



## Reply to comment on “Penetration of corrosive species into copper exposed to simulated O<sub>2</sub>-free groundwater by time-of-flight secondary ion mass spectrometry (ToF-SIMS)”

### ARTICLE INFO

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### 1. Introduction

Based on the results from our in-depth ToF-SIMS measurements of copper samples after exposure to simulated ground water relevant for final disposal of nuclear waste, we recently published a research article entitled “Penetration of corrosive species into copper exposed to simulated O<sub>2</sub>-free groundwater by time-of-flight secondary ion mass spectrometry (ToF-SIMS) in Corrosion Science [1]. In a correspondence article, referred to as Comment herein, the authors made comments on our paper, questioned our interpretation of the ToF-SIMS data, and argued that there is no risk for such penetration of corrosive species into Cu and, thus, no risk for corrosion failure of Cu canisters under repository conditions [2]. The background information of the Cu corrosion system, our focus of the research question, a short summary of relevant literature, the description of the ToF-SIMS measurements, the results presented as in-depth elemental profiles and as 2D/3D elemental maps showing the spatial distribution of corrosive species H, S, O and Cl from the sample surface down to the inside of the Cu matrix, as well as the discussion and implication of the results can be found in our original research paper [1].

The Comment concerns mainly *i*) the fundamental interpretation of the ToF-SIMS data where it is claimed that a region of pronounced penetration into the metal exists under a thin layer of corrosion products, and *ii*) the discussion of results in the context of geologic repository conditions. In this Reply article, we address each of the raised issues, and give our explanations and rebuttal arguments. We believe that the debate is helpful not only for improving our current understanding of the scientific questions involved in the system, but also for identifying the knowledge gap that needs further studies.

### 2. Basic interpretation of ToF-SIMS data

The Comment raised several questions about our data interpretation: the existence of a region of “pronounced penetration” under the corrosion product film; the effect of surface roughness; the illustration in Fig. 2 (Fig. 12 in ref. 1); and the correlation between the depth profiles

and 2D/3D maps. Below we give our explanation and rebuttal to the Comment, point by point.

*Existence of a region of “pronounced penetration”* – The ToF-SIMS depth profiles (Figures 3a, 5a, 7, 10 and 11 in our paper [1]) show clearly that below the region showing maximum signal intensity of the dominant corrosive species, O and S, there is a region where the signals of corrosive species H, S, O and Cl decrease gradually with increasing depth. Meanwhile, the Cu signal remains quite stable at the level of the Cu matrix. Moreover, in the 2D elemental maps, it is clear that Cu grains are visible within this depth range, so there is no doubt that in this region pronounced penetration of the corrosive species occurred as a result of the exposure. It is striking that an increase of the exposure temperature from 22 °C to 60 °C caused a large extension of the pronounced penetration region into the Cu matrix.

The authors of the Comment suggest an alternative interpretation of our data, i.e., this “pronounced penetration” region is part of the corrosion product film, based on a previous laboratory study (focusing on the growth of the corrosion product film) where the measured thickness of the corrosion product film was about 1 micrometre after one month exposure under similar conditions [3]. They also point out the discrepancy in the thickness of the corrosion product film measured by gravimetric method and by the ToF-SIMS method, and compare the calculated thickness of the corrosion product film from different exposure conditions and different studies. Here, we emphasize that it is important to consider how the boundary between the corrosion product film and the metal matrix is defined, at both macroscopic and microscopic scales. Moreover, one has to take into account the differences between the measuring methods that can affect significantly the accuracy of the results, and the possible instantaneous, local or averaging nature of the method. It is common in practice that different measuring methods (e.g., electrochemical, gravimetric, and various profiling techniques) may give different values of the thickness of the corrosion product film and also large scattering between parallel samples, especially when there is no sharp boundary between the corrosion product film and the metal matrix. With the gravimetric method, the end result is an average of film growth on the entire exposed surfaces over the

