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► **To cite this version:**

C. Cannes, D. Rodrigues, N. Barré, D. Lambertin, S. Delpech. Reactivity of uranium in geopolymers, confinement matrices proposed to encapsulate MgZr waste. *Journal of Nuclear Materials*, 2019, 518, pp.370-379. 10.1016/j.jnucmat.2019.03.024 . hal-02323355

HAL Id: hal-02323355

<https://hal.science/hal-02323355>

Submitted on 22 Oct 2021

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Reactivity of uranium in geopolymers, confinement matrices proposed to encapsulate MgZr waste

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Abstract

The U reactivity has been examined in three geopolymer (GP) formulations: GP, GP containing 1.25 M of NaF (GP-NaF) and GP containing 1.25 M of NaF and a double concentration of NaOH (GP-NaF-NaOH). In a previous study, two mechanisms representative of uranium oxidation in basic aqueous solutions have been proposed, depending on the ratio of the fluoride and hydroxide ions concentrations ($R_{F/OH}$). For $R_{F/OH} < 1$, U is protected by the oxides layer UO_{2+x} (mechanism A), while for $R_{F/OH} > 1$, U is continuously corroded (mechanism B). We have exploited the results on the GP pH evolution to understand the uranium behavior in geopolymers. With NaF at the saturated concentration in the geopolymers, if $pH > 13.8$, $R_{F/OH}$ is lower than 1, while for $pH < 13.8$, this ratio is higher than 1. Moreover, the pH would be stabilized at 13.4 for GP and GP-NaF and 14.1 for GP-NaF-NaOH. The ratio $R_{F/OH}$ can thus reach values higher than 1 in GP-NaF but not in GP-NaF-NaOH. Consequently, mechanism A can be applied for the U behavior in GP and GP-NaF-NaOH and mechanism B can occur in GP-NaF because of the pH decrease. The open circuit potential measurements confirm that in GP and GP-NaF-NaOH, U is protected by the oxides layer UO_{2+x} while in GP-NaF, corrosion is observed after 10 days. In GP and GP-NaF-NaOH, the presence of the redox couple UO_{2+x}/UO_2 has been put in evidence by electrochemical impedance spectroscopy. This technique confirms a different behavior of uranium in GP-NaF. In the presence of fluoride ions, cracks in the GP have been observed and a great quantity of uranium oxide has been produced.

Keywords

Uranium, corrosion, geopolymer, fluoride ions, electrochemical measurements.

1. Introduction

In France, nuclear facilities such as gas cooled reactors UNGG (Natural Uranium Graphite Gas) have to be decommissioned. Prior to disposal, the radioactive waste must be conditioned in a stable and confined form. Concrete encapsulation is one strategy to manage the low level waste by isolation from the environment. The major risk of this type of metal confinement is its corrosion by interstitial water, resulting in hydrogen release. It seems then primordial to understand the reactivity of the metal nuclear waste to propose the safest storage of the conditioned waste packages.

The UNGG fuel cladding material was based on Mg-Zr alloy [1, 2]. To manage the Mg metal waste, the strategy is to use a confinement matrix with a highly alkaline pore solution. Consequently, works have been dedicated to the behavior of Mg-Zr in Ordinary Portland Cement (OPC), mineral binder widely used for conditioning low level waste and geopolymers (GP), alumino silicate material [3,4]. Among the investigated materials, the lowest volume of hydrogen produced by aqueous corrosion has been measured in the sodium-based GP. Moreover, fluoride ions are known to inhibit efficiently the corrosion of Mg and its alloys [3-9]. A formulation has then been proposed to encapsulate Mg-Zr waste: a sodium based GP containing fluoride ions.

After the dismantling process, the magnesium cladding is isolated, but potentially contaminated with the fuel made of uranium (trace levels). It is therefore important to understand the uranium reactivity in confinement matrices proposed for Mg-Zr waste. Whereas the uranium oxidation is well documented in aqueous solution, only few studies concern the uranium corrosion in cementitious materials. However, the occurrence of the uranium oxidation in the nuclear waste storage context is studied regarding to: (i) hydrogen formation by aqueous corrosion; (ii) hydrogen reaction with uranium to form uranium hydride, which is known for its pyrophoric properties [10]. Some experiments have been carried out by X-ray powder diffraction and X-ray tomography to understand the uranium behavior in Blast Furnace Slag (BFS) / Ordinary Portland cement (3:1) [11]. In this study, UO_2 has been identified as the dominant corrosion product and no UH_3 has been detected over the 50-week period examined. Initially, a mixt oxidation by O_2 and H_2O would occur, followed by an aqueous corrosion regime during the early stage of hydration. After hydration, the cement permeability is reduced. Uranium oxidation is therefore slowed by the decreasing diffusion of oxidant. The corrosion of uranium in waste forms is also described in a report [12]. The main results presented concern BFS/OPC and Pulverized Fuel Ash (PFA)/Ordinary

Portland cement (3:1). It is shown that the corrosion rate is dependent on the oxygen content and the water availability. The uranium oxidation first proceeds rather by oxygen than by water until anaerobic conditions have been established. After cement hydration, the corrosion kinetic decreases linearly with time due to limitation on the water supply. The authors have also reported that in BFS/OPC cement, UO_2 and UO_3 can form a number of hydrated calcium urinates and uranium-substituted calcium silicate hydrates. In the literature, we can find a third report concerning the uranium oxidation in matrices [13]. Results obtained in the British Nuclear Fuel Limited and the Pacific Northwest National Laboratory have been described. They concern grouts composed of BFS and OPC with different water to cement ratio and magnesium phosphate cement. For some formulations, bentonite has been added to decrease the hydraulic permeability. Normal grouts show corrosion rates near those observed for U metal in anoxic water, while a factor of 2 to 3 decrease in corrosion rate is observed for dry grouts or for OPC with bentonite.

In this context, we were particularly concerned on the uranium behavior in geopolymers containing fluoride sodium, which could be proposed for the Mg-Zr waste confinement. As the pore solution of such materials has a basic pH, our work has first been focused on the reactivity of uranium in alkaline solution, with a particular attention on the role of fluoride ions [14]. In this reference, we have built the potential – pH diagram, which shows a passivation zone for basic aqueous solutions: depending on the redox conditions, uranium is protected from corrosion by the solid phase UO_2 , U_4O_9 , U_3O_7 , U_3O_8 or UO_3 . Our thermodynamic calculations have also demonstrated that the uranium fluoro complexes UF_4 and UO_2F_2 cannot be formed in basic solutions containing 1.25 M of fluoride ions. Experiences carried out in basic solutions containing fluoride ions have put in evidence an opposite behavior of hydroxide and fluoride ions on the uranium oxidation process: F^- ions induce the continuous uranium corrosion whereas OH^- ions protect the metal against the corrosion. Two mechanisms have then been proposed according to the ratio of the fluoride and hydroxide ions concentration [14].

