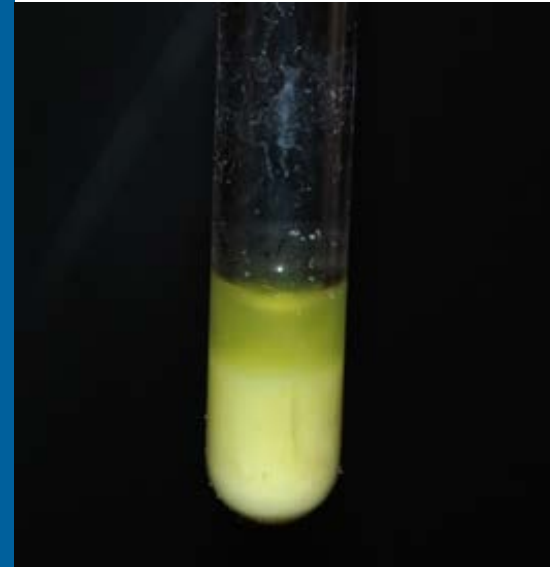


SEPTEMBER 10-13, 2017
MONTREAL MARRIOTT CHATEAU CHAMPLAIN
MONTREAL, QC CANADA



PROGRESS TOWARD MITIGATING URANYL PEROXIDE PRECIPITATION AND CONTROLLING PU BEHAVIOR ON TITANIA



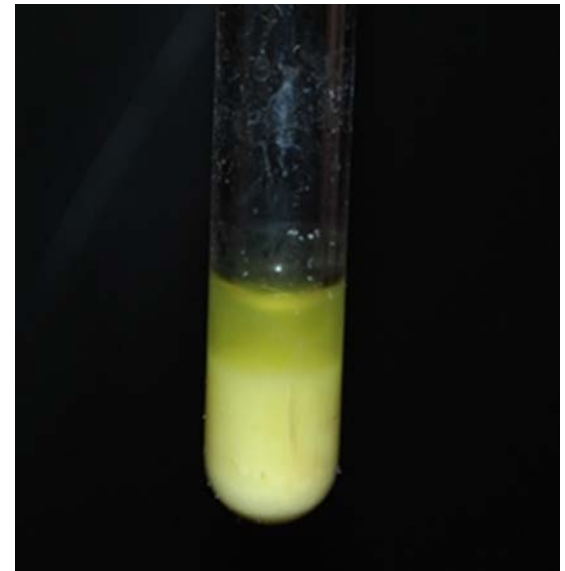
AMANDA YOUKER

Chemist

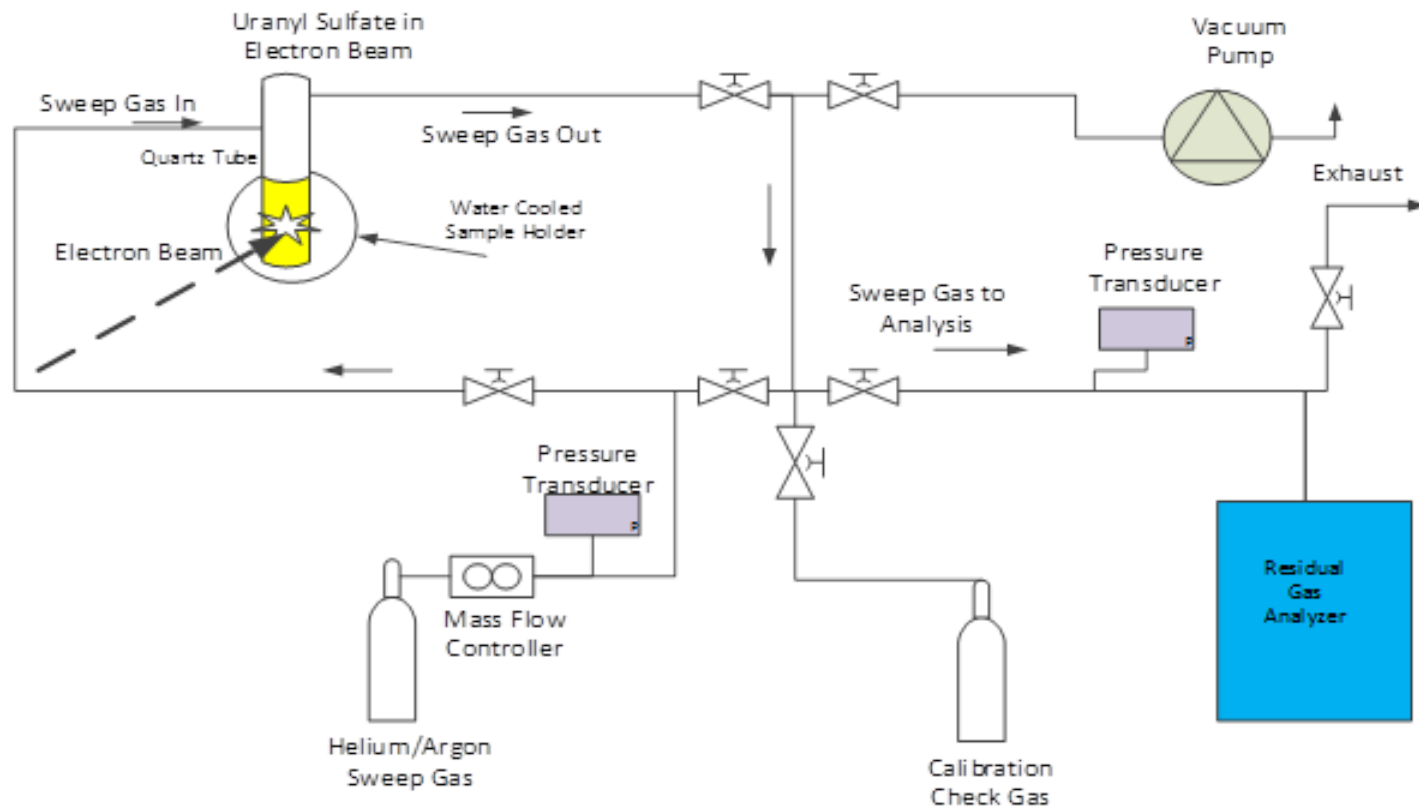
Sergey Chemerisov, Michael Kalensky,
Alex Brown, Kevin Quigley, Tom Brossard,
James Byrnes, and George F. Vandegrift

LEU URANYL SULFATE SOLUTION FOR MO-99 PRODUCTION

- Radiolysis of water produces hydrogen and hydrogen peroxide.
- No large pH changes expected during irradiation in sulfate media
- Hydrogen peroxide is an important radiolysis product. Buildup of peroxide can lead to precipitation of uranyl peroxide
- Products of nitrate radiolysis do lead to peroxide destruction
- Products of sulfate radiolysis do NOT affect peroxide destruction
- Precipitation of uranyl peroxide occurred during irradiation of LEU uranyl sulfate solutions at our 3 MeV Van de Graaff accelerator

