

**Military Technical College
Kobry El-Kobbah,
Cairo, Egypt.**



**16th International Conference
on Applied Mechanics and
Mechanical Engineering.**

PLUTONIUM USAGE AND MANAGEMENT IN PWR AND COMPUTING AND PHYSICAL METHODS TO CALCULATE PU

A. E. Mohamed*

ABSTRACT

In this paper, I discuss and show the advanced computing and physical methods to calculate Pu inside the nuclear reactors and glovebox and the different solutions to be used to overcome the difficulties that affect on safety parameters and on reactor performance, and analysis the consequences of plutonium management on the whole fuel cycle like Raw materials savings, fraction of nuclear electric power involved in the Pu management. All through two types of scenario, one involving a low fraction of the nuclear park dedicated to plutonium management, the other involving a dilution of the plutonium in all the nuclear park.

KEYWORDS

Physical methods, PuO₂, Plutonium degradation, Doppler effect, Void effect.

* Research professor at BRNO University of Technology, Institute of Energy, Czech Rep.,
Main research fields: Nuclear reactors Engineering and Physics, PU material radiation and
nuclear materials. Tel: 002 01147602039, Email: ashraf.mohamed@saudieng.org.

INTRODUCTION

Main limitations due to the enhancement of the plutonium content are related to the coolant void effect as the spectrum becomes faster, the neutron flux in the thermal region tends towards zero and is concentrated in the region from 10 keV to 1 MeV. Thus, all captures by Pu240 and Pu242 in the thermal and epithermal resonance disappear and the Pu240 and Pu242 contributions to the void effect become positive. The higher the Pu content and the poorer the Pu quality, the larger the void effect.

The core control in nominal or transient conditions. Pu enrichment leads to a decrease in κ_{eff} and the efficiency of soluble boron and control rods. Also, the Doppler effect tends to decrease when Pu replaces U, so, that in case of transients the core could diverge again if the control is not effective enough.

As for the voiding effect, the plutonium degradation and the Pu240 and Pu242 accumulation after multiple recycling lead to spectrum hardening and to a decrease in control.

One solution would be to use enriched boron in soluble boron and shutdown rods.

All fissile materials must be accounted for, following any operation that causes plutonium debris, such as separation Pu from minor actinides, cutting or machining, the waste crumbs are brushed into a tray and weighed. The weight for all materials- both usable and residue- must be within a gram of the total weight prior to cutting. This system of weights and records, maintained by a dedicated computer network, verifies that all the laboratory's plutonium can be accounted for at any time -day or night-. As plutonium is dangerous, the world's most dangerous substance .Plutonium occurs naturally in trace quantities in uranium ore, but most plutonium is produced from irradiation of uranium in nuclear reactors. There are 18 different isotopes of plutonium all of which are unstable and decay into other elements by emitting various types of radiation. Because of radioactivity, a piece of plutonium is warm to the touch and the danger from swallowing plutonium is not much greater than from other heavy metals such as lead or mercury.

Inside the laboratories' plutonium, plutonium 239 is an essential fuel for nuclear weapons and is the form of plutonium most often used in them. So, all handling of plutonium is done in a glovebox to protect workers from any airborne particles. The air pressure in the glovebox is slightly lower than the pressure in the room, which is lower than in the hall, and so on. This pressure control assures that the flow of air is always directed inward to contain and capture any plutonium that might escape from the glovebox in an accident A complex air handling system is needed that includes electrical power fans and a complete backup systems. A filtration system prevents leakage of any potentially dangerous materials into the atmosphere

But inside the nuclear power reactors, we deal with plutonium by accounting it through analysis methods and equations with application of these equations according to the kinds of the reactors, reactors core, fissile materials, mass and other factors.

In this paper, (first part of three parts that deal with accounting plutonium inside the nuclear reactors (first and second parts) and the last part will deal with plutonium inside the laboratories' plutonium by accounting plutonium critical mass, methods that use in the glovebox that deal with plutonium, equations use in the glovebox and laboratories' plutonium and the second and third parts will be published later), we will discuss the methods and experiments use in some kinds of nuclear reactors.

