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LANL Overview

Roberta Mulford

MET-1 (Actinide Processing Support)

Manufacturing Engineering & Technology Division

JOWOG 22/2 – Actinide Chemical Technology

July 9-13, 2012

AWE, Aldermaston, UK

Associate Directorate-Plutonium Science and Manufacturing

- **ADPSM Mission Statement**
  - The Plutonium Science and Manufacturing Directorate provides world-class, safe, secure, and reliable special nuclear material research, process development, technology demonstration, and manufacturing capabilities that support the nation's defense, energy, and environmental needs.

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Actinide Engineering and Science (MET-1)

- **Mission Statement**
  - We safely and efficiently process plutonium, uranium, and other actinide materials to meet national program requirements, while expanding the scientific and engineering basis of nuclear weapons-based manufacturing, and while producing the next generation of nuclear engineers and scientists.

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Actinide Process Chemistry (NCO-2)

- **Mission Statement**
  - Actinide Process Chemistry (NCO-2) safely and efficiently processes plutonium and other actinide compounds to meet the nation's nuclear defense program needs. All of our processing activities are done in a world class and highly regulated nuclear facility. NCO-2's plutonium processing activities consist of direct oxide reduction, metal chlorination, americium extraction, and electrorefining. In addition, NCO-2 uses hydrochloric and nitric acid dissolutions for both plutonium processing and reduction of hazardous components in the waste streams. Finally, NCO-2 is a key team member in the processing of plutonium oxide from disassembled pits and the subsequent stabilization of plutonium oxide for safe and stable long-term storage.

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Aqueous Chloride Processing

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Brenda Griego
Joe Ray Martinez
Sylvia Nunn (Form-B from NCO-5)
Victor Salazar
Chester Smith
Felix Valdez (Form-B to NCO-4)

Nitrate Processing

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Georgette Ayers
Yvonne Martinez
Greg Ortega
Marvin Romero
Felice Valdez

PSM Organizational Responsibilities

Equipment Lifecycle

	Phase I	Phase II	Phase III	Phase IV
	Technology Development & Demonstration	Implementation	Operations & Maintenance	D&D
Deliverables	•SON •TS&R •Technology Development •Technology Assessment Rpt •Proj Approval & Funding	•F&OR •Design Change Package •Equipment Procurement •Fabrication & Installation •Construction •As-Built Config. •Maintenance Program •Testing & Startup Plan	•Testing & Startup •Process Qualification with WI's •Operator Training & Qualification •ORR/RA •Operations •Maintenance •Terminate Operations	•D&D Plan/Design •D&D •Waste Disposition •Area Turnover •Project Closeout
Divisions				
IPM	S S S R	S → S	S R	S → S
MET	R → R	S → S	R S S R S	S → S
NCO	S S	S S S → S	S S R → R S S	S → S
NPI	S	R → R	S → S	R → R
FOD	S S	S → S	S → S	S → S

R – Accountable for delivery of milestone S – Support required to deliver milestone

Stage Gates

Line of Responsibility

Aqueous Nitrate Processing at Los Alamos

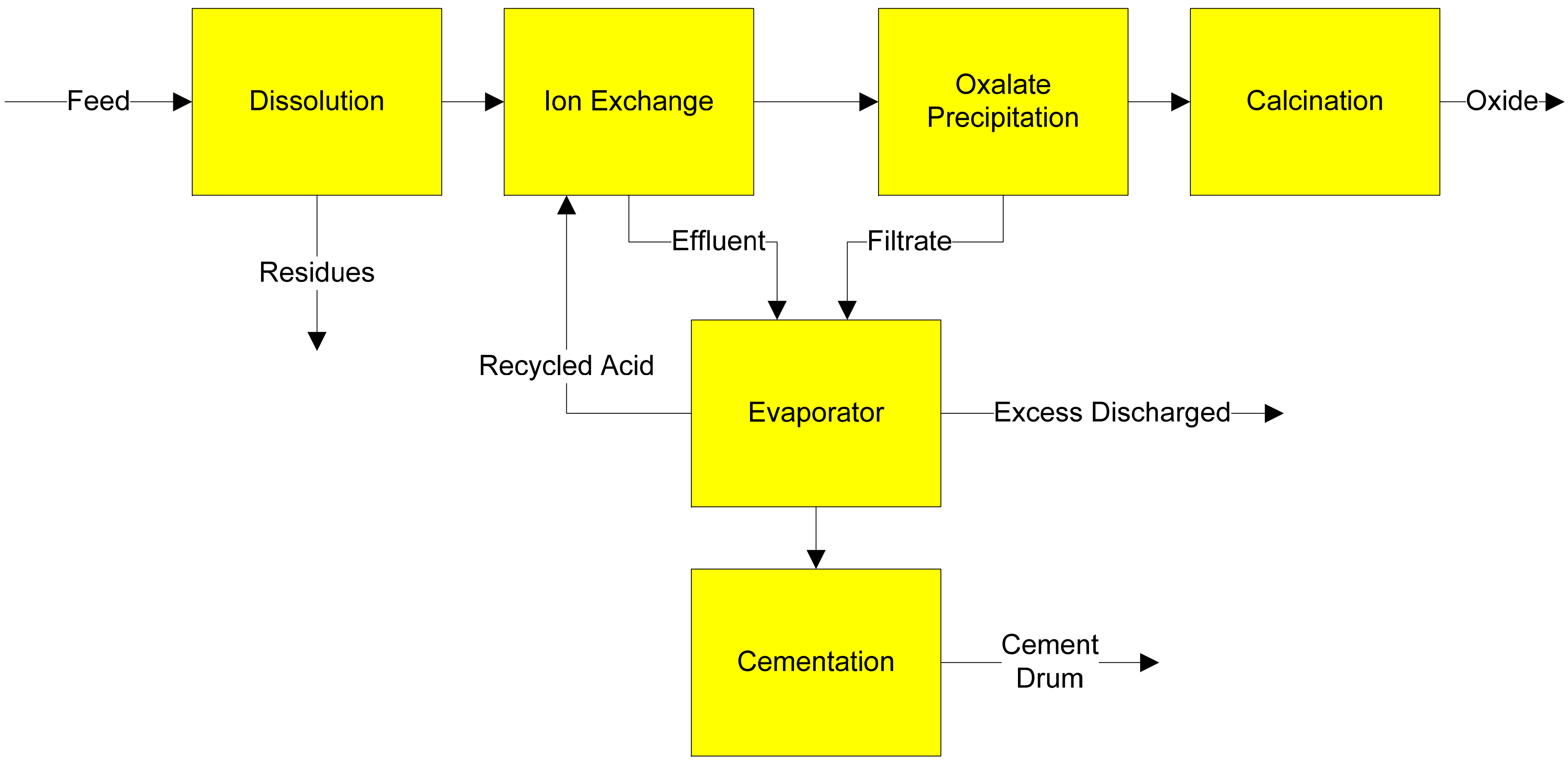
Casey Finstad, Mary Ann Stroud

Roberta Mulford, presenter

Presented to JOWOG 22-2
July 10, 2012

Aldermaston Weapons Establishment

Aqueous Nitrate Flowsheet shows 4 major steps



Ceramic or metal feed is from several sources

- **Vault**
  - Oxides (LZB, PMB), residues, sweepings (VTB)
- **Casting Skulls, Anode Heels**
  - Suspect chloride oxide
- **PuBe**
  - High purity mixed metal oxides

Pu residues are dissolved, usually in a batch process

- Add 15.6M* nitric acid
- Add HF
- Sparge with argon or air to mix
- Slowly add feed

Dissolution requires time and often, fluoride catalysis

- **Reflux ~96 ^{o}C for at least 4 hours**
  - Evaporation and Condensation

$PuO_2 + 6HNO_3 \xrightarrow{HF}$
$Pu(NO_3)_6^{-2} + 2H_2O + 2H^+$

$Pu + 6HNO_3 \xrightarrow{HF}$
$Pu(NO_3)_6^{-2} + 2H_2 + 2H^+$

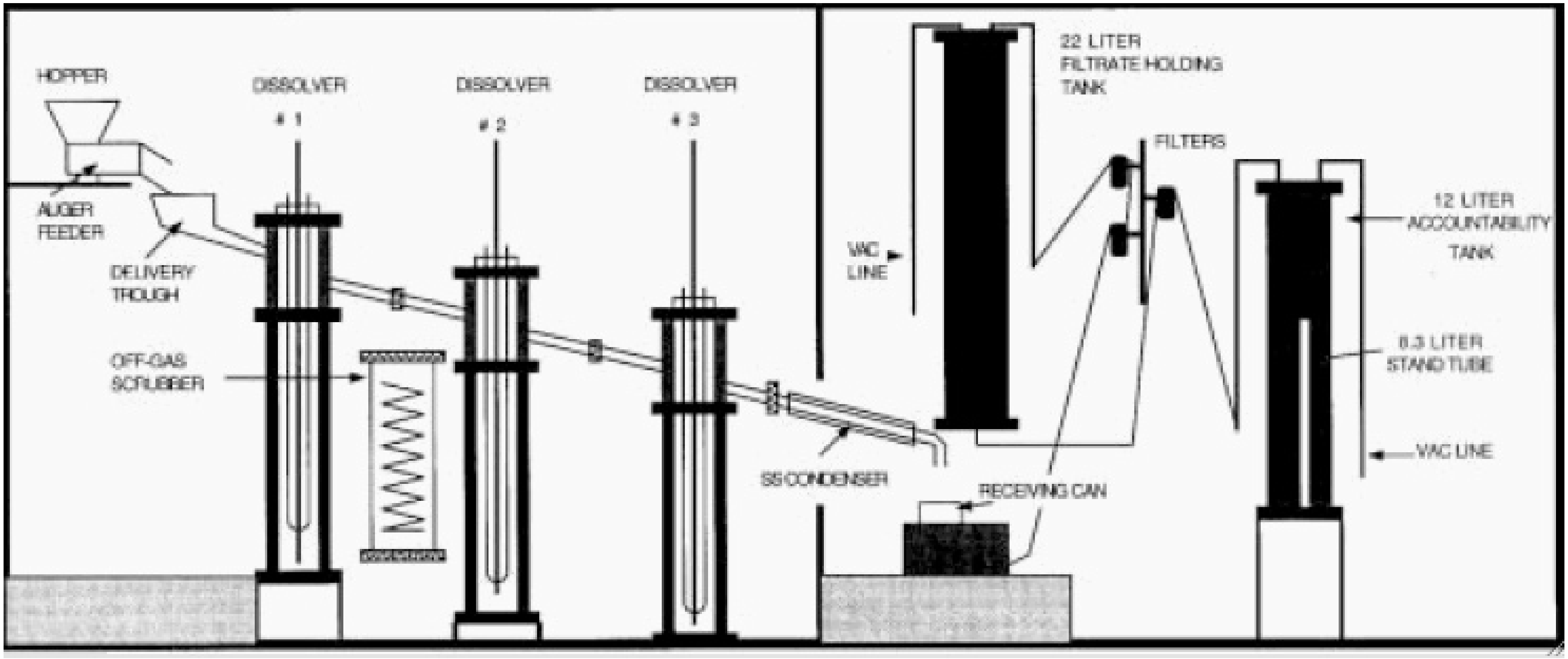
Fluoride ion removed from system after dissolution

- **Add aluminum nitrate**

$$Al(NO_3)_3 + 6HF \rightarrow AlF_6^{-3} + 3H^+ + 3HNO_3$$

- **Filter and Rinse**
- **Chloride concentration determination**
  - determination as necessary, based on feed (e.g. skull)

Cascade Dissolvers can provide continuous feed process for larger quantities



- **Ensure air is flowing to airlift**
- **Bring acid in dissolvers to ~90-100 C**
- **Add feed with CaF2 into hopper**
- **Start acid drip**

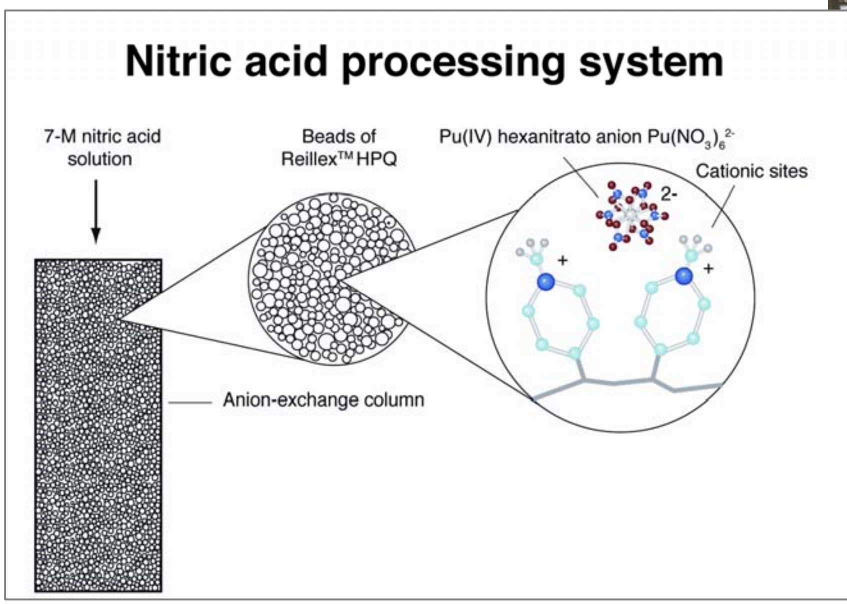
Ion Exchange requires preparation of feed and column

- **Feed Treatment**
  - Verify SNM
  - Adjust Molarity ~ 7M
  - Optional Peroxide Treatment
    - Pu(VI) -> Pu(IV)

- **Condition column**
  - ~7M nitric acid
  - 10 liters added at 30 liter/hour

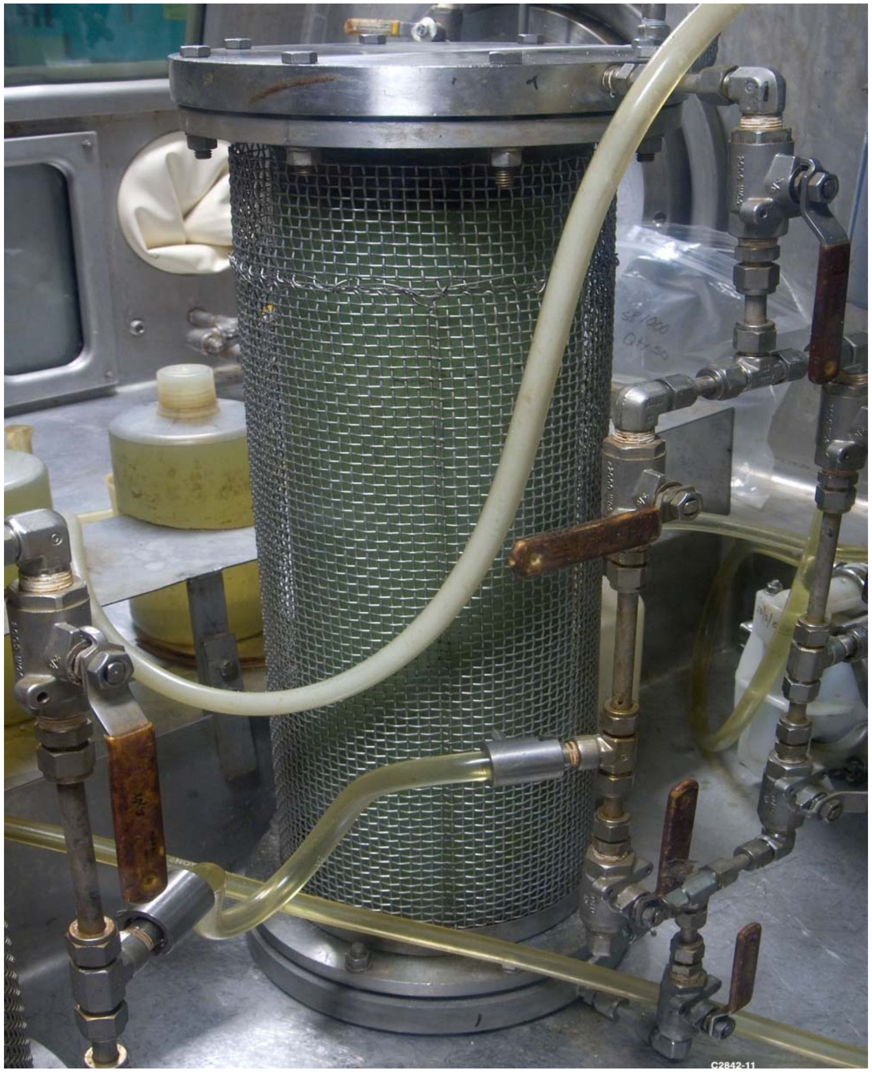
Ion Exchange selectively captures plutonium

- **Pumped through the three serial columns**
- **Loading Rate varies with Pu concentration**
  - 50-90 liters/hr



Plutonium purified by washing ion exchange column

- 5M acid
- Varying Volumes
- 50-70 liters/hr

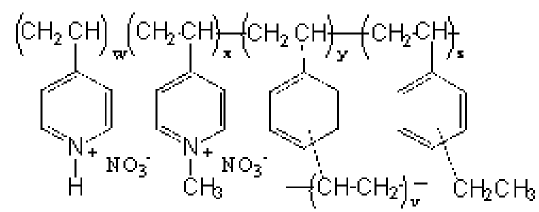


Plutonium usually recovered from ion exchange as Pu(IV)

- **Elute column**
  - 0.45M acid
  - 40-50 liters/hr
  - ~90 liters
    - reducing
  - Hydroxylamine
    - convert to Pu(III)
    - optional

Technical Safety Requirements govern ion exchange resin lifetime and maintenance

- **Resin can degrade, evolve H_2**
  - Polyvinyl pyridine
  - Max. 5 years
  - Max. 500 Mrad exposure
  - Resin kept wet
- **Pressure Release Valves**
  - Set point <25 psig
  - Inspected annually



Reillex™ HPQ

Plutonium recovered as a solid Pu(III) oxalate precipitate

- **Reduce Pu(IV) to Pu(III) (Hydroxylamine nitrate)**

  $2Pu(NO_3)_4 + 2NH_2OH{\cdot}HNO_3 \rightarrow 2Pu(NO_3)_3 + 2H_2O + N_2 + 4HNO_3$

  80-100% stoichiometric excess

- **Add oxalic acid** 10% stoichiometric excess

  $2Pu(NO_3)_3 + 3\ H_2C_2O_4 \rightarrow Pu_2\ (C_2O_4)_3 + 6HNO_3$

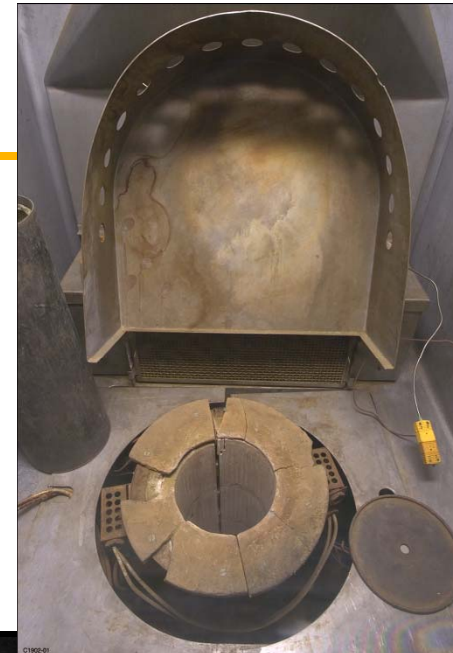
- **Filter and wash**
  - Oxalate Filtrate to Evaporator

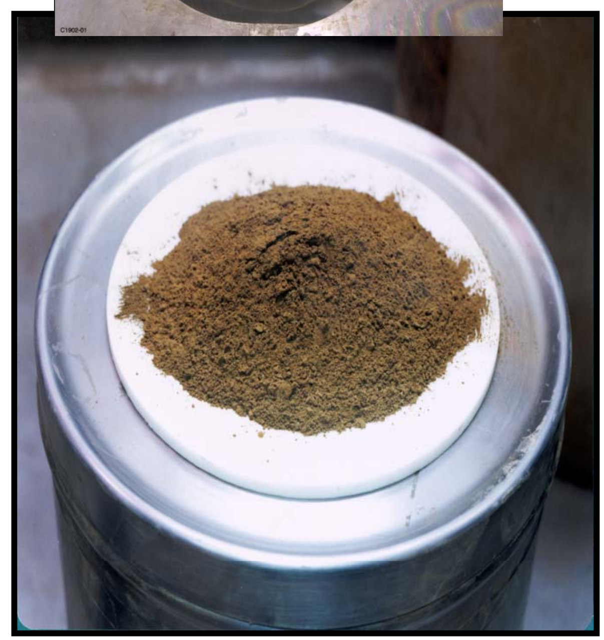
- Pu (IV) Oxalate can be obtained if required

