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Vitrification Programme in China

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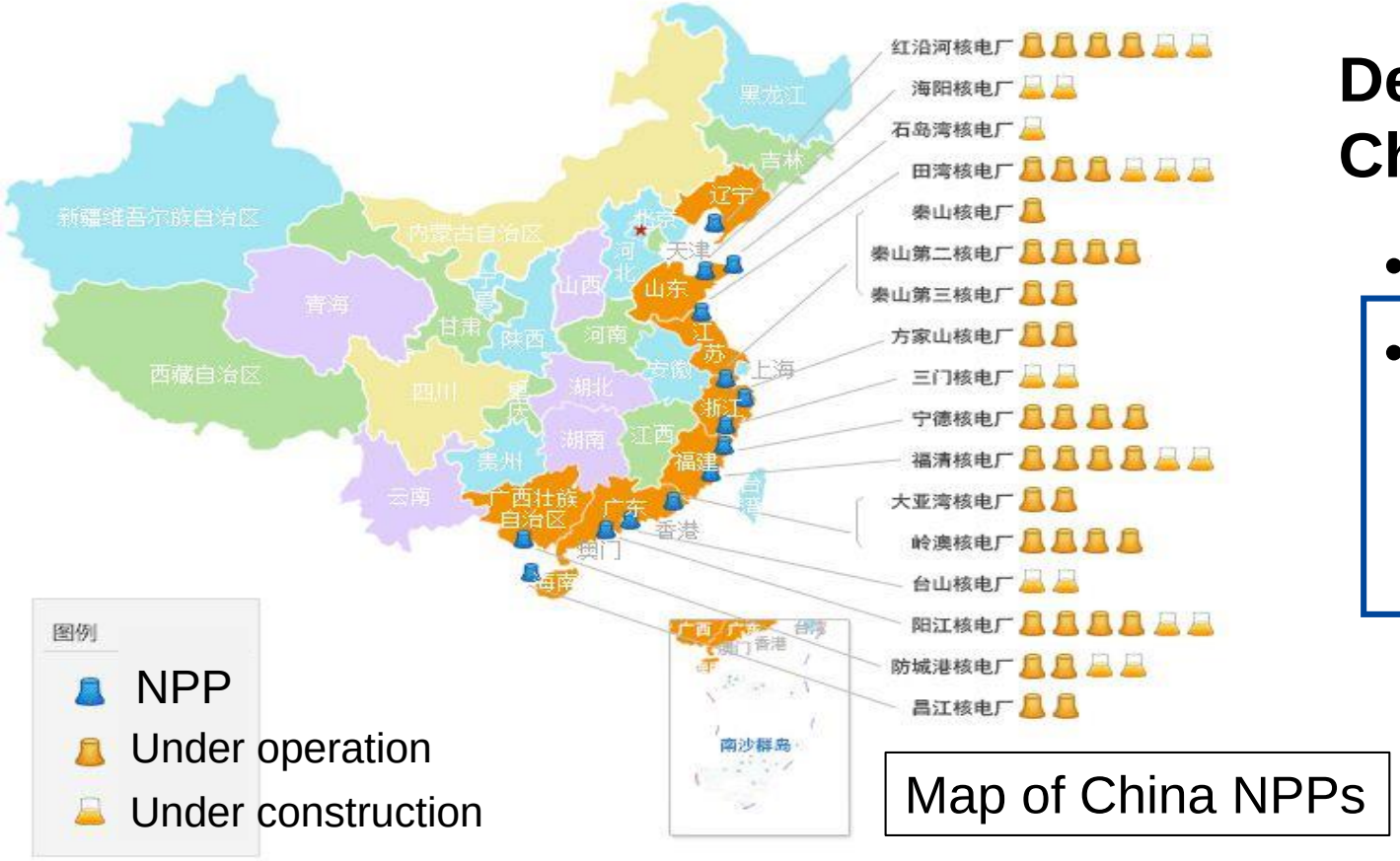
Background - fast growing of China nuclear power

Reactors under construction: 18 (2018 data)



Map of China NPPs

Development plan of China nuclear power:

- 2020: 58 GW
- 2035: 150 GW
  - ~10% of the total
  - 2nd world largest NNPs country

- By 2035, 50,000 m^3 of HLW will be produced from reprocessing
- Legacy waste (HLW) is going to be vitrified soon

