

## **Chemical activity of noble gases Kr and Xe and its impact on fission gas accumulation in the irradiated UO<sub>2</sub> fuel.**

**Marcin Szuta**

Institute of Atomic Energy, Otwock-Świerk 05-400, Poland,  
E-mail: mszuta@cyf.gov.pl

### **Abstract**

It is generally accepted that most of the insoluble inert gas atoms *Xe* and *Kr* produced during fissioning are retained in the fuel irradiated at a temperature lower than the threshold.

Experimental data imply that we can assume that after irradiation exposure in excess of  $10^{18}$  fissions/cm<sup>3</sup> the single gas atom diffusion can be disregarded in description of fission gas behaviour.

It is assumed that the vicinity of the fission fragment trajectory is the place of intensive irradiation induced chemical interaction of the fission gas products with UO<sub>2</sub>.

Significant part of fission gas product is thus expected to be chemically bound in the matrix of UO<sub>2</sub>.

From the moment of discovering the rare gases (helium, neon, argon, krypton, xenon and radon) at the end of XIX century until to the beginning of sixties years of XX century it was considered that the noble gases are chemically inactive.

The nobility of rare gases started to deteriorate after when the first xenon compound was found by Barlett in 1962. Barlett showed that the noble gases are capable of forming what one could consider as normal chemical compounds, compelling chemists to readjust considerably their thinking regarding these elements.

In a burst of activity in the years that followed, a number of compounds of noble gases have been reported.

Experiments with mixture of noble gases, coupled with theoretical calculations, provide strong evidence for direct bonds between Ar, Kr, or Xe atoms and the U atom of the CUO molecule.

Because of its positive charge, the UO<sub>2</sub><sup>2+</sup> ion, which is isoelectronic with CUO, should form even stronger bonds with noble gas atoms, which could lead to a growing number of complexes that contain direct noble gas – to –actinide bonds.

Considering the huge amount of gas immobilised in the UO<sub>2</sub> fuel the solution process and in consequence the re-solution process of rare gases is to be replaced by the chemical bonding process. This explains the fission gas accumulation in the irradiated UO<sub>2</sub> fuel.

## 1. Introduction

It is generally accepted that most of the insoluble inert gas atoms  $Xe$  and  $Kr$  produced during fissioning are retained in the fuel irradiated at a temperature lower than the threshold [1-11]. Some authors [1-7] assume random diffusion of gas atoms to grain boundaries and consider the effect of trapping the atoms at inter-granular bubbles until saturation occurs. Others [12-13] confirmed that bubbles tend to concentrate in the grain boundaries during irradiation. Likewise, some authors [8-11] further assume that most of the gas atoms are retained in solution in the matrix of grains being there immobilised or are precipitated into small fission gas bubbles.

In a very early publication (1964) in Journal of Nuclear Materials MacEwan and Stevens [8] in the work "Xenon Diffusion in  $UO_2$  (some complicating factors)" have proved experimentally that an appreciable fraction ( $F$ ) of the fission xenon was immobilised after irradiation exposure in excess of  $10^{15}$  fissions/cm<sup>3</sup>. In fig. 1 are plotted the fractions,  $F$ , of trapped xenon in the specimens for both the sintered and single-crystal specimens. A tolerable fit to each set of results was obtained with an exponential law expression,  $A[1-\exp(-\alpha n)]$ , where  $n$  was the number of fission events/cm<sup>3</sup> and  $A$  and  $\alpha$  are constants.

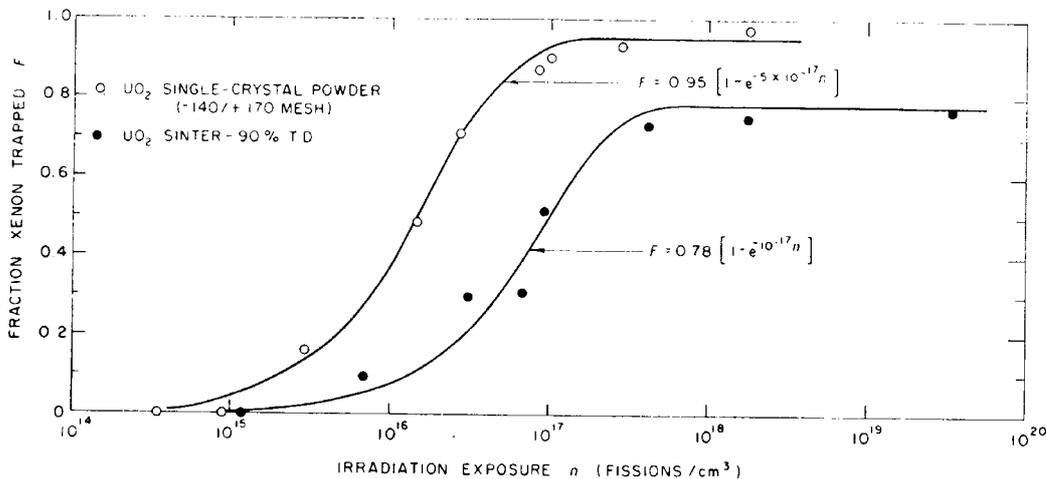


Fig.1. A plot showing how the fraction of the fission xenon trapped after annealing for a short period at 1400 °C varies as a function of the prior irradiation exposure [8].

It is clearly seen from the fig. 1 that after irradiation exposure in excess of  $10^{18}$  fissions/cm<sup>3</sup> both for the single crystal specimen and the sintered  $UO_2$  significant portion of xenon is immobilised namely 95 % and 78 % respectively.

MacEwan and Stevens underlined that if it were assumed that all xenon was free to migrate, the diffusion coefficient for xenon decreased by a factor of 1000 for the single crystal  $UO_2$  and by a factor of 20 for the sintered  $UO_2$ .

Several years later in 1972 Samsonov and Fray [14] have carried out an in-pile investigation from 1 to 400 MWD/t(U). They observed releases of 3 isotopes of xenon and obtained different decreases for the apparent diffusion coefficient: by a factor of 5 to 6 powers of ten for  $Xe^{133}$ , 2 to 4 powers for  $Xe^{135}$  and 1 to 3 powers for  $Xe^{138}$ . They also observed saturation after about irradiation exposure in excess of  $10^{18}$  fissions/cm<sup>3</sup>. This is illustrated below in fig. 2.

A remarkable fact is that the values of apparent diffusion coefficients of  $Xe^{133}$ ,  $Xe^{135}$  and  $Xe^{138}$  after irradiation beside that the coefficients decreased but also its order is in reverse.



