

Dissolution studies on molybdenum-based inert matrix fuels for the transmutation of minor actinides

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Rationale

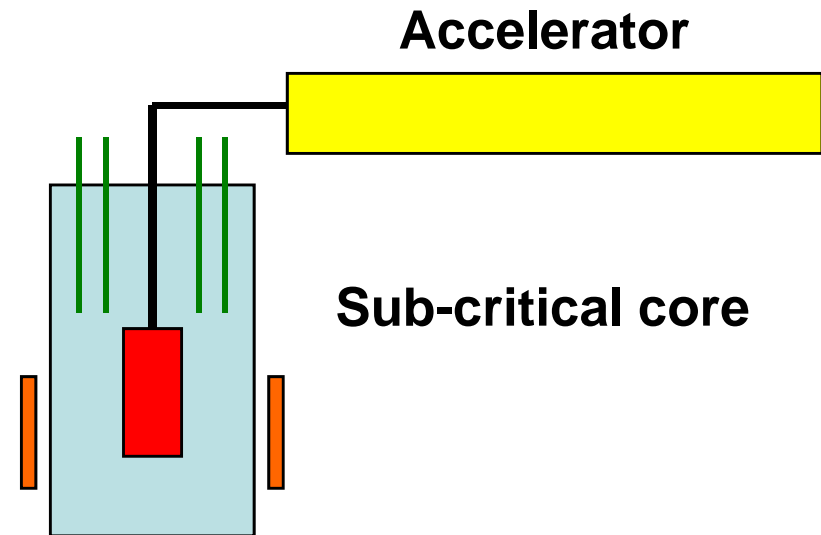
- New reactor concepts, novel fuels and their reprocessing
 - Studied in several European countries
 - However, by different scientific communities
 - Weak interaction

- Irradiation - Separation:
ASGARD closes the cycle



Inert Matrix Fuels (IMF)

- Promising fuel candidate for MA transmutation in ADS reactors
- Heterogeneous recycling
- High content of Pu and MA
- ^{238}U free
- Inert matrix
 - thermal properties
 - Low absorption of neutrons
 - Good radiation stability
 - (Pu,MA)-oxide/MgO (CerCer)
 - **(Pu,MA)-oxide/ ^{92}Mo (CerMet)**



ADS « FUEL CYCLE »

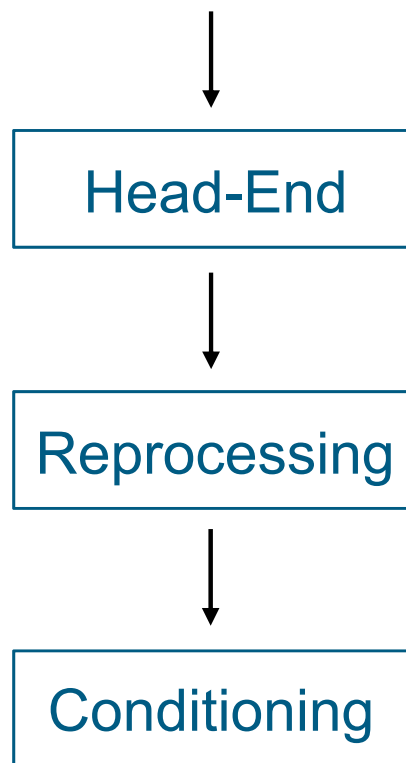
- ☺ High content of minor actinides
- ☹ Necessity to often recycle (core stability)
- ☹ Specific fuels, specific separation processes?
- ☹ Waste management of inert matrix *elements*

Potential problems during reprocessing of IMF

Goal: Recovery of ^{92}Mo



CerMet (Pu,MA)-oxide/ ^{92}Mo



- Complete or selective dissolution
- Polymeric Mo species at high acid and Mo concentrations (precipitation problem)
- TBP: Mo is not extractable
- DIAMEX/SANEX: Mo extractable, masking agents are needed (e.g. oxalic acid)
- Recovery of ^{92}Mo is desirable

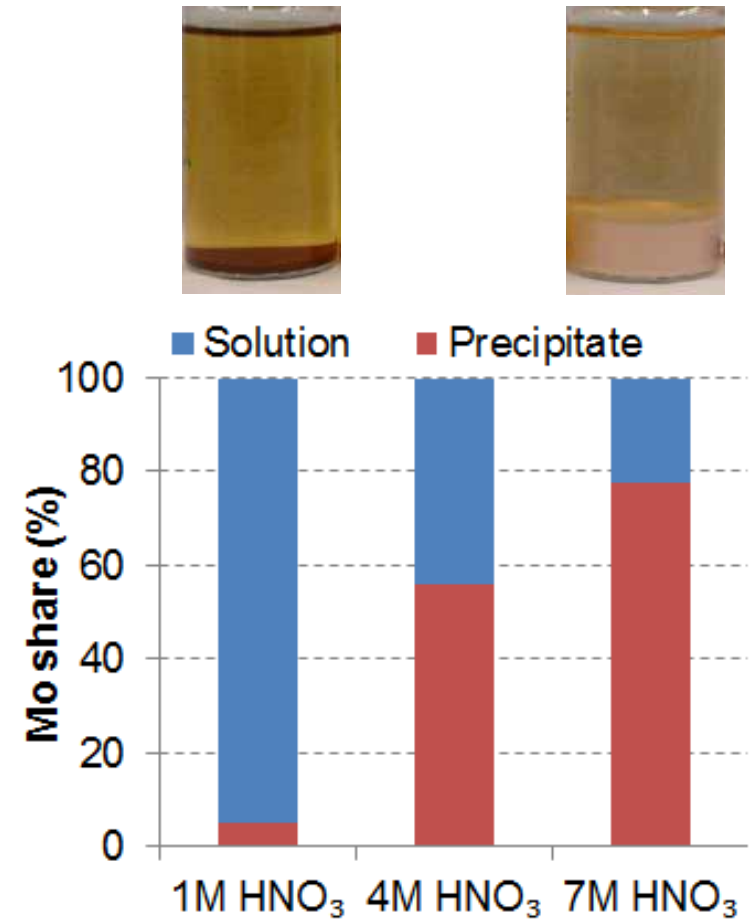
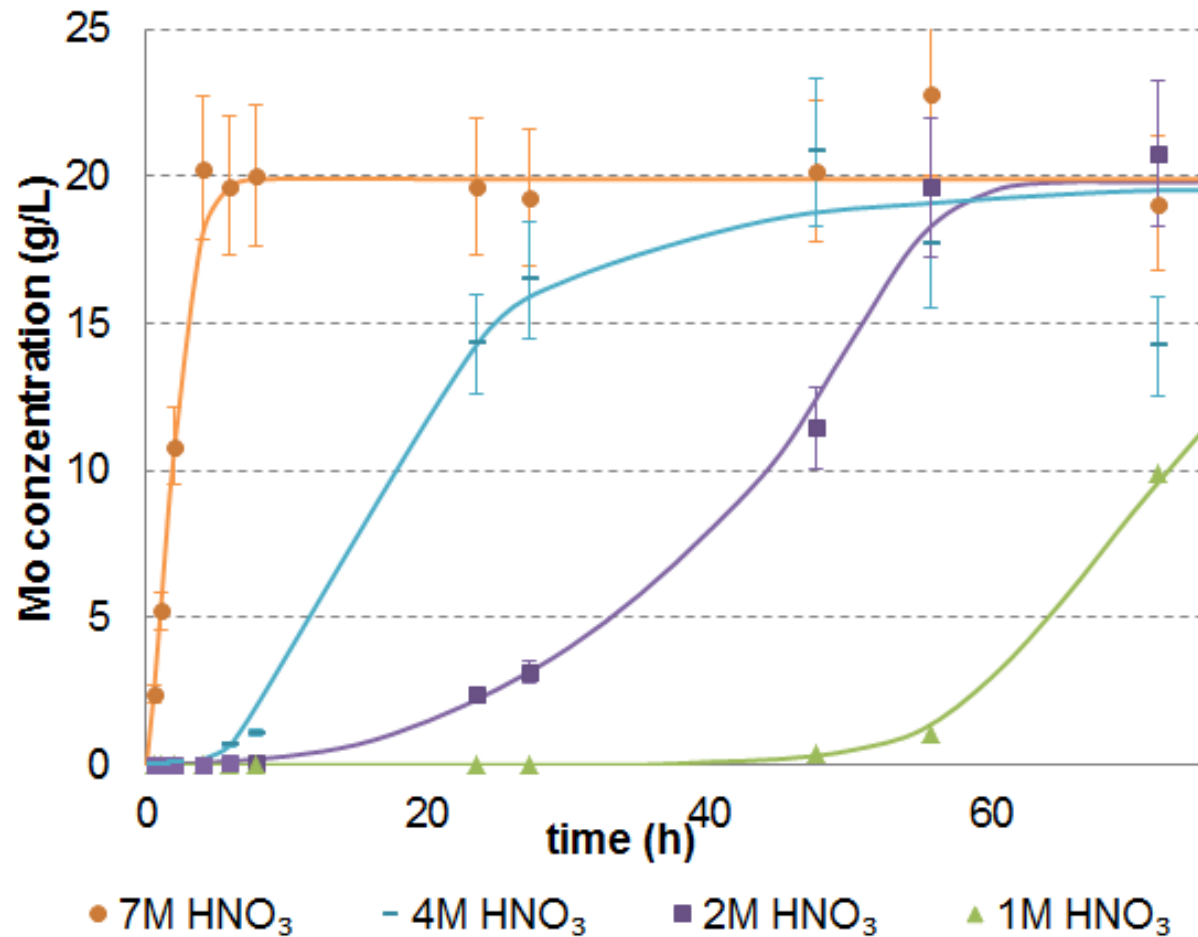
Ideal situation: Separation of Mo during dissolution process

Objective

- Preparation of reference samples
 - Mo
 - Mo/CeO₂
 - Mo/PuO₂
- Characterization
 - Density measurements
 - SEM
 - XRD
- Dissolution experiments
 - HNO₃ concentration
 - Temperature
 - Influence of Fe(III)
- Speciation
 - Electrospray Ionisation Mass Spectrometry