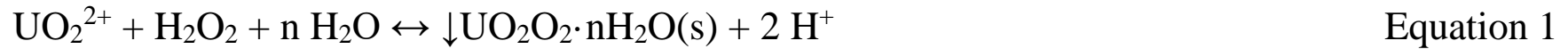


VAN DE GRAAFF EXPERIMENTS



- 0.5 and 2.0 mL uranyl sulfate (DU, NU, and LEU) samples irradiated
- Gases measured in sweep gas via RGA
- Samples temperature controlled
- Various dose rates applied to samples

PRODUCTION AND DECOMPOSITION OF URANYL PEROXIDE



- Radiolysis of water generates hydrogen peroxide and can react with uranyl ion to form uranyl peroxide
- Two forms of uranyl peroxide can form studtite (n=4) and meta-studtite (n=2)
- Two different mechanisms proposed by Silverman et. al. for uranyl peroxide decomposition (equation 2&3 and equation 4&5)
- Temperature and addition of a catalyst play a role as well

DIFFERENT SOURCES OF URANIUM

Solution	Cr (ppm)	Fe (ppm)	Ni (ppm)	Cu (ppm)	Pt (ppm)	NO ₃ ⁻ (mM)
NU - 140 g-U/L	<0.25	<0.1	<0.05	0.41	0.54	0
DU - 185 g-U/L	9.6	81	6.3	4.2	0.02	500
LEU - 148 g-U/L	1.1	18	2.7	1.3	<0.01	0

