Chemical Processing Activities for ^{99}Mo production by (γ,n) and (n,γ) reactions using enriched ^{100}Mo and ^{98}Mo targets

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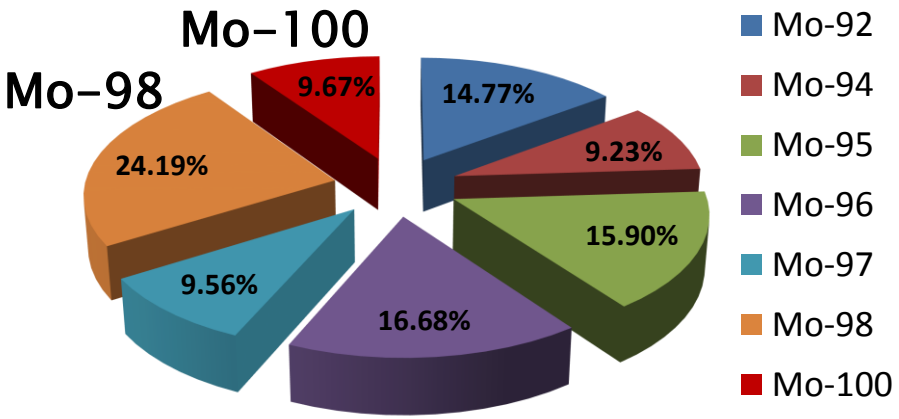
ANL support to NorthStar

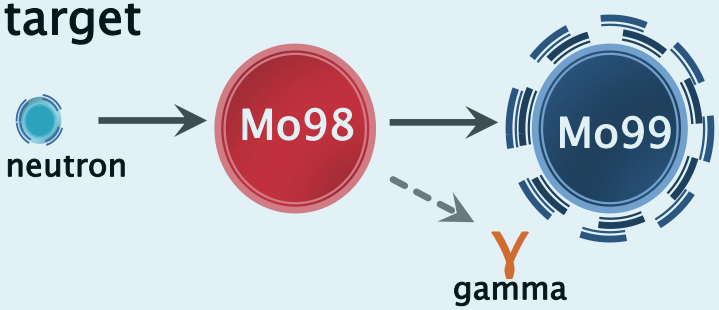
- Irradiation of sintered Mo targets using electron linac
- Chemical processing of irradiated targets
- Optimization of sintered Mo disks for density and dissolution kinetics
- Large scale dissolution process (300-600g of Mo per batch)
- Front-End purification of irradiated Mo
- Recycle process to recover valuable enriched ^{98}Mo and ^{100}Mo
- Radiation stability studies at VDG

Production of $^{99}Mo/^{99m}Tc$ without U targets

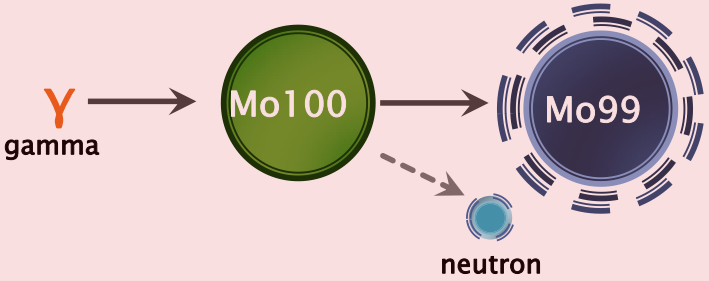


Enriched Mo-100 is available for ~$1000 per gram for kg quantities!!!