PHYSICAL ACCOUNTING METHODS FOR ADJUSTING FISSILE ENRICHMENT

It is well accepted that reactivity should be controlled by uranium enrichment (U235/U) in nuclear reactors that only uranium is used for nuclear materials based on the assumption that only U235 contributes to reactivity and U238 does not contribute to it. If uranium and plutonium mixed (MOX) fuel is used in Light Water Reactors, reactivity can be controlled by uranium enrichment, plutonium content as $(x=Pu/(U+Pu))$ and fissile plutonium fraction (Pu^*/Pu) based on the assumption that U235 and fissile plutonium (Pu239 and Pu241) equally contribute to reactivity and U238, Pu238, Pu240 and Pu242 do not contribute to it. In this case fissile enrichment is given as :

$$\begin{aligned} (U235+Pu^*)/(U+Pu) &= U/(U+Pu) U235/U + Pu/(U+Pu) Pu^*/Pu \\ &= (1-x) U235/U + x Pu^*/Pu \end{aligned}$$

This equation is used for reactivity control when using MOX fuel in LWR.

A multiplication factor 'K' can be accounted by:

$$K = \nu \Sigma f / (\Sigma a + L)$$

where

- ν is the number of neutrons released per fission event.
- Σf is the macroscopic fission cross section of the fuel atoms in a unit volume.
- Σa is the macroscopic absorption cross section of all atoms in a unit volume.
- L is the neutron lost by leakage from a unit volume.

For the assembly to be critical, we get the following:

$$L + \Sigma a.p = \nu \Sigma f - \Sigma a.fuel = N_h (P A_1 Y_1 + (1 - P) B_2 Y_2) ,$$

where

- N_h is the total number of heavy atoms per unit volume
- P is the plutonium content.
- A_1 and B_2 are the isotopes compositions of plutonium and uranium, and
- Y_1 and Y_2 correspond to $(\nu \sigma_f - \sigma_a)$ of plutonium and uranium, respectively

σ_f and σ_a are microscope cross section for fission and absorption of an atom.

$$\Sigma a = \Sigma a.fuel + \Sigma a.p \text{ 'non fuel materials'}$$

Here, F_i is defined by Y_i/Y_{239} and Y_{239} approximately corresponds to reactivity worth of Pu_{239} . Thus, if F_i is equivalence factor by which each uranium and plutonium isotopes must be adjusted to be an 'equivalent Pu' which generally corresponds to Pu_{239} , then the following equation can be obtained:

$$P \sum_i (A_i F_i) + (1 - P) \sum_j B_j F_j = (L + \Sigma_a.p) / N_h Y_{239} .$$

The right side of the equation is calculated by L and N_h which are inherently determined when reactor core design is fixed, and $\Sigma_a.p$ and Y_{239} which have been evaluated in literatures of nuclear data. Therefore, the value of the right side of the equation is considered to be constant. So, given the critical size of a fast reactor with fuel of a certain isotopic composition, the fissile enrichment of alternative composition can be determined by using the left side of previous eq. So, the right side of the equation is defined as equivalent fissile content (E_{239}):

$$P \sum_i (A_i F_i) + (1 - P) \sum_j (B_j F_j) = E_{239}$$

Then, plutonium content 'P' can be finally given by the following relation:

$$P = (E_{239} - \sum_j (B_j F_j)) / (\sum_i (A_i F_i) - \sum_j (B_j F_j))$$

If $(U_{235}+Pu^*)/(U+Pu)$ is put into E_{239} and F for U_{235} , Pu_{239} and Pu_{241} is set to be 1.0 and that for U_{238} , Pu_{238} , Pu_{240} and Pu_{242} to 0.0, then the above equation is written by:

$$\begin{aligned} P &= ((U_{235} + Pu^*) / (U + Pu) - (U_{235}/U)) / ((Pu_{239}/Pu) + (Pu_{241}/Pu) \\ &\quad - (U_{235}/U)) \\ &= ((U_{235} + Pu^* / U + Pu) - (U_{235}/U)) / ((Pu^*/Pu) - (U_{235}/U)). \end{aligned}$$

PuO₂

Plutonium-based materials have for many years been studied in connection to their usage in nuclear energy applications. Due to the restrictions in handling plutonium for fewer experiments have been done on PuO_2 the magnetic susceptibility of PuO_2 has been found to take a small and constant value of 5.4×10^{-4} emu/mol.