- VDG experiments used different sources of uranium
- Various metal ions were present in solution
- LEU used at VDG because it will be used for experiments at linac
- Nitrate radiolysis products lead to destruction of hydrogen peroxide

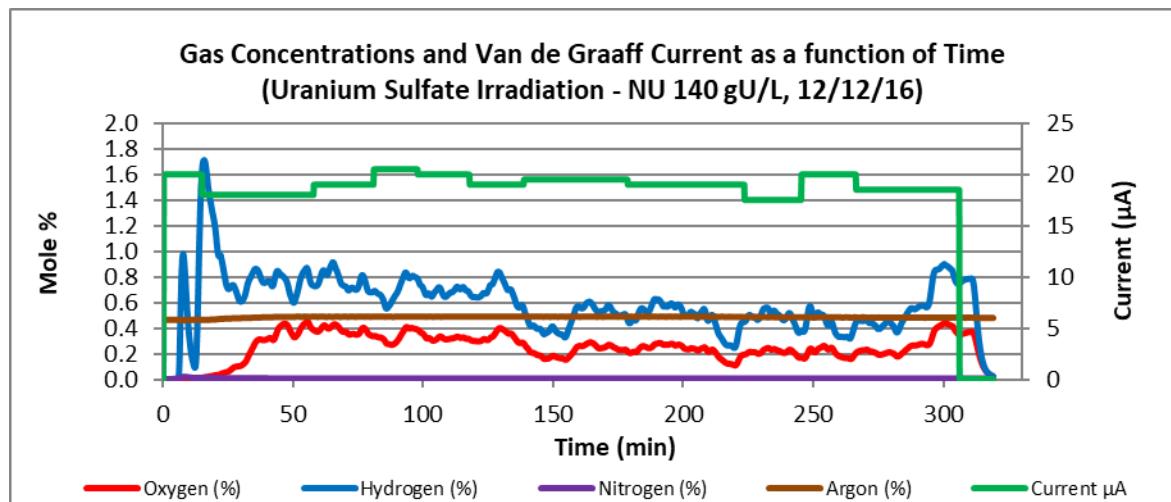
NU AND DU VDG RESULTS

Sample Type	Sample Temp (°C)	Average Current (µA)	Estimated Total Dose (Mrad)	Dose Rate (Mrad/min)	Measured H ₂ O ₂ (µM)	Precipitation	Gas Generation H ₂ (µmoles/Mrad)	Gas Generation O ₂ (µmoles/Mrad)	Overall H to O Ratio	Apparent Steady State Time (min)	Measured H:O Ratio @ Steady State
NU	62	19	13,600	44	130	NO	0.045	0.019	2.4	60	2.0
NU - 30µM/L H ₂ O ₂ added	64	20	15,800	47	390	Delayed ¹	0.079	0.036	2.2	45	2.2
NU - 17µM/L H ₂ O ₂ added	80	20	16,000	48	60	NO	0.089	0.043	2.1	60	2.0
NU - 170µM/L H ₂ O ₂ added	60	18	17,300	42	610	NO	0.065	0.031	2.1	83	2.1
NU - 4300µM/L H ₂ O ₂ added	60	18	10,300	41	540	YES	0.075	0.049	1.5	140	2.1
NU - 2300µM/L H ₂ O ₂ added	60	17	13,300	41	60	YES	0.122	0.087	1.4	140	2.0
NU - 50µM/L H ₂ O ₂ added	63	20	15,800	46	800	Delayed ²	0.101	0.046	2.2	42	2.1
NU - 240µM/L H ₂ O ₂ added	63	20	15,000	47	840	NO	0.104	0.047	2.2	50	2.1
NU - 130µM/L H ₂ O ₂ added	60	18	15,000	41	880	NO	0.100	0.043	2.4	130	2.2
DU - 50µM/L H ₂ O ₂ added	63	19	12,200	48	100	NO	0.011	0.005	2.2	25	2.2
DU - 55µM/L H ₂ O ₂ added	63	20	14,900	46	6	NO	0.011	0.005	2.5	30	2.5

