

Chapter 3

Solution of Fission Products in UO_2

“As things stand, I find it very difficult to assume such a degree of ‘bursting,’ but we’ve had so many surprises in nuclear physics that one can’t very well say it’s impossible.”

Lise Meitner

Letter to Otto Hahn, Dec. 21 1938

3.1 Introduction

UO_2 is the standard nuclear fuel used in modern, conventional power reactors (e.g. PWR, BWR and AGR). The oxide phase of fissile uranium provides the necessary thermodynamic stability required in operating conditions. It then follows that an extensive knowledge of the properties of this material is necessary. Unfortunately, experimental research is costly, especially if fission products are considered. Therefore, computer simulation is a desirable alternative. In this chapter, an attempt is

made to clarify the situation of the existing, but conflicting sets of data concerning the solution of defects corresponding to fission products.

3.2 Previous Work

3.2.1 The Chemical State of Fission Products

As mentioned previously in Chapter 1, fission products will vary chemically and physically, such that absolute yield is not the only important consideration. Several attempts have been made to classify fission products into categories based on their chemistry [37, 140], see Figure 3.1. The chemical state of fission products is important in that the chemical state influences the physical properties of the fuel, e.g. thermal conductivity, swelling, melting point, etc. [37].

												III _B	IV _B	V _B	VI _B	VII _B	
I _A	II _A											B	C	N	O	F	Ne
Li	Be											Al	Si	P	S	Cl	Ar
Na	Mg	III _A	IV _A	V _A	VI _A	VII _A		VIII		IB	II _B	Ga	Ge	As	Se	Br	Kr
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	In	Sn	Sb	Te	I	Xe
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	Tl	Pb	Bi	Po	At	Rn
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Fr	Ra	Ac			
Fr	Ra	Ac															

Figure 3.1: The chemical state of fission products, where orange denotes volatile fission products, grey denotes metallic precipitates, blue denotes oxide precipitates and green indicates products in solid solution. Elements labelled with more than one colour denote the possibility of an alternate chemical state, with the preferential chemical state denoted by the top colour.

The noble gases Kr and Xe are insoluble in UO₂ and migrate to grain boundaries [141], dislocations or pre-existing pores [142, 143] where they aggregate into bubbles which lead to fuel swelling. Fuel swelling is a performance limiting factor and therefore, understanding the behaviour of Kr and Xe is imperative to improving fuel performance. Several studies have focused on the determination of the position of Kr and Xe within the UO₂ lattice and this will be discussed further in Section 3.3. The other volatile fission products, the halogens Br and I, are not considered in this work (and in fact have a much lower yield than Kr or Xe). However, other studies have concentrated on the determination of their behaviour in UO₂. Iodine, for example, has been found to diffuse two orders of magnitude faster than Xe [144], and therefore tends to be released in the fuel clad gap. Unlike the noble gases kryp-

ton and xenon, bromine and iodine are chemically reactive with other species in this gap [145]. In fact, it has been suggested that iodine may react with the zircalloy fuel cladding material thus leading to stress related cracking [146]. Until this issue has been settled, reactor design must account for non-appreciable concentrations of iodine in the fuel cladding gap.

A number of other fission products precipitate out of solution in the form of a complex oxide, which is referred to as the “grey phase.” The composition of grey phase precipitates will vary with fuel composition and reactor history, though the main constituents include Ba, Zr and U, see Figure 3.1. The most commonly reported precipitates are perovskites of the type $[\text{Ba}_{1-x-y}\text{Sr}_x\text{Cs}_y](\text{U}, \text{Pu}, \text{Ln}, \text{Zr}, \text{Mo})\text{O}_3$ which are essentially substituted BaZrO_3 [147].

The fission products found in solid solution include Sr, Y, Nb and the lanthanide ions. The extent of Sr solubility is dependent on the metal to oxygen ratio. For example, the solubility of Sr is over ten times higher in UO_2 than $\text{UO}_{1.94}$ [37]. It has also been suggested that Sr is more soluble than its chemical relative Ba [148]. It is then likely that Sr will remain in the fuel while Ba will precipitate in the grey phase. It has also been observed that chemical relatives Ce and Zr exhibit different solubilities, where Ce is more soluble than Zr [149]. Concentrations of CeO_2 in excess of what is the result of fission (at usual burnups) have shown complete solubility in a range of UO_2 non-stoichiometries down to room temperature. ZrO_2 is only soluble above 1350°C.

The remaining quarter of fission products will precipitate out of solution in the form of metallic inclusions. These precipitates are known as the “white phase,” and are comprised mainly of 4d transition metals Mo, Tc, Ru, Rh and Pd [37].

