

# An alternative structure of $\text{Pu}_4\text{O}_9$ (“ $\text{PuO}_{2.25}$ ”) incorporating interstitial hydroxyl rather than oxide

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## Abstract

Bond length/bond strength relationships are applied to the  $\text{Pu}_4\text{O}_9$  (“ $\text{PuO}_{2.25}$ ”) structure proposed by others and support one Pu(V) with a central hydroxyl ion but not a central oxide ion nor formation of Pu(VI). Bond distances and bond strengths are normal for a central ion of unit charge, and reconcile the finding that cell dimensions are so minimally changed from those of  $\text{PuO}_2$ . Substitution of hydroxyl for oxide accounts for the “excess” oxygen content of  $\text{PuO}_{2.265}$ , yielding  $\text{PuO}_2(\text{OH})_{0.249}$ . The short range, local order (structure) of the “ $\text{Pu}_4\text{O}_9$ ” entity is alternatively formulated as  $\text{Pu}_4\text{O}_8\text{OH}$ .

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## 1. Introduction

In a remarkable study Haschke et al. [1] established that, under conditions 50–350 °C, reaction of  $\text{PuO}_2$  with  $\text{H}_2\text{O}$  yielded *hydrogen gas and increased oxygen content in the solid*. The composition of the resulting fluorite-related solid phase was described as  $\text{PuO}_{2+x}$  with  $x=0.265$ . We rewrite their formula as  $\text{Pu}_4\text{O}_{8+4x}$  to indicate its derivation from  $\text{Pu}_4\text{O}_8$ , the unit cell of  $\text{PuO}_2$ . Although their oxygen content,  $x=0.265$  exceeds this value, at  $x=0.25$  they reach composition  $\text{Pu}_4\text{O}_9$ , a structure they propose contains a central oxide ion and hexavalent plutonium. This new material has cell dimensions scarcely increased over those of  $\text{PuO}_2$  (5.404 Å vs. 5.3975 Å) in spite of the placement of the extra oxide ion at body center, enclosed by the close-fitting subcell of eight oxide ions. The dominant X-ray scattering arises from plutonium, indicating that the plutonium lattice positions remain essentially unchanged.

Other authors have described [2,3] such plutonium compound(s) as hyper-stoichiometric  $\text{PuO}_{2+x}\cdot\text{H}_2\text{O}$

in which water or hydroxyls are necessary components based upon consideration of experimental characterization data including extensive XPS and EXAFS data sets.

Following the Haschke article, Petit et al. [4] published first-principle, theoretical studies of  $\text{Pu}_4\text{O}_9$ , a structure similarly fluorite based and containing a body-centered *oxide* ion. Contrary to Haschke’s conclusions, theirs favored two *pentavalent* plutonium constituents over a cell with one *hexavalent* plutonium.

The strength of the experimental work by Haschke et al., is in their demonstration that, under certain conditions, water can react with  $\text{PuO}_2$  to yield hydrogen and form a product containing oxygen in excess of stoichiometric  $\text{PuO}_2$ . Yet, we are forced to the conclusion that both the Haschke and Petit structures are significantly in error, specifically, in that they both depend on an oxide ion at body center.

The Pu–O relationships (described in the following) as applied to the structure of the oxygenated reaction product, “ $\text{Pu}_4\text{O}_9$ ” support the following outcomes:

1. A hydroxyl ion at body center.
2. Oxidation of a Pu(IV)–O to Pu(V)=O, at a bond distance of 1.9 Å.

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3. Explain the minimal cell size increase over that of  $\text{PuO}_2$ .
4. Substitution of hydroxyl for oxygen accounts for  $\text{PuO}_{2.265}$ , yielding  $\text{PuO}_2(\text{OH})_{0.249}$  and  $\text{Pu}_4\text{O}_8(\text{OH})_{0.996}$  for the cell.

Furthermore, data emerging in press and referenced briefly herein [2,3] suggest that the structure and speciation inherent in the hyper-stoichiometric  $\text{PuO}_{2+x}$  material needs to be seriously reconsidered.

### 1.1. Zachariasen bond length/bond strength formulations

Development of the body of actinide bond lengths has a long history including: Pauling's [5] definition of bond strength as ion valence divided by its coordination number; and Zachariasen's [6] derivation of the dependence of bond lengths on coordination number.

The interpretations in this paper utilize the 1978 Zachariasen bond length/bond strength formulations [7]. Based on data from well-established actinide structures, he formulated equations relating bond strengths to observed bond lengths. These equations largely supplanted the use of ionic radii sums, which did not account for the observed variation. Although little referenced in modern literature, these summary equations and accompanying tables encompass both oxygen and halogen compounds of the *d* and *f* elements [7].

