Separation, Purification, and Clean-Up Developments for MIPS and SHINE

Argonne National Laboratory

Mo-99 Topical Meeting

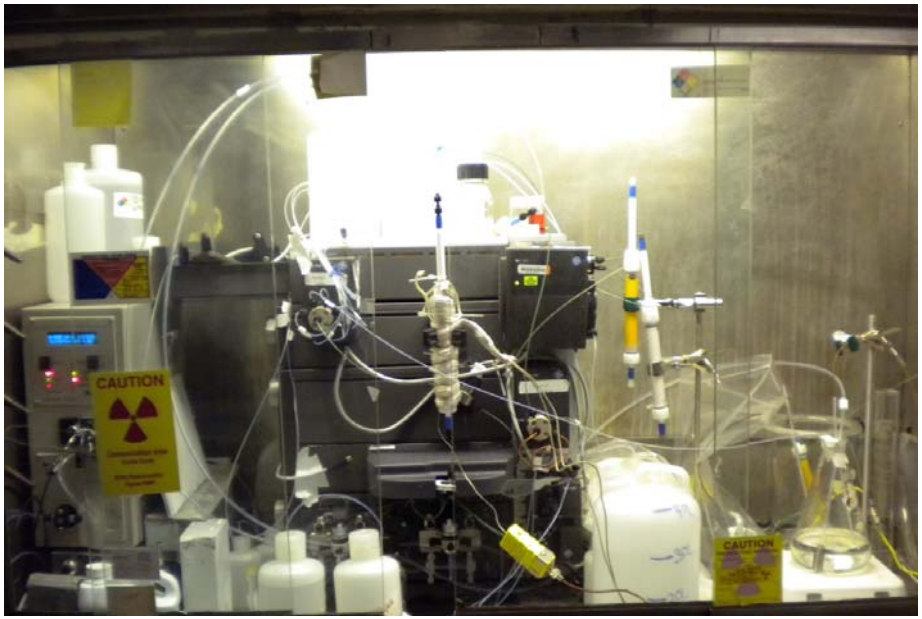
Santa Fe, New Mexico
December 4 – 7, 2011

MIPS and SHINE

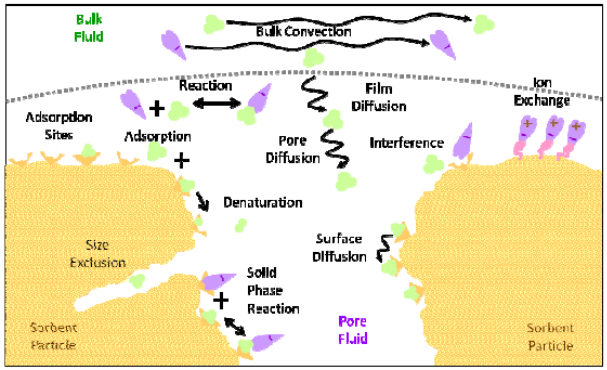
- Argonne is assisting 2 potential domestic suppliers
- Babcock and Wilcox Technical Services Group (BWTSG) – Medical Isotope Production System (MIPS)
- Morgridge Institute for Research (MIR) – Subcritical Hybrid Intense Neutron Emitter (SHINE)
- Pure titania sorbent to separate Mo-99 from uranyl nitrate and uranyl sulfate solutions
- LEU-Modified Cintichem process is being considered for Mo purification

Mo-99 Separation

- S110 (pure titania sorbent) is the top candidate for Mo-99 separation and recovery column
- S110 replaces S80 which has been discontinued
- S110 outperforms S80
- Plant-scale column has been designed for BWTSG
- Plant-scale column design will be available for MIR in ~ 1 week
- Mo-99 recovery continuously being optimized
- Oxidizing agents have been added to water wash and strip solutions to help improve Mo-99 recovery

