Current Progress in R&D on Pyrochemical Partitioning Technology in the Czech Republic

Jan Uhlíř

Nuclear Research Institute Řež plc

Czech Republic

uhl@ujv.cz

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P&T concept under development in the Czech Republic

Czech P&T program is based on the development of closed fuel cycle of advanced reactor systems, chiefly on the Molten Salt Reactor system concept with fluoride salts based liquid fuel, the fuel cycle of which is based on pyrochemical fluoride partitioning of spent fuel.

Molten Salt Reactor (MSR) represents one of promising advanced reactor type, which can be operated as actinide burner (transmuter) incinerating transuranium fuel.

MSR – An burner has to be operated in closed cycle mode, based on the on-line reprocessing technology. The on-line reprocessing should be linked with the fresh transuranium fuel processing to continuously refill the new fuel into the reactor system.

The P&T program has also a close connection to the development of MSR – Th breeder technology.

Main Czech R&D project devoted to pyrochemical partitioning technology

MIT project: "Fluoride reprocessing of spent fuel of GEN-IV reactors" (2006 – 2011)

- R&D project devoted to pyrochemical fuel cycle technologies focused mainly to fluoride separation processes suitable for MSR technology including thorium - uranium fuel cycle and separation of transuranics
- Solved by NRI Řež

- The project has a close link to another MIT project called **"Nuclear system SPHINX with molten fluoride salts based liquid nuclear fuel"** solved by consortium of Czech research and industrial institutions and companies.

(MIT = Ministry of Industry and Trade of the Czech Republic)

Fluoride pyrochemical partitioning

Czech activities in development of pyrochemical partitioning technologies are devoted to reprocessing of selected advanced fuel types of GEN-IV reactor systems and are focused on two fluoride technologies:

- Fluoride volatility method
- Electrochemical separation processes from fluoride molten salt media

Both pyrochemical partitioning technologies under development meet the requirements of MSR fuel cycle. This is caused by the fact that MSR fuel is constituted by a mixture of molten fluorides and the technology has to be resistant to a very high radioactivity of fuel entering the process.

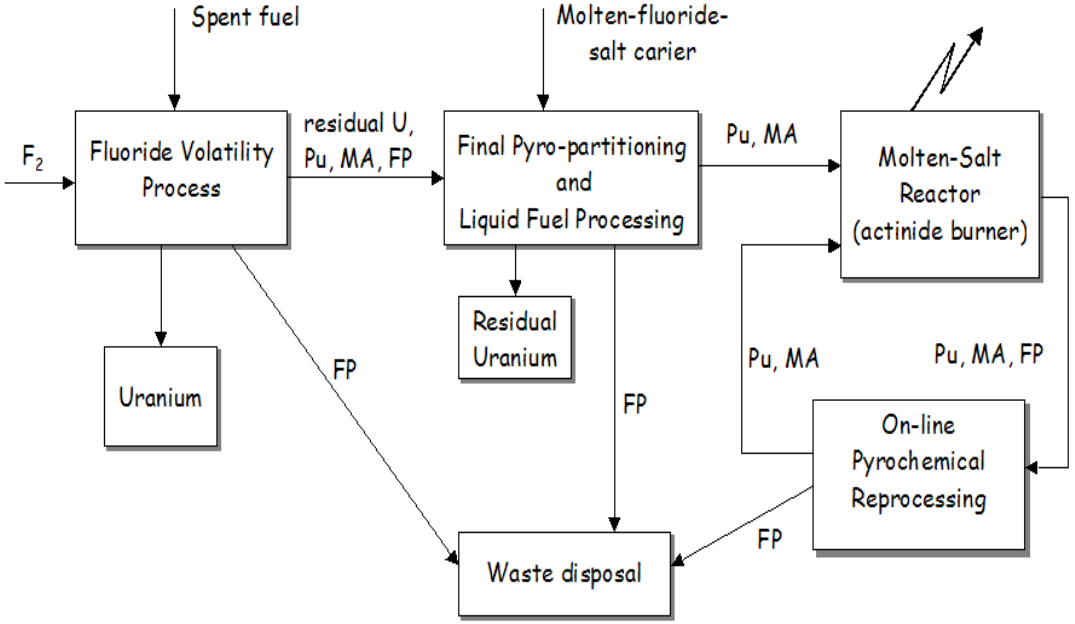
R&D on Fluoride Volatility Method

Principles of reprocessing by FVM:

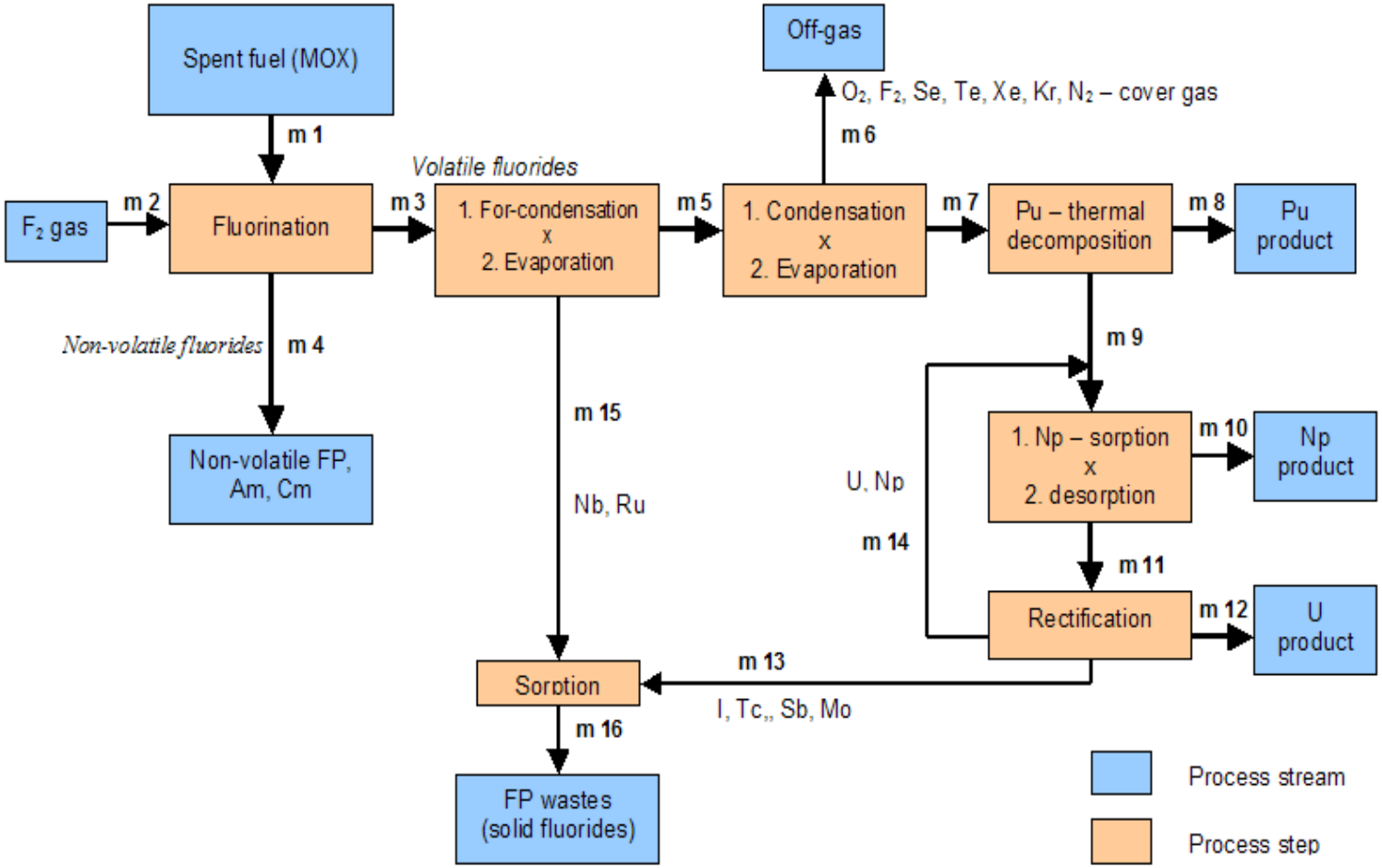
- The FVM technology is based on direct fluorination of spent fuel by fluorine gas
- The separation process comes out from the specific property of uranium, neptunium and partially of plutonium to form volatile hexafluorides, whereas most of fission products and transplutonium elements present in spent fuel form non-volatile trifluorides.