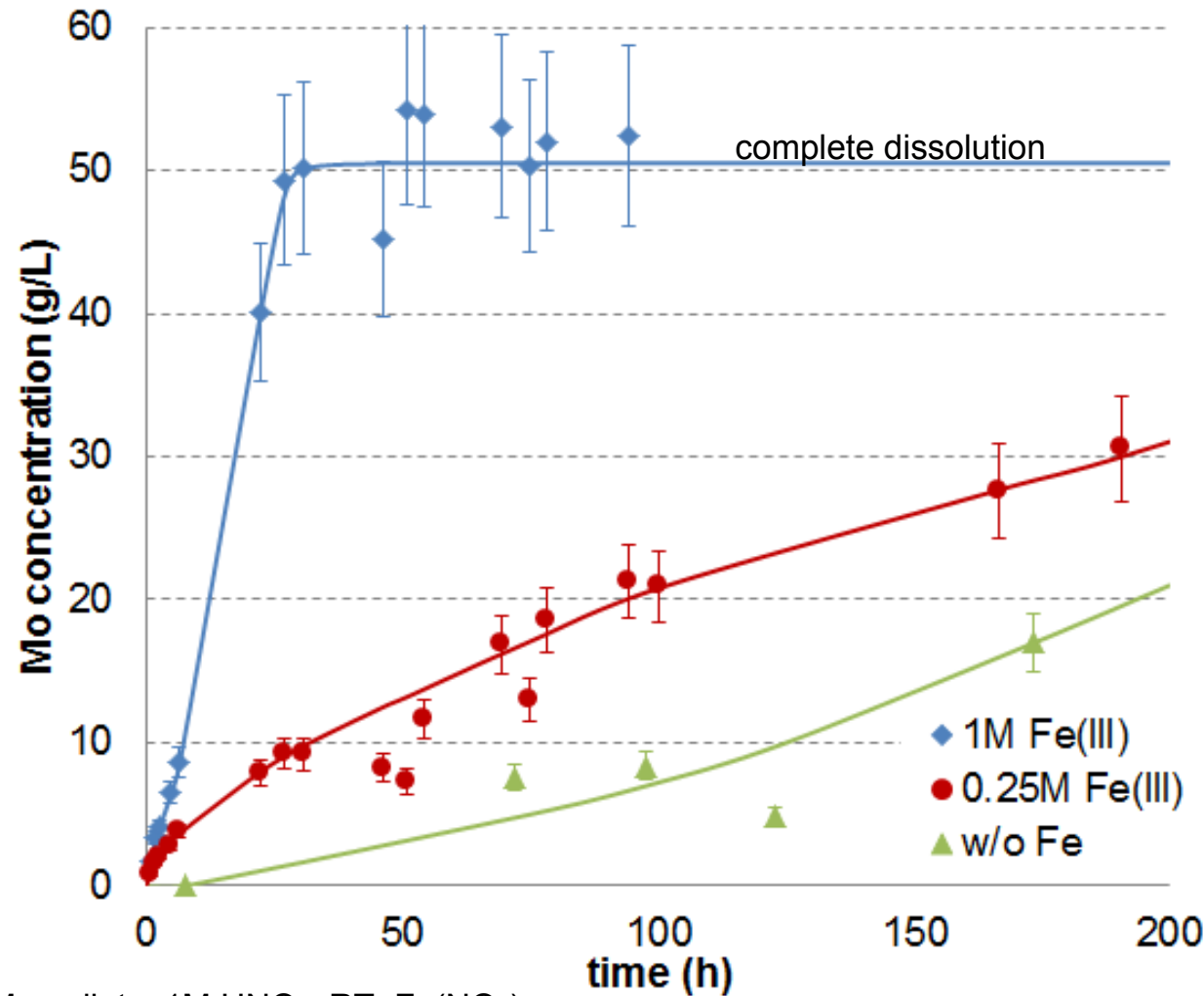
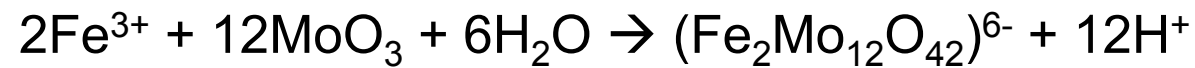


Mo pellet dissolution



Mo pellets (P = 640 MPa, argon atmosphere, T_S = 1600 °C, ρ_S = 91.5%TD), HNO₃, RT

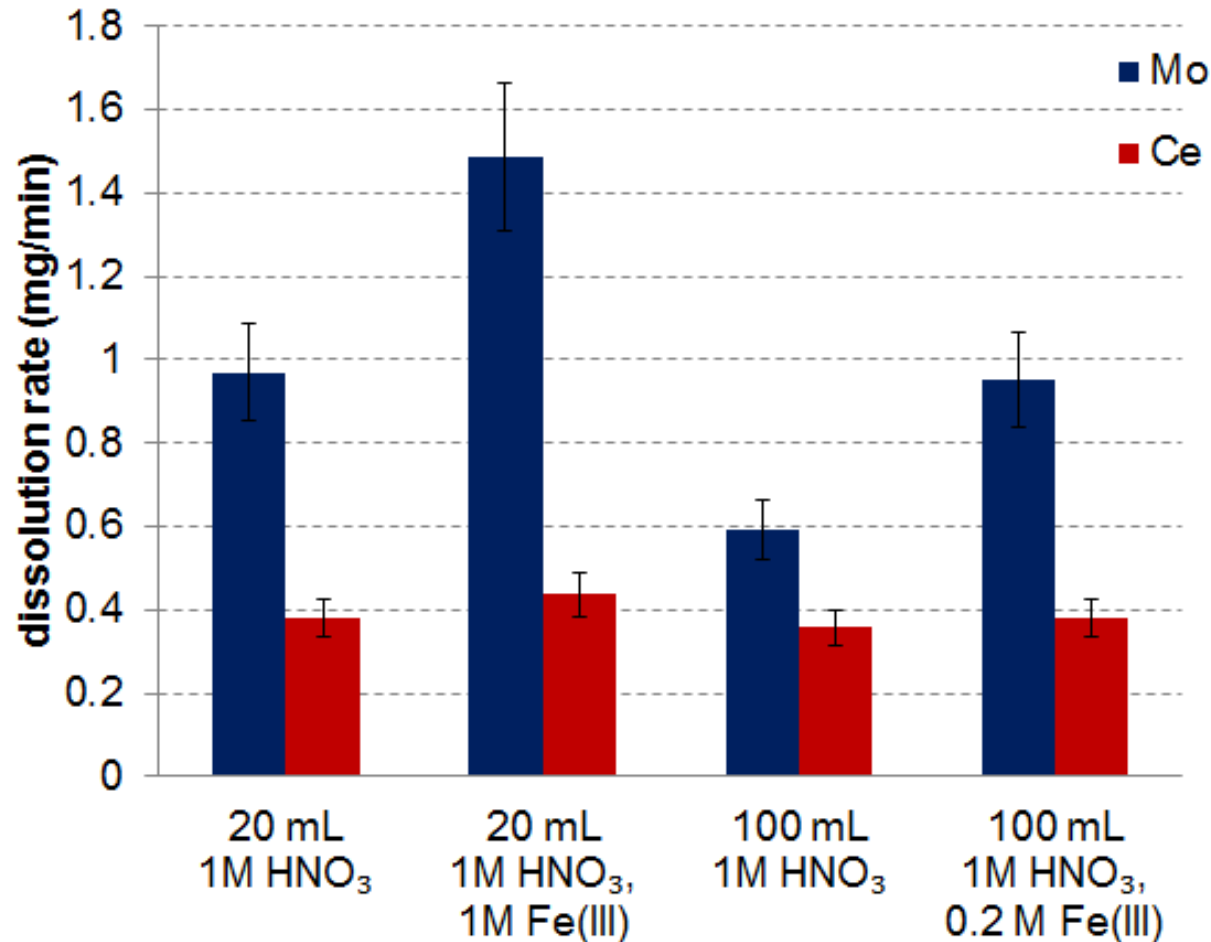
Influence of iron



- Fe(III) increases solubility
- Fe(III) increases dissolution velocity significantly
- Complete dissolution Mo:Fe 1:2