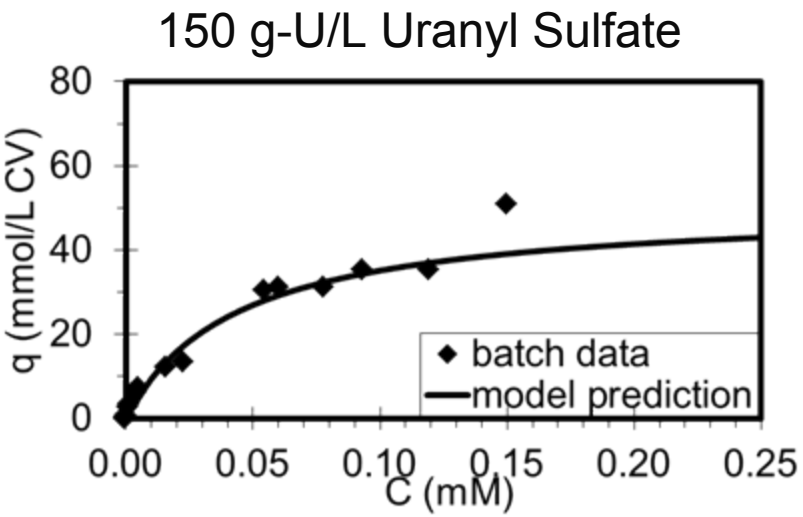


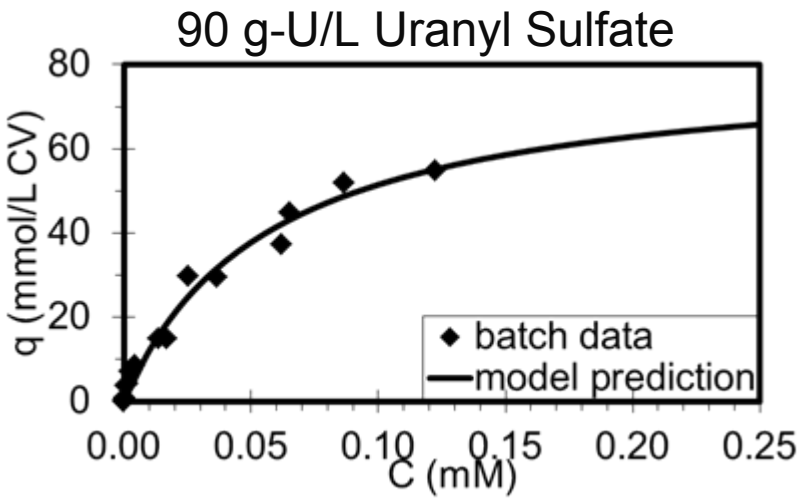
From Batch to Column…



- Batch data input into VERSE (Versatile Reaction Separation) simulator
- Data specific to VERSE code for column design
- Langmuir-type adsorption via batch contact experiments
- Mo breakthrough column tests
- Preliminary plant-scale column design
- Small-scale column tests
- Modified plant-scale column design

Langmuir Data for Uranyl Sulfate





- Batch data fit to Langmuir model for 150 and 90 g-U/L uranyl sulfate solutions
- Langmuir data in batch mode yields a good estimate of “a” linear parameter for Langmuir model
- Data used to predict conditions for Mo breakthrough curve experiments
- Mo breakthrough column tests give a good estimate of “b” non-linear parameter for Langmuir model

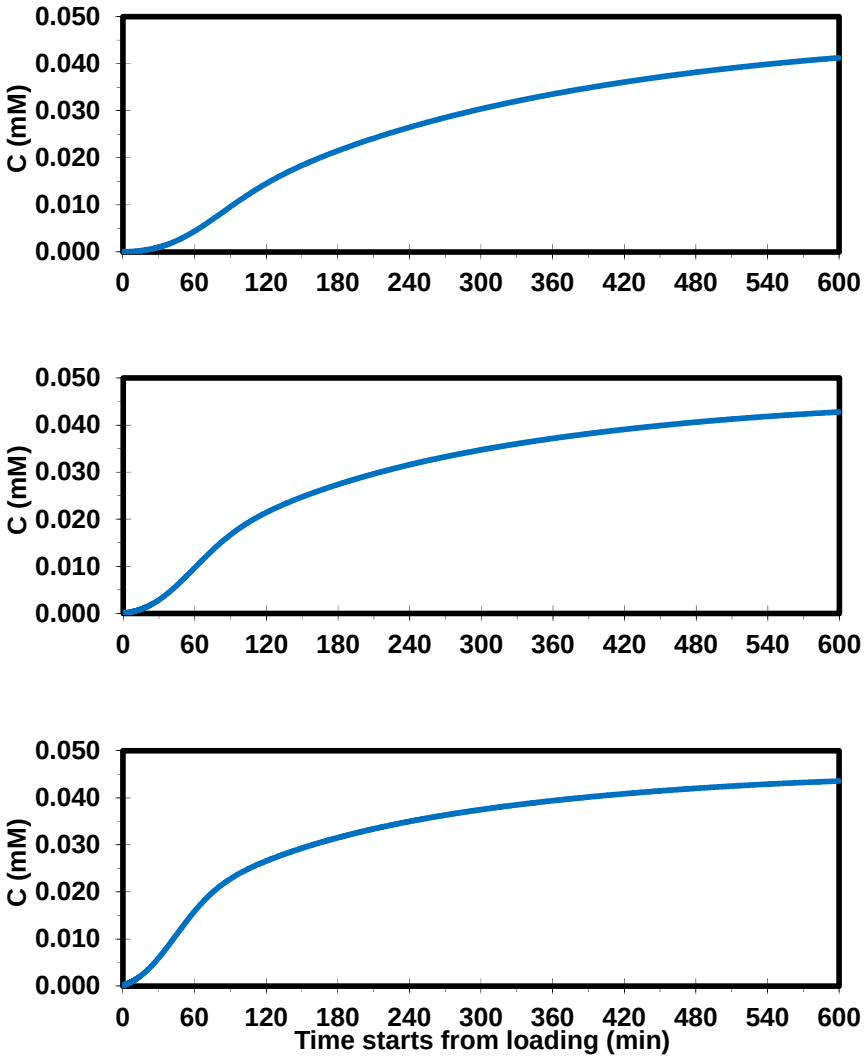
$$q_i = \frac{a_i \cdot C_i}{(1 + b_i \cdot C_i)}$$