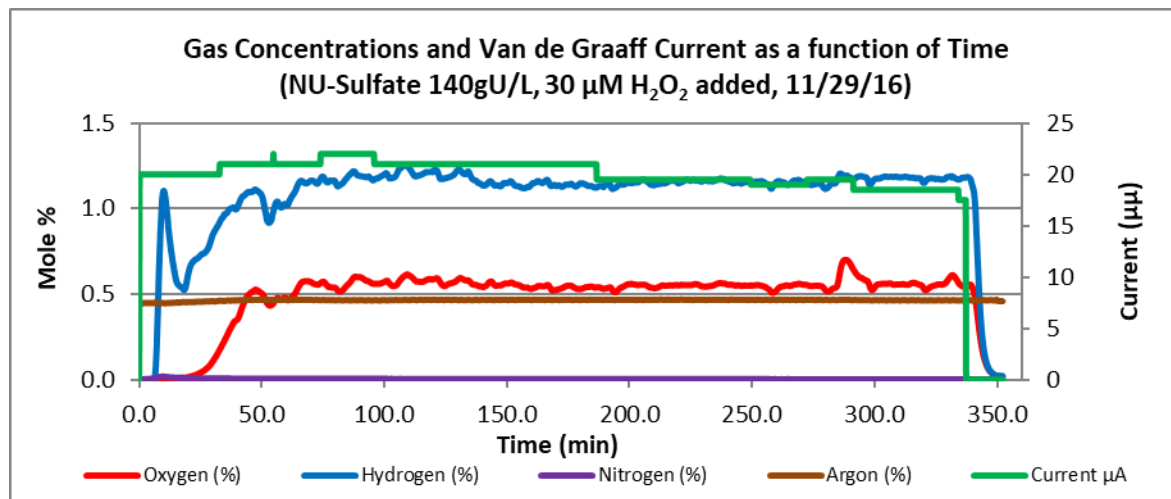
¹Sample was cloudy on 12/07/16, and precipitate was observed on 12/22/16. ²Precipitate was observed on 12/06/16.

- Hydrogen peroxide added prior to irradiation because precipitation did not occur in 2014-2015
- Delayed onset of precipitation where it occurred 8-21 days after irradiation
- Apparent steady state (gas generation rates stabilize) and overall H₂:O₂ ratios shown
- DU solutions – lower gas production and no precipitation
- Solubility limit of hydrogen peroxide is ~ 1 mM

