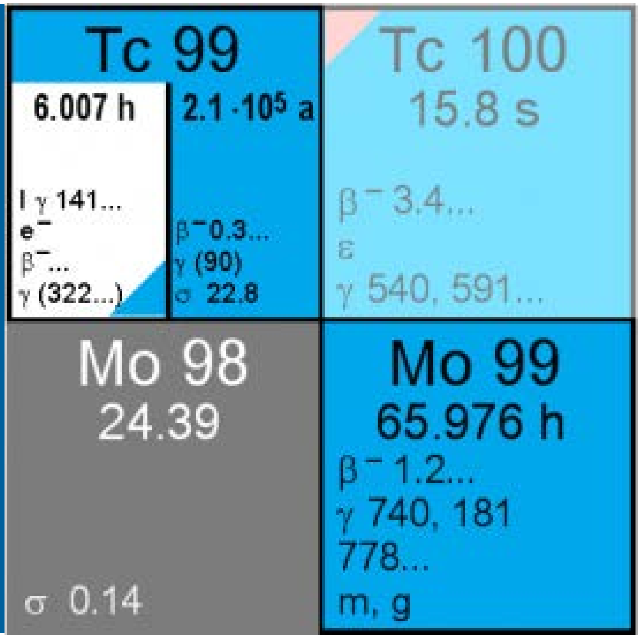
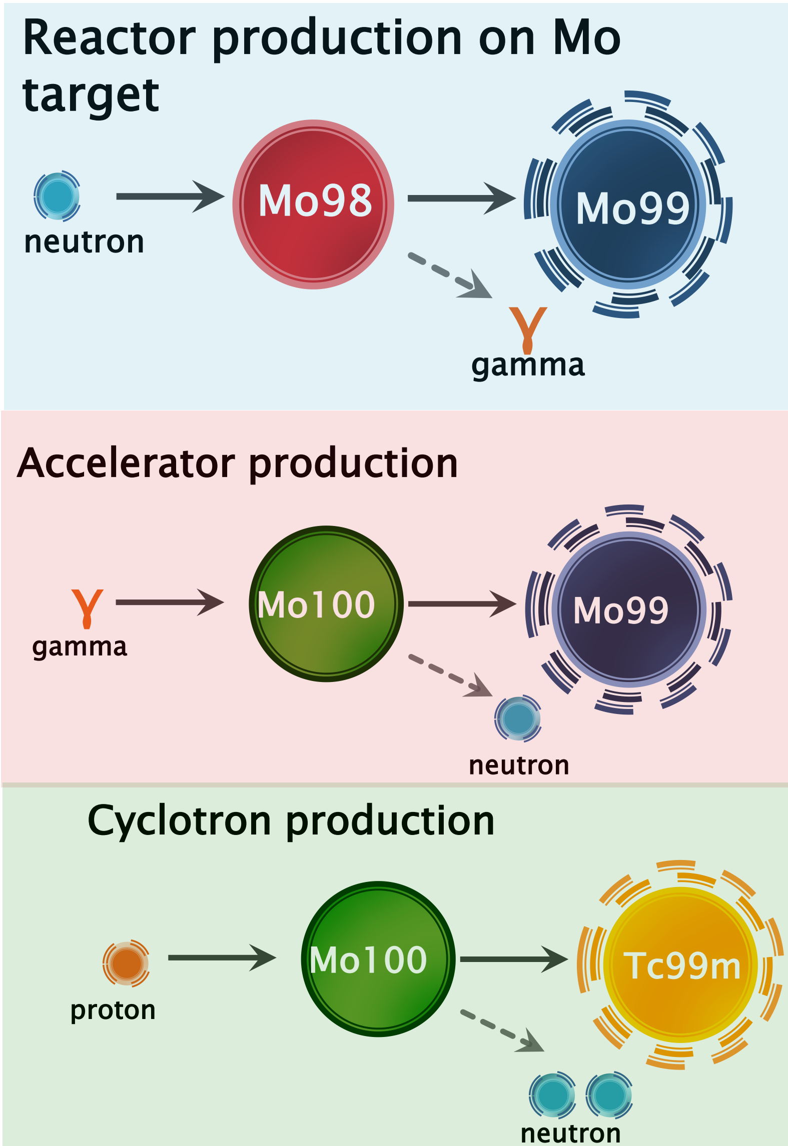
CHEMICAL PROCESSING FOR NON-URANIUM PRODUCTION OF ^{99}MO/^{99M}TC

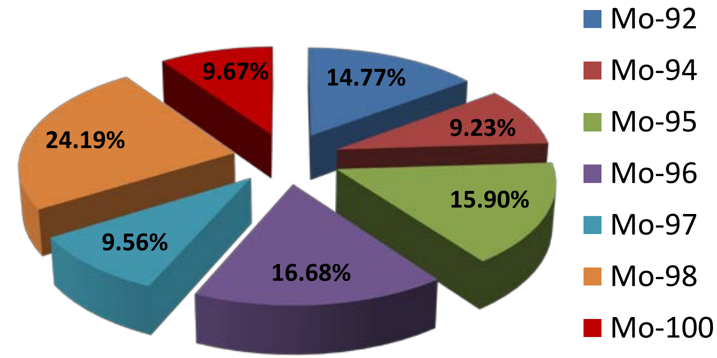


P. TKAC, K.E. WARDLE, M.A. BROWN, A. MOMEN, D.A. ROTSCH, J.M. COPPLE, S.D. CHEMERISOV, R. GROMOV, G.F. VANDEGRIFT

September 11-14, 2016
2016 Mo-99 Topical Meeting

WHAT ARE THE ALTERNATIVES?





