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REVIEW OF ACTINIDE NITRIDE PROPERTIES WITH FOCUS ON SAFETY ASPECTS

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Review of Actinide Nitride Properties with Focus on Safety Aspects

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This report provides a review of the potential advantages of using actinide nitrides as fuels and/or targets for nuclear waste transmutation. Then a summary of available properties of actinide nitrides is given. Results from irradiation experiments are reviewed and safety relevant aspects of nitride fuels are discussed, including design basis accidents (transients) and severe (core disruptive) accidents. Anyway, as rather few safety studies are currently available and as many basic physical data are still missing for some actinide nitrides, complementary studies are proposed.

Keywords: Nitride Fuel, Actinide Nitrides, Safety, Fast Reactors, Transmutation

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アクチノイド窒化物の特性と窒化物燃料の安全性に関するレビュー

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本報告は、長寿命核種の核変換用ターゲットあるいは高速炉用新型燃料として期待されているアクチノイド窒化物の開発状況についてレビューしたものである。報告値のあるアクチノイド窒化物の物性データを整理したほか、これまでに実施されてきた照射試験から得られた知見を要約した。照射健全性については、通常時の燃料挙動に加えて、関心が持たれている過渡時及び事故時の挙動に関する報告も含めた。しかし、事故時の燃料安全性に関するこれまでの研究例は少なく、超高温物性データの取得と併せて、今後の窒化物燃料炉心の安全性確認のために必要な研究項目を提案した。

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1. INTRODUCTION

This report is written in the frame of the CEA/JAERI implementing agreement on waste transmutation technology. Both CEA and JAERI are involved in research studies to solve this key issue of the nuclear energy, which is waste management. Among the different possibilities to manage nuclear wastes, transmutation of actinides and fission products in advanced reactors¹ would allow to have a practically closed nuclear cycle, the ideal goal being what is sometimes called Self-Consistent Nuclear Energy System (SCNES) (ref. 18).

The interest of using actinide nitrides for waste transmutation technology is developed in section 2.

Section 3 provides a summary of the available knowledge about fabrication, physical properties and high temperature behaviour of actinide nitrides.

Section 4 recalls the available data on irradiation of nitride fuels, including experimental results gained both by CEA, by JAERI and by other research institutes (bibliographic study).

Nevertheless, it is known (and developed in section 3) that, at high temperature, some actinide nitrides could dissociate, giving nitrogen in the gas phase and leading to a possible surface melting of the actinide under the metallic form. Therefore, a major concern about the use of actinide nitrides in reactor is their behaviour at high temperature, mainly under potential incident or accident situation. CEA industrial partners consider a clear view on this problem as a prerequisite before funding more research on this topic. So, section 5 of this report focus on the safety aspects, related to the high temperature behaviour of actinide nitrides both under normal, transient and severe accident conditions.

Finally, items to be investigated in future research work are indicated in section 6.

2. MOTIVATIONS FOR USING NITRIDES

In the huge majority of nuclear reactors, oxide fuels are used. Their behaviour is well known and they are usually considered as very good fuels, let's say reference fuels. Also, reprocessing plutonium from spent fuel and reusing it as mixed oxide (MOX) fuel is nowadays an industrial reality. So in an oxide fuel based reactor, as a first approach, it looks reasonable to try to transmute minor actinides under oxide form. It is the reason why actinide oxides currently receive the first priority in CEA studies on nuclear materials.

Now, we should answer the question: "why to try to develop alternate fuels as nitride fuels, and why to try to transmute minor actinides under nitride form?" Indeed, both the type of nitride to be considered and the motivation to develop it, may depend on some specific objectives, on the chosen fuel cycle, including reprocessing strategy and the type of reactor to be used. This is shown in the following parts 2.1 to 2.4, and based on one of these possible fuel cycles (double strata, with dry reprocessing and use of an accelerator driven system (ADS)) nitrides are the major research topic about nuclear materials in JAERI.

¹ In this report, advanced reactor means any type of innovative nuclear reactor allowing both electricity production and waste transmutation. Then in this report, we will speak mainly of transmutation of minor actinides but we should keep in mind that, as much as possible, transmutation should apply also to fission products.

2.1 Fast Breeder Reactors and General Motivation for Nitride Fuels

Fast breeder reactors are not directly in the scope of the waste transmutation technology, although they may constitute one part of the nuclear power considered in some closed advanced nuclear cycles. Then, as many past studies on nitride fuels were performed for a potential application to fast breeder reactors, it is difficult to ignore it in the present report. Finally, some points presented in this part are not specific to the breeding objective, but are general to any use of nitride fuels as presented in the next parts of this section 2.

Hereunder considerations have been mainly extracted from reference 21.

Oxide fuels have been widely studied for fast breeder reactors and their suitability, including the capability to achieve high burn-up, has been demonstrated. Due to their very good behaviour and the large know-how gained in the past, they are considered as reference fuels. Nevertheless, three main drawbacks concerning oxide fuels can be quoted:

- non compatibility of oxide fuels with the sodium,
- rather low heavy atom density, leading to a large reactivity drop,
- low safety margins in some operating situations.

To avoid the above problems several types of fuels have been studied, such as metallic fuel and carbide fuel. The first one was much studied, mainly in the USA, through the Integral Fast Reactor (IFR) programme developed at Argonne National Laboratory. Nevertheless, metallic fuel would lead to a complete change of the nuclear cycle (fabrication and reprocessing) and a risk of formation of eutectic with the clad would dramatically reduce the safety margins in incident or accident situation. Carbide fuel was studied in the past but most studies were abandoned due to its pyrophoricity and to difficulties for its reprocessing.

So nitride fuel is considered as the most suitable candidate, if we want to avoid the drawbacks mentioned here above about oxide fuels. For such a fuel, a classical composition is $(U_{0.8}Pu_{0.2})N$.

The high density, and more precisely the high heavy atom density, of mixed uranium-plutonium nitride fuel (about 40% higher than oxide fuels, see section 3.7) constitutes an advantage in terms of breeding. Furthermore, it allows to reduce the reactivity drop with burn-up, and so to increase the residence time in reactor.

The melting temperature of mixed uranium-plutonium nitride fuel depends on the nitrogen pressure but it is close to that of the oxide fuel. As the thermal conductivity of nitride fuel is about 6 times higher than that of the oxide fuel, it is a serious advantage for nitride fuel as regards safety. For a given linear power, the fuel temperature will be lower ("cold fuel") and so the safety margins will be larger. Or, with the same safety margins as with oxide fuels, the linear power could be increased and the core volume could be reduced. This advantage can also be thought as allowing fatter and fewer pins in a reactor, or a higher coolant temperature, a cooler interior, or some combination of these benefits.

The excellent compatibility of nitride fuel with sodium is a supplementary major advantage as regards a potential clad failure. The only reaction with the coolant should be a very slow reaction with oxygen impurities contained in the sodium. Therefore, a failed assembly could remain without major problem in the reactor and the managing of failed assemblies should be easier and less penalising for the loading factor. At low temperature (20 to 60°C), the compatibility of nitride pellets with water is good, too. Finally, at ambient temperature, the compatibility with air is good, too.

Except the high temperature behaviour of nitride fuel, which will be addressed in more details in the following sections of this report, another drawback has to be mentioned. Natural nitrogen is constituted at 99.635% by the isotope 14. By (n,p) reaction, this isotope would produce ^{14}C , which constitutes a supplementary waste. Then, ^{14}N presents neutronic characteristics close from those of oxygen, and so, because of neutron captures, a supplementary enrichment of plutonium would be necessary compared to carbide fuels. Finally, these neutron captures on ^{14}N would lead to an additional gas release (helium and hydrogen) compared to the oxide. To avoid these problems, the solution consists of an enrichment of nitrogen into ^{15}N , to a level close to 99.9 % in order to match the admissible release rates. Several enrichment processes exist: cryogenic distillation of NO, chemical exchange NO/HNO₃ and chromatographic process. The so-called NITROX process, based on chemical exchange NO/HNO₃ can lead to very high enrichment and could be used for an industrial production of several tons per year. Some rough estimates of the enrichment cost of nitrogen have been published in literature. The figures are much spread out depending on the authors. In any cases, complementary studies should allow optimising these processes and significantly reducing the costs. Furthermore, ^{15}N may be recovered within the fuel cycle, and so the necessary amount could be much limited.

2.2 Plutonium and Minor Actinide Transmutation in Fast Reactors

Fast reactors were initially conceived as fast breeder reactors. Nevertheless, in the nineties, one major motivation for going on in developing fast reactors was their capability to transmute plutonium and minor actinides and so, to participate in the nuclear waste reduction.

2.2.1 Homogeneous Recycling of Minor Actinides in Regular Fast Reactor Cores

As a first step, one can envisage a rather simple strategy in which minor actinides and plutonium are recycled together. It means that the reprocessing technology would not need to separate minor actinides from plutonium. To obtain a significant reduction in radio-toxicity, this approach implies to recycle at least both plutonium, americium and curium. So, if we think of oxides, this approach would lead to a MOX fuel containing uranium, plutonium and some amounts of minor actinides. Such a fuel was successfully irradiated in France in the so-called SUPERFACT experiment. Indeed, the good behaviour of this oxide fuel was demonstrated.

Nevertheless, if we want to avoid the drawbacks reported in 2.1 about oxide fuels, we can think of nitride fuels in fast reactors. In such a case the relevant fuel would consist of a mixed (uranium-plutonium-minor actinides) nitride.

2.2.2 Heterogeneous Recycling of Minor Actinides in Regular Fast Reactor Cores

Currently, many studies in CEA are rather related to heterogeneous recycling of minor actinides in regular fast reactor cores. In such a strategy, reprocessing should allow the separation of minor actinides from plutonium. Then, plutonium and minor actinides should be in the same core. Plutonium (and probably neptunium) would be associated to uranium as standard fuel for the core. Minor actinides would be located at the core periphery, as incineration targets in sub-assemblies.

Two different strategies can be considered in the case of this heterogeneous recycling.

The first one is the one-through strategy. It consists of a unique irradiation at extremely high burn-ups (more than 90 % of actinides have to be fissioned) with direct storage of the residue. This strategy avoids reprocessing of the spent targets but the targets should

withstand very high damage doses. So, it is thought that a two-phase material is necessary for this approach. The actinide compound should be dispersed -with a particle size to be optimised- in an inert matrix. The main criteria that this inert material should fulfil are discussed in ref. 13. We will quote the main points: a small neutron cross-section (neutron saving, no production of other wastes), good thermal and mechanical properties and good resistance to irradiation damages. Here again, most of the current studies in CEA are relevant to actinide oxides in oxide inert matrices (e.g. the ECRIX or CAMIX experiments). Nevertheless, due to their very good properties relevant to the criteria to be fulfilled, nitride materials are among the promising candidates and some nitrides are studied in CEA experiments (e.g. TiN as an inert matrix, in MATINA experiment). In such a case the target could be, for instance AmN (or (Am,Zr)N, ... without forgetting similar curium compounds) dispersed in TiN or ZrN, or dispersed in oxide inert matrices (MgO, ...).

The second strategy is the multi-recycling strategy. The transmutation should be done through relatively low burn-up irradiations separated by reprocessing. So, this strategy implies many reprocessing operations and relies on small loss fractions during reprocessing. On the other hand, due to the lower burn-up, conditions to be fulfilled by the targets are less drastic. In such a case, the same type of targets as quoted just above may be considered. Furthermore, if they can withstand the irradiation conditions, which are less severe than in the previous case, we could also think of simpler compounds as solid solutions (e.g. (Am,Zr)N) which should simplify the multi-reprocessing.

2.2.3 CAPRA and CADRA Programmes

In France, and in Europe, the initial objective of the CAPRA programme (in French: "Consommation Accrue de Plutonium dans les Réacteurs Avancés", which means enhanced consumption of plutonium in advanced reactors) was to define fast reactor cores optimised to burn as much plutonium as possible. Then, the objectives were extended to explore the feasibility of a reactor dedicated to the incineration of a large amount of plutonium and of minor actinides (and long lived fission products). Finally, a specific programme called CADRA (in French: "Consommation des Actinides et des Déchets dans les Réacteurs Avancés", which means consumption of actinides and wastes in advanced reactors) was launched in 1999 to fulfil this latest objective.

2.2.3.1 CAPRA Programme

The so-called CAPRA 1994 reference core is based on oxide fuel. The feasibility of this core was demonstrated on a neutronic point of view, but the real feasibility issue is the fuel behaviour and its capacity to achieve the requested burn-ups. An irradiation programme is still in progress to answer this question.

Core calculations were also performed with mixed nitride core and with the same design as for the CAPRA oxide reference core. In fact, the reference oxide core is characterised by a dilution concept to reduce the fuel inventory. Therefore, the larger heavy atom density of nitride fuel forced to more dilution, i.e. to an adaptation of the smear density of the fuel. These calculations show a comparable burning effect as with oxide fuel, with an increase of the residence time and lowering the integrated dose and mean enrichment.

Furthermore, as long as we deal with oxide fuels, and taking into account of the necessary compatibility with the PUREX reprocessing process, the maximum plutonium concentration is limited to 45%. For a higher level of plutonium burning, further increase of the plutonium content is needed. Nitride fuel allows this possibility while being quite compatible with the PUREX reprocessing process (ref. 9). So mixed (uranium-plutonium)

nitride with plutonium concentrations in between 60 to 80% are probably the most promising fuel to solve this issue. Here again, for getting better material properties, the addition of a compound such as zirconium could be envisaged.

Then, for a maximum level of plutonium burning and for use of very degraded plutonium, uranium free fuels could be considered. Plutonium nitride or plutonium-zirconium nitride are serious candidates in this respect. They can be considered either under a classical pellet shape (with a small diameter) or under a more innovative concept, which would consist of spherical particles poured into the annular space between the external clad tube and an inner tube. Another solution would consist of associating the plutonium nitride to an inert material matrix.

2.2.3.2 CADRA Programme

Three main scenarios to be studied in the CADRA programme have been defined (ref. 31).

The first one consists of diluting the minor actinides (mainly neptunium, americium and curium) into the CAPRA fuel. Such a scenario would lead to a minor actinide content of about 10wt% and consequences of such an amount on the CAPRA core and on the CAPRA fuel has to be analysed. Of course, if we refer to the CAPRA oxide reference core, this study is relevant to oxides. Nevertheless, we can also think of more advanced CAPRA nitride cores for higher plutonium burning as stated in the previous part. In such a case the studies would become relevant to a mixed (uranium-plutonium-minor actinide) nitride or even, thinking of uranium free fuel to mixed (plutonium-minor actinide) nitride. As previously stated the addition of a stabilising compound as zirconium can also be considered.

The second scenario consists of concentrating americium and curium in incineration targets located at the periphery regions of the CAPRA core, while neptunium should be included in the CAPRA fuel. In this case, the minor actinide concentration in the targets should be about 50wt%. Again, if we refer to the CAPRA oxide reference core, this study should be mainly relevant to oxides. Nevertheless, as for heterogeneous recycling of minor actinides in regular fast reactor cores (part 2.2.2) nitrides (with higher actinide content) could present a great interest due to their excellent properties. Finally, if a CAPRA nitride core were considered, the interest for minor actinide nitride as targets would be enhanced. So, (U,Pu,Np)N and (Pu,Np)N would be relevant fuels. (Am,Cm)N with the addition of an inert matrix would be a relevant target.

The third scenario considers that all the minor actinides (except, neptunium, which could possibly follow the plutonium route) are managed in a "second stratum" in specific fast reactors dedicated to the transmutation: the CADRA reactors. In such a scheme, the "dedicated fuel" is mainly composed of minor actinides, while the complement in heavy metals would be constituted of fissile isotope as Pu or ^{235}U , or even of ^{233}U if a thorium cycle is considered. A priori, the burn-up to be achieved with such fuels is about 15 to 20at%. So, irradiation damage should be rather limited and a solid solution can be considered. The major selection criteria to determine the fuel to be used in such a case are a good thermal conductivity (cold fuel concept, i.e. a fuel operating at a rather low temperature while keeping a high linear power rating), a high heavy atom density (the higher the density, the harder is the neutron spectrum and the more efficient is the transmutation), a good crystal structure symmetry without phase transformation. Based on these criteria, nitride is again one of the most promising materials. The major restriction for its use is the uncertainty about its high

temperature behaviour, which is the main motivation for writing this report. In this case, we would deal with mixed nitrides containing more than 50wt% of minor actinides.²

Nevertheless, still relevant to the third scenario, achieving a high burn-up (more than 50at%) should be preferable to avoid too many costly recycling operations. In such a case, mechanical behaviour of the fuel would become a major concern and a composite fuel, as an inert matrix fuel type, should be considered. So, most of the mechanical stress should be withstood by the inert material. In such a case the mean heavy atom density would be much lower than in the previous case and the thermal properties would be lower in most of the cases (except if we think of metal as inert matrix material). However, the advantage gained on the better mechanical behaviour of such fuels could overcome these drawbacks. Again, to maintain as far as possible the "cold fuel" concept, actinide nitrides should be a promising possibility.