Mo pellets, 1M HNO₃, RT, Fe(NO₃)₃

Dissolution of mixed Mo/CeO₂ pellets

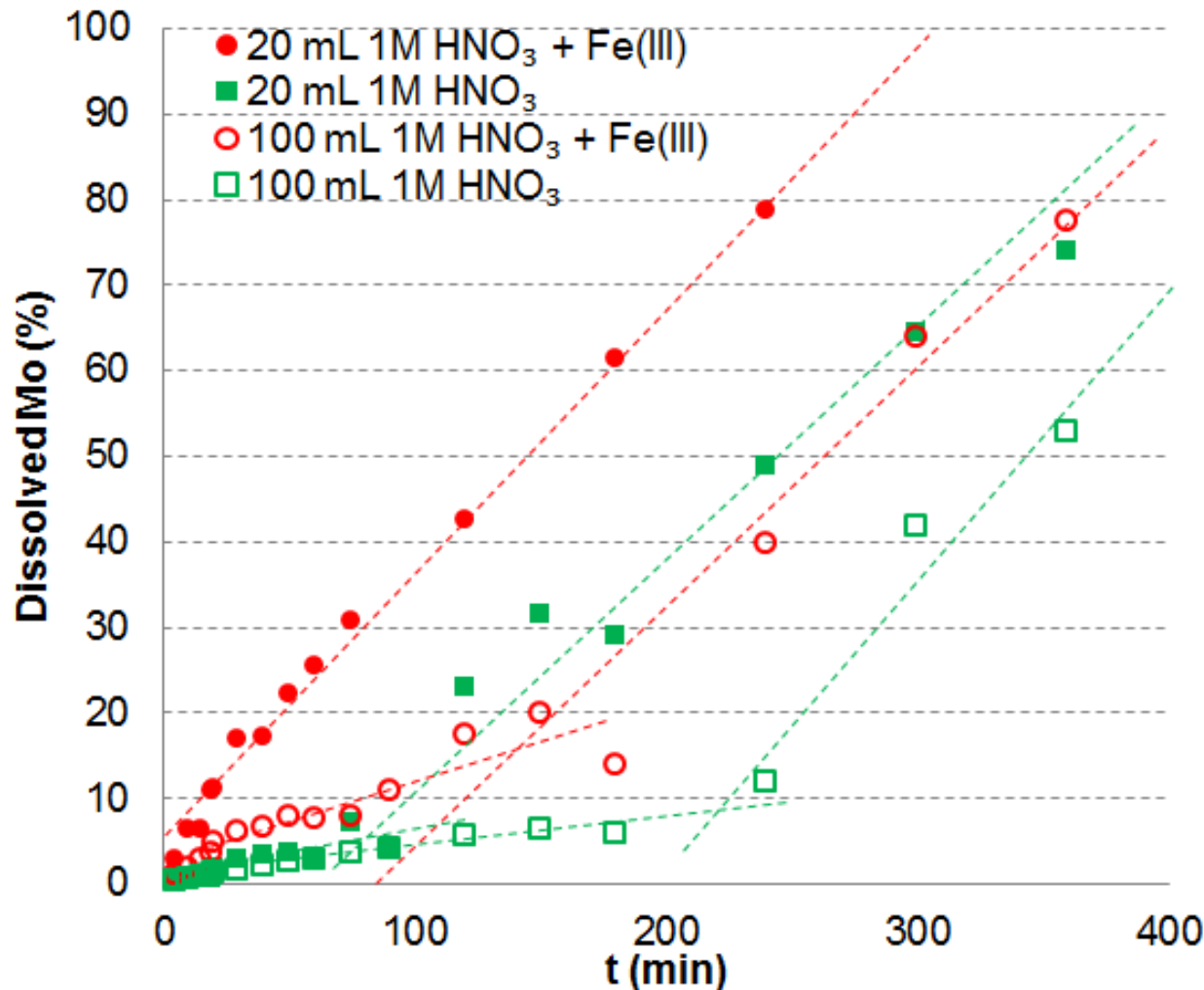


- Initial dissolution rate of Ce is not influenced
- Initial dissolution rate of Mo is higher
 - In the presence of iron
 - In 20 mL acid

Mo/CeO₂ (60/40wt.%) pellets (P = 640 MPa, argon atmosphere, T_S = 1600 °C, ρ_S = 89.3%TD), RT

Dissolution of mixed Mo/CeO₂ pellets

Mo dissolution



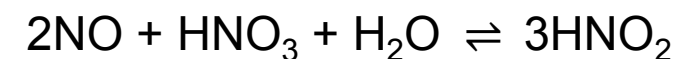
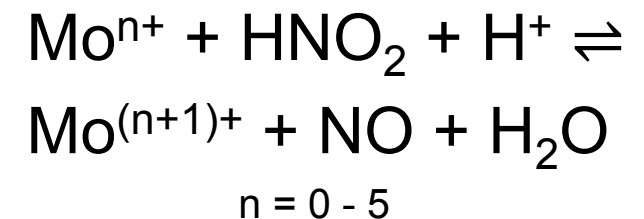
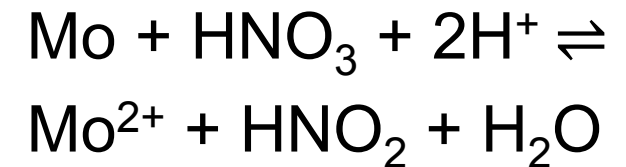
Mo/CeO₂ (60/40wt.%) pellets, RT, Fe(III):Mo ratio 2:1

Elcheikh et al., Annali di chimica 1983.

Delwaille et al., Chem. Eng. J. 2011.

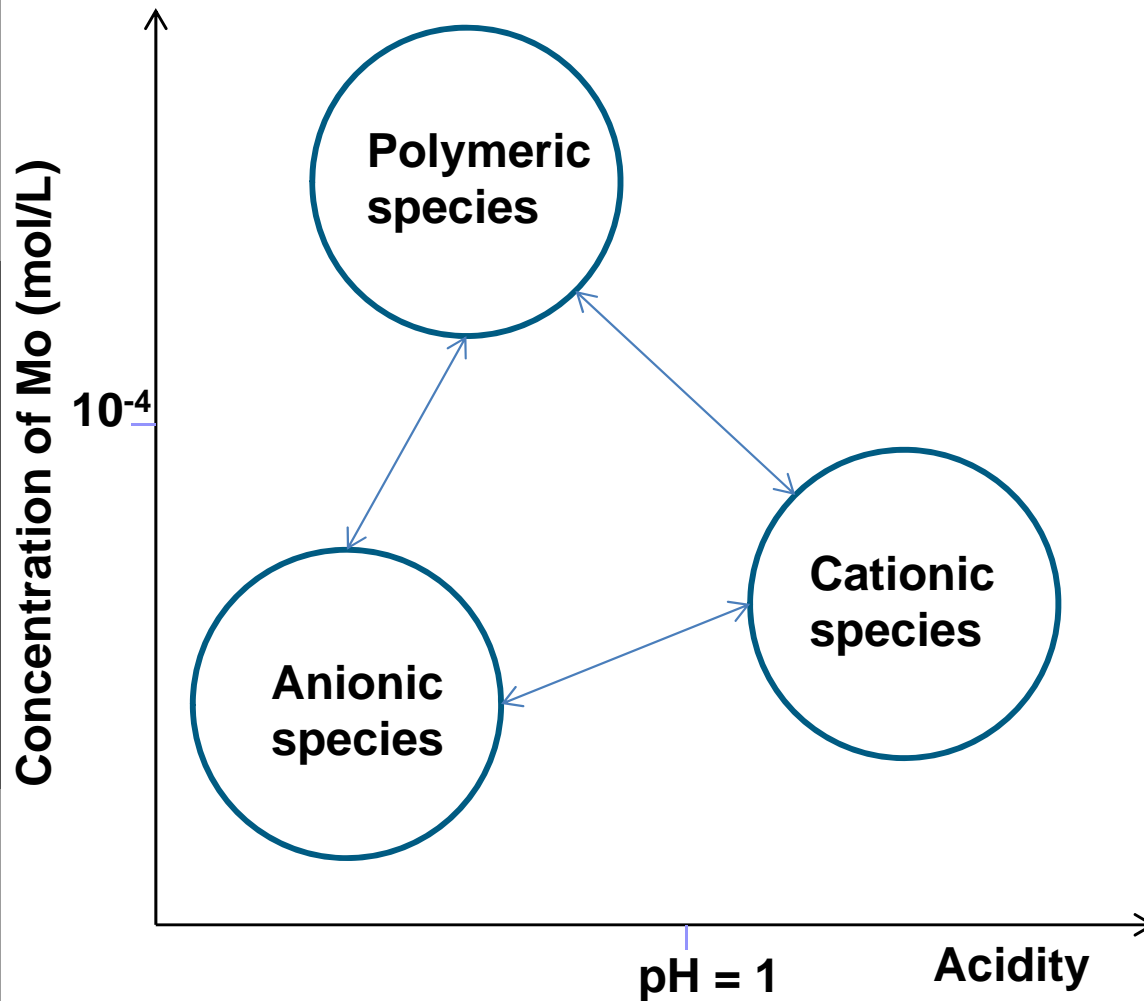
Haleem and Aal, J. Mat. Process. Tech. 2008.