- Enriched Mo-100 is available for ~$1000 per gram for kg quantities!!!
- Different generator technology is required

ADVANTAGES AND DISADVANTAGES OF ALTERNATIVES

- Advantages
  - Lower start-up costs
  - Commercial availability
  - Fast post-irradiation processing
  - Easier licensing procedure
  - Less costly waste disposal (no fission products)
- Disadvantages
  - Lower production yields
  - Use of enriched Mo targets
  - Lower specific activity, which leads to requiring a different generator technology

❖ Use of commercial reactors for production of Mo-99 using Mo98(n,γ)Mo99

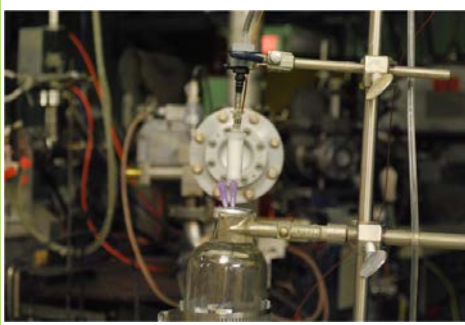
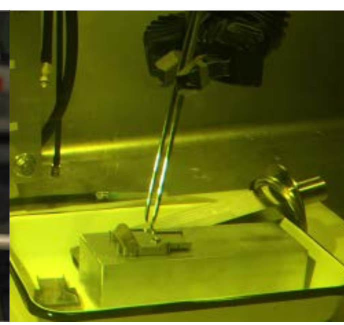
❖ Electron accelerator technology using Mo100(γ,n)Mo99

❖ Availability of medical cyclotrons for direct production of Tc-99m world-wide

– Up to 70Ci of Tc-99m can be produced in two 6-h irradiations (500µA and 24MeV)
– Short half-life requires very quick post-irradiation processing

WORK AT ARGONNE

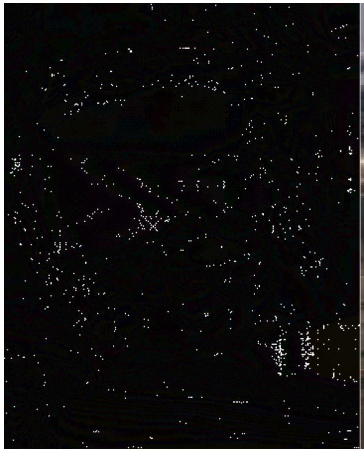
- Radiation studies
- Irradiation and processing of Mo targets using an electron linac
- Dissolution studies to optimize Mo target properties
- Large-scale dissolution studies with up to 600g of Mo
- Recycle of enriched Mo-98 or Mo-100 material

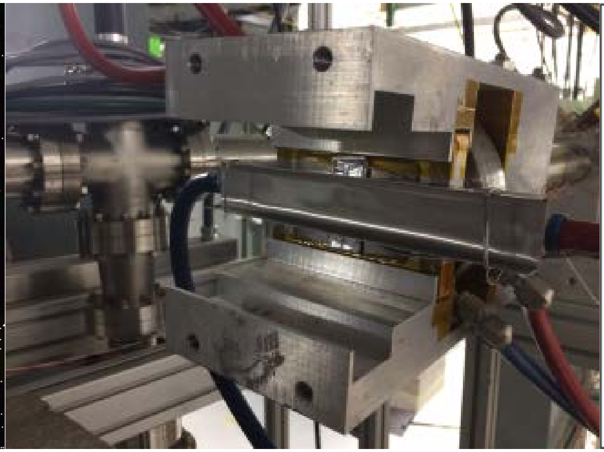



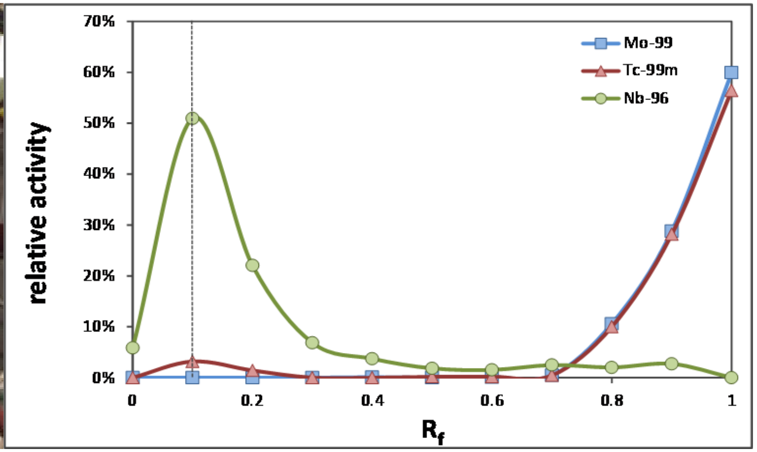

IRRADIATIONS PERFORMED IN FY16

- The goal was to determine if Sn-stabilized peroxide can affect the radiochemical purity of the Tc/Mo product
  - Four UHP natural Mo targets irradiated
  - One 97.4% Mo-100 enriched target irradiated

