Development of pyrochemical treatment process for used molten salt fast reactor fuels: novel process for removal and vitrification of fission products in molten salt

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Background and purpose

- As one of the promising systems for MA transmutation, the authors have been proposing a chloride MSFR since 2015.
- Reprocessing of the spent chloride fuel salt is required for increasing effectiveness of MA transmutation.
- There are very limited studies on fuel cycle process for chloride fuel salt.
- **A new reprocessing process composed of several pyrochemical steps based on the developed technology for metallic fuels reprocessing which meets the following requirements,**
  - **Technically feasible**
  - **Capable of ^{37}Cl recycling**
  - **Applicable to NaCl, NaCl-$CaCl_2$, etc.**

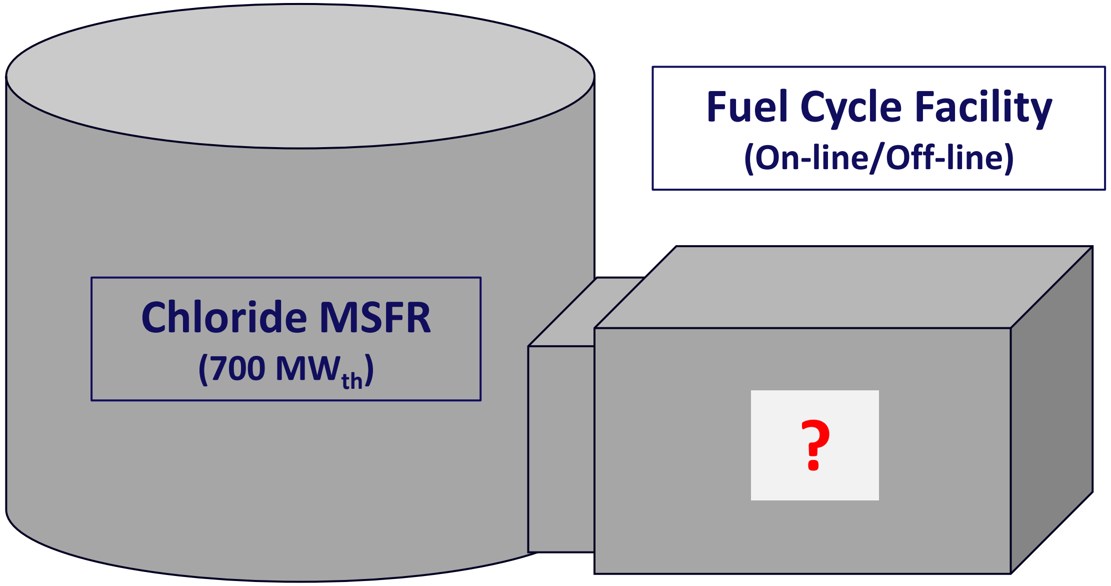
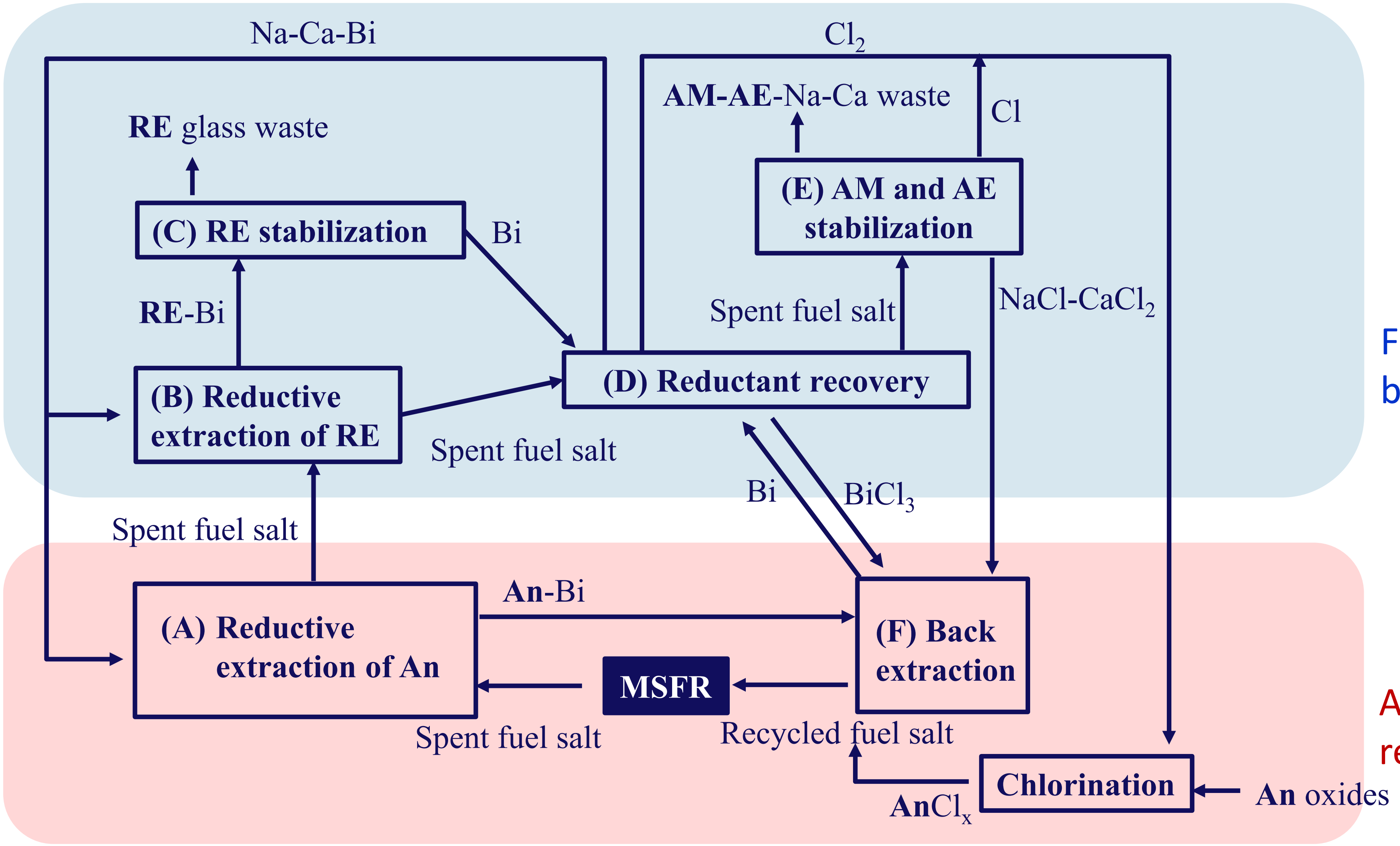


Image of Integrated Molten Salt Fast Reactor (IMSFR)

[ref] Mochizuki, H., Neutronics and thermal-hydraulics coupling analysis using the FLUENT code and RELAP5-3D code for a molten salt fast reactor, Nuclear Engineering and Design, 368, 110793 (2020).

