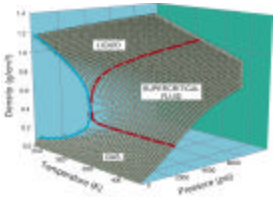
2000 ANS/ENS International Meeting
Washington DC, Nov. 14, 2000

The Deployment of Supercritical Fluid Extraction for Moisture Measurements in Impure Plutonium Oxides

LA-UR-00-2911

W.K. Hollis, A.M. Martinez, K.A. Brandt[a], B.S. Bender[b], and J.B. Rubin[c],

Applied Chemical Technology Group (C-ACT)
[a] Quality Management Group (ESH-14)
[b] Actinide Process Chemistry Group (NMT-2)
[c] Plutonium Metallurgy Group (NMT-16)
Los Alamos National Laboratory
Los Alamos, New Mexico 87545



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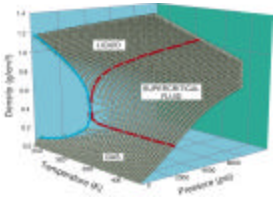
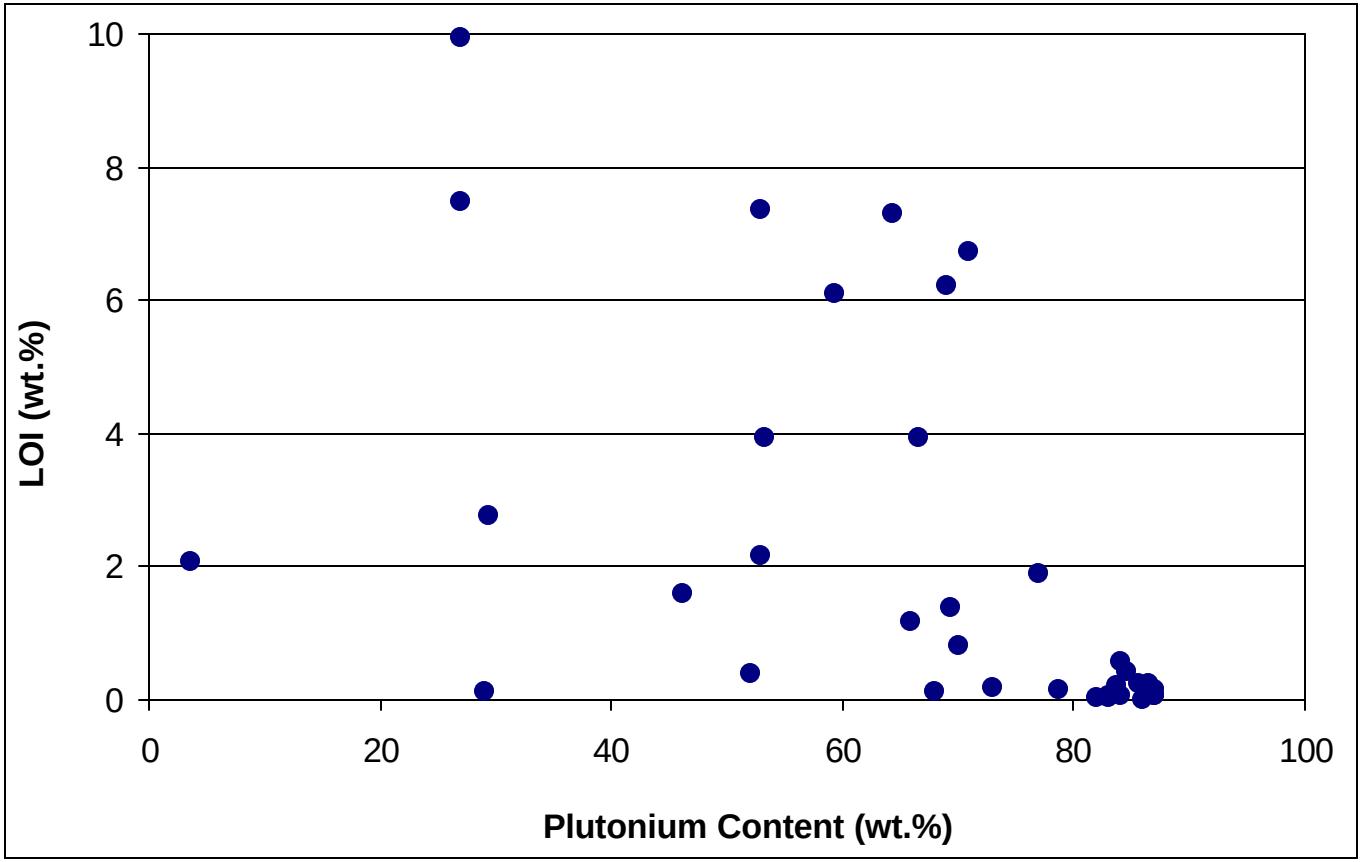
Statement of the Problem with Long-term Storage of PuO_2

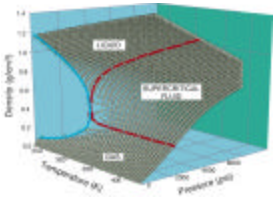
- Hydrogenous material mixed with pure/impure plutonium oxide powder may cause hydrogen production (through radiolysis) and pressurization of the welded canisters
- DOE-STD-3013-94/99 calls for material to be thermally stabilized by calcining at 950°C for at least two hours
- Thermal stabilization to be verified by Loss On Ignition at 1000 °C for at least one hour - weight loss not to exceed 0.5 mass %



