ANL Activities in Support of Accelerator Production of ^{99}Mo through the γ/n reaction on ^{100}Mo

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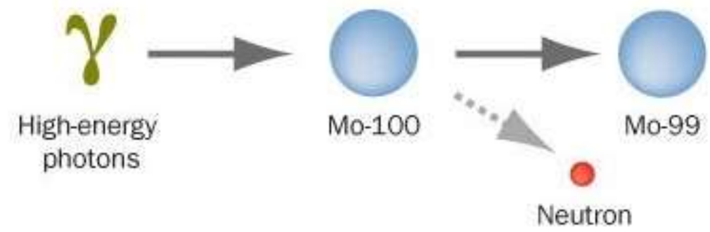
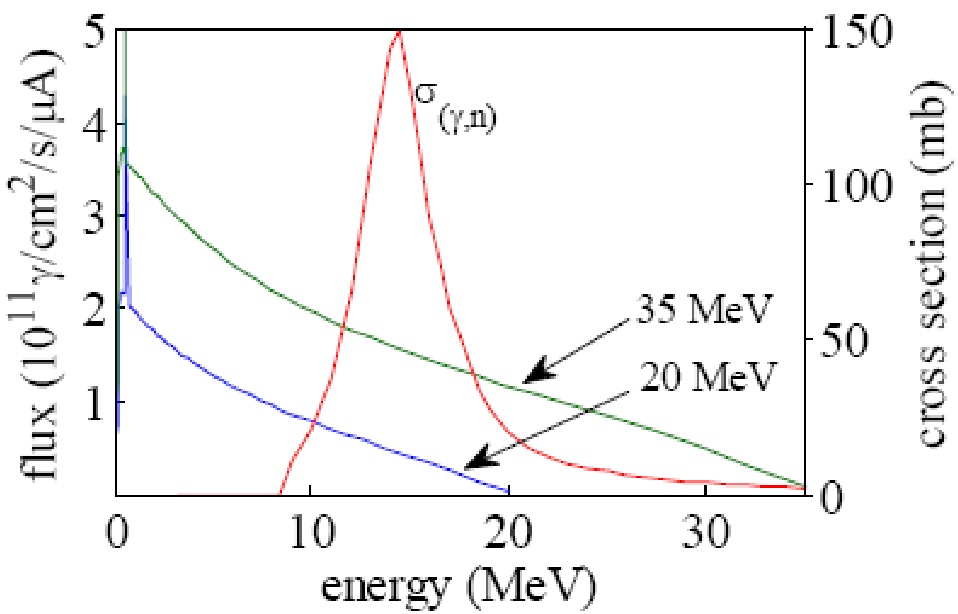
Accelerator Based Production of ^{99}Mo

- ANL and LANL are assisting NorthStar in development of accelerator based production of ^{99}Mo through the ^{100}Mo(γ,n)^{99}Mo reaction.
- Enriched ^{100}Mo is commercially available for ~$1000 per gram for kg quantities.
- High energy photons are created from a high power electron beam through bremsstrahlung.