- HNO₂ autocatalysis

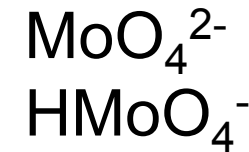


- Incubation period
 - Shortened by higher HNO₂ concentration in 20 mL

Molybdenum speciation in strongly acidic media



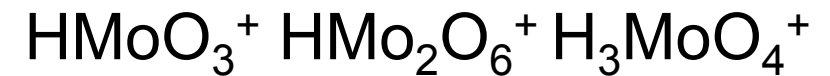
Anionic species



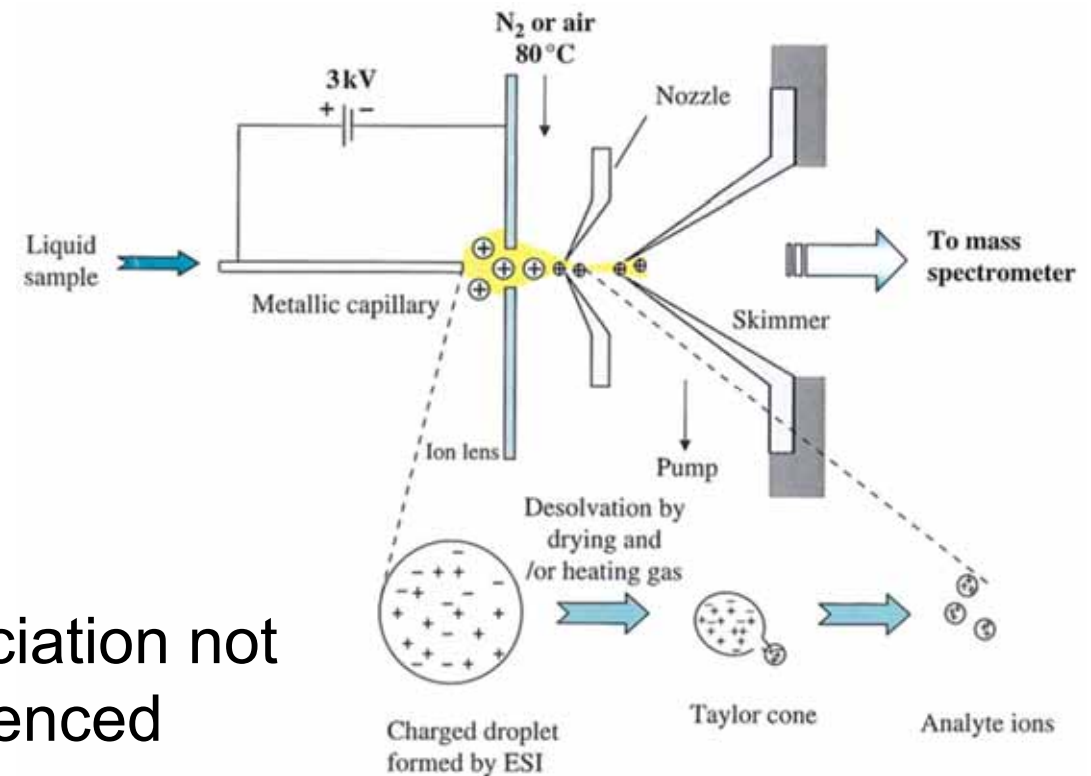
Polymeric species



Cationic species



Nano Electrospray Ionization process

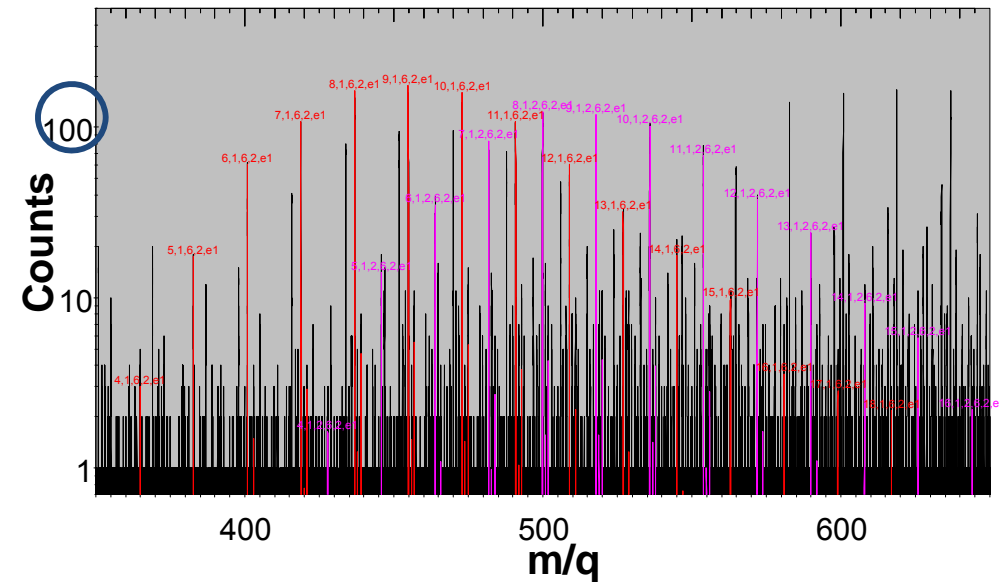
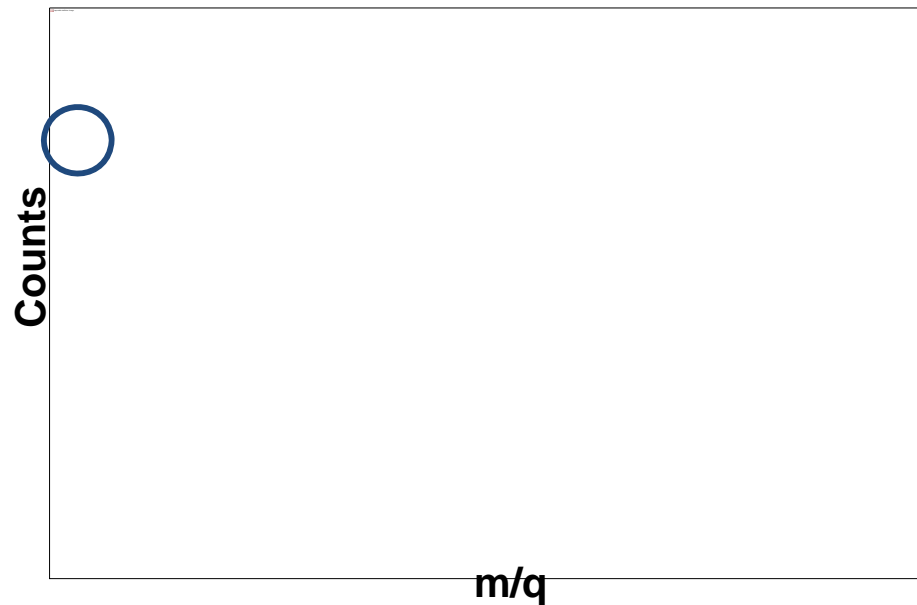


- + very soft ionization
 - + no fragmentation
 - + minor species detectable
 - + less artifacts formed (cf. conventional ESI)
 - + ToF covers large mass range
 - + isobaric resolution
 - only charged species detectable
- } Speciation not influenced

ESI-ToF: natMo versus ⁹⁸Mo

Mo 91	Mo 92	Mo 93	Mo 94	Mo 95	Mo 96	Mo 97	Mo 98	Mo 99	Mo 100
14.53	9.15	15.64	16.67	3.60	24.36	65.970 h	9.82	14.6	
Nb 90	Nb 91	Nb 92	Nb 93	Nb 94	Nb 95	Nb 96	Nb 97	Nb 98	Nb 99
10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2	10.2

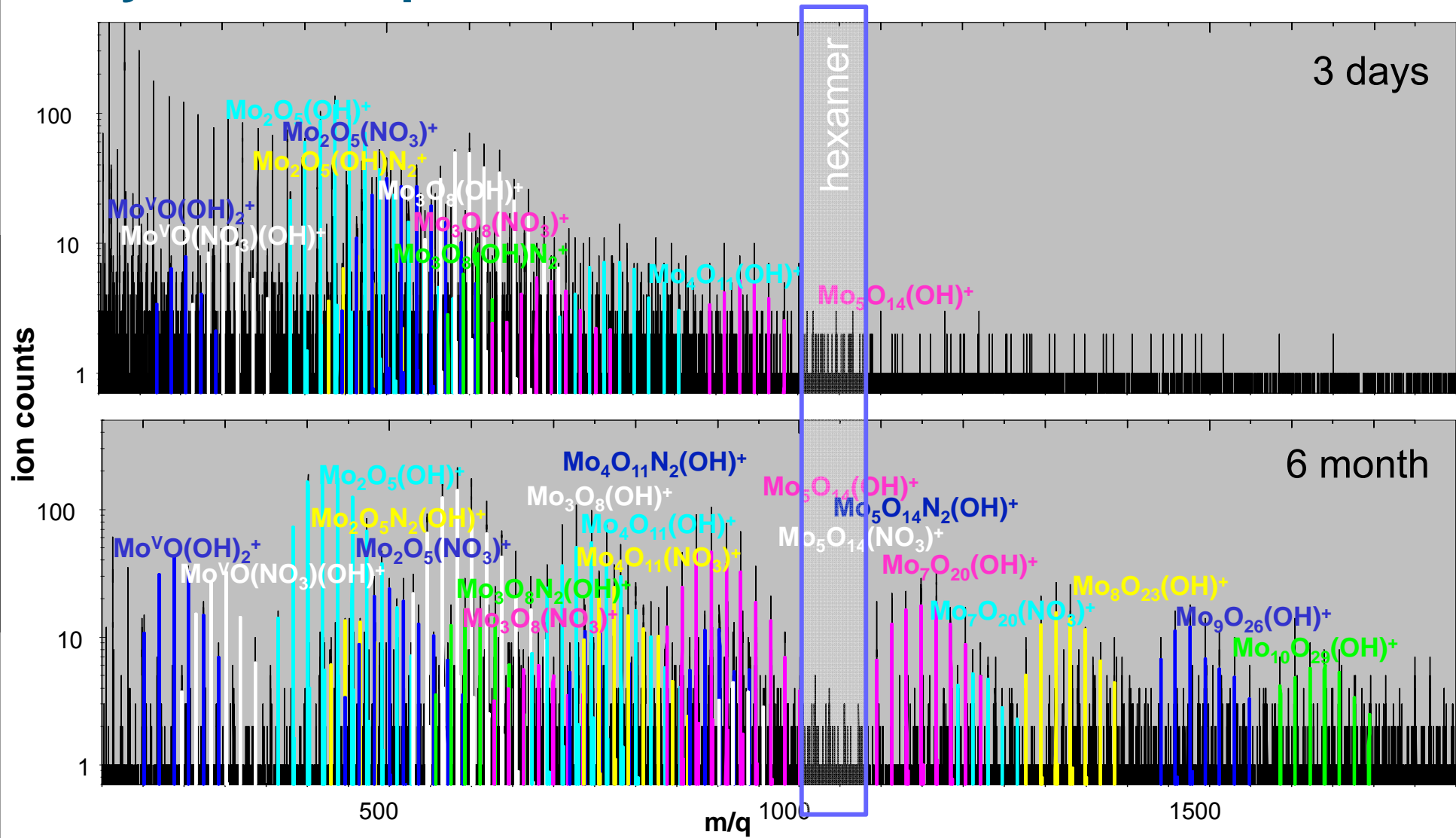
Mo 97	Mo 98	Mo 99
24.36	65.970 h	9.82
Nb 96	Nb 97	Nb 98
10.2	10.2	10.2