Mo, g	Activity at EOB, mCi						R_f=0.9±0.1		H_2O_2 used	H_2O_2 used, mL/g
	^{99}Mo	^{90}Mo	^{93m}Mo	^{95m}Nb	^{95}Nb	^{96}Nb	^{99}Mo	^{99m}Tc		
UHP, 1.13	16.5	2.8	ND	0.79	0.11	2.34	91.3%	89.5%	30% NS	13.3
UHP, 1.05	15.3	1.8	0.01	0.79	0.07	1.98	99.7%	96.5%	50% Sn-stab	9.5
UHP, 1.06	13.5	2.2	ND	0.72	0.06	1.89	99.5%	95.8%	50% Sn-stab	18.9
UHP, 1.03	16.1	2.5	ND	0.83	0.07	2.22	99.3%	94.6%	30% NS	9.7
^{100}Mo, 2.09	123.2	ND	0.04	0.05	ND	ND	98.4%	98.3%	50% Sn-stab	31







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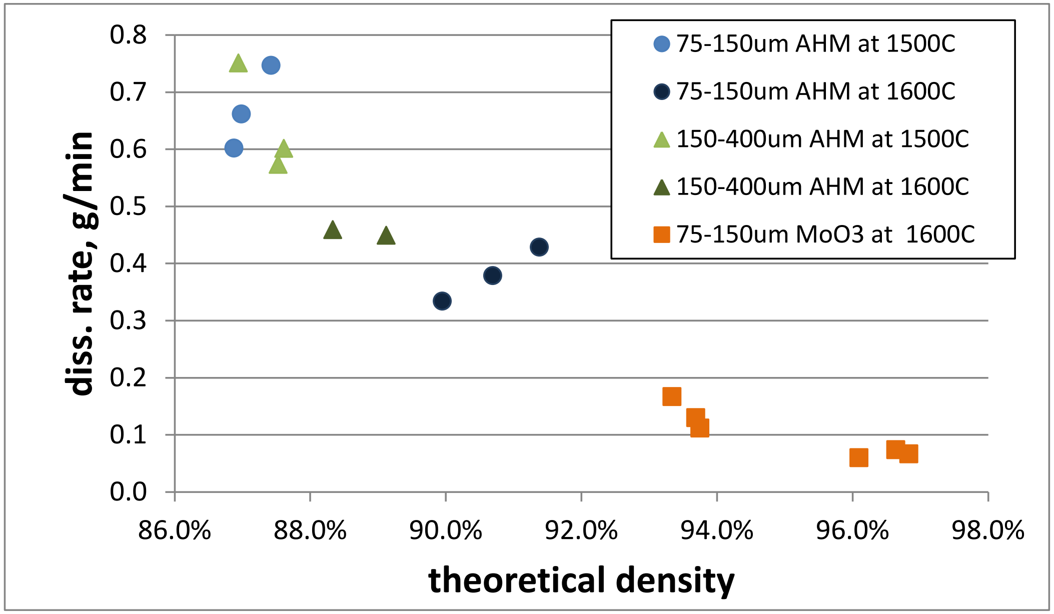
SMALL-SCALE DISSOLUTIONS – ORNL DISKS