Therefore, our work is now focused on the uranium behavior in geopolymers containing fluoride ions to evaluate the risk of its presence inside the primary package of MgZr waste. This study is mainly based on (i) the exploitation of results reported in the literature, both on the U reactivity in basic solution and on the pH evolution of geopolymers pore solution and (ii) the electrochemical measurements carried out on uranium incorporated in geopolymers as a function of time and GP formulation. Two techniques have been selected: monitoring the open circuit potential (OCP) with time and electrochemical impedance spectroscopy (EIS) at

OCP. Three formulations have been studied: a geopolymer (GP), a geopolymer containing 1.25 M of NaF (GP-NaF) and a geopolymer containing a double concentration of NaOH (GP-NaF-NaOH).

2. Experimental

2.1. Geopolymers preparation

The formulation of the geopolymer (GP) is reported in the Table 1. First, an activation solution was prepared by dissolving sodium hydroxide (NaOH pellets, Sigma-Aldrich, purity 99.9 %) in a commercial silicate solution, the Betol 39T (Woellner, composed of 27.80 wt% SiO₂, 8.30 wt% Na₂O and 63.90 wt% H₂O). The solid phases, the metakaolin (Argical M1000, composed of 54.4 wt% SiO₂; 38.4 wt% Al₂O₃; 7.2 wt% impurities) and the sand (Fulchiron, reference VX800LS, silica sand with a D50 of 800 μm), were mixed with a mass ratio sand/metakaolin of 1.5. When the temperature of the activation solution has decreased until room temperature, the powders mixture (Metakaolin + sand) is added to the activation solution under stirring at 200 rpm. The rotation speed is then increased to 400 rpm for 2 minutes and 1000 rpm for 3 minutes.

To prepare the geopolymer containing fluoride ions (GP-NaF), sodium fluoride (NaF, Sigma Aldrich, purity 99.9 %) is added to the activation solution to obtain a concentration of 1.25 mol.L⁻¹ (0.012 wt%). In the “results and discussion” part, the fluoride concentration is expressed in mol.L⁻¹ to easily compare the results with the ones obtained in solution and reported in the reference [14].

A third formulation of geopolymer (GP-NaF-NaOH) was prepared by adding a quantity of NaOH twice as big as in GP-NaF (Table 1).

2.2. Electrochemical measurements

A three-electrode cell was used for the electrochemical measurements: a working electrode (uranium foil), a counter electrode (platinum wire) and a quasi-reference electrode (platinum wire). The electrochemical set-up is reported in the Figure 1.

The uranium foil (0.02 cm of thickness) was supplied by the Institut de Physique Nucléaire of Orsay. The uranium electrodes were cut with a chain saw (PRESI model Mecatome T210) at a rate of 2200 rpm to obtain surfaces comprised between 0.9 and 1.22 cm². The uranium electrodes were rinsed with water and cleaned by nitric acid (10 M) until a shiny appearance (around 2-3 min). Then they were rinsed with water, ethanol and air-dried. The uranium

electrodes were placed into a Pyrex tube (diameter: 8 mm), sealed on the top by a silicon paste (CAF 4).

The platinum wire (diameter: 1 mm, Goodfellow purity 99.9%) was cleaned with ethanol and heated until bright-red color with a blowtorch.

Just after mixing, 50 mL of geopolymer were introduced in a plastic container (3.5 cm in diameter and 5 cm in height). The three electrodes were incorporated in the GP and the electrochemical measurements were regularly achieved *in situ* from the first day of incorporation until almost the hundredth day.

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 10^5 and 0.1 Hz, with 10 frequencies values per logarithmic decade.

2.3. Sample preparation for characterization

To characterize the uranium surface, the GP has been cut with a chain saw (PRESI model Mecatome T210) at a rate of 2200 rpm at different angles and with a manual advance of the table (maximum 0.5 mm/s) to release the uranium electrode. In the case of strong uranium corrosion, a black powder has been stacked on the surface of the electrode and around this one through the GP. The uranium electrode has been rinsed with ethanol. The largest amount of black powder has been recovered, air-dried and analyzed by XRD.

2.4. XRD analysis

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 (θ - θ) equipped with a Cu anode ($K_{\alpha 1} = 1.54178 \text{ \AA}$). Acquisition was performed with a point scintillator NaI detector from 20° to 80° with 0.02° step size. Phase identification was performed with DIFFRACPlus software (release 2018, Bruker AXS) using powder diffraction files (ICDD PDF4+2018).

3. Results and discussion

3.1. Summary and exploitation of results reported from literature

We have shown in a previous paper that the uranium corrosion depends strongly on the ration $[F^-]/[OH^-]$ noted $R_{F/OH}$ [14]. Two mechanisms have been proposed as a function of $R_{F/OH}$. To understand the uranium reactivity in geopolymers, it seems to us important to summarize the

results obtained in basic solution containing fluoride ions. Moreover, the pH of the GP pore solution is initially very alkaline but evolves during its ageing. We have then analyzed results from literature to establish the variation of the ratio $R_{F/OH}$ as a function of the pH [19, 20] and the variation of the GP pore solution pH with time [21, 22].

Behavior of uranium in basic solutions (Summary of the results reported in the reference [14])

The main results published in this reference are summarized in this paper to understand the reactivity of uranium in GP, which have a basic pore solution. The behavior of uranium has mainly been examined by electrochemistry (voltammetry, OCP and EIS measurements) in alkaline solutions containing or not NaF. Two mechanisms, given in the Table 2, have been proposed as a function of the ratio $R_{F/OH}$:

- Mechanism A, if $R_{F/OH} < 1$: No corrosion

Uranium metal is not stable in aqueous solution. It is oxidized into UO_2 . According to the redox conditions, the uranium(IV) can be further oxidized by oxygen into uranium(VI) to form the hyper stoichiometric oxides UO_{2+x} , such as U_4O_9 , U_3O_7 , U_3O_8 or UO_3 [14-18]. The uranium metal is protected by the oxides layer and the electrochemical behavior is defined by the U(VI)/U(IV) redox couple.

- Mechanism B, if $R_{F/OH} > 1$: Corrosion

In the presence of NaF, the fluoride ions diffuse through the uranium oxides layer and cause its desquamation. The uranium metal is no longer protected and is corroded into UO_2 . The potential of the uranium is then fixed by the U(IV)/U(0) redox couple and the proposed mechanism includes 4 steps: 1) the charge transfers (oxidation of uranium and reduction of oxygen or water), 2) diffusion of fluoride ions, 3) adsorption of fluoride ions and desorption of UO_2 , 4) desorption of fluoride ions.

