DISTRIBUTION SHEET

To	From	Page 1 of 1
PFP Process Engineering	Plutonium Process Support Laboratories	Date September 6,1994
Project Title/Work Order		EDT No. 119585
Precipitation of Plutonium from Acidic Solutions Using Magnesium Oxide		ECN No. NA

Name	MSIN	Text With All Attach.	Text Only	Attach./ Appendix Only	EDT/ECN Only
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ENGINEERING DATA TRANSMITTAL

1. EDT 119585

2. To: (Receiving Organization) PFP Process Engineering	3. From: (Originating Organization) Plutonium Process Support Labs.
4. Related EDT No: NA	
5. Proj/Prog/Dept/Div: WAE	6. Cog/Proj Engr: S. A. Jones
7. Purchase Order No: NA	
8. Originator Remarks: For Release	9. Equip/Component No: NA
	10. System/Bldg/Facility: 234-5Z
11. Receiver Remarks:	12. Major Assm Dwg No: NA
	13. Permit/Permit Application No. NA
	14. Required Response Date: 9/6/94

15. **DATA TRANSMITTED**

(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev No.	(E) Title or Description of Data Transmitted	(F) Impact Level	(G) Reason for Transmittal	(H) Originator Disposition	(I) Receiver Disposition
1	WHC-SD-CP-TP-077	-	0	Precipitation of Plutonium from Acidic Solutions Using Magnesium Oxide	SQ	1	1	1

16. **KEY**

Impact Level (F)	Reason for Transmittal (G)	Disposition (H) & (I)
1, 2, 3, or 4 see MRP 5.43 and EP-1.7	1. Approval 2. Release 3. Information 4. Review 5. Post-Review 6. Dist (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment 4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

17. **SIGNATURE/DISTRIBUTION**
(See Impact Level for required signatures)

(G) Reason	(H) Disp	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp
1	1	Cog./Proj. Eng	S. A. Jones	9-1-94	T5-12						
1	1	Cog./Proj. Eng. Mgr.	C. S. Sutter	9/1/94	T5-12						
1	1	QA ~~G. W. Upington~~	D. R. GROTH	9/1/94	T4-19						
1	1	Safety	S. E. Nunn	9/2/94	T4-18						
1	1	G. B. Chronister		9/2/94	T5-04						
1	1	J. F. Durnil		9/2/94	T5-55						
1	1	L. T. Nirider		9/1/94	T5-53						

18. S. A. Jones Signature of EDT Originator — Date: 9-6-94	19. ~~M. W. Gibson~~ Authorized Representative for Receiving Organization — Date: 9/6/94	20. C. S. Sutter Cognizant/Project Engineer's Manager — Date: 9/1/94

21. DOE APPROVAL (if required) Ltr No. _____
- ☐ Approved
- ☐ Approved w/comments
- ☐ Disapproved w/comments

RELEASE AUTHORIZATION

Document Number:	WHC-SD-CP-TP-077, REV 0
Document Title:	PRECIPITATION OF PLUTONIUM FROM ACIDIC SOLUTIONS USING MAGNESIUM OXIDE
Release Date:	9/6/94

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This document was reviewed following the procedures described in WHC-CM-3-4 and is:

APPROVED FOR PUBLIC RELEASE

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WHC Information Release Administration Specialist:

Kara Broz — 9/6/94

(Signature) — **(Date)**

SUPPORTING DOCUMENT		1. Total Pages ~~13~~ 116
2. Title Precipitation of Plutonium from Acidic Solutions Using Magnesium Oxide	3. Number WHC-SD-CP-TP-077	4. Rev No. 0
5. Key Words plutonium, precipitation, hydroxide, magnesium, 10 L KMB 9/6/94 APPROVED FOR PUBLIC RELEASE	6. Author Name: S. K. Jones Signature Organization/Charge Code 8E120/K6F6G	

7. Abstract

Magnesium oxide will be used as a neutralizing agent for acidic plutonium-containing solutions. It is expected that as the magnesium oxide dissolves, the pH of the solution will rise, and plutonium will precipitate. The resulting solid will be tested for suitability to storage. The liquid is expected to contain plutonium levels that meet disposal limit requirements.

