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Computational Study of the Substitution of Early Actinides and Ce into Zirconolite

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Abstract

Substitutions of tetravalent early actinides (Th – Am) and Ce into the ceramic nuclear waste form zirconolite, $\text{CaZrTi}_2\text{O}_7$, have been analysed using hybrid Density Functional Theory in conjunction with the Periodic Electrostatic Embedded Cluster Method. Substitutions on to both Zr^{4+} and Ca^{2+} sites were modelled, with Fe^{3+} and Al^{3+} used for charge balancing. The mean displacements of a central region of ions in the cluster indicated redox behaviour which was then confirmed through analysis of spin density data. Strong correlations were found between the substitution energies of these ions and the ratio of the ionic radii of substituents and substituted ions. Similar redox behaviour and substitution energies were seen for substitutions of Ce^{4+} and Pu^{4+} into the lattice. Spin density data of molecular $\text{M}(\text{OH})_n$ ($\text{M} = \text{Ce}, \text{Th} - \text{Am}, n = 3 - 5$) showed a preference for the +3 oxidation state for later actinides - as seen in the zirconolite clusters.

Keywords: Zirconolite, DFT, PEECM, Spin Density

1. Introduction

In the United Kingdom, the current stockpiling of plutonium-containing materials, accumulated from the reprocessing of spent nuclear fuel, has been identified as an unacceptable long-term strategy [1]. Potential solutions include re-use *via* conversion to Mixed Oxide (MOX) Fuels or immobilisation and disposal in a Geological Disposal Facility (GDF) [2, 3]. Immobilisation is the atomistic substitution of radioisotopes into a waste form [4, 5]. These must be able to withstand self-radiation damage and geologic processes, to prevent leaching over geologic time scales and hence allow the safe isolation of nuclear materials from the biosphere. Candidate waste forms for high level nuclear waste include borosilicate glasses and ceramics [5–7]. While borosilicate glasses are able to achieve a waste loading of around 25 wt% - around 15 wt% more than is expected of ceramic waste forms [7, 8] - they are less preferable than ceramics due to their lower leaching resistance.

The ceramic zirconolite $\text{CaZrTi}_2\text{O}_7$ was characterised by Rossell in the 1980s [9] and identified by the Australian National University as a potential material for use as part of the multi-phase waste form SYNROC (SYNthetic-ROCK) [5, 7, 10, 11]. Zirconolite-2M, (Fig. 1) the polytype analysed within this work, is comprised of TiO_5 and TiO_6 polyhedra separated by alternating layers of seven-coordinated (by oxygen) Zr^{4+} sites and eight-coordinated Ca^{2+} sites [12, 13]. Other polytypes of zirconolite (such as the 4M polytype) can be formed through

an increase in waste load and other variances in material production [14–17]. The presence of natural actinide-containing zirconolite samples [18] and the ability to accommodate heavy elements onto either the Ca^{2+} or Zr^{4+} sites indicates the geologic durability of zirconolite and its compositional flexibility. Substitutions of other cations, such as Fe^{3+} , Mg^{2+} and Al^{3+} onto the Ti^{4+} sites [10, 12, 13, 18–20] can be used to balance the charge for substitutions of trivalent or tetravalent ions onto the Ca^{2+} site.

Figure 1: Zirconolite-2M Unit Cell. Light blue indicates Ti^{4+} ions, green – Zr^{4+} , red – O^{2-} and dark blue – Ca^{2+} .

Molecular Dynamics (MD), periodic Density Functional Theory (DFT) and ionic potential models have been used to study zirconolite computationally. MD studies focussed on the modelling of low-energy alpha decay events involving uranium and plutonium in both pristine and Pu-doped zirconolite [21–24]. Periodic DFT was used to describe the electronic structure [25], study intrinsic defects [26] and investigate the potential build up of He following alpha decay [27]. Substitution energies of both tri- and tetravalent Ce and Pu into the zirconolite lattice were calculated using an ionic potential model [28]. Isolated substitutions onto a Ca^{2+} site were found to be energetically favourable, while substitutions onto Zr sites were energetically unfavourable. This is largely driven by coulombic factors following altrivalent substitutions onto Ca^{2+} , and resulting steric factors following isovalent substitutions onto Zr^{4+} . The total defect energy associated with substitutions of Fe^{3+} onto Ti^{4+} , as well as actinide substitutions onto Ca^{2+} , is positive - indicating that the additional and necessary charge balancing substitutions make the overall substitution energetically unfavourable.

In this study, hybrid DFT within the Periodic Electrostatic Embedded Cluster Method (PEECM) is used to calculate the changes in geometry and electronic structure of the zirconolite lattice following single and double substitutions of tetravalent early actinides (Th–Am) and cerium onto the Ca^{2+} and Zr^{4+} sites. The use of Fe^{3+} and Al^{3+} for charge balancing is discussed. Substitution energies for all of these systems are calculated and compared with those found in previous calculations.

2. Computational Details and Methodology

All calculations were performed using TURBOMOLE 7.2 and 7.3 [29]. Settings were left at default except for the self-consistent field (SCF) orbital shift (0.5), initial SCF damping value (5.7) and the integration grid size (M4). The GGA-level PBE [30] and hybrid PBE0 [31] functionals were used in conjunction with def2-SVP basis sets for all atoms smaller than and including Ce. For the actinides, the basis sets employed are labelled "def-SVP" by Turbomole, but this description is ambiguous. The actinide basis sets are actually of higher quality than SVP, employing a (14s13p10d8f1g) / [10s9p5d4f1g] contraction [32, 33]. Small core Effective Core Potentials (ECP) were used for Zr, Ce (28 electrons) and all actinides (60 electrons) [34, 35].