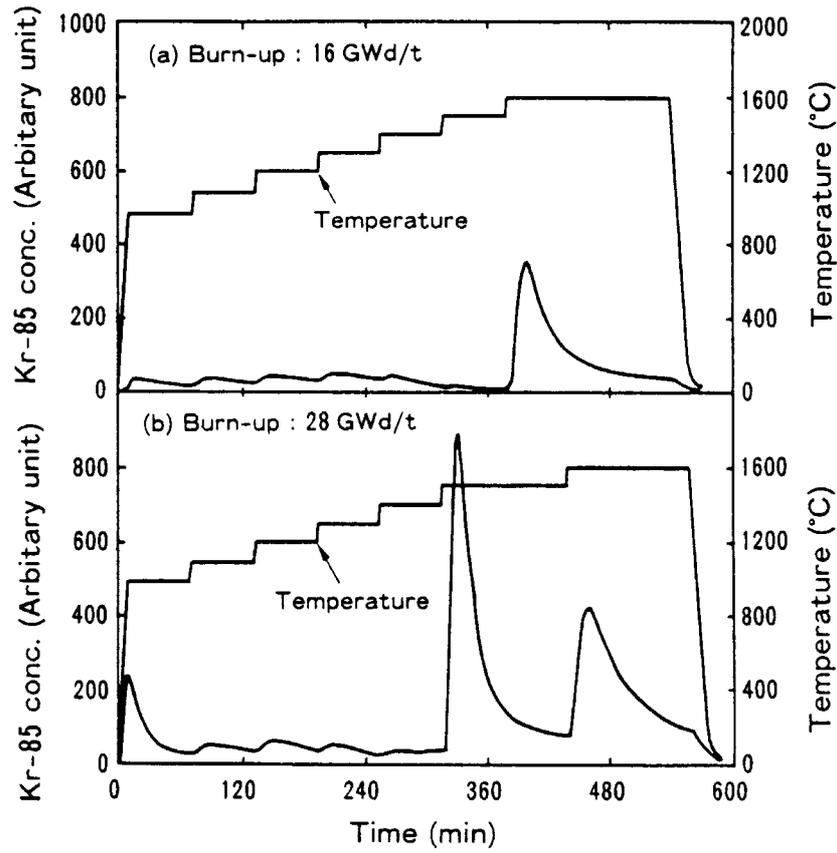


Fig. 3.  $\text{Kr}^{85}$  release on stepwise temperature ramp [12].

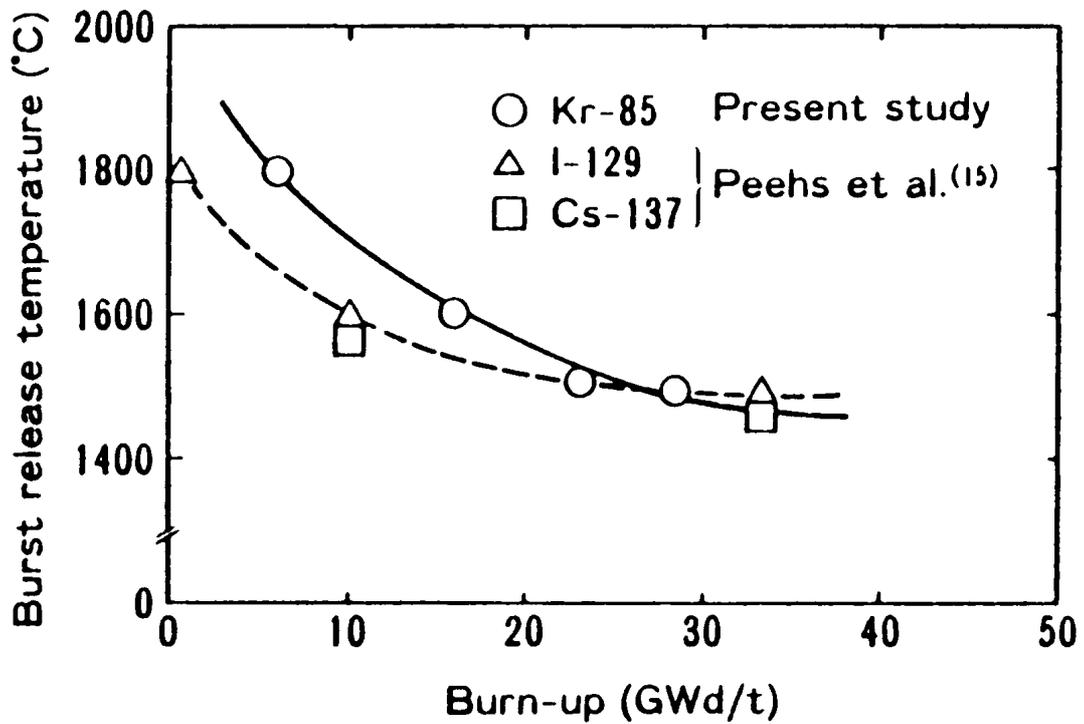


Fig. 4. Burn-up dependence of critical temperature for onset of burst release [12].

The critical temperature for the onset of the high temperature burst release is plotted against fuel burn-up in Fig. 4. The diagram indicated that the bursts release temperature becomes lower with increasing burn-up.

The same tendency has been reported by Vitanza et al. [15], who measured the fuel centreline temperature of instrumented fuel rods in the Halden Reactor. The fractional fission gas release of the rods was above 1%. This burn-up dependence of burst release temperature is attributable to the increases of fission gas inventory in the grain boundaries and the density of the grain boundary bubbles at higher burn-ups. The Vitanza's curve is shown in Fig. 5.

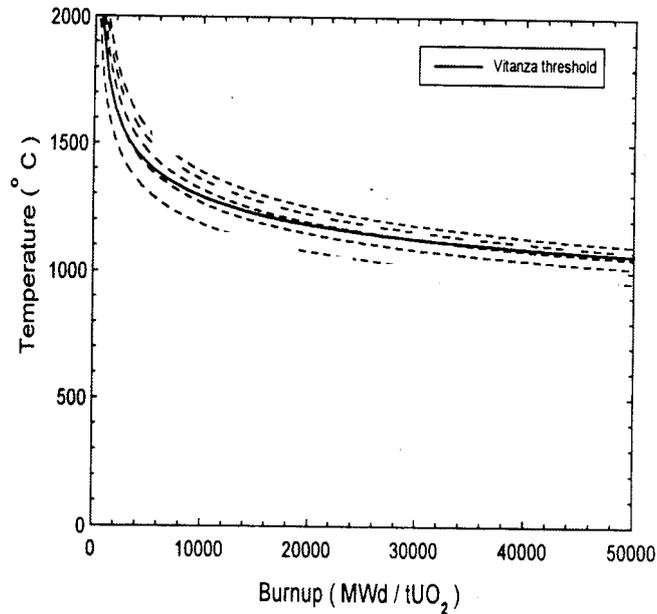


Fig. 5 Incubation time (burn-up) as a function of the centre temperature [15].

The critical temperature for high temperature burst release is about 1800 °C for low burn-up ( about 7 MWd/kgU ) and decreases to about 1500 °C for high burn-up ( 30 MWd/kgU ).

The point defects induced by radiation begin to recover at 450 – 650 °C and are completely almost recovered above 850 °C, while defect clusters of dislocations and small intragranular bubbles require 1150 – 1450 °C [16].

Thermal recovery of radiation defects and microstructure change in irradiated UO<sub>2</sub> fuels studied by X – ray diffraction and transmission electron microscopy lead to the conclusion that the gas release kinetics from irradiated UO<sub>2</sub> is determined by the kinetics of thermal recovery of the radiation induced defects.