Mission and objectives of Fluoride Volatility Method

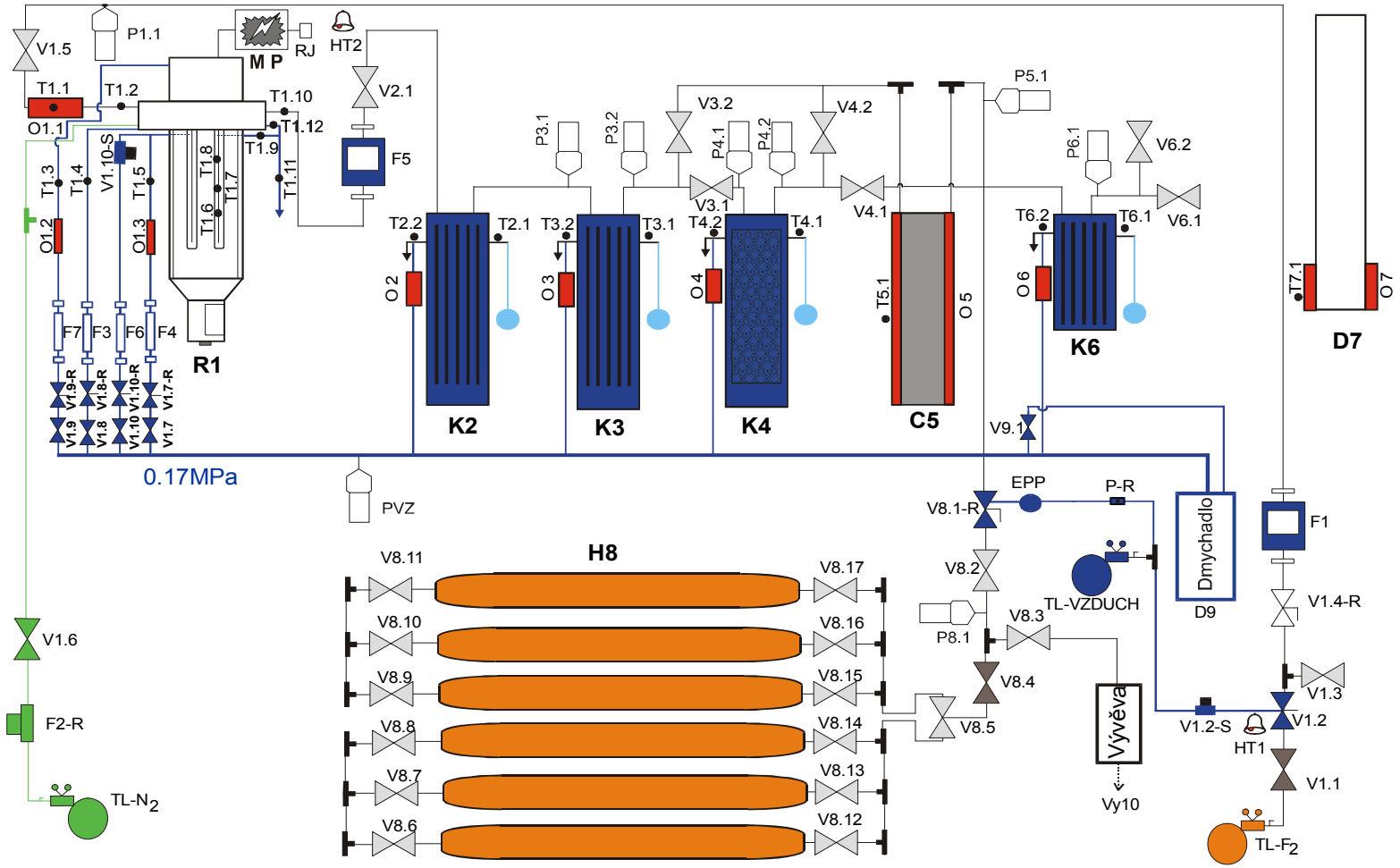
- **Reprocessing of such types of oxide fuels from LWR or FR, which could be hardly reprocessed by aqueous technologies** *(inert matrix fuels, TRU-fuels, fuels with very high burn-up, short cooling time, high concentration of Pu, different cladding material etc.)*
- **Reprocessing of metallic and carbide fuels**
- **Primary processing of TRU-fuel for MSR – An-burners**
- **Separation of a maximum fraction of uranium component from Pu, MA and FP.**