Pyrochemical reprocessing of spent chloride fuel salt

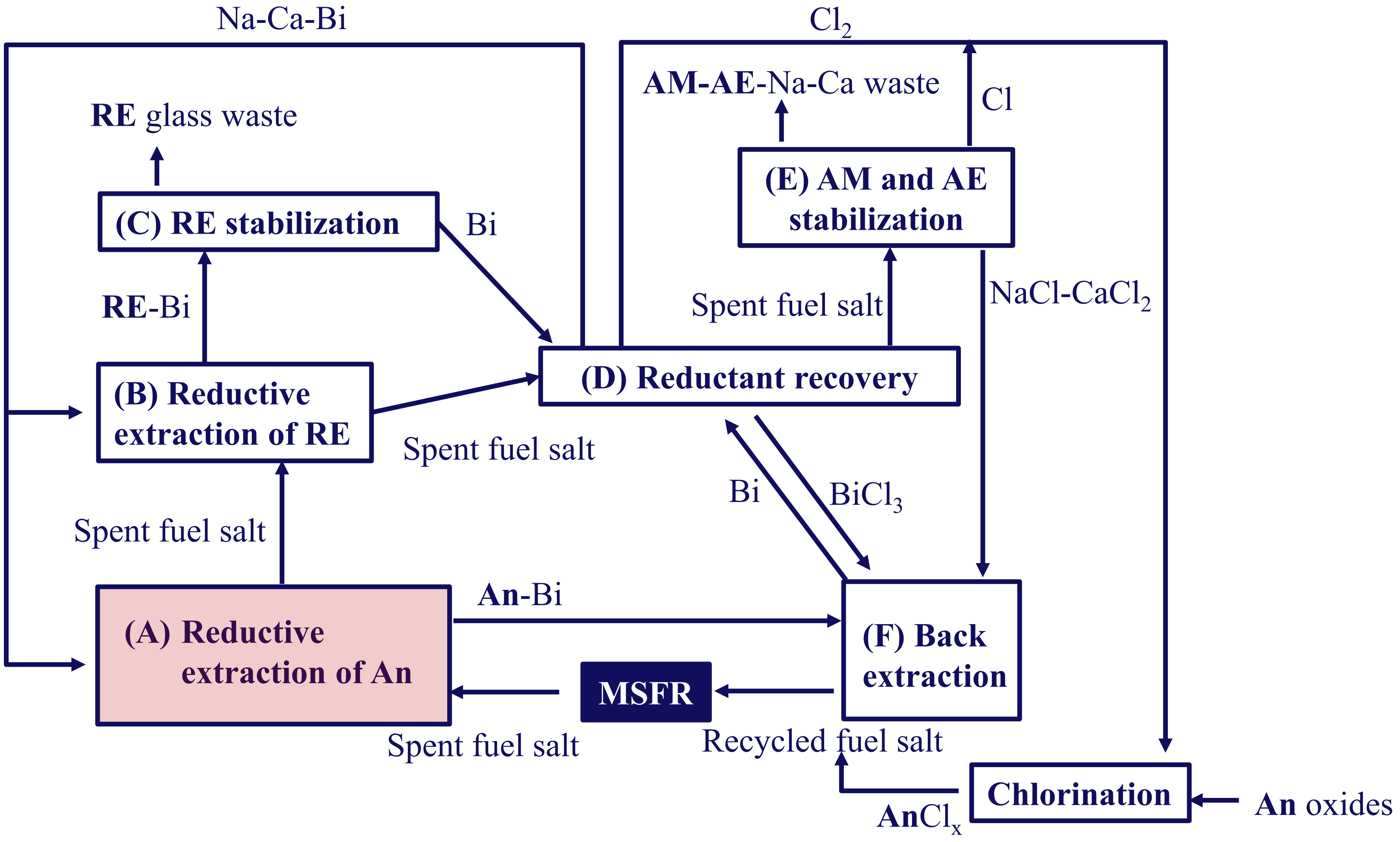


An: Actinides
RE: Rare earths
AE: Alkaline earths
AM: Alkalis Metal
MSFR: Molten Salt Fast Reactor

Fission products removal to be stabilized in a waste form

Actinides recovery to be recycled as new fuel salt

Pyrochemical reprocessing of spent chloride fuel salt



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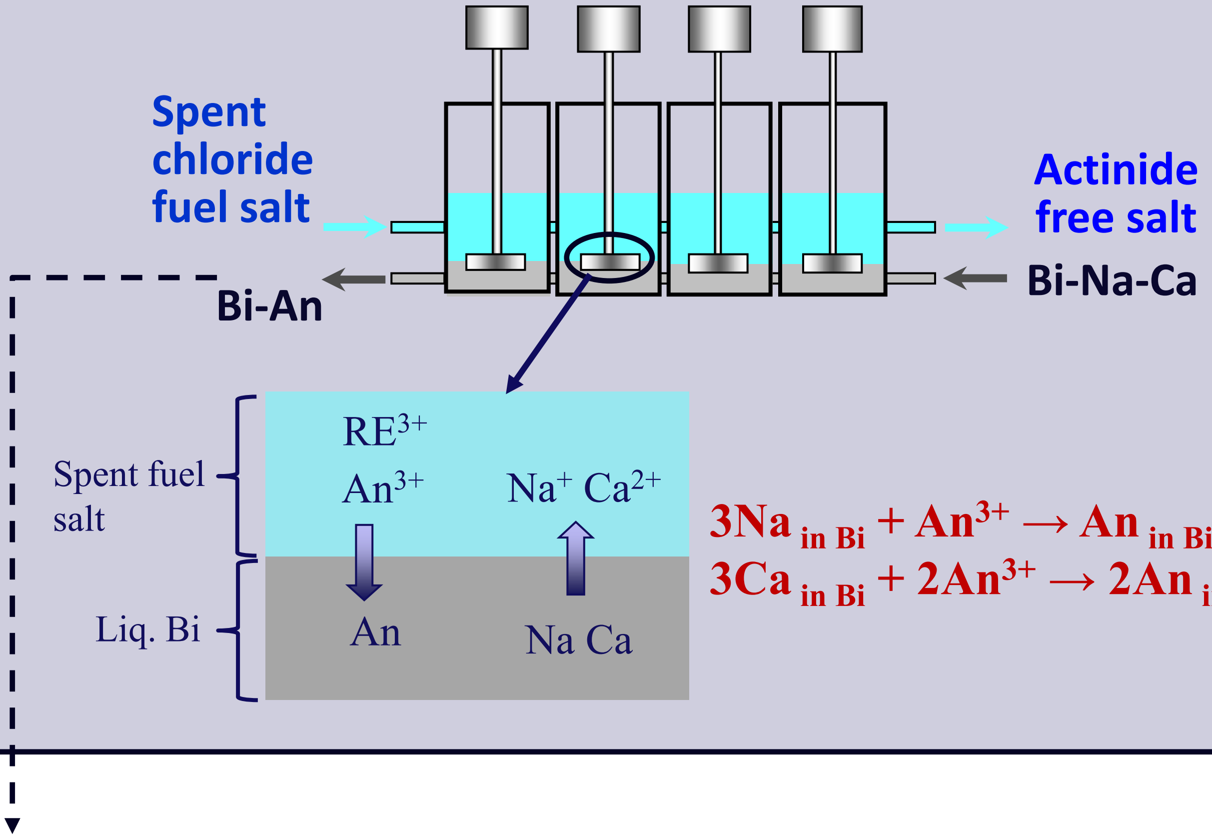
(A) Reductive extraction of actinides

Actinides recovery from the spent chloride fuel salt to be recycled as new fuel salt