Data for Pu(IV)–O, Pu(V)–O and Pu(VI)–O distances, important to this paper, are fit by the logarithmic equations:  $D(s) = D_1 - B \ln(s)$ ; where  $D(s)$  is the bond length at bond strength ( $s$ ) and  $D_1$  is the bond length at unit bond strength,  $s=1$ .

For plutonium–oxygen bonds,  $D_1$  values for Pu-III, IV, V and VI are: 2.142, 2.094, 2.08 and 2.06 Å, respectively [7]. For Pu–O bond strengths of unity or less,  $B=0.35$  is constant. However, the multiplier “ $B$ ” increases as  $0.35 + 0.12(s - 1)$  for bond strengths greater than unity, notably in structures containing the actinide (V) and (VI) dioxy cations,  $\text{MO}_2^+$  and  $\text{MO}_2^{2+}$ .

For Pu(III)–F bonds the values for  $B$  and  $D_1$  are 0.40 and 1.992, respectively. These values are necessary for the demonstration example provided in the next section.

For plutonium and oxygen constituents of a structure, the sum of bond strengths to their neighbors is equal to their respective valences (usually to within 5%). Zachariasen noted that the sesquioxides display larger deviations, possibly a result of super structure or disorder; the C-type having two kinds of metal ions, and the A-type two kinds of oxygen ions [8]. In 1980 (his last paper) he summarized experience in part, as, “The remarkable fact is that the equation,  $D(s) = D_1 - B \ln(s)$ , normally predicts the bond length to 0.02 Å when  $s$  is known” [9].

Fig. 1 displays a plot of the function  $D(s) = D_1 - B \ln(s)$  for Pu–O bonds for the Pu(V) valence state (note:

when only bond lengths are provided, the LOG form having both  $B$  and  $s$  as variables makes it inconvenient to estimate ( $s$ ) values between 1 and 2. However, the function is essentially linear for  $s$  values between 1 and 2 and is fit by the equation,  $Ds = -0.3243(s) + 2.402$ , (max deviation = 0.003 Å) relating  $D(s)$  and ( $s$ ) and over this range. Curves for all the oxidation states are similar, their bond distance values being displaced from a Pu(V value) at a given bond strength by the difference in their  $D_1$  values; namely, 0.014 Å longer for Pu(IV) and 0.02 Å shorter for Pu(VI) than for Pu(V).

### 1.2. Application of Zachariasen's formulas

The utility of the approach is presented briefly in two examples where the Zachariasen relationships unequivocally predict correct structural changes in selected Pu compounds containing coordinated oxygen atoms.

#### 1.2.1. The location of the light atoms, oxygen and fluorine, in PuOF [10]

Zachariasen found that he had erred when he earlier utilized ionic radii to assign the positions of the light atoms O and F in trivalent plutonium oxyfluoride. In PuOF each plutonium atom is coordinated by two sets of four anions, at 2.569 and 2.385 Å. Since the ionic radius of  $\text{O}^{2-}$  is greater than that of  $\text{F}^{1-}$ , the longer distance was originally assigned to Pu–O. He later interchanged the oxide and fluoride positions based on the following arguments [8]:

- (i) The (–2) oxide charge, shared by 4 Pu (III)'s yields Pu–O bond strengths,  $s=0.5$ , and dictates assignment of the shorter bond distance to oxygen.
- (ii) The (–1) fluoride charge, shared equally by 4 Pu(III)'s, yields Pu–F bond strengths,  $s=0.25$ , and thus the longer Pu–F bond distance.
- (iii) Comparison of the bond strength sums makes the interchange clearly preferable.

Original selection: Pu–4O, 2.569 Å;  $s=0.2952$ ; Pu–4F, 2.385 Å;  $s=0.3745$ .

Old Bond strength sum: Pu = 2.68; O = 1.18; F = 1.50.

Interchanged positions: Pu–4O, 2.385 Å,  $s=0.4997$ ; Pu–4F = 2.569 Å,  $s=0.2363$ .

New Bond strength sum: Pu = 2.94 Å; O = 2.00; and F = 0.95.

#### 1.2.2. Prediction of the correct structure for BaPuO<sub>3</sub>

The structure was originally assigned as perovskite-type, with the 2.18 Å Pu–O bonds aligned along the cell edges. Application of Zachariasen's formulas in 1983, predicted an increased Pu–O bond distance of 2.236 Å, necessitating rotation of the  $\text{PuO}_6$  octahedra off the cell edges. A definitive 1988 neutron study confirmed both predictions [11].