- low intensity
- superimpose
- Long measurement time

- higher intensity
- clearly to identify

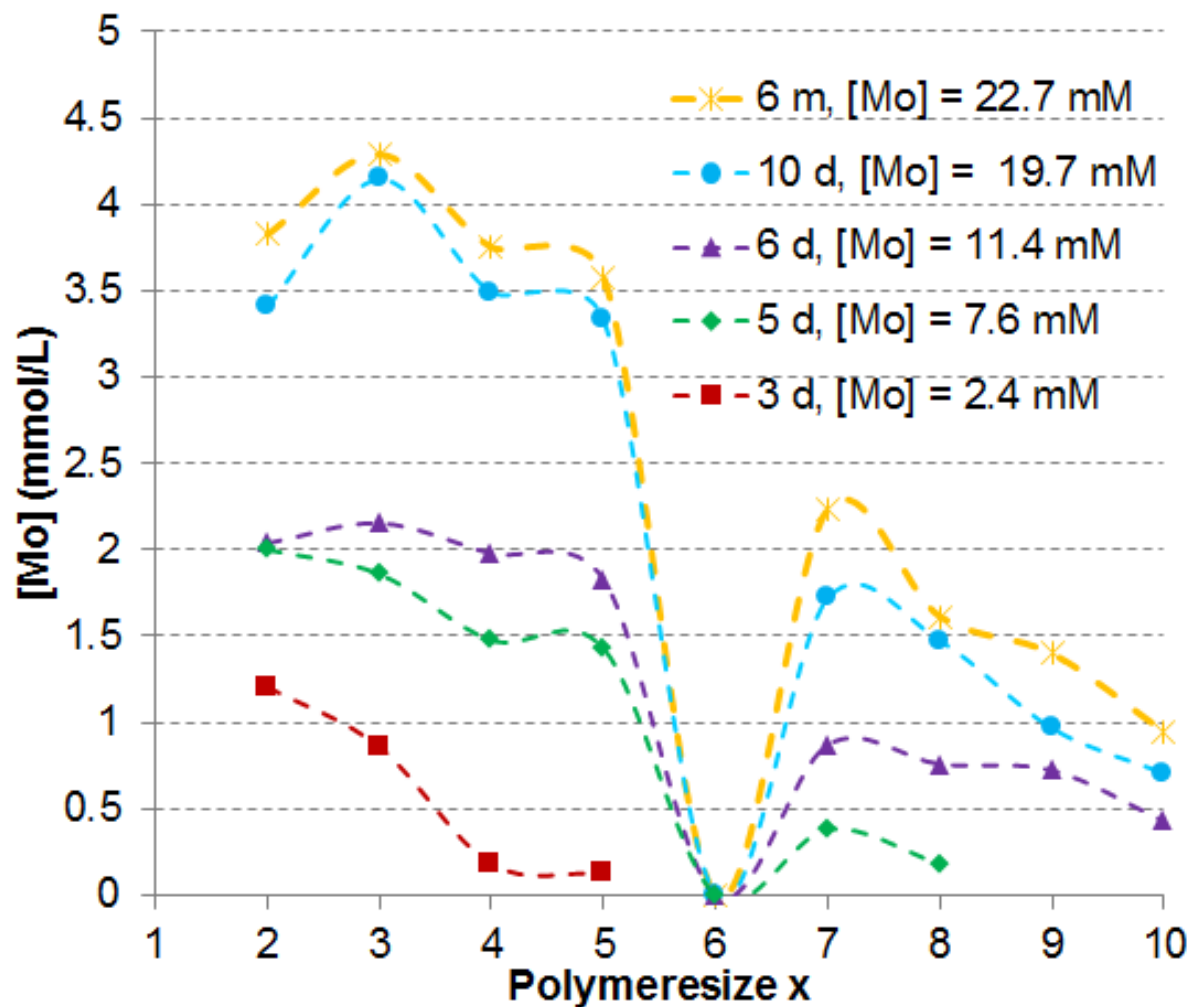
Molybdenum speciation



Mo pellet, 1M HNO₃, 60 °C

Molybdenum speciation

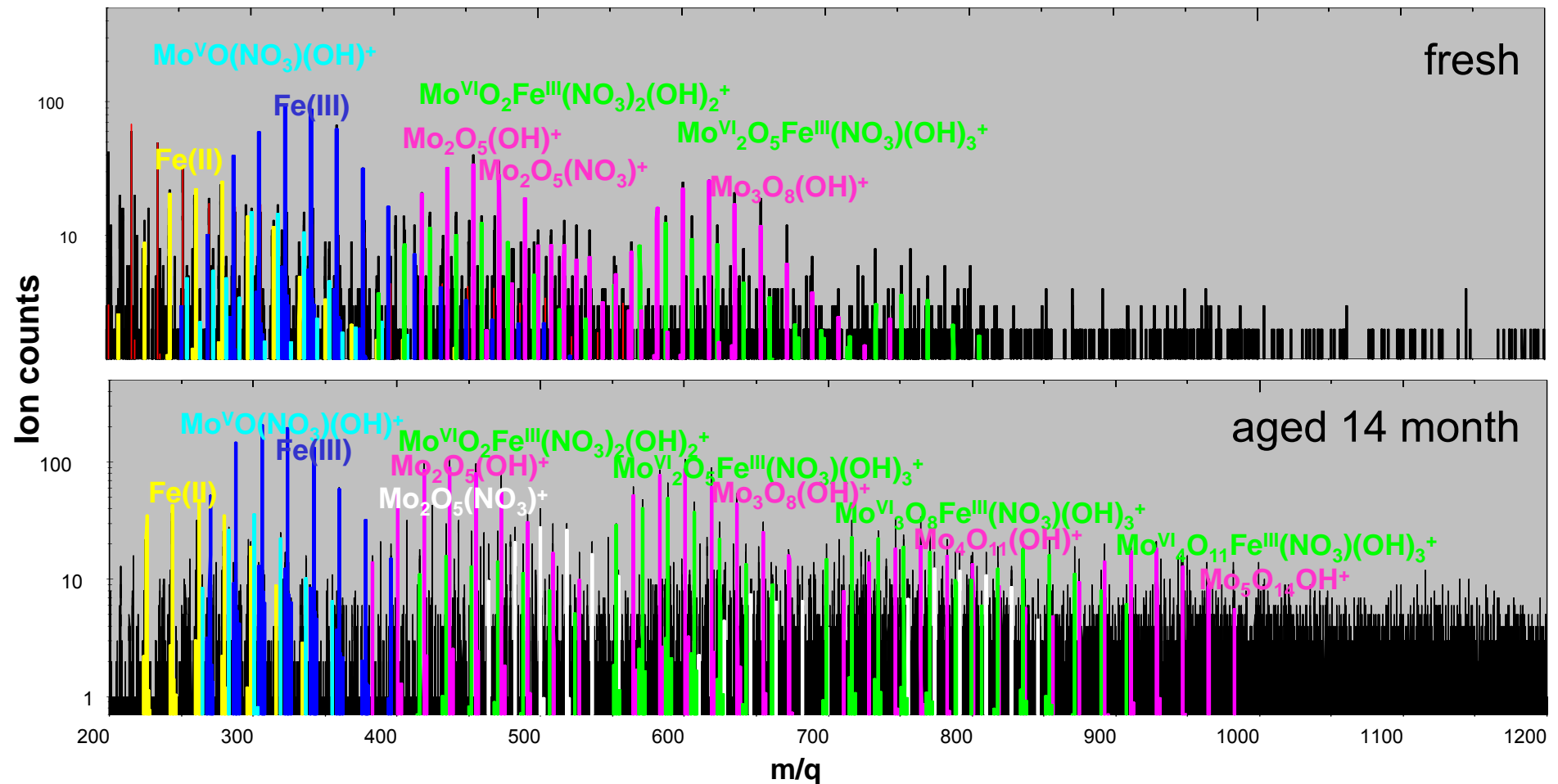
Time dependence



Mo pellet, 1M HNO₃, 60 °C

- Polymerization increases with concentration/time
- No hexamer

Molybdenum speciation: Influence of iron



10mM ^{98}Mo , 1M HNO_3 , 10mM Fe(III) , 60 °C

- Mixed Mo-Fe species are formed
- Polymeresize increases over time

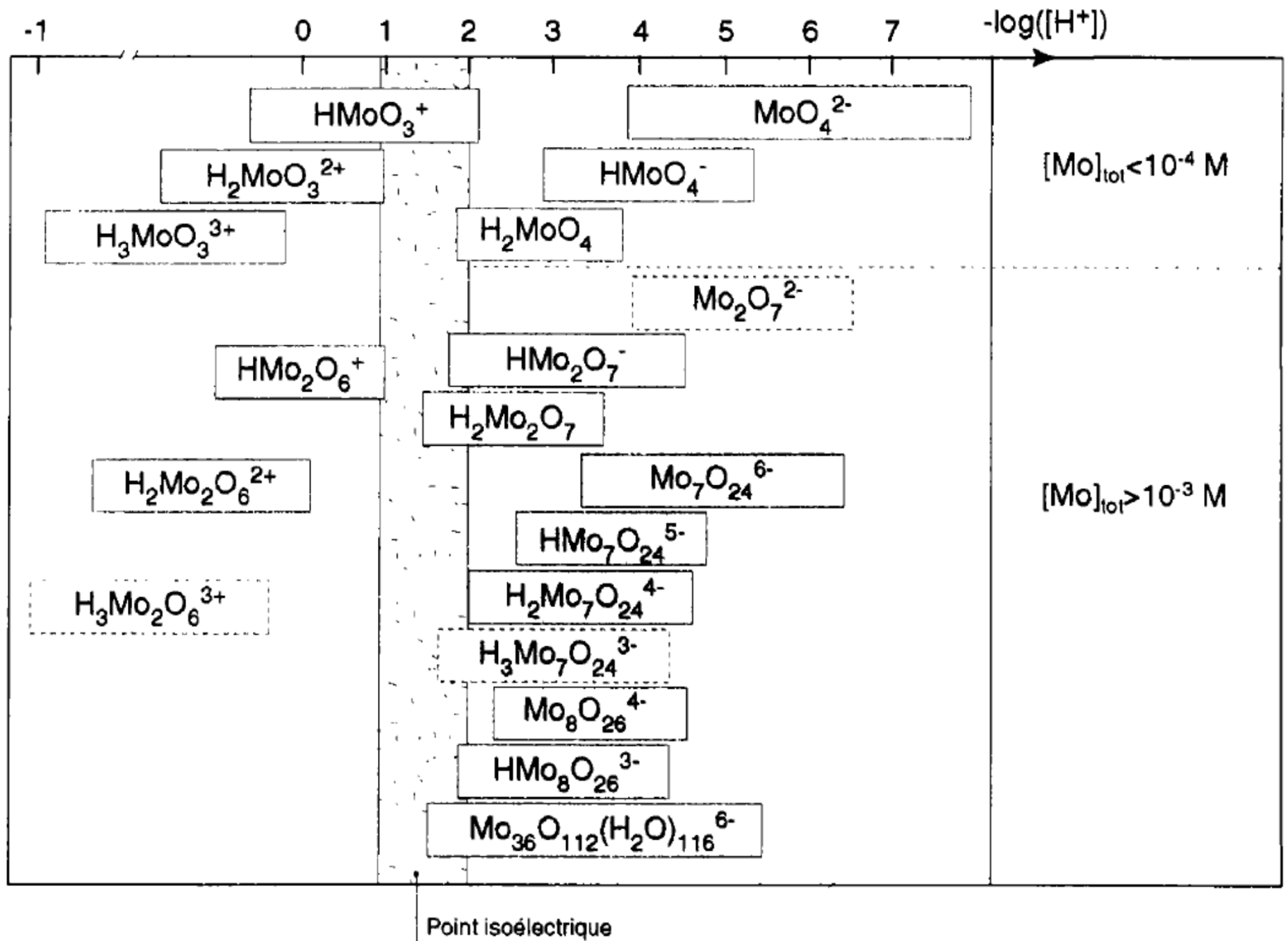
Conclusions and Outlook

