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Fabrication, Properties and Irradiation behaviour of MOX, Carbide and Nitride Fuels, Inert Matrix Fuels with and without Minor Actinides

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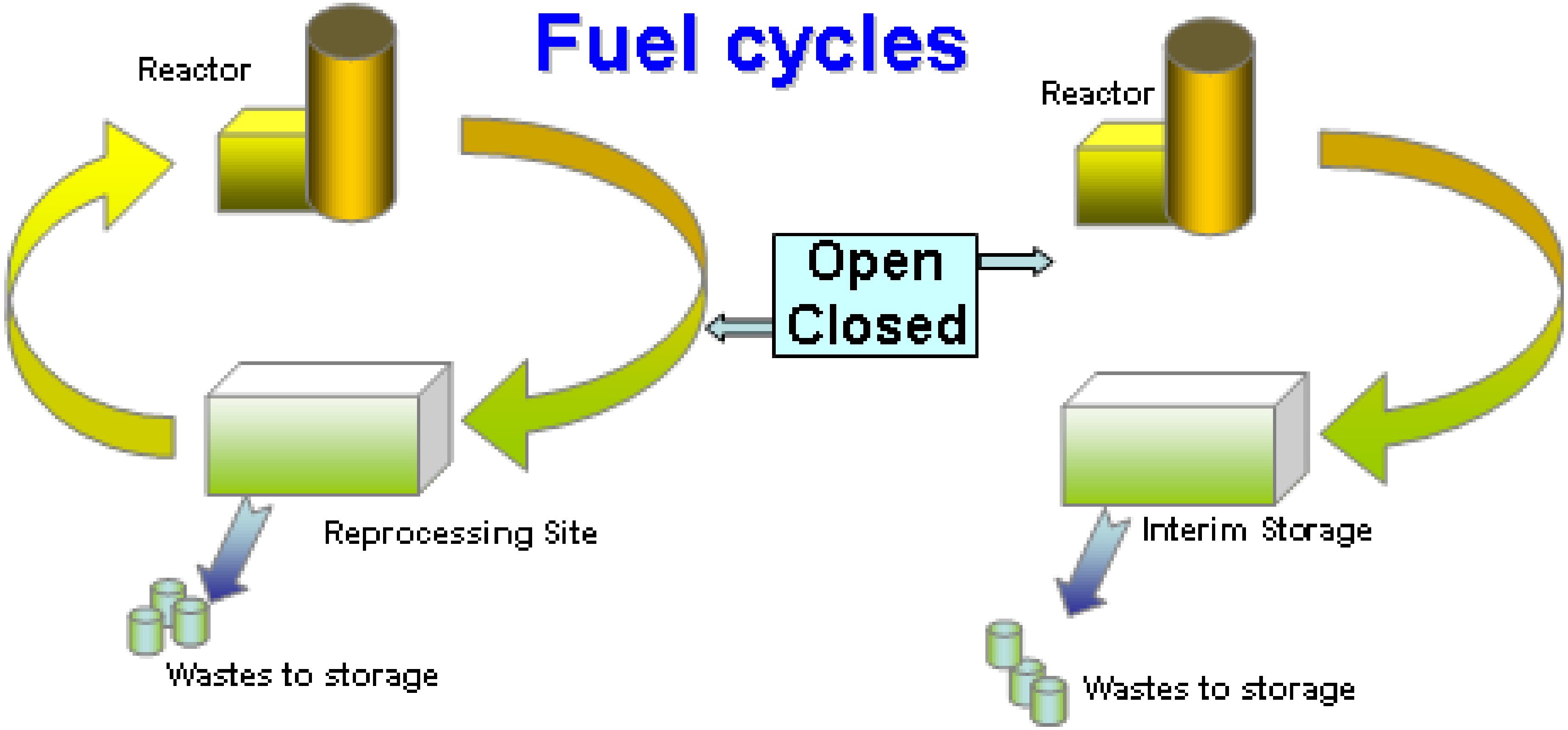
Fuel cycles



The nuclear fuel cycle is called "closed" when plutonium is extracted from spent fuel and remanufactured into nuclear fuel for breeder or light water reactors, and "open" when spent reactor fuel is disposed of without plutonium recovery.

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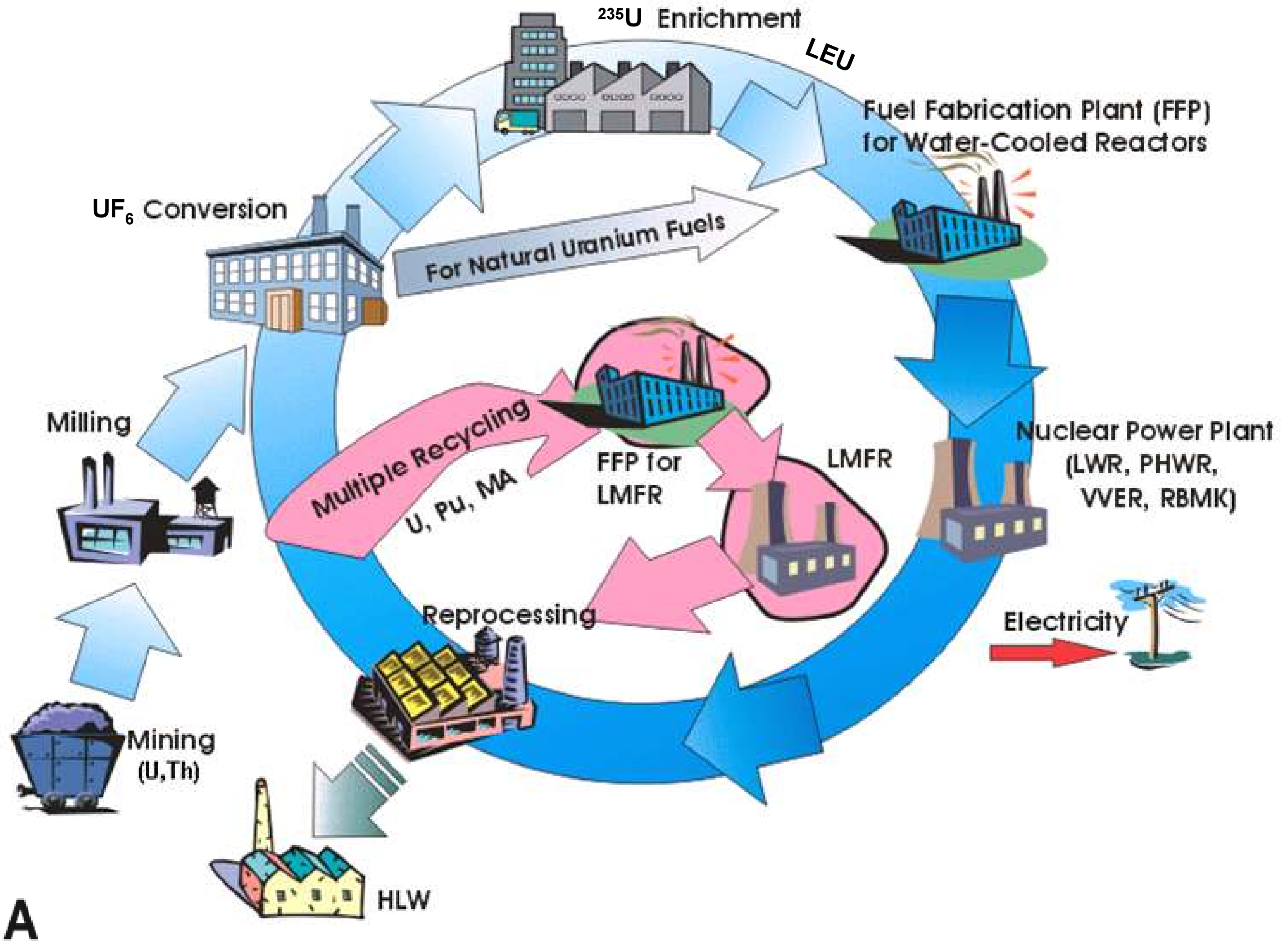
Nuclear Fuel Cycle

OBJECTIVES :

1. Effective Utilization of Resources (Fissile / Fertile)
2. Improved Fuel Cycle Economy
   - (i) High Burn – up
     - a) increased residence time in the reactor
     - b) less waste volume generation
   - (ii) Maximum Fuel Utilization
   - (iii) More Cost Effective Fuel Fabrication Methods
3. Proliferation Resistance
4. Reduction in Strategic Nuclear Material Stock Pile
5. Waste Generation and Its Characteristics

238U - 239Pu Closed Fuel cycle for SFR with multiple recycling of U, Pu and MA.

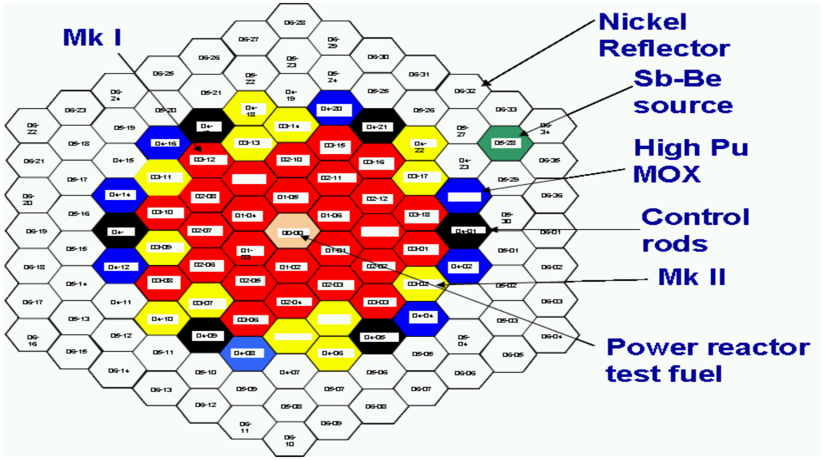
[DU, RepU & NatU could be used as fertile materials in fuel and blanket assemblies]



Fuels for Fast Reactor

Fast reactors could be used with diverse fuel types and compositions including plutonium and minor actinides. They can be used either as BREEDERs to produce more fissile than consume or BURNERs to transmute the transuranium elements in the high level waste. Fast Reactor fuels should have the capability to operate at high heat ratings and achieve high burn up. The need for compact core and high heat ratings implies that the fuel pins be of very small diameter and separated from one another by narrow coolant channels .Thus the fuel should meet the following requirements :

High fissile atom density
Good thermal conductivity
Good compatibility with cladding & coolant
As few moderating atoms as possible
Low swelling from fission products



The concentration of fissile material , namely plutonium in the fuel is much higher than that in a thermal reactor and the fuel fabrication technologies for fast reactor are accordingly more challenging. Alloys containing uranium and plutonium or solid solutions of the oxides or carbides or nitrides of uranium and plutonium are used as the fast reactor fuels

Steps in Manufacturing of Fuel Pin

The major steps in manufacturing of UO_2 / $(U,Pu)O_2$ and (U,Pu)C / (U,Pu)N fuel pins are :

Preparation of feed powders

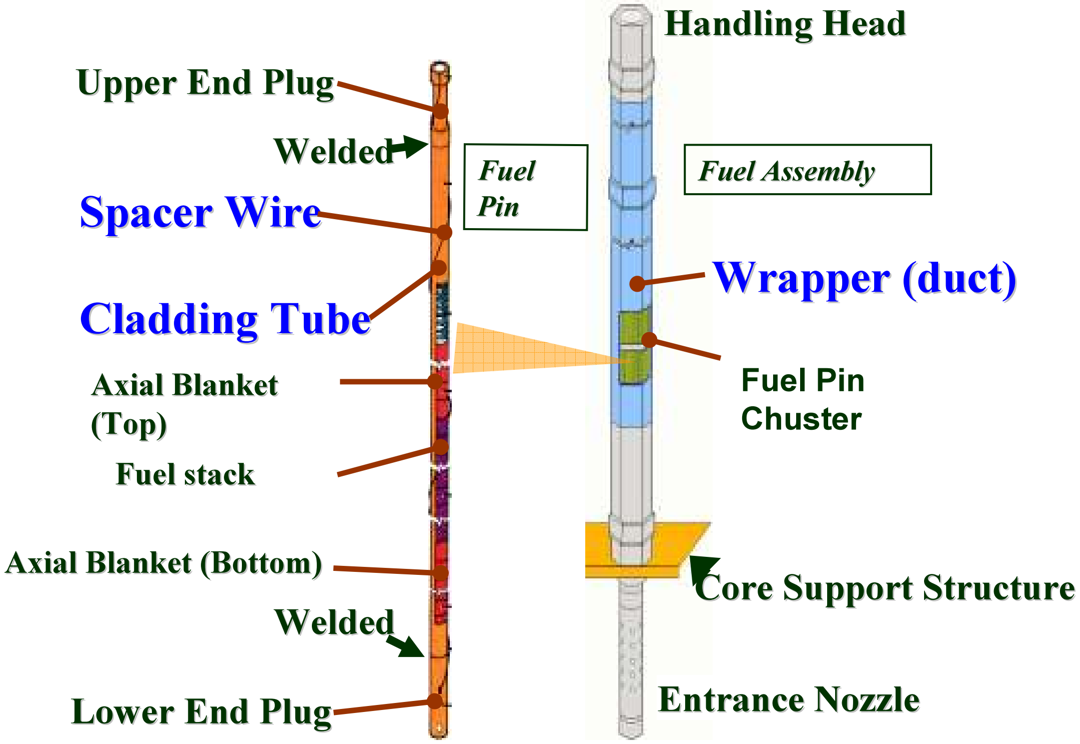
Fabrication of sintered pellets of controlled diameter , L/D ratio , density and microstructure

Inspection of pellets

Loading of accepted pellets in one end welded SS cladding tube

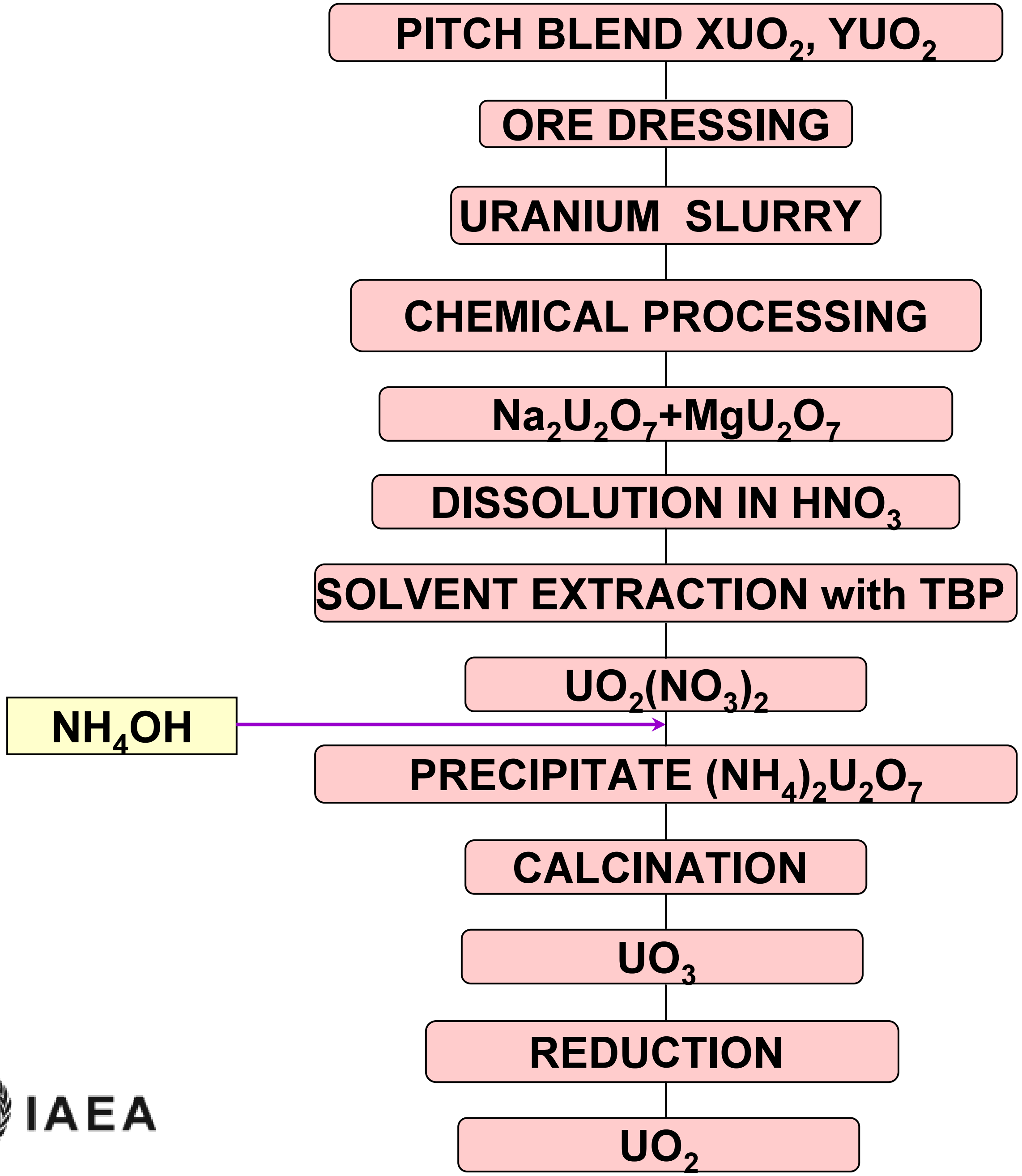
Encapsulation with helium as filler gas

Wire wrapping of fuel rods and assembly making.



