Fuel cycle aspects of Molten Salt Reactor technology

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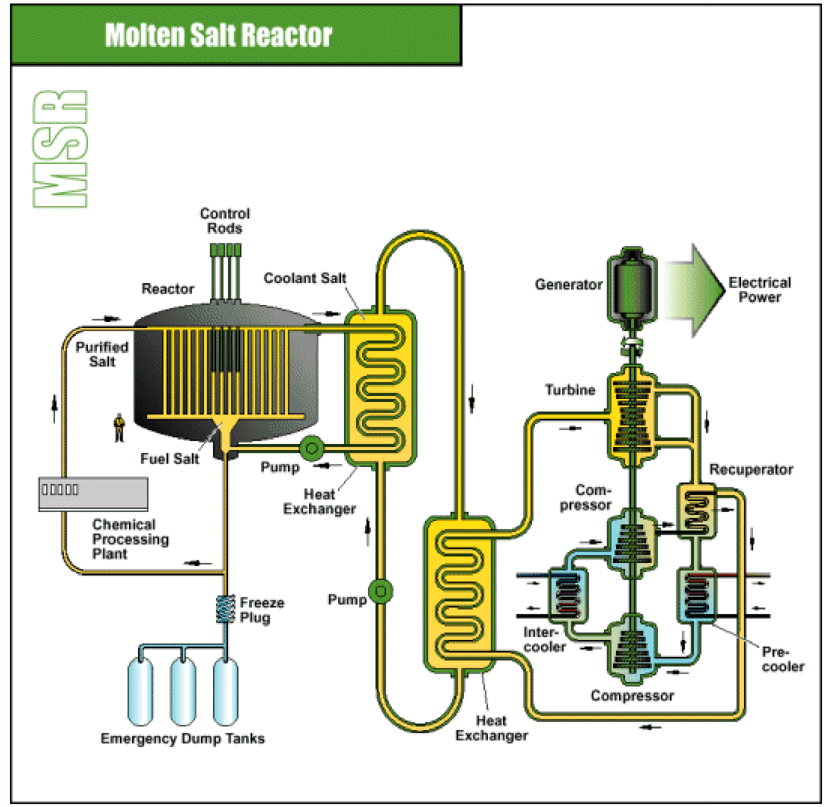
MSR – non classical reactor type

- Specific features of MSR comes out from the use of liquid (molten-salt) fuel circulating in the primary circuit.

- MSR can be operated either as thorium breeder (in thermal or fast/resonance spectrum) within the ^{232}Th – ^{233}U fuel cycle or as actinide transmuter (in resonance/epithermal spectrum) incinerating transuranium fuel.

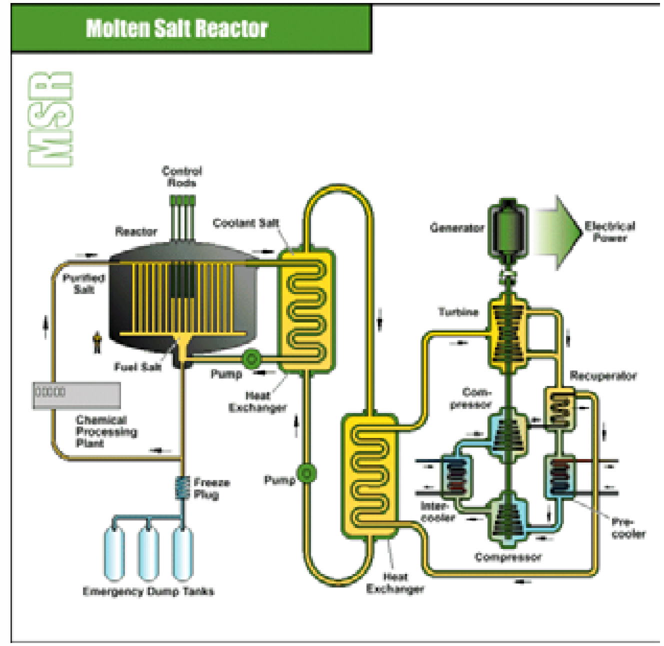
- Typical fuel: fluorides of actinides dissolved in fluoride carrier salt.