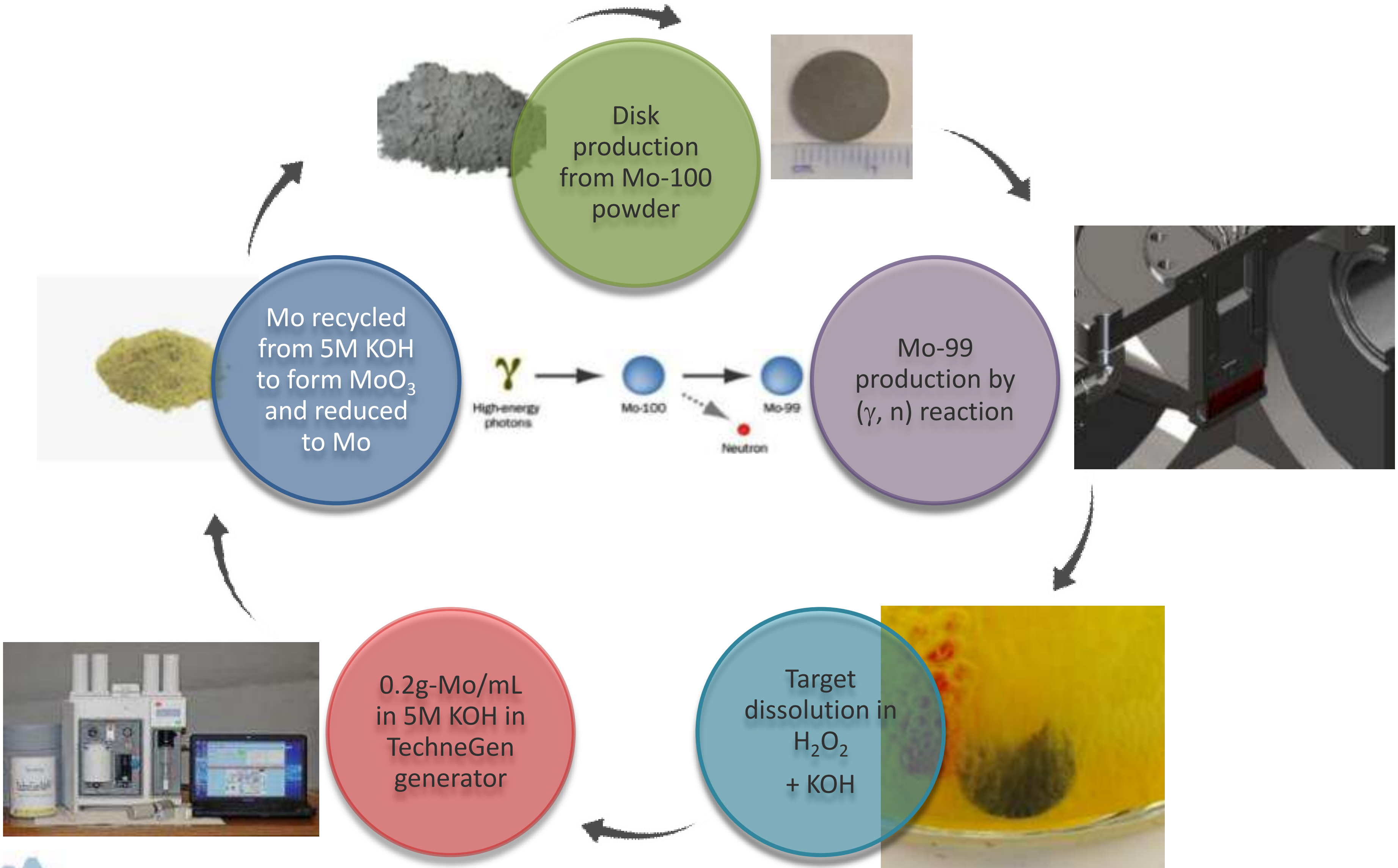
$$Y_{m,E_0} = N_m \int_{E_{th}}^{E_0} \sigma_m(\gamma,n)\Phi_{E_0}(E)dE$$

N_m – atom density of material m
E_{th} – threshold energy in m
$\Phi_{E0}(E)$ – photon fluence spectrum
$\sigma(\gamma,n)$ – cross section



Average bremsstrahlung photon spectra produced with 20- and 35-MeV electron beams in a Mo target compared to the photonuclear cross section of ^{100}Mo.

Molybdenum cycle

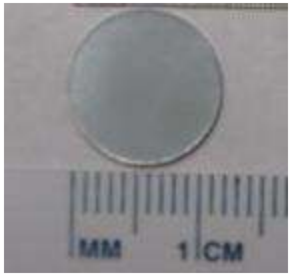


Disks production

MoO_3 reduced by disk manufacturer to Mo powder and sintered

MoO_3

Mo powder



- Disks provided by NorthStar (also getting disks from ORNL)
- Every disk is characterized by a 3 digit code "**ABC**" e.g. "791"
- **A**= powder treatment before pressing
- **B**= disk pressing parameters
- **C**= sinter conditions

Disk density determined from dimensions of the disks and divided by density of Mo metal (10.22g/mL)

GOAL: Find conditions for the production of Mo disks with high packing density (>92%) and good dissolution rates

Dissolution of Mo sintered disks in 30% H_2O_2

- $2Mo(s) + 10H_2O_2 = [Mo_2O_3(O_2)_4(H_2O)_2]^{2-} + 2H_3O^+ + 5H_2O$
- Initial pH≈5, after dissolution pH ≈1-2
- 1 Mo disk ~1g, 40mL of 30% H_2O_2 at 70°C, H_2O_2:Mo molar ratio ~35

auto-destruction of hydrogen peroxide to water and oxygen:

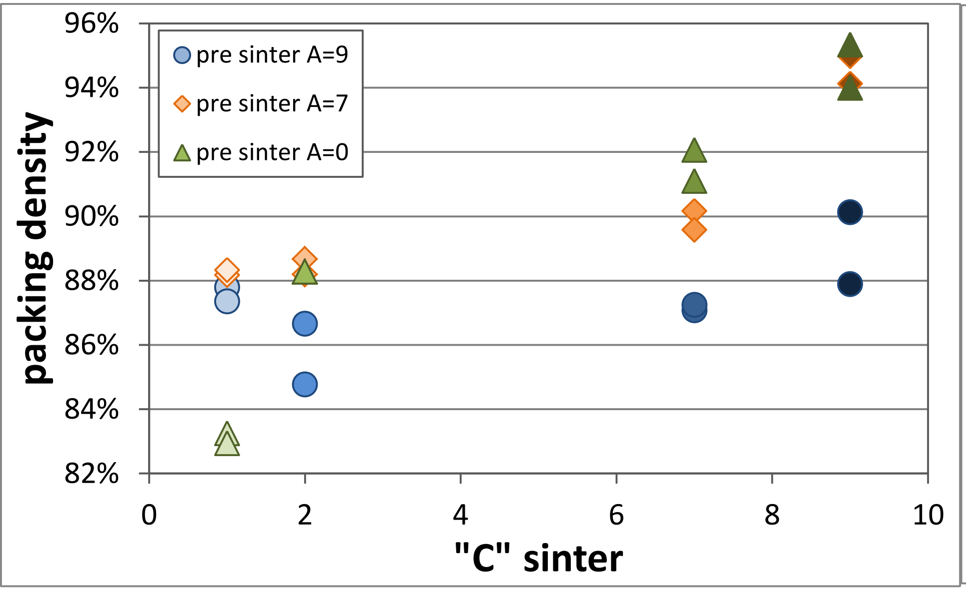
$$2H_2O_2 = 2H_2O + O_2$$

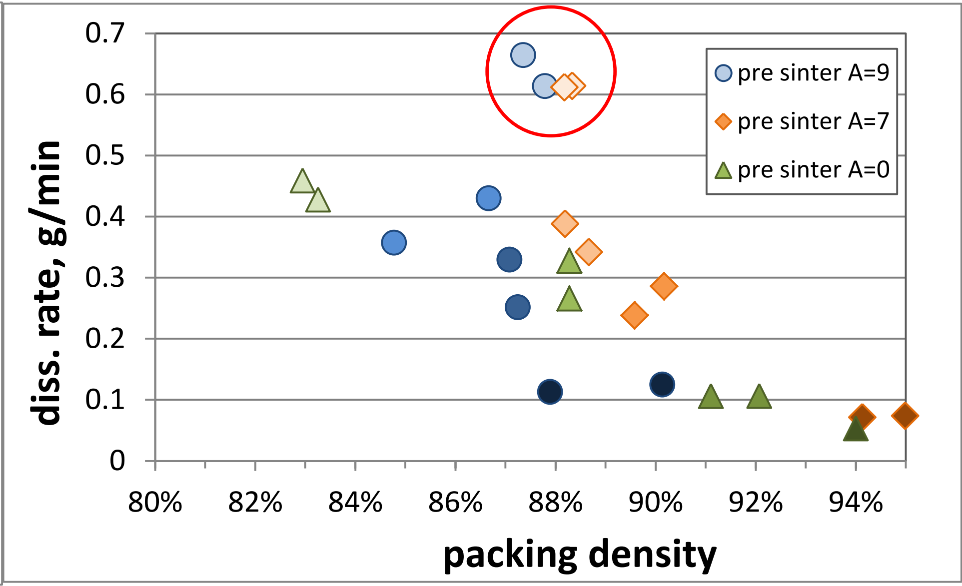
After dissolution KOH added to make **0.2g-Mo/mL in 5M KOH**

$$2[Mo_2O_3(O_2)_4(H_2O)_2]^{2-} + 8KOH = 4K_2MoO_4{\cdot}(H_2O)_2 + 5O_2$$

Effect of sinter conditions on density and dissolution

- **Pre-sinter conditions A=0, 7, 9**
- **Pressing conditions B=4**
- **Sinter conditions C=1, 2, 7, 9**





