



1858-40

School on Physics, Technology and Applications of Accelerator Driven Systems (ADS)

19 - 30 November 2007

ADS Fuels for Partitioning & Transmutation

Frodo KLAASSEN NRG Fuels, Actinides & Isotopes 1755 ZG Petten The Netherlands

ADS fuels for Partitioning & Transmutation

Frodo Klaassen Nuclear Research and consultancy Group (NRG) Westerduinweg 3 / P.O. Box 25 1755 ZG PETTEN, the Netherlands

klaassen@nrg-nl.com

Sylvie Pillon Commissariat à l'Énergie Atomique (CEA) Centre du Cadarache

School on Physics, Technology and Applications of ADS, ICTP, Trieste, 30 November 2007

Content

- 1. Fuel development : needs and organisations
- 2. ADS Fuel specification : what is an ADS fuel?
 - Fuel requirements
 - Fuel types : oxides, nitrides, metal alloys
 - EUROTRANS selection
- 3. ADS Fuel behaviour under irradiation
 - Current knowledge on ADS fuels (and targets)
 - Comparison with MOX fuel containing Am and Np
 - Experiments in HFR and Phénix

BREAK

Content

- 1. Fuel development : needs and organisations
- 2. ADS Fuel specification : what is an ADS fuel?
 - Fuel requirements
 - Fuel types : oxides, nitrides, metal alloys
 - EUROTRANS selection
- 3. ADS Fuel behaviour under irradiation
 - Current knowledge on ADS fuels (and targets)
 - Comparison with MOX fuel containing Am and Np
 - Experiments in HFR and Phénix
- 4. ADS Fuel fabrication
 - Issues linked to the fuel composition
 - Impact on the processes
 - Status of the R&D and needs
- 5. Results from EUROTRANS
- 6. Conclusions-Summary



ADS fuel specification: strategy

- * Double strata strategy (MA burning)
 - U-free fuels or TRU fuels
 - Typically 30 to 50% Pu
 - 70% Am and 30% Cm
 - Np included or not (depending on the P&T scenario)
 - High burn-up
- * Integrated ADS fuel cycle (TRU burner)
 - Typically 4 to 6 t TRU/year
 - Reprocessing and TRU separation
 - Pyrochemistry or pyro/hydro mixed system
 - Fuel refabrication

ADS fuel specification: requirements

- * Fuel compatibility with coolant
 - EUROTRANS : Pb coolant (Pb/Bi for the demonstrator)
 - Options are:
 - He coolant (gas)
 - Na coolant
 - Pb or Pb/Bi
- * Fuel compatibility with cladding
 - Na : austenitic steels : 15-15Ti (AIM1)
 - Peak cladding temperature : 650°C
 - Pb, Pb/Bi : ferritic-martensitic steels T91 (9Cr-1Mo)
 - Peak cladding temperature : 550°C
 - He : ceramic composite based on SiC
 - Peak cladding temperature : 1100°C

The best thermal conductivity and TRU density

 $\Delta G_{f}^{0}(298K)$ Melting point or Thermal conductivity Actinide compounds temperature of Density (g/cm^3) at 1273K (W.m⁻¹.K⁻¹ (kJ/mol) decomposition (°C) Pu-Am-Cm-40Zr 22 1327 9.61 NpO₂ 2550 11,14 -720 The best thermal- PuO_2 , Pu_2O_3 2390, 2360 11,46 -730 dynamical stability AmO_2, Am_2O_3 2175, 2205 11,71 -620, Cm_2O_3 377 --2830 (12 atm N₂) 17 NpN The highest melting PuN 2675 (1 atm N₂) 13 -150 and good cond. 2570 (1 atm N2) AmN --CmN >1400 -90 NpC_{1-x} 1654, 2050 -70, -100 PuC_{1-x}, Pu_2C_3 13,6 -70 Am_2C_3 Intermediate NpS properties -342 2347 PuS -360 AmS -CmS >1550

3 main candidates: metal, oxide and nitride

Fuels: past experience (FBR)

	Mixed Oxide	Mixed Nitride	Metal alloys		
	(U,Pu)O ₂	(U,Pu)N	U-Pu-Zr		
Compatibility with Pb or Pb/Bi	yes	yes	no		
Compatibility with clad	yes	Ves	yes		
Fuel temperature limit	melting point (solidus : ~2800°C)	nitride decomposition (~1700°C, influence of the atmopshere)	eutectic reaction with clad . 725°C with U-Pu-Zr : Na bond		
Behaviour under irradiation	moderate swelling accommodated by the clad in FBR temperature conditions 25% achieved : limitation by the clad damage dose	high swelling accommodated by the free volume 15 at% achieved : limitation not yet known	high swelling accommodated by the clad 20 at% BU achieved : limitation by the fuel/clad chemical interaction		
Fabricability	Easy (wet and dry process)	Complex due to the first Ditridation phase from oxides	Pyrophoricity		
Solubility in molten salts	yes	yes	yes		
Solubility in nitric acid	yes	yes	yes		
Application to ADS	- inert matrix to improve the thermal behaviour	-inert matrix to improve the stability at high temperature -high AmN volatility (fabrication issue) -C14 production from the N14 : (n, p) reaction	-only for Na-cooled ADS - Na bonding required - high Zr content to improve the melting point - high Am volatility (fabrication & irradiation issue)		

Chemical stability of (ADS) oxide fuels

- * U-free fuels have poorer thermal & thermodynamic properties compared to U-based fuels
 - Lower performance in pile





Chemical stability of (ADS) oxide fuels



Thermal conductivity of (ADS) oxide fuels NG

- * U-free fuels have poorer thermal & thermodynamic properties compared to U-based fuels
 - Lower performance in pile