2.3 Plutonium and Minor Actinide Transmutation in Sub-critical Reactors

In the frame of the Japanese programme on partitioning and transmutation technology (OMEGA Programme), sub-critical ADS with nitride fuel has been designed in JAERI for transmutation of minor actinides. In this system, a minor actinide-loaded sub-critical core is driven by a high-intensity proton accelerator (several tens of MW beam) and fast neutrons enable efficient transmutation of minor actinides. Again, nitride is chosen as a fuel material for ADS because of excellent thermal (high thermal conductivity and high melting temperature) and neutronic properties (high heavy metal density leading to hard neutron spectrum). The mutual solubility of actinide mononitrides (including neptunium, americium, curium, etc), the good compatibility with potential coolant (both Na and Pb-Bi) and the applicability to pyrochemical reprocessing technique are supplementary advantages of nitride fuel as regards its application to ADS and to the general fuel cycle. The mutual solubility enables a flexible fuel composition according to the core design. Although Na had been considered as coolant following the manner of liquid metal cooled fast reactor, the recent JAERI design study is focused on Pb-Bi coolant. Pb-Bi cooled system has an advantage in safety aspect although its thermal characteristics are inferior to Na. The applicability to pyrochemical reprocessing of nitride fuel is further commented in section 2.4. Table 1 summarises major parameters of the JAERI's design Pb-Bi cooled ADS (ref. 16). Fuel is a mononitride solid solution containing minor actinides as a primary component and in this case, Pu is added to the fuel in order to keep k_{eff} nearly constant at 0.95 during operation³.

The design study of ADS is also underway in Europe and in the USA. In the USA, the Accelerator-driven Transmutation of Waste (ATW) programme was launched to lighten a burden of the waste disposal at Yucca Mountain site. Nevertheless, due to the American past experience (IFR programme), metallic fuel is considered as a reference fuel material for the moment. In France, the studies on ADS concept began in 1998, with setting up an R&D programme aimed at the possible construction of an experimental demonstration unit in the framework of a European project, open to international exchanges. The current schedule should lead to the selection of technical and safety options in 2002. Feasibility and definition

² Anyway we should keep in mind that oxide fuels remain a reference for the French programme and that nitrides are studied as an interesting alternative. Indeed, if oxide fuels containing more than 50wt% of minor actinides can achieve the conditions imposed for this CADRA concept, due to the very good knowledge on oxides, they would probably be chosen.

³ Actually, transmutation of plutonium itself is out of the scope of the OMEGA programme. Indeed, it is extracted in reprocessing and high level radioactive wastes do not contain significant amount of plutonium.

studies should be completed by 2006. Then construction could begin. So the type of fuel is not yet definitely decided, but for the reasons already developed, nitride fuel could be chosen.

2.4 General Recycling Strategy

Regarding the classical PUREX recycling technology, as it is currently used in France, the excellent solubility of nitrides in nitric acid is a major advantage. Especially, as stated in section 2.2.3.1, if we consider the use of high plutonium content fuels (let's say 60 to 80%) in a CAPRA core, oxide fuels would not be anymore compatible and we should really use nitride fuels.

The concept of "double strata fuel cycle" as proposed and studied in JAERI is composed of the power reactor fuel cycle (the first stratum) and the minor actinide transmutation cycle (the second stratum). In this concept, each stratum evolves independently: the first stratum will be optimised for the safe and economical use of plutonium, and the second stratum will aim the efficient reduction of long-lived minor actinides and fission products. Nitride fuel has been chosen for this second stratum. The spent fuel is reprocessed by pyrochemical technology in LiCl-KCl eutectic melt. Although the pyrochemical process was initially developed in Argonne National Laboratory (the U.S.A.) for reprocessing of metallic fuel, it could be applicable to nitride fuel. Indeed, nitride fuel is also a good electric conductor and the free energy changes for the formation of chlorides from minor actinide nitrides and from most of fission product nitrides are similar to the case of metallic fuel.

It is possible to reprocess the conventional (U,Pu)N fuel for advanced fast reactor, with or without ^{15}N enriched nitrogen, by pyrochemical process. Anyway, as already discussed, using ^{15}N enriched nitrogen will be required (mainly for avoiding ^{14}C production). The pyrochemical process is probably more convenient for recovery of expensive ^{15}N enriched nitrogen gas compared with a conventional wet process.

Pyrochemical process presents also advantages for treating spent minor actinide fuel with significant large decay heat and fast neutron emission as regards radiological protection of the operators. Compactness of the facility leading to cost reduction of reprocessing and strong resistance against potential proliferation problem are also expected.

The reference flow sheet for processing nitride fuel for minor actinide transmutation is shown in Figure 1. The chopped (minor actinide-plutonium) mixed nitride fuel is put into anode and directly subjected to electrorefining in LiCl-KCl eutectic melt. Plutonium and minor actinides are recovered together at liquid Cd cathode. Nitriding of plutonium and minor actinides is carried out by flowing nitrogen gas into liquid Cd cathode after the electrorefining.

So far, JAERI has investigated the molten salt electrorefining of nitride fuel that is a primary process of pyrochemical reprocessing. The experimental study covers:

- the electrolysis of UN, NpN and PuN at anode in LiCl-KCl eutectic melt,
- the release of nitrogen gas from nitride fuel,
- the electrochemical measurements of dissolution and deposition at the electrodes,
- the recovery of U, Np and Pu metal at solid/liquid cathode and the nitriding behaviour of the cathode deposits.

At laboratory scale, more than ten grams of plutonium could be recovered at liquid Cd cathode with high plutonium concentration by electrorefining of PuN. From now, nitriding procedure suitable for the next fuel pin fabrication should be investigated.

3. FABRICATION, PHYSICAL PROPERTIES AND HIGH TEMPERATURE BEHAVIOUR OF ACTINIDE NITRIDES: AVAILABLE KNOWLEDGE

Selected physical properties of the actinide nitrides relevant to our study are given in Table 2 to Table 8. Density and thermal conductivity data are also plotted in Figure 2 and Figure 3, together with actinide dioxide data. The following parts 3.1 to 3.11 provide complementary information, with focus on the fabrication processes and vaporisation behaviour, when available.

Note: Very few relevant data are available for curium-based nitrides. Nevertheless, to reduce significantly the activity of the residual materials sent to a deep geological storage, in any case both americium and curium should be transmuted (ref. 33). So curium-based nitrides should also be considered.

3.1 Uranium Nitride

Uranium nitride (UN) is not of direct interest for waste transmutation. It is treated in this report because it is the most studied actinide nitride, and because some unknown properties of other actinide nitrides should be rather close from those of uranium nitride. Furthermore, its well-known dissociation at high temperature is one of the major reasons, for having some concerns on the high temperature behaviour of other actinide nitrides.

3.1.1 Fabrication Processes

A variety of fabrication methods have been used to produce UN. The most common methods are: nitration of metallic uranium in N_2 or NH_3 , nitration by arc melting, hydride route, sol-gel route, and carbothermic reduction from UO_2 .

This last process is probably the only one that could be used at an industrial stage. It relies on the reaction: $UO_2 + 2C + 0.5N_2 \rightarrow UN + 2CO$.

It consists of mixing and grinding UO_2 powder with graphite and heating under N_2 atmosphere at about 1773K. The drawback of this method is the rather high content of carbon and oxygen as impurities in the final product. Typical impurities of oxygen can be around 0.1wt% (ref. 23).

The densification of UN powders is difficult to achieve by usual sintering techniques. Sintering below 1873K yields pellets of about 80% of theoretical density as a maximum value. Sintering above 1973K would lead to the decomposition of UN. So, to produce dense UN pellets, isostatic hot pressing of pre-compacted UN should be used. Then, densities as high as 96% of the theoretical density can be obtained (ref. 14).

As an illustration, in ref. 19, the synthesis of UN tablets was performed using nitrogen with 5% hydrogen mixed gas stream, at 1773K for 28.8ks. Then, the tablets were ground for 172.8ks by a ball mill. After grinding, nitride powder was pelletised, and then sintered at 1923K for 10.8ks and at 2023K for 10.8ks under an Ar gas stream. The final density of

sintered pellets was 92.7% of the theoretical density. They contained oxygen up to 0.6wt% and carbon up to 0.2wt%.

It is to note that in all relevant papers, carbothermic reduction is performed under an open stream of nitrogen. With enriched nitrogen, for economical reason, it is clear that a closed nitrogen circuit, with on line trapping of CO should be used. It looks quite possible but it has never been done.

3.1.2 Physical Properties, High Temperature Behaviour

Selected physical properties of uranium nitrides are reported in Table 2.

When heated under vacuum atmosphere, above 1973K, uranium nitride decomposes. Nitrogen evaporates and a metallic uranium phase, liquid at high temperature, appears at the grain boundaries. As the homogeneity range of UN_{1-x} is very narrow, less than 4% of nitrogen release from UN is enough to precipitate the liquid metal phase. Under inert atmosphere, this dissociation of UN occurs at higher temperature and the kinetics has to be taken into consideration (ref. 21).

This behaviour has been studied by a number of authors. A plot of the decomposition pressure of uranium nitride in equilibrium with liquid, taken from ref. 23, is given in Figure 4. Over the two-phase region $UN(sol) + U(liq)$, equilibrium pressure of nitrogen is not so large: about 100Pa at 2500K (see also, ref. 29). The partial pressure of uranium over UN, taken from ref. 39, is given in Figure 5. This low partial pressure causes U metal to be formed during evaporation of UN. A more recent experimental study, (ref. 19) is in agreement with these results. Finally, congruent vaporisation of UN occurs at $3103 \pm 30K$, at $3.5 \times 10^5 Pa$ nitrogen (ref. 8). To prevent the decomposition of UN up to this temperature, the nitrogen pressure should be, at least, equal to this value of $3.5 \times 10^5 Pa$.

Although thermal properties of solid uranium nitride are known, no experimental data exist about those at liquid state. In the only report (ref. 34) dealing with them, these properties are estimated from those of solid UN, by extrapolation under some assumptions. Therefore, the following estimated values for the liquid phase should be cautiously considered. Thermal expansion coefficient: $21.6 \times 10^{-6} K^{-1}$.

Density: $14.24/(1 + 8.07 \times 10^{-5} T)$ (in $g.cm^{-3}$, not far above the melting point).

Heat capacity: $49.9201 + 6.4694 \times 10^{-3} T$ (in $J.mol^{-1}.K^{-1}$, $T \leq 8500 K$).

Enthalpy: $H(T) - H(298) = 55452.1 + 49.9201 T + 3.2347 \times 10^{-3} T^2$ (in $J.mol^{-1}$, $T \leq 8500 K$).

Total vapor pressure over UN in liquid region: $\log(P_T) = 4.9968 - 24048/T + 0.51735 \log(T)$ (P_T in atm). Partial pressures of U, N_2 and UN are also estimated in reference 34.

Thermal conductivity: $24.3 W.mol^{-1}.K^{-1}$.

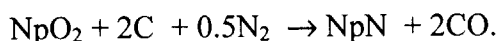
3.2 Neptunium Nitride

As soon as we deal with nuclear waste transmutation, neptunium, together with americium and curium, is one of the actinides to be transmuted. As discussed in part 2, neptunium could be transmuted either in homogeneous or in heterogeneous mode. So we could consider either a mixed (uranium–plutonium–neptunium) nitride or a minor actinide based mixed nitride (neptunium–americium–curium) nitride. In any case, the properties and behaviour of neptunium nitride should be known.

3.2.1 Fabrication Processes

As for uranium nitride, we will deal with carbothermic reduction method, as it is the most suited method for a possible industrial fabrication process. Reference 40 gives a description of the method used in JAERI, which is summarised hereafter.

First, the NpO_2 , and graphite powders were blended with a C/NpO_2 ratio of 2.2 in order to have a carbon excess, as regards the basic relation:

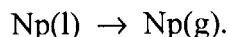
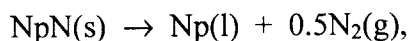


The mixture was then compacted into disks of 12mm in diameter and about 2mm thick. The NpN synthesis was carried out in two steps: at 1823K for 36ks in a pure N_2 stream for completing the carbothermic reduction, then at 1723K for 54ks in a N_2 -8% H_2 stream for removing excess carbon. Then, green pellets were prepared under a pressure of about 300MPa. Sintering was carried out at 2000K in a N_2 -8% H_2 stream. The final density of sintered pellets was over 90% of the theoretical density, for sintering times of 72ks. After the two synthesis steps, the oxygen and carbon impurities were 0.03wt% and 0.09wt%, respectively.

3.2.2 Physical Properties, High Temperature Behaviour

Selected physical properties of neptunium nitride are reported in Table 3.

Vaporisation behaviour of neptunium nitride was studied in JAERI by mass spectrometry with a Knudsen cell, from 1690 to 2030K (ref. 27). The samples were prepared by carbothermic reduction method. Partial pressure of Np gas over NpN (solid) was found to be in between those of U over UN and Pu over PuN . The calculated free energy of formation of NpN was also between those of UN and PuN . The proposed decomposition mechanism is:



It means that, as it is the case for UN , NpN may decompose into liquid metal and nitrogen gas. However in a more recent study (ref. 27), the same authors report that when NpN is co-loaded with PuN in the Knudsen cell, due to the nitrogen pressure derived from congruent vaporisation of PuN , no liquid phase occurs anymore.

3.3 Plutonium Nitride

As discussed in part 2, plutonium-based nitrides should be the most relevant compound when using a nitride fuel for waste transmutation. Usually, plutonium should be associated to other actinides although in the objective of a U free fuel (c.f. CAPRA programme) it could be considered by itself. In any case, the knowledge of its properties is necessary to understand the properties and the behaviour of mixed nitrides containing plutonium.

3.3.1 Fabrication Process

A suitable route for obtaining PuN is the hydride route, i.e.; the reaction of $\text{PuH}_{2.7}$ with NH_3 or N_2 at quite low temperature (ref. 23).

However, here again the carbothermic reduction process looks more suitable for a potential industrialisation. The process is similar to the one described for UN and NpN .

For instance, the following process, reported in ref. 38, yielded final impurities in PuN as low as 0.12wt% in carbon and 0.06wt% in oxygen. First, the PuO₂ and graphite powders were blended with a C/PuO₂ mole ratio of 2.5 in order to have a carbon excess, as regards the basic relation:



The mixture was then compacted into disks of 12mm in diameter and about 2mm thick. The PuN synthesis was carried out in two steps: at 1740K in a pure N₂ stream for completing the carbothermic reduction, then at 1595K for 18ks in a N₂–H₂ gas stream (H₂/N₂=3) for removing excess carbon.

3.3.2 Physical Properties, High Temperature Behaviour

Selected physical properties of plutonium nitride are reported in Table 4.

In ref. 39, vaporisation behaviour of plutonium nitride up to 2000K is reported. A short summary is provided in part 3.7.2. As shown in Figure 5, the partial pressure of Pu over PuN is much larger than that of U over UN.

Furthermore, as the enthalpy of formation of Pu(g) is smaller than that of U(g), the vaporisation behaviour of PuN differs from that of UN: instead of preferential vaporisation of nitrogen, Pu and N₂ vaporise congruently (e.g. ref. 29). The congruent melting point is estimated in ref. 45: 3103±50K at 5±2MPa nitrogen.

Although thermal properties of solid plutonium nitride are relatively well known, no experimental data exist about those at liquid state. As for UN, reference 34 is the only report dealing with them. The properties being estimated from those of solid PuN, by extrapolation under some assumptions, the following estimated values for the liquid phase should be cautiously considered.

Thermal expansion coefficient: $39.0 \times 10^{-6} \text{ K}^{-1}$.

Density: $16.15/(1 + 1.75 \times 10^{-4} T)$ (in g.cm⁻³, not far above the melting point).

Heat capacity: $49.9201 + 1.168 \times 10^{-2} T$ (in J.mol⁻¹.K⁻¹, T≤8000 K).