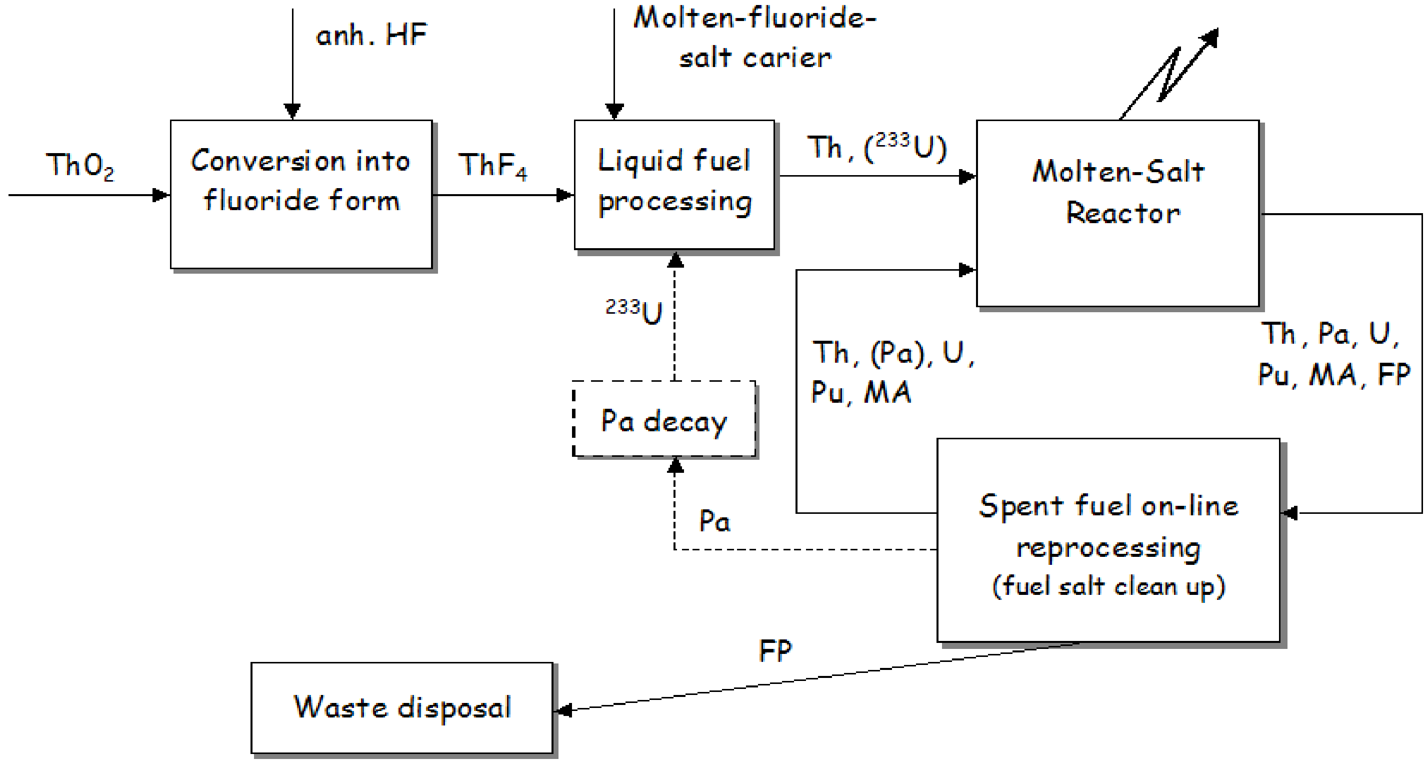
MSR – thorium breeder

- MSR is the only reactor system from the GEN IV reactor family for which the thorium fuel is considered.
- ^{233}U is the only fissile material in the thorium – uranium fuel cycle
- MSR – Th breeder with higher breeding cannot be operated without the on-line reprocessing

- Typical fuel: ThF_4 and UF_4 dissolved in $^{7}LiF – BeF_2$ carrier molten salt.



Fuel cycle technology in MSR system



Mission of MSR fuel on-line reprocessing

To keep the reactor in steady-state conditions by continuous cleaning-up of the primary (fuel) circuit salt.

q **To clear away neutron poisons like Xe, Kr, lanthanides**

q **To extract freshly constituted fissile material or its precursors**
- **Desirable reaction in the reactor core (MSR – Th-breeder):**

  ^{232}Th (n,γ)® ^{233}Th(β^{-})® ^{233}Pa(β^{-})® ^{233}U
- **Undesirable reaction:** **^{233}Pa(n,γ)® ^{234}Pa(β^{-})® ^{234}U**

q **To secure refilling of fresh fuel into fuel (primary) circuit**

(reprocessing technology is connected with fresh fuel feeding)

Technologies proposed for on-line reprocessing

Reprocessing technologies proposed for MSR fuel cycle are generally pyrochemical, majority of them are fluoride technologies. 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.

Main separation techniques proposed for on-line reprocessing of MSR fuel

Originally proposed by ORNL:

- **Gas extraction (He-bubbling)**
- **Fluoride volatilization processes**
- **Molten-salt / Liquid metal extraction processes**

New technique under present development:

- **Electrochemical processes**

Selection of carrier molten salt for MSR system

Special attention has to be paid to the selection of carrier molten salt, which must exhibit several basic properties:

- Appropriate melting point and viscosity
- Good thermal conductivity
- Low vapor pressure
- Radiation stability and good neutronic parameters
- Chemical and thermodynamic stability
- Compatibility with structural materials
- Sufficient solubility of actinides (Th, Pa, U)
- Reprocessability by adequate separation techniques

FLIBE melt was selected by ORNL as the best candidate fulfilling nearly all the criteria

^{7}LiF-BeF_2 (acronym FLIBE, melting point 456 °C, the only problem is the reprocessability due to limited electrochemical stability).

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Molten salt carrier selection for reprocessing technology

Chosen melts should meet some suitable basic characteristics:

- Low melting point
- High solubility of actinides and fission products
- High electrochemical stability
- Appropriate physical properties (electrical conductivity, viscosity etc.)
- Compatibility with some structural materials used in electrochemistry

Unfortunately, no melt fulfilling all the requirements was found.

Suitability of individual molten salt carriers for on-line reprocessing of MSR fuel

Carrier salt of MSR primary (fuel) circuit:

^{7}LiF-BeF_2 (called FLIBE)

Suitable for fuzed salt volatilization, noble gas extraction and partially for molten salt/liquid metal extraction

However, FLIBE is insufficiently electrochemically stable.

Fluoride melts suitable for electrochemical separations

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

Carrier salt of MSR primary (fuel) circuit:

$^{7}LiF\text{-}BeF_2$ - m.p. 456 °C

However, FLIBE is insufficiently electrochemically stable.

Carrier salts proposed for electrochemical separation processes:

$LiF\text{-}BeF_2$ *(limited use for insufficient electrochemical stability)*

LiF-NaF-KF (FLINAK) - m.p. 454 °C *(also insufficient electrochemical stability)*

$LiF\text{-}CaF_2$ - m.p. 766 °C *(electrochemically stable, but difficult to handle due to high melting point)*

Possible solution – to use two of them or all three melts successively for gradual separation of individual MSR fuel components.

Suitable electrochemical separation processes:

Cathodic deposition method

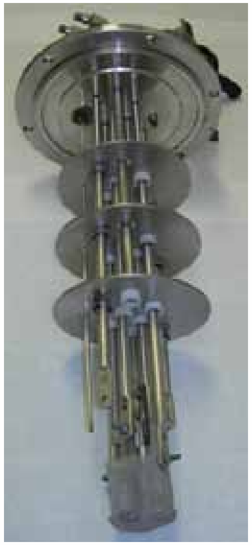
Anodic dissolution method

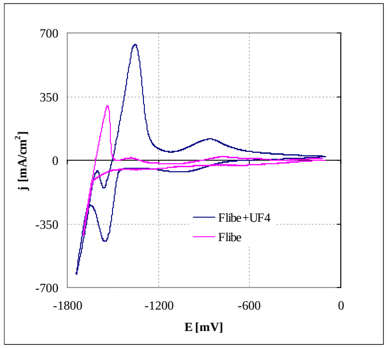
Laboratory research on electrochemical separation from fluoride molten-salt media

- The electrochemical measurements have been carried out in a laboratory nickel electrolyser under inert atmosphere in a three-electrode set-up.