Loss on Ignition

Unsuitability for Impure Materials





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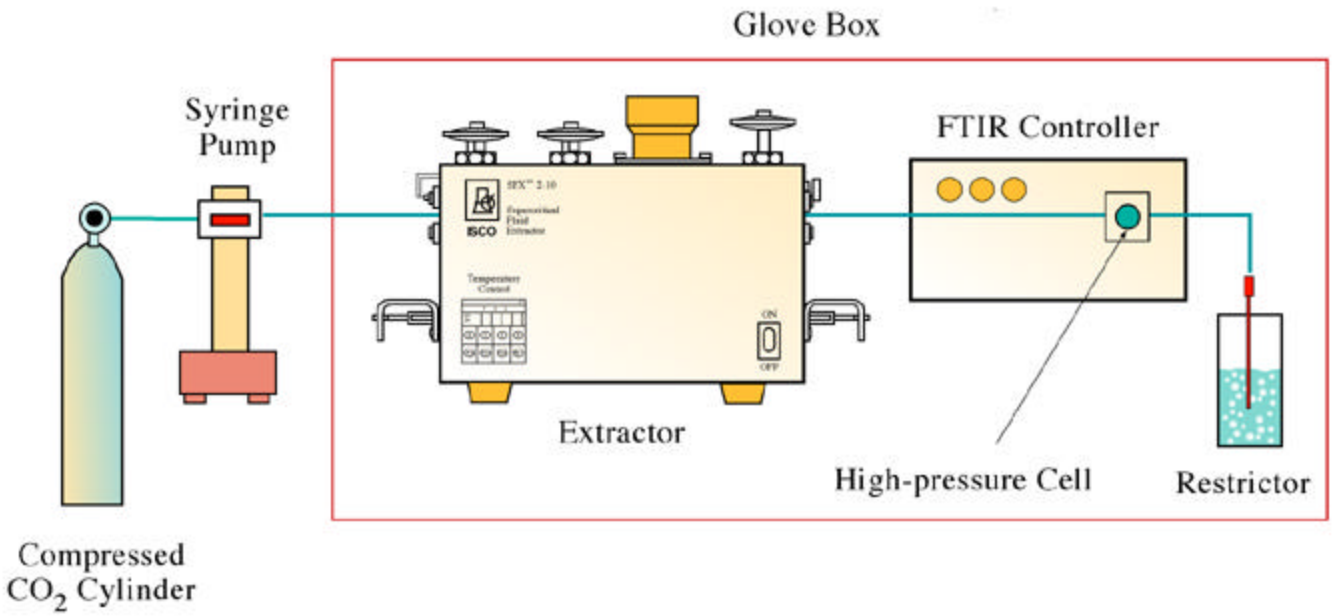
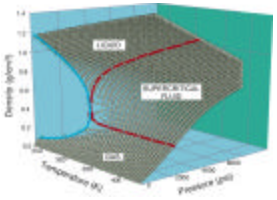
SFE Schematic

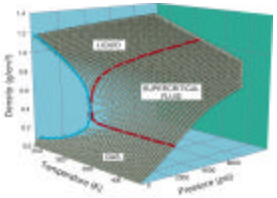




SFE - Requirements

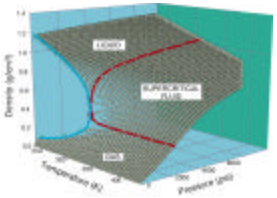
- Initial capital cost
  - ≈ 50 K

Annual operating cost
  - ≈ 10 K
- Personnel requirements
  - 1 technician (2-person rule observed)
- Facility requirements
  - Glovebox



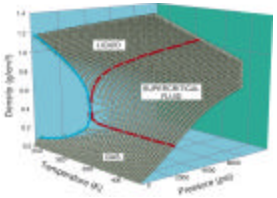
SFE - Advantages

- Advantages
  - **Large sample size (£20 g)**
  - **Short analysis time (30 - 60 minutes)**
  - **Minimal to no liquid waste generation**
  - **Data collection is automatic**
  - **DOE approved method**