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exposure time, and the procedure used to remove the corrosion product may largely affect the result. Besides, if the corrosion is not uniform, which is often true at microscopic scale, the measured surface area has a large influence on the result. In our ToF-SIMS measurements, the focus was to probe the penetration of corrosive species into the Cu matrix, so we selected a small local area ( $450\ \mu\text{m} \times 450\ \mu\text{m}$ ) of the surface that is quite smooth for the analysis. The local thickness of the corrosion product film measured by the ToF-SIMS analysis is expected to be small in comparison with that of other areas where more severe corrosion attack occurred. The film thickness measured by ToF-SIMS can be compared with the samples measured in a similar way, but should not be compared directly with other thickness data measured by different methods on larger areas. Importantly, the ToF-SIMS results reveal the existence of a region of “pronounced penetration”, as described clearly in our paper, which is not part of the corrosion product film. This is a new finding achieved by using the ToF-SIMS technique. In this context, the comparison between the thicknesses of the corrosion product film measured by different techniques in different studies is not really meaningful to this extent of precision.

To provide further evidence of the pronounced penetration, here we give an example of new results from our recent Nano-SIMS measurement of a cross-section of the Cu sample, see Fig. 1. The cross-section sample for Nano-SIMS measurement was a lift-out cut by focused ion beam (FIB), and the sample will also be used for subsequent TEM analysis. The Nano-SIMS data show non-uniform distribution of H and S at the depth of several micrometres, not only along the indicated grain boundary but also within the grains on both sides of the grain boundary, confirming pronounced penetration several micrometres down in the sample. Whereas another sample exposed to the same ground water but at  $22\ ^\circ\text{C}$  showed much less penetration of H and S. The measurement is ongoing and the results will be further analysed and reported after completion of the TEM measurement and data analysis.

### 2.1. Effect of roughness

In the “final project report” of our research project [4], we presented SEM images showing nodular-like corrosion products formed on some areas of the sample surfaces, while porosity was evident in the films under some exposure conditions. Moreover, the SEM images disclosed that the film morphology only occasionally followed the original grinding grooves. Therefore, although there might have been grinding grooves in

the surface region of the Cu samples before exposure, the surface morphology of the films was influenced much more significantly by the exposure conditions than by the original surface finish. As mentioned in our paper, there are already many literature reports about the morphology, composition and structure of the corrosion products, since most of the studies focused on the corrosion reactions on the metal surface and the growth of the corrosion product film. To address an important gap of knowledge, our study has focused on the penetration of corrosive species into the Cu matrix, which is missing in the literature but crucial knowledge needed to understand the potential risk of degradation of the material integrity during the extremely long period of service. Since a rough surface topography and thickness variation of the corrosion products can create some ambiguity when it comes to interpretation of SIMS depth profile data, we selected a smooth surface area without visible nodular growth or porosity for the ToF-SIMS analysis, as in previous works [5]. Although the selection of analysis location might have some influence on the accuracy of the thickness of the corrosion product film, there is no real problem in the interpretation and analysis of the ToF-SIMS data, especially the penetration of detected species into the Cu matrix. Further, we emphasize that the ion images and also the macro images from the SIMS revealed very little effect of film topography. In addition, the mass resolution, which would be affected almost immediately by considerable surface roughness, remained well above 4500–5000 with well-shaped gaussian peaks for the elements shown in the paper. This indicates that the surface roughness is not a contributing factor that can be deemed to have any serious impact on the interpretation of the SIMS data. We have now also completed the ToF-SIMS depth profile analysis with Nano-SIMS analysis of the cross sections as described above to again confirm the penetration and accumulation of the corrosive species inside the Cu matrix.

### 2.2. The illustration in Fig. 2

Fig. 2 schematically illustrates the corrosion mechanism involving penetration of the corrosive species into the Cu matrix, which has been revealed by our ToF-SIMS measurements. The extent of such corrosion penetration depends on many factors, such as the exposure time, the S content of the exposure environment, and in particular the temperature of the ground water. The main point of the Fig. 2 is to show how such corrosion mechanism could be operative in the Cu corrosion system, rather than to show exactly the depth of the pronounced penetration for