Calcination converts oxalate to oxide

- **Calcine for approximately 6 hours at 600 ^{o}C**

$$Pu_2(C_2O_4)_3 + 2O_2 \rightarrow 2PuO_2 + 6CO_2$$





Evaporator removes contaminants from acid solutions

Products

- **Recycled Acid**
  - Molarity preserved
- **Bottoms**
  - Salts
  - Liquid

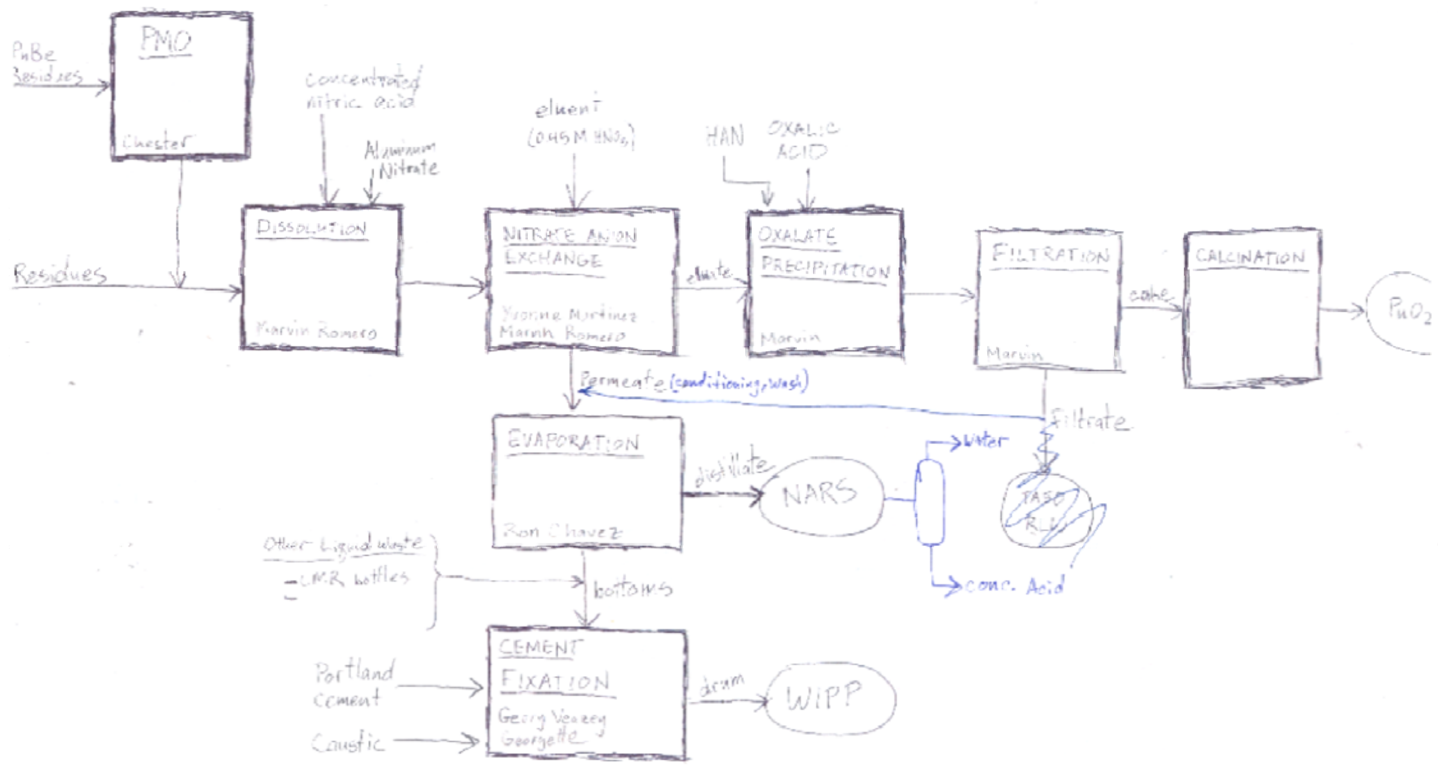
Cement Fixation stabilizes salt residue waste for disposal

- **Immobilize RCRA waste constituents**
- **TRU waste sent to WIPP**

Summary

- **Process optimized over 60 years**
- **Improvements**
  - Resins changed over time to improve stability
  - Acid distillation and reuse an important innovation
  - Air brake installed recently to prevent backflow to acid tank
- **Challenges**
  - High chloride feeds can cause difficulties

Aqueous Nitrate process notes and personnel



Establishing an Americium-241 Oxide Production Capability at the Los Alamos National Laboratory. LA-UR-12-21319

Louis D. Schulte, Technical Lead, MET-1

Co-Authors and Acknowledgements

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- Benjie Martinez (NPI-8) Project Manager.
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- Sheldon Apgar & Christopher Thorn for design, drawings & mechanical work.
- Steve McKelvey for scheduling, project controls. Bradley E. Skidmore Process Engineering.

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- Dan Gonzales (RP-3) and Adam Davis (AET-2) for dose assessment work, Drew Kornreich (AET-2) for analysis & project documentation.

Who Wants This Stuff?

- Nuclear decay by nearly monoenergetic alpha emissions—5.44 and 5.49 MeV—with an associated high yield of 59.6 keV gamma emissions. Glenn Seaborg called ^{241}Am "The Most Useful Actinide Isotope".

  - The largest $^{241}AmO_2/Be$ (AmBe) neutron sources, and the majority of these sources, are used for oil and natural gas well-logging purposes. ^{241}Am has a half-life (432 years) useful for sources because this relatively high-specific activity (3.43 curies per gram) provides good neutron source efficiency, useful neutron flux ranges, and steady neutron output for years in an AmBe source.

  - Ionization smoke detectors use $^{241}AmO_2$. The alpha emission finds use in measurement of thin films, gas densities, and as a source of alpha ionization.

  - Low-energy gamma emission transmission/absorption and backscatter measurements, primarily for determination of thickness of materials/coatings, density and radiographic measurements. Both the alpha and gamma signatures find use in calibration of instrumentation.

Well Logging Application

What is Current State of ^{241}Am Availability?

- About 14 kg $^{241}AmO_2$ added to the National Isotope Center in early 1980s. A "glut" of $^{241}AmO_2$ on the market has become a "shortage" over 25 years.

  - Domestic USA $^{241}AmO_2$ sales were discontinued in 2004/2005.

  - Recent sales (2004) ~$1,000 / g. Set by1980s material recovery prices.

  - Sustainable domestic production of $^{241}AmO_2$ is needed for the future (at a higher price).

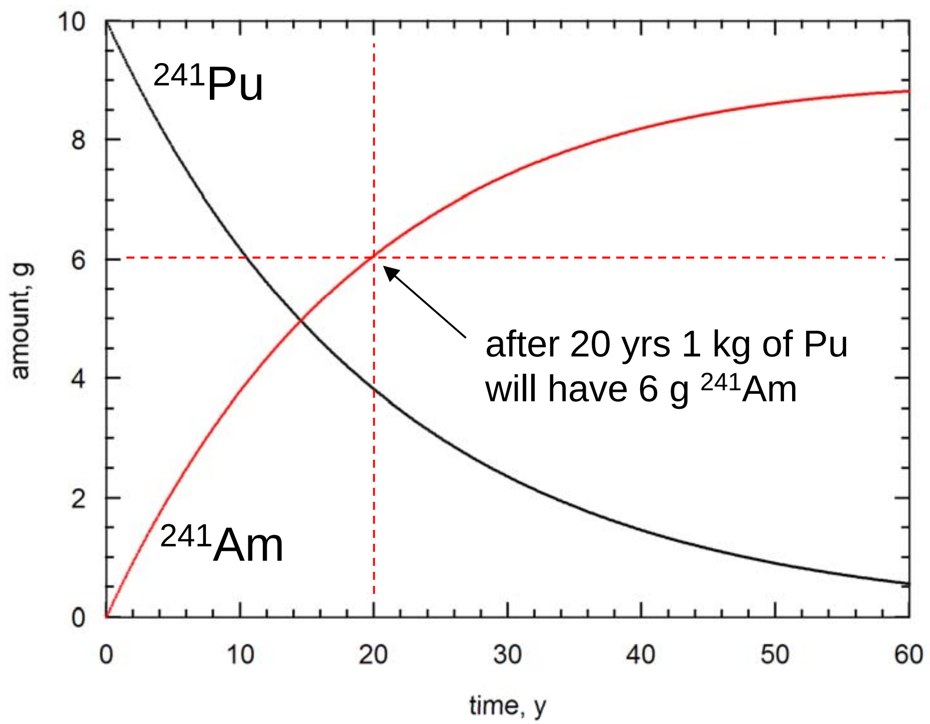
  - Path forward possible from recycle of weapons Pu.

  - LANL now funded to "Establish an Americium-241 Oxide Production Capability".

Where does ^{241}Am come from?

All ^{239}Pu from reactors contains a small percentage of ^{241}Pu

$$^{241}Pu \xrightarrow{t_{1/2} = 14.4 \text{ years}} {}^{241}Am + \beta^-$$



$$^{241}\text{Am} \xrightarrow{t_{1/2} = 432 \text{ years}} {}^{237}\text{Np}$$

$+ \alpha$ (~5.5 MeV)

$+ \gamma$ (59.5 KeV), 30%

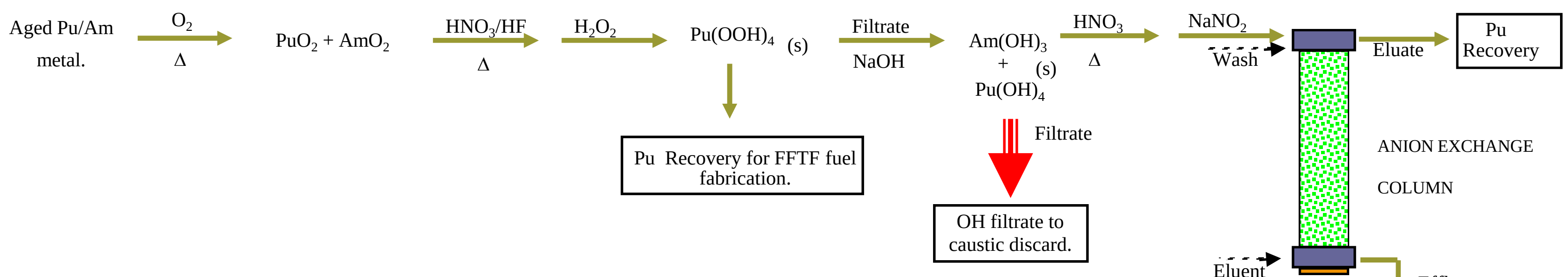
^{241}Am Specific Activity = 3.43 Ci/g (~100 % by alpha decay)

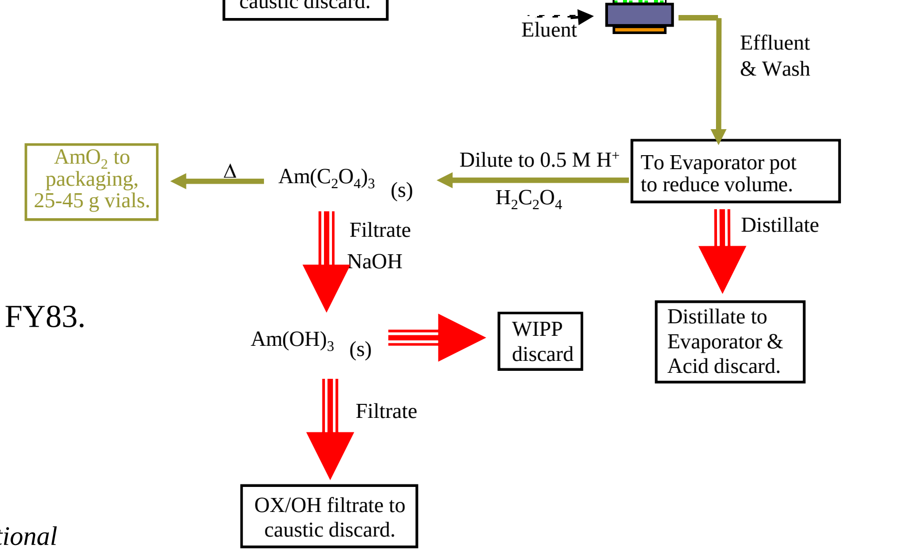
Radiation

Alpha (a) charged helium nucleus, shield with paper.
Beta (b) charged electron, shield with thin Al sheet.
Gamma (g) photon, very penetrating (energy dependent), shield with Pb.
Neutron (N) neutral particle, very penetrating, shield with concrete/water.

The high alpha specific activity of ^{241}Am means we handle it in a facility and gloveboxes designed for confinement of alpha materials.

$^{241}AmO_2$ Production at LANL 1979-1984



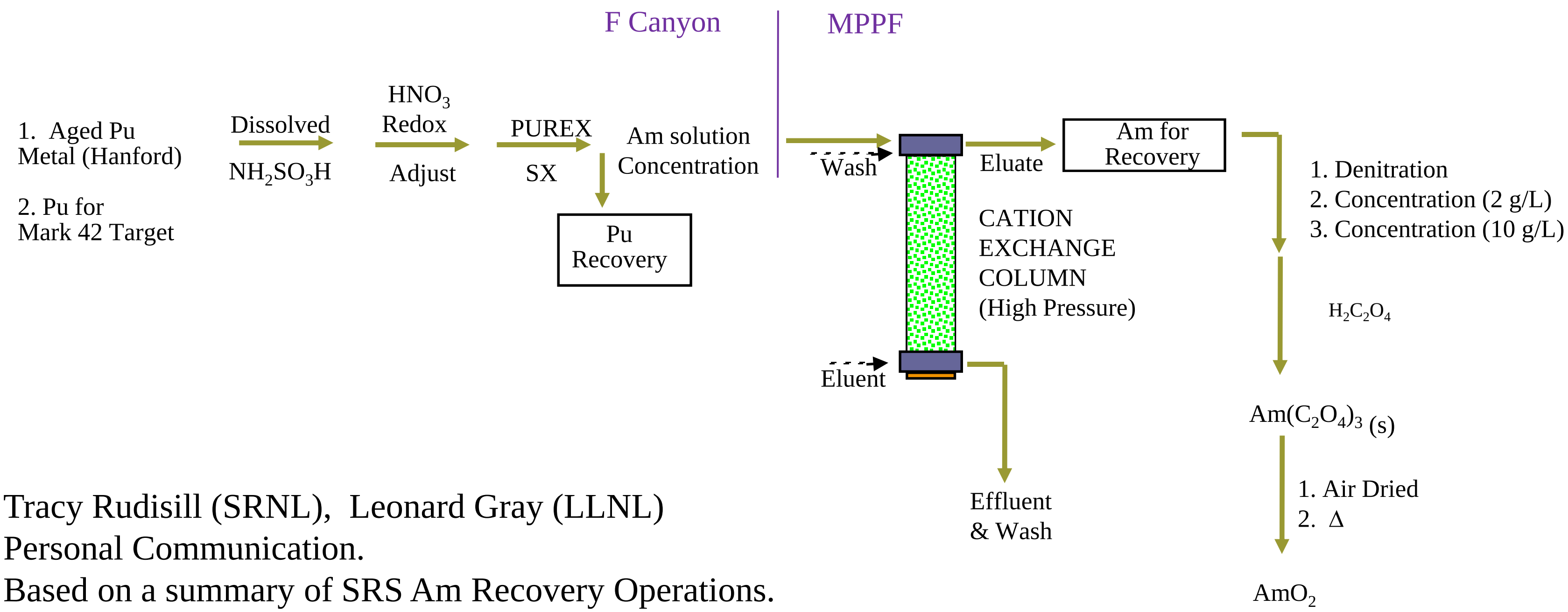


- $^{241}AmO_2$ produced from 79-84 for ORNL isotope sales.
- 2.7 kg $^{241}AmO_2$ product in FY83. About **6.5 kg total**.
- Recovery efficiency improved from 60% to 90%.
- 1 mR whole body, 10 mR extremity per g $^{241}AmO_2$ product in FY83.

LAUR-83-2962 T. Blum, J. Parker, M. Romero, D. Yearwood.
"Americium Oxide Production at LANL: Recovery Up – Exposures Down"

H. Ramsey, D. Clifton, S. Hayter, R. Penneman, E. Christensen.
"Status of Americium-241 Recovery and Purification at the Los Alamos National Laboratory" Transplutonium Elements Production and Recovery, ACS Symposium Series 161, pp 75-91, 1980. J. Navratil and W. Schulz Editors.

$^{241}AmO_2$ Production at SRNL 1978-1981 (simplified)



Tracy Rudisill (SRNL), Leonard Gray (LLNL)
Personal Communication.
Based on a summary of SRS Am Recovery Operations.

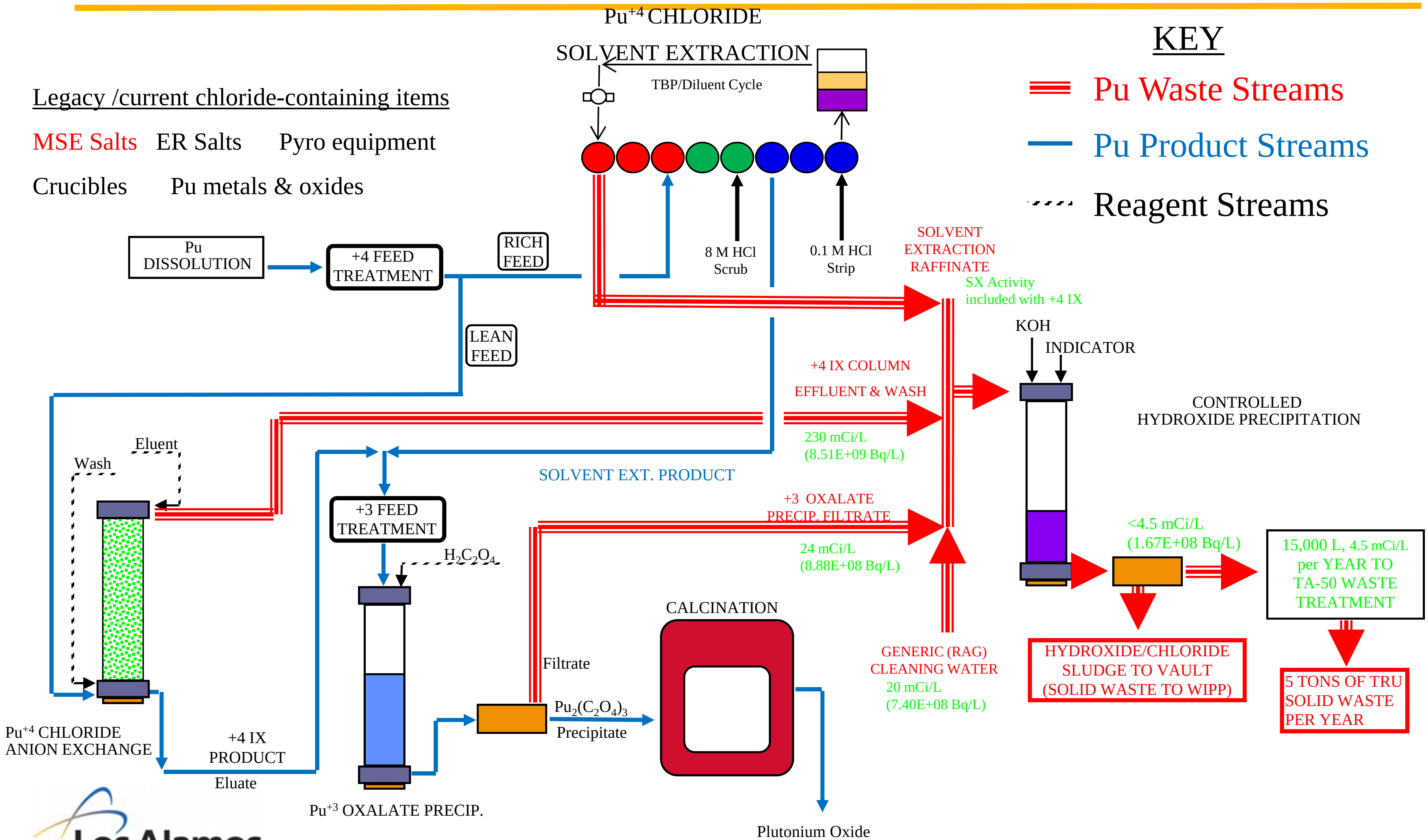
$^{241}AmO_2$ produced from 7/78 to 6/81 for ORNL isotope sales.

About 7 kg total $^{241}AmO_2$ in two campaigns in F Canyon/MPPF.
(Multi-Purpose Processing Facility).

