Effects of Nitrate on Potassium Perrhenate($KReO_4$) Volatilization

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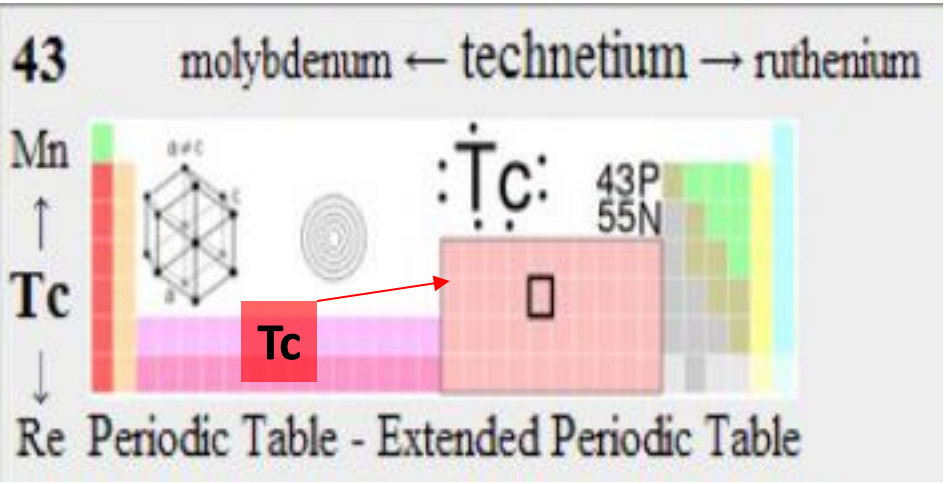
Outline

- Background
- Experimental
- Results and Discussion
  - **The path of Tc/Re volatilization**
  - **The effect of nitrate- at low temperature**
  - **The effect of nitrate- at high temperature**
- Conclusion

Background-The concern of Tc

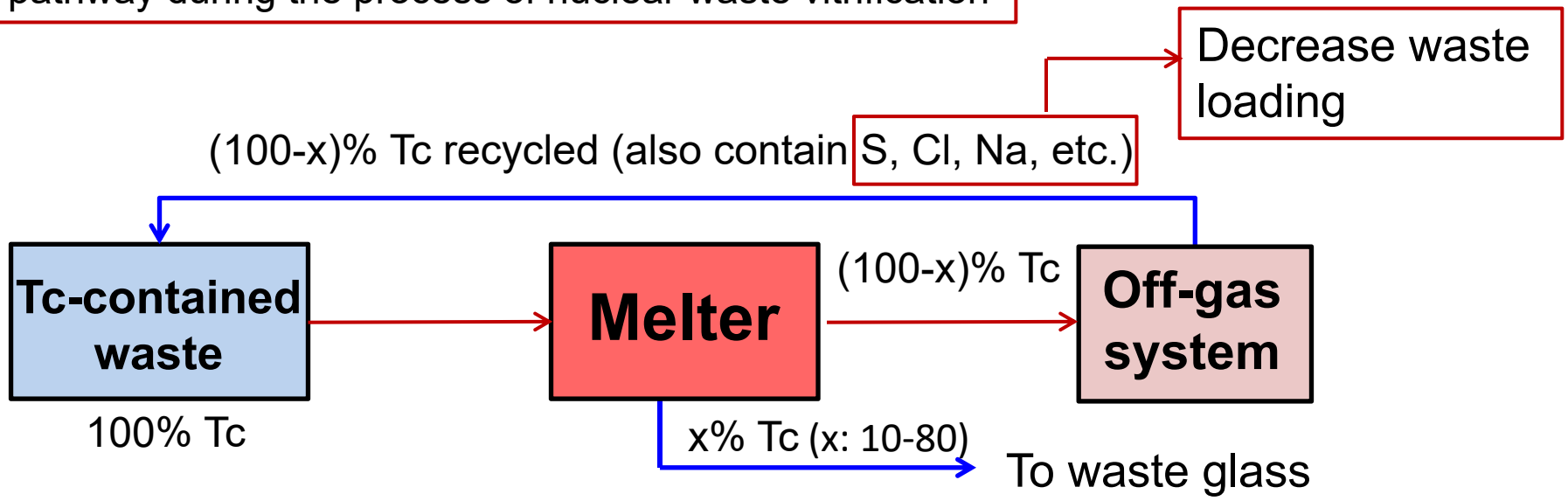


Tc-99

- Long half-life: 2.1×10^5 years
- High yield: 6.1% (^{235}U fission)
- High solubility and mobility of TcO_4^- (the dominant species)