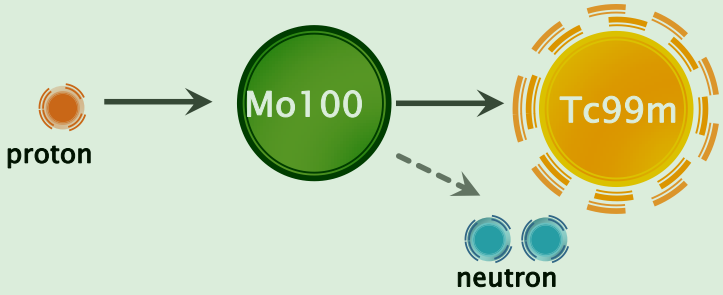
Reactor production on Mo target



Accelerator production

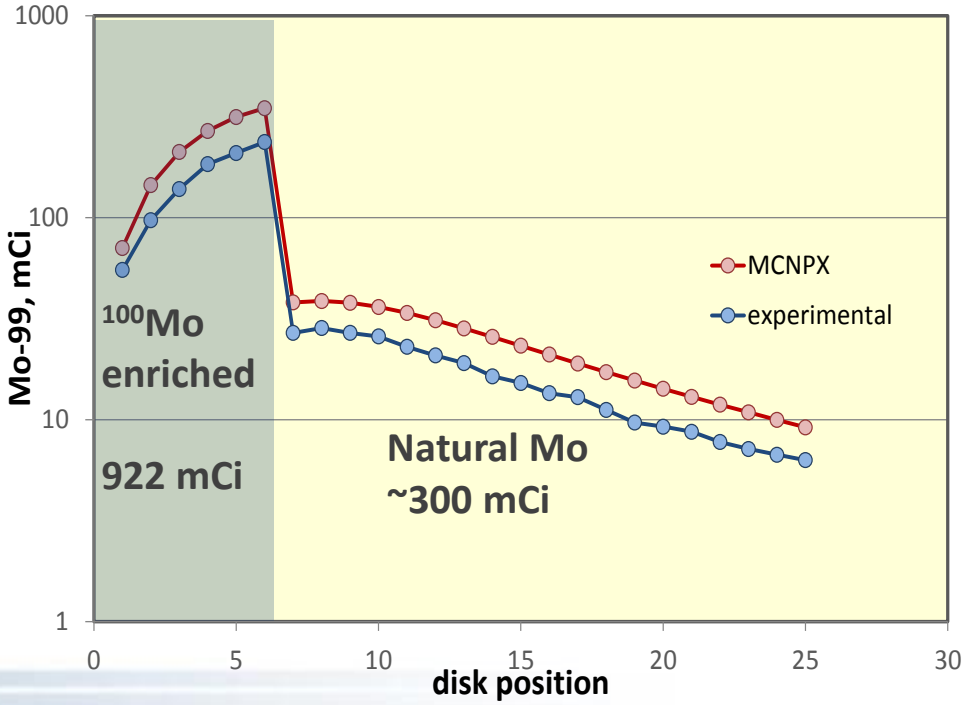


Cyclotron production

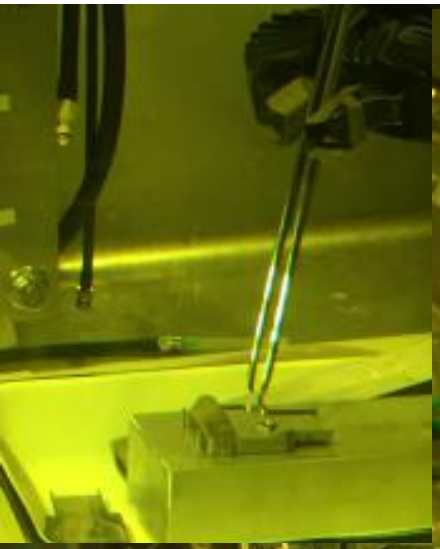
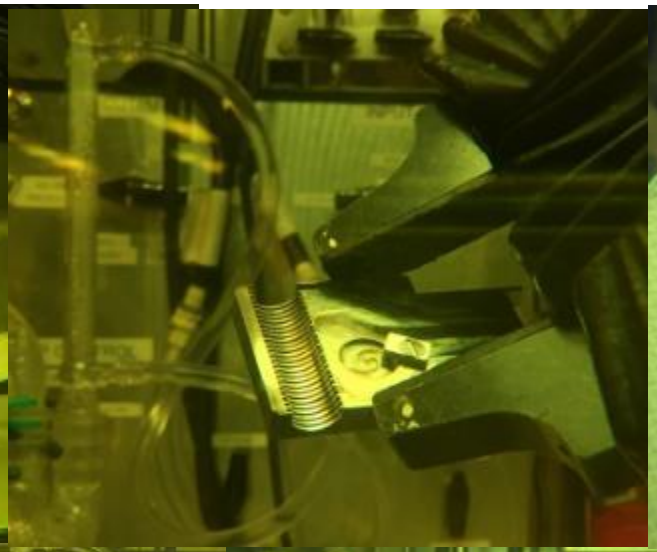
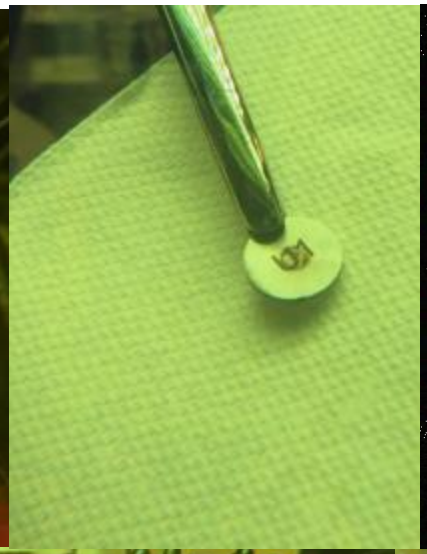