Process flow-sheet of Fluoride Volatility Method



Experimental technological line FERDA in NRI Řež plc



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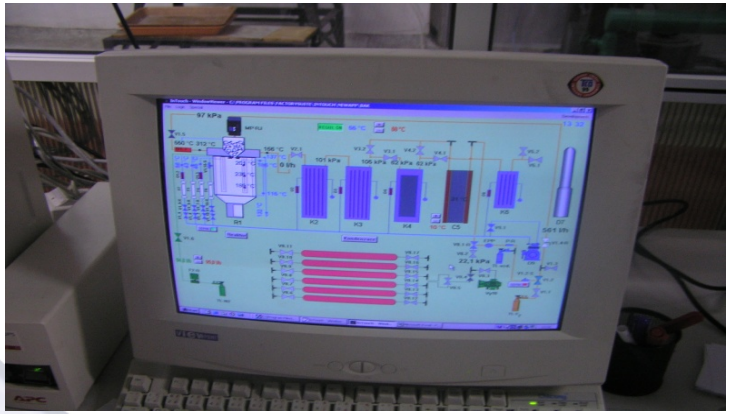
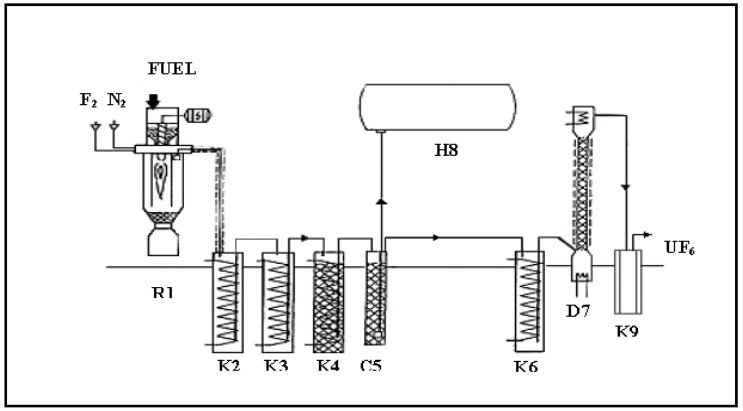




Flame fluorination reactor of the FERDA line

Main parts:

- el. motor with gearbox
- •screw doser
- •body of the fluorinator
- •burning chamber
- •container for non-volatile fluorides
- •metallo-ceramic filters
- •pseudo-fluidized bed part
- •fluorine gas pre-heater
- •air cooling system
- •stand for gas distribution

Main structural materials:

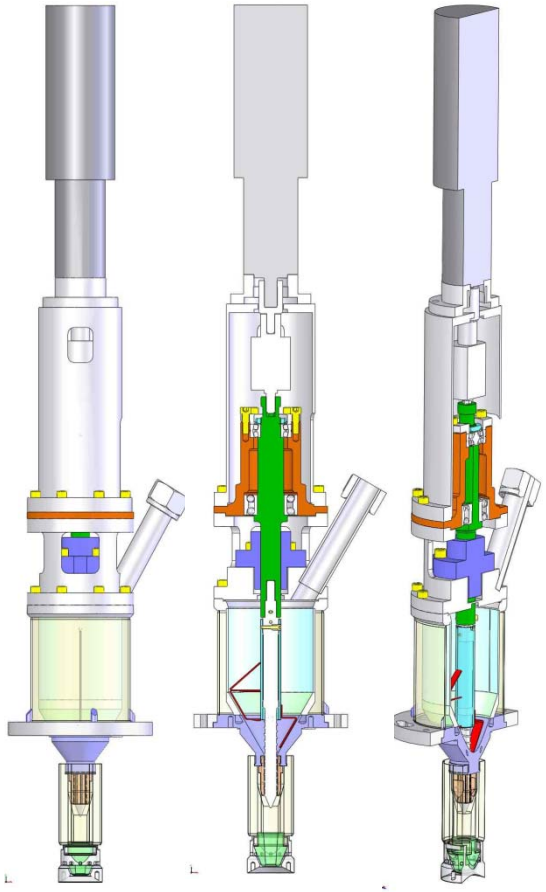
- • Nickel and nickel alloys)

Short term capacity:

- 3 kg /hour

Original feeder-head after long run experiment

Flame fluorination reactor of the FERDA line



Reconstruction of upper part

Now it works!

Current status – future plans

Basic demonstration of FVM was verified

Further engineering development is necessary

- **Powdered uranium oxide dosing problem was solved**
  - New redesigned feeder is under long-run tests
- **Remote control operation**
  - Some fittings and connecting parts will have to be redesigned to fulfill requirements of of remote control and decontamination processes
- **Verification with irradiated fuel**
  - Hot cell construction is planned

Perspectives of Fluoride Volatility Method

Fluoride Volatility Method has a good potential to be used within the fuel cycles of advanced reactor types for reprocessing of selected advanced oxide fuel types, metallic and carbide fuels.

The main attractiveness of the technology is in the extreme radiation resistance of used chemical agents (fluorine gas, inorganic fluorides), non presence of any neutron moderating agents and in the possible compactness of the whole process.

Another possible use of FVM can be as the fuel cycle “Front-end” technology of MSR – An-burner, as it completely converts oxides into fluorides – a chemical form of MSR fuel.