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9. Impact Level SQ

10. **RELEASE STAMP**

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DATE SEP 06 1994
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MASTER

CONTENTS

PRECIPITATION OF PLUTONIUM FROM ACIDIC SOLUTIONS USING MAGNESIUM OXIDE

1.0 TEST ITEM IDENTIFICATION

Magnesium oxide will be used as a neutralizing agent for acidic plutonium-containing solutions. These solutions may be, but are not limited to, Argonne chloride scrap solutions or laboratory waste solutions. Additional items may be tested if the method of separating the plutonium from solution to form a stable, storable solid is successful. In addition, the solid/liquid mixture may be transferred to Room 187 for magnetic separation testing. Any other testing will be done under separate test plans.

2.0 GENERAL DESCRIPTION

Plutonium (IV) is only marginally soluble in alkaline solution. Precipitation of plutonium using sodium or potassium hydroxide to neutralize acidic solutions produces a gelatinous solid that is difficult to filter and an endpoint that is difficult to control. If the pH of the solution is too high, additional species precipitate producing an increased volume of solids separated.

The use of magnesium oxide as a reagent has advantages. It is added as a solid (volume of liquid waste produced is minimized), the pH is self-limiting (pH does not exceed about 8.5), and the solids precipitated are more granular (larger particle size) than those produced using KOH or NaOH.

$$MgO(s) + 2H^{+} \rightarrow Mg^{++} + 2OH^{-}$$
$$Pu^{4+} + 4OH^{-} \rightarrow Pu(OH)_4\downarrow$$

Following precipitation, the raffinate is expected to meet criteria for disposal to tank farms. The solid will be heated in a furnace to dry it and convert any hydroxide salts to the oxide form. The material will be cooled in a desiccator. The material is expected to meet vault storage criteria.

3.0 CRITICALITY SAFETY LIMITS

No special test conditions are required. Liquid testing will be performed in a glovebox with a 250-g limit and a 10-L/container maximum volume with no maximum total volume. All items in the unit mass are to be separated from any other unit mass by at least 10 in. (25 cm). Dry air atmosphere for

open storage of active powders will be provided in a desiccator with Drierite* desiccant. The glovebox with the furnace has a 4 x 400-g plutonium limit with no vessel to exceed 4-L in volume. The total volume of all vessels associated with any one unit mass may not exceed 10 L, and all items of any one unit mass are to be separated from any item of any other unit mass by at least 10 in (25 cm).

4.0 INSTRUMENTS AND CALIBRATION

A Mettler 2000** electronic balance will be used to weigh solids produced in the precipitation step.

The temperature being experienced by the plutonium materials contained in a crucible in the furnace will be estimated with an integral thermometer on the Thermolyne*** muffle furnace. It is not necessary to determine the exact time-temperature history of the plutonium material in the crucible.

5.0 FACILITIES, EQUIPMENT, AND MATERIALS

5.1 FACILITIES

Preparation of nonradioactive materials will be performed in Room 191 of the 234-5Z Building. This facility is the Plutonium Process Support Laboratories "cold" laboratory. Room 191 contains top-loading balances, hotplates, and fume hoods suitable for preparing reagents and testing surrogates.

Glovebox 179-4 in Room 179 of the 234-5Z Building will be used for testing involving solutions. This glovebox is configured for and governed by Criticality Prevention Specification CPS-L-114-00020, Set D, which provides for one 250-g plutonium unit mass with unlimited H/X, a 10-L maximum single container size, and an unlimited number of containers. All items associated with any one unit mass are to be separated from another unit mass by at least 10 in. (25.4 cm).

Glovebox 179-10 in Room 179 of the 234-5Z Building will be used for furnace operations. This glovebox is configured for and governed by Criticality Prevention Specification CPS-L-114-00020, Set F, which provides

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*Drierite is a trademark of Hammond Drierite Company.

**Mettler 2000 is a trademark of Mettler Instrument Corporation.

***Thermolyne is a trademark of Thermolyne Corporation.

for four 400-g plutonium unit masses with unlimited H/X*. a 4-L maximum container size, and a maximum 10-L total volume container size for any one unit mass. All items associated with any one unit mass are to be separated from another unit mass by at least 10 in (25.4 cm).

5.2 EQUIPMENT

The following equipment will be used:

Thermolyne muffle furnace (located in glovebox 179-10)
Mettler 2000 electronic balance
Stirring hotplate.