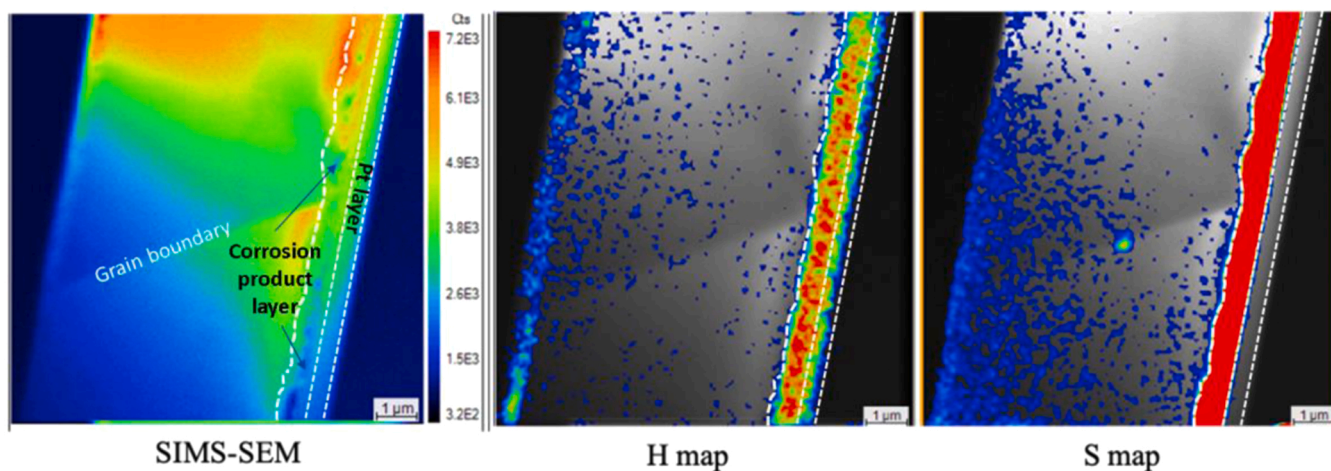


Fig. 1. Nano-SIMS mapping of a FIB-cut lift-out cross-section of the Cu sample after 4 months' exposure in the simulated ground water at  $60\ ^\circ\text{C}$  (the same sample as in our paper [1]). Left: SIMS-Secondary electron image; Middle: Map showing H-distribution; Right: Map showing S-distribution. The blue dots show the signals of H in the H map and S in the S map, while the right-side thin layer (yellow and red colour) is the corrosion product film. Note the micrometre scale of the maps and a thin Pt layer on the surface deposited for FIB cutting. The Nano-SIMS measurement was performed at The Chemical Imaging Infrastructure of Chalmers University of Technology/Gothenburg University, Sweden, using a NanoSIMS 50L instrument (CAMECA) using a  $\text{Cs}^+$  beam with 50 nm spatial resolution. Colour bare shows accumulated counts ranging from black ( $3.2\text{E}2$ ) to red ( $7.2\text{E}3$ ).