Legacy /current chloride-containing items

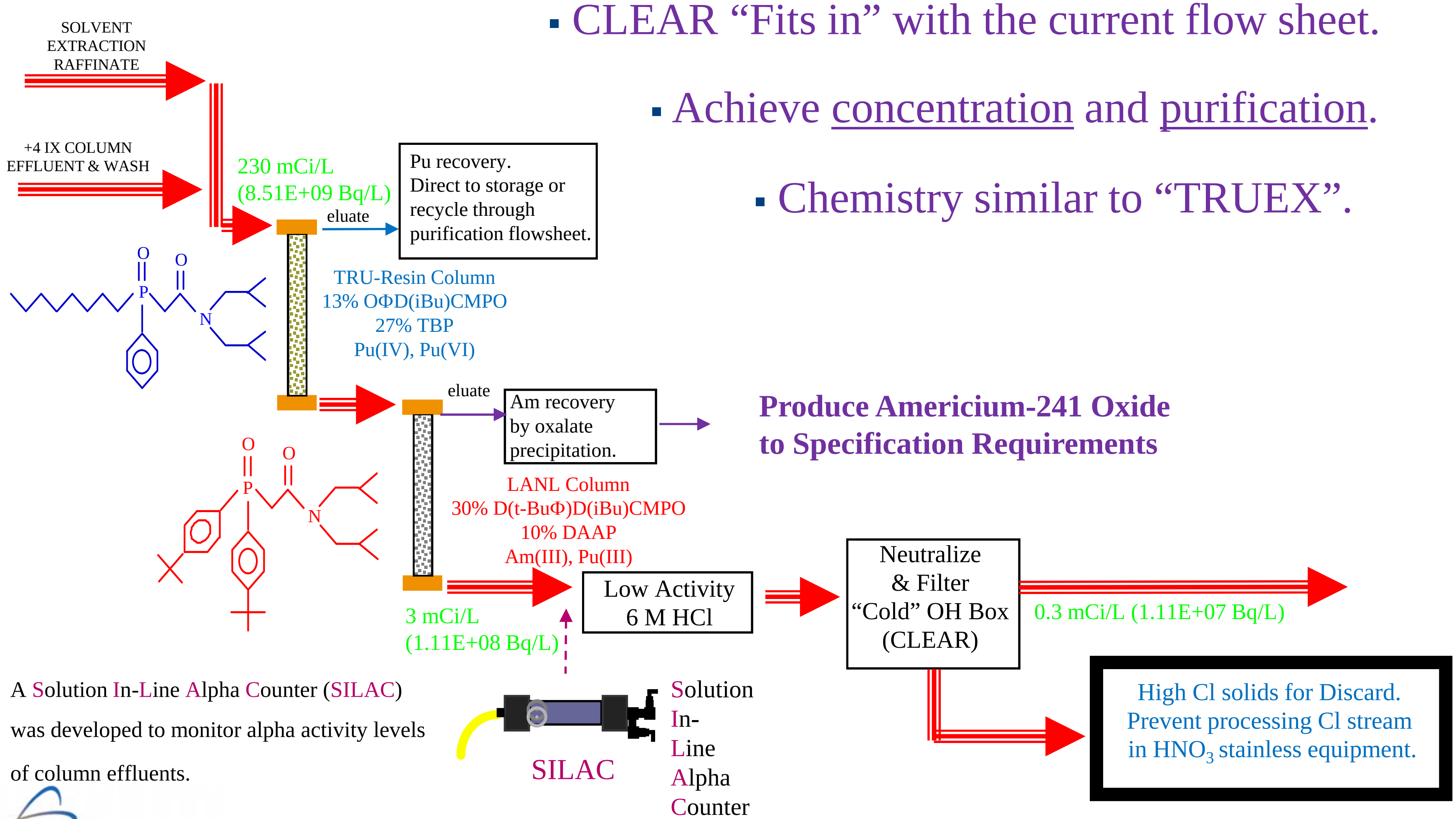
MSE Salts ER Salts Pyro equipment

Crucibles Pu metals & oxides



Chloride Extraction for Actinide Recovery (CLEAR)

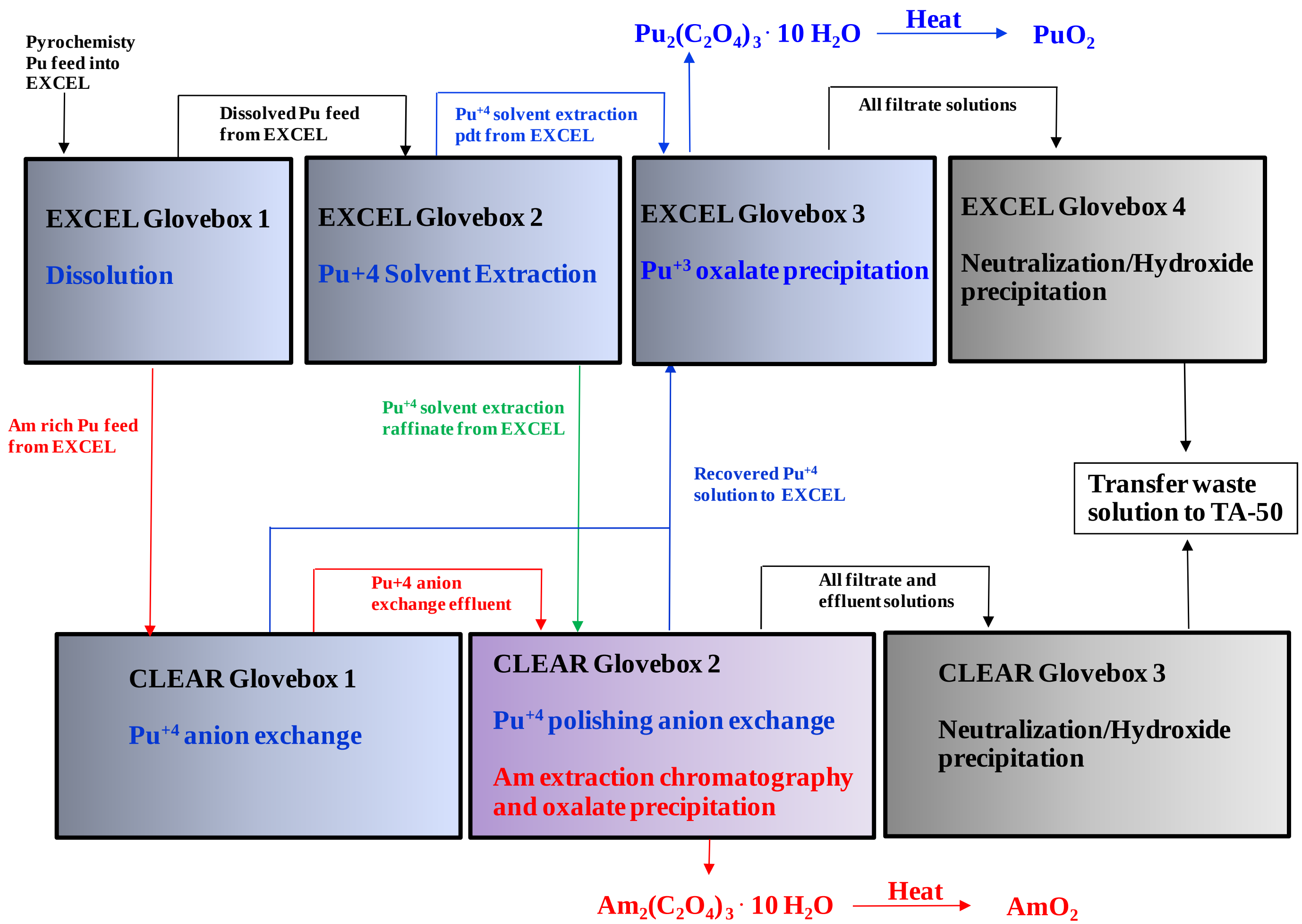
- CLEAR "Fits in" with the current flow sheet.
- Achieve concentration and purification.
- Chemistry similar to "TRUEX".



Produce Americium-241 Oxide to Specification Requirements

A Solution In-Line Alpha Counter (SILAC) was developed to monitor alpha activity levels of column effluents.

Integration of EXCEL and CLEAR Glovebox Lines



Establish Capability Schedule Overview

1.02.02 Construction | 1.02.03 Startup | 1.02.04 "Pre Ops"

Time zero 11/28/12 | 1.5 Years | 2.5 Years | 3.0 Years

1.02.02 Construction
Complete utility piping, electrical, sheetmetal. Testing of glovebox hardware, dose assessment, containers, establish analysis capabilities.

1.02.03 Startup
Criticality safety, procedures, MSA, RA, QA.

1.02.04 "Pre Ops"
Initial operations. Analysis of products. CRM/WRM Work.

$^{241}AmO_2$ Product Specification

Quantity	Specification
^{241}Am isotopic purity	^{241}Am > 99% …^{243}Am < 1% weight by Gamma NDA method (TIMS, RC alternate method).
$^{241}AmO_2$ chemical purity	> 95% by weight from Calorimetry NDA method (TIMS, RC alternate method).
Pu content	< 1.0% by weight (with allowed uncertainty) by Gamma NDA method for ^{239}Pu (TIMS, RC alternate method).
Pu isotopics	No spec requirement or measurement typically reported, only assumptions for ^{wp}Pu. Can be measured and reported from TIMS.
Trace elements	< 0.5% by weight for any individual trace element measured and reported by ICP-AES and ICP-MS.
^{237}Np	No spec requirement , but typically measured and reported by ICP-AES and ICP-MS.

Analysis Methods

Activity	Above Specification Non-Routine Analysis	95% Specification Routine Analysis
Sample dissolution, aliquoting and separation	All	All
Am assay (TIMS)	All	Primary by NDA, need periodic TIMS measurement
Am isotopic (TIMS)	All	Primary by NDA, need periodic TIMS measurement
Pu assay (TIMS)	All	Primary by NDA, need periodic measurement
Pu isotopic (TIMS)	All	Primary by NDA, need periodic measurement
Trace elements on oxide (ICP-AES/MS)	All	All
Np by radiochemistry	All	periodic
Anions (Cl & F)	periodic	periodic
NDA/Calorimetry for ^{241}Am assay	All	All
NDA/Gamma for ^{239}Pu, ^{243}Am	All	All

$^{241}AmO_2$ Assay - Calorimetry

- Calorimetry: thermal power generated by radioactive decay on a bulk item.

- Calorimetry is arguably the most important measurement tool to quantify the amount of $^{241}AmO_2$ in items from production operations. Direct value for Ci/g.

- Required for MC&A (Material Control and Accountability) purposes.

- "Bulk item" measurement means that measured value is tied to the balance measurements of the $^{241}AmO_2$ and the innermost container.

- Standards program exists for calorimetry based on calibrated $^{238}PuO_2$ WRM items. No new standards (WRMs) are planned for use in calorimetry. Utilize the known half life and decay heat of ^{241}Am (3+ significant figures).

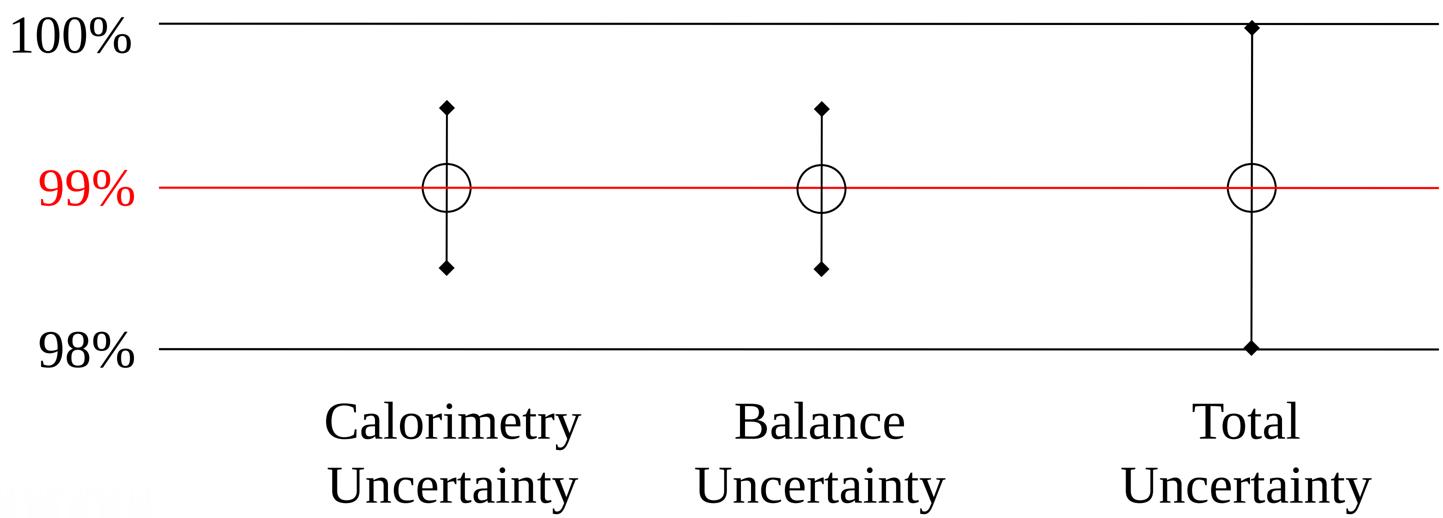
- Alternate methods that provide independent verification measurements, independent qualification, and higher precisions can be made by TIMS isotope dilution and RC on aliquot samples. CRMs/WRMs planned for TIMS & RC.

$^{241}AmO_2$ Calorimetry & Balance Measurement Uncertainties

- Calorimetry: Uncertainty values for calorimetry measurements on production $^{241}AmO_2$ items are expected to be +/- 0.5% at the 95% confidence level.

- Balance: Measurement uncertainty in our production environment is nominally about +/- 0.5% at the 95% confidence level. Regardless of other measurements. Between 2 & 3 significant figures, report 3.

Assume a particular lot of $^{241}AmO_2$ is 99.0% chemical purity



$^{241}AmO_2$ Radiopurity Specification >99%

- Radiopurity greater than 99% by weight is synonymous with "isotopic purity" and can also be defined as the summation of americium nuclides other than ^{241}Am being less than 1% of the total.

- LANL will assume ^{243}Am content less than 1% by measurement as adequate proof that radiopurity specification greater than 99% has been met for production operations. Only tracer quantities of ^{242}Am or ^{242m}Am on site, not considered credible to have gross contamination (1%) of $^{241}AmO_2$ product materials.

- NDA gamma methods easy to qualify for ^{243}Am contamination. ^{243}Am is relatively easy to detect in small quantities because of prominent high E gamma rays associated with its ^{239}Np daughter, and further (beta) decay to ^{239}Pu.

- It is the intent of the project to develop NDA gamma methods to quantify $^{243}Am/^{241}Am$ ratios to "less than" 1% values in ^{241}Am.

- Alternate methods that provide independent verification measurements, independent qualification, and higher precision can be made by TIMS and RC on aliquot samples. <u>New standards (WRMs) are planned for $^{243}Am/^{241}Am$ to provide tighter error bars and verification of NDA gamma measurements.</u>

Pu Content: Part of Historical Specification as < 0.5 and <1%

- Pu content very important to MC&A (materials control and accountability) of SNM. Less than 1% Pu values in batches of 30 g ^{241}Am would keep Pu "sub-accountable" (<0.5 g) for MC&A.

- It is the intent of the project to develop NDA gamma methods to quantify ^{239}Pu/^{241}Am ratios in order to generate "less than" 1% Pu values in ^{241}Am. Utilize approximate isotopic ranges of weapons Pu for calculations of total Pu.

- Concerns about the measurement uncertainty for the ^{239}Pu/^{241}Am ratio by gamma ray NDA, and allowance of this uncertainty might be noted in the specification. More difficult than gamma analysis of ^{243}Am.

- Pu < 1.0% by weight (with allowed uncertainty) by Gamma NDA method. Alternate methods provide independent verification measurements, independent qualification, and higher precision can be made by TIMS and RC on aliquot samples. New standards (WRMs) are planned for ^{239}Pu/^{241}Am to provide tighter error bars and verification of NDA gamma measurements.

- 11/2/10 External Review of the "Establish $^{241}AmO_2$ Production Capability Project.", commissioned by DOE NP (Office of Nuclear Physics), recommended certification of "standards" by an external laboratory such as NBL (New Brunswick Laboratory).

- LANL has developed a plan for NBL certification of LANL methods of measurement CRM of key attributes of ^{241}Am content (assay), ^{243}Am /^{241}Am, and ^{239}Pu /^{241}Am. Very great certainty and small error bars can be achieved in these attributes for the CRM and WRM materials.

- The $^{241}AmO_2$ CRM would provide a common and well characterized reference material for LANL destructive analysis for the life of the project. This material has a unique potential value outside the project for others due to the extensive certification required.

- The $^{241}AmO_2$ WRM would be utilized as verification standards for NDA gamma methods to quantify ^{243}Am /^{241}Am, and ^{239}Pu /^{241}Am ratios to "less than" 1% values in $^{241}AmO_2$ production.

Trace Elements

- "Raw Material Specification" for $^{241}AmO_2$ received from the DOE Office of Science matches AMP-xxx data sheets. Historical specification requirements are no more than 0.5% by weight (<5,000 microgram/gram) of any measure inert trace element impurity in $^{241}AmO_2$.

- The ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) and ICP-MS (Inductively Coupled Plasma-Mass Spectrometry) are utilized to measure trace element impurity levels. Al, B, Be, Bi, Ca, Cd, Co, Cr, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Zn, Zr.

- It is anticipated that residual and ingrown ^{237}Np content and U content will be adequately measured by ICP methods for routine $^{241}AmO_2$ production, and only occasionally measured for process knowledge by more precise radiochemical methods.

- LANL ICP instrumentation is currently calibrated against NIST traceable materials. No $^{241}AmO_2$ reference materials are needed.

- 1 mR whole body, 10 mR extremity per g $^{241}AmO_2$ product in FY83. LAUR-83-2962 T. Blum, J. Parker, M. Romero, D. Yearwood. *"Americium Oxide Production at LANL: Recovery Up – Exposures Down"*. Gradual ~3 fold reduction in whole body and ~8 fold reduction in extremity exposure per gram of ^{241}Am produced over the years from 1979 to 1983.

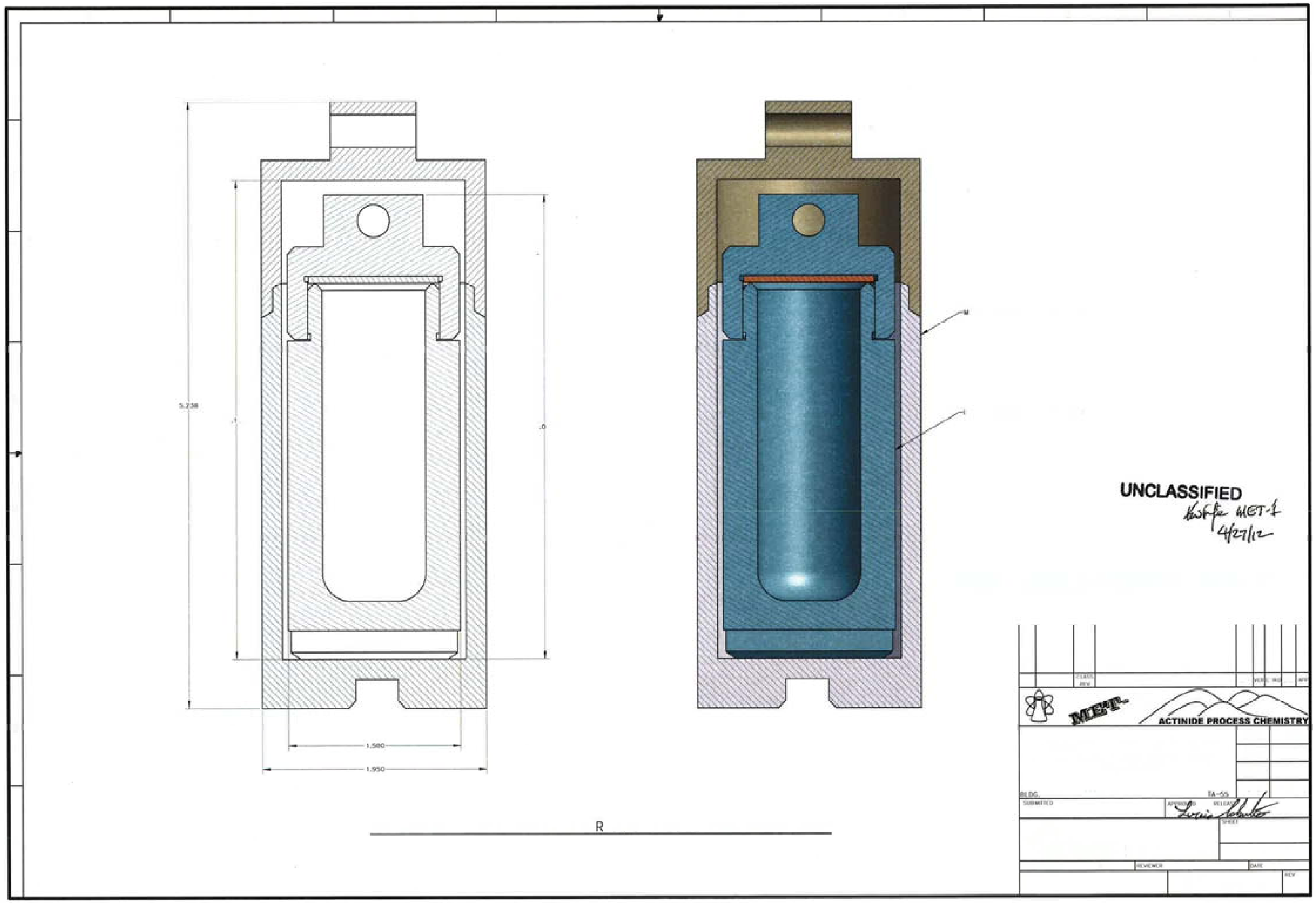
- Modeling (MCNP5) of unit operations for $^{241}AmO_2$ production today shows 1.2 mR whole body, 6 mR extremity per g $^{241}AmO_2$ product. LAUR-12-xxxx, Adam Davis, Daniel Gonzalez. *"Preliminary Radiological Assessment of Americium Recovery Operations"*.

- Extremity dose is the toughest issue. Handling solid materials is the source of most dose. Many unique point-source shields and tools have been developed.

- Attention to operational details, shielding, and improving worker skill all can contribute to reducing exposure in glovebox operations. Operational experience and improvements are likely to provide better understanding of high dose operations and further methods to optimize/reduce personnel dose. Automation of some steps.

