Development of Fluoride Volatility Reprocessing Technology

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Fluoride pyrochemical partitioning

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Czech activities in development of pyrochemical partitioning technologies are devoted to reprocessing of selected advanced fuel types of GEN-IV reactor systems. They 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.

Principles of reprocessing by Fluoride Volatility Method

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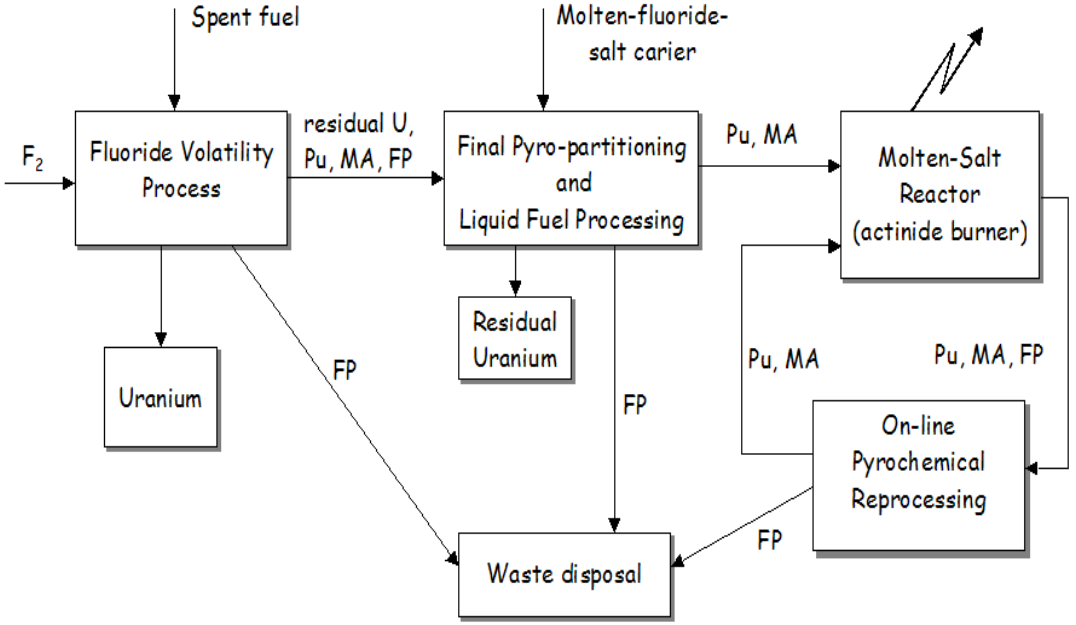
The technology is based on direct fluorination of spent fuel by fluorine gas.

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.**



Main steps of FVM – Fluorination reactions

uranium:

$UO_2\,(s) + 3F_2\,(g) \rightarrow UF_6\,(g) + O_2\,(g)$

$U_3O_8\,(s) + 9F_2\,(g) \rightarrow 3UF_6\,(g) + 4O_2\,(g)$

plutonium:

$PuO_2\,(s) + 2F_2\,(g) \rightarrow PuF_4\,(s) + O_2\,(g)$

$PuO_2\,(s) + 3F_2\,(g) \rightarrow PuF_6\,(g) + O_2\,(g)$

$PuF_4\,(s) + F_2\,(g) \leftrightarrow PuF_6\,(g)$

lanthanides:

$2Ln_2O_3\,(s) + 6F_2\,(g) \rightarrow 4LnF_3\,(s) + 3O_2\,(g)$

minor actinides:

$NpO_2\,(s) + 3F_2\,(g) \rightarrow NpF_6\,(g) + O_2\,(g)$

$NpO_2\,(s) + 2F_2\,(g) \rightarrow NpF_4\,(s) + O_2\,(g)$

$NpF_4\,(s) + F_2\,(g) \leftrightarrow NpF_6\,(g)$

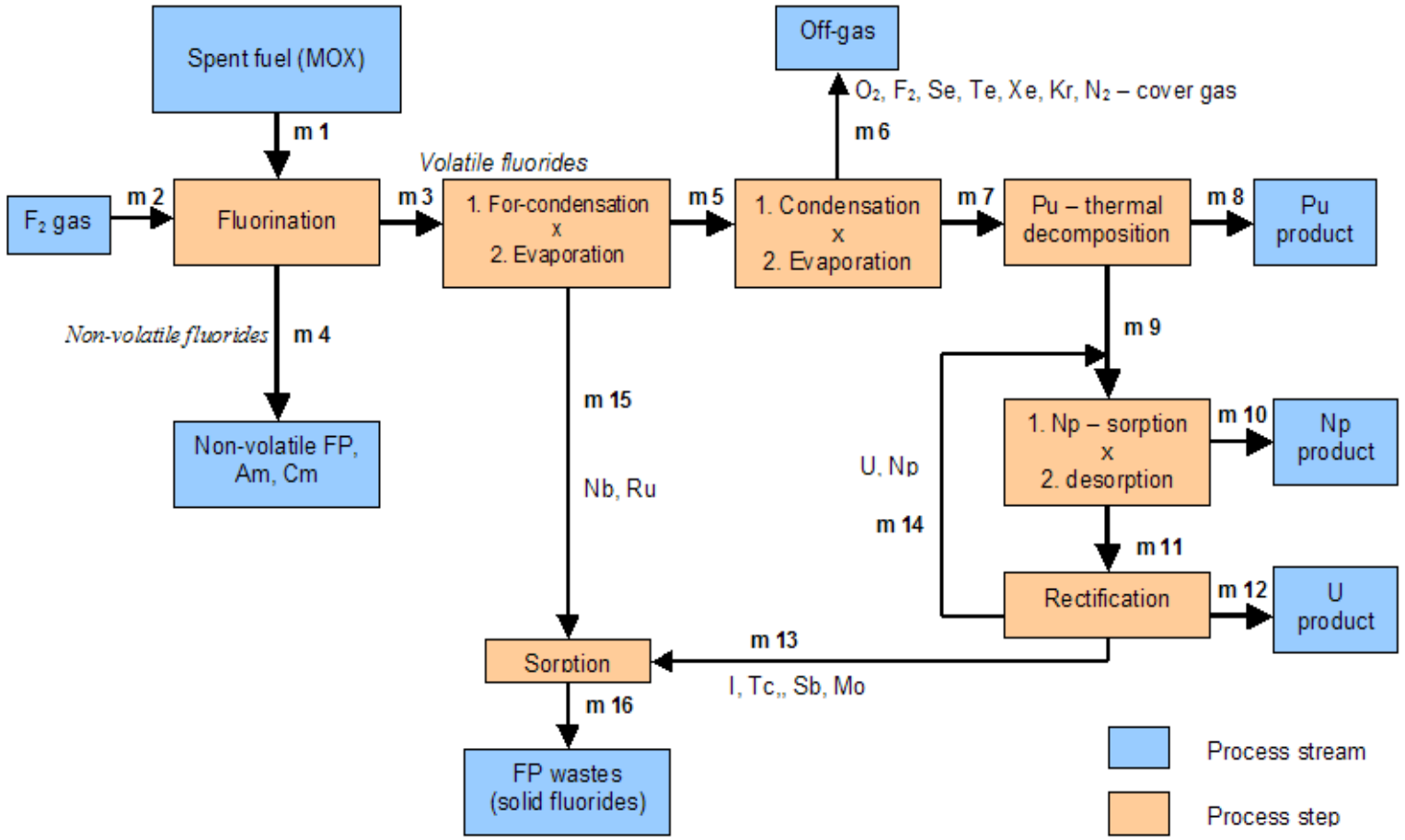
$2Am_2O_3\,(s) + 6F_2\,(g) \rightarrow 4AmF_3\,(s) + 3O_2\,(g)$

$2Cm_2O_3\,(s) + 6F_2\,(g) \rightarrow 4CmF_3\,(s) + 3O_2\,(g)$

Presumed Selected Products of Spent Fuel Fluorination

Volatile fluorides	Non-volatile fluorides	
UF_6	**AmF_3**	LaF_3
NpF_6	**CmF_3**	YF_3
PuF_6	**PuF_4**	InF_3
MoF_6	CsF	PmF_3
TcF_6	SrF_2	SnF_4
SeF_6	ZrF_4	RbF
TeF_6	PrF_3	AgF
RuF_5	SmF_3	BaF_2
NbF_5	EuF_3	ZnF_2
IF_5	GdF_3	NdF_3

