

Understanding Uranium Binding Mechanisms and Speciation on Stainless Steel - 17462

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ABSTRACT

Stainless steels have been exposed to nitric acid solutions containing natural uranium under similar conditions to those found in reprocessing plants. Solution and solid analysis of the stainless steel samples has been undertaken to describe the contamination phenomenon. General corrosion of the surface was seen to take place over the month-long experiments. Contamination has been shown on all exposed surfaces. Solution analysis indicates that an equilibrium state is reached after 2 weeks exposure to the 12 M HNO₃. Surface analysis through autoradiography and X-ray absorption near edge structure (XANES) indicate that multiple mechanisms of uptake may occur and consequently concentrated regions of contamination may be produced.

INTRODUCTION

Reprocessing of spent nuclear fuel is currently undertaken in the United Kingdom. This takes place through application of the plutonium uranium redox extraction (PUREX) process at the thermal oxide reprocessing plant (THORP) and Magnox plants at Sellafield, Cumbria. Both plants are due to cease operations by 2018; this will be followed by post operational clean out. A large quantity of material will be handled during this process; furthermore, a significant proportion will have come in to contact with radionuclide-containing liquor. The PUREX process necessitates nitric acid at room temperature to boiling point, consequently materials that can withstand the corrosive, oxidising environment are utilised. Primarily this is Zircaloy but a widely used secondary material is low carbon austenitic stainless steel, particularly grade 304L (nitric acid grade) NAG. For example, in THORP there is roughly 320 km of stainless steel piping and over 1000 stainless steel vessels.[1] It has been shown that radioactive material can become bound to the surface in a process sometimes referred to as plate-out.[2] This poses a problem for the clean out process due to the associated hazards to workers, the general public and the environment.

Decontamination is a possible solution to this issue producing material that can be disposed of to a lower level waste stream or potentially even leaving it reusable or recyclable. As such, research is taking place to understand the binding mechanism and define a decontamination methodology that most effectively removes the

contaminant. Most of the literature focusses on the latter subject but there is limited work looking at fission product, uranium and transuranic binding mechanisms. Moreover, prior studies investigating solution-based contamination have mostly taken place over short time lengths.[3-6]

It has also been shown that 304L steel undergoes corrosion in acidic, oxidising media. General working conditions of the material mean that in up to 8 M HNO₃ at boiling point only low uniform dissolution of the surface should be seen. However at higher acidity and with the presence of oxidising species (such as Np^{VI} or corrosion product Cr^{VI}), the material can be pushed in to a transpassive state. Resultantly the material will undergo intergranular corrosion.[7] Consequently, over longer time lengths, surface structure will evolve producing features which might favourably interact with a contaminant.

By investigating the corrosion and contamination of stainless steel over a period of one month, this study investigates how uranium binds and whether corrosion affects the uptake.

EXPERIMENTAL

Materials and Sample Preparation

Type 304L (1.4307) steel was received to a 2B finish from Aalco Manchester; the elemental composition is given in Table 1.

TABLE I. Elemental composition of received 304L stainless steel

Elem	C	Si	Mn	P	S	Cr	Ni	Nb	Fe
wt%	.023	.3	1.6	.032	.001	18.3	8.06	.03	Bal.

Prior to receipt the sheet had been hot rolled, was heat treated at 1100°C, and the solution annealed by quenching with water and air. Lastly the mill scale was removed. At the University of Manchester, the steel was then cut in to coupons of size 2 cm x 2 cm x 0.4 cm (Fig. 1). One face of the material was ground with silicon carbide paper (P120 to P2500) and polished (using 6 µm diamond paste followed by 1 µm).

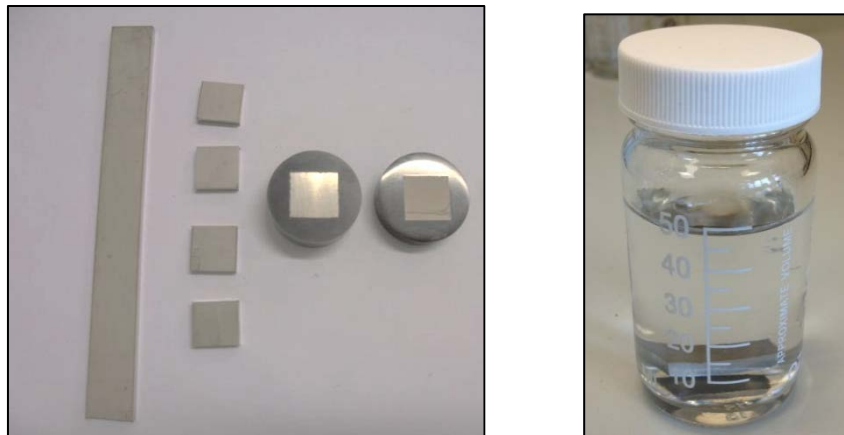


Fig. 1. Stainless steel preparation and experimental setup in jar containing 1g/L uranyl nitrate hexahydrate