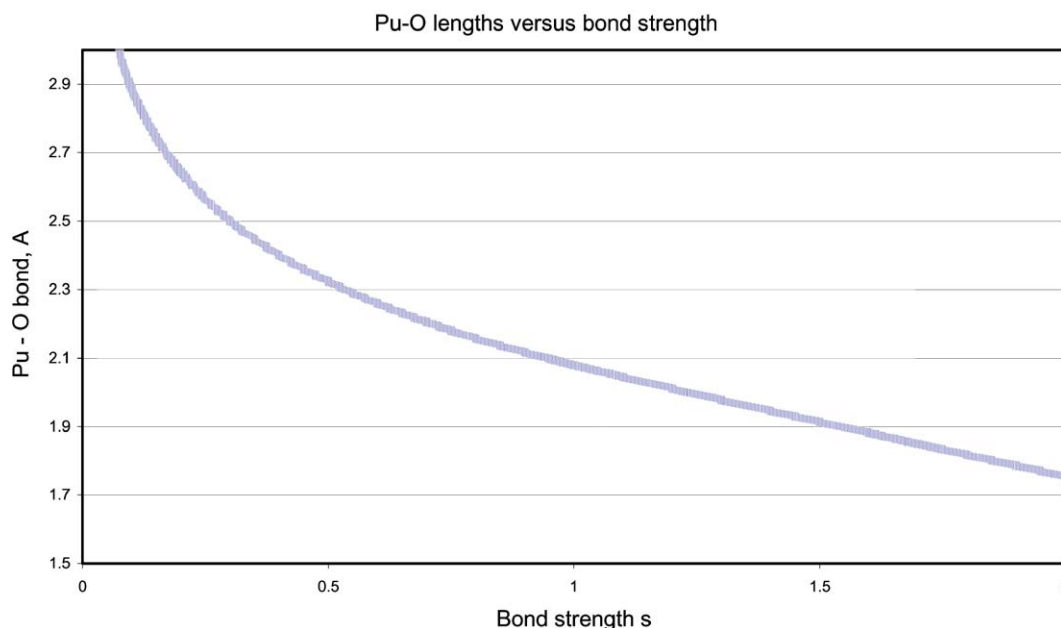


Fig. 1. Zachariasen formula bond length plotted versus bond strength using equation described in text for Pu(V)–O bonds.

Both Pu(V)=O and Pu(VI)=O dioxo bond lengths are increased by coordination. It is customary to formally denote the actinide  $MO_2^+$  and  $MO_2^{2+}$  cations as double bonded. At bond strength  $s=2$ , the Pu(V)=O bond distance is very short, 1.75 Å and that of Pu(VI)=O 1.73 Å. Bond distances this short occur rarely. Usually, bonding to other ions in the structure reduces the M=O bond strength and lengthens the multiple bond, providing a range of *longer distances*. We retain the double bond formality, but recognize that its strength is more often less than 2. Pertinent to the introduction of a Pu(V)=O component in the structure of  $Pu_4O_9$ , the  $M(V)=O$  distances in  $KPuO_2CO_3$  are estimated as 1.84 Å, increasing to 1.87 Å, after allowing for weak bonds to potassium ions [12].<sup>2</sup> When not specifically determined,  $s$  values and corresponding bond distances can be estimated for  $MO_2^+$  and  $MO_2^{2+}$  ions after calculating  $s$  values from distances provided for groups coordinated to them in the equatorial band, and subtracting their sum from the  $M$  valence. Bond strengths, thus determined by difference, are subject to a 5% error that is transferred to bond distance uncertainty. In the just cited case, 5% of  $V$ , yields an error in  $s$  of 0.25. From the slope of the equation fitting  $s$  values between 1 and 2, this suggests an error of 0.08 Å in the 1.87 Å derived distance.

In summary, these examples demonstrate the use of Zachariasen's relationships and the utility of discriminating between plausible ligated species. The PuOF

example is particularly germane because of the crystal chemical similarities between the F and OH ligands.

### 1.3. Application to $Pu_4O_9$ ( $PuO_{2.25}$ ) and the body centered oxide ion

The value for the cell edge of cubic  $PuO_{2+x}$  of highest oxygen content [1], is 5.404 Å yielding a body diagonal of 9.36 Å. The added oxygen is placed at the body center [1,4], midway along the diagonal at 4.68 Å. The Pu(IV)–O distance along this diagonal is 2.33 Å at  $s=0.5$ . However, increasing the valence to Pu(V) yields  $s=1.5$  and the smaller value of 1.91 Å for the Pu(V)=O bond distance. Allowing  $2 \times 1.4$  Å for the Van Der Waal (VDW) radii sum of the two oxygens, center and the O–Pu(V), and adding the Pu(V)–O distance of 1.9 Å, yields  $2.8 + 1.9 = 4.7$  Å which agrees well with experimental value of 4.68 Å for half the body diagonal.