In most cases , the UO_2 axial blanket is part of the fuel rod and loaded in both ends of the fuel pellet stack

UO_2 POWDER PRODUCTION



PITCH BLEND XUO_2, YUO_2

ORE DRESSING

URANIUM SLURRY

CHEMICAL PROCESSING

$Na_2U_2O_7+MgU_2O_7$

DISSOLUTION IN HNO_3

SOLVENT EXTRACTION with TBP

$UO_2(NO_3)_2$

NH_4OH

PRECIPITATE $(NH_4)_2U_2O_7$

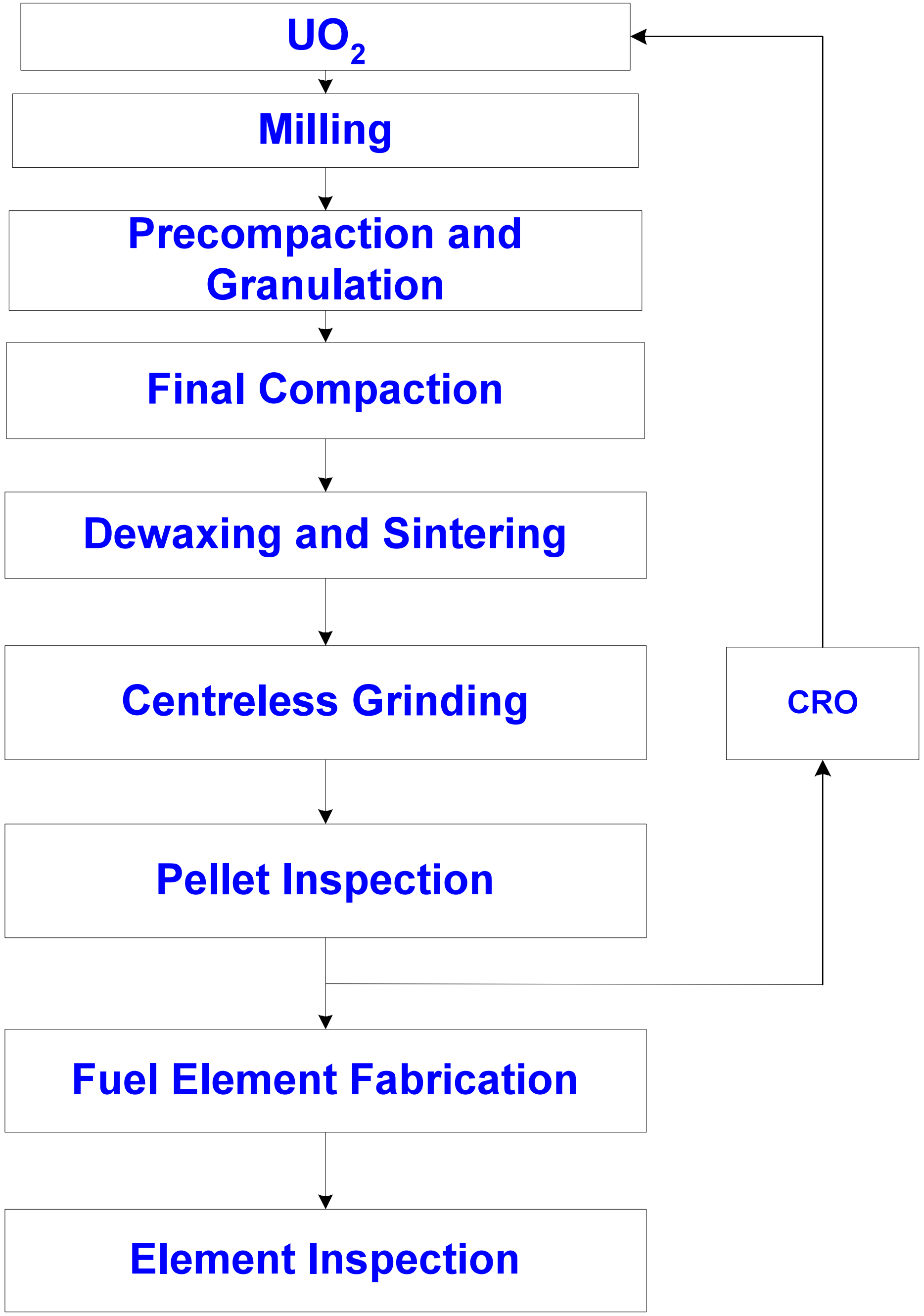
CALCINATION

UO_3

REDUCTION

UO_2

Fabrication of UO_2 fuel elements



UO_2

Milling

Precompaction and Granulation

Final Compaction

Dewaxing and Sintering

Centreless Grinding

Pellet Inspection

Fuel Element Fabrication

Element Inspection

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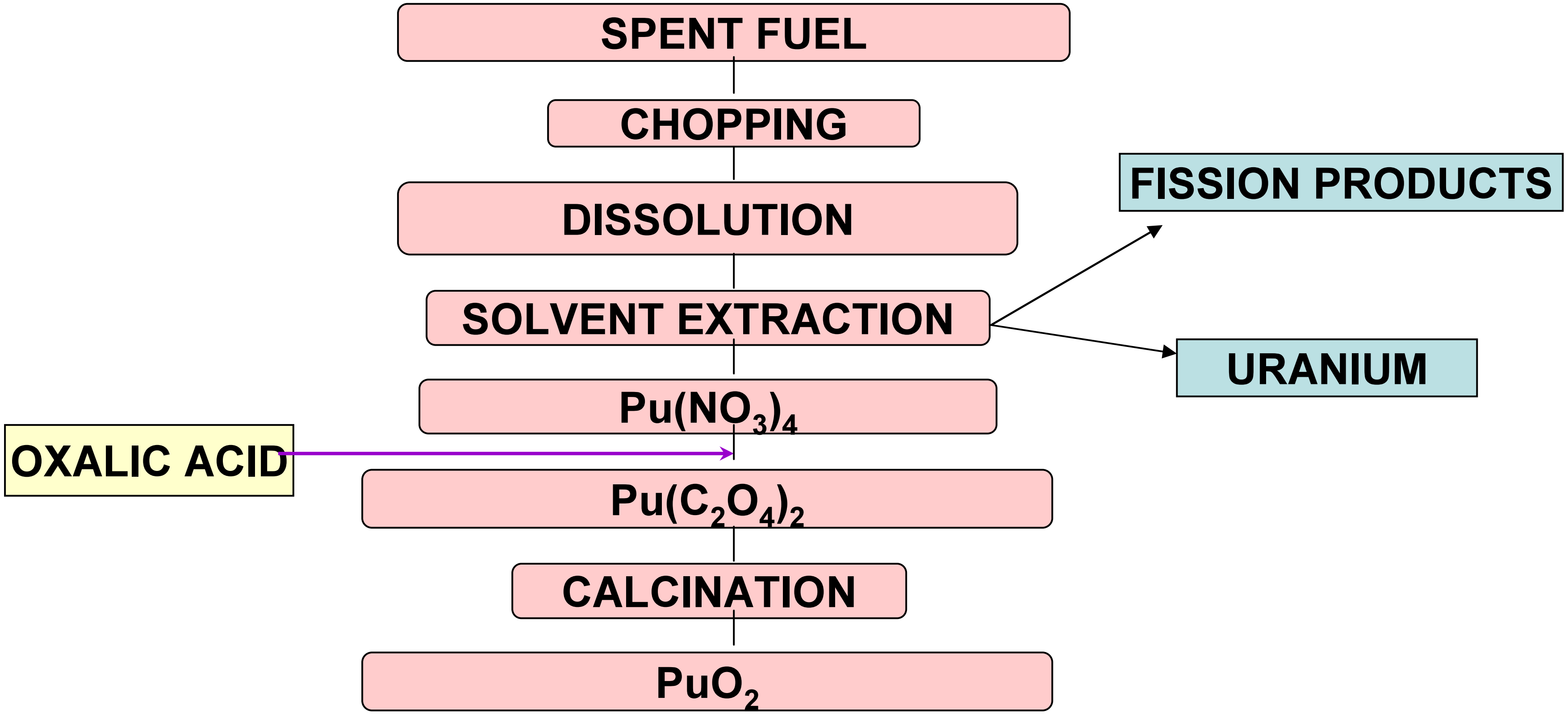
PuO_2 POWDER PRODUCTION



SPENT FUEL

CHOPPING

DISSOLUTION

SOLVENT EXTRACTION

FISSION PRODUCTS

URANIUM

$Pu(NO_3)_4$

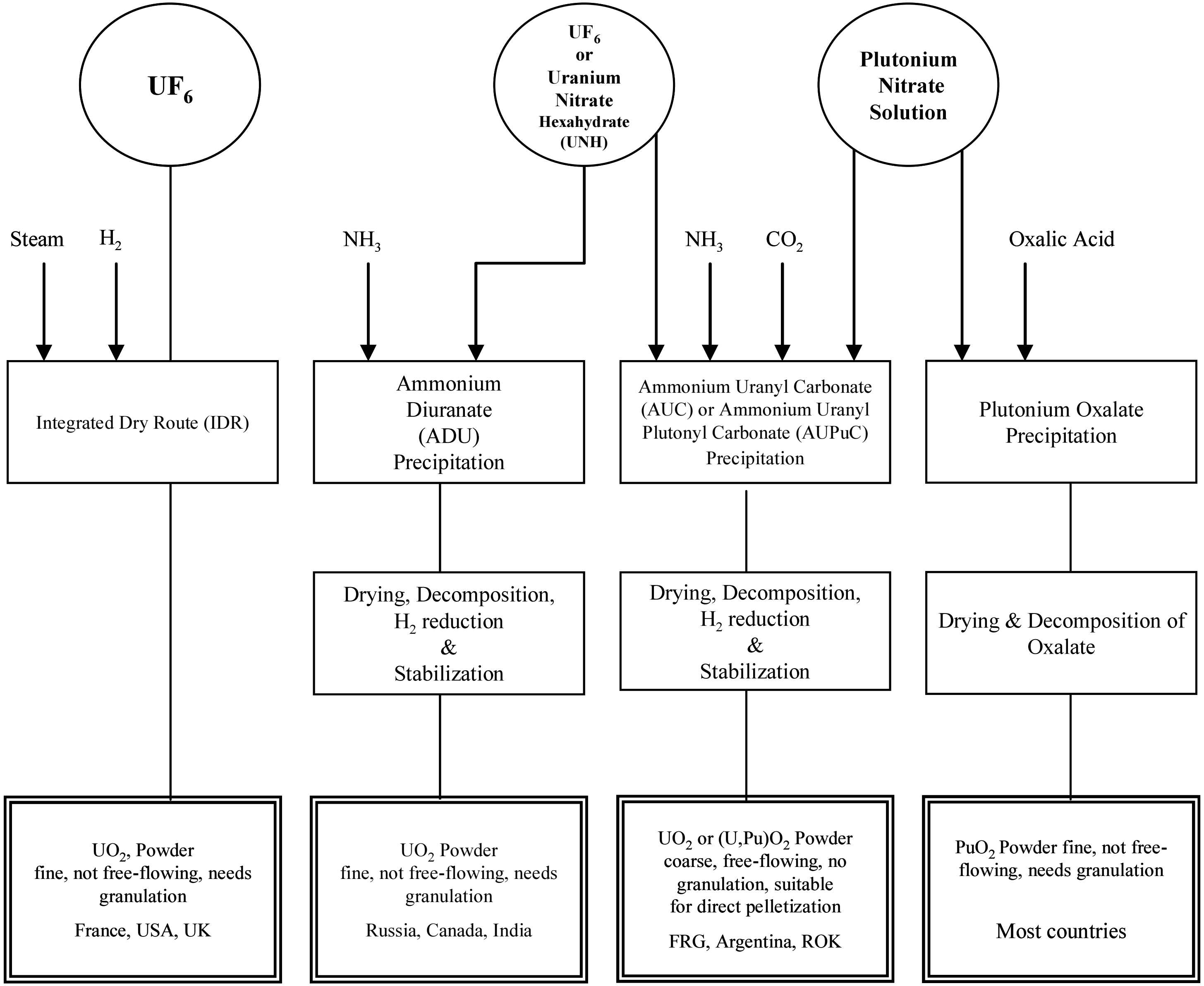
OXALIC ACID

$Pu(C_2O_4)_2$

CALCINATION

PuO_2

Industrial Processes for Fabrication of UO_2, PuO_2 & $(U,Pu)O_2$ Powders



UF_6

Steam

H_2

Integrated Dry Route (IDR)

UO_2, Powder
fine, not free-flowing, needs granulation

France, USA, UK

UF_6
or
Uranium
Nitrate
Hexahydrate
(UNH)

NH_3

Ammonium
Diuranate
(ADU)
Precipitation

Drying, Decomposition,
H_2 reduction
&
Stabilization

UO_2 Powder
fine, not free-flowing, needs granulation

Russia, Canada, India

NH_3

CO_2

Ammonium Uranyl Carbonate (AUC) or Ammonium Uranyl Plutonyl Carbonate (AUPuC) Precipitation

Drying, Decomposition,
H_2 reduction
&
Stabilization

UO_2 or $(U,Pu)O_2$ Powder
coarse, free-flowing, no granulation, suitable
for direct pelletization

FRG, Argentina, ROK

Plutonium
Nitrate
Solution

Oxalic Acid

Plutonium Oxalate
Precipitation

Drying & Decomposition of
Oxalate

PuO_2 Powder fine, not free-flowing, needs granulation

Most countries

Challenges in MOX Fuel Fabrication

UO_2 and PuO_2 are iso-structura (CaF_2type FCC), completely solid soluble at stoichiometric composition and have very similar thermodynamic and thermo - physical properties.Hence, the manufacturing processes of UO_2 and $(U,Pu)O_2$ are similar. The oxide fuels are generally used in the form of "pellets" and manufactured by powder metallurgy (P/M) processes.

The main process steps in "powder - pellet" routes are:

i) preparation of oxide powder;
ii) granulation of oxide powder in some cases;
iii) cold – pelletization; and
iv) high temperature sintering in hydrogen atmosphere.

The major challenges in the P/M route are "radiotoxic dust hazard" associated with the generation and handling of large quantities of very fine powders of UO_2, highly radiotoxic PuO_2 and oxides of minor actinides and the poor flow-ability of the powder. The isotopes of plutonium, in particular, ^{238}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu are also associated with emission of beta-gamma radiations and neutrons. Hence, fabrication processes have to be carried out in a shielded facility. The type of shielding depends on beta – gamma activity.

Properties of Oxide , Carbide , Nitride and Metallic Fuels for Fast Reactors

Properties	$(U_{0.8}\,Pu_{0.2})O_2$	$(U_{0.8}\,Pu_{0.2})C$	$(U_{0.8}\,Pu_{0.2})N$	U-19Pu-10Zr
Theoretical Density g/cc	11.04	13.58	14.32	15.73
Melting point ºK	3023	2750	3070	1400
Thermal conductivity (W/m ºK) 1000 K	2.6	18.8	15.8	25
2000 K	2.4	21.2	20.1	
Crystal structure (Type)	Fluorite	NaCl	NaCl	γ (>973 K)
Breeding ratio	1.1 - 1.15	1.2 – 1.25	1.2 - 1.25	1.35 - 1.4
Swelling	Moderate	High	High	High
Handling	in air	Inert atmosphere	Inert atmosphere	Inert atmosphere
Compatibility - clad	Average	Carburization	Good	Eutectics
coolant	Average	good	good	good
Dissolution & reprocessing amenability	Demonstrated on industrial scale for aqueous and pilot scale for pyro-processes	Process not yet demonstrated on industrial scale	Dissolution easy but risk of C^{14} in reprocessing	Pyro-processing demonstrated on pilot plant scale

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Chemical Reactivity of Powders

UO_2, PuO_2, ThO_2	Air handling at Room Temprature
UO_2	Converts to low density U_3O_8 when heated in air. Therefore $(U\text{-}Pu)O_2$ fuel pellets are sintered in reducing atmosphere –N_2+7%H_2/ Ar+8%H_2.
PuO_2	Can be handled in air. When heated in reducing atmosphere beyond 1300-1400°C converts to BCC-Pu_2O_3.
ThO_2	Inert, can be sintered in either oxidizing or reducing atmospheres.
MC & MN	Pyrophoric & susceptible to oxidation & hydrolysis. Has to be handled in Inert atmosphere

Relative advantages and disadvantages of oxide, carbide, nitride and metallic fuels, with and without minor actinides, for LMFR

Fuel	Advantage	Disadvantage
Oxide	-Proven burn up >25 at % -industrial scale fabrication & irradiation experience -High creep rate, negligible PCMI -High melting temperature -Good stability at high temperature for Am_2O_3 & Cm_2O_3 (up to 5%)	-Very low dissolution rate of pure PuO_2 and plutonium-rich MOX in nitric acid -Likelihood of chemical interaction with Na/cladding material -Poor thermal conductivity -Powder processing route of fuel fabrication is associated with the problem of radio toxic dust hazard
Carbide	-Hard spectrum (small fraction of Pu required for reactivity balance) -High thermal conductivity favouring high linear rating of fuel rod -Proven to 18 at %	-Pyrophoric (must be handled and fabricated in inert gas atmosphere) -Powder processing route of fuel fabrication is associated with the problem of radio toxic dust hazard -High vapour pressure of AmC (vaporizes at <1500 K in vacuum)
Nitride	-Hard spectrum (small fraction of Pu required for reactivity balance) -High thermal conductivity -Test fuel pins have demonstrated proven burn up of 20 at % -High solubility rate in nitric acid	-Pyrophoric (must be handled and fabricated in inert gas atmosphere) -Powder processing route of fuel fabrication is associated with the problem of radio toxic dust hazard -Small creep rate leading to: pellet – clad mechanical interaction (PCMI) -Production of ^{14}C by $^{14}N(n,p)$ reaction. -To avoid ^{14}C formation, ^{15}N enrichment in necessary -To avoid dissociation of AmN, temperature of fuel fabrication should be below 1800 K
MetallicFuel (U-Zr and U-Pu-Zr)	-Hard spectrum (small fraction of Pu required for reactivity balance) -High thermal conductivity -Proven to 20 at % in EBR-II -Simplified fabrication, involving melting and casting which avoids the problem of radiotoxic dust hazard	-Low melting temperature (Pu must be alloyed with Zr) -Volatility of Am (rapid cooling of molten alloy during fabrication) -Large swelling rate requires large sodium bonded pellet clad gap -Alpha contaminated Na waste -pyro processing

Oxide Fuels for Sodium Cooled Fast Reactors

\# Simplicity and less number of process steps in fabrication, and maturity of UO2 and MOX fuels fabrication industry;

\# High melting point and good chemical stability of UO2 and MOX fuels;

\# Satisfactory chemical compatibility of UO2 and MOX with sodium coolant and stainless steel cladding;

\# Considerable and satisfactory irradiation database of UO2 and MOX fuels to high burn up in thermal and fast reactors;

\#. Well advanced safety analysis based on large number of out-of-pile and in-pile experimentsworld wide, simulating incidental and accidental conditions;

\# Industrial scale experience in reprocessing of spent UO2 and MOX fuels.

Technology Already Demonstrated

France and UK have demonstrated all the steps of SFR fuel cycle including fabrication, irradiation, reprocessing and re-fabrication on an industrial scale with MOX fuel.

Japan has also industrial scale manufacturing experience of MOX fuel for JOYO and MONJU.

Russia has industrial scale manufacturing and high burn up irradiation experience of UO2 fuel containing HEU in BOR-60, BN-350 and BN-600.

The Indian PFBR-500 will also use MOX as the driver fuel.