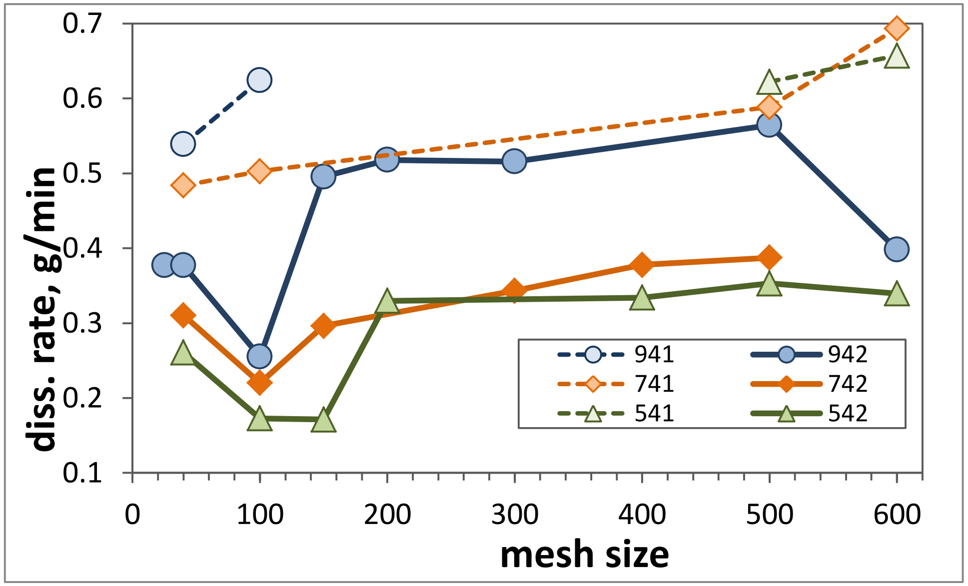
- packing densities increase with stronger sintering conditions
- stronger sinter "C" conditions lead to the lowest dissolution rates
- **the best dissolving disks are with stronger pre-sinter (A=7-9) and weaker sinter conditions (C=1-2)**

Effect of Mo powder size

- Pre-sinter conditions A=5, 7, 9
- Pressing conditions B=4
- Sinter conditions C=1, 2

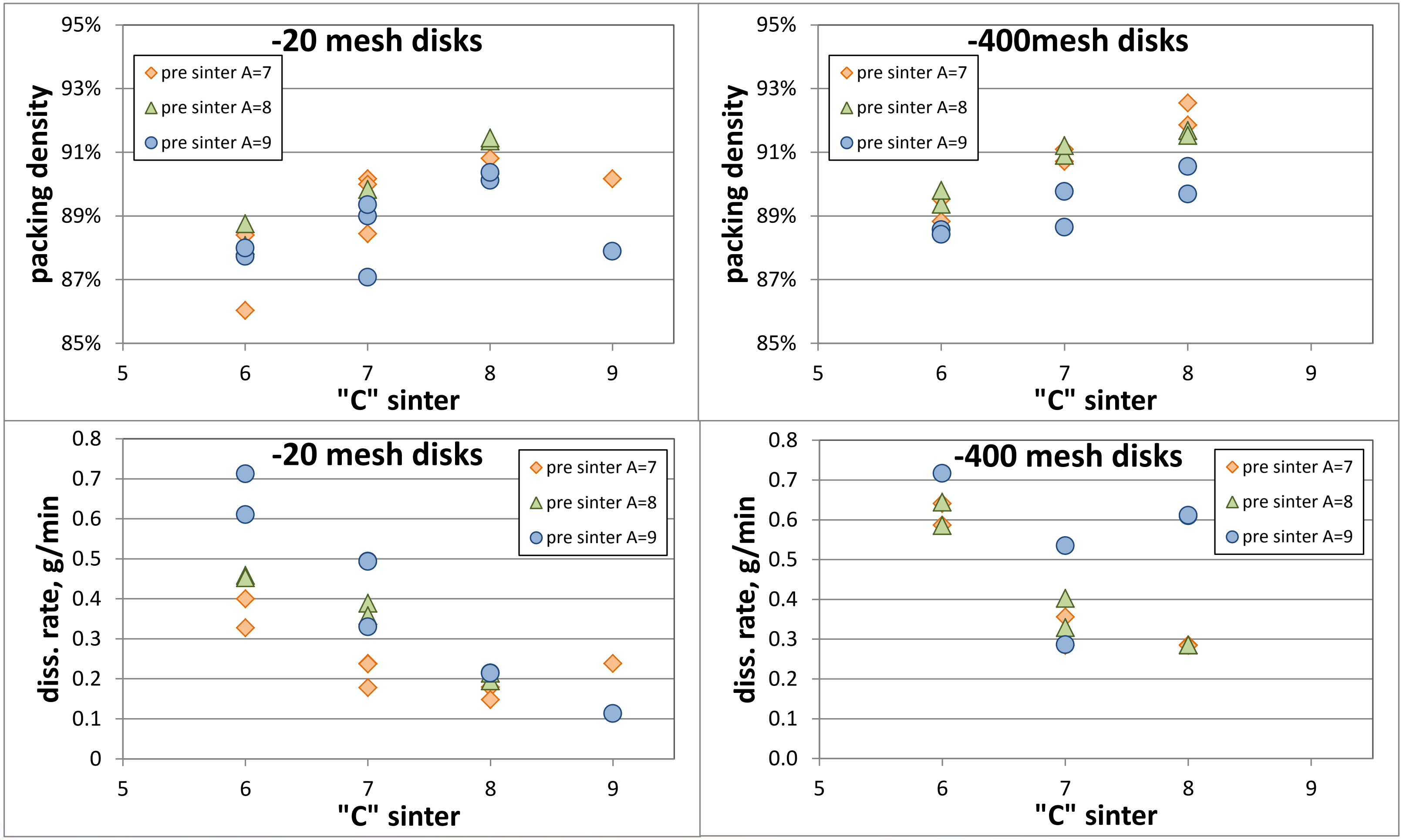
mesh	25	40	100	140	200	300	400	500	-500
Particle size, µm	710-841	400-710	150-400	105-150	74-105	45-74	37-45	25-37	<25