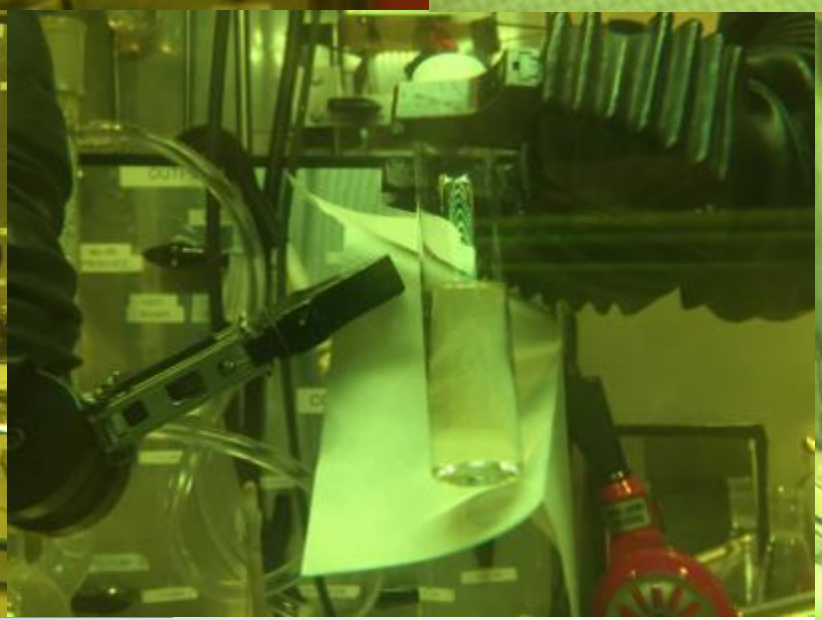
FY 15 production of ^{99}Mo at ANL

^{100}Mo (position)	^{99}Mo in 6 disks, Ci	power	Current	Time, hrs.	Energy
99% (1-6)	0.92	4kW	95μA	19	42 MeV
97.4% (3-8)	2.9	7.56kW	180μA	21	42MeV
95.1% (3-8)	2.2	7.56kW	180μA	19	42MeV
99% (3-8)	4.2	7.77kW	222μA	24.4	35MeV

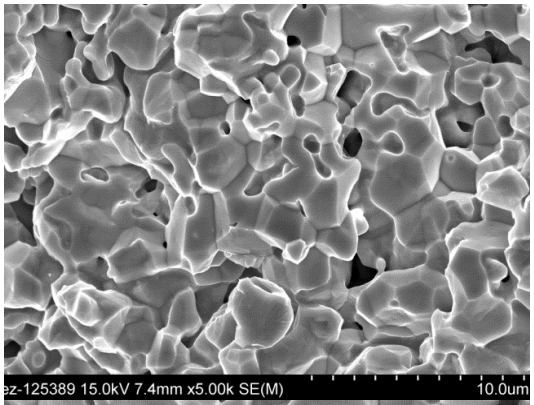


Processing of irradiated disks

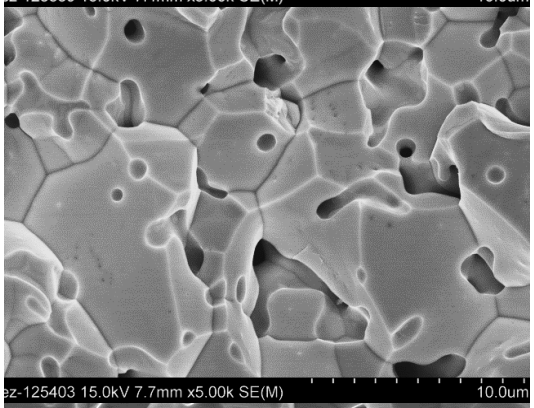




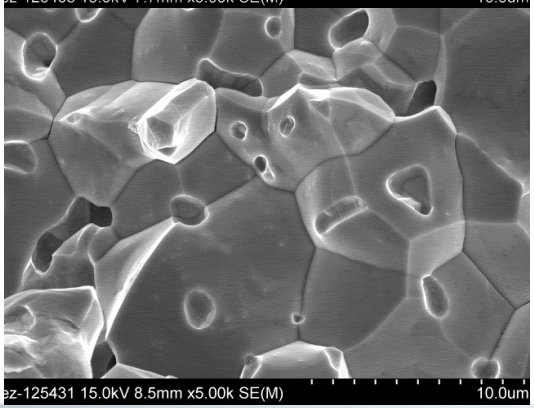

Optimizing sintered Mo disks production (ANL &ORNL)



1400°C
Density = 89.7%
Open Porosity = 7.1%
Diss. Rate = 0.623 g/min



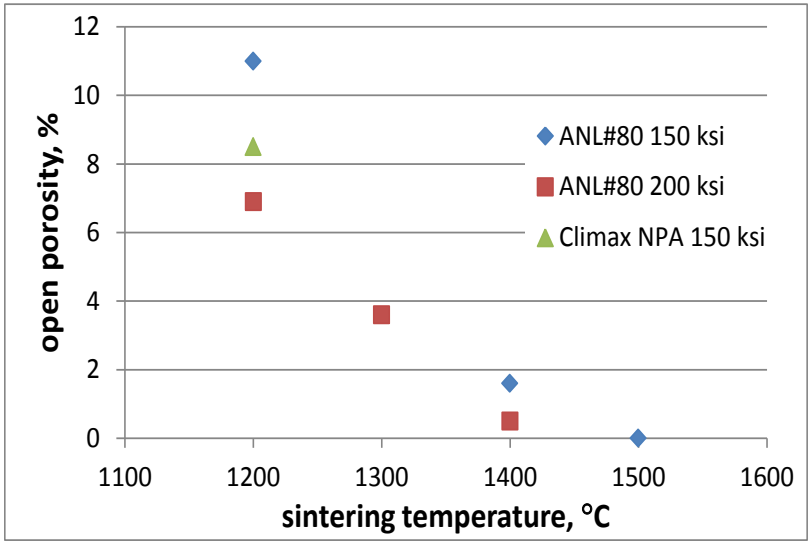
1500°C
Density = 91.9%
Open Porosity = 0.2%
Diss. Rate = 0.361 g/min