Enthalpy: $H(T) - H(298) = 29496 + 49.9201 T + 5.841 \times 10^{-3} T^2$ (in J.mol⁻¹, T≤8000 K).

Total vapor pressure over PuN in liquid region: $\log(P_T) = -9.7188 - 15234/T + 3.984 \log(T)$ (P_T in atm). Partial pressures of Pu, N₂, PuN and Pu₂ are also estimated in reference 34.

Thermal conductivity: $15.5 \text{ W.mol}^{-1}.\text{K}^{-1}$.

3.4 Americium Nitride

For minor actinide transmutation, it has been seen in part 2 that americium nitride could be an interesting compound for transmutation, both in fast reactor, in CADRA type core, or in ADS. Depending on the case, it should be considered either as a fuel constituent (together with uranium and/or plutonium) or as a target (with inert matrix).

3.4.1 Fabrication Process

Synthesis of AmN from metal or from hydrides was reported in the 60's and 70's. In case we think of a nuclear cycle based on pyro-reprocessing, americium should be recovered by electrolysis under the metallic form. So, the metallic route for obtaining AmN should be relevant.

Nevertheless, the carbothermic reduction method is again considered as the best one for a possible industrialisation. Synthesis of AmN by carbothermic reduction method was performed at JAERI and the method, hereafter shortly summarised, is reported in ref. 41.

The reaction of carbothermic reduction is expressed by:



The major difficulty in the synthesis of AmN is due to the vapor pressure of pure Am metal, which is high comparing with that of U or Pu. The carbothermic reduction was performed at 1573K for 6120s with a purified N₂ gas stream. After the reduction was completed (no more production of CO detected) the furnace atmosphere was changed to N₂+4%H₂ again for 6120s at 1573K in order to decrease the oxygen and carbon impurities. This temperature is considered as close from the maximum one to avoid the vaporisation loss of americium. So, in spite of this subsequent sweeping, oxygen was detected in the prepared samples, which were analysed by X-ray diffraction. Although no quantitative measurement was performed, it is also thought that residual carbon was not efficiently removed by the N₂+4%H₂ sweeping. Efforts will have to be made to reduce these impurities.

3.4.2 Physical Properties, High Temperature Behaviour

Selected physical properties of americium nitride are reported in Table 5. It will be noted that many basic data are not available.

About the high temperature behaviour, there is a peculiar problem for AmN. The ground state of neutral Am gas atom is so stable that the Am vapour pressure over any Am-bearing substance is significantly high compared with the similar substance of the other actinides. This causes a mass loss problem, particularly during the fabrication stage, in particular during the sintering of the nitride fuel. It is the reason why, in the fabrication process here above described, the temperature was limited to 1573K.

The only study relevant to the vaporisation behaviour of AmN is reported in ref. 30. In fact, this study was made from experimental results on the vaporisation behaviour of a PuN sample, which contained 1.3at% of ²⁴¹Am, as a daughter of ²⁴¹Pu. It is shortly summarised in part 3.9.

3.5 Curium Nitride

Practically, no physical data are available for curium nitride. The molar weight is 261.0067 g. Lattice constant was reported as 0.5041 and 0.5027nm. (see ref. 12). This leads to a theoretical density of 13.6g/cm³ and a heavy atom density of 12.9g/cm³.

3.6 (Uranium–Neptunium) Mixed Nitride

As reported in ref. 3, solid solutions of (uranium–neptunium) mixed nitride were obtained at JAERI by heating mixtures of UN and NpN in a N₂+8%H₂ gas stream at 2023K for 180ks. UN and NpN were previously synthesised by carbothermic reduction method, mixed, and compacted into green pellets. Carbon and oxygen impurities were lower than 0.05wt% in all the fabricated pellets.

Selected physical properties of (U_{0.75}Np_{0.25})N, (U_{0.50}Np_{0.50})N and (U_{0.25}Np_{0.75})N are reported in Table 6.

3.7 (Uranium-Plutonium) mixed nitride

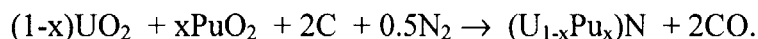
(Uranium-Plutonium) mixed nitrides have been studied for a potential use in fast reactors for the reasons given in part 2. The usual composition is $(U_{0.8}Pu_{0.2})N$. Although we can think to much higher plutonium concentrations in the frame of the CAPRA programme, except otherwise stated, we will deal hereafter with $(U_{0.8}Pu_{0.2})N$ fuel as it is the composition which was the most extensively studied.

3.7.1 Fabrication Processes

Fabrication processes are essentially similar to the ones described for uranium nitride.

For instance, the method used at PSI (Switzerland), following the sol-gel route, is described in reference 15. Very low residual carbon and oxygen impurities were achieved in the final pellets. Micro-spheres with plutonium content up to 75at% were also obtained.

Nevertheless, the carbothermic reduction mentioned as previously described is probably the most interesting method for a potential industrial application. After mixing UO_2 and PuO_2 powders with graphite, the carbothermic reduction is performed at a temperature of 1823K, following the reaction:



For instance, in ref. 19, exactly the same operating parameters as those used for producing uranium nitride were used for mixed $(U_{0.8}Pu_{0.2})N$ and yielded the same quality of pellets (see 3.1.1).

In ref. 1, a detailed fabrication process and the influence of fabrication parameters are reported. First, the UO_2 , PuO_2 and graphite powders were heated respectively under Ar-8%H₂, dry air and vacuum. Then, they were blended and the resulting powder was compacted into disks of 12mm in diameter and 1 to 2mm thick. The carbothermic reduction was carried out at 1823K for 36ks in a N₂-8%H₂ stream. Argon gas was used for heating and cooling, at temperatures under 1673K. Then the (U,Pu)N disks obtained were milled into fine powder, polyethylene glycol was added as a binder (in most cases) and the powder was compacted into green pellets under a pressure of 200 to 400MPa. Sintering was carried out at 1873-2053K for 18ks using either Ar-8%H₂ or Ar or N₂-8%H₂ stream. Wax-type pore former was used for controlling the density of sintered pellets. Depending on the fabrication parameters the final density of sintered pellets ranged from 78.6 to 95.1% of the theoretical density. They contained 0.02 to 0.18wt% of oxygen and 0.11 to 0.30wt% of carbon.

A similar process was used at CEA and yielded average values of 0.05wt% in oxygen and 0.1wt% in carbon as impurities. It is reported in ref. 7, where the mechanism and the kinetics of the reactions are studied.

Finally, we should quote that for studying the effect of fabrication process during irradiation, still from carbothermic reduction synthesis, two other variants were used when fabricating pellets for the NILOC experiment (see section 4.2). One of them, the direct pressing, consisted of cold-compacting the reaction product of the carbothermic reduction in the form of cylindrical clinkers directly into the required shape of the green pellets for sintering. In this way, one grinding dirty step of the conventional route is avoided. The second variant consisted of producing the clinkers in the form of granules, which were directly pressed. The objectives aimed through these variants consisted of taking advantage of the stable clinker structure after synthesis and obtaining a final porosity of 15 to 20%. So,

re-densification under irradiation should not occur and swelling up to high burn-up should be accommodated (ref. 10).

3.7.2 Physical Properties, High Temperature Behaviour

UN and PuN form a solid solution whatever the U/Pu ratio. However, especially in the Pu-rich domain, significant positive deviation from the Vegard's law was observed on the lattice parameters and so the solution cannot be treated as an ideal solution (ref. 39). Selected physical properties of $(U_{0.8}Pu_{0.2})N$ are reported in Table 7.

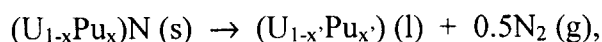
Vaporisation behaviour of (uranium-plutonium) mixed nitrides of various U/Pu ratios was experimentally studied in JAERI and reported in ref. 39. The nitrides were fabricated by the carbothermic reduction method and the vaporisation was studied up to 2000K by using a quadrupole mass spectrometer with a Knudsen effusion cell. The determined partial pressures of U and Pu over $(U_{1-x}Pu_x)N$ are shown in Figure 5. The partial pressure of Pu is much larger than that of U. It might result in the depletion of PuN near the surface layer of a sample in the case of free vaporisation but was not observed in these experimental conditions.

About the free evaporation behavior of $(U_{0.8}Pu_{0.2})N$ mixed nitrides, a calculation is reported in reference 23. It is shown that, at 2000K and as a function of the $N/(U+Pu)$ ratio, the total gas pressure of (N_2+U+Pu) above the mixed nitride exhibits a minimum. This minimum, located in the narrow single-phase region, corresponds to a quasi-congruent evaporation. Considerable amounts of Pu can be lost into the gas phase before the specimens become two-phased., $(U,Pu)N(s)+(U,Pu)(l)$.

One experiment, reported in ref. 19, aimed at determining the initial decomposition temperature of $(U_{0.8}Pu_{0.2})N$. A fragment of pellet was heated up to 3273K under a helium gas flow, with 200K temperature steps. Nitrogen released from the sample was measured through the thermal conductivity change of the flowing gas. Release of nitrogen initiated between 2073 and 2273K, while significant release was observed at 2673 and 2873K. These significant releases are attributed to thermal decomposition with vaporisation of U or Pu metal. The nitrogen pressure in the incoming flowing gas was calculated to be such that $\log(p(N_2),MPa)=-5.7$. So, the detection of initial nitrogen release is quite consistent with the equilibrium nitrogen pressure over UN and PuN, as given in Figure 4.

Another experimental study, reported in ref. 32, helps in understanding the temperature behaviour of mixed uranium-plutonium nitride above 2000K. Several $(U_{0.77}Pu_{0.23})N$ pellets were fabricated by carbothermic reduction method and sintering. The density was 80 to 85% of the theoretical density, residual impurities were about 0.03wt% for carbon and ranged from 0.05 to 0.76wt% for oxygen. The experiments were carried out using a direct electrical heating apparatus allowing a radial temperature gradient within the pellet (5mm in diameter). The duration of experiments varied between 300s and 324ks. The working atmosphere was either helium or nitrogen. The maximum temperature at the centre of the pellet was 2700K. The pellet was observed before and after the thermal test. Up to 2000K, the stability of all the pellets (including those with high values of oxygen impurities forming oxinitride inclusions in the material) was good.

Above 2000 K, important densification and grain growth of the pellets was observed. For experiments under helium atmosphere, a metallic phase represented by uranium-plutonium alloys, segregated into the grain boundaries. This phenomenon is due to the dissociation of the mixed nitride following the reaction:



taking into account that the plutonium-gas pressure over the mixed nitride is much higher than that of uranium gas (see Figure 5). So, the Pu/U ratio changes and a strong Pu depletion was observed above 2200K. The U-rich liquid metallic phase migrated toward the low temperature region, i.e. the periphery of the pellet. The pellets heated under helium collapsed at temperatures around 2500K.

Nevertheless, the experiments performed under nitrogen atmosphere show that, as long as oxygen impurities are not above 0.15wt%, the decomposition of (uranium-plutonium) mixed nitride can be prevented (at least up to 2700K) by replacing helium with nitrogen at atmospheric pressure.

As a summary, we can say that the behaviour of (U,Pu)N pellet under vacuum or under helium atmosphere is complex. Above 2000K, U-rich liquid alloys segregate at the grain boundary due to the simultaneous loss of Pu and nitrogen from the grain surface. However, the process is considered as a rather slow process, which is rate-determined by the atomic transport in the (U,Pu)N matrix. As is the case with UN, at the stage where the liquid phase segregates, the partial pressure of nitrogen is not prohibitively large. Under nitrogen atmosphere, and up to 2700K, the decomposition of (U,Pu)N does not occur.

Finally, although thermal properties of solid (uranium-plutonium) nitride are relatively well known, no experimental data exist about those at liquid state. As for UN and PuN, reference 34 is the only report dealing with them. The properties being estimated from the ones of solid $(U_{0.8}Pu_{0.2})N$, by extrapolation under some assumptions, the following estimated values for the liquid phase should be cautiously considered.

Thermal expansion coefficient: $22.8 \times 10^{-6} K^{-1}$.

Density: $14.36/(1 + 8.65 \times 10^{-5} T)$ (in $g.cm^{-3}$, not far above the melting point).

Heat capacity: $49.9201 + 6.8291 \times 10^{-3} T$ (in $J.mol^{-1}.K^{-1}$, $T \leq 8600 K$).

Enthalpy: $H(T) - H(298) = 43764.2 + 49.9201 T + 3.4145 \times 10^{-3} T^2$ (in $J.mol^{-1}$, $T \leq 8600 K$).

Total vapor pressure over $(U_{0.8}Pu_{0.2})N$ in liquid region:

$\log(P_T) = 3.0073 - 22886/T + 0.98591 \log(T)$ (P_T in atm).

Thermal conductivity: $20.5 W.mol^{-1}.K^{-1}$.

3.8 (Neptunium-Plutonium) Mixed Nitride

As discussed in part 2, (plutonium-minor actinide) mixed nitride and so (plutonium-neptunium) nitride is a relevant material for some CADRA scenarios or for accelerator driven systems. Due to the neighbour properties of Pu and Np, this type of fuel, with relatively small amounts of Np added to Pu (or to the (U,Pu) mixture) could also be used in most of other transmutation scenarios.

(Neptunium-plutonium) mixed nitride pellets of different Np/Pu ratios were fabricated in JAERI by heating mixtures of NpN and PuN previously synthesised by carbothermic reduction from the oxides. The mixed powders were pressed into green pellets under about 300MPa and heated at 2023K in a N_2 -8% H_2 mixed gas stream for 90 to 180ks. The formation of a solid (Np,Pu)N solution was completed in all cases. The lattice parameter increased with PuN content in the solution, but a positive deviation from the Vegard's law between NpN and PuN was observed (ref. 26).

Selected physical properties of $(Np_{0.67}Pu_{0.33})N$ and $(Np_{0.33}Pu_{0.67})N$ are represented in Table 8.

The vaporisation behaviour of (Np,Pu)N was investigated in the range from 1270 to 2010K by Knudsen-effusion mass spectrometry (ref. 3, 26). The pressures of Np(g) showed a similar temperature dependence with that over Np(l), which suggested the precipitation of liquid neptunium during the measurements. On the other hand, rather complicated temperature dependence was found for Pu(g) over the mixed nitride solid solutions. At temperature higher than 1773K, the slope of logarithmic pressures of Pu(g) versus the reciprocal temperature was similar with the pressure over PuN and it depended on the concentration of the solid solution. At temperatures lower than 1473K, the temperature dependence approached that over Pu(l) and the composition dependence was very weak. At intermediate temperatures, a transition stage was observed (c.f. Figure 6). So, although further study is needed, the vaporisation behaviour of (Np,Pu)N seems to have both characteristics of NpN (incongruent vaporisation precipitating liquid neptunium) and PuN (congruent vaporisation).

3.9 (Plutonium-Americium) Mixed Nitride

As discussed in part 2, (plutonium-minor actinide) mixed nitride and so (plutonium-amerium) nitride is a relevant material for some CADRA scenarios or for accelerator driven systems. Furthermore, we should notice that in any case plutonium nitride contains some quantity of americium since ^{241}Am is a daughter of ^{241}Pu .

No synthesis of intentionally added americium in plutonium nitride has been reported.

The only reported study on high temperature behaviour of (plutonium-amerium) mixed nitride is a JAERI study (ref. 30). In fact, it is a subsequent analysis of experimental results obtained when measuring the vaporisation behaviour of PuN by using a mass spectrometer (ref. 39). In this study, the PuN sample contained 1.3at% of ^{241}Am , as a daughter of ^{241}Pu . A large ion signal of mass 241 was noted in the initial heating run on the mass spectrometer. The analysis of the phenomenon, by thermodynamic consideration, yields the following explanation for the vaporisation behaviour of $(\text{Pu}_{0.99}\text{Am}_{0.01})\text{N}$, at relatively low temperature, say 1473K. First, due to its equilibrium vapour pressure and its large diffusion coefficient, nitrogen is preferentially lost from the surface. The N/(Pu+Am) ratio decreases and as in the same time Am vapour pressure has significantly increased, AmN congruent vaporisation can occur. Therefore, in a second step, americium and nitrogen are preferentially lost versus plutonium ($0.9976 > \text{N}/(\text{Pu}+\text{Am}) > 0.9855$ at 1473K). Finally, the N/(Pu+Am) ratio reaches a point where the PuN component (which is in great excess due to americium depletion at the surface during the second step) vaporises congruently.