DOT Certified Type "A" SFC Shipping Container "Outer" 23

“Innermost” and “Middle” Container (LANL working design)



End of Presentation

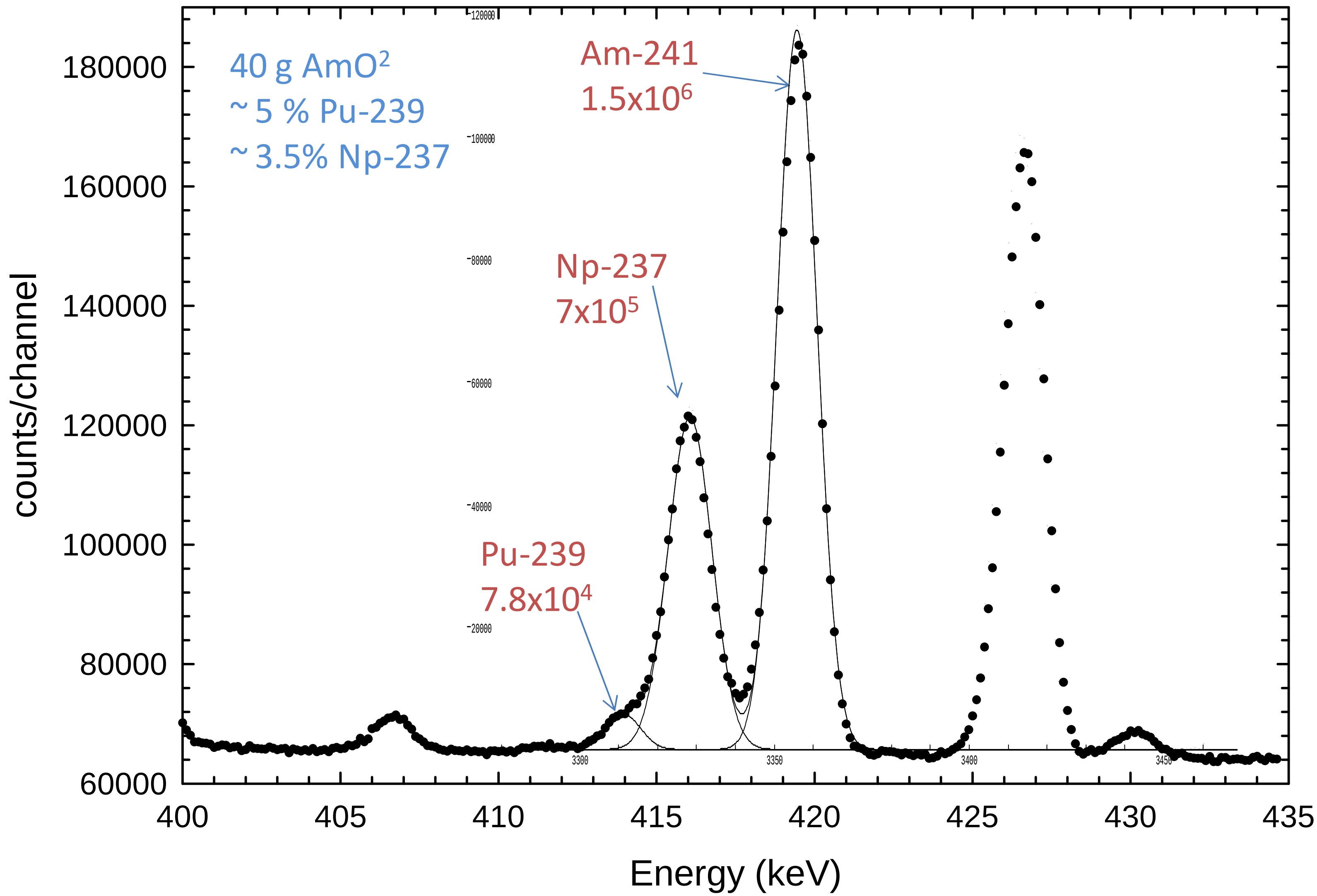
Results for MSE Residues Batched for 1 SX run

Run	Pass	Vol. (L)	Alpha mCi/L (Bq/L) Before resins	Alpha mCi/L (Bq/L) After resins	% alpha Removed	Resin(s)	Resin Eluates
30	1	17	2700	49	98.19	0.54 L column 100 g Reilly HPQ	? g Pu
			9.99E+10	1.81E+09			
						1.8 L D(tBuPh)D(iBu)CMPO resin	0.47 g Pu 14.4 g Am
31	1	23	2454	3.52	99.86	0.54 L column 100 g Reilly HPQ	? g Pu
			9.08E+10	1.30E+08			
						1.8 L D(tBuPh)D(iBu)CMPO resin	0.10 g Pu 17.4 g Am
32	1	16	1620	2.26	99.86	0.54 L column 100 g Reilly HPQ	2.37 g Pu
			5.99E+10	8.36E+07			
						1.8 L D(tBuPh)D(iBu)CMPO resin	0.062 g Pu 7.83 g Am

2 Additional SX runs of Batched MSE Residues

Run	Pass	Vol. (L)	Alpha mCi/L (Bq/L) Before resins	Alpha mCi/L (Bq/L) After resins	% alpha Removed	Resin(s)	Resin Eluates
35	1	19	3130 1.16E+11	3.63 1.34E+08	99.88	1.8 L D(tBuPh)D(iBu)CMPO resin	1.25 g Pu 16.9 g Am
36	1	18	2460 9.10E+10	1.47 5.44E+07	99.94	1.8 L D(tBuPh)D(iBu)CMPO resin	3.78 g Pu 13.4 g Am
37	1	19	2460 9.10E+10	2.63 9.73E+07	99.89	1.8 L D(tBuPh)D(iBu)CMPO resin	3.18 g Pu 13.3 g Am
38	1	20	2900 1.07E+11	0.576 2.13E+07	99.98	1.8 L D(tBuPh)D(iBu)CMPO resin	0.613 g Pu 13.8 g Am
39	1	14	2430 8.99E+10	0.66 2.44E+07	99.97	1.8 L D(tBuPh)D(iBu)CMPO resin	1.83 g Pu 9.87 g Am

Am-241 Oxide Gamma-Ray Spectrum



- “Raw Material Specification” for $^{241}AmO_2$ received from the DOE Office of Science silent on Pu isotopics. No historical specification requirements.

- Historical AMP-xxx data shows approximate isotopic information for “reactor“ Pu utilized for the $^{241}AmO_2$ campaign 1979-1984. No precise Pu isotopics reported.

- It is the intent of the project to develop NDA gamma methods to quantify $^{239}Pu/^{241}Am$ ratios in order to generate “less than” 1% Pu values in ^{241}Am.

- Utilize approximate isotopic ranges of weapons Pu for calculations of total Pu in routine $^{241}AmO_2$ production. Occasional/periodic TIMS measurements of Pu isotopics can be performed.

- Pu isotopics by TIMS a mature technology at LANL.

Am 1/2 life from *"^{241}Am - Comments on evaluation of decay data"*

by V. P. Chechev and N. K. Kuzmenko, Sept., 2009

^{241}Am 1/2 life (years) = $t_{1/2}$ = 432.6 plus/minus 0.6 years

^{241}Am decay constant lambda (λ, years) = $\ln 2/(t_{1/2})$ = 0.00160

$N/No = e^{-\lambda t}$ N = number of atoms or amount after time t

N_o = number of atoms or amount at time 0 (t_o)

$A = \Delta N/\Delta t = \lambda N$ A = decay rate

^{241}Am activity (A) in Ci/g = 3.430

- 3.43 Ci/g is the accepted activity value for 100% isotopic purity, 100% chemical purity americium-241 **metal**.

$^{241}AmO_2$ Formula Weight and Ci/g Calculation

^{241}Am Formula Weight calculation

ISOTOPE	Isotope Weights	FW of AmO_2
^{241}Am	241.0568	273.0556
^{nat}O	15.9994	

Chemical Purity of AmO_2	Theoretical Ci/g Purity of AmO_2	Theoretical % ^{241}Am wt of $^{241}AmO_2$
100%	3.028	88.28%
99%	2.998	87.40%
96%	2.907	84.75%
95%	2.877	83.87%
94%	2.847	82.98%

Container Geometry & Weight Issues

LANL innermost container (4/27/12)						approximate	approximate
Nitronic 60 SST		without lid	with lid	$V = \pi r^2 h$	$S = 2 \pi r h$	weight (g)	weight (lb)
	diameter (in)	height (in)	height (in)	volume (cm^3)	surface area (cm^2)	container	container
inner	0.9	2.75		29	50		
outer	1.5	3.25	4	94	99		
delta volume				65		524	1.2
				More precise values from drawings			
			inner volume	28.2		613	1.33
LANL middle container (4/27/12)						approximate	approximate
Nitronic 60 SST		without lid	with lid	$V = \pi r^2 h$	$S = 2 \pi r h$	weight (g)	weight (lb)
	diameter (in)	height (in)	height (in)	volume (cm^3)	surface area (cm^2)	container	container
inner	1.6	3.25		107	105		
outer	1.95	4.20	5.30	206	166		
delta volume				98		788	1.7
				More precise values from drawings			
			inner volume	403.9		767	1.68
Nominal Dimensions for SAVY-4000 containers for PF-4 vault				MAR limit for MT 44 ($^{241}AmO_2$) is 84 g ^{241}Am in a SAVY 4000			
3 quart SAVY 4000 appears suitable as an overpack				per TA55-DOP-091,R1			
	Inner	Inner	Overall	Overall	Gross	Tare	Payload Max.
	diameter (in)	height (in)	diameter (in)	height (in)	weight (lb)	weight (lb)	weight (lb)
12 quart	8.99	12.76	10.00	13.95	49	11.9	37.1
8 quart	7.75	10.26	8.85	11.45	44	9.3	34.7
5 quart	6.60	8.76	7.70	9.95	40	7.4	32.6
3 quart	5.45	6.76	6.55	7.95	33	5.6	27.4
1 quart	3.67	4.38	4.77	5.98	22	3.3	18.7
Dimensions of existing Type A SFC (Drawing # 90Y-219998) has an overall OD length of 11.75" without the nut.						270 Ci limit (78.9 g ^{241}Am)	
Assumes existing SFC has 1/2" wall thickness. Plug leaves ~7.5" useful length inside container.							
						approximate	approximate
Dimensions of existing Type A SFC.				$V = \pi r^2 h$	$S = 2 \pi r h$	weight (g)	weight (lb)
	diameter (in)	height (in)		volume (cm^3)	surface area (cm^2)	stainless container	stainless container
inner	2.06	10.5		573	438		
outer	3.06	12		1446	744		
delta volume				873		6981	15.4

Software Quality Assurance

John MacDonald, Cameron Turner, Sonya Lee

Roberta Mulford, presenter

Presented to JOWOG 22-2
July 10, 2012

Aldermaston Weapons Establishment

Software Quality Assurance Concerns Reliability, Cost

- **Processes rely on software for governance, process record acquisition**
- **Software testing is critical**
- **Software maintenance must be facile**
  - Minimize down time
  - Process replacement necessary if software obscure
- **Safety and reliability must be demonstrable**
- **Good engineering practise, industry-wide standards**

Testing usually constitutes Software Quality Assurance

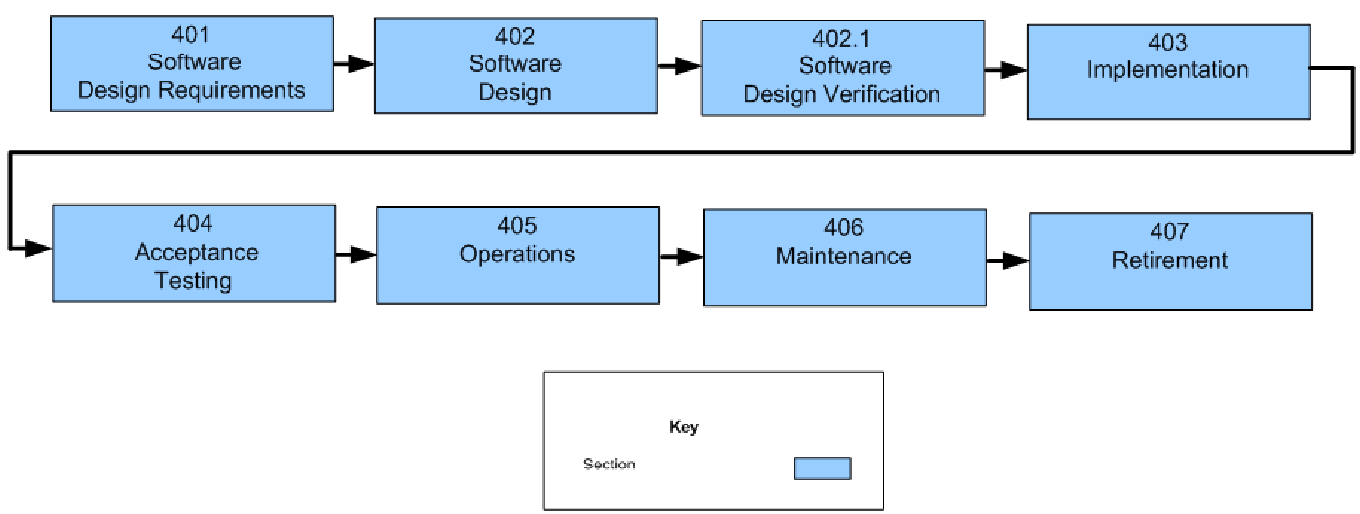
- **Testing examines**
  - Software-hardware interface
  - Human factors
  - Algorithm
  - Required outputs
  - Reproducibility
  - Environmental factors
  - Other factors

SQA Implemented throughout Software Life Cycle

ASME NQA-1 1997
Subpart 2.7
Software life cycle activities

As found in section 102 - **Software life cycle:** the activities that comprise the evolution from conception to retirement. The software life cycle typically includes the software development cycle and the activities associated with operation, maintenance and retirement.

Subpart 2.7 Section 400 SOFTWARE ENGINEERING METHOD
Contains the following sections:

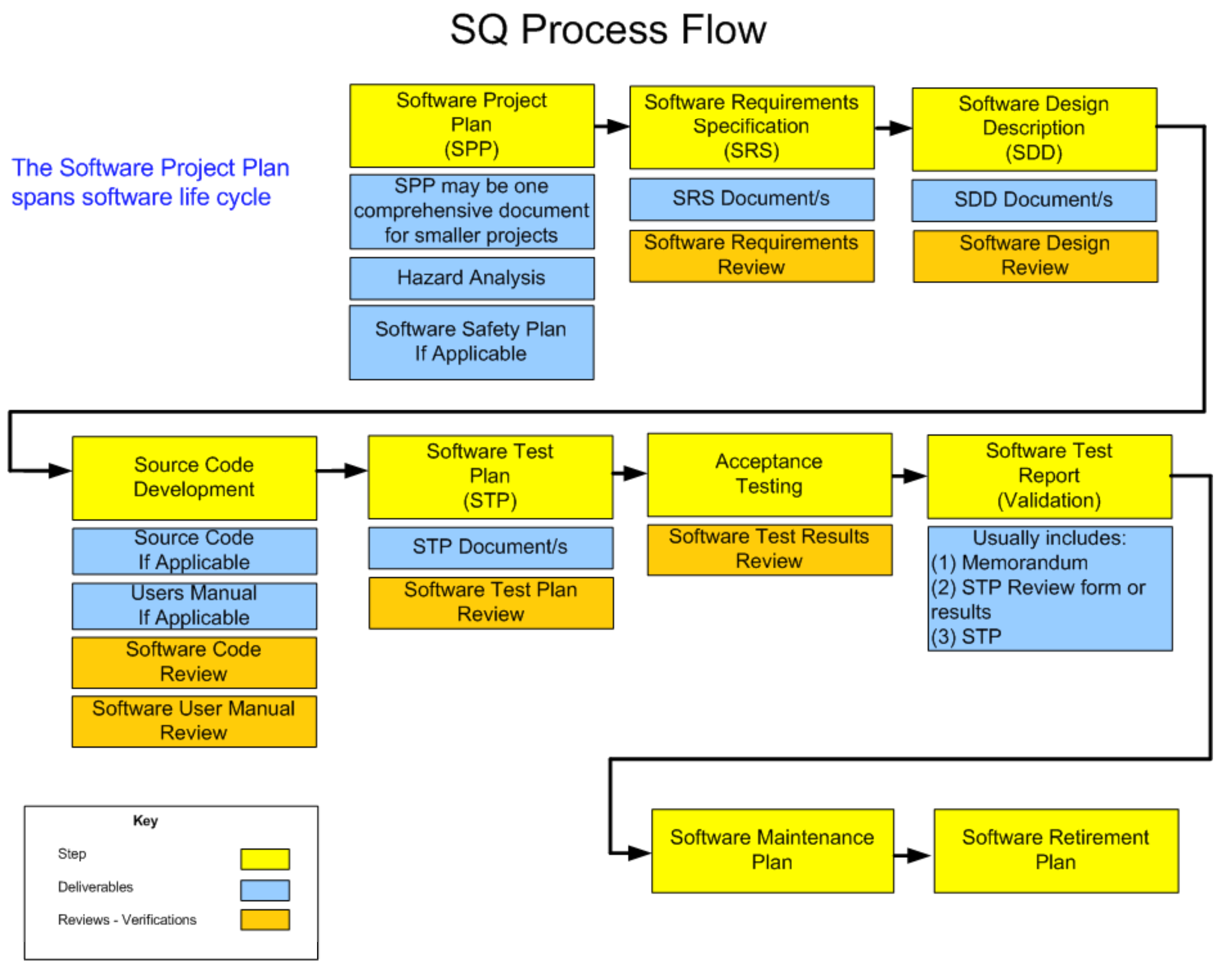


Maintenance of software facilitated by sound SQA

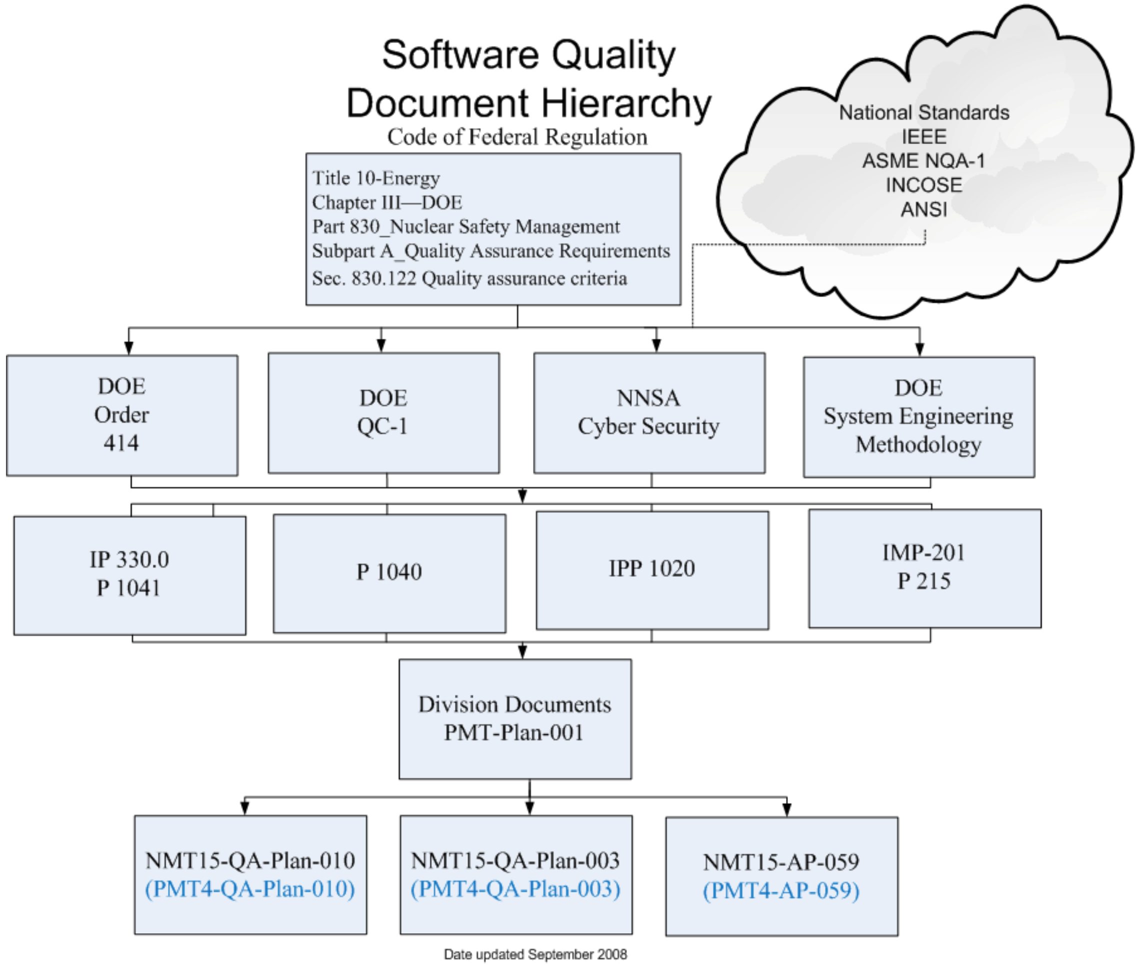
- **Software maintenance can be demanding**
  - Hardware upgrades
  - Software and operating system upgrades
  - Revised requirements
  - Version control and necessary bug fixes

- **Experience tells us that capabilities can be lost to inability to upgrade software or hardware**

