Impeding $^{99}$Tc(IV) mobility in novel waste forms

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Technetium ($^{99}$Tc) is an abundant, long-lived radioactive fission product whose mobility in the subsurface is largely governed by its oxidation state. Tc immobilization is crucial for radioactive waste management and environmental remediation. Tc(IV) incorporation in spinels has been proposed as a novel method to increase Tc retention in glass waste forms during vitrification. However, experiments under high-temperature and oxic conditions show reoxidation of Tc(IV) to volatile pertechnetate, Tc(VII). Here we examine this problem with ab initio molecular dynamics simulations and propose that, at elevated temperatures, doping with first row transition metal can significantly enhance Tc retention in magnetite in the order Co > Zn > Ni. Experiments with doped spinels at 700 °C provide quantitative confirmation of the theoretical predictions in the same order. This work highlights the power of modern, state-of-the-art simulations to provide essential insights and generate theory-inspired design criteria of complex materials at elevated temperatures.
Technetium ($^{99}$Tc) is an abundant long-lived radioactive fission product present in used nuclear fuel and waste generated from nuclear fuel reprocessing. Owing to its long half-life (2.1 × 10^{5} years) and relatively high fission yield (~6%), $^{99}$Tc can generate the greatest radiation dose in the vicinity of a waste repository, and for a much longer time compared with other fission products, such as $^{90}$Sr and $^{137}$Cs (with half-life ~30 years)\(^1\). In addition, $\text{TcO}_2^-$ is highly soluble and weakly adsorbed in the near-field, while Tc(IV) is highly adsorbable to geological materials and clays\(^2\). Thus, soluble and weakly adsorbed Tc(IV) in the near-field, while Tc(VII) is highly volatile. Tc(IV) is less volatile\(^3,8,9\). Tc(VII) may be effectively retained in the final waste glass\(^4–7\). Retention of Tc in the glass is generally improved by reducing conditions since Tc(IV) is less volatile\(^6,8,9\). Tc(VII) may be effectively reduced to Tc(IV) by Fe(II) in oxide and sulfide minerals or by Fe(II) adsorbed to mineral surfaces such as iron oxides or aluminium oxides\(^9–17\). However, retention of Tc is still limited because of re-oxidation of Tc(IV) back to Tc(VII)\(^18–21\). Consequently, simply reducing Tc(VII) to Tc(IV) before vitrification is unlikely to stabilize Tc and prevent its volatilization as Tc(VII). An alternative approach would be to trap Tc(IV) in the lattice of a metal oxide by co-precipitation. Spinel is an attractive target for Tc stabilization during vitrification because of their physical and chemical stability under the high temperatures used in preparing borosilicate glasses\(^4,6\). In this respect, efficient incorporation and high retention of Tc by glass-incorporated spinels is very important for radioactive waste management and offers substantial economic benefit because of reduction in the amount of glass needed to immobilize $^{99}$Tc.

Magnetite ($\text{Fe}_3\text{O}_4$) has a cubic inverse spinel structure, where the oxygen anions form a slightly distorted face-centred-cubic sublattice and the iron cations occupy tetrahedral and octahedral interstitial sites. In the [001] direction, two types of layer stacking occur: A layers with tetrahedral Fe(III) and B layers with O and octahedral Fe(II)/Fe(III) (see Fig. 1). Marshall et al.\(^8\) showed that Tc(VII) can be reduced to Tc(IV) and incorporated into the magnetite structure under high pH conditions (pH 10.5–13.1). They also observed that Tc(IV) incorporation occurred at the octahedral sites and remobilization of Tc(IV) was limited during subsequent air oxidation. Kobayashi et al.\(^8\) observed Tc(IV) incorporation into the magnetite structure at pH 6 and pH 7.5 (ref. 22). However, magnetite oxidizes to maghemite ($\gamma$–$\text{Fe}_3\text{O}_4$) in oxidic conditions or under high temperature through maghemitization, where all the Fe(II) atoms oxidize to Fe(III), while the oxygen sublattice remains unchanged\(^23\). When maghemitization takes place, iron atoms diffuse towards the surface, leaving octahedral cation vacancies\(^23,24\). As a result, maghemitization could lead to re-oxidation of Tc(IV) because of the increase in Fe(III), a highly efficient oxidizing agent\(^4\). Sidhu et al.\(^23\) suggested that incorporation of trace elements into magnetite stabilizes Fe(II) and suppresses maghemitization by decreasing electron mobility. The majority of experimental studies on Tc retention are conducted at low temperatures, while theoretical studies employ static structural models that neglect temperature effects.