ADS fuel specification: main fuel types

- * TRU oxides
 - Low thermal conductivity
- ty development
 - Improvement with inert matrix of high conductivity
- * TRU nitrides



Considered in Europe

EUROTRANS

/ Japan / (US)

- Low stability at high temperature
 - AmN is especially volatile
- ¹⁴C production from (n,p) reaction on ¹⁴N
 - Improvement with inert matrix of high stability
 - ¹⁵N enrichment
- * TRU metal alloy
 - Low melting point
 - Increase of Zr content
 - Na bond



Inert matrices fuels (IMF) for ADS

- * Inert matrix provides a fertile-free (Uranium-free) diluent in which the (minor) actinide phase is incorporated
- * Inert Matrix Fuels improve the fuel properties
 - Thermal conductivity higher than that of UO_2
 - Thermal stability higher than that of AmN
 - High melting point (higher than the Actinide compound)
- * Inert Matrix Fuels improve the fuel performance
 - Clad corrosion (fission product retention)
 - High burnup (local)
 - Stability under irradiation

ADS fuels: many requirements !

- * Good thermal properties
 - High melting point
 - High thermal conductivity
 - High thermal stabilty
- * Good chemical properties
 - Compatible with coolant, clad and compound of MA
- * Resistant to neutron, FP and alpha radiation
 - Cubic crystal structure (isotropic deformation)

- * Low activation
 - -Waste reduction
 - Ability to be reprocessed and recycled
 - Aqueous process
 - Molten salts process
- * Fabricability
- Compatibility with glasses (final storage)

Inert Matrices for ADS: selection for EUROTRANS

				Chemical compatibility with						
Inert matrix		Crystal lattice	Thermal properties	neutron activation	AnO ₂	AnN	Zry	Acier	Na	H ₂ O
st-ZrO ₂		+	-	+	+ (solid solution)		+	+	+	+
oxide	MgO	+	+	+	- (eutectic)		?	+	+	-
	Al ₂ O ₃	- (hexagonal)	+	+	- (eutectic)		+	+	+	+
	Y_2O_3	+	-	+	+ (solid solution)		?	+	-	-
	CeO _{2-x}	+	-	+	+ (solid solution)		-	+	-	+
	MgAl ₂ O ₄	- (monoclinic)	+	+	- (eutectic)		+	+	+	+
	$Y_3AI_5O_{12}$	+	+	+	+		+	+	+	+
	CePO ₄	- (monoclinic)	-	+	+		?	?	-	+
	ZrSiO ₄	- (tetragonal)	- (decomposition)	+	+		?	?	-	+
carbide, nitride	SiC	-(hex./cubic)	+	+	-	-	-	-	+	+
	¹¹ B ₄ C	- (trigonal)	- (vapor pressure)	+		-		-	+	+
	¹¹ BN	-(hex./cubic)	- (vapor pressure)	- (¹⁴ C)					+	+
	Si ₃ N ₄	- (hexagonal)	- (vapor pressure)	- (¹⁴ C)				+	+	+
	CrN		- (vapor pressure)	- (¹⁴ C)						
	TiN	+	+	- (¹⁴ C)	+	+		?	+	?
	YN	+	+	- (¹⁴ C)		+ (solid solution)		?	?	- (hygroscopic)
	ZrN	+	+	- (¹⁴ C)	-	+ (solid solution)		-	+	+
	CeN	+	+	- (¹⁴ C)		+ (solid solution)		?	?	-
	AIN	- (hexagonal)	- (vapor pressure)	- (¹⁴ C)	- (?)	+		+	+	-
	Cr	+	+	+	- (eutectic ?)	- (eutectic)	+	+	+	-(H ₂ hazard)
metal	V	+	+	+	- (eutectic ?)	- (eutectic)	+	+	+	-(H ₂ hazard)
	W	+	+	+	+	+	+	+	+	-(H ₂ hazard)
	Мо	+	+	- (⁹⁵ Mo)	+	+	+	+	+	-(H ₂ hazard)
	Nb	+	+	- (⁹⁴ Nb)			-		+	-(H ₂ hazard)
	Acier	+	_	+	- (eutectic)	- (eutectic)	+	+	+	-(H ₂ hazard)

ADS Inert Matrix Fuels (IMF)

- * Composition of IMF is a compromise between:
 - Volume of inert matrix higher than 55-60%
 - To optimise the composite microstructure
 - Inert matrix surrounding fissile particles
 - Improve the quality of the pellet surface
 - Reduce the matrix cracking
 - To keep good thermal properties when mixed with fissile particles
 - For an easier fabrication process
 - Volume of inert matrix as low as possible
 - To increase the transmutation rate
 - To reduce the core size
 - Easier reactivity control



Inert Matrix Fuels: selection for EUROTRANS

- 1. CERCER fuels (composite CERamic-CERamic)
 - (Pu, Am,-Np,Cm-)O_{2±x} + MgO or ZrO₂
 - MgAl₂O₄, the most studied matrix under irradiation (good stability under neutron), was not retained
 - Idem for YAG $(Y_3AI_5O_{12})$
- 2. CERMET fuels (composite CERamic-METal)
 - (Pu,Am,-Np,Cm-) O_{2±x} + Mo
 - Cr, V not retained : non compatible with TRU oxide
 - W not retained : too absorbent

Inert Matrix Fuels: selection for EUROTRANS

- CERCER fuels (composite CERamic-CERamic)
 (Pu, Am,-*Np,Cm*-)O_{2±x} + MgO or ZrO₂
- 2. CERMET fuels (composite CERamic-METal)
 (Pu,Am,-*Np,Cm*-) O_{2+x} + Mo
- 3. Nitride fuel (solid solution)
 - (Pu,Am,-Np,Cm-)N + ZrN

TiN not retained (bi-phased composite: no impact on the AmN stability)
YN not retained (hygroscopic)

