



# Role of fluoride ions on the uranium oxidation mechanism in highly alkaline solutions

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## ABSTRACT

This research is focused on understanding uranium oxidation to predict the behavior of uranium contaminated Mg alloy waste in confinement matrices. The environment of the matrix proposed for the magnesium encapsulation, based on geopolymer material, imposes basic conditions and the presence of fluoride ions (corrosion inhibitor of the Mg alloy). This work demonstrates the opposite behavior of the hydroxide and fluoride ions on the uranium oxidation: the fluoride ions induce the corrosion of uranium, whereas the hydroxide ions protect the metal against corrosion by making an anionic barrier at the uranium/solution interface. Two mechanisms are proposed, depending on the  $[\text{OH}^-]/[\text{F}^-]$  ratio. In absence of fluoride ions, or if  $[\text{OH}^-]/[\text{F}^-] > 1$ , the mechanism corresponds to a single step, the charge transfer characteristic of the  $\text{UO}_2/\text{UO}_{2+x}$  system. Uranium metal is thus protected from corrosion by the oxides layer. By contrast, if  $[\text{OH}^-]/[\text{F}^-] < 1$ , uranium is corroded, the fluoride ions diffuse through the oxides layer and cause its desquamation. This phenomenon has to be taken into account for the confinement of uranium contaminated Mg waste in geopolymers matrices containing fluoride ions.

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## 1. Introduction

Since 1990, the nuclear decommissioning research of first-generation reactors has been under way. In France, we are particularly concerned by the large volume of waste generated by the gas cooled reactors UNGG (Natural Uranium Graphite Gas). The dismantling process is notably dedicated to the fuel assembly, which is constituted of the fuel cartridge (containing the graphite carbon core, the Mg-Zr alloy cladding and the uranium metal tube) and the glassy carbon covering [1,2]. The first step of this process is the physical separation of the fuel cartridge from the glassy carbon covering. The second step involves extracting the uranium tube from the Mg-Zr sheath and separating it from the graphite core. The magnesium cladding is thus isolated, but contaminated with U (about 5% by weight). Therefore, three types of waste are generated: (i) the glassy C covering and the graphite C core; (ii) the uranium tube and (iii) the magnesium alloy sheath.

For better management, radioactive waste is classified according to: their mass radioactive activity, low (FA), medium (MA) or high activity (HA), and their half-life period, very short < 100 days (VTC),

short < 31 years (VC) or long lived > 31 years (VL). The MA-VL waste will be stored in geological storage sites. The U contaminated Mg-Zr cladding would be encapsulated into a confinement matrix and stored in primary packages. After a curing phase, the primary packages would be sealed and placed in a concrete container. The major risk of this type of metal confinement is their corrosion by interstitial water, resulting in hydrogen release. The production of this gas can cause irreversible damage to the primary package and the package's sealing.

The potential-pH diagrams of magnesium and uranium show a common passivation zone for pH greater than 10 [3]. Indeed, for this pH range, Mg and U are respectively oxidized into solid phases,  $\text{Mg}(\text{OH})_2$  and  $\text{UO}_2$ ,  $\text{UO}_3$  or  $\text{U}_3\text{O}_8$ , which can reduce the corrosion rate. The strategy is to propose a material providing a high pH environment for the storage of both magnesium alloy and uranium. Moreover, the inhibition effect of fluoride ions on the corrosion of Mg and its alloys has been reported [4–16]. Some works have been dedicated to the matrix formulation for Mg-Zr encapsulation by measuring the corrosion rate in Portland cement and geopolymer containing sodium fluoride [12,13]. It has been concluded that sodium-based geopolymers are good candidates for the Mg-Zr confinement. One main advantage of this material is its strongly basic interstitial solution, close to pH 14. On the other hand, the pH decreases from 14 to 12 during the setting phase [17–20] because

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the formation of Al-Si-Al bridges consumes hydroxide ions during the polymerization [21].

Before considering the geopolymers as materials for Mg-Zr cladding (contaminated with uranium) waste encapsulation, it seems primordial to evaluate the risk of uranium corrosion in such confinement matrix. For that purpose, it is important to understand the chemical reactions of uranium in the environment imposed by the geopolymers. Therefore, our work is focused on the uranium metal reactivity in highly alkaline solutions and the effect of fluoride ions addition. A large number of publications have been devoted to the uranium oxidation in aqueous solution as a function of pH, temperature and oxygen content [22–30]. Nevertheless, few of them have been dedicated to basic media with pH lower than 12 [31–36] and there is a notable lack of data on the reactivity of uranium in highly basic solutions (higher than 12).

In our study, three approaches have been adopted to understand the mechanism of uranium oxidation with or without NaF:

- (i) Thermodynamic calculations;
- (ii) Electrochemical (cyclic voltammetry and electrochemical impedance spectroscopy) and potentiometric measurements on uranium electrode as a function of pH (from 14 to 11) and the NaF content;
- (iii) Solid phase characterization after immersion in basic aqueous solutions containing fluoride ions.

## 2. Experimental section

### 2.1. Chemical reagents and alkaline fluoride solutions preparation

Sodium hydroxide (Sigma Aldrich, purity 99.9%) and sodium fluoride (Sigma Aldrich, purity 99.9%) were used as received without further purification. All solutions were prepared using deionized water (18 M $\Omega$  cm). Solutions at different pH were prepared by dilution from a solution at pH 14. The pH was controlled by a pH meter (Eutech Instruments pH 510) and pH papers.