For all temperature up to 1000 K, so that the crystal electric field (CEF) ground state has been suggested to be a G₁ single. On the other hand, recent neutron inelastic experiments have suggested a separation of 123 meV between the G₁ ground state and the first excited G₄ triple state. This value is however, in complete disagreement with that derived from the susceptibility measurements. In a simple model, a separation of 123 meV corresponds to a susceptibility of -10×10^{-4} emu/mol, and requires a deviation from T constant behaviour above $T = 400$ K. In order to investigate the magnetic ground state of PuO_2 , we have performed O₁₇ NMR measurements, for the first time, on this system. The powder sample used in our O₁₇ NMR was prepared by oxidizing Pu metal powder in O₂ gas containing O₁₇. X-ray diffraction patterns confirmed a cubic fluorite PuO_2 structure for our sample. The O₁₇ NMR spectra were measured using a superconducting magnet and a phase

coherent pulsed spectrometer at several temperatures between 6 and 70 K with the following notices:

1. The O17 NMR spectrum at (T=6.2 K). We have obtained a narrow spectrum with half-width of ~ 8 KHz. The narrow spectrum is very similar to those in the paramagnetic state of NpO₂ and UO₂, suggesting that there is no quadrupole splitting and no appreciable anisotropic NMR shift at the O sites. In PuO₂, however, we have observed neither spectrum broadening nor splitting through the temperature region studied. This confirms the absence of magnetic ordering or structural distortions. At least, down to 6K. The Knight shift values are estimated to be $\{K \sim 0.01\%$, and are nearly temperature independent. This agrees with the temperature independent magnetic susceptibility in PuO₂.
2. We also plot the temperature dependence of 1/T in PuO₂ where "the temperature dependence of 1/T measured at H=9.6 T for PuO₂. The 1/T value was measured by the saturation-recovery method using standard spin-echo techniques. Recovery of the nuclear magnetization from a saturation pulse was found to follow in all cases a single-exponential functional form. The 1/T value in PuO₂ is 2-3 orders of magnitude smaller than those in the paramagnetic state of other actinide dioxides. This small 1/T is attributed to the non-magnetic CEF ground state of PuO₂. The 1/T gradually decreases with decreasing temperature below 50 K. For the relaxation process in PuO₂, we may expect contributions from Pu-5* spins in the first-excited G₄ triplet state. These contributions, however, should be more important at high temperatures, since the G₁ to G₄ splitting is suggested to be more than 100 meV in PuO₂. At low temperatures, we can also expect relaxation processes caused by phonons and/or by a small quantity of magnetic impurities, to the extent that they exist. To completely derive the 1/T mechanisms in PuO₂, further experimental effort in a wider temperature range is certainly required.

PLUTONIUM PROPERTIES

We evaluate the plutonium parameters DE (energy difference), DS (entropy difference), DV (volume difference) and U for the A-P model. This occurs in two stages. DV and DE come from consideration of the S-a' transformation, assuming that DS is known. DS and U come from fitting the measured temperature dependence of the lattice constant, assuming DV and DE are known. Some iteration is required, as the two stages are weakly coupled through the value of DS. For Pu-Ga alloys, we know that DV at room temperature is linear with atomic Ga concentration X from data for the a'-phase tabulated where:

$$\Delta V = (3.05 - 0.197 X) \text{ cm}^3 / \text{molL.}$$

We assume that DE is linear with X and use the known transformation temperature at zero pressure of 1.4 and 1.9% at Ga alloys given of 223 and 163 K. We find $DE = (646 - 172X) \text{ cal/molL.}$

As a check, we calculate the transformation pressure at 300 K for Pu-2 at % Ga and find 5.1 kbal. Report an onset pressure of 4 kbal for Pu-2 at %.

