Development of a Simple Reprocessing Process Using Selective Precipitant for Uranyl Ions

- Fundamental studies for evaluating the precipitant performance -

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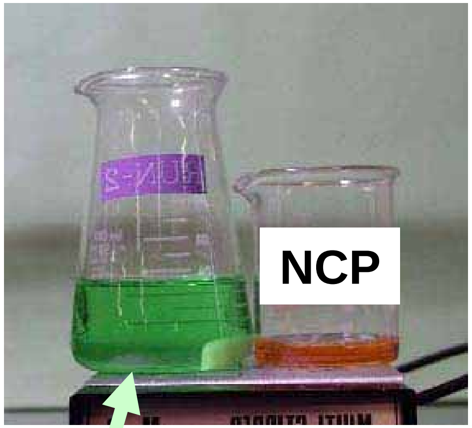
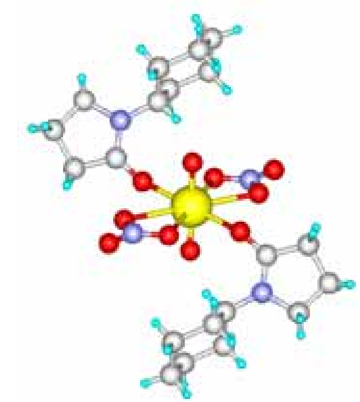
Background



UO_2^{2+} + FP in HNO_3

Precipitation

Rapidly

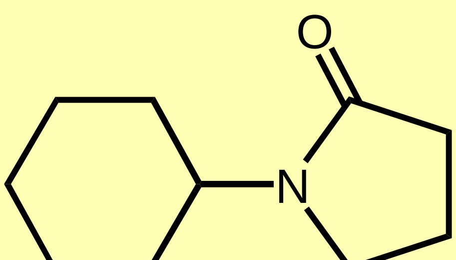


U-NCP precipitate
$UO_2(NO_3)_2(NCP)_2$

Filtration
Washing

Filterability : Good

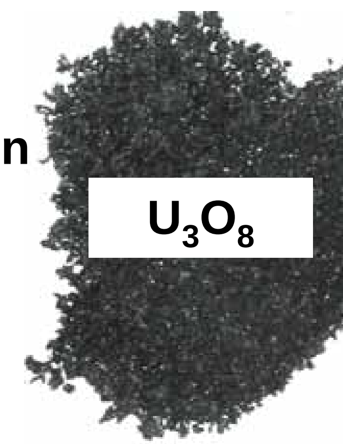
N-Cyclohexyl-2-Pyrrolidone



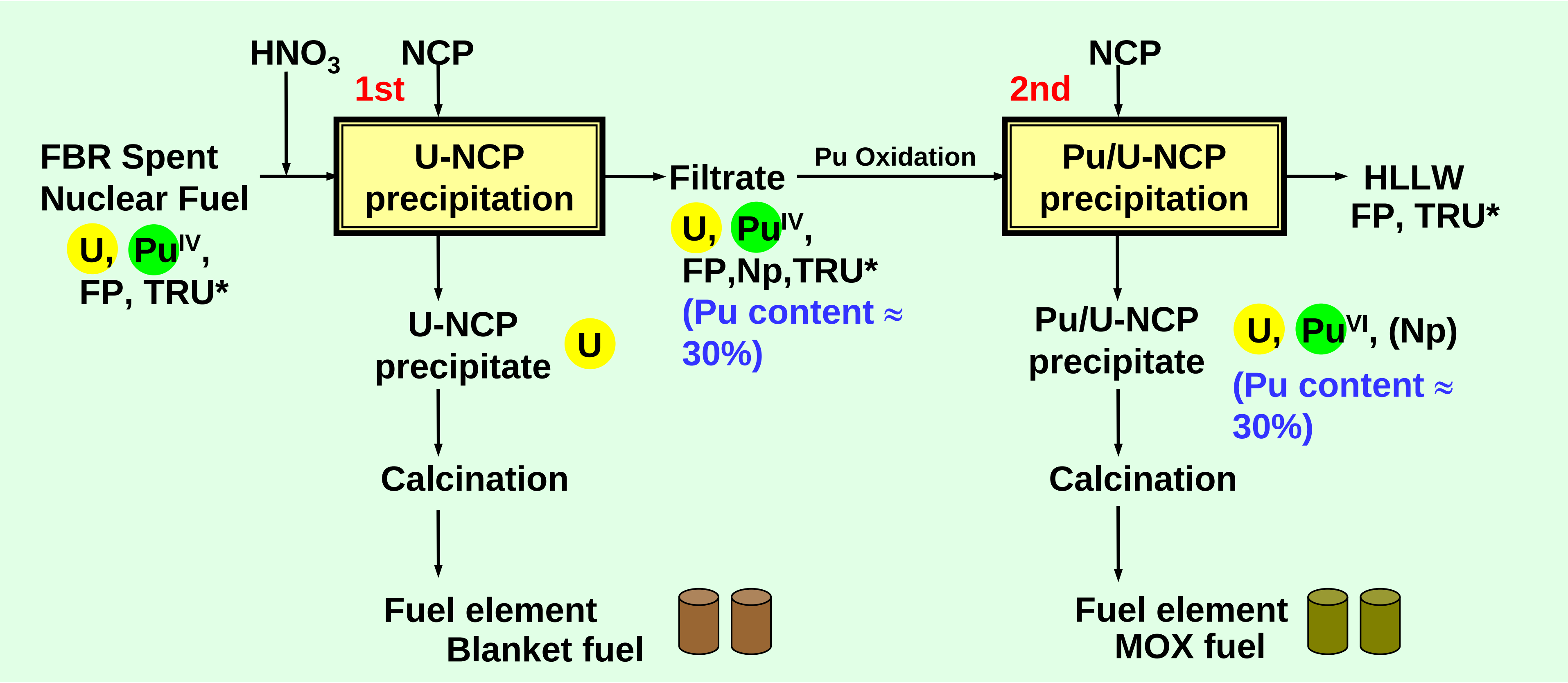
NCP consists of C, H, O, N.
Fully combustible

Calcination

800 ºC
2h



Flow Diagram of the Simple Reprocessing Process for FBR Spent Nuclear Fuels Using NCP.