3.10 (Plutonium-Curium) Mixed Nitride

As discussed in part 2, (plutonium-minor actinide) mixed nitride is a relevant material for some CADRA scenarios or for accelerator driven systems.

$(\text{Pu}_{0.6}\text{Cm}_{0.4})\text{N}$ has been recently synthesised in JAERI (ref. 42) by the carbothermic reduction method. The starting material was $(\text{Pu}_{0.6}\text{Cm}_{0.4})\text{O}_{2-x}$, which resulted from an original CmO_2 batch kept for 30 years, thus allowing formation of ^{240}Pu from ^{244}Cm . As described for other nitrides, an excess of carbon was used. C/(Cm+Pu) molar ratios of 3.2 and 1.6 were tested. The carbothermic reduction was performed at 1773K in a nitrogen gas flow for 14.4ks. Then a subsequent heating with N_2 -4% H_2 gas was performed for 14.4ks to remove the residual carbon. Finally a 18ks heating at 1743K in nitrogen was performed. A

solid solution was obtained, although Cm and Pu oxides were detected when the excess of carbon was the lowest.

The lattice parameters measured from this fabrication was 0.4948nm when the largest excess of carbon was used. This value is in reasonable agreement when applying the Vegard's law with the values reported for PuN and CmN, suggesting an ideal solution between these two nitrides. A higher lattice constant (0.497nm) was measured for the sample synthesised with the lowest carbon excess, suggesting that some oxygen was dissolved in the material.

3.11 Actinide Nitride and Inert Compounds

As discussed in section 2, the combination of minor actinides and an inert matrix under a nitride form can be interesting both as minor actinide targets (e. g. (Am,Zr)N or (Am,Y)N) or as a fuel in which minor actinide should be the major component (e.g. (Pu,Am,Zr)N) both for CADRA cores and for accelerator driven systems.

Currently very few data exist on these materials.

3.11.1 (Uranium-Zirconium) Mixed Nitride

Data on (Uranium-Zirconium) mixed nitride are interesting as a representative of other (Actinide-Zirconium) mixed nitrides. Nevertheless, as it is not directly relevant to transmutation technology, we give hereunder a very short summary.

(Uranium-Zirconium) mixed nitride was fabricated in PSI (Switzerland) following the sol-gel route. A description of the fabrication process can be found in references 15 and 35. In the latest reference, the impurity levels are given and both carbon and oxygen contents are high (around 2% in most of the cases) and so the final product was indeed a mixture of (U,Zr)(N_{1-x}C_x) and (U,Zr)O₂.

In Russia, (Uranium-Zirconium) mixed nitride was studied and some sparse data (thermal conductivity, Young's modulus, creep) were made available to CEA through a collaboration agreement with MINATOM.

3.11.2 (Plutonium-Zirconium) Mixed Nitride

Fabrication and characterisation of (Pu,Zr)N was performed at JAERI for providing basic information for evaluating feasibility of nitride fuel for the ADS (ref. 4, 5 and 6).

Plutonium nitride was prepared by carbothermic reduction of PuO₂ and ZrN powder was bought from a manufacturer. PuN and ZrN powders were mixed and compacted into thin disks and heated in N₂-8%H₂ mixed gas stream at 1673K for 18ks for homogenisation. The previous procedure was repeated three times. Then, the disks were ground, compacted into green pellets and sintered in Ar gas stream at 2003K for 18ks. Finally, the pellets were heated again in N₂-8%H₂ mixed gas stream at 1673K for the control of stoichiometry. Plutonium concentrations were 40 and 60wt%. Solid solutions were obtained and the lattice parameters followed the Vegard's law between PuN and ZrN. Lattice parameters of 0.4643 and 0.4712nm were measured for Pu concentrations of 40 and 60wt%, respectively. The density of the pellets was 90-95% of the theoretical density. Carbon and oxygen impurities, higher than for PuN were mainly attributed to the starting ZrN powder. Carbon (0.25wt% in the case of 60wt% Pu) is assumed to be dissolved in (Pu,Zr)N, while oxygen (0.44 and 0.94wt% in the case of 40 and 60wt% Pu, respectively) was mainly in a oxide phase, detected by X-Ray diffraction. Finally, in supplementary experiments, the oxygen content of (Pu,Zr)N could be lowered to about 0.2wt.% by adding small amount of carbon before initial mixing.

Thermal conductivity of (Pu,Zr)N was also measured at JAERI (unpublished results). For instance, we can give the following values for (Pu_{0.4}Zr_{0.6})N: 10.1 W.m⁻¹K⁻¹ at 1000K, 11.8 W.m⁻¹K⁻¹ at 1200K, 13.0 W.m⁻¹K⁻¹, at 1400K and 13.9 W.m⁻¹K⁻¹ at 1600K.

Fabrication and characterisation of (Pu,Zr)N pellets is also planned in PSI (Switzerland) in the frame of a PhD thesis co-funded by CEA and PSI. The Pu/Zr ratio should be 20/80. Two fabrication processes are planned: one similar to that already used in JAERI; another in which the carbothermic reduction should be applied to (Pu,Zr)O₂ micro-spheres with carbon, obtained by sol-gel process from carbon and Pu(NO₃)₄⁻ and ZrO(NO₃)₂⁻ solutions.

3.11.3 Other Actinide Nitride and Inert Matrices

PuN pellets containing TiN as an inert matrix were recently fabricated and characterized in JAERI (ref. 6). The fabrication process was exactly the same as for (Pu,Zr)N (see previous part). Plutonium concentration was 50wt%. Two separate phases were identified: a PuN phase and a TiN phase. It was calculated from the lattice parameters that 0.7at% of PuN only dissolved in TiN and 0.3at% of TiN in PuN. The density of the pellets was 76% of the theoretical density only. Carbon and oxygen impurities, higher than for PuN were mainly attributed to the starting TiN powder. Most of oxygen impurities (0.76wt%) are contained in an oxide phase. Fabricating PuN (then PuN plus minor actinide nitrides) pellets containing TiN as an inert matrix, such as they could be suitable for transmutation purpose (higher density, etc...) would require further improvements. It looks preferable in a first step to concentrate on different material as (Pu,Zr)N.

As yttrium is well known for its stabilising properties, (Am_{0.1}Y_{0.9})N was recently synthesised in JAERI in order to evaluate its properties. Of course, (americium-zirconium) mixed nitride is also a promising compound, but it has not been synthesized yet.

4. BEHAVIOR UNDER IRRADIATION

Irradiation experiment results of nitride fuels are rather sparse. Up to now, only UN, PuN and mixed (U,Pu)N fuels have been irradiated. Some plans for irradiating (Pu,Zr)N are foreseen. After a description of the different fuel concepts to be envisaged, available results from CEA, from JAERI and from others are presented.

4.1 Fuel Concepts to Be Envisaged

Three major aspects have to be taken into account for designing a fuel element for nitrides (ref. 21).

- The good thermal conductivity of nitride fuels allows operating as "cold fuels". So the nitride fuels should keep a rather large margin as regards their maximum operating temperature. In order to preserve this advantage, the concepts considered up to now are based on a rather small gap between the fuel and the clad. It was possible to obtain high linear powers, which could not be reached with oxide fuels. A core concept with fatter and fewer pins compared to oxides could be another way to take advantage of the good thermal conductivity of nitride fuels.

- As discussed later on in this report, one of the major problems with nitride fuels is the swelling rate, which is higher than for oxide fuel: the necessary space for accepting this swelling should be designed.
- Both in a breeding objective and in a CADRA dedicated core objective, one of the major advantages of nitrides is their large heavy atom density (see Figure 2). To preserve this advantage the smear density of the fuel should be high enough. As this objective is contradictory with the previous one, a compromise should be found.

From these considerations, several fuel designs can be considered. We will give some more details for the helium-bonded and sodium-bonded pins, as there are the only ones for which irradiation experiments and safety evaluation have been reported. Complementary information can also be found in ref. 23.

4.1.1 Sodium-Bonded Pins

This concept consists of filling the pellet-clad gap with sodium. Due to the excellent thermal conductivity of sodium, the advantage provided by the good thermal conductivity of nitride fuel can be fully exploited. The pellet-clad gap can be large, while still having a low surface temperature of the fuel. So swelling, which should be reduced due to the low temperature, can be accommodated and a high pellet density (about 90-95% of the theoretical density) can be chosen. Furthermore, the fuel temperature should remain quasi-constant throughout the irradiation.

This solution was not chosen as a reference for the French programme because of difficulties for manufacturing and reprocessing, and for potential safety problems, as loss of sodium bond. Such a loss could result either from a crack in the clad, or from partial sodium boiling and bubble formation, or from formation of fission gas bubbles within the sodium bond during an eventual transient.

This concept should allow obtaining higher burn-up than the helium-bonded concept. The question to be answered is: "Can the sodium be acceptable both for reprocessing and for safety?"

4.1.2 Helium-Bonded Pins

Due to above-mentioned difficulties with the sodium-bonded pins, the gas-bonded pin concept was elaborated and used in many experiments. In this concept, helium is chosen for its good thermal conductivity, compared to other gases, and for its (chemically) inert characteristics. Anyway, a pellet-clad gap of 100 to 250µm is regarded as a maximum to avoid too high surface temperatures. The porosity is uniformly distributed within the fuel. This concept is suitable for a smear density of 75-80%, with pellet densities of 80-85% of the theoretical density. Lower density pellets would probably not withstand irradiation, while higher density pellets could probably not withstand a high burn-up because of swelling (see sections 4.2 to 4.4).

This concept was the reference concept of the French nitride programme (see section 4.2), launched in 1985, with its two variants as regards linear power: 45kW/m (as for oxides) or 73kW/m. As it will be discussed later in this report, with such a concept, an initial pellet-clad gap of 100µm is usually closed at 2-3at% burn-up and the fuel-clad mechanical interaction has to be considered during most of the irradiation when designing the clad (thick clad). This behaviour leads to a large temperature decrease of the fuel at the beginning of the irradiation. Usually, initial temperature is basically 500K more than with sodium bonding.

Then, when the gap is closed, the temperature becomes comparable to the case with sodium bonding.

4.1.3 Nitrogen-Bonded Pins

Although only very sparse experimental data are available on this concept, it can be an alternate to helium-bonded pins. Indeed, thermal conductivity of nitrogen is poorer than the one of helium, so it would lead to higher fuel temperature.

Nevertheless, as explained in section 3, high temperature dissociation of some nitrides can be prevented under a nitrogen pressure. For instance, for uranium nitride, the plenum volume of the fuel element may be adjusted in order to achieve equilibrium of slightly nitrogen-deficient UN and an acceptable pressure of nitrogen. For mixed uranium-plutonium nitrides, as stated in section 3.7.2, under nitrogen atmosphere, and up to 2700 K, the decomposition of (U,Pu)N does not occur.

4.1.4 Venting Pins

The leading idea for this concept consists of "opening" the fuel pins in order to release the fission gases. It assumes excellent fuel-coolant compatibility, which is the case for nitride and sodium. In such a concept, the clad cannot play anymore its function of safety barrier. So, another barrier has to be envisaged in the reactor design.

Such a pin should be associated to sodium bonding. So, the pin plenum could be suppressed, and the pin could be shorter. In fact, the balance between this advantage and the drawbacks of such a concept (necessity to clean up the upper plenum of the vessel, safety barriers...) is not straightforward. A complete technical and economical study only, should allow seeing if it can be developed. Currently, it is not considered as a priority.

4.1.5 Vibro-Compacted Fuels

Most of the time, whatever the pin design is, the pin is filled with pellets, either regular or annular pellets. The diameter is chosen slightly smaller than the inner pin diameter for mechanical reason when fabricating and to accommodate the fuel swelling during irradiation. Of course, the pellet fabrication is a well-known process and most of the irradiation experiments are performed with pellets. Nevertheless, at least one other concept has to be mentioned: it is the vibro-compacted fuel concept.

It consists of filling the pin with granulates, then vibrating the pin to compact these small fuel spheres. The sol-gel process was successfully used at PSI (Switzerland) to fabricate such nitride granulates. Experience on vibro-compacted fuel was also gained in Russia, including irradiation experiments.

The foreseen advantages of such a method are:

- an easier fabrication process, without grinding, so without pollution of the hot cells (or glove-boxes) by actinide dust.
- no problem for accommodating swelling within the pin.
- the fuel temperature should be still lower than with a pellet concept. Due to the vaporisation behaviour of AmN, this could be interesting for some advanced fuels containing large amounts of AmN.

Anyway, to obtain a smear density of about 80% with spherical particles, different particle sizes have to be used: "big" particles of several hundreds of μm and "small" ones of some tens of μm . Nevertheless, in case of a clad failure, we should guarantee that no "small"

particle could escape. Finally, a smear density higher than 80% cannot be achieved and it could be prohibitive for using such a concept in view of actinide burning.

4.2 Irradiation Results from CEA

In France, the first irradiation experiment of nitride fuels was performed in the RAPSODIE reactor at Cadarache. It consisted of irradiating three sodium-bonded pins at 750W/cm and 3.1at%. No failure was observed, and the global behaviour was very similar to those of carbide fuels, which were irradiated in the same experiment.

Then another programme was launched in 1985, in collaboration with ITU Karlsruhe. The objective was to demonstrate the capability for nitrides to achieve high burn-up. ($U_{0.8}Pu_{0.2}$)N fuel in He-bonded pins was used.

Preliminary experiments NILOC 1 and NILOC 2 were performed in the HFR reactor in Petten (the Netherlands) in 1986-1987 to study beginning of life (BOL) in-pile behaviour up to 0.5at%. The fabrication process (see part 3.7.1) of the pellets and the initial size of the fuel-clad gap (and so of the initial fuel temperature) were the main parameters studied. In fact, the linear powers were higher than expected (up to 106.5kW/m) and in most of the cases, the inner fuel temperatures were calculated to be in between 1773 and 2173K. So, data on the high temperature behaviour of nitride fuel could be gained.

In NIMPHE 1 experiment, 11 pins were irradiated in a capsule, in the PHENIX reactor at Marcoule. The linear power was about 45kW/m and a burn-up of 7at% was reached. Non-destructive post irradiation examination (PIE) was performed for one pin only. The main conclusion was that the pellet-clad gap was closed (large swelling). The remaining pins were supposed to be re-irradiated in PHENIX (NIMPHE 1bis) to achieve a higher burn-up. Finally, because of priority choices in CEA and because of PHENIX problems the idea of re-irradiating these pins was abandoned.

In the NIMPHE 2 capsule, 5 nitride pins and 2 carbide pins (with different geometry than in NIMPHE 1) have been irradiated at about 73kW/m and now, a burn-up of 6.3at% has been achieved. No examination has been performed yet. The capsule is still in PHENIX. When the reactor re-starts, it could be possible to pursue the irradiation in order to achieve a higher burn-up.

Anyway, from these very sparse experimental results, and also from the knowledge of other experiments described in next parts, the following specific points could be deducted about the in-pile behaviour of ($U_{0.8}Pu_{0.2}$)N fuel (ref. 21).

The concept of "cold fuel" was confirmed. For instance, in NIMPHE 1, calculations were performed with a linear power of 40kW/m. The calculated fuel temperatures were 1473K for the inner temperature and 1273K for the surface temperature. In NILOC 2, for a linear power of 100kW/m, the inner temperature was 2173K and the surface temperature was 1773K, still far below the melting temperature in spite of this very high linear power. Anyway, it should be kept in mind that in the case of nitrides, even below the melting temperature, vaporisation behaviour could be a safety concern (see section 5).

At low temperature (let's say under 1500K) the free swelling rate of nitride fuel is practically temperature independent: about 1%/at% (to be compared to 0.6%/at% in the case of oxide fuel). Then, the swelling rate increases with temperature. Of course, this swelling rate decreases when the fuel-clad interaction occurs. In a He-bonded pin, as in NIMPHE, due to swelling, the initial fuel-clad gap of 230µm was closed at about 5at% burn-up. Then the

fuel is really at low temperature. Calculations performed in the frame of NIMPHE 1bis showed that the mechanical interaction is still acceptable up to 15at%. Anyway, as during most of the irradiation duration the fuel-clad interaction occurs, the pin design should consider enough void (usually as pellet porosity) to accommodate the swelling. So, in order to achieve high burn-up, the smear density should remain rather low. In the case of the NIMPHE experiment a 15at% burn-up was aimed with a smear density of 78%. To achieve 20at%, a smear density as low as 70% should probably be used. In the case of a sodium-bonded pin, the gap should be large enough to avoid fuel-clad interaction throughout the irradiation. Finally, as a result of the NILOC experiment, it was shown that besides the porosity, the thermal stability of the pellet should be quantified. In fact in the NILOC experiment the pellets fabricated through the conventional route showed some densification. The pellets fabricated from direct pressing of the clinkers from the carbothermic reduction in the form of granules did not densify. So the open porosity could be kept, it should allow fission gas release and smaller swelling rate (ref. 10).