SQA was systematically implemented in ARIES Program software development



Regulatory Drivers and Standards Govern Implementation of SQA at Los Alamos



Various SQA Standards Can Be Compared

QC-1 Rev 10, Feb 10, 2004	IEEE	TBP 306	Draft IPP 1004 5/1/2007 & LIR 308-00-05.1 12/29/2006	DOE Systems Engrg Methodology	NQA-1 SubPart 2.7	Title 10: Energy CFR 830.122 Quality Assurance Criteria	DOE O 414
Continuous Quality Improvement	1061-1998 Software Quality Metrics Methodology	2.1.1 Project Planning	Product Engineering Process	System Design	100 General	Criterion 3--Management / Quality Improvement	Criterion 5 - Work Processes & Criterion 6 - Design
Software Quality Assurance	730-2002 Software Quality Assurance Plans	1.2 Objectives	Software Quality Assurance	Develop Quality Assurance Plan	100 General	Criterion 1--Management / Program	Criterion 1 Program
Continuous Process Improvement	1061-1998 Software Quality Metrics Methodology	2.9.2 Software Support Concept and Assurance	Project Management	Develop Project Plan	204 Problem Reporting and Corrective Action	Criterion 3--Assessment / Management Assessment	Criterion 3 Quality Improvement
Risk Assessments	1540-2001 Software Life Cycles - Risk Management	2.1 Project Control	Risk Management	Risk Management	101 Software Engineerng	Criterion 9--Management / Quality Improvement	Criterion 10 Independent Assessments
Training	1063-2001 Software User Documentation	1.2 Life Cycle Support and Training	Formal Training and Qualification Process	Organizational Training	NQA-1 Part 1 Rqmts	Criterion 2--Personnel Training and Qualification	Criterion 2 Personnel Training & Qualification
Planning	1490 - 2003 Guide for Adoption of PMI Standard & IEEE 1058- 1998 Software Project Management Plans	2.1.1 Project Planning	Project Management Process	Develop Project Plan	202 Review	Criterion 3--Assessment / Management Assessment	Criterion 9 Management Assessment & Criterion 10 Independent Assessment
Metrics	1061-1998 Software Quality Metrics Methodology	2.3 Product Identification and Traceability	Software Project Tracking & Oversight Process	Develop Quality Assurance Plan	204 Rptg and Corrective Action	Criterion 5--Performance / Work Processes	Criterion 9 Management Assessments
Design Definition	1016-1998 Software Design Descriptions	2.5.2 Design Process	Product Engineering Process	Functional Design	401 Software Design Req	Criterion 6--Performance / Design	Criterion 6 Design
Functional Design	1016-1998 Software Design Descriptions	2.5.2 Design Process	Product Engineering Process	Functional Design	402 Software Design	Criterion 6--Performance / Design	Criterion 6 Design
System Design	1016-1998 Software Design Descriptions	2.5.2 Design Process	Product Engineering Process	Functional Design	402.1 Software Design Veri	Criterion 6--Performance / Design	Criterion 6 Design
Procurement	1062-1998 Practice for Software Acquisition	2.7.1 OTS Software Procurement	Procurement Process	Initiate Procurement	300 Software Acquisition	Criterion 7--Performance / Procurement	Criterion 7 Procurement

Standards Are Extensive and Comprehensive

QC-1 Rev 10, Feb 10, 2004	IEEE	TBP 306	Draft IPP 1004 5/1/2007 & LIR 308-00-05.1 12/29/2006	DOE Systems Engrg Methodology	NQA-1 SubPart 2.7	Title 10: Energy CFR 830.122 Quality Assurance Criteria	DOE O 414
Test and Verification - Acceptance	829-1998 Standard Test Documentation	2.8.1 Product Acceptance Process	Verification and Validation	Acceptance Testing	404 Acceptance Testing	Criterion 8-- Inspection and Acceptance	Criterion 8 Inspection and Acceptance Testing
Programming	1061-1998 Software Quality Metrics Methodology	2.1.2 Project Control	Product Engineering Process	Acceptance Testing	404 Acceptance Testing	Inspection and Acceptance Testing	Criterion 8 Inspection and Acceptance Testing
Installation and Acceptance	829-1998 Standard Test Documentation	2.8.1 Product Acceptance Process	Verification and Validation	Acceptance Testing	404 Acceptance Testing	Inspection and Acceptance	Criterion 8 Inspection and Acceptance
Operation	1362-1998 Concept of Operations	2.8.3 Site Production Acceptance	Quality Assurance Process	Plan transition to Operational Status	405 Operation	Criterion 4-- Documenrts and Records	Criterion 8 Inspection and Acceptance
Corrective Action	1044-1993 Standard Classification for Software Anomalies	2.3 Product Identification and Traceability	Tracking and Oversight	Risk Management	204 Problem Reporting and Corrective Action	Criterion 10-- Assessment / Independent Assessment	Criterion 10 Independent Assessments
Records	All Engineering Standards	2.3.2 Identification Schema	Configuration Management	Project Management	201 Document ation	Criterion 4-- Documenrts and Records	Criterion 4 Documents and Records
Configuration Management	828-1998 Software Configuration Management	2.6.1 Records Management Process	Configuration Management	Project Management	203 Software Config Mgmt	Criterion 4-- Management / Documenrts and Records	Attachment 5 Supplemental Safety SQ Requirements
Procedures	ANSI/IEEE Std. 610.12-1990 Software Dev. Life Cycle	2.0 Software Process Implement Guidance	Software Product Engineering Process	Project Management	203 Software Config Mgmt	Criterion 4-- Management / Documenrts and Records	Criterion 1 Program
Libraries	All Engineering Standards	2.3.4 Program Management	Generate Operating Documentation	Project Management	405 Application documentation	Criterion 4-- Management / Documenrts and Records	Criterion 1 Program
Verification and Validation	1028-1997 Software Reviews	Product Acceptance	Verification and Validation	Quality Reviews	404 - 405 Acceptance testing	Inspection and Acceptance	Criterion 8 Inspection and Acceptance
Assessments	Under Development	Product Acceptance	Tracking and Oversight	Quality Reviews	202 Review	Management Assessment	Criterion 9 Management Assessments
Requirements	830-1998 Software Requirements Specifications	Product Definition	Requirements Management	Requirements Definition	401 Software Design Require ments	Criterion 3-- Management / Quality Improvement	Criterion 6 Design
Retirement	1219-1998 Software Maintenance	Program Management	Software Project Management	Plan transition to Operational Status	407 Retirement	Criterion 3-- Quality Improvement	Criterion 5 - Work Processes

Customer Satisfaction Requires a Methodical Approach

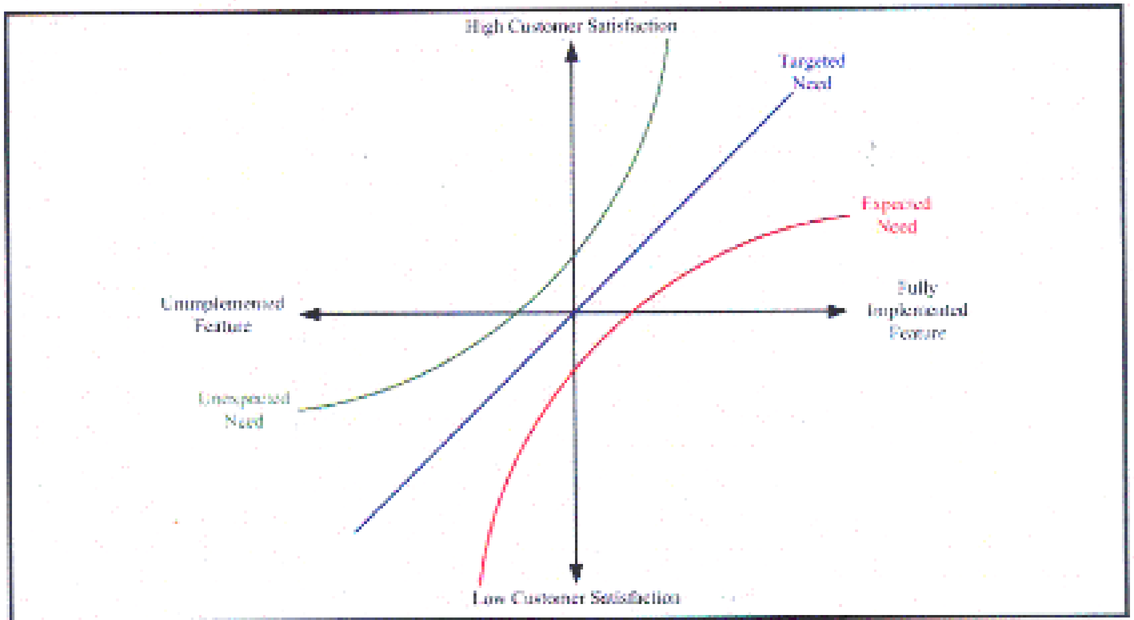


Figure 5. Customer Needs and Satisfaction versus Implementation Quality

The Kano diagram

Prof. Noriaki Kano

Customers have explicit requirements and implicit expectations

Early implementation of SQA identifies real needs and expectations

Cost-benefit Analysis
Supports Lifecycle Application of SQA

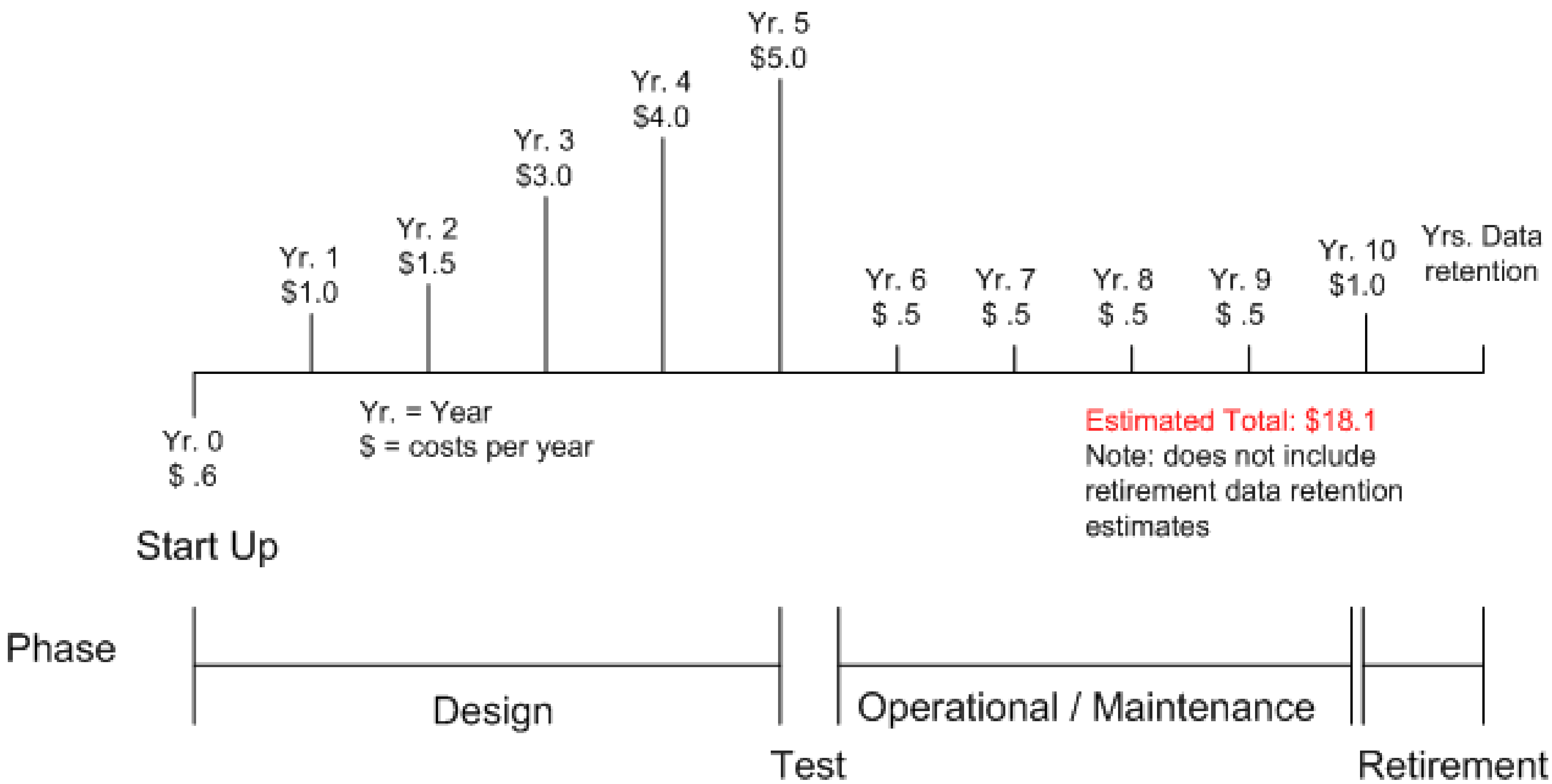
- [(Cost of software development) + (Cost of SQ activities)] = Costs

- [(Down system cost per week) + (Security impacts per week) + (Safety estimated costs of an event per week) + (Productivity loss per week) + (Impact on community, state, society) + (Impact on current project) + (Impact on future projects)] = Costs

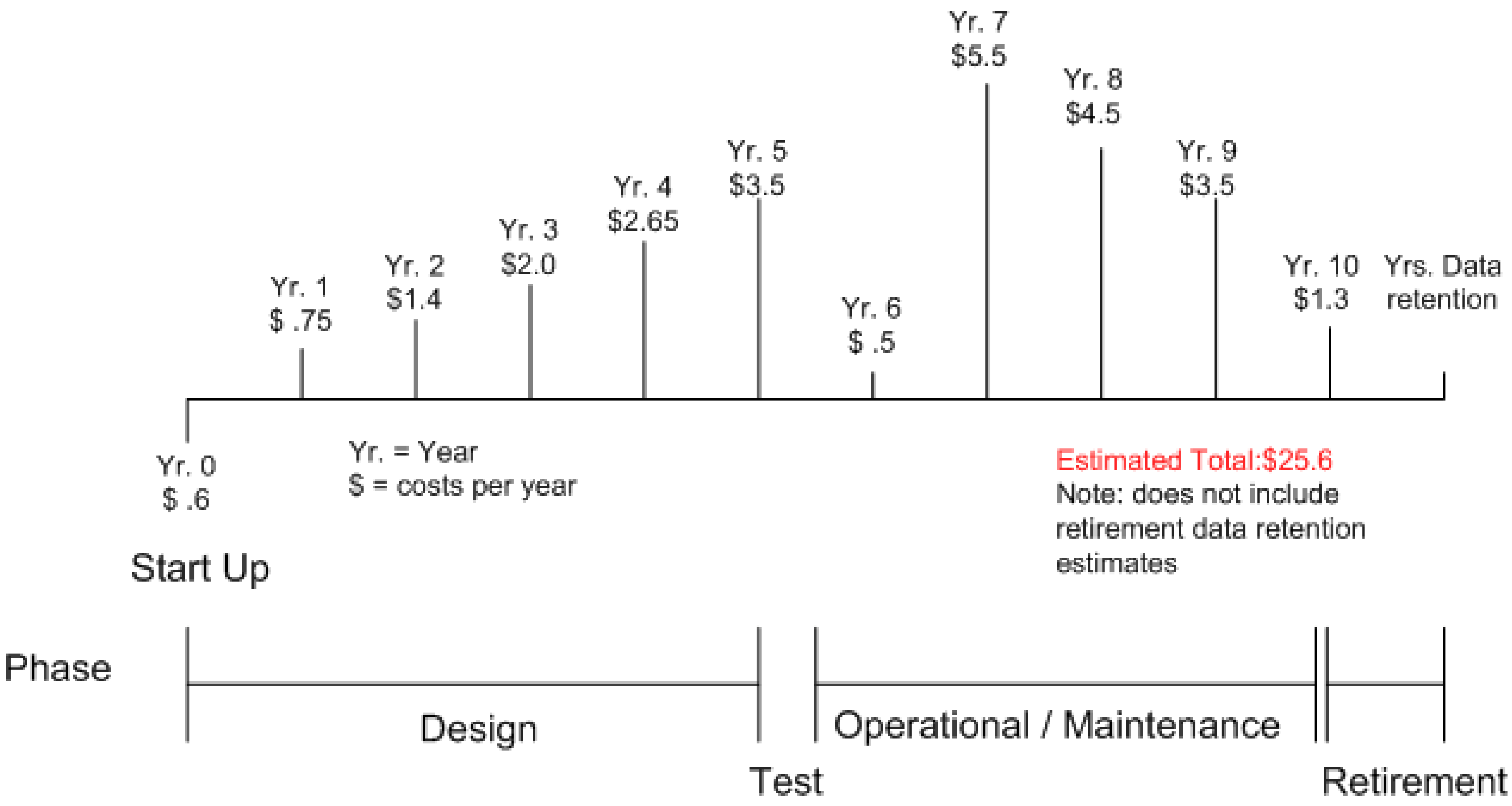
- (Red costs – Blue costs) = difference presents a return on investment (ROI) number.

Cost of Software development	Cost of SQA Activities	Costs	Down System Cost per week	Impacts Security week	Impacts Safety week	Productivy Loss week	Impact on community, state, society	Impact on Project	Impact on Future Projects	Costs	Difference ROI
$300	$200	$500	$12	$20	$25	$12	$1,000	$60	$1,000	$2,128	$1,628.10

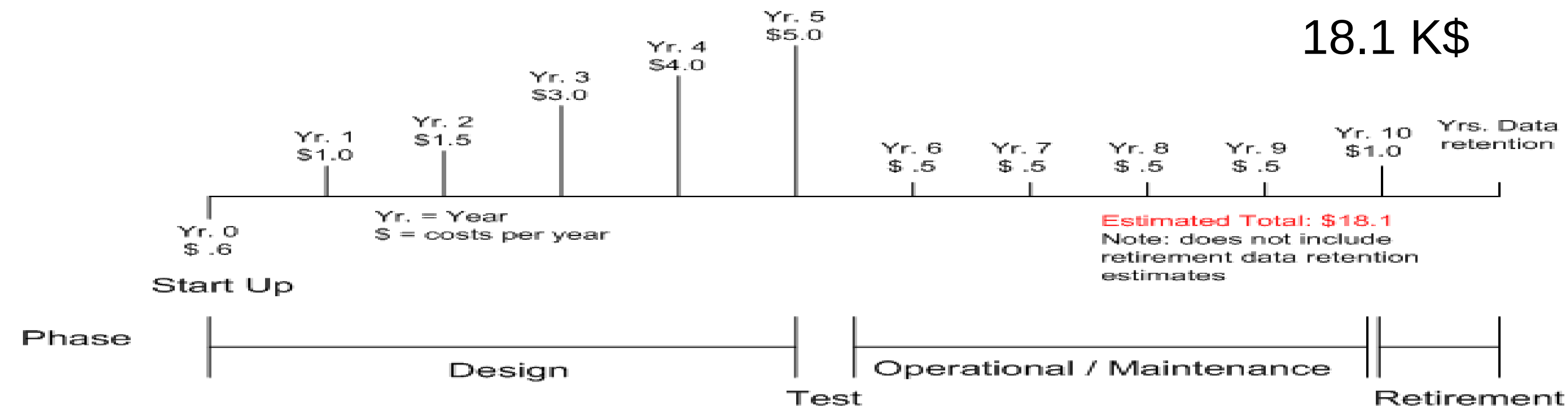
SQA Distributed Over Software Lifecycle Adds Cost Early in Lifecycle

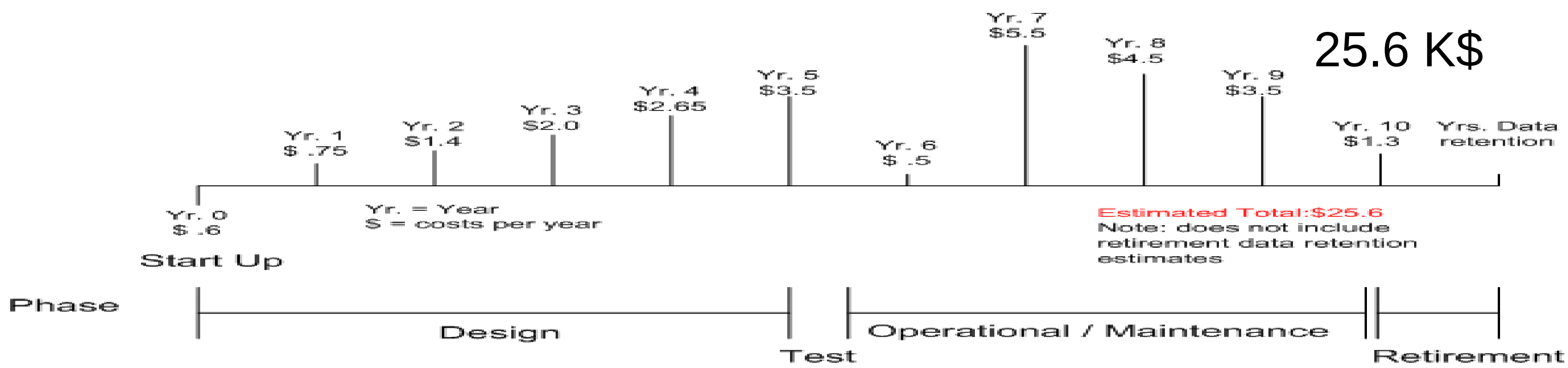


Legacy or “Archeologial” Software Documentation is Difficult and Expensive



Comparison of Documentation Strategies indicates value of attention to SQA throughout software lifecycle





Summary

- SQA is required by regulation: Title 10: Energy CFR 830, and DOE Order 414 supporting documents.
- SQA testing has caught issues that without SQ activities would have gone unnoticed until the system was in a production mode of operation.
- The need exists for sound SQA, based on prior experiences with failures such as those cited in section 4.
- SQA produces documents supporting software throughout the life cycle and retirement.
- SQA requires greater attention and focus on the software than a programmer would normally give to the software.
- SQA reduces the risk of failure associated with software.
- SQA requirements can incorporate safety and security requirements.
- SQA uses a graded approach of activities dependent on safety or security level.
- SQA is good engineering practice.