We next assume that DS and U are independent of X and fit the Pu242-Ga lattice constant measured using neutron diffraction to find

$$\Delta S = 1.96 \text{ cal/molK} \quad \text{and} \quad U = 3280 \text{ cal/mol} .$$

In this stage of the fitting process, the low temperature data also determine the phonon gruneisen constant $\gamma = 0.49$, which is needed to correct the measured lattice constants for ordinary vibrational thermal expansion. The fits are somewhat poorer than those obtained with an earlier but they are satisfactory considering the much broader scope of the A-P model. The value of U is in fair agreement with the energy difference of 2780 cal/mol found by the invar model. It is unnecessary to assume anomalous properties liquid plutonium to explain its melting behaviour. The calculated compressibility is similar to that of cerium, consistent with the observed minimum in the plutonium-melting curve. The fitted parameters are collected in both molar and atomic units. The critical point for plutonium happens to fall in the liquid state and can not be observed directly. Lattice constants calculated with the A-P model are plotted versus Ga concentration in the panel. In agreement with experiment, Ga suppresses the first order transition between the d- and a- phase by driving the zero-pressure transformation temperature to negative, via the linear Ga dependence of DE. The lower panel shows the d-a transition temperature (t_0) versus.

PU241/PU239 ATOM RATIO IN PRESSURIZED HEAVY WATER REACTORS

Data on the isotopic composition of Pu produced in power reactors are required for knowing the fissile content of Pu when used as a fuel in fast reactors. This information is useful to determine the α -specific activity of Pu, which is required to calculate the weight percentage of Am241 in any Pu sample as well as for the determination of Pu concentration by radiometric methods. The atom ratios of different Pu isotopes in a Pu sample are obtained by thermal ionization mass spectrometry (TIMS), which requires a detailed chemical separation procedure. This increases the amount of analytical effort. There are many instances where such data, for the determination of atom ratios of Pu isotopes, using the data obtained by alpha spectrometry and by thermal ionization mass spectrometry. With these correlations, the atom ratios of different Pu isotopes except for the one involving Pu241, could be obtained with reasonable accuracy (2-5%). The uncertainty on the correlation involving Pu241 was large due to its relatively short half-life (14.32 yr) which necessitates the availability of Pu samples with known irradiation and cooling history. Thus an attempt was made to develop a simple and independent method for determining Pu241/Pu239 atom ratio. This method is based on the determination of total α and total β activity of Pu isotopes using a suitable liquid scintillation counter. Pu241 being a soft β -emitter ($\beta = 20 \text{ keV}$) with a half-life of about 14.32 yr. It was considered worthwhile to measure the β activity of Pu241 in any Pu solution using liquid scintillation counting (LSC). To circumvent the problem of knowing the exact amount of Pu taken in the LSC vial for counting, ratio of the β due to Pu241 with respect to total α activity, also measured by LSC, due to other Pu isotopes was used.

The ratio of the β activity to total α activity was correlated with the amount of Pu241 with respect to the other Pu isotope in the sample as given below:

$$\frac{(A_{\beta}(\text{Pu 241}))}{(N(\text{Pu241}) \lambda_{241})} / \frac{(A_{\alpha}(\text{Pu 238}) + A_{\alpha}(\text{Pu239}) + A_{\alpha}(\text{Pu240}) + A_{\alpha}(\text{Pu241}))}{(N(\text{Pu238}) \lambda_{238}) + (N(\text{Pu239}) \lambda_{239}) + (N(\text{Pu240}) \lambda_{240}) + (N(\text{Pu242}) \lambda_{242})},$$

where

- N denotes the number of atoms,
- A denotes the activity.

Denoting α and β count rates by T_{α} and T_{β} ; the atom ratio of two isotopes as R, the previous equation may be written as:

$$(T_{\beta} / T_{\alpha}) = (R_{1/9} \lambda_1) / ((R_{8/9} \lambda_8) + \lambda_9 + (R_{0/9} \lambda_0) + (R_{2/9} \lambda_2)),$$

where the subscripts 8, 9, 0, 1 and 2 stand for Pu238, Pu239, Pu240, Pu241 and Pu242, respectively;

$$R_{1/9} = (T_{\beta} / T_{\alpha}) ((R_{8/9} \lambda_8) + \lambda_9 + (R_{0/9} \lambda_0) + (R_{2/9} \lambda_2)) / \lambda_1$$