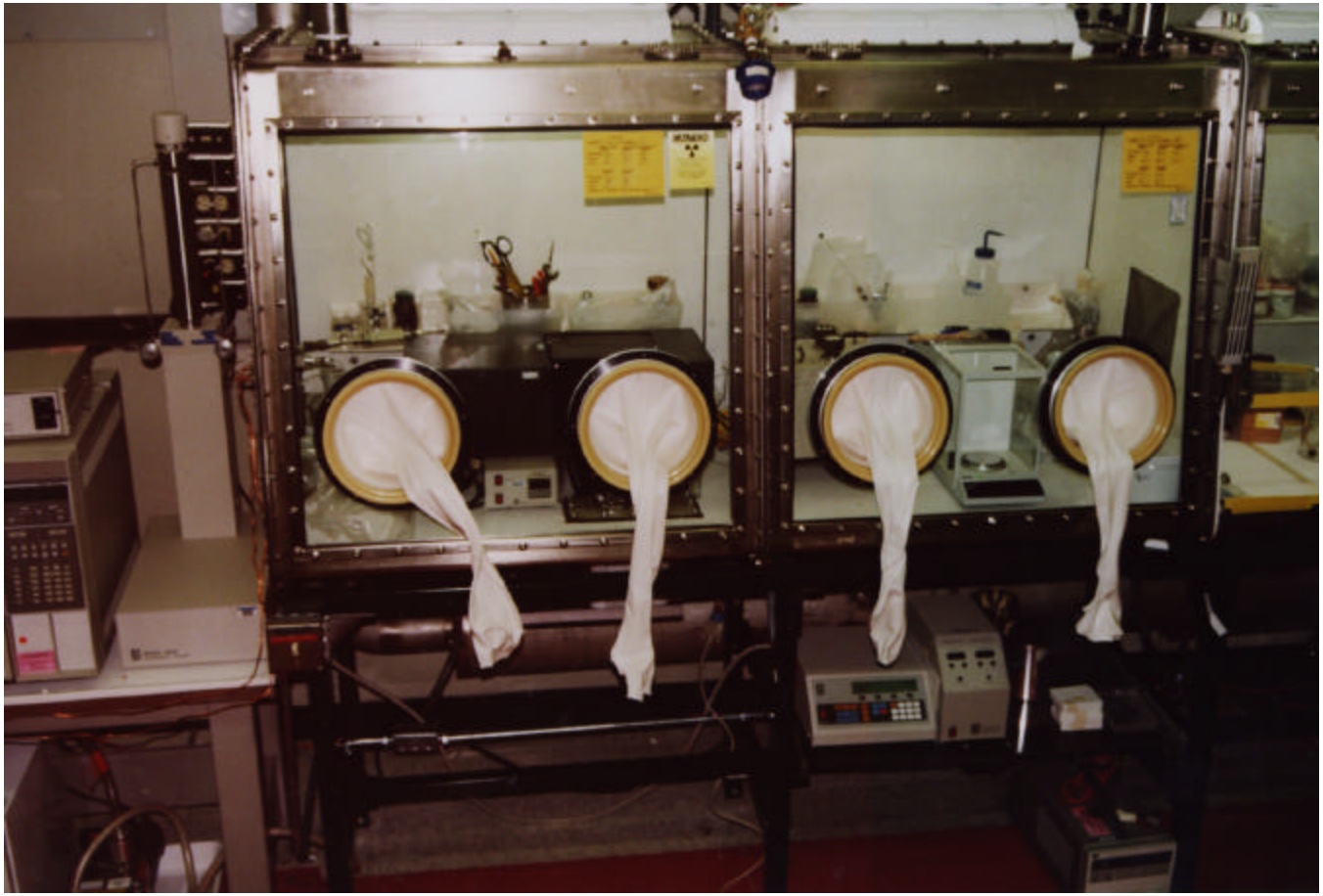


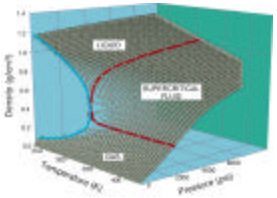
SFE - Disadvantages

- Disadvantages
  - **Plugging with high salt samples**
  - **FTIR window susceptible to acid attack**
  - **Hydrates problematic**



LANL
SFE / FTIR Glovebox Assembly





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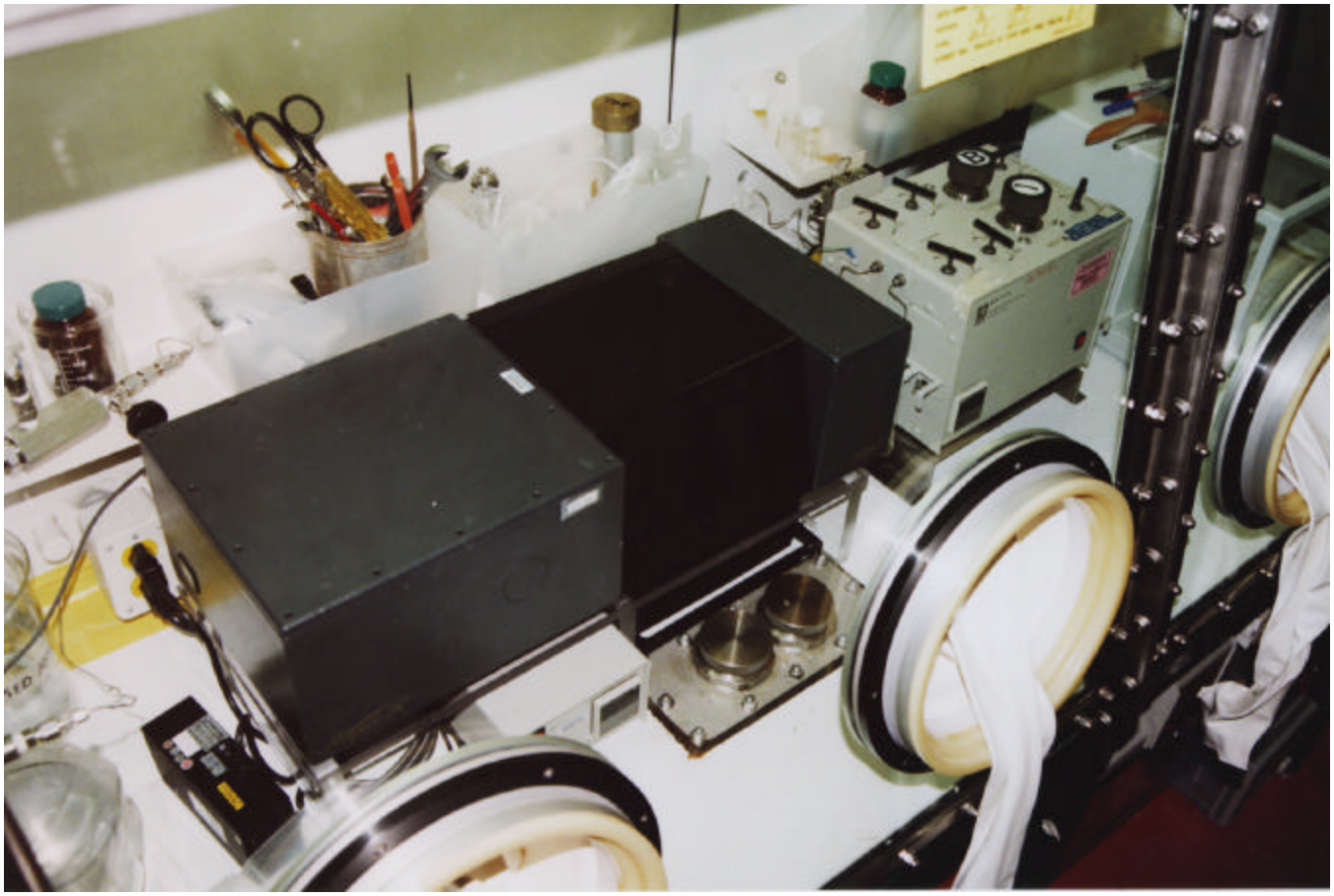

