



Nuclear Process & Radio-Analytical Chemistry

Class Notes – Section 3.1

Bismuth Phosphate & REDOX Processes

Chung-King Liu



Major Plant Operating Periods

Fuel Reprocessing

T-Plant	1944 - 1956
B-Plant	1945 - 1952
REDOX	1952 - 1967
PUREX	1956 - 1972 and 1983 - 1988

Nuclear Materials Processing

Fuel Fabrication	1944 - 1987
Plutonium Finishing Plant	1949 -
U-Plant Uranium Recovery	1952 - 1957
UO₃ Plant	1952 - 1972 and 1984 - 1993



Major Plant Operating Periods

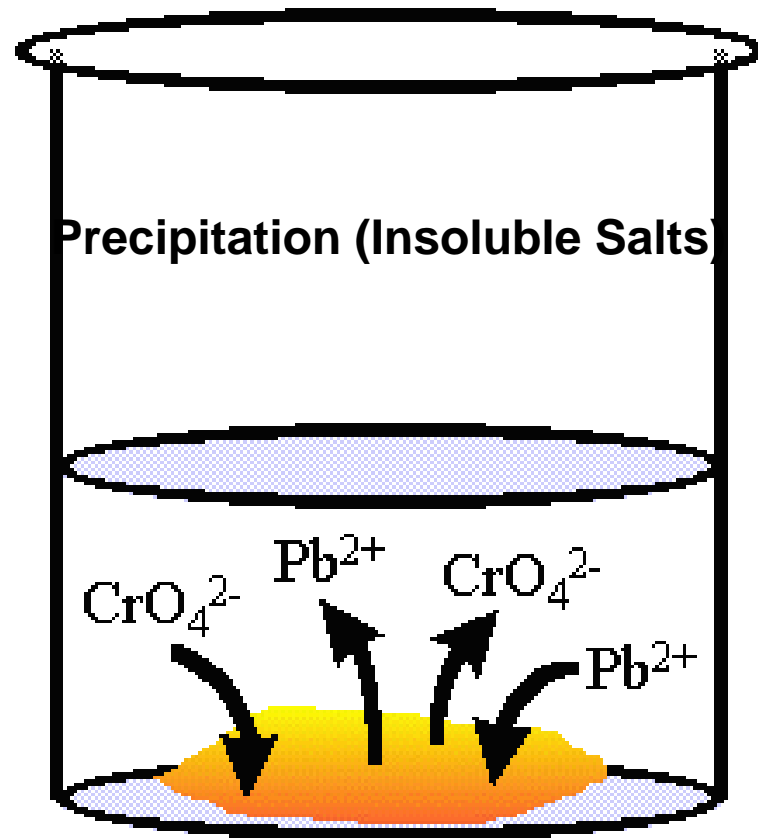
By-Product and Waste Processing

Waste Scavenging (U-Plant)	1953 - 1957
Cs and Sr Recovery (B-Plant)	1967 - 1985
Cs and Sr Encapsulation (WESF)	1974 - 1985
Waste Evaporators	1952 -

Selected Chemical properties of various oxidation # for actinides

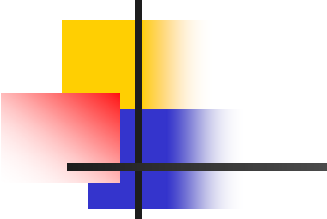
Oxidation #	F ⁻¹	(PO ₄) ⁻³	(SO ₄) ⁻²
+2	PPT	PPT	Partial PPT
+3	PPT	PPT	PPT
+4	PPT	PPT	PPT
+5	Soluble	Soluble	Soluble
+6	Soluble	Soluble	Soluble

Precipitation (insoluble salts)



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Stable oxidation states of selected elements



Element	+1	+2	+3	+4	+5	+6	+7	+8
Titanium		○	○	●				
Vanadium		○	○	●	●			
Chromium		●	●	○	○	●		
Manganese		●	○	●	○	○	●	
Iron		●	●	○		○		
Cobalt		●	●					
Nickel		●	○	○				
Strontium		●						
Yttrium			●					
Molybdenum		○	○	●	●	●		
Technetium		○	○	●	○	○	●	
Silver	●		○	○				
Cesium	●							
Barium		●						
Lanthanides			●					
Lead		●		○				
Polonium		○		●		○		
Radium		●						
Actinium			●					
Thorium				●				
Protactinium				○	●			
Uranium			○	○	○	●		
Neptunium			○	○	●	○	○	
Plutonium			○	●	○	○		
Americium			●	○	○	○		
Curium			●	○				



Redox reagents for used in nuclear process industry

Strong oxidizing agents

($\text{Pu}^{+3}/\text{Pu}^{+4} \rightarrow \text{Pu}^{+6}$):

- 1) $\text{K}_2\text{Cr}_2\text{O}_7$
- 2) KMnO_4
- 3) Ag^{+2}
- 4) NaBiO_3 (Sodium Bismuthate)
- 5) Ce^{+4}



REDOX reagents for used in nuclear process industry

Strong reducing agents ($\text{Pu}^{+4} \rightarrow \text{Pu}^{+3}$):

- 1) Zn metal
- 2) Fe^{+2}
- 3) NaI (I^{-1})
- 4) $\text{NH}_2\text{OH}.\text{HNO}_3$ (hydroxylamine nitrate)
- 5) Ti^{+3} & U^{+4}



Common Oxidation States

In $\text{HNO}_3/\text{HNO}_2$ solution, majority of each actinide will be shown the following oxidation states:

Actinide	Oxidation #
Am	+3
Pu	+4
Np	+5
U	+6

Radioactive elements

<table border="1" style="margin: auto;"> <tr> <td colspan="2" style="text-align: center;"> UOX 45 Gwd/t (4 years cooled) </td> </tr> <tr> <td style="text