Supporting Information for:

Cesium and Strontium Contamination of Nuclear Plant Stainless Steel: Implications for Decommissioning and Waste Minimization

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**S1. Steel Composition and SEM Analysis of Steel Surface**

**Table S1.** Chemical Composition (wt. %) of AISI Type 304L stainless steel.

|   | Cr  | Ni  | C   | Mn  | Si  | P   | S   | N   | Fe   |
|---|-----|-----|-----|-----|-----|-----|-----|-----|------|
|   | 18.15 | 8.6 | 0.055 | 1.38 | 0.45 | 0.04 | 0.005 | 0.038 | Bal. |

**Figure S1.** Typical morphology of type 304 stainless steel surfaces after immersion in: (A) 3 M, (B) 6 M, and (C) 12 M HNO₃, and (D) 1 mM NaOH aqueous solution, at 60 °C for 30 days. The arrows in image (C) show the attacked ferrite stringers (scale bar = 50 μm).
S2. GD-OES Depth Profiling

For a quantitative assessment of the elemental depth distribution of steel samples, it is necessary to correlate the GD-OES measurement time with depth of analysis. In this work, the depth of a GD-OES crater generated after 20 seconds of sputtering was determined using laser confocal microscopy (Figure S2). Assuming a constant sputtering rate, time can then be converted into depth by an appropriate scaling calculation. However, as the sputtering rate of a sample could be affected by changes in the composition of a material, the depth equivalent data can only be considered as an estimate.

The crater depth was measured to be 761 ± 59 nm, corresponding to an average sputtering rate of 38 ± 3 nm s\(^{-1}\). The presentation of GD-OES profiles as a function of sputtered depth (Figures 1, 4, and S3) reveals the surface oxide thickness after acid and alkaline passivation treatment as 6 ± 1 nm and 12 ± 1 nm, respectively. This result is consistent with a 316L stainless steel passivation kinetic study which reported a film thickness of 4.8 nm after immersion in 6 M HNO\(_3\) for 24 hours. An equilibrium film thickness was not obtained in this 24 hour study and therefore our reported value of ~6 nm after 720 hours is likely to be reasonable.

Figure S2. (A) Optical image, and (B) surface topography profile of GD-OES crater formed on the surface of type 304 stainless steel after 20 seconds of continuous sputtering. The steel specimen was contaminated in 1 mM NaOH at 60 °C for 30 days prior to GD-OES measurement.
Figure S3. GD-OES elemental depth profiles of type 304 stainless steel after contamination in 12 M HNO₃. The O and Sr signals are scaled by a factor of 10 and 100, respectively, for clarity. The x-axis is expressed as “sputtering time” and estimated “sputtered depth”. For detail on the conversion of time to depth, please see SI section 2. Note, the data presented in this Figure is the same at that presented in Figure 1-C of the manuscript, however the x-axis of the above graph has been shortened to allow easy comparison of O data collected for this sample with the other samples shown in Figure 1.
S3. XPS Analysis