AHM Recycled

75-150µm AHM reduced to 91±25µm Mo

150-400µm AHM reduced to 204±37µm Mo

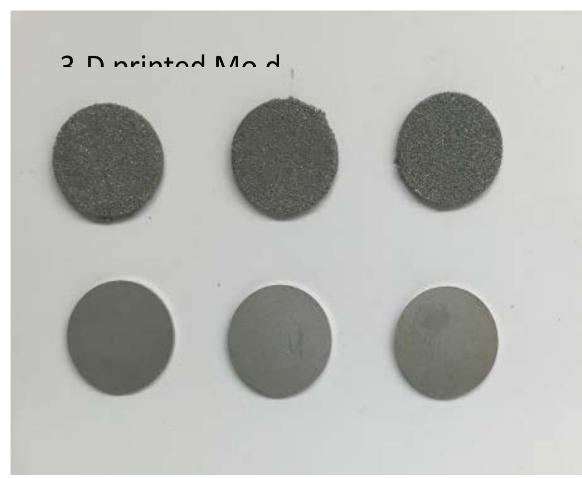
MoO_3 Recycled

75-150µm MoO_3 reduced to 125-155µm Mo

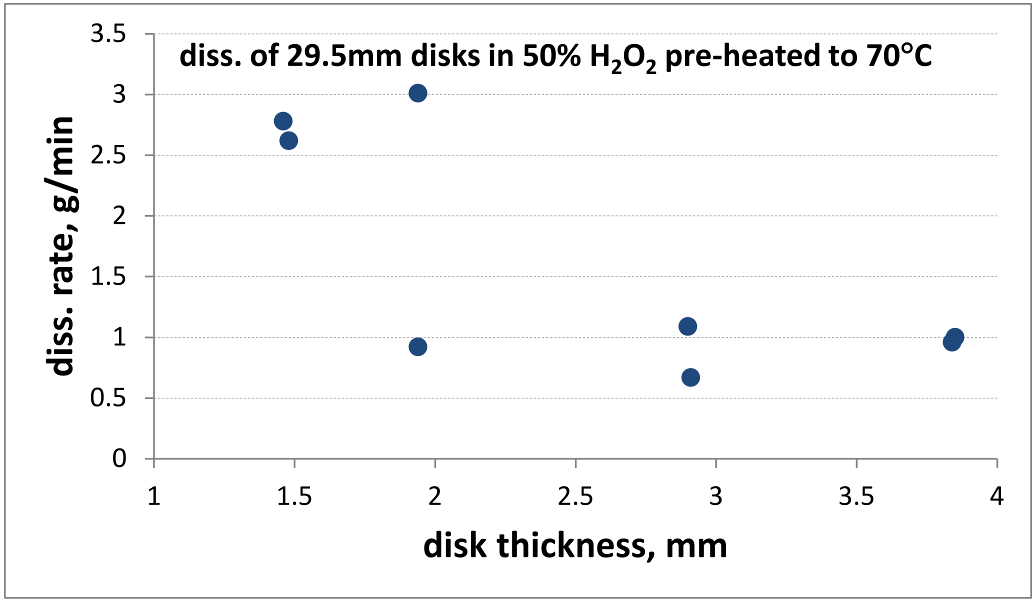
Agglomerates of 1-10µm Mo particles

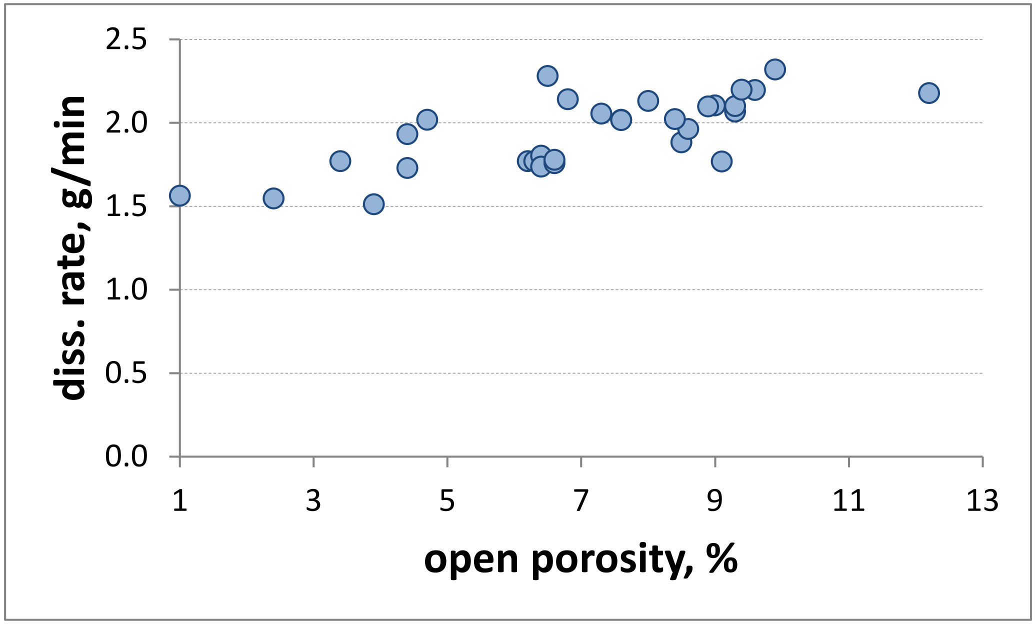
Laser-melt 3D printed Mo disks

- Disks broke down into small pieces
- Wire-like particles
- Longer diss. time vs. sintered
- Opposite trend on open porosity



SMALL-SCALE DISSOLUTIONS 29MM DISKS-ORNL DISKS





- ~29.5mm disks
- 9-24g per disk
- Very good dissolution rates for up to 4mm thick disks

- 29x0.5mm disks
- 87-93% theoretical density

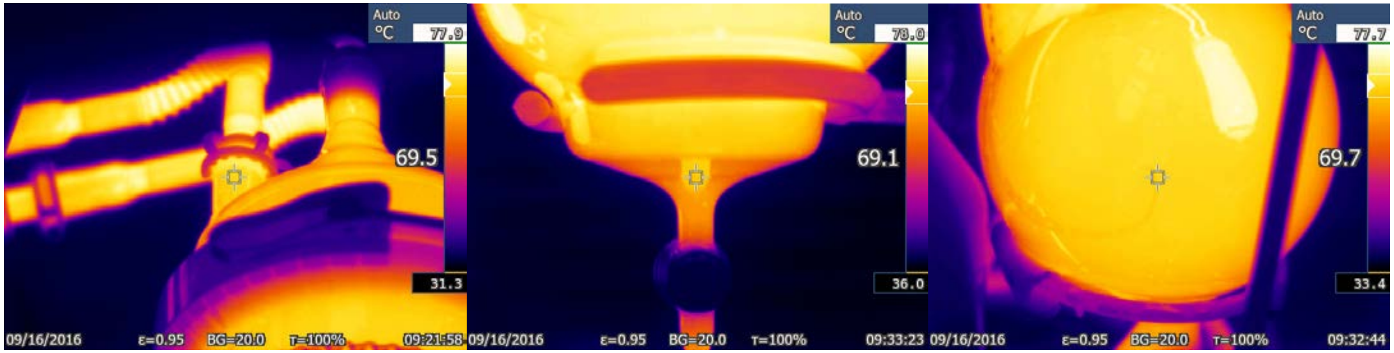
LARGE-SCALE DISSOLUTION
600G OF SINTERED MO DISKS