2.1. Periodic Electrostatic Embedded Cluster Method

Using the PEECM allows for a localised area, such as the area surrounding a vacancy or a defect [36], to be analysed. Hybrid functionals are straight forward to use, an advantage over periodic DFT [37]. In naturally occurring zirconolite samples, the ratio of Ti/Zr ions is variable. For simplicity, zirconolite with the integer unit formula ($\text{CaZrTi}_2\text{O}_7$) is used throughout this study. Through the use of the PEECM [36], the periodic zirconolite system is split up into three parts. Region 1 is the central 110 atom cluster (Fig. 2) which is produced using the VESTA [38] graphical software by initially repeating the 88 ion unit cell in all directions before reshaping the

cluster to a near spherical shape while making it stoichiometric. An inner region of the cluster, made up of 17 atoms (2 Ca, 9 O, 4 Ti and 2 Zr) is allowed to relax during geometry optimisations, with all other atomic coordinates in the cluster remaining fixed. The central cluster is treated fully quantum mechanically (QM) and is surrounded by an intermediate region. This intermediate region, region 2, in which cations are replaced by all-electron ECPs and anions are replaced by formal charges, prevents the QM region from being over-polarised by the surrounding infinite point charge (PC) region (region 3) which recreates the Madelung potential of the bulk of the system. The ECP18SDF [39], ECP18MHF [40] and CRENBSECP [41] all-electron ECPs were used for Ca, Ti and Zr respectively in region 2.

Figure 2: The 110-atom zirconolite cluster, sites A-D refer to substitution sites for early actinides. Light blue indicates Ti^{4+} ions, green – Zr^{4+} , red – O^{2-} and dark blue – Ca^{2+} .

2.2. Substitutions: Kröger-Vink Notation and Energies

Substitutions of early actinides and Ce have been performed on four different sites. Sites A and B (shown in Fig. 2) are Zr sites, with A being used for both the singly- and doubly-substituted systems and B used only for doubly-substituted systems. Similarly, for substitutions onto Ca sites, sites C and D were used. To describe each type of substitution, or specific substitutions of a certain type, the Kröger-Vink notation is used. The general form of the notation is:

$$M_S^C$$

in which M represents the substituting ion, S is the site on which it has been substituted and C is the charge of the substituent relative to the site which it occupies. A net single positive charge is represented by $\bullet$, a net negative charge is represented by $\prime$ and a net neutral charge is represented by $\times$. Examples presented in this work include tetravalent Pu substituted isovalently onto a Zr^{4+} site – $\text{Pu}_{\text{Zr}}^{\times}$ – and tetravalent Np substituted altrivalently onto a Ca^{2+} site as well as two Fe^{3+} substitutions onto Ti^{4+} sites for charge balancing; $\text{Np}_{\text{Ca}}^{\prime\prime} + 2 \times \text{Fe}_{\text{Ti}}^{\prime}$.

M	Ce	Th	Pa	U	Np	Pu	Am
M_{Zr}^X							
Mean	0.049	0.081	0.044	0.053	0.049	0.044	0.040
Max (atom)	0.180 (O)	0.292 (O)	0.091 (Ti)	0.173 (O)	0.167 (O)	0.140 (O)	0.133 (O)
M-Site (A)	0.087	0.156	0.069	0.108	0.106	0.098	0.100
$M_{Ca}^X + 2 \times Fe'_{Ti}$							
Mean	0.063	0.100	0.108	0.158	0.162	0.064	0.064
Max (atom)	0.144 (O)	0.149 (O)	0.261 (O)	0.824 (Fe)	0.847 (Fe)	0.153 (O)	0.151 (O)
M-Site (C)	0.086	0.112	0.111	0.177	0.164	0.066	0.069
$2 \times M_{Zr}^X$							
Mean	0.076	0.123	0.064	0.081	0.078	0.073	0.068
Max (atom)	0.181 (O)	0.297 (O)	0.101 (O)	0.186 (O)	0.163 (O)	0.163 (O)	0.148 (O)
M-Site (A)	0.087	0.153	0.056	0.111	0.106	0.097	0.098
M-Site (B)	0.065	0.112	0.100	0.114	0.081	0.081	0.089
$2 \times (M_{Ca}^X + 2 \times Fe'_{Ti})$							
Mean	0.143	0.162	0.148	0.144	0.144	0.146	0.082
Max (atom)	0.342 (O)	0.497 (Fe)	0.408 (O)	0.337 (O)	0.338 (O)	0.342 (O)	0.160 (O)
M-Site (C)	0.133	0.147	0.082	0.113	0.107	0.106	0.068
M-Site (D)	0.123	0.075	0.063	0.100	0.077	0.079	0.041

Table 1: Displacements following single and double substitutions onto the Ca and Zr sites. Only site A and both sites, A and B, are used for single and double substitutions onto Zr-sites respectively. Only site C, and both sites C and D, are used for single and double substitutions onto Ca-sites respectively. Maximally displaced atoms are denoted by their element symbol. All values are in Ångström.

Substitution energies (E_{Sub}) are calculated via equation 1

$$E_{Sub} = E_{An_{Zr}^X} + E_{Zr^{4+}} - (E_{Zirconolite} + E_{An^{4+}}) \quad (1)$$

where $E_{An_{Zr}^X}$ is the energy of the substituted cluster within the PEECM, E_X is the energy of cation X, and $E_{Zirconolite}$ is the energy of the unsubstituted zirconolite cluster.