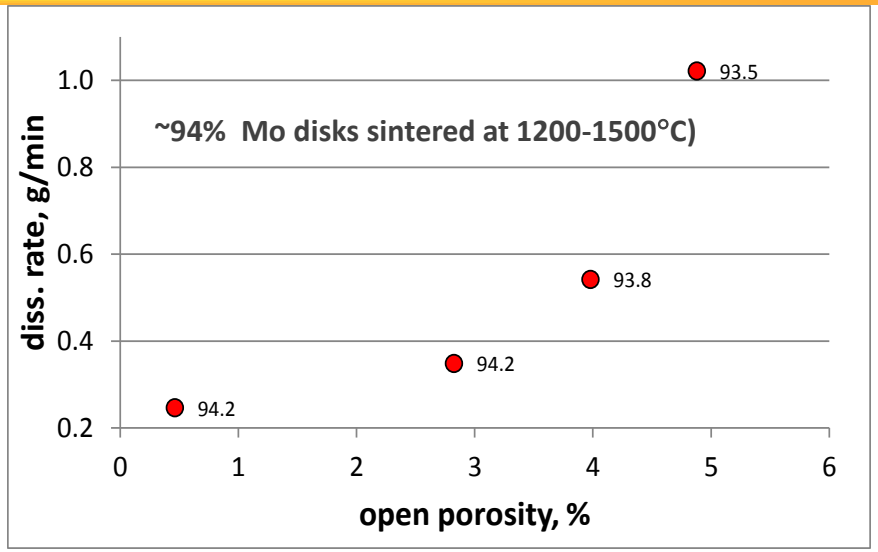


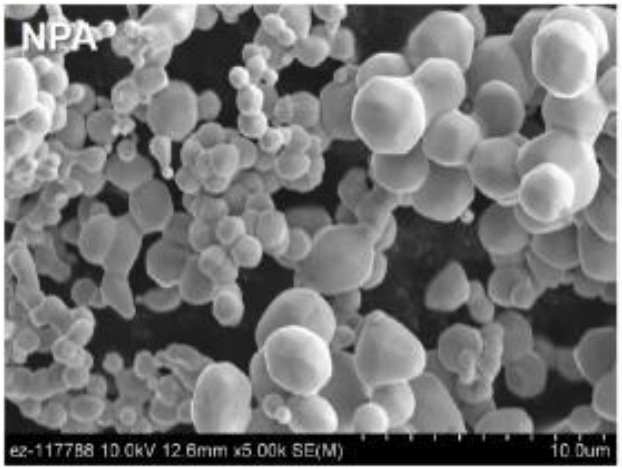
1600°C
Density = 94.0%
Open Porosity = 0%
Diss. Rate = 0.186 g/min

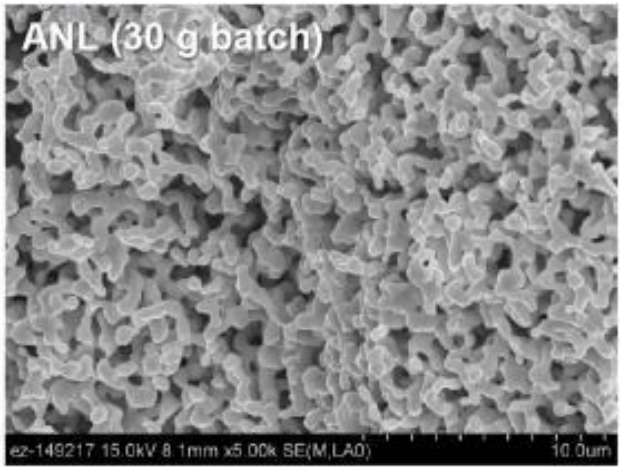
SEM Images provided by Steve Nunn (ORNL)

Optimizing sintered Mo disks production (ANL &ORNL)





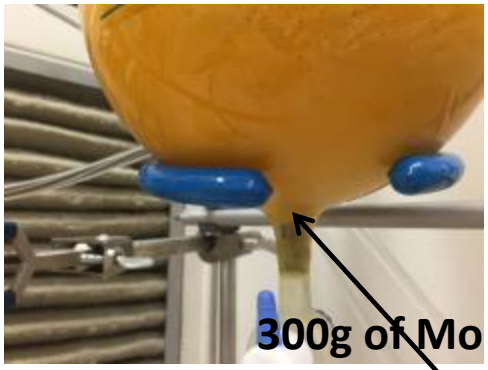


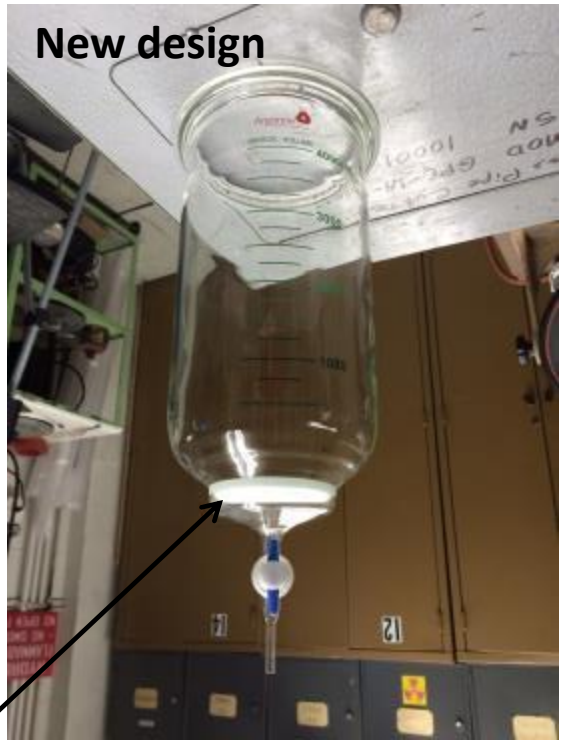


SEM Images of As-received Commercial NPA Powder and Reduced Small Batch (30 g) of ANL Recycled MoO_3 Powder. SEM images provided by Rick Lowden (ORNL).