Considering the efficiency values of α and β counting by LSC as h_{α} and h_{β} , respectively and the observed α and β count rates by T_{α} and T_{β} , respectively; the above equation can be re-written as:

$$R_{1/9} = (T_{\beta} h_{\alpha} / T_{\alpha} h_{\beta}) ((R_{8/9} \lambda_8) + \lambda_9 + (R_{0/9} \lambda_0) + (R_{2/9} \lambda_2)) / \lambda_1$$

$$R_{1/9} = (\eta_{\alpha} / \eta_{\beta}) (T_{\beta} / T_{\alpha}) ((R_{8/9} \lambda_8) + \lambda_9 + (R_{0/9} \lambda_0) + (R_{2/9} \lambda_2)) / \lambda_1$$

$$R_{1/9} = ((\eta_{\alpha} / \eta_{\beta})) \text{ X-VALUE} .$$

$$R_{1/9} \sim \text{ X-VALUE} .$$

Thus, a correlation between $R_{1/9}$ obtained by thermal ionization mass spectrometry and X-value calculated from (T_{β}/T_{α}) determined by LSC and using the atom ratios of other Pu isotopes was established for determining Pu241/Pu239 atom ratio. It may be mentioned that atom ratios of other Pu isotopes can be obtained from the previously developed correlations. It is essential to confirm that the efficiency values of α as well as β counting by LSC have not changed after established the correlation. Otherwise, suitable correlation must be incorporated into the LSC data by using a Pu standard sample of known isotopic composition.

PU IONS DILUTED IN A METALLIC MATRIX

A comparison of actinide (U,Np,Pu) atoms diluted in Pd was provided by Russian scientists .U diluted in Pd is non-magnetic .A simple rigid –band model works surprisingly well assuming that the U 5f states contribute to the filling of the Pd 4d band for low concentrations .Once the 4d band is filled up (which happens at 8% U) U moments start to develop ,which is manifest by ,the kondo effect in electrical resistivity .The 4d- band filling is reflected also by the fast decrease of g (also clearly evidenced in the Th-Pd system).when the 5f states start to be occupied in UPd, g

starts to rise again. The complete depletion of the 5f states does not happen in the Np-Pd system, apparently due to the higher 5f count in Np compared to U. The Np doping leads to the fast suppression of the spin-fluctuation maximum in the susceptibility of Pd, but still contributes to U. The Np doping leads to the fast suppression of the spin-fluctuation maximum in the susceptibility of Pd, but still contributes by a Curie term of 2.0 mb/Np leading to an upturn at low T. Effective moments m_{eff} exceeding 1.1 mb/Pu were indicated also in the Pu-Pd system (doping up to 2% Pu). Although for higher concentrations the m_{eff} values decrease, magnetic Pu ions clearly exist. The fast decrease of the susceptibility of the Pd matrix (much faster than in the Np-Pd system) has to be again interpreted as due to the 4d band filling. These facts support the idea that a certain reduction of the 5f count comparing to the Pu metal favours the Pu magnetic moment formation.

Pu in intermetallic compounds By analogy to U, the importance of a minimum actinide spacing has been recognized as prominent precondition for the formation of magnetic moments. Similar to U and Np,

It is expected that for Pu systems also an additional hybridization with the valence states plays a role in the suppression of magnetism, when the large inter-plutonium spacing, $d_{\text{Pu-Pu}}$, and the small direct 5f-5f overlap would allow for magnetism. Besides the 5f-5f overlap and the 5f-ligand hybridization, so, we can compare magnetic properties of U, Np and Pu compounds, especially of the isostructural ones, with similar inter-actinide spacing and type of coordination. Generally, Np compounds exhibit (with few rare exceptions) a similar or stronger tendency to magnetism than their U counterparts. The reasons can be seen in a higher number of 5f electrons (about 4 comparing to 3 or little less in typical U intermetallic) which makes the correlations in the f states more important and induces a certain contraction of the 5f orbitals, reducing the 5f-5f overlap for the same inter-actinide spacing. Continuing further to Pu, the tendency to magnetic order becomes much weaker and, excluding actinide laves phases AnFe_2 , which are driven by the 3d-3d coupling (PuFe_2 is ferromagnet with $T_c = 564$ K), the ordering temperatures of Pu compounds typically do not reach those of U or Np counterparts. As to other Pu laves phases with transition metals, most of them are weakly magnetic ($\text{PuMn}_2, \text{PuCo}_2, \text{PuNi}_2, \text{PuRu}_2, \text{PuIr}_2$).