- Dissolution of Mo is complex (precipitation phenomena), addition of Fe(III) improves solubility and kinetics
- CeO_2 dissolves slower than Mo
- Semi-warm tests with Mo/PuO_2 pellets
- Mo(V) + Mo(VI) was detected in nano ESI ToF MS
- Larger polymers form over time
- mixed Fe/Mo Species → improved solubility
- Dissolution of Mo pellets in presence of Fe(III)

Acknowledgements

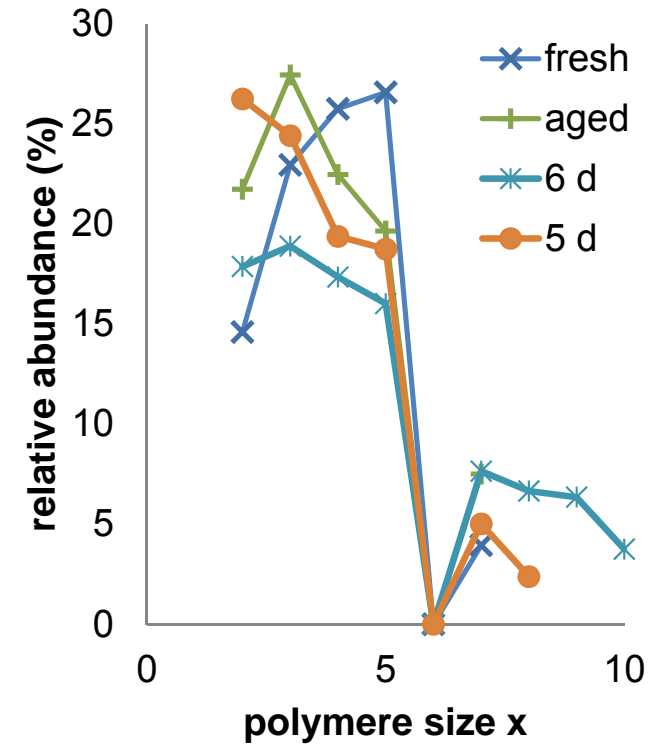
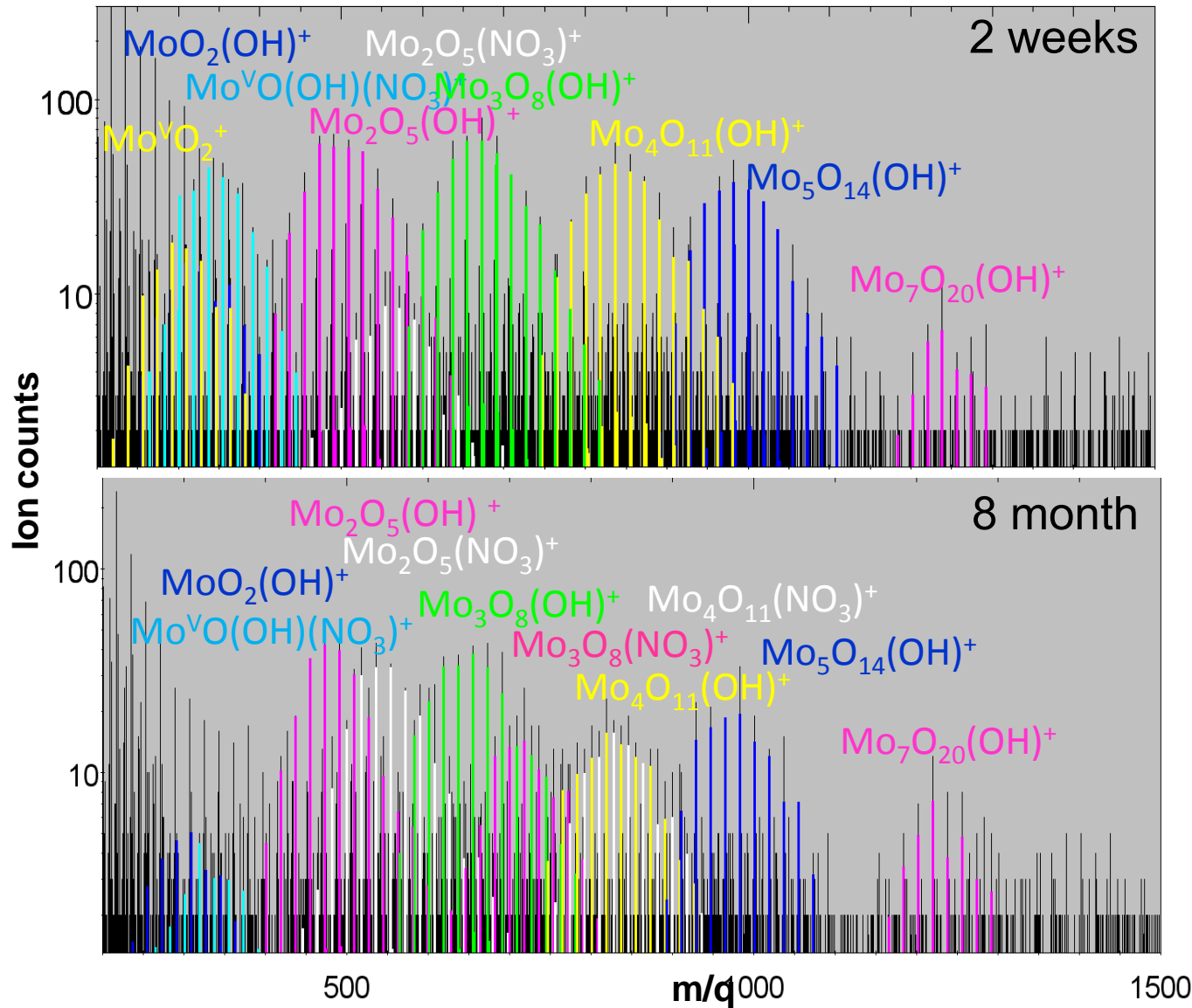
- All co-workers
- Fabian Sadowski
- Andreas Hartmann
- NRG Petten
- KIT-INE

Thank you for your kind
attention!