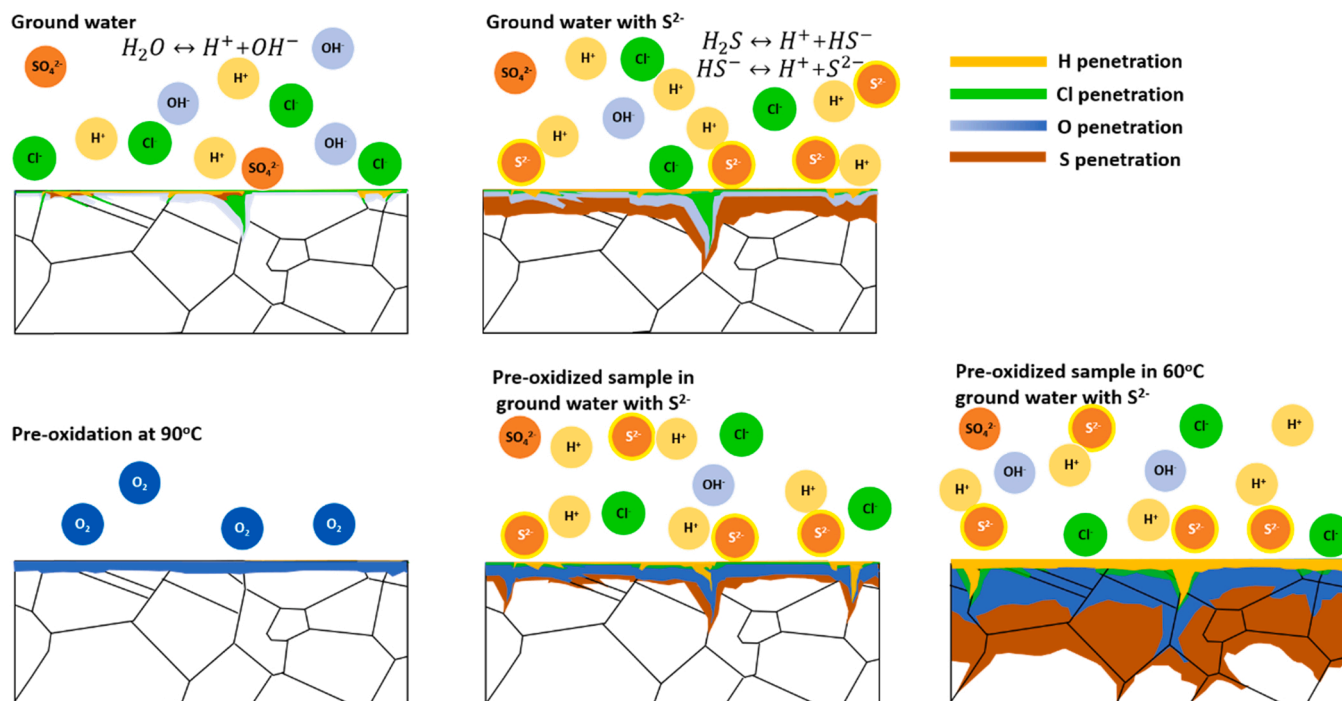


Fig. 2. Illustration of penetration of corrosive species into the Cu microstructure under different exposure conditions.

a specific exposure.

In a recent high-quality scientific paper published in *Nature Communications* (referred to as NC paper herein), the authors reported “One dimensional wormhole corrosion in metals” [6], which exhibits many similarities to what we observed by the ToF-SIMS and Nano-SIMS imaging of the Cu samples, i.e., apparent discontinuous corrosive species present inside the metal matrix. By using state-of-the-art SEM- and TEM-based techniques, including FIB-SEM 3D reconstruction (tomography), STEM-HAADF imaging and STEM-EDX chemical mapping, and 4D-STEM, the authors of the NC paper demonstrate a-dimensional (1D) wormhole corrosion process that can occur inside the metals. Fig. 1 in ref. 6 illustrates the differences between 3D, 2D, and 1D corrosion, and also shows that the SEM cross-section reveals dot-like corrosive species along some grain boundaries. Supported by theoretical DFT simulations, the authors could explain fast growth of wormholes in the diffusion-induced grain boundary migration zone, which was attributed to extremely high levels of vacancies. Moreover, the NC paper analysed the local strains associated with the 1D wormholes, and mentioned that intergranular oxide may also form a percolated network similar to the 1D wormhole corrosion. Although the experimental examples shown in this paper were mainly molten salt systems, as pointed out by the authors, such 1D wormhole corrosion may also occur in other localized corrosion systems, such as stress-corrosion and sulfidation-induced cracking. One can speculate if the fast pathways found in our SIMS studies also may form a percolated network similar to that in the 1D wormhole corrosion.

In the Cu corrosion system, the ground water contains a high amount of Cl<sup>-</sup> ions and also a certain level of S-species, which are involved in the aqueous corrosion process and may have synergetic corrosion actions with H and O species since the 2D ToF-SIMS elemental maps show their co-segregation at local sites in the Cu matrix [1]. The inward diffusion of the corrosive species is coupled to and promoted by the chemical reactions occurring at the interface between Cu and the electrolyte and/or the corrosion product film. It is well known that a high Cl content accelerates the corrosion processes. Moreover, the increase of temperature, although only from 22 °C to 60 °C, greatly enhanced the penetration of the corrosive species into the Cu matrix, which indicates

that the elevated temperature provides a large driving force for the penetration. An analogue situation is that an increase of temperature of an aqueous NaCl solution to 50–90 °C is sufficient to cause the breakdown of passive film on stainless steel (which otherwise is quite stable), leading to fast corrosion at local sites. In fact, little is known about what could happen inside the Cu microstructure in the corrosion processes where corrosive species, such as Cl and S species co-exist in the aqueous environment. Obviously, more detailed studies using state-of-the-art techniques, especially high-resolution structural and chemical imaging techniques available today, are needed to achieve fundamental understanding of the complex corrosion processes inside the Cu microstructure, as exemplified by our ToF-SIMS/nano-SIMS measurements and the SEM/TEM analyses reported in ref. 6.