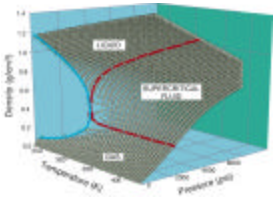

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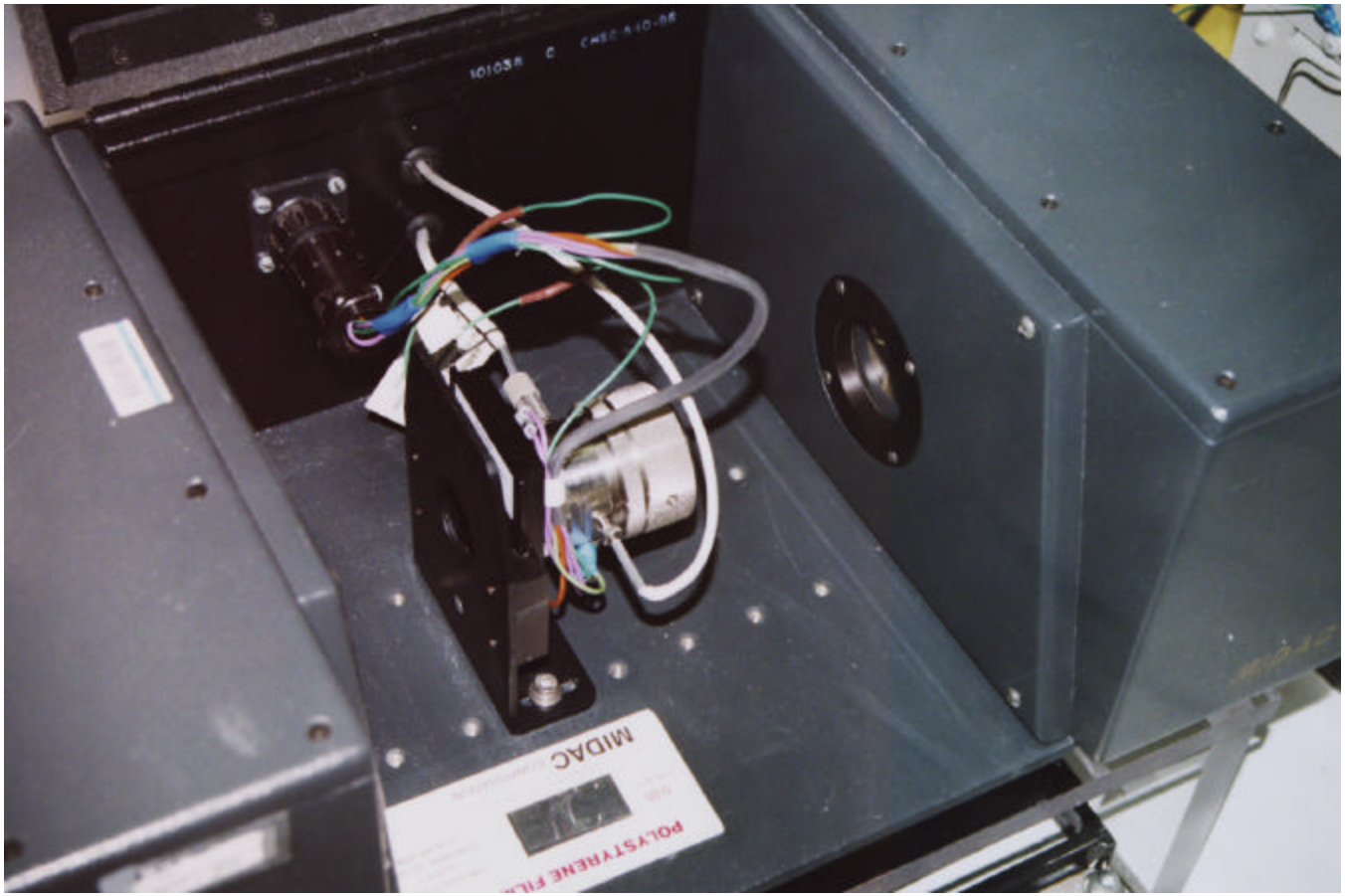
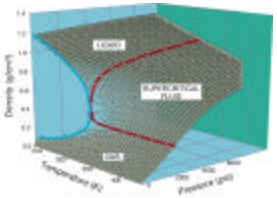
High-Pressure FTIR Cell





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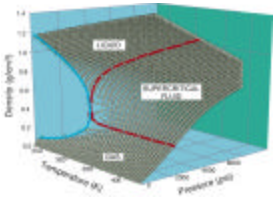
Cumulative Work (SFE)

Extracted Matrix	Dates	Number of Extractions
Aluminum Oxide, Al_2O_3	9/96	3
Ammonium Molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	4/97	2
Calcium Sulfate Dihydrate, $CaSO_4\cdot 2H_2O$	4/97 - 8/97	9
Cerium(IV) Oxide, CeO_2	12/96 - 8/97	28
Magnesium Sulfate Heptahydrate, $MgSO_4\cdot 7H_2O$	9/96 & 5/97	4
Magnesium Phosphate Octahydrate, $Mg_3(PO_4)_2\cdot 8H_2O$	5/99	3
Sodium Borate Decahydrate, $Na_2B_4O_7\cdot 10H_2O$	5/99	3
Thorium Oxide, ThO_2	7/97	3
Water, H_2O	9/96 - 7/97	44
Zirconium Oxide, ZrO_2	9/96 - 3/97	15
Empty Vessels, Aluminum & PEEK	2/97 - 7/97	6
Plutonium Oxide, PuO_2	**9/96 - present**	**123**
Total Number of Extractions	243	



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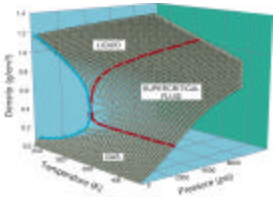
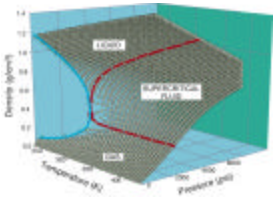
LANL Observations

- 950°C calcine removes water
- Minimal water re-uptake in vault storage for most material tested
- For ***VERY*** pure oxides, LOI can be used for routine moisture analysis
- For impure oxides, LOI is unsuitable



Deployment Schedule -
Supercritical CO_2 extraction

- Manufacturer has implemented design modifications to equipment for this application
- SFE to be installed at RFETS no later than 5/1/00
- SFE to be installed at Hanford (PFP) no later than 10/1/00



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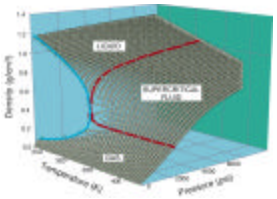
Deployment Status -

Supercritical CO_2 extraction - RFETS

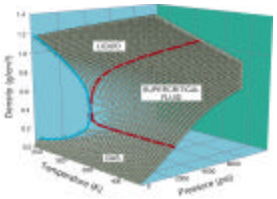
- Bi-weekly conference calls initiated 12/3/99
- MOU signed on 12/14/99
- Design Criteria Document completed 1/17/00
- Equipment purchased by RFETS and procured by LANL on 2/18/00
- RFETS operators trained at LANL during the week of 2/21/00
- RFETS equipment shipped to RFETS on 3/3/00
- RFETS “cold” installation set for 4/3/00
- Installation in Glovebox 12/1/00