Nevertheless, in the presence of fluoride ions, if hydroxide ions are sufficiently concentrated ($R_{F/OH} < 1$), they prevent the fluoride ions diffusion by making an anionic barrier. The uranium metal is consequently protected against corrosion.

For example, we have reported the evolution with time of OCP measurement on uranium electrode in several electrolytes from pH 11 to 14 containing or not NaF (the OCP values have been recalculated in this work against the Pt reference electrode used for the measurements in the geopolymers). In conditions of no corrosion ($R_{F/OH} < 1$, mechanism A),

the OCP is controlled by the redox system U(VI)/U(IV). The OCP values depend on the O₂ content in the electrolyte and so, on the amount of U(VI) formed. By contrast, in the presence of NaF ($R_{F/OH} > 1$, mechanism B), we observe a decrease of OCP with time. A corrosion of uranium has been evidenced by the formation of a solid deposit, identified by XRD as UO₂.

Variation of $R_{F/OH}$ as a function of the pH (analysis based on the studies reported in the reference [19] and [20])

We have shown that the behavior of uranium in basic solution depends strongly on the ratio $R_{F/OH}$. In the experiments we realized in solution [14], the amount of NaF is fixed at 0.125 M, which is lower than its solubility. Then, the ratio $R_{F/OH}$ could easily be manageable. In geopolymers, the amount of NaF introduced (1.25 M) is higher than its solubility. To correlate the behavior of uranium with the pore solution composition, it is necessary to know the $R_{F/OH}$ ratio. This ratio is not easily controlled because the solubility of NaF depends on pH. Therefore, if we consider only saturated solution (concentration of NaF higher than 1 M), the ratio $R_{F/OH}$ is only controlled by the pH of the solution. Nagorski and Nowosselow have performed experimental studies on the solubility of NaF in NaOH solutions at various temperatures [19]. The results of this work have been reported by Seidell [20] and we have used them to draw the variation of the ratio $R_{F/OH}$ as a function of pH in solution saturated with NaF at 20°C (Figure 3). For pH higher than 13.8, the $R_{F/OH}$ ratio is lower than 1. In this case, the mechanism A would occur and no corrosion of uranium is expected. On the contrary, corrosion would be observed for pH lower than 13.8 because, in this case, the $R_{F/OH}$ ratio is higher than 1.

Variation of the GP pore solution pH with time (analysis based on the references [21] and [22])

As the uranium behavior depends strongly both on the pH and the NaF concentration, we have to take into account the evolution of the interstitial solution composition during the setting time. The pore solution composition of GP varies with time and a strong decrease of pH is measured just after preparation of the matrix [21]. The graph presented Figure 4 shows the variation with time of the GP interstitial solution pH measured in the reference [21], when GP is in contact with air. The pH variation is explained by the reactivity of the hydroxide ions. The initial pH is very high because the activation solution used to prepare the geopolymers is a very alkaline solution. Then, the formation of the Al-Si-Al bridges

consumes OH^- during the polymerization reaction, causing a decrease of the pH [21]. When the GP structure is stabilized, some hydroxide ions remain in the pore solution, involving a high pH value. Nevertheless, for the GP sample in contact with the atmosphere, the hydroxide ions react with the dissolved carbonic acid to form carbonates in solution. The pH decreases markedly until 10.5 after one year [22]. Nevertheless, in our experimental conditions (see the electrochemical set-up Figure 1), the contact of the geopolymer with the CO_2 contained in the atmosphere is limited by the cap on the top. The pH of our samples should then vary according to the "without air" experimental conditions and should not decrease until a pH of 10.5.

We observe on Figure 4 that the pH varies linearly after 50 days. The Y-intercept of this line indicates a pH of 12.6. The strong pH decrease observed for the short times corresponds to the GP polymerization reaction. Considering the experimental conditions described by Pouhet [21,22], the initial NaOH concentration is estimated at 8.4 M. The polymerization period is estimated from the curve evolution of Figure 4 at 30 days. After this period, the pH is close to 12.6, corresponding to a NaOH concentration close to 0.04 M. We can conclude that the polymerization of GP consumes 8.36 M of NaOH. In our experimental conditions, in GP and GP-NaF, the initial concentration of hydroxide is 9.2 M. After polymerization, we can assess that the NaOH concentration is close to 0.8 M corresponding to a pH close to 13.9. When GP-NaF-NaOH is prepared, the initial concentration of NaOH is 14.6 M and the pore solution pH is close to 14.8. After the polymerization phase, the decrease of pH measured by Pouhet is very low and, without CO_2 , it varies from 12.6 to 12.1 after one year (Figure 4). By extrapolation to our conditions, we can expect stabilization at pH 13.4 for GP-NaF and 14.1 for GP-NaF-NaOH.

Then, the pH critical value of 13.8 (determined in Figure 3) that characterizes the limit between the two behaviors of uranium would be reached in GP-NaF but not in GP-NaF-NaOH.

3.2. Experimental results

As corrosion is a redox reaction, it can be studied by electrochemical techniques. The open circuit potential (or the potential at zero current) at the selected metal in a medium is a good indicator of its reactivity, since this potential is imposed by the redox reaction occurring at the interface. Electrochemical Impedance Spectroscopy is an interesting technique for understanding the reactivity of redox compounds and to access to data on the evolution of the

interface metal/electrolyte. This method has already been applied to study the corrosion of metal or alloy embedded in a cement-based-material [23-31]. Since OCP and EIS (recorded at the OCP) measurements have the advantage not to alter the metal sample/medium interface, the uranium reactivity has mainly been examined by using both methods with only one sample, *in situ* and during a long time range.

Open circuit potential measurement in matrices

In solution, when uranium metal is corroded, its OCP is fixed by the U(IV)/U(0) redox couple, whereas if no corrosion occurs, the OCP is fixed by the U(VI)/U(IV) redox couple. Consequently, OCP has regularly been measured on uranium electrode immersed in the studied GP (Figure 5) from the first day until the almost hundredth day. These values can be compared to the uranium potential measured in solution (Figure 2).

- In GP and GP-NaF-NaOH, the uranium OCP evolution with time and the OCP values are similar to the one measured in solution in the case of $R_{F/OH} < 1$ (corresponding to the corrosion mechanism A). That is in agreement with our previous analysis of pH evolution in GP. In GP-NaF-NaOH, we have shown that the ratio $R_{F/OH}$ is never higher than 1 because the pH does not decrease under 14.1. Then the mechanism A can be applied: UO_2 formed instantaneously at the U interface is oxidized by oxygen to the hyper stoichiometric UO_{2+x} . . The nature of UO_{2+x} depends on the amount of free soluble oxygen in the medium. Whatever the nature of the oxide layer, its protection against uranium metal corrosion is sufficient to prevent, during the time range considered, hydrogen and uranium hydride production.