### 2.2. Uranium pretreatment

The uranium foil (0.02 cm of thickness) was supplied by the Institut de Physique Nucléaire of Orsay. The foil appeared black and powdery.

The uranium foil was cut to prepare the electrodes (0.75–1.25 cm<sup>2</sup>). The electrodes were then cleaned with nitric acid (10 M), rinsed with water, ethanol and finally air-dried for 15 min. After this treatment, the uranium had a shiny appearance.

### 2.3. Electrochemical experiments

Electrochemical measurements were carried out using a three-electrode cell: uranium as a working electrode (surface between 0.75 and 1.25 cm<sup>2</sup>), platinum wire (diameter 1 mm, GoodFellow, 99.95% purity) as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. Measurements were carried out using a potentiostat (AMETEK model VersaSTAT 4) piloted by the VersaStudio software. Electrochemical Impedance Spectroscopy (EIS) diagrams were recorded at the open circuit potential with 10 mV amplitude. Frequency ranged between 10<sup>5</sup> and 0.1 Hz, with 10 frequencies values per logarithmic decade.

### 2.4. Uranium characterization

The uranium surface was characterized by X-ray diffraction

(XRD). The XRD patterns were collected by an X-ray powder diffractometer (XRD, D8 Advance, Bruker AXS) in a Bragg–Brentano geometry ( $\theta$ - $\theta$ ) equipped with a Cu anode ( $K_{\alpha 1} = 1.54178$  Å). Acquisition was performed with a point scintillator detector from 20° to 80° with 0.02 steps. Phase identification was performed with DIFFRACPlus software (version 16, 2013, Bruker AXS) using powder diffraction files (ICDD PDF4+2016).

Surface characterization of uranium was performed according to the air oxidation time. The shape of the diffractogram lines recorded before acid treatment showed that uranium was probably oxidized in several oxidation states and formed compounds such as UO<sub>2</sub>, U<sub>3</sub>O<sub>7</sub>, U<sub>3</sub>O<sub>8</sub> and U<sub>4</sub>O<sub>9</sub>. Uranium electrodes were treated in 10 M HNO<sub>3</sub> until the brilliant aspect of the uranium metal was obtained and the characteristic lines of the metal were visible by XRD. After a few hours in air, the metal was covered again with a layer of uranium oxides.

A 3D laser scanning microscope VK X200 - Keyence was used to determine the uranium topography after chemical stripping and after having been in contact with different media. This microscope combined halogen light and laser light (408 nm).

## 3. Results and discussion

### 3.1. Thermodynamic calculations

Calculations have been undertaken to build the potential-pH diagram of uranium in a basic aqueous solution by using the HSCChemistry 5.11 program (Fig. 1). In this recent version of the program, the databases have notably been completed with the uranium species U<sub>4</sub>O<sub>9</sub> and U<sub>3</sub>O<sub>7</sub>. The diagram demonstrates that the metallic state is not stable in an aqueous solution. Depending on the redox conditions, it is oxidized into UO<sub>2</sub>, U<sub>4</sub>O<sub>9</sub>, U<sub>3</sub>O<sub>7</sub>, U<sub>3</sub>O<sub>8</sub>

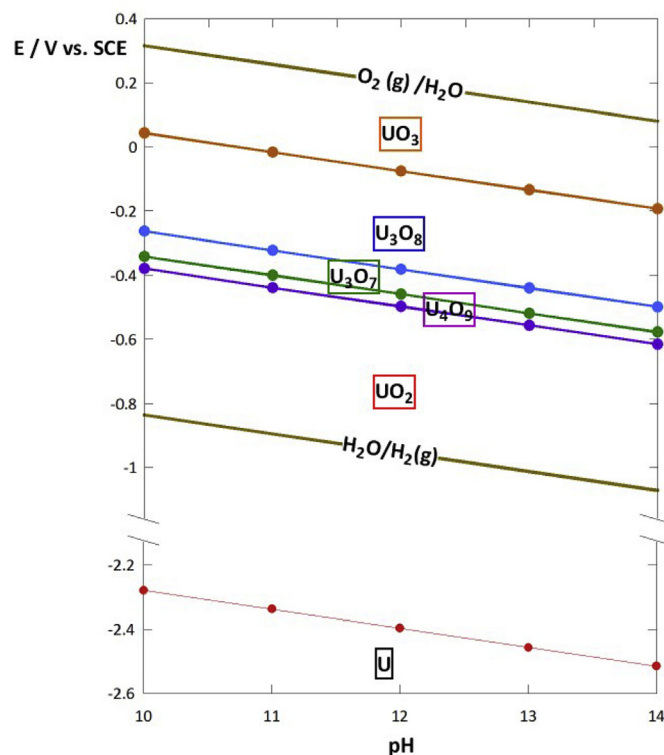


Fig. 1. Stability zones of various uranium oxide compounds and the thermodynamic potential of the H<sub>2</sub>O/H<sub>2(g)</sub> and O<sub>2(g)</sub>/H<sub>2</sub>O redox couples in the domain of alkaline solutions. The dotted lines correspond to the uranium systems.

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