Background – China nuclear waste management policy

HLW

ILW/LLW

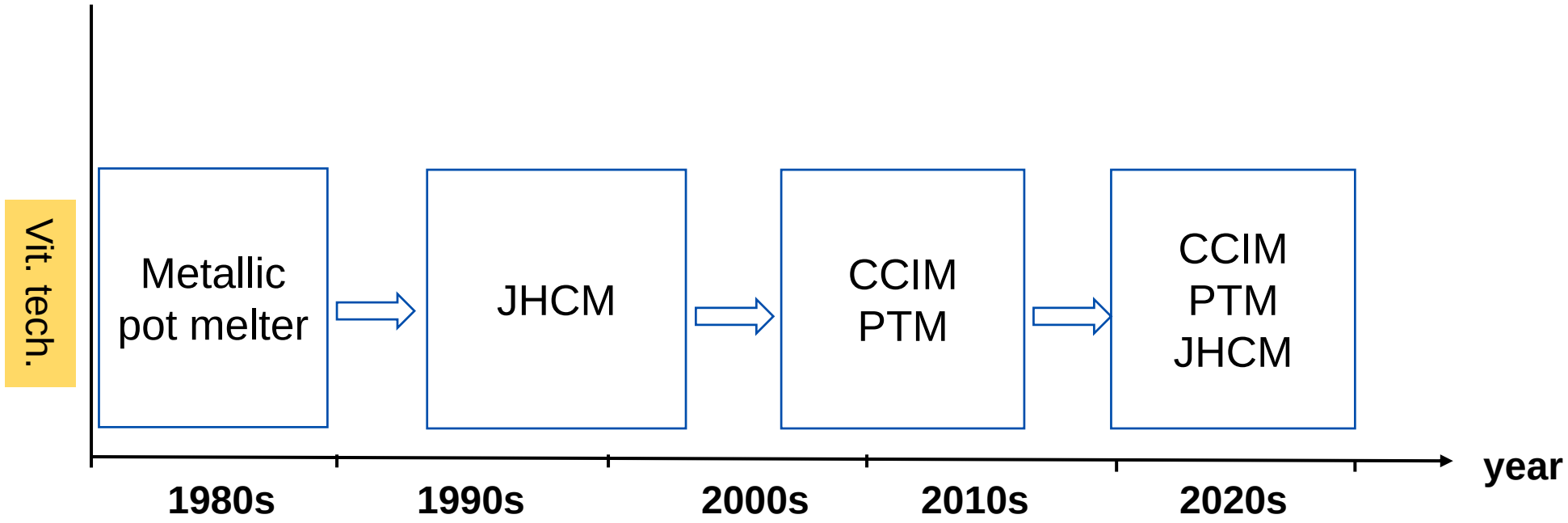
Optional

(from NPPs)