Fabrication Processes for MOX

Powder – pellet route (both mechanical mixing & co-precipitation)

Sphere-pac or Vibro-sol process

Sol-Gel Microsphere Pelletisation process

The technology of fabrication of plutonium bearing fuels like MOX for Fast Breeder Reactors has now been mastered industrially by many countries like Belgium , France , India , Germany , Great Britain and Russian Federation

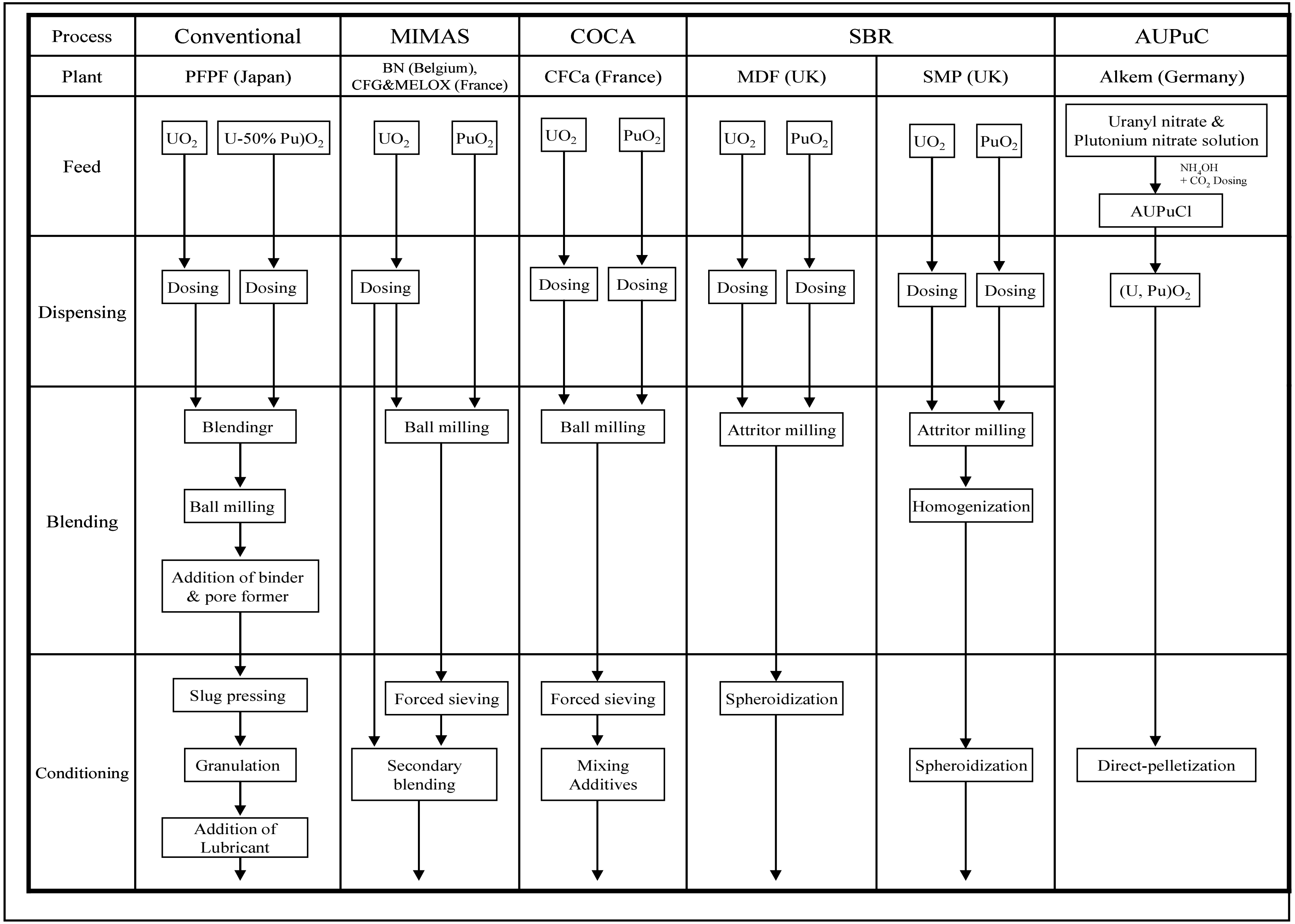
When fabrication of fuels containing minor actinides like americium , curium and long lived fission products or transmutation fuels is considered, dust production and consequent radiation exposure to personnel could limit the applicability of the process consisting of co-milling , cold compaction and sintering. Therefore , alternate fabrication routes that are more amenable to remotization and automation should be considered .

Processes utilized for Fabrication of $(UPu)O_2$ Fuel Pellets

1. COobroyage CAdarche (COCA) process of France
2. Micronized Master Mix (MIMAS) process of Belgium and France,
3. Short Binder less Route (SBR) of UK
4. Oxide Co-milling (OCOM)
5. Ammonium Uranium Plutonium Carbonate (AUPuC) processes of Germany

COCA, SBR, OCOM and AUPuC have been used for fabrication of MOX fuel pellets for fast reactors and MIMAS is mostly used for fabrication of MOX fuel for thermal reactors

Industrial Processes for MOX Fuel Manufacturing



Process	Conventional	MIMAS	COCA	SBR		AUPuC
Plant	PFPF (Japan)	BN (Belgium), CFG&MELOX (France)	CFCa (France)	MDF (UK)	SMP (UK)	Alkem (Germany)
Feed	UO_2 U-50% Pu)O_2	UO_2 PuO_2	UO_2 PuO_2	UO_2 PuO_2	UO_2 PuO_2	Uranyl nitrate & Plutonium nitrate solution NH_4OH + CO_2 Dosing AUPuCl
Dispensing	Dosing Dosing	Dosing	Dosing Dosing	Dosing Dosing	Dosing Dosing	$(U, Pu)O_2$
Blending	Blendingr Ball milling Addition of binder & pore former	Ball milling	Ball milling	Attritor milling	Attritor milling Homogenization	
Conditioning	Slug pressing Granulation Addition of Lubricant	Forced sieving Secondary blending	Forced sieving Mixing Additives	Spheroidization	Spheroidization	Direct-pelletization

Powder – Pellet route

Preparation of feed UO_2 and PuO_2 powders

Mixing of powders in either planetary ball mill or attritor to get homogeneous powder mixture

Pre-compaction & granulation

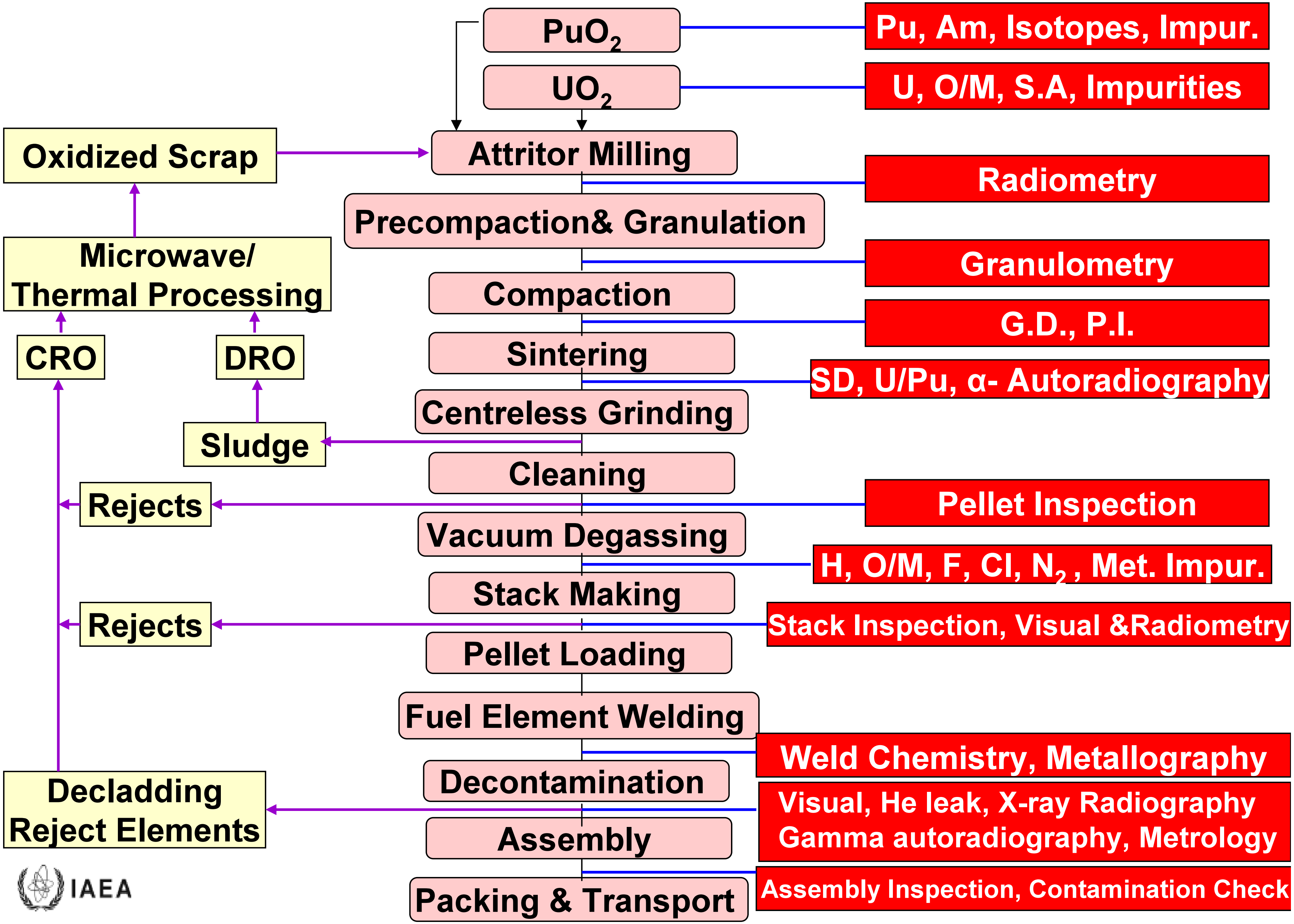
Cold compaction

High temperature sintering in hydrogen atmosphere

Centreless grinding

The distribution and the homogeneity of the constituents is an important consideration since it affects the safety and reliability of the fuels. The presence of the Pu rich regions in the pellet affects the fuel performance since they act as hot spots generating high temperatures and releasing more fission gases. This also causes problem during reprocessing operations since these pellets will not dissolve completely in nitric acid without addition of HF. Hence it is essential to avoid such regions by adopting proper manufacturing procedures leading to high degree of micro-homogeneity

MOX Fuel Fabrication Flow-sheet



PuO_2 — Pu, Am, Isotopes, Impur.

UO_2 — U, O/M, S.A, Impurities

Attritor Milling — Radiometry

Precompaction& Granulation — Granulometry

Compaction — G.D., P.I.

Sintering — SD, U/Pu, α- Autoradiography

Centreless Grinding

Cleaning — Pellet Inspection

Vacuum Degassing — H, O/M, F, Cl, N_2 , Met. Impur.

Stack Making — Stack Inspection, Visual &Radiometry

Pellet Loading

Fuel Element Welding — Weld Chemistry, Metallography

Decontamination — Visual, He leak, X-ray Radiography Gamma autoradiography, Metrology

Assembly — Assembly Inspection, Contamination Check

Packing & Transport

Oxidized Scrap

Microwave/ Thermal Processing

CRO

DRO

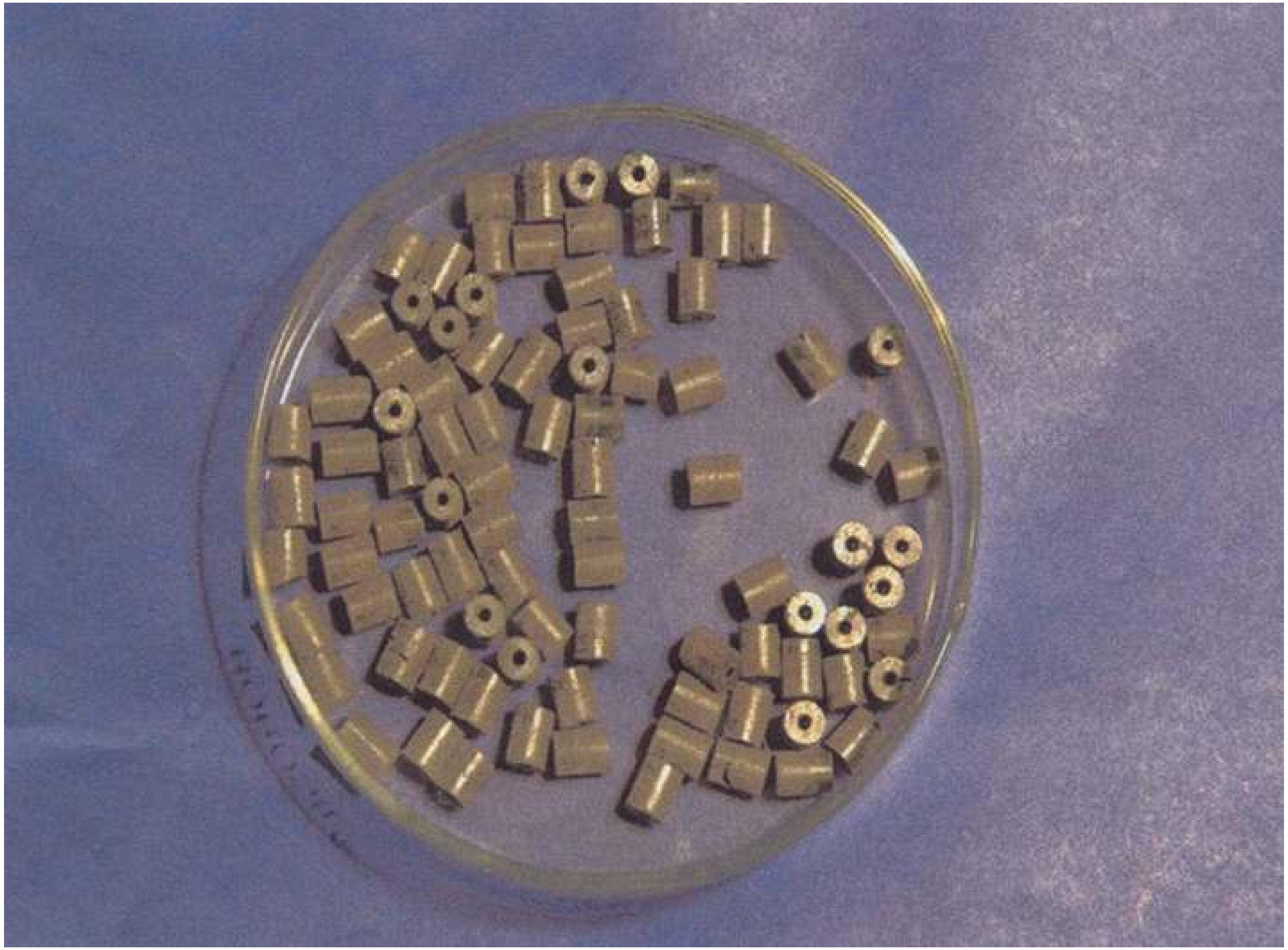
Sludge

Rejects

Rejects

Decladding Reject Elements

Annular MOX Pellets for Fast Reactor



Advanced Fabrication Processes

Vibro – sol or sphere – pac process

The vibro – sol or sphere – pac process consists of the preparation of sol – gel derived microspheres of diameter 50 - 1000µm by internal or external gelation process starting from heavy metal nitrate feed solution. The mixed oxide gel microspheres are dried and sintered to high density (≥96%T.D) which is subsequently packed in the cladding tube by vibratory compaction. The principal advantages of this process are the avoidance of the handling and generation of fine powders, less number of fabrication steps, maximum number of flexibility of operation, a high degree of micro - homogeneity of fissile species and amenability to automation and remotisation.

Sol – gel microspher pelletisation process (SGMP)

This is an advanced concept for the fabrication of high density fuel pellets retaining most of the manufacturing advantages of powder – pellet route and vibro – sol process. The SGMP process utilises sol – gel derived dust free and free flowable calcined gel microspheres of mixed oxide as feed materials for pellet compaction and sintering. High density fuel pellets with tailor made microstructure suitable for thermal and fast reactors could be fabricated by SGMP process.

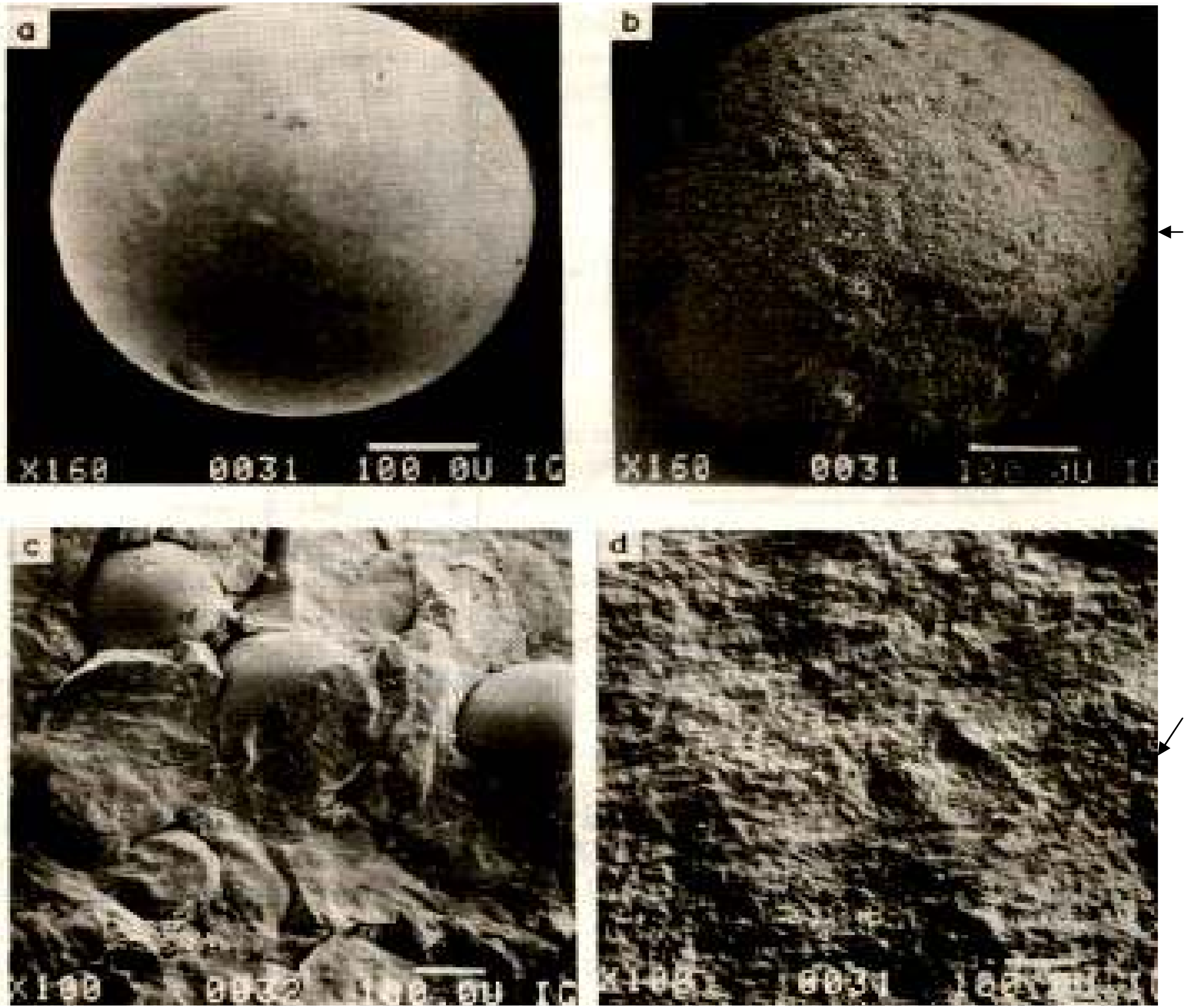
Sol-Gel Based Processes for Fuel Manufacturing

Sphere-pac or Vibro-sol Fuel

High density oxide / carbide / nitride fuel microspheres of two to three sige fractions (~750 , ~100 and ~10 micron) are loaded in one end welded fuel cladding tubes and subjected to vibratory compaction. It is possible to prepare fuel pins of smear density in the range of 80 – 85%T.D.