R&D on Electrochemical separation of An/Ln from molten fluoride media

Development of separation technology suitable for on-line reprocessing of MSR fuel

Carrier salt of MSR primary (fuel) circuit:

^{7}LiF-BeF_2 (called FLIBE) or ^{7}LiF-BeF_2-NaF

However, FLIBE is insufficiently electrochemically stable.

Carrier salts proposed for electrochemical separation processes:

^{7}LiF-BeF_2 or ^{7}LiF-BeF_2-NaF *(limited use)*

LiF-NaF-KF (called FLINAK)

LiF-CaF_2

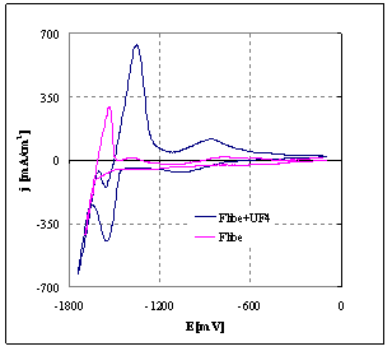
Electrochemical separation processes under development:

Cathodic deposition method

Anodic dissolution method

Laboratory research on electrochemical separation from fluoride molten-salt media

- The electrochemical measurements have been carried out in a laboratory nickel electrolyser under inert atmosphere in a three-electrode set-up.
- High-temperature electrolyser was designed for fluoride carrier melts (temperature range 750 – 850 °C)
- A specially designed reference electrode based on the Ni/Ni^{2+} red-ox couple was developed.
- Linear Potential Sweep Cyclic Voltammetry Method has been used as the measurement technique.



Evaluated red-ox potentials and reaction mechanism in various carrier salts

Melt	**FLIBE(-Na)**	E [V] vs. Ni/Ni^{2+} in FLIBE	
Studied reaction	*mechanism*	*Potential without / with separator*	
Melt decomposition	one-step	-1.50	-
Uranium reduction	two-step	-0,90	-1,40
Thorium reduction	No reduction		
Lanthanides reduction (La, Nd, Pr, Gd)	No reduction		

Melt	**FLINAK**	E [V] vs. Ni/Ni^{2+} in FLINAK		**$LiF-CaF_2$**	E [V] vs. Ni/Ni^{2+} in $LiF-CaF_2$	
Studied reaction	*mechanism*	*Potential without / with separator*		*mechanism*	*Potential without separator*	
Melt decomposition	one-step	-2.05/ -1,80	-	one-step	-2.30	-
Uranium reduction	two-step	-1.20/ -0,25	-1.75/ -1,54	two-step	-1.40	-1.85
Thorium reduction	two-step	-0.70	-2.00	N/A	N/A	N/A
Neodymium reduction	two-step	-1.00/ -0,70	< -2.05/ < -1,80	one-step	-2.00	-
Gadolinium reduction	two-step	-1.01 / -0,95	< -2.05/ < -1,80	one-step	-2.10	-
Europium reduction	two-step	-0.75	-1.95	one-step	< -2.30	-
Strontium reduction	not observed	<-2.05	-	N/A	N/A	N/A
Zirconium reduction	complicated	from-1.40*	-1.80*	N/A	N/A	N/A

A survey of the studied red-ox potentials

Red-ox couple	LiF-NaF-KF	LiF-CaF_2	LiF-BeF_2	LiF-NaF
	Ref. Ni/Ni^{2+} in FLINAKu	Ref.. Ni/Ni^{2+} in LiF-CaF_2	Ref. Ni/Ni^{2+} in LiF-BeF_2	Ref. Ni/Ni^{2+} in LiF-NaF
U^{3+}/U^{0}	-1.75	-1.90	-1.4	-1.4
U^{4+}/U^{3+}	-1.20	-1.40		(-0.8) – (-1.25)
U^{5+}/U^{4+}	+0.40	-		not-detected
U^{6+}/U^{5+}	+1.40	-		not-detected
Th^{x+}/Th^{0}	~ -2.00	-1.70	out of window	-
Th^{4+}/Th^{x+}	-0.70	-		-
Nd^{2+}/Nd^{0}	< -2.05	-2.00	out of window	out of window
Nd^{3+}/Nd^{2+}	~ -1.00	not-detected		-1.3
Gd^{2+}/Gd^{0}	< -2.05	-2.10	out of window	-1.35
Gd^{3+}/Gd^{2+}	~ -1.00	not-detected		-0.55
Eu^{3+}/Eu^{x+}	~ -0.75	not-detected		-0.2
Eu^{x+}/Eu^{0}	-1.95	< -2.30		out of window
Zr^{4+}/Zr^{x+}	-1.50	-		-
Zr^{x+}/Zr^{0}	-1.80	-		-
Sr^{2+}/Sr^{0}	< -2.05	-		-
La^{3+}/La^{0}	< -2.05	-	out of window	-
Pr^{3+}/Pr^{0}	< -2.05	-	out of window	-
Sm^{2+}/Sm^{0}	-0.8	-	-	out of window
Sm^{3+}/Sm^{2+}	out of window	-	-	-1.2