- No significant effect on density for disks sintered at C=1, 2
- Disks made of finer particles (higher mesh) dissolve faster



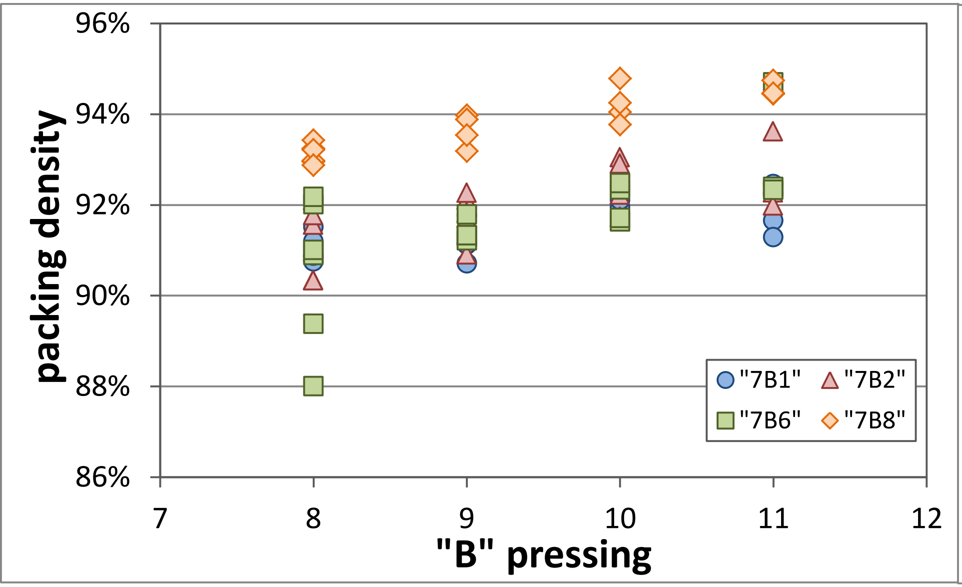
Effect of Mo powder size

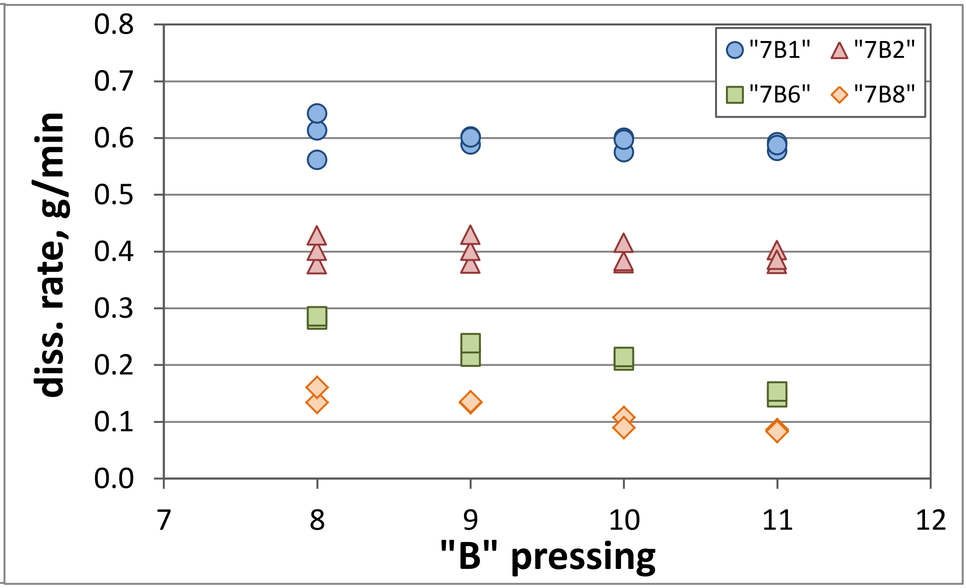
- Pre-sinter conditions A=7, 8, 9
- Pressing conditions B=4
- Sinter conditions C=6, 7, 8, 9