Figure 1 | The B-truncated (octahedral Fe) $\text{Fe}_3\text{O}_4(001)$ structure. (a) Top view and (b) side view of surface structure. Red and cyan circles represent oxygen and iron, respectively. A (blue circle) can be either Fe or Tc and B (yellow circle) can be either Fe or an impurity atom (Ni/Zn/Co).
tional structural parameters). These observations imply that (i) within the surface layer the oxidation state of Tc is essentially Tc(IV) and (ii) at 25 °C (the glass-feed stage) reduced Tc(IV) is the prevalent oxidation state. However, the completely opposite picture emerges at high temperatures, 600 °C or higher. Tc moves above the surface, dragging coordinating surface oxygens along with it (see Supplementary Movie 1). The local Tc geometry is consistent with a tetrahedral Tc(VII)O₄ species, with two or three of the coordinating oxygens dynamically connected to Fe atoms on the surface (Fig. 2c). Analysis of g(R) for Tc–O pairs shows a peak at 1.79 Å (Fig. 2b, lower panel), an almost 10% reduction compared with the Tc(IV)–O distance at 25 °C. This change is compatible with the shorter Tc(VII) – O distances of ~1.75 Å as determined by XAFS (Supplementary Table 2 and refs 22, 33). From this observation, we infer, that beginning at 600 °C, Tc oxidation is in process, commensurate with the tetrahedrally coordinated Tc transitioning to TcO₄⁻. In addition to the system with Tc at the surface, we also examined a system with Tc at an inner lattice site at 600 °C. The calculated g(R) gives the distance between Tc and O as 2.01 Å, consistent with the reduced Tc(IV) in magnetite. As shown in Supplementary Fig. 2, Tc remains in the same layer throughout the simulation timescale. When comparing the energetics of the configurations with Tc below or at the surface layer, the energy with Tc below the surface is 2.5 eV higher than when Tc is at the surface. This implies that there is a thermodynamic driving force that will eventually move Tc out to the surface.

Experimental. Tc-magnetite samples, heated from room temperature to 600 °C and then cooled back to room temperature, were analysed to determine the Tc oxidation state using XANES as shown in Fig. 2d. In the figure, the grey diamonds and black line indicate the measured data and a linear combination fit, respectively, for Tc-magnetite samples, while the red and blue lines represent the contribution from Tc(IV) and Tc(VII), respectively. At 25 °C, the spectrum of the sample shows only Tc(IV) (feed, red) but no Tc(VII) (blue), indicating that all Tc in the sample is in its reduced form. In the sample heated to 600 °C, however, the spectrum shows a mixture of both Tc(IV) and Tc(VII). All these observations are compatible with the simulations.

Effects of dopants on Tc retention. To simulate the effect of dopants on the Tc redox chemistry and immobilization, we modified the magnetite by substituting one surface Fe atom with Ni, Zn or Co (~1% wt each) at a site close to Tc. This choice was motivated by earlier experiments by Sidhu et al., who observed stabilization of Fe(II) and suppression of maghematization when first row transition metal dopants were present in magnetite even at concentrations ~1 wt %. The atomic density profiles along the surface normal from AIMD at 600 °C in the presence of the doping elements are shown in Fig. 3 (Co) and Supplementary Fig. 3 (Ni and Zn), exhibiting an increase in Tc retention in the order Co > Zn > Ni.

In the case of Ni, the Tc population is bi-modal where Tc remains mostly on top of the surface with only a small population within the top surface layer. In the case of Zn, the bi-modal Tc distribution is shifted towards a larger Tc population within the surface. Analysis of trajectories also shows that the distance between Tc and the coordinating O fluctuates between 1.71 and 1.92 Å, compatible with an equilibrium between Tc(VII) and Tc(IV) oxidation states (see Supplementary Fig. 4). This behaviour implies that Ni and Zn only partially, and to a similar degree, hinder Tc oxidation. Finally, in the presence of Co, Tc remains almost in its entirety within the surface at all times indicative of a Tc(IV) state. We examined Tc(IV) stabilization in the presence of Co by conducting a simulation starting with TcO₄⁻ on top of the surface. As shown in Supplementary Movie 2, Tc(VII) rapidly migrates into the surface becoming Tc(IV), within 1.5 ps of simulation time.

To validate these findings, we prepared three different magnetite samples doped with ~10% wt of Ni, Zn and Co. Details on the preparation of samples can be found in the Methods section. The samples were heated at 700 °C in a furnace.
for 1 h, and the remaining Tc was measured (see Supplementary Table 3). Gravimetric measurement showed that doping with Co resulted in the highest Tc retention (29% wt) compared with less than half that amount for Zn (12% wt) and ~1/8 of that for Ni (4% wt). No detectable amount of Tc was found in the Tc-magnetite sample prepared without dopant and treated at 700°C. We also performed XANES measurements for the samples prepared at 25 and 700°C (see Supplementary Methods for details) and confirmed our theoretical prediction of the highest Tc retention with Co dopant at high temperature, as shown in Supplementary Table 4 and Fig. 3b and Supplementary Fig. 5.