The stainless steel coupons were then placed in vials with the preferential side to be exposed to the contaminant facing upwards. Solutions of 12 M nitric acid were prepared containing 1 g/L uranyl nitrate hexahydrate (Fig. 1).

50 mL of each solution was pipetted over the stainless steel. Controls were also run in acidic solution without contaminant and also a standard solution without coupon. The samples were stored in a drying oven held at 50°C for 1-31 days.

Upon removal of the steel from solution, deionised water was used to rinse the surface. This was done in order to remove standing acidic solution from the coupon and avoid post-immersion contamination. Any contaminant removed during the wash is assumed to have been so weakly bound that it is not relevant to this study. The samples were then left to dry.

Microscopy

Optical microscopy (AxioLab.A1, Carl Zeiss Jena GmbH, Jena, Germany) was used to image the surfaces. The data were processed with Axio Vision Software (Carl Zeiss MicroImaging GmbH, Jena, Germany).

Autoradiography

Autoradiography was undertaken using a Typhoon 9410 variable mode imager. The BAS-IP MS storage phosphor screen (Amersham BioSciences) was exposed for 71 hours. Following exposure, the screen was scanned using a HeNe laser with pixel sizes of 25 – 50 μm . Finally the autoradiographs were analysed using OptiQuant software.

X-ray Absorption Near Edge Structure (XANES)

Microfocus x-ray spectroscopy and mapping of the stainless steel coupons took place at beamline I18 of the Diamond Light Source. I18 has a double crystal monochromator, a working energy range of ~ 2 – 20 keV and a maximum focus of ~ 2 µm x 2 µm. XANES analysis was undertaken using Demeter.

RESULTS AND DISCUSSION

Corrosion

Optical micrographs of the stainless steel coupons exposed to uranium containing nitric acid over the period of a month are shown in Fig. 2. These images show the general corrosion of the surface until the grain structure is fully revealed by the end of the 1-month exposure.

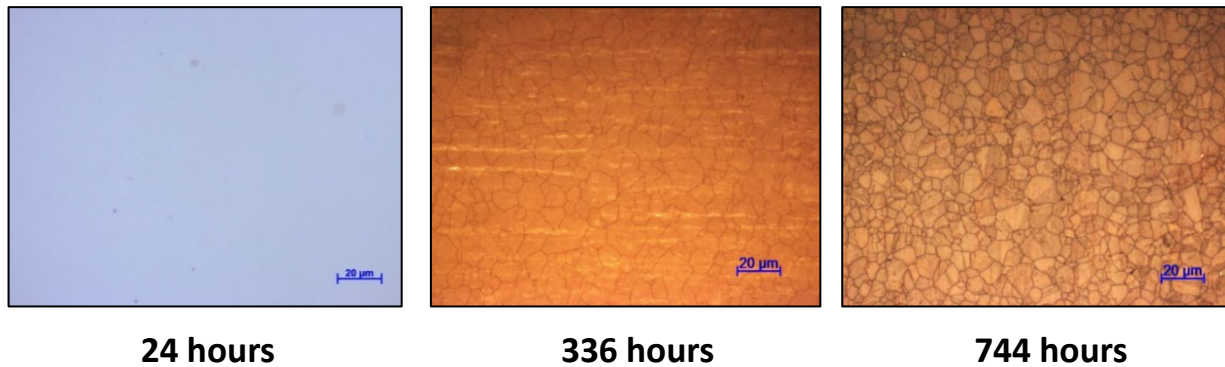


Fig. 2. Optical micrographs of polished 304L steel after submersion in 12 M HNO3 over varying time lengths

Fig. 3 shows the corrosion rate of 304L stainless steel in contact with the various combinations of nitric acid concentration and radionuclides. Weight loss determination was obtained through the use of the following rate of corrosion (Eq. 1):

$$\text{millimetres per month} = \frac{(7290 \times W)}{(A \times d \times t)} \quad (\text{Eq. 1})$$

Where W is weight loss (kg), A is total surface area (m²) of the coupon, d is the density of the sample (kg/m³) and t is time length of exposure (seconds).