- Density increases with increasing “C”
- Dissolution rate decreases with increasing “C”
- -400 mesh disks dissolve faster then -20 mesh



Effect of pressing conditions cont.

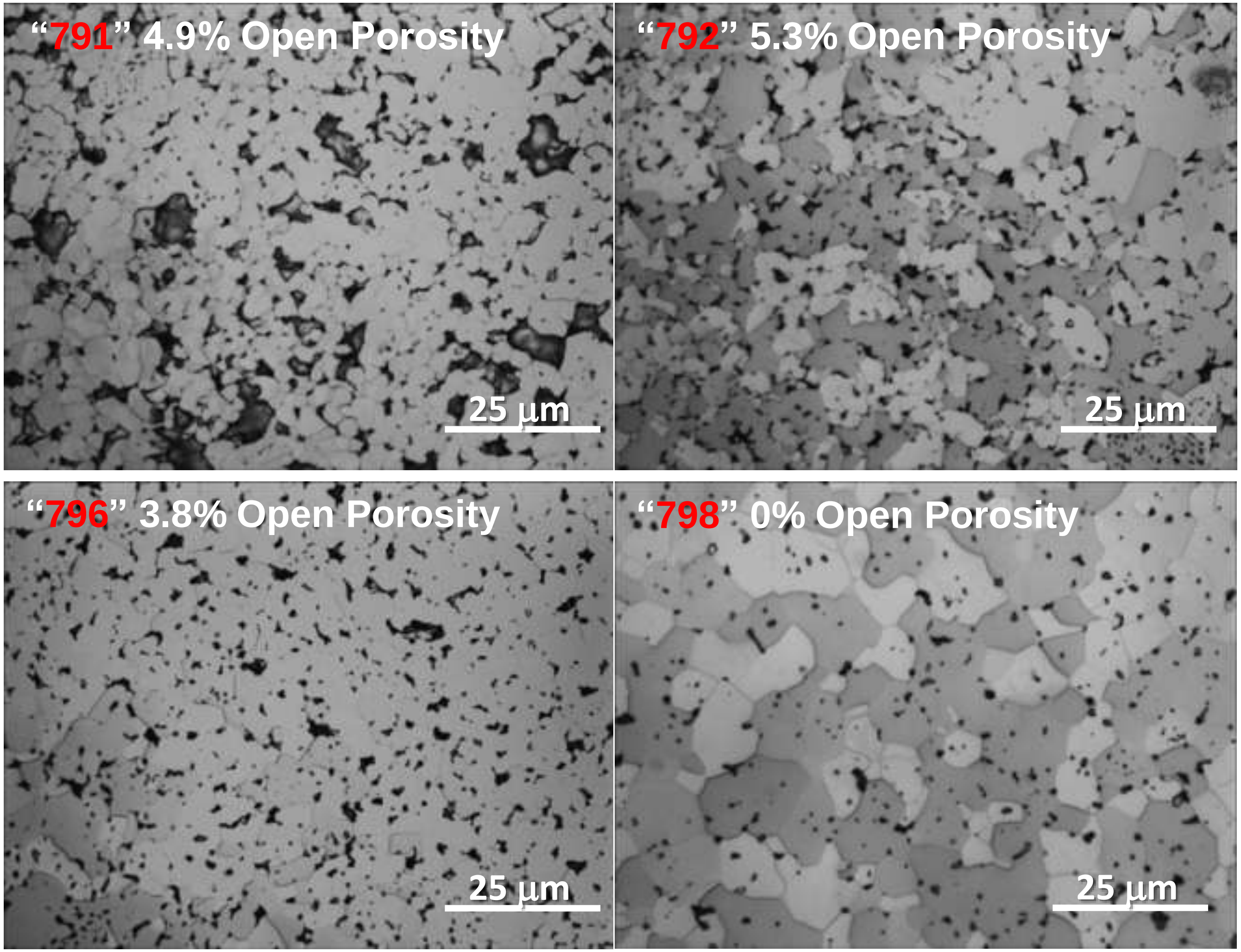
- **Pre-sinter conditions A=7**
- **Pressing conditions B=8-11**
- **Sinter conditions C=1, 2, 6, 8**