Large scale dissolution processing

75g batch diss.
50% vs. 30% H_2O_2
Total processing time
1h40min vs 4hrs





Dissolution in H_2O_2 >>> evaporation/ H_2O_2 destruction >>> Fe co-precipitation of Zr&Nb >>> filtration >>> KOH added to make ~200g/L Mo in ~5M KOH

Large scale dissolution processing

Large scale dissolution processing

Large scale dissolution processing

#	H_2O_2, %	diss. vessel, L	Mo, g	dissolution, hrs	evaporation, hrs	total, hrs	concentration step
1	50	2	75	0.5	1.5	2	open to atm.
2	50	2	75	0.5	1.2	1.7	open to atm.
3	**30**	**2**	**75**	**0.5**	**3.5**	**4**	**open to atm.**
4	50	5	300	2	5.8	7.8	vacuum
5	50	5	300	2.7	6	8.7	vacuum
6	50	5	300	2	6.8	8.8	vacuum
7	**30**	**5**	**300**	**1.4**	**6.4**	**7.8**	**vacuum**
8	**50**	**5**	**300**	**1.5**	**0.6**	**2.3**	**vacuum**
9	**50**	**5**	**300**	**1.3**	**0.7**	**2.2**	**vacuum**

Removal of Zr and Nb

pH	Removal of Zr and Nb, %					
	filtration 0.22µm	0.7% vol Fe(III)	4% vol Fe(III)	0.7% vol Fe(III)+Fe(II)	4% vol Fe(III)+Fe(II)	10mg/mL HZO
12	99.9	99.0	98.9	99.5	99.7	99.9
13	99.9	99.9	99.1	100	99.7	100
14	99.3	99.2	99.6	99.3	99.6	99.5
5M OH^-	72.5	73	76.8	73.3	73.7	84.4

pH	Removal of Zr and Nb with 1µl/mL 30% H_2O_2, %					
	filtration 0.22µm	4% vol Fe(III)	4% vol Fe(III)+Fe(II)	10% vol La(III)	magnetite Fe_3O_4	10mg/mL HZO
12	82.4	83.2	75.4	95.4	16.8	76.8
13	74.4	77.8	99.8	100	83.5	99.9
14	19.6	37.2	95.3	77.6	3	45.7
5M OH^-	7.6	37.6	62.1	55.2	2	15.6

Fe=1M, La=10mg/mL

Large scale recovery of Mo by precipitation

- 1.5L of spent generator solution in 5M KOH containing ~300 g of Mo (MURR samples)
- **80% of K removed in AcA precipitation**
- Mo precipitate washed with conc. HNO_3 (~7.5L of HNO_3 per wash, up to 9-10 washes are needed) **~75L of conc. HNO_3 used per batch**
- Remove residual HNO_3 by heating
- Final Mo product as MoO_3 ready for reduction

Mo recovery: ~95%, product MoO_3
K concentration in purified product <100mg-K/kg-Mo

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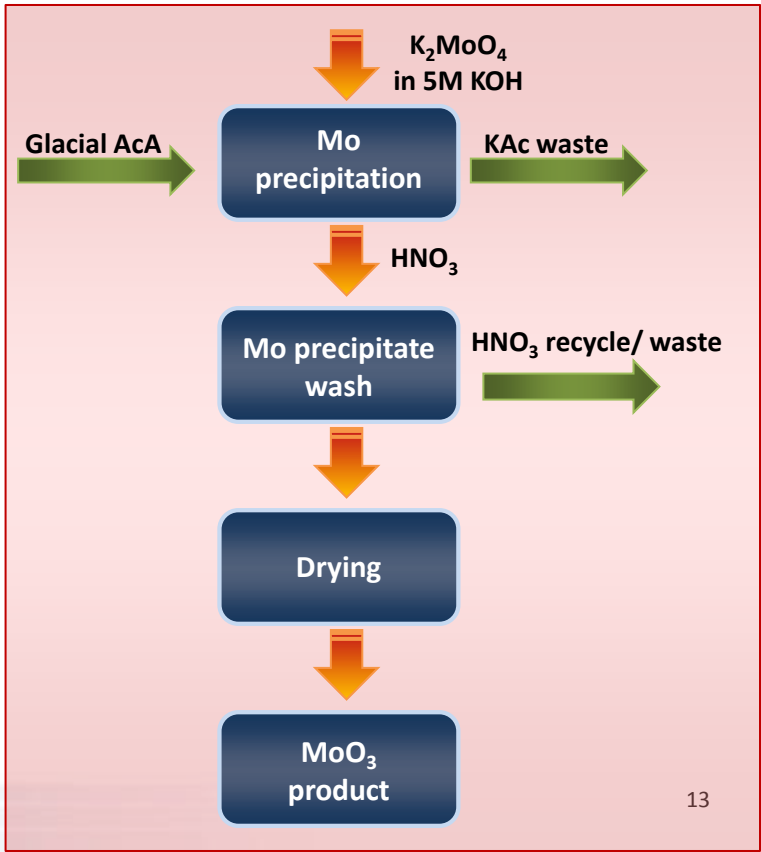
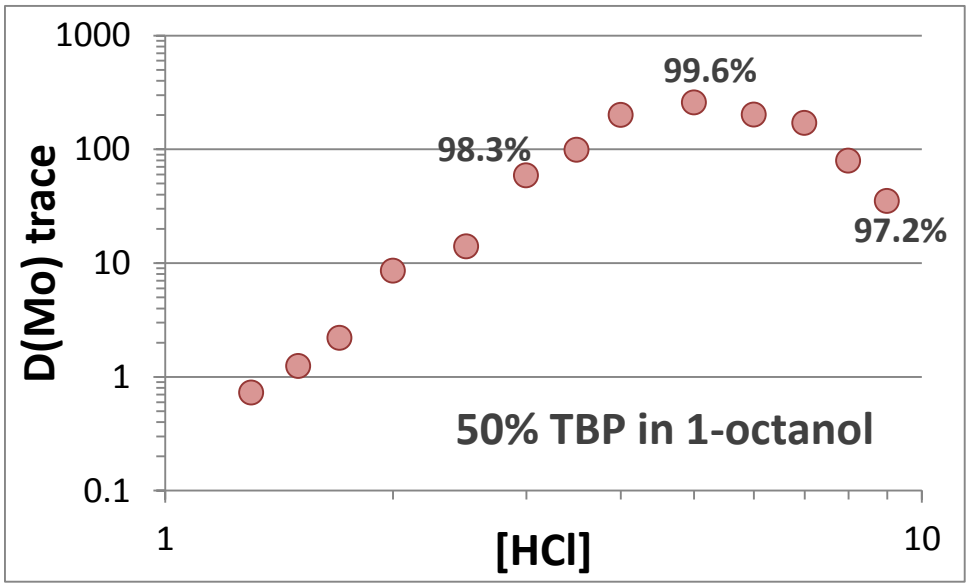
http://link.springer.com/article/10.1007/s10967-015-4357-1