Fig. 3 shows an initially high corrosion rate of the stainless steel upon submersion in the nitric acid followed by rapid plateauing that is maintained across the month of exposure.

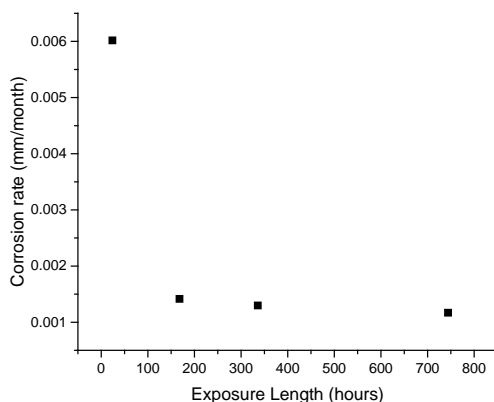


Fig. 3. Corrosion rate of 304L stainless steel in 12 M HNO₃ over a one month time period

Measurement of the corrosion product concentration in solution was undertaken through the use of inductively coupled plasma optical emission spectrometry (ICP-OES). The level of iron and chromium in solution is given in Fig. 4.

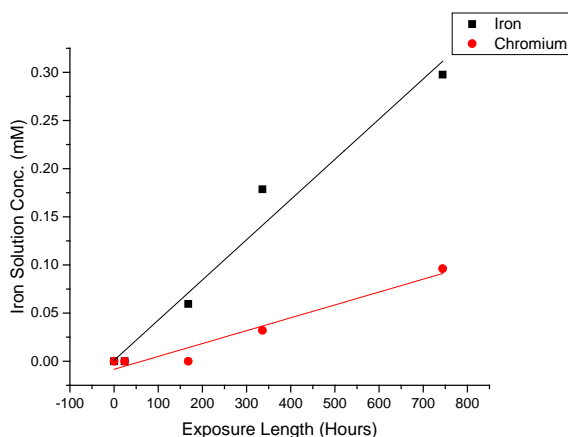


Fig. 4. ICP-OES measurements of iron and chromium solution concentration against length of exposure to 12 M HNO₃

The presence of corrosion products in solution once again indicates that across the month of exposure to 12 M HNO₃ there is a relatively consistent corrosion rate of the stainless steel surface.

Contamination

Solution and surface analysis was utilised to determine the amount of uranium that was bound to the surfaces of the stainless steel over the time length of exposure. The level of uranium in solution was followed using ICP-OES. It was seen in the control containing no stainless steel that minimal uranium was adhered to the

glassware itself. After correcting for this loss of uranium, the concentration of the contaminant on the stainless steel is plotted in Fig. 5.

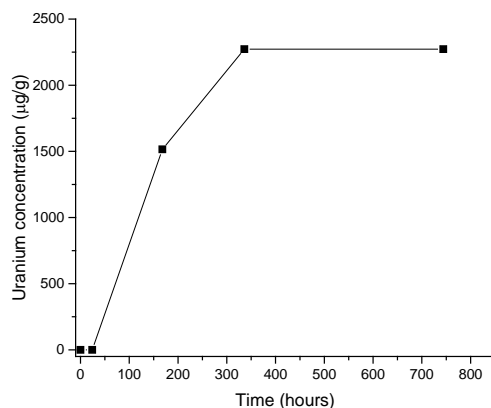


Fig. 5. ICP-OES derived uranium uptake on 304L stainless steel in 12 M HNO₃ over a one month period

The uptake was seen to reach an equilibrium state after 14 days in solution. It was found that the adsorption kinetics were best described when fitted to Ho's pseudo second order kinetic model (Fig. 6).[8] This provides a $k_2(U)$ of 2.8×10^{-5} g/µg hr. This suggests that the rate determining step of the contamination phenomena is chemisorption, which describes a valent interaction between the surface and contaminant.

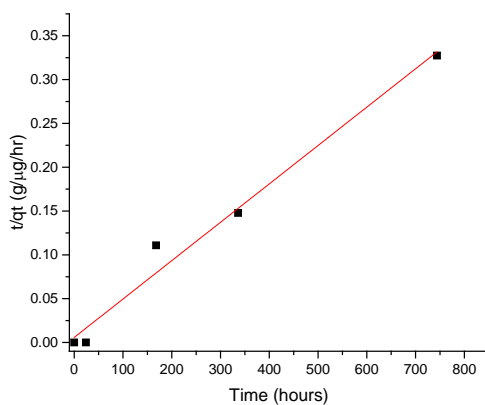


Fig. 6. Kinetics of uranium uptake on to stainless steel in 12 M HNO₃ from Ho's pseudo second order kinetic equation

Analysis of the stainless steel surface itself was initially conducted using autoradiography. An example screen is shown in Fig. 7.