Pu and U are precipitated together. **High nuclear proliferation resistance**

Whole process can be carried out in HNO_3 solution. **Simple and economical**

NCP consists of C, H, O, N (Fully combustible). **Reduce the amounts of HLLW**

Objectives

1. Investigation of selective precipitation by NCP

Precipitation test of U and Pu by NCP

Does NCP precipitate U(VI) and Pu(VI) in high yields?

Decontamination factors in this process

Does NCP precipitate fission products?

Examination of resistance to γ-ray radiation

Does NCP have sufficient resistance for precipitation?

2. Development of high-performance precipitants

Evaluation of the performances

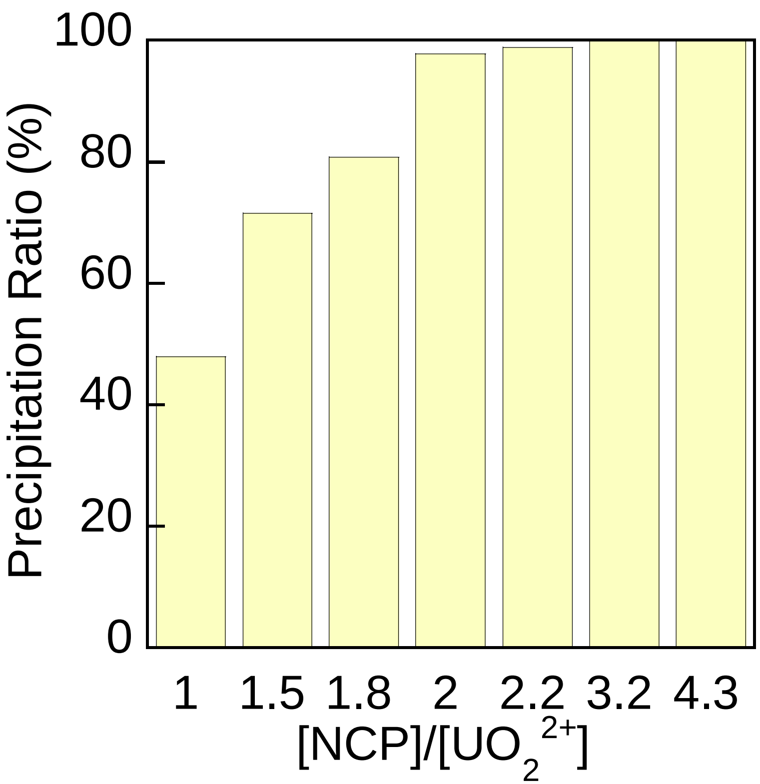
Precipitation ability

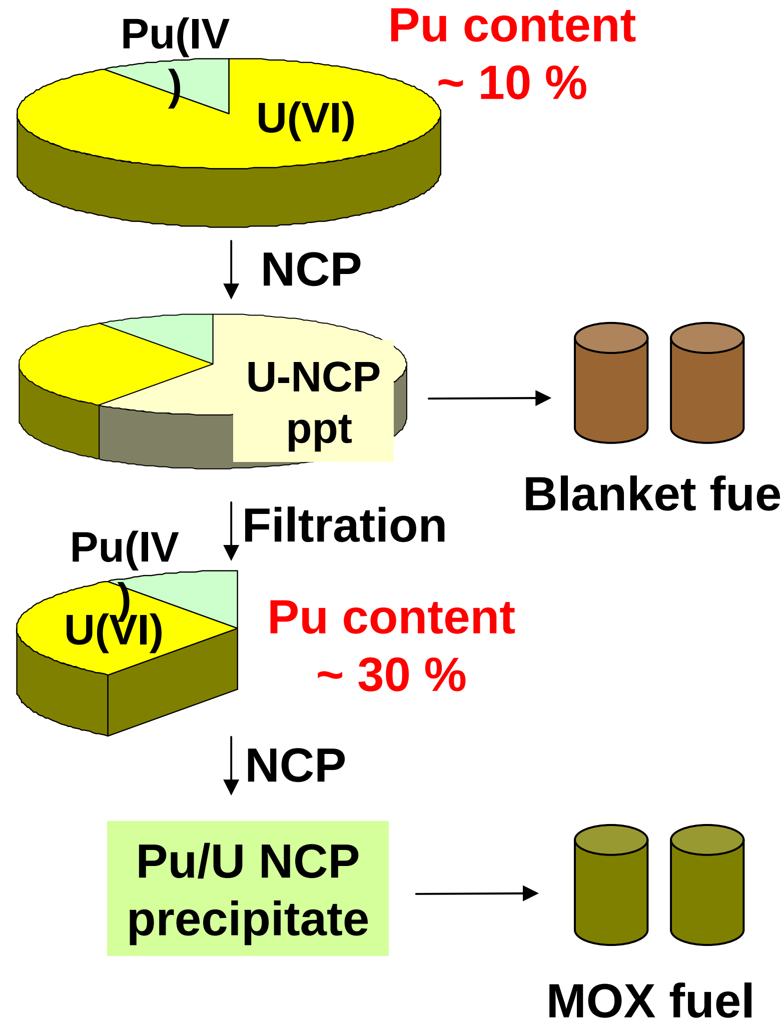
Decontamination factors

Resistance to γ-ray radiation (*N*-*n*-butyl-2-pyridone)

Precipitation Ratios of Uranyl Ion by NCP

1M UO_2^{2+} in 3 M HNO_3 at 25 °C



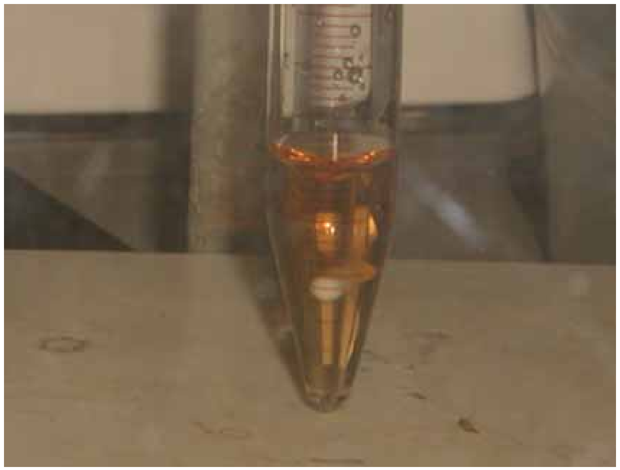


Precipitation ratios can be controlled by the amounts of NCP.