Concept of reductive extraction

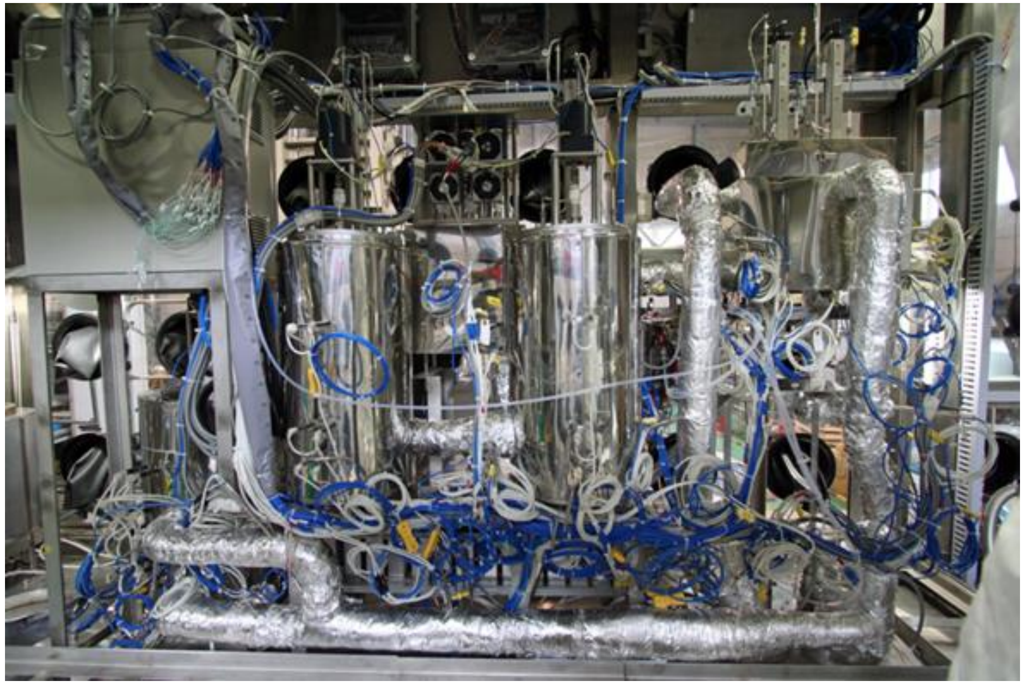


$$3Na_{\text{in Bi}} + An^{3+} \rightarrow An_{\text{in Bi}} + 3Na^{+}$$
$$3Ca_{\text{in Bi}} + 2An^{3+} \rightarrow 2An_{\text{in Bi}} + 3Ca^{2+}$$

An in liq. Bi are chlorinated at (F) Back extraction.

$$An_{\text{in Bi}} + Bi^{3+}_{\text{in NaCl-CaCl2}} \rightarrow \underline{An^{3+}_{\text{in NaCl-CaCl2}}} + Bi$$

Recycled as new fuel salt

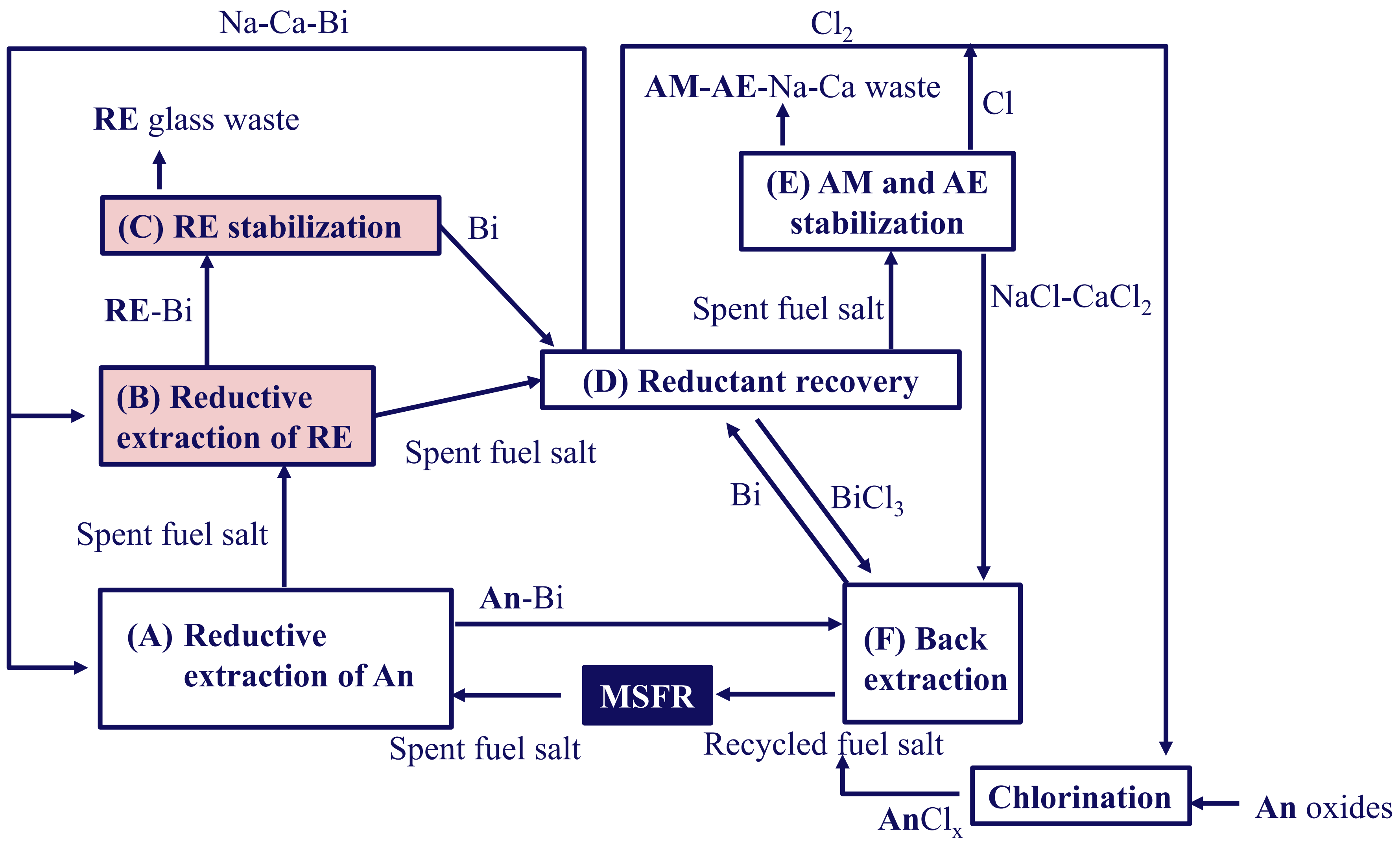


Photograph of the **industrial scale apparatus of reductive extraction for LiCl-KCl/liquid Cd system** in pyrochemical reprocessing of the spent metallic fuel.

Applicable to both (A) and (B) reductive extraction steps

[ref] T.Koyama and M. Iizuka, "Chapter 18: Pyrochemical fuel cycle technologies for processing spent nuclear fuels", p.457-520, R.Taylor edited, "Reprocessing and recycling of spent nuclear fuel", Woodhead Publishing, ISBN 978-78242-212-9 (2015).