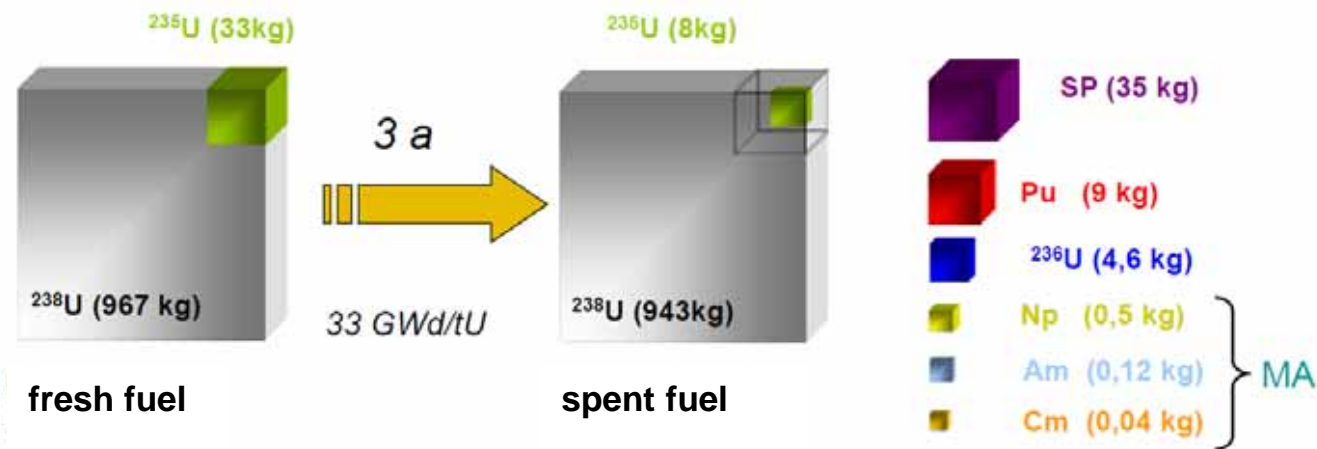


Speciation of Mo as function of time

^{98}Mo metal < 10 mmol/L; 0.5 mol/L HNO_3

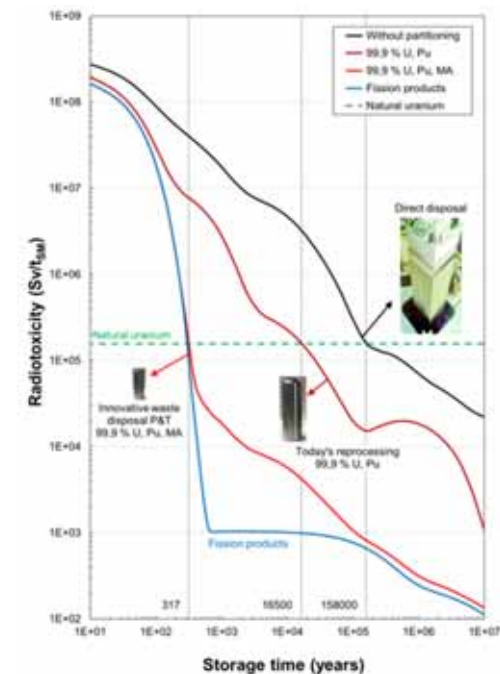


Introduction

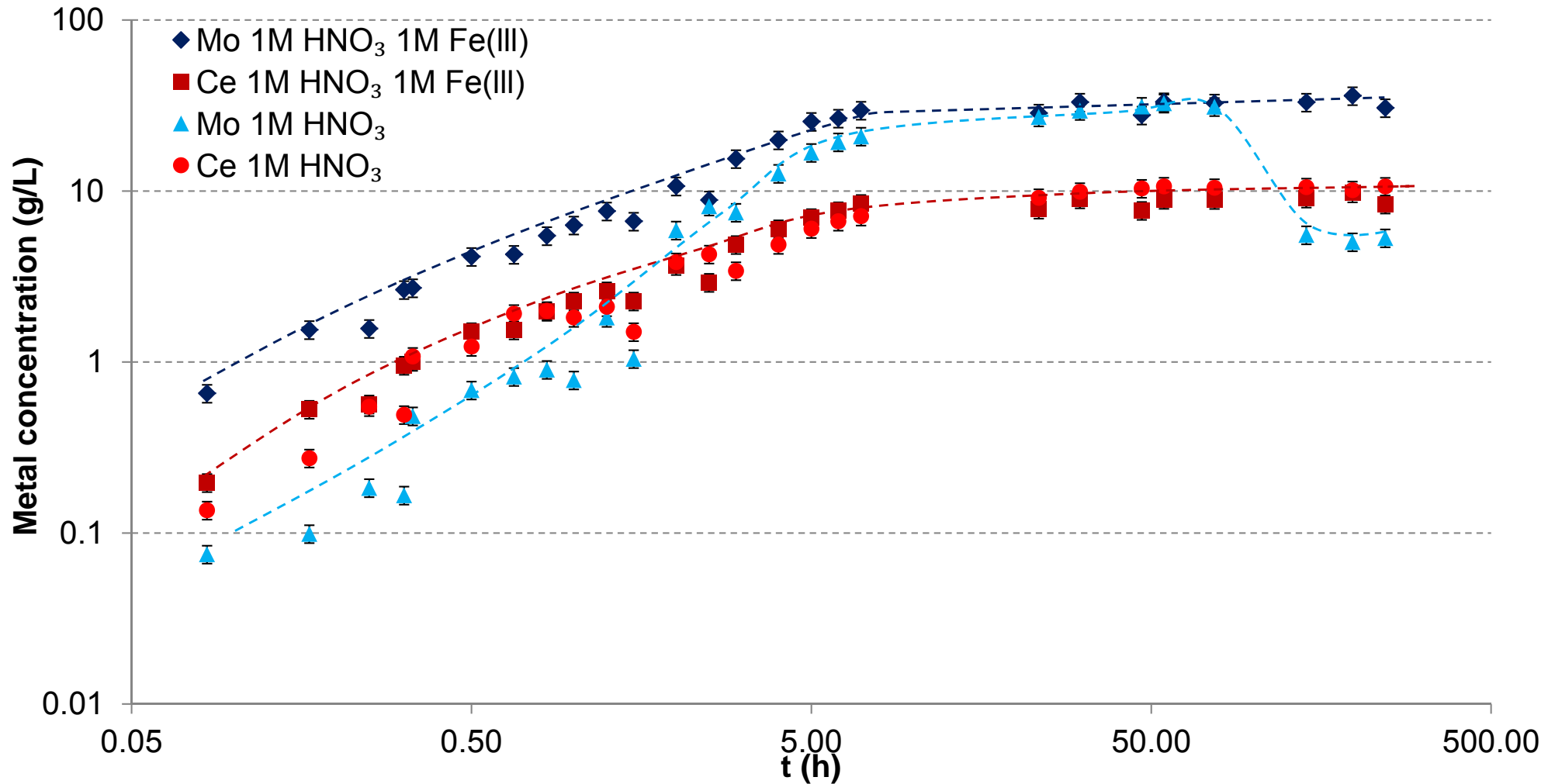


Future policy: recycle all the actinides (P&T)

- ⇒ To reduce quantity, radiotoxicity, heat and impact on waste management
- ⇒ To decrease the HLW repository space
- ⇒ To increase resistance to proliferation risks