Equilibrium constants and free energy estimates. To best connect with the experimental observations, we determined the ratio of the equilibrium populations between the two different oxidation states of Tc(IV) ([Tc(IV)] and Tc(VII) ([Tc(VII)]). This can be achieved by integrating the area under the atomic density profiles for Tc in Fig. 3. An equilibrium constant between the two populations, determined as the ratio $K_{eq} = \frac{[\text{Tc}]_\text{in}}{[\text{Tc}]_\text{out}}$, was used to calculate the Gibbs free energy for this equilibrium from the relation $\Delta G = RT \ln K_{eq}$, where $R$ is the gas constant and $T$ is the absolute temperature. Negative values indicate that the equilibrium favours a higher population of Tc(IV). Table 1 summarizes the computed values of $K_{eq}$ and $\Delta G$, as well as the measured Tc retention for the different doping agents Ni, Zn, and Co. These results show a remarkable agreement between the theoretical prediction and experimental validations, not only in terms of relative order but also in magnitude. The underlying reason is based on the increase in the reducing capacity of the Tc-containing spinels upon doping. This can be quantified by the difference in energy between the Fermi level, $E_F$, and the Tc HOMO energy from the projected DOS.

| Doping   | $K_{eq}$ | $\Delta G$ (kJ mol$^{-1}$) | Exp. retention (%wt) | $\Delta E_{gap}$ (eV) |
|----------|----------|---------------------------|----------------------|-----------------------|
| Tc       | 0.15     | 12.4                      |                      | 1.5                   |
| Tc/Ni    | 0.56     | 14.3                      | 4                    | 3.5                   |
| Tc/Zn    | 2.79     | 12                        | 12                   | 1.03                  |
| Tc/Co    | 21.80    | 23.1                      | 29                   | 1.12                  |

Tc implies system without dopant. Relative populations determined as a ratio from the computed $K_{eq}$ values. Experimental values correspond to the amount of Tc remaining in the doped magnetite after exposure to 700°C. $\Delta E_{gap}$ represents the energy difference between the Fermi level $E_F$ and the Tc HOMO energy from the projected DOS.

Discussion

In conclusion, we propose that standard reduction potentials of transition metal ions relative to those of parent spinel, combined with their available oxidation states, can be a useful diagnostic tool for identifying appropriate additives. The reduction potential for magnetite ranges from +0.22 to +0.66 V (ref. 34), while those for Co$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ are −0.28, −0.26 and −0.76 V, respectively35, and in principle Co$^{2+}$ and Ni$^{2+}$ should have similar and limited effect upon Tc retention, while Zn$^{2+}$ should have a more pronounced influence. However, Co$^{3+}$ with a wide range of redox values towards Co$^{3+}$ (refs. 35, 36), it greatly increases the overall reducing capacity of the spinel material. This is reflected in the increased stabilization of the Tc $d$-states, see Table 1. Both simulations and experimental show that cobalt is by far the most effective additive for Tc retention compared with the undoped magnetite. We postulate that Tc retention, during the glass vitrification, can be controlled by balancing the redox capacity of oxide materials and doping agents. The current study underscores the impact of complex models incorporating both electronic structure and temperature effects that reveal the critical variables needed for predictive materials’ design.

Methods

Density functional theory (DFT) parameters. Spin-polarized DFT simulations were performed with periodic boundary conditions (3D PBC) as implemented in the CP2K package37. The Perdew, Burke and Ernzerhof (PBE) generalized gradient approximation was used for the exchange-correlation functional38. The core electrons were described by the norm-conserving pseudopotentials39, while the valence wave functions were expanded in terms of double-zeta quality basis sets optimized for condensed systems to minimize linear dependencies and superposition errors40. An additional auxiliary plane wave basis set with a 500-Ry cutoff was used to calculate the electrostatic terms. The GGA + U scheme was used to provide more accurate electronic structure for the localized $d$-orbitals. The Hubbard parameter ($U$) of 3.5 eV was taken for the Fe $3d$ states, which results in a work function of 5.32 eV, in good agreement with that obtained by Pentcheva el al.28 Owing to large supercell simulations, the $\Gamma$-point approximation was used for the Brillouin zone integration.

