Study of SIMFUEL corrosion under hyper-alkaline conditions in the presence of silicate and calcium

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ABSTRACT

Cement has been considered as a possible material present in the Deep Geological Disposal (DGD) [1] . In order to determine the effect of cementitious waters on the oxidation of the surface of Spent Fuel (SF), a series of electrochemical experiments were performed, to study the influence of two main components of cementitious water: calcium and silicate.

Test solutions with Na_2SiO_3 and/or $CaCl_2$ were prepared at pH 12 and NaCl 0.1 mol·dm^{-3} as ionic medium. A 3 at.% doped SIMFUEL was used to perform cyclic voltammetric (CV), potentiostatic and corrosion potential (E_{CORR}) experiments. After potentiostatic and E_{CORR} experiments, the SIMFUEL surface was analyzed using X-Ray Photoelecton Spectroscopy (XPS).

The results showed that the presence of silicate decreased the SIMFUEL oxidation between -100 mV and 300 mV. When Ca^{2+} was added, the whole oxidation process was shifted to higher potentials which indicated a protective effect of the combination of Ca^{2+} and SiO_3^{2-} . The XPS results obtained after potentiostatic experiments at 200 mV showed that the presence of silicate partially suppressed the oxidation of SIMFUEL, as indicated by the contribution of both U(IV) and U(V) XPS to the U $4f_{7/2}$ band (~ 38%). After the addition of calcium, the predominant uranium oxidized state contribution on the surface was U(V) (40%). After the E_{CORR} experiments, the E_{CORR} values were similar either with or without silicate in solution (-80 mV and -70 mV respectively). The resulting surface also exhibited a similar composition. When calcium was added to the electrolyte, the E_{CORR} value was suppressed to -105 mV, and XPS showed that the surface was less oxidized than with the other two electrolytes.
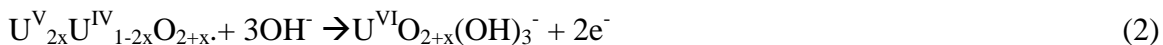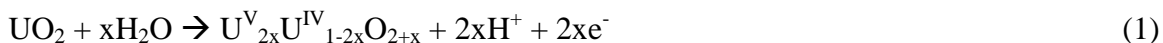
INTRODUCTION

In the spent fuel near field many reactions between the water and the spent fuel (SF) can occur depending on the solution composition, redox conditions, and pH. Experimental studies with actual SF are expensive and complex. In order to assess the SF performance some studies have been carried out using SF analogues such as SIMFUEL [2]–[4].

Cement has been proposed for use in the deep geological disposal to seal possible cracks in the different structures. Waters in contact with cementitious materials have high pH values and contain silicate and calcium ions [5], [6]. However, SF corrosion under these conditions has not been extensively studied.

Some studies on the influence of very alkaline pH values on UO_2 dissolution have been published [7], [8]. Santos et al. [9] studied the influence of pH on the corrosion of SIMFUEL by

performing CV and potentiostatic experiments and analyzing the surface by XPS. The authors proposed the subsequent oxidation mechanism (1) and (2) at high pH:

$$UO_2 + xH_2O \rightarrow U^V_{2x}U^{IV}_{1-2x}O_{2+x} + 2xH^+ + 2xe^- \tag{1}$$

$$U^V_{2x}U^{IV}_{1-2x}O_{2+x}.+ 3OH^- \rightarrow U^{VI}O_{2+x}(OH)_3^- + 2e^- \tag{2}$$

The effect of SiO_3^{2-} on the corrosion of 1.5 at.% doped SIMFUEL was also studied at pH=9.5 by Santos et al. [10]. The authors determined that SiO_3^{2-} could not prevent the first oxidation step (1) but it suppressed the subsequent reaction from ($U^V_{2x}U^{IV}_{1-2x}O_{2+x}$) to U(VI) phases (reaction (2)). This was attributed to the adsorption of silicate on the fuel surface promoting the precipitation of a U(VI) hydrated phase at high corrosion potentials.

The presence of Ca^{2+} was also studied at pH = 9.5 by Santos et al.[11] using a 1.5 at.% doped SIMFUEL. They observed that Ca^{2+} had a similar effect to that of SiO_3^{2-}. Calcium could prevent the first oxidation step but it inhibited further oxidation of the ($U^V_{2x}U^{IV}_{1-2x}O_{2+x}$) layer to U(VI) surface species. The authors proposed two different possible mechanisms: the inhibition of the $UO_2(OH)_{2ads}$ precursor on the ($U^V_{2x}U^{IV}_{1-2x}O_{2+x}$) surface, and/or the blockage of O^{2-} anions transfer reaction from the oxidized fuel surface to the bulk of the electrode.