If the point defects, defect clusters of dislocations and small intra-granular bubbles are thermally recovered at the temperatures below 1450 °C, a natural question concerns nature of forces which immobilise the noble gases. Hence an additional trapping process of inert gas atoms with the uranium dioxide material is suspected to occur.

The process of strong binding of the fission gas fragments with the irradiation defects is described in the literature as a process of chemical interaction with UO<sub>2</sub>[17]. It is important to remind here the MacInnes and Winter's remark [17] that the crucial assumption concerning the fuel for long time was that the fission gases and volatile fission products, principally Xe and Cs, have no effect on the chemical state of the fuel. This seems reasonable if these fission products have been released from the fuel, but its validity must be called into question if a fraction is distributed within the grains as single atoms. Since these atoms tend to precipitate from the fuel, they will interact with the thermally-generated point defects in the UO<sub>2</sub> lattice.

It is assumed further that the vicinity of the fission fragment trajectory is the place of intensive irradiation induced chemical interaction of the fission gas products with UO<sub>2</sub> [3].

We can further assume that above a limiting value of fission fluency (burn-up) a more intensive process of irradiation induced chemical interaction occurs. Significant part of fission gas product is thus expected to be chemically bound in the matrix of UO<sub>2</sub>.

## 2. Chemical activity of noble gases

From the moment of discovering the rare gases (helium, neon, argon, krypton, xenon and radon) at the end of XIX century until to the beginning of sixties years of XX century it was considered that the noble gases are chemically inactive.

The nobility of rare gases started to deteriorate after the first xenon compound was found by Barlett in 1962 [18]. Barlett showed that the noble gases are capable of forming what one could consider as normal chemical compounds, compelling chemists to readjust considerably their thinking regarding these elements.

### 2.1. The general noble gases characteristic.

The ability of the noble gases to combine with other atoms is relatively limited because their closed-shell electronic structures are extremely stable. This ability would be expected to increase with decreasing ionisation energy and decreasing energy promotion to states with unpaired electrons. This is clearly seen in the Table 1 [19-20] presenting the basic chemical and physical properties of the noble gases. Except the helium, which has the outer shell configuration 1s<sup>2</sup>, the other elements of the periodic group have the outer shell configuration s<sup>2</sup>p<sup>6</sup>. The helium group gases do not form stable positive ions because of high ionisation energy. The noble gases show negative electron affinity and that is why they do not form anions. In the standard conditions the noble gases occur in the atomic form since they do not attach and do not give up the electrons and because of that they do not show trend to form chemical bonds.

Table 1. Chemical and physical properties of the noble gases [19-20]

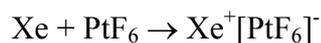
Element	Outer shell configuration	First ionisation energy [eV]	Second ionisation energy [eV]	Promotion energy np <sup>6</sup> →np <sup>5</sup> (n+1)s <sup>1</sup> [eV]	Electron affinity [eV]	Boiling point [°C]	% by volume in the atmosphere
<sup>2</sup> He	1s <sup>2</sup>	24.59	54.42	19.8	0.077	-268.9	5.2·10 <sup>-4</sup>
<sup>10</sup> Ne	2s <sup>2</sup> 2p <sup>6</sup>	21.56	40.96	16.6	-0.40	-246.0	1.8·10 <sup>-3</sup>
<sup>18</sup> Ar	3s <sup>2</sup> 3p <sup>6</sup>	15.76	27.63	11.5	-0.36	-185.9	0.93
<sup>36</sup> Kr	4s <sup>2</sup> 4p <sup>6</sup>	14.00	24.36	9.9	-0.40	-153.2	1.1·10 <sup>-3</sup>
<sup>54</sup> Xe	5s <sup>2</sup> 5p <sup>6</sup>	12.13	20.98	8.3	-0.42	-108.1	8.7·10 <sup>-6</sup>
<sup>86</sup> Rn	6s <sup>2</sup> 6p <sup>6</sup>	10.75	18.00	6.8	–	-62.0	vestigial

It is known that the noble gases can be trapped in clathrates. In the clathrates, atoms of noble gases are trapped in the lattice of the host substance. There are no chemical bonds between the gas atoms and the surrounding atoms in the usual sense, but instead, only weak Van der Waal forces. The element therefore escapes when the host crystal melts or dissolves [19-21].

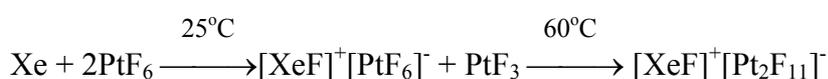
The rare gases form one of the most abundant classes of constituents of our Universe. The beautiful octet rule led scientists to accept the nonreactivity of rare gases until 1933, when Linus Pauling suggested [22] from considerations of ionic radii of different elements

that molecules like XeF<sub>6</sub> and KrF<sub>6</sub> and perhaps unstable compounds XeF<sub>8</sub> and H<sub>4</sub>XeO<sub>6</sub> should be preparable. However, attempts to synthesise rare-gas –containing molecules were not successful at that time [23].

It took about 30 years until the first rare-gas-containing chemical compound was found. After the observation that O<sub>2</sub> reacts with PtF<sub>6</sub> to give the compound [O<sub>2</sub><sup>+</sup>][PtF<sub>6</sub><sup>-</sup>], Neil Barlet [18] recognised that since the first ionisation energy of Xe (Xe→Xe<sup>+</sup> 12.3 eV≡1169kJ/mol) is almost identical with that of molecule O<sub>2</sub> (O<sub>2</sub>→O<sub>2</sub><sup>+</sup> 1177 kJ/mole), an analogous reaction should occur with Xe. He obtained a red solid by reaction of Xe with PtF<sub>6</sub> in the room temperature:



Present knowledge indicates that the reaction is more complicated and that the xenon oxidation sequence is following [19]:



The key idea for this discovery was the similar ionisation potentials of O<sub>2</sub> and Xe.

## 2.2. Examples of rare gas compounds

In a burst of activity in the years that followed after the discovery of the first halogen compound, a number of compounds of noble gases have been reported, especially with xenon. It is observed, that the rare gases make reaction with the most electronegative elements, such as fluorine and oxygen. Later it has been shown that Xe (sometimes Kr) form bonds also with other non-metals, and even with some metals.

While many of these can be regarded as metastable species, several are actually thermodynamically stable compounds and can be obtained commercially. Very shortly after the discovery of rare compounds, specialists made considerable contributions to the understanding of their chemistry [24].

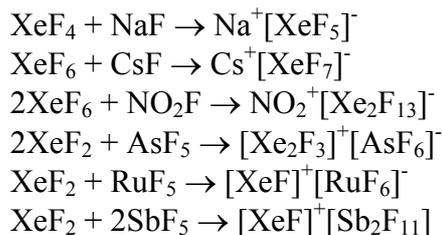
Xenon reacts directly only with F<sub>2</sub>, but compounds in oxidation states from II to VIII are known, some of which are exceedingly stable and can be obtained in large quantities. The more important compounds and some of their properties are given in Table 2.