Pyrochemical reprocessing of spent chloride fuel salt



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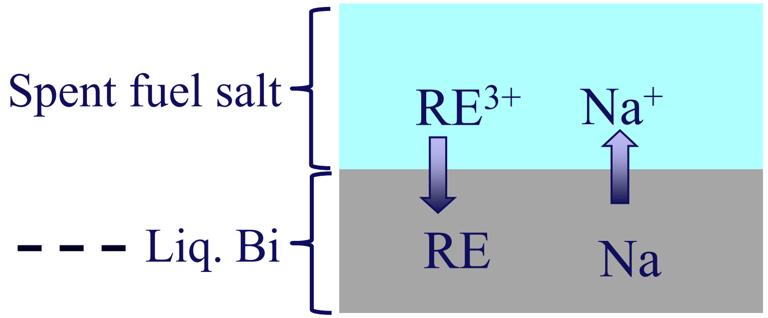
(B) Reductive extraction of RE and (C) RE stabilization

(B) Reductive extraction of RE

Bi-RE



$$3Na_{\text{in Bi}} + RE^{3+} \rightarrow RE_{\text{in Bi}} + 3Na^{+}$$

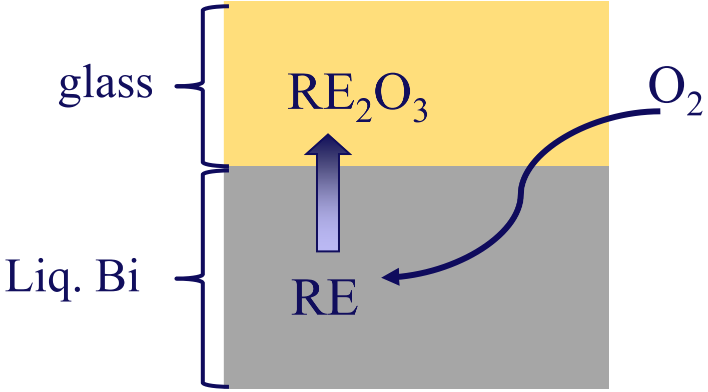
(C) Stabilization of the extracted RE

Selective oxidation of rare earths due to higher oxygen affinity of rare earths than Bi

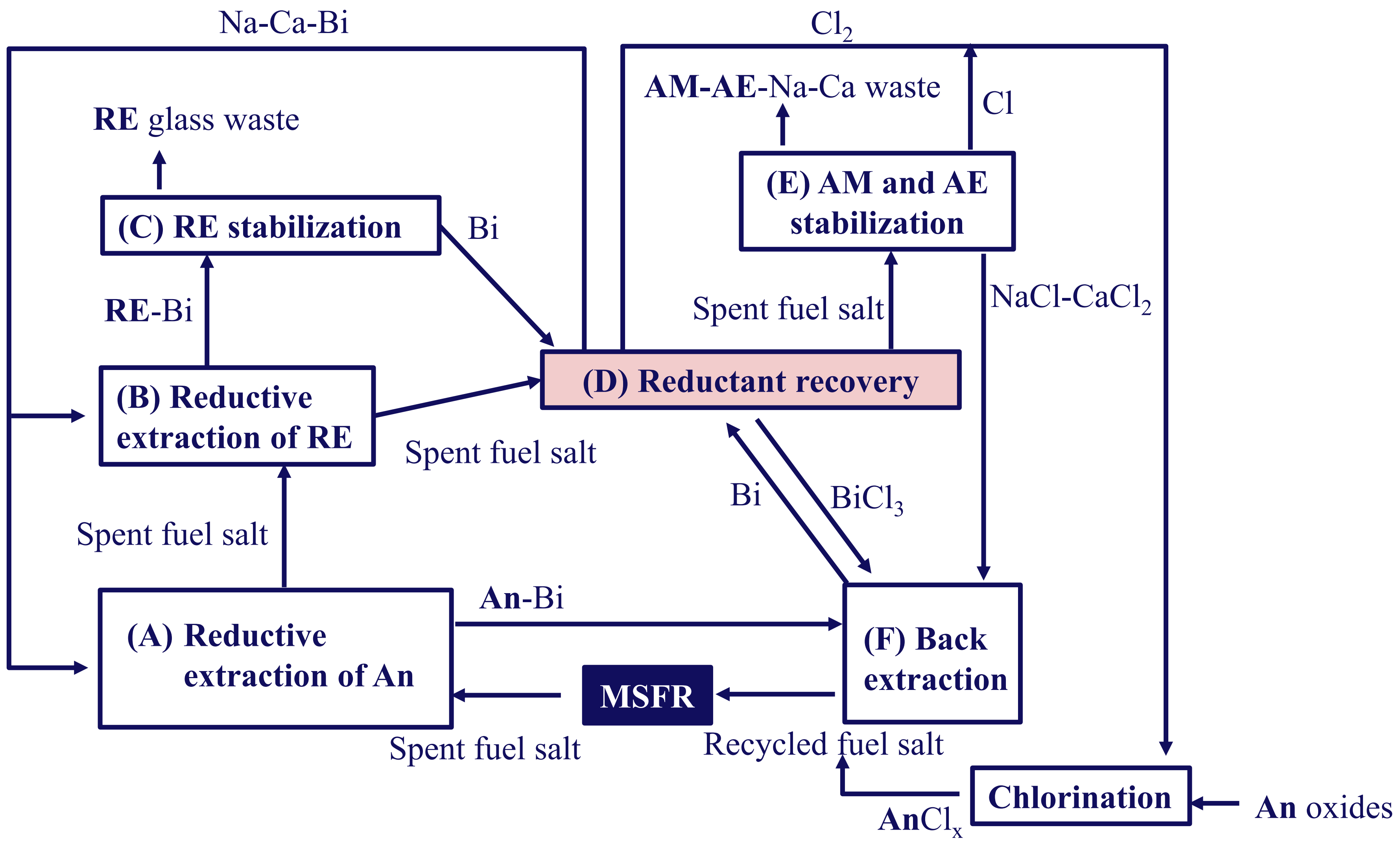
$$Bi_xRE + 3/2O_2 \rightarrow 1/2RE_2O_3 + xBi$$