- A specially designed reference electrode based on the Ni/Ni^{2+} red-ox couple was developed.

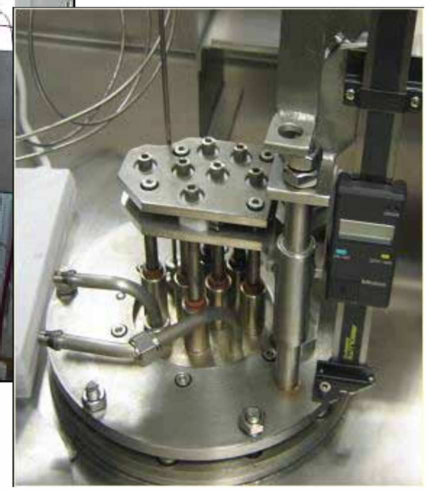
- Linear Potential Sweep Cyclic Voltammetry Method has been used as the measurement technique.





Instrumentation

Two nitrogen glove-boxes with built-in electrolysers sealed by removable flange.

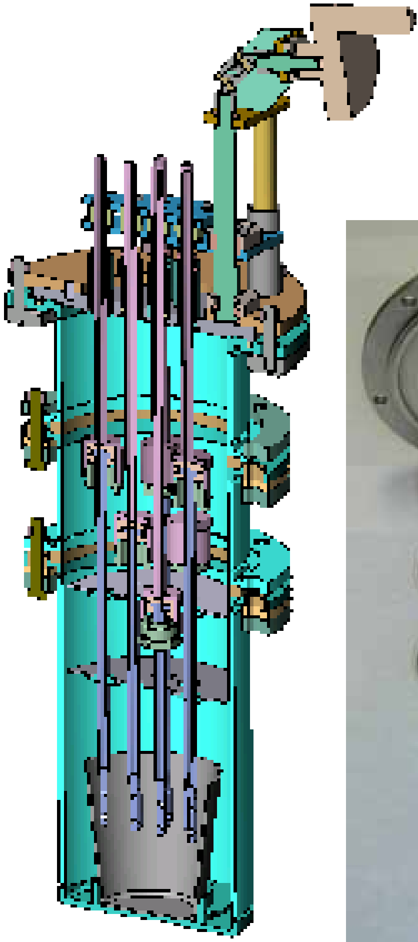


HEKA PG 310 potentiostat:

Compliance Voltage: $\pm 20\ V$
Output Current: $\pm 2\ A$

Instrumentation

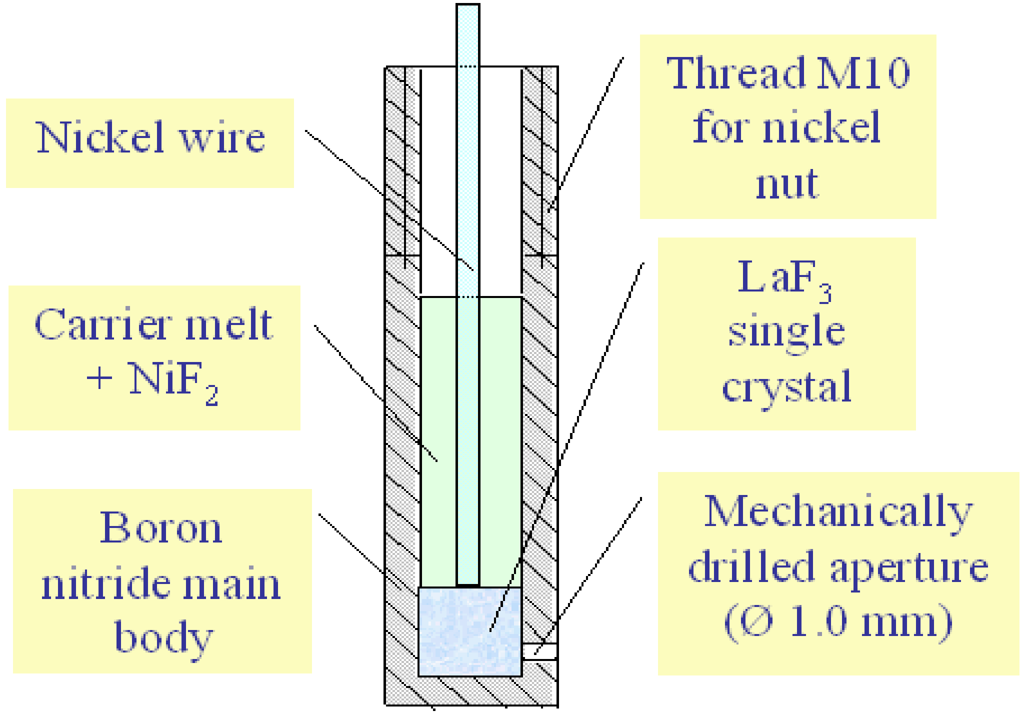
Electrolyser made of Ni/Ni-based alloy (INCONEL 625) placed in a furnace offering homogenous thermal field up to 1000°C.



Measurements

Electrochemical measurements in FLiNaK, FLiBe, LiF-CaF_2:

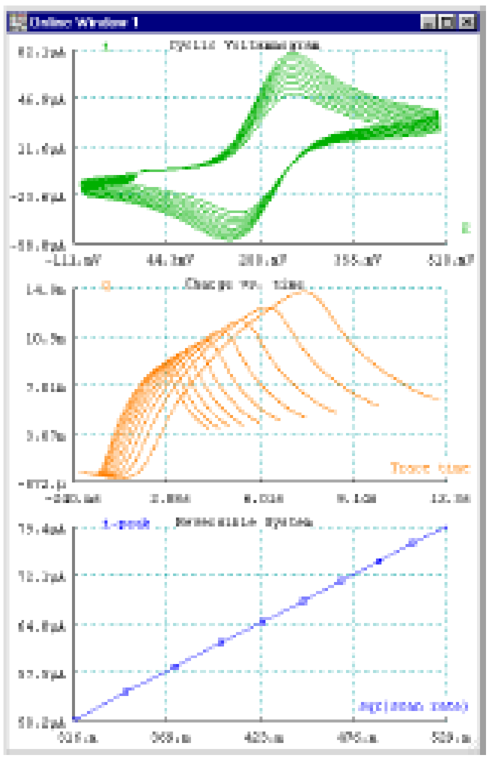
- Using W, Mo, Ni, GC working electrodes
- Glassy-carbon crucible
- Pt or Ni/Ni^{2+} reference

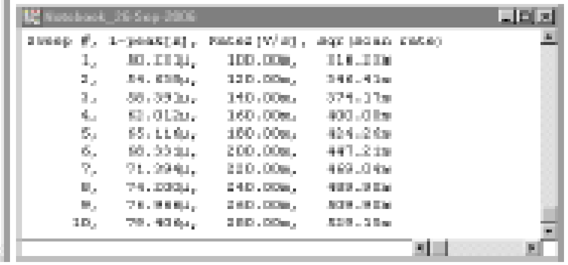


Measurements

Systems containing actinides *(U, Th)* and Lanthanides *(Eu, Gd, Sm, La, Pr, …)* are studied by variety of electrochemical methods.