Sol-Gel Microsphere Pelletization(SGMP)

Sol-gel derived soft or hard microspheres are directly compacted to pellets and sintered at ~1700°C in hydrogen atmosphere. Hard microspheres retain their individual identity even after pelletization and sintering resulting in black-berry structures with microsphere boundaries and open porosity. Soft microspheres having low crushing strength disintegrate during pelletization resulting in pellets without microsphere boundaries



Relatively
hard
microsphere

Porous & soft
microsphere

Blackberry
structure
showing
microsphere
boundaries

Microstructure
showing no
boundaries

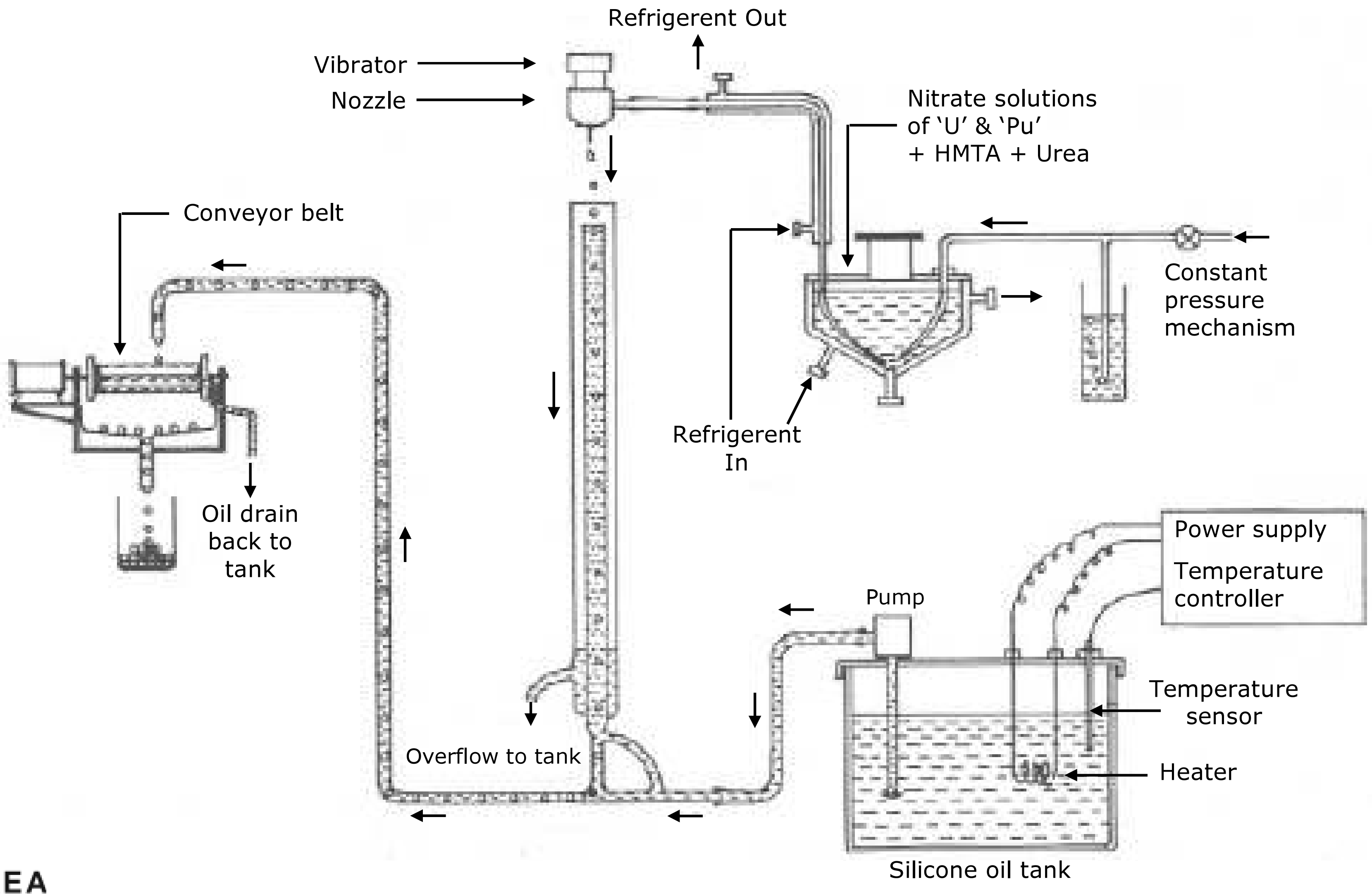
Sol – Gel Processes for Fuel Fabrication (Sphere-pac & SGMP processes)

1. Preparation of sol or broth from nitrate solutions of uranium and plutonium (nitrate solutions with urea and ammonium nitrate for EGU, urea and HMTA for IGU)
2. Droplet formation by vibratory nozzel
3. Droplet gelation in NH_3 gas and NH_4OH bath (for EGU) or silicon oil bath at 90±1°C which decomposes HMTA to release ammonia for the conversion of droplets into hydrous gei-microspheres (for IGU). Microwave heating can also be used in place of silicon oil bath
4. Washing of gel – microspheres :

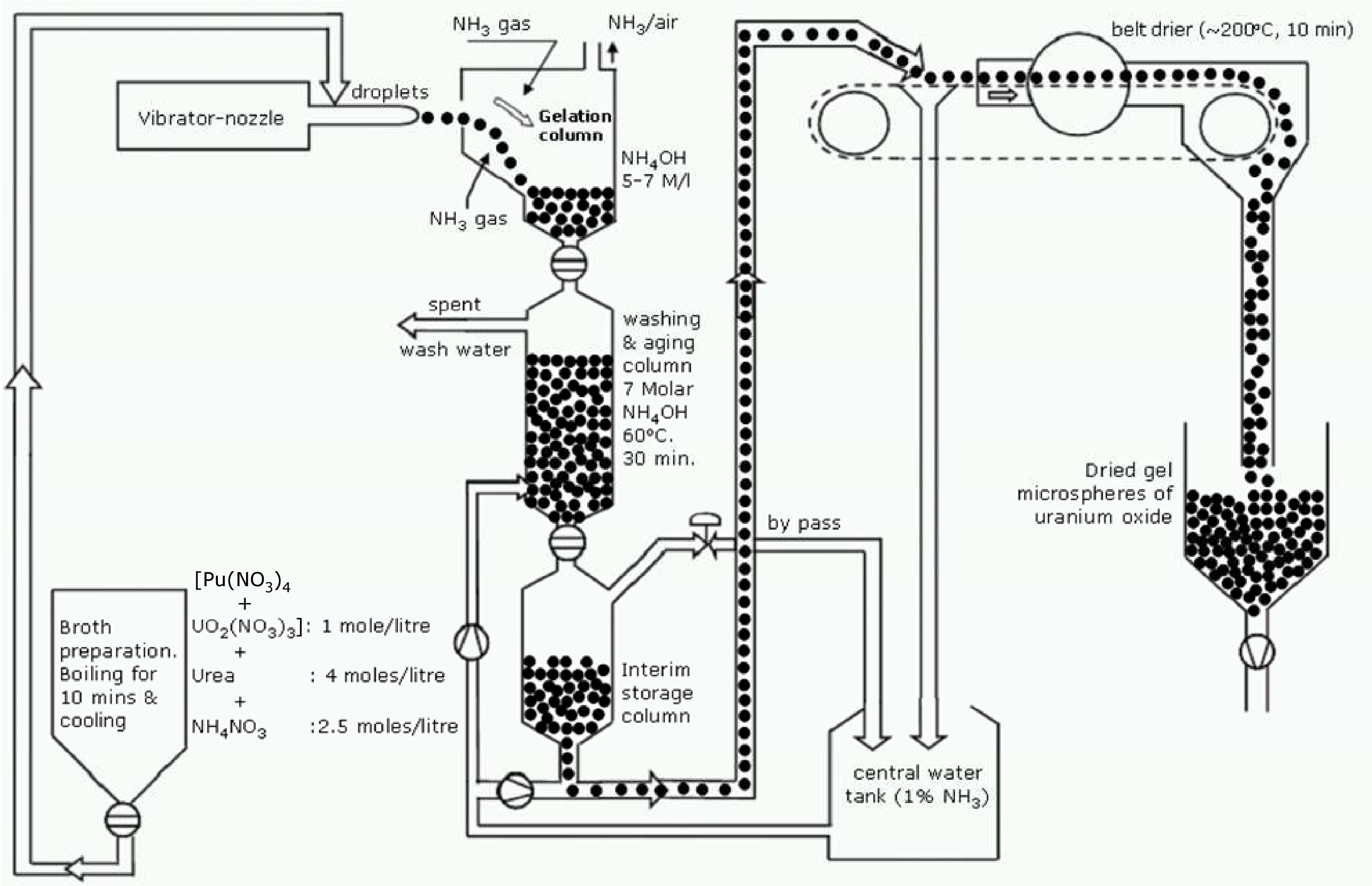
   i) In EGU , 1% ammonia solution for removal of ammoniumnitrate

   ii) In IGU , CCl_4 is used to remove oil and 3M NH_4OH solution to remove ammonium nitrate
5. Drying of gel – microspheres on a continuous belt-dryer at 200 - 250°C
6. Sintering at ~ 1600°C to produce high density $(UPu)O_2$ microspheres

Internal Gelation Process



External Gelation Process



Advantages of Sol-Gel Processes

1. A high degree of micro-homogeneity is attained in MOX fuel as uranium and plutonium nitrate solutions are mixed prior to gelation

2. Generation and handling of fine UO_2 and PuO_2 are avoided . Hence the problem of radiotoxic dust hazards associated with conventional powder – pellet route is significantly minimized

3. Dust free and free-flowing microspheres facilitate remote and automated manufacturing of fuel pins by vibro-sol or SGMP processes

4. The sol-gel facility could be easily integrated with spent fuel reprocessing plant and could be utilized for manufacturing of MOX containing minor actinide oxides

Advantages of Sol Gel Microsphere Pelletization Process

\# Radiotoxic dust hazard and pyrophoricity hazard are minimized;

\# Dust-free and free-flowing microspheres facilitate automation and remotization;

\# Fabrication steps for monocarbide and mononitride fuel pellets are significantly reduced;

\# Excellent microhomogenity is ensured in fuel pellets because U and Pu are mixed as nitrate solutions;

\# Fabrication of relatively low-density pellets (~85% T.D.) with "open" pore structure specified for He-bonded FR fuel pins is possible without addition of pore former.

Importance of Thermo-physical Properties of Nuclear Fuel

The performance of nuclear fuel in power reactors is largely dependent on its thermo-physical properties and their changes with temperature and irradiation. Experimental data on properties such as **Melting point**, **Thermal conductivity**, **Thermal expansion** are required for fuel design, performance modeling and safety analysis . The variables that influence these properties of fuel are **composition**, **temperature (T)**, **density**, **microstructure** and **stoichiometry (O/M, C/M, N/M)** of fuels .

Melting point and **thermal conductivity** of the fuel play a crucial role in determining the power to melt of the fuel and decides the operating linear heat rating. Melting point depends on the **fuel composition**, **stoichiometry** and **burn up**. The thermal conductivity of nuclear fuel affects the temperature profile which in turn influences almost all important processes such as **fission gas release**, **swelling**, **grain growth** etc. and limits the linear power . The changes in thermal conductivity occur during irradiation by the formation of fission-gas bubbles, porosities, build-up of fission products and by the change of fuel stoichiometry.

The coefficient of thermal expansion (CTE) is needed to calculate stresses occurring in the fuel and cladding on change in temperature. The difference between the coefficients of thermal expansion of the fuel and the cladding determines the status of the fuel-clad gap when the fuel element is brought to power. In safety analysis, the values of thermal expansion data are required in determining the gap conductance and thus the stored energy .

Melting Point

UO2 melts at higher temperature than PuO2. MOX fuels melt at a temperature between that of pure UO2 and PuO2. The deviation from the stoichiometry and burn up lowers the melting temperature

Tm (UO2) = 3120 ± 30 K & Tm (PuO2) = 2701 ± 35 K

i) Effect of Pu content :

Mixed oxide fuel melts incongruently. Solidus /liquidus temperature (T_S)/(T_L) of unirradiated **MOX** fuel of stoichiometric composition is estimated by the Adamson correlations :

T_S (K) = $3120.0 - 655.3y + 336.4y2 - 99.9y3$

T_L (K) = $3120.0 - 388.1y - 30.4y2$

where y is the PuO2 content in molar fractions.

ii) Effect of Stoichiometry :

The change in solidus and liquidus temperatures as function of O/M ratio and Pu fraction is given by the following relation:

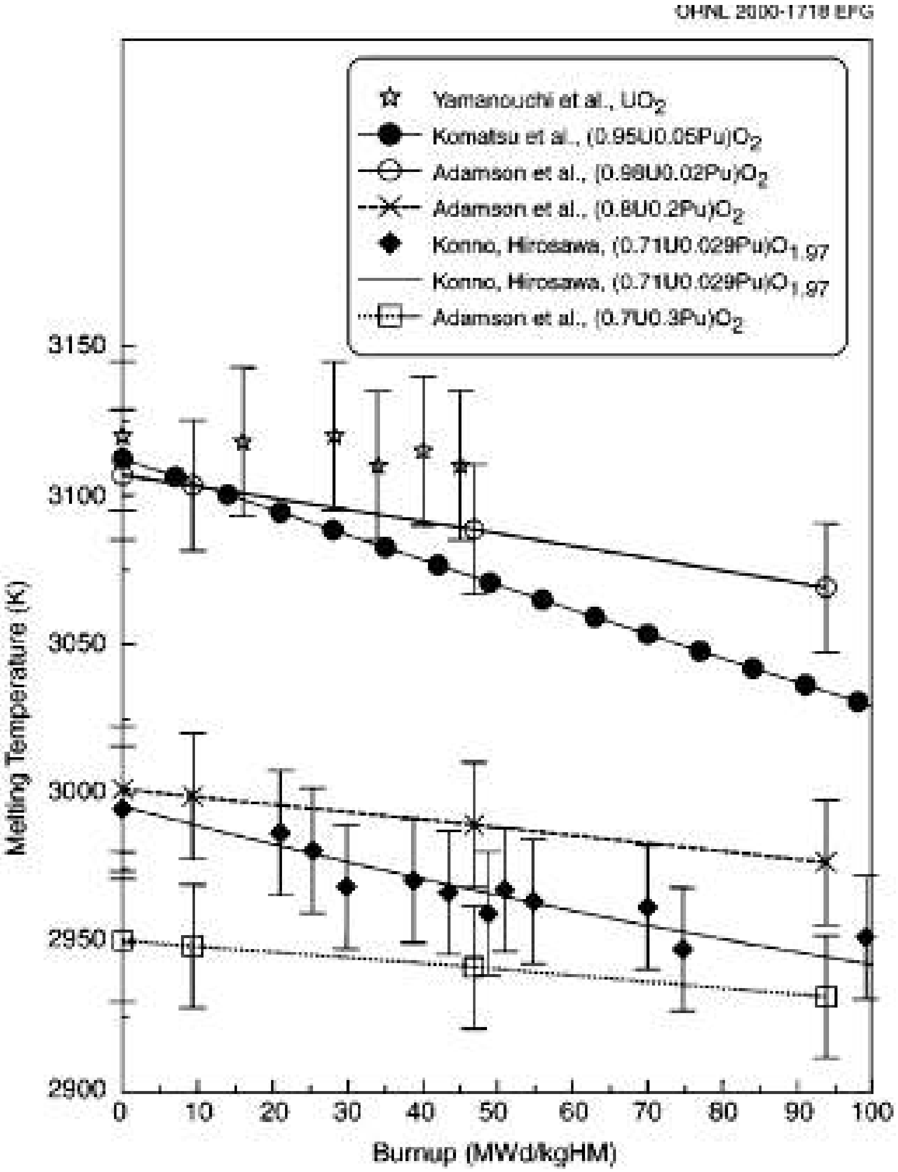
$\Delta Ts = -(1000-2850y)*(2.00-O/M)$

$\Delta T_L = -(280-5000y3)*(2.00-O/M)$

Where y is the Pu fraction.

This relation is valid for an O/M ratio of 1.94 to 2.00.

Effect of Burn up on Melting Temperature for MOX Fuel with different PuO2 content



Thermal conductivity

Thermal conductivity measurements

Thermal conductivity of a solid can be measured by two methods:

1. By determining the stationary heat flow through the specimen (steady state) which gives k directly
2. By determining the variation of the temperature at a fixed plane, that is a specimen surface, due to an induced non-stationary heat flow (transient) thermal diffusivity, α is obtained.

The thermal conductivity (k) is derived from the measured values of thermal diffusivity data by using the relation:

$k = \alpha \rho Cp$

where ρ is the density of the material and Cp its specific heat at constant pressure.

Since the second method is more versatile and requires smaller specimen, it has become a standard method for determining k

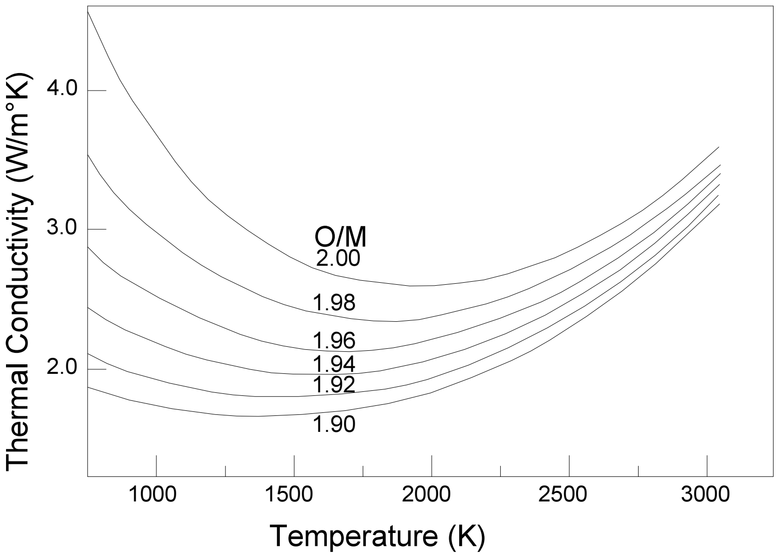
Thermal conductivity of 100% dense stoichiometric and hypostoichiometric MOX fuel

A detailed comparison of stoichiometric oxide fuels shows that the thermal conductivity of both uranium dioxide and mixed dioxide are comparable. Thermal conductivity and melting point are higher at exact stoichiometric composition. Recommended relation for $(U_{0.8}Pu_{0.2})O_{2-x}$ between temperature (k) and thermal conductivity (W/m.K) as function of x is

$$K_{100} = (0.037 + 3.33x + 2.37 * 10^{-4} T)^{-1} + 78.9 * 10^{-12}T^{3}$$

This equation is valid for the temperature range of 500-2 000 °C, over the range $0<x<0.1$ and is valid for PuO_2 content of about 20%.