3.2.2 Calculation of Fission Product Solution Energy

Motivated by the fundamental diversity of uranium dioxide and subsequently its technological importance, great interest has been placed upon this material. To reiterate, experimental studies on this material are very difficult indeed, given the extreme conditions of greatest technological importance. UO₂ thus lends itself to reliable theoretical studies. Early studies on defects in UO₂ [150] demonstrated the viability of pair potential calculations, deriving suitable parameters and calculating a range of defect energies which were in accord with the experimental data of the time.

These early studies prompted the development of more refined studies. Later studies calculated with increased accuracy: defect formation, clustering, migration and solution energies [151–153]. Initial fission product studies were confined to the volatile fission products Xe and Kr [154–158], which determined the solution sites of these fission products as a function of stoichiometry.

Of particular relevance to this work is that of Grimes and Catlow [36], whose paper on the stability of fission products provides a review of the experimentally demonstrated behaviour of fission products and proceeds to discuss the development of a theoretical model which incorporates all of the constituents required to simulate the properties of fission products in UO₂ at thermodynamic equilibrium. The calculations of that study were carried out at the atomistic level, employing the methodology described in Chapter 2. The work considered the solution of fission products at existing trap sites. With the eventuality of fission products outnumbering existing trap sites, the energy to form trap sites was included. In order to facilitate this, trap site equilibria for Frenkel and Schottky intrinsic defects had to be calculated. From these calculations, Grimes and Catlow were able to predict equilibrium solution sites for many fission products at different stoichiometries.

It was found that the equilibrium solution site is stoichiometry dependent. For example, the low energy solution site for Xe in hypo-stoichiometric UO_{2-x} and stoichiometric UO₂ was the neutral tri-vacancy. However, for hyper-stoichiometric UO_{2+x}, the lowest energy site was the uranium vacancy. Similar behaviours were observed for other fission products. The calculated low energy solution sites for Xe, Cs and Rb were all substantiated by experiment [159], but there exists no other experiment with which to compare the remaining data.

The solution of oxides was also considered using this model (e.g. Cs₂O, BaO, La₂O₃ and ZrO₂). A significant aspect of this model is that it is able to predict the differences in the variation of solubility with stoichiometry exhibited by fission product compounds. There is certainly room to expound the behaviour of the components of fission product precipitates with changing fuel history.

There have also been recent *ab initio* UO₂ point defect studies [160–162]. These studies employ the local-density approximation and apply it to density-functional theory. The defect energies are calculated using a linear muffin-tin orbital supercell method. In this supercell method, a characteristic region is defined and then repeated periodically. Due to the complexity of these calculations, the supercells are rather small, for example 12 and 24 atoms in the work of Petit *et al.* [161]. A limitation of this type of calculation is that the atoms surrounding the defect are not permitted to relax on account of the defect.

In regard to formation energies of oxygen and uranium vacancies, interstitials and Frenkel pairs as well as Schottky trio defects, the *ab initio* results are in good agreement with the aforementioned classical studies. However, those authors contest that there are discrepancies with the classical studies when confronting the issue of the location of Kr atoms [160]. This was due to a misunderstanding of the definitions of solution and incorporation energy as defined by Grimes and Catlow [36]. Once

corrected, the *ab initio* and classical results agree remarkably well. The discrepancy and its origin are discussed in detail in Section 3.3 and have been previously published in a letter by Stanek *et al.* [163].

3.3 Location of Krypton Atoms in UO_2

In a recent paper, Petit *et al.* [160] discussed their results concerning an *ab initio* study of the location of krypton in UO_2 . The results from this study were compared to similar studies, which employed different techniques, namely experimental [142,164] (Rutherford backscattering) and theoretical (energy minimization based on pair potentials) [36]. The paper concludes that their result (of the neutral tri-vacancy trap site providing the lowest solution energy for Kr) is in agreement with experiment, but in contradiction with previous theoretical studies. Petit *et al.* suggest that the “crude approximation made in semi-empirical (pair potential) schemes can explain some of the discrepancies with the results obtained in the present study.” It is our understanding that it is not the approximations inherent to pair potentials, but rather a misinterpretation of terms which has led to the discrepancy and in fact the two sets of results agree remarkably well.

3.3.1 Discussion

In the previous work by Grimes and Catlow [36], two definitions were given for the energy associated with placing fission products in the UO_2 lattice. The first was the incorporation energy (i.e. the energy to place a fission product at a pre-existing trap site). The energies of two atomic configurations must be calculated: the empty trap site and the fission product at the trap site. Then, the incorporation energy is given by:

$$\text{incorporation energy} = \text{energy of fission product in trap site} - \text{energy of empty trap site}$$

Inherent in this definition is the assumption that there are more trap sites than fission products. Given the large defect energy of trap sites (defined as the calculated energy to remove the appropriate ions from the lattice to infinity), this is unlikely to be the case. Therefore, a second definition was made, the solution energy. This assumes that for the fission product to be accommodated in the lattice, the energy to form the trap site in equilibrium with the majority Frenkel intrinsic defects must be accounted for. The solution energy is then:

$$\text{solution energy} = \text{incorporation energy} - \text{equilibrium trap formation energy}$$

Of course the equilibrium trap formation energy is a strong function of stoichiometry. The energies for equilibrium trap formation are given in Tables 3.1 and 3.2, where Table 3.1 denotes how each energy is calculated and Table 3.2 provides the corresponding values [36].