Table 2. Principle xenon compounds [19]

Oxidation state	Compound	Form	Mp [°C]	Structure	Remarks
II	XeF <sub>2</sub>	Colorless crystals	129	Linear	Very soluble
IV	XeF <sub>4</sub>	Colorless crystals	117	Square	Stable
VI	XeF <sub>6</sub>	Colorless crystals	49.6	Complex	Stable
	CsXeF <sub>7</sub>	Colorless solid			
	Cs <sub>2</sub> XeF <sub>8</sub>	Yellow solid			Stable to 400 °C
	XeOF <sub>4</sub>	Colorless liquid	-46	Octahedral	Stable
	XeO <sub>2</sub> F <sub>2</sub>	Colorless crystals	31		Metastable
	XeO <sub>3</sub>	Colorless crystals			Explosive, stable in solution
VII	XeO <sub>4</sub>	Colorless gas	-35.9	Tetrahedral	Highly explosive
	XeO <sub>3</sub> F <sub>2</sub>	Colorless gas	-54.1		

When xenon and fluorine are mixed together, only a small amount of energy by heating up the mixture is needed to initiate the formation of fluorides. According to the amount of reagents there can be formed three different products:  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  [19,20,25]. Formation of bonds in these three fluorides can be explained by the theory of covalent bonds [20]. It is worth to underline that xenon difluoride obtained commercially has found a relatively widespread use as a fluorinating agent and has useful applications in semiconductor processing for etching silicon.

The three fluorides  $\text{XeF}_2$ ,  $\text{XeF}_4$  and  $\text{XeF}_6$  can be used to form anionic species in reactions such as [19].



A group of rare-gas molecules, krypton and xenon hydrides  $\text{HRgY}$ , where Rg is a rare gas and Y is an electronegative fragment, have been identified in low-temperatures matrices [26]. The first observed  $\text{HRgY}$  compounds were triatomic  $\text{HXeY}$  ( $Y = \text{H}, \text{Cl}, \text{Br}, \text{I}$ ) and  $\text{HKrCl}$  molecules [27, 28].

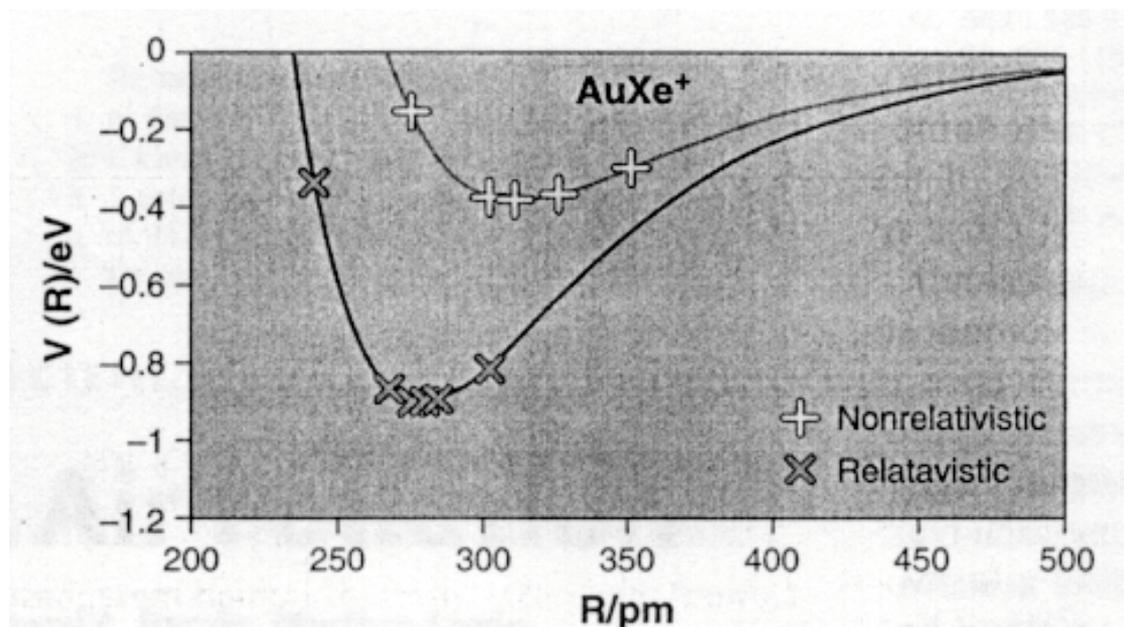


Fig. 6. The role of relativity. In the atomic  $\text{AuXe}^+$ , roughly half of the Au-Xe bond strength arises from relativistic effects.  $V$ , bonding energy;  $R$ , interatomic distance (Copied from [33]).

Another complex compounds were obtained as  $\text{HXeNCO}$  [26],  $\text{HXeNC}$  [26],  $\text{HKrCN}$  [29],  $\text{HXeSH}$  [30],  $\text{HXeOH}$  [31] and  $\text{HXeNCO}$  [32].

Pyykko[33] recalls, that Seidel and Seppelt [34] take noble gas bonds a step further, reporting a bulk compound held together by covalent bonds between gold and xenon. If gold were a truly noble metal and xenon a truly noble gas, such an Au-Xe bond would be impossible. In actual fact, noble metals such as platinum and gold have a rich chemistry. It

has been theoretically predicted [35] that  $\text{XeAuXe}^+$ , which has the same number of valence electrons in similar molecular orbitals as the  $\text{ClAuCl}^-$  anion, should possess short, strong covalent bonds between xenon and gold. The lighter rare gases were predicted to form similar, but more weakly bound systems. The simpler diatomic species, such as  $\text{AuXe}^+$ , were also predicted. The authors [34] characterised  $[\text{AuXe}_4]^{2+}$  ion, in which the Xe atoms act as electron donors to the electron-deficient  $\text{Au}^{2+}$  ion.

Two of the predicted species,  $\text{AuXe}^+$ , and  $\text{XeAuXe}^+$ , have been observed experimentally by mass spectroscopy [36].

Relativity plays a large role in stabilising these Au-Xe compounds; about half of the Au-Xe bonding energy comes from relativistic effects (see Fig. 6). The high nuclear charge of gold accelerates the 6s valence electrons to high speeds when they dive near the nucleus. In a simple picture, the consequent relativistic mass increase compresses and stabilises the valence 6s shell. This relativistic stabilisation of the 6s shell makes covalent bonds to gold anomalously strong and short [33].

There is very interesting report on bonding between noble gas atoms and an actinide metal atom uranium. The developments began with the observation that the  $\text{CUO}$  molecule, which has been trapped in noble gas matrices, exhibits notably different spectroscopic behaviour in the presence of Ar, Kr, or Xe than in matrices of pure Ne [37].