Disks, mm	H_2O_2 (L)	Water condensed from diss., L	Diss. time, h	Evaporation time, h	Total time, h	Total diss. rate, g/min
26x1	9.5	5.4	2.5	1.5	4.5	2.2
26x1	9.0	5.9	2.75	1	4.0	2.5
26x1	6.5	4.3	2.0	1.5	3.8	2.7
29.5x0.5	6.8	4.7	1.8	0	2.3	4.42

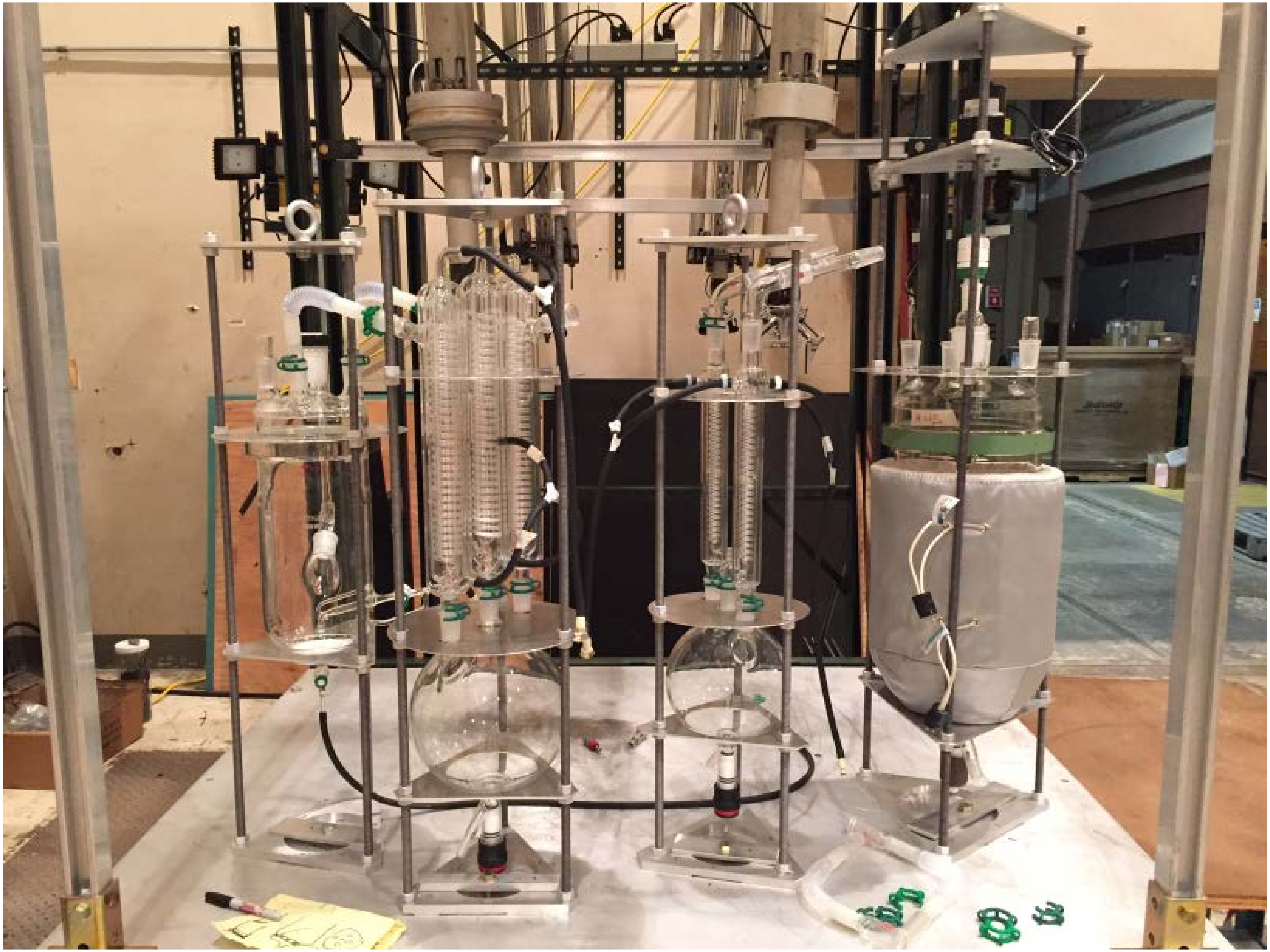
Last 26x1mm dissolution – 900mL of water condensed in 15min

