

Partitioning and Conditioning Options Based on Chinese High-Level

Liquid Waste Full Partitioning Process- 11440

Xuegang LIU*, Jingming XU*, Jing CHEN*, Jianchen WANG*,
Jin CHEN*, and Shaowei LI*
Institute of Nuclear and New Energy Technology,
Tsinghua University, Beijing, China 102201

ABSTRACT

China has decided to construct a large-scale spent fuel(SF) reprocessing plant in about 2020 and fulfill closed nuclear fuel cycle. High level liquid waste(HLLW) is generated as a by product of SF reprocessing, and its management is of great concern. Though vitrification is maturely employed in commercial reprocessing plants, HLLW partitioning is considered as a significant advancement in future reprocessing and promising to be in commission in China's reprocessing plant.

A HLLW partitioning process, so called TRPO process, was proposed in early 1980s and has been in continuous study for thirty years. The most significant milestones in the history of research, development and demonstration on TRPO full partitioning process has been introduced in this paper. All results confirm that the process is effective and feasible to partition minor actinides(MA), Sr and Cs from HLLW.

Considering the flexibility of the process and practical separation demands, partitioning and conditioning (P&C) scheme should be determined prior to further work. The process includes feed adjustment in front end, extractive separations and waste conditioning. The most possible four P&C options are introduced in the paper, including process description, material flow calculation and waste forms. In the view of waste reduction, the above four options are discussed.

INTRODUCTION

China has set the guideline to boost the construction of nuclear power plant and fulfill closed fuel cycle. The first commercial spent fuel reprocessing plant is expected to finish construction in around 2020-2025 with the capacity of 800 tU/a. At a rough estimation, annual generation of High Level Liquid Waste(HLLW) is about 5,000 cubic meters. The management of HLLW released from reprocessing process(PUREX process) is of great concern. Though vitrification is the internationally recognized standard to minimize the environmental impact resulting from HLLW,

much effort has been put into the implement of HLLW partitioning in China, and partitioning is considered as the pith of the new generation of spent fuel reprocessing. Much effort has been taken to attach partitioning process with PUREX process.

RESEARCH ON TRPO FULL PARTITIONING PROCESS

In the early 1980s, Trialkyl phosphine oxide (TRPO) was found to have good extractive performance for U, Pu and An(III) in acidic media. A partitioning process, so-called TRPO process, was proposed by ZHU[1] with the extractant of TRPO/kerosene to remove actinides from HLLW. Based on the separative performance of TRPO, two additional processes were introduced consecutively to remove strontium and cesium respectively from the raffinate of TRPO extraction, becoming “TRPO Full Partitioning Process”. In the next thirty years, the full partitioning process has been under continuous and systematic study, including chemical properties, extractive behaviors, equipment developments and hot tests[2-5].

In the full partitioning process, TRPO/OK is used to extract U, Pu and minor actinides (MA) (Np, Am, Cm) from HLLW. Then dicyclohexano-18-crown-6 (DCH18C6)/n-octanol is to extract strontium from the raffinate. Cesium is removed by adsorption or extraction from the raffinate of Sr extraction. The process diagram of the full partitioning process is shown in Fig. I.

