

Microgravimetric corrosion studies on UO_2 thin film models

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For a reliable assessment of the long-term storage behaviour of spent fuel a mechanistic understanding of the interactions of the waste forms with the surrounding environment is indispensable. A potential failure of the technical barriers can result in contact of the fuel matrix with groundwater possibly under oxidizing conditions leading to corrosion and dissolution of the fuel and therewith the release of radionuclides. Carbonate and bicarbonate are important groundwater constituents assumed to influence UO_2 dissolution due to their strong complexation of the UO_2^{2+} ion. Studies of several authors revealed a mechanistic picture of the process [1-4]. Anyhow, additional information about the corrosion process such as the mass change is strongly needed to verify these mechanistic approaches and to determine all the processes involved.

A widespread and highly sensitive method to study mass changes is the quartz crystal microbalance. Actinide compound thin films sputtered onto the piezoelectric quartz crystal electrodes can be designed as model systems for spent fuel with a reduced complexity therefore being suitable for single effect studies [5].

UO_2 thin films were used in electrochemical studies with the electrochemical quartz microbalance (ECQM) in combination with other characterisation methods, as there are X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Atomic force microscopy (AFM) and Scanning electron microscopy (SEM). Our studies were conducted to measure the influence of carbonate and other groundwater constituents on the dissolution behaviour of UO_2 . In 0.01 M NaCl solution and with addition of HCO_3^- mass change and current response in potential sweep cycles from $-992 \text{ mV}_{\text{SHE}}$ up to $+508 \text{ mV}_{\text{SHE}}$, and $+708 \text{ mV}_{\text{SHE}}$ respectively, and back to $-992 \text{ mV}_{\text{SHE}}$ were recorded. Insignificant differences are observed comparing the tests at pH 5 and pH 8 in the chloride solution, whereas addition of bicarbonate caused significant changes. The reversible surface reaction proposed for the potential region between $-800 \text{ mV}_{\text{SHE}}$ to $0 \text{ mV}_{\text{SHE}}$ for pH values above 5, easily seen in the combination of voltammogram and mass information for the chloride system, is suppressed in 0.01 M NaHCO_3 solution. In the following potential region ($>0 \text{ mV}_{\text{SHE}}$) the superposition of different reactions is observed. Here the competition between the growth of a $\text{UO}_{2.33}$ layer [2], leading to a mass increase of the electrode by O^{2-} incorporation, and the dissolution of UO_2^{2+} from the electrode surface into the aqueous phase can be directly observed in the case of the non-complexing electrolyte

whereas in the carbonate system the dissolution process is dominating. The clear onset of the dissolution reaction, combining a strongly increasing current and a strong mass decrease of the electrode, can be seen around $100 \text{ mV}_{\text{SHE}}$. The mass signal exhibits at least two different rates. For the carbonate system, in the first view unexpected, a lower overall mass loss is seen than for the non-complexing system. For carbonate, a strong complexing agent for UO_2^{2+} , an increase in the solubility is found in leaching experiments because the formation of protective U(VI) corrosion product layers (e.g. schoepite) on the UO_2 surface seems prevented at carbonate concentrations $\geq 10^{-3} \text{ M}$ [2]. Anyhow the behaviour may be explained by the earlier assumed formation of an U(VI)CO_3 layer [2,4] on the electrode surface. In the cathodic sweep the significant reduction peak around $0 \text{ mV}_{\text{SHE}}$ seen in the chloride system is missing for the carbonate containing system. The identification of this reaction with the reduction of corrosion products is corroborated by the strongly suppressed mass increase in the cathodic sweep at potentials $< 400 \text{ mV}_{\text{SHE}}$ compared to the one observed in the chloride system. Going to more reductive potentials the second reductive peak around $-700 \text{ mV}_{\text{SHE}}$ is broadened and shows a complex behaviour of the mass signal in the carbonate system. It is assumed that several reactions are superimposed in this region. Actual investigations are disposed to elucidate these processes.

In the contribution a short introduction into the film preparation and its possibilities will be given. The main aspect will deal with the ECQM corrosion studies in carbonate containing systems and the characterisation of the reaction products from the electrochemistry experiments.

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