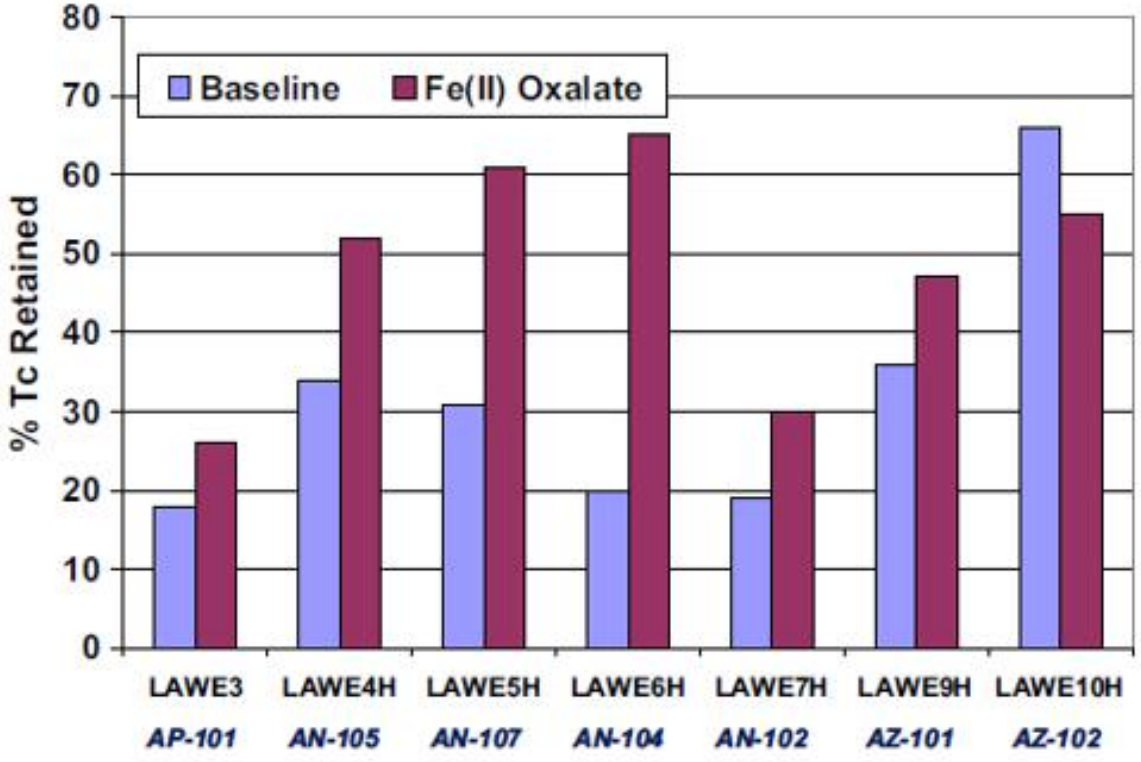
Re: as a nonradioactive surrogate

Tc pathway during the process of nuclear waste vitrification



Background-Effect factors on Tc/Re volatilization

Redox



Measured single-pass Tc retentions for seven waste glass formulations with and without ferrous oxalate

Tc retention almost increases with the addition of reductant

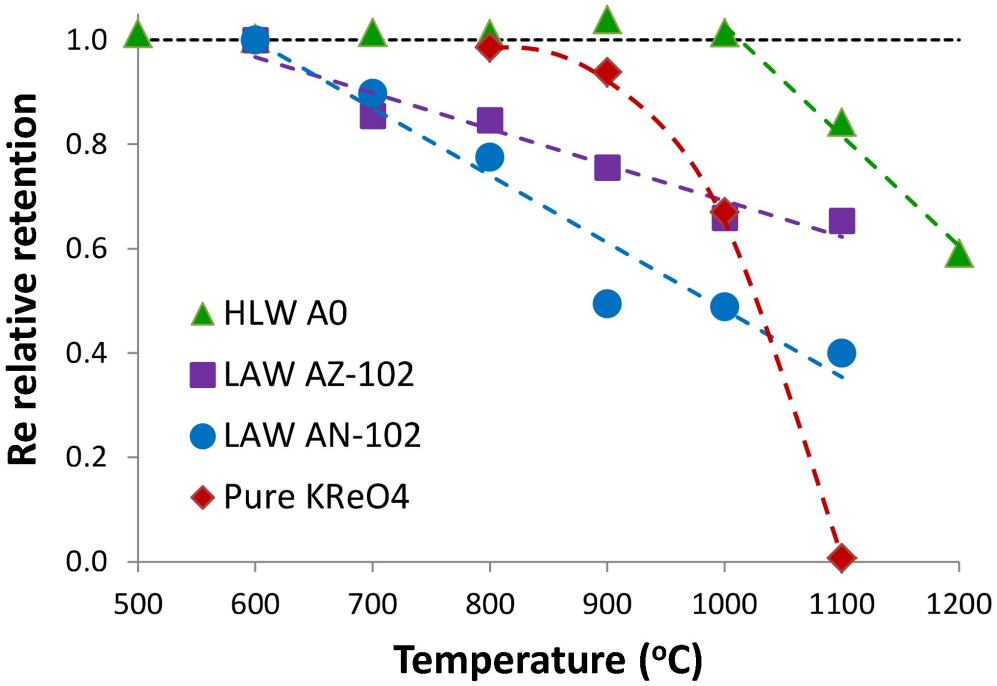
Pegg, Ian L. "Behavior of technetium in nuclear waste vitrification processes." *Journal of radioanalytical and nuclear chemistry* 305.1 (2015): 287-292.