2.3. Projected Density Of States

In order to produce a Projected Density of States (PDOS), a Mulliken population analysis (MPA) was performed on the optimised structures. From the results of the MPA, TURBO-MOLE generates a PDOS through a broadening of the calculated discrete energy levels using Gaussian functions which are then superimposed. The Fermi energy is then assigned to the occupied orbital with the highest energy. The difference between the two discrete energies of the lowest unoccupied (LUMO) and highest occupied molecular orbital (HOMO) can be used as an analogue for the band gap, but it is an overestimation. This overestimation arises as the discrete energy levels are not directly comparable with band gaps which are a bulk property. Also, the HOMO-LUMO energy difference is calculated at the gamma point - the centre of the first Brillouin zone. Zirconolite has an indirect band gap [25], meaning the energy gap at the gamma point will be a further overestimation of the natural band gap.

2.4. Spin Density

Natural Population Analysis (NPA) was used to calculate spin densities on all ions following substitution. Spin density data are calculated in part to reveal the oxidation state of ions in the system. As an example, Pu(IV) has four unpaired f -electrons and so the spin density value for this ion will be approximately 4. Should the Pu ion be reduced to Pu(III), the spin

density would increase to around five - as the ion has gained an electron.

Figure 3: PBE0 Projected Density of States of unsubstituted zirconolite.

3. Results And Discussion

3.1. PDOS and Choice of Functional

To determine which functional would be best to use, embedded clusters were modelled using the PBE and PBE0 functionals. The 17 atom inner region of each cluster (as described in section 2.1) underwent geometry optimisation. MPA was then run on both clusters. For the reasons mentioned in section 2.3, the calculated value of $E_{LUMO} - E_{HOMO}$ should be larger than the experimental band gap of 3.6 eV [42]. Indeed, that is what is found for the PBE0 value (4.40 eV) while the PBE value is an underestimation at 2.20 eV. This is in line with the tendency of GGA functionals to underestimate the band gap of

M	Ce	Th	Pa	U	Np	Pu	Am
M_{Zr}^X	4.55	4.18	0.36	1.64	2.98	4.01	3.89
$2 \times M_{Zr}^X$	4.54	3.65	0.69	0.90	2.41	3.48	3.63
$M_{Ca}^{\cdot\cdot} + 2 \times Fe'_{Ti}$	1.24	3.06	1.93	3.16	3.49	1.31	2.37
$2 \times (M_{Ca}^{\cdot\cdot} + 2 \times Fe'_{Ti})$	2.23	2.38	1.68	2.05	2.48	2.07	1.42

Table 2: $E_{LUMO} - E_{HOMO}$ for single and double tetravalent substitutions onto Ca^{2+} and Ti^{4+} sites. All values in eV

M	Ce	Th	Pa	U	Np	Pu	Am
M_{Zr}^X (A)	-	-	<u>0.00</u>	1.96	2.94	3.96	5.00
$2 \times M_{Zr}^X$ (A)	-	-	<u>0.01</u>	1.95	2.95	3.95	5.00
$2 \times M_{Zr}^X$ (B)	-	-	<u>0.00</u>	<u>1.08</u>	2.91	3.94	4.99
$M_{Ca}^{\cdot\cdot} + 2 \times Fe'_{Ti}$ (C)	<u>0.99</u>	0.00	0.96	1.98	2.97	<u>4.91</u>	<u>5.91</u>
$2 \times (M_{Ca}^{\cdot\cdot} + 2 \times Fe'_{Ti})$ (C)	0.02	0.00	0.96	1.98	2.98	4.02	<u>5.91</u>
$2 \times (M_{Ca}^{\cdot\cdot} + 2 \times Fe'_{Ti})$ (D)	0.03	0.00	<u>0.04</u>	1.96	2.97	4.00	<u>5.88</u>

Table 3: Spin density values of substituted ions following single and double M_{Zr}^X and $M_{Ca}^{\cdot\cdot} + 2 \times Fe'_{Ti}$ substitutions. Values not related to a 4+ charge state are underlined.

insulators and sometimes incorrectly characterise them as conductors [43]. Comparison of our PBE0 data with a previously calculated PDOS using the PBE functional [26] shows a similar composition of the valence band edge – made up of oxygen p orbitals – and the conduction band edge – made up of Ti d orbitals (Fig. 3). Hence, the PBE0 functional provides a more accurate value for the band gap while also agreeing with previous PBE data for the make-up of the valence and conduction band edges of zirconolite. It is therefore used throughout this work.

3.2. Geometric Changes of Substituted Systems

The optimised coordinates of the unsubstituted system were used as the initial coordinates for the substitution calculations. The same 17 atomic sites (section 2.1) were then optimised. The displacement D of these atoms from their respective sites within the unsubstituted cluster is then calculated through equation 2

$$D = \sqrt{(x_{sub} - x_{unsub})^2 + (y_{sub} - y_{unsub})^2 + (z_{sub} - z_{unsub})^2} \quad (2)$$

where A_{sub} refers to cartesian coordinates of specific atoms in the substituted system, and A_{unsub} refers to Cartesian coordinates in the optimised unsubstituted system. The displacements, following actinide and Ce^{4+} substitution, of the optimised 17 atoms in the system are summarised in Table 1. Typically, an oxygen ion is most displaced for each of the systems considered. Mean displacements for all optimised ions are fairly small following substitutions on the Zr site and slightly larger following substitutions onto the Ca site. This is due to the additional substitution of two Fe^{3+} ions into the lattice, causing a greater degree of disturbance to the local geometry. A reduction in mean displacement is seen across the actinide series for both the single and double M_{Zr}^X substitutions, with Pa a slight outlier. This is likely due to less re-ordering of the surrounding lattice being required for later actinides, as they have an ionic radius which is closer to that of Zr^{4+} . Of note are the