Glass

Cement

Background – China nuclear waste vitrification R&D



- R&D of nuclear waste vitrification draws attention in China in the past decade

(I) JHCM
-Vitrification Plant China (VPC) Programme

VPC: the first nuclear waste vitrification facility in China

Phase 1

Phase 2

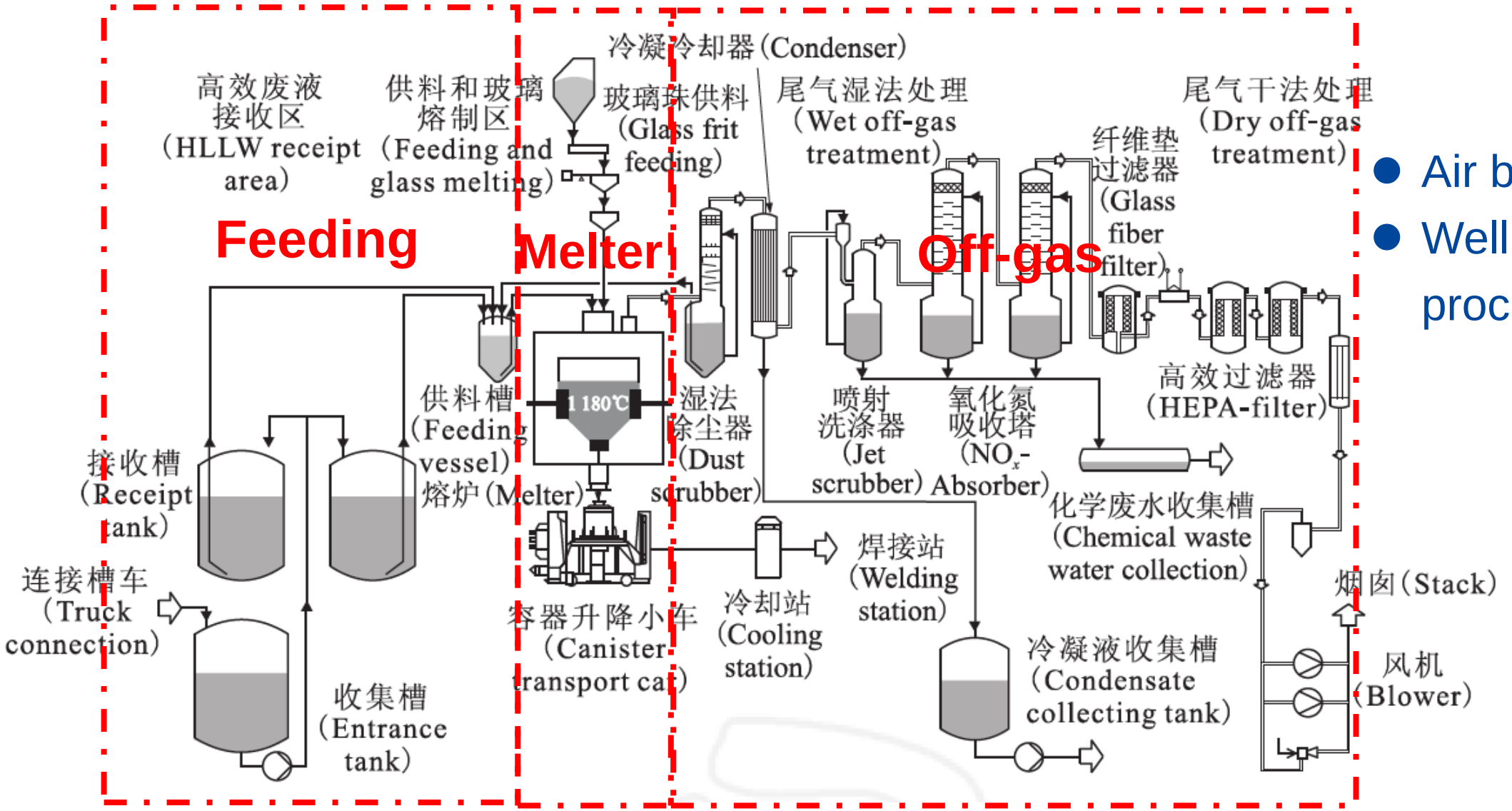
VPC programme (Phase 1) – glass formulation

w/%

氧化物 (Oxides)	从前玻璃 (Former glass)		候选玻璃 (Candidate glass)		预选玻璃 (Preselect glass)		最后推荐玻璃 (Final recommend glass)	
	玻璃料 (Frit)	废物玻璃 (Waste glss)	玻璃料 (Frit)	废物玻璃 (Waste glss)	玻璃料 (Frit)	废物玻璃 (Waste glss)	玻璃料 (Frit)	废物玻璃 (Waste glss)
SiO_2	59.80	50.23	50.96	42.55	53.76	44.89	53.76	44.89
B_2O_3	22.00	18.48	14.68	12.26	14.68	12.26	14.68	12.26
Na_2O	5.00	4.20	7.04	5.88	5.25	4.38	5.25	4.38
Li_2O	2.30	1.93	2.61	2.18	2.61	2.18	2.61	2.18
Al_2O_3	3.50	2.94	4.43	3.70	4.43	3.70	4.43	3.70
CaO	5.40	4.54	8.05	6.72	8.05	6.72	8.05	6.72
MgO	1.00	0.84	5.23	4.37	5.23	4.37	5.23	4.37
TiO_2	1.00	0.84	1.01	0.84	-	-	-	-
BaO	-	-	5.99	5.00	5.99	5.00	4.16	3.50
V_2O_5			-	-	-	-	1.79	1.50
Sb_2O_5			-	-	-	-	0.60	0.50
玻璃料中氧化物合计 (Total in frit)	100.00	84.00	100.00	83.50	100.00	83.5	100.00	84.00
废液中氧化物合计 (Total in HLLW)[1)]	16.00	16.00		16.00		16.00		
添加的氧化物(Additives)								
BaO		-		-		-	-	
Sb_2O_5			-	0.500		0.500	-	
V_2O_5			-		-	-	-	
$SO_3^{2)}$			-	0.586		0.586		0.586
废物玻璃中氧化物总计 (Total,glass frit+waste oxides)		100.00		100.00		100.00		100.00