GAS ANALYSIS RESULTS FOR NU SAMPLES

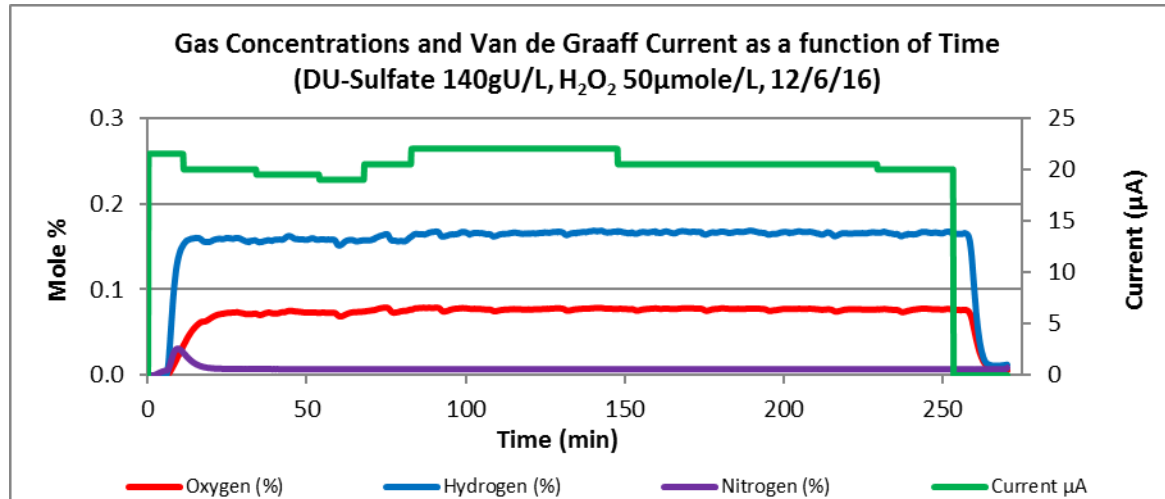


- No precipitation

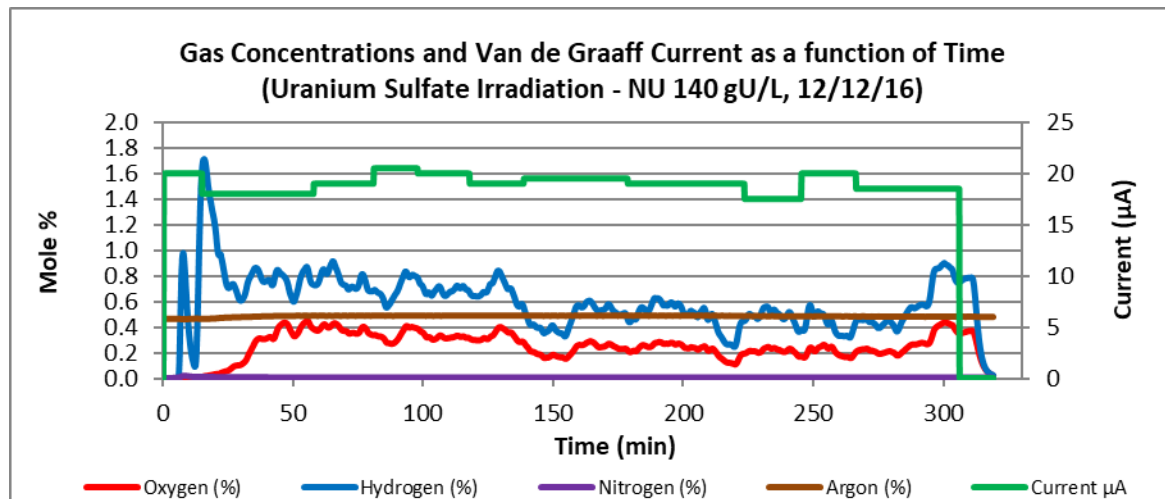


- Delayed precipitation

DU RESULTS COMPARED TO NU RESULTS



- DU sample



- NU sample

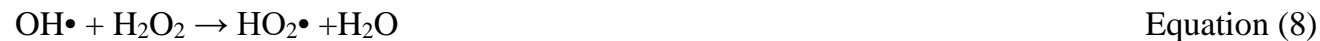
LEU VDG RESULTS

Sample Type	Sample Temp (°C)	Average Current (μA)	Estimated Total Dose (Mrad)	Dose Rate (Mrad/min)	Measured H ₂ O ₂ (μM)	Precipitation	H ₂ (μmoles/Mrad)	O ₂ (μmoles/Mrad)	Overall H to O Ratio	Apparent Steady State Time (min)	Measured H:O Ratio @ Steady State
LEU	64	20	16,728	46	100	YES	0.135	0.054	2.5	60	2.3
LEU	62	19	13,990	43	17	YES	0.146	0.060	2.4	60	2.3
LEU - Fe ⁺² @1000ppm	66	21	17,994	50	1300*	NO	0.025	0.010	2.4	55	2.4
LEU - Fe ⁺² @1000ppm	32	5	4,150	12	2100*	NO	0.011	0.002	5.4	252	3.1
LEU - Fe ⁺² @500ppm	66	22	18,519	51	16*	NO	0.039	0.017	2.3	50	2.3
LEU - Fe ⁺² @500ppm	29	4	3,295	9	440*	NO	0.057	0.023	2.5	107	2.3
LEU - Fe ⁺² @200ppm	30	4	3,575	10	2600*	NO	0.048	0.019	2.5	173	2.4
LEU - Cu ⁺² @500ppm	34	5	4,541	12	1600*	YES	0.066	0.027	2.5	N/A	N/A
LEU - Fe ⁺² & Cu ⁺² @100ppm	28	4	1,112	9	860*	NO	0.032	0.011	2.7	N/A	N/A
LEU - Fe ⁺³ @250ppm	30	4	1,336	11	1600*	NO	0.030	0.009	3.2	N/A	N/A

