

How does Iron influence the dissolution behavior of Mo based generation IV reactor fuel? New insights using *nano* ESI-TOF-MS.

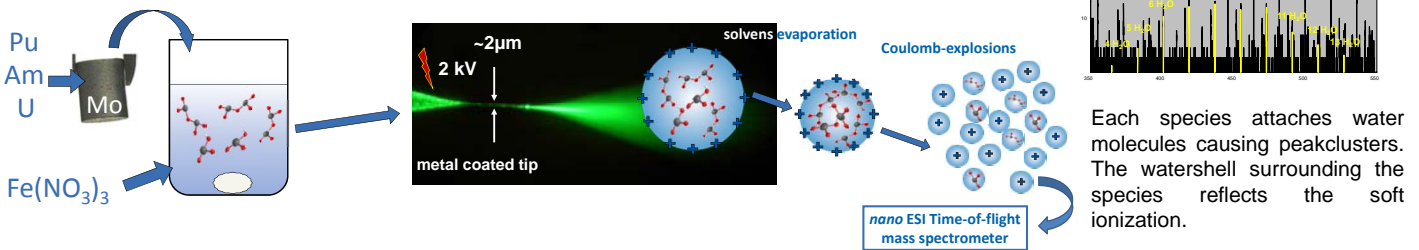
M. Cheng^{1,2}, M. Steppert¹, E. Ebert³, C. Walther¹

1. Institute for Radioecology and Radiation Protection (IRS), Leibniz University Hannover, Germany. 2. Institute for Nuclear Waste Disposal (INE), Karlsruher Institut für Technologie (KIT), Germany. 3. Institute of Energy and Climate Research (IEK-6), Forschungszentrum Jülich GmbH, Germany.

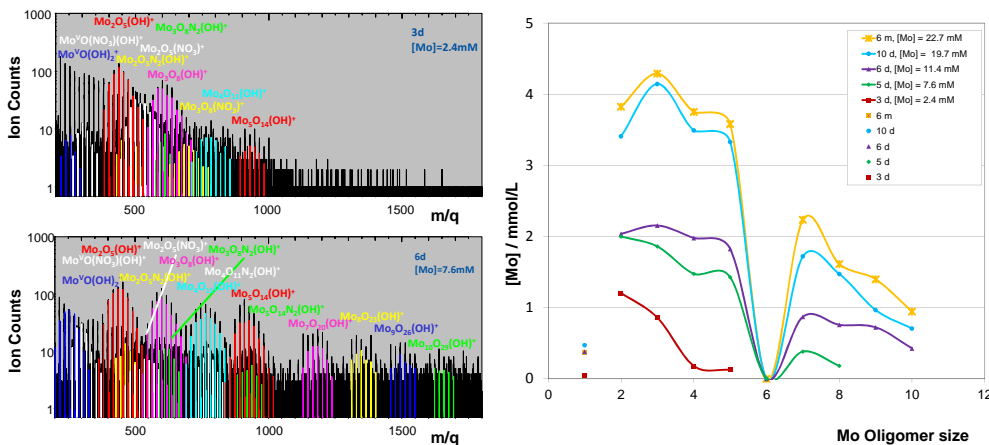
Background and objectives

The development of new reactor types of Generation IV demands new types of fuel with high thermal stability. One option for the reactor fuel, the application of molybdenum as inert matrix for the fissile material (*i.e.* Pu and Am), is investigated in the ASGAR-D-project (Advanced fuels for Generation IV reactors: Reprocessing and Dissolution). During the reprocessing steps fissile material has to be separated from the matrix, most likely in liquid-liquid extraction steps, in order to recycle it. As Molybdenum shows poor solubility as well as slow dissolution kinetics in nitric acid, strategies are needed to enhance the dissolution process of the matrix. The addition of Fe(III) leads to an increased solubility of the Molybdenum matrix and enhances the dissolution kinetics. In order to understand the effect of Fe(III) on the process, the solution species Mo forms in the presence of Iron are investigated by means of nano-electrospray ionization mass spectrometry^[1-3].

Principle of ESI-TOF

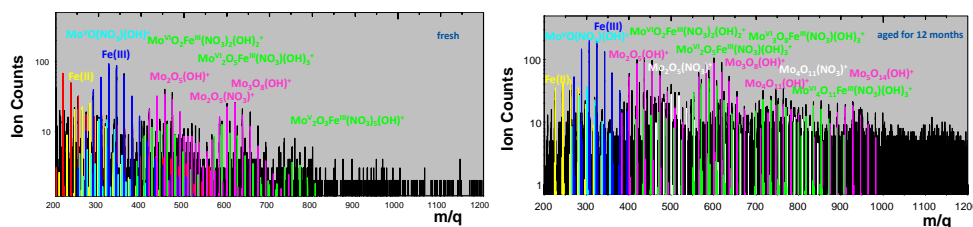


⁹⁸Mo metal pellets: solution species during dissolution



- sum formulas and relative abundances of the solution species
- with higher concentrations larger oligomers form
- hexameric species absent in all samples
- Mo-dimeric is dominant species
- solubility kinetics rather slow
- about 5% of Mo present in oxidation state +V: $\text{Mo}^{\text{V}}\text{O}(\text{NO}_3)(\text{OH})^+$ [4]
- the relative abundances of large polymeric species increases with decreasing acidity

Addition of $\text{Fe}(\text{NO}_3)_3$ solution to ⁹⁸Mo metal pellets dissolution



- Mo metal pellets dissolved faster
- mixed Mo-Fe species form
 - $\text{Mo}^{\text{VI}}\text{O}_2\text{Fe}^{\text{III}}(\text{NO}_3)_2(\text{OH})_2^+$,
 - $\text{Mo}^{\text{VI}}\text{O}_5\text{Fe}^{\text{III}}(\text{NO}_3)(\text{OH})_3^+$,
 - $\text{Mo}^{\text{VI}}\text{O}_8\text{Fe}^{\text{III}}(\text{NO}_3)(\text{OH})_3^+$,
 - $\text{Mo}^{\text{VI}}\text{O}_{11}\text{Fe}^{\text{III}}(\text{NO}_3)(\text{OH})_3^+$
- might be responsible for faster dissolution and for not forming precipitates

Conclusions

- Correlation between acidic strength and polymerization: the relative abundances of large polymeric species increases with decreasing acidic strength.
- At high acid concentration, Mo(VI) shows a strong tendency to dimerize in accord with [5].
- Mixed species of Mo and Fe are formed.
- The dissolution of Mo metal pellets will be enhanced by addition of $\text{Fe}(\text{NO}_3)_3$ and precipitates are not forming in aged solution.

Acknowledgements

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