-X. Wang et al., (2013)

VPC programme (Phase 1) – glass formulation



- Air bubbler used
- Well working of processing

Flow diagram of PVA vitrification facility in KIT

-X. Wang, et al., (2013)

VPC programme (Phase 1) – glass formulation

China standard

KIT test data

Beijing test data

参数(Parameters)	数值(Data)		
	EJ1186-2005[6]	INE	CIAE
密度(Density)	2.5～2.8 g/cm³	2.67 g/cm³	2.65 g/cm³
粘度(Viscosity)	1 150 ℃:(50±15) dPa·s	(32±1.6) dPa·s	(29.2±1.4) dPa·s
	950 ℃:(550±100) dPa·s	(379±24) dPa·s	(309.5±5.9) dPa·s
电阻率	1 150 ℃:(7±2) Ω·cm	7.43 Ω·cm	(6.54±0.18) Ω·cm
(Electrical resitivity)	950 ℃:(22±5) Ω·cm	22.79 Ω·cm	(19.87±0.31) Ω·cm
结晶倾向	φ<5%,730～750 ℃/28 d	φ<3%	φ<5%
(Crystallization tendency)			
MCC-1 浸出率	总失重应小于 15 g/m²;Na、Si、B、Cs、U 的归	(10.96±0.75) g/m²	(9.50±0.16) g/m²
(MCC-1 leaching rate)	一化元素浸出率均应小于 1 g/(m²·d)(Total	B 0.91 g/(m²·d)	B 0.659 g/(m²·d)
	mass loss <15 g/m²;leaching rate of Na,Si,	Na 0.82 g/(m²·d)	Na 0.675 g/(m²·d)
	B,Cs,U <1 g/(m²·d))	Si 0.52 g/(m²·d)	Si 0.354 g/(m²·d)
		Cs 0.75 g/(m²·d)	Cs 0.863 g/(m²·d)
		La -	La 2.4×10^{-4} g/(m²·d)
Soxhlet 浸出率	行标无要求(No requests)	(168±13) g/m²	(190.33±26.94) g/m²
(Soxhlet leaching rate)			
均匀性(Homogeneity)	均匀(Yes)	均匀(Yes)	均匀(Yes)

- Acceptable of glass properties
- No yellow phase

-X. Wang, et al., (2013)

(II) CCIM
-The latest vitrification technology

Principle

- Induced current supplied by inductor and HF generator

Advantages

- No refractories & internal electrodes
- No corrosion & erosion problems
- Long life-time
- Available high operating temperature
- Easy start-up & shut-down…

- Fundamental study
- Process and key technology study
- Pilot and engineering application study

(III) PTM
- Plasma torch melter

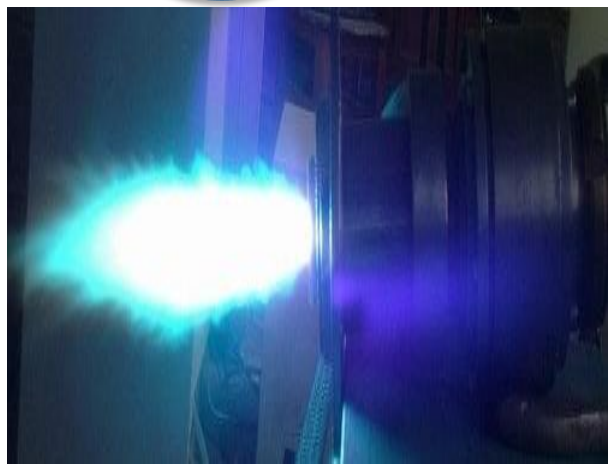
Target wastes: LLW (working clothes/gloves, insulation cotton, paper, spent filter etc.) from NPPs

PTM

Pyrolysis — Utilizing the thermal plasma to break the chemical bonds

Gasification — Incomplete oxidation of the organic components, producing combustible gases or syngas