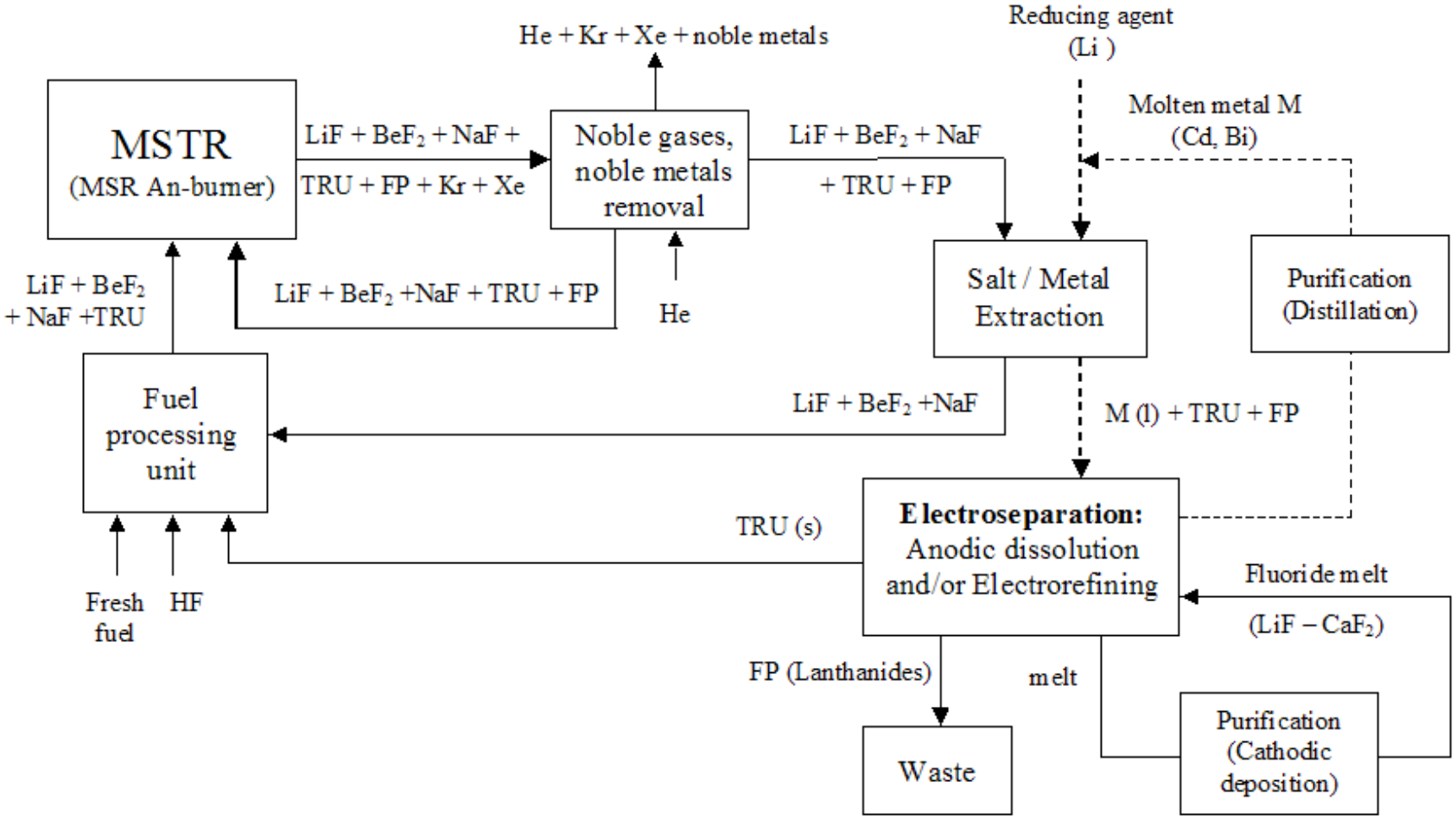
Separation possibilities of selected actinides and lanthanides