Plutonium Oxide Characteristics

Jacquelyn Lopez and Dave Wayne

Presented by: Roberta Mulford

MET-1 (Actinide Processing Support)

Manufacturing Engineering & Technology Division

JOWOG 22/2 – Actinide Chemical Technology

July 9-13, 2012

AWE, Aldermaston, UK

Purpose

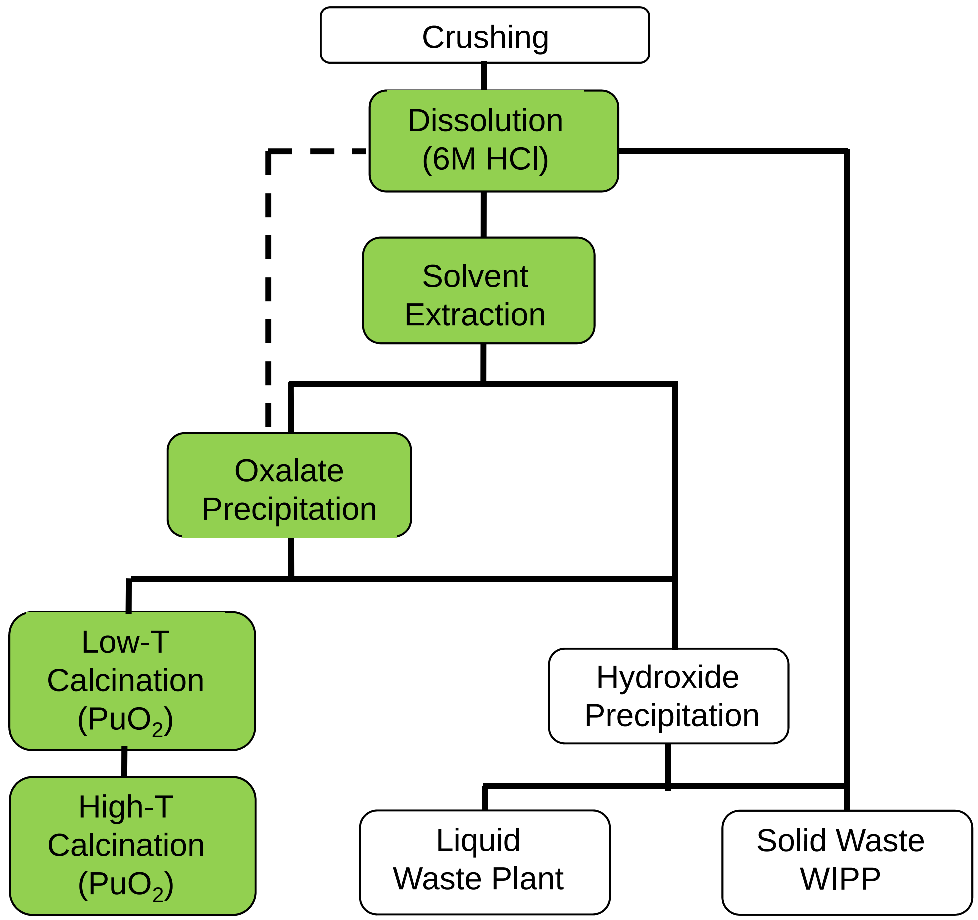
- Characterize plutonium oxide processed through aqueous and high temperature operations.
- Gather analytical and characterization results of items with known process history.
  - Processing documentation
  - Pu Assay
  - Analytical chemistry
  - Physical analysis
  - Moisture content
- Review information for any distinguishing characteristics based on the material and/or process to identify trends

Analysis Plan

- Recovery Processes:
  - Aqueous Chloride- recovery of chloride based feed items
  - Aqueous Nitrate- recovery of non-chloride based feed items
  - Metal Oxidation- low temperature metal oxidation ~475-575°C
- High Temperature and Blending Processes:
  - ARIES stabiliation- Calcination at ~950-1040°C for 2.2 hrs
  - MOX stabilization- Calcination at 650°C for 6 hrs
  - DOR stabilization-Calcination at 850°C for 8 hrs
  - 94-1 3013 stabilization- Calcination at 1025°C for 4 hrs
  - Other stabilization- Calcination at 750°C for 8 hrs

Operation Capabilities

- Aqueous Chloride Processing



Operation Capabilities

- Typical Aqueous Chloride Processing Input Feeds

ER salt

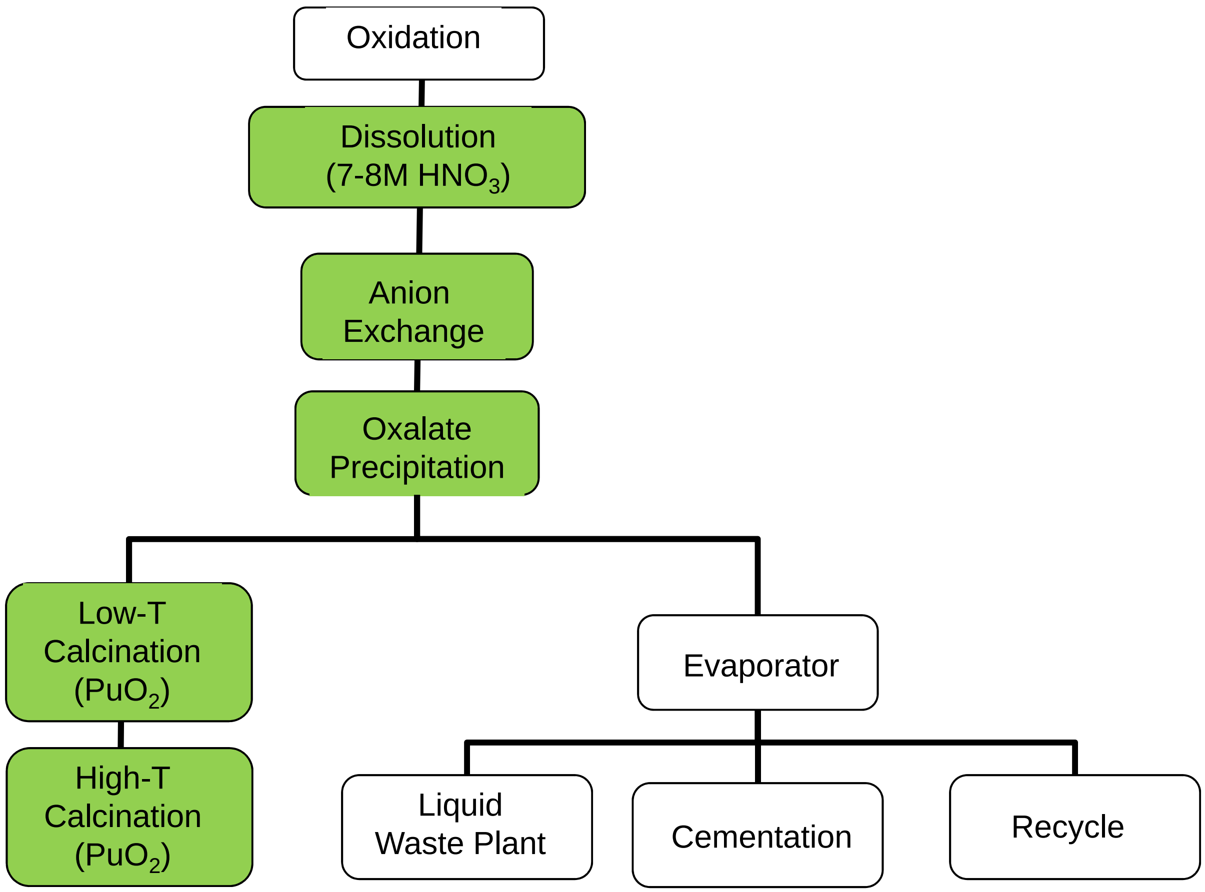
ER Crucible

Anode heel

MSE metal and salt

Operation Capabilities

- Aqueous Nitrate Processing



Operation Capabilities

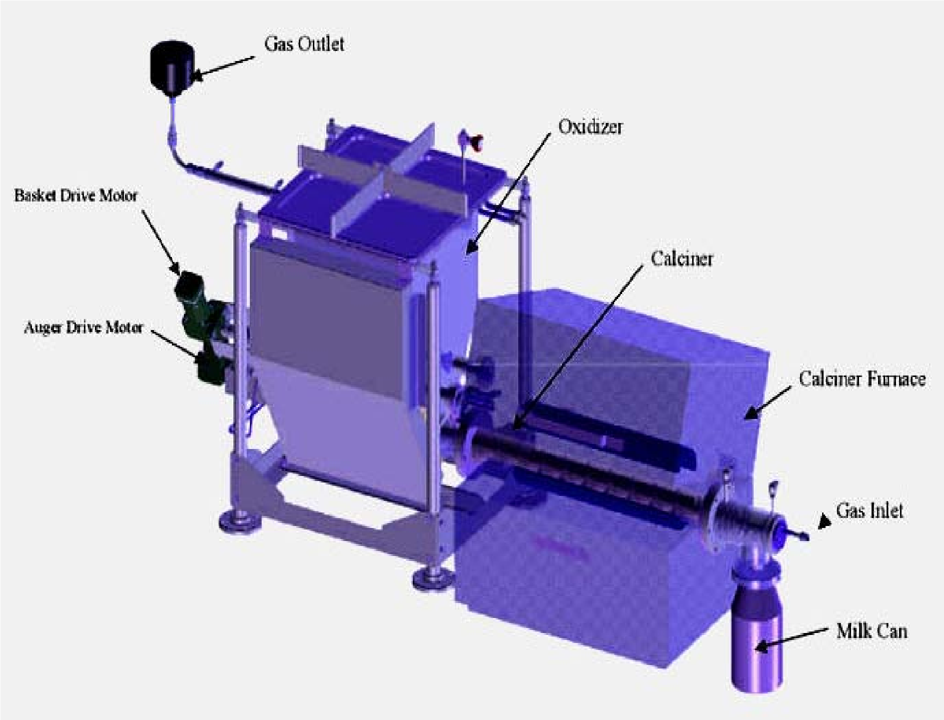
- Typical Aqueous Nitrate Processing Input Feeds
  - Pu metal turnings
  - Casting skulls from Coalescence
  - Anode heel from Electro-refining
  - Sand, Slag, and Crucible (SS&C) from metal production during PuF_4-Ca^0 reduction
  - Ashes formed from the treatment of Pu bearing combustible material
  - Any other non-chloride based residues

ARIES Oxide Processing

- <u>ARIES (Advanced Recovery & Integrated Extraction System)</u>

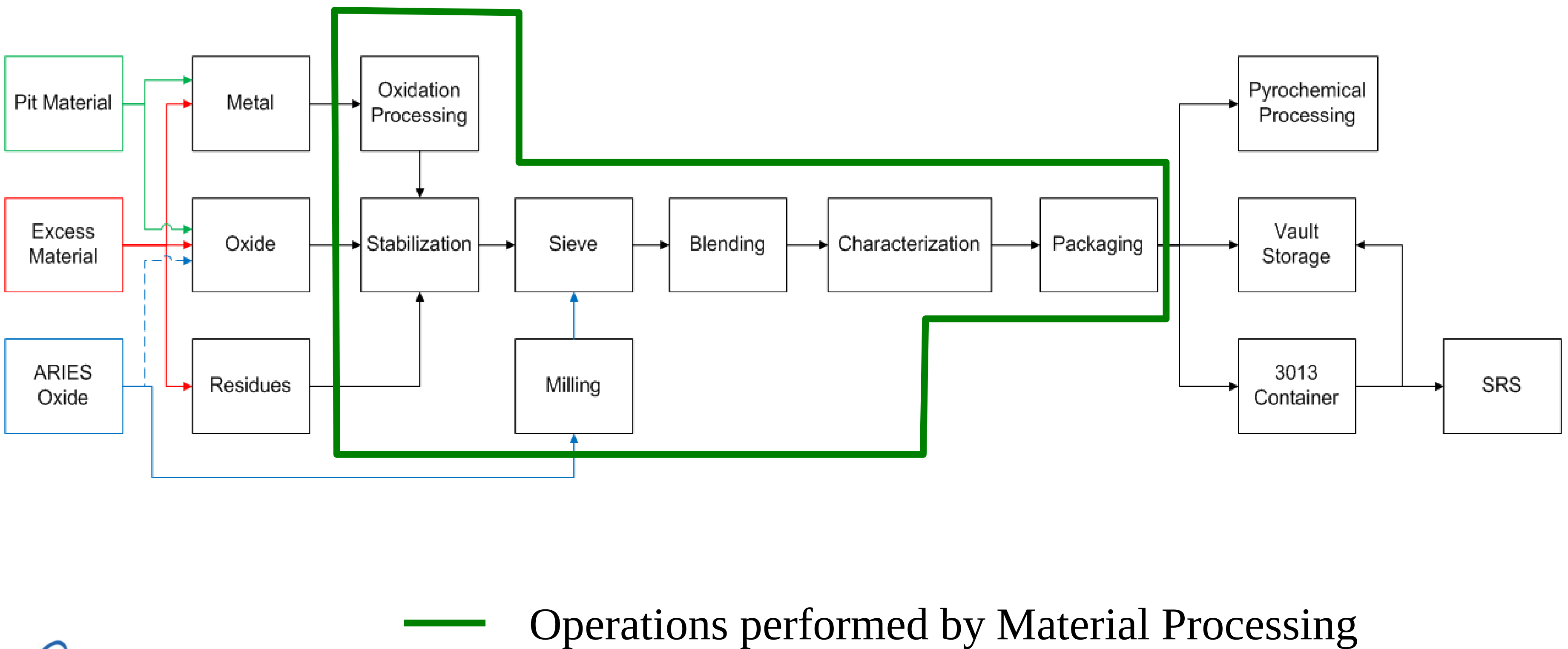
❖ Pu extracted from old weapons
  - Pu → high-purity oxide: DMO
  - Ignition / Oxidation: rotating perforated basket: ~475-575^{o}C, 75%O_2 / 25% He, ~2 L/min He; 1.5 L/min O_2
  - Total O_2 > amt. needed for stoichiometric PuO_2
  - Calcination: screw calciner, ~950-1040^{o}C, 132 min., same gas mix
  - Product Oxide: sieved, milled, blended; physical & chemical analysis; packaged for long-term storage

- Direct Metal Oxidation (DMO-2) Furnace / Calciner



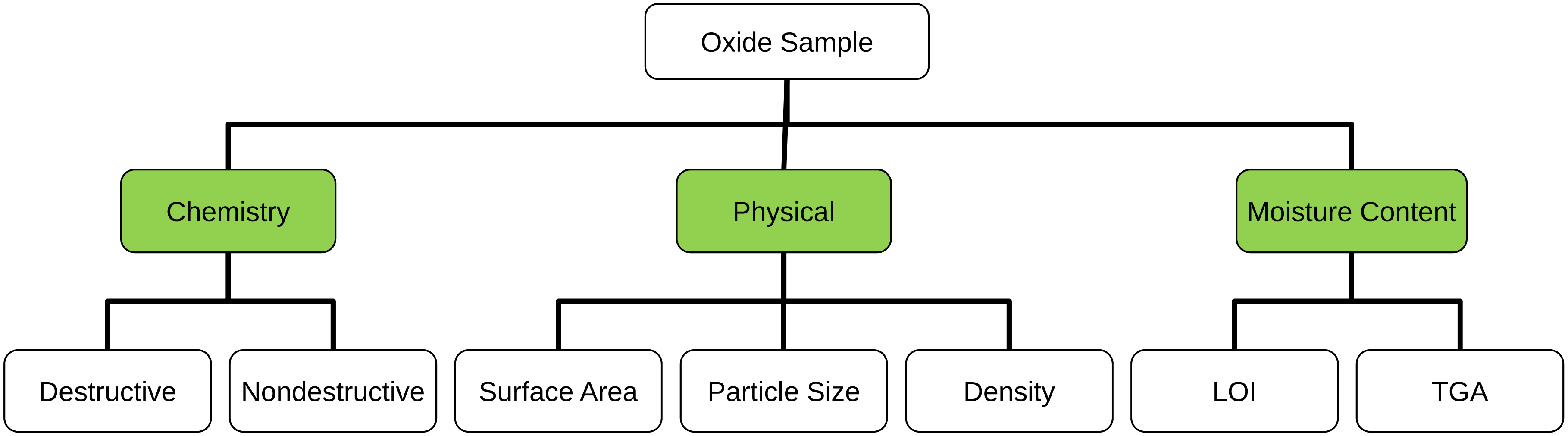
Operation Capabilities, continued

- High Temperature Stabilization



Operation Capabilities, continued

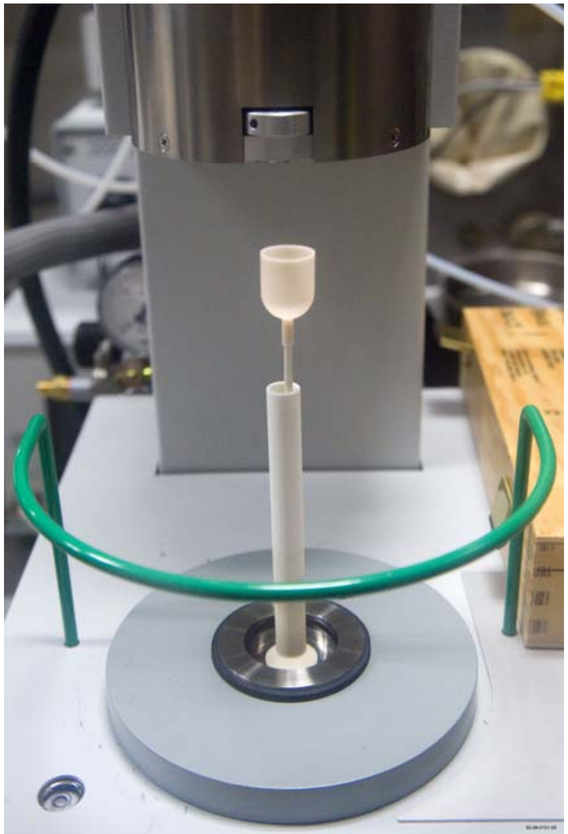
- Oxide Characterization



Why TGA?

- Loss-on Ignition

- Thermal Analysis



Why TGA?

- Analysis required for Packaging & Shipping PuO_2 in 3013 welded steel cans
- Loss On Ignition (LOI) insufficient for many reasons:
  - **Does not address possible weight gain**
  - **Does not distinguish between H_2O & other volatiles**
  - **No knowledge of temperature *vs*. time constraints**
  - **Large samples / Overnight analysis**
  - **Severe restrictions on sample handling**
- Upper Limits for Moisture in Packaged PuO_2
  - **Max. H_2O permissible by LOI = 0.15 wt. %**
  - **Max. H_2O permissible by TGA-MS = 0.32 wt. %**

Analysis Overview

- Reviewed process information between 1997-2011
  - Feed material
  - Material Type
  - Calcination temperatures for conversion from oxalate to oxide
  - Stabilization temperatures
  - Characterization techniques used
  - Project (historical process information)
  - Pictures of material
  - Any process variations
    - Acid molarity adjustments
    - Purification process, if used
    - Sieving and Blending times
    - Processing issues

Observations

- General
  - All current Pu oxide products processed in the same room
  - Analytical samples were taken post calcination
  - Most analytical information was taken as part of experimental plans or to verify composition as part of existing project requirements
  - The results are identified by project but the feed items came from multiple sources. Mostly LANL processed material but also LLNL, Rocky Flats, and Hanford.
  - It took a lot of experimental work to develop our current processes and its still ongoing
  - Types of equipment is important
  - Human technique is most important

Observations

- Aqueous Processing
  - Aqueous Chloride incoming feed generally between 10-35% Pu assay if crucible or residue, if MSE salt, it can be >50%
  - Aqueous Nitrate incoming feed generally >40% Pu assay
  - Large volumes of solutions are necessary to achieve high Pu assay, >50 L per 1000g of Pu assay solution from dissolution with IX and SX. Complete flow sheet and ~40 L without SX.
  - Dissolution is the first step and key in determining how much Pu can be recovered
  - High product assay can be achieved (>80%) without SX
  - The nitrate process has a more consistent recovery