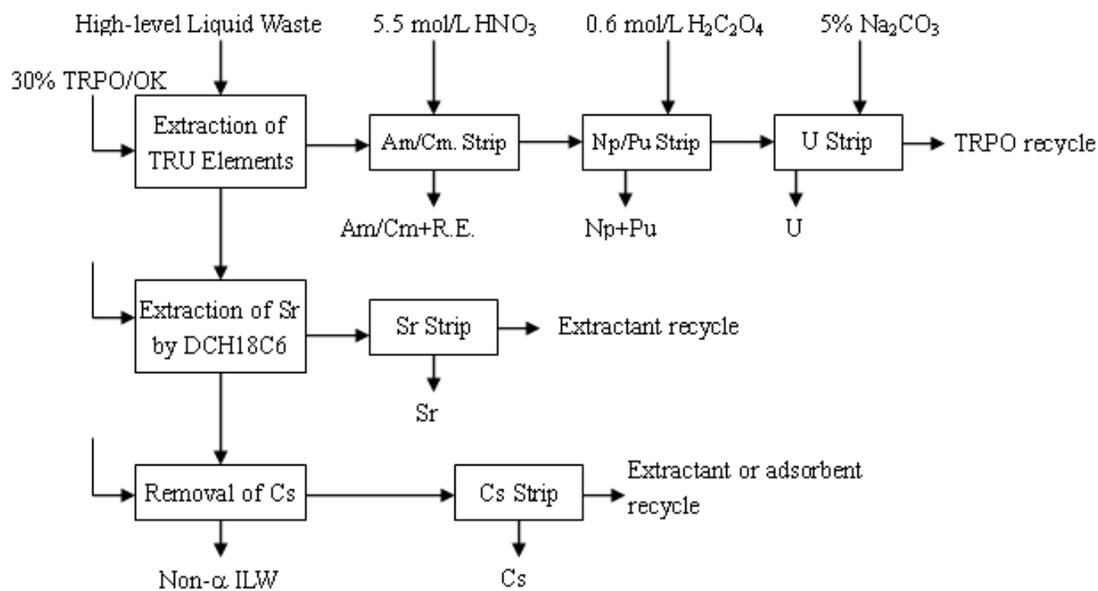


Fig.I The diagram of the full partitioning process

- Hot tests of the process were conducted in 1988-1989 and 1992-1993 in hot cells of ITU with the genuine HLLW generated from PWR spent fuel (~33GWd/tU) reprocessing[6]. The results demonstrated high separative performance of TRPO/OK for U, Pu and An(III).
- Full partitioning process with the removal of Sr by DCH18C6 and Cs by potassium titanium

hexacyanoferrate (KTiFC) adsorption was carried out in 1996 in hot cells of INET, Tsinghua University, China. Instead of power HLLW, the feed in this test was genuine Chinese defence HLLW with high salinity[7]. The results meant full partitioning process is feasible to treat Chinese defence HLLW arising in 1960s.

- And then the partitioning of defence HLLW was in progress, both in technology research and equipment development. In 2005, a pilot test facility was finished construction aiming to testify the full partitioning process with key equipments, including extractive columns and $\phi 70$ centrifugal contactors. Three consecutive separative units were employed to consecutively separate MA, Sr and Cs by means of TRPO/OK, DCH18C6/n-octanol and KTiFC respectively. Except for Cs separation unit, all equipments were in good conditions in the scheduled twice consecutive runs(>72 h in each) and got satisfied separation results[8].
- To improve the performance of full partitioning process, the adsorption of Cs was replaced by 25,27-Bis(2-Propyloxy) Calix[4]-26,28-Crown-6 (iPr-C[4]C-6)/n-octanol extraction. After a series of R&D work, a >120h's consecutive hot test was conducted in 2009. The exciting experimental results make us confident in the full partitioning process and consider it as the recommended process to treat Chinese defence HLLW.

The summary of above research activities are shown in Table I.

Table I Summary of key research activities on Chinese partitioning process

		Hot test 1	Hot test 2	Pilot test	Hot test 3
Year		1992	1996	2005	2009
Feed		Genuine HLW from WAK	Genuine Chinese defence HLLW	Simulated defence HLLW	Genuine Chinese defence HLLW
Total feed Volume		~ dozens of ml	~ 130 ml	~ 15 m ³	~4 L
Running period		~ 3 h	~ 6 h	2*72 h	~ 160 h
Performance	SF _U	>700	~10E4	>3000	>3000
	SF _{Pu}	>950	695	>1000 ^a	>1500
	SF _{Am}	>3200	666	>500 ^a	>4000
	SF _{Sr}	unimplemented	>2500	~250	>10E4
	SF _{Cs}	unimplemented	>200	-- ^b	>10E4

a: Pu and Am was represented by Zr and Nd respectively.

b: The result was unreachable.