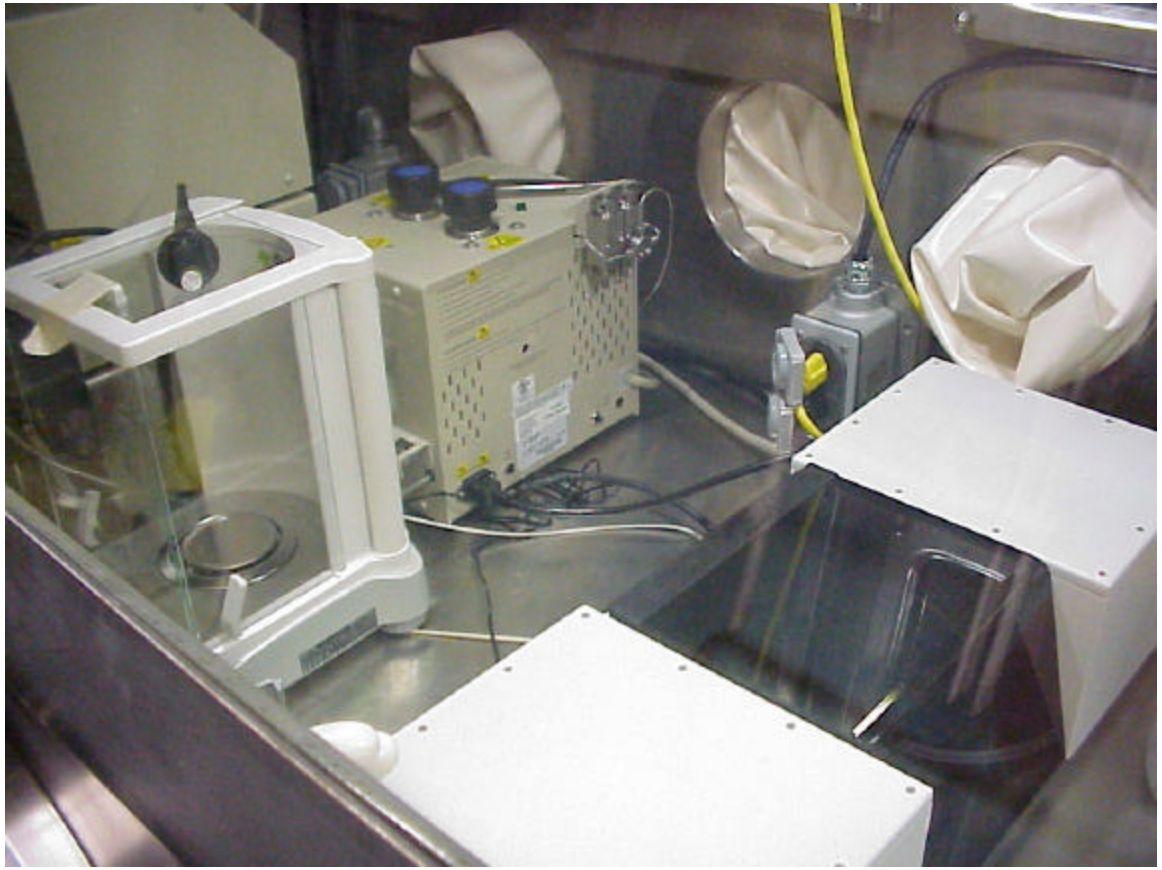
Deployment Status -

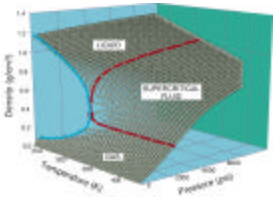
Supercritical CO_2 extraction –PFP

- Bi-weekly conference calls initiated 11/24/99
- MOU signed on 1/3/00
- Equipment purchased by PFP and shipped to LANL on 8/15/00
- PFP operators trained at LANL during the week of 8/28/00
- PFP equipment shipped 9/1/00
- PFP installation and pasted ORR 9/18/00
- Hot Samples Processed beginning 9/25/00