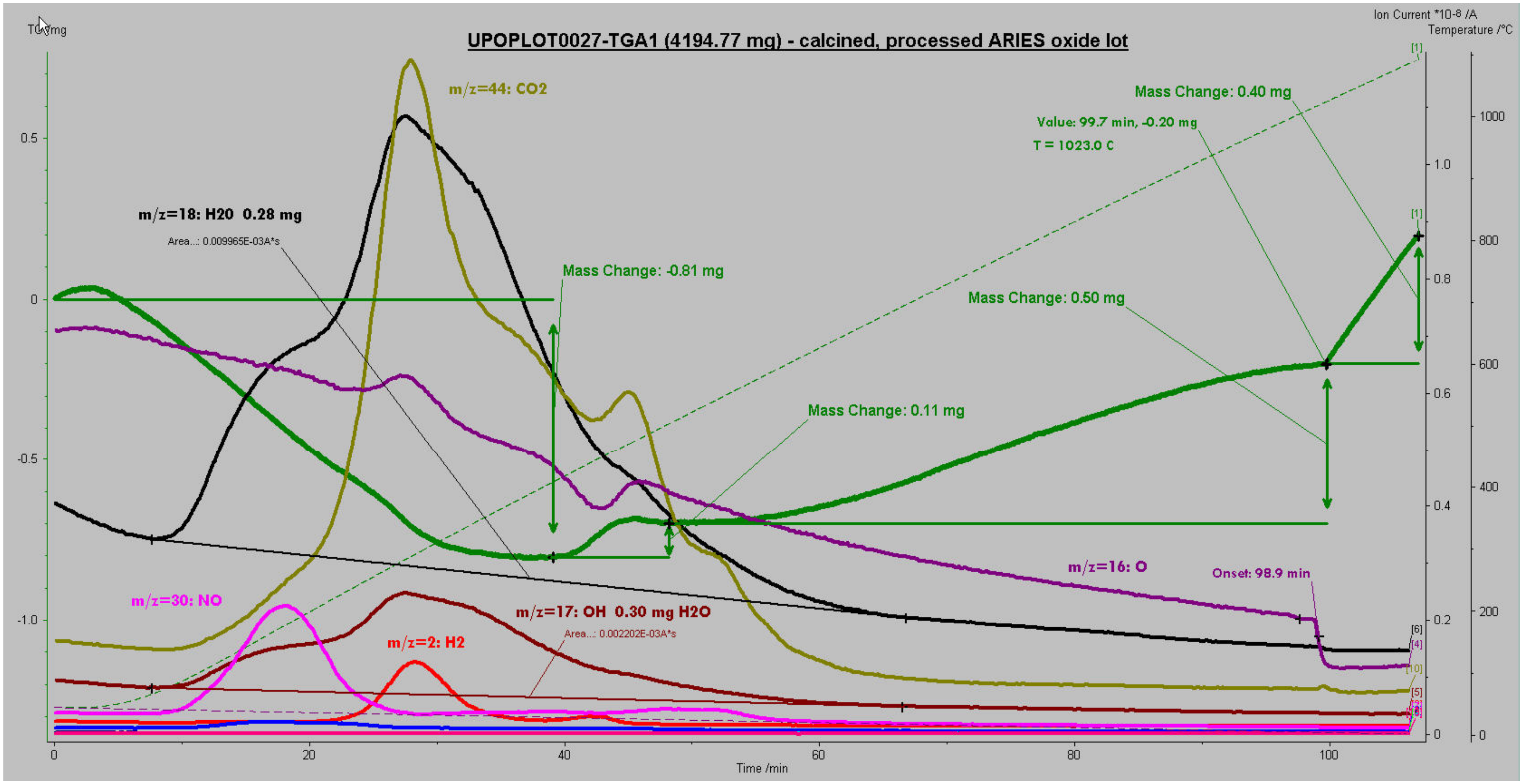
Observations

- Oxide Processing
  - Oxide products were typically 82-86% Pu assay when IX or SX were used
  - Oxide products were typically 73-86% Pu assay without SX
  - Residues not processed through Aq. were typically 60-78% Pu assay
  - 3013 processing avg. calcination loss was 91.9 g (3.5 wt%)
  - DOR processing avg. calcination loss was 25.9 g (0.81 wt%)
  - MOX processing avg. calcination loss was 2172.2 g (55.25 wt%)
  - The lower the assay the higher the calcination loss (g)
  - Type of calcination boat can affect oxide product due to cross contamination, but is minimal

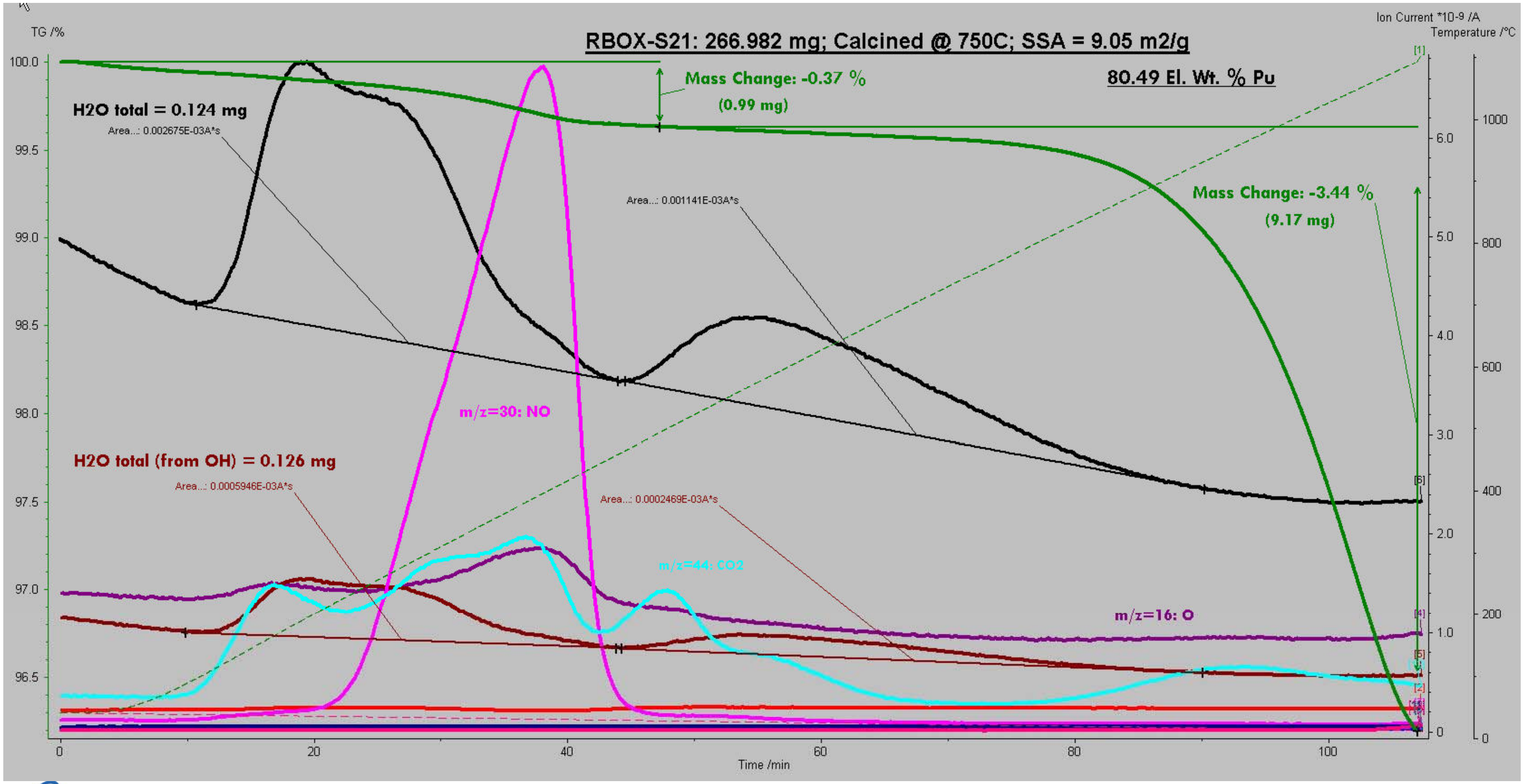
Observations

- Thermal Trends
  - PuO2 from different process paths → Different thermal behavior
  - <u>ARIES</u>: complex trimodal PSD, very low SSA, miniscule volatile content: H_2O and CO_2 dominate, NO always present, may see H_2 peaks. Possible oxidation of sub-stoichiometric oxides dominates high-T behavior (wt. gain). Considerations include initial particle size, oxygen levels in TGA furnace. Uncalcined PuO_2 may deposit Ga_2O_3.
  - <u>MR&R / MIS</u>: relatively simple unimodal PSD, high & variable SSA, significant volatile content: H_2O and NO dominate, CO_2 always present, other ligands such as SO_2 may also appear @ high T. Weight loss behavior dominated by salt volatilization – no Cl peaks seen (abundance sensitivity problem due to Ar).

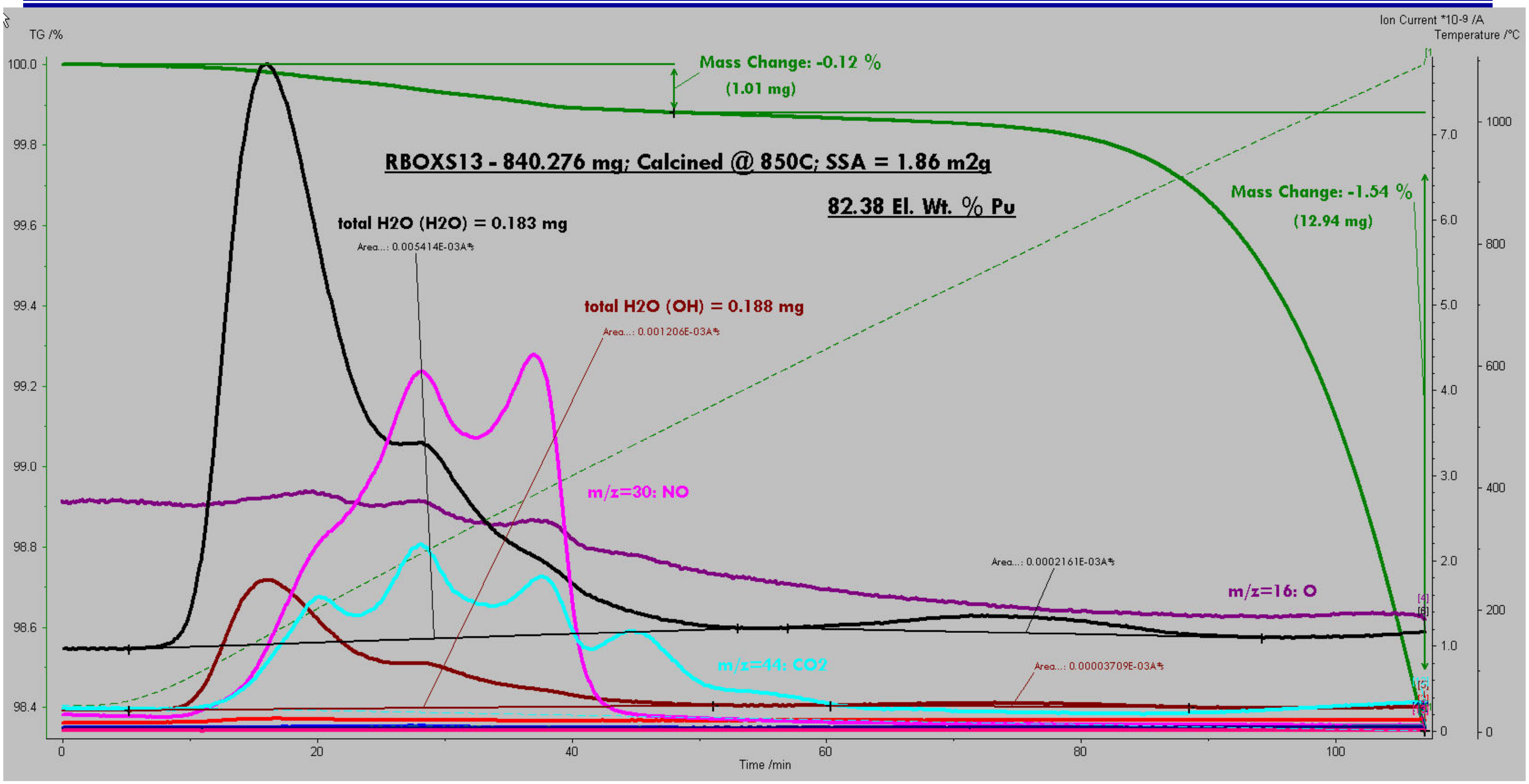
A Typical ARIES PuO_2 Calcined, Processed Lot



MR & R Sample: High Surface Area, 750°C Calcination

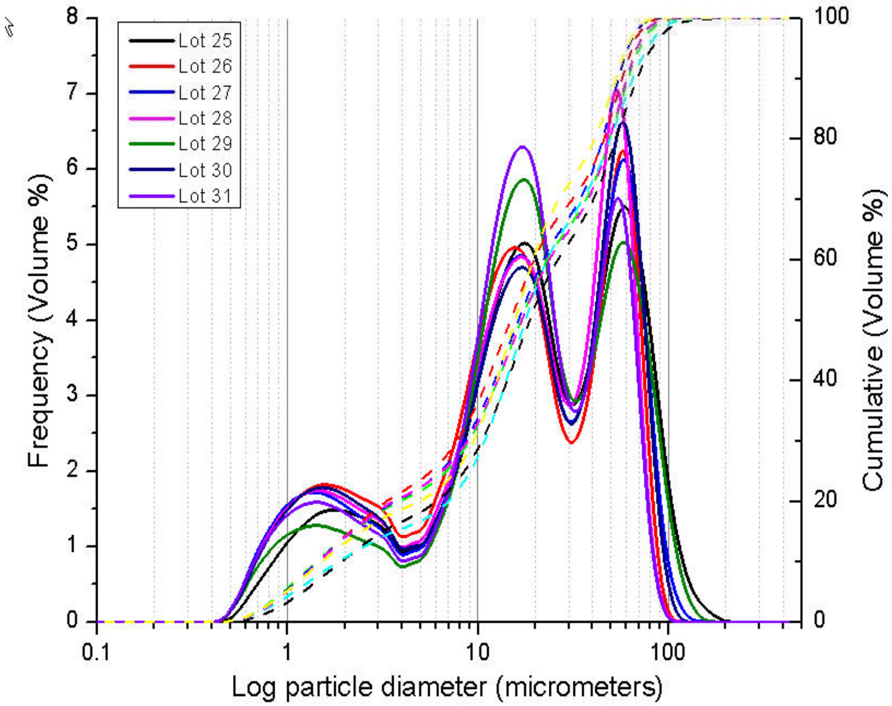


MR & R Sample – Low Surface Area, 850^{o}C Calcination

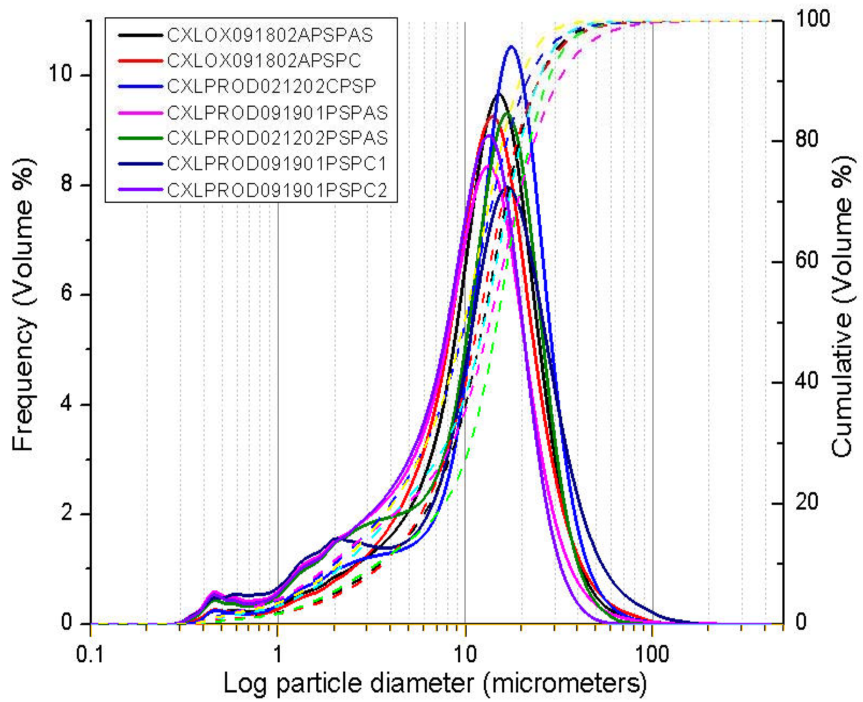


Characteristics of Process PuO_2: Particle Size Distribution

- Processed ARIES Oxide



- MIS / MR&R Impure Oxide



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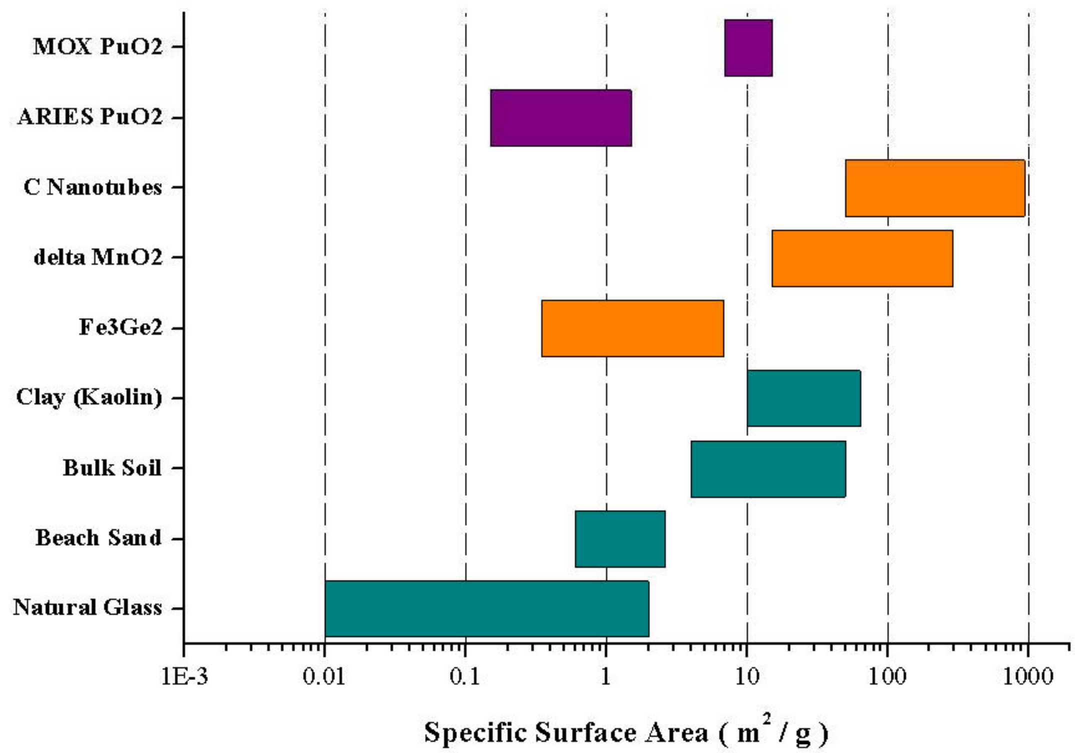
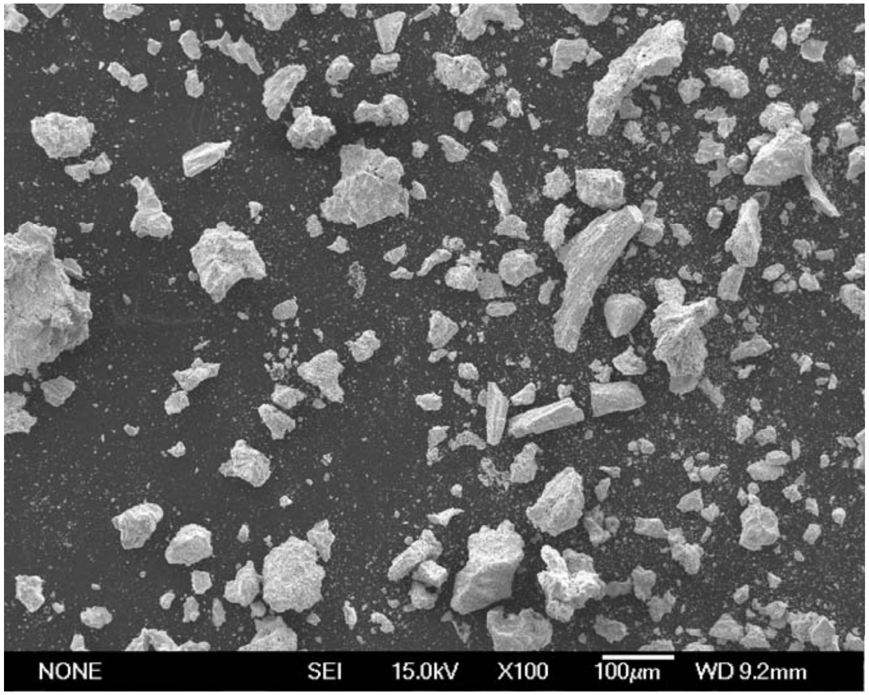
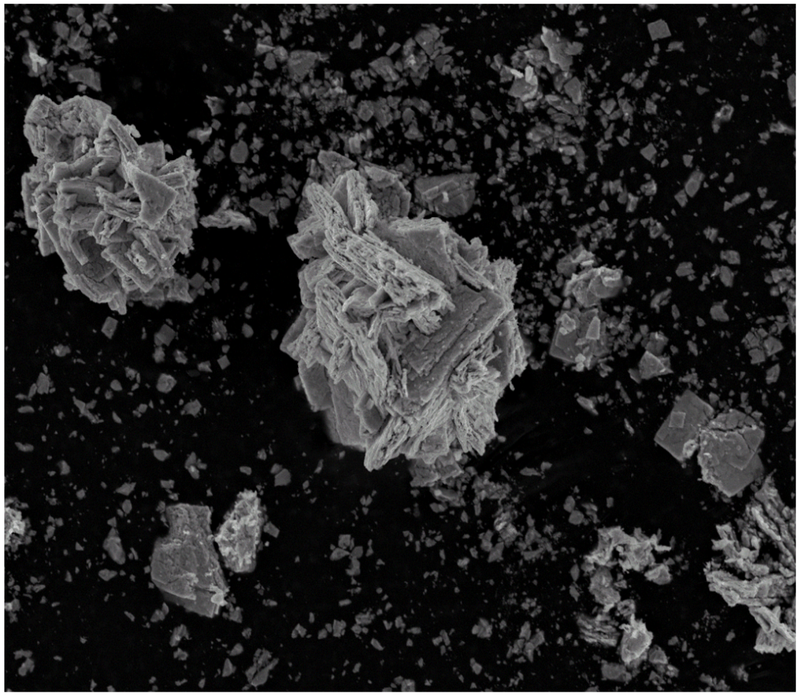
Specific Surface Area: Significant variation depending on process path