Electrolytic experiments follow basic electrochemical studies





U deposit on Ni electrode

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 fission products (lanthanides)

Carrier melt	Separation presumed possible	Separation presumed impossible
FLIBE	U / Th U / Nd, Gd, Sm, Eu, Pr	Nd / Gd
FLINAK	U / Th U / Nd, Gd, La, Sm, Eu, Pr, Sr Th / La, Pr, Sr, Zr, Eu	Th / Nd, Gd Nd / Gd U / Zr
LiF-CaF_2	U / Th U / Nd, Gd, Sm, Eu, Pr Th / Nd, Gd, Sm, Eu, Pr U,Th / Nd, Gd, Sm, Eu, Pr	U / Nd Nd / Gd

MSR core design

There are two possibilities of the MSR reactor core design:

- One-fluid (single-fluid) system **– fissile and fertile materials are mixed together**

- Two-fluid (double-fluid) system **– with separate channels of fissile and fertile fuel components**

One-fluid system:

- **Significantly simple construction – relatively low breeding factor (~1.04)**

Two-fluid system:

- **Complicated reactor core design – excellent breeding factor (~1.1 – 1.13)**

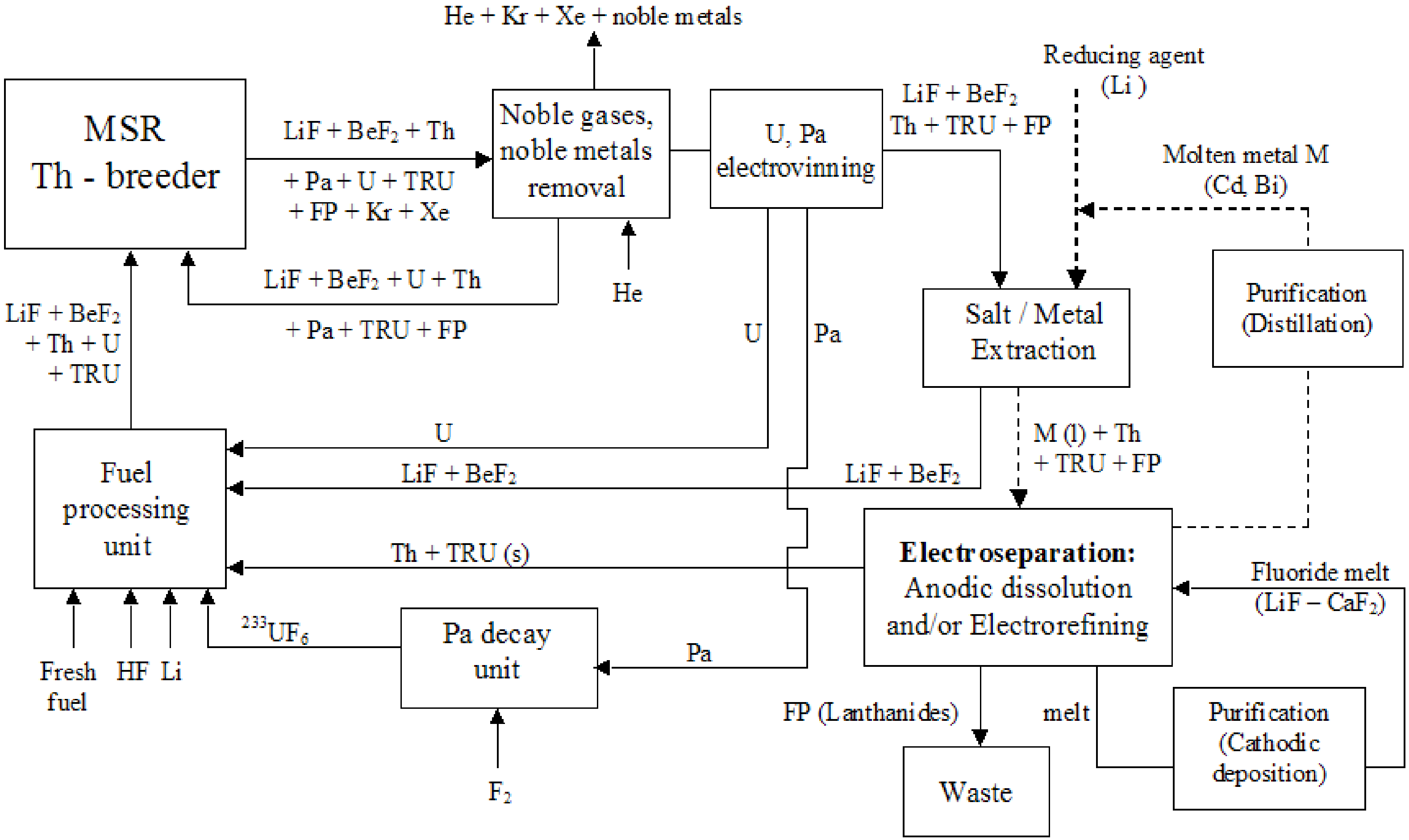
One-fluid MSR on-line reprocessing design

- **To extract neutron poisons represented namely by fission products**
- **To separate freshly breeded fissile material ^{233}U or its precursor ^{233}Pa.**

As the fissile and fertile materials are present together in the single primary (fuel) circuit, the reprocessing technology must be able to separate all fuel and fission products components dissolved in the carrier salt.