Background-Effect factors on Tc/Re volatilization

Inorganic Salt

Waste	Single-pass retention (%)	
	Tc	Re
AP-101	18	25
AN-105	34	43
AN-107	31	39
AN-104	20	36
AN-102	19	27
AZ-101	36	NA
AZ-102	66	57

Pegg *et al.*, VSL-10R1920-1 (2010)
Pegg *et al.*, VSL-11R2260-1 (2011)



Kim *et al.*, JNCS (2015); Xu *et al.*, JNM (2015)

Tc/Re shows different volatility in different kinds of waste glass feeds

Background-Effect factors on Tc/Re volatilization

Inorganic Salt

AN-102 (Hanford site)

	Feed[a] (M)
Na^+	5.98 E + 00
K^+	2.92 E − 02
Al	2.72 E − 01
Ca	5.14 E − 03
Cr	1.69 E − 03
P	4.27 E − 02
Si	2.68 E − 03
NO_3^-	1.89 E + 00
NO_2^-	8.32 E − 01
SO_4^{2-}	6.20 E − 02
PO_4^{3-}	< 1.26 E − 02
Cl^-	4.35 E − 02
OH^- (free)	1.69 E + 00
^{99}Tc	4.60 E − 05
U (mg/L)	7.80 E + 00
TIC (mg/L)	1.09 E + 04
TOC (mg/L)	4.66 E + 04

AN-103 (Hanford site)

	Feed[a] (M)
Na^+	4.99 E + 00
K^+	1.17 E − 01
Al	8.40 E − 01
Ca	2.00 E − 03
Cr	1.40 E − 03
Si	3.40 E − 03
NO_3^-	9.98 E − 01
NO_2^-	8.66 E − 01
SO_4^{2-}	9.00 E − 03
PO_4^{3-}	5.90 E − 03
Cl^-	8.50 E − 02
OH^- (free)	1.87 E + 00
^{99}Tc	3.07 E − 05
U (mg/L)	4.08 E + 00
TIC (mg/L)	3.68 E + 03
TOC (mg/L)	5.68 E + 02

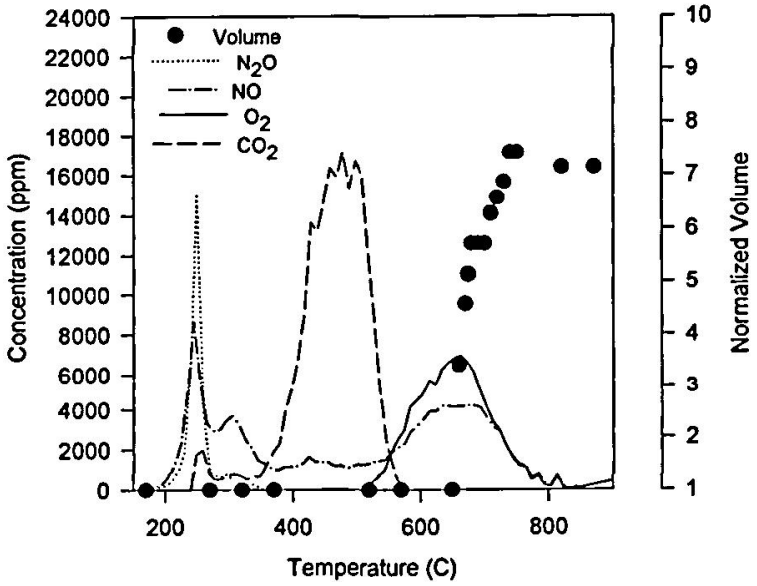
Compositions of the feed of the AN-102 and AN-103 samples

Nuclear waste contains various inorganic salts (nitrates/nitrites, chlorides, sulfates)