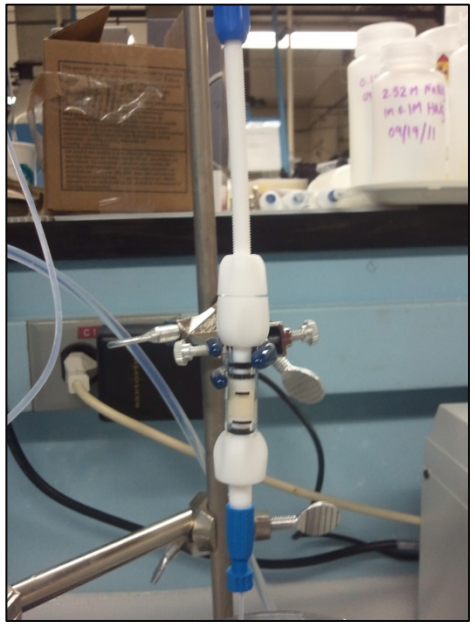
Mo Breakthrough Column Designs – 90 g-U/L

Sorbent	*ID* (cm)	*L* (cm)	*CV* (mL)	u_s /*L* (min^{-1})	u_s (cm/min)	Mo amount *(meq/CV)	ΔP (atm)	Flowrate (mL/min)	To achieve a complete breakthrough curve	
									Time (hr)	Volume* (mL)
S110	0.66	1	0.34	3	3	0.0032	0.01	1.0	> 10	> 616
S110	0.66	1	0.34	4	4	0.0032	0.01	1.4	10	821
S110	0.66	1	0.34	5	5	0.0032	0.01	1.7	10	1026
S110	1.0	1	0.8	3	3	0.0074	0.01	2.4	> 10	> 1414
S110	1.0	1	0.8	4	4	0.0074	0.01	3.1	10	1885
S110	1.0	1	0.8	5	5	0.0074	0.01	3.9	10	2356
S110	1.0	1.5	1.2	3	4.5	0.0111	0.01	3.5	> 10	> 2121
S110	1.0	1.5	1.2	4	6.0	0.0111	0.02	4.7	10	2827
S110	1.0	1.5	1.2	5	7.5	0.0111	0.02	5.9	10	3534
S110	1.0	2.0	1.6	3	6	0.0148	0.02	4.7	> 10	> 2827
S110	1.0	2.0	1.6	4	8	0.0148	0.03	6.3	10	3770
S110	1.0	2.0	1.6	5	10	0.0148	0.04	7.9	10	4712

- 0.045 mM Mo - ~20X higher than actual Mo concentration expected
- Lower Mo concentration may take 15 – 20 hours to achieve full Mo breakthrough with S110
- Loading velocities range from 3 – 10 cm/min
- Experiments have been completed with 0.66 cm ID x 1 cm L and 1 cm ID x I cm L S110 columns

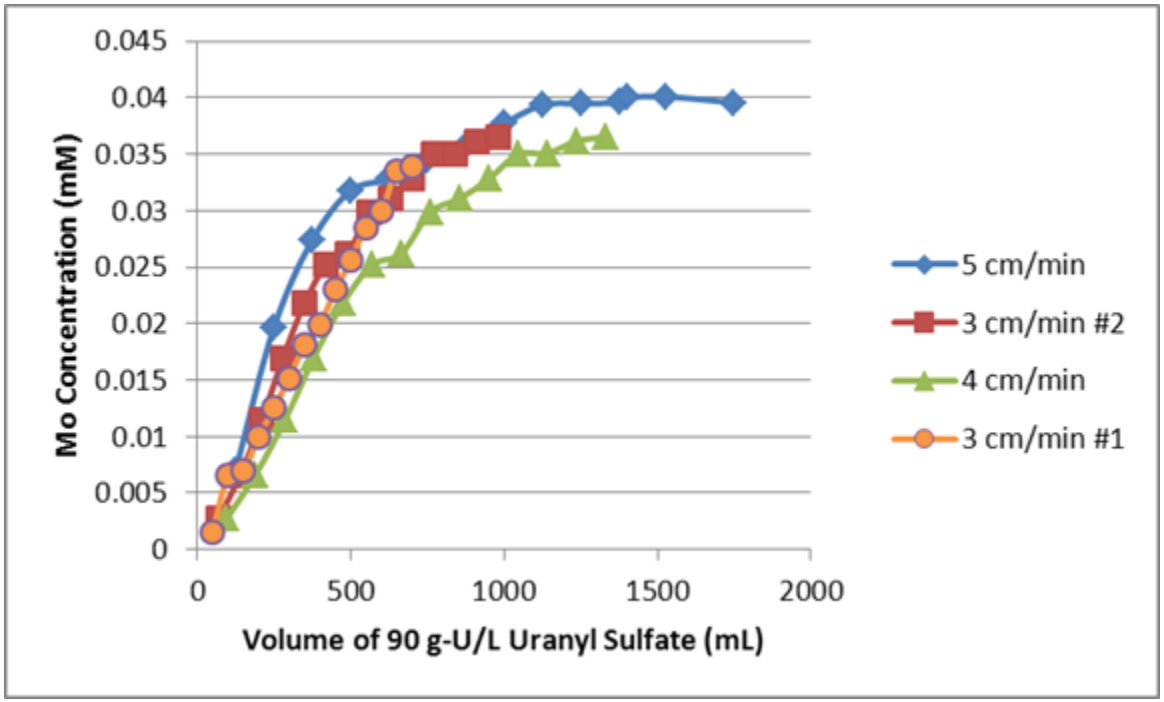
VERSE Mo Breakthrough Simulations - 90 g-U/L