Particularly striking is the contrast of PuNi_2 with ferromagnetic UNi_2 and NpNi_2 . Only PuPt_2 is ferromagnet ($T_c = 6$ K, ordered magnetic moment $m = 0.2$ mb/f.u.) somewhat higher ordering temperatures were found for equiatomic binaries PuSi ($T_c = 72$ K, m_{eff} in the paramagnetic state 0.72 mb, compared to $T_c = 120$ K in USi and PuPt ($T_n = 44$ K, compared to $T_c = 27$ K in UPt and $T_n = 27$ K in NPPt). Important few magnetic cases also include PuPt_3 ($T_n = 40$ K, $m_{\text{eff}} = 1.3$ mb/f.u.), PuPd_3 ($T_n = 24$ K, $m_{\text{eff}} = 1.0$ mb), and PuGa_3 ($T_c = 20$ K, $m = 0.2$ mb/f.u. or $T_n = 24$ K, depending on structure modification, both having $m_{\text{eff}} = 0.78$ mb, the only exception being the antiferromagnetic PuRh_3 while URh_3 and NpRh_3 are non-magnetic spin fluctuators. Easier comparison between U, Np, and Pu is possible for ternary compounds as those (unlike binaries) form large isostructural groups but, unfortunately, for many compounds only the structure is known. Exceptions are PuNiGa and PuCoGa which crystallize in the ZrNiAl structure type and are non-magnetic, whereas UNiGa , UCoGa and NpNiGa order magnetically. Remarkably, the discovery of superconductivity

in PuCo Ga 5 and PuRhGa5 has initiated a broader study of the actinide '115' compounds. In the UtGa5 group, magnetic order appears only for T=Ni, Pd , and Pt .

The particular cases of T=Co,Rh,Ir , which are very weak pauli paramagnets is clearly due to the 5f –d hybridization which is usually weak for the very late transition metals but gets stronger when moving to the left within each series. The respective Np compounds exhibit different types of antiferromagnetic order (e.g. ,NpCoGa5 has $T_n = 47$ k). PuCoGa5 ,PuRhGa5 , as well as PuNiGa5 are non-magnetic , the first two have a superconducting ground state. We can conclude that also in the '115' series the Pu compounds exhibit weaker magnetic properties than their Np and even U isotype. An interesting systematics can be drawn also from binaries of the rocksalt type ,namely actinide monpnictides and monochalcogenides, the properties of which are well known. U and Np chalcogenides (AnSi,AnSe,AnTe) are magnetic metals whereas Pu chalcogenides ,despite their quite larger atomic volume, remain weakly paramagnetic semi-metals. This is different from Pu pnictides (as PuSb) that are magnetic metals similar to U and Np pnictides. PuSb in particular is a very well documented case of magnetic Pu compound with extended set of microscopic information. Photoelectron spectroscopy deduced the 5f states out of the Fermi level and concluded their localization , while neutron diffraction identified a 5f5 ground state with ordered magnetic moments 0.75 mb /Pu. To test whether a reduced 5f count would be obtained by the LDA+U calculations in such case, leading eventually to Pu magnetic moments, we performed the LDA+U calculations also on PuSb(both around meanfield ,AMF ,and fully localized limit , FLL ,LSDA+U). In case of AMF-LSDA+U ,the hybridization with Sb electronic states leads to a lower 5f occupancy ($n_{5f}=5.2$) than in , e.g., in d/Pu and the total magnetic moment 0.76 mb /Pu in good agreement with experiment. In case of FLL-LSDA +U , yielding the magnetic moment of 0.87 mb /Pu and 5f occupancy $n_{5f}=5.0$. My AMF-LSDA+U calculation for Pu chalcogenides (PuTe) , which have one more conduction electron and less charge transfer from Pu towards the anion, gave the proper non-magnetic ground state. The FLL-LSDA+U calculations produce a magnetic solution in this case.Phase transition in d plutonium alloy.

