Aqueous and Pyrochemical reprocessing of thorium fuel

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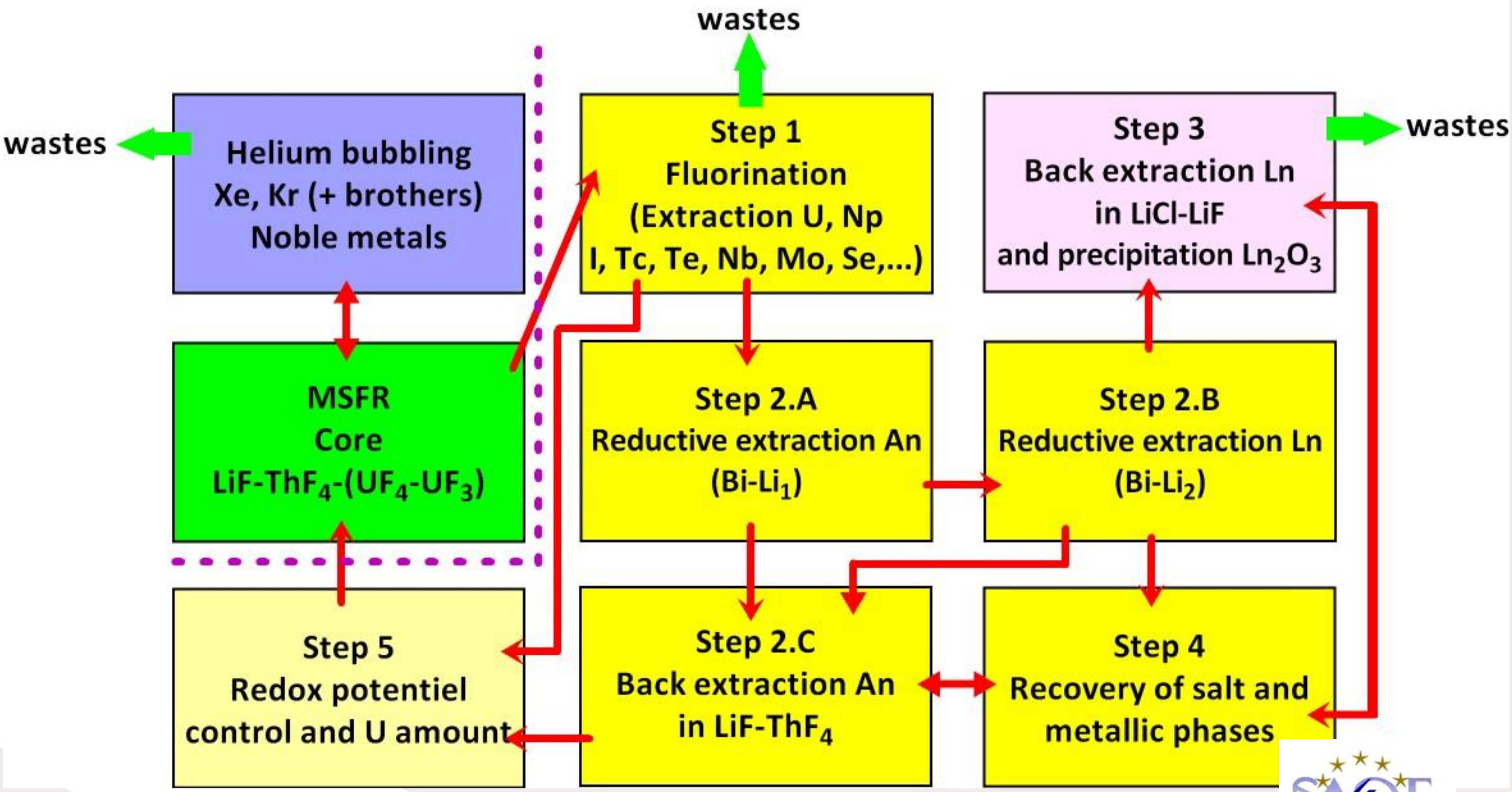
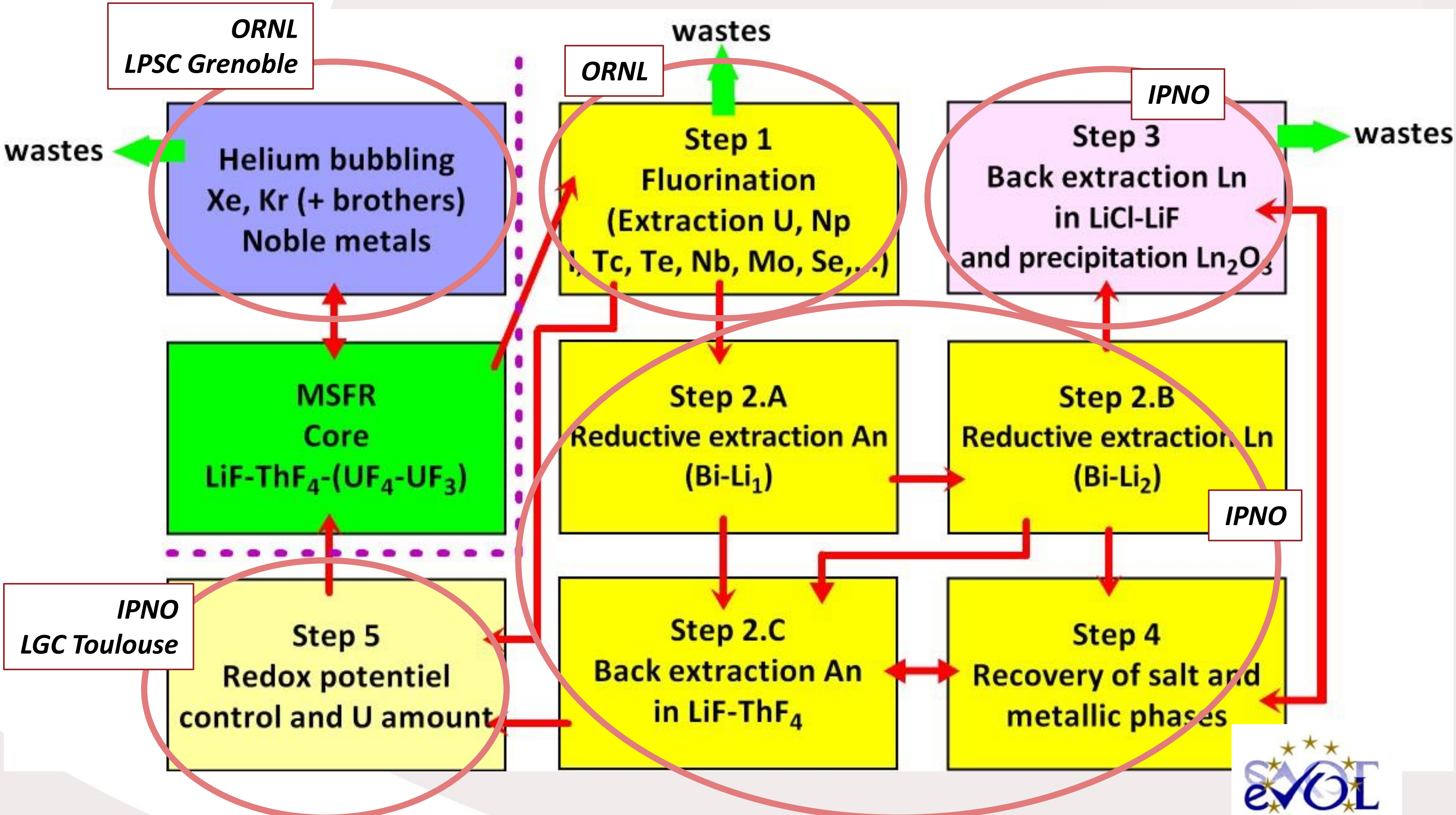
Thorium fuel reprocessing