In the present study, SIMFUEL corrosion has been studied in more representative cementitious waters by using a hyper-alkaline medium containing SiO_3^{2-} and/or Ca^{2+}.

EXPERIMENTAL SET UP

The SIMFUEL electrode (WE) was prepared from a 3 at.% doped UO_2 pellet made by Canadian Nuclear Laboratories (Chalk River, Ontario, Canada). The procedure used to prepare the electrode from the pellet slice has been described previously [12]. Before an experiment, the electrode was polished with 1200 grit SiC paper to remove any oxidized surface phases.

A three compartment cell was used to perform all experiments. The counter electrode was a platinum net and the reference electrode (RE) was a commercial saturated calomel electrode (SCE) (Fisher Scientific). The cell was placed in a Faraday cage to minimize interference from electrical noise.

The 0.1 mol.dm^{-3} NaCl (Caledon, 99.0%) solutions were prepared using Milli-Q water (ρ=18.2 MΩ·cm). The pH was adjusted to 12 by adding NaOH or HCl when necessary (Na$^+$-OH$^-$ electrolyte). Na$_2$SiO$_3$ (Aldrich) was used to prepare the 10^{-2} mol·dm^{-3} SiO_3^{2-} electrolyte. CaCl$_2$ (Fisher Scientific) was used to add 10^{-3} mol·dm^{-3} of calcium to the SiO_3^{2-} electrolyte (Ca^{2+}-SiO$_3^{2-}$ electrolyte).

Data were recorded using a Solatron Potentiostat. Cyclic voltammetric (CV), potentiostatic, and corrosion potential (E$_{CORR}$) experiments were carried out with the three electrolytes. Prior to an experiment, the electrolyte was purged with an Ar stream supplied by BOC (UK) and a cathodic cleaning performed at -1400 mV to reduce any oxidized surface layer. CV experiments were performed between -1200 mV and 400 mV (vs. SCE) using a scan rate of 10 mV·s^{-1} in a stirred solution. For potentiostatic experiments, the potential applied between the WE and the RE was 200 mV for 1 hour. E$_{CORR}$ experiments were also performed. The data obtained were recorded using the Corrware and Corrview software (Scribner Associates).

After each potentiostatic experiment and each E$_{CORR}$ experiment, the WE surface was analyzed by XPS in order to determine the oxidation of the solid surface. The spectra were

deconvoluted into contributions from U^{IV}, U^{V} and U^{VI} using the methodology published by Santos et al. [10].

RESULTS AND DISCUSSION

Cyclo – voltammetric measurements (CV)

The CV measurements show the change in current density as a function of the potential applied at a scan rate of $10mV.s^{-1}$. These curves provide qualitative information on the kinetics of the reactions occurring on the SIMFUEL surface.

Figure 1 shows that, in the presence of SiO_3^{2-} the current density in the potential region between -100 mV and 300 mV is decreased compared to the current measured in the NaOH electrolyte. In the solution containing both Ca^{2+} and SiO_3^{2-}, the onset of oxidation does not start until the potential is 60 mV more positive than in the other two solutions.
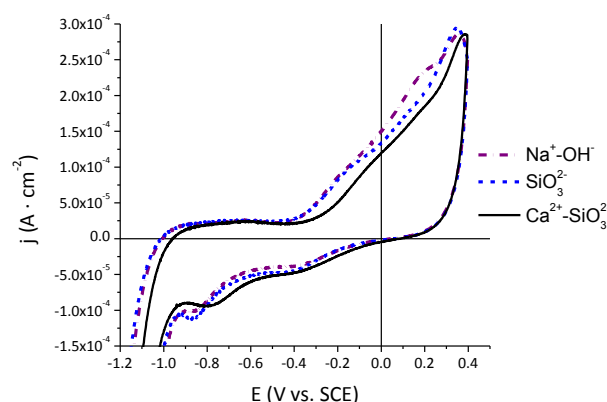
Figure 1 CV curves obtained with Na^+-OH^-, SiO_3^{2-} and Ca^{2+}-SiO_3^{2-} electrolytes

Since, thermodynamically, oxidation of UO_2 becomes possible at approximately at -400 mV (vs. SCE) (reaction (1)) [13], Figure 1 indicates that the presence of SiO_3^{2-} in the solution slightly suppresses the oxidation of the initially formed $U^V_{2x}U^{IV}_{1-2x}O_{2+x}$ to the more soluble $U^VO_2^{2+}$ (and the formation of U(VI) phases) which occurs between -100 and 300 mV[13]. When both Ca^{2+} and SiO_3^{2-} are present the UO_2 matrix is stabilized. However, CVs are rapid experiments and to determine in more detail the influence of each ion on the oxidation reactions, potentiostatic experiments were performed.