5.3 MATERIALS

The following materials will be used:

Test solution
22-mL sample vials
MgO (from reagent chemicals or ground crucible)
pH paper
Drierite (located in desiccator in glovebox 179-10)
White vinyl tape
Green fabric tape
Blue-bottom, H/X $\leq$ 2 fissile stickers
Green-bottom, H/X $\leq$ 20 fissile stickers
Pink-bottom H/X $\geq$ 20 fissile stickers
Fine-point permanent marking pen
Red wax pencil
One-pint ice cream cartons
Small polyvinyl chloride bag
Filter paper
Filter funnel
Magnetic stir bar
Crucible
Crucible handling tongs.

6.0 SAFETY

Criticality and radiological safety considerations are largely those attendant to glovebox operations with plutonium materials. Safety will be ensured by rigid adherence to Criticality Prevention Specifications CPS-L-114-00010, -00020, -00030, -00040, and -01900, and Plutonium Finishing Plant Radiation Work Procedures.

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*The H/X ratio is the amount of hydrogen (usually water) to the amount of fissile material (usually plutonium).

Special safety precautions are required for high-temperature processing of plutonium in a glovebox. Good practices for glovebox work with high-temperature equipment will be followed. Glovebox gloves will be tied back from the furnace when not in use and the area around the furnace will be kept free of combustible materials. The crucible and any other hot items will be handled with tongs.

7.0 MAINTENANCE AND FAILURES

No special maintenance is required. Failures are not anticipated; however, failures can be corrected, and testing, if interrupted, can be resumed from any point without adverse consequences. Similarly, any test site access interruption will not lead to damaging temperatures or spoiled plutonium product because the maximum temperature, and time at that temperature, experienced by plutonium-bearing solids, the crucible, or the furnace is not critical.

8.0 TEST DATA

Weights and volumes of materials used, initial and final pH values, initial concentrations of plutonium and americium, time-temperature history data for the calcination step, and final plutonium and americium concentrations measured will be entered into a controlled laboratory notebook.

9.0 PERSONNEL

Plutonium Process Support Laboratories personnel will write test plans, perform tests, document results, analyze data, and write test reports.

Plutonium Finishing Plant Analytical Laboratory personnel will provide analytical measurements for plutonium concentrations.

Plutonium Finishing Plant Operations personnel will provide letters of instruction, review and approve test plans, provide test solutions, and provide funding.

Plutonium Finishing Plant Safety Assurance personnel (i.e., Industrial, Nuclear, and Criticality Safety) will review and approve test plans and test results.

Quality Assurance personnel will review and approve test plans.

10.0 WITNESSES

No witnesses are required.

11.0 PROCEDURE

1. Load solution into Glovebox 179-4.
2. Place pink-bottom H/X $\geq$ 20 fissile sticker on outside of hood of Glovebox 179-4.
3. Record visual appearance of solution in controlled laboratory notebook.
4. Transfer approximately 15 mL of solution to a vial.
5. Label the vial with sample ID.
6. Send the 15-mL sample to Plutonium Finishing Plant Analytical Laboratory for H^+, Pu, and Am concentration analyses.
7. Based on the H^+ result, calculate the amount of MgO required to neutralize the solution as follows:

$$\text{weight MgO} = \frac{\text{volume solution x molarity } H^+}{\text{40.3 g/mole MgO}} \times \frac{1}{2}$$

8. Weigh the amount of MgO calculated in step 7.
9. While stirring the solution, slowly add MgO. In the controlled notebook, note any visible changes in the solution.
10. If no undesired effects, such as heating or foaming, are observed, continue to add MgO until the amount calculated in step 7 has been added.
11. Continue to stir the solution until all the added MgO has dissolved, or for a minimum of one hour.
12. Measure solution pH using color-indicating paper strip..
13. If solution remains acidic, calculate the amount of MgO required to neutralize the solution using the following calculation:

$$\text{weight MgO} = \frac{\text{volume solution x } 10^{-pH}}{\text{40.3 g/mole MgO}} \times \frac{1}{2}$$

14. Repeat steps 7 through 13 until the solution pH remains basic.

15. Allow the solution to stand (do not stir) at least 8 hours. If the supernate appears cloudy after 8 hours, allow it to stand an additional 24 hours and proceed with the following steps regardless of the clarity of supernate.

16. Take an approximate 10- to 15-mL sample of the supernate. Do not disturb the solids at the bottom of the container.

17. Send the sample to Plutonium Finishing Plant Analytical Laboratory for Pu and Am concentration analysis.

18. If magnetic separation testing will be applied to the test material, set it aside until notified by Engineering/Environmental Demonstration Laboratory engineer of readiness to receive the material. Otherwise, continue to step 19.