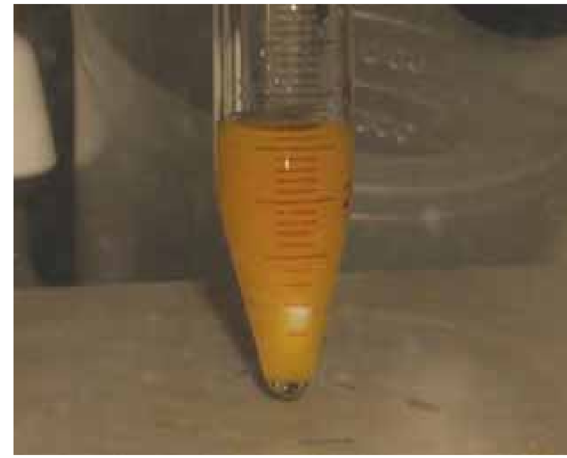
Pu contents can be readily adjusted.

Precipitation test of Pu(VI) by NCP

$[PuO_2^{2+}]$ = 40 mM in 1.5 M HNO_3
at room temperature

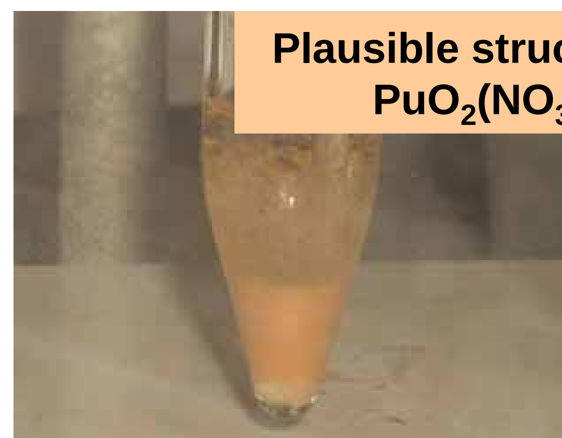


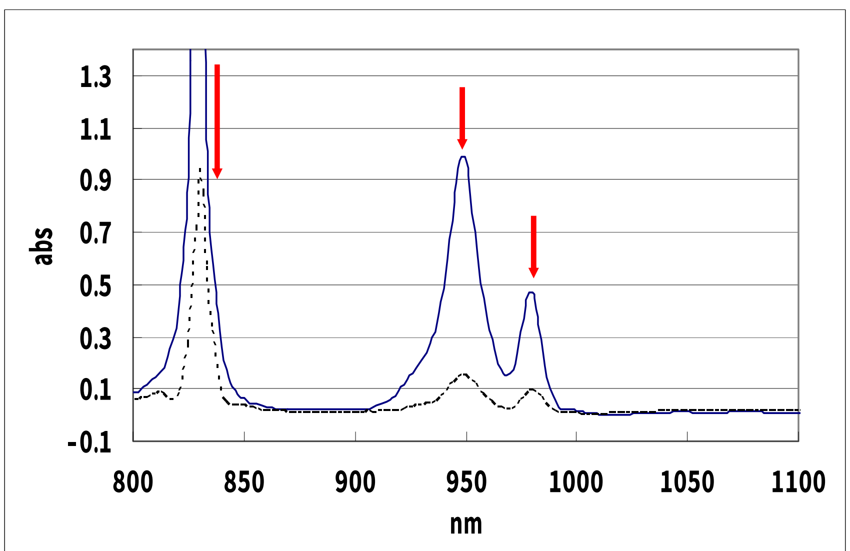
Added
0.40M NCP



After centrifuge

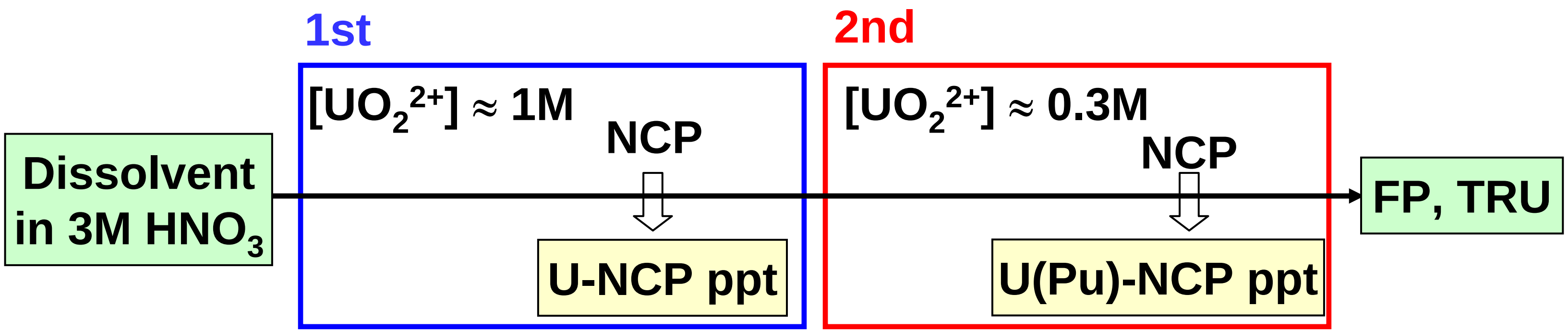
Plausible structural formula
$PuO_2(NO_3)_2(NCP)_2$





Precipitation ratio of Pu(VI) = 83 %

Decontamination factors in the Reprocessing Process by Using NCP



	Ba^{2+}	$RuNO^{3+}$	Ce^{3+}	Nd^{3+}	ZrO^{2+}	MoO_2^{2+}	ReO_4^-
DF (1M UO_2^{2+})	>100	>100	22	20	6	27	20
DF (0.3M UO_2^{2+})	>100	>100	>100	100	46	≈100	≈100

ReO_4^- was used as a simulated ion of TcO_4^-.