Reaction heat: ~2.6kW

Chiller used: 1.7kW cooling capacity at 20°C



LARGE-SCALE DISSOLUTION OF SINTERED MO DISKS



MO RECYCLE PROCESS

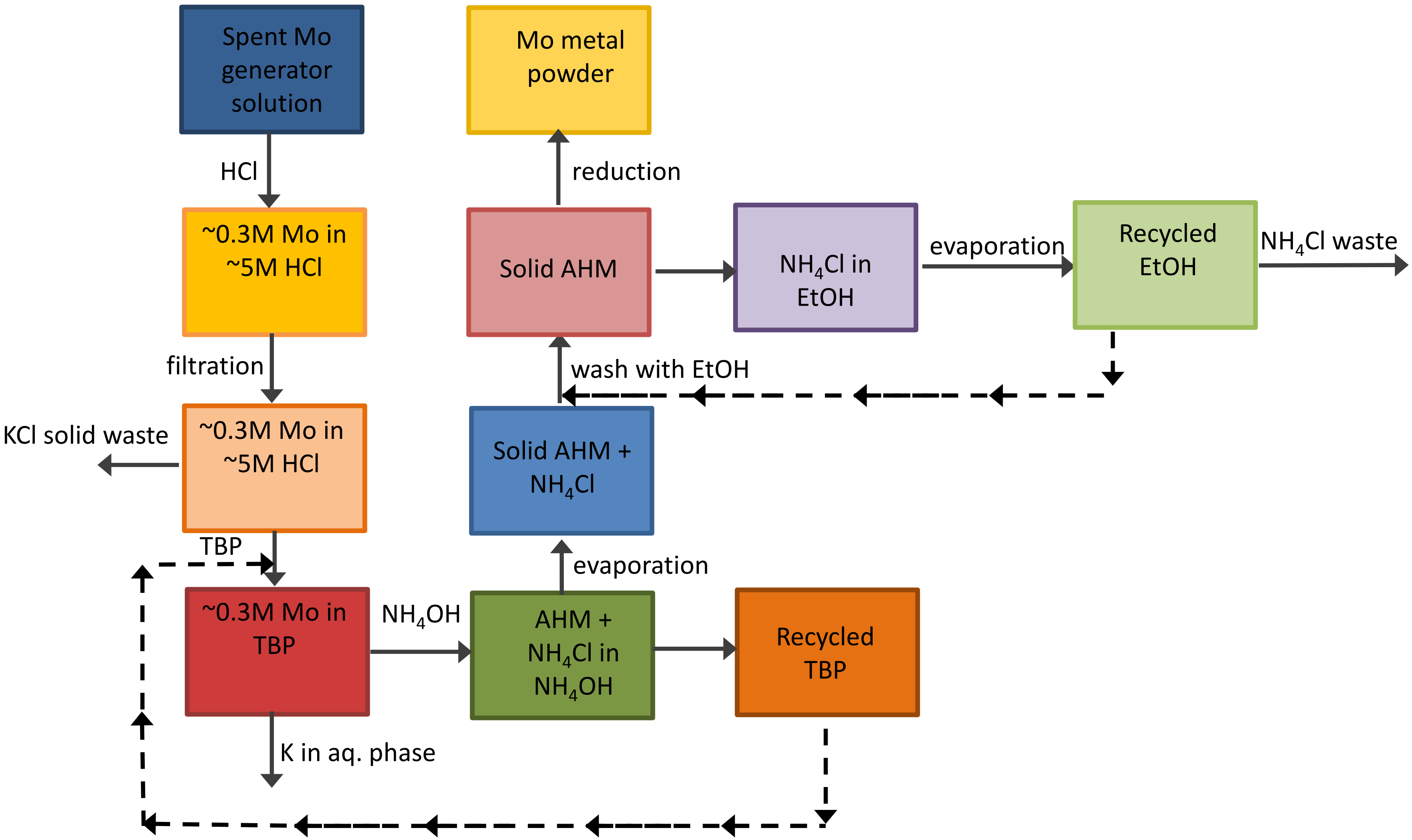
SPENT GENERATOR SOLUTION

- Need to be recycled to reuse enriched Mo-98, Mo-100 material for economic production
- Generator solution contains ~2kg of K per kg of Mo

REQUIREMENTS

- Recycling capacity of up to 400g/day
- High recovery yield
- No introduction of other elements that can lead to side reaction products
- Recycled material ≤100mg-K/kg-Mo – separation factor required SF=1×10^4
- Automated process