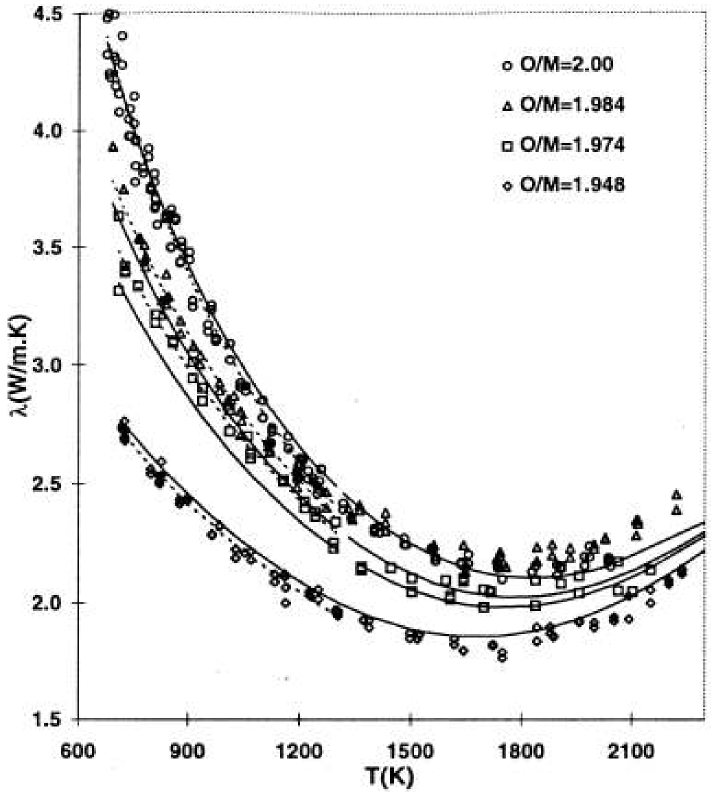
Figure 36 shows the variation of thermal conductivity for 100% dense stoichiometric and hypostoichiometric mixed oxide. The effect of O/M is more prominent at low temperatures (below 1 000 K) than at high temperatures of around 3 000 K.



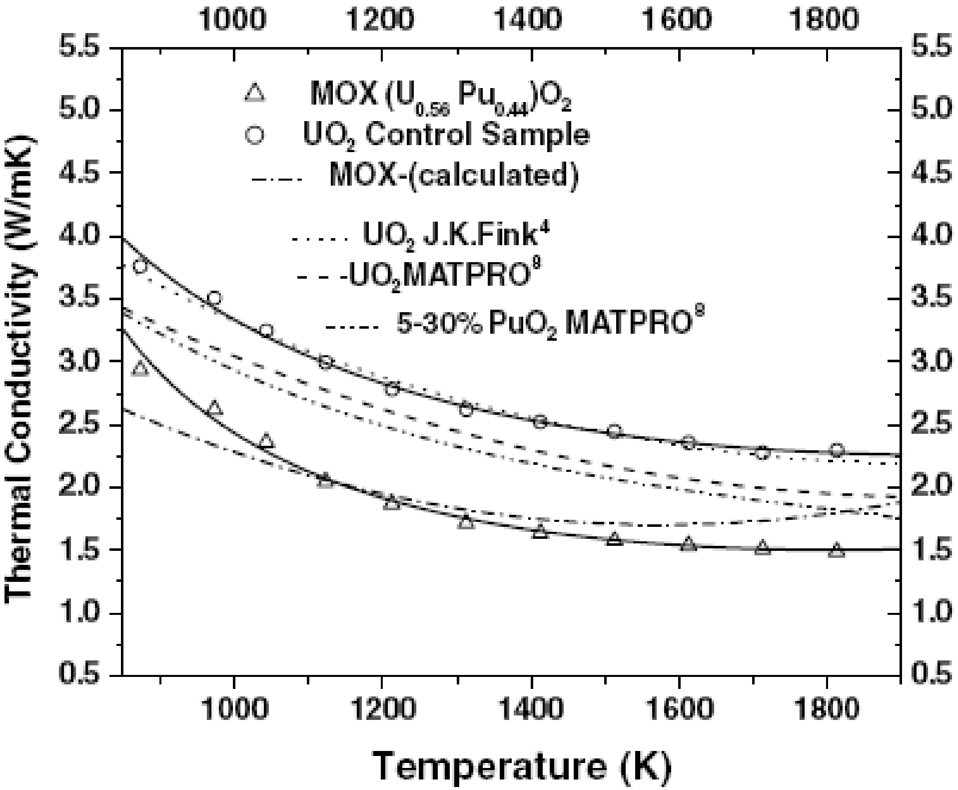
Effect of Plutonium Addition on Thermal Conductivity

In general , thermal conductivity is sensitive to Pu content and decreases with increase in the Pu content at a given temperature . This decrease in thermal conductivity is more prominent at lower temperatures.

Thermal conductivity ofUO$_2$-15%PuO$_2$



Thermal conductivity of UO2-44%PuO2



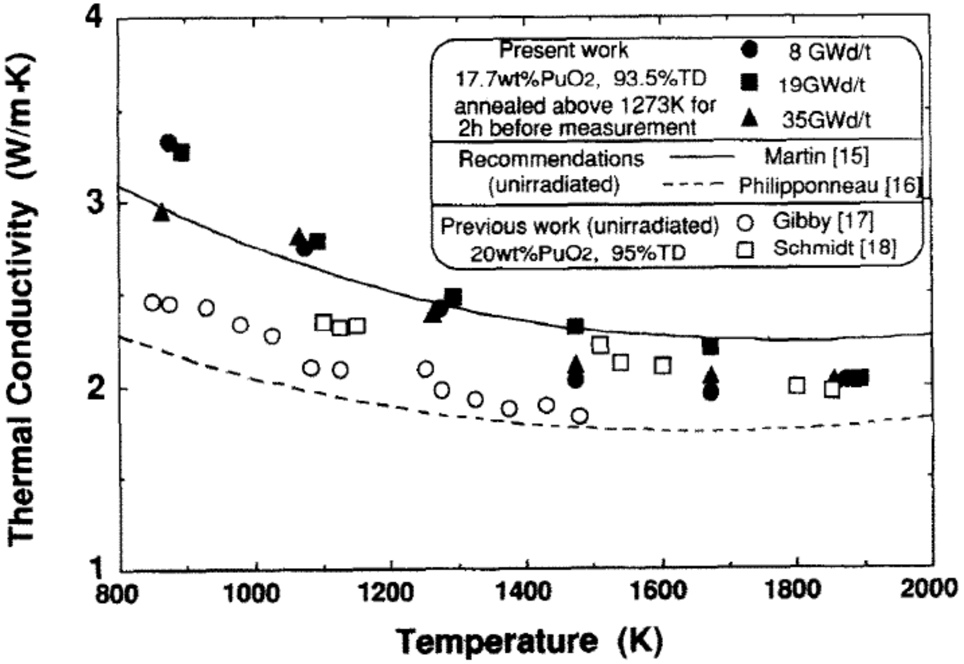
Effect of Porosity on Thermal Conductivity

Pores, like any other defect, scatter phonons and reduce the thermal conductivity.

$$k_M = [(1-P)/(1+\beta P)]\, k_{100}$$

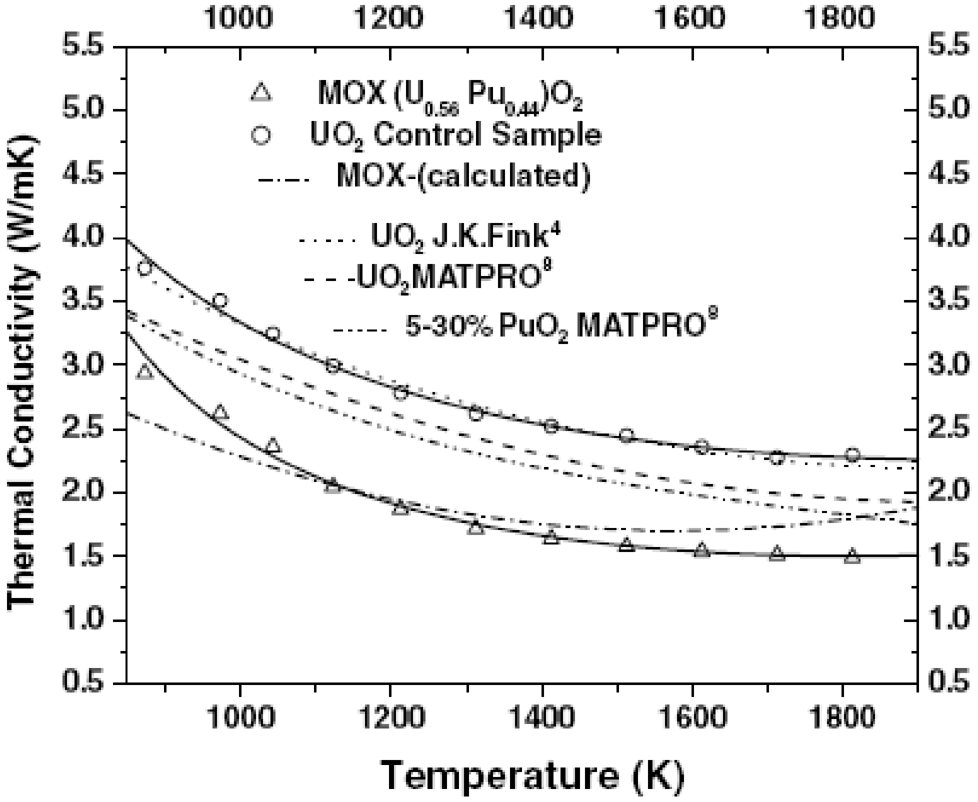
where P is the porosity fraction and β is a constant and is 2.

Effect of Burn up on Thermal conductivity



Thermal conductivity variations with burn up are not significant for mixed oxide fuel

Thermal Conductivity of UO2 – 44%PuO2 (95%T.D) as a function of Temperature



Thermal conductivity decreases with increase in temperature and follows a 1/(A + B*T) relation and expressed by the equation

$k= 1/(-0.61 + 1.42 * 10^{-3} T - 3.93 * 10^{-7} T^{2})$

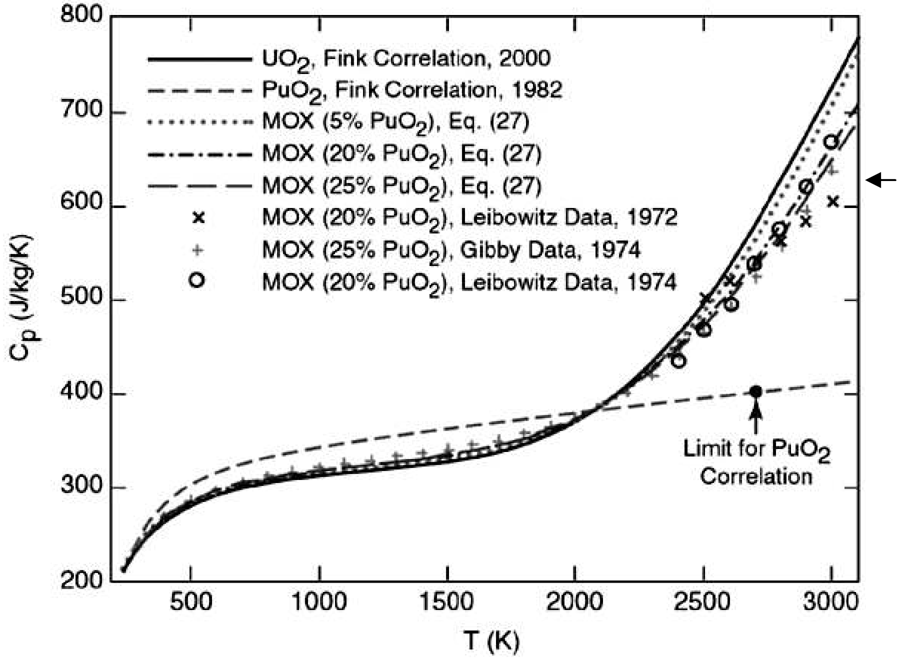
Thermal conductivity of UO2-44%PuO2 was found to be 1.80 W/m K while the same for UO2- 30% PuO2 was 2.33 W/m K at 1 000 °C.

Specific Heat

For a mixture of UO2 and PuO2, the specific heat capacity of the solid is determined by combining the contribution from each constituent in proportion to its weight fraction. For example, the heat capacity for solid MOX [(U $_{1-y}$ Pu $_{y}$)O2] fuel is expressed as

$$C_p\,(T, \mathrm{MOX}) = (1-y)\, C_p\,(T, \mathrm{UO_2}) + y\, C_p\,(T, \mathrm{PuO_2})$$

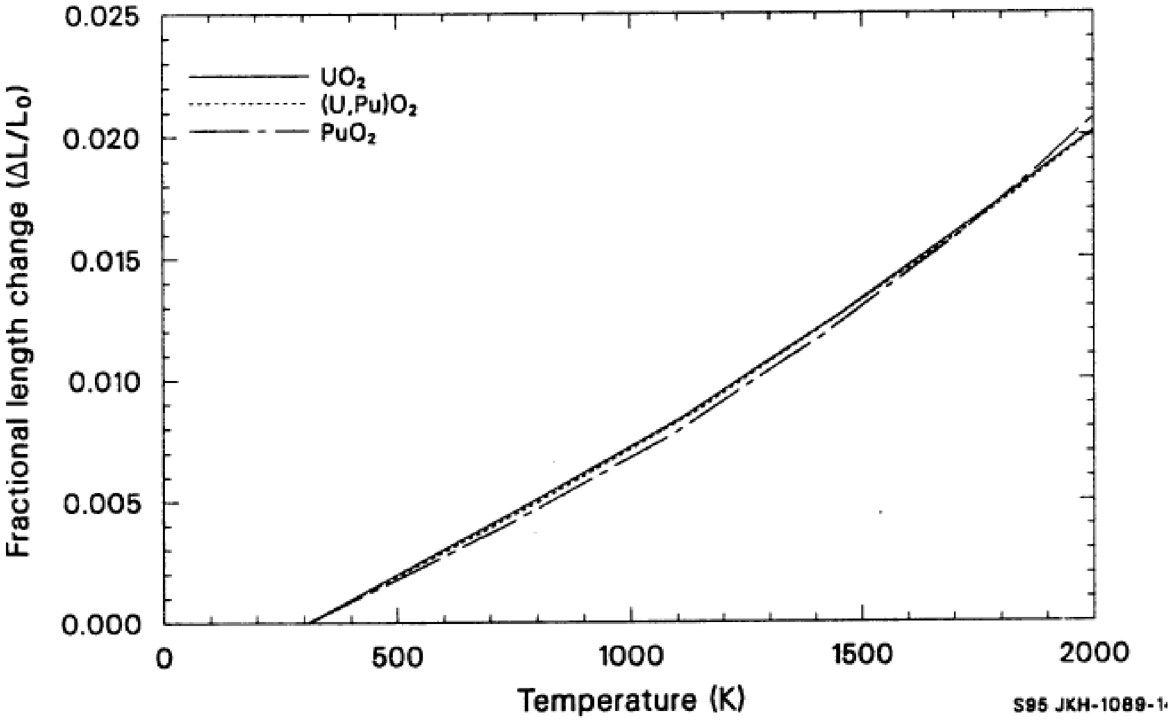
where y is the mole fraction of PuO_2



←Specific heat capacity of UO_2 , PuO_2 and MOX plotted against temperature

Coefficient of Thermal Expansion

Both UO_2 and PuO_2 have identical coefficient



Thermal Expansion curves for UO2 , PuO2 and (U0.8Pu0.2)O2+x

Fuel Failure and Irradiation Behaviour

For safe operation , the integrity of the cladding shall be maintained during irradiation and at least up to the target burn-up. Cladding integrity in Fast Breeder Reactor fuel pin may be affected due to :

1. Mechanical defects
2. Mechanical interaction between pin , spacer and wrapper
3. Fuel Clad Mechanical Interaction (FCMI)
4. Fuel clad Chemical Interaction (FCCI)

FCMI has been largely overcome by suitable fuel pin design such as lower smear density , annular pellet etc.

FCCI is caused by the migration of oxygen and volatile fission products to the fuel surface due to severe operating conditions and generally low density of the oxide fuel. FCCI consists mainly of the oxidation of constituents of the cladding material , particularly chromium , in the presence of cesium, molybdenum, tellurium and iodine.

Irradiation capabilities of MOX Fuel

The post irradiation examination has led to the conclusion that the behaviour of MOX fuel is not a life limiting factor for fuel pins , even under the stringent high burn up requirements .The main observations confirming this are :

 # A moderate fuel swelling rate , even at high burn up and no dramatic degradation of heat transfer properties

 # Problems of mechanical and chemical interaction between fuel and cladding can be overcome with adequate pin design . Recommended variations include using a moderate linear heat rating and increased pin diameter , resulting in a lower fuel surface temperature , a greater cladding thickness and lower oxygen to metal (O/M) ratio

 # In case of pin failure , no major reaction of the fuel with coolant , which might lead to a great loss of fissile material or to a rapid development of secondary failures or to failure propagation within the assemblies , have been observed.

On the basis of the excellent results obtained with MOX fuel , it is currently believed that the target burn up of 200 GWd / t (HM) for future large FBRs can be reached with MOX fuel

Irradiation Experience of MOX Fuel in SFR

Mixed uranium plutonium oxide (MOX) has been the driver fuel for most of the demonstration, prototype and commercial SFRs. Hence, the irradiation experience of MOX fuel in fast reactor are much more compared to other type of SFR fuels

More than 300,000 MOX fuel pins made by conventional powder – pellet route have been mostly irradiated in fast reactors in Europe , Russia and Japan

MOX fuel rods (~1000) made by vibro-pac have also been irradiated in BN-350 and BN-600 at a burn up ≤ 130 GWd/t(HM) . ~ 16000 vibro compacted fuel rods were irradiated even more than this burn up in BOR-60.

Only some experimental fuel pins irradiated in test and prototype reactors throughout the world have attained burn up more than 210 GWd/t(HM)

Restructuring in Irradiated MOX Fuel in Fast Reactor

Four distinct regions are observed when operated at a linear heat rating of 40 kW/m . These are as follows :

1. Innermost region is central void resulting from the transport of as fabricated porosity up the temperature gradient to the fuel centre;

2. Fuel surrounding the void consists of dense grains that are elongated radialy. Zones of increased plutonium content may also be observed within the columnar grain region;

3.Outside the columnar grain is a region where temperatures are sufficiently high for grain growth to take place by volume diffusion. These equiaxed grains are slightly elongated in the direction of temperature gradient with their boundaries containing gas bubbles and fission product inclusions;

4. Fuel between the equiaxed grain growth region and the cladding retain its original microstructure and density and is called the unstructured region or as fabricated structure. Fuel in this region operates at temperature below ~ 1200°C where mobilities are low and therefore the fuel tends to retain most of its original characteristics.