. The presence of uranium inside the primary package of MgZr has no damaging effect on the safety of the confinement.

- In GP-NaF, the variation of OCP measured on U metal electrode with time is different. During the first days, the presence of fluoride ions does not have any effect on the OCP. On the contrary, after 10 days, the OCP decreases significantly to -0.7 V/Pt. This trend is also observed in basic aqueous solution and the OCP values are close to the one measured at pH 12.5 in the presence of NaF, when the $R_{F/OH}$ is higher than 1. Based on the results of Pouhet detailed before [22], the ratio $R_{F/OH}$ becomes higher than 1 after the GP polymerization phase (about 30 days). In GP-NaF, mechanism B (uranium corrosion) occurs when the pH of the GP pore solution decreases under 13.8. That is observed after a period of 10 days. This period seems shorter than the expected one (30 days to reach a pH of 13.9) but the geopolymer composition was not exactly the same that the one studied by Pouhet.

We can then suppose that in geopolymers, the uranium reactivity is the same as in basic solutions. In the absence of fluoride ions or if $R_{F/OH} < 1$, UO_2 is oxidized into UO_{2+x} and U metal is protected against the corrosion by this oxides layer. The hydroxide ions constitute an effective electrostatic barrier and the fluoride ions cannot approach the U metal surface. However, if $R_{F/OH} > 1$, the fluoride ions diffuse through the oxides layer and cause its desquamation. The uranium metal is then continuously corroded into UO_2 .

In GP, U metal would then be protected against the corrosion by the passive layer composed of UO_2 and the hyper stoichiometric oxides UO_{2+x} (mechanism A).

By contrast, in GP-NaF, both mechanisms can be observed. During the first days, the pH is very high. The hydroxide ions are enough concentrated to constitute an effective barrier against the fluoride ions diffusion through the oxide layer. The uranium is then not corroded during this period (mechanism A). However, as the pore solution pH decreases, the fluoride ions become more concentrated than the hydroxide ions and the second mechanism (B) occurs. The uranium metal is corroded into UO_2 .

In GP-NaF-NaOH, the amount of free OH^- in the pore solution is enough to protect the metal against corrosion (mechanism A).

Electrochemical Impedance Spectroscopy

The impedance diagrams are recorded on uranium electrode incorporated in GP (Figure 6). The Nyquist diagrams (variation of the imaginary part Z_i of the impedance as a function of the real part Z_r) show a quasi-vertical curve characteristic of a capacitive. However, the impedance values are relatively small. This behavior can be related to the one described in solution at pH 14 [14]. It can be attributed to the presence of a redox system UO_{2+x}/UO_2 at the uranium surface. In the impedance diagrams, there would be two contributions: the charge transfer U^{VI}/U^{IV} and the formation of the passivating layer composed of the oxides uranium. The impedance diagrams also show no significant variation with time. This result suggests that the interface does not evolve drastically.

The impedance diagrams obtained GP-NaF are reported Figure 6B. After about 30 days, the impedance decreases and diffusion impedance appears (characterized by a phase at 45° at low frequencies). After 50 days, the electrical connection has been lost. These results put clearly in evidence a different behavior of uranium in the presence of fluoride ions in the GP.

However, in the GP-NaF-NaOH, the evolution of the impedance diagrams recorded on uranium electrode is totally different from GP-NaF (Figure 6C). We can observe a capacitive behavior until 56 days. The reactivity of uranium in this GP formulation is close to that

observed in GP without NaF. The ratio $R_{F/OH}$ is lower than 1. The uranium is protected by a layer composed of the oxides UO_2 and UO_{2+x} .

The electrolyte resistance can be measured by EIS. It corresponds to the values measured at high frequencies for Z_i equal to zero. The evolution of the electrolyte resistance on a Pt electrode in GP, GP-NaF and GP-NaF-NaOH is given in Figure 7 (left). The use of a Pt electrode has for objective to characterize only the electrical contribution of the matrices. We observe a fast increase of this resistance during the first days and a stabilization after 60 days for GP and GP-NaF. After 100 days, R_e measured in GP-NaF-NaOH is not yet stabilized probably because the high amount of NaOH. In GP-NaF and GP-NaF-NaOH, the values are similar and lower than the one measured in GP. That can be explained by the presence of NaF in the pore solution which increases the conductivity of the electrolyte more than NaOH. The excess of NaOH introduced in GP-NaF-NaOH does not bring a supplementary increase of the conductivity.

R_e was also measured on uranium electrodes. In this case, the resistance measured at high frequencies is the sum of the resistance of the pore solution (measured on Pt electrode) and the layer covering the uranium surface. We have then chosen to present the variation of $(R_e(U)-R_e(Pt))$, which is only characteristic of the resistance at the uranium/covering layer interface (Figure 7 (right)).

For GP-NaF, during the first 50 days, the resistance values are the lowest. That means that the solid phase formed at the uranium surface in GP-NaF is less protective than the one formed in GP and GP-NaF-NaOH. Moreover, in this geopolymer containing fluoride ions, we can observe a high increase of the resistance after 50 days. This can be attributed to the loss of electrical connection due to the high uranium corrosion. This is in good agreement with the results presented above.

In GP and GP-NaF-NaOH during 60 days, the resistance values are the same. The uranium surface is protected by a passive layer. For the longest period, we observe an increase of the resistance in GP-NaF-NaOH. This could be attributed to a supplementary resistance due to the adsorption of hydroxide ions in this geopolymer containing the highest amount of NaOH.

Observation of the geopolymer and the uranium surface after curing

The pictures of the geopolymers GP and GP-NaF with the uranium electrodes are reported Figure 8. Without NaF (GP, picture on the left) or with NaF but in presence of a double concentration of NaOH (GP-NaF-NaOH, data not shown), no crack has been formed after

about 100 days of U incorporation. By contrast, we observe cracks, only in the vicinity of the uranium electrodes (picture on the right), for the geopolymer containing NaF (GP-NaF).

The uranium electrode has been extracted from the matrices by cutting the samples with a chain saw. The uranium surface is covered by a thin, compact, black solid phase, which can be attributed to the superoxides UO_{2+x} layer. After immersion in the geopolymer containing the sodium fluoride salt (GP-NaF), the uranium surface is highly corroded (Figure 8). A black solid phase has been formed around the uranium electrode. The solid phase has been collected and analyzed by XRD (Figure 9). By comparison with the experimental diagram of UO_2 and the ICDD pattern 04-008-2456 calculated for UO_2 , the results show that uranium is corroded into UO_2 . This is in good agreement with the mechanism proposed above: in GP-NaF, uranium is continuously corroded into UO_2 when the pH of the pore solution decreases. The formation of cracks in the geopolymer around the electrode can be explained by the production of either UO_2 , an expansive oxide compound [32] or H_2 , formed by reduction of water during the corrosion reaction. It should be interesting to measure by gas chromatography the hydrogen release to understand if the corrosion of uranium in presence of fluoride ions is an aqueous or a gaseous reaction.