19. Decant as much clear solution as can be decanted without disturbing the solids settled at the bottom.

20. When all possible clear solution has been decanted, suspend the solids and filter the slurry What are the solids and slurry placed in now? Is that on the materials list?.

21. Consolidate the raffinate and place it in a poly bottle.

22. Remove the pink-bottom H/X $\geq$ 20 fissile sticker from the original container and destroy it.

23. Place a new pink-bottom H/X $\geq$ 20 fissile sticker on the poly bottle used in step 22 to contain the raffinate.

    a. List EL. WT as *.

    b. Change ID number to PPSL-XXX-R.

24. Change the pink-bottom H/X $\geq$ 20 fissile sticker on outside of glovebox hood.

25. Place green-bottom H/X $\leq$ 20 fissile sticker near filtrate.

    a. List EL. WT as amount in original solution.

    b. Change ID number to PPSL-XXX-P.

26. Place green-bottom H/X $\leq$ 20 fissile sticker on outside of glovebox 179-4 in vicinity of the filtrate.

    a. List EL. WT as amount in original solution.

    b. Change ID number to PPSL-XXX-P.

27. Allow the solids to air dry.

28. Transfer air-dried solids to glovebox 179-10, which contains the muffle furnace. Observe criticality spacing requirements.

29. Place a green-bottom H/X $\leq$ 20 fissile sticker on the outside of glovebox 179-10.

30. Adjust criticality inventory list.

31. Plug muffle furnace into utility outlet.

32. Tie unused gloves away from muffle furnace surfaces.

33. Weigh and record the weight of a crucible in the controlled laboratory notebook.

34. Transfer the dried solids (including filter paper) to the weighed crucible.

35. Weigh the loaded crucible. Record the weight of the loaded crucible in the controlled laboratory notebook.

36. Place the loaded crucible in the muffle furnace. Record the time and muffle furnace temperature in the controlled laboratory notebook.

37. Move the green-bottom, H/X $\leq$20 fissile sticker located on the window of glovebox 179-10, to a position near the muffle furnace.

38. Temporarily affix the package sticker to the muffle furnace door handle.

39. Tie working gloves away from muffle furnace surfaces.

40. Heat muffle furnace to 500°C (or other temperature dictated by vault storage requirements).

41. Leave loaded crucible in muffle furnace at least 1 hour.

42. When the loaded crucible has been in the muffle furnace a minimum of 1 hour, turn the muffle furnace setpoint to 0°C.

43. Allow the loaded crucible to cool in the muffle furnace until the muffle furnace temperature has cooled to a minimum of 300°C.

44. Transfer the loaded crucible to the desiccator as follows:

    a. Remove desiccator lid.

    b. Position glovebox floor handle down to ensure fouling of the greased sealing surface does not occur.

    c. Using tongs, carefully withdraw the loaded crucible from the muffle furnace.

d. Promptly place the loaded crucible in the desiccator, and replace desiccator lid.

45. Allow the loaded crucible to cool in the desiccator 2 hours or longer.

46. Remove the fissile stickers from the muffle furnace and the window near the muffle furnace and destroy them.

47. Put a blue-bottom, H/X $\leq$2 fissile sticker on the desiccator.

48. Put a blue-bottom, H/X $\leq$2 fissile sticker on the glovebox window.

49. Update glovebox inventory list.

50. Weigh an empty 1-lb slip-lid can with lid.

51. Record the tare weight in the controlled laboratory notebook and on the empty 1-lb slip-lid can.

52. Update glovebox inventory list.

NOTE: Do not leave the loaded crucible or the loaded 1-lb slip-lid can open or unsealed and out of the desiccator for longer than required to effect the transfer and weighing operations.

53. After the loaded crucible has cooled in the desiccator at least 2 hours:

a. Withdraw the loaded crucible from the desiccator.

b. Working over a stainless steel tray, quickly but carefully transfer the contents of the crucible to the tared 1-lb slip-lid can. Tap and, if necessary, scrape the crucible to remove all contents.

c. Transfer any spilled crucible contents from the stainless steel tray into the slip-lid can.

d. Weigh the loaded 1-lb slip-lid can with lid.

e. Record the gross weight in the controlled laboratory notebook.

f. Return the 1-lb slip-lid can to the desiccator.

g. Update glovebox inventory list.