MO RECYCLE PROCESS – SOLVENT EXTRACTION



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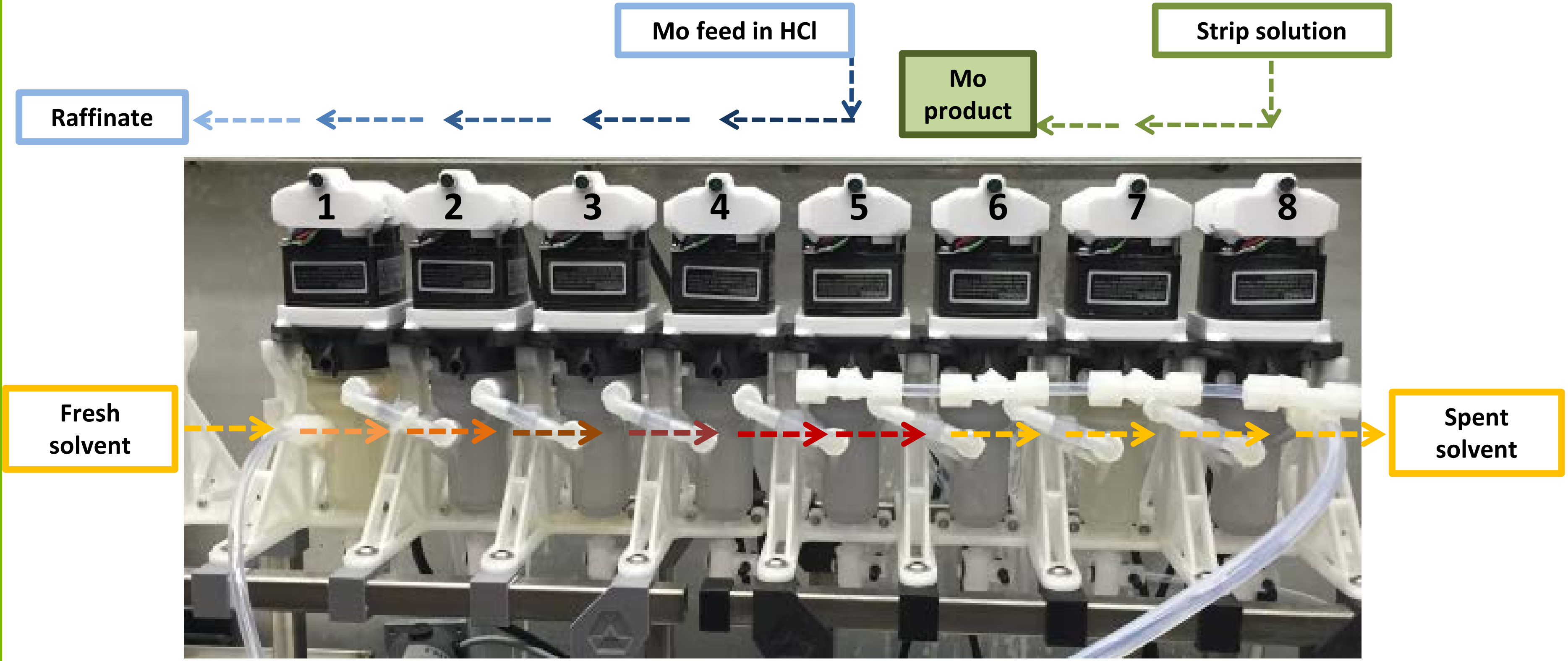
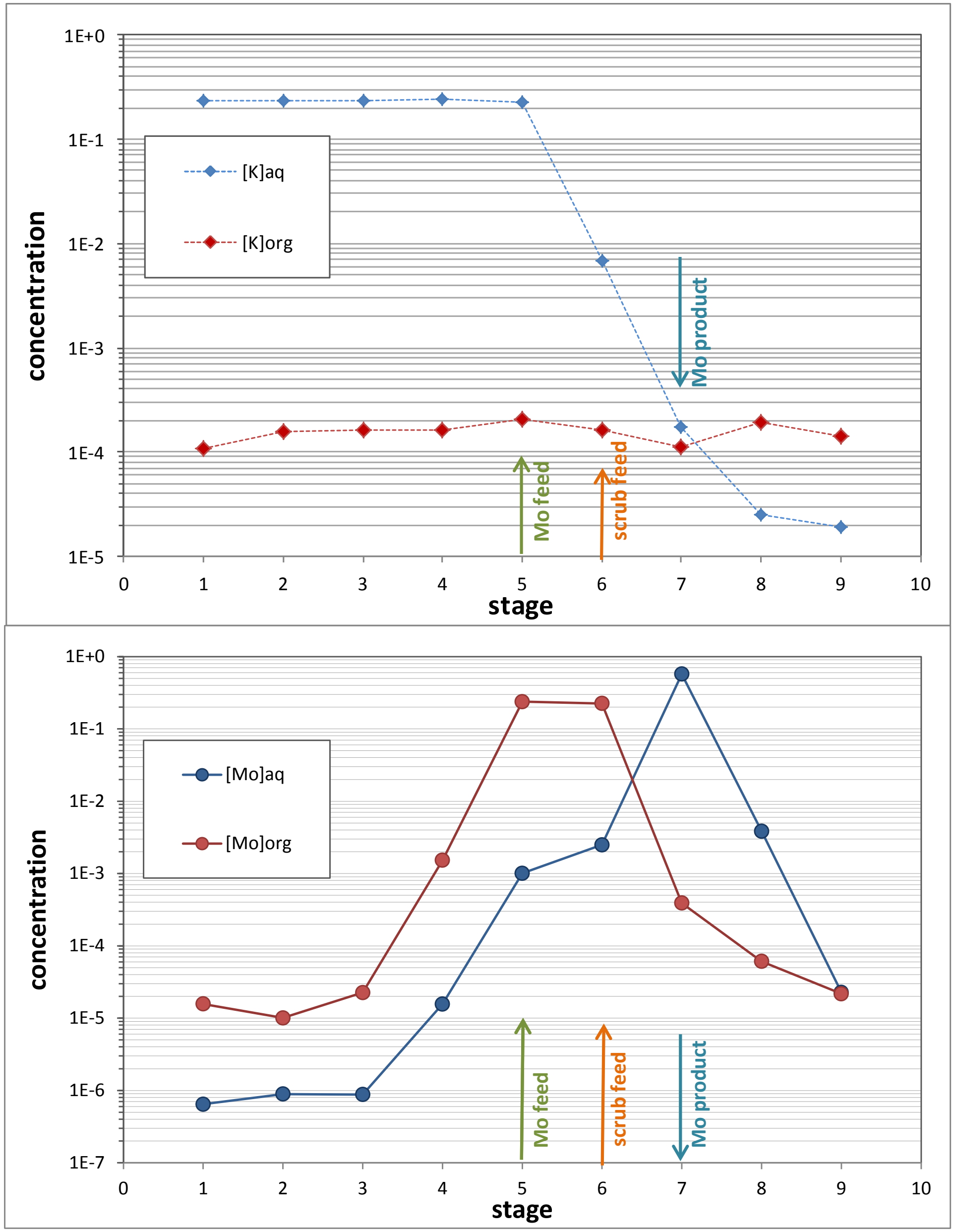
PLASTIC 3D PRINTED COUNTERCURRENT CENTRIFUGAL CONTACTOR