X-ray photoelectron spectroscopic measurements were carried out to determine the elemental composition of the passive layers formed on type 304 stainless steel, where the influence of solution composition was investigated. The XPS spectra of the Fe 2p and Cr 2p photoelectron positions for the four contaminating matrices are shown in Figure S4. It is clear that no significant deviation of the binding energy positions occurs, suggesting that the fundamental Fe and Cr oxide components are independent of solution composition. On the other hand, the relative proportion of the Fe and Cr in the film is strongly influenced by the solution (i.e. passivating medium). The reduced Fe 2p signal after acid passivation treatment is due to an increased Fe solubility at low pH, whereas a similar effect occurs for Cr under basic conditions. The Fe 2p$_{1/2}$ and 2p$_{3/2}$ peaks at 724.6 and 710.7 eV, respectively, are associated with Fe$_2$O$_3$.$^3$ Furthermore, the contributions at 719.8 and 706.7 eV are due to metallic Fe,$^4$ likely corresponding to photoemission from bulk material. It is important to note that the feature at ~ 720 eV in the spectrum from the alkaline sample may also be ascribed to the Fe 2p$_{3/2}$ satellite, where the presence of the corresponding Fe 2p$_{1/2}$ satellite at 733.1 eV supports this assignment.$^3$ In addition, the feature at ~ 742 eV may also be identified as a daughter peak of one of the Fe 2p peaks, although an exact assignment remains unclear.$^5$ The Cr 2p$_{1/2}$ and Cr 2p$_{3/2}$ peaks at 586.2 and 576.7 eV, respectively may be assigned as Cr$_2$O$_3$.$^6$ For a similar reason outlined for Fe, elemental Cr was also identified by the corresponding photoelectron lines at 583.4 and 574.1 eV. These results reveal that, in combination with the GD-OES data, a fundamental structure of the passive layer is a Cr$_2$O$_3$ layer underneath a Fe$_2$O$_3$ over layer. The relative concentrations of these two components are highly sensitive to the solution pH, where Cr grows at the expense of Fe oxide under acidic conditions. The surface enrichment of Fe after alkaline pH treatment is also apparent, although this effect is more subtle owing to the high Fe oxide content in the passive film formed by atmospheric exposure. The increased Fe stability within the passive film under alkaline conditions has important ramifications for the identification of Cs present in the steel material as the Cs 3d photoelectron are likely to be masked by the more prominent Fe 2p peaks (Figure S4). Thus, despite an increased amount of Cs accumulating on the steel surface at alkaline pH (see Table S3), no Cs could be detected by XPS on the steel surface after contamination under alkaline solution conditions.
**Figure S4.** XPS high-resolution spectra of (A) Fe 2p, and (B) Cr 2p photoelectron peaks of 304 stainless steel as a function of passivation treatment.
S4. Sr and Cs Sorption and Kinetic Modelling

The Ho model pseudo-second order kinetic fits are shown in Figure S5. The model is described in the main paper.

Figure S5. Ho pseudo-second order kinetic fits for the adsorption of Sr and Cs onto type 304 stainless steel from (A) 3 M, (B) 6 M, and (C) 12 M HNO₃, and (D) 1 mM NaOH solution, at 60 °C.

The rate of adsorption for the Lagergren pseudo-first order model is dependent on the sorption capacity of the substrate, which is expressed as:

$$\frac{dq_t}{dt} = k(q_e - q_t)$$

where $q_e$ is the equilibrium uptake (g m⁻²) and $k$ is the first order rate constant (hr⁻¹). The integrated form over the boundary conditions $t = 0$ to $t = t$ and $q_i = 0$ to $q_i = q_t$ is

$$\log(q_e - q_t) = -kt + \log(q_e)$$

Therefore a plot of $\log(q_e-q_t)$ against $t$ will yield a linear relationship of gradient -k and a y-intercept of $\log(q_e)/kq_e^2$ is obtained. A fundamental disadvantage of this kinetic model is that
some knowledge of the equilibrium sorption capacity must be known. In this work, the maximum $q_t$ value measured for each individual sorption was taken as $q_e$. The pseudo-first order kinetic plots are shown in Figure S6 for all for systems studied, where the pseudo-first order rate constant can be determined by the gradient of the fit.

**Figure S6.** Lagergren pseudo-first order kinetic fits for the sorption of Sr and Cs on type 304 stainless steel from (A) 3 M, (B) 6 M, (C) and 12 M HNO$_3$, and (D) 1 mM NaOH, at 60 °C.