Summary Fuel selection for ADS

- * Uranium-based (fertile) fuels
 - MOX: $(U,Pu)O_2$ with minor actinides
 - Nitrides (U,Pu)N etc.
- Inert Matrix Fuels provide an attractive alternative (more efficient TRU burning, option to tailor properties, etc.)
- * Inert Matrix fuels:
 - CERCER fuels, based on MgO or ZrO₂
 - CERMET fuels, based on Mo
 - Nitrides, based on ZrN

Spinel as Inert Matrix

- Magnesium aluminate spinel was, for a long time, thought to be the ideal inert matrix
- * MgAl₂O₄ was intensively investigated
 - Good radiation resistance (neutrons / alpha)
 - Good chemical stability
 - Relatively high thermal conductivity > UO_2
 - Ability to accommodate displacements (dpa)
- * In the end spinel was discarded as Inert Matrix, but we have learned a lot from the experiments on spinel

IMF behaviour under irradiation: spinel-based CERCER with U or Pu



- * THERMHET (1997) in Siloe (CEA, France)
 - UO₂ (40 wt%) + MgAl₂O₄ at low burn-up (1.3 at%)
 - Prepared by powder mixing of UO₂ and spinel





- * Spinel, known to be resistant to neutron, is not resistant to FP damaging!
 - Fracturation after strong swelling
 - Void filling (Thermocouple hole, fuel/clad gap, fuel porosity)
 - High swelling estimated at ~15 vol%

Results EFTTRA T4ter irradiation in HFR

- * EFTTRA T4ter:
 - 25 wt% UO₂ (20% enriched) mixed with spinel
 - Irradiation of 652 full power days in HFR
 - Burn-up ~ 150 GWd/m³
 - Similar results as THERMHET:
 - Volume swelling of 11 vol%
 - Increase of the cladding diameter due to swelling





NZG

X-ray diffraction shows amorphisation of spinel

- * Consequences of the spinel damaged by FP
 - Amorphisation of the crystal structure





Annealing of fission product damage



* FP damages annealed at temperature above 1100°C

Conclusions for spinel

- * Micro-dispersed actinide phases in spinel
 - Spinel is very sensitive to high energy fission products
 - Large swelling due to amorphisation of spinel
 - THERMHET irradiation, J. Noirot et al., J. Nucl. Mater. **320** (2003), 117
 - EFTTRA T4ter, Klaassen et al. J. Nucl. Mater. **319** (2003), 108
 - At high irradiation temperatures, FP damage may be annealed
 - Helium production (in transmutation) gives high porosity and additional swelling
- Macro-dispersed actinide phases in spinel may offer better irradiation performance

Dispersion of the actinide phase



MACRO

Fission product damage confined to the fissile particle

MICRO

Fission product damage in the inert matrix as well.

Dispersion of the actinide phase

- * Damage by FP is localised within a shell of 10µm around the fissile particle
 - Large fissile particles limits the matrix damaging



Micro- vs Macro-dispersion of the actinide phase

- * A strict control of the distribution and size of the fissile particles is required
 - Impact on the fabrication process not negligible



No fuel swelling



Swelling of ~15 vol%

Micro- vs Macro-dispersion of the actinide phase

- * A strict control of the distribution and size of the fissile particles is required
 - Impact on the fabrication process not negligible



100.m Swelling of ~15 vol%

Matrix damaging around macromasses

OTTO = Once Through incineration

- * Geo-chemically stable inert matrices for Pu-burning
 - Insoluble in nitric acid
 - Suitable for final storage
- * Zirconia-based IMF
 - Cubic phase, i.e. single phase system (Zr,Y,Pu,Er)O_{2-x}
 - Excellent irradiation performance
 - Low thermal conductivity
- * Spinel matrix with (Zr,Y,Pu,Er)O_{2-x} compound
 - Two phase system with (Zr,Y,Pu,Er)O_{2-x}
 - Micro-dispersed (fissile particles < 25 μm) and micro-dispersion tested (fissile particles ~ 200-250 μm)



OTTO: Joint project NRG / PSI / JAERI*

Cap sule	Composition	Dispersion	Fissile phase	Pu _{fis} (BOI)	Supplier	Instrum entation	
			vol%	g/cm ³			
1	(Zr,Y,Pu,Er)O ₂	Solid solution	single phase	0.37	PSI	-	
2	(Zr,Y,Pu,U)O ₂	Solid solution	single phase	0.34	JAERI	-	
3	(Zr,Y,Pu,Er)O ₂ +MgAl ₂ O ₄	<25 µm	20.8	0.32	NRG	TC	
4	(Zr,Y,Pu,U)O ₂ +MgAl ₂ O ₄	<25 µm	20.7	0.31	JAERI	TC	
5	(Zr,Y,Pu,Er)O ₂ +MgAl ₂ O ₄	200-250 μm	19.7	0.31	NRG	TC	
6	(Zr,Y,Pu,U)O ₂ +MgAl ₂ O ₄	200-250 μm	19.7	0.30	JAERI	-	
7	(Pu,U)O ₂	Solid solution	single phase	0.39	PSI	TC	

Solid solution

OTTO studies:

Micro-dispersed

Macro-dispersed

* Now JAEA

Dispersion of the actinide phase



MACRO

Fission product damage confined to the fissile particle

MICRO

Fission product damage in the inert matrix as well.
X-ray images after irradiation



Capsule 1

Zirconia-based IMF No swelling Capsule 2 Behaviour like UO₂

Spinel-based IMF Capsule 3 Micro-dispersed Swelling due to amorphisation Capsule 4

Spinel-based IMFCapsule 5Macro-dispersedNo swelling
in spinelCapsule 6

MOX-reference Capsule 7



$(Zr, Y, Pu, Er)O_{2-x}$ is a good IMF

No swelling

Behaviour similar to UO₂

Rather high fission gas release: 6–9 % at a burn-up ~ 20 GWd/tU (eq.)