Conversion of a corner Pu(IV) to Pu(V) has the following effects: Increasing  $s=0.5$  to 1.5 for the Pu(V)=O bond on the diagonal, leaves unchanged its seven other Pu–O oxygen bonds at  $s=0.5$  for a bond sum of  $3.5 + 1.5 = 5$ . This has the strong implication that the cell dimensions will show little size change from those of  $PuO_2$  itself. Withdrawal of the oxygen 0.42 Å along the body diagonal from its tetrahedral site lengthens somewhat the Pu(IV)–O bonds on the threefold axis. This may account for the direction and magnitude of the +0.007 Å change in cell dimensions (5.3975–5.404 Å). Oxygen volume assignment in compounds containing Pu(V) is  $18 \text{ Å}^3$ , and is applicable for oxide, hydroxyl, and water [12] (see footnote 2). Using

<sup>2</sup>For the preceding paper, which established  $KPuO_2CO_3$  see Ref. [13].

$18 \text{ \AA}^3$  for the nine oxygen atoms per unit cell provides a volume for  $\text{Pu}_4\text{O}_9$  of  $162 \text{ \AA}^3$  vs.  $158 \text{ \AA}^3$  observed.

However, a surprising result arises with the bond strength sum around the central oxide. Octahedral coordination at the body center by the 6 face-centered plutonium (IV) ions occurs at distances of half the cell edge, or  $2.702 \text{ \AA}$ . This Pu–O bond distance corresponds to  $s=0.176$ , and an oxygen valence sum of 1.06, compared to a Pu(IV)–O distance of  $2.72 \text{ \AA}$  calculated for  $s=\frac{1}{6}$ . (Note: the bond strength sum normally agrees to within 0.1 valence units and the bond length to  $0.02 \text{ \AA}$  when  $s$  is known.) This further substantiates a central ion of *unit charge*, and the strong possibility of a central hydroxyl ion instead of an oxide ion. A central oxide ion requires  $s=\frac{2}{6}$ , and a much shorter bond distance of  $2.48 \text{ \AA}$  (not observed). An oxide ion centered in the cubic array of eight oxygen ions would likely expand the lattice by repulsion. Hydrogen bonding by the hydroxyl ion, as well as its lower charge, would attenuate repulsion. Haschke<sup>1</sup> reported  $\text{PuO}_{2.265}$  as the “oxide” content of the solid without discussing that it exceeded the  $\text{O}=2.25$  limit imposed by  $\text{Pu}_4\text{O}_9$ . Further supporting our proposal for  $\text{Pu}_4\text{O}_8\text{OH}$ , their value of 0.265 for the “oxygen” excess over  $\text{PuO}_2$  is obtained directly as a result of substituting hydroxyl for an oxygen in  $\text{Pu}_4\text{O}_9$  (that is  $17/16 \times 0.25 = 0.2656$ ).

## 2. Other structures

Although a central hydroxyl ion can account for the bulk of the increased oxygen uptake, additional structures are needed to account for spectroscopic observations. In a definitive study of  $\text{PuO}_2$  samples exposed to both water vapor and oxygen, Begg et al. [3], fit the reduced EXAFS data for  $\text{PuO}_{2+x}$  and independently proposed a Pu(V)=O presence but the fit required five to eight Pu–O distances ranging from 1.8 to  $3.6 \text{ \AA}$  for the nearest neighbor Pu–oxygen distances.

## 3. Summary and conclusions

The short range, local order (structure) of the “ $\text{Pu}_4\text{O}_9$ ” entity is better described as  $\text{Pu}_4\text{O}_8\text{OH}$ .

Bond strength/bond length arguments justify the location of a hydroxide ion in a  $\text{PuO}_2$  structure rather than a central oxide, providing an alternative interpretation for the experimental data on plutonium dioxide oxidation by water. A central oxide is rejected on the basis of its bond sum. Similarly rejected is increasing the valence to Pu(VI) on the basis of the sum about such a Pu(VI)=O moiety. The bond strength sum around the Pu(V)=O moiety is normal, and support

minimal cell dimension change. In contrast, Pu(VI)=O at  $s=2.0$  requires that the seven remaining Pu(IV)–O bonds increase from  $s=0.5$  to 0.571, that is ( $7 \times 0.571 + 2.0 = 6$ ), resulting in cell dimensions not present for a Pu(V)=O moiety. Zachariasen’s bond strength/bond length relationships are based upon a multitude of actinide structures that support this contention.

There may be some displacement of the hydroxyl off body center, slightly relieving its distance from the remaining seven interior oxygen atoms. However, formation of a peroxy group as observed in uranium (VI) structures is ruled out by bond strength arguments. This alternative view of the structure with a hydroxide is more consistent with XPS [2] and EXAFS [3] data.

The bond strength/bond length arguments considered together with the XPS and EXAFS spectroscopic observations do call for more work to unequivocally determine the short and long range structural changes manifested when  $\text{PuO}_2$  is corroded by water. It would be particularly useful to perform neutron diffraction studies to augment the interpretation provided by these other techniques.

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