Conceptual flow-sheet of MSR on-line reprocessing technology

One-fluid system



Two-fluid MSR on-line reprocessing design

Fissile fluid circuit:

- **To extract neutron poisons represented namely by fission products**

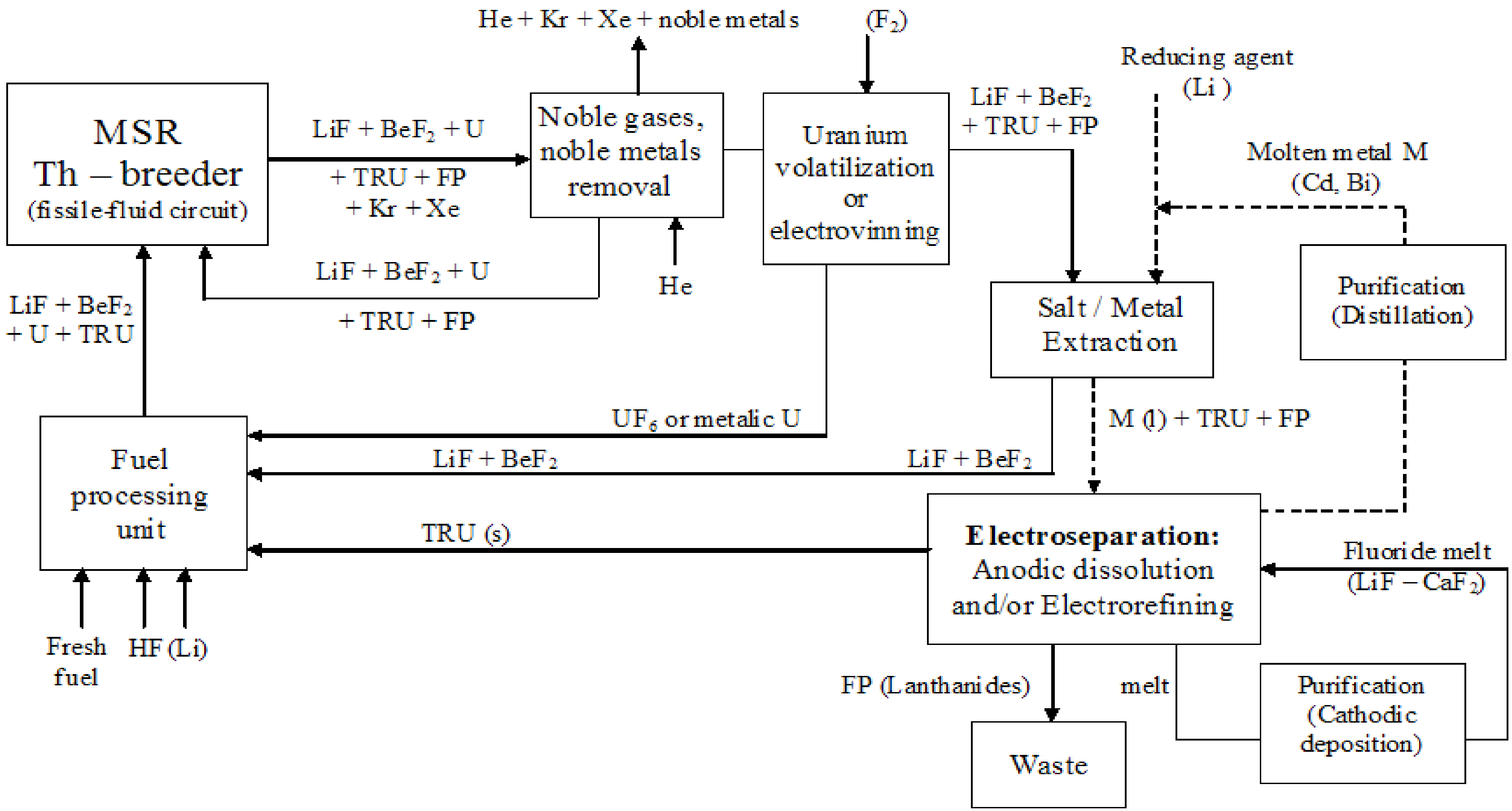
Fertile fluid circuit:

- **To separate freshly breeded fissile material ^{233}U or its precursor ^{233}Pa.**

As the partitioning technology used for the reprocessing of fissile-fluid circuit could be similar to those proposed for the one-fluid system (evidently without the Pa and Th separation), the partitioning of the fertile fluid circuit could be significantly simplified.

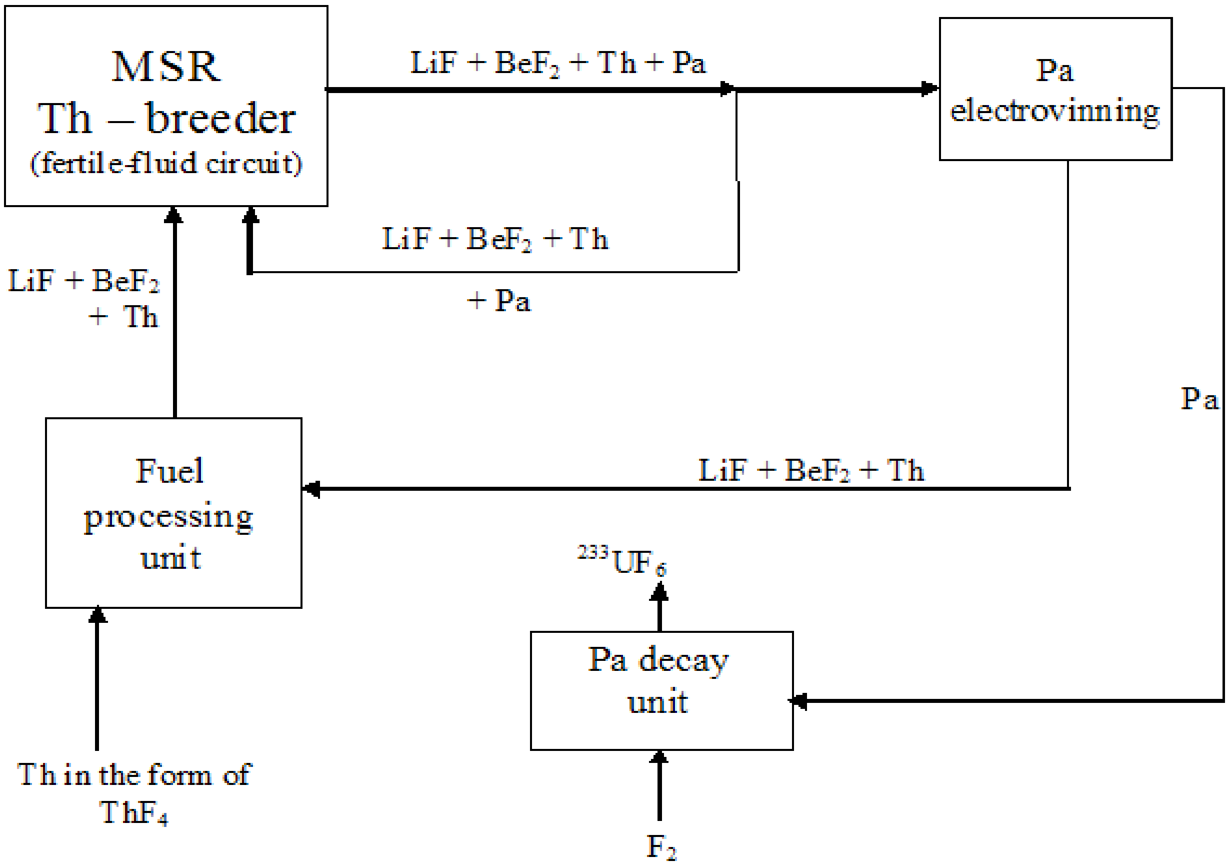
Conceptual flow-sheet of MSR on-line reprocessing technology