Potentiostatic experiments

The evolution of the current density as a function of time at 200 mV was recorded and integrated over the period of oxidation to yield the total charge used in oxidation (Q_A). The results are shown in Figure 2A. Over the first few minutes the charge (Q_A) due to oxidation does not change significantly in NaOH and the SiO_3^{2-} solution, but decreases at longer times indicating the presence of silicate suppresses the oxidation slightly. When both Ca^{2+} and SiO_3^{2-} are present the extent of oxidation is very significantly suppressed confirming that this combination inhibits the oxidation of the UO_2. These results are consistent with the less rigorous

CV experiments which showed the lowest current density at 200 mV was observed with Ca^{2+} and SiO_3^{2-} present.

 After the potentiostatic experiments, the SIMFUEL electrode was analyzed by XPS and the deconvolution of the U 4f bands into contributions from U^{IV}, U^V and U^{VI} are shown in Figure 2B. Consistent with expectations from the potentiostatic experiments, the extent of oxidation of the UO_2 surface was the greatest after anodic oxidation in the NaOH solution, lower after oxidation in the silicate solution, and least after oxidation in the solution containing both Ca^{2+} and SiO_3^{2-}.
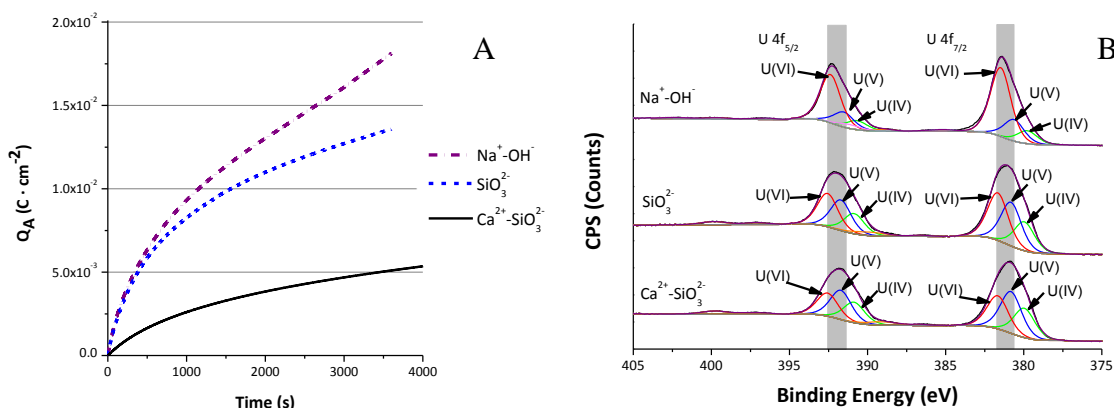

Figure 2 (A) Comparison of all the anodic charges obtained by the integration of the current densities and **(B)** the resulting U4f XPS band of the WE.

 Although not shown here, the XPS survey spectrum detected both Ca^{2+} and SiO_3^{2-} on the surface of the electrode after potentiostatic oxidation. While the exact chemical state of both the Ca^{2+} and the SiO_3^{2-} remains uncertain, it is possible their incorporation into surface layers blocks the incorporation of O^{2-} ions required for oxidation of the UO_2 surface.

Corrosion potential measurements

 In corrosion experiments, the E_{CORR} of the SIMFUEL electrode was measured over an exposure period of 24 hours in each of the three electrolytes. The evolution of E_{CORR} with time of exposure to the three solutions is shown in Figure 3A. Initially, E_{CORR} increased rapidly to approximately -300 mV in all three solutions. Subsequently, the behavior of the potential varied depending on the electrolyte. In the NaOH electrolyte, E_{CORR} increased to a steady-state value of -80 mV after approximately 3 hours.

 In the presence of SiO_3^{2-}, E_{CORR} increased more slowly achieving a steady-state value of approximately -70 mV by the end of the exposure period. This value is similar to that obtained in the NaOH electrolyte but took considerably longer to achieve, suggesting that, while the extent of oxidation was similar in the two electrolytes, oxidation of the surface was much slower when SiO_3^{2-} was present.