Rare earths oxides stabilization in a glass matrix

$$RE_2O_3 \xrightarrow{+\text{ glass}} RE_{\text{in glass matrix}}$$



Pyrochemical reprocessing of spent chloride fuel salt



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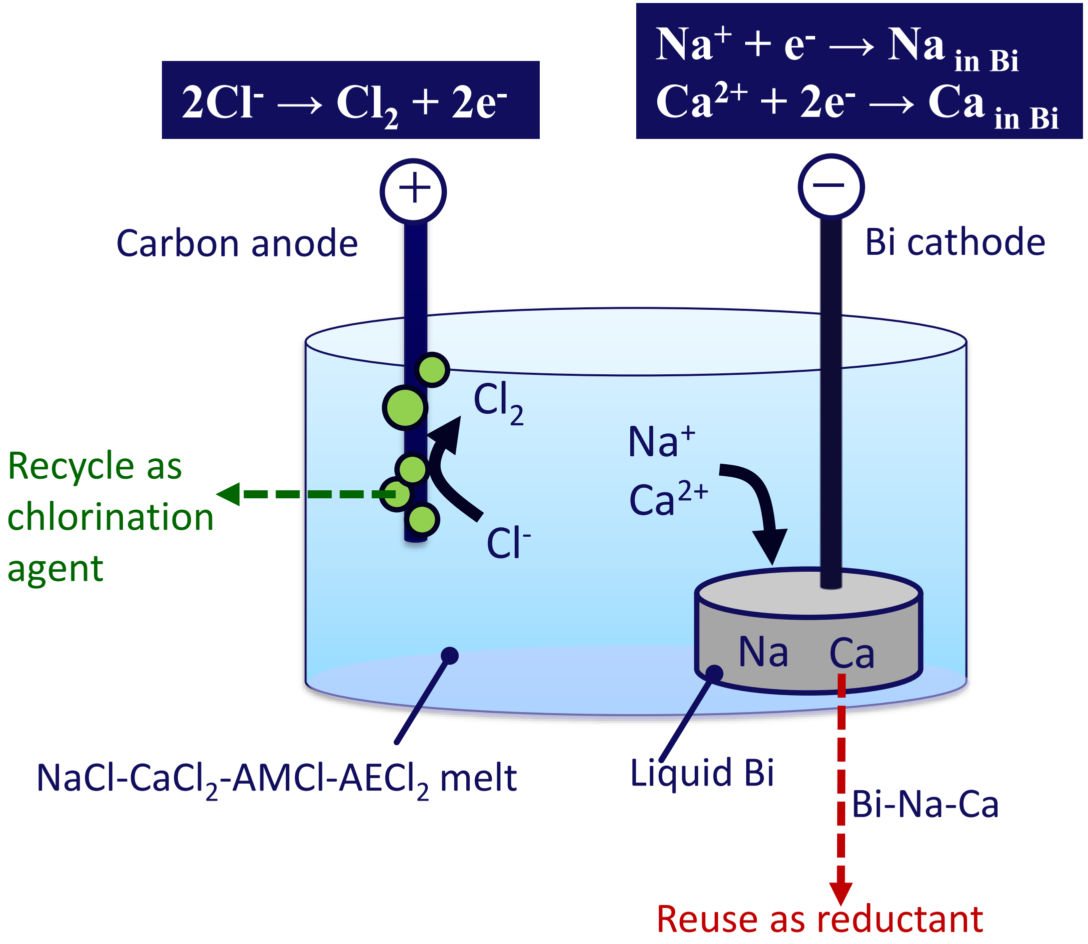
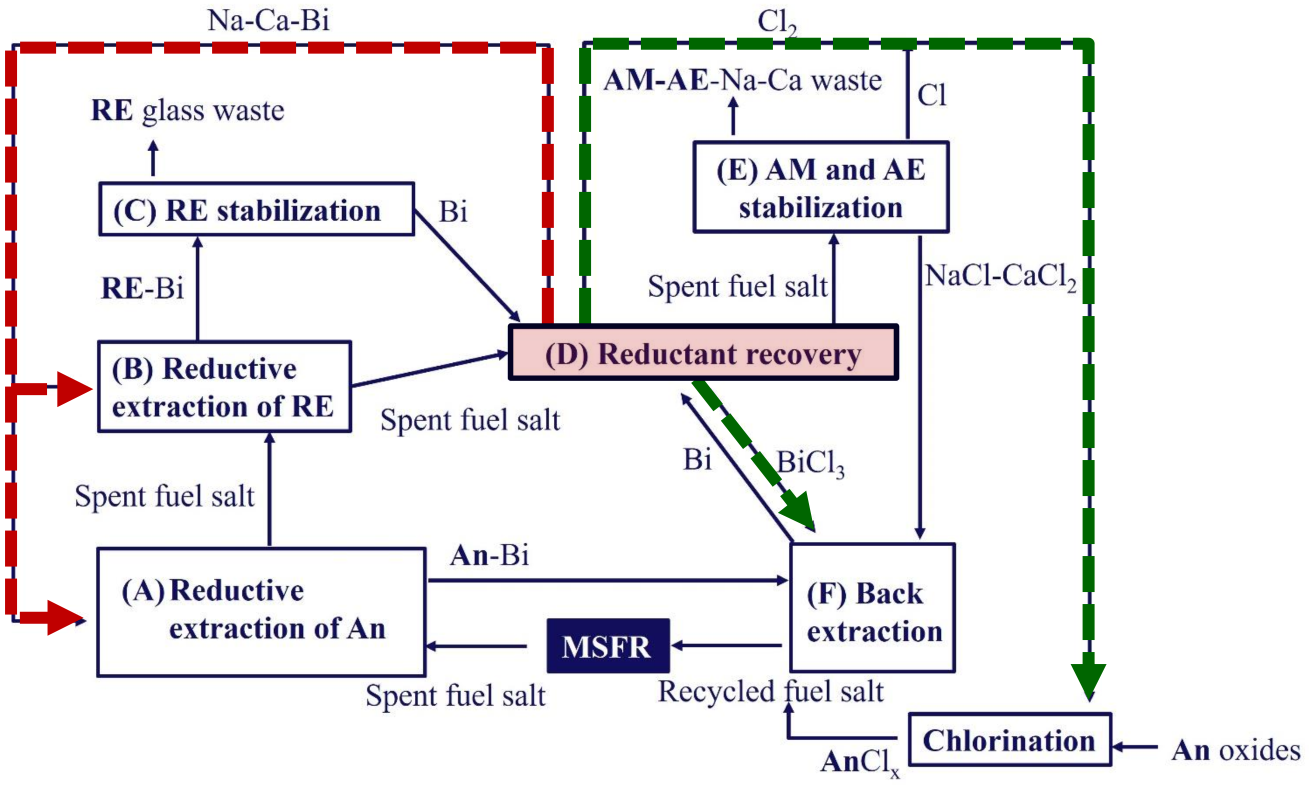
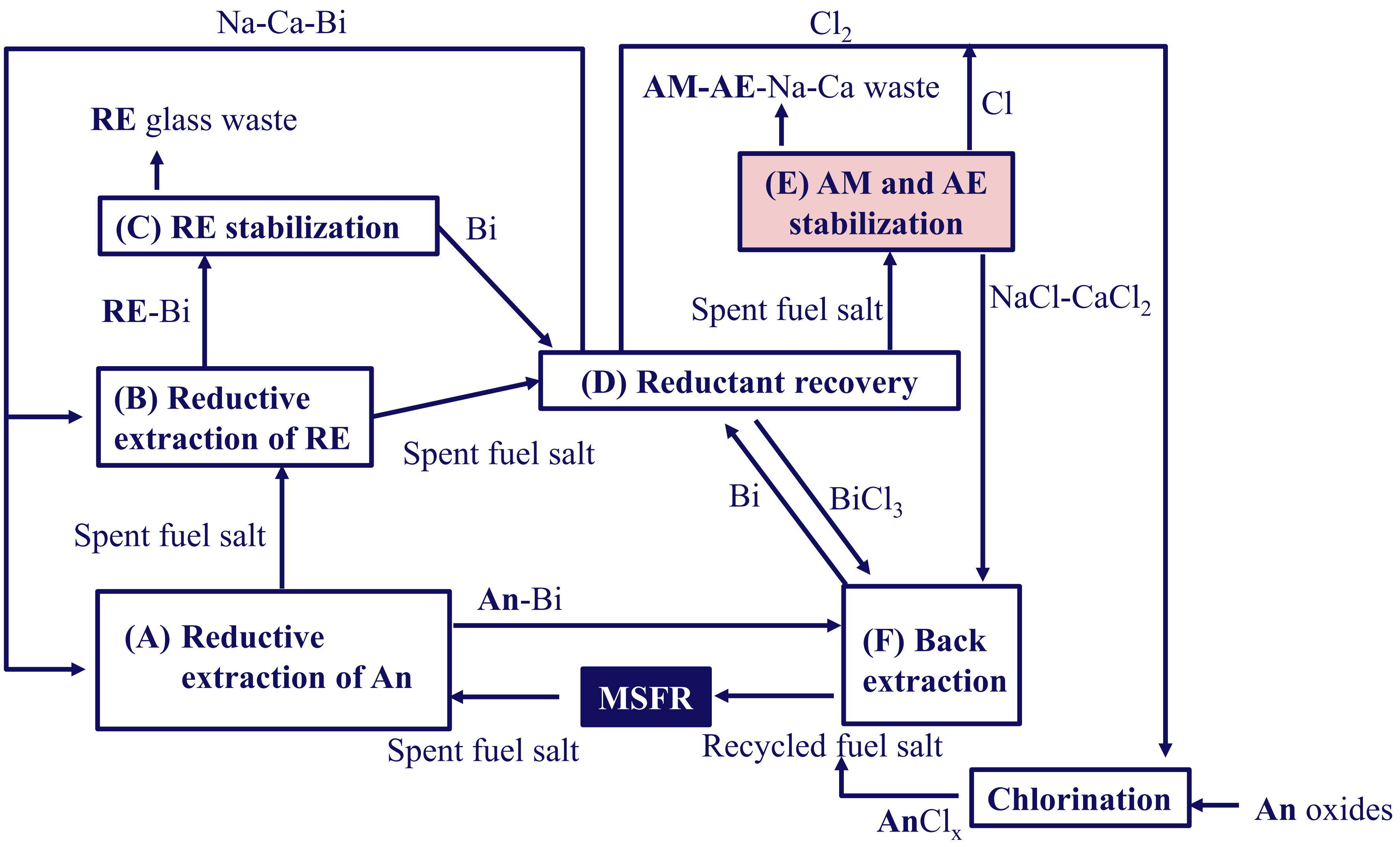
(D) Reductant recovery