- Specific Surface Area varies markedly for Pu Oxides produced by different methods:
  - Oxidation in DMO: 0.1 – 1.0 m^2/g (typically ~0.2 to 0.35 m^2/g)
  - Oxidation in Air (no calcination): ~7 m^2/g (one sample)
  - Oxalate Precipitation (calcination to ~650°C) : 7 – 14 m^2/g (LANL's MOX Pu Polishing Program)



SEM: ARIES vs. MOX





Observations

- Chemistry Trends
  - Iron (Fe), Magnesium (Mg), Aluminum (Al), Molybdenum (Mo), Phosphorous (P), and Tungsten (W) high for oxide produced from Aq. Chloride processing
  - Calcium (Ca), Thorium (Th), Uranium (U), Bismuth (Bi) higher for oxide produced from Aq. Nitrate processing
  - After stabilization, chloride concentrations are similar between Aq. Chloride products vs. Aq. Nitrate products (~125 ppm)
  - Material processed from metal oxidation and no aqueous processing was the cleanest, and represents a baseline

Sample Results- Aq. Chloride with & without SX

	Lot ID	MT	Concentration (ppm)					
			Ca	K	Mg	Na	F	Cl
	04272-CC-075	52	133	83	12	85	50	30
	RBXSFY05-4	52	27	82	119	142	100	20
	RBXSFY05-6	52	11	92	412	72	120	250
	RBXSFY05-18	52	61	171	11	64	<40	<40
SX	RBXSFY06-1	52	33	81	67	63	<90	<90
	RBXSFY06-2	52	49	86	375	67	<90	140
	RBXSFY06-3	52	16	76	1390	59	160	150
	RBXSFY06-4	52	35	91	602	71	160	170
	RBXSFY06-5	52	24	92	55	72	60	150
	RBOX	52	2680	5	2090	670	526	
OX	RBOX	52	1460	1100	3840	99		
	RBOX	52	1600	1400	3900	210	510	3100
	RBOX	52	1100	6500	1200	1000	837	10352

Averages	SX	43	95	338	77	108	130
	OX	1710	2251	2758	495	624	6726

Sample Results- Aq. Chloride with & without SX

		Concentration (ppm)									
Lot ID	MT	Al	Cr	Fe	Ni	Si	Ga	Ta	Th	Ti	W
04272-CC-075	52	55	32.7	111	28	195	17.6	4.3	0.4	4.6	51.3
RBXSFY05-4	52	84	43.8	340	35	156	9.9	8.9	0.2	5.9	195
RBXSFY05-6	52	<20		278	11	100	5.8	3.2	<0.1	1.5	104
RBXSFY05-18	52	56	22		23	223	8.1		3.6	15	86
RBXSFY06-1	52	25	93		64	141	29		0.4	1.9	87
RBXSFY06-2	52	58	88		155	214	24		1.2	3.5	137
RBXSFY06-3	52	23	37		57	128	8.8		0.3	2.0	88
RBXSFY06-4	52	<20	39		66	78.1	14		0.3	1.7	96
RBXSFY06-5	52	32	68		82	110	19		0.1	1.6	94
RBOX	52	92	5.3	1000	260	300	150	99	110	13	110
RB0X	52	8.5	36	29	18	1100	21	87	6.5	2.9	49
RBOX	52	48	34	66	22	1500	39	84	9.1	10	55
RBOX	52	47	31	210	93	500	20	160	160	11	120
Averages	SX	48	53	243	58	149	15	5.5	0.8	4	104
	OX	49	27	326	98	850	58	108	71	9.2	84

Sample Results- Aq. Nitrate vs. Aq. Chloride

			Concentration (ppm)					
Lot ID	**MT**	**Feed**	**Ca**	**K**	**Mg**	**Na**	**F**	**Cl**
04272-CC-075	52	Chloride	133	83	12	85	50	30
RBXSFY05-4	52	Chloride	27	82	119	142	100	20
RBXSFY05-6	52	Chloride	11	92	412	72	120	250
RBXSFY05-18	53	Chloride	61	171	11	64	<40	<40
RBXSFY06-1	52	Chloride	33	81	67	63	<90	<90
RBXSFY06-2	52	Chloride	49	86	375	67	<90	140
RBXSFY06-3	52	Chloride	16	76	1390	59	160	150
RBXSFY06-4	52	Chloride	35	91	602	71	160	170
RBXSFY06-5	52	Chloride	24	92	55	72	60	150
RBXSFY05-10	53	Nitrate	143	93	4.4	72	200	80
RBXSFY05-11	53	Nitrate	118	90	18	70	180	210
RBXSFY05-12	53	Nitrate	99	101	<3	79	120	40
RBXSFY05-13	53	Nitrate	84	87	5	67	90	100
RBXSFY05-14	53	Nitrate	191	88	5.6	69	100	90
RBXSFY06-9	54	Nitrate	92	89	11	69	60	170

Averages	Nitrate	121.2	91.3	8.8	71.0	125.0	115.0
	Chloride	43.2	94.9	338.1	77.2	108.3	130.0

Sample Results- Aq. Nitrate vs. Aq. Chloride

			Concentration (ppm)									
Lot ID	MT	Feed	Al	Fe	Ni	Si	Mo	Ga	P	Th	U	W
04272-CC-075	52	Chloride	55	111	28	195	5.2	17.6	98.2	0.4	105	51.3
RBXSFY05-4	52	Chloride	84	340	35	156	9.8	9.9	542	0.2	116	195
RBXSFY05-6	52	Chloride	20	278	11	100	18.3	5.8	283	<0.1	115	104
RBXSFY05-18	53	Chloride	56		23	223	182	8.1	215	3.6		86
RBXSFY06-1	52	Chloride	25		64	141	18	29	406	0.4		87
RBXSFY06-2	52	Chloride	58		155	214	22	24	281	1.2		137
RBXSFY06-3	52	Chloride	23		57	128	16	8.8	374	0.3		88
RBXSFY06-4	52	Chloride	20		66	78.1	10	14	166	0.3		96
RBXSFY06-5	52	Chloride	32		82	110	14	19	132	0.1		94
RBXSFY05-10	53	Nitrate	20	98	41	162	6.8	19.6	43.6	5470	3220	10.8
RBXSFY05-11	53	Nitrate	19	97	86	118	12.8	16.5	43.6	531	2180	21
RBXSFY05-12	53	Nitrate	22	47	30	105	11	0.7	42	371		5.4
RBXSFY05-13	53	Nitrate	19	50	32	113	7.5	2.6	38	470		6.9
RBXSFY05-14	53	Nitrate	19	15	29	129	2.9	1.4	41	708		15
RBXSFY06-9	54	Nitrate	19		59	192	5.3	1.0	77	981		14

Averages	Nitrate	19.7	61.4	46.2	136.5	7.7	7.0	47.5	1421.8	2700.0	12.2
	Chloride	41.4	243.0	57.9	149.5	32.8	15.1	277.5	0.8	112.0	104.3

Sample Results- Calcination

Project	Pu Assay (g)	Pre Calcination Net wt (g)	Initial wt%	Post Calcination Net wt (g)	Final wt%	Loss due to Heating (g)
3013	2060.02	2673.58	82.56%	2514.61	86.27%	-91.90
DOR	1593.77	3223.7	84.78%	2981.93	85.30%	-25.96
MOX	1541.63	3931.81	36.6%	1759.59	88.14%	-2172.21
Other	667.50	819.9	80.53	806.04	81.85%	-13.3

- MOX stabilization- Calcination at 650°C for 6 hrs (min)
- DOR stabilization-Calcination at 850°C for 8 hrs (min)
- 94-1 3013 stabilization- Calcination at 1025°C for 4 hrs (min)
- Other stabilization- Calcination at 750°C for 8+ hrs (min)

Sample Results- Testing the Trends

			Concentration (ppm)											
Lot ID	**MT**	**Feed**	Al	Ni	Si	Ca	K	Bi	Mg	Na	Ga	P	Th	W
RBXSFY05-19	53	LEXC-PO-0006	49	125	218	200	85	6240	84	66	41	24	307	17
RBXSFY05-21	53	LEXC-PO-0009	45	131	179	188	83	6720	67	65	53	68	307	19
RBXSFY05-22	53	LEXC-PO-0010	83	143	277	180	88	4380	71	69	51	86	271	30

- LEXC-PO-000X were unknown because they had already been packaged in 2000. So can we figure out where it came from?
  1. Compare to process averages. Are there any abnormal compositions? Yes, high bismuth
  2. Are there any similarities to any of the processes? Yes, they are high in Th and Ca and low in Mg and W like nitrate history.
  3. Is there any other information; particle size, surface area, etc? No
  4. Any similarities to known process history samples? Yes, one item processed through chloride operations and solvent extraction and another item that was from pyrochemistry but did not go through aqueous processing.

Sample Results

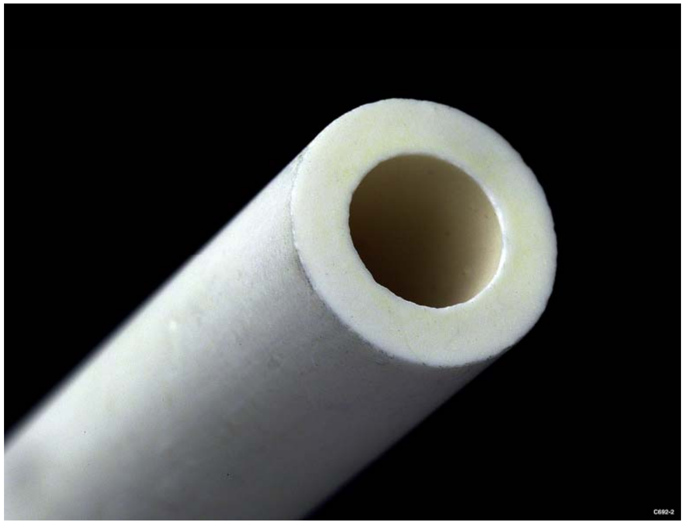
5. Based on process knowledge and comparison to chemical process averages, was it processed through nitrate or chloride processing? Nitrate
6. Research process history. Was some information found, if so what? Yes, item was found on LAMCAS and the history revieled it was processed through nitrate operations in the mid-1990s and the feed came from pyrochemistry. I later found research papers describing work that was done which supports what these items were.

Future Work

- Look at more available data
  - Physical characteristics like particle size and surface area
  - TGA data
- Look at kinetics of aqueous processing and mass balances to help identify/validate possible trends
- Look at what process impurities are being introduced during processing
- There is still more historical information available

Beryllium Oxide Sparge Tube Experiment in Pyrochemical Plutonium Operations

Process Engineer: J. Matt Jackson



Background

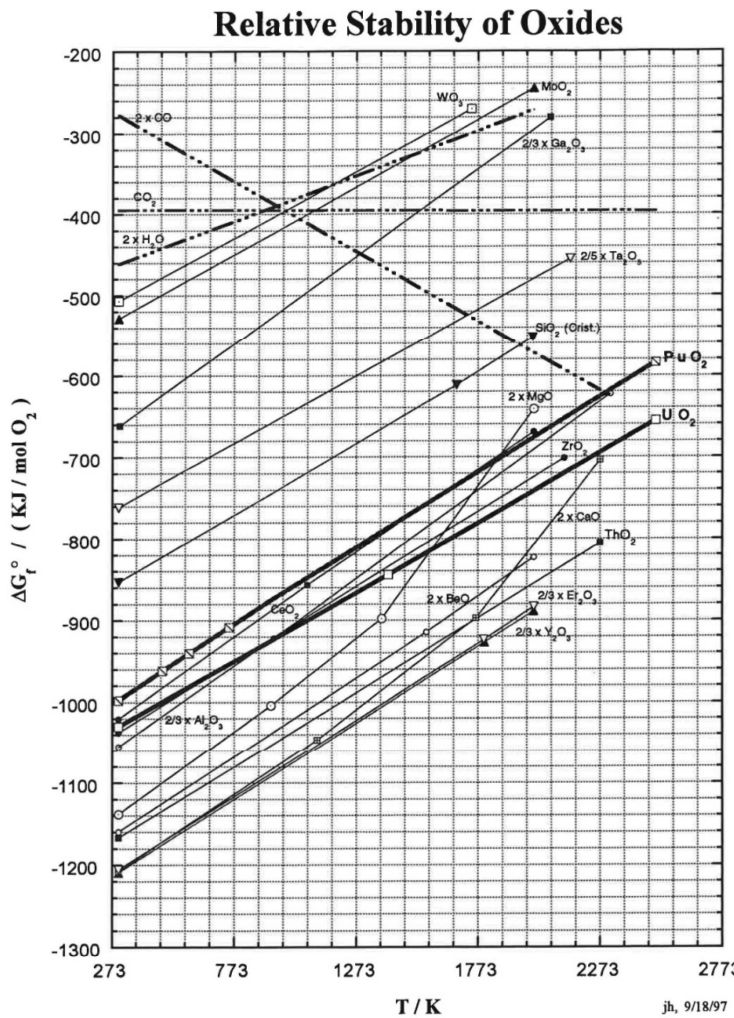
- Ceramic sparge tubes are used to deliver anhydrous chlorine gas to the Multiple Cycle Direct Oxide Reduction (MCDOR), and the Metal Chlorination (MC) Processes at LANL.
  - The MCDOR process reduces plutonium oxide to plutonium metal using calcium metal. The reaction takes place at 850 C in a molten calcium chloride solvent salt. The byproduct of the reaction is calcium oxide which is then oxidized using chlorine gas to regenerate the solvent salt.
  - The MC process chlorinates Pu metal directly for either a short time (30 minutes) for the purpose of Am extraction, or for a long time (6 hours) for the purpose of $PuCl_3$ production.
- Currently Magnesium Oxide (MgO) sparge tubes are used in the process discussed above.

The Problem

- MgO sparge tubes fail at a high rate. Sparge tubes fail in both processes due to thermal shock and fragility. Additionally MgO sparge tubes fail in both processes due to chemical deterioration. In MC a MgO sparge tube has a one run service life.
- Efforts to replace MgO with AlO2, Y2O3, Ta, and SiAlON have been unsuccessful (SiAlON performed well in MCDOR but extremely poorly in MC).

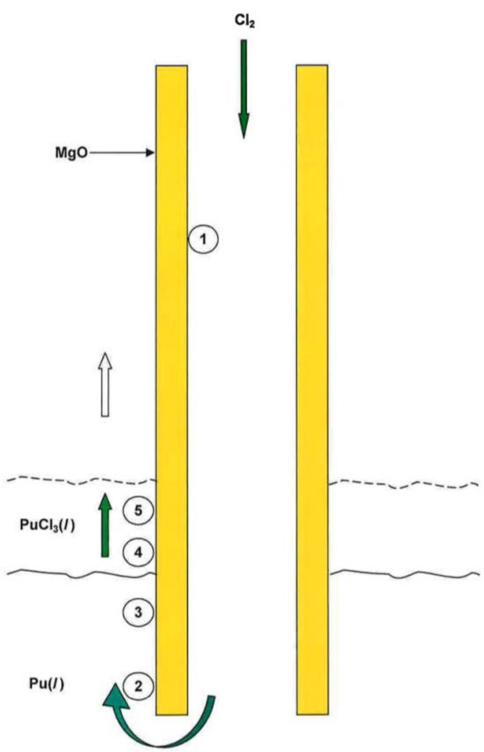
Why BeO?

- BeO exceptionally stable oxide
- Gibbs Free Energy Predictions
- Thermal Properties
- Material Toughness/Durability
- Better Wetting Properties



MC Gibbs Predictions

MgO Sparge Tube in Metal Chlorination



(1) $MgO(s) + Cl_2(g) \rightarrow MgCl_2(l) + 1/2\ O_2(g)$, $\Delta G^0_{1200K} = +\ 7.3$ kJ ; $\Delta G_{1200K} < 0$, if $P_{Cl2} > 2.08\ (P_{O2})^{1/2}$

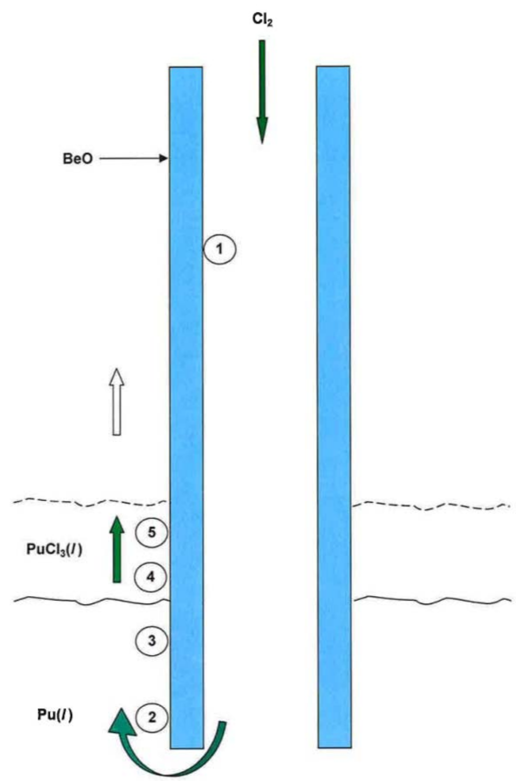
(2) $MgO(s) + 1/2\ Pu(l) \rightarrow 1/2\ PuO_2(s) + Mg\ (l)$, $\Delta G^0_{1200K} = +\ 59.0$ kJ

(3) $Pu(l) + 3/2\ Cl_2(g) \rightarrow PuCl_3(l)$, $\Delta G^0_{1200K} = -\ 698.1$ kJ

(4) $2\ MgO(s) + PuCl_3(l) + 1/2\ Cl_2(g) \rightarrow 2\ MgCl_2(l) + PuO_2(s)$, $\Delta G^0_{1200K} = -\ 109.1$ kJ

(5) $MgO(s) + 2/3\ PuCl_3(l) \rightarrow 1/3\ Pu_2O_3(s) + MgCl_2(l)$, $\Delta G^0_{1200K} = -\ 22.7$ kJ

BeO Sparge Tube in Metal Chlorination



(1) $BeO(s) + Cl_2(g) \rightarrow BeCl_2(g) + 1/2\ O_2(g)$, $\Delta G^0_{1200K} = +\ 108.9$ kJ

(2) $2\ BeO(s) + Pu(l) \rightarrow PuO_2(s) + 2\ Be\ (s)$, $\Delta G^0_{1200K} = +\ 161.4$ kJ

(3) $Pu(l) + 3/2\ Cl_2(g) \rightarrow PuCl_3(l)$, $\Delta G^0_{1200K} = -\ 698.1$ kJ

(4) $2\ BeO(s) + PuCl_3(l) + 1/2\ Cl_2(g) \rightarrow 2\ BeCl_2(g) + PuO_2(s)$, $\Delta G^0_{1200K} = +\ 93.8$ kJ

(5) $2\ BeO(s) + PuCl_3(l) + 1/2\ Cl_2(g) \rightarrow 2\ BeCl_2(g) + 1/2\ Pu_2O_3(s) + 1/4\ O_2(g)$, $\Delta G^0_{1200K} = +\ 172.6$ kJ

BeO Advantages

- Beryllium oxide has a thermal conductivity of 330 $WK^{-1}m^{-1}$ and a coefficient of thermal expansion of 6.5×10^{-6} (At room temperature). Magnesium oxide has a thermal conductivity of 45 $WK^{-1}m^{-1}$ and a coefficient of thermal expansion of 10.4×10^{-6} (At room temperature). Therefore the BeO sparge tube would be much less susceptible to failure due to thermal shock.
- Beryllium oxide has a Knoop hardness of 2000 while MgO has a Knoop Hardness of 692.
- The more durable material of construction would result in fewer failed runs due to broken sparge tubes.

Tests Conducted (Thus Far)

- 1 run in MC (Americium Extraction)
- 1 run in MCDOR

MC Run Summary

- Run was a typical MC with 1/3 turnings and 2/3 DOR metal.
- Samples drawn from melt using quartz pipette (Results Pending).
  - 1 sample pre chlorination.
  - 1 sample after 15 minutes of chlorination.
  - 1 sample after 40 minutes of chlorination.
- Sample taken from salt after breakout (Results Pending).
- Dose rate monitored throughout the run.
  - Background: 2.6 mr/hr At Insertion: 6.0 mr/hr High: 7.4 mr/hr
- Mass of sparge tube was measured before and after run. Approximately 0.6 g was lost. Small amount of tapering could be seen at Pu submerged tip.
- Further Testing Planned this FY.

MCDOR Run Summary

- Run was a typical MCDOR operation with 4 reductions and 3 salt regenerations.
- Samples Taken (Results Pending):
  - 1 sample of plutonium oxide feed.
  - 1 sample after 1st , 2nd, and 3rd salt regeneration.
  - 1 sample after final reduction.
  - 1 sample of metal product after break out.
  - 1 sample of substance from downstream particulate filter.
- Dose rate monitored through duration.
- Mass and dimensions of sparge tube were monitored throughout the run. A total of 3.5 grams were lost over 315 minutes of operation. ID and length were unchanged. OD reduced from 0.362” to .345”.

Questions?

MIS Sample: Oxalate Precipitation