Computational models. To study Tc incorporation in magnetite with and without dopants, we used a 2 × 2 × 2 supercell in all simulations to minimize periodic images. Optimization of the bulk structure of magnetite had a cell parameter of 8.391 Å, which agrees well with experimental data (8.390 Å (ref. 41)). Using this optimized cell parameter, we constructed a magnetite(001) surface model terminated at an octahedral Fe sublattice, since it is known to be the most stable surface structure in magnetite. A more recent surface model was also considered42, but was found not to have significant impact on the present problem, see SI. Our model system consisted of a symmetric slab with seven octahedral and six tetrahedral Fe sublattices (384 atoms) with a vacuum region of 12.5 Å between slabs. To study Tc incorporation, one surface octahedral Fe was replaced with Tc, followed by structural optimization. We also optimized a structure with one octahedral Fe in the third layer replaced by Tc. For the doping studies, we substituted a surface Fe atom with Co, Ni or Zn (~1 wt%) at a lattice position close to Tc. In all simulations, we fixed the atomic positions of the four bottom atomic layers.

AIMD simulations. AIMD simulations were performed with and without Tc at 25°C and with the dopants Co/Ni/Zn at 600°C with the Nose–Hoover thermostat for NVT ensemble and a time step of 1.0 fs. Each simulation was equilibrated for at least 20–28 ps, and the last 10–12 ps of the trajectories was used for the analysis. Owing to the big computational cost of high-temperature simulations, we chose lower range of vitrification temperatures (600°C) while experiments were performed at somewhat higher temperatures (~700°C).

Spinel synthesis and XAFS analysis. Ni-, Zn-, or Co-doped Tc-incorporated magnetite was synthesized at high pH (~13). Three solutions of 0.05 M Ni, Zn and Co in distilled deionized water (DDI) were prepared using analytical-grade NiCl$_2$, ZnCl$_2$ and CoCl$_2$. Technetium solution (0.001 M) was prepared by spiking 10,000 p.p.m. NaTcO$_4$ stock solution into 1 M NaOH solution. Synthesized Fe(OH)$_3$ dry powder (0.09 g) was mixed with 5 ml of NiCl$_2$, ZnCl$_2$ or CoCl$_2$ solution in 20-ml poly vials and shaken on an orbital shaker (120 r.p.m.) for 24 h at room temperature (RT). After 24 h shaking, 15 ml of the Tc-spiked 1-M NaOH was added to each vial and heated in an oven at 75°C for 72 h. After cooling to RT, the precipitates were separated using 0.45-μm filters and washed using ~120 ml DDI.
Icenhower, J. P., Qafoku, N. P., Martin, W. & Zachara, J. M.

References

1. Koteog, K. V., Pavlov, O. N. & Shvedov, V. P. in Advances in Inorganic Chemistry and Radiochemistry (eds Emelius, H. J. & Sharpe, A. G.) Vol. 11, 1–90 (Academic Press, 1968).
2. Luyks, F. in Technetium in the Environment (eds Desmet, G. & Mynteraene, C.) 21–27 (Springer, 1986).
3. Chen, F., Burns, P. C. & Ewing, R. C. Near-field behavior of 99-Tc during the oxidative alteration of spent nuclear fuel. J. Nucl. Mater. 278, 225–232 (2000).
4. Muller, I. S., McKeown, D. A. & Pegg, I. L. Structural behavior of Tc and I ions in aqueous-based magnetite dispersions: Effect of pH and redox potential. J. Colloid Interf. Sci. 197, 407–416 (1998).
5. Darab, J. G. & Smith, P. A. Chemistry of technetium and rhenium species in heterogeneous electron transfer from Fe(II)-containing geological material. Environ. Sci. Technol. 1244–1249 (1999).
6. Fan, D. C., Chin, S. F. & Anderson, M. A. Redox equilibria of iron oxides in aqueous-based magnetite dispersions: Effect of pH and redox potential. J. Colloid Interf. Sci. 311, 94–101 (2007).
7. CRC Handbook of Chemistry and Physics 7th edn (CRC Press, 1994-1995).
8. Hamdani, M., Singh, R. N. & Chartier, P. CoO and Co-based spinel oxides bifunctional oxygen electrodes. Int. J. Electrochem. Sci. 5, 556–577 (2010).
9. VandeVondele, J. et al. Quickstep: fast and accurate density functional calculations using a mixed gaussian and plane wave approach. Comput. Phys. Commun. 167, 103–128 (2005).
10. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 77, 3865–3868 (1996).
11. Goedecker, S., Teter, M. & Hutter, J. Separable dual-space Gaussian pseudopotentials. Phys. Rev. B 54, 4148–4170 (1996).
12. VandeVondele, J. et al. Adsorption and incorporation of transition metals at the magnetite Fe(III) (001) surface. Phys. Rev. B 92, 075440 (2015).
13. Ravel, B. & Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 12, 537–541 (2005).

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Author contributions
All authors provided input for the manuscript. M.-S.L. contributed to the planning and executed the simulations and analysed the data, W.U., G.W. and W.W.L. performed the experiments and related data analysis. R.R. provided pseudopotentials for the calculations and contributed to the analysis of the data. V.-A.G. planned and supervised the research. M.-S.L., R.R. and V.-A.G. jointly wrote the manuscript with input from all authors.

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