In 30 years of research, the full partitioning process has proven to be promising for the treatment

of HLLW. Technically, it is feasible to separate MAs, Sr and Cs from HLLW one by one. But the full partitioning process attached with commercial reprocessing process is and should be quite different from the one to treat defence HLLW. Because much more concerns focus on the economic issue and secondary waste of partitioning. As a waste treatment procedure, partitioning process has to meet the demand of higher economy and as less waste as possible. In order to boost the implement of partitioning process attached with commercial reprocessing process, a series of researches on process simplification and waste management have been conducted, including lanthanides(III)/actinides(III) separation[9,10,11], co-extraction of Sr/Cs from TRPO raffinate[12] and HLLW concentration/denitration.

This paper is trying to discuss the HLLW partitioning and conditioning (P&C) options on the basis of experimental results and find out their benefits. It will help us to determine the most feasible process for further R&D. Though all the discussions are on the basis of experiments, technical details will not be elaborated. Due to the high radiation and radiotoxicity, high level waste and/or TRU (α emitting) waste are focuses of our attention. Neither ordinary low/intermediate waste nor secondary waste will be involved in this paper. Economical issues are excluded.

TRPO FULL PARTITIONING PROCESS AND REGARDING P&C OPTIONS

Front end: denitration and concentration

To meet the demand of TRPO/OK extraction, the acidity of feed should be 1.0-1.2 mol/L HNO_3 . Considering that the typical acidity of 1AW generated from PUREX process is 2-3 mol/L, a front end process is necessary to modify the HLLW. Highly active liquid waste concentration using the formaldehyde denitration process is widely used in current reprocessing plants in France and Japan[13], so denitration/concentration is introduced as the front end treatment process. HLLW concentration process is also helpful to reduce the volume of HLLW, which results in the reduction of partitioning facility scales and secondary waste generation.

The majority of HLLW is arising from PUREX U/Pu coextraction cycle(1AW raffinate, whose composition can be calculated by ORIGEN 2 and PUREX parameters). Waste solution from hull wash and purification cycle also flows to HLLW tank. Some elemental concentrations in HLLW, such as K, Mn and Na increase due to the addition of technical agents in PUREX. Furthermore, it is recognized that precipitates occur during denitration/concentration process and later concentrated HLLW interim storage. Experimental results show that most Zr and Mo will precipitate before extraction. Taking all the above factors into consideration, the front end treatment of HLLW includes 1AW denitration/concentration, interim storage of concentrated HLLW and solids filtration.

The composition of feed solution(1AF) to TRPO partitioning process is depicted in Table II.

Table II The composition of feed to partitioning process

Average Burnup: 45 GWd/tU

Specific volume: 1600L/tU; [HNO₃]=1.0-1.2 mol/L

Component	Concentration /g·L ⁻¹
Ru+Rh+Pd	4.54
Tc	0.76
Zr	0.75 ^a
Mo	0.36 ^a
Sr+Cs	3.30
K	4.00 ^b
Na	14.00 ^b
RE+Y	10.85
U	1.45
TRU	1.39
Others	8.22 ^b
Total	49.63

a: With the assumption that 80% of Zr and 90% of Mo precipitates into sludge

b: Besides their existence in spent fuel, more K, Na and Mn are from their addition in PUREX process.

Partitioning Options

The full partitioning process was proven to be technically feasible into several ways. Here, four partitioning options are addressed as following:

- Option 1: Direct vitrification of entire HLLW (reference option)

This option has no difference from current vitrification process widely employed in commercial reprocessing plants[13]. In this option, HLLW is directly sent into vitrification process after concentration/denitration/storage, together with all precipitates generated during these processes. All components in original HLLW will be solidified into glass.