Background-Effect factors on Tc/Re volatilization

Inorganic Salt

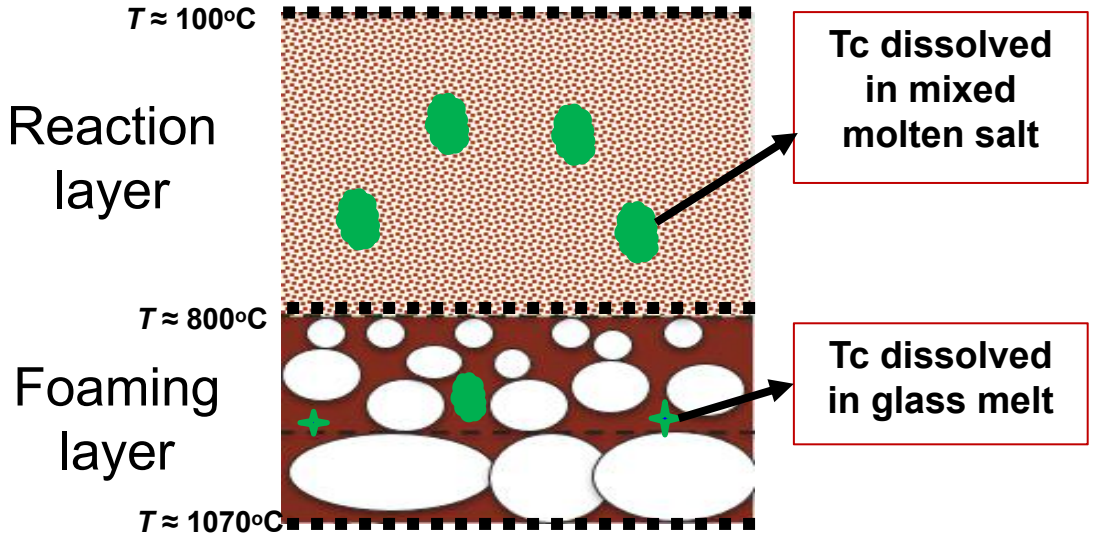
Evolved gas composition and volume expansion



Elemental retention

	100℃	700℃	1000℃
Cl	67	56	49
S	100	72	48
Re	**100**	**94**	**93**

Reaction and foaming layer in Cold-cap



Decomposition of inorganic salt occurred in the reaction layer of cold-cap, which affect Tc/Re retention, however, the detail is not clear

J.G Darab, E.M Meiers, A.P Smith; Mater. Res. Soc. Proc., 556 (1999), p. 215

Xu *et al.*, JACerS (2015), (2016); Dixon *et al.*, EST (2015)

Background-The argument of Tc/Re volatilization path

Congruent evaporation of $MTcO_4$ melt

$$MTcO_4(s/l) \rightarrow MTcO_4(g)$$

Decomposition of $MTcO_4$ melt

$$2MTcO_4(l) \rightarrow Tc_2O_7(g) + M_2O\ (s/l/g)$$

Migge H. Simultaneous Evaporation of Cs and Tc during Vitrification-A Thermochemical Approach [J]. Materials Research Society Symposium Proceedings, 1990, 176: 411-417.

Kim D S, Soderquist C Z, Icenhower J P, *et al*. Tc Reductant Chemistry and Crucible Melting Studies with Simulated Hanford Low-Activity Waste, PNNL-15131 [R]. Richland, WA, US: Pacific Northwest National Laboratory, 2005.

Motivation

- **The Tc/Re volatilization path**
- **Effects of nitrate on $KReO_4$ volatilization**

Experimental

Crucible test

Sample	Total/g
Pure Re	2
Pure N	2
1Re4N	2
1Re2N	2
1Re1N	2
1Re0.5N	2
1Re0.25N	2

Muffle furnace

From RT to 500~1300℃ at the rate of 5℃/min (interval: 100 ℃)