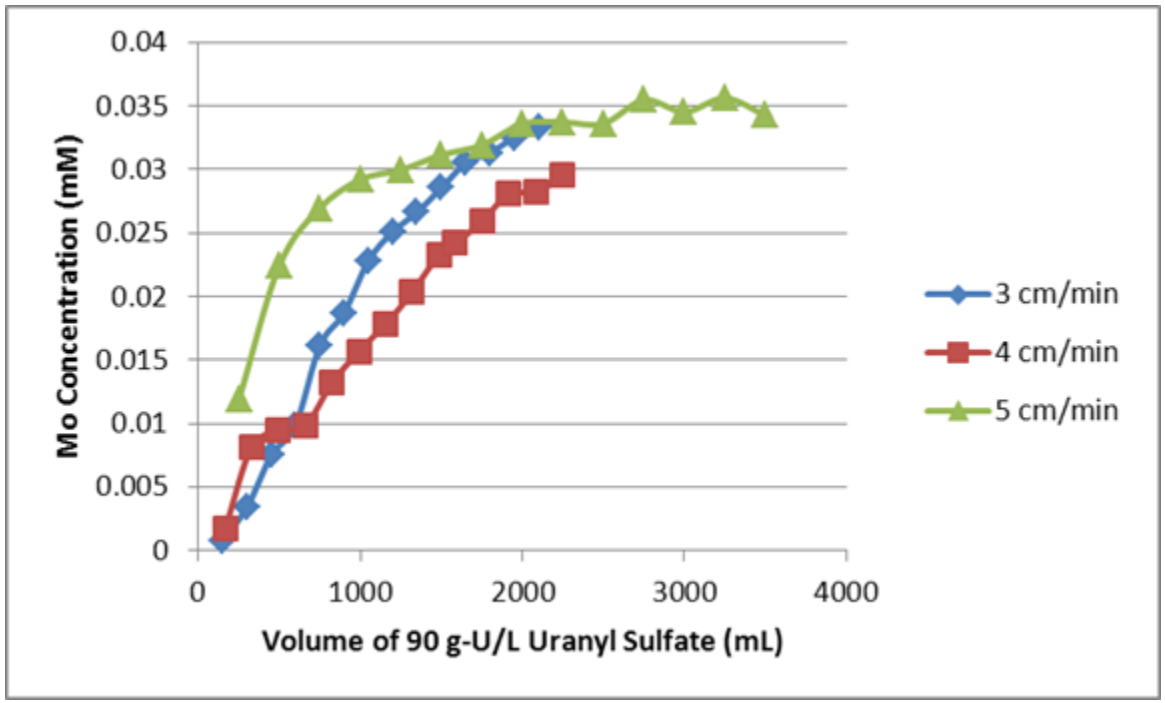
- Mo breakthrough curve simulations
- Loading velocities for 3, 4, and 5 cm/min with a column length of 1 cm
- Breakthrough occurs earlier when loading velocity is increased
- 0.66 cm ID x 1 cm L S110 column

0.66 cm ID x 1 cm L Results



- VERSE predicted full Mo breakthrough achieved after >616, 821, and 1026 mL are passed through column at 3, 4, and 5 cm/min
- S110 performs better than expected based on VERSE predictions
- Mo breakthrough is not achieved after 980 mL at 3 cm/min and 1330 mL at 4 cm/min are passed through the column
- Full Mo breakthrough achieved after 1750 mL of solution are passed through the column at 5 cm/min

1 cm ID x 1 cm L Results



- VERSE predicted full Mo breakthrough would occur after >1414, 1885, 2356 mL are passed through the column at 3, 4, and 5 cm/min
- Mo breakthrough is not achieved after 2100 mL at 3 cm/min and 2247 mL at 4 cm/min are loaded onto the column
- Mo surprisingly begins to breakthrough more rapidly at 3 cm/min rather than at 4 cm/min
- Full Mo breakthrough achieved after 3500 mL of solution are passed through the column at 5 cm/min

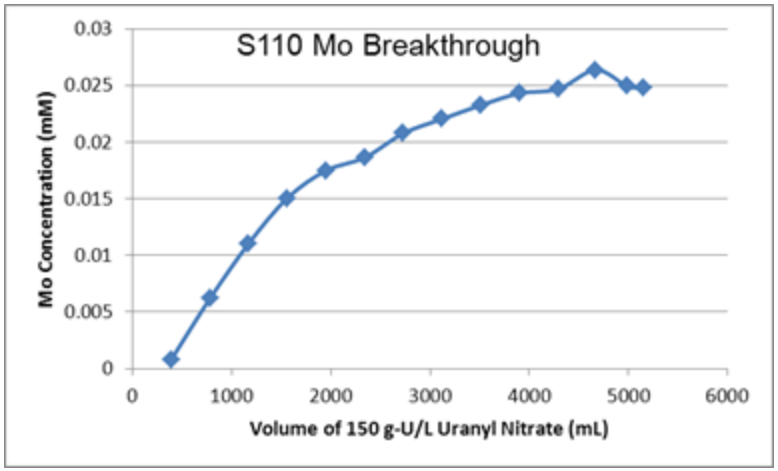
Mo-99 Separation Updates for Uranyl Nitrate