### 2.3. Correlation between the depth profiles and 2D/3D maps

The ToF-SIMS results have a high depth resolution due to a small step of ion sputtering, and the data include a large number of sequential 2D images, which can be displayed in different ways. To limit the space and number of figures in the paper [1], the 2D elemental maps in our paper were presented with relatively large depth intervals, especially for the sample with a large depth of pronounced penetration. The 3D elemental images were reconstructed in a similar way as in 3D tomography, where one can take slices in different ways or rotate the 3D images to view the spatial distribution of the corrosive species in the analysed volume. The x, y, z scales were chosen to suit the size of the figures. The 3D images may give an impression that is different from the series of 2D images, but this is not a real problem of the interpretation of the results. It seems that the authors of the Comment misunderstood the message of the ToF-SIMS results. Regarding the comment on “only one analysis technique was used”, we already mentioned in our paper that other results obtained from different characterization methods will be published separately. Moreover, our TEM analysis of the FIB-cut cross-section samples is ongoing, which will provide more detailed information at micro/nano-scale levels. The new results from Nano-SIMS (Fig. 1 is one example) and TEM analysis will be reported in coming publications.

We note that the authors of the Comment focus on the ambiguous

definition of the thickness of corrosion product film, rather than reading and understanding the clear evidence in the ToF-SIMS results. Based on above explanations and arguments, we disagree with the Comment claiming that our interpretation of the ToF-SIMS data is incorrect. Instead, we want to stress that many of the localized corrosion processes that may operate under current exposure conditions are still not fully understood. Very long exposure periods and addition of gamma-radiation, which is known to generate high levels of atomic H on the Cu surface, may complicate the uncertainties even further.

### 3. Repository conditions and implication of the ToF-SIMS results

The Comment raised questions mainly on the following issues: our discussion on the diffusion and speculation of the penetration depth; and discussion about the relevance to the S-induced SCC and preferential intergranular corrosion observed in three relevant studies reported in literature. Below we give our arguments and rebuttal to the Comment, point by point.

#### 3.1. Diffusion and penetration depth

The ToF-SIMS data in our paper clearly show the existence of a region of “pronounced penetration” under the corrosion product film. Moreover, the logarithmic plots of the depth profiles (Supplemental material in ref. 1) and the channel-like features in the 3D elemental images indicate the occurrence of deep penetration at certain local sites, which may extend to a much larger depth than the termination of the ion sputtering. Based on these experimental observations, we discuss the diffusion of the corrosive species along the grain boundaries and bulk diffusion towards grain interior. Similar to the estimation in a SKB Technical Report compiling the diffusion data [7], we speculate the possible depth of penetration over a long period of time. The authors of the Comment firstly deny the existence of the pronounced penetration, then argue that the diffusion kinetics should follow the square root of time. In our reply above, we give our rebuttal arguments and provide further evidence to demonstrate the existence of a region of pronounced penetration of the corrosive species. The diffusion kinetics of square root of time is true only for simple diffusion processes driven by concentration gradients. However, as shown in the 2D ToF-SIMS elemental images, the corrosive species H, S, O and Cl often co-segregate at the same sites within the Cu matrix, which indicates that inward diffusion is coupled to and promoted by the chemical reactions involving chemical dissociation of  $H_2O$  or reaction with  $H_2O$ , as well as oxidation-sulfidation along certain fast pathways inside the Cu microstructure. Such diffusion process could be much faster than simple diffusion processes driven by concentration gradients. The 1D wormhole corrosion mechanism reported in ref. 6 is a good example of localized fast corrosion inside metals. It should be mentioned that within large Cu grains there may be pervasive, low degrees of lattice disorientation and coincident site lattice boundaries (seen as twin domains), which can promote the penetration of the corrosive species. Therefore, we disagree with the Comment that the corrosion process in this complex system follows a slow kinetics in which the penetration depth increases as the square root of time. In all, based on the observation of the pronounced penetration and co-segregation of the corrosive species, as well as the deep penetration along fast pathways, we have good reasons to believe that the penetration of the corrosive species within Cu matrix could be much faster than the slow bulk diffusion.