	Separation presumed possible	Separation presumed impossible
LiF-NaF-KF	U/Nd, Gd, La, Pr,Eu	Th/Nd,Gd
	U/Th	Nd/Gd
	Th/La,Pr,Sr,Zr,Eu	U/Zr
	U/Sr	
LiF-CaF2	U/Gd,Th,Eu	U/Nd
	Th/Eu,Nd,Gd	Nd/Gd
	Eu/Nd,Gd	
LiF-BeF2	U/Nd,Gd	Nd/Gd
	U/Th	
LiF-NaF	U/Nd, Gd, Sm, Eu	Nd, Gd
	Gd/Eu,Sm	

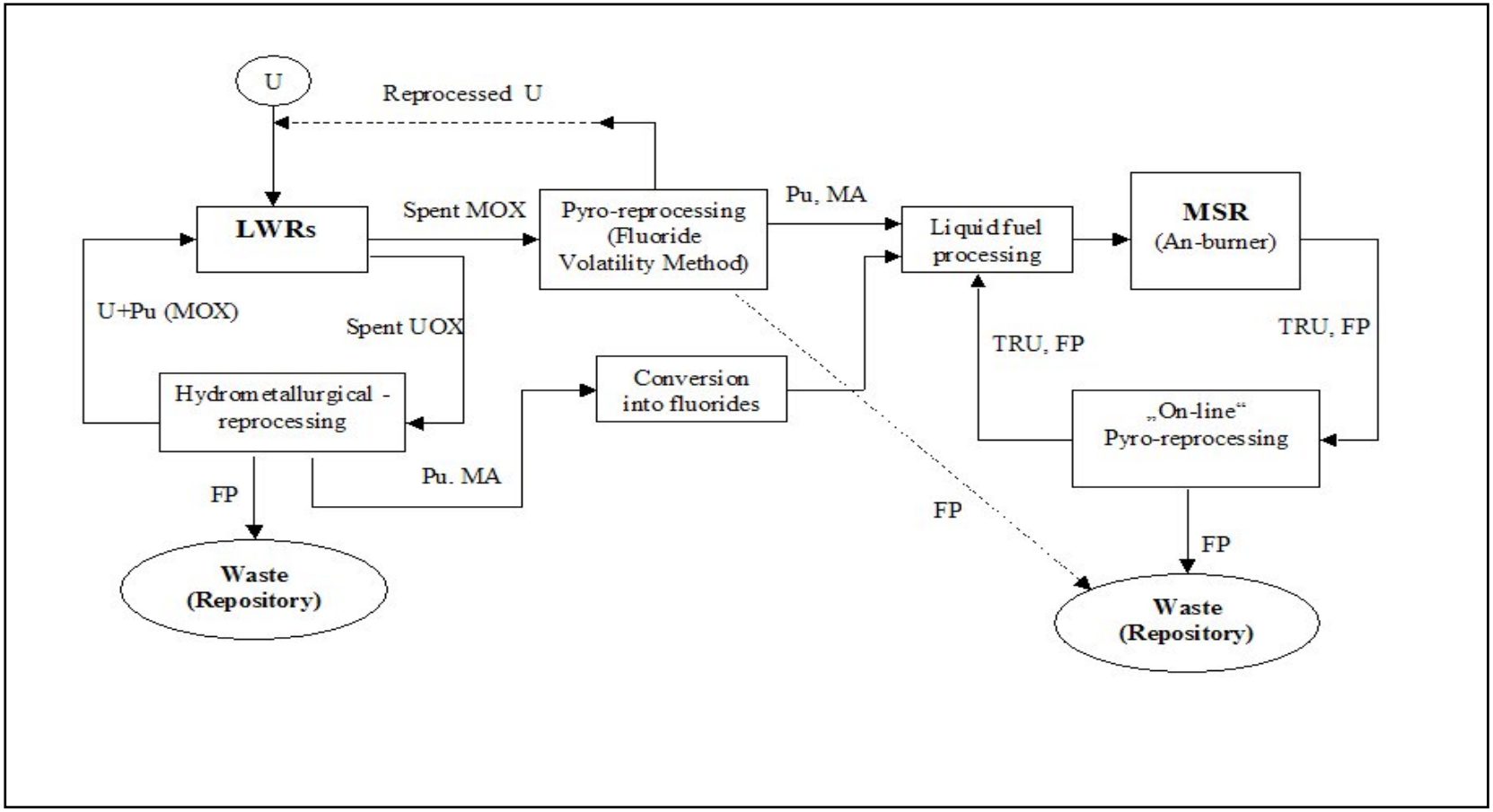
Flow-sheeting of MSR on-line reprocessing technology