Studies present experimental data on transformation of four plutonium –gallium alloys with 1, 1.7, 2.5 and 3.5 % Ga under isostatic pressure at 25 c in the Bridgman dilatometer. Large-volume d phase expectedly collapses at quite low pressures and it transforms directly from d to a' phase with possible traces of g -phase . All the observation indicate that d----a' transformation occurs through the martensite mechanism in cooling . The data show that the change in the specific volume of the d-phase alloy under the positive pressure is accompanied by the work which is expended for the d---a' transformation. This means that the energy level of the alloyed d-phase is lower than that of the a' phase. On the other hand , it is well known that the unalloyed a phase is more favourable energetically than the unalloyed d-phase and that a-----d phase transition at the room temperature occurs when a tensile stress of 0.35 GPa is applied curves presented allow for the explicit determination of the d-a transformation energy as a function of gallium concentration in the alloy through the calculation of GpdV integral at the inelastic segment of the compression curve . Energy per gallium mole in alloy is almost independent of the gallium content. This show on the existence of a stable gallium complex in d plutonium that exists in alloys with the Ga content ranging from 1 % to 3.5 % the energy of such complex can be expressed as

$$DE = 67 - 100 \times \text{KJ/mole Ga.}$$

where X is the molar fraction of Ga in Pu-Ga alloy . In this case , the enthalpy of intermetallic compound Pu₃Ga is 42 kJ/mole that is close to the value of Pu₃Ga enthalpy.

The pattern of the transition of gallium alloyed d -plutonium under the high pressure to the a' -phase state can be seen from the plot of the Helmholtz free energy as a function of the specific volume .Internal energy of different phases of plutonium is given by the following equation:

$$E_s = 9 B_m / 2 D_e \cdot (s^{1/3} - 1)^2 + C$$

where ; B_m and D_e are the bulk models and equilibrium density for phase at ' P=0' and ' T=0' respectively , and C_e are constants determining the minimum energy for each phase.

All found curves have been calculated using bulk modules B₁=30 GPa for the d phase, B₂=50 GPa for the a' phase, the slope of the common tangent to curves FV for the two phases determines the pressure of the phase transformation at the thermodynamically equilibrium state. And other curves show that the transition occurs with changing pressure. This is concrete evidence of the absence of the thermodynamic equilibrium, the presence of hysteresis ,also indicates the absence of thermodynamic equilibrium .It is well known that at temperatures of 130-150 oC the remaining d phase gets enriched in gallium during the d--a' transformation. This kinetic process may be responsible for the formation of the thermodynamically non-equilibrium state .The tension of the P= - 0.35 GPa applied to a -plutonium corresponds, the a- d transformation in unalloyed plutonium at standard temperature with phase energy difference of 1.2 kJ/mole .This value is much less than TDS in the a---d transformation (3.6 kJ/mole at 300 k and DS= 12 J/mole). Lack of the information about the a---d transformation in tension do not allow a direct comparison of the transition energies in pure and alloyed plutonium as the fraction of d phase that therewith results is unknown .

The transition from the a' phase to the pure a phase may be accompanied with the energy release of 3.6-10 kJ/mole, depending on the gallium concentration. This energy is likely the energy of pure a'- phase lattice deformation in a'-phase formation due to the capture of gallium and plutonium are bonded forming in Pu₃Ga and this bond in the a' phase disappears, we can determine from the d---a' transformation under pressure at constant temperature the Helmholtz free energy difference. This difference appears to be close to the plutonium -gallium alloy formation enthalpy .Other curves show the d plutonium alloy enthalpy calculated using expression ,divided by mole of the sum of nuclei of plutonium and complexes Pu₃Ga as a function of the molar fraction of gallium in Pu-Ga alloy.

Two experimental points obtained with the method of drop calorimetry fall on this calculated curve. This means that results of the calorimetric measurements and experiments on the d---a' transformation under pressure are in agreement . The studies suggest that the formation of d-phase plutonium alloy can be represented

into the crystalline lattice of metallic plutonium based on this model, we can determine the dependence of the alloy density on the gallium content as the density of the metallic plutonium and Pu₃Ga mixture. Alloy densities versus Ga concentration calculated using the above mentioned model. The straight lines 'obey' the Vegard rule.