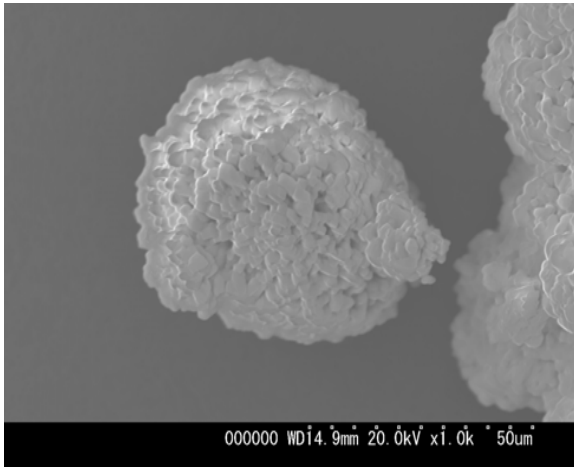
1st treatment (1M UO_2^{2+}) : DFs of Ba^{2+} and $RuNO^{3+}$ are more than 100.

2nd treatment (0.3M UO_2^{2+}) : DFs of most of FPs (except ZrO^{2+}) can be achieved >100.

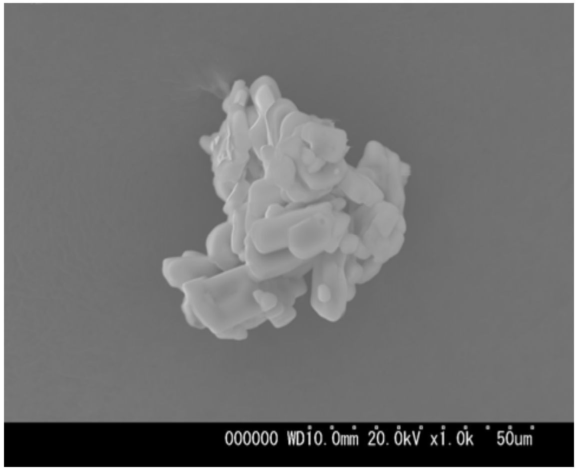
$$DF = \frac{[FP]_S/[UO_2^{2+}]_S}{[FP]_P/[UO_2^{2+}]_P}$$

$[FP]_S$, $[UO_2^{2+}]_S$: Concentrations of FP and UO_2^{2+} in treated solution
$[FP]_P$, $[UO_2^{2+}]_P$: Concentrations of FP and UO_2^{2+} in precipitate

SEM images of U-NCP precipitate (× 1000)



1 M UO_2^{2+}



0.3 M UO_2^{2+}

	Ba^{2+}	$RuNO^{3+}$	Ce^{3+}	Nd^{3+}	ZrO^{2+}	MoO_2^{2+}	ReO_4^-
DF (1M UO_2^{2+})	>100	>100	22	20	6	27	20
DF (0.3M UO_2^{2+})	>100	>100	>100	100	46	≈100	≈100

Rough surface condition

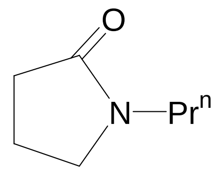
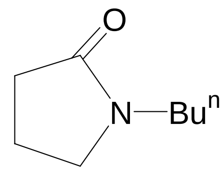
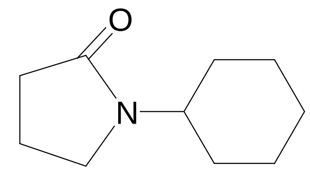
↓

Efficient washing of precipitate

↓

Higher DFs

Evaluation of Precipitants Capability (Precipitation ability for UO_2^{2+})

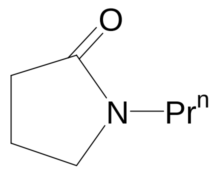
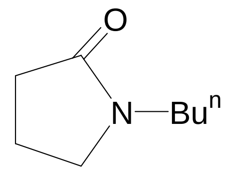
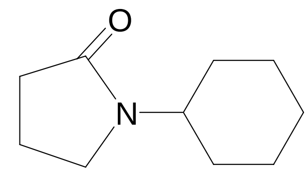
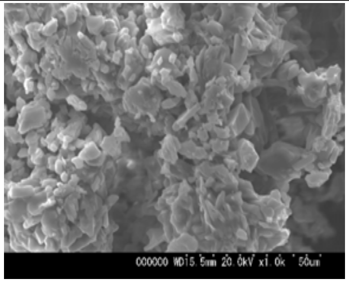
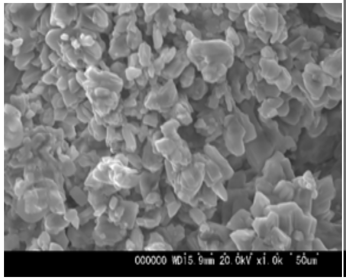
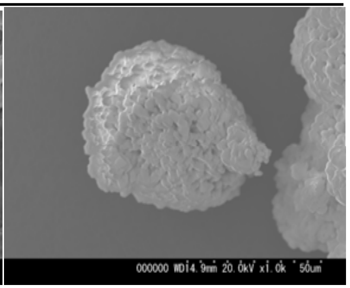
	NProP	NBP	NCP
			
log P [a]	0.88	1.37	2.16
Precipitation ratio of UO_2^{2+} ion [b]	58%	67%	73%

[a] Hydrophobicity (P = octanol/water partition coefficient of precipitant).
[b] Condition : [precipitant]/[UO_2^{2+}] = 1.5 in 3M HNO_3 at 25 ºC.