Two-fluid system, fissile fluid circuit



Conceptual flow-sheet of MSR on-line reprocessing technology

Two-fluid system, fertile fluid circuit



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Mutual link between reactor physics and chemical technology of on-line reprocessing

The mutual link between MSR physics and the on-line reprocessing is extremely strong.

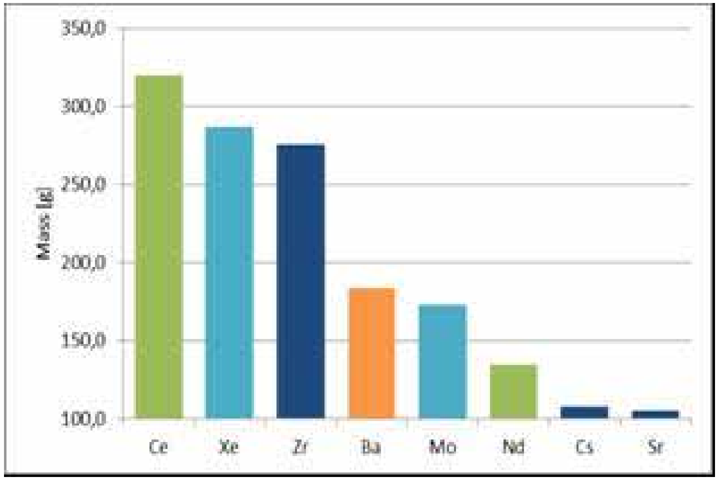
Instantaneous fissile power affects the capacity of on-line reprocessing; the rate of reprocessing has the retroactive effect on the quantity and concentration of fissile material. The rate of protactinium removal affects the breeding factor of the reactor system.

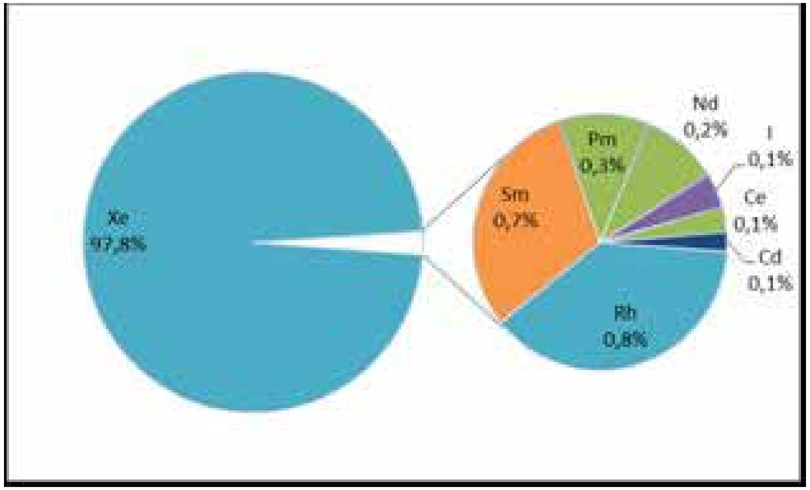
Another interconnection between chemistry and reactor physics is based on the fact that fission reaction is oxidative process, which must be chemically compensated to keep reductive conditions in the fuel circuit to minimize corrosion of structural material (nickel alloys).

If we wish is to maximize the breeding of ^{233}U, then our task is not only to extract protactinium as soon as possible, but also to identify the main neutron poisons among fission products in fuel circuit. It can be done on the basis of their production rates and neutron capture cross section.

The knowledge of these data can finally determine the technology of chemical partitioning and the details of the conceptual reprocessing flow-sheet.

Computation made by Monte Carlo code MCNPX v 2.7 with ENDF/B VII library (two-fluid MSR core configuration)

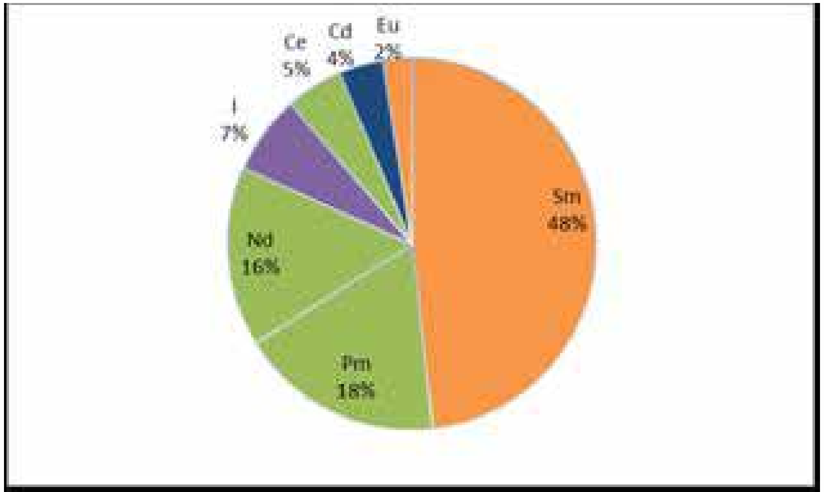




Figures: Mass production of main fission products originated from fresh fuel after one-day reactor operation