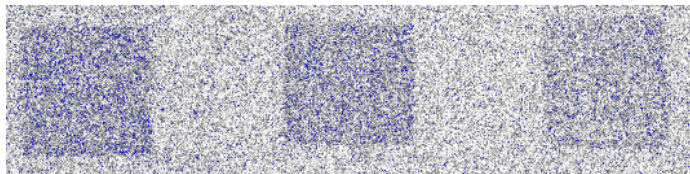


Fig. 7. Example autoradiography screen after exposure to 3 stainless steel coupons that were exposed to 12 M HNO₃ containing uranium for 14 days.

This technique showed the presence of uranium on all surfaces tested; on the resolution of the technique, this contamination appears to be uniform. Currently the results are qualitative and concentrations cannot be extracted from the screens. However, it has been shown elsewhere that quantitative results are possible through the use of an internal solution standard and is in progress for uranium contaminated steel.[9]

Further study of the stainless steel contamination was undertaken using the I18 beamline at the Diamond Light Source. Mapping of the surface and XANES was undertaken on a range of samples held over varying time lengths. It was seen that the contamination was localised in hot spots and not uniform across the surface. Uranium L_{III}-edge spectra were collected, calibrated, background subtracted and normalised to a standard position of E₀; a value unique to each element representing a core-electron binding energy. This produced extremely similar signals, which were compared to literature standards. A representative example signal for a polished sample held for 31 days is shown in Fig. 8.

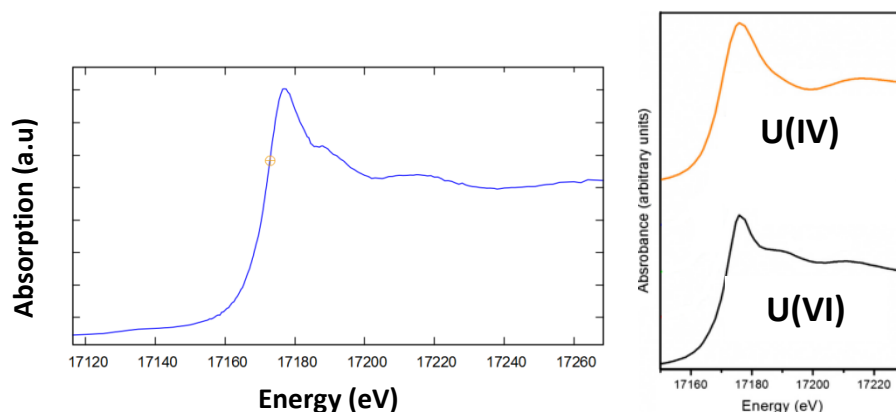


Fig. 8. XANES U L_{III} edge produced from 1 month exposed 304L coupon and reference edges for uranium

Accounting for differences in matrices of the uranium signal, it can be said that the spectra displays U(VI)-like features. This indicates that a redox process is not playing a role in the contamination phenomena. Previous study by Dombovári et al. (2007) investigated uranium binding on stainless steel tubing through a pilot plant model system.[6] They concluded that the primary mechanism of contamination was coprecipitation with iron, chromium and nickel making up the passive oxide

surface layer. Through X-ray photoelectron spectroscopy (XPS) analysis, they concluded that the primary contaminant was also U(VI). Furthermore the signal produced was correlated with that of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

CONCLUSIONS

The uptake of uranium on to stainless steel over a one-month period in conditions replicating those found in a reprocessing facility has been investigated. Over the study general corrosion was seen to occur; by one month of exposure, the grain structure of the 304L steel was revealed. Contamination was shown to occur on all samples through the use of ICP-OES, autoradiography and XANES analysis. Solution analysis indicates that an equilibrium state has been reached within 2 weeks of exposure of the steel to the 12 M HNO_3 solution. Fitting of the uptake to Ho's pseudo second order kinetic model indicates a chemisorption process. Autoradiography proved the presence of uranium on the stainless steel surface and appeared to indicate a uniformity of the contamination across the material. Conversely results of the X-ray absorption spectroscopy (XAS) mapping showed concentrated regions of higher activity that could be characterised as U(VI). This suggests there are potentially differing mechanisms of uptake. No conclusions can be drawn on the relationship of corrosion with contamination but further study is underway over longer time lengths.

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