Date of Run	Column Size (ID x L)	Velocity (cm/min)	Sorbent	%Mo in Effluent	%Mo in Washes	%Mo Recovered	Stripping Agent
09/15/11	1.5 x 3.1	9	S40	16.0	0.6	86.0	1 M NH_4OH
09/21/11	1.5 x 6.2	3	S110	1.0	0.6	88.0	1 M NH_4OH
09/23/11	1.5 x 6.3	5	S110	1.0	1.0	85.0	1 M NH_4OH
09/26/11	1.5 x 2.6	5	S40	32.0	0.3	80.0	1 M NH_4OH
09/28/11	1.5 x 6.3	10	S110	1.0	0.1	77.0	1 M NH_4OH
09/30/11	1.5 x 6.3	7.5	S110	2.0	0.1	85.0	1 M NH_4OH
10/06/11	1.5 x 6.2	7.5	S110	7.3	0.8	73.0*	1 M NH_4OH
10/12/11	1.5 x 6.2	3	S110	7.0	1.0	89.0*	1 M NH_4OH

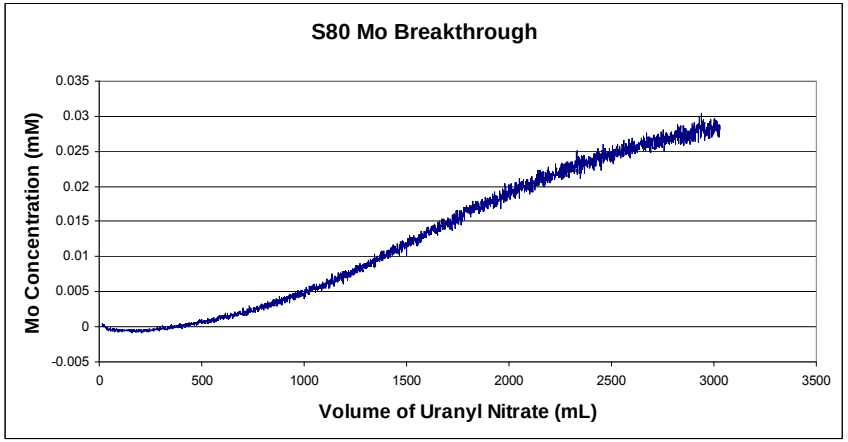
- Feed solution ~150 g-U/L uranyl nitrate, stable Mo, and Mo-99
- Column tests performed with S40 and S110 with 60 Å pores
- S110 outperforms S40 which had a significant amount of Mo in effluent
- Mo recoveries varied from 73 – 89%
- Stripping velocity had little effect on Mo recovery
- 0.5 wt.% $KMnO_4$ added to first water wash for runs on 10/06 and 10/12

S110 vs. S80 for Mo Breakthrough

S110 Mo Breakthrough Results



S80 Mo Breakthrough Results



- 1 cm ID x 1.6 cm L column with a linear velocity of 13 cm/min
- 5 L for S110 compared to 3 L for S80 for almost full Mo breakthrough to occur
- Mo breakthrough occurs more rapidly with S110 compared to S80
- Current plant-scale column designs for uranyl nitrate solutions using S80 should work for S110

Effects of Temperature

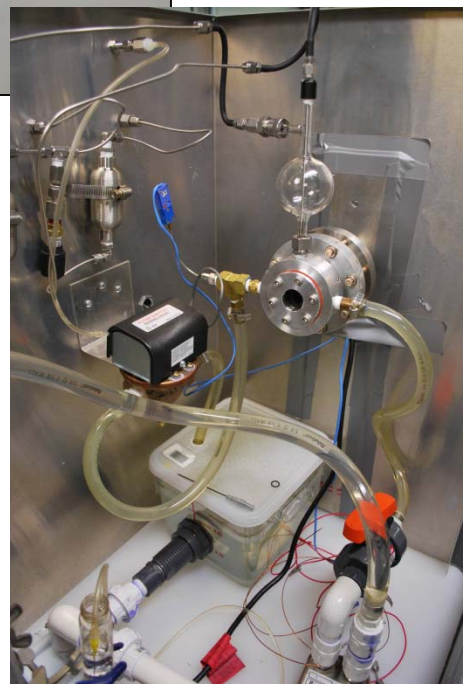
Sorbent	Solution	K_d, Mo, (mL/g) 20°C	K_d, Mo, (mL/g) 40°C	K_d, Mo, (mL/g) 60°C
S110	90 g-U/L uranyl sulfate	2600	3500	6200
S110	150 g-U/L uranyl nitrate	7000	12000	21000