Melting — Adding glass additives and melting with ash residue to glass



Plasma arc

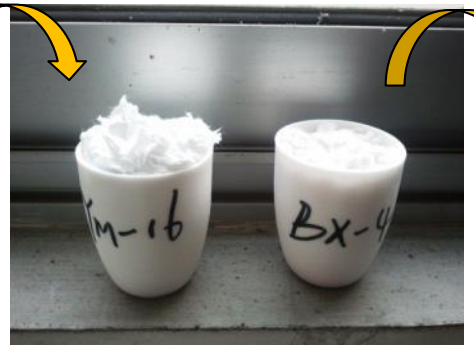
Glass pouring

Glass waste-form

PTM – Glass formulation

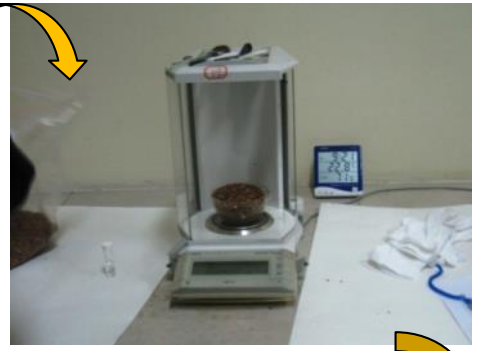
- Select typical waste from NPPs
- Analyze of the incinerated residues
- Add glass forming reagents + melt glass
- Characterize glass waste-form

①Typical waste

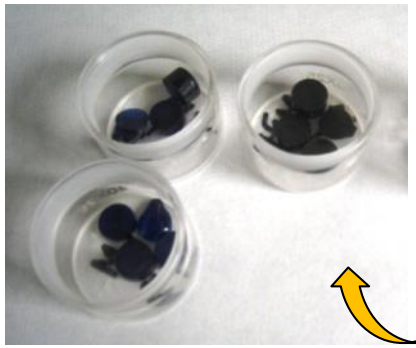


②Shredding

③Incineration



④Glass forming additives



⑨Vitrified samples

⑧Annealing

⑦Pouring

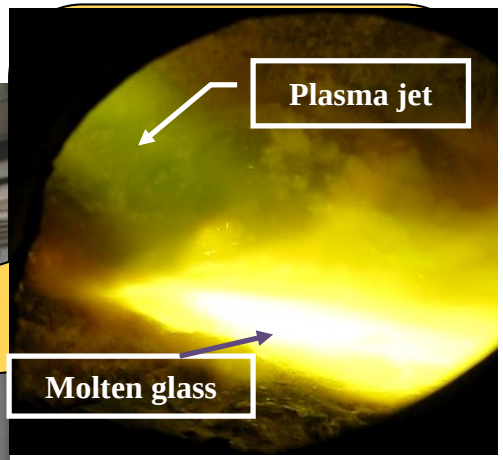
⑥Melting

⑤Mixing

PTM – Pilot test

Glass additives

Simulated waste



(IV) Waste-form development

- Glass-ceramics
- FeP glass

Glass-ceramics

Barium borosilicate glass

（improve sulfate solubility）

Zirconolite, titanite phases

（improve TRUs solubility）

Melting-thermal treatment

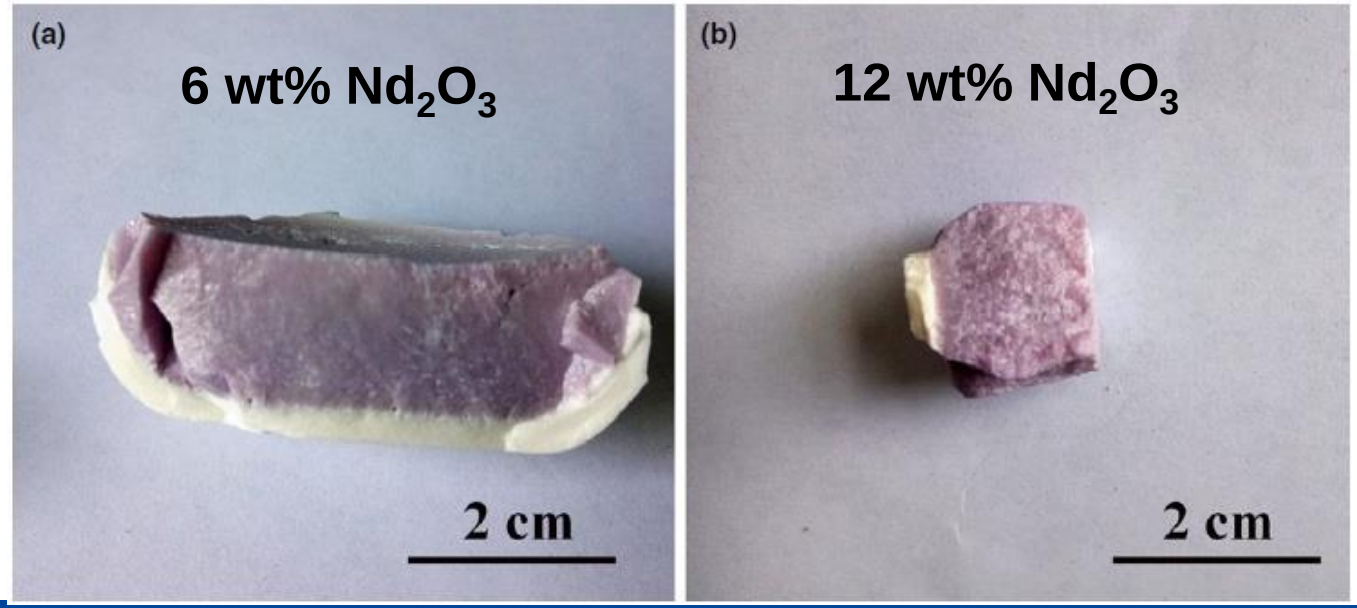
Barium borosilicate glass-ceramics containing zirconolite, titanite phases