54. Add appropriate stickers as follows:

a. Remove the 1-lb slip-lid can from the desiccator.

b. Remove the blue-bottom, H/X $\geq$2 from the desiccator and place it on the 1-lb slip-lid can.

c. If moisture pickup determinations will be made, move the package to the Mettler 2000 electronic balance. Otherwise, move the package out of the work area until it is removed to other storage.

d. Update inventory list to indicate plutonium content, volume, and location of the slip-lid can and crucible.

12.0 DISPOSITION OF TEST ITEM

At the completion of testing, test materials will be stored or disposed of according to appropriate operating procedures.

13.0 REPORTS

Status will be reported in Plutonium Process Support Laboratories Weekly Reports. The final status report will be issued as a supporting document.

14.0 DATA SHEETS

Data sheets will be maintained in a controlled laboratory notebook.

15.0 REFERENCES

Criticality Prevention Specification, CPS-L-114-00010, Westinghouse Hanford Company, Richland, Washington.

Criticality Prevention Specification, CPS-L-114-00020, Westinghouse Hanford Company, Richland, Washington.

Criticality Prevention Specification, CPS-L-114-00030, Westinghouse Hanford Company, Richland, Washington.

Criticality Prevention Specification, CPS-L-114-00040, Westinghouse Hanford Company, Richland, Washington.

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Peretrukhin, V. F. and V. I. Spitsyn, 1982, "Electrochemical Determination of the Oxidation Potentials and the Thermodynamic Stability of the Valence States of the Transuranium Elements in Aqueous Alkaline Media," *Bulletin of the Academy of Sciences USSR, Division of Chemical Sciences*, Vol. 4, pp. 826-831.

APPENDIX A
CRITERIA FOR DISPOSAL OF SOLUTIONS TO D-4 DRAIN

APPENDIX A

CRITERIA FOR DISPOSAL OF SOLUTIONS TO D-4 DRAIN

Organics are not present in disposal solutions. Disposal solutions will contain nitrates and will go to an evaporator.

Arsenic, barium, cadmium, mercury, and selenium are not present in disposal solutions. These toxic metals are not permitted.

Specifically mentioned (approved) in the Part A Permit Application are the *following:*

Sodium hydroxide
potassium hydroxide
sodium nitrite,
ferric nitrate
nitric acid
chrome*
lead*
silver*
carbon tetrachloride**
aluminum nitrate
aluminum fluoride
potassium fluoride
magnesium nitrate
calcium nitrate
other minor trace metal ions

Plutonium, americium, and uranium are acceptable but the quantity in total grams (or volume and concentration) and the uranium enrichment or the isotopic distribution needs to be known. Only nuclear material item transfer amounts are of interest.

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*Notify Plutonium Finishing Plant Environmental Engineering of concentration and quantity.

**Only trade quantities are present (water soluble).

APPENDIX B
JOB SAFETY ANALYSIS

JOB SAFETY ANALYSIS

Job Description: Precipitation of Plutonium from Acidic Solutions using Magnesium Oxide

Component: Plutonium Process Support Laboratories Building/Area: 234-5Z

Prepared by: S. A. Jones

Date: Initials: Review Dates:

SAFETY EQUIPMENT REQUIRED	TOOLS AND EQUIPMENT REQUIRED	JOB PREPARATION
Special Work Permit (SWP) Clothing Gloves, Surgeons'	Beaker Filter funnel Muffle furnace Crucible Balance Stirring hotplate	Ensure necessary equipment is in place and operating properly. Review Radiation Work Procedures and Criticality Prevention Specifications CPS-L-114-00020, -00030, -00040, and -01900
	HAZARDOUS MATERIALS	RELATED REQUIREMENTS
	Plutonium oxide	Radiation Work Permit yes Criticality Safety Specification yes

JOB STEP	HAZARD	HAZARD CONTROL AND PROTECTIVE EQUIPMENT
1. Bag out 15-mL sample solution to hood in Room 187.	Handling fissile materials	Work will be performed in accordance with approved procedures.
2. Transfer solution to Plutonium Finishing Plant Engineering Laboratory to determine Pu and Am concentrations in solution.		
3. Perform precipitation and filtration steps.	No hazards exist; work performed in glovebox	
4. Prepare muffle furnace and load with hydroxide precipitate in crucible.		
5. Maintain temperature for 2 hours.		
6. Cool for at least 2 hours in desiccator.		
7. Clean and put away equipment.	Handling fissile material	