Capsule 4 cladding failure

NZG





Macro-dispersion in spinel





Halo around the fissile particle due to f.p. damage in spinel

Macro-dispersed zirconia in spinel

Macro-dispersion limits irradiation damage from fission products



Halo around the fissile particle due to f.p. damage in spinel



Matrix damaging around macromasses OTTO irradiation, conclusions



- * An actinide depletion of 50% and a Pu transmutation of 60% was reached
- * The performance of the inert matrices can be rated as follows:

Zirconia-based inert matrix fuels	+	(solid solution)
Spinel-based inert matrix fuels:	+/-	(macro-dispersed)
		(micro-dispersed)

Am-241 transmutation

Transmutation scheme for Am-241:
 requires on average 2.5 neutrons
 produces 0.75 He-atom per initial Am-atom



The helium production due to ²⁴²Cm decay is one order of magnitude larger than fission gas production Contributes to the fuel swelling and pin pressurisation

EFTTRA T4 & T4bis; two irradiations to study Am transmutation

- * EFFTRA-T4 and T4bis experiments (1999) in HFR (EFTTRA group)
 - First irradiation tests of AmO₂ (11 wt%)+MgAl₂O₄
 - Prepared by infiltration of a porous spinel skeleton (ITU)
 - Homogeneous (micro)-dispersion of the fissile phase
 (3 μm-sized Am-particles)
 - Pellet diameter = 5.4 millimetre
 - Transmutation up to 99.8 % of Am-241 !!

EFTTRA T4 & T4bis; two irradiations to study Am transmutation

* EFFTRA-T4 / T4bis pellets







EFTTRA T4 & T4bis; two irradiations to study Am transmutation

	EFTTRA T4	EFTTRA T4 bis
Reactor	HFR Petten	HFR Petten
Irradiation time	358.4 FPD	652.6 FPD
Fissile phase	AmO _x	AmO _x
Fissile content	12.5 wt%	12.5 wt%
	$(11.2 \text{ wt}\%^{241}\text{Am})$	$(11.2 \text{ wt}\%^{241}\text{Am})$
Thermal fluence ($E < 0.7 \text{ eV}$)	$5.8 \cdot 10^{25} \text{ m}^{-2}$	$9.7 \cdot 10^{25} \text{ m}^{-2}$
Fast fluence ($E > 0.1$ MeV)	$16.8 \cdot 10^{25} \text{ m}^{-2}$	$21.3 \cdot 10^{25} \text{ m}^{-2}$
Actinide depletion	~ 28 %	~ 50 %
Burn-up	96 % (²⁴¹ Am)	99.8 % (²⁴¹ Am)
Power (W/cm)	40 / 70 (min/max)	40 / 65 (min/max)
Fuel central temperature	~ 700°C	$\sim 700^{\circ}\mathrm{C}$



Ceramographies of EFTTRA T4

 $\frac{T4}{28 \text{ at\% BU}}$ Sw.=18 vol%
0,4g Am/cm³
Released He = 20%
Released FG = 5%



- * The accumulation of He in gas bubbles seems to be the major cause of swelling (> #30vol%)
 - This swelling rate should have favored the gas release thanks to the pore interconnection (creation of release paths)
 - As observed on nitride, metal, carbides and UOX or MOX fuels
 - The abnormal retention could be due to the amorphisation/nanocristallisation of the crystal structure

Release of helium at higher temperatures

- * Significant gas release is observed when IMF is heated at temperature around 1600K (out-of-pile observation)
- * Correlation with the fuel restructuring (similar to the RIM effect)



Am-241 transmutation loop

- * In EFTTRA T4bis, Am-241 was transmuted for 99.8%
- * Now the Am-concentration is increasing again
 - Decay of Pu-241 !!



Comparison with MOX fuel containing MA SUPERFACT experiment (1988) in Phénix

Fuel	P _{lin} (W/cm)		BU _{max} (at%)	T _{clad} (°C)	
	BOL	EOL	EOL	BOL	EOL
2% Np	385	350	6.6	613	604
2% Am	379	346	6.48	612	603
20%Am+20%Np	174	286	4.1	603	595
45% Np	197	302	4.56	603	595
(U, Pu)O ₂	402	353	7.38	618	609







Comparison with MOX fuel containing Am NRG and Np

mm³ of gas/g of fuel



* Fission gas release very similar to that of MOX fuel

Comparison with MOX fuel containing Am NRG and Np



* Fission gas release very similar to that of MOX fuel

Comparison with MOX fuel containing Am and Np



Low He production



High He production

Intermediate conclusion

- Swelling (>~15 vol%) due to the amorphisation of the crystal structure
 - (TANOX, THERMHET, OTTO, EFTTRA T4)
 - Sensitive matrices: YAG (Y₃Al₅O₁₂) and spinel
 - Gas retention enhancement
- Macrodispersion (dispersion of MA compounds >100 µm) limits the damaged volume of inert matrix (THERMHET, ROX, OTTO, TANOX)
 - Strict control of the particle dispersion and particle size
 - More complex fabrication process
 - Content of particles limited
- * Damage annealing above 1200°C (MATINA1)
 - Swelling limited to 5 vol%







(Zr, Y, Pu, Er)O₂ in HFR 50 at% BU C. HELLWIG, U. KASEMEYER Journal of Nuclear Materials 319 (2003) 87-94

Intermediate conclusion

Objectives of the current R&D:

- Optimise the transmutation rate and capacity of the TRU-fuels
 - Reach higher fission rate (up to 90% in moderated flux)
 - Increase the MA content (from 0.7 to ~5 g/cm³)
- Directions:
 - Enhance the He release during irradiation
 - By providing release paths as soon as the irradiation starts
 - New IMF microstructure with open porosity
 - By increasing temperature with Pu addition
 - (Pu,Am)O₂ + inert matrix





(Zr, Y, Pu, Er)O₂ in HFR 50 at% BU C. HELLWIG, U. KASEMEYER Journal of Nuclear Materials 319 (2003) 87-94

Intermediate conclusion

- Objectives of the current R&D:
 - Optimise the transmutation rate and capacity of the TRU-fuels
 - Reach higher fission rate (up to 90% in moderated flux)
 - Increase the MA content (from 0.7 to ~5 g/cm³)
- Directions:
 - Enhance the He release during irradiation
 - Select inert matrices more resistant to the FP damage at temperatures < 1000-1100°C
 MgO, ZrO₂, Mo
 - Test new Am compounds to reduce oxygen potential and limit the clad corrosion
 - $Am_2Zr_2O_7$ (pyrochlore)



- * A key issue
 - High neutron source (of ²³⁸Pu and ²⁴⁴Cm)
 - High thermal constraint (heat release of ²³⁸Pu and Cm isotopes)

Isotop	Period (year)	Activity (x10 ¹⁰ Bq/g)	Neutron source (n.g ⁻¹ .s ⁻¹)	Heat release (W/g)	Ingestion dose factor (x10 ³ Sv/g)
Np 237	2,14x10 ⁶	0,00261	0	0	0,028
Pu 238	87,7	63,4	2511	0,568	630
Pu 239	24390	0,227	0,02	0,002	2,6
Pu 240	6540	0,843	905,6	0,007	9,8
Pu 241	14,3	382	0	0,003	90
Pu 242	3,87x10 ⁵	0,0141	1678	0	0,15
Am241	432	12,7	1,2	0,115	150
Am 242m	152	36,0	150	0,004	410
Am 243	7380	0,736	0	0,007	8,8
Cm 243	28,5	170	0	1,685	1300
Cm 244	18,1	299	5892	2,825	1800
Cm 245	8530	0,633	5448	0,006	7,6

* Minor actinides in solution

No industrial experience is available today!

- 250 g $^{\rm 243+241}Am$ /I : #25 W/I
 - Typical concentration for a chemical operation of precipitation
- 250 g ²⁴⁴Cm/l : #700 W/l
- Industrial experience : 10 W/I (FP concentrates at La Hague)
- * Minor actinides in solid state
 - 1 m² of powder bed kept below 80°C must not exceed
 ⇒ 0.5 mm of thickness with natural cooling (air, room temperature)
 - \Rightarrow 5 mm of thickness with forced cooling

NZG

- * Implementation in hot cells with heavy shielding and remote handling
 - Reduction of the volume for cost reduction (process compaction)
 - Simple process
 - Limitation of the control steps
 - Limitation of liquid and solid waste treatment
 - Development of robust processes
 - Limitation of the maintenance
 - Simple process
- * Avoid powder handling
 - More difficult to cool
 - Risk of dust retention and accumulation

NZG

- * R&D limited by the hot lab availability
 - In Europe, only 2 labs (CEA, ITU)
 - In Japan, 1 lab (JAEA)
 - In USA, 3 labs (INL, LANL, ORNL)
- * R&D limited by the hot lab capacity

	ATALANTE	MA-LAB	TRU-HITEC
²⁴¹ Am	1700 g	2000 g	10 g
²⁴² Am	2 g	0,1 g	-
²⁴³ Am	30 kg	34 g	0,2 g
²⁴³ Cm	110 g	0,14 g	-
²⁴⁴ Cm	70 g	5 g	0,02 g
²³⁷ Np	-	9600 g	10 g



- Wet processes for [liquid ==> solid] conversion have great potential
 - SOL-GEL (internal or external gelation process)
 - direct synthesis of flowable, dust free MA particles (>100 µm)
 - clean installation, easier maintenance after material removing (operator intervention)
 - suppression of dirty operation of mechanical granulation
 - but concentrated solution : 200 to 360 g/l
 - continuous cooling throughout process (tanks, pipes, transfer tubing, vessels, etc...)
 - Risk of hydrolysis, radiolysis of organic compounds used for the gelification









Before aging

- * Pressing & sintering
 - Use of organic lubricant is necessary for an industrial scale
 - Radiolysis and thermolysis issue
 - quick degradation of the lubricant property
 - further de-cohesion of the green pellets

Innovative development required (such as automatic lubrication of press dies)







Pressing & sintering

After aging

- Use of organic lubricant is necessary for an industrial scale
- Radiolysis and thermolysis issue
 - quick degradation of the lubricant property
 - further decohesion of the green pellets

Innovative development required (like automatic lubrication of press dies)







Assembly, mounting and storage

- * Neutron radiation ==> implementation necessarily in hot cell with remote handling
- * Heat control ==>continuous cooling (blowing engine)
 - very large cells to enable S/A handling (EFR S/A overall length : 4.8 m)
 - ancillary equipment (crane, etc...) in hot cells

S/A mounting, transport and storage in shielded cells

Simplified fabrication process: SpherePAC

- * SPHEREPAC (called VIPAC when molten salts processes)
 - Direct filling by vibropacking of fuel granules into the pin
 - Avoid granulation, pressing and sintering steps
 - the simplest, the most robust and compact process
 - Large experience existing in Russia
 - less intensive controls and only on welded pins (cleanness)
 - density and actinide distribution in pins
 - Select inert matrices able to be co-precipitated with actinides :
 - MgO, ZrO₂

Issues for SpherePAC fuels

- Optimisation of the filling to reach smeared density of ~ 85% th.d.
 - Selection of convenient granulometry classes
- * Segregation issue to be addressed
 - when mixing inert matrix and actinide compounds
- * Assess the impact of the fuel performance
 - Initial load of MA, fission rate, corrosion, ...
 - Thermal conductivity
- * Irradiation tests required !!