Linked to its higher swelling rate, compared to oxide, nitride fuel releases less fission gases. For instance, at 10at% the release rate is less than 30% (to be compared to oxide: 80 to 85%). Anyway, at higher burn-up (over 15at%), even with nitride fuel, the release rate should become significant and a sufficient expansion volume should be preserved when designing the pin (except if we think of venting pins). Furthermore, if non-enriched nitrogen were used, nuclear reactions on ^{14}N should produce about 16% of additional gas.

As the sesquinitrides do not exist a chemical reaction between the fuel and the clad is unlikely. However, experimental results to confirm this good compatibility with the clad are very sparse. In the early experiments performed in the RAPSODIE reactor, a hardening, linked to internal nitridation with cracking was observed on the hottest part of one of the pins. All the NIMPHE 1 micrographic examinations show an intact clad at 5at%. A good compatibility was also observed in Russia, up to 10at% in the BOR60 reactor. Nevertheless the good fuel-clad compatibility should be checked for very high burn-ups.

As already mentioned in section 2.1, the excellent compatibility of nitride fuel with sodium is a supplementary advantage as regards a potential clad failure. The only reaction with the coolant should be a very slow reaction with oxygen impurities contained in the sodium. Nevertheless, at very high burn-ups, the absence of reaction with some fission products should be checked.

High temperature behaviour of actinide nitride was described in section 3. As an illustration, we can quote that in the NILOC experiments, auto-radiographic examinations showed that, when the fuel inner temperature was over about 1900K, a radial redistribution of plutonium occurred: lower content at the centre, enrichment at the periphery. The appearance of a metallic phase looks possible only above a high temperature, which has to be determined. However, it is probably above 2200-2300K.

4.3 Irradiation Results from JAERI

Although there was a small irradiation program of UC, U(C,N) and UN in the beginning of the 70's, the practical irradiation campaign of nitride fuel at JAERI started in 1990. So far the irradiation of four (U,Pu)N fuel pins in two capsules was completed in the Japan Material Testing Reactor (JMTR). The post irradiation examinations were carried out in the Reactor Fuel Examination Facility of JAERI.

The first capsule (88F-5A) contained two He-bonded (U,Pu)N fuel pins with different gap width between pellet and cladding. The cladding material was 316-type austenitic steel with 9.40mm in diameter and 0.51mm in thickness. Temperature change in the fuel pellet was monitored by a thermocouple inserted into the pellet by micro-drilling technique. The second capsule (89F-3A) contained two He-bonded (U,Pu)N fuel pins with different cladding material: 316-type austenitic steel and ferritic steel with similar dimensions as mentioned above. Mixed nitride (U,Pu)N pellets were prepared by carbothermic reduction of $0.8\text{UO}_2 + 0.2\text{PuO}_2$ mixtures. The oxygen and carbon impurities were analysed to be around 0.1-0.2wt%, which are typical values for technological grade of (U,Pu)N fuel. The pellet density was controlled at ~85% to mitigate fuel-cladding mechanical interaction at higher burnup. A “thermally stabilised pellet”, in which relatively large pores are dispersed in a high-density fuel matrix, was used in this irradiation campaign. Accordingly, the smear density of the fuel pin was controlled at ~80% of the theoretical density.

The maximum burn-up and linear heat rate of the fuel pins were estimated at 4.1at%, 65kW/m in the 88F-5A capsule, and at 5.5at%, 73kW/m in the 89F-3A capsule. The maximum temperature of the fuel pellet at beginning of life is calculated at 1573-1673 K. No failure was observed in the irradiated fuel pins.

The results of the post irradiation examinations were described in detail in JAERI technical reports (in Japanese) and published in ref. 2 and 3. Typical results are summarised below.

(1) Fuel irradiation performance up to 5.5at% was demonstrated under the irradiation condition.

(2) Temperature decrease in the centre of the pellet with increasing burn-up was observed. Initially this temperature was about 1673K, then it decreased to about 1473K. This suggested that the initial gap was closed due to the swelling of fuel pellet, yielding an increase of gap conductance.

(3) Distribution of actinides and solid fission products almost corresponded to those estimated from neutron fluence. Caesium only exhibited a migration to lower temperature region.

(4) The increase of fuel pin diameter at the maximum reading point was 0.04mm ($\Delta D/D=0.4\%$), which suggests that significant fuel-cladding mechanical interaction did not occur yet under the irradiation condition.

(5) The macro-structure of fuel pellet changed from that of before irradiation. It might be caused by the inhomogeneity of relatively large pores artificially introduced in pellet fabricating stage. A restructuring might be accelerated by in-pile densification in the beginning stage of irradiation.

(6) However, fission gas release (FGR) was only 2-3%, which corresponds at less than 1%/at%. In addition to the low fuel temperature, low open porosity in the pellet could contribute to this extreme low FGR.

(7) Contrary to the macro-structure, there was little difference in the micro-structure of (U,Pu)N fuel matrix observed before and after the irradiation.

(8) Pellet swelling rate calculated from the change in pellet density was 0.5~1.0%/at%. This value was considered to involve the contribution of both free swelling before the contact of pellet and cladding and constraint swelling after the contact.

(9) The inner surface of austenitic and ferritic stainless steel did not show any sign of chemical interaction with fuel pellet under the irradiation condition.

Following the irradiation tests of (U,Pu)N fuel at JMTR, an irradiation experiment at the fast test reactor JOYO was started in 1994 under the joint research programme of JAERI and JNC. Two He-bonded (U,Pu)N fuel pins, in which Pu/(U+Pu) ratio is 19.3wt% (18.6at%), were fabricated in JAERI using the similar manner as the fuels irradiated at JMTR. In this case, however, ^{235}U enriched uranium up to 19.39wt% was used to secure enough linear power. Austenitic steel tube with 8.5mm in diameter and 0.45mm in thickness was used for cladding material. Fuel stack length of each (U,Pu)N fuel pin is 200mm. The fuel pins assembled into a special irradiation rig were irradiated at JOYO for 5 cycles until September 1999.

The maximum linear power and burn-up were estimated at 78kW/m and 4.5at%. Non-destructive post irradiation examinations were started in the end of 1999 and no failure of (U,Pu)N fuel pins was detected. Destructive post irradiation examinations have been carried out in hot cells of both JAERI and JNC since the second half of 2000.

Furthermore, the irradiation of U-free nitrides such as PuN pellets containing so-called inert matrix nitrides such as ZrN and TiN are planned. One or two fuel pins encapsulated will be irradiated at JMTR from the first half of 2002. The design study of the fuel and licensing of the irradiation is underway.

4.4 Other Irradiation Results

A summary of American experimental results about the irradiation of nitride fuels is provided in ref. 22.

UN had been developed in the USA since the sixties, as a candidate fuel for space nuclear reactors. Over 100 helium-bonded pins were irradiated in thermal reactors with various parameters as cladding nature, cladding temperatures, burn-ups (up to 4.5at%), fuel densities (80 to 96% of the theoretical density), grain sizes and stoichiometries. Then, approximately 90 UN pins were tested in the EBR-II and FFTF fast reactors. Some trends were drawn from these irradiation results. No pin failure occurred in spite of relatively high test-temperatures (up to 1900K fuel centreline). Metallic fission products, mainly ruthenium, migrated to the fuel pellet surface and into the cladding. High-density fuels released less fission gas than low-density fuels. Large fission gas pores formed in the centre of low-density UN fuel pellets, while the high-density fuel showed no evidence of restructuring or cracking.

On the other hand, over 140 (U,Pu)N fuel pins were irradiated as part of the U.S. Liquid Metal Fast Breeder Reactor (LMFBR) programme. The variable parameters were the pin concept (cladding material and thickness, He and Na bonding, with and without shroud tube), the nitride density (80 to 90% of the theoretical density), the smear density (75 to 86% of the theoretical density), the linear power (67 to 107kW/m), the cladding temperature (825 to 950K) and the burn-up. Some pins failed in the earliest experiments, probably due to fuel-cladding mechanical interaction or to defective welds. Indeed, the failures occurred mainly in pins with small gaps and high smear density. Some of them were apparently related to high temperature fuel swelling. Mixed nitride fuel showed relatively low fission gas release (usually around 10%), and swelled at approximately 1.5vol%/at%. Unfortunately, results of the most successful irradiation test (the K-4 test) are not available. In this test, 8 (U,Pu)N pins (fuel density: 96.8% of the theoretical density, smear density 79.4%) achieved a 9.6at% burn-up without failure. The linear power was 85kW/m, while the cladding temperature was 825K.

Only very few irradiation experiments, quoted in ref. 13, were performed on PuN. They were performed at Hanford (the U.S.A.) in the sixties. Three small PuN wafer samples were irradiated in the MTR reactor at estimated surface heat fluxes as high as $950\text{W}/\text{cm}^2$. The sample density was greater than 95% of the theoretical density. Preliminary post-irradiation examination results are available on one PuN sample, which was irradiated at an estimated average burn-up of 20×10^{20} fissions/ cm^3 . Visual examinations of the sample indicated initial melting followed by immediate re-solidification when good contact was made with the aluminium heat sink. No obvious micro-structural changes of the non-melted portion of the sample occurred during the irradiation. The X-ray diffraction pattern of the irradiated PuN sample suggests severe lattice damage.

In addition, several nitride fuel irradiation experiments were performed in Russia. For example, $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ was irradiated in the BOR60 reactor at $100\text{kW}/\text{m}$. It is likely that 4at% burn-up was achieved with apparently no problem. Unfortunately, no detailed information is available.

5. EVALUATION OF NITRIDE SAFETY

5.1 General Remarks

As reported in the previous section, nitride fuel shows good irradiation behavior up to about 10at% burn-up, under steady condition. However, due to the high temperature properties of actinide nitrides, as described in section 3, concerns are given on their behavior under transient and accidental conditions. These concerns include:

- A metallic liquid phase can appear on the surface of fuel pellets, which could result in fuel-cladding chemical interaction (FCCI).
- Vaporized gaseous species, especially $\text{Pu}(\text{g})$, may condense onto the inner surface of the cladding tube.
- Fission product gas contained in fuel pellet causes a high swelling with increasing temperature, then an abrupt release into the plenum can occur.
- In core disruptive accident (CDA) scenarios, if very high temperature are reached, severe fuel-coolant (Na) interaction may happen.
- In CDA scenarios, dissociated nitrogen gas causes pressure increase in reactor vessel up to several tens of bars.

Well-known U-N phase diagram indicates a rather narrow single phase region of UN. For example, a slight decrease of N/U ratio from unity results in phase transition into two-phase region of $\text{U}(\text{l})+\text{UN}(\text{s})$. However, UN exists as a single phase over very wide range of nitrogen pressure. This indicates that properties of "single-phase" UN may depend on the nitrogen partial pressure equilibrated with UN. Although some reports concern about the pressure increase in the fuel pin or reactor vessel, nitrogen partial pressure over $\text{U}(\text{l})+\text{UN}(\text{s})$ is not so high, for example, about 10^{-3}atm at 2500K . So, the pressure in the system where $\text{U}(\text{l})+\text{UN}(\text{s})$ exists can not exceed this equilibrated nitrogen partial pressure. The same remark applies to PuN except for the non-existence of higher nitrides such as Pu_2N_3 and PuN_2 .

As indicated in section 3, we can find many reports dealing with vapor pressure measurements over nitride fuel under equilibrium condition and phase relations of U-N

system. On the other hand, there are few reports dealing with phase relationships of Np-N, Pu-N, Am-N and Cm-N systems and several reports are dealing with thermal and thermodynamic properties of solid UN, PuN and (U,Pu)N. Then we can find only two reports dealing with nitride behavior over 2273K (ref. 19 and 32, already quoted in section 3.7.2). Thermal and thermodynamic properties of solid UN, PuN and (U,Pu)N at liquid state are seen only in reference 34, which deals with density, heat capacity, enthalpy, vapor pressure, thermal conductivity and viscosity. Furthermore, we must note that these data at liquid state are not experimentally measured but estimated by extrapolation under some assumptions and so, they should be very cautiously considered. In addition to high temperature behavior under equilibrium condition, phenomenal and kinetic study is important in assessing the safety aspects.

As it was mentioned in section 4, Matzke described the in-pile behavior of (U,Pu)N pellets in detail in his well-known book, Science of Advanced LMFBR Fuels (ref. 23). The vapor pressure of Pu(g) over (U,Pu)N is much higher than that of U(g). Therefore, selective evaporation of Pu(g) and N₂(g) should occur at the surface and at grain boundaries of (U,Pu)N fuel pellets. This behavior differs from that of UN (for which a precipitation of U liquid phase occurs) and it can explain the Pu depletion at the surface of (U,Pu)N observed in the experiments. This is possibly a Pu diffusion-controlled process in the solid phase. In parallel, the N/(U+Pu) ratio is expected to change until the total pressure of U(g), Pu(g) and N₂(g) comes to a minimum (see section 3.7.2). Then considerable amounts of Pu can be lost into the gas phase before the specimens become two-phased, MN(s)+M(l). At the point of precipitation of liquid phase, the equilibrium pressure of N₂(g) becomes rather low.

The evaluation of nitride fuel safety depends on many factors. Of course, it depends on the type of reactor (fast breeder, fast actinide burner, ADS, ...), on the core design, on the precise geometry of the reactor. Then, a fundamental element is the type of nitride fuel (composition of the mixed nitride, ¹⁵N enrichment...). Indeed, we have seen in the previous parts that some nitrides may exhibit rather different high temperature behaviour. Finally, considering a fuel at beginning of life or end of life can also lead to different results because of many structural and chemical changes during the irradiation. In fact, very few studies are available on the evaluation of nitride fuel reactors. They are presented in this section.

5.2 Reactor Safety under Normal and Off-Normal Transient Conditions

5.2.1 Specific Behaviour of Nitride Fuel

Independently of the type of reactor considered, a recent British study relevant to the safety of nitride fuels in normal and transient conditions (ref. 24) is summarised hereunder.

First, the kinetics of vaporisation was assessed through specific calculations. Gas phase transport through the fuel along the interconnected pores was modelled by solving transport, diffusion and mass conservation equations. It is to note that basic data, mainly on (Zr_{1-x}Pu_x)N was missing and assumptions were made. So the presented results may depend on some of these assumptions, as for instance the Xe fission gas release, which is of critical importance for calculating the pellet swelling. In such a calculation, transient temperatures are not calculated from neutronic data and as a function of an unprotected event, but they are a priori estimated. A maximum inner temperature of 2250K was assumed during the transient, at the inner surface of the annular pellet. The temperature was assumed to come back to initial temperature (1250K) within 2s. As a result and globally speaking, the high temperature behaviour described in section 3.7.2 is confirmed. (U_{0.8}Pu_{0.2})N fuel is stable under normal

operating conditions. Anyway, due to assumptions made (mainly fuel evaporation rate and Xe release rate), it is concluded that further detailed investigation should be required to assess the behaviour under temperature transients.

Besides this high temperature behaviour study, the paper presents a performance study of nitride fuel, using the NITRAF code, which is based on the TRAFIC code -previously used for oxide fuel performance evaluation- but specially dedicated to nitride fuels. $(U_{1-x}Pu_x)N$, PuN and $(Zr_{1-x}Pu_x)N$ fuel pellets were considered, in nitrogen gas atmosphere. Scoping calculations allowed concluding that a $(Zr_{0.61}Pu_{0.39})N$ fuel pin with 700 μ m cladding should survive up to 40at% burn-up, either at 70kW/m or at 55kW/m of initial linear power (decreasing respectively to 50 and 35kW/m at end of life).

5.2.2 Fast Breeder Reactors

Studies about the behaviour of a large fast-breeder nitride core during unprotected transients were performed at CEA in the frame of the European Fast Reactor (EFR) programme. Preliminary general tendencies, compared to oxide cores, were first given in reference 21. Then they were reported in reference 11. It should be noted that the dissociation behaviour of the nitride fuel was not taken into account, so some results have to be cautiously considered, and further analysis is needed.

