Dissolution of unirradiated MOX fuel in the presence of metallic iron

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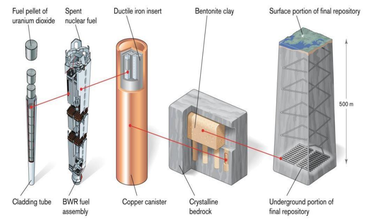
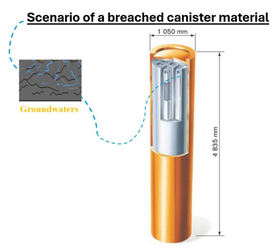
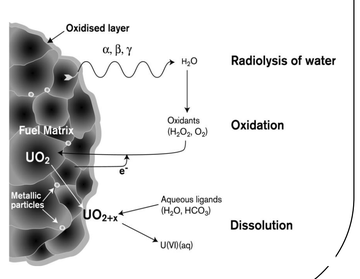
1 Background

- Spent nuclear fuel(SNF) contains ~ 95% UO_2 matrix, with the remaining 5% as fission products (Sr,I,Cs,Xe,Tc), and transuranic elements(Pu,Np,Am,Cm).
- It contains highly radioactive isotopes and generate decay heat.
- By 2045, ~ 12,000 metric tons of SNF are predicted to be generated from the Swedish nuclear facilities, with final disposal planned in a deep geological repository.







2 Objectives

Investigate the dissolution behavior of unirradiated MOX fuel in the presence of metallic iron and to evaluate the effect of repository relevant reductants (Fe(II), dissolved H_2 and iron corrosion products) on its oxidative dissolution.

3 Design and Experimental Methodology

- Autoclave: Stainless steel vessel (total volume of 1 L, 131 bar, 350 °C) with two valves in the lid to allow sampling of liquids and purging of gases.
- Metallic iron foil (0.125 g, 0.1 mm thick, 1.56 cm² surface area) and 2 g of iron powder were used.
- Synthesis of the Swedish Forsmark ground water compositions and 10-2 solution.

Table 1. Chemical compositions of synthetic groundwaters. Concentrations in mmol/L

ID	Na	K	Ca	Mg	HCO_3	Cl	SO_4	Si	Br	Fe(II)	Sr	pH
02A	96.57	0.93	22.21	10.04	2.07	148.9	5.28	0.22	0.3	0.04	0.1	7.19

- The iron foil and iron powder was pre corroded in 800 ml of synthetic Forsmark groundwaters in the absence of the MOX pellet using the autoclave.
- Un-irradiated MOX pellet was used as a simulant for α- field of old spent fuel , with specific alpha-activity of the pellet was 1.71 GBq/gMOX.
- The MOX fuel pellet was annealed in Ar+ 5% H_2 at 1200 °C , with a 20 °C/min heating and cooling rate.
- Long term MOX leaching experiment(407 days) was carried out in the presence of iron.

Table 2. Composition and dimensions of the used 10 wt.% MIMAS-MOX pellets.

Oxide composition			Pu/Am isotopic composition June 2019		Dimensions	
UO_2	PuO_2	AmO_2			Diameter	Height
89.76 wt.%	10.23 wt.%	0.01 wt.%	^{238}Pu	1.32%		
			^{239}Pu	64.37%		
			^{240}Pu	26.60%	8.08 mm	3.27 mm
			^{241}Pu	2.54%		
			^{242}Pu	5.05%		
			^{241}Am	0.12%		

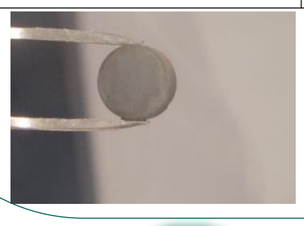


Figure 1. Image of the unirradiated MOX pellet.

Figure 2. Autoclave (Parr instrument, USA)

4 Results and Discussion

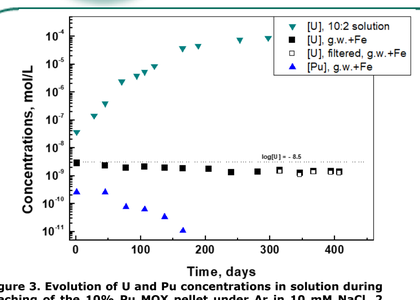


Figure 3. Evolution of U and Pu concentrations in solution during leaching of the 10% Pu MOX pellet under Ar in 10 mM NaCl, 2 mM $NaHCO_3$ solution and in Forsmark groundwater in presence of Fe(s).

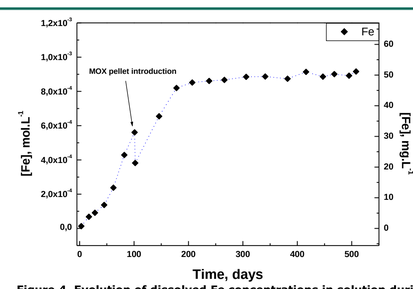


Figure 4. Evolution of dissolved Fe concentrations in solution during the entire leaching experiment .

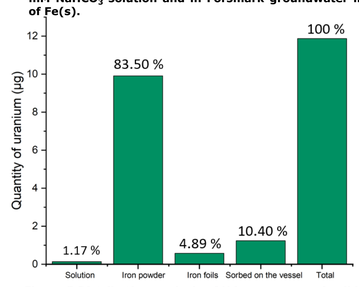


Figure 5.Distribution analysis of U in aqueous and solid phases.