Electrochemical recovery of Cl_2 and the reductant (Na, Ca) for reductive extraction at steps (A) and (B)





Pyrochemical reprocessing of spent chloride fuel salt



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(E) AM and AE stabilization

Conversion of AM and AE chlorides to other chemical form with chlorine recovery

AM and AE removal from LiCl-KCl melt by absorbing them in the frame of zeolite

- ✓ Feasible process for metallic fuel reprocessing
- ✓ Applicable to waste form production for chloride fuel salt final disposal

but

- ✓ Absorption of Ca (base salt) together with FP in zeolite structure
- ✓ Chlorine recovery required in MSFR reprocessing

Another process is necessary for chloride fuel salt reprocessing.

Recycle as chlorination agent

Possible process*

$T \leq 600°C$

$$2AMCl + 2NH_4H_2PO_4 \rightarrow AM_2O{\cdot}P_2O_5 + H_2O + 2NH_4Cl$$

$$AECl_2 + 2NH_4H_2PO_4 \rightarrow AEO{\cdot}P_2O_5 + H_2O + 2NH_4Cl$$

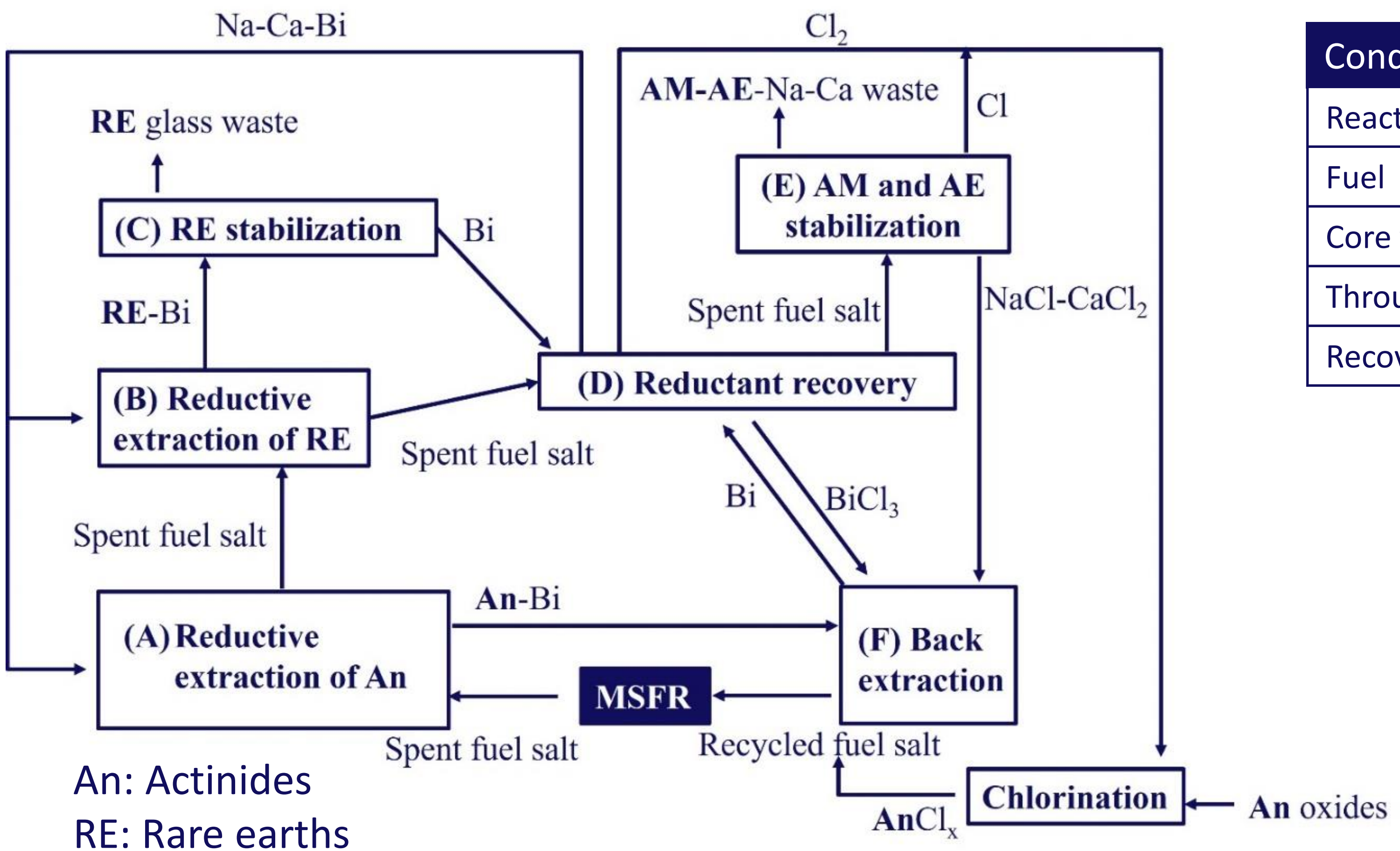
$+ Fe_2O_3$ $T > 1000°C$

Stabilized as Iron phosphate

Stable waste form

*B. J. Riley et al., Journal of Nuclear Materials, 529 (2020) 151949.

Mass balance evaluation of actinides and FP at reprocessing of the spent chloride fuel salt from MSFR (700 MWth)



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Condition for mass balance evaluation	
Reactor	700MWth MSFR
Fuel	$NaCl-CaCl_2-30\%(PuCl_3,UCl_3,UCl_4)$
Core volume	$14m^3$
Throughput	122L/30days
Recovery Ratio of actinides	99.9%

Mass balance evaluation to confirm the feasibility

Basic properties measurements of actinide and fission products in $NaCl\text{-}CaCl_2$ melt

Data required for mass balance calculation

Thermodynamic properties of actinides and fission products

- Distribution behavior between liquid Bi and salt at reductive extraction step
- Distribution behavior between liquid Bi and glass at RE stabilization step

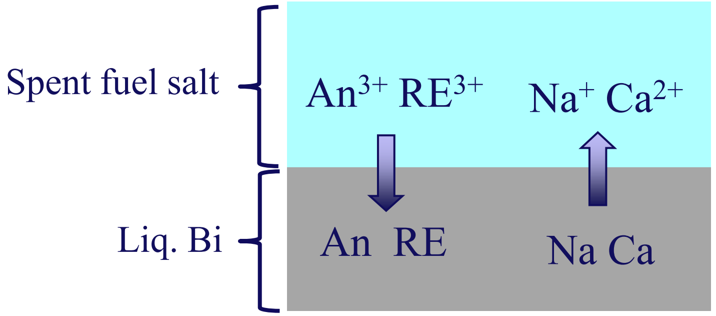
→ Not enough data available so far

We have measured thermodynamic properties of actinides and fission products in $NaCl\text{-}CaCl_2$ melt and demonstrated RE stabilization.