Mixed Uranium –Plutonium Carbide (MC)

&

Mixed Uranium – Plutonium Nitride (MN)

Fuel for Fast Reactor

Different Routes for preparation of MC&MN

1. Direct synthesis by arc-melting;

2. Hydriding - dehydriding of bulk metal (to form fine metal powder) followed by carburization and nitridation with methane/propane and nitrogen for obtaining fine powders of MC and MN respectively;

3. Carbothermic reduction of oxide-carbon mixture in vacuum/argon and flowing nitrogen for preparation of MC and MN respectively

The carbothermic reduction of oxides is the most attractive route for large scale production and has , therefore , been studied extensively in all the laboratories associated with the development of MC and MN fuels.

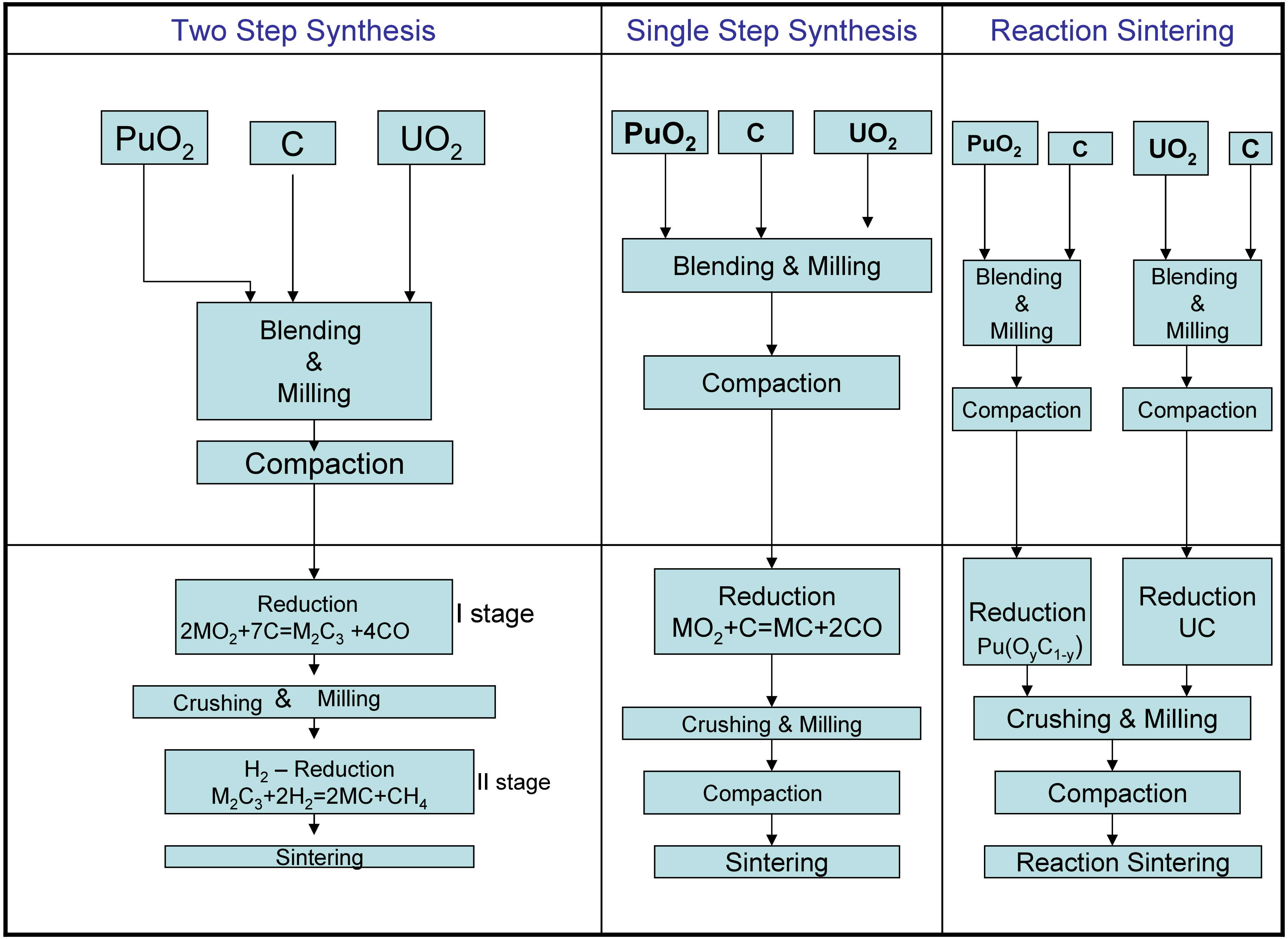
Carbothermic Synthesis of (UPu)C from Oxide

The simplified chemical equation for the production of monocarbide by carbothermic reduction of oxide is represented by :

$$\mathbf{MO_2 + 3\,C \;=\; MC + 2\,CO}$$

Where MO_2 is either a mechanical mixture or solid solution of UO_2 and PuO_2. During carbothermic reduction , the control of the partial pressure of CO is very important since the evolution of this gas not only constitutes the primary reduction mechanism but also controls the kinetics of the reaction

DIFFERENT CARBOTHERMIC REDUCTION PROCESSES FOR SYNTHESIS OF MIXED URANIUM PLUTONIUM **CARBIDE**



Two Step Synthesis

PuO_2 C UO_2

Blending & Milling

Compaction

Reduction $2MO_2+7C=M_2C_3+4CO$ I stage

Crushing & Milling

H_2 – Reduction $M_2C_3+2H_2=2MC+CH_4$ II stage

Sintering

Single Step Synthesis

PuO_2 C UO_2

Blending & Milling

Compaction

Reduction $MO_2+C=MC+2CO$

Crushing & Milling

Compaction

Sintering

Reaction Sintering

PuO_2 C | UO_2 C

Blending & Milling | Blending & Milling

Compaction | Compaction

Reduction $Pu(O_yC_{1-y})$ | Reduction UC

Crushing & Milling

Compaction

Reaction Sintering

Synthesis of (UPu)C

Single Step Synthesis

Single step solid state synthesis is the simplest technique for preparation of MC. In this method , MC end product always contain M_2C_3 second phase and residual oxygen and nitrogen impurities. This is because oxygen and nitrogen act as carbon equivalents and replace “C” in MC lattice to form the compound $(U,Pu)(O_xN_zC_{1-x-z})$ where x , z and their summation is less than 1.0

Two Step Synthesis

Two step solid state synthesis is an improvement over the single step synthesis and aims at the preparation of single phase MC with very low oxygen and nitrogen contents and practically no loss of plutonium by volatilization . In the first step , carbothermic reduction at a relatively low temperature with excess carbon ensures that only M_2C_3 is formed. In the second step , M_2C_3 is crushed , milled and treated with hydrogen at ~ 1123K in order to reduce it to MC and remove free carbon as methane.

Reaction Sintering

Three step “Reaction Sintering” process involves separate preparation of UC and plutonium oxycarbide from their respective oxides. The low temperature of plutonium oxycarbide formation minimizes the Pu loss by volatization. In the third step , UC and Plutonium oxycarbide powders are blended , compacted and subject to reaction sintering

Carbothermic Synthesis of (U,Pu)N from Oxide

The overall chemical reaction : $MO_2 + 2C + \frac{1}{2} N_2 = MN + 2CO$

Nitrogen plays the dual role of the reactant and the carrier for the removal of CO

The ideal way to obtain nearly single phase MN with very low oxygen , carbon and higher nitride is to use ~ 10% excess carbon in the oxide – carbon mixture , a synthesis temperature of 1550°C in flowing N_2 followed by $N_2 + H_2$ for the removal of excess carbon and then cooling in argon atmosphere to avoid any higher nitride formation

The principal methods of consolidation of MC and MN powders or microspheres in the form of small diameter fast reactor fuel pins

- **Cold pelletization of the powder into pellets followed by sintering in reducing atmosphere**
- **Direct pressing of clinkers into pellets followed by sintering**
- **Vibratory compaction of the granules, microspheres or crushed clinkers in cladding tubes**
- **Sol-gel microsphere pelletization.**

Process Flow Sheet for Fabrication of (U,Pu)C Pellets

UO_2

Graphite

PuO_2

Milling & Grinding

Process control

Tableting

Carbothermic Reduction
At 1673K in vacuum

Crushing

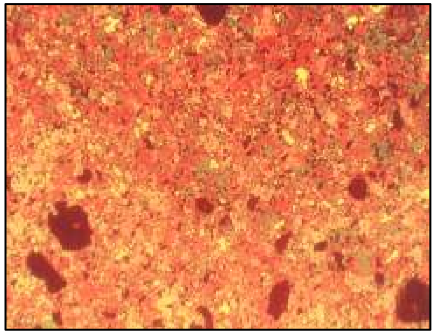
Milling

Process control

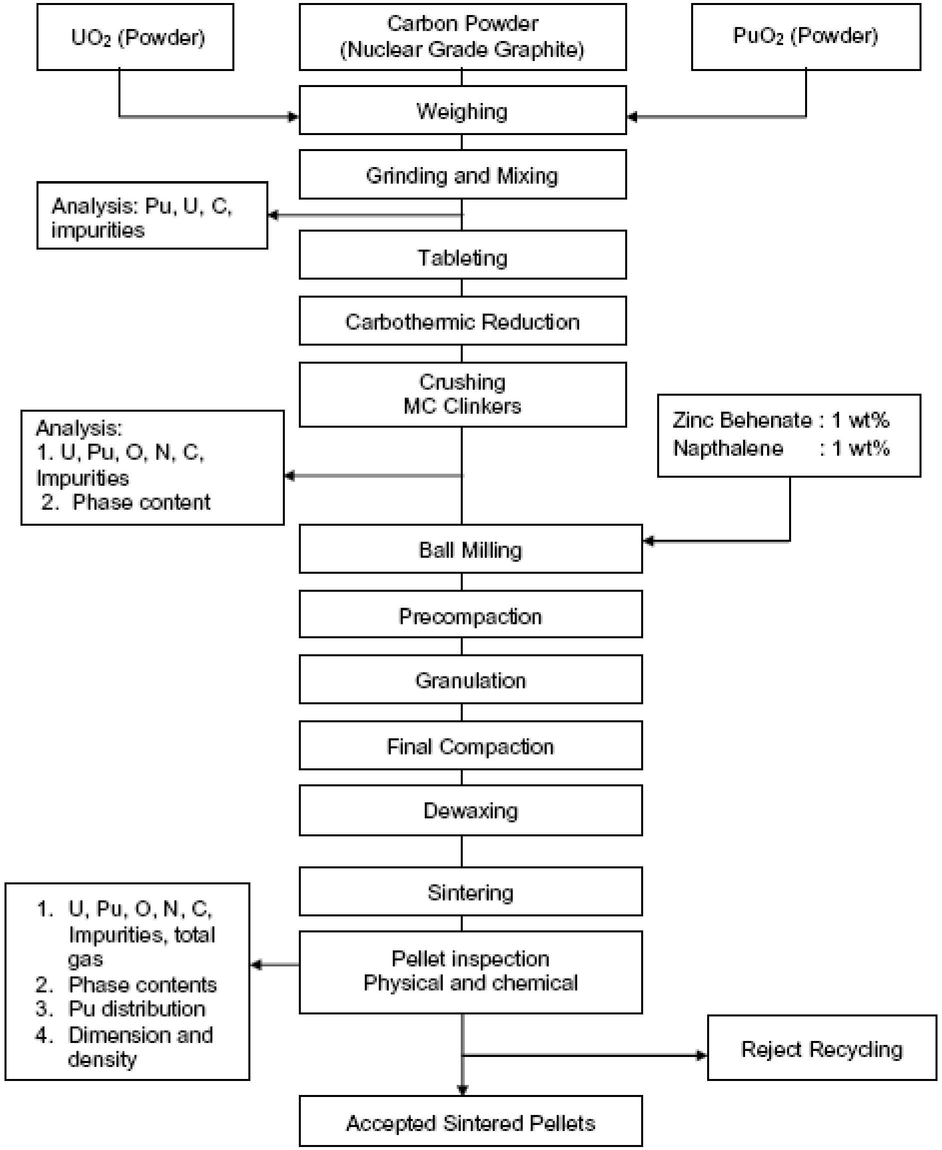
Compaction

Sintering
At 1923K in Ar-8%H_2

Pellet Inspection



Process steps followed in India for preparation of plutonium rich (U,Pu)C pellets for FBTR by the 'single step' "carbothermic synthesis" route in a static bed.



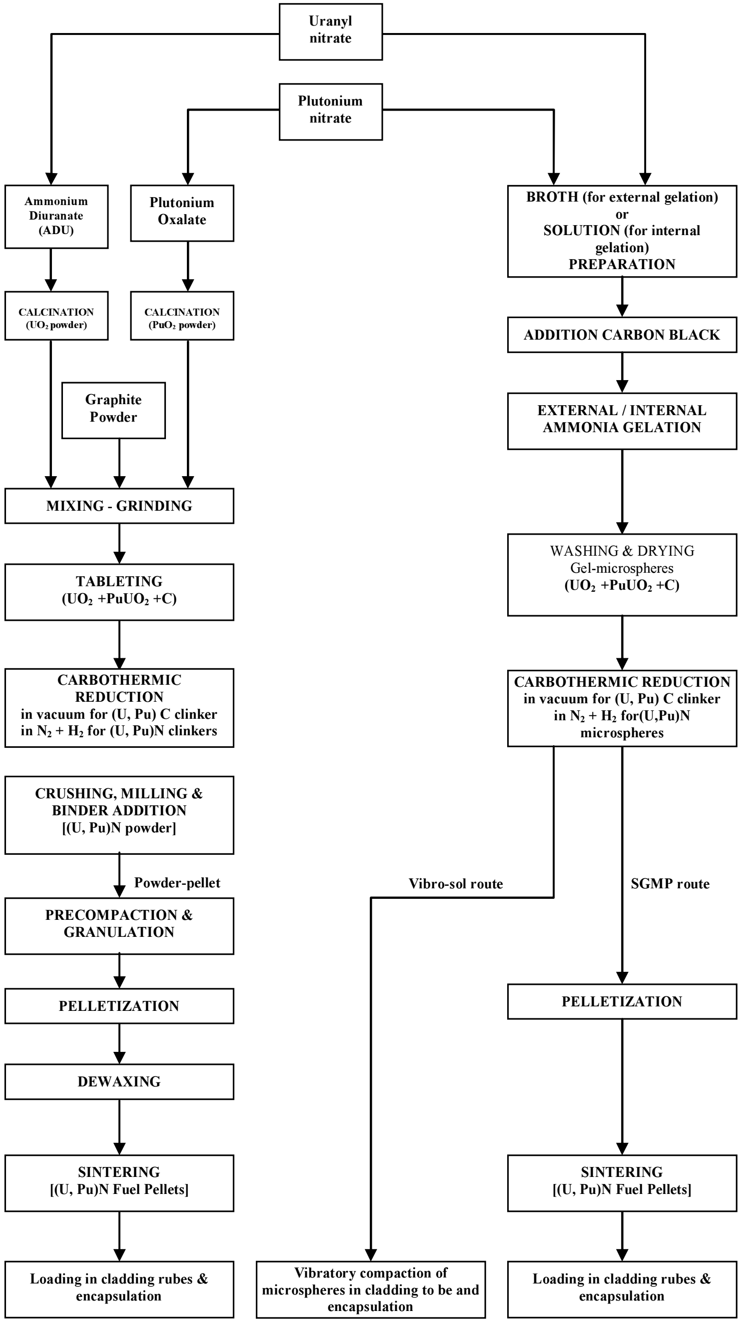
Comparison of Process Steps for Oxide and MC / MN Fuel Pellet Manufacturing

	Basis	Oxide	Carbide / Nitride
1.	Principal steps in fabrication	I)Co-milling of UO_2 & PuO_2 II)Compaction III)Sintering	I)Mixing of UO_2, PuO_2 & Carbon II)Tableting III)Carbothermic reduction IV)Crushing V)Milling VI)Compaction VII)Sintering
2.	Glove box atmosphere	Air	Inert gas: Ar or N_2 containing < 20 ppm each of O_2 & moisture
3.	Process controls	I)O/M II)Pellet density	I)C/M or N/M II)O, C & N contents of powder and pellet III)MO_2, M_2C_3 & MC_2 or MO_2, MN_2 & M_2N_3 contents of powder and pellets IV)Pellet density
4.	Additional equipment for (U,Pu)C fabrication		I)High temperature furnace for carbothermic reduction II)O, N and C analysers III)Trace oxygen & moisture monitors IV)Personnel safety oxygen monitors V)Inert gas system – once through or recirculation–purification

Sol-Gel based processes for MC & MN

Sphere – pac or Vibro sol & SGMP processes are similar to oxide fuel manufacturing , only carbon is added to the sol prior to gelation in order to obtain oxide microspheres containing carbon . These microspheres are used as feed material for the subsequent processes involving synthesis of mixed carbide or mixed nitride

Powder-Pellet & Sol – Gel Microsphere Pelletization Processes for MC / MN Pellet Manufacturing



Uranyl nitrate

Plutonium nitrate

Ammonium Diuranate (ADU)

Plutonium Oxalate

CALCINATION (UO_2 powder)

CALCINATION (PuO_2 powder)

Graphite Powder

MIXING - GRINDING

TABLETING (UO_2 +$PuUO_2$ +C)

CARBOTHERMIC REDUCTION
in vacuum for (U, Pu) C clinker
in N_2 + H_2 for (U, Pu)N clinkers

CRUSHING, MILLING & BINDER ADDITION [(U, Pu)N powder]

Powder-pellet

PRECOMPACTION & GRANULATION

PELLETIZATION

DEWAXING

SINTERING [(U, Pu)N Fuel Pellets]

Loading in cladding rubes & encapsulation

BROTH (for external gelation)
or
SOLUTION (for internal gelation)
PREPARATION

ADDITION CARBON BLACK

EXTERNAL / INTERNAL AMMONIA GELATION

WASHING & DRYING
Gel-microspheres
(UO_2 +$PuUO_2$ +C)

CARBOTHERMIC REDUCTION
in vacuum for (U, Pu) C clinker
in N_2 + H_2 for(U,Pu)N microspheres

Vibro-sol route

SGMP route

Vibratory compaction of microspheres in cladding to be and encapsulation

PELLETIZATION

SINTERING [(U, Pu)N Fuel Pellets]

Loading in cladding rubes & encapsulation

Advantages of Sol Gel Microsphere Pelletization Process

Radiotoxic dust hazard and pyrophoricity hazard are minimized;

Dust-free and free-flowing microspheres facilitate automation and remotization;

Fabrication steps for monocarbide and mononitride fuel pellets are significantly reduced;

Excellent microhomogenity is ensured in fuel pellets because U and Pu are mixed as nitrate solutions;

Fabrication of relatively low-density pellets (~85% T.D.) with "open" pore structure specified for He-bonded FR fuel pins is possible without addition of pore former.