Fabrication processes for nitride fuels



- 1. Fabrication of (Pu, Am, Zr)O₂ + *free* C as starting material
 - − Powder metallurgy → powder
 - Sol-gel process → beads
 - Am is alternatively infiltrated into porous beads
- 2. Carbothermic reduction from oxides:
- 3. Shaping
Fabrication processes for nitride fuels

- * Nitride fuel fabrication is a more complex process : additional step of oxide nitridation by carbothermic reduction
- 1. Fabrication of (Pu, Am, Zr)O₂ + *free C* as starting material
- 2. Carbothermic reduction from oxides (Pu, Am, Zr)O_{x+u} + xC +1/2N₂ +uH₂ → (Pu, Am, Zr)N + uH₂O+ xCO
 - Intermediate products : carboxide, carbonitrides, oxide, carbide
 - Nitridation temperature limited by the AmN vaporisation at low temperature (~1500°C)
 - Product of good quality difficult to synthesize (incomplete reaction)
- 3. Shaping (grinding, sieving, pressing, sintering)



Fabrication processes for nitride fuels

- (Pu,Zr)N for CONFIRM fabricated by this fabrication route
- Density of (Pu_{0.3},Zr_{0.7})N
 ρ ~ 80% T.D.



Stability of AmN



- * AmN shows volatile behaviour at relative low temperatures of ~ 1800 K
- * This may severely limit the application of minor actinide nitride fuels



Conclusions and summary : fuel fabrication

- * Wet processes for shaping particles or granulates
 - To avoid powder handling and dust dissemination (cleanness)
 - To simplify the process
 - VIPAC, SPHEREPAC process is an objective for the future
- * Impact of the fabrication process on the fuel performance process must still to be assessed
 - A compromise between the simplification of the fabrication process and the increase of the fuel performance will have to be found

- * ECRIX : AmO_{1.6}+ MgO
 - micro-dispersed
 - 0.7 g Am/cm³
 - 200 mm
 (≈ 2,75 g of Am with
 95 % of ²⁴¹Am)
- * Objective
 - Test MgO
 - Fission rate = <u>30 at%</u>
 - Role of the flux moderation





- * Role of the flux moderation
 - ECRIX B (¹¹B₄C)
 - Irradiation time =
 670 EFPD
 - Transmutation rate = 80 %
 - End of irradiation : December 2007
 - ECRIX H (CaH₂)
 - Irradiation time = 340 EFPD
 - Transmutation rate = 90%
 - End of irradiation : October 2005



- * Role of the moderator
 - Reach higher burnup by limiting the irradiation







* Role of the moderator: to reach a higher burn-up by limiting the damage dose on the clad

Experiments in Phénix: CAMIX/COCHIX

- * Objective:
 - Test new Am compounds, microstructures, and MgO
 - Fission rate = 30 at% ⇒ irradiation time = 340 EFPD

⇒ Transmutation rate = 90 %



Sol. Solution





Macro-dispersed



Experiments in Phénix: CAMIX/COCHIX

* CAMIX/COCHIX

- 0,7 g Am/cm³, height of the column = 100 mm
- CAMIX 1 : Sol. Sol. (Am_{0.06},Zr_{0.78},Y_{0.16})O_{2-x}
- CAMIX 2 : CERCER micro. $(Am_{0.2}, Zr_{0.66}, Y_{0.14})O_{2-x}$ in MgO particule size 40 < ϕ < 60 μ m
- COCHIX 3 : CERCER macro. $(Am_{0.2}, Zr_{0.66}, Y_{0.14})O_{2-x}$ in MgO particule size 100 < ϕ < 125 μ m (30% vol of the matrix damaged)





* Standard Phénix capsule

- 19 pins (length : 1.80 m, ϕ : 5.65-6.55 mm)
 - 8 experimental transmutation fuel pins
 - Fuel column : 10 cm
- * 2 irradiation cycles
 - half 2007 → beginning 2009
 - 240 EFPD, 4th ring in the core, flux 4.10^{15} n.cm².s⁻¹



Experiments in Phénix: FUTURIX FTA



- * Composition of the FUTURIX-FTA device
- * Nitride pins to be irradiated later

Futurix FTA in Phénix





FUTURIX-FTA pin design

He-bonded pin



HELIOS planned in HFR

- * Five pins containing 0.7 grams ²⁴¹Am /cm³
- * Objectives
 - Test pyrochlore compound of Am
 - Test Mo matrix
 - Confirm the effect of temperature on the He release



- Test porous inert matrix to favour the He release

Helios	Composition	Fuel length (mm)	Fuel diameter (mm)	Volume (cm3)	Actual Density (g.cm-3)	Stack weight (g)	%Pu	%Am
1	Am2Zr2O7-MgO	62.0	5.458	1.451	3.96	5.748	0.00%	<mark>17.84%</mark>
2	ZrYAmO2	60.7	5.43	1.406	5.92	7.497	0.00%	<mark>12.17%</mark>
3	ZrYPuAmO2	60.5	5.43	1.401	5.85	7.555	7.85%	<mark>12.12%</mark>
4	ZrYAmO2/Mo	59.5	5.44	1.383	8.85	12.110	0.00%	7.88%
5	PuAmO2/Mo	63.1	5.41	1.450	10.00	14.246	12.50%	2.97%



Nitride experiment in HFR

- * CONFIRM
 - Irradiation of 2 nitride pins (Pu,Zr)N as precursor of ADS nitride fuels
 - $-(Pu_{0.3},Zr_{0.7})N$ irradiated
 - $-(Pu_{0.2},Zr_{0.8})N$ also fabricated
 - Started on 25 November 2007
 - Linear heat rate = 450 W/cm
 - -6 cycles (150 EFPD)



CONFIRM

- * Twee pins with (Pu,Zr)N fuel
- * Linear heat rate ~ 450 W/cm
- * Hafnium shield with a thickness of van 0.5 mm



EUROTRANS

- * Eurotrans is a 6th European Framework Programme
 - From 2005 2009, budget ~ 50 M€
 - Dedicated to the design & performance of an ADS demonstrator
 - Various core designs are studied, and two inert matrix fuel types are considered for MA burning
 - MgO CerCer Slightly better transmutation rate
 - Mo CerMet Better safety characteristics

Why Molybdenum metal ?