Recovery of Mo by solvent extraction (tributyl phosphate)



Distribution ratio:

$$D_{Me} = \frac{[Me]_{org}}{[Me]_{aq}}$$

K distribution ratio

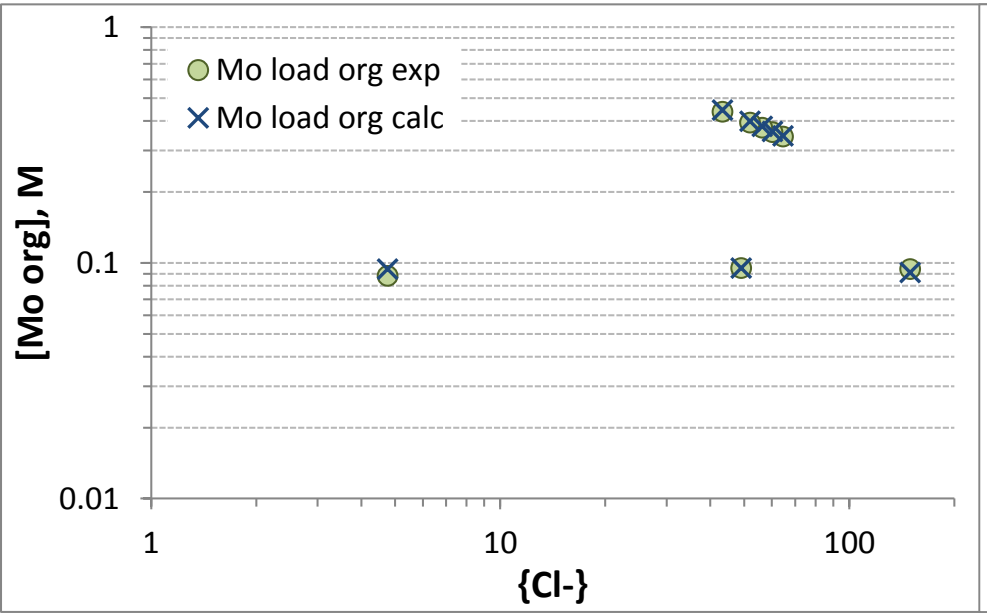
$D_K = 1 \times 10^{-4} - 1 \times 10^{-5}$

Mo, M	HCl, M	Extr. %
0.35	7.1	97.6%
0.36	6.9	97.5%
0.38	6.8	97.1%
0.40	6.6	97.4%
0.45	6.2	97.2%