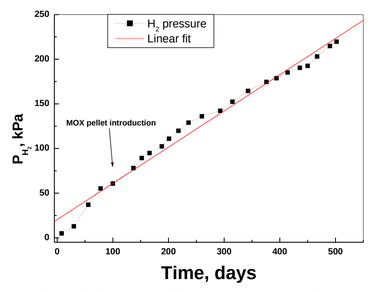


Figure 6. Evolution of Hydrogen pressure in the autoclave

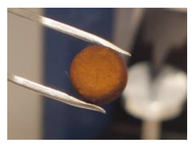
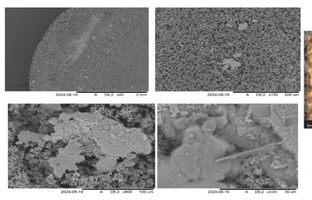


Figure 7. Image of the MOX pellet surface at the end of the leaching experiment.



The SEM-EDX analysis suggests that the precipitates primarily consists of Fe containing compounds

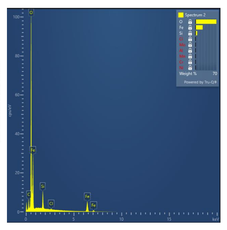


Figure 8. SEM micrographs of the leached MOX pellet in synthetic Forsmark groundwater in the presence of iron.

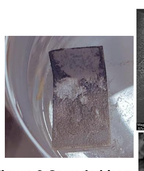
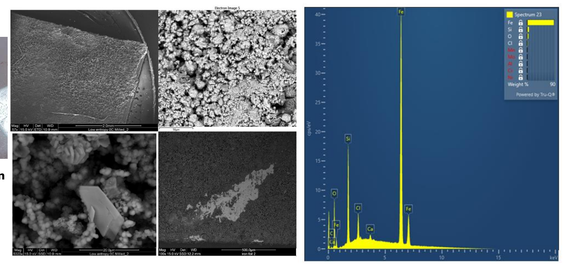
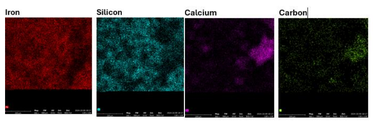


Figure 9.Corroded iron foil





Based on the SEM-EDX analysis, iron corrosion products such as Fe hydroxide, Fe hydroxy-carbonate or calcite seems most likely formed.

Figure 10.SEM-EDX micrographs, spectrum and mapping on the corroded iron foils

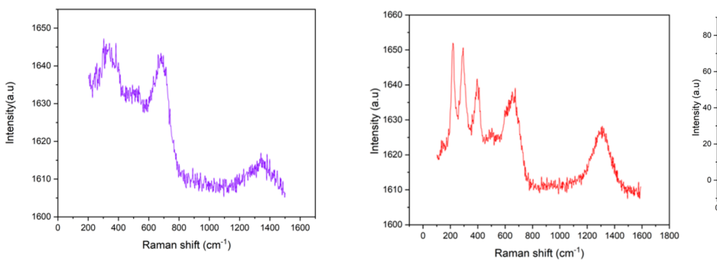
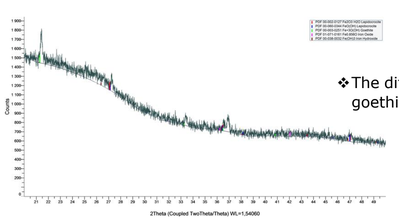


Figure 11: Raman spectra of the precipitates found on the leached MOX pellet.

Figure 12 : Raman spectra of the precipitates found on the surface of the corroded iron foils

- The resulting Raman spectrum in Fig 11. was compared to reference spectra of akageneite (β-FeOOH) and lepidocrocite, showing significant similarities and indicating that the precipitates are likely composed of Fe(III) oxyhydroxide.
- The spectra shown in Fig 12. align well with calcite ($CaCO_3$), chukanovite ($Fe_2(OH)_2CO_3$), and ankerite ($CaFe^{2+}(CO_3)_2$).



- The diffractogram matches with some peaks for a variety of Fe(III) oxides such as lepidocrocite, goethite, akageneite, and Fe(III) hydroxide.

Figure 13: XRD patterns of the red deposit or precipitates formed on the surface of the leached MOX pellet.

5 Conclusions

- The corrosion of an unirradiated MOX fuel pellet containing 10% Pu (specific alpha activity 1.7 GBq/g) was investigated under Ar atmosphere in simulated granitic groundwater from Forsmark, Sweden in the presence of metallic iron foils and iron powder.
- The Fe(II) concentrations increased from 5.6 10^{-4} M after 101 days and MOX pellet insertion to 9.2 10^{-4} M at test termination.
- No traces of oxidized uranium were observed in the active autoclave during the whole duration (407 days) of the test; the uranium concentrations (from 2.9 10^{-9} M at start to 1.2 10^{-9} at the end) are in good agreement with the lower range of UO_2(am) solubility.
- Anoxic iron corrosion products such as ankerite, chukanovite were detected on the iron foils while several Fe(III) compounds including goethite, lepidocrocite and akageneite were formed on the surface of the MOX pellet.
- This study shows that the anoxic corrosion of iron in granitic Forsmark groundwaters completely inhibits the oxidative dissolution of a MOX pellet with a very high specific alpha activity.
- Leaching experiments on un-irradiated MOX pellets, while interesting as highly α-doped UO_2 samples, also remain relevant in the context of the long-term disposal of spent MOX fuel.

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