THORIUM FUEL	
Liquid fuel (molten salt reactor) **ThF_4**	**Solid fuel** **ThO_2**
Recovery of fissile material (^{233}U) **for sustainable energy**	
Separation FPs/MA to decrease waste toxicity	
Gaseous FP extraction **Redox potential control** **Control of fertile/fissile ratio**	
Pyrochemical treatment	**Aqueous treatment**

Pyrochemical reprocessing : case of molten salt reactor



Pyrochemical reprocessing : case of molten salt reactor



	Extraction process	Comments	State
The state of the elements depends on the redox conditions of the fuel salt. The redox conditions are given by the ratio U(IV)/U(III) which varies from 100 to 10. Therefore the redox potential of the salt is ranging between -3.0V and -3.3V.			
Es	RE1		
Cf	RE1		
Bk	RE1		
Cm	RE2		CmF_3
Am	RE1		AmF_3
Pu	RE1		PuF_3
Np	RE1		NpF_3
U	FLUO		UF_4/UF_3
Pa	STOP + FLUO		PaF_4
Th	CORE		ThF_4
Ac	RE1		AcF_3
Ra	RE1		RaF_2
Bi	FLUO	Bi produced at metallic and liquid state. Can form BiF_3 gas under fluoration. Can also form BiNi alloys with structural materials	Bi
Pb	FLUO	Pb produced at metallic and liquid state.	Pb
Er	RE2		ErF_3
Ho	RE2		HoF_3
Dy	RE2		DyF_3
Tb	RE2		TbF_3
Gd	RE2		GdF_3
Eu	RE2		EuF_3