*NaF was added as a complexant

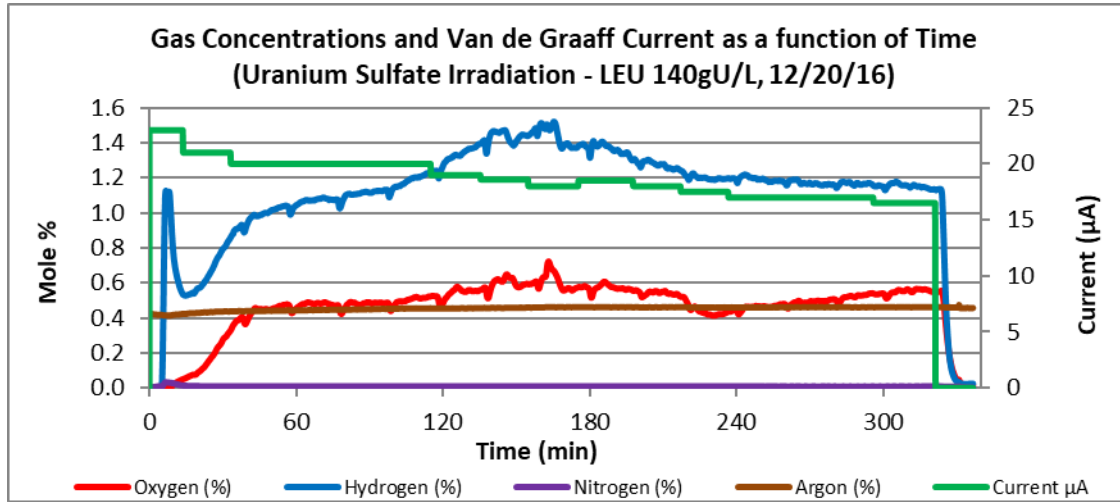
- Precipitation occurred in LEU solutions without additional catalysts added
- 200 ppm Fe²⁺, 250 ppm Fe³⁺, and 100 ppm Fe²⁺ with 100 ppm Cu²⁺ prevented precipitation
- Total dose and dose rates applied to samples were varied
- Temperatures were also varied

PEROXIDE DESTRUCTION BY Fe^{2+}

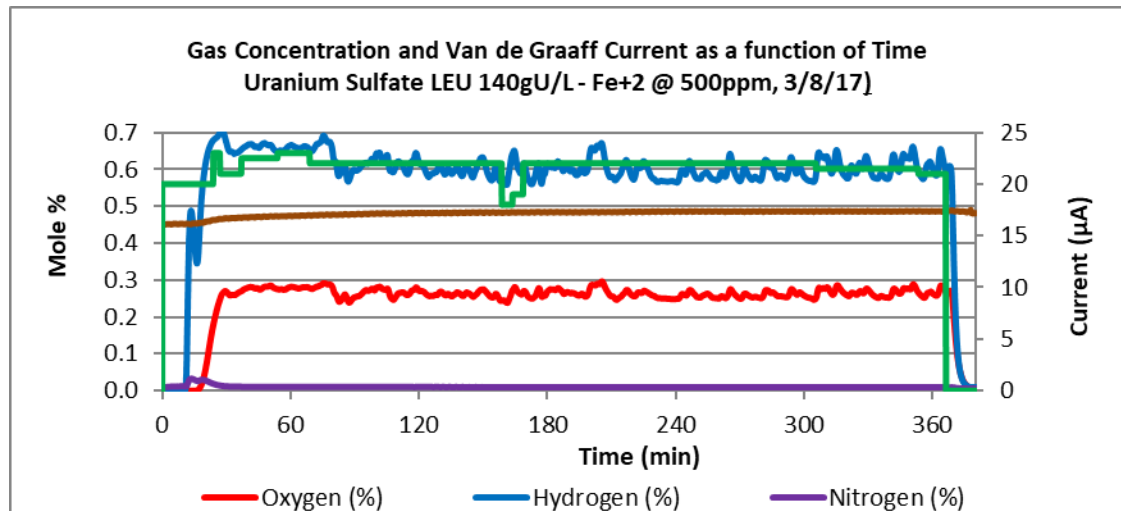


- Total gas production decreases significantly when Fe^{2+} is present
- A possible explanation may be that Fe^{3+} is acting as an electron scavenger (Fenton reaction, Fe^{2+} is oxidized to Fe^{3+} by peroxide to form the OH radical (equation 7))
- The radical goes on to decompose hydrogen peroxide. It also becomes the chain breaker by oxidizing Fe^{2+} to Fe^{3+}
- Fe^{3+} can interact with solvated electron to form Fe^{2+} , which is why Fe^{2+} and Fe^{3+} were both effective at catalyzing peroxide destruction