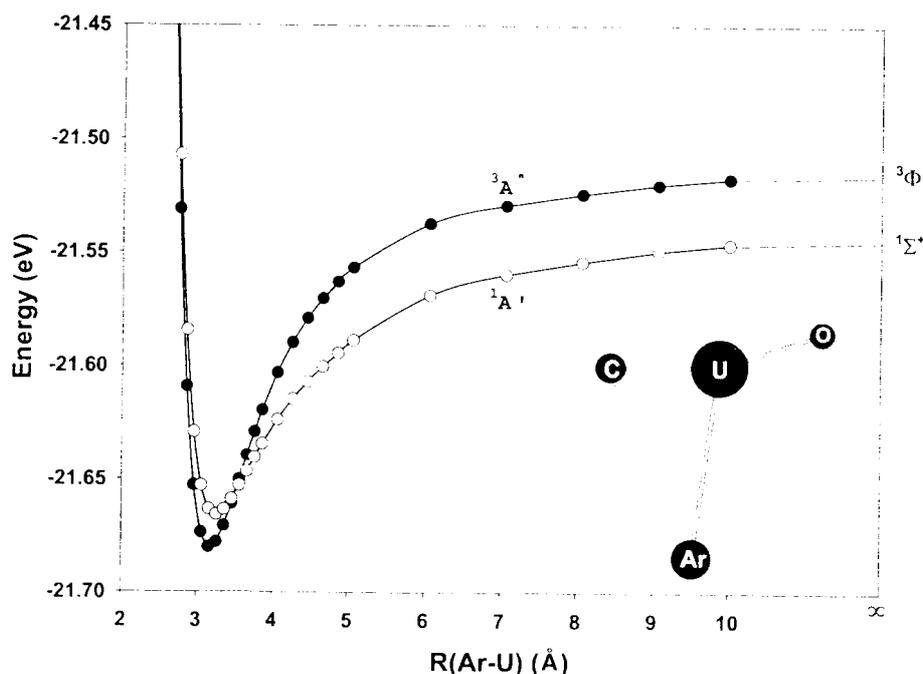


Fig. 7. Potential energy curves for the  $^1\text{A}'$  and  $^3\text{A}''$  states of  $\text{CUO}\cdot\text{Ar}$  as a function of the U-Ar distance. The inset figure lower right shows the optimised structure of the  $^3\text{A}''$  state of  $\text{CUO}\cdot\text{Ar}$ . The U-Ar bond length in this complex is 316 pm. (copied from [37])

Experiments with mixture of noble gases using the infrared spectroscopy (IR), coupled with theoretical calculations, provide strong evidence for direct bonds between Ar, Kr, or Xe atoms and the U atom of the  $\text{CUO}$  molecule [37].

Calculations on  $\text{CUO}\cdot\text{Ar}$  were carried out with the  $\text{CUO}$  molecule in its  $^1\Sigma^+$  ( $^1\text{A}'$ ) ground state and its low-lying  $^3\Phi$  ( $^3\text{A}''$ ) excited state, where the Greek state designations are for the linear geometry of  $\text{CUO}$ , whereas the designations in parentheses are appropriate for the  $\text{CUO}\cdot\text{Ar}$  molecule. It is found that  $\text{CUO}\cdot\text{Ar}$  is a planar molecule with a  $^3\text{A}''$  ground state in which a bent  $\text{CUO}$  fragment is bound to the Ar atom primarily through the U atom (see Fig.

7). The Ar atom interacts most significantly with the U and C atoms. Figure 7 shows a slice through the calculated potential energy surfaces of the  $^3A''$  ground state and  $^1A'$  excited state of CUO·Ar as a function of the U-Ar distance. Orbital analysis of the calculations on  $^3A''$  and  $^1A'$  CUO·Ar indicates that, the Ar atom serves as a base that donates electron density into an empty U 6d orbital [37].

The density functional theory (DFT) calculations predict that the interaction of a Kr or Xe atom with CUO is stronger than that of an Ar atom. The stabilisation of the  $^3A''$  ground state of CUO·Kr and CUO·Xe are 1.1 and 3.6 kcal/mol greater than that in CUO·Ar, respectively. The calculated U-Kr and U-Xe distances, 324 and 330 pm, respectively, are shorter than the sums of the crystal radii (341 and 358 pm, respectively) [37].

To explore the notion of multiple CUO·Ar<sub>x</sub> species further, it was calculated the structures of CUO·Ar<sub>x</sub> (x=2 to 6) complexes. The theoretical results provide strong support for the binding of multiple Ar atoms to a single CUO molecule. The binding of two or more Ar atoms continues to favour the triplet form of CUO [37].

The authors believe that the experimental and the theoretical data presented in their report [37] make a strong case for the interactions between the U atom of CUO and the noble gas (Ng) atoms. The U-Ng bond distances are short, and the U-Ng interaction is strong enough to change the spin state of the CUO molecules. Because of the positive charge, the UO<sub>2</sub><sup>2+</sup> ion, which is isoelectronic with CUO, should form even stronger bonds with noble gas atoms, which could lead to growing number of complexes, that contain direct noble gas – to – actinide bonds.

### 3. Discussion

The examples of rare gas compounds presented above show that noble gas chemistry is much richer than it would be expected. New chemical bonds between strange bedfellows, like noble metals, actinides and noble gases, can still be found.

Since the examples of rare gas compounds presented above are formed by applying the classical chemical methods, the more the noble gas species in the conditions of neutron and fission fragments irradiation of the UO<sub>2</sub> fuel type can be expected.

This assumption is suggested by the fact that the ClXeCl has been found to form after irradiation with 501.7 nm laser light of Cl<sub>2</sub>-doped xenon matrices. It appears that after excitation of the Cl<sub>2</sub> there is little or no barrier for the rearrangement to ClXeCl [38].

The fission fragments are stripped of about 20 electrons along most of their paths in the medium in which the fission takes place. The high positive charge of the fragments was estimated by Bohr (1940, 1941) [39-40]. He assumed that the equilibrium is reached, e.g. that the probabilities for electron capture or loss by the ion are equal when the ionic velocity and the velocity of the electrons within the ion is the same. Lamb (1940) [41] considered the electrons within the decelerating medium as practically free and assumed that the kinetic energy of these electrons relative to the ion is, at equilibrium, equal to the ionisation energy of the outermost electrons within the ion.

Knipp and Teller (1941) [4] and Ozeroff (1949) [42] computed the fission particle charge states. The equilibrium charge states in various solids of several ions were measured in the energy range 10 – 100 MeV by Leischner (1966) [43]. Measurements on <sup>79</sup>Br and <sup>127</sup>I by Moak et al., (1968) [44] are of particular interest here, since these two ions may be considered as typical fission fragments. Their most probable charge states are plotted versus ion energy in Figs 8 and 9. We see that charges of the two groups of fission fragments are about 22 at the beginning of their paths and decrease slowly, and are still 10 at 10 MeV, e.g. near the end of their paths.

Fission fragments are at the same time very energetic and highly charged particles; they interact strongly with electrons of the material losing their energy mainly by ionisation but also by elastic collisions with atoms as a whole [45].

The kinetic energy of the two fragments is about 160 MeV. . But the energy  $\nu$  that each fission event delivers directly to the lattice of the irradiated material via atomic collisions does not exceed 10 MeV [45]. The energy given directly to the lattice, via atomic collisions, is  $5,4 \pm 1.5$  MeV for the median heavy fragment, and only  $3.3 \pm 1.5$  MeV for the median light fragment. It is therefore assumed that each fission event dissipates roughly 10 MeV (from 5 to 15 MeV) through atomic collisions in fissile materials [46].