COUNTER CURRENT CENTRIFUGAL CONTACTORS



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RECOVERY OF MO BY SOLVENT EXTRACTION BACK END PROCESSES

Evaporation

NH_4OH solution

NH_4Cl
$(NH_4)_6Mo_7O_{24}$

Differential solubility in ethanol-water mixture

Solid mixture
NH_4Cl
$(NH_4)_6Mo_7O_{24}$

NH_4OH waste

NH_4Cl solid waste

$(NH_4)_6Mo_7O_{24}$

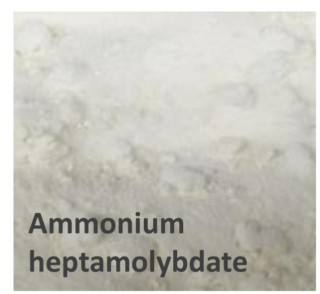
heat

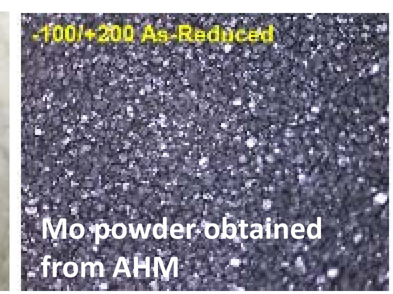
MoO_3 product

~98% recovery yield for Mo

AHM particle size distribution

~50% -40/+100 mesh	400-149µm
~40% -100/+200 mesh	149-74µm
~10% -200 mesh	<74µm





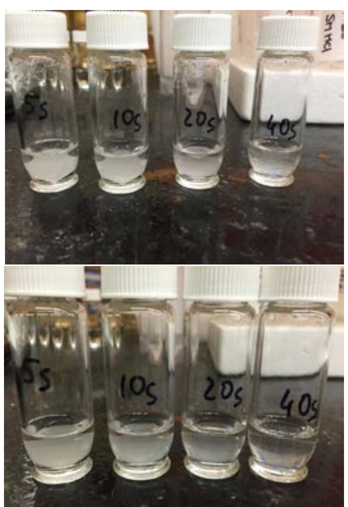
RECOVERY OF MO BY SOLVENT EXTRACTION BACK END PROCESSES

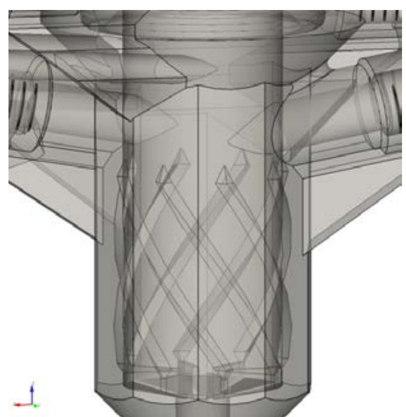
	~5M HCl	strip	Ammonium molybdate
	ppm (mg/kg-Mo)		
K	4.2E5	193	< 41
Na	2.6E3	2.7E3	< 43
P	2.5E3	2.7E3	< 111
Mg	70	133	< 19
Al	79	154	< 35
Ti	27	59	17
Fe	< 66	96	< 42
As	31	20	71
Zr	< 0.76	10	20
Nb	1.7	1.6	1.6
Cd	1.7E3	1.6E3	1.4E3
Sn	1.2E3	N/A	1.2E3
Te	97	71	79
W	3.2E3	3.0E3	2.2E3

COMPLEXITY OF STRIPPING

$\boldsymbol{MoO_2^{2+}}$	$MoO_2(OH)^+$ $H_3MoO_4^+$ $HMoO_3^+$ MoO_3 $HMoO_4^-$ H_2MoO_4	$Mo_2O_5^{2+}$ $HMo_2O_5^{3+}$ $HMo_2O_6^+$ $H_2Mo_2O_6^{2+}$ $H_3Mo_2O_6^{3+}$	$Mo_3O_{11}^{4-}$ $Mo_4O_{14}^{4-}$ $HMo_6O_{21}^{5-}$ $\boldsymbol{Mo_7O_{24}^{6-}}$ $HMo_7O_{24}^{5-}$ $H_7Mo_{12}O_{41}^{3-}$ $HMo_{24}O_{78}^{3-}$	MoO_4^{2-}

pH 1 **pH 3** **pH 7**





CONCLUSIONS

- **Dissolution rates of disks from recycled Mo material depends on Mo particle size**

  Mo reduced from AHM has good properties for sintered disks

  Mo reduced from MoO_3 lead to fine Mo particles – affects dissolution rate

- **3D printed disks in early stage of development show different dissolution characteristics**

  slower dissolution vs. sintered Mo disks

  opposite trend of dissolution rate on open porosity

- **Developed process and equipment for quick dissolution of up to 600g of sintered Mo disks**

  total processing time for 600g of Mo is ~4hrs

  hot cell mock up

- **Developed an efficient recycle process for enriched Mo material with high recovery yields**

  automated solvent extraction using 3D-printed centrifugal contactors

  good particle size distribution of recovered AHM

ACKNOWLEDGMENTS

FUNDING

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