- Batch studies performed as a function of temperature after 24 hours of contact
- K_d values ~2X higher for sulfate and 3X higher for nitrate in going from 20-60°C
- Solution is not heated prior to column loading due to heat loss in the pump
- Temperature of solution entering column is not 60°C but column is kept at 60°C
- Stainless steel coils wrapped in heat tape were added before and after the column
- Mo adsorption is significantly affected by temperature
- If temperature is controlled better, more Mo may adsorb
- 2 – 5% Mo typically observed in effluent
- VERSE column sizes are designed to be able to adsorb at least 2X more Mo than needed

Mo-99 Separation Wrap-Up

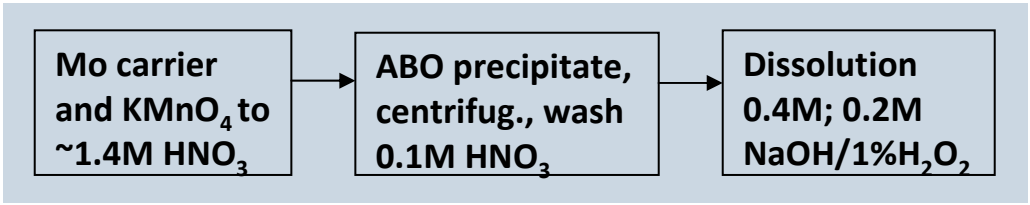
- S110 can be used to separate Mo-99 from LEU uranyl nitrate or uranyl sulfate solutions
- Current plant-scale column designs for BWTSG using S80 will work for S110 as well
- Plant-scale column designs are almost complete for MIR
- Recovery of Mo-99 continuously being optimized
- Small-scale column experiments will be done for MIR when plant-scale design is complete
- Mini-MIPS/SHINE experiments will provide useful data regarding the fate of other fission products in the separation, recovery, and purification processes

Radiolytic Stability of Mo-ABO Precipitate



- Precipitation of Mo with alpha-benzoin oxime is an important step in Cintichem purification process
- Mo yields unaffected when up to 1000 Ci of Mo-99 was processed in a single Cintichem run
- If production yields are higher, primary concern is that ABO will radiolytically breakdown and Mo yields will decrease
- Several 6-day kCi per batch are expected for processing
- Van de Graaff (VDG) accelerator was used to irradiate the Mo-ABO precipitate at doses equivalent to ~160 kCi of Mo-99
- Stability of the precipitate was examined after irradiation

ABO Irradiation at Van de Graaff

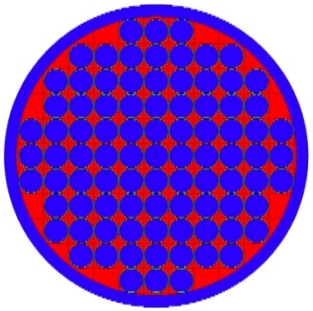


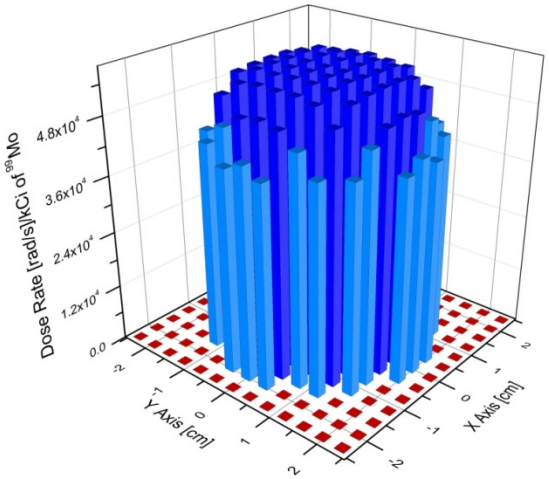
Before irradiation (24.4GRad)

After irradiation

- ABO precipitate
- Centrifuge, discard solution
- Irradiate (0.1 M HNO_3)
- Transfer to filter vial
- Wash with 0.1 M HNO_3
- Centrifuge
- Dissolve in 0.4 M NaOH/1%H_2O_2
- Centrifuge
- Dissolve in 0.2 M NaOH/1%H_2O_2
- Centrifuge
- Rinse with 0.2 M NaOH
- Count filter, HNO_3, NaOH fraction