4. Conclusions

In regard to the analysis of the reported data in the literature, the electrochemical measurements and the observation of both the geopolymers and the uranium surface after curing, the behavior of uranium in the three selected geopolymers have been summarized in the Table 3. In geopolymers, the uranium behavior is the same as the one previously described in basic solutions. Two mechanisms can be proposed depending on the ratio of the fluoride and hydroxide ions concentration ($R_{\text{F/OH}}$). Without NaF (GP) or with NaF and a double concentration of NaOH (GP-NaF-NaOH), the uranium metal is protected against corrosion by the oxides UO_{2+x} layer (mechanism A). By contrast, in the presence of fluoride ions (GP-NaF), because the pore solution pH decreases, the ration $R_{\text{F/OH}}$ can reach values higher than 1. In this case, the protective layer is desquamated and so, the uranium is continuously corroded (mechanism B). Cracks have been observed in the vicinity of the uranium electrode and can be explained by the high production of uranium oxides, which are expansive products or by the hydrogen gas formed by aqueous corrosion.

Acknowledgement

This work was supported by the interdisciplinary NEEDS project funded by ANDRA, CNRS, EDF, AREVA, CEA and IRSN.

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Figure captions:

Figure 1: Set-up for electrochemical measurements on uranium electrode incorporated in 50 mL of geopolymers (diameter of the plastic pots: 3.5 cm and height: 5 cm).

Figure 2: Variation of the uranium Open Circuit Potential (OCP) as a function of time in basic solutions containing or not NaF (0.125 M) [14].

Figure 3: Variation of the $R_{F/OH}$ ratio with pH in saturated solutions of NaF at 20°C (analysis of data from references [19] and [20]).

Figure 4: Variation of GP pore solution pH with time (analysis of the data reported by Pouhet [21]).

Figure 5: Variation of the uranium Open Circuit Potential (OCP) as a function of the immersion time in the three geopolymers (GP, GP-NaF and GP-NaF-NaOH).

Figure 6: Variation of the Nyquist and Bode diagrams recorded on uranium electrode as a function of immersion time in the three studied geopolymers GP (A), GP-NaF (B) and GP-NaF-NaOH (C) at OCP ($\Delta E = 10 \text{ mV}$; $F = 10^5 \text{ to } 10^{-1} \text{ Hz}$).

Figure 7: Evolution of the electrolyte resistance R_e measured on Pt electrode (left) and ($R_e(U) - R_e(Pt)$) corresponding to the difference between the electrolyte resistance measured on U and on Pt (right) with time.

Figure 8: Photos of uranium electrode and electrochemical set-up in the geopolymers GP and GP-NaF after curing (diameter of the plastic pots used for the electrochemical measurements: 3.5 cm and height: 5 cm).

Figure 9: Diagram XRD of the solid phase formed at the uranium surface after immersion in a geopolymer with NaF (black curve). Comparison with the diagram of the UO_2 solid phase and the ICDD pattern 04-008-2456 (grey curve and grey markers).