The precipitation abilities are high enough to adjust Pu contents.

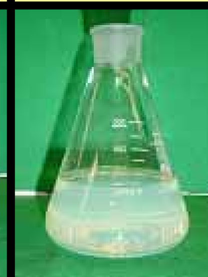
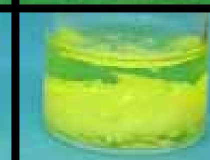
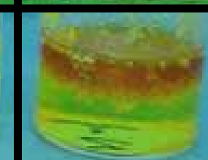
Decontamination factors?

Comparison of decontamination factors

Precipitant	NProP	NBP	NCP
			
log P_{cal}	0.88	1.37	2.16
Ba^{2+}	> 100	> 100	> 100
Ce^{3+}	> 100	> 100	22
Nd^{3+}	> 100	> 100	20
$RuNO^{3+}$	> 100	> 100	> 100
ZrO^{2+}	≈ 100	91	6
MoO_2^{2+}	> 100	≈ 100	27
ReO_4^-	> 100	16	20
SEM image ($\times$ 1000)			

Resistance of NCP to γ-ray Radiation

$$\text{NCP in 3M } HNO_3 \xrightarrow{^{60}Co\ \gamma\text{-ray}} \xrightarrow[([NCP]/[UO_2^{2+}] = 3)]{UO_2^{2+}} \text{U-NCP precipitate}$$

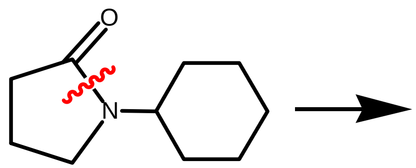
Irradiated dose	**0 Gy**	**100 kGy**	**200 kGy**	**1 MGy**	**3 MGy**
Appearance of NCP					
Appearance of ppt					
Precipitation ratio*	**99.9** %	**99.9** %	**44.3** %	**22.1** %	**10.9** %

NCP has sufficient resistance to γ-ray (>>3.3 kGy).

γ-ray radiation order in NCP precipitation

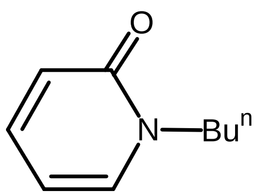
~ 3.3 kGy (6.5 kGy/h $\times$ 30 min)

Decomposition of NCP by γ-ray radiation

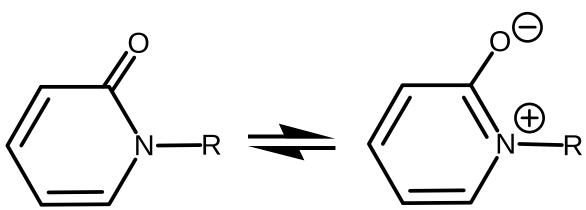


Decomposition

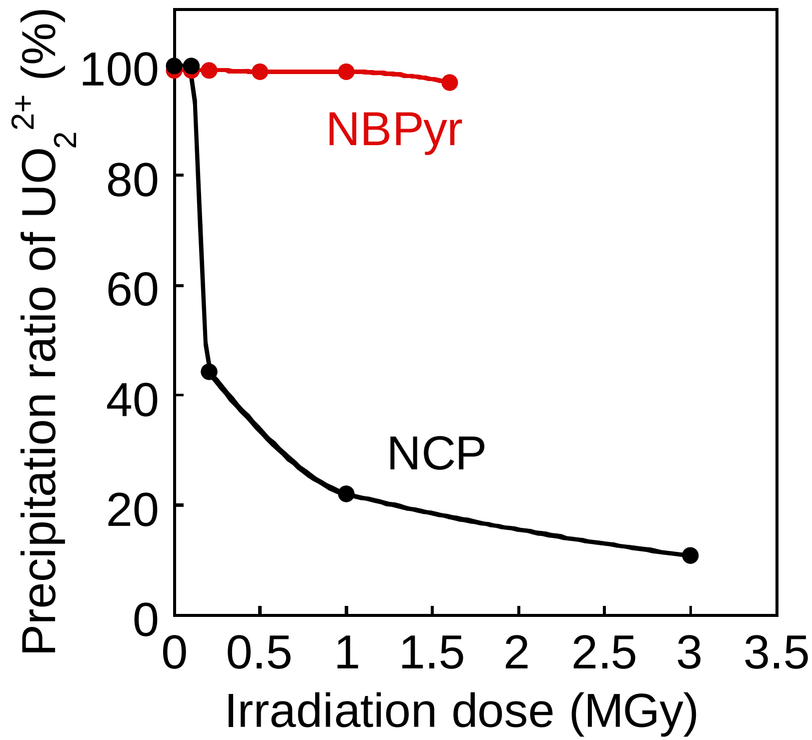
NCP



NBPyr (*N*-*n*-butyl-2-pyridone)



Pyridone derivatives would have higher resistance to γ-ray radiation.



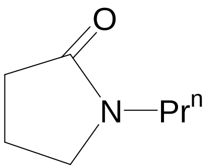
Conclusion

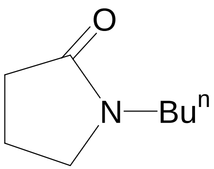
It was confirmed that NCP is applicable to our proposed reprocessing process for FBR spent fuels.

Fundamental studies ⇄ Engineering studies

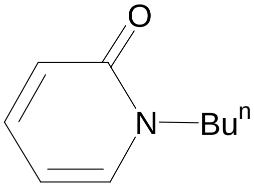
The performances of alternative precipitants were examined.

Lower hydrophobic precipitants such as NProP and NBP give higher DFs.





NBPyr has higher resistance to γ-ray radiation, which could reduce the cost for reprocessing.