$U_{Ca}^{\cdot\cdot}$ and $Np_{Ca}^{\cdot\cdot}$ systems, in which one of the Fe^{3+} ions is displaced by >0.8 Å. According to one definition, that defects are formed following a displacement over 0.75 Å [23], this implies that these Fe^{3+} ions are occupying defect sites within the lattice. The ion initially occupies a five-coordinate Ti-site and, following optimisation, moves to fill an empty region of space near the centre of the cluster. This is shown in Figure S1 in the supplementary information. No other clear trends in the mean displacement, maximum displacement and displacement from the M-site – the site onto which An is substituted – are seen across the actinides for single substitutions onto the Ca or the Zr sites. Similar behaviour, except for >0.8 Å displacements for some charge balancing ions, is seen for the double substitutions with slightly larger mean and maximal displacements overall. This is to be expected, with more substitutions causing greater disruption to the geometry of the system. In conclusion, there is generally only a small change to the local geometry of the zirconolite cluster following heavy element substitution.

3.3. PDOS of Substituted Systems

Following the substitution of actinides into the cluster, f-states are introduced within the conduction and valence bands and between them. This has the effect of reducing the value of $E_{LUMO} - E_{HOMO}$ (Table 2) for the $E_{M_{Zr}^X}$ systems. PDOS of the substituted systems are given in the supplementary information (SI Figs. S2-5). $E_{LUMO} - E_{HOMO}$ generally increases from Pa to Am as the energies of the introduced f states are close to that of E_{LUMO} for Pa_{Zr}^X and decrease to an energy lower than E_{HOMO} for Am_{Zr}^X (SI Fig. 2). This is in line with f-state stabilisation across the 5f series [44]. A similar trend is also seen for double substitutions onto the Zr sites. The addition of d-states due to the presence of Fe^{3+} within the cluster following substitution onto Ca sites complicates the PDOS, with the result that there is no discernible trend in $E_{LUMO} - E_{HOMO}$ across the actinide series.

M	Ce	Th	Pa	U	Np	Pu	Am
M_{Zr}^X	5.58	11.42	8.51	7.91	7.04	5.98	4.57
$2 \times M_{Zr}^X$	11.48	23.65	16.85	15.90	14.46	12.26	9.36
$(M_{Ca}^{..} + 2 \times Fe'_{Ti})$	30.47	35.42	33.68	32.16	31.37	31.07	28.74
$2 \times (M_{Ca}^{..} + 2 \times Fe'_{Ti})$	60.08	71.13	66.40	64.85	63.24	61.12	57.87

Table 4: Substitution energies of single and double substitutions onto the Ca and Zr sites. All values are in eV.

M	Ce	Th	Pa	U	Np	Pu	Am
$(M_{Ca}^{..} + 2 \times Al'_{Ti})$							
Mean	0.162	0.152	0.157	0.158	0.160	0.074	0.074
Max (atom)	0.811 (Ti)	0.784 (Ti)	0.778 (Ti)	0.771 (Ti)	0.737 (O)	0.199 (O)	0.198 (O)
M-Site (C)	0.224	0.161	0.184	0.184	0.206	0.092	0.096
$2 \times (M_{Ca}^{..} + 2 \times Al'_{Ti})$							
Mean	0.140	0.123	0.153	0.135	0.140	0.143	0.115
Max (atom)	0.257 (Al)	0.255 (O)	0.274 (O)	0.229 (Al)	0.253 (Al)	0.256 (Al)	0.348 (Al)
M-Site (C)	0.183	0.167	0.126	0.159	0.163	0.163	0.121
M-Site (D)	0.257	0.218	0.151	0.227	0.208	0.199	0.074

Table 5: Displacements following substitutions onto Ca^{2+} using Al^{3+} charge balancers. Sites C and D refer to Ca-sites which actinides are substituted onto. Element symbols in brackets refer to the maximally moved atom. All values are in Ångström.

3.4. Spin Density of Substituted Systems

The spin densities of the substituted ions are given in Table 3. As the Th_{Zr}^X and Ce_{Zr}^X calculations are closed-shell, there are no spin density data for these systems or the corresponding double substitutions. Singly substituted Ce^{4+} , Pu^{4+} and Am^{4+} are reduced to trivalent species following substitution onto the Ca site. Electrons gained by these ions originate from several oxygen ions surrounding the charge-balancing Fe. Both substituted Am ions are reduced in the $2 \times Am_{Ca}^{..} + 2 \times Fe'_{Ti}$ system. Additionally, Pa on the Zr site - in all cases - and one of the substituted U ions in the double U_{Zr}^X system are oxidised, with the electron shared over multiple Ti ions.

Figure 4: Modified zirconolite lattice containing Ge - in grey - with remaining titanium ions denoted by pink (site 1) and dark blue (site 2)

In order to further probe the movement of these electrons, the cluster was modified to contain only one or two Ti ions, with all other Ti sites occupied by Ge ions. Ge was chosen as, by contrast to Ti, it is redox inactive in the 4+ oxidation state.