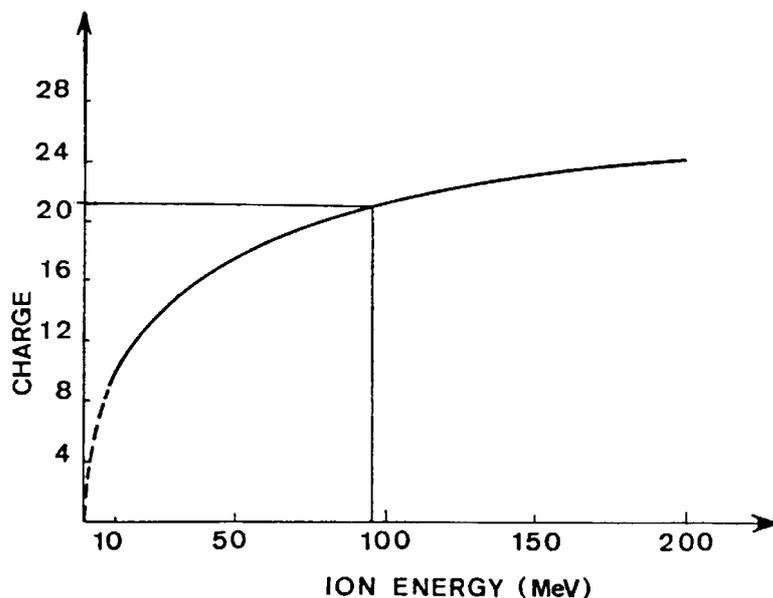


Fig. 8. Most probable charge state for  $^{79}\text{Br}$  ions in solids versus ion energy [44].

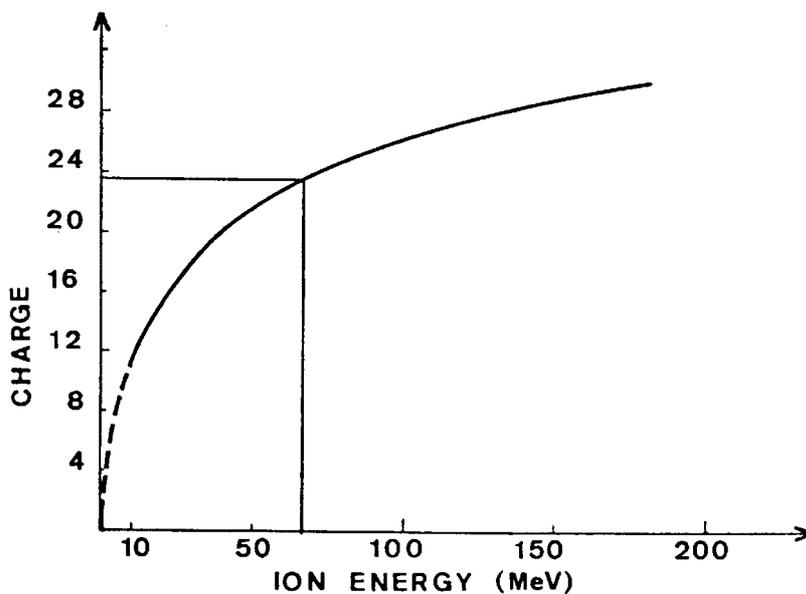


Fig. 9. Most probable charge state for  $^{127}\text{I}$  ions in solids versus ion energy [44].

95 % of the initial fission fragment energy is finally lost through ionisation processes, e.g. to electrons with the huge rate of 5 to 10 MeV energy loss per atomic distance. Whatever the

material, this energy is ultimately converted into heat, but there is an important difference in behaviour between a metal and an insulator.

In an insulator (e.g.  $\text{UO}_2$ ), energy lost by ionisation can only diffuse through the slow and weak electron-phonon and phonon-phonon interactions. Weak because electrons diffuse by phonons lose only a small amount of energy in each collision. Slow because the relaxation times of electron-phonon and especially phonon-phonon collisions are slow. Therefore ionisation may induce very large thermal effects in insulators (thermal spike) [46].

It is interesting to know the maximum number of Frenkel pairs created by one fission event. The number of Frenkel pairs created is directly connected to the energy given to the lattice by each fission event. Its approximate value is  $N = v/(2E_d)$ , where  $E_d$  is the displacement threshold energy,  $v$  is indeed the energy actually given to the lattice. This means that  $v$  is not the sum of all primary energies but the sum of all primary energies minus the fraction of these energies lost by ionisation.

But of course, some of these defects created are immediately annealed, even if the irradiated lattice is completely frozen. This anneal, very difficult to estimate, is due to recombination of opposite defects, either athermally by overlapping of damaged regions or by spontaneous recombination of very close Frenkel pairs, or thermally in thermal spikes.

A commonly accepted value of  $E_d$  is 25 eV. So the maximum number of Frenkel pairs created by one fission event is then 200 000 [45].

In  $\text{UO}_2$  dislocations are observed very soon after the beginning of the irradiation. Dislocation loops about 25 Å in diameter and with density of  $10^{16} \text{ cm}^{-3}$  are seen for a dose of  $4.3 \times 10^{15}$  fissions/ $\text{cm}^3$ . After  $6 \times 10^{16}$  fissions/ $\text{cm}^3$ , the average diameter is 100 Å. When the dose increases, the loop density in  $\text{UO}_2$  becomes saturated at about  $2 \times 10^{16}$  fissions/ $\text{cm}^3$  but the average loop size increases.

Whapham and Sheldon in 1965 described the nature of point defect clusters in  $\text{UO}_2$  [47]. They concluded that vacancy clusters are observed only after  $10^{20}$  fissions/ $\text{cm}^3$  while the clusters observed after  $4.3 \times 10^{15}$  or  $3.7 \times 10^{17}$  fissions/ $\text{cm}^3$  are interstitial dislocation loops.

As a conclusion, displacement cascades in fissile materials are characterised by the generation of a very high point defects concentration, immediately followed by an intense thermal spike.

Keeping in mind that the  $\text{UO}_2$  fuel is highly defected, ionised with very energetic and highly charged fission fragments, it appears that during irradiation there is little or no barrier for the formation of rare gas atoms compounds with the  $\text{UO}_2$  molecule and fission products. There would be a strong interaction between the U atom of  $\text{UO}_2$ , fission products and the noble gas (Ng) atoms. This further implies that significant part of the fission fragments after dissipating all their energy and stopping in the material being still highly ionised at the end of their paths react chemically with the fuel.

Fission products are frequently divided into four general categories: noble gases, volatile elements, semi-volatiles, and non-volatiles. About 300 different fission products exist in a nuclear reactor core. The rare gases Xenon (*Xe*) and to a lesser extent Krypton (*Kr*), are two of the more abundant fission products. About 15% of fission products are rare gases; *Xe* (90%) and *Kr* (10%).