- ✓ Redox potential of actinides and lanthanides
- ✓ Distribution behavior of fission products (lanthanides, alkali, alkaline earth) between liquid Bi and salt
- ✓ Demonstration of RE stabilization step

Distribution behavior between liquid Bi and NaCl-$CaCl_2$ melt in terms of separation factor

Reductive extraction tests to measure separation factor in liquid Bi/NaCl-$CaCl_2$ melt system



$$3Na_{\text{in Bi}} + An^{3+}\,(RE^{3+}) \rightarrow An_{\text{in Bi}}\,(RE_{\text{in Bi}}) + 3Na^{+}$$
$$3Ca_{\text{in Bi}} + 2\,An^{3+}\,(RE^{3+}) \rightarrow 2\,An_{\text{in Bi}}\,(RE_{\text{in Bi}}) + 3Ca^{2+}$$

(Separation factor of **rare earths** based on Ce) $= \dfrac{X_{\text{M in salt}} * X_{\text{Ce in Bi}}}{X_{\text{M in Bi}} * X_{\text{Ce in salt}}}$

	La	Pr	Nd	Gd
RUN1	**3.2**	**0.84**	**0.86**	**4.1**

(Separation factor of **Sr, Cs and Ce** based on Na) $= \dfrac{(X_{\text{M in salt}})^{1/n} * X_{\text{Na in Bi}}}{(X_{\text{M in Bi}})^{1/n} * X_{\text{Na in salt}}}$

	Sr	Cs	Ce
RUN2	**3.0×10^{-2}**	**1.8**	**3.3×10^{-4}**

Mass balance evaluation

Redox potential measurement of actinide and fission products in NaCl-CaCl$_2$ melt

Electrochemical measurements in NaCl-CaCl2 melt containing actinide or fission product chlorides

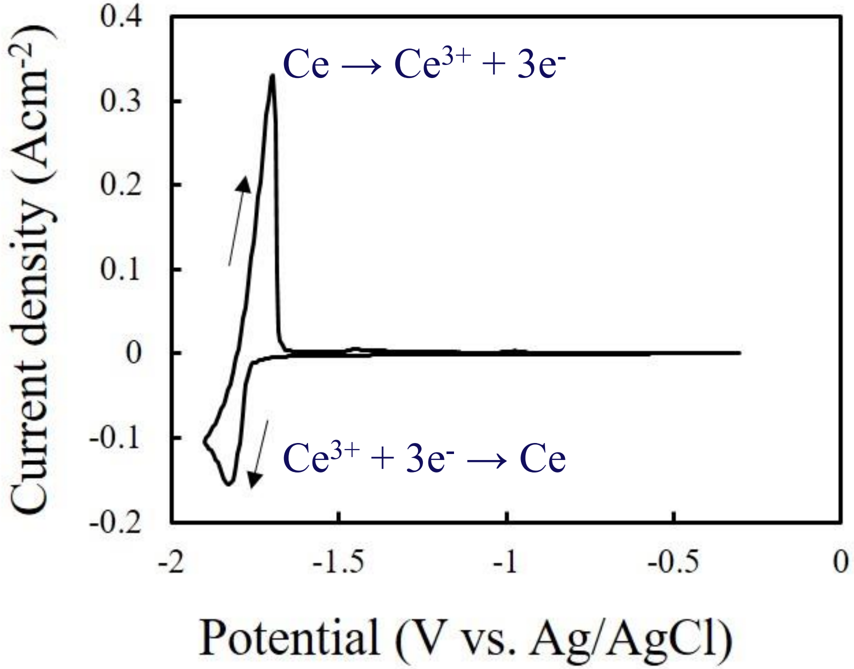


Fig. Cyclic voltammogram using W in NaCl-CaCl$_2$-1.05mol%CeCl$_3$(823 K) melt. Scan rate: 50 mVs^{-1}.

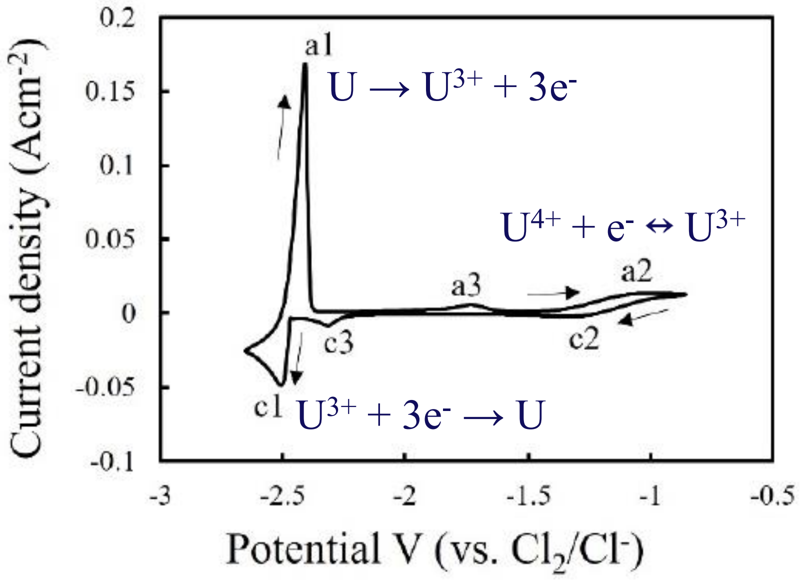


Fig. Cyclic voltammogram using W in NaCl-CaCl$_2$-0.255 mol%UCl$_3$(823 K) melt. Scan rate: 50 mVs^{-1}.

Formal standard redox potential of Ce^{3+}/Ce
$E^{0'}$= -2.941 (V vs. Cl$_2$/Cl$^-$)

Formal standard redox potential of U^{3+}/U
$E^{0'}$ = -2.325 V (vs. Cl$_2$/Cl$^-$) at 823 K

Mass balance evaluation

T. Murakami et al., KURNS Progress report 2022, CO9-2.

Distribution behavior between liquid Bi and NaCl-$CaCl_2$ melt in terms of separation factor

No separation factor of **Pu and minor actinides (Np, Am, Cm) in liquid Bi/NaCl-$CaCl_2$ reported**

Reported values of separation factor of **Pu and minor actinides (Np, Am, Cm)** in liquid Bi/LiCl-KCl melt system was used for mass balance evaluation

	Separation factor based on Pu
Am	**1.5**
Cm	**3.6**

H. Moriyama et al., J. Alloy. Compds., 271-273 (1998) 587-591.

	Separation factor based on U
Pu	**13**
Np	**11**

M. Kurata et al., J. Nucl. Mater., 227 (1995) 110-121.

Mass balance evaluation

RE distribution between glass and Bi at RE stabilization step

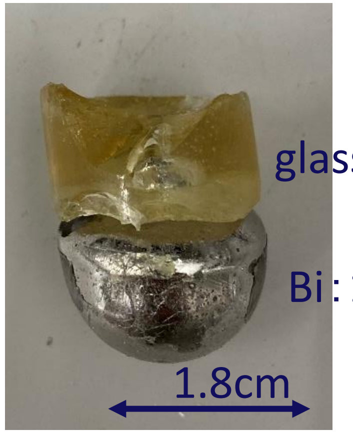
Bi-Ce alloy

glass

Alumina tube

1100℃ for 2 h

RUN1



glass : 4.4544 g

Bi : 18.8822 g

1.8cm

1100℃ for 55 min

RUN2

glass : 4.0944 g

Bi : 18.8355 g

1.8cm

	RUN1	RUN2
A: Ce in glass (g)	6.98×10^{-2}	3.99×10^{-2}
B: Ce in Bi (g)	1.82×10^{-4}	1.73×10^{-4}
Ce distribution =A/(A+B)	0.997	0.996

All of Ce transferred from Bi to glass

	RUN1	RUN2
C: Bi in glass (g)	0.708	0.339
Bi distribution =C/(C + Bi weight after RUN)	3.6×10^{-2}	1.8×10^{-2}

Almost all of Bi remained as metal
Shorter heating time→smaller Bi transferred to glass

Further decrease of the Bi loss by adding reducing agent to induce the following reactions.