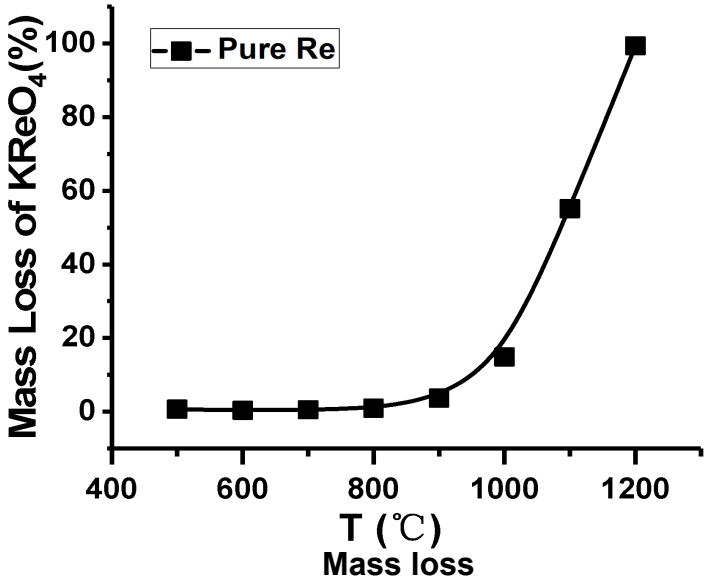
Cooling

Micro-test

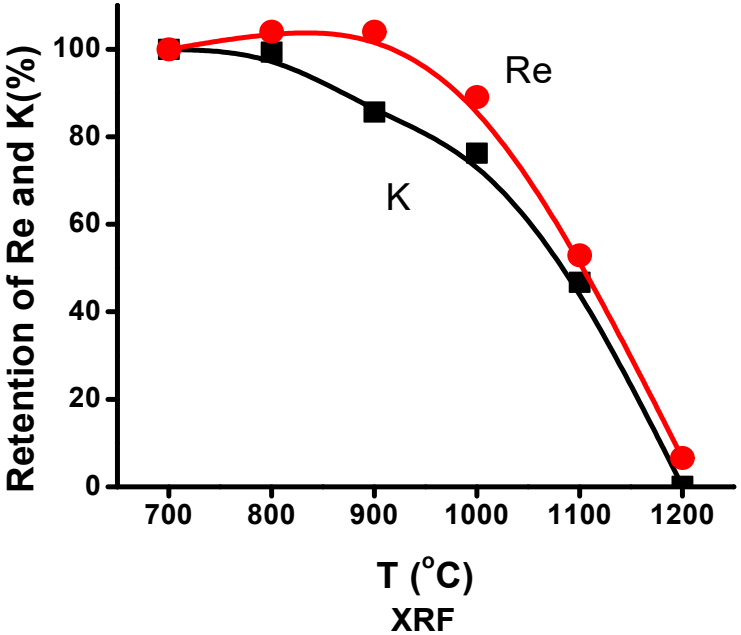
TG-DSC
GC-MS

Mass loss
XRD
XRF, CHNS/O

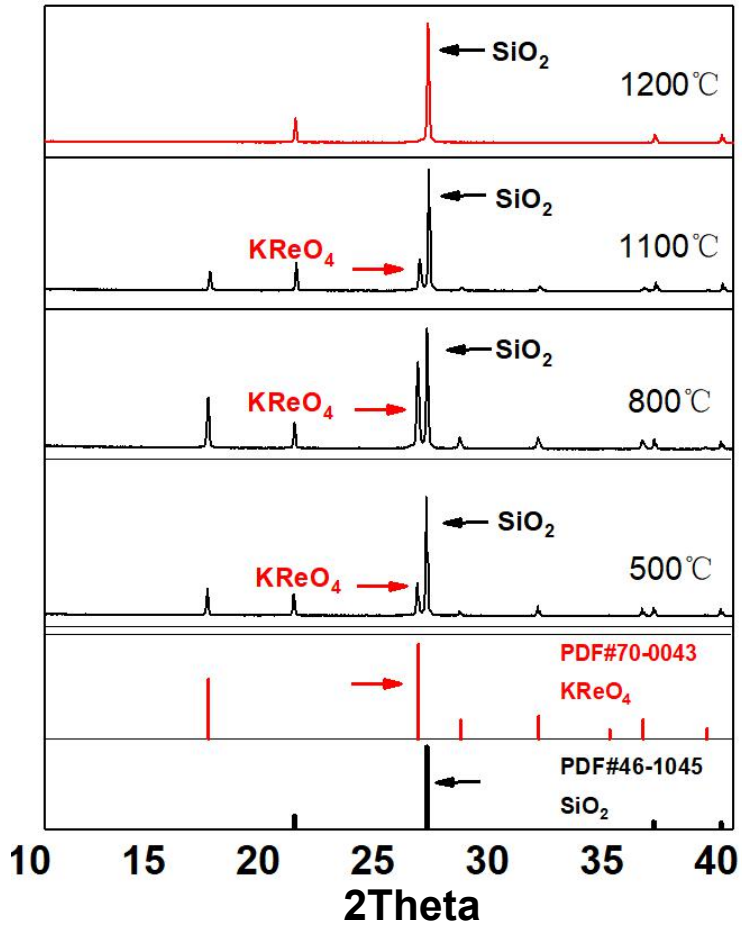
Results & Discussion-The Tc/Re volatilization path