packing densities for the disks with C=1:	90.7-92.6%	diss. rates: ~0.6 g/min
packing densities for the disks with C=2:	90.3-93.6%	diss. rates: ~0.4 g/min
packing densities for the disks with C=6:	89.4-94.7%	diss. rates: ~0.28-0.14 g/min
packing densities for the disks with C=8:	93-94.7%	diss. rates: ~0.16-0.08 g/min (heating)

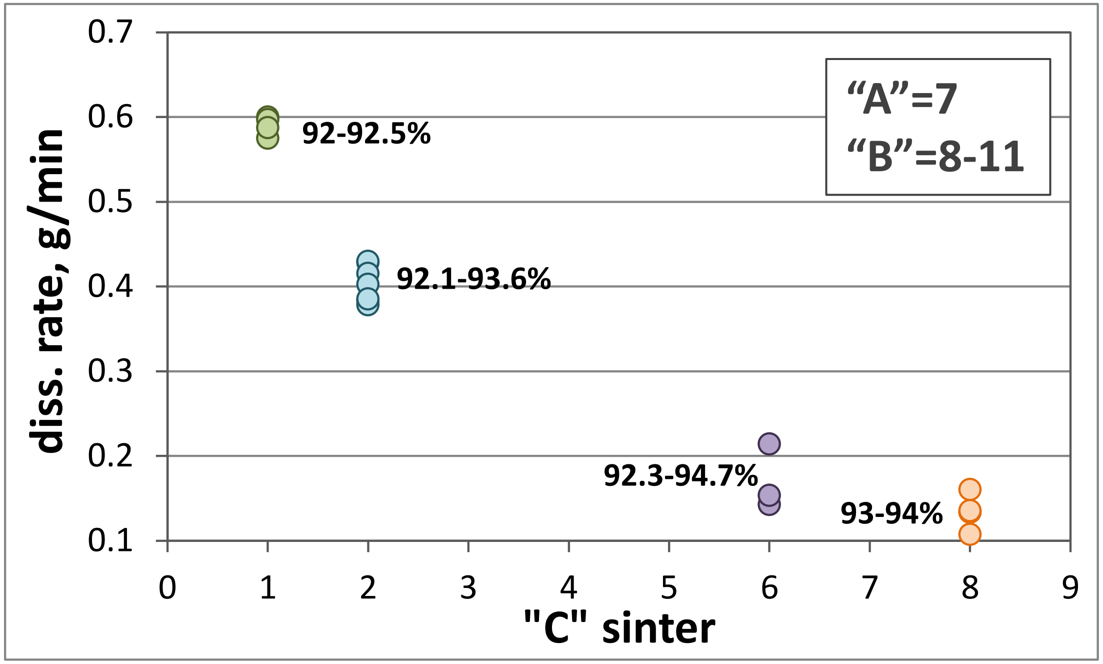
Effect of pressing conditions cont.



Optical micrographs of "791", "792" "796" and "798" disks provided by ORNL

Dissolution - summary

Dissolution rates of disks pre-sintered at A=7 and sintered at different conditions with densities ~92-94%