Installed SFE System at Hanford PFP





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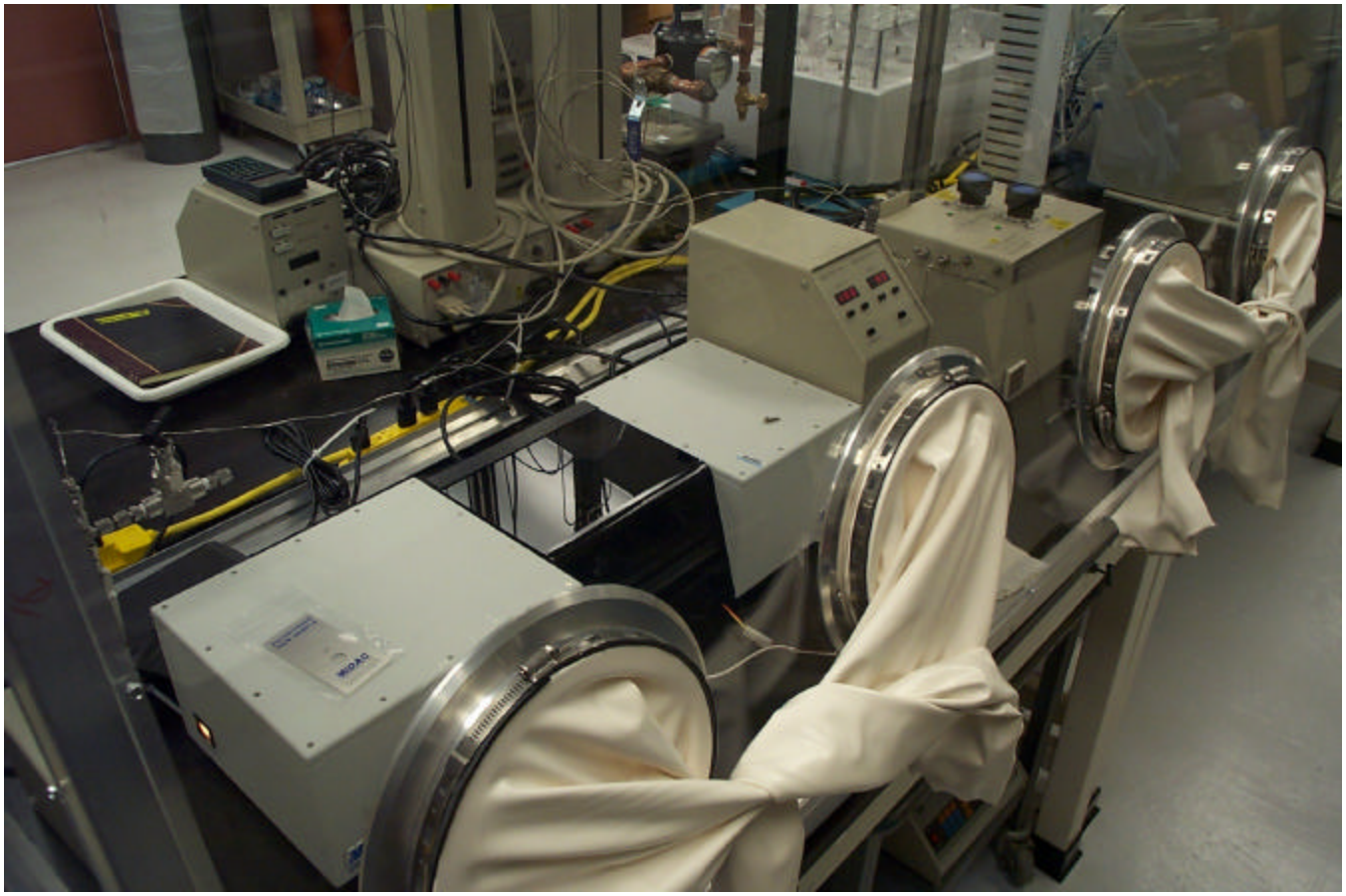
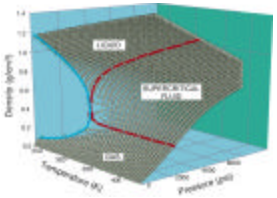
RFETS / PFP Operator Training





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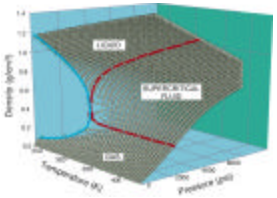
Continuing Development of the SFE Technique

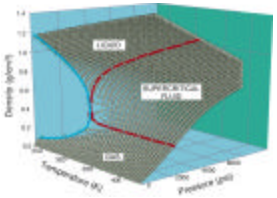
- Plugging with high salt (chloride) samples
  - Automated back-pressure regulator
- FTIR window susceptible to acid attack
  - Surveillance of samples (spot testing ?), alternate materials for windows
- Hydrates problematic
  - Thermal stabilization should address this
- Hydroxides



Acknowledgements

- K Hakonson *: Applied Chemical Technology Group (C-ACT)*
- E. Wilson : *Actinide Chemistry Group (NMT-2)*
- M. Brugh and Y. Mazza : *RFETS*
- S. Hurlbut and D. Johnston : *Handford PFP*
- R. Greene and P. Liescheski : *ISCO*

This work is performed as part of the 94-1 R&D Project (Rick Mason, Project Leader)



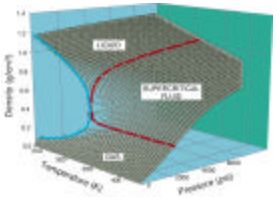
On-Line Resources

- MIS web-page :

w10.lanl.gov:80/orgs/nmt/nmt6/PuRD/index.htm

- Supercritical Fluids Facility web-page :

www.scrub.lanl.gov



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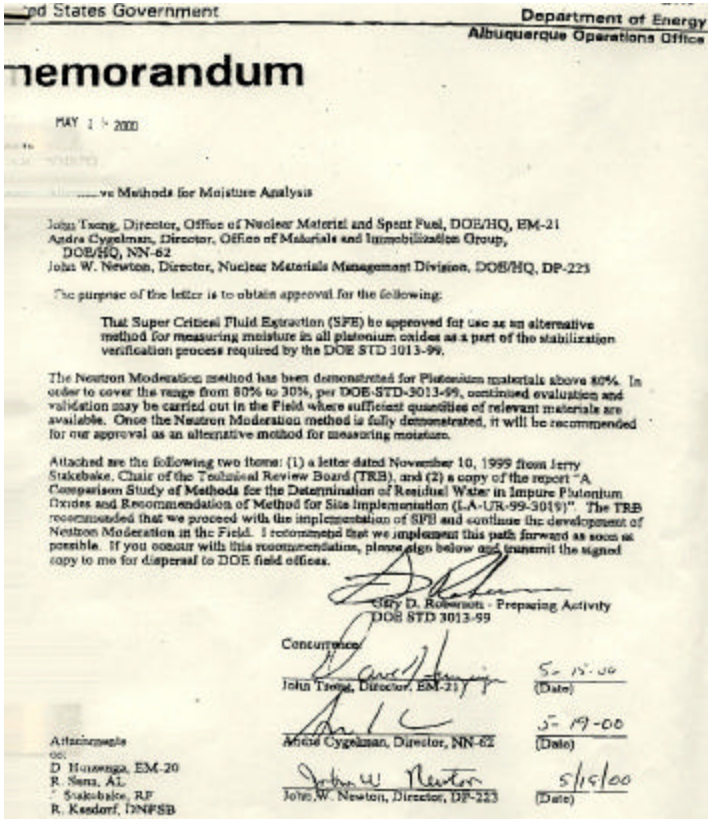
Alternative Method Approval



...ed States Government

Department of Energy
Albuquerque Operations Office

...memorandum

MAY 1 - 2000

...ve Methods for Moisture Analysis

John Tseng, Director, Office of Nuclear Material and Spent Fuel, DOE/HQ, EM-21
Andre Cygelman, Director, Office of Materials and Immobilization Group, DOE/HQ, NN-62
John W. Newton, Director, Nuclear Materials Management Division, DOE/HQ, DP-223

The purpose of the letter is to obtain approval for the following:

That Super Critical Fluid Extraction (SFE) be approved for use as an alternative method for measuring moisture in all plutonium oxides as a part of the stabilization verification process required by the DOE STD 3013-99.