Mass loss



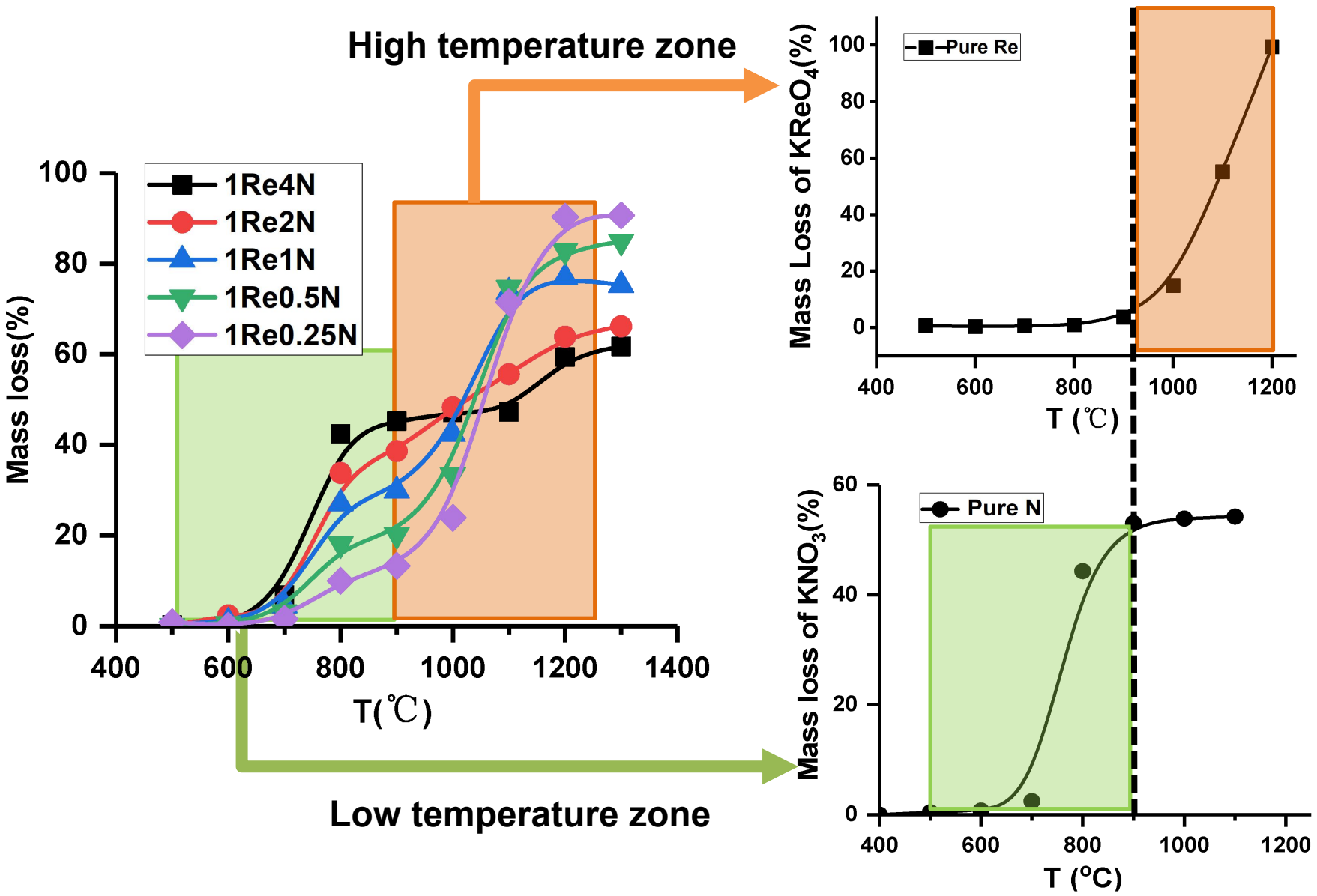
XRF



XRD

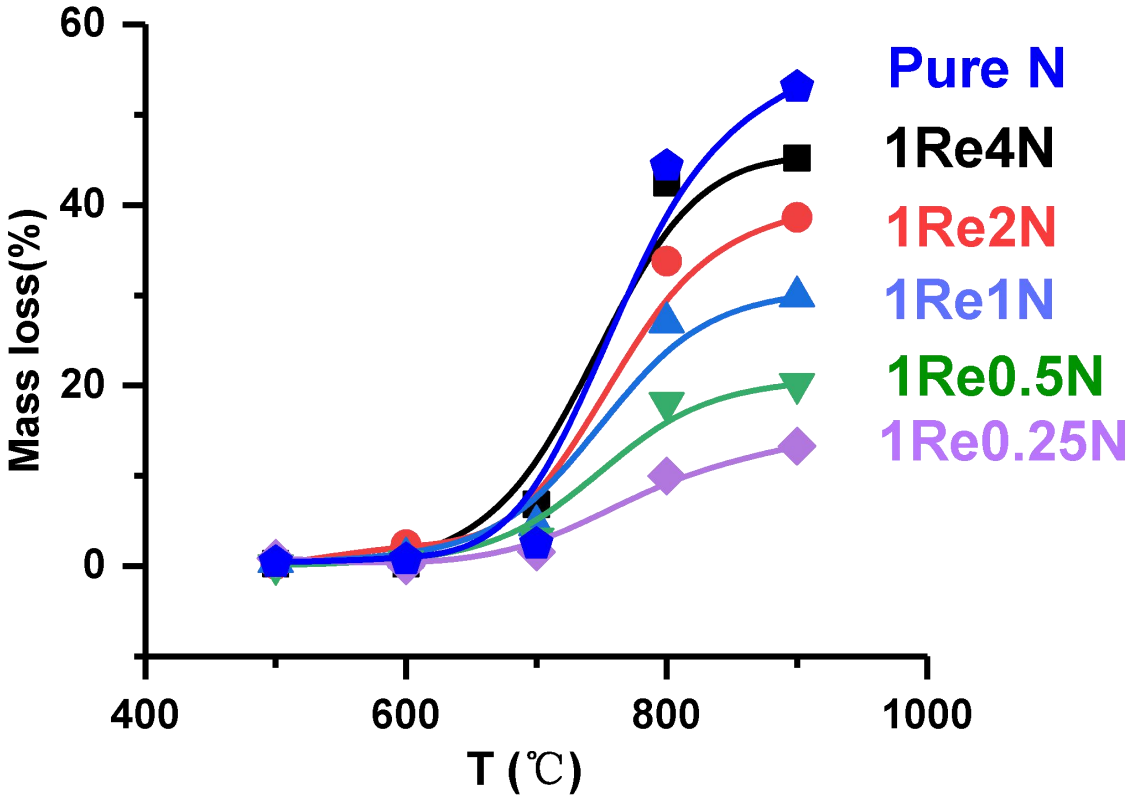
1. K, Re congruently lost between 800℃ to 1200℃
2. $KReO_4 + SiO_2 \xrightarrow{\Delta} KReO_4(g) + SiO_2$