Pyrochemical reprocessing : Results obtained in the frame of EVOL project

Sm	RE2	SmF_2 can be also stable (depends on redox conditions)	SmF_3
Pm	RE2	No data	PmF_3 ?
Nd	RE2		NdF_3
Pr	RE2		PrF_3
Ce	RE2	Can also be oxidized to CeF_4 gas by fluorination	CeF_3
La	RE2		LaF_3
Ba	CORE		BaF_2
Cs	CORE		CsF
I	FLUO		I
Sb	FLUO	Sb produced at metallic and liquid state. Can form SbF_5 gas by fluorination. Formation of NiSb alloys possible.	Sb
Sn	FLUO	Sn produced at metallic and liquid state. Can form SnF_4(g) gas by fluorination at 800°C. Formation of Ni_3Sn, Ni_3Sn_2 and Ni_3Sn_4 alloys possible.	Sn
In		E=-3,36: RE seems possible but activity coefficients of In in Bi required to conclude	InF_3
Cd	He	E=-2.87V. Cd is produced at metallic and liquid or gaseaous state (T_{vap}=765°C). So extraction by He bubbling.	Cd
Zr	He	E=-4.2V. ZrF_4 is gaseous at 912°C. Can be extracted with He and F_2(g)	ZrF_4
Y	RE2	E=-5,13	YF_3
Sr		E=-5,45	SrF_2
Rb		E=-4,77	RbF
Br	FLUO		Br(-)
Ge	He	Ge produced at metallic state. Can produce GeF_2 gas by fluorination. Ni_2Ge alloys possible	Ge
Ga	FLUO	Ga produced at metallic and liquid state. All Ga fluoride are gaseous. No data about Ni-Ga alloys	Ga

Pyrochemical reprocessing : Results obtained in the frame of EVOL project

Cu	He	CuF_2 after oxydation by $F_2(g)$. CuF_2 logK=-2,5 at 800°C for $CuF_2(g)$. RE possible	Cu
Ni	He	NiF_2 by fluorination. Not gaseous. RE possible	Ni
Co	He	E = -2.83V. CoF_3 by fluorination. Gas at 900°C. RE possible	Co
Fe	He	E=-3.07V. Extraction possible by He bubbling depending on redox conditions. RE seems possible depending on activity coefficients of Fe in Bi and solubilities in Bi.	Fe/FeF_2
Mn		Formation of MnF_3 under fluorination but MnF_3 is not a gas. Reduction of MnF_2 to Mn in Bi pool possible by RE1 and RE2. Efficiency calculation required activity coefficients of Mn in Bi	Mn et MnF_2
Cr		idem Mn	
V			
Ti			
Sc	RE1 ?	E = -4,86. RE possible. Requirement of activity coefficients in liquid Bi.	ScF_3
Ca	CORE		CaF_2
K	CORE		KF
Cl	FLUO		$Cl(^-)$
S	FLUO	Li_2S for E< -3,43V. All the fluoride sulfurs are gaseous. Formation of $SF_6(g)$ by fluorination.	S et $S(^{-2})$
F	CORE		$F(^-)$
O	FLUO	$O_2(g)$ by fluorination	$O(^{2-})$
B	He	$BF_3(g)$ in the redox conditions of the salt	$BF_3(g)$
Be	CORE		BeF_2
Li	CORE		LiF

Pyrochemical reprocessing : Conclusion

- Proposition of a complete reprocessing scheme

- Identification for each element of an appropriate extraction method

- Identification of missing data

    - *Experimental determination requirement*

    → *Efficiency determination*

- Development of experimental device to test all reprocessing steps

- ***THOREX Process***

    - Dissolution in nitric acid/HF/$Al(NO_3)_3$
    - Liquid-liquid (Co) Extraction Th/U by TBP 30%
    - Selective back-extraction of Th and U

- ***Interim 23 Process*** *(retained by India)*

    - Dissolution with nitric acid
    - Selective liquid-liquid extraction of U by TBP 5%
      (Thorium in the wastes)

Dissolution

- Dissolution time in boiling conditions > 30-40h
- Solution very corrosive
  - Use of special steels
  - Addition of Al
- Partial dissolution of oxide (residues = blue thorine)
- Partial dissolution of zircaloy clad
  - Impact ?