It is worth to be noted that the inert gases Kr and Xe are practically not formed directly by fission, but originate by  $\beta$ -decays from the precursors.  $\text{Se}^{85}$ ,  $\text{Se}^{87}$ ,  $\text{Br}^{88}$ , and  $\text{Br}^{89}$  are precursors for the krypton and  $\text{Sn}^{131}$ ,  $\text{Sn}^{132}$ ,  $\text{Sb}^{133}$ ,  $\text{Sb}^{134}$ ,  $\text{Te}^{135}$ ,  $\text{I}^{137}$ ,  $\text{I}^{138}$  and  $\text{I}^{139}$  are the precursors for the xenon. That is why the prompt fission yield for the  $\text{Kr}^{85\text{m}}$ ,  $\text{Kr}^{87}$ ,  $\text{Kr}^{88}$ ,  $\text{Kr}^{89}$  and for the  $\text{Xe}^{131}$ ,  $\text{Xe}^{133}$ ,  $\text{Xe}^{135}$ ,  $\text{Xe}^{137}$ ,  $\text{Xe}^{138}$ ,  $\text{Xe}^{139}$  are equal zero [48-52].

This that the inert gases Kr and Xe mostly are not formed directly by fission, but originate from the precursors imply, that the precursors which are not gas atoms can easier chemically react with the  $\text{UO}_2$  fuel than the rare gas atoms. We can assume that the precursor already chemically bond with the fuel decaying to the rare gas atom do not change the electron shell of the compound and remain chemically bonded. It means that the rare gas atoms are chemically bound with the  $\text{UO}_2$  fuel after decaying of the precursors which chemically reacted with the fuel.

It has been known for over a century that in the presence of an electric discharge or electron beam gas atoms become embedded into the electrodes and the walls of the vessel containing the gas [53]. It was this observation which suggested to workers at the AECL Laboratories at Chalk River that a similar phenomena may operate on the fission gases within fuel pins during irradiation. This they proved by irradiating UO<sub>2</sub> pellets in the presence of natural xenon. After irradiation they mass analysed the gas and took drilled cores from selected positions in the pellets and they found that indeed some of the natural xenon had been sorbed into the surface of the fuel [54]. Whilst the gases embedded by electrical discharge were only lightly attached to solid surfaces and could easily be released by slight heating, the xenon was found to be very firmly attached to the UO<sub>2</sub> surfaces such that only 1% of the attached gas could be removed after annealing samples for 12 hours at 1400 °C. This was the first of many experiments, which showed that the mechanism and kinetics of the phenomenon were complicated.

Uranium dioxide irradiated to a burn-up greater than about  $3.2 \times 10^{19}$  fissions/cm<sup>3</sup> between 800 and 1600 °C is always found to contain a high concentration of matrix fission-gas bubbles [55]. The bubble nucleation density is virtually independent of both temperature and dose rate at about  $10^{17}$  bubbles/cm<sup>3</sup> [56-57]. Whapham and Sheldon [58] suggest, on the grounds of repeated low temperature irradiation of UO<sub>2</sub> fuel with intermediate annealing, that the gas trapped in the bubbles may be knocked back into the matrix as a result of the action of fission fragments. This effect we assume to enhance the chemical bonding process as the gas atoms from the bubbles become ionised by the fission fragments.

The phenomenon observed in the above quoted work [56-57] allows to conclude that the rate of the chemical bonding process is markedly higher than the fission gas trapping rate in the bubbles.

Keeping in mind that the gas release kinetics from irradiated UO<sub>2</sub> is determined by the kinetics of thermal recovery of the radiation induced defects and associating it with the idea of the noble gas atoms trapped in clathrates (where no chemical bonds between gas atoms and the surrounding occur), we can postulate that in point defects, dislocation loops and gas bubbles the rare gas atoms with the closed-shell electronic structure can be immobilised. In this sense, there exists no true diffusion for the fission gas in the UO<sub>2</sub> fuel.

It appears necessary in this discussion to recall the conclusion of the panel discussion of the International Seminar on Fission Gas Behaviour in Water Reactor Fuels, held in Cadarache, France 26-29 September 2000. Namely “The notion of diffusion coefficient of the fission gas atoms should be verified and if we resign from the term *re-resolution* then what we should assume instead”.

It is very important to recall also that solubility of rare gas atoms in uranium alloys or ceramics is so low that it has not been measured. In perfect crystals, the order of magnitude of the solubility is  $10^{-10}$  in the most favourable cases. This figure may be increased up to  $\approx 10^{-5}$  in the vicinity of dislocations. So, considering the huge amount of gas immobilised in the UO<sub>2</sub> fuel, the solution process and in consequence the re-resolution process of rare gases is to be replaced by the irradiation enhanced chemical bonding process. This explains the huge fission gas accumulation in the irradiated UO<sub>2</sub> fuel.

#### 4. Conclusions

Noble gas chemistry is much richer than it would be expected.

Since the rare gas compounds are formed by applying the classical chemical methods, the more the noble gas species in the conditions of neutron and fission fragments irradiation of the UO<sub>2</sub> fuel type can be expected.

As the irradiated UO<sub>2</sub> fuel is highly defected, ionised with very energetic and highly charged fission fragments, it appears that during irradiation there is little or no barrier for the formation of rare gas atoms compounds with the UO<sub>2</sub> molecule and fission products. This further implies that significant part of the fission fragments after dissipating all their energy and stopping in the material being still highly ionised at the end of their paths react chemically with the fuel.

This that the inert gases Kr and Xe mostly are not formed directly by fission, but originate from the precursors imply, that the precursors which are not gas atoms can easier chemically react with the UO<sub>2</sub> fuel than the rare gas atoms. It is assumed that the precursor already chemically bonded with the fuel decaying to the rare gas atom do not change the electron shell of the compound and remain chemically bonded.

The rate of the chemical bonding process is markedly higher than the fission gas trapping rate in the bubbles.

The rare gas atoms with the closed-shell electronic structure can be immobilised in point defects, dislocation loops and gas bubbles and be released by recovery of the radiation induced defects. In this sense, there exists no true diffusion for the fission gas in the UO<sub>2</sub> fuel.

Considering the huge amount of gas immobilised in the UO<sub>2</sub> fuel and a very low solubility of rare gas atoms in the uranium dioxide fuel, the term *re-solution* is to be replaced by the irradiation-enhanced chemical bonding process. This explains the huge fission gas accumulation in the irradiated UO<sub>2</sub> fuel.