BaBSi glass-ceramics (Nd effect)

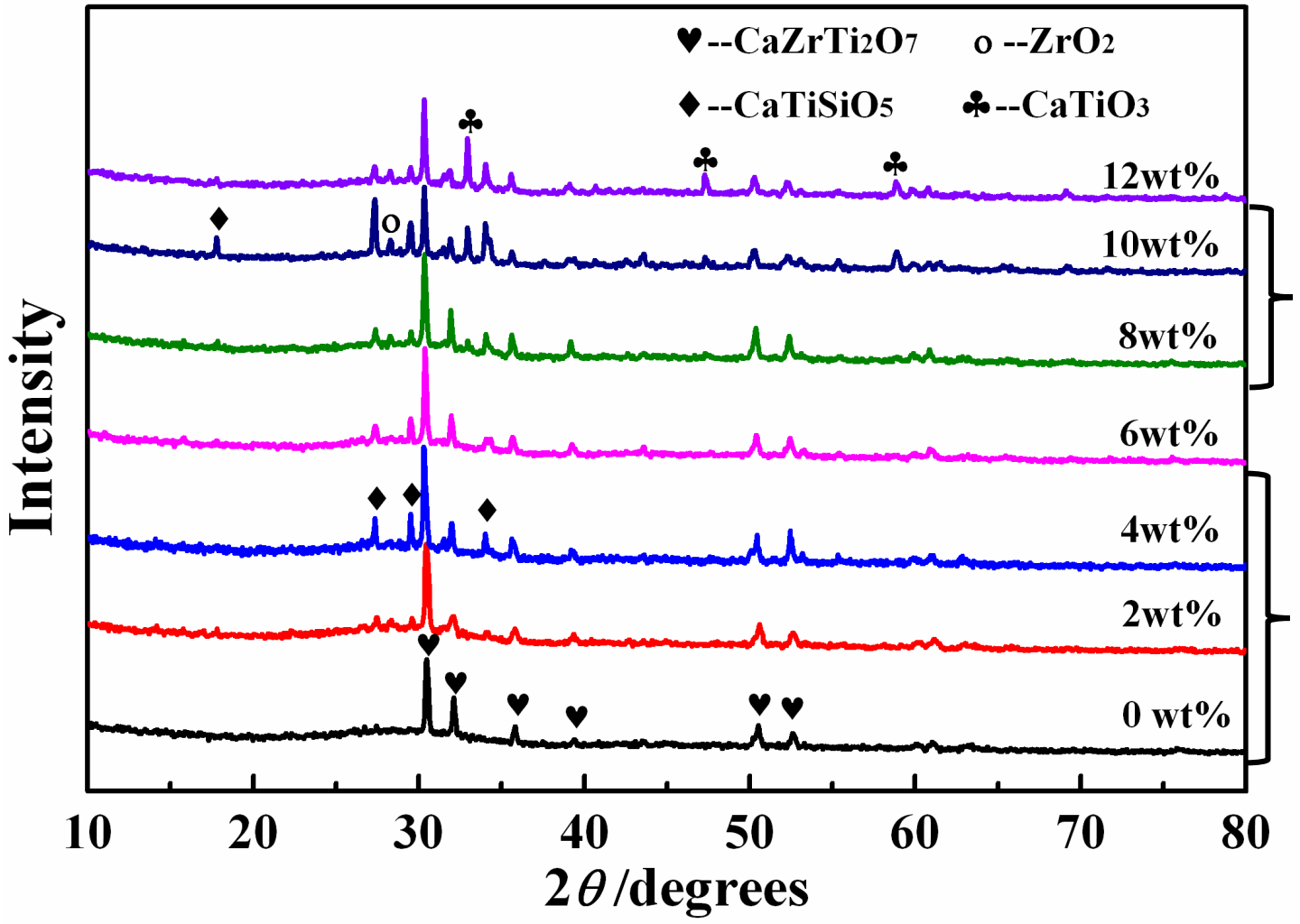
Composition of glass-ceramics (wt%)