GAS ANALYSIS RESULTS FOR LEU SAMPLES



- No catalyst – precipitation occurred



- 500 ppm Fe²⁺ - precipitation did not occur

CONCLUSIONS FROM VDG PEROXIDE EXPERIMENTS

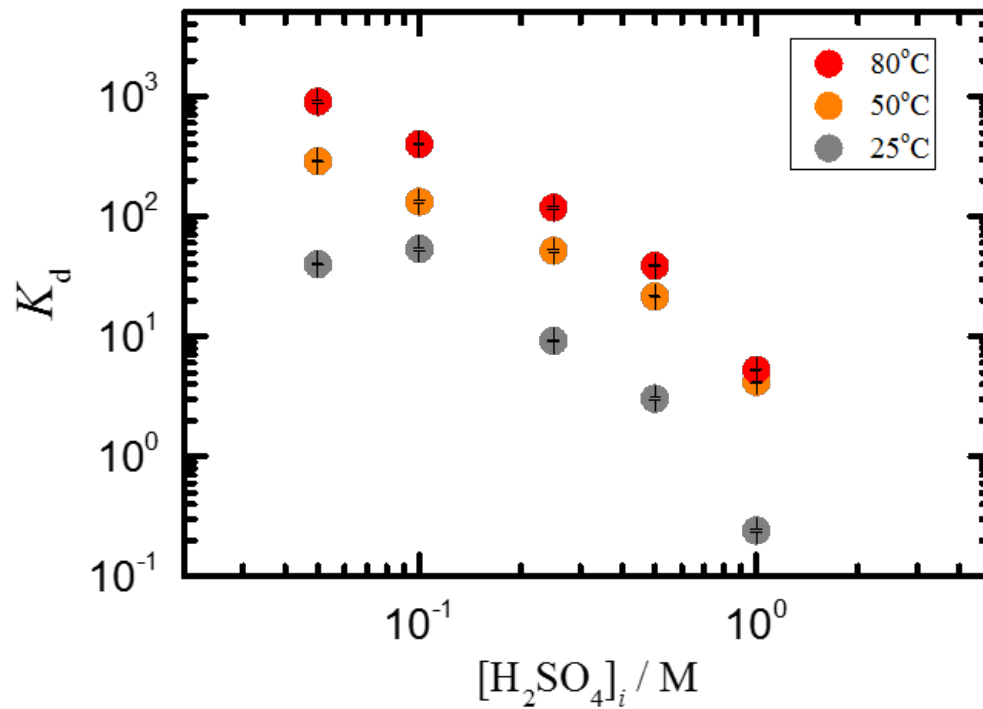
- Precipitation of uranyl peroxide occurred in LEU samples without additional catalysts
- Temperature and catalyst concentration play an important role in preventing uranyl peroxide precipitation
- 200 ppm Fe^{2+} , 250 ppm Fe^{3+} , and 100 ppm Fe^{2+} with 100 ppm Cu^{2+} all were successful at preventing precipitation
- Delayed onset of uranyl-peroxide precipitation is concerning
- Mini-AMORE experiments will follow
 - Fissioning and higher power densities in mini-AMORE
- LEU samples will be irradiated with and without catalysts to look for uranyl peroxide precipitation

LEU URANYL SULFATE SOLUTION FOR MO-99 PRODUCTION

- ~30 times more Pu-239 from LEU compared to HEU
- Avoid generation of GTCC waste - ≥ 1 nCi/g Pu-239
- Set of tracer experiments to investigate Pu behavior on titania in a sulfate media
- Examined ways to control Pu behavior
- Collected batch data
- Tested batch data results in small-scale column setting

PU ADSORPTION ON TITANIA

- Batch study results suggest better adsorption at higher temperature and lower acid concentration