Multiple M_{Zr}^X ($M = Pa$ and U) systems were tested in which a single Ti was placed on each Ti-site with all other sites occupied by Ge to see if a situation would arise in which the lone Ti ion was fully reduced, in contrast to all Ti systems where the electron is shared across multiple Ti ions. This was found to be the case when the Ti was located in a five-coordinate site at the edge of the cluster, denoted Ti(1), highlighted in pink in Fig. 4. A similar method was used to create systems in which all but two Ti-sites were occupied by Ge ions. A Ti ion was kept on the Ti(1) while a second Ti ion was placed on each remaining Ti-site until both Ti ions were fully reduced. Following the double Pa and double U substitutions, both substituent actinides were oxidised. One unpaired electron from each ion localised on Ti(1) and Ti(2) - another five-coordinate titanium within the central region of the cluster. Ti(2) is highlighted as navy blue in Fig. 4. It appears that the presence of five-coordinate Ti-sites close to substitution sites causes Pa and U to be oxidised in these systems.

The Pa ion on site B is oxidised in the $2 \times (Pa_{Ca}^{..} + 2 \times Fe'_{Ti})$ system and the lone electron also localises onto Ti(1). This behaviour may be related to the redox potentials of the substituting ions. The oxidation and reduction potentials of Pa(IV)/Pa(V) and Ti(IV)/Ti(III) are 0.10 and 0.19 V respectively [45, 46]. The total potential ($E^\circ = E_{Red.} - E_{Oxid.}$ where $E_{Red.}$ and $E_{Oxid.}$ are the reduction and oxidation potentials respectively) is positive (0.09 V) which in turn makes the Gibbs Free energy (ΔG° of this reaction (equation 3) negative (n is the number of electrons involved in the process and F the Faraday Constant) and hence the oxidation of Pa and concurrent reduction of Ti is favourable energetically.

$$\Delta G^\circ = -nFE^\circ. \quad (3)$$

The oxidation of U(IV) and reduction of Ti(IV) is also favourable as the oxidation potential for U(IV)/U(V) has been

Figure 5: Correlations between the substitution energy (E_{sub}) and the ratio of the Shannon radii of substituents and the substituted ion.

a) M_{Zr}^X substitutions ($R^2 = 0.977$), b) double M_{Zr}^X substitutions ($R^2 = 0.971$), c) $M_{Ca} + 2 \times Fe_{Ti}'$ substitutions ($R^2 = 0.953$), d) double $M_{Ca} + 2 \times Fe_{Ti}'$ substitutions ($R^2 = 0.994$). Pa is oxidised in both Figures 5a) and 5b). Pu is reduced in Fig. 5c) but no Shannon data exists for the eight-coordinate Pu^{3+} ion. Am and Ce are reduced in both Figures 5c) and 5d). In order to compare across the series of tetravalent actinides, cerium and all ions which have been reduced or oxidised are not included in the calculation of R^2 .

found to be between -0.62 and -0.27 V [47, 48], leading to a positive E_{cell}^o value of 0.46 to 0.81 V. This indicates the oxidation of U(IV) when substituted into these systems is also energetically favourable. We consider the behaviour of the later actinides later in the paper in section 3.6.3.

3.5. Substitution Energies

Substitution energies for single and double substitutions onto the Zr and Ca sites were calculated (Table 4) and strong correlations were found between them and the ratio of the Shannon radii of the substituent and substituted ions (Fig. 5). In order to compare across the series of tetravalent actinides, cerium and all ions which have been reduced or oxidised are not included in the calculation of R^2 . For all systems ($R^2 > 0.95$) and a decrease in substitution energy across the actinide series is seen. This is due to a reduction in the ionic radii of the substituted species which, in turn, causes less of a perturbation to other ions in the local environment upon substitution. A more than doubling of the substitution energies is seen when comparing singly with doubly substituted systems. This implies that if the level of substitution were to be increased further then the substitution energy would increase at a greater-than-linear rate, as the surrounding zirconolite structure is perturbed to a greater degree. Energies for substitutions onto Ca sites are substan-

tially larger (3-6 $\times$) than corresponding substitutions onto Zr sites. This is likely due to the additional substitution of Fe^{3+} ions onto Ti^{4+} sites required for charge balancing.

In comparison to previous computational research by Gilbert et al, the calculated value of the Pu_{Zr}^X defect energy is in good agreement at 5.98 eV vs 5.05. This is in contrast to our PEECM Ce_{Zr}^X substitution energy of 5.58 eV vs 9.02 eV as calculated by Gilbert. Ce^{4+} is often used as a non-radioactive surrogate for Pu^{4+} and this is supported by the similarities we see in our energetic data on isolvalent substitution, unlike Gilbert's findings. Furthermore, similar values for Ce_{Ca}^{X} and Pu_{Ca}^{X} have been calculated, 30.47 and 31.07 eV respectively. Again, this indicates a similarity between the energetics of plutonium and cerium substitution into the zirconolite lattice. These values are also in fairly good agreement with Gilbert et al's sums of the corresponding substitution energies of 27.47 eV and 30.45 eV for Ce and Pu respectively. This includes the defect energies of two Fe^{3+} substitutions onto two different Ti sites in the former case. This similarity between cerium and plutonium is highlighted in Figure 5, with the exception of Figure 5c as no Shannon radius data for an eight coordinate Pu^{3+} ion exist, and is corroborated by similar electronic behaviour shown *via* spin density in section 3.4.

