washed pieces described in Glove Test #2. The dark spot where the dried plutonium nitrate originally was deposited had lightened considerably.

EXPERIMENTAL - EXPOSURE OF GLOVE PIECES TO FREON® AND HNO₃

Two pieces, each approximately 4½" X 3", of the test glove were cut from near the portion where the pieces for the foregoing tests were taken. After weighing, one was submerged in 200 mL of Freon® 113 contained in a 500-mL Erlenmeyer flask that was kept stoppered. The other piece was similarly submerged in 200 mL of 3.15M HNO₃. After one week at room temperature, the pieces were removed, washed well with water, dried by blotting with lint-free Kimwipes®, and reweighed.

The pieces were resubmerged into the same respective liquids for one more week at room temperature. They were again removed, washed well with water, blotted dry, and reweighed. These treated pieces are being returned to you in plastic bags for your observation. The only noticeable difference I could detect was that the orange-colored middle layer of the glove piece treated in the acid had turned a dark tan. There was no other indication of any reactivity between the glove pieces and the liquids.

Results of the weighings were:

	<u>Immersed in Freon® 113</u>	<u>Immersed in 3.15M HNO₃</u>
Initial wt, g	23.87	26.42
After one week's submersion, g	25.78	26.90
After two weeks' submersion, g	25.86	26.96

Over the two-week period, the piece immersed in the Freon® did have a weight gain of 8.3 wt%; that in the 3.15M HNO₃, 2.0%.

CONCLUSIONS

Freon® 113 was not effective, under our test conditions, in removing dried plutonium nitrate from Hypalon® gloves or from Pyrex® glassware,

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even under conditions of a high degree of agitation in the vicinity of the plutonium deposit. Nitric acid, 18% or 3.15M, was quite efficient in doing the same job, due to the much greater solubility of plutonium nitrate in the aqueous solvent as compared to that in the Freon®. So, if you are considering the use of either Freon® 113 or 18% HNO₃ as decontaminating agents, I would certainly choose the latter based on our tests. Use of the former as a high velocity liquid for decontamination would also necessitate further process treatment of the Freon® in order to recover plutonium removed strictly by physical impingement. Treatment of acid-recovered plutonium nitrate to recover Pu should not be as complicated.

However, since proper test conditions for other decontaminating methods are not available in the Separations Technology Laboratory, such techniques should not be ruled out until they can be proven ineffective.

After two week's immersion in either Freon® 113 or in 3.15M HNO₃, there was very little change in the physical character of the Hypalon® glove pieces so tested. The piece immersed in the Freon® did undergo an 8% weight gain.

HPH/h

Enclosures to ENM copy only: Uncontaminated glove pieces in plastic bags;

Original Polaroid Photos.

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Figure 1

Original Glove Piece With Deposited Pu Nitrate In Center

Figure 2

Experimental Setup For Washing Glove Pieces with Liquids

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Figure 3

Glove Piece After Freon Wash Showing Residual Pu In Center

Figure 4

Glove Piece After Acid Wash Only - Pu Removed

NORTH ASYMMETRICAL GLOVE

8YLY30 (3-87)

On Cuff - B 3550

Immersed 2 weeks in 18% HNO₃

NORTH ASYMMETRICAL GLOVE

8YLY30 (3-87)

On Cuff - B 3550

Immersed 2 weeks in Freon 113