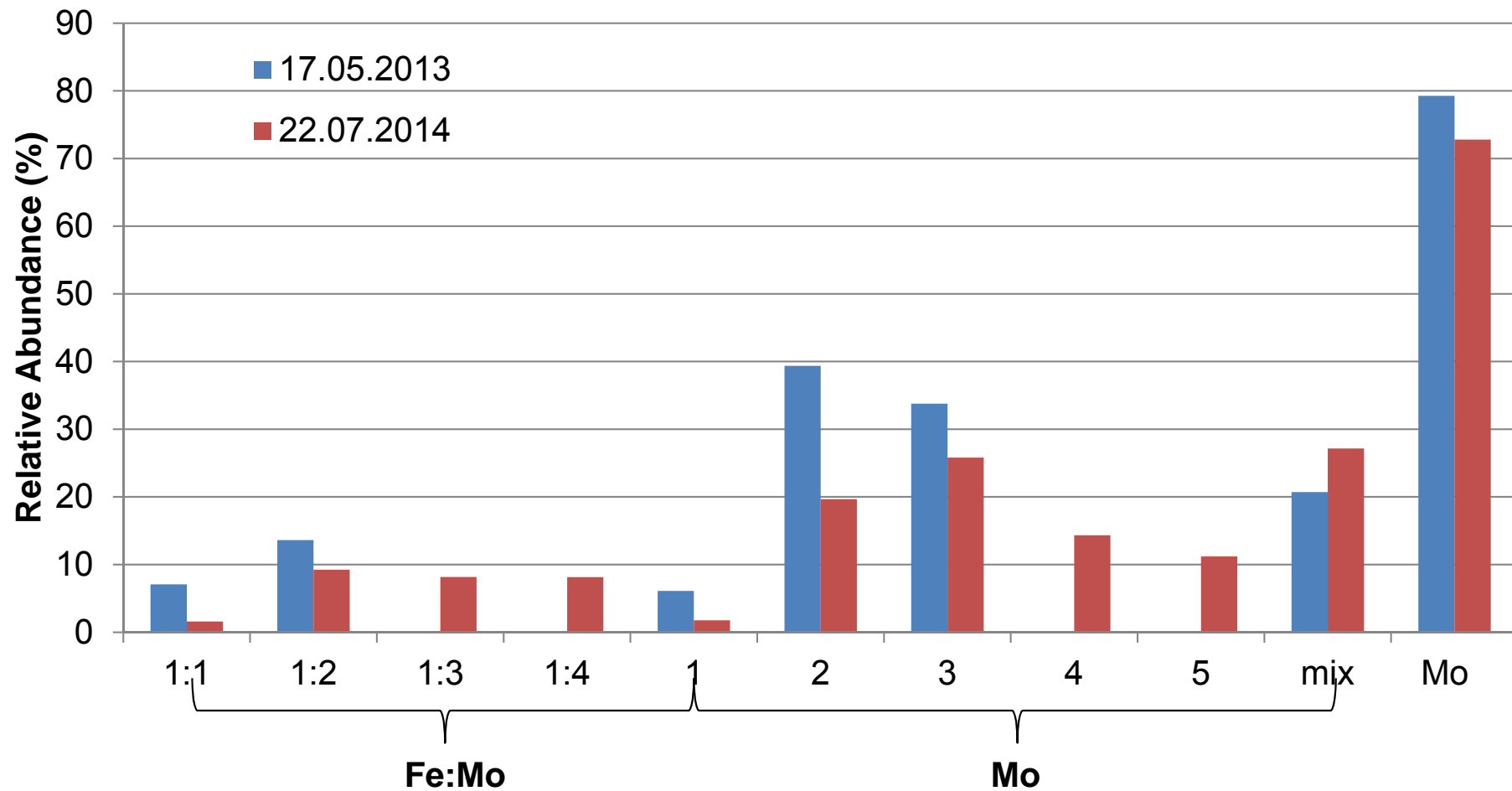
Dissolution of mixed Mo/CeO₂ pellets



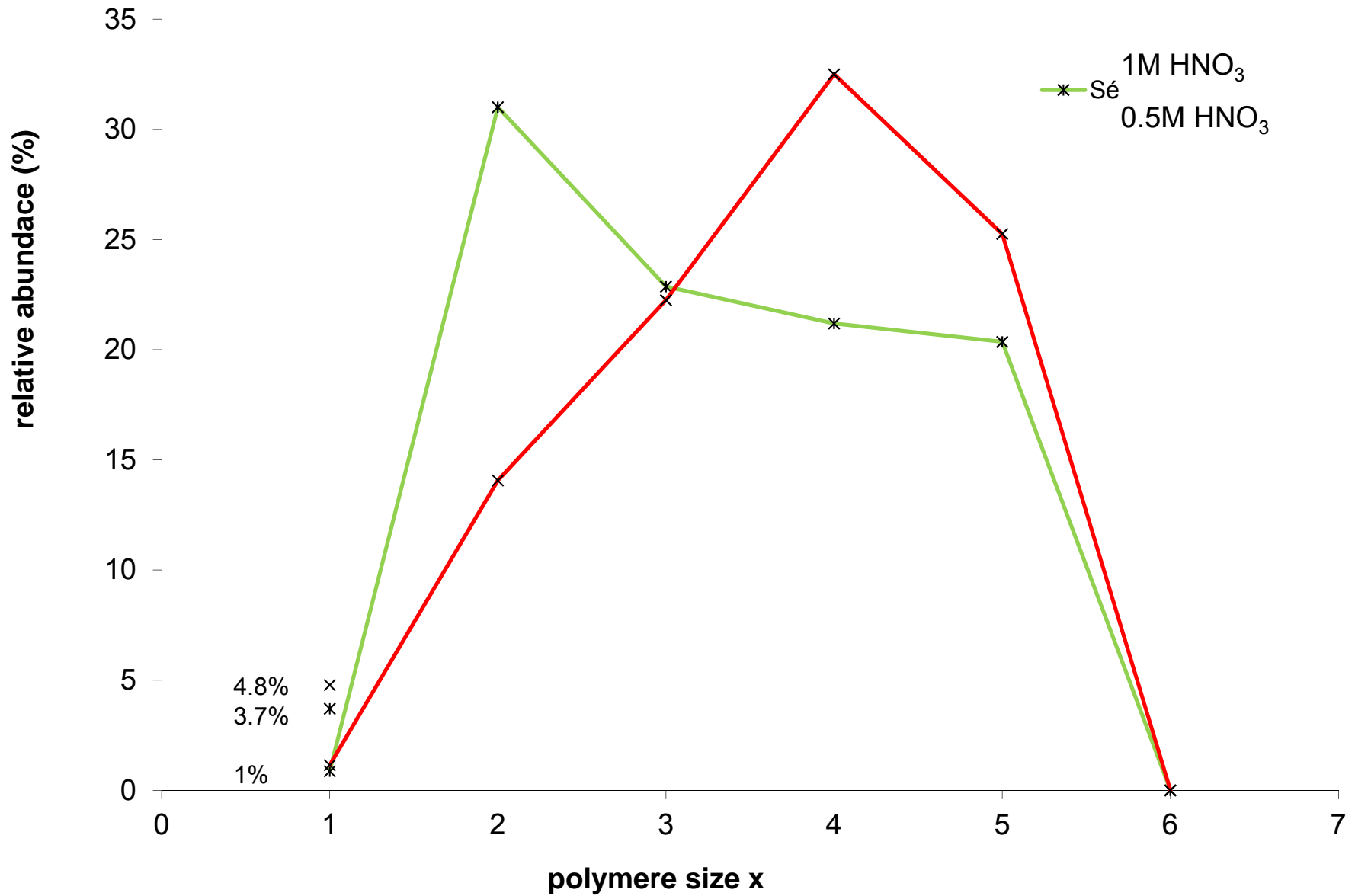
Dissolution of molybdenum and cerium from mixed Mo/CeO₂ 60/40 pellets (1 g) in 20 mL 1 mol/L HNO₃ without Fe(III) or containing 1 equivalent of Fe(III) per equivalent of Mo at room temperature.

Molybdenum speciation: Influence of iron

Time dependence



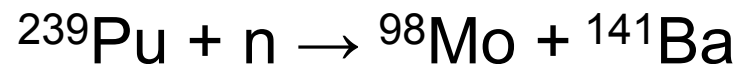
Speciation of Mo as function of acidity



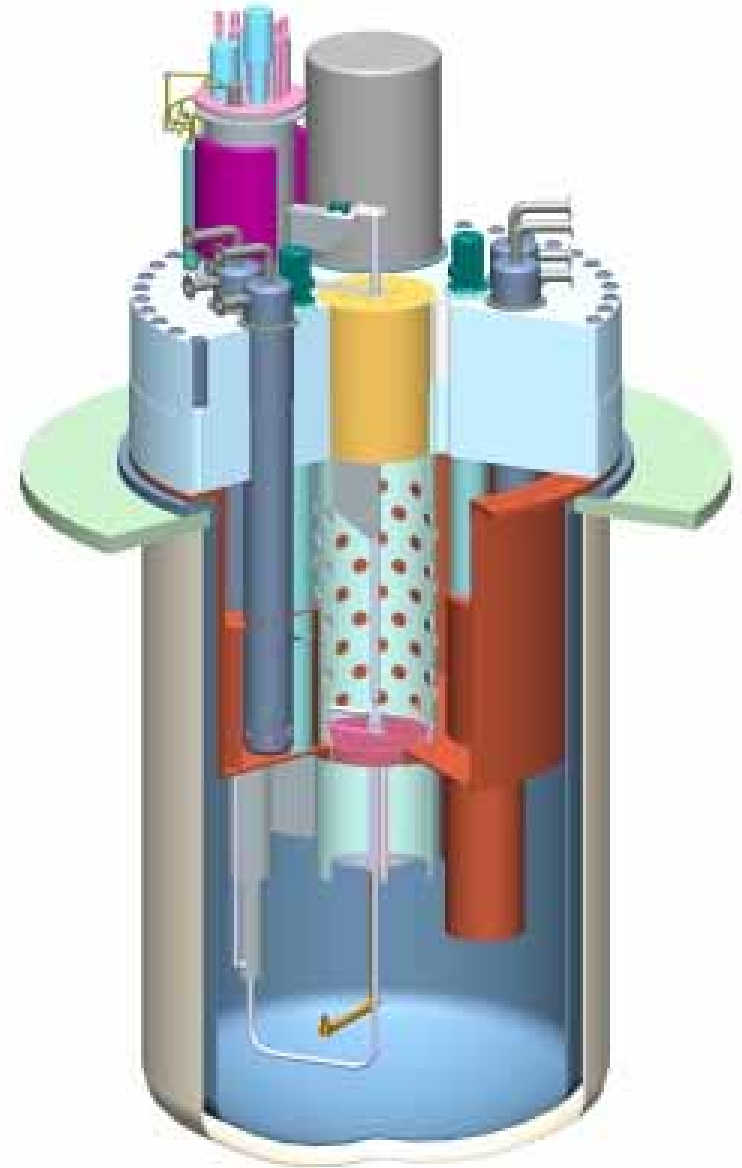
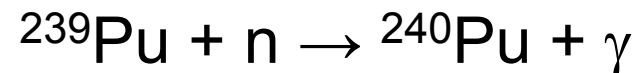
Transmutation in accelerator driven systems

- Spallation
 - Proton beam
 - Lead or lead-bismuth target
 - 30-40 fast neutrons

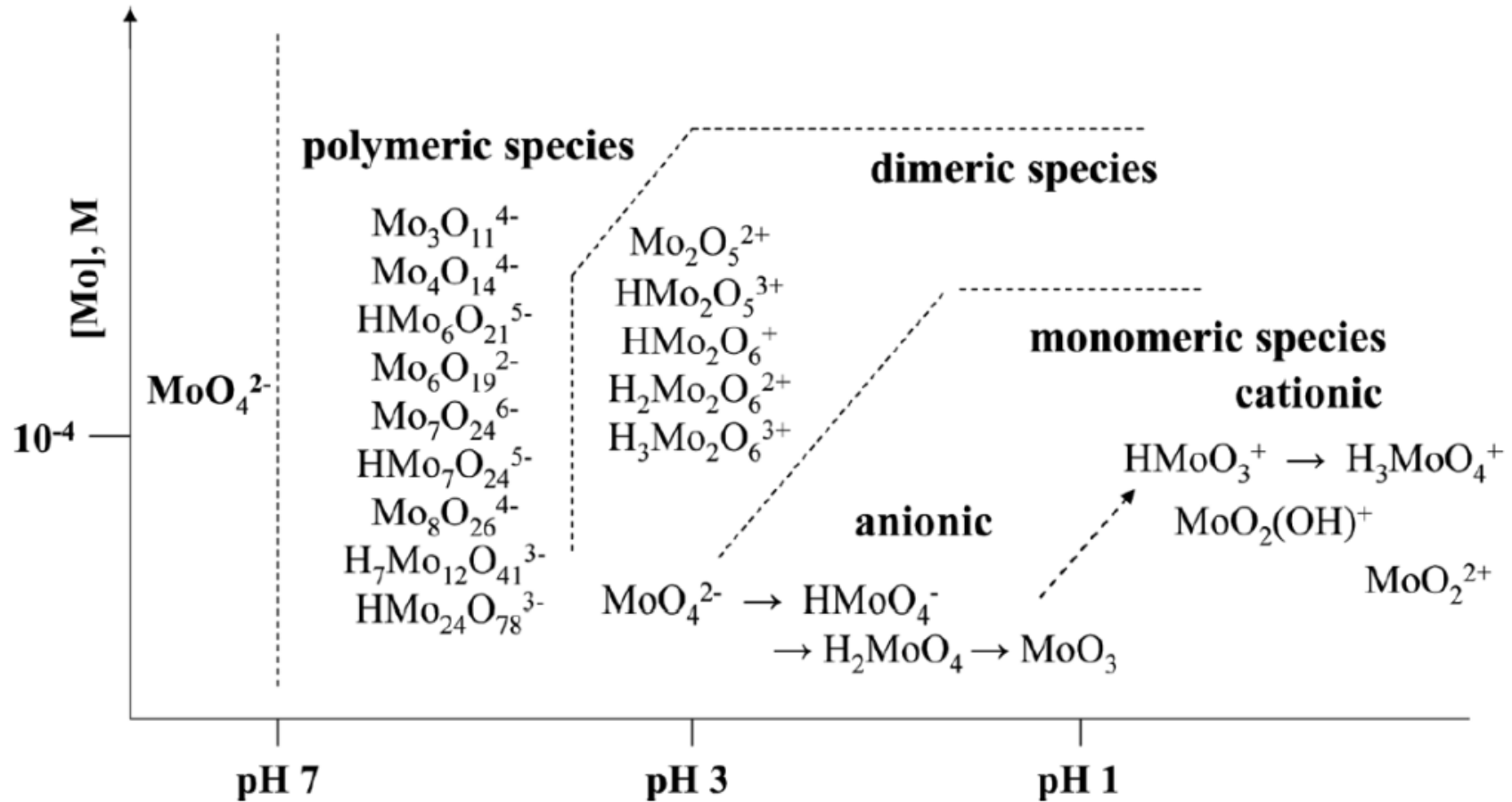
- Fission reaction



- Neutron capture



Mo speciation



Schematic diagram of Mo(VI) speciation in aqueous phase as a function of pH