$1.5Si + Bi_2O_{3\ in\ glass} = 2Bi + 1.5SiO_2$ (ΔG^0 = -790 kJ (at 1373 K))

$1.5C + Bi_2O_{3\ in\ glass} = 2Bi + 1.5CO_2$ (ΔG^0 = -385 kJ (at 1373 K))

Mass distribution calculation of reprocessing the used chloride fuel salt from MSFR (700 MWth)

Table Mass balance of actinides and fission products

		Recycled as new fuel salt (%)	Stabilized in glass waste form (%)	Stabilized in phosphate glass waste form (%)
Actinide	U	99.9	0.1	-
	Np	99.9	0.1	-
	Pu	99.9	0.1	-
	Am	99.7	0.3	-
	Cm	95.7	4.3	-
Lanthanide	La	3.6×10^{-1}	96.2	-
	Ce	1.3	98.2	-
	Pr	1.6	97.9	-
	Nd	1.7	97.9	-
	Gd	2.8×10^{-1}	93.0	-
Alkaline earth	Sr	6.0×10^{-2}	2.5×10^{-1}	1.5
Alkali	Cs	4.2×10^{-2}	8.7×10^{-2}	39

Almost all of actinides are recovered to be recycled as new fuel salt

at the same time

✓ Most of rare earths stabilized in waste form

Mass distribution calculation in glass waste form

Table Amount of waste form produced

step	Waste form	amount
RE stabilization	Borosilicate glass containing 10 wt% RE	100 kg / month
AE and AM stabilization	Iron phosphate glass containing 26 wt% AM and AE	6.9 kg / month

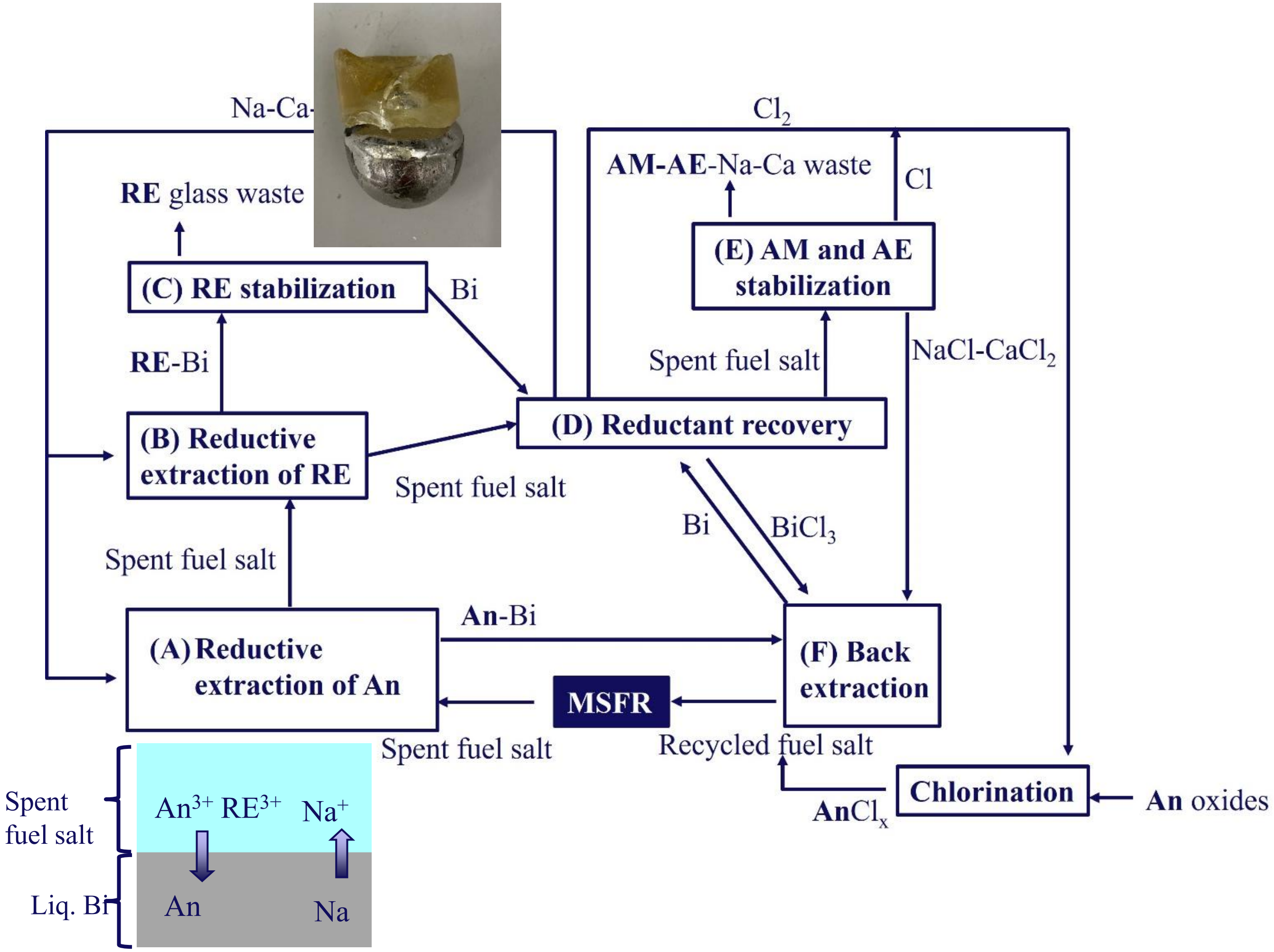
	Composition in borosilicate glass containing 10 wt% RE (mol)
U	6.19×10^{-1}
Pu	1.27×10^{-1}
Np	1.26×10^{-3}
Am	1.85×10^{-2}
Cm	8.82×10^{-2}
La	5.63
Ce	1.81×10
Pr	8.95
Nd	3.14×10
Gd	1.32
Sr	4.28×10^{-3}
Cs	1.13×10^{-3}

Important information for evaluating its heat and leachability

➡ Footprint of geological disposal site

Summary

- **A proposal of reprocessing process of chloride fuel salt meeting the following requirements,**
  - **Technically feasible**
  - **Applicable to NaCl, NaCl-CaCl$_2$, etc.**
  - **Capable of ^{37}Cl recycling.**
- **Mass balance evaluation of actinides and fission products based on their basic thermodynamic properties**
  - almost all of actinides recycled as new fuel
  - stabilization of fission products in waste form
- **Novel vitrification process for RE stabilization**
  - almost all of RE stabilized in glass
  - most of Bi left as metal to be recycled



Pyrochemical reprocessing process of chloride fuel salt

Thank you for your attention !

Aknowledgement :

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