The Neutron Moderation method has been demonstrated for Plutonium materials above 80%. In order to cover the range from 80% to 30%, per DOE-STD-3013-99, continued evaluation and validation may be carried out in the Field where sufficient quantities of relevant materials are available. Once the Neutron Moderation method is fully demonstrated, it will be recommended for our approval as an alternative method for measuring moisture.

Attached are the following two items: (1) a letter dated November 10, 1999 from Jerry Stakebake, Chair of the Technical Review Board (TRB), and (2) a copy of the report "A Comparison Study of Methods for the Determination of Residual Water in Impure Plutonium Oxides and Recommendation of Method for Site Implementation (LA-UR-99-3019)". The TRB recommended that we proceed with the implementation of SFE and continue the development of Neutron Moderation in the Field. I recommend that we implement this path forward as soon as possible. If you concur with this recommendation, please sign below and transmit the signed copy to me for dispersal to DOE field offices.

Gary D. Robertson - Preparing Activity
DOE STD 3013-99

Concurrence:

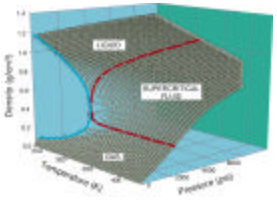
John Tseng, Director, EM-21 — 5-15-00 (Date)

Andre Cygelman, Director, NN-62 — 5-19-00 (Date)

John W. Newton, Director, DP-223 — 5/15/00 (Date)

Attachments
cc:
D. Hunzenga, EM-20
R. Sena, AL
J. Stakebake, RF
R. Kendorf, DNFSB

- **Method approved for STD-3013-99 on May 19, 2000**
- **"..alternative method for measuring moisture in all plutonium oxides.."**



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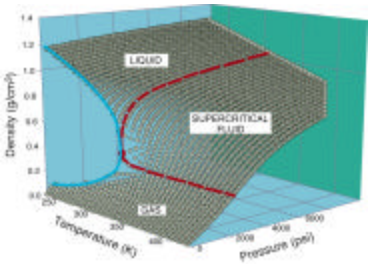
Data Summary - CCLANL025

As–received, 0.06 wt.% H_2O	Measured moisture content, average wt. % loss	Standard deviation, s,[1] of the measurements and (number of runs)
LOI	7.79	1.08 (2)
IGA total H_2O (300°C) + total H_2 (950°C) data	0.07	0.02 (3)
SFE	0.05	0.02 (2)
Neutron Moderation	0.31	0.03 (2)
Spiked to 0.36 wt.% H_2O		
LOI	7.03	0.16 (2)
IGA, total H_2O (300°C)	0.40	0.01 (2)
IGA, total H_2 (950°C)	0.41	0.06 (3)
SFE	0.54	0.16 (7)
Neutron Moderation	0.38	0.07 (2)
Spiked to 0.74 wt.% H_2O		
LOI	6.83	0.04 (2)
IGA, total H_2O (300°C)	0.74	0.10 (3)
IGA, total H_2 (950°C)	0.95	0.06 (3)
SFE	1.19	0.32 (7)
Neutron Moderation	0.63	0.01 (2)
Re-calcined		
LOI	4.99	0.49 (2)
IGA, total H_2O (300°C)	< 0.03	— (3)
IGA, total H_2 (950°C)	< 0.03	— (3)
SFE	< 0.03	— (2)
Neutron Moderation	0.37	0.04 (2)



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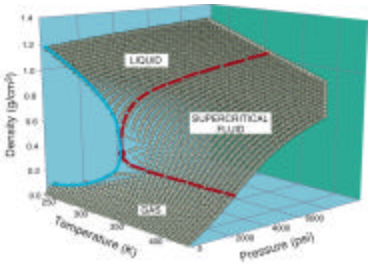
Data Summary - High Pu

($MgSO_4 \cdot 6H_2O$ spiked)

	Average moisture Content (wt. %)	Standard deviation, s,[1] of (n) moisture content measurements	
As–received			
LOI	0.46	0.00	(2)
IGA @ 300°C	0.17	0.00	(2)
IGA @ 900°C	0.22	0.01	(2)
SFE	< 0.03	—	(2)
TGA @ 300°C	0.43	—	(1)
TGA @ 1000°C	1.20	—	(1)
Neutron Moderation	-0.01	—	(1)
Spiked to 0.3 wt.% H_2O			
LOI	0.82	0.02	(2)
IGA @ 300°C	0.26	0.04	(3)
IGA @ 900°C	0.36	0.01	(3)
SFE	0.12	0.04	(6)
TGA @ 300°C	0.26	—	(1)
TGA@ 1000°C	0.64	—	(1)
Neutron Moderation	0.16	0.02	(3)
Spiked to 0.7 wt.% H_2O			
LOI	0.90	0.01	(2)
IGA @ 300°C	0.37	0.16	(3)
IGA @ 900°C	0.29	0.01	(3)
SFE	0.21	0.06	(7)
TGA @ 300°C	0.21	—	(1)
TGA@ 1000°C	0.67	—	(1)
Neutron Moderation	0.29	0.01	(3)
Re-calcined			
LOI	x.xx	x.xx	(2)
IGA @ 300°C	—	—	(x)
IGA @ 900°C	—	—	(x)
SFE	< 0.03	—	(2)
TGA @ 300°C	< 0.20	—	(1)
TGA@ 1000°C	0.21	—	(1)
Neutron Moderation	-0.08	0.03	(3)



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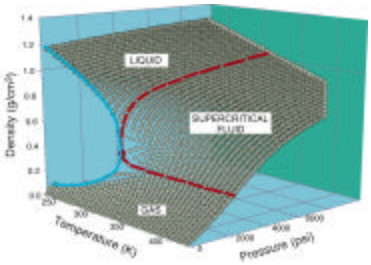
Data Summary - High Pu

($CaSO_4 \cdot 2H_2O$ spiked)