- * Molybdenum has excellent prospects
 - TANOX irradiation (40 wt% UO₂ in Mo) has shown good irradiation behaviour
 P. Dehaudt et al., *IAEA Technical Comittee Meeting on Research of Fuel aimed at Low Fission Gas Release*. Oct. 1-4, 1996. Moscow, Russia, IAEA TECDOC 970 (1997)
 - High melting point (~ 3000 K),
 - High thermal conductivity (~ 100 W/mK at 1500 K)
 - Reprocessible
 - Easy fabrication compared to ceramic IMF
- * But molybdenum has adverse neutronics properties
 - Relatively high absorption cross section
 - Neutron capture in Mo-98 leads to the production of long-lived Tc-99

Molybdenum has seven stable isotopes

* Only Mo-95 has a high cross section for thermal neutrons



Molybdenum has seven stable isotopes

- * For fast neutrons, the absorption cross sections are quite similar for all isotopes
- * The production of Tc-99 becomes a more important issue



Molybdenum depletion in ⁹⁵Mo

- Neutronic properties can be improved by depletion in Mo-95 and / or in Mo-98
- * Urenco & NRG studied depletion of Mo in ⁹⁵Mo *
 - Mo depletion (<1% ⁹⁵Mo) can be achieved
 - Costs of depletion are relatively low
 - Thermal cross section of Mo can be reduced significantly
- * In a similar way, depletion in Mo-98 can be achieved

* K. Bakker et al., Nucl. Technology 146 (2004), 325

Molybdenum depletion in ⁹⁵Mo

- * For the following procedure was designed for the production of Depleted Mo (DepMo)
- * Separation into three fractions
 - Light fraction (enriched in Mo-92, Mo-94)
 - Heavy fraction (enriched in Mo-98, Mo-100)
 - Middle fraction(containing the Mo-95) → Tails
- Light and heavy fractions are mixed to achieve the lowest Mo-95 content
- * Urenco Stable Isotopes has optimised for this scenario

URENCO process for depleting Mo

- * The enrichment (depletion) process for Mo is similar to the enrichment of uranium
- * Conversion is achieved by reduction to Mo-metal



Final isotopic composition

- * After depletion and conversion to metal, a typical blend was made with Mo-95 < 1%
- * But in principle, any isotopic composition can be achieved

	Natural	Light	Heavy	Typical blend
Isotope	at%	at%	at%	at%
92	14.84	~ 90 %		14.0
94	9.25			1.4
95	15.92			0.9
96	16.68			1.9
97	9.55			5.3
98	24.13) ~ 90 %	42.5
100	9.63		J	34.0

Molybdenum issues

- Now we have produced DepMo and established a successful fabrication route for DepMo-based CerMets
- * Question:

What is the optimum isotopic composition of DepMo?

- * Three criteria have to be balanced:
 - Parasitic absorption of neutrons by DepMo
 - Limit Tc-99 production
 - Minimise costs of depletion of Mo

Three criteria

- * Assessment of:
 - Parasitic absorption
 - Tc-99 production
 - Costs of depletion

* For different reactor types:

- Light Water Reactor
- Gas-Cooled Fast Reactor
- Accelerator Driven Systems
- * For various DepMo mixtures
 - Light fraction only (~ 90% Mo-92)
 - Produced DepMo with Mo-95 ~ 1%
 - DepMo with Mo-98 ~ 2 % (low Tc-99 production)

σ_{abs} ⁹⁹Tc (capture) / ⁹⁹Tc (fission) SWU needed / material loss

NZG

Results: σ_{abs} and Tc-99 production

Energy averaged absorption cross section σ_{abs} (barn)

	Natural Mo	Light fraction	LWR DepMo	FR DepMo	
		~ 90% Mo-92	~ 1% Mo-95	~ 2% Mo-98	
LWR	0.983	0.217	0.252	0.870	
GCFR	0.203	0.087	0.151	0.152	
ADS	0.129	0.066	0.091	0.106	

Ratio Tc-99 production: ⁹⁹Tc (capture in Mo) / ⁹⁹Tc (fission An)

	Natural Mo	Light fraction	LWR DepMo	FR DepMo	
		~ 90% Mo-92	~ 1% Mo-95	~ 2% Mo-98	
LWR	0.148	0.001	0.200	0.012	
GCFR	2.385	0.008	3.226	0.196	
ADS	1.680	0.006	2.273	0.138	

For LWR, Tc-99 production increases by ~ 20 % For fast reactor systems, depletion in Mo-98 is necessary

Conclusions for Molybdenum

- * Molybdenum is a very promising inert matrix material
- * Adverse neutronic properties can resolved by depletion in Mo-95 / Mo-98
 - Process developed by URENCO
 - Costs are reasonable in relation to potential benefits
 - DepMo can be used also for U-Mo MTR fuel
- * Fabrication of CERMETs has been sucessfully achieved
- * We are eagerly waiting for the test irradiations
 - FUTURIX FTA in Phenix
 - HELIOS in High Flux Reactor (HFR)
 - DepMo / PuO₂ irradiation in BR-2 (LWR-Deputy programme)

Last, but not least: Fabrication is easy!