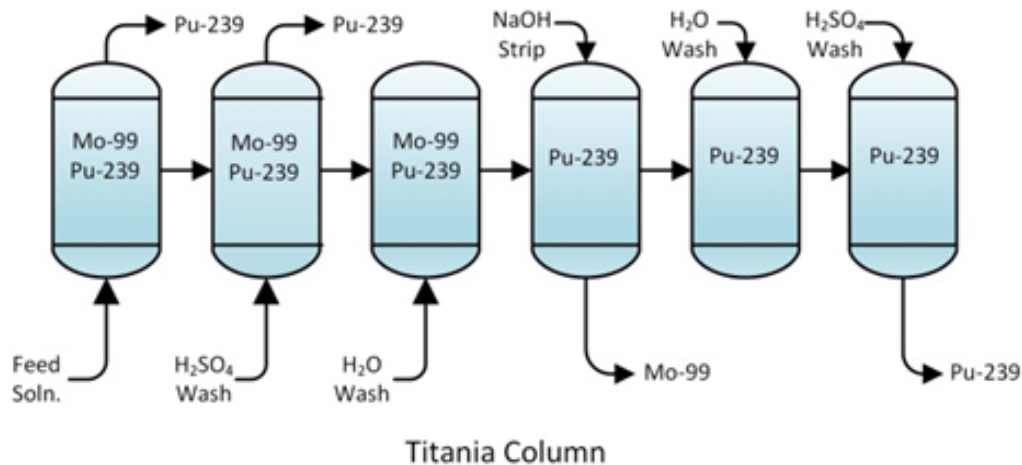


COLUMN STUDY: TEMPERATURE EFFECTS

Sample	%Pu-239 80°C	%Pu-239 25°C
Column Effluent #1	8.7	20.4
Column Effluent #2	7.7	33.3
pH 1 H ₂ SO ₄ Wash	0.7	6.4
H ₂ O Wash #1	0.1	0.4
1 M NaOH Strip	0.03	0.04
H ₂ O Wash #2	0.0008	0.002
1 M H ₂ SO ₄ Wash	62.8	37.8
Sorbent contact with 1 M H ₂ SO ₄	4.5	2.6
Remaining Activity	15.2	0

- 0.66 cm X 1 cm L titania column
- Direct down-scale column for plant-scale design
- 13.3 cm/min loading velocity and 6.7 cm/min stripping velocity

COLUMN STUDY: EFFECT OF H⁺



- Less than 1% Pu-239 when first acid wash is pH 1 H₂SO₄
- >35% Pu-239 when first acid wash is 0.5 M H₂SO₄
- Final acid wash can be used to remove additional Pu-239
- 0.66 cm X 1 cm L titania column
- Direct down-scale column for plant-scale design
- 13.3 cm/min loading velocity and 6.7 cm/min stripping velocity

HOW TO CONTROL PU BEHAVIOR ON TITANIA

- Temperature and acid wash concentration
- Decreasing temperature below 80°C affects Mo adsorption on titania – not recommended
- Increasing the acid wash concentration to 0.5 or 1 M H₂SO₄- recommended because results have shown no Mo losses
- Results given below for Mo-99 down-scale column run with Pu-239

Sample	%Mo-99	Sample	%Mo-99
Column Effluent #1	0.009	Column Effluent #1	0.03
Column Effluent #2	0.016	Column Effluent #2	0
0.5 M H ₂ SO ₄ Wash #1	0.007	1 M H ₂ SO ₄ Wash #1	0.014
H ₂ O Wash #1	0.004	H ₂ O Wash #1	0
1 M NaOH Strip	100	1 M NaOH Strip	100
H ₂ O Wash #2	0.1	H ₂ O Wash #2	0.1

FUTURE WORK WITH AMORE AND MINI-AMORE

- AMORE – 20 L LEU UO_2SO_4 solution for production of up to 20 Ci Mo-99 EOB – DU target – electron linac
- Mini-AMORE – dry-well in target solution vessel where small volumes of uranyl sulfate solution will be irradiated
- Various catalysts will be tested to combat uranyl peroxide precipitation as part of mini-AMORE
- Pu-239 behavior will be followed in more representative conditions for Mo-99 production as part of AMORE



ACKNOWLEDGEMENTS

- The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory (“Argonne”). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.
- Work supported by the U.S. Department of Energy, National Nuclear Security Administration's (NNSA's) Office of Defense Nuclear Nonproliferation, under Contract DE-AC02-06CH11357.