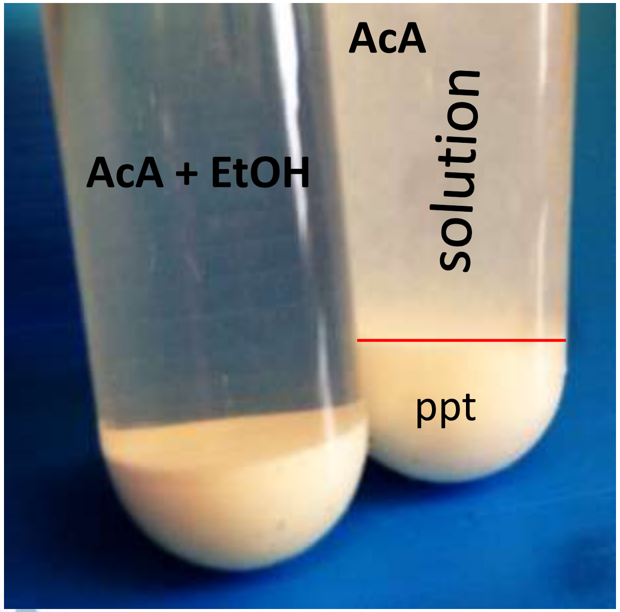
- Best dissolving disks are pre-sintered at higher temperature A=7-9 and sintered at C=1-2
- Densities for fastest dissolving disks (A=7-9, C=1-2) can be increased ≥92% by increased pressing parameter "B"
- Dissolution rates for disks with >90% density are mostly affected by "C" sintering conditions

Mo recovery

- Mo solution 0.2g-Mo/mL in 5M KOH: 1.8kg of K per 1kg of Mo
- Final product: **~25 ppm K** – ~99.999% of K needs to be removed,
- **>98% of Mo recovered**

Purification from potassium

Mo in 5M KOH precipitated using glacial CH_3COOH, CH_3CH_2OH or their mixture (H_2SO_4 also tested)



- Small-scale experiments with 1-5 mL of K_2MoO_4
- EtOH precipitate Mo as K_2MoO_4
- more ppt forms with AcA – Mo-acetate interaction cloudy solution containing Mo develops over time
- EtOH + AcA – no ppt. over time

Mo recovery

step	reagent	K removed	Mo loss	solution
Mo ppt	AcA; EtOH/AcA	65-75%	0-3%	cloudy; clear
wash 1	AcA	10-15%	<1%	clear
wash 2	HNO_3	5-10%	0-15%	cloudy
diss. + ppt	H_2O+NH_4OH - AcA ppt	0-5%	0 -3%	cloudy
wash 3	HNO_3	<0.5%	0-15%	cloudy
wash 4	HNO_3	<0.1%	0-2%	clear
wash 5	HNO_3	<0.1%	<0.5%	clear
wash 6	HNO_3	<0.1%	<0.5%	clear
wash 7	HNO_3	<0.1%	<0.5%	clear
wash 8	HNO_3	<0.1%	<0.5%	clear

HNO_3 wash

First 4 steps – 95-99% of potassium removed

99.9% purification – 1500 ppm of K

Optimizing Mo recovery – first washing steps are the most critical

Mo ppt formed after AcA – can be filtered

Mo ppt formed after HNO_3- very fine – cannot be filtered (0.2µm)

Mo recovery - potassium analysis

Mo precipitate after final wash – dissolved and analyzed by K^+ ISE, ICP-MS, ICP-OES

Sample matrix		Detection limit for K			Issues		
Mo	K	K^+ ISE	ICP-MS	ICP-OES	K^+ ISE	ICP-MS	ICP-OES
8000 ppm	0.2 ppm	0.2-0.4 ppm	>0.2 ppm	>1 ppm	Cation interfere	100 ppm TDS	Detection limit
25 ppm K/Mo							

#	ppt	wash	wash	Diss.+ppt	Wash 5x	K ppm/Mo		Mo yield
						K^+ ISE	ICP-MS	
A	EtOH	AcA	HNO_3	NH_4OH/AcA	HNO_3	54 ppm	103 ppm	100%
B	AcA/EtOH	AcA	HNO_3	NH_4OH/AcA	HNO_3	45 ppm	96 ppm	96.7%

~99.997% of K removed

Mo recovery - summary and future plans

- Good Mo recovery **97-100%** obtained if HNO_3 washes allowed to sit for several hours
- Purification of potassium **<100 ppm** (99.997% removed) – work continues
- XRD characterization of Mo precipitate – converting to MoO_3
- Side products purification experiments upcoming

Al, Zr, Nb, Rh, Sb (50 ppm/Mo), W (400 ppm/Mo)

If no selective purification:

Nb and W follow Mo (100%)

Al = 30-40 ppm (60-80%)

Sb = <20 ppm (30-40%)

Zr = ~1.4 ppm (2-3%)

Rh = ~0.6 ppm (~1%)

Possible purification options for side products

- Precipitation after dissolution of Mo target
- Cation exchange

    - before loading into generator

    - during Mo recovery process

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