- The flow-sheet concept comes out from the former results achieved by ORNL team during MSRE and MSBR projects and from the current progress in electrochemical separation studies
- The reprocessing technology is based on primary total (non-selective) “Molten-salt / Liquid metal” reductive extraction from MSR carrier salt and on subsequent electrochemical separation processes:
  - Anodic dissolution method (selective electrochemical oxidation of reduced elements according to the differences in their red-ox potentials)
  - Cathodic deposition method (selective electrochemical reduction of dissolved ions in molten carrier salt)

Conceptual flow-sheet of MSTR-SPHINX on-line reprocessing technology (MSR – actinide burner)



P&T concept - Double strata strategy with MSTR in second stratum



Conclusions

- Successful solution of MSR/MSTR fuel cycle technologies represents an essential precondition for future deployment of MSR systems.
- Fluoride pyrochemical separation methods seem to be promising technologies for their use within these fuel cycles.
- Current R&D effort and achieved results offer a prospect, that the MSR/MSTR fuel processing and reprocessing will be solved successfully.

Acknowledgements

The author is greatly appreciative of the support of the Ministry of Industry and Trade, Radioactive Waste Repository Authority and EC-EURATOM (FP7 project ACSEPT), which made this work possible.

Almost the end of my presentation, but this begins some questions ……

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Now we have to solve problems caused by the use of uranium – plutonium fuel cycle:

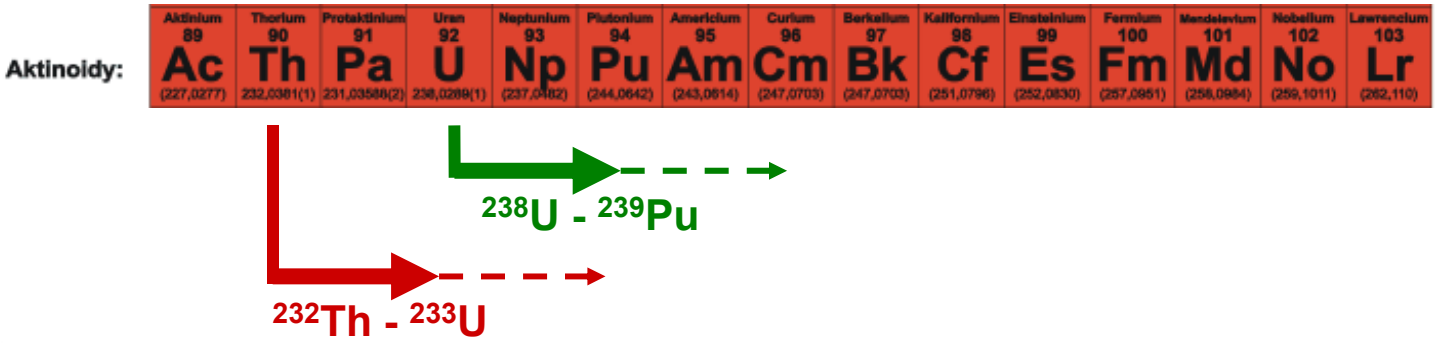
- Partitioning of higher actinides (Np, Pu, Am, Cm)
- Difficult fabrication of Am and especially Cm fuel
- How complete will be burning (transmutation) of Am and Cm in fast reactor systems ?

And what about the gradual transition to the thorium – uranium fuel cycle to completely eliminate these problems ?!!!

- It brings new technical problems and difficulties
- It can be effective only with liquid fuel
- It was never fully verified
- <u>But it could push forward the frontiers of nuclear technology !</u>

Possibilities and challenges of thorium

- **Uranium – plutonium fuel cycle ($^{238}U \rightarrow {}^{239}Pu$)**
  - Excellent breeding in fast spectrum neutrons
  - Production of transplutonium elements (Am, Cm)
  - Fabrication problems with Am and Cm
  - PUREX, UREX, Pyrochemical technologies
- **Thorium – uranium fuel cycle ($^{232}Th \rightarrow {}^{233}U$)**
  - ^{233}U is not natural isotope (once-through fuel cycle is not possible)
  - Excellent breeding in thermal spectrum neutrons
  - Minimized production of plutonium, no higher (transplutonium) actinides
  - Sustainability problems with solid fuel (^{233}Pa – long decay half-life, high cross-section)
    - Optimal with liquid fuel and on-line reprocessing (MSR)
  - THOREX, Pyrochemical methods



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