M	Ce	Th	Pa	U	Np	Pu	Am
$(M_{Ca}^{2+} + 2 \times Al_{Ti}^{3+})$	3.12	3.67	1.77	3.18	3.71	1.63	2.68
$2 \times (M_{Ca}^{2+} + 2 \times Al_{Ti}^{3+})$	2.34	2.78	1.77	2.25	2.94	2.19	2.09

Table 6: $E_{LUMO} - E_{HOMO}$ for substitutions onto Ca^{2+} using Al^{3+} charge balancers.

M	Pa	U	Np	Pu	Am
$(M_{Ca}^{2+} + 2 \times Al_{Ti}^{3+})$ (C)	0.96	2.05	3.08	<u>5.05</u>	<u>6.11</u>
$2 \times (M_{Ca}^{2+} + 2 \times Al_{Ti}^{3+})$ (C)	1.02	2.07	3.09	4.16	<u>6.11</u>
$2 \times (M_{Ca}^{2+} + 2 \times Al_{Ti}^{3+})$ (D)	<u>0.02</u>	2.07	3.09	4.16	<u>6.04</u>

Table 7: Spin density values of substituted ions with Al^{3+} charge balancers. Values not indicative of a 4+ charge state are underlined.

3.6. Al^{3+} Charge Balancing

In order to examine the effect of using different charge balancers, single and double substitutions onto the Ca site have been performed using Al^{3+} as a charge balancer. Unlike Fe^{3+} , Al^{3+} is not redox active and hence its inclusion should allow for a better understanding of the redox behaviour of substituted An.

3.6.1. Geometric Changes

Similarly to the calculations discussed in section 3.2, the displacement of 17 ions from their original positions in the lattice were calculated following substitution of Ce or An. These results are summarised in Table 5. In contrast to systems which include Fe^{3+} for charge balancing, there is a larger number of ions exhibiting large displacements following substitutions of actinides or Ce and two Al^{3+} ions into the lattice. As both Al^{3+} (0.68 Å) and Fe^{3+} (0.69 Å) have similar ionic radii, this is not due to the relative sizes of the charge balancing ions. For substitutions of Ce, Th, Pa and U, the maximally displaced ion is mainly a Ti^{4+} while for Np it is an oxygen ion. Also, unlike the iron systems, the maximal displacement in doubly-substituted systems is smaller than in the singly-substituted systems, except for Pu and Am. The same Ti-site in which the Fe^{3+} ion is maximally displaced in the double Np_{Zr}^{2+} system (SI Fig. 1), is maximally displaced in these systems into the same void space within the cluster. This movement is not seen in the doubly-substituted systems, leading to lower mean displacements in these systems compared to the corresponding singly-substituted systems. Additionally, while no clear trend exists for the mean displacements across the substituted actinides, this value is significantly smaller for single substitutions of Pu and Am and the double substitution of Am into the lattice.

3.6.2. PDOS

Generally, the calculated values for $E_{LUMO} - E_{HOMO}$ (Table 6) are similar to those calculated for the Fe^{3+} charge balanced systems. No general trend can be seen for these values across the actinide series. The conduction band edge, typically made up of Ti d character, doesn't rise as sharply, implying this region of the PDOS (SI Figs. 5 and 6) is now made up of states from

both the substituted Al^{3+} and already present Ti^{4+} . Both single and double substitutions involving Ce^{4+} result in large peaks of f character around the conduction band edge. Similarly to other systems, a reduction in the energy of the f-states across the actinide series can be seen through observation of the PDOS.

3.6.3. Spin Density

Table 7 shows that the spin density data are very similar to the Fe^{3+} charge balanced systems. The electron from the second of the two Pa ions in Pa_{Ca}^{2+} is localised onto the Ti(1) site – similarly to $Pa_{Ca}^{2+} + 2 \times Fe_{Ti}^{3+}$ systems detailed in section 3.3. Electrons which localise on the reduced Pu and Am ions originate from several oxygen ions within the cluster in Fe^{3+} charge balanced systems. Use of Al^{3+} , which is not redox active helps elucidate the more complicated redox behaviour of corresponding systems using iron as a charge balancer. Indeed, use of a redox inactive charge balancer shows that, following single substitutions, Ce, Pu and Am all oxidise a specific oxygen highlighted as gold in Figure 6. Double substitutions of Am, in which both Am ions are reduced, oxidise two oxygens, the second of which is highlighted in black. This is supported by corresponding reduction and oxidation potentials for Ce/Pu/Am(IV)/(III) (1.7, 1 and 2.6 V respectively [46]) and O^{2-}/O^{-} (-1.5 V [49]) which correspond to a very positive values for E° (3.2, 2.5 and 4.1 V for Ce, Pu and Am respectively). As stated earlier, this implies these processes are energetically favourable (equation 3). These results are also supported by the geometric data in section 3.6.1, showing that disruption to the lattice is lessened for substitutions of Ce, Pu and Am. The larger ionic radii of trivalent Ce, Pu and Am are closer to that of the substituted Ca^{2+} radius (1.26 Å) and substitutions of ions of a similar size will result in less disruption to the lattice.

Figure 6: Zirconolite cluster with oxidised oxygen sites (gold, black) and substituted Ca sites (both navy) highlighted.