MCNPX Simulations and Mo Recovery Results





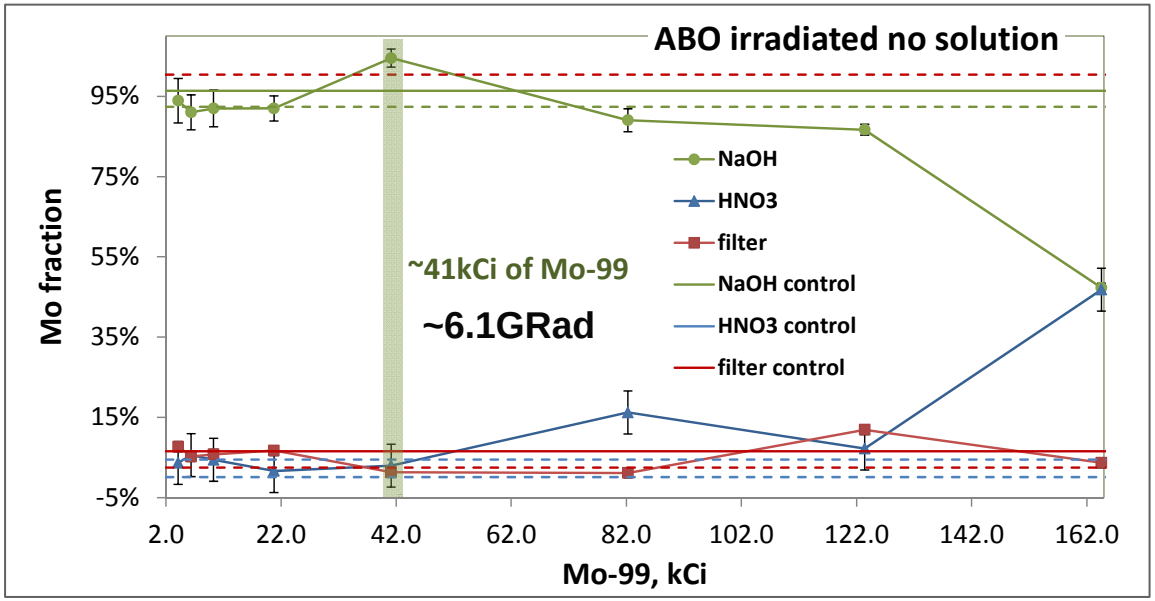
MCNPX calculations

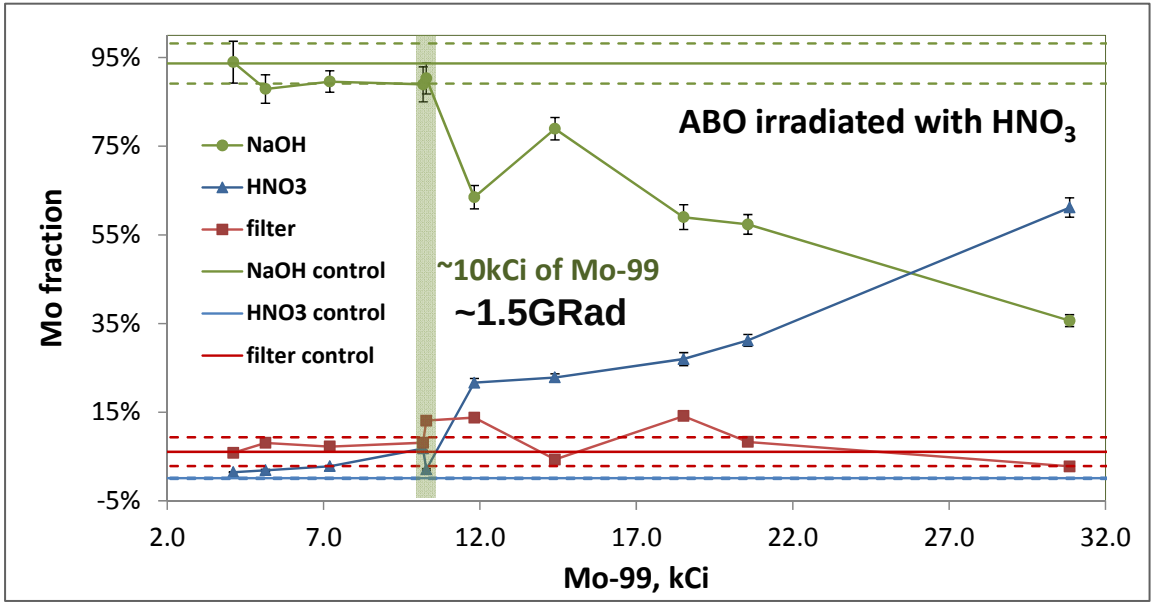
20 minutes (Cintichem process) is eq.

~62.5 MRad/ 1 kCi of ^{99}Mo

If modeled as a single layer ABO **~150 MRad per 1 kCi of Mo-99**

(more conservative)





Four Potential Clean-Up Methods, If Required

- Methods listed below assume a uranyl sulfate solution

1. Anion Exchange of uranyl sulfate complexes
2. Direct Solvent-Extraction Process for Uranyl Sulfate
3. Precipitation of Uranyl Ion as Uranyl Peroxide
4. Conversion to nitrate media followed by UREX processing

Least Favorable Options for Clean-Up

- Anion exchange of uranyl sulfate complexes will not work because of the low capacity of the resins (1-2 meq/g and ~500 kg of resin for 200 L at 150 g-U/L)
- Direct solvent-extraction process for uranyl sulfate could work but the concentrations of trioctyl ammonium sulfate (TOA) and trioctyl phosphate (TOPO) and stripping conditions need to be determined
- Precipitation of uranyl ion as uranyl peroxide is problematic because it cannot be filtered or centrifuged
- The last two options could work but both would require a significant amount of R&D

Conversion to Nitrate Media Followed by UREX

- Steps
  - Addition of $Ca(NO_3)_2$ dissolved in 1 M HNO_3 to the irradiated uranyl sulfate solution in a stirred vessel; addition rate, stirring speed, and temperature must be set to optimize the morphology and size of the crystals formed to allow facile filtration
  - Passing the slurry into a filtration system to collect and wash the precipitate
  - UREX processing of the filtrate
  - Precipitation of uranium as ammonium diuranate and its filtration
  - Conversion of uranium to UO_3
  - Dissolution of UO_3 in sulfuric acid
  - Reconstitution to the uranyl-sulfate/0.1 M-sulfuric-acid target solution
  - Potential recycle of uranium from ammonium diuranate filtrate
  - Treatment of waste streams generated for storage and final disposal
- All process steps are used commercially and well understood
  - Minimum R&D is required to design processing facility