Figure 1

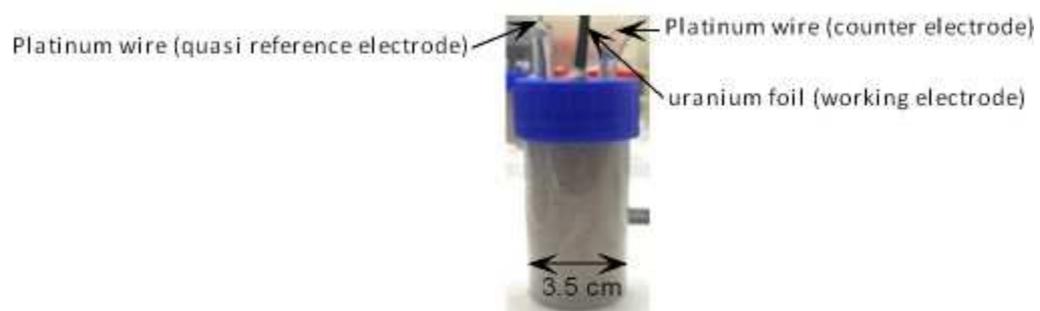


Figure 2

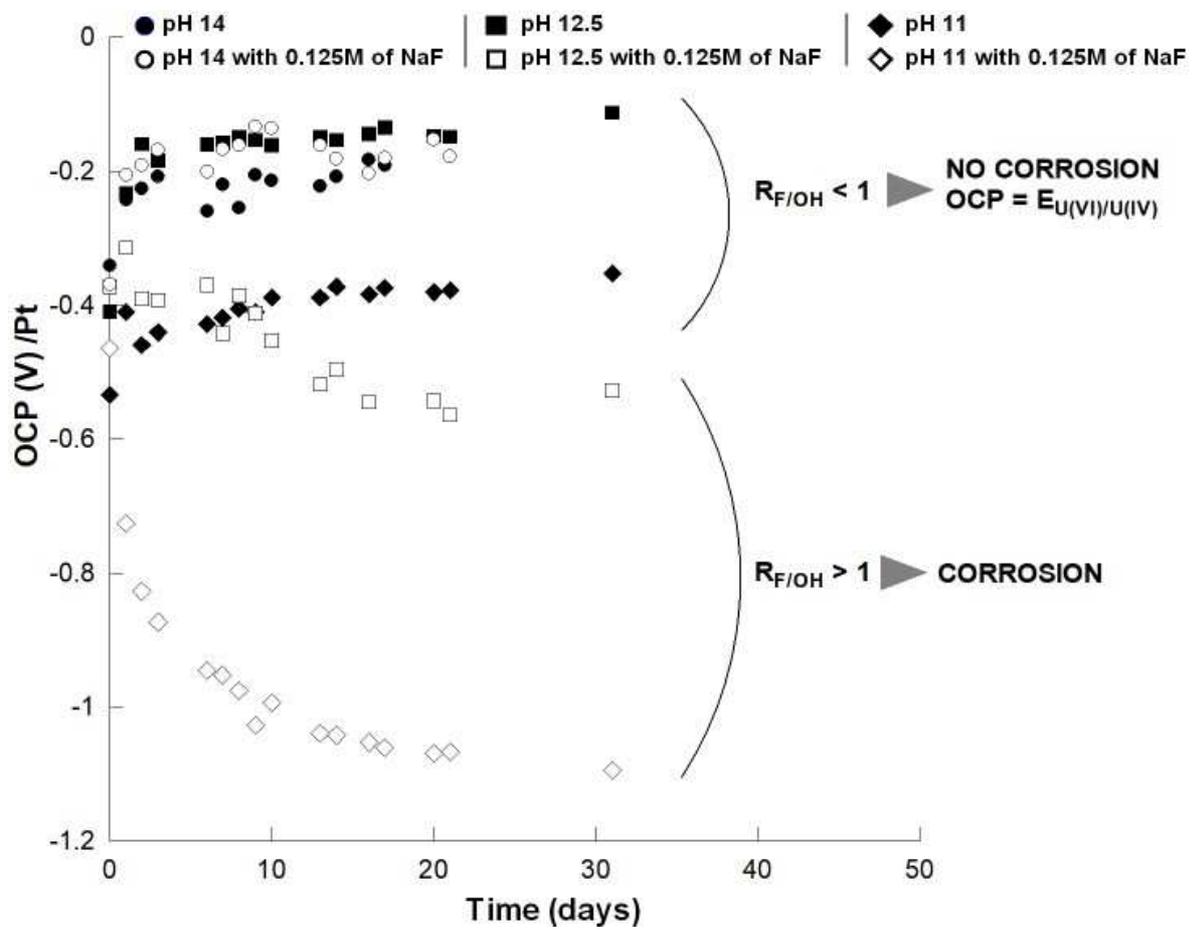


Figure 3

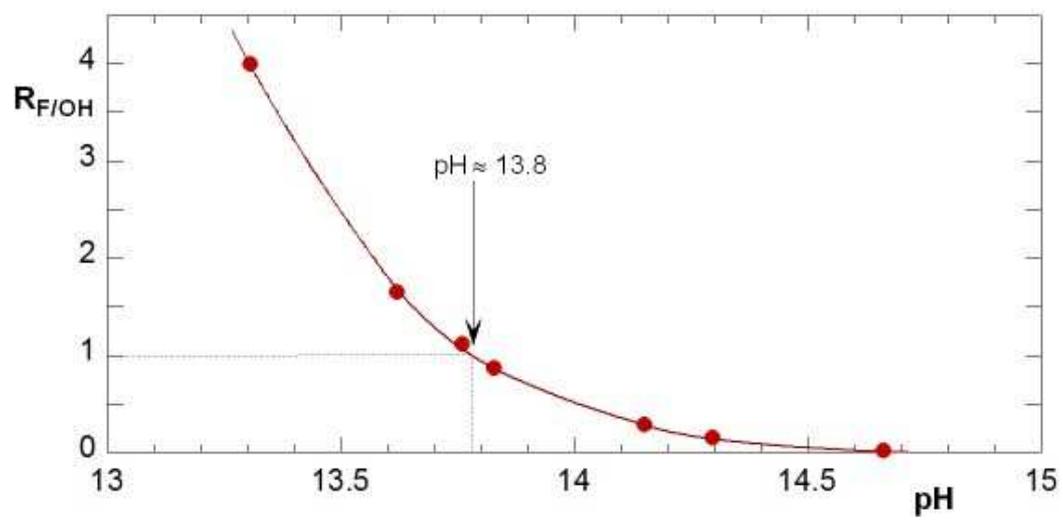


Figure 4

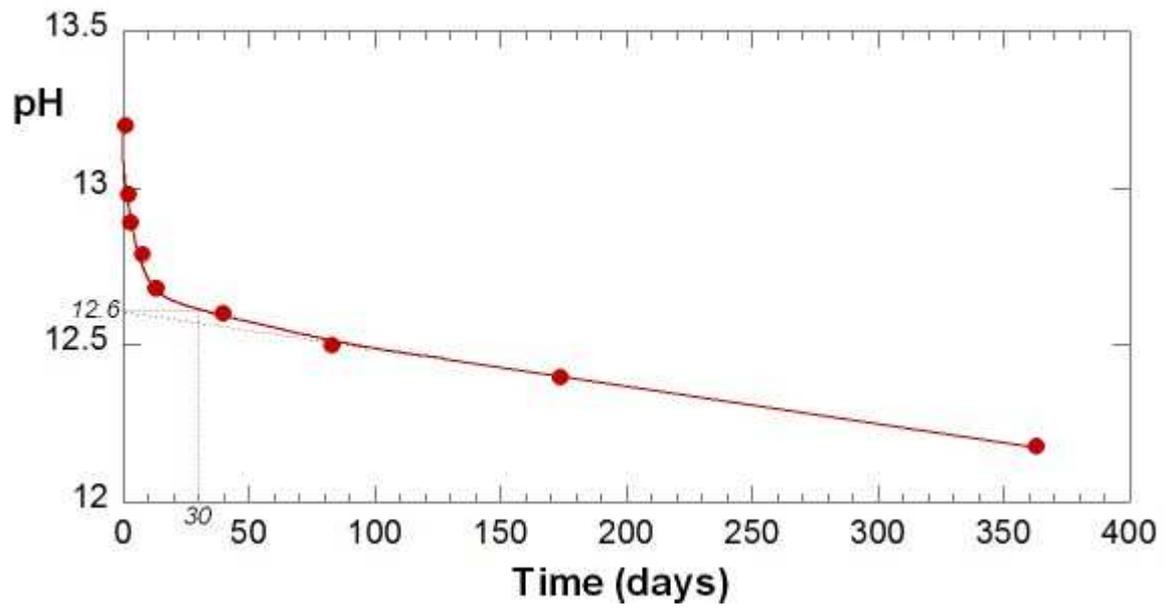