- In case of a rapid Unprotected Loss of Flow (ULOF) driven transient, similar phenomena occur for the nitride core and for the oxide core. The positive (sodium density and Doppler) and the negative (expansion of the control rod supports) feedback effects equilibrate so that the net reactivity becomes zero. The reactor reaches an equilibrium state with a reduced power level and a cooling by natural convection. However, for the oxide core, the large positive sodium density feedback effect and the large negative Doppler constant play an unfavourable role. The sodium reaches its boiling temperature at its maximum. Although its positive sodium density effect is as important as for the oxide core, the nitride core exhibits a more favourable behaviour. Therefore, the sodium maximum temperature is lower than for the oxide core: the sodium should not boil.
- In case of a slow unprotected transient overpower (UTOP) with a nitride core, the power increase is more rapid, the fuel temperature is lower, the sodium and cladding temperatures are higher than for an oxide core. Fuel melting is delayed compared to oxide but sodium boiling and cladding failures could be reached earlier. Nevertheless, the favourable aspect of this behaviour is that an increase in sodium temperature could help for a rapid detection of the incident.
- In case of an unprotected fast transient overpower (UFTOP), the peak power and the fuel temperatures are much smaller with a nitride core compared to an oxide core. Therefore, the nitride core provides a more efficient Doppler feedback effect during the transient and a substantial margin to melting after transient.

A recent safety analysis in transient conditions, for a nitride core, sodium-cooled, 1500MWe, fast breeder reactor is presented in ref. 18. A 99.9% ^{15}N enrichment is assumed and the operating linear power was chosen to 27kW/m to really use the concept of cold fuel and to enhance the safety margins. Both He-bonded and Na-bonded pins concepts are studied. As a result of the calculations, any unprotected event considered in this study -Unprotected Loss of Flow (ULOF) and Unprotected Transients Overpower (UTOP)- yields a quick return to a safe steady state situation, with an intact core geometry and without coolant (sodium) boiling. This is mainly due to the very good "self-controllability" of the nitride core (passive

shutdown capability induced by the inherent negative feedback reactivity). For example, in the ULOF case, as the flow rate decreases, the temperatures of coolant and cladding increase and the negative feedback reactivity effect of core radial expansion and control rod axial expansion decreases the core power. So, the core temperature decreases and the maximum calculated sodium temperature is 1147K, to be compared to sodium boiling point: 1203K. In the UTOP case, safety criteria are still fulfilled but the fuel temperature reaches 2033K. Regarding the pin concept, sodium-bonded pin is safer at ULOF, while helium bonded pin can be better at UTOP: both of them are practicable as regards the safety aspect.

So, more studies about the behaviour of nitride fuels under transient conditions should be recommended, with focus on non-boiling condition of sodium coolant. But it looks that the behaviour of a nitride core should be safe as regards transient conditions.

5.2.3 Fast Burning Reactors

Preliminary studies about the behaviour of a CAPRA type nitride core during a transient were performed in France. A 3600MWt core was considered. First, behaviour versus core loading variations was calculated. Then ULOF and Unprotected Loss of Heat Sink (ULOHS) driven transients were calculated. Many hypotheses were necessary. The following general tendencies, compared to oxide cores, are reported in ref. 21:

- In case of loading variations due to secondary pumps speeding-up or to reactivity increase, the nitride core quickly comes back to a stable operating condition. At the end of the transient, both temperature and power are slightly lower than for an oxide core.
- At ULOF, thanks to more favourable feedback coefficients (higher Doppler and lower sodium void), thermal power decreases from the beginning of the transient (and faster than for an oxide core). It is to note that these good results are independent of the calculation hypothesis and are really due to the intrinsic properties of the nitride fuel.
- At ULOHS, all the steam generators are dried and very high temperatures can be reached on some structures. The calculation of such a "slow" transient depends on the core and reactor design. Here a CAPRA oxide type core was chosen. The result is that a long time is necessary before getting general boiling, while general boiling would be reached in one hour and a half for a European Fast Reactor (EFR).

The first tendencies from this study are favourable for the nitride core. It reacts more quickly than an oxide core (less inertia) and in any case, maximum temperatures and powers are lower. However, these preliminary calculations involved many hypotheses and they should be confirmed.

Finally, we can quote the reference 43, in which a study of several transients for a PuN CAPRA-type core is briefly reported. Few details are given, and due to the poor knowledge of PuN, the results should be considered as very preliminary. In case of design basis transients, the main mitigating effect is the feedback from the expansion of the control rod supports. No phase changes occur in case of ULOF, inner cladding melting can be reached in case of a slow UTOP. For beyond design basis initiated transients, the first phase change is melting of the inner clad.

5.2.4 Accelerator Driven Systems

Currently, only some preliminary scoping calculations have been published regarding the safety of ADS. For example, we can quote a preliminary analysis of the deterministic

safety potential of ADS (ref. 36). From neutronic considerations, it shows that compared to critical reactors, ADS has a definite advantage concerning transient overpower events due to an important margin of the “negative reactivity”. On the contrary, ADS is less stable against thermal-hydraulically driven accidents in which the spallation source is not cut, because of less important feedback effects in power reduction.

Other interesting papers relevant to the safety of ADS can be found. Nevertheless, no specific safety analysis is available for nitride fuel loaded ADS. Performing such analyses should be done in the near future.

5.3 Reactor Safety under Severe Accident Conditions

Very few things exist on the study of a hypothetical severe accident involving a nitride fuel.

One evaluation is reported in ref. 44. As stated here above, the first point to recall is that a nitride fuel core presents a good passive shutdown capability on the transient conditions. Once the transient occurs, the reactor power is lowered by the negative reactivity feed back by the Doppler and by axial fuel expansion. The reactor tends to recover a stable point and actually, the probability of occurrence of a Core Disruptive Accident (CDA) is very low. It was, however, studied in this paper for licensing procedure of the expected future advanced fast breeder reactors. Emphasis was given to mechanical and thermal consequences that challenge the integrity of the primary coolant boundary, particularly due to the nitrogen gas generated by the dissociation of nitride fuel. The study is performed through a computer code, on a 1600MWt, vibro-pack fuel with Na bonding core. Some missing data regarding nitride fuel were derived from oxide fuel. Five study cases, more and more severe, are presented. In some case, stabilisation can be recovered. Then if an early dispersion of the fuel is considered (at 1673K due to the fission gases and nitrogen production), local core damage can occur. In the worst case, involving a complete core meltdown, N_2 pressures up to 5MPa can be reached in the reactor vessel. So the thickness of the reactor vessel and of the primary circuit should be 170mm to maintain integrity: it is unrealistic for the primary system.

Except the paper here above summarised, we are not aware of other severe accident studies for nitride cores. Due to the hypotheses made for the sparse studies reported in section 5.2 and due to high thermal conductivity of nitrides (which can become of critical importance for severe accident studies: see below), the rather good behaviour of nitride fuel as regard normal and off-normal transients cannot be extrapolated to severe accident conditions.

For instance, in a Bethe-Tait type accident, we assume that all coolant is lost. It causes a core meltdown and a quasi-spontaneous re-criticality due to gravity collapse leading to core disassembly. The time span is few milliseconds. So, due to the slow diffusion processes involved in the high temperature behaviour of nitride fuels, we cannot assume any equilibrium vapour pressure over the nitride fuel as reported in the sparse published papers and discussed in section 3. Then, the total vapour pressures over the stoichiometric compounds have to be examined.

Another concern about possible very severe accident with a nitride core is the following. Let's assume that a very high temperature of the fuel (let's say about 5000K) can be reached⁴.

⁴ Such a high temperature was calculated for a severe accident scenario, with a non-optimised core. It can probably not be reached as soon as the core design is better optimised.

Then the clad should have melted, the coolant sodium should be liquid, and due to the good thermal properties of the nitride fuel, a considerable amount of heat should be quickly transferred to the sodium coolant. It should result in a very rapid boiling of the sodium, practically similar to an explosion.

Clearly, although the probability of occurrence of a core disruptive accident is lower than with an oxide fuel, complementary studies, including experiments, are needed for investigating the safety of nitride fuels under severe accident conditions.

6. FUTURE PROSPECTS

6.1 On Going and Planned Programmes

In order to complement the data, which have been reviewed in this report, some studies are currently on going or planned in several research institutes.

At JAERI, we can quote several topics as irradiation tests, fabrication and property measurements of nitride fuel, which are going on or in planning stage.

As stated in section 4.3, the irradiation of two ($U_{0.8}Pu_{0.2}$)N fuel pins at fast test reactor JOYO was completed and post-irradiation examinations (PIEs) are underway. Following non-destructive PIEs, destructive PIEs start in the latter half of 2000 in the hot cells of both JAERI and JNC. On the other hand, a capsule irradiation test at JMTR is planned aiming at knowing the irradiation behaviour of U-free nitride fuel from 2002. Pellets of (Pu,Zr)N and PuN+TiN are candidate fuel materials for the moment. The design and licensing study has been just started.

AmN and (Pu,Cm)N prepared by carbothermic reduction are characterized in detail by chemical analysis. High temperature properties of AmN are examined under a joint research with ORNL. A “Module for TRU High Temperature Chemistry” (TRU-HITEC) is to be constructed in the Nuclear Fuel Cycle Safety Engineering Facility (NUCEF) of JAERI for gram-scale experiments of Am and Cm. The experiments will start in the fiscal year 2003. On the other hand, as JAERI’s double-strata fuel cycle relies on nitride fuel and pyrochemical separation, re-fabrication of nitride from electrochemical deposits is one of the subjects to be examined in the near future. Such a fabrication technology and characterization of the nitride “fuel” will complement the demonstration of the feasibility of the whole cycle.

High temperature data for heat capacity and thermal expansion, which are important for safety analysis, are scarce compared with other properties such as thermal conductivity. In JAERI those of NpN, PuN and the solid solutions are measured. During the design study of ADS, the important subjects from the viewpoint of safety of nitride fuel will be clarified.

From the French side, as stated in section 4.2, the NIMPHE 2 capsule is still in PHENIX. Although no decision has been taken yet, when the reactor re-starts, it could be possible to pursue the irradiation in order to achieve a high burn-up. Then, besides the CEA/JAERI collaboration, CEA is involved in several other international collaborations and programmes dealing with actinide nitrides.

In the frame of a CEA agreement with Russia (CEA/MINATOM collaboration agreement), work is going on in Russia about fabrication of ($U_{0.55}Pu_{0.45}$)N, ($U_{0.4}Pu_{0.6}$)N and

(Pu_{0.4}Zr_{0.6})N fuel. Currently, calculations on the irradiation performance of these fuels are also underway for preparing a forthcoming irradiation in the BOR-60 reactor.

As already quoted in section 3.11.2, CEA is co-funding and so directly implicated, in a PhD thesis, which is underway at PSI (Switzerland) for studying the properties of (Pu,Zr)N.

CEA is also directly involved in a European programme, co-ordinated by Sweden. This is the CONFIRM programme. It is a four-year programme, which is just starting and which includes the following studies relevant to nitride fuels.

- Safety of nitride fuels:
 - UN samples will be heated up to 3073K and the stability of the fuel will be assessed from post-test chemical analyses and scanning electron microscopy (SEM-EDX).
 - Small samples of UN will be heated in a tungsten coil to high temperatures in a sealed chamber under a high pressure of nitrogen, then the samples will be analysed. Different heating rates will be studied.
 - Limitations in linear ratings for uranium free nitrides with varying concentrations of AmN will be explored by theoretical modelling of pins bonded with helium, nitrogen and sodium.
 - In order to check the impact of ¹⁵N enrichment, a set of partitioning and transmutation scenarios with various types of fast spectrum, ¹⁵N enriched nitride, burning cores will be elaborated. The amount of ¹⁴C directed to the secondary waste stream will be calculated for each of the scenarios.
- Modelling and optimisation of uranium free oxide and nitride fuel pellet, pin and assembly design, for the purpose of identifying a plausible high burn-up fuel type for an ADS demo facility. Modelling and optimisation for the plutonium nitride pellets to be irradiated within the project.
- Fabrication and characterisation of optimised (Pu,Zr)N fuel pins (this part of the CONFIRM project will be done by PSI (Switzerland) and is linked to the PhD thesis work already mentioned).
- Development of a fabrication process for (Am,Zr)N pellets, starting with Pu before moving to Am. The fabricated samples will be characterised in terms of composition, density, microstructure, thermal conductivity, heat capacity and high temperature stability.
- Irradiation of (Pu,Zr)N fuel pins at temperatures similar to those in liquid metal cooled cores (outer cladding temperature of about 773K). A 10at% burn-up is expected, with linear power of 60-70kW/m. Tests of pin performance during a power transient may be performed.

Finally, in Russia a (Pu,Zr)N irradiation will start in the BOR60 reactor from October 2000. Besides, 30 UN assemblies should be irradiated in the BR10 reactor by 2002.

6.2 Other Suggested Studies

Currently planned and on going programmes here above mentioned should provide interesting answers to improve the current knowledge on actinide nitrides. Anyway, some other studies can be suggested in order to assess definitively the possibility of using nitrides for nuclear waste transmutation.

First, further experimental studies should be performed on basic high temperature properties of PuN, (U,Pu)N, (Pu,Zr)N, and minor actinide nitrides AmN, CmN, (Pu,Am)N, (U,Am)N, (Pu,Am,Zr)N... Although these are challenging experiments, these studies should

include thermodynamic property measurements up to very high temperatures (including the liquid phase), phase diagram studies, kinetics of vaporization behavior.

Further irradiation experiments should aim at checking the capacity of nitride fuel to achieve high burn-ups, at understanding the swelling phenomenon (role of porosity...) and studying the thermal-chemical evolution of the fuel at high burn-up (more than 50at%). Besides, americium (and if possible, curium) loaded fuels should be irradiated.

More sophisticated safety studies for core disruptive accidents, as a function of the fuel characteristics, the core and the reactor geometry should be undertaken. These studies should be cross-checked through experiments. This should allow determining what are the real safety criteria for a nitride-fuelled reactor. Besides, it should allow a better evaluation of the safety margins and it should allow designing specific safety devices to avoid any possibility of a core disruptive accident (concept of intrinsically safe reactor). Such safety studies should be done for any type of nitride-fuelled reactor but it is particularly lacking for ADS.

Finally, besides the safety-related aspects, we will mention that studies for economical ^{15}N enrichment should be recommended.

7. CONCLUSION

Using nitride fuels in view of a closed nuclear fuel cycle including nuclear waste transmutation should provide many advantages compared to oxides. Among these advantages, detailed in section 2 of this report, we will focus on two major ones: the very good thermal conductivity and the heavy atom density. The first one allows working with a "cold" fuel, with enhanced margins as regards melting conditions. The second one yields a harder neutron spectrum and so, more efficiency as regards the transmutation rate. These advantages look so promising for an advanced nuclear cycle and advanced reactors that, for the last ten years, nitrides have become the major actinide form to be studied in JAERI.

Nevertheless, two drawbacks have to be mentioned. One is the necessity to use highly enriched ^{15}N . It looks quite possible. Current concerns are rather on the economical side. However, one can expect a significant cost reduction if further studies to improve the process were realised. The second one is the possible vaporisation of some nitrides below their boiling point and the incidence of such behaviour on the safety of a nitride core reactor. This point was the major motivation for drafting the present report. Indeed, CEA industrial partners consider a clear view on this problem as a prerequisite before funding more research on nitride fuels.

Several fabrication processes can be envisaged for nitride fuels. Among them, carbothermic reduction method is now a well-established process, which yields good quality fuels with a reasonably low content in carbon and oxygen as main impurities. Nevertheless, as nitrogen enriched at more than 99% in ^{15}N should be used, for a reasonable cost of production, in an industrial process the nitrogen stream gas should be recycled. This seems quite feasible although it was never realised up to now.

Most of basic physical (and chemical) properties of actinide nitrides, necessary for understanding and evaluating their in-pile behaviour (including safety relevant aspects), are relatively well known as long as we deal with UN, PuN and (U,Pu)N mixed nitrides. Nevertheless, complementary data would be needed on the kinetics of their vaporisation behaviour and practically nothing is available as soon as we want to deal with liquid

properties. Basic data become very sparse, and are often unknown for other actinide nitrides of interest in waste transmutation. As regards safety aspects, which are of major concern, high temperature behaviour of these nitrides should be studied as an important priority.