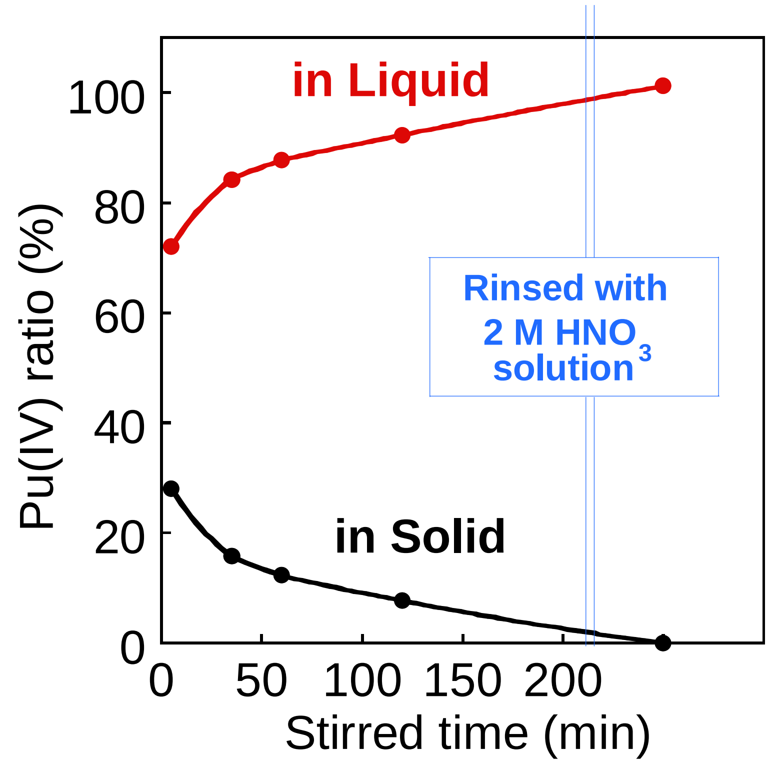


Our reprocessing process is flexible.

Precipitation test of Pu(IV) with U(VI) by NCP

U : 0.67 M
Pu: 0.06 M
in 2 M HNO_3

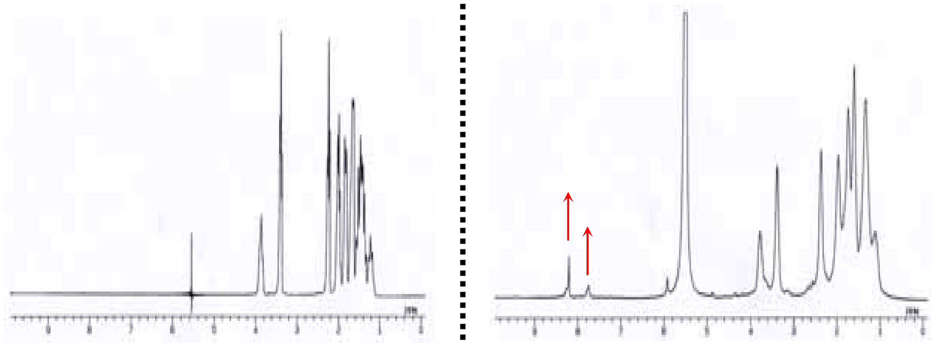
NCP
(1.4 mol/mol U)