Figure 5

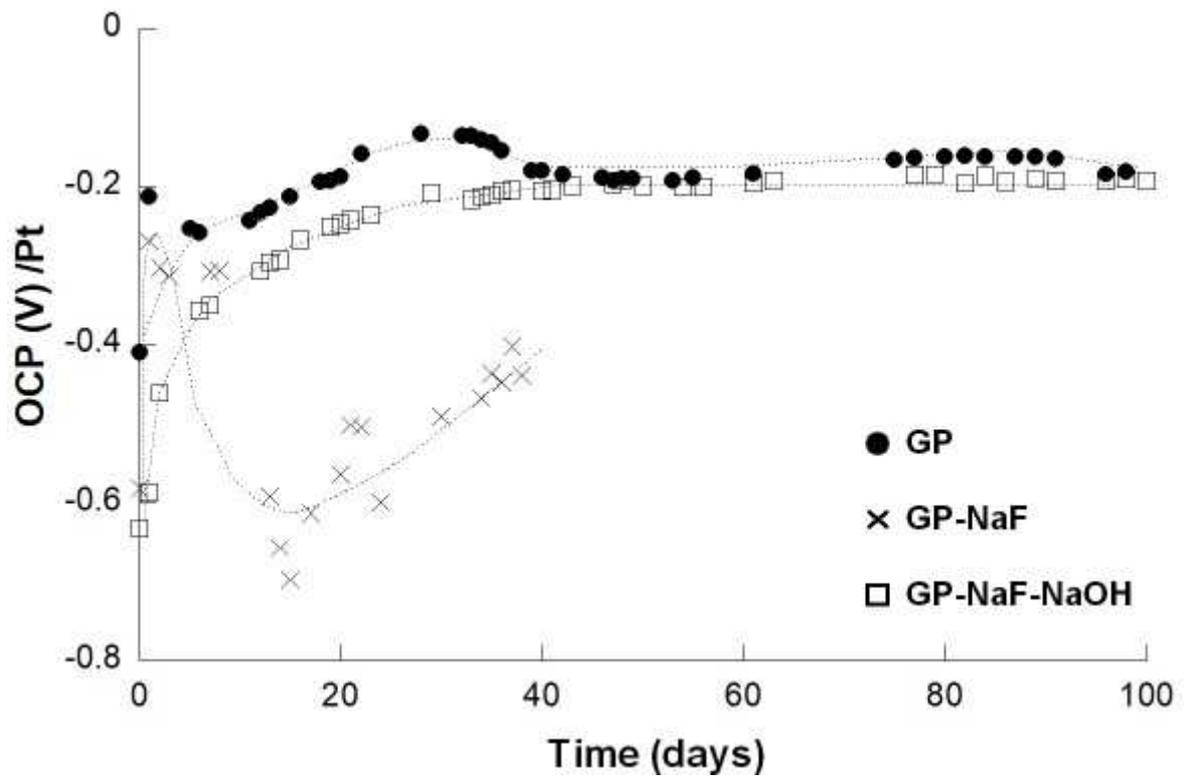


Figure 6

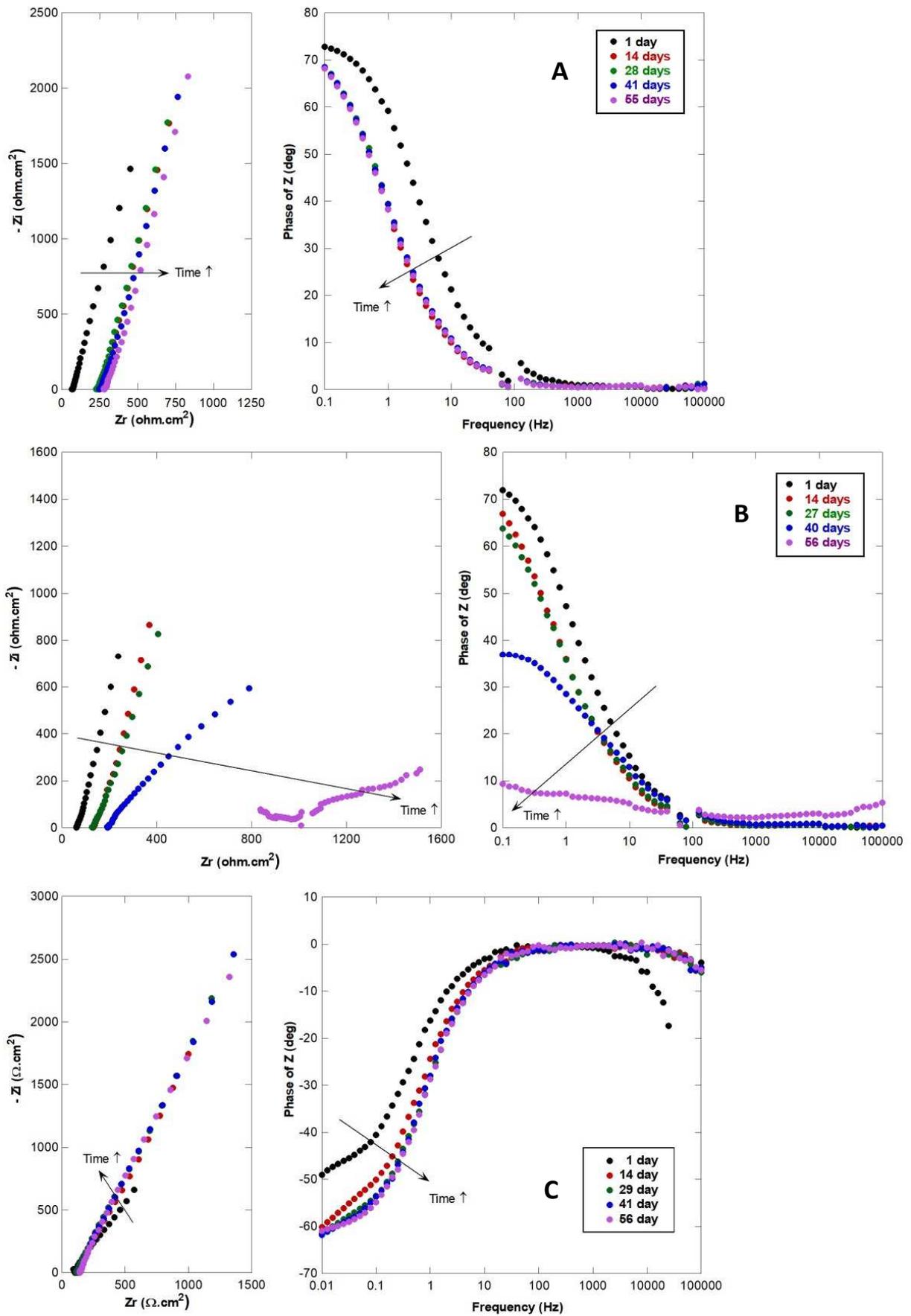


Figure 7

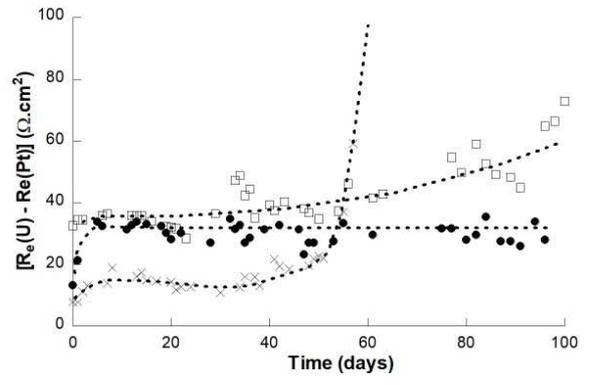
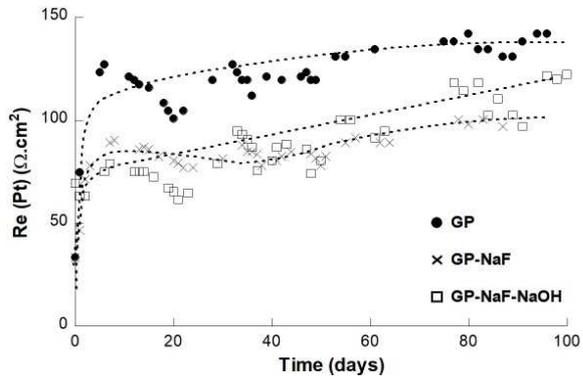