Results & Discussion-The effect of nitrate



Results & Discussion-The effect of nitrate-at low temperature

Mass loss



Mass loss of mixed samples and pure N

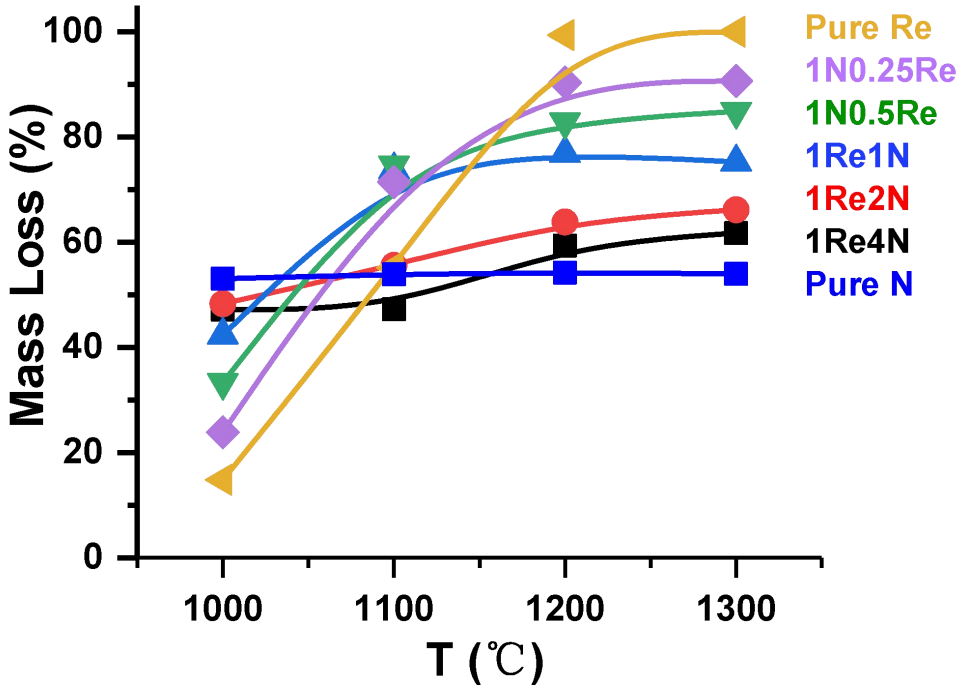
1. With increase of N ratio, mass loss in mixed samples is closer to that of pure N
2. No new phases are formed at low temperatures

XRD semi-quantitative analysis

1Re0.25N	SiO_2	■	■	■
	KNO_3	■		
	$KReO_4$	■	■	■
	Amorphous phase			
1Re0.5N	SiO_2	■	■	■
	KNO_3	■		
	$KReO_4$	■	■	■
	Amorphous phase			
1Re1N	SiO_2	■	■	■
	KNO_3	■		
	$KReO_4$	■	■	■
	Amorphous phase			
1Re2N	SiO_2	■	■	■
	KNO_3	■		
	$KReO_4$	■	■	■
	Amorphous phase			
1Re4N	SiO_2	■	■	■
	KNO_3	■		
	$KReO_4$	■	■	■
	Amorphous phase			
T/°C		700	800	900