Thermo physical properties of Carbides and Nitrides

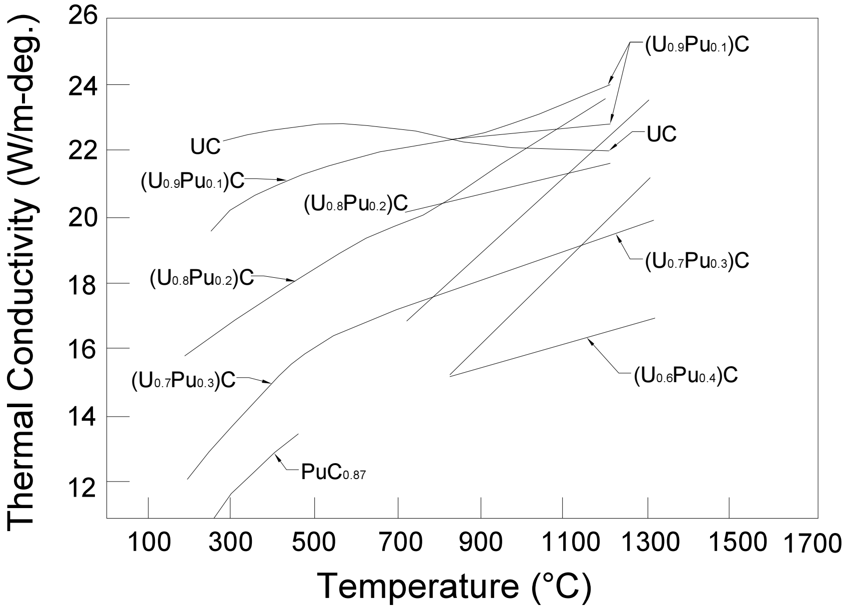
Melting Point

The melting point of pure UC is reported as as 2 780 ± 25 K .The melting temperature of PuC is 1 875 ± 25 K . The melting temperatures of U_2C_3 and Pu_2C_3 are given as 2 100 and 2 285K, respectively . The solidus temperature of($U_{0.8}Pu_{0.2}$) C and ($U_{0.8}$ Pu0 $_{0.2}$) $_2C_3$ are 2750 ± 30 and 2 480 ± 50 K, respectively .

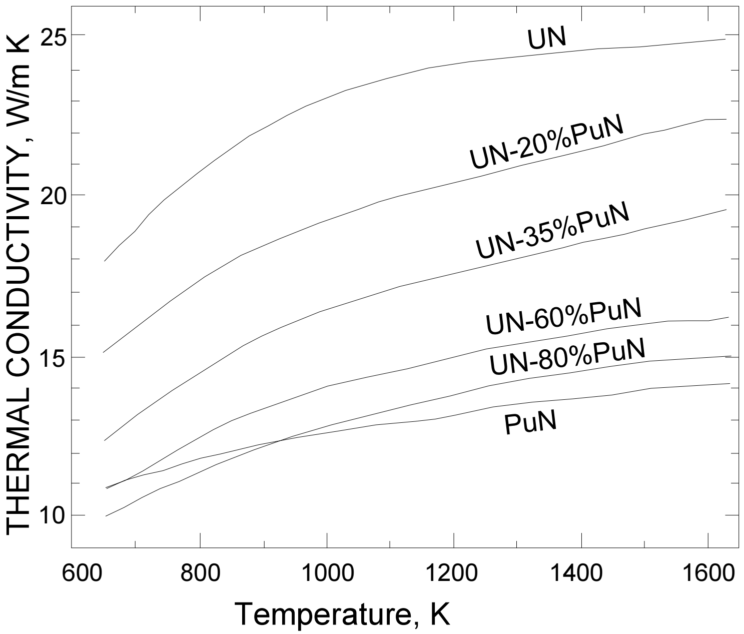
The melting temperatures of UN and PuN are given as 3 035±40 K and 2 843±30 K, respectively . The melting temperature of($U_{0.8}Pu_{0.2}$) N is given as 3 053 ± 20 K .

Thermal Conductivity of Carbide and Nitride

Thermal conductivity of MC
with varying amount of Pu



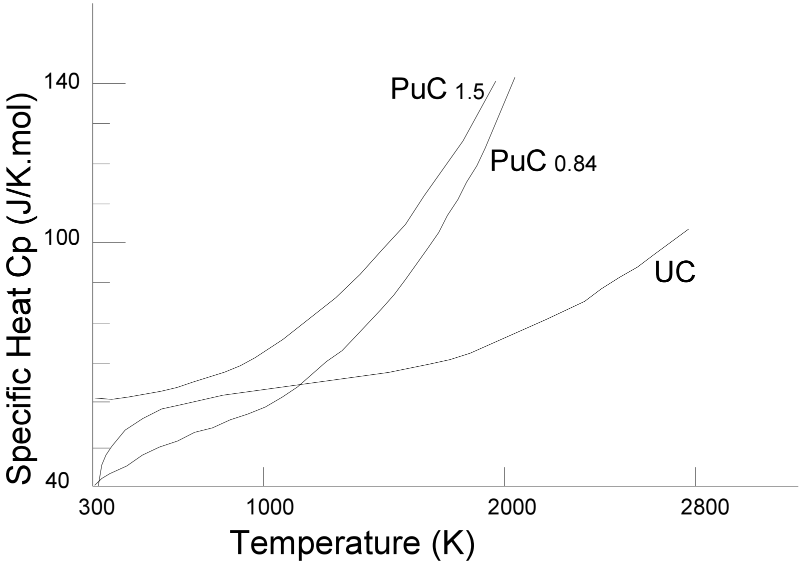
Thermal conductivity of MN
with varying amount of Pu



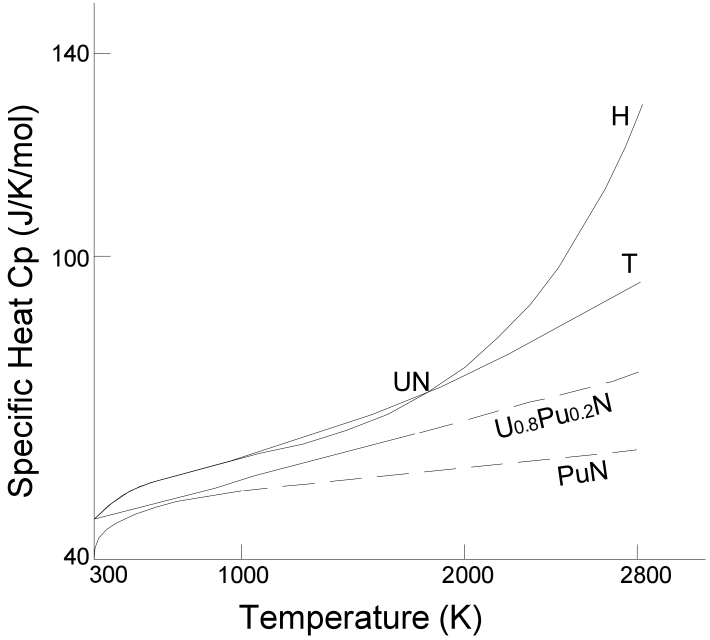
Advanced ceramic fuels such as carbides and nitrides have higher thermal conductivities and lower melting points than oxide fuels . The thermal conductivity of mixed carbide fuels increases with temperature, which has a distinct advantage over oxide fuel .

Specific Heat of MC & MN

Heat capacities of UC, PuC and MC pellets



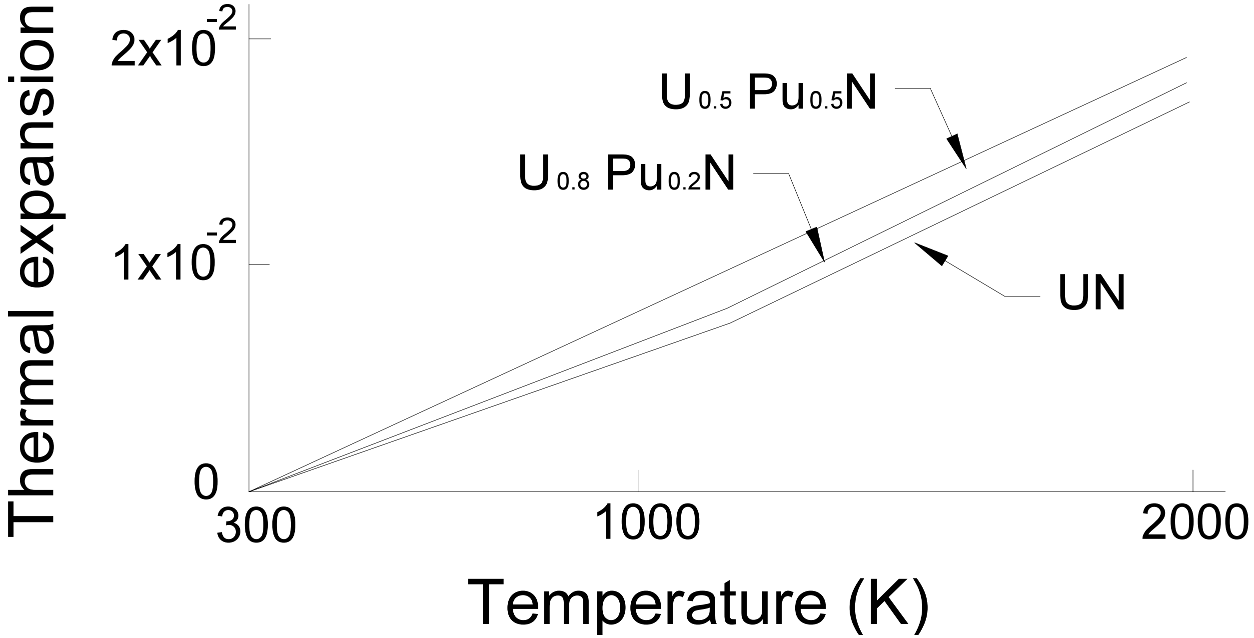
Heat capacities of PuN and MN pellets



Coefficients of Thermal Expansion for Carbides

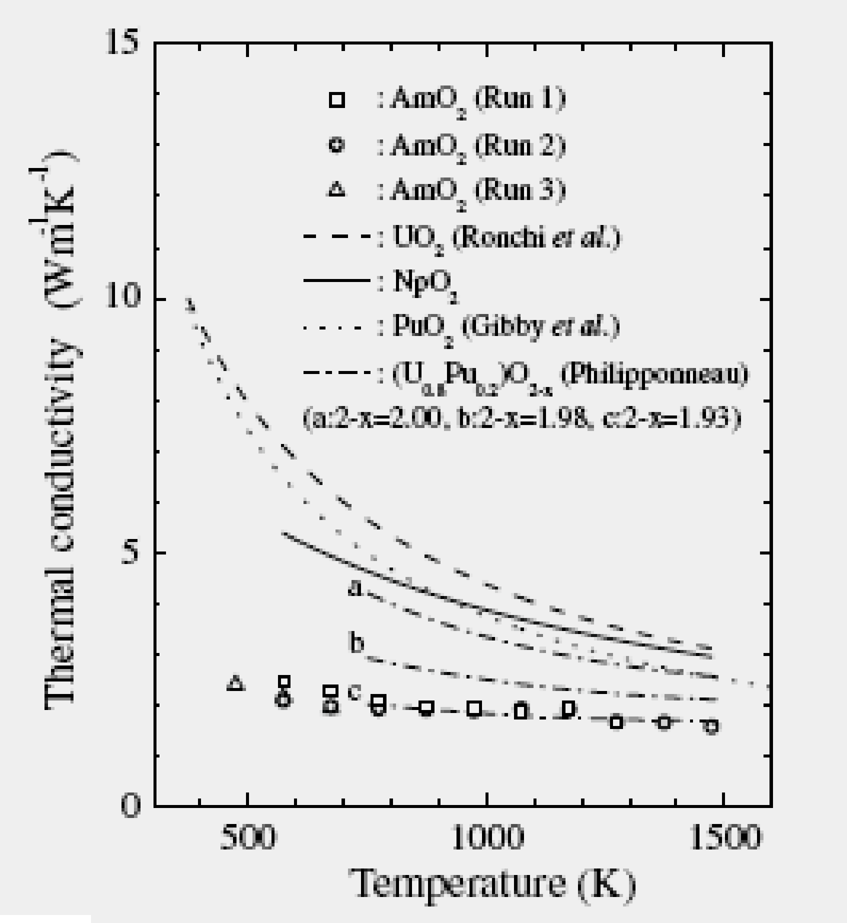
Material	CTE x10^{-6}/^{o}C (at 25^{o}C)	Mean CTE x10^{-6}/^{o}C (25-1 000^{o}C)
UC	10.1	11.2
PuC	8.5	10.8
(U,Pu)C	8.8	11.9
U_2C_3	10.7	10.6
Pu_2C_3	12.9	14.9
$(U,Pu)_2C_3$	9.6	11.2

Expansion curves for UN, PuN and MN pellets



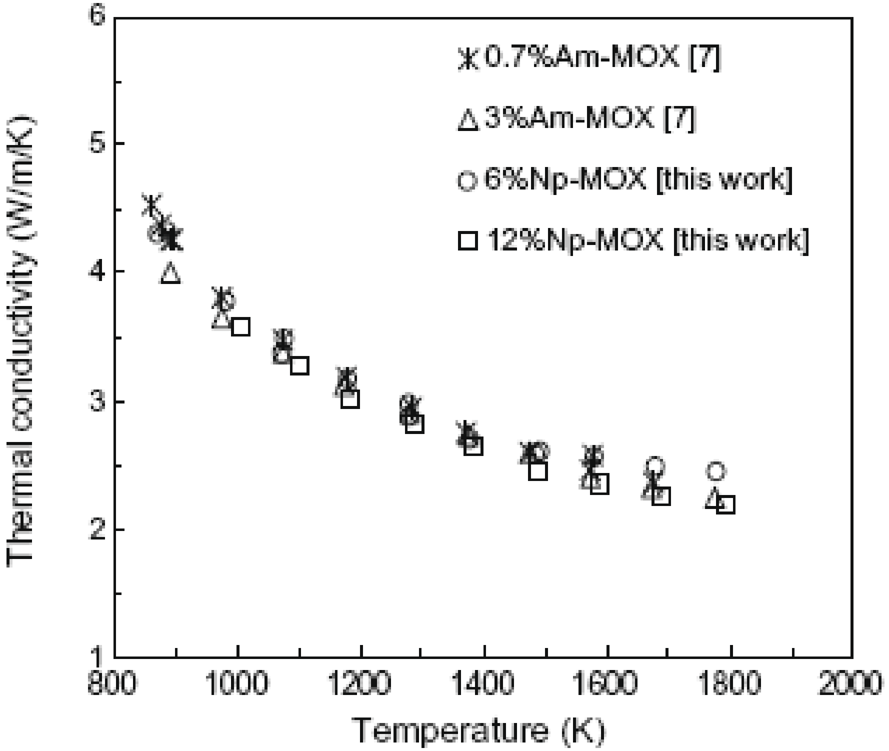
Thermo physical properties of fuels containing MA

Oxide fuel with MA

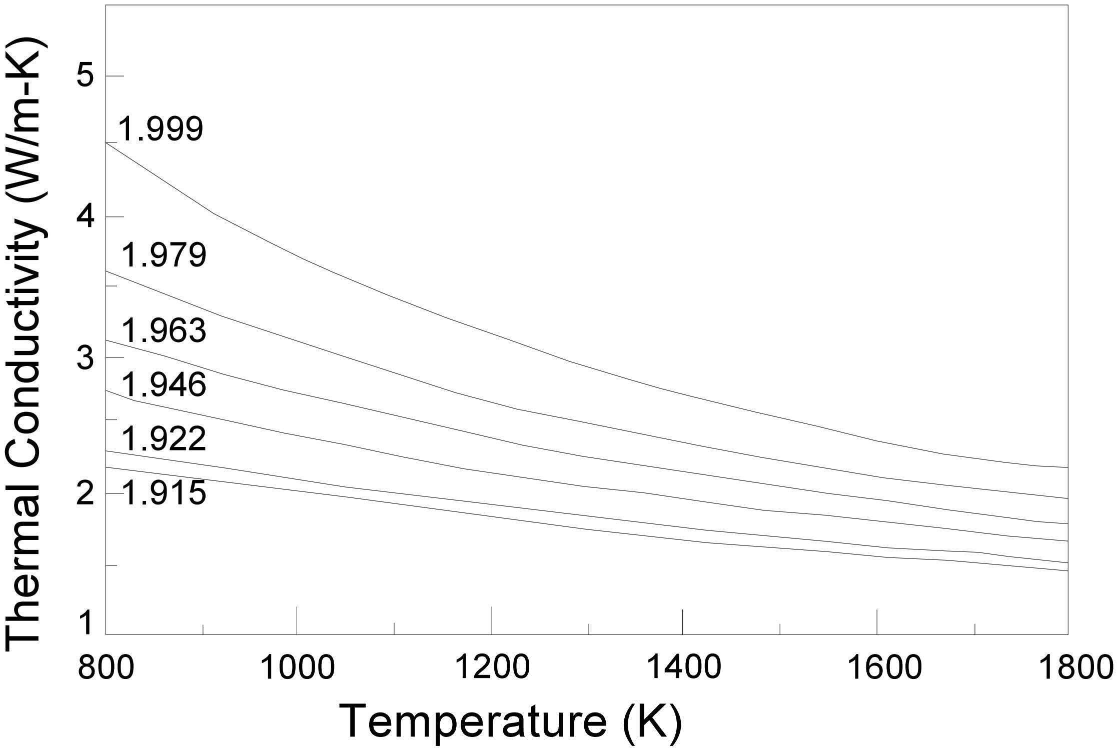


The thermal conductivities of AmO2-x and NpO2 decreased with increasing temperature in the temperature range investigated. This temperature dependence of the thermal conductivities of AmO2and NpO2 was similar to that of UO2, PuO2 and (Uo.8 Pu0.2)2-x

Thermal conductivities of $(U,Pu,Np)O_2$ and $(U,Pu,Am)O_2$ solid solutions at temperatures from 900 to1 770 K