 When both Ca^{2+} and SiO_3^{2-} are present, the increase in E_{CORR} was very slow and the final value at the end of the exposure period was lower at approximately -105 mV, Figure 3A. At the end of the 24 hours, E_{CORR} was still increasing slightly suggesting oxidation was possibly still occurring.

Figure 3B shows the XPS spectra recorded at the end of each experiment. For the experiments in electrolytes with and without SiO_3^{2-} the distribution of the three oxidation states (U^{IV}, U^V, U^{VI}) was very similar consistent with the similar final E_{CORR} values. However, when both Ca^{2+} and SiO_3^{2-} were present, the UO_2 surface was considerably less oxidized as expected since the final E_{CORR} achieved was lower. Closer inspection of the deconvoluted U 4f peaks show it is the fraction of U^V in the electrode surface which is suppressed in this last experiment, indicating that, in the presence of both Ca^{2+} and SiO_3^{2-}, it is the oxidation of UO_2 to $U^V_{2x}U^{IV}_{1-2x}O_{2+x}$ that is suppressed.

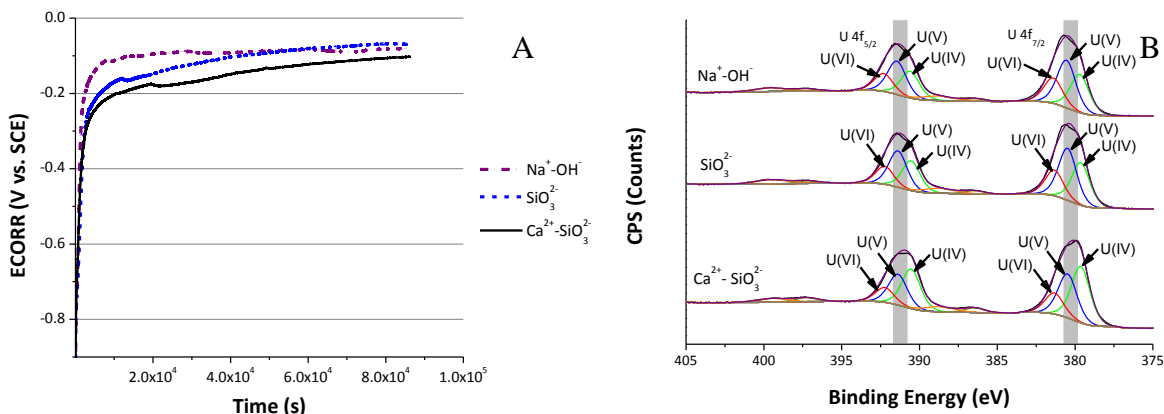**Figure 3 (A)** E_{CORR} measurements on the 3 at.% doped SIMFUEL in contact with Na^+-OH^- electrolyte (segmented line); SiO_3^{2-} electrolyte (dot line); Ca^{2+}-SiO_3^{2-} electrolyte (black line); **(B)** the resulting U4f XPS band of the WE

CONCLUSIONS

The corrosion of 3 at.% doped SIMFUEL exposed to a hyper-alkaline medium and to this electrolyte containing either SiO_3^{2-} or SiO_3^{2-} and Ca^{2+} has been studied.

The CV scans showed that when SiO_3^{2-} is present the rate of oxidation of UO_2 to $U^V_{2x}U^{IV}_{1-2x}O_{2+x}$ is unaffected while the subsequent oxidation of this layer to U^{VI} is slower. When both Ca^{2+} and SiO_3^{2-} are present under hyper-alkaline conditions the surface is stabilized against oxidation to $U^V_{2x}U^{IV}_{1-2x}O_{2+x}$, the potential required for this reaction being increased by approximately 60mV.

These effects were confirmed by the results of potentiostatic experiments (at 200 mV) followed by XPS analyses. Charge measurements showed a higher extent of oxidation in NaOH than in this electrolyte with added SiO_3^{2-}. This was confirmed by the XPS analyses. When both Ca^{2+} and SiO_3^{2-} were present the oxidation rate and overall extent of oxidation were significantly reduced. This was again confirmed by XPS.

In corrosion experiments, measurements showed that in the presence of both Ca^{2+} and SiO_3^{2-} electrolyte the E_{CORR} was considerably lower than in the other two electrolytes and XPS confirmed the surface was considerably less oxidized.

ACKNOWLEDGMENTS

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