Concluding Remarks

- S110 will be used for Mo-99 separation and recovery columns for MIPS and SHINE
- Column stripping and loading conditions will continue to be optimized
- Future irradiations will take place at Argonne using the linac (mini-MIPS/SHINE experiments)
- Mo-ABO radiolytic stability tests show that ~10 kCi Mo-99 can be purified via the Cintichem process without losses due to ABO degradation
- If solutions need to be cleaned up, conversion to nitrate followed by UREX processing is the best option

Acknowledgements

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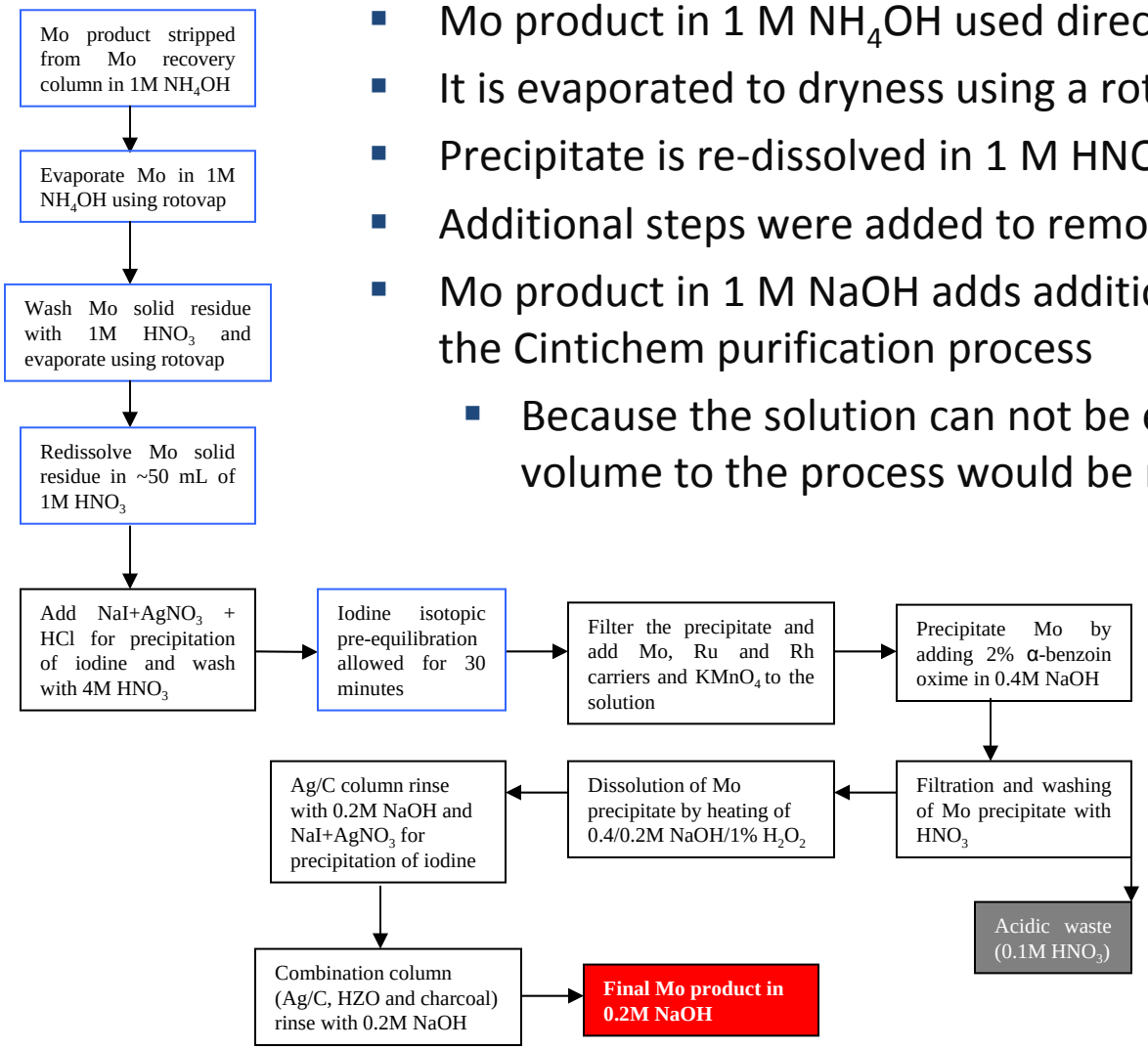
Modified LEU-Modified Cintichem Process



- Mo product in 1 M NH_4OH used directly from column run
- It is evaporated to dryness using a rotary evaporator
- Precipitate is re-dissolved in 1 M HNO_3
- Additional steps were added to remove iodine
- Mo product in 1 M NaOH adds additional complications to the Cintichem purification process
  - Because the solution can not be evaporated, the feed volume to the process would be much too large