Process flow-sheet of Fluoride Volatility Method



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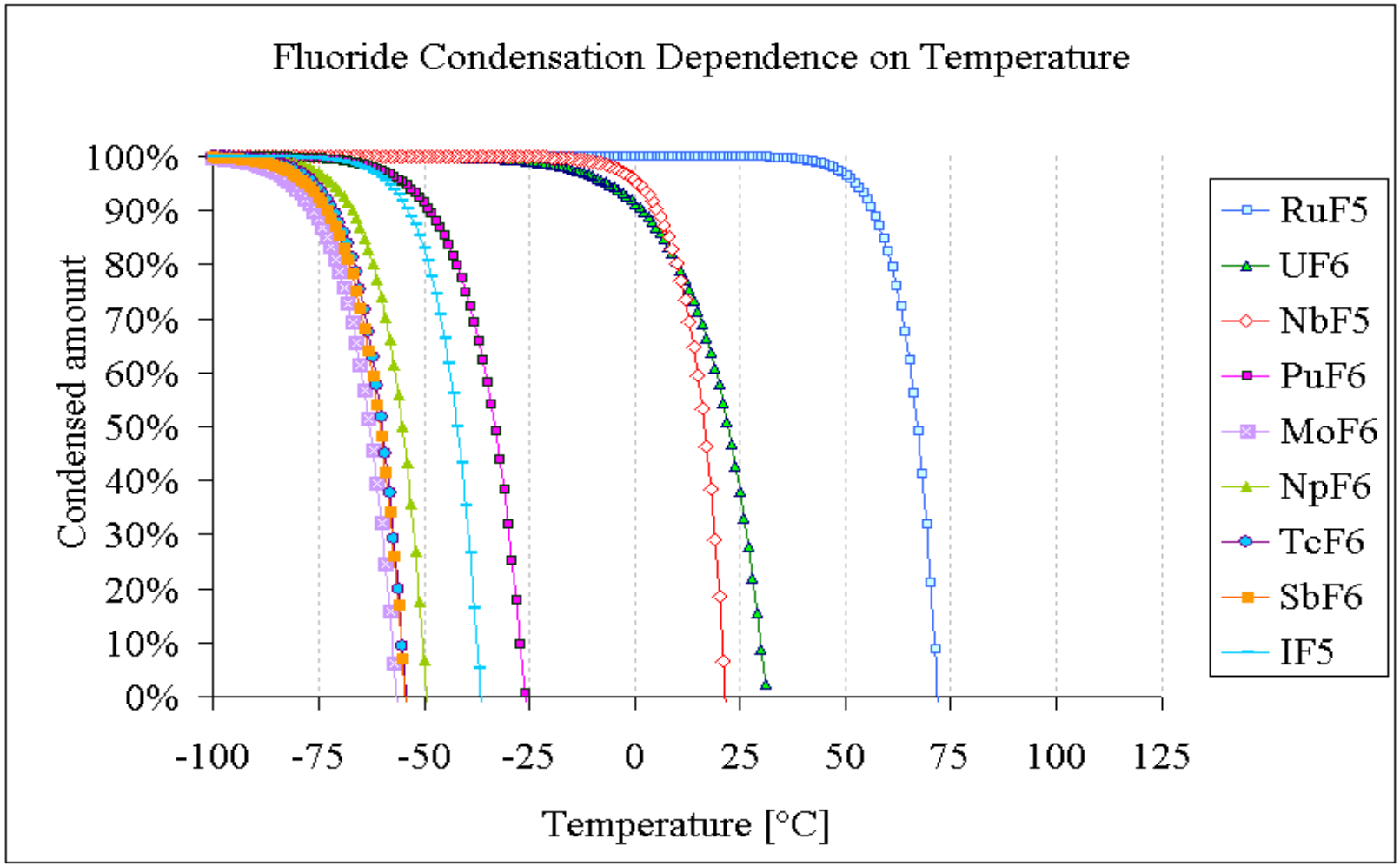
Calculation of volatile fluorides condensation

LWR (VVER) spent fuel, 200% surplus of fluorine gas at fluorination



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Achieved separation efficiencies of selected spent fuel components by using Fluoride Volatility Method