Samples	SiO_2	B_2O_3	Na_2O	BaO	CaO	TiO_2	ZrO_2	Nd_2O_3
Nd–0	27.50	11.00	5.50	11.00	12.77	18.19	14.03	0
Nd–2	26.50	10.60	5.30	10.60	12.77	18.19	14.03	2
Nd–4	25.50	10.20	5.10	10.20	12.77	18.19	14.03	4
Nd–6	24.50	9.80	4.90	9.80	12.77	18.19	14.03	6
Nd–8	23.50	9.40	4.70	9.40	12.77	18.19	14.03	8
Nd–10	22.50	9.00	4.50	9.00	12.77	18.19	14.03	10
Nd–12	21.50	8.60	4.30	8.60	12.77	18.19	14.03	12

Photos of glass-ceramics



BaBSi glass-ceramics (Nd effect)



$CaZrTi_2O_7$+
$CaTiSiO_5$+
ZrO_2+
$CaTiO_3$

$CaZrTi_2O_7$+
$CaTiSiO_5$

XRD patterns with different contents of Nd_2O_3

L. Wu, *et al*., (2016).

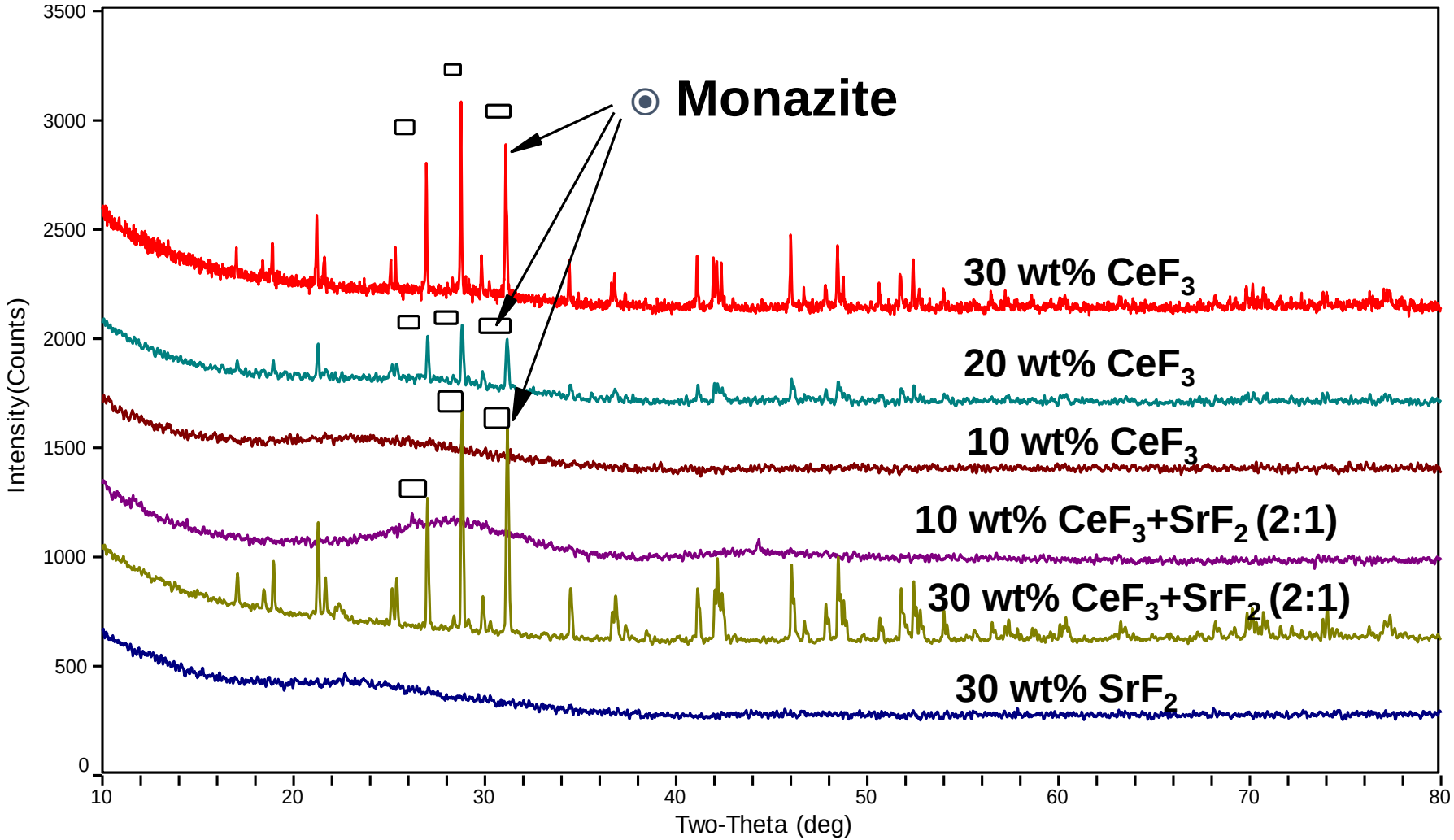
Fluoride wastes from molten salt reactor (MSR)

- MSR utilizes liquid molten fluoride salts as coolant, or even the fuel in the molten salt mixture

- Reprocessing includes fluorination, distillation to separate uranium and other FPs from fluoride salts

- Typical simulated fluoride wastes (mol%)
  - 18.8LiF-23.8NaF-57KF-0.1MgF_2-0.3PF(SrF_2-SrF-CeF_3)
  - 8.4CsF-8.3SrF_2-37.8SmF_3-29.7ZrF_4-15.8CeF_4

FeBP glass immobilization of fluorides



XRD patterns of FeBP glasses

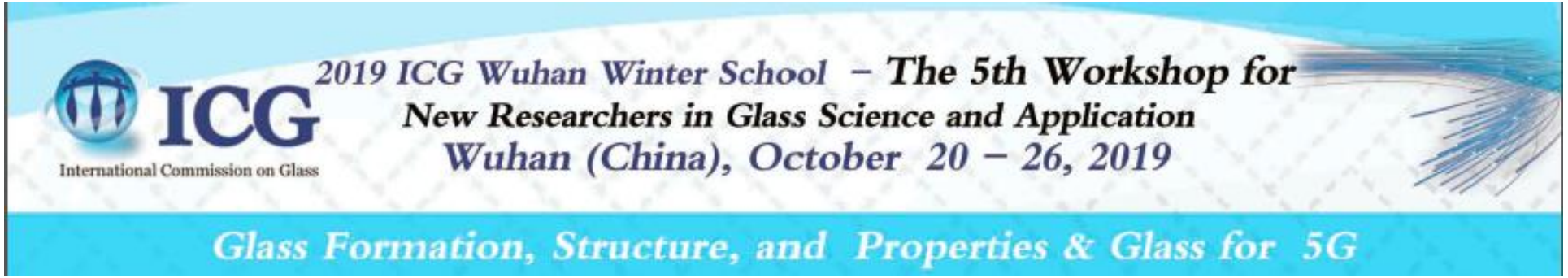
- Monazite formed when CeF_3 ≥20 wt%.
- No crystallization when SrF_2 =30 wt%.

Y. Qiao *et al*., (2016).

Summary

- R&D of China nuclear waste vitrification started at the early 1980s, and revived at the end of 2010s
- R&D programme mainly includes:
  - The process of JHCM, CCIM, PTM
  - Waste glass formulation
  - Glass-ceramics, FeP glass
  - Radiation effects on glass
- R&D of nuclear waste vitrification in China is highly needed

ICG Wuhan Winter School



Proposing to have a glass corrosion school in 2020 (2021?)

- **Financial support available for international students**
- **Homepage of ICG: http://www.icglass.org/**