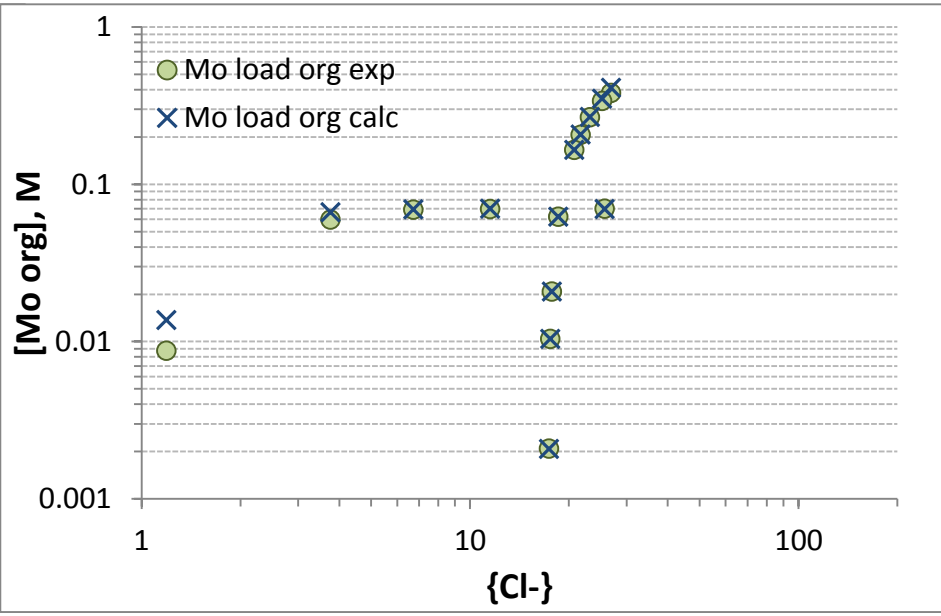
50% TBP in 1-octanol

Recovery of Mo by solvent extraction-extraction modeling

50% TBP in 1-octanol



30% TBP in tetrachloroethylene

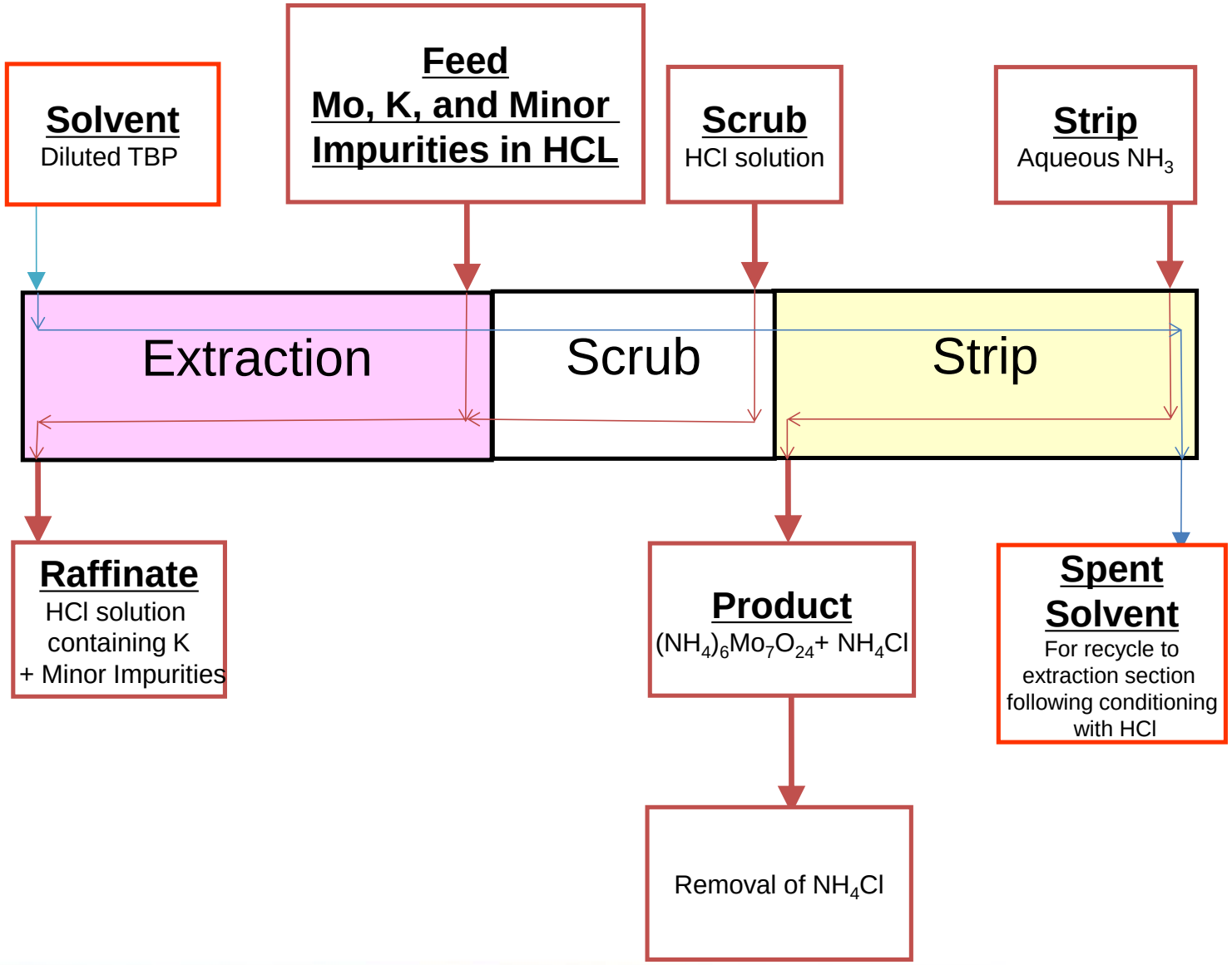


Extraction constants determined for two Mo-TBP species:

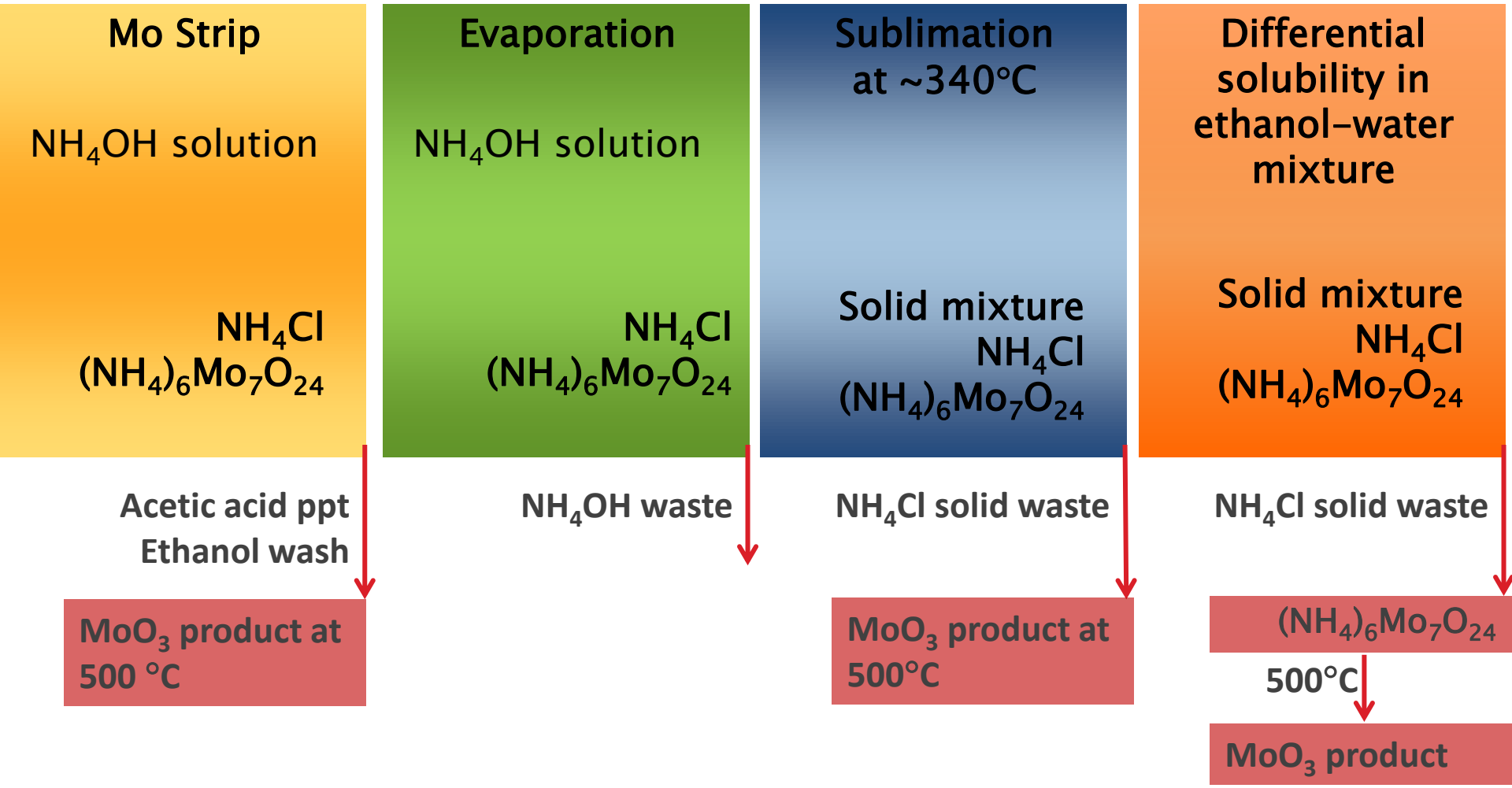
$HMoO_2Cl_3 \cdot 2TBP$

$MoO_2Cl_2 \cdot (TBP \cdot HCl)_2$

Recovery of Mo by solvent extraction



Recovery of Mo by solvent extraction-back end processes



Recovery of Mo by solvent extraction


Mo ppt after wash with AcA and EtOH


Mo ppt after heating at 500°C


Ammonium molybdate $(NH_4)_6Mo_7O_{24}\cdot xH_2O$

~500g of MoO_3 sent to ORNL for reduction to Mo metal and production of sintered Mo disks


Mo ppt after heating at 500°C

Recovery of Mo by solvent extraction

	Mo in KOH	5M HCl	strip	ammonium molybdate	MoO_3
	ppm (mg/kg-Mo)				
B	ND	ND	2.0	9.1	ND
Na	9439	9712	24.7	10.9	9.3
Mg	29.6	21.7	4.8	4.0	5.1
Al	8.3	8.46	2.8	ND	ND
Si	ND	ND	ND	ND	ND
P	ND	ND	1838	ND	ND
Ti	26.7	64.1	37.3	13.7	12.4
Cr	ND	ND	5.2	ND	ND
Mn	1.9	0.55	0.4	ND	ND
Fe	ND	ND	ND	ND	ND
Co	ND	ND	ND	ND	ND
Ni	ND	ND	0.8	ND	ND
Cu	5255	7.7	23.3	ND	7.8
Zn	12.4	ND	24.6	2.4	3.1
Zr	0.6	0.37	0.1	ND	ND
Nb	2.8	1.53	1.5	2.9	2.7
Sn	86.2	19.2	22.3	24.0	20.5
Sb	4.7	4.1	4.2	ND	ND
Cs	0.8	0.66	0.7	0.2	0.1
W	237	259	138	164	159
K	**1933673**	**1217949**	**454**	**257**	**233**
K (%)	**100%**	**63.0%**	**0.023%**	**0.013%**	**0.012%**

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