Another kinetic model tested was the Elovich model (Figure S7). In the Elovich equation, the overall rate of analyte removal from solution is derived from competing adsorption and desorption processes, which is expressed as:

$$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}$$

where $q_t$ is the amount sorbed at time t, $\alpha$ is the initial sorption rate (g m$^{-2}$ hr$^{-1}$) and $\beta$ is a constant related to the rate of desorption (m$^2$ g$^{-1}$). The integrated form over the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_i$ is

$$\frac{e^{\beta q_t}}{\beta} = \alpha t + \frac{1}{\beta}$$
Rearranging into the linear form yields

\[ q_t = \frac{1}{\beta} \ln(t + t_0) - \frac{1}{\beta} \ln t \]

where

\[ t_0 = \frac{1}{\alpha \beta} \]

In order to simplify this kinetic model, it is often assumed that \( \alpha \beta t > 1 \) i.e. the contribution of \( t_0 \) is negligible. The rate equation then becomes:

\[ q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t \]

When the \( q_t \) is plotted against \( \ln t \), a linear plot of gradient \( 1/\beta \) and a \( y \)-intercept of \( \ln(\alpha \beta)/\beta \) is obtained. The corresponding kinetic plots are shown in Figure S7 for all for systems studied, where the values of \( \beta \) and \( \alpha \) can be calculated from the slope and intercept of the fits, respectively.

![Figure S7](image)

**Figure S7.** Elovich kinetic fits for the sorption of Sr and Cs on type 304 stainless steel from (A) 3 M, (B) 6 M, and (C) 12 M HNO\(_3\), and (D) 1 mM NaOH, at 60 °C.
The statistical results of the Ho, Lagergren, and Elovich kinetic fits are summarized in Table S2. It can clearly be seen that the Lagergren and Elovich equations do not give reasonable R^2 values and in all cases Sr and Cs sorption behavior can be more accurately described by Ho pseudo-second order kinetics.

**Table S2.** Comparison of the co-efficient of determination (R^2) values obtained from the linear plots of the Ho, Lagergren, and Elovich kinetic models used to characterize Sr and Cs sorption onto type 304 stainless steel

| Solution Composition | Ho 2nd order R^2 | Lagergren 1st order R^2 | Elovich R^2 |
|----------------------|-----------------|-------------------------|-------------|
|                      | Sr   | Cs   | Sr   | Cs   | Sr   | Cs   |
| 3 M HNO₃             | 0.997| 0.995| 0.137| 0.688| 0.778| 0.644|
| 6 M HNO₃             | 0.991| 0.987| 0.861| 0.600| 0.727| 0.901|
| 12 M HNO₃            | 0.994| 0.996| 0.819| 0.419| 0.947| 0.992|
| 1 mM NaOH            | 0.995| 0.989| 0.850| 0.956| 0.930| 0.895|

**Table S3.** Calculated equilibrium sorption capacity (qₑ), second order rate constant (k₂), and initial sorption rate (h) from Ho pseudo-second order kinetic analysis of Sr and Cs accumulation onto type 304 stainless steel

| Solution Composition | qₑ / g m⁻² | k₂ / 10⁻² m² g⁻¹ hr⁻¹ | h / g m⁻² hr⁻¹ |
|----------------------|------------|------------------------|---------------|
|                      | Sr         | Cs                     | Sr            | Cs            | Sr        | Cs        |
| 3 M HNO₃             | 3.6 ± 0.1  | 5.0 ± 0.1              | 1.5 ± 0.1     | 1.9 ± 0.1     | 0.2 ± 0.1 | 0.5 ± 0.1 |
| 6 M HNO₃             | 5.9 ± 0.2  | 5.0 ± 0.2              | 1.1 ± 0.1     | 1.5 ± 0.1     | 0.4 ± 0.1 | 0.4 ± 0.2 |
| 12 M HNO₃            | 6.8 ± 0.1  | 5.0 ± 0.1              | 1.0 ± 0.1     | 6.5 ± 0.3     | 0.4 ± 0.1 | 1.6 ± 0.2 |
| 1 mM NaOH            | 11.0 ± 0.3 | 5.6 ± 0.2              | 1.4 ± 0.1     | 1.0 ± 0.1     | 1.7 ± 0.2 | 0.3 ± 0.1 |

**SI References**

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