	Average moisture Content (wt. %)	Standard deviation, s,[1] of (n) moisture content measurements
As–received		
LOI	0.23	< 0.01 (2)
IGA @ 300°C	0.02	0.00 (2)
IGA @ 900°C	0.06	0.01 (2)
SFE	< 0.03	— (1)
Neutron Moderation	-0.03	0.00 (2)
Spiked to 0.3 wt.% H_2O		
LOI	1.07	0.02 (2)
IGA @ 300°C	0.36	0.02 (2)
IGA @ 900°C	0.37	0.04 (2)
SFE	0.31	0.04 (7)
Neutron Moderation	0.20	0.05 (2)
Spiked to 0.7 wt.% H_2O		
LOI	1.25	— (1)
IGA @ 300°C	0.63	0.08 (2)
IGA @ 900°C	0.70	0.01 (2)
SFE	0.67	0.03 (6)
Neutron Moderation	0.73	0.10 (2)
Re-calcined		
LOI	x.xx	x.xx (2)
IGA @ 300°C	0.02	0.00 (2)
IGA @ 900°C	0.03	0.00 (2)
SFE	< 0.03	— (2)
Neutron Moderation	-0.10	0.05 (2)



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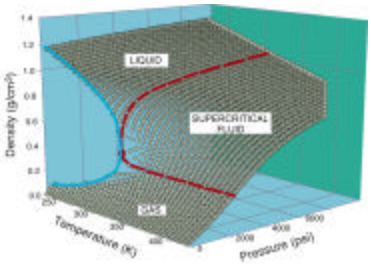
Data Summary - High U

	Average moisture Content (wt. %)	Standard deviation, s,[1] of (n) moisture content measurements	
As–received, pre-calcined			
LOI	-2.09	0.16	(2)
IGA @ 300°C	0.17	0.00	(2)
IGA @ 900°C	0.22	0.01	(2)
SFE	0.05	0.01	(2)
Neutron Moderation	-0.18	0.03	(3)
As–received, calcined			
LOI	0.02	0.08	(2)
IGA @ 300°C	< 0.03	—	(2)
IGA @ 900°C	< 0.03	—	(2)
SFE	< 0.03	—	(2)
Neutron Moderation	-0.13	0.01	(2)
Spiked to 0.3 wt.% H_2O			
LOI	1.07	0.02	(2)
IGA @ 300°C	0.34	0.04	(2)
IGA @ 900°C	0.39	0.01	(2)
SFE	0.34	0.02	(7)
Neutron Moderation	0.08	0.01	(2)
Spiked to 0.7 wt.% H_2O			
LOI	9.45	9.78	(2)
IGA @ 300°C	0.65	0.08	(2)
IGA @ 900°C	0.61	0.05	(2)
SFE	0.73	0.02	(7)
Neutron Moderation	0.56	0.02	(3)
Re-calcined			
LOI	1.05	0.02	(2)
IGA @ 300°C	0.12	0.01	(2)
IGA @ 900°C	0.13	0.00	(2)
SFE	< 0.03	—	(2)
Neutron Moderation	-0.05	0.02	(3)



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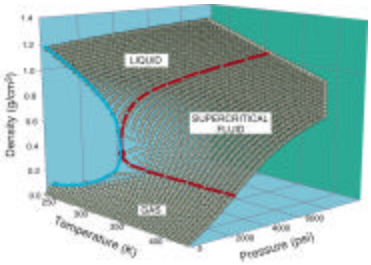
Data Summary - High Mg

	Average moisture Content (wt. %)	Standard deviation, s,[1] of (n) moisture content measurements	
As–received, pre-calcined			
LOI	2.84	0.75	(2)
IGA @ 300°C	0.46	0.03	(2)
IGA @ 900°C	0.42	0.18	(3)
SFE	0.08	0.01	(2)
TGA	1.72	—	(1)
Neutron Moderation	0.25	0.08	(2)
As–received, calcined			
LOI	4.15	0.24	(2)
IGA @ 300°C	0.26	0.01	(2)
IGA @ 900°C	0.29	0.01	(2)
SFE	< 0.03	—	(2)
TGA	2.15	—	(1)
Neutron Moderation	0.02	0.02	(2)
Spiked to 0.06 wt.% H_2O			
LOI	3.68	0.65	(2)
IGA @ 300°C	0.37	0.05	(2)
IGA @ 900°C	0.29	0.19	(3)
SFE	0.06	0.03	(7)
TGA	2.17	—	(1)
Neutron Moderation	- 0.01	0.12	(2)
Spiked to 0.15 wt.% H_2O			
LOI	3.90	0.12	(2)
IGA @ 300°C	0.45	0.05	(2)
IGA @ 900°C	0.42	0.01	(2)
SFE	0.16	0.01	(7)
TGA	1.77	—	(1)
Neutron Moderation	0.07	0.06	(2)



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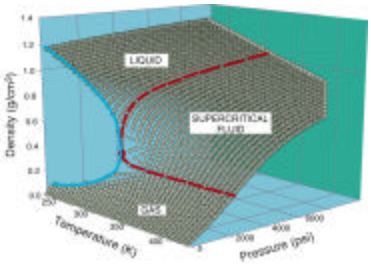
Data Summary - High Mg

Spiked to 0.3 wt.% H_2O			
LOI	3.74	0.13	(2)
IGA @ 300°C	0.70	0.01	(2)
IGA @ 900°C	0.68	0.01	(2)
SFE	0.32	0.02	(7)
TGA	1.80	—	(1)
Neutron Moderation	0.08	0.01	(2)
Spiked to 0.5 wt.% H_2O			
LOI	3.36	0.16	(2)
IGA @ 300°C	0.55	0.02	(2)
IGA @ 900°C	0.87	0.01	(2)
SFE	0.49	0.04	(7)
TGA	1.94	—	(1)
Neutron Moderation	0.44	0.07	(2)
Spiked to 0.7 wt.% H_2O			
LOI	4.01	0.16	(2)
IGA @ 300°C	1.09	0.00	(2)
IGA @ 900°C	1.29	0.01	(2)
SFE	0.72	0.06	(4)
TGA	2.28	—	(1)
Neutron Moderation	0.74	0.01	(2)
Re-calcined			
LOI	3.31	0.04	(2)
IGA @ 300°C	0.19	0.02	(2)
IGA @ 900°C	0.47	0.04	(3)
SFE	0.03	—	(1)
TGA	1.64	—	(1)
Neutron Moderation	-0.08	0.07	(2)



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