Liquid-liquid extraction

- Formation of 3rd phase (low solubility of Th-TBP in organic solvent)
- Formation of slag (Th-DBP complexes very stable in organic phase) (DBP produced by TBP radiolysis and hydrolysis)

Conclusion and perspectives

Dissolution

- Combine physical and chemical techniques (sonochemistry, electrochemistry)
- Impact of fuel fabrication techniques and microstructure
  - Addition of elements during the fabrication (MgO)

Extraction

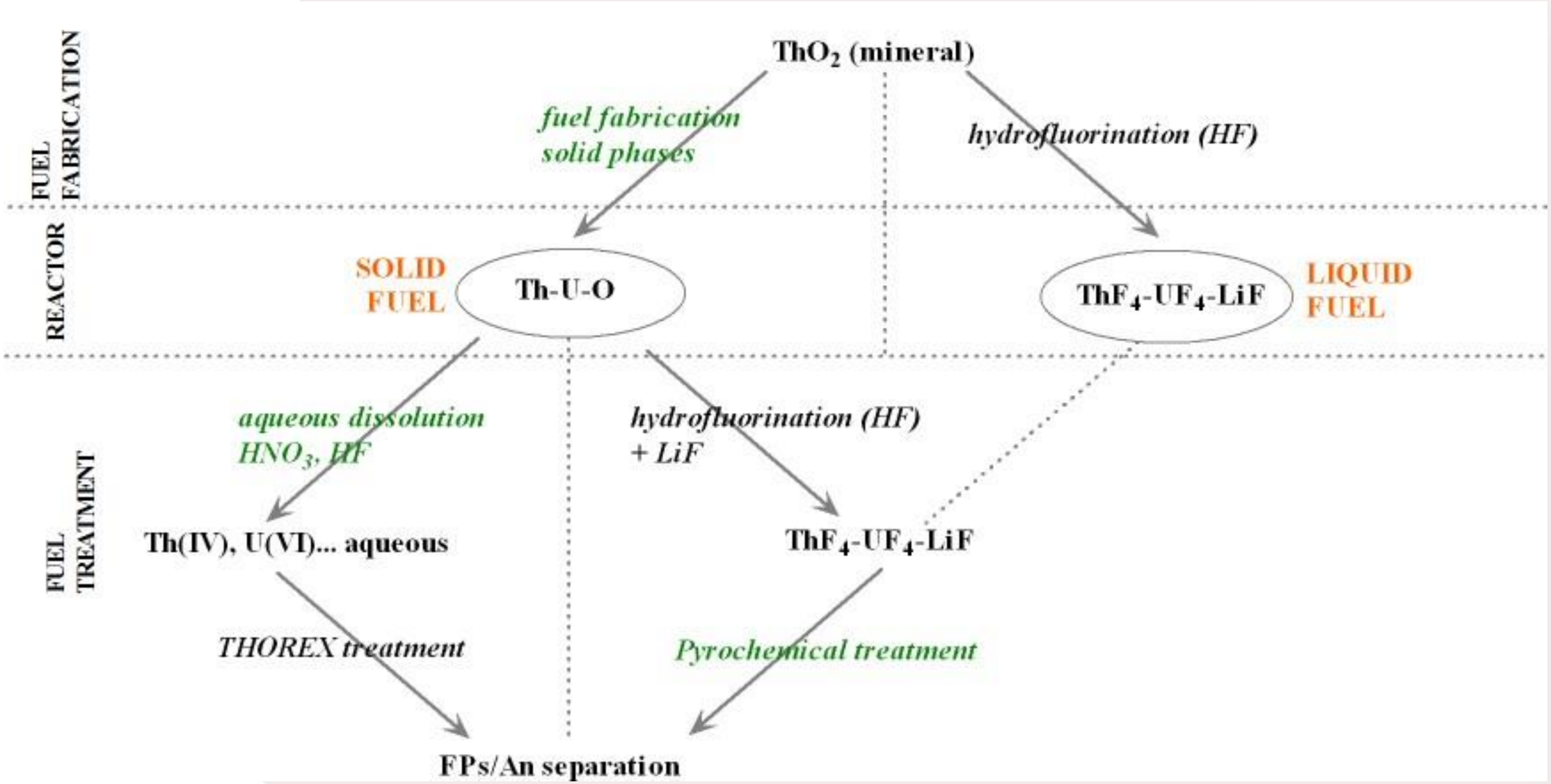
- Study of alternative extractive molecules (monoamide ?)

Alternative

- Pyrochemical treatment for solid oxide fuel ?

Valorize the knowledge on thorium chemistry in molten salt at high temperature.

Conclusion and perspectives



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Thanks for your attention….