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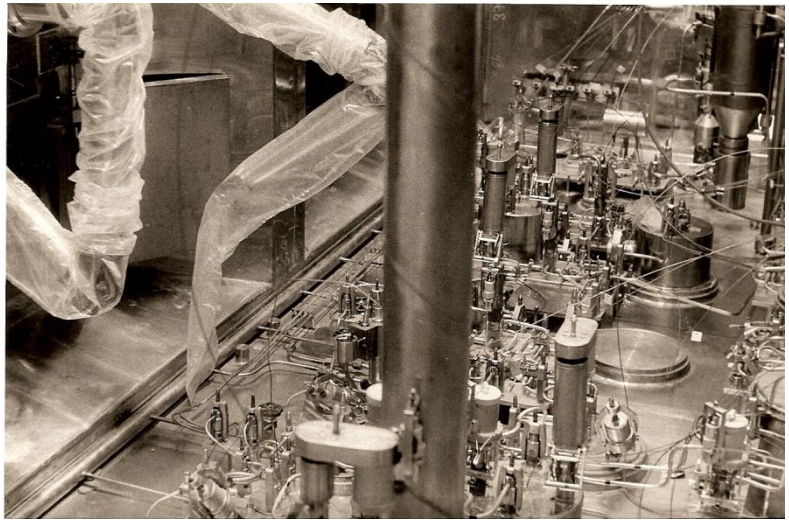
Chemical elements	Separation efficiency (%)
U	95 – 99.5
Pu	~98 – 99.5
Np	~60 – 70
Nb, Ru	~95 - 99
Am, Cm	Individually inseparable (in non-volatile fluoride stream)
FP forming solid fluorides	Individually inseparable (in non-volatile fluoride stream)

* ***The fluorination process can be controlled in that mode of operation to convert all plutonium only to solid PuF_4 and steer it to non-volatile fluoride stream. Then the separation efficiency of uranium reaches max. 95 %.***

History of FVM development

- 1950s – 1960s: US - Oak Ridge National Laboratory – *MSR program*
- 1970s: Russia (USSR) - NIIAR (RIAR) – *FREGAT experimental line*
- 1970/80s: France – CEA Fontenay-aux-Roses – *Attila facility*
- 1980s: Russia (USSR) in cooperation with Czechoslovakia – NIIAR – *FREGAT-2 technological line*

- 2005 – 2008: Japan – Hitachi – *FLUOREX process*
- 2000 – nowadays: Czech Republic – NRI Řež: *FERDA technology*



Present R&D:
Experimental technological line FERDA in NRI Řež plc

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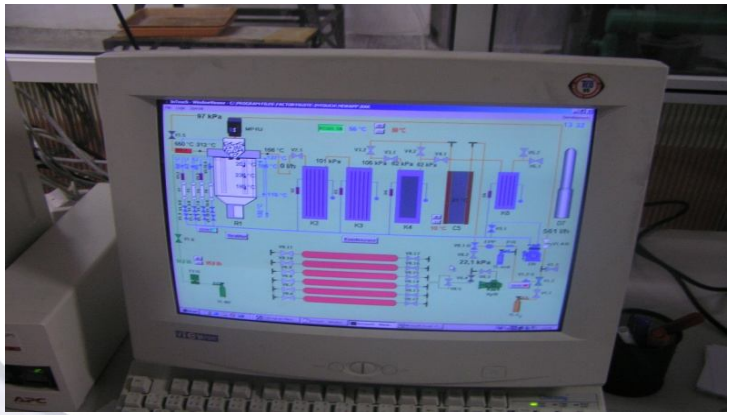
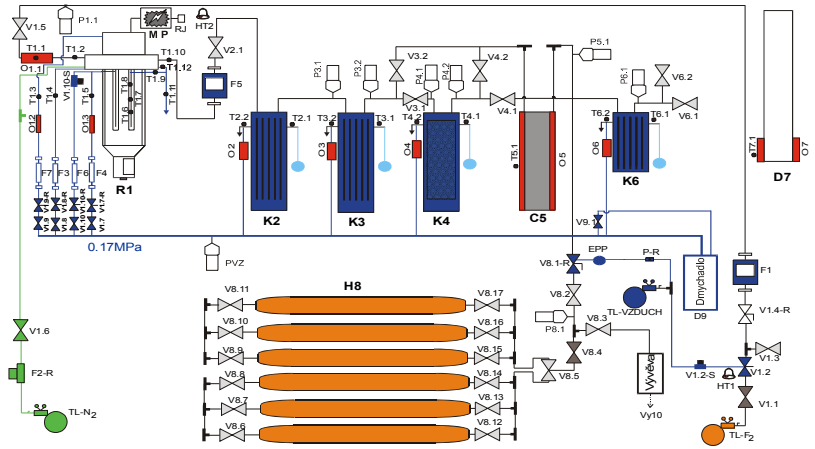
Experimental Technological Line FERDA in the NRI Řež plc





Flame Fluorination Reactor of the FERDA line

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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

Current status – future plans

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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 remote control and decontamination processes
- **Verification with irradiated fuel**
  - Hot cell construction is planned

Prospects of Fluoride Volatility Method

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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.

Thank you for your attention

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