Trap Site	UO _{2-x}	UO ₂	UO _{2+x}
oxygen vacancy	nil	$\frac{1}{2}E_F$	E_F
uranium vacancy	E_S	$E_S - E_F$	$E_S - 2E_F$
di-vacancy	$E_S - B_{DV}$	$E_S - \frac{1}{2}E_F - B_{DV}$	$E_S - E_F - B_{DV}$
neutral tri-vacancy	$E_S - B_{NTV}$	$E_S - B_{NTV}$	$E_S - B_{NTV}$
charged tetra-vacancy	$2E_S - B_{CTV}$	$2E_S - E_F - B_{NTV}$	$2E_S - E_F - B_{NTV}$

Table 3.1: The effective energy to form a trap site, where E_S is the Schottky trio formation energy = 13.34eV; E_F is the Frenkel pair formation energy = 6.82eV; B_{DV} is the binding energy of a di-vacancy = 3.24eV; B_{NTV} is the binding energy of a neutral tri-vacancy = 4.93eV; B_{CTV} is the binding energy of a charged tetra-vacancy = 8.89eV. Reproduced from [36].

We are now in a position to understand the confusion. Petit *et al.* [160] calculated incorporation energies which were then erroneously compared to the solution energies of Grimes and Catlow [36]. Petit *et al.* [160] found the discrepancy puzzling since the agreement between the two sets of calculations is correct for simple point defects (interstitial, oxygen and uranium vacancies) but very poor for more complex structures (divacancy and neutral tri-vacancy). This discrepancy can easily be explained. The trap site formation energy for simple point defects is either negligible or zero, whereas for more complex defect structures there is a more substantial trap site formation energy, see Table 3.2. For example, there is a 5eV disparity between the trap site formation energies of an oxygen vacancy and a neutral tri-vacancy in stoichiometric UO₂.

Trap Site	UO _{2-x}	UO ₂	UO _{2+x}
oxygen vacancy	0.0	3.41	6.82
uranium vacancy	13.34	6.51	-0.31
di-vacancy	10.09	6.68	3.27
neutral tri-vacancy	8.41	8.41	8.41
charged tetra-vacancy	17.78	10.96	4.13

Table 3.2: Calculated values for trap site formation energies in eV, according to Table 3.1, reproduced from [36].

To rectify the discrepancy, the pair potential trap site formation energies of Grimes and Catlow [36] are added to the *ab initio* incorporation energies of Petit *et al.* [160], resulting in hybrid *ab initio*/pair potential values, see Table 3.3. Unfortunately, there is insufficient past data from which to formulate *ab initio* trap site formation energies [161, 165, 166].

Krypton location	Grimes (pair potential)			Petit (hybrid <i>ab initio</i> /pair potential)		
	UO_{2-x}	UO_2	UO_{2+x}	UO_{2-x}	UO_2	UO_{2+x}
interstitial	13.3	13.3	13.3	14.2	14.2	14.2
oxygen vacancy	9.9	13.3	16.8	8.0	11.4	14.8
uranium vacancy	17.2	10.3	3.5	16.3	9.5	2.7
di-vacancy	12.5	9.0	5.7	12.5	9.0	5.7
neutral tri-vacancy	9.5	9.5	9.5	9.8	9.8	9.8
charged tetra-vacancy	19.1	12.3	5.5	-	-	-

Table 3.3: Comparison of calculated solution energies of a krypton atom in uranium dioxide

3.3.2 Conclusion

When corrected for trap site formation energy, the hybrid *ab initio* results agree remarkably well with the pair potential results, especially for those complex defect structures which provide the most stable solution sites. However, what should also be noted from these studies is the predicted preference for Kr solution at di-vacancies in stoichiometric UO₂. Furthermore, that these two studies agree does not invalidate the agreement with experiment. The experimental work was conducted on Xe, which is a considerably larger atom than Kr and consequently, solution is expected at the larger neutral tri-vacancy trap, despite the chemical similarity of Kr and Xe. Of course, a hybrid *ab initio*/pair potential calculation is not entirely satisfactory. Therefore, it would be beneficial to calculate the equilibrium solution site energies *ab initio*. It is accepted that good quality *ab initio* simulations are inherently more reliable than pair potential calculations. However, in the event of a more complete comparison between the techniques, attention should also be paid to the difference between large unit cell simulations [160] and isolated defect cluster calculations that relate to the infinite dilute limit.