An(IV)/An(III)	An	Pa	U	Np	Pu	Am
Actinide Reduction	E_{Red}	-1.9	-0.52	0.15	1.00	2.60
Oxygen Oxidation	E_{Oxid}	-1.50	-1.50	-1.50	-1.50	-1.50
	E_{Cell}	-0.4	0.98	1.65	2.50	4.10
An(IV)/An(V)	An	Pa	U	Np	Pu	Am
Ti (IV) Reduction	E_{Red}	0.19	0.19	0.19	0.19	0.19
Actinide Oxidation	E_{Oxid}	-0.1	-0.62	-0.75	-1.1	-0.84
	E_{Cell}	0.29	0.81	0.94	1.29	1.03

Table 8: Reduction and oxidation potentials of An (Pa-Am) with corresponding O^{2-}/O^- and Ti^{4+}/Ti^{3+} reactions. Data shows the oxidation of Pa(IV) and concurrent reduction of Ti(IV) is more favourable than the reduction of Pa(IV) and concurrent oxidation of O^{2-} . The opposite is true for Am.

M	Ce	Th	Pa	U	Np	Pu	Am
$(M_{Ca}^{2+} + 2 \times Al_{Ti}^{3+})$	26.89	32.10	30.39	29.21	28.39	28.46	26.05
$2 \times (M_{Ca}^{2+} + 2 \times Al_{Ti}^{3+})$	54.16	65.05	60.61	58.91	57.37	55.27	52.26

Table 9: Substitution energies of single and double substitutions onto the Ca sites with Al^{3+} used for charge balancing. All values are in eV.

The redox data of the An(IV) ions (from Pa - Am) and concurrent reactions (reduction of Ti^{4+} and oxidation of O^{2-} for actinide oxidation and reduction respectively) are collated in Table 8. The overall behaviour, oxidation of early An (Pa) and reduction of later An (Am) can hence be explained as the result of two competing redox processes. Across the series, these processes both become more energetically favourable. The difference in E° between the oxidation and reduction processes for Pa is 0.69 V, while the difference between the reduction and oxidation processes for Am is 3.07 V. The reduction of later actinides is due to the reduction process becoming increasingly more favourable in comparison to oxidation.

3.6.4. Substitution Energies

Substitution energies for the single and double ($M_{Ca}^{2+} + 2 \times Al_{Ti}^{3+}$) systems were calculated and the values are presented in Table 9. The calculated energies are generally lower than the corresponding substitutions using Fe^{3+} as a charge balancer. The general trend across the actinides discussed earlier is also

present in these systems and is shown in Figure 7. Strong correlations are again seen between the substitution energy and the ratio of the Shannon radii of the substituent actinide and substituted Ca^{2+} . Am is an outlier for both systems as it is reduced. For the doubly-substituted systems, Ce and Pu exhibit similar energetic properties, in agreement with calculations discussed previously.

3.7. $M(OH)_n$ Calculations

To further understand the reduction of Ce and the later actinides (Pu, Am) following substitution onto Ca sites, calculations of small molecules $M(OH)_n$, where $n = 3 - 5$, and $M = Ce$ and $Th - Am$, were performed. Both symmetrised (D_{3h} , T_d and D_{3h} for $n = 3-5$ respectively) and non-symmetrised structures were optimised, the energy difference between the non-symmetrised and symmetrised structures are shown in Table 10. Symmetrised systems exhibited imaginary modes found through vibrational analysis resulting in non-symmetrised systems being more stable in all cases, and hence, the calcula-

Figure 7: Correlations between the substitution energy (E_{sub}) and the ratio of the Shannon radii of substituents and the substituted ion. a) $M_{Ca}^{2+} + 2 \times Al_{Ti}^{3+}$ substitutions ($R^2 = 0.973$), b) double $M_{Ca}^{2+} + 2 \times Al_{Ti}^{3+}$ substitutions ($R^2 = 0.993$). Pu is reduced in Fig. 7c) but no Shannon data exists for the eight-coordinate Pu^{3+} ion. Am is reduced in both Figures 7a and 7b). In order to compare across the series of tetravalent actinides, cerium and all ions which have been reduced or oxidised are not included in the calculation of R^2 .

M	Th	Pa	U	Np	Pu	Am	Ce
n = 3	0.00	-1.03	-0.73	-0.78	-1.61	-0.38	-1.61
n = 4	0.00	0.08	-2.05	-0.93	-2.68	-2.25	0.00
n = 5	-	0.00	-1.33	-0.57	-2.37	-2.17	-

Table 10: Energy difference (eV) between non-symmetrised and symmetrised $M(OH)_n$ molecules, negative values indicate that the non-symmetrised molecules are more stable.

Figure 8: Correlation ($R^2 = 0.980$) between $E_{(3\rightarrow4)}$ and the $3/4+$ redox potentials of the early actinides. In order to compare across the actinide series, cerium is not included in the calculation of R^2 .

tions described in this section are on the non-symmetrised systems. Closed shell calculations ($Th(OH)_4$, $Ce(OH)_4$, $Pa(OH)_5$) produced geometries close to the symmetrised structures.

3.7.1. Energetics of $M(OH)_n$

The energy gain following the formation of $An(OH)_{n+1}$ molecules from $An(OH)_n$ ($E_{(n\rightarrow n+1)}$) is calculated through equation 4,

$$E_{(n\rightarrow n+1)} = E_{(n+1)} - (E_n + E_{OH_{Neut}}) \quad (4)$$

where $E_{(n+1)}$ is the energy of the molecule with the additional $\cdot OH$ molecule, E_n is the energy of the ligand before addition and $E_{OH_{Neut}}$ is the energy of the neutral $\cdot OH$ molecule. The results for $n = 3/4$ and $n = 4/5$ are shown in Table 11. All values are negative, as M-O bonds are formed for each of these processes.