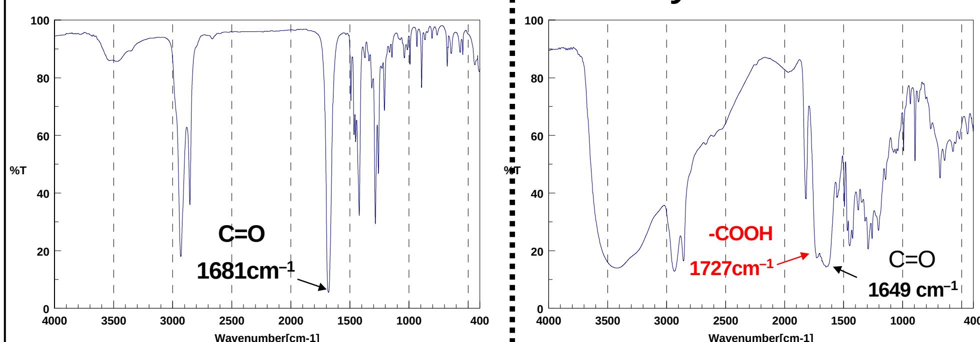
Possible Mechanism of NCP Decomposition

^{1}H NMR spectra

- Peaks became broadening.
- Peaks appeared in lower fields

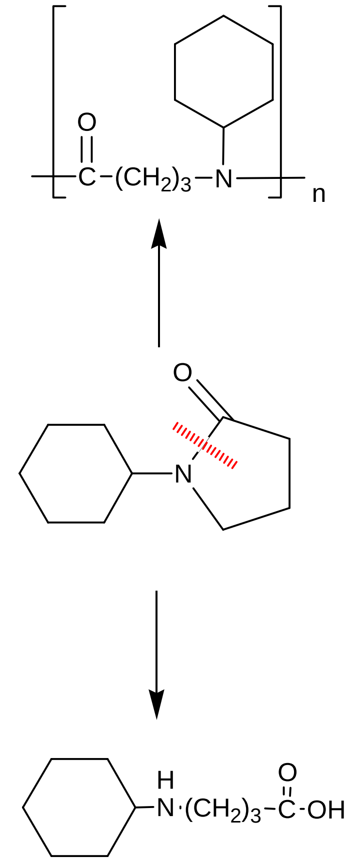


non-irradiated NCP 3 MGy irradiated NCP

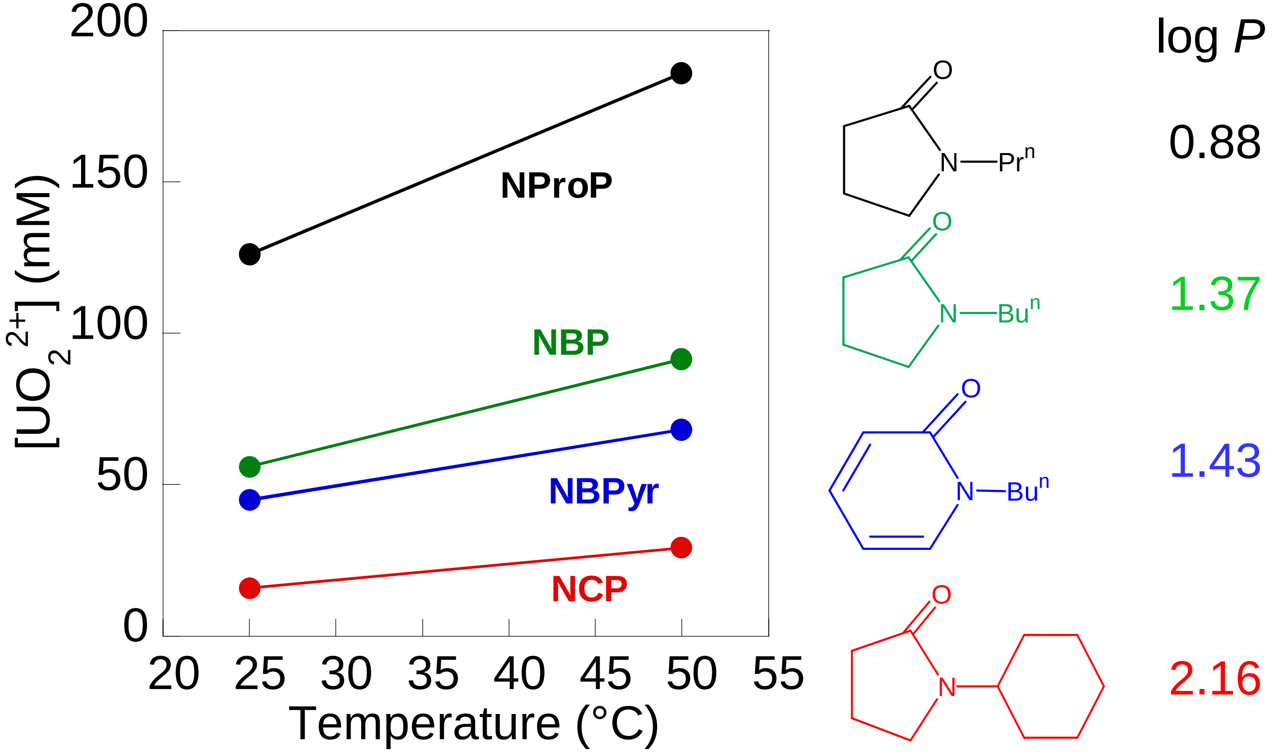


IR Spectra

The peak at 1727 cm^{-1} could be assigned to carboxyl group.



Solubility of uranyl precipitant in nitric acid solutio



A precipitant with higher precipitation ability (lower solubility) and higher decontamination ability would solve the problems.

Resistance of NCP to Radiation

$$\text{NCP} \xrightarrow{\alpha\text{- and } \gamma\text{-rays radiation}} \text{Decompose?}$$

Spent Nuclear Fuel of FBR

γ-ray radiation dose ~ 6.5 kGy/h

⇩

Retention time for precipitation (~30 min)

⇩

γ-ray radiation order in NCP precipitation ~ 3.3 kGy

U / Pu / FPs (γ-ray) → Precipitator (30 min) ← NCP

Precipitator (30 min) → Filtration → U/Pu-NCP ppt ; FPs (γ-ray)

Does NCP have enough Resistance under γ-ray radiation? (>3.3 kGy)

Precipitation Ratios of Uranyl Ion by NCP in nitric acid (3M)

$[UO_2^{2+}]$ (M)	*T* (°C)	$[NCP]/[UO_2^{2+}]$	Precipitation ratios (%)
0.3	25	2.1	96.0
0.3	25	3.1	99.3
0.3	25	4.2	99.8
0.3	50	2.1	89.9
0.3	50	3.1	98.6
0.3	50	4.2	99.5

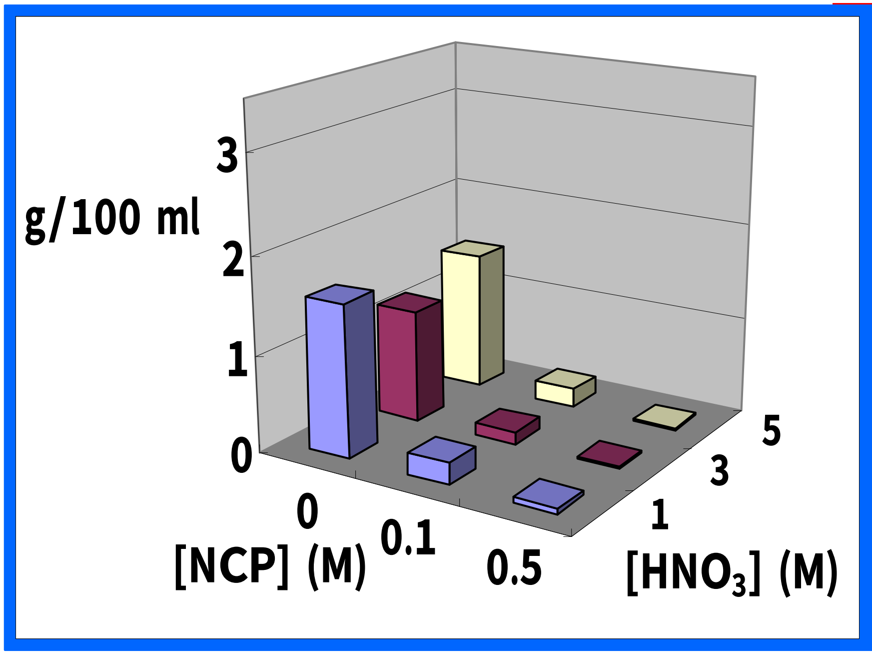
U(VI) can be recovered by NCP with high yield.