#### 3.2. Relevance to S-induced SCC and preferential intergranular corrosion

Three references have reported important experimental studies of S-induced SCC of Cu in the context of risk assessment of corrosion failure of Cu canisters for geological disposal of nuclear waste. In an early study in Japan, it was found that the presence of sulphide ( $Na_2S$ ) in simulated sea water can cause S-induced SCC of Cu, and the critical S content was

found to be 0.01 M, below which SCC was not observed. However, preferential intergranular corrosion was observed at lower S content level [8]. Later, in a similar study in Sweden, S-induced SCC of Cu was also observed, and the critical S content was found to be 0.001 M. Again, preferential intergranular corrosion was observed at lower S content level [9]. In a more recent joint study by Finish and Swedish researchers, where more measurements and analyses were performed, again, S-induced SCC of Cu was observed. The critical S content was confirmed to be 0.001 M, and preferential intergranular corrosion was observed at lower S content level [10]. These studies clearly show that in the presence of tensile strains, S-induced SCC of the Cu material can occur, within the time scale of only several days. We note that in the latter two studies, the experiments were performed at 90 °C, and the critical S content was 10 times lower than in the first study where the experiment was performed at ambient temperature. These findings suggest a significant effect of the elevated temperature. Even at lower S levels, preferential intergranular corrosion was repeatedly observed. It is noteworthy and surprising that the authors of the Comment try to find alternative explanations to the S-induced SCC, in spite of all the experimental evidences. In our opinion, our SIMS observations of the pronounced penetration and deep penetration along fast pathways, as well as the joint actions of the corrosive species provide a reasonable explanation for the S-induced SCC of the Cu material, including the intergranular corrosion observed at lower S levels. The main argument in the Comment, which disagrees with our reasoning, is based on their belief that no pronounced penetration of S occurs inside the Cu matrix, in spite of all observations by different research groups in different countries. Unfortunately, the authors restrict their mechanistic explanations to uniform and very slow corrosion of Cu, without considering the complexity of the corrosion system and the corrosion mechanisms that can lead to localized and fast corrosion inside the Cu material. Referring to our ToF-SIMS data and Nano-SIMS results (Fig. 1) one could say that the authors only consider S and H to be integrated in the corrosion products while, in fact, our data show that these and other elements (O and Cl) are spread to a much deeper part of Cu.

The authors of the Comment mentioned their Comment on our earlier paper published in 2022 [11], trying to find alternative explanations to the observed S-induced SCC [12]. In fact, we have provided extensive explanations and replies to the comments, and based our arguments on our own and others experimental results as well as on theoretical calculations that suggest the possibility for S-induced SCC [13].

### 4. Conclusions

Our ToF-SIMS results published recently [1] provide clear evidence for the existence of a region of pronounced penetration and co-segregation of the corrosive species H, S, O and Cl under the corrosion product film, and also for deep local penetration along some fast pathways. The penetration and accumulation of the corrosive species within the Cu matrix was greatly enhanced by the increase of the exposure temperature in artificial groundwater from 22 °C to 60 °C. Our interpretation of the data is based on a solid knowledge of the ToF-SIMS technique and data analysis, as well as on careful considerations of eventual artifacts that might be caused by the surface roughness, etc.

The authors of the Comment consider the effects of groundwater exposure to Cu to be restricted to the formation of corrosion products in which elements, such as H, S, O and Cl, are integrated. However, our ToF-SIMS data and other data including Nano-SIMS results which are underway, provide ample evidence that these elements are not confined to corrosion product films but are spread from the groundwater along grain boundaries and other fast pathways much deeper into the interior of Cu. This makes the corrosion system and concomitant corrosion mechanisms much more complex, in particular if also considering the addition of gamma-radiation.

We believe that there is a knowledge gap regarding the corrosion



mechanism leading to pronounced penetration and fast localized penetration of the corrosive species inside the Cu microstructure. Further research is necessary by utilizing state-of-the-art techniques, especially high-resolution structural and chemical imaging based on SEM/TEM and ToF-SIMS/Nano-SIMS. The complexity of the corrosive environment as well as joint/synergistic actions of the corrosive species should be considered in order to achieve a fundamental understanding of the corrosion process that is needed for reliable risk assessment of the Cu canister used in geological disposal of nuclear waste.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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