Distribution of fission products capture rate leaving the MSR core

Distribution of fission products capture rate entering the reprocessing unit



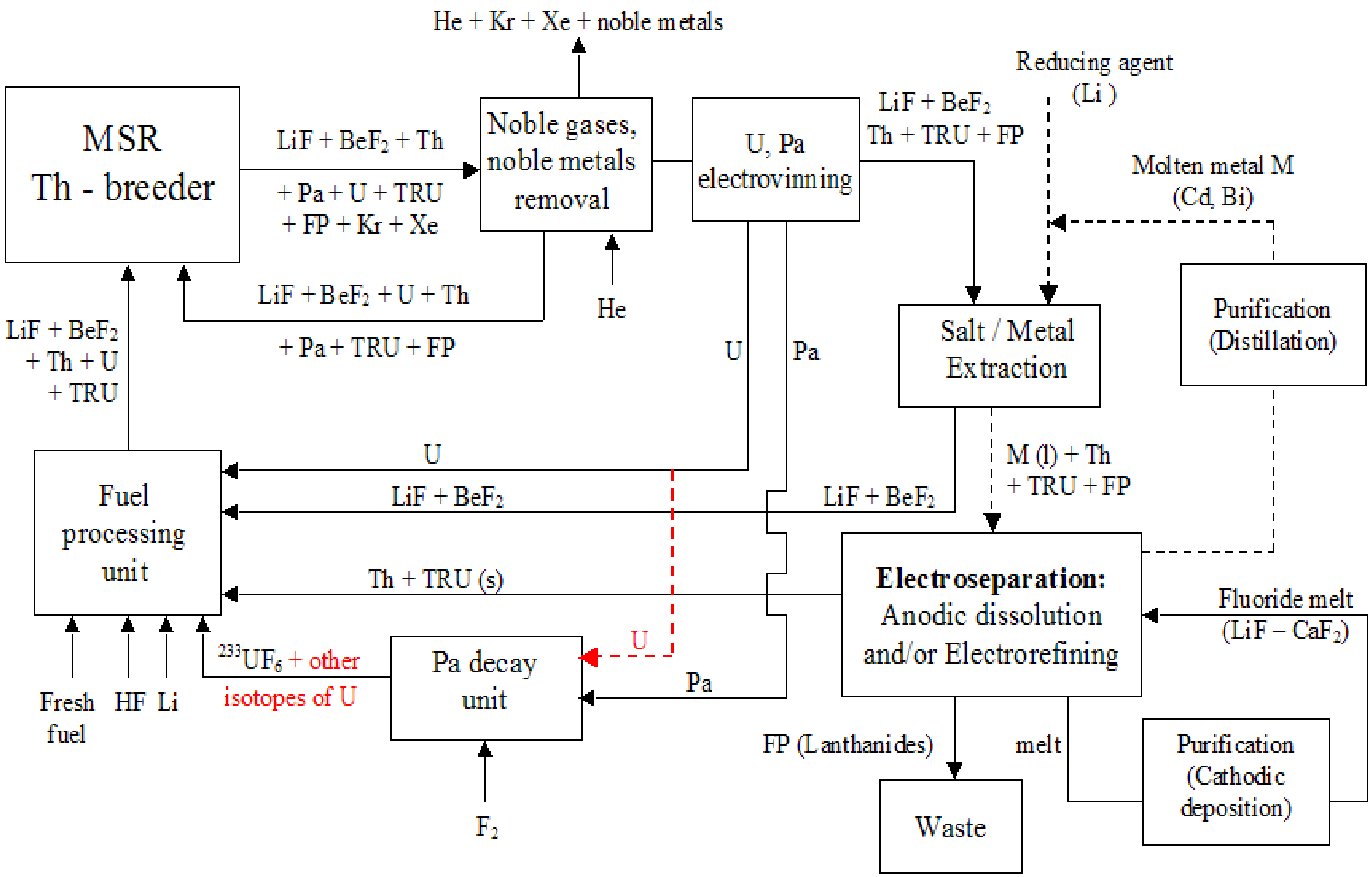
Study made by Evžen Losa and Milan Štika

Non-proliferation issues, physical protection

- q Special attention must be paid to uranium and protactinium management including the protactinium extraction technology. To ensure the highest breeding ratio, Pa removal has to be as fast as possible.
- q There are two possibilities how to increase a proliferation resistance and/or physical protection
  1. Denaturation by adding of ^{238}U into the fuel circuit Þ a very problematic way, which destroys all benefits of Th –U fuel cycle
  2. Denaturation by mixing of extracted Pa with uranium from the fuel circuit Þ a prospective way, which increases the radioactivity of uranium fuel due to mixing of ^{233}U with ^{234}U and especially with ^{232}U producing highly radioactive decay products.
- q MSR fuel technology is extremely difficult to master, most steps of the process have to be realized in hot cells, all final technology has to be placed in the reactor site, ^{233}U can be denatured.