Results & Discussion-The effect of nitrate-at high temperature

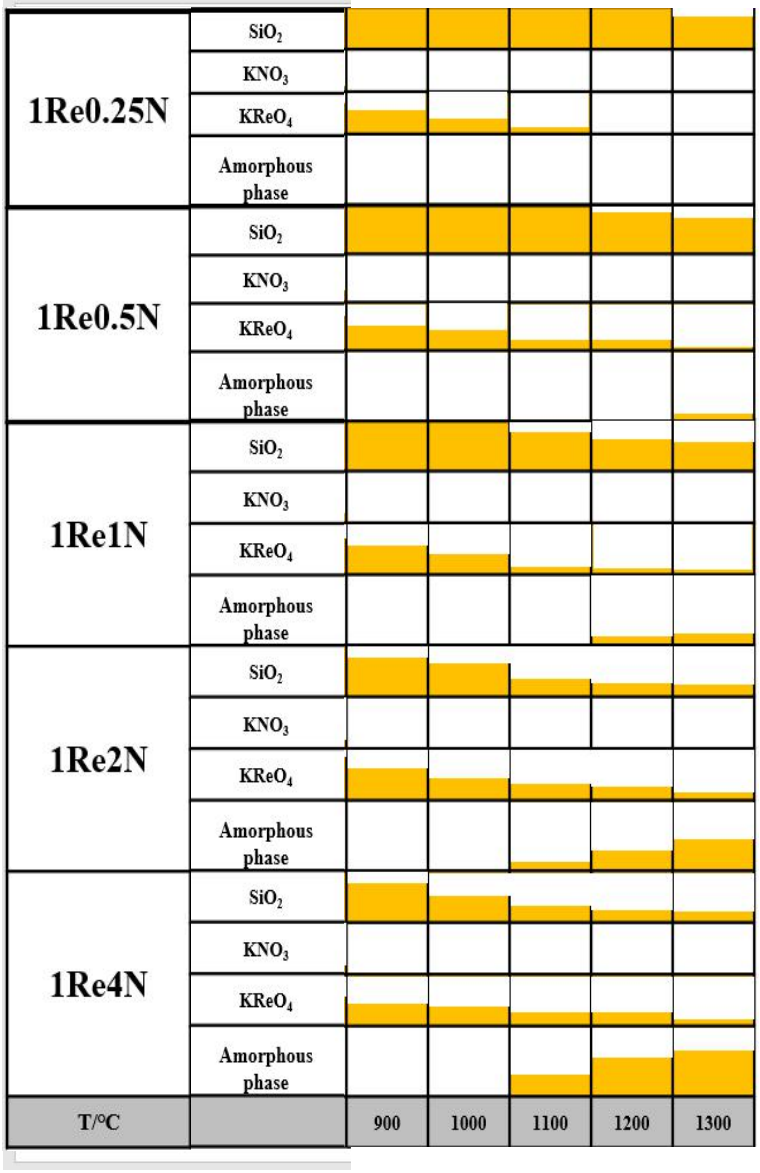
Mass loss



Mass loss of mixed samples at high temperature zone

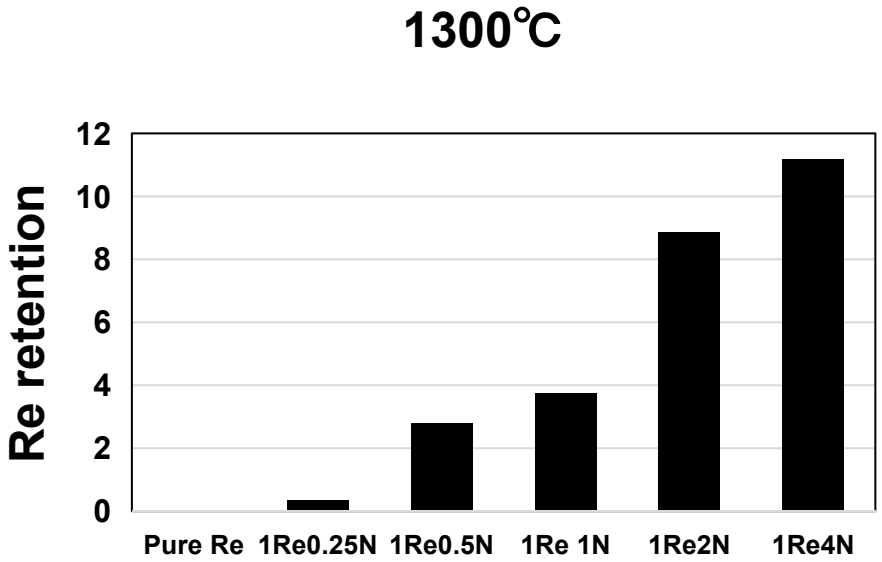
1. The mass loss in mixed samples at temperature above 1000℃ is higher than pure N, but lower than pure Re
2. Amorphous phase appear at high temperature zone

XRD semi-quantitative analysis



Results & Discussion-The effect of nitrate-at high temperature

Re retention



1. At 1300℃, Re still retained in the mixed samples, whereas all Re was gone in pure Re
2. At 1300℃, Re retention in mixed samples increases with the increase of N ratio

Conclusion

1. At the designed system, $KReO_4$ evaporates by

$$KReO_4(l) \xrightarrow{\Delta} KReO_4(g)$$

2. At the low temperature : $KReO_4$ starts to evaporate at 600℃ when Re:N＜1, because $KReO_4$ and KNO_3 formed an eutectic body
3. At the high temperature : after the addition of KNO_3,the mass fraction of amorphous increases, which leads to the increase of retention of Re

Thanks for your attention