Composites, 30 vol.% microspheres

Leading ideas for MA-IMF design

From transmutation experiments (such as EFTTRA T4bis, we have optained a good insight in the most important isssues and how to influence them

Try to limit volume swelling by:

- * Promoting Helium release:
 - Providing open porosity
 - By increasing the temperature
- * Alternatively other inert matrices with better retention properties are also considered, such as metals



Providing Open porosity

Open porosity, up to 50% of total porosity, is obtained in MgO matrix:

- > sintering under nitrogen pressure
- > double pressing before sintering



Experiments performed by CEA Density is 85-90%T.D. while open porosity remains high

Increase of temperature

- * Implantation experiments of Helium in spinel and zirconia indicate that:
 - onset of Helium release: about 800 Kelvin
 - completion of release : about 1600 Kelvin

Fuel temperatures must be higher than about 1400 C

- * Fuel temperature increase:
 - Addition of Plutonium in order to study the effect of temperature on release and swelling
 - Adjustment of thermal design (increase of initial gap)

Next experiment: Helios

- * In HELIOS, many of the lessons learned will be used
 - Irradiation in HFR, ~ 250 300 full power days
 - MgO with open porosity
 - Zirconia with / without Pu to address helium release mechanism
 - Testing of Mo as metal matrix

Pin	Composition	Target Am	Target Pu	Expected	Specified act. dens.	
nr.		density	density	T.D.	(based on 100% T.I) .)
		g/cm ³	g/cm ³	%	g/cm ³	
1	Am ₂ Zr ₂ O ₇ +MgO	0.7		90%	0.78	
2	$(Am,Zr,Y)O_2$	0.7		90%	0.78	
3	$(Am, Pu, Zr, Y)O_2$	0.7	0.25	90%	0.78 / 0.28	
4	(Zr,Am,Y)O ₂ +Mo	0.7		95%	0.74	
5	(Pu,Am)O ₂ +Mo	0.3	1.2	95%	0.74 / 1.26	

Power densities in HELIOS +HELIOS1 MgO + Am2Zr2O7 HELIOS2 (Y,Zr,Am)Ox HELIOS3 (Y,Zr,Pu,Am)Ox HELIOS4 Mo + (Y,Zr,Am)Ox Linear heat rate (W/cm)

Irradiation time (fpd)

Addition of plutonium: increase of temperature to promote helium release





Summary HELIOS

- * HELIOS provides an irradiation test to study the release options for helium
 - To optimise the transmutation of Am
- * Study of CerCer and CerMet matrices
- * Two methods are being tested:
 - Providing open porosity (in MgO)
 - Fuel temperature increase by addition of Plutonium
- * Five Am-containing inert targets will be irradiated, starting from 2008 in HFR
NZG

Conclusions and summary : fuel composition

- * ADS fuels are composed of:
 - High content of TRU
 - Degraded thermal properties
 - Degraded fuel performance in pile compared to U+Pubased fuels
 - 55-60 vol% of inert matrix
 - To improve the thermal properties of the fuel
 - Melting point, thermal conductivity, stability at high temperature,...
 - To improve the fuel quality

NZG

Conclusions and summary : fuel composition

- * ADS fuel can be:
 - An oxide composite :
 - Reference: (Pu,-Np-,Am,Cm)O₂+MgO, Mo and ZrO₂ (He bond or Pb bond)
 - A nitride solid solution
 - Reference: (Pu,-Np-,Am,Cm)N + ZrN (He, Pb or Na bond)
 - A metal alloy
 - Reference: Pu-Np-Am-Cm-40Zr (Na bond)
 - Knowledge on oxide fuels is the largest in Europe
 - Several Irradiation tests now completed,
 - Several irradiation tests to be completed
 - Others in preparation and started in 2007
 - New PIE results on nitride should be available soon

Conclusions and summary: fuel performance

- * Inert matrices have been selected for
 - Their good thermal properties (higher than that of UO_2)
 - Their compatibility with the TRU compound, the coolant, the clad
 - Their resistance to neutron, FP recoil damage
 - MgO, ZrO₂ for TRU oxide
 - ZrN for TRU nitride
- * ADS fuels must be designed to accommodate
 - The swelling due to the inert matrix damage (FP recoil)
 - Depends on the inert matrix (sensitivity to amorphisation)
 - Beneficial effect of the irradiation temperature (>1100°C) and macrostructure
 - The swelling due to the He production
 - Beneficial effect of the irradiation temperature and microstructure (open porosity)

NZG

Conclusions and summary: fuel performance

- * ADS fuel performance (Linear power & BU) is limited
 - By the melting of (Pu,-Np-Am,Cm)O₂ or the eutectic reaction between (Pu,-Np-Am,Cm)O₂ and the inert matrix
 - By the vaporisation of (Pu,-Np-,Am,Cm, Zr)N
 - The cladding damage and clad corrosion
- * Not so many hot labs in Europe to handle TRUs
 - CEA (ATALANTE), ITU (MA-lab), NRG (Act. Lab)
 - Only small quantities of Am and Cm
- * Simplification, automation, compaction, robustness
 - heavy shielding, remote handling & cooling throughout process
 - from conversion to S/A storage and transport
 - limited fabrication possibilities

Conclusions and summary : fuel fabrication

- * Wet processes for shaping particles or granulates
 - To avoid powder handling and dust dissemination (cleanness)
 - To simplify the process
 - VIPAC, SPHEREPAC process is an objective for the future
- * Impact of the fabrication process on the fuel performance process must still to be assessed
 - A compromise between the simplification of the fabrication process and the increase of the fuel performance will have to be found