Conceptual flow-sheet of MSR on-line reprocessing technology with increased PRPP

One-fluid system



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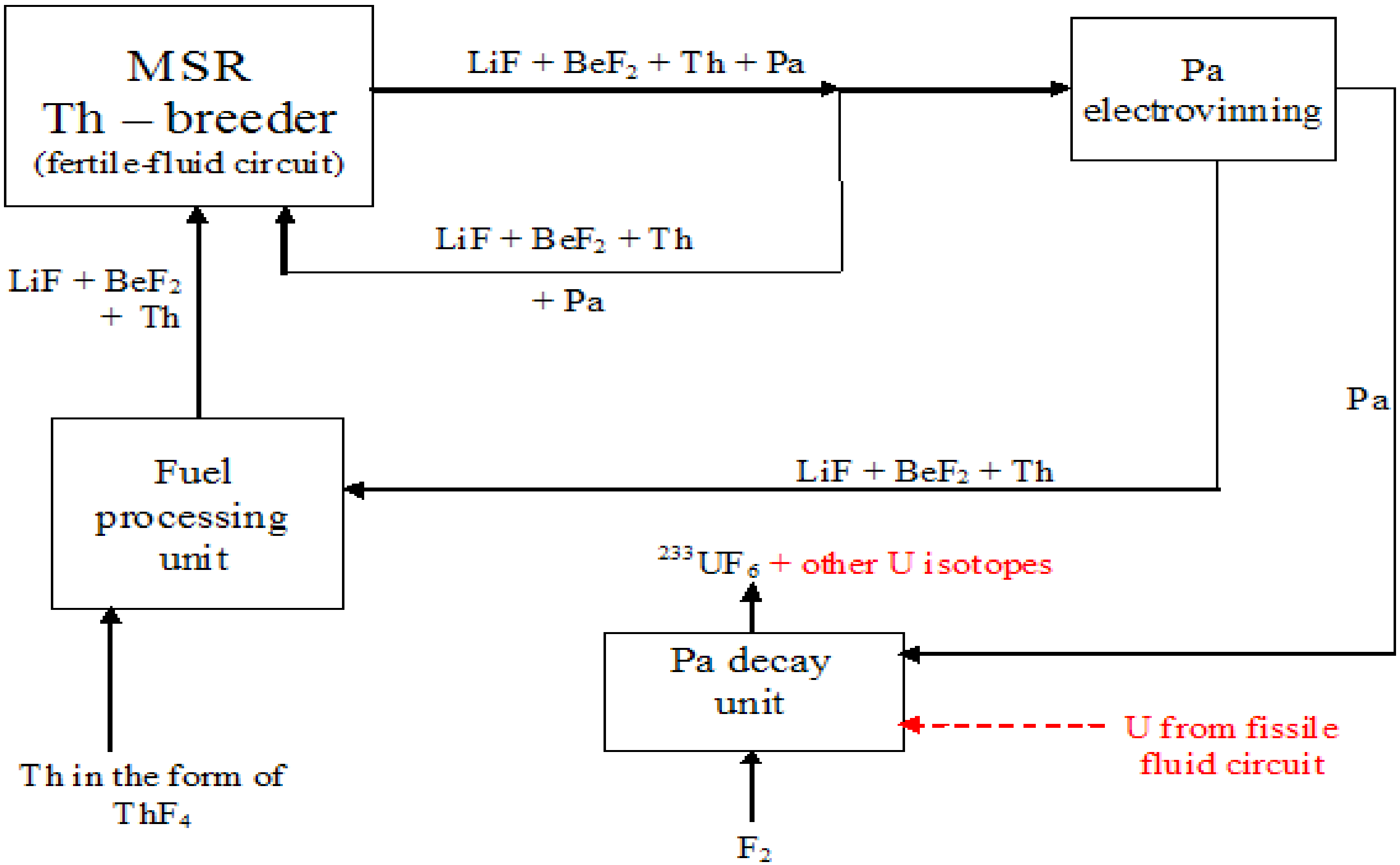
Conceptual flow-sheet of MSR on-line reprocessing technology with increased PRPP

Double-fluid system, fertile fluid circuit

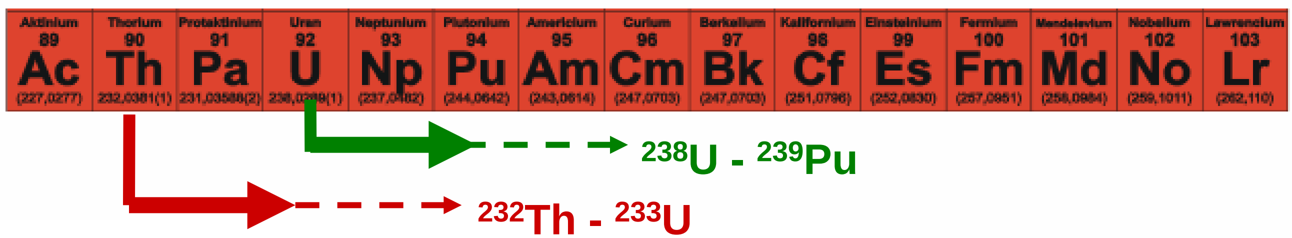


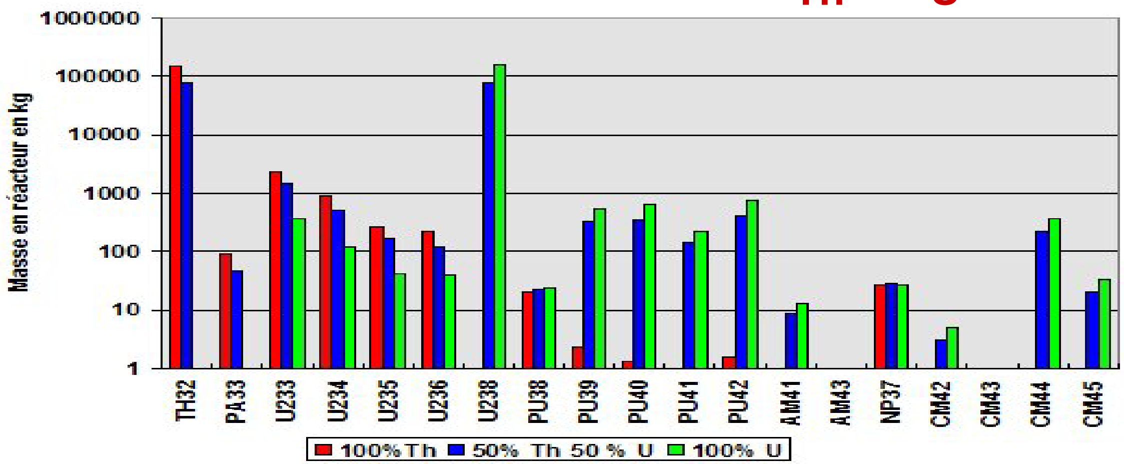
Conclusions

There are two main benefits in using thorium as the MSR fuel:

- Minimizing of long-lived radioactive waste
  - There is practically no production of higher actinides within the Th – U cycle
- Sustainable development of nuclear power
  - MSR is the reactor type, where the Th-breeding factor can be positive (about 1.04 in “one-fluid system” and more than 1.1 in “two-fluid system” with separated U and Th circuits)

Actinides:





Courtesy of
Dr. David Lecarpentier, EDF

Thank you for your attention

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