Irradiation experiments of nitride fuels are rather sparse and are limited to uranium, plutonium, and mixed uranium-plutonium nitrides. Several pin concepts can be considered: each provides advantages and drawbacks. Anyway, the sparse available irradiation results are relevant to nitride fuel pellets in sodium or helium bonded pins only.

It is confirmed that the nitride fuel operating temperature is lower than the oxide fuel one, providing higher margin as regards safety. Free swelling rates are generally about 1%/at%. They are higher for high-density fuels, which release less fission gases. Nevertheless, large uncertainties remain to calculate this swelling rate in different conditions. In particular, the exact contribution of different factors to the swelling rate (mainly the porosity) should be investigated. Furthermore, due to this rather high swelling, fuel-cladding interaction has to be carefully examined, mainly on a mechanical point of view, but also as regards the fuel-cladding chemical compatibility. Linked to higher swelling rate, compared to oxide, nitride fuel releases less fission gases. Up to now a maximum burn-up of 9.6at% was achieved in an American experiment with mixed (U,Pu)N under fast neutron circumstances. As regards the transmutation objective, the possibility of achieving higher burn-up should be demonstrated.

Up to now, no specific safety experiment was performed with nitride fuel. Very sparse studies have been done through calculations. As a general trend, nitride fuel is safe under normal and off-normal transient condition. Due to its good passive shutdown capability, it rapidly comes back to a safe stable situation. Anyway, due to the lack of knowledge on basic properties of nitride fuels, the results of these studies should be confirmed. Furthermore, for some transient situations, non-boiling of the coolant should also be confirmed. Finally, only one study exists as regards core disruptive accident situation. Although the probability of occurrence is extremely low (passive shutdown capability of nitride fuel), it should be studied in more details. Such a study should consider both the type of reactor and its design, the type of fuel considered, and the kinetic aspects of the vaporisation of the relevant nitride. In particular, we will note that in the sparse studies summarised in this report, only (U,Pu)N was considered. For a CAPRA or an ADS nitride fuel, AmN should be a major component. Its peculiar dissociation behaviour can lead to quite different results as regards safety aspects.

On going and planned studies in different research-institutes should provide a useful and necessary complement to the current knowledge about nitride fuels. Anyway some complementary studies are still necessary to fully demonstrate the feasibility of a nitride-based advanced nuclear cycle.

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TABLES

Table 1 Major parameters of the JAERI design Pb-Bi cooled ADS

Table 2 Physical properties of uranium nitride (UN)

Table 3 Physical properties of neptunium nitride (NpN)

Table 4 Physical properties of plutonium nitride (PuN)

Table 5 Physical properties of americium nitride (AmN)

Table 6 Physical properties of uranium-neptunium mixed nitrides ((U,Np)N)

Table 7 Physical properties of uranium-plutonium mixed nitride ((U_{0.8}Pu_{0.2})N)

Table 8 Physical properties of neptunium-plutonium mixed nitrides ((Np,Pu)N)

Table 1: Major parameters of the JAERI design Pb-Bi cooled ADS

Core thermal power	820 MW
Core height	1000 mm
Core radius	1200 mm
k_{eff} (Initial/Max./Min.)	0.95/0.95/0.94
Linear power rating (Max./Ave.)	520/300 W/cm
Power density (Max./Ave.)	310/180 MW/m ³
MA/Pu inventory	2500/1660 kg
Fuel	(MA,Pu)N, inert matrix ZrN initial Pu fraction 40% N-15 enriched
Pin pitch-to-diameter ratio	1.5
Coolant temperature (In/Out)	603/703 K
Coolant velocity (Max.)	2 m/s
Sodium void coefficient	-4.8% dk/k
Doppler coefficient	$-3.7 \times 10^{-4} \text{T dk/dT}$
Burnup swing	1.8%
Variation in beam power	30%
MA transmutation rate	500 kg/cycle (20%/cycle)

Table 2: Physical properties of uranium nitride (UN)

Property (unit)	Value and/or comments	Reference
Molar weight (g)	252.0356	
Crystal structure symmetry space group lattice constants (nm)	Face centred cubic (no transition in the solid phase reported) Fm3m a = b = c = 0.4889	8
Density (g.cm ⁻³) Heavy atom dens. (g.cm ⁻³)	14.325 13.529	From above data
Melting point (K)	3123 at 2.5 atm. Nitrogen 3103 ± 30 at 3.5 bar Nitrogen (congruent)	8 8
Heat capacity (J.mol ⁻¹ .K ⁻¹)	54.149 + 2.2807x10 ⁻³ T + 4,372x10 ⁻⁶ T ² – 681251 T ⁻² (298 < T < 3000 K)	8
Thermal conductivity (W.m ⁻¹ .K ⁻¹)	4.64 + 0.02326 T – 5.96x10 ⁻⁶ T ² (473 K < T < 2073 K) i.e. 19.06 at 773 K; 24.59 at 1273 K 20.4 at 773 K ; 24.3 at 1273 K	23 From graph reading in 3
Entropy (J.mol ⁻¹ .K ⁻¹)	62.43 ± 0.22 at 298.15 K	17
Enthalpy of formation (J.mol ⁻¹)	-290000 ± 3000 at 298.15 K	17
Enthalpy (J.mol ⁻¹)	H(T) – H(298.15) = 54.149 T + 1.14035 T ² + 1.4573 x 10 ⁻⁶ T ³ + 681251 T ⁻¹ – 18569.4 (T < 3103 K)	From C _p and H ₂₉₈ above
Linear thermal expansion coefficient (K ⁻¹)	8.6 x 10 ⁻⁶ at 773 K 9.4 x 10 ⁻⁶ at 1273 K 9.8 x 10 ⁻⁶ at 1773 K 10.0 x 10 ⁻⁶ at 2273 K	From graph reading in 8 and 23

Table 3: Physical properties of neptunium nitride (NpN)

Property (unit)	Value and/or comments	Reference
Molar weight (g)	251.0549	
Crystal structure symmetry space group lattice constants (nm)	Face centred cubic (no transition in the solid phase reported) Fm3m a = b = c = 0.48971	3
Density (g.cm ⁻³) Heavy atom dens. (g.cm ⁻³)	14.199 13.407	From above data
Melting point (K)	3103 K at 1 MPa Nitrogen (congruent)	20
Heat capacity (J.mol ⁻¹ .K ⁻¹)		
Thermal conductivity (W.m ⁻¹ .K ⁻¹)	14.5 at 773 K 17.3 at 1273 K	From graph reading in 3
Entropy (J.mol ⁻¹ .K ⁻¹)	Not available Estimated at 60.79 at 298.15 K in ECN-T base	ECN-T base
Enthalpy of formation (J.mol ⁻¹)	Not available Estimated at -299200 at 298.15 K in ECN-T base	ECN-T base
Enthalpy (J.mol ⁻¹)		
Linear thermal expansion coefficient (K ⁻¹)		

Table 4: Physical properties of plutonium nitride (PuN)

Property (unit)	Value and/or comments	Reference
Molar weight (g)	253 (for ^{239}Pu)	
Crystal structure symmetry space group lattice constants (nm)	Face centred cubic (no transition in the solid phase reported) Fm3m $a = b = c = 0.49049$	45
Density (g.cm^{-3}) Heavy atom dens. (g.cm^{-3})	14.241 13.453	From above data
Melting point (K)	3103 ± 50 at 5 ± 2 MPa Nitrogen (congruent)	45 (estimation)
Heat capacity ($\text{J.mol}^{-1}.\text{K}^{-1}$)	$45.002 + 0.01542 T$ ($T < 3000$ K)	28
Thermal conductivity ($\text{W.m}^{-1}.\text{K}^{-1}$)	$3.361 + 0.01859 T - 9.5 \times 10^{-6} T^2$ ($473 \text{ K} < T < 1773 \text{ K}$) i.e. 12.06 at 773 K; 11.63 at 1273 K 10.8 at 773 K ; 11.5 at 1273 K	Suggested in 23 From graph reading in 3
Entropy ($\text{J.mol}^{-1}.\text{K}^{-1}$)	64.8 at 298.15 K	45
Enthalpy of formation (J.mol^{-1})	-299200 ± 2600 at 298.15 K	45
Enthalpy (J.mol^{-1})	$H(T) - H(298.15) = 45.002 T + 0.00771 T^2 - 14102.7$ ($T < 3000$ K)	28
Linear thermal expansion coefficient (K^{-1})	$11.2 \times 10^{-6} \leq \alpha \leq 13.8 \times 10^{-6}$ at about 1273 K	23

Table 5: Physical properties of americium nitride (AmN)

Property (unit)	Value and/or comments	Reference
Molar weight (g)	257.0067	
Crystal structure symmetry space group lattice constants (nm)	Face centred cubic (no transition in the solid phase reported) Fm3m $0.4991 \leq a = b = c \leq 0.5005 \pm .0005$ (sparse values reported by different authors)	37
Density (g.cm ⁻³) Heavy atom dens. (g.cm ⁻³)	$13.616 \leq d \leq 13.731$ $12.874 \leq \text{had} \leq 12.983$	From above data
Melting point (K)	N.A.	
Heat capacity (J.mol ⁻¹ .K ⁻¹)	N.A.	
Thermal conductivity (W.m ⁻¹ .K ⁻¹)	N.A.	
Entropy (J.mol ⁻¹ .K ⁻¹)	N.A.	
Enthalpy of formation (J.mol ⁻¹)	-294000 at 1600 K	30 (estimation)
Enthalpy (J.mol ⁻¹)	N.A.	
Linear thermal expansion coefficient (K ⁻¹)	N.A.	

Table 6: Physical properties of uranium-neptunium mixed nitrides ((U,Np)N)

Property (unit)	Value and/or comments			Reference
Compound	(U _{0.75} Np _{0.25})N	(U _{0.50} Np _{0.50})N	(U _{0.25} Np _{0.75})N	
Molar weight (g)	251.7890	251.5452	251.3001	
Crystal structure symmetry space group lattice constants (nm)	Face centred cubic Fm3m a = b = c = 0.48901	Face centred cubic Fm3m a = b = c = 0.48914	Face centred cubic Fm3m a = b = c = 0.48971	3
Density (g.cm ⁻³) Heavy atom dens. (g.cm ⁻³)	14.302 13.506	14.277 13.482	14.237 13.444	From above data
Melting point (K)				
Heat capacity (J.mol ⁻¹ .K ⁻¹)				
Thermal conductivity (W.m ⁻¹ .K ⁻¹)	16.7 at 773 K 21.7 at 1273 K	15.8 at 773 K 19.6 at 1273 K	15.0 at 773 K 18.2 at 1273 K	From graph reading in 3
Entropy (J.mol ⁻¹ .K ⁻¹)				
Enthalpy of formation (J.mol ⁻¹)				
Enthalpy (J.mol ⁻¹)				
Linear thermal expansion coefficient (K ⁻¹)				

Table 7: Physical properties of uranium-plutonium mixed nitride ((U_{0.8}Pu_{0.2})N)

Property (unit)	Value and/or comments	Reference
Molar weight (g)	252.29	
Crystal structure symmetry space group lattice constants (nm)	Face centred cubic Fm3m a = b = c ≈ 0.4890	1
Density (g.cm ⁻³) Heavy atom dens. (g.cm ⁻³)	14.3 13.5	From above data
Melting point (K)	3053 (to be used cautiously: in reference 34, melting temperatures given for UN and PuN are not coherent with more recently assessed values, given in Table 2 and Table 4)	34
Heat capacity (J.mol ⁻¹ .K ⁻¹)	45.38 + 0.0109 T	34
Thermal conductivity (W.m ⁻¹ .K ⁻¹)	scattered data : 15.1 to 16.7 at 773 K 17.6 to 19.7 at 1273 K 19.4 to 21.8 at 1773 K 19.8 at 1273 K	From graph reading in 23 21
Entropy (J.mol ⁻¹ .K ⁻¹)		
Enthalpy of formation (J.mol ⁻¹)		
Enthalpy (J.mol ⁻¹)	H(T) – H(298.15) = 45.38 T + 0.00544 T ² – 14008 (T < 3000 K)	34
Linear thermal expansion coefficient (K ⁻¹)	7.9 × 10 ⁻⁶ at 773 K 8.7 × 10 ⁻⁶ at 1273 K 10.0 × 10 ⁻⁶ at 1773 K	From graph reading in 23

Table 8: Physical properties of neptunium-plutonium mixed nitrides ((Np,Pu)N)

Property (unit)	Value and/or comments		Reference
Compound	(Np _{0.67} Pu _{0.33})N	(Np _{0.33} Pu _{0.67})N	
Molar weight (g)	253.3722	255.6894	
Crystal structure symmetry space group lattice constants (nm)	Face centred cubic Fm3m a = b = c = 0.49002	Face centred cubic Fm3m a = b = c = 0.49033	3
Density (g.cm ⁻³) Heavy atom dens. (g.cm ⁻³)	14.303 13.512	14.406 13.617	From above data
Melting point (K)			
Heat capacity (J.mol ⁻¹ .K ⁻¹)			
Thermal conductivity (W.m ⁻¹ .K ⁻¹)	11.9 at 773 K 13.8 at 1273 K	11.5 at 773 K 12.8 at 1273 K	From graph reading in 3
Entropy (J.mol ⁻¹ .K ⁻¹)			
Enthalpy of formation (J.mol ⁻¹)			
Enthalpy (J.mol ⁻¹)			
Linear thermal expansion coefficient (K ⁻¹)			

FIGURES

- Figure 1** JAERI reference flow sheet for reprocessing nitride fuel in the second stratum
- Figure 2** Density of actinide nitrides, compared to actinide dioxides
- Figure 3** Thermal conductivity of actinide nitrides, compared to actinide dioxides
- Figure 4** Decomposition pressure of UN and PuN in equilibrium with liquid (from ref. 23)
- Figure 5** Vapour pressure of U and Pu above $(U_{1-x}Pu_x)N$ (from ref. 39)
- Figure 6** Vapour pressure of Np and Pu above $(Np_{1-x}Pu_x)N$ (from ref. 3)

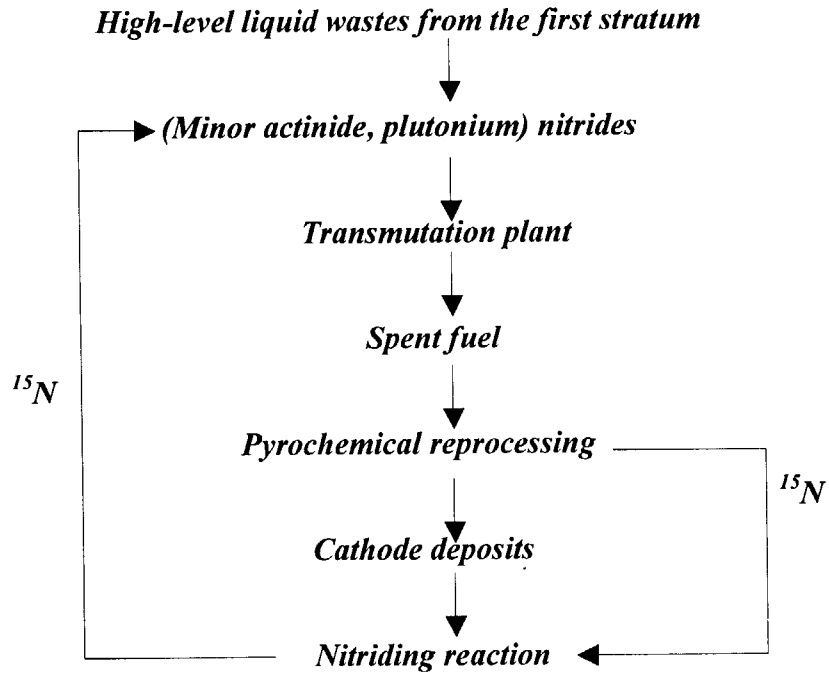


Figure 1: JAERI reference flow sheet for reprocessing nitride fuel in the second stratum