## References

- [1] R. Hargreaves, D. M. Collins, *J. Br. Nucl. Energy Soc.* 15 (1976) 311.
- [2] R. G. Bellamy, J. B. Rich, *J. Nucl. Mater.* 33 (1969) 64.
- [3] H. Zimmermann; *J. Nucl. Mater.* 75 (1978) 154.
- [4] R. J. White, M. O. Tucker, *J. Nucl. Mater.* 118 (1983) 1.
- [5] T. Nakajima, H. Saito, *Nucl. Engrg. Des.* 101 (1987) 267.
- [6] Kenichi Ito, Ryo Iwasaki and Yoshihiko, *J. Nucl. Sci. Technol.* 22 (1985) 129.
- [7] J. Rest, A. W. Cronenberg, *J. Nucl. Mater.* 150 (1987) 203.
- [8] J. R. Mac Iwan, W. H. Stevens, *J. Nucl. Mater.* 11(1964) 77.
- [9] I. L. F. Ray, H. Thiele, H. Matzke; *J. Nucl. Mater.* 188 (1992) 90.
- [10] T. Aoki, S. Koizumi, H. Umehara, K. Dgotu; Fission gas release behaviour of high burn-up fuel during power ramp tests; *Proceedings of a technical committee Meeting hold in Pembroke, Ontario, Canada, 28 April-1 May, 1992.*
- [11] M. Szuta; *J. Nucl. Mater.* 210(1994)178.
- [12] Katsumi Une and Shinji Kashibe, *J. Nucl. Sci. Technol.* 27 [11] (1990) 1002.
- [13] J. Burbach, H. Zimmermann, KfK 3997, (1985).
- [14] B.W. Samsonov, A. K. Frey; *SAARI – P135, Melekes, 1972.*
- [15] C. Vitanza, E. Kolstad, U. Gracioni, *Proc. of the American Nuclear society, Topical Meeting on Light Water Reactors Performance, Portland, Oregon, May 1979, p. 361.*
- [16] Y. Nogita, K. Une, *J. Nucl. Sci. Tech.* 30, 900(1993).
- [17] D. A. McInnes, P. W. Winter, *J. Phys. Chem. Solids* Vol.49, 143(1988).
- [18] N. Barlett, *Proc. Chem. Soc.* 6 (1962) 218.

- [19] F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann; *Advanced Inorganic Chemistry*, John Wiley & Sons, New York 1999.
- [20] K. Łyczko, *Chemistry of the noble gases*; *Wiadomości Chemiczne*, 2002, 56,p 771-792.
- [21] L. Stein, *Radichemica Acta* 32,(1983)p. 163-171.
- [22] L. Pauling, *J. Am. Chem. Soc.* 1933,55, p.1895.
- [23] M. Pettersson, J. Lundell, M. Rasanen, *Eur.J. Inorg. Chemistry* 1999, p. 729-737.
- [24] M. Lorenz, M. Rasanen and V.E. Bondybey; *J. Phys. Chem. A* Vol. 104, No. 16 (2000), 3770 – 3774.
- [25] C.R. Bieler, K.E. Spence, K.C. Janda, *J. Phys.Chem.* 95, 1991, p. 5058-5064.
- [26] M. Petersson, J. Lundell, M. Rasanen; *Eur. J. Inorg. Chem.* 1, 1999, p. 729.
- [27] M. Petersson, J. Lundell, M. Rasanen; *J. Chem. Phys.*, 102, 1995, p.6423.
- [28] M. Petersson, J. Lundell, M. Rasanen; *J. Chem Phys.* 103, 1995, p. 205.
- [29] M. Petterson, J. Lundell, L. Khriachtchev, M. Rasanen, *J. Chem. Phys.* 109, 1998 p. 618.
- [30] M. Petterson, J. Lundell, L. Khriachtchev, E. Isoniemi, M. Rasanen, *J. Am. Chem. Soc.* 120, 1998, p.7979.
- [31] M. Petterson, L. Khriachtchev, J. Lundell, , M. Rasanen, *J.Am. Chem. Soc.* 121, 1999, p.11904,
- [32] M. Petterson, L. Khriachtchev, J. Lundell, , S. Jolkkonen, M. Rasanen, *J. Phys. Chem. A* 104, 2000, p3579.
- [33] P. Pyykko; *Science*, Vol 290, 2000, p. 64.
- [34] S. Seidel, K. Seppelt; *Science* vol. 290, 2000, p. 117.
- [35] P.Pyykko, *J. Am. Chem. Soc.* 117, 1995, p.2067.
- [36] D. Schroder, H. Schwarz, J. Husak, P. Pyykko, *Inorg. Chem.* 37, 1998, p. 2067.
- [37] J. Li, B. E. Liang, L. Andrews; *Science* Vol. 295 (March 2002) p.2242-2245.
- [38] C.R. Bieler, K.E. Spence, K.C. Janda; *J. Phys. Chem.* 95, 1992, p. 5058-5064.
- [39] N. Bohr, , 1940, *Phys. Rev.* 58, 654,
- [40] N. Bohr, 1941, *Phys. Rev.* 59, 654,
- [41] J. Knipp, E. Teller, 1941, *Phys. Rev.* 59, 659.
- [42] J. Ozeroff, 1949, KAPL Rept., 205,
- [43] E. Leischner, 1966, UNILAC Rept. (heidelberg) 1, 66.
- [44] C. D. Moak, H. O. Lutz, L. B. Bridwell, L. C. Nothcliffe, S. Datz, 1968, *Phys. Rev.* 176, 427.
- [45] J. Leteurtre, Y. Quere; *Irradiation effects in fissile materials*; North-Holland Publishing Company-Amsterdam – 1972
- [46] J. Lindhard, P. V. Thomsen, 1962, Sharing of energy dissipation between electronic and atomic motion, in : *Radiation damage in solids*, Vol. 1, (IAEA, Vienna) 65.
- [47] A. D. Whapham, B. E. Sheldon, 1965, *Phil. Mag.* 11, 1175.
- [48] A. A. Grieshilov, W. W. Kolobashkin, S. I Dementev, *Produkty mgnoviennovo delenia  $U^{235}$ ,  $U^{238}$ ,  $Pu^{239}$  v intervale 0–1 cz*, Atomizdat, Moskva,1969,
- [49] a) B. S. Dzelepov, L. K. Peker, V. O. Sergeev, *Schemy raspada radiaktyvnykh jader,  $A < 100$* , Izdatelstvo “Nauka”, Moskva, 1966.  
b) B. S. Dzelepov, L. K. Peker, V. O. Sergeev, *Schemy raspada radiaktyvnykh jader,  $A > 100$* , Izdatelstvo Akademii Nauk SSSR, Moskva, 1963.
- [50] M. Masalska, J. Masalski, *Tablica izotopow, Postepy Techniki Jądrowej*, Vademecum, Nr 16 (278), 1960,
- [51] C. M.Lederer, J. M. Hollander, I. Perlman, *Table of Isotopes*, Sixth Edition, 1968.
- [52] N. Gusev, V. Maskovitz, G. Obvincev, *Gamma-izlucene radioaktyvnykh izotopov i produktov delena; Gosudarstvennoe Izdatelstvo Fiziko-Matematicheskoy Literatury*, Moskva, 1958.
- [53] J.A. Turnbull, *Radiation Effects*, Vol. 53, 1980, pp. 243-250.
- [54] W.B. Lewis, J.R. MacEwan, W.H. Stewens, R.G. Hart, *Proceedings of the 3<sup>rd</sup> UN Conference on the Peaceful Uses of Atomic Energy*, May (1964).

[55] R.M. Cornell, *J. Nucl. Mater.* 38(1971)319-328

[56] R. S. Nelson, *J. Nucl. Mater.* 31(1969)153.

[57] J. A. Turnbull, R. M. Cornell, *J. Nucl. Mater.* 41(1971)156.

[58] A. D. Whapham and B.E. Sheldon, *Nucl. Appl.* 2 (1966)123.