KINETICS OF PHASE TRANSFORMATIONS IN PU-GA ALLOYS.

We can form the kinetics of phase transformation in Pu-Ga alloys by the following kinds:

- 1- Kinetics of formation of Pu₃Ga from a δ matrix in Pu-Ga alloys.
- 2- Kinetics of eutectoid phase decomposition in Pu-Ga alloys.
- 3- Kinetics of martensitic transformation in Pu-Ga alloys.

Kinetics of formation of Pu₃Ga from a δ matrix in Pu-Ga alloys: this kinetics – model calculations were performed to study the formation of Pu₃Ga from a δ matrix of Pu-Ga as a function of alloy composition, obviously, as already anticipated the higher the temperature is, and therefore the higher the thermodynamic force is, the shorter the time for Pu₃Ga formation is, as can be concluded from the temperature – time – transformation (TTT) curves were shown. The higher the Ga composition is, the shorter the time for transformation is, because of the evolution of the thermodynamic driving force with alloy composition. This study also shows that at low temperatures the kinetics of phase formation is rather slow, and therefore from an experimental standpoint, we can understand why the determination of the two-phase region is inaccurate. The time for formation found with this model and its kinetics database is compatible with those found experimentally.

Kinetics of eutectoid phase decomposition in Pu-Ga alloys: this kinetics modelling was applied to the study of diffusion δ → δ' + Pu₃Ga with the diffusion controlled TRAnsformation (DICTRA). The TTT curve associated with a 5% rate of transformation for the two separate reactions. Close to the temperature of the eutectoid decomposition, the time for transformation is about $1.5 \cdot 10^6$ years, which means that Pu has long time decayed before equilibrium could be reached. This matter was confirmed by modelling the true eutectoid reaction. Although some versions of the phase diagram describe meta stable equilibrium eutectoid transformation is definitely inhibited by diffusion alone.

Kinetics of martensitic transformation in Pu-Ga alloys: to study the early stage of the δ → δ' isothermal martensitic transformation. The model of martensite nucleation proposed by scientists, and successfully applied to Fe-Ni alloys, was adopted. In this model, the main idea is that a heterogeneity must pre-exist beyond a critical size, and rapidly transforms in a martensite, this embryo must go through a number of growth steps that are thermally activated. In the present case, since detailed experimental information is lacking, a rate control reaction at the higher Ga contents (i.e., between 1.0 and 2.0 % Ga) that involves the δ to γ (around -130 °C) and δ to δ' (around -160 °C and -90 °C at 1.9 and 0.7 % Ga, respectively) transformations, as suggested by scientists, was proposed to explain the transition from double to single C-shape of the TTT curves with a decrease in Ga content. Despite the constraints imposed on the model parameters, the results shown that account fairly well for the

change in temperature and time scale of the early stage of martensite nucleation with alloy composition, and for the transition from double to single C- curve with a decrease in Ga composition, in agreement with those from reference. As a final note, the scenario proposed here only illustrates the feasibility of explaining the transition from double to single C- curve (sorry, I will not include this curves in this studies, but in the next papers for summery), and more in site work on time-resolved structural information as a function of temperature is required to bring a definite answer.

CONCLUSION

The 441 reactors around the world produce about 100 tonnes of plutonium and about 10 tonnes of minor actinides annually, in spent fuel, some of which is separated through reprocessing. While the recycling of plutonium as MOX fuel derives additional energy from this resource, it does little to address the issue of growing plutonium inventories.

In this first part paper, we review and discuss some methods and experiments to control and manage Pu and Pu isotopes inside some nuclear reactors.

REFERENCES

- [1] S. Kern et al., Phys. Rev. B59, 104 (1999).
- [2] M. Colarieti-Tosti et al., Phys. Rev. B65, 195102 (2002).
- [3] G. Rophael and R.Lallement, Solid State Commun., 6, 383 (1968).
- [4] Y.Tokunaga, 'NMR Studies of Actinide Dioxides', Pu Confernc. (2006).
- [5] D.Alamelu. dete.ef Pu. dec. (2006).
- [6] S. K. Aggarwal, D. Alamelu and P.M. Shah, Radiochim. Acta 81, 129 (1998).