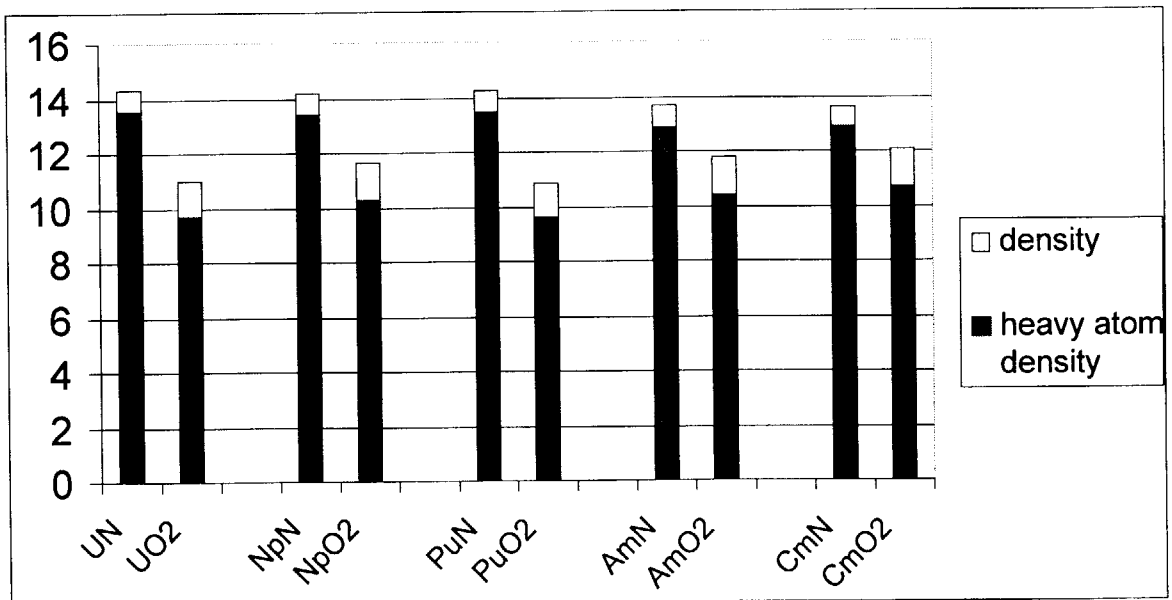


Figure 2: Density of actinide nitrides, compared to actinide dioxides

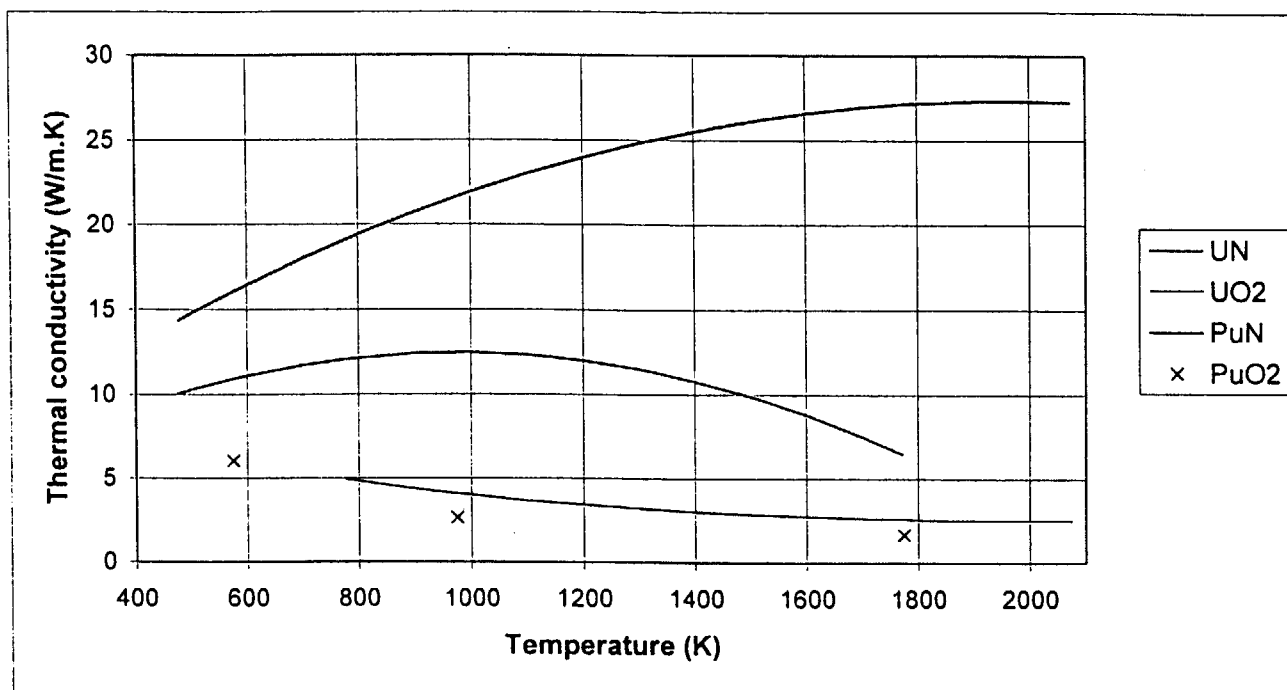


Figure 3: Thermal conductivity of UN, PuN, compared to UO_2 and PuO_2

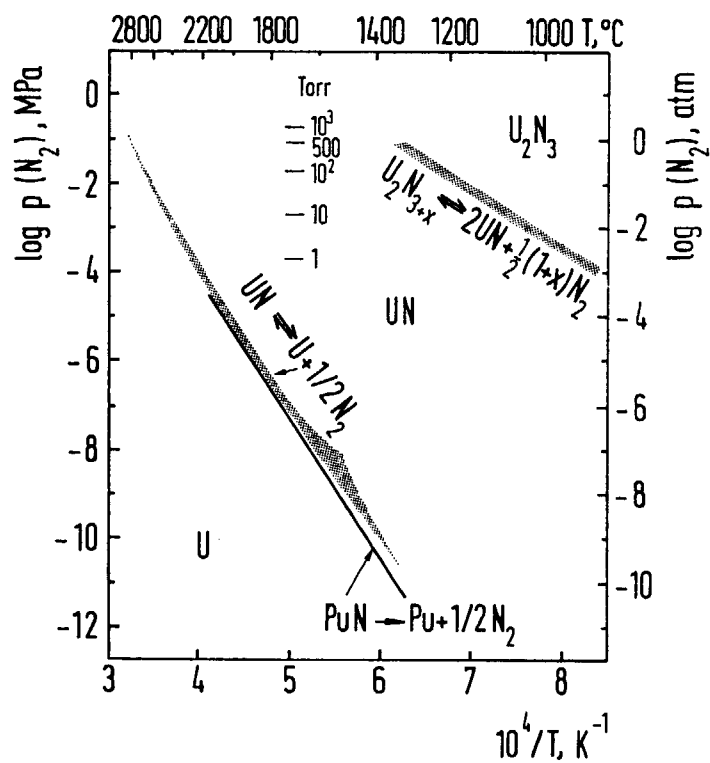


Figure 4: Decomposition pressure of UN, PuN in equilibrium with liquid (from ref. 23)

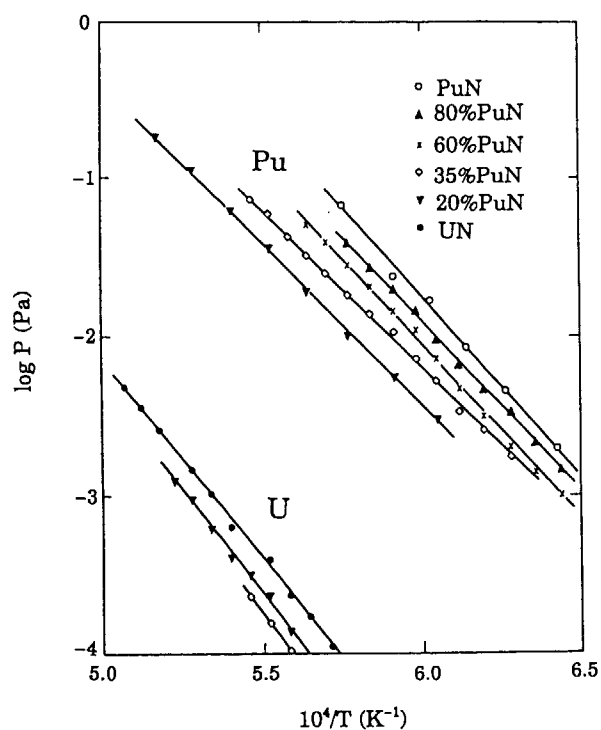


Figure 5: Vapour pressure of U and Pu above $(U_{1-x}Pu_x)N$ (from ref. 39)

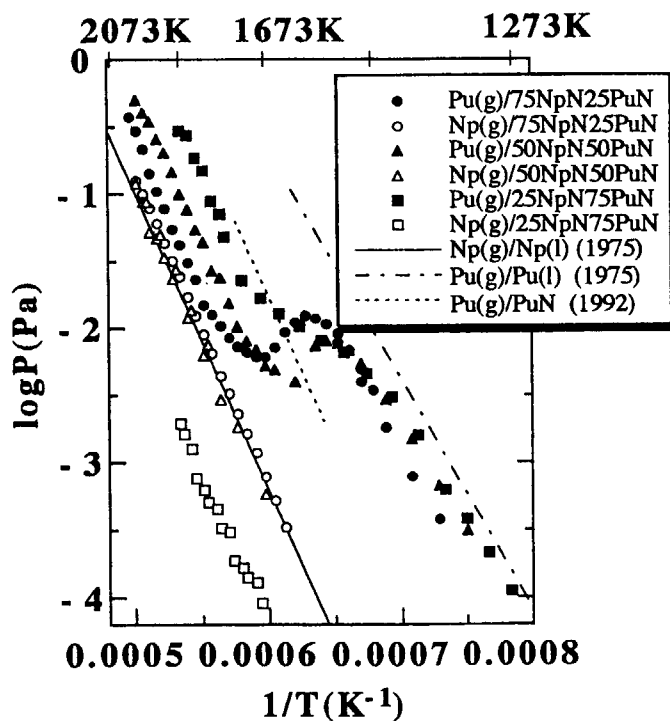


Figure 6: Vapour pressure of Np and Pu above $(Np_{1-x}Pu_x)N$ (from ref. 3)

国際単位系 (SI) と換算表

表1 SI基本単位および補助単位

量	名称	記号
長さ	メートル	m
質量	キログラム	kg
時間	秒	s
電流	アンペア	A
熱力学温度	ケルビン	K
物質	モル	mol
光度	カンデラ	cd
平面角	ラジアン	rad
立体角	ステラジアン	sr

表3 固有の名称をもつSI組立単位

量	名称	記号	他のSI単位 による表現
周波数	ヘルツ	Hz	s^{-1}
力	ニュートン	N	$m \cdot kg / s^2$
圧力, 応力	パスカル	Pa	N / m^2
エネルギー, 仕事, 熱量	ジュール	J	$N \cdot m$
工率, 放射束	ワット	W	J / s
電気量, 電荷	クーロン	C	$A \cdot s$
電位, 電圧, 起電力	ボルト	V	W / A
静電容量	ファラド	F	C / V
電気抵抗	オーム	Ω	V / A
コンダクタンス	ジーメンズ	S	A / V
磁束	ウェーバ	Wb	$V \cdot s$
磁束密度	テスラ	T	Wb / m^2
インダクタンス	ヘンリー	H	Wb / A
セルシウス温度	セルシウス度	$^{\circ}C$	
光束	ルーメン	lm	$cd \cdot sr$
照度	ルクス	lx	lm / m^2
放射能	ベクレル	Bq	s^{-1}
吸収線量	グレイ	Gy	J / kg
線量当量	シーベルト	Sv	J / kg

表2 SIと併用される単位

名称	記号
分, 時, 日	min, h, d
度, 分, 秒	$^{\circ}, ', ''$
リットル	l, L
トン	t
電子ボルト	eV
原子質量単位	u

$$1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}$$

$$1 \text{ u} = 1.66054 \times 10^{-27} \text{ kg}$$

表4 SIと共に暫定的に維持される単位

名称	記号
オングストローム	\AA
バ	b
バ	bar
ガ	Gal
キュリー	Ci
レントゲン	R
ラ	rad
レ	rem

$$1 \text{ \AA} = 0.1 \text{ nm} = 10^{-10} \text{ m}$$

$$1 \text{ b} = 100 \text{ fm}^2 = 10^{-28} \text{ m}^2$$

$$1 \text{ bar} = 0.1 \text{ MPa} = 10^5 \text{ Pa}$$

$$1 \text{ Gal} = 1 \text{ cm} / s^2 = 10^{-2} \text{ m} / s^2$$

$$1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$$

$$1 \text{ R} = 2.58 \times 10^{-4} \text{ C} / \text{kg}$$

$$1 \text{ rad} = 1 \text{ cGy} = 10^{-2} \text{ Gy}$$

$$1 \text{ rem} = 1 \text{ cSv} = 10^{-2} \text{ Sv}$$

表5 SI接頭語

倍数	接頭語	記号
10^{18}	エクサ	E
10^{15}	ペタ	P
10^{12}	テラ	T
10^9	ギガ	G
10^6	メガ	M
10^3	キロ	k
10^2	ヘクト	h
10^1	デカ	da
10^{-1}	デシ	d
10^{-2}	センチ	c
10^{-3}	ミリ	m
10^{-6}	マイクロ	μ
10^{-9}	ナノ	n
10^{-12}	ピコ	p
10^{-15}	フェムト	f
10^{-18}	アト	a

(注)

- 表1-5は「国際単位系」第5版, 国際度量衡局 1985年刊行による。ただし, 1 eV および 1 uの値はCODATAの1986年推奨値によった。
- 表4には海里, ノット, アール, ヘクタールも含まれているが日常の単位なのでここでは省略した。
- barは, JISでは流体の圧力を表わす場合に限り表2のカテゴリーに分類されている。
- EC閣僚理事会指令ではbar, barnおよび「血圧の単位」mmHgを表2のカテゴリーに入れている。

換算表

力	N (=10 ⁵ dyn)	kgf	lbf
	1	0.101972	0.224809
	9.80665	1	2.20462
	4.44822	0.453592	1

$$\text{粘 度 } 1 \text{ Pa} \cdot \text{s} (N \cdot \text{s} / m^2) = 10 \text{ P (ポアズ)} (g / (cm \cdot s))$$

$$\text{動粘度 } 1 m^2 / s = 10^6 \text{ St (ストークス)} (cm^2 / s)$$

圧	MPa (=10 bar)	kgf/cm ²	atm	mmHg (Torr)	lbf/in ² (psi)
	1	10.1972	9.86923	7.50062×10^3	145.038
力	0.0980665	1	0.967841	735.559	14.2233
	0.101325	1.03323	1	760	14.6959
	1.33322×10^{-4}	1.35951×10^{-3}	1.31579×10^{-3}	1	1.93368×10^{-2}
	6.89476×10^{-3}	7.03070×10^{-2}	6.80460×10^{-2}	51.7149	1

エネルギー・仕事・熱量	J (=10 ⁷ erg)	kgf·m	kW·h	cal (計量法)	Btu	ft·lbf	eV
	1	0.101972	2.77778×10^{-7}	0.238889	9.47813×10^{-4}	0.737562	6.24150×10^{18}
	9.80665	1	2.72407×10^{-6}	2.34270	9.29487×10^{-3}	7.23301	6.12082×10^{19}
	3.6×10^6	3.67098×10^5	1	8.59999×10^5	3412.13	2.65522×10^6	2.24694×10^{25}
	4.18605	0.426858	1.16279×10^{-6}	1	3.96759×10^{-3}	3.08747	2.61272×10^{19}
	1055.06	107.586	2.93072×10^{-4}	252.042	1	778.172	6.58515×10^{21}
	1.35582	0.138255	3.76616×10^{-7}	0.323890	1.28506×10^{-3}	1	8.46233×10^{18}
	1.60218×10^{-19}	1.63377×10^{-20}	4.45050×10^{-26}	3.82743×10^{-20}	1.51857×10^{-22}	1.18171×10^{-19}	1

$$1 \text{ cal} = 4.18605 \text{ J (計量法)}$$

$$= 4.184 \text{ J (熱化学)}$$

$$= 4.1855 \text{ J (15 } ^{\circ}C)$$

$$= 4.1868 \text{ J (国際蒸気表)}$$

$$\text{仕事率 } 1 \text{ PS (仏馬力)}$$

$$= 75 \text{ kgf} \cdot \text{m} / \text{s}$$

$$= 735.499 \text{ W}$$

放射能	Bq	Ci
	1	2.70270×10^{-11}
	3.7×10^{10}	1

吸収線量	Gy	rad
	1	100
	0.01	1

照射線量	C/kg	R
	1	3876
	2.58×10^{-4}	1

線量当量	Sv	rem
	1	100
	0.01	1