- Option 2: Partitioning process with only TRPO extractive cycle to remove MAs from strong radioactive Sr/Cs stream.

Only one extraction cycle by TRPO/OK is implemented in this option. The 1AF is extracted with TRPO/OK. U, Pu, An(III)+RE(III), Tc, Zr and most Mo in feed solution are loaded into organic phase. By fractional back extractions, all extracted components in organic phase are divided into three streams: (1) all Am/Cm, REs and ~75% of Tc are stripped with 5.5 mol/L HNO₃; (2)all Np/Pu, Zr and most Mo are stripped with oxalic acid; (3)U with part of Tc is stripped with carbonate. The TRPO/OK extraction and back extraction scheme is similar to that in Fig. I.

The raffinate of TRPO extraction are composed of all high radioactive Sr+Cs and other fission products. This stream will be conditioned as final waste without further separation.

- Option 3: Option 2 attached with separation of Sr and Cs

Option 3 is on the basis of Option 2 with an additional extraction cycle for Cs and Sr. Instead of Sr and Cs separation one by one, coextraction process for Cs/Sr has been developed. All Sr+Cs are recovered from the raffinate of TRPO extraction. Due to the similar extractive properties, about half of K, Rb and ~30% of Ba in raffinate are also extracted into organic phase and stripped into Sr+Cs product stream. Liquid waste free of Sr and Cs belongs to ILW.

- Option 4: Option 2 attached with separation of lanthanides(Lns) from minor actinides (Ans) (mainly Am and Cm)

Option 4 is another derived process based on Option 2. An extraction process with bis-(2, 4, 4-trimethylpentyl) dithiophosphonic acid (HBTMPDTP), which is purified from the commercial product Cyanex 301 is implemented to treat the back extraction stream containing Am/Cm and RE. Trivalent Am/Cm can be separated from rare earth elements. Option 4 also has two extraction cycles, TRPO and Cyanex301. Similar to Option 2, the raffinate from TRPO extraction will be conditioned without any separation.

Waste Conditioning

Each partitioning option is associated with different waste conditioning options. For example, the α -emitting waste stream can be vitrified or temporary stored in the form of oxide. In this paper, the discussions only focus on four types of waste:

(1) **High-level TRU waste**, for example, the glass produced by direct vitrification of the entire HLLW. Vitrification is the only way to condition high-level TRU waste because of its high radiation and permanent hazard. The loading capacity of waste oxides in glass is considered as 20% w/w for oxides.

(2) **High-level waste**. It has strong radiation mainly from Sr and Cs, but free of TRU elements. Vitrification process is implemented to condition high-level waste. Because there is no TRU elements solidified in the glass, the isolation time of waste glass is required no more than 1,000a. The loading capacity of waste oxides is also assumed as 20% w/w for oxides.

(3) **Low or intermediate level TRU waste**. It contains TRU elements, but scarcely Sr or Cs. Pu/Np back extraction stream, Am/Cm streams with or without RE are regarded as this type of waste. In this paper, it is recommended to condition this waste in the form of oxides because TRU oxides has low heat generation, stable chemical properties and if necessary, easy to vitrify.

(4) **Low or intermediate level waste**. The waste containing scarce Sr, Cs and TRU elements belongs to this type of waste. Cementation is used to condition this waste with an average loading rate of 13% w/w for nitrates.

P&C MODEL AND MATERIAL FLOW ANALYSIS

Fig. II-a to Fig.II-d shows four P&C options considered in this study and associated material flows.