Figure 8

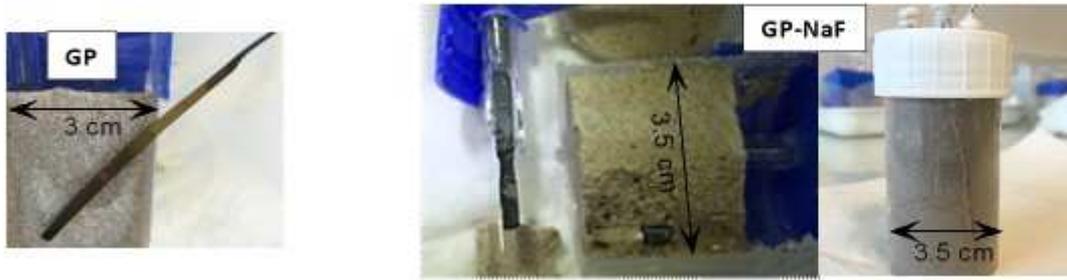
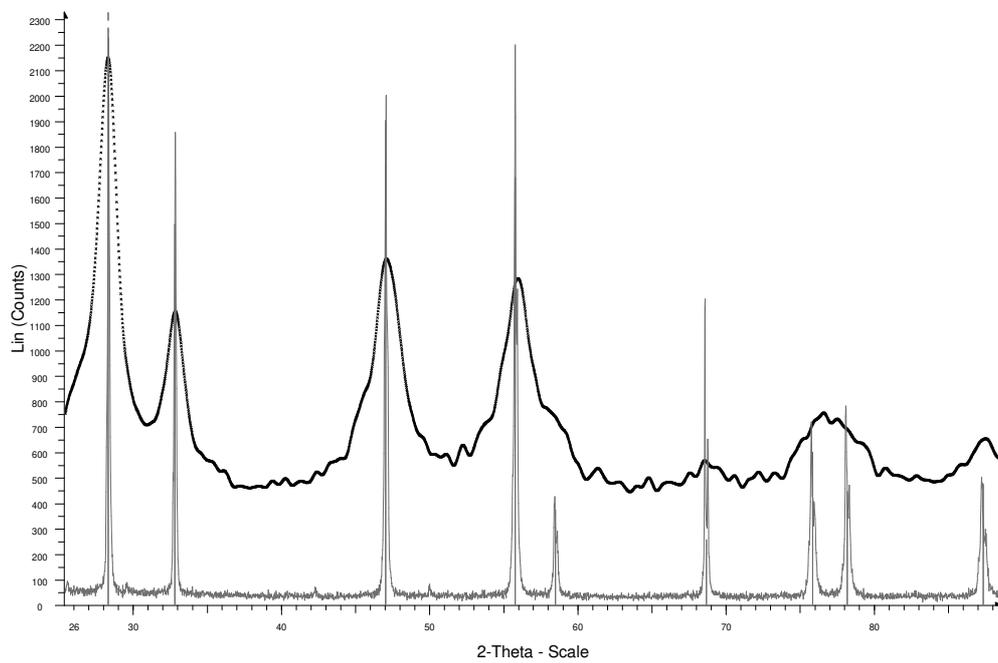


Figure 9



Tables

Table 1: Chemical composition for 100 mL of geopolymer ($\text{Al}_2\text{O}_3 - 3.8 \text{ SiO}_2 - \text{Na}_2\text{O} - 12.5 \text{ H}_2\text{O}$) containing NaF (1.25 mol.L^{-1} , 0.012 w%).

| | GP | GP-NaF | GP-NaF-NaOH |
|---|------------|---------------|--------------------|
| | weight (g) | | |
| Betol 39T (SiO_2 27.8w%, Na_2O 8.3 w%, H_2O 63.9 w%) | 47.87 | 47.87 | 47.87 |
| NaOH | 7.57 | 7.57 | 15.14 |
| Distilled water | 5.14 | 5.14 | 5.14 |
| NaF | 0 | 2.29 | 2.29 |
| Metakaolin | 42.13 | 42.13 | 42.13 |
| sand | 84.27 | 84.27 | 84.27 |
| total | 189.27 | 189.27 | 189.27 |

Table 2: Mechanisms proposed for the behavior of U metal in basic solutions as a function of the ratio $[F^-]/[OH^-]$ ($R_{F/OH}$) in the reference [14]

| Mechanism A | Mechanism B |
|--|---|
| $R_{F/OH} < 1$ | $R_{F/OH} > 1$ |
| No corrosion | Corrosion |
| Protective layer of UO_{2+x} | No protective layer |
| <p>Charge transfer reaction</p> $UO_2 + 2xOH^- \rightarrow UO_{2+x} + xH_2O + 2xe^-$ | <p>Corrosion reactions</p> $U + s + 4OH^- \rightarrow UO_{2,s} + 2H_2O + 4e^-$ $O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{or}$ $4H_2O + 4e^- \rightarrow 4OH^- + 2H_2$ <p>Fluoride ions diffusion</p> $F^-_{\text{solution}} \rightarrow F^-_{\text{metal interface}}$ <p>Desorption of UO_2</p> $UO_{2,s} + F^-_{\text{metal interface}} \rightarrow F^-_{,s} + UO_2$ <p>Desorption of F^-</p> $F^-_{,s} \rightarrow F^- + s$ |
| OCP controlled by the redox system U(VI)/U(IV) contained in the protective layer of UO_{2+x} | OCP controlled by the corrosion reaction of U^0 into $U^{IV}O_2$. |

Table 3: Mechanisms proposed for the behavior of U metal in the geopolymers

| GP | GP-NaF-NaOH | GP-NaF | |
|--|--|--|--|
| No fluoride ions | pH stabilization (30 days) = 14.1 | pH stabilization (30 days) = 13.4 | |
| $R_{F/OH} < 1$ | $R_{F/OH} < 1$ | $R_{F/OH} < 1$ If pH > 13.8 | $R_{F/OH} > 1$ If pH < 13.8 |
| Mechanism A | Mechanism A | Mechanism A | Mechanism B |
| No corrosion Protection of U by oxides layers | No corrosion Protection of U by oxides layers | No corrosion Protection of U by oxides layers | U corrosion Formation of uranium oxides Possible formation of H ₂ Cracks of GP |