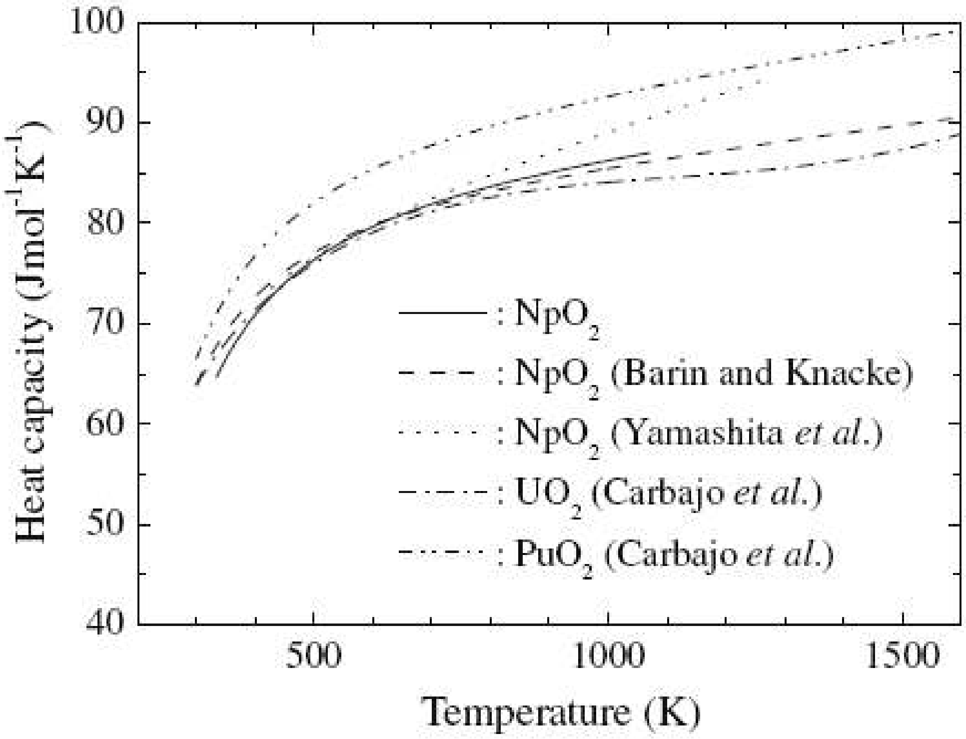


Thermal conductivities of (U0 $_{0.68}$Pu $_{0.3}$Am $_{0.02}$)O $_{2-x}$ as a function of temperature for different O/M ratios



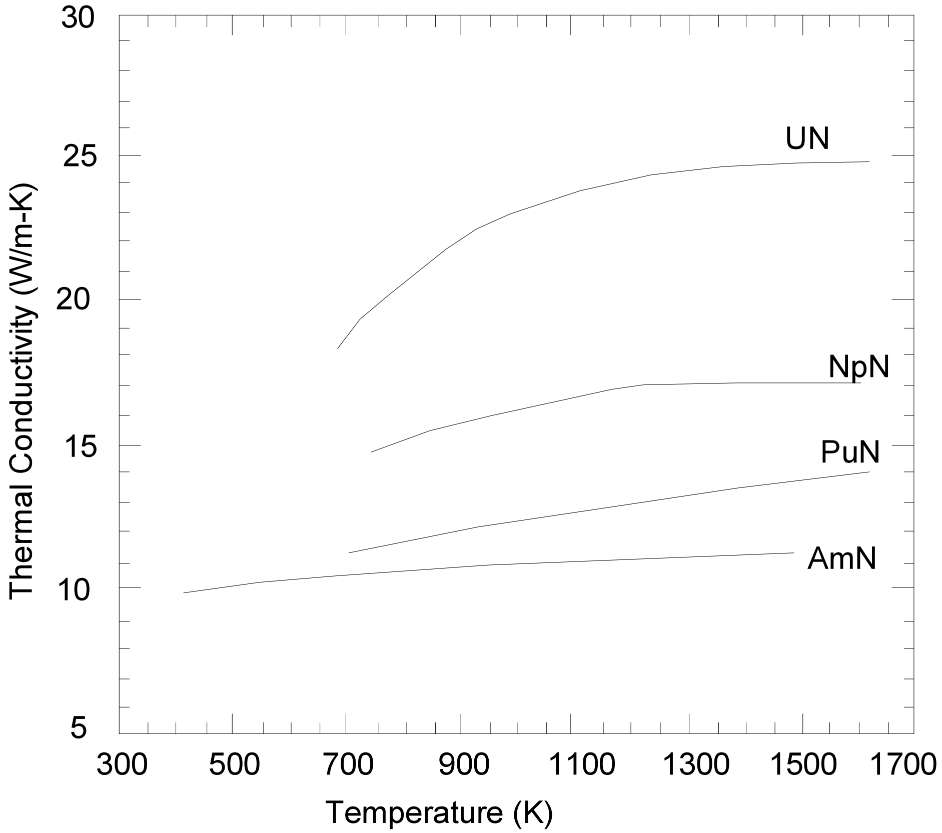
Thermal conductivities of 2%Am–MOX decrease with increasing temperature and larger deviations of O/M ratios from 2.00. The effect of O/M ratio on the thermal conductivity is large and is significant especially in the low temperature region

Heat capacity of NpO2, together with those of UO2 and PuO2 as a function of temperature



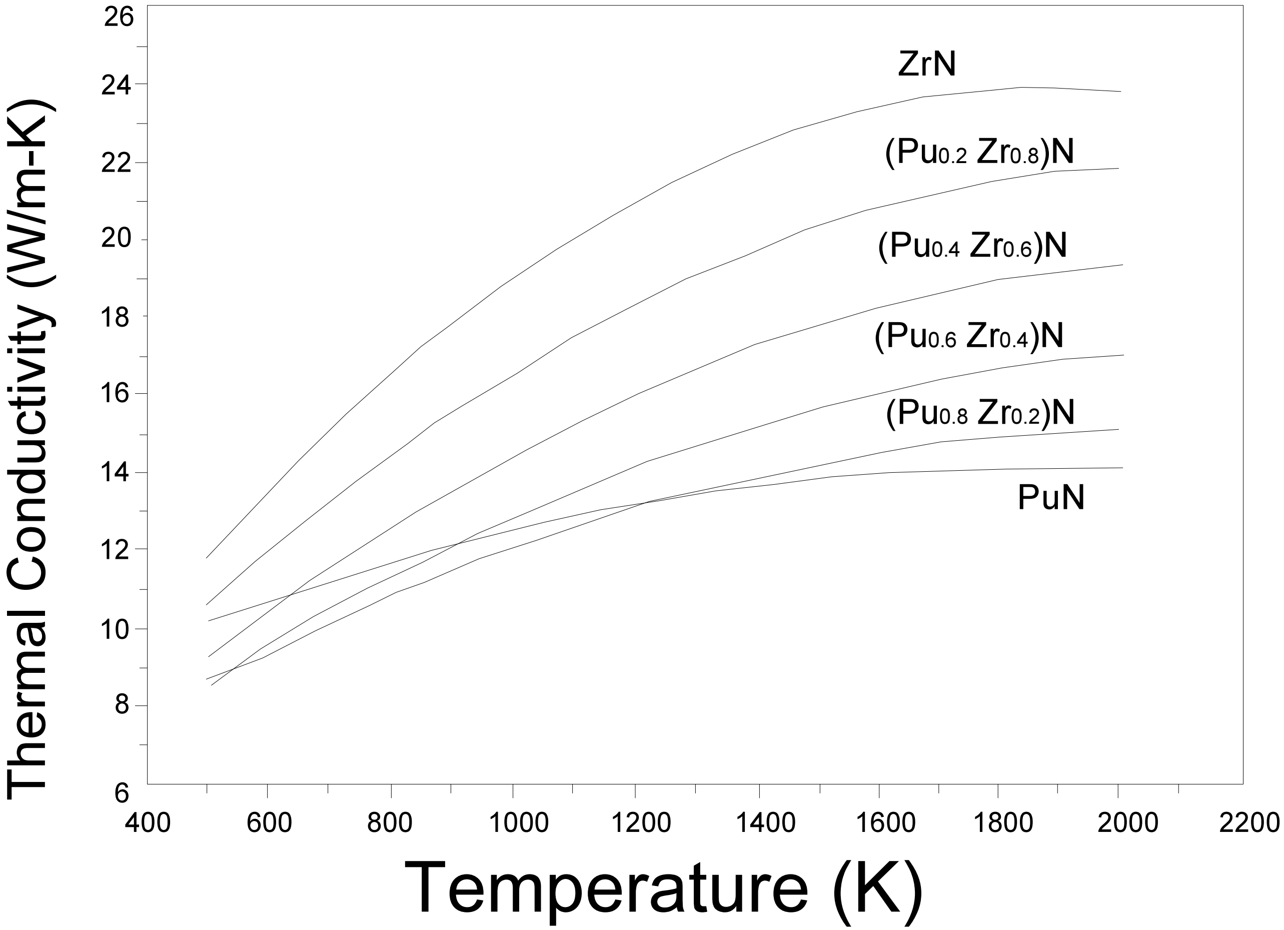
The heat capacity of NpO2 was determined by drop calorimetry and was found slightly larger than that of UO2 and about 7% smaller than that of PuO2

The thermal conductivity values of UN, NpN, PuN and AmN

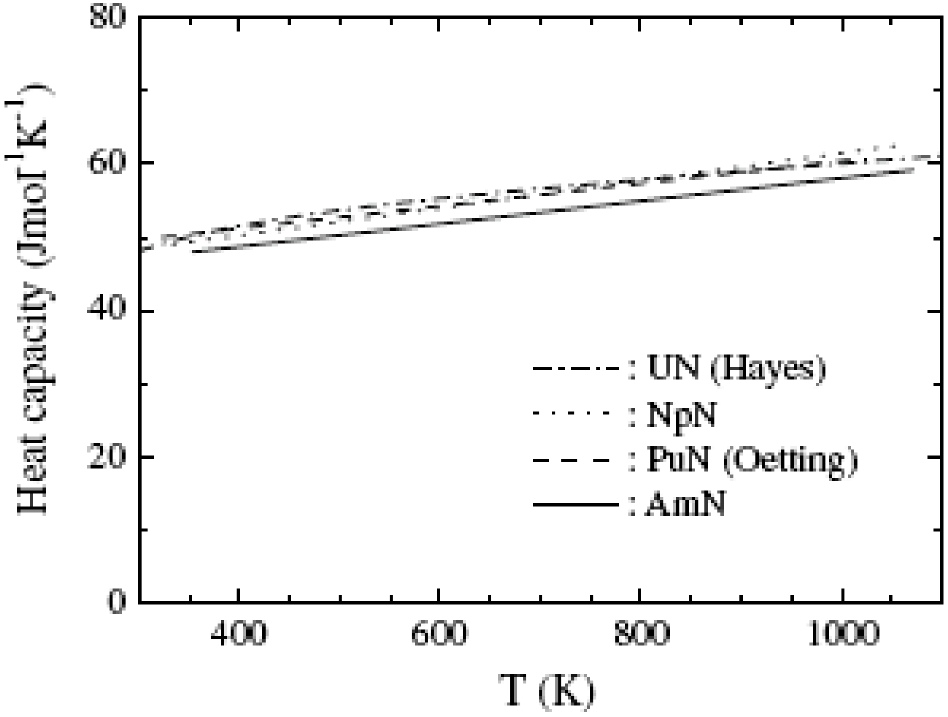


The thermal conductivities of UN, NpN and PuN are found to have a tendency to increase gradually with temperature , while to decrease with the atomic number of the actinide element component because of the decrease of electronic contribution . The solid solutions of the mononitrides show temperature dependence similar to those of two component nitrides each and possess intermediate thermal conductivity values.

Thermal conductivity of ZrN, PuN and (Zr,Pu)N

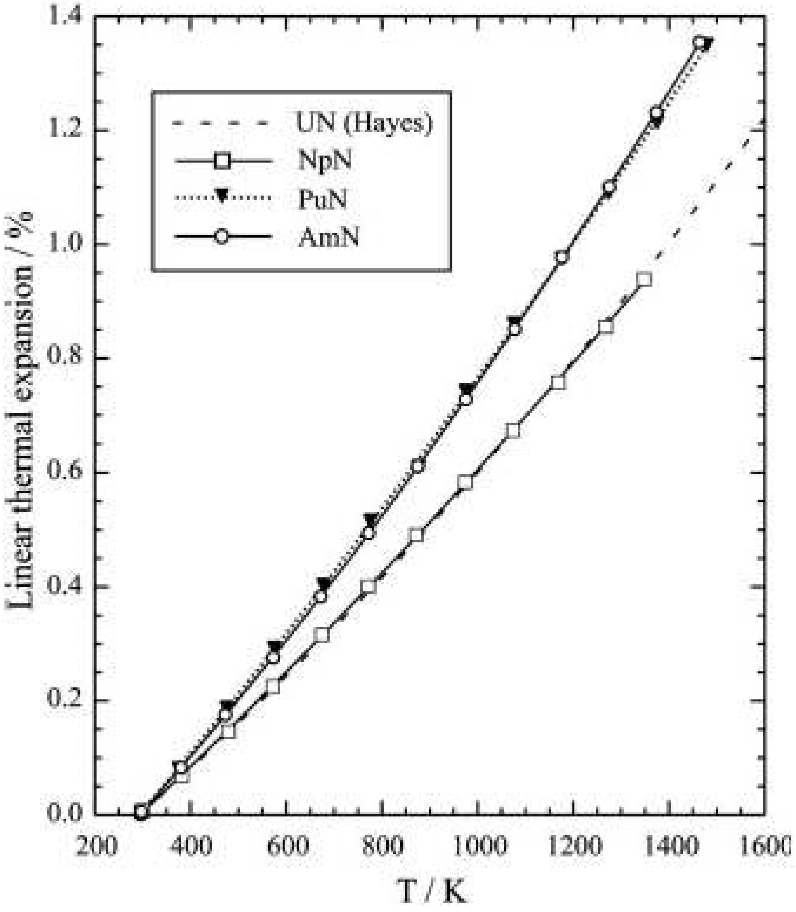


Specific heat values UN, NpN, PuN, AmN



The heat capacity of AmN is found to be slightly smaller than those of UN, NpN and PuN.

Linear expansion coefficients for UN, NpN, PuN, AmN



The thermal expansions of AmN and PuN are found to be close to each other and larger than that of UN, whereas the thermal expansion of NpN was nearly the same as that of UN

Irradiation Experience of MC and MN Fuels for Fast Reactor

During the 1970s and early 1980s , 470 MC fuel rods were irradiated in EBR-II and another 200 fuel rods were irradiated in FFTF. The parameters explored included:

sodium or helium bond,

variation in cladding type,

(316, D9, 321 stainless steels and ferritic HT-9 and nickel based PE-16),

variation in pellet density (84% TD for solid fuel pellets and 97% TD for annular pellets),

variation in pellet cladding gap size (0.13 -0.2 mm)

both pellet and sphere-pac fuel

In most cases all the fuel pins containing high density pellets failed whereas pins containing low density pellets survived. FCMI was found to be too severe for pellet densities more than 85% T.D.

Irradiation Experience of MC and MN in France , Germany , UK and Russia

In France, the (U,Pu)C fuel pins with 71% T.D. smear density reached a burn-up of 12 at.% with clad deformation of 1 to 3%.

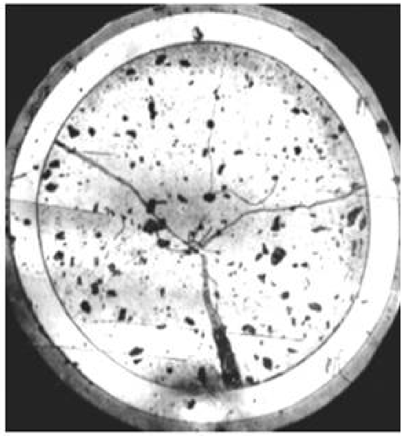
The German mixed carbide fuel irradiation program (75% TD smear density, 800 W/cm) was successfully tested under power cycling and transient conditions.

In UK , the mixed carbide pin irradiation program was successful with low smear density (70% T.D.) vibro-packed fuel of about 1 000 W/cm, with target burn up of 100 GWd/t.

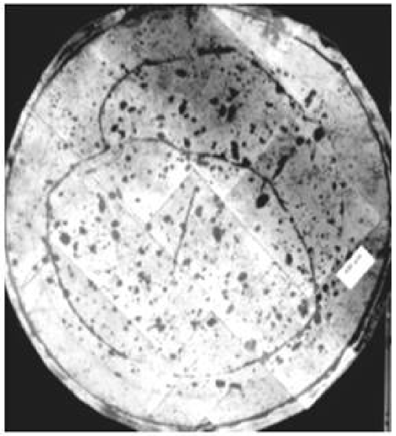
Russian experience shows that carburization of austenitic stainless steel cladding in case of pure MN (content of O and C less than 0.2% of each) is 2.5 times lower than that of low purity MN. For MN with 0.2–0.5% O and 0.3–0.5% C, the depth of carburization was ~ 50 µm for He-bonded fuel at burn-up of 8.2 at%.

Irradiation Performance of Plutonium rich Mixed Carbide Fuel

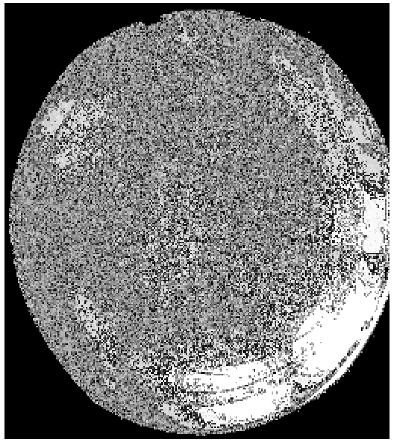
25 GWd/t BURN-



50 GWd/t BURN-



100 GWd/t BURN-



155 GWd/t BURN-

With increasing burn up beyond 50 GWd / t , cracking pattern changed to circumferential with the closure of fuel – clad gap indicating a restrained swelling phase.

A progressive reduction in porosities was observed on the fuel microstructure with increasing burn up indicating that Pu rich carbide , on account of its lower melting point , exhibit sufficient plasticity to accommodate swelling as a result of FCMI by creeping.

Distinct porosity free peripheral zones were observed at the burn up of 155 GWd / t

The major concern was the significant increase in dimensions of SS316 hexagonal wrapper and fuel pins and degradation in their mechanical properties

Inert Matrices for Plutonium and Minor Actinide bearing Fuels

Oxide Ceramics :

Zirconia , Thoria , Ceria and Magnesia

Complex Oxides :

Zircon ($ZrSiO_4$) and Spinel ($MgAl_2O_4$)

Non-oxide Ceramics :

Silicon Carbide , Zirconium Carbide & Nitride and Aluminium Nitride

Advanced Fuels with Minor Actinides (MAs)

Nitride is a candidate material of advanced fuels for fast reactors and for transmutation of minor actinide elements such as Np, Am and Cm because of its advantageous thermal and neutronic properties. Nitride fuels are attractive primarily due to high thermal conductivity relative to actinide oxides, high actinide density, and simple phase equilibria – only a rock salt (face-centered cubic) phase is known to form in the Np, Pu, Am, and Cm systems.

The major issue confronting the use of this fuel is the need to enrich nitrogen in the ^{15}N isotope in order to avoid production of large amounts of ^{14}C in reactor through the $^{14}N\ (n,p)\ ^{14}C$ reaction.

Typically, ZrN, TiN, YN, or AlN are proposed as the inert matrix phase for nitride fuels as target material for ADS. Nitrides containing minor actinides are synthesized by the carbothermic reduction technique using their oxides as the starting material

Irradiation Performance of MN Fuel

The irradiation performance database for MN fuels is substantially smaller than that for MC fuels. Compared to MC fuels, MN fuels exhibit less fuel swelling, lower fission gas release, and are considerably easier to reprocess; however, the problem of the production of biologically hazardous ^{14}C in nitride fuels fabricated using natural nitrogen poses a considerable concern for the reprocessing of MN fuels .

Thank You

For

Kind Attention