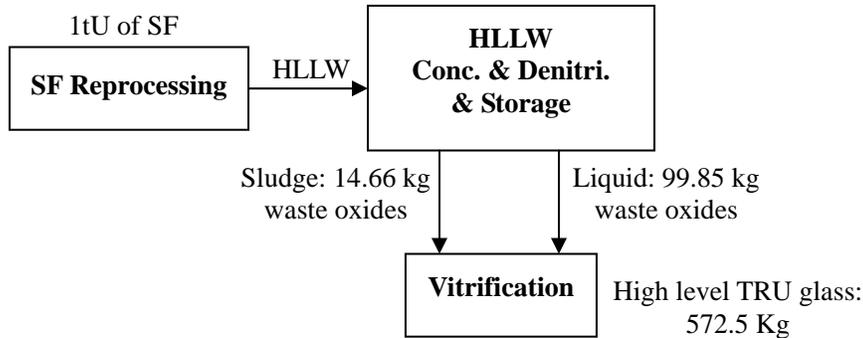


Fig. II-a P&C reference Option: Vitrification of entire HLLW

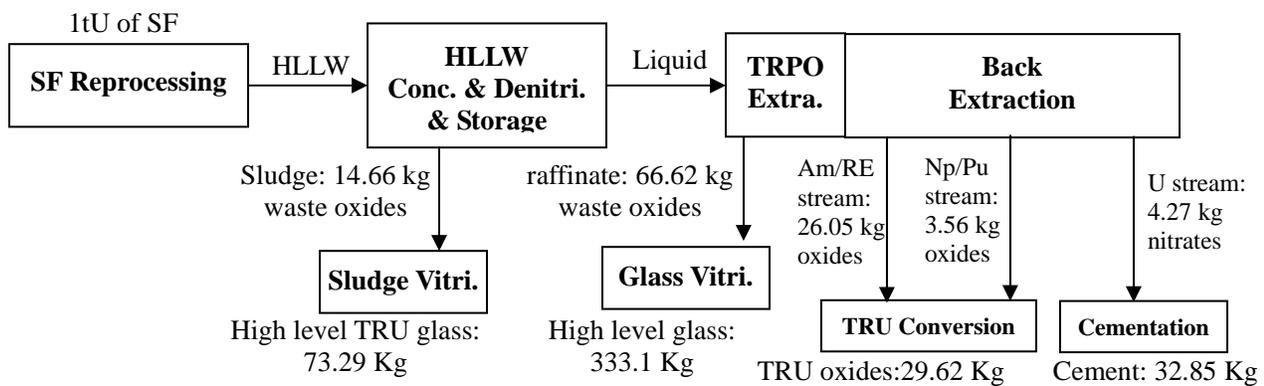


Fig. II-b P&C Option 2: TRU partitioning from HLLW

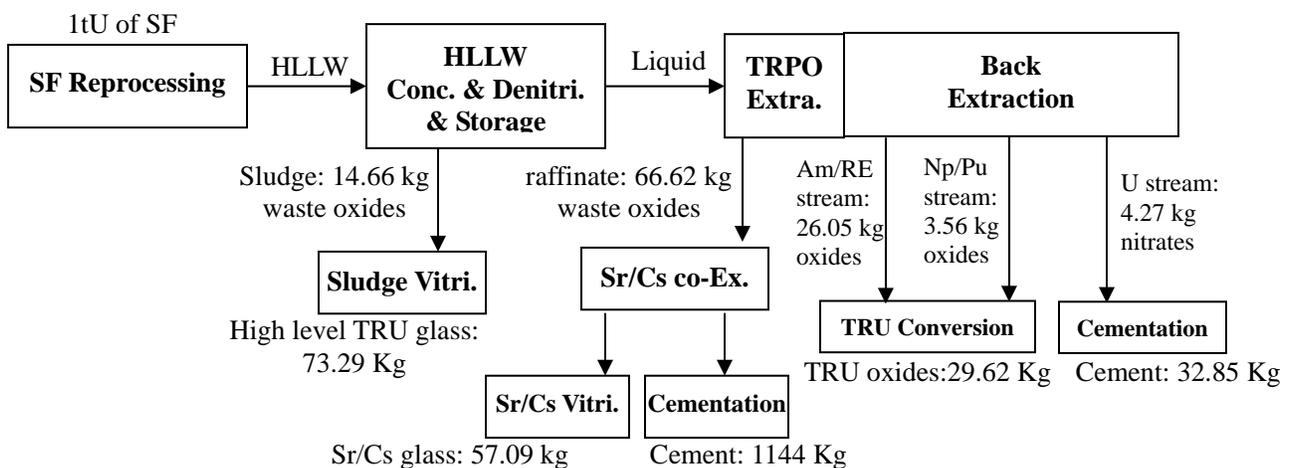


Fig. II-c P&C Option 3: TRU + Sr/Cs partitioning from waste

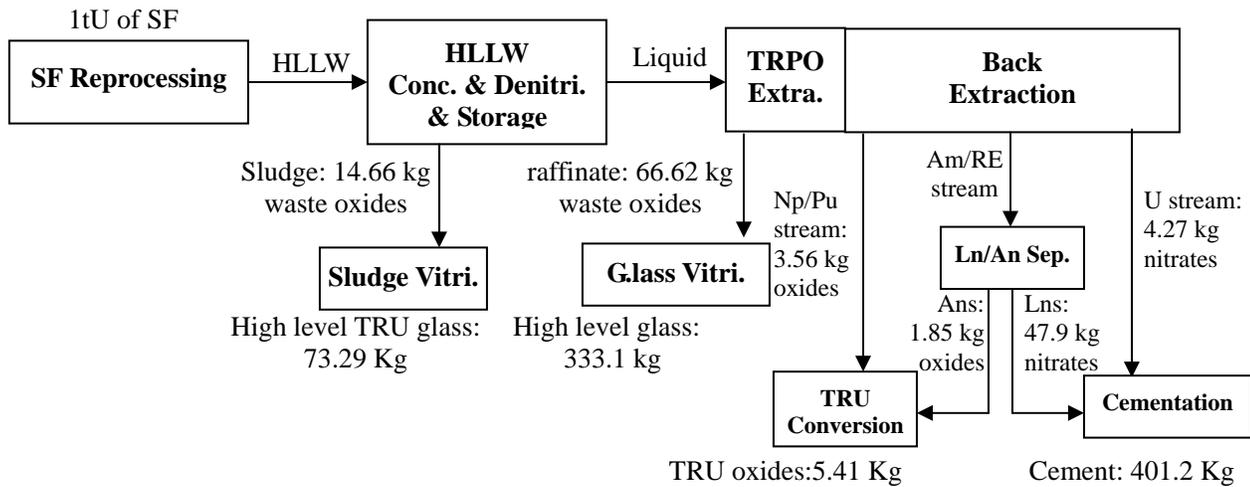


Fig. II-d P&C Option 4: TRU + Ln/An partitioning from waste

EVALUATION OF WASTE GENERATION

Reduction of high level glass

Table III shows the high level glass generations in each P&C options. The reduction rate is defined as the ratio of decreased glass mass to reference option. Comparing with other options, option 3 (TRU and Sr/Cs partitioning) generates the least amount of glass, including 73.29 kg of TRU glass resulting from sludge vitrification and 56.7 kg Sr/Cs glass. The benefit of glass reduction is mainly from Sr/Cs partitioning from other salinity components. However, the calculation is on the assumption that the loading capacity of “pure” Sr/Cs oxides in glass is as same as other low thermal emitting oxides. Even if the high loading of Sr/Cs had no negative impact on the properties of immobilization matrix, the extremely high thermal release would require more disposal space and ventilation. It will decrease the benefit from Sr/Cs partitioning, and for its industrial employment, tremendous efforts are required to develop new type of Sr/Cs glass formulation, safety containers of condition, transportation and disposal and etc.

It should also be mentioned that in all options, except for the reference one, high level glass includes 73.29kg TRU glass and α -free high level (HL) glass. The α -free glass is required much shorter isolation time and is more favorable in longer time scale. It might be stored/conditioned in near surface instead of deep geological disposal. The management of α -free glass is similar to current vitrified HLLW glass in industrial vitrification facilities, which lasted for several years. The near surface storage of α -free glass has opened new perspectives for high level waste management, and enabled us to reconsider the benefit and expense of Sr/Cs separation. Because vitrification and management of glass with much higher Sr/Cs ratio present more challenges, the

value of Sr/Cs separation is limited. Therefore, Options without Sr/Cs separation (Option 2 or 4) will be more feasible to be employed in China's reprocessing plant in 2020s.

Table III High level glass generations and reduction rates

	Glass weight /kg·tSF ⁻¹	comments	Reduction rate
Option 1 (Reference option): Vitri. Of entire HLLW	572.5	TRU glass	--
Option 2: TRU partitioning with TRPO process	406.4	73.29 kg TRU glass 333.1 kg HL glass	29.0%
Option 3: TRU and Sr/Cs partitioning	130.4	73.29 kg TRU glass 56.7 kg Sr/Cs glass	77.2%
Option 4: TRU and Ln/An partitioning	406.4	73.29 kg TRU glass 333.1 kg HL glass	29.0%

Reduction of α waste

Table IV shows α waste generations in each P&C options. The reduction rate is defined as the ratio of decreased α waste to α waste generated in reference option. The similar reduction rates in three partitioning options also reflect that the TRPO extraction cycle provides high efficiency for α nuclides selection from HLLW.

Thanks to Ln/An partitioning, option 4 has the least α waste generation among four options. Due to the existence of 73.3 kg of TRU glass, the partitioning of Ln/An improves the reduction rate little though the Ln/An partitioning process performs effective to decrease TRU oxides from 29.6 kg to 5.4kg. Therefore, options without Ln/An partitioning will be more favored for industrial application.

Table IV α waste generation and reduction rates in four P&C options

	α waste /kg·tSF ⁻¹	comments	Reduction rate
Option 1 (Reference option): Vitri. Of entire HLLW	572.5		--
Option 2: TRU partitioning with TRPO process	102.9	73.3kg TRU glass and 29.6 kg oxides	82.0%
Option 3: TRU and Sr/Cs partitioning	102.9	73.3kg TRU glass and 29.6 kg oxides	82.0%
Option 4: TRU and Ln/An partitioning	78.7	73.3kg TRU glass and 5.4 kg oxides	86.3%

CONCLUSION

Since 1980s, Chinese full partitioning process has been under continuous and systematic study, including chemical properties, extractive behaviors, equipment developments and hot tests. The most important four milestones in the history of full partitioning process development are introduced. The successful research activities proved the feasibility to implement in partitioning HLLW released from commercial reprocessing plant in the near future.

Because the full partitioning process exhibits high flexibility in waste partitioning, it is necessary to clear and determine the most promising partitioning and conditioning scheme among all options. Four P&C options were analyzed.

- The front end treatment (concentration/denitration/storage) has obvious impact on the final waste. Because solids occur during the process and it will be conditioned as high level TRU glass, which is the most undesirable waste form.
- Sr/Cs partitioning process gives great contribution for volume reduction of vitrified glass at the price of increased heat generation in glass and more space and ventilation. If α -free high level waste can be stored in near surface, the separation of Sr/Cs from other α -free components will have less value.
- TRPO partitioning process has high efficiency to reduce α waste. The later Ln/An separation by CYANEX 301 decreases the long lived α oxide waste further to $\sim 1/5$. Due to the existence of high level TRU solids in front end treatment, Ln/An separation brings little benefit to total α waste reduction.
- Taking all above factors into consideration, it is recommended that the implement of Chinese full partitioning process should focus on
 - a. partitioning with only TRPO extraction cycle into two major waste streams(long-lived TRUs/Lns stream and high level Sr/Cs/FPs stream). as depicted in Option 2 and
 - b. the management of precipitates arising during its front end.

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