$E_{(3\rightarrow4)}$ exhibit strong correlation ($R^2 = 0.980$) with the $+3/4$ redox potentials of the corresponding actinides (Fig. 8). For later actinides it becomes increasingly unfavourable to form molecules containing An(IV) from the An(III) counterparts. This behaviour, that An(III) is more favourable later in the actinides, is in agreement with the results seen for the zirconolite calculations. $E_{(4\rightarrow5)}$ data provide a similar result with the lower oxidation state being more favoured for later actinides. The larger difference between the values of $E_{(4\rightarrow5)}$ for earlier actinides imply an increase in the stability of Pa(V) and U(V) compared to later actinides. This is also in agreement with results for zirconolite.

M	Th	Pa	U	Np	Pu	Am	Ce
$E_{(3\rightarrow4)}$	-5.68	-5.62	-5.08	-4.43	-3.87	-2.58	-3.50
$E_{(4\rightarrow5)}$	-	-4.47	-3.48	-2.55	-1.56	-1.38	-

Table 11: Energy gained (eV) following the formation of $An(OH)_{n+1}$ molecules from $An(OH)_n$

3.7.2. Spin Density of Molecular Calculations

The spin densities of the actinides in each $M(OH)_n$ system are collected in Table 12. These data indicate that the later actinides tend to exhibit increasing amounts of reduction, shown by the tendency for actinide spin density to increasingly deviate from an integer value. This is exemplified by the central Am in $Am(OH)_5$ which is much closer to being Am(IV) than Am(V) (spin density = 4.78). This corroborates previous computational research which also indicated a preference for reduction for Pu and Am compared to earlier actinides in AnO_2 systems [44, 50, 51]. The spin density of the surrounding oxygen atoms in all molecules decreases across the series (Table 13) highlighting the movement of electrons to the central actinide ion. The higher coordination of substituted Am on the Ca site within the PEECM cluster compared to these molecular systems could result in the preference for reduction of Am seen in both the small molecular and large cluster calculations (compared to earlier actinides) to be exacerbated.

An	Th	Pa	U	Np	Pu	Am	Ce
n = 3	1.05	2.10	3.15	4.17	5.19	6.20	1.04
n = 4	-	1.07	2.13	3.19	4.33	5.41	-
n = 5	-	-	1.16	2.32	3.45	4.78	-

Table 12: Spin density values for all M in the $M(OH)_n$ systems. All M except Am^{5+} exhibit the M(n) oxidation state.

An	Th	Pa	U	Np	Pu	Am
n = 3	-0.02	-0.03	-0.05	-0.06	-0.06	-0.07
n = 4	-	-0.02	-0.03	-0.05	-0.09	-0.10
n = 5	-	-	-0.03	-0.07	-0.09	-0.15

Table 13: Average spin density values of all oxygen ions in each molecule. Larger negative values indicate greater oxidation

4. Conclusion

In this study, DFT has been used in conjunction with the PEECM to model the single and double substitution of tetravalent actinides and Ce onto Zr and Ca sites within the zirconolite lattice. The effects on the local geometry, electronic structure,

and energetic properties were analysed along with a discussion of the redox behaviour of the substituted system. The effect of the choice of charge balancer was also explored, with Fe^{3+} and Al^{3+} substitutions onto Ti^{4+} sites modelled to balance alternative substitutions onto Ca^{2+} sites.

Analysis of the displacement of 17 innermost ions of the cluster from their original positions showed that the local geometry is not, in general, significantly perturbed following substitution into the lattice. Generally, no trend of the mean displacements of the system is seen for the single and double M_{Zr}^X systems across the actinide series. Substitution of Pa^{4+} results in oxidation to Pa^{5+} and the effect on the local geometry is less than for the substitution of U^{4+} which is not oxidised. This structural behaviour arises because the radius of Pa^{5+} is more similar to the radius of the substituted Zr^{4+} . Similarly, the reduction of Ce, Pu and Am when substituted onto Ca sites is indicated by lower than expected mean displacements compared to other substituents. This result is corroborated by molecular calculations performed at the same level of theory which indicated a preference for later actinides to be reduced.

For all types of system modelled, the increase in stability of the f-orbitals across the early actinides is seen within the PDOS. The additional substitutions of Fe^{3+} and Al^{3+} for charge balancing causes greater disruption to the electronic structure – especially to the conduction band, made up Ti d-orbitals in the unsubstituted system.

Strong correlations were found between the substitution energy of actinides into the zirconolite lattice and the Shannon radii of the substituents and substituted ions. Substituent An which showed redox character, Pa_{Zr}^X , $\text{Ce}_{\text{Ca}}^{\cdot\cdot}$, $\text{Pu}_{\text{Ca}}^{\cdot\cdot}$ and $\text{Am}_{\text{Ca}}^{\cdot\cdot}$, exist as outliers to this trend.

Ce^{4+} and Pu^{4+} behave similarly following substitution, both in terms of their redox and energetic changes. This implies that Ce^{4+} is an appropriate non-radioactive surrogate for Pu^{4+} in the context of experimental studies of waste immobilisation.

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6. Supplementary Information

The PDOS of all systems and a figure indicating geometric changes for the $\text{Np}_{\text{Ca}}^X + 2 \times \text{Fe}_{\text{Ti}}'$ structure.

7. Data Availability

The raw data required to reproduce these findings are available to download from <https://data.mendeley.com/datasets/kdn28v6rn8/1>
DOI: 10.17632/kdn28v6rn8.1.

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