Precipitation ratios of UO_2^{2+} by NCP in 3M HNO_3

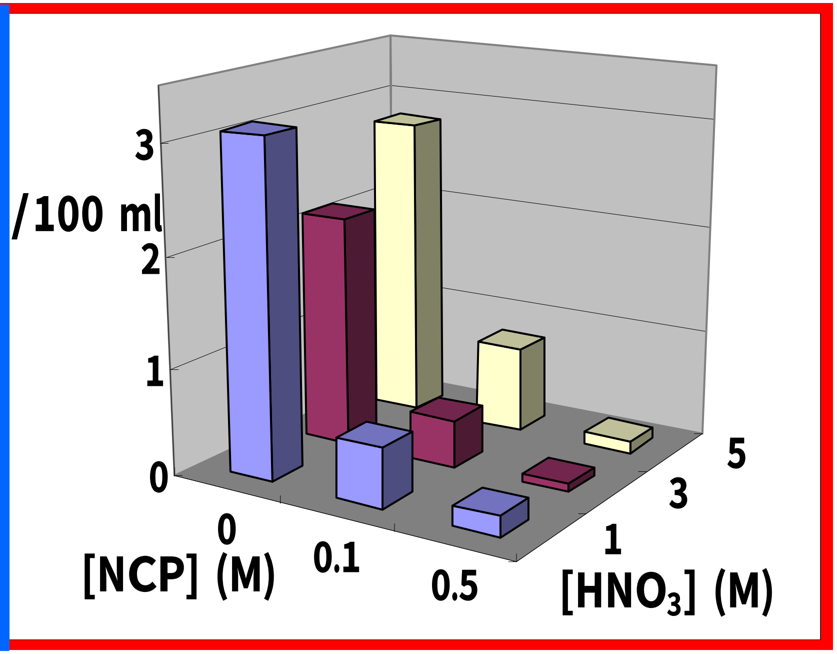
$[UO_2^{2+}]$ (M)	$[NCP]/[UO_2^{2+}]$	Precipitation ratio (%)
0.9	1.5	66.0
	1.8	80.7
	2.2	98.8
	3.2	99.9
0.3	2.1	96.3
	3.1	99.4
	4.2	99.8
	5.2	99.8
0.1	1.9	89.4
	2.8	97.5
	3.8	99.2

Solubility of $UO_2(NO_3)_2(NCP)_2$ precipitate

25°C

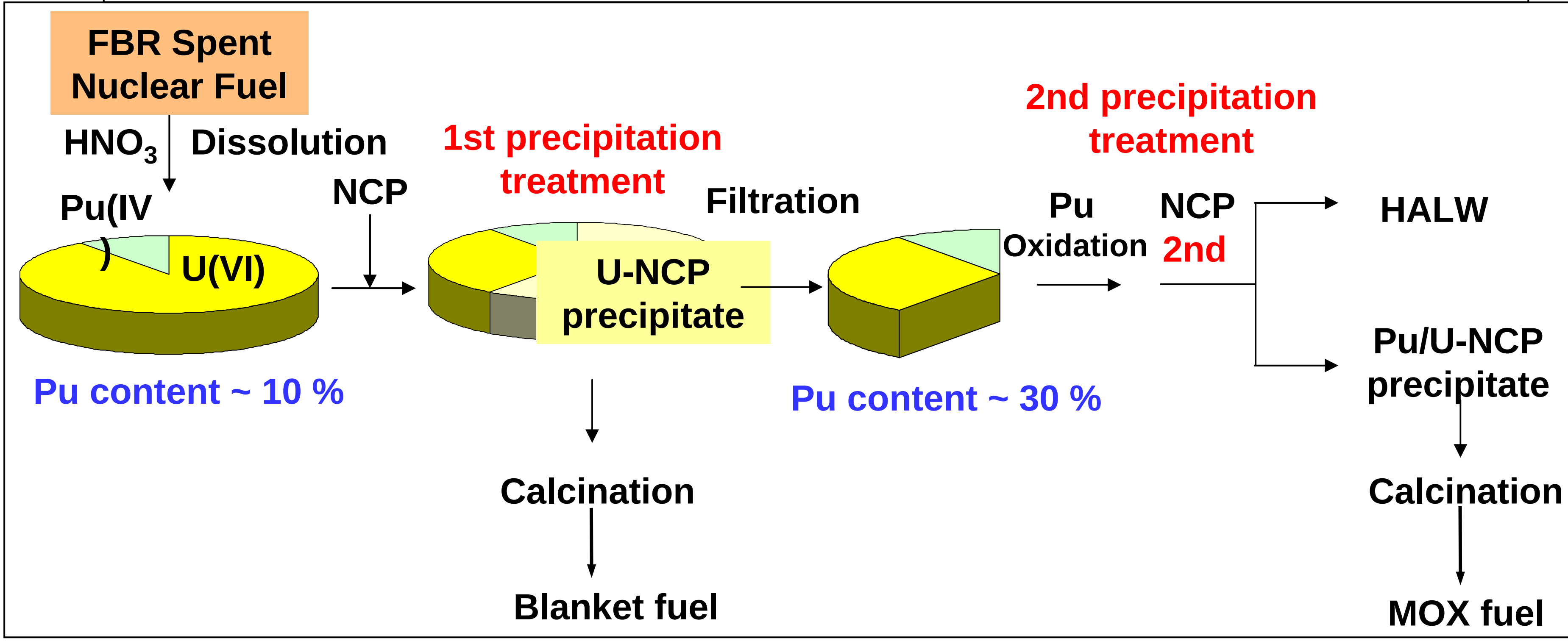


50°C



A Simple Reprocessing Process for Spent FBR Fuels Using NCP

Direct recovery of U and Pu mixture to satisfy a high Pu content in MOX fuel from nitric acid solution of spent nuclear fuels



Pu and U are precipitated together. → **High nuclear proliferation resistance**

Whole process is in HNO_3 solution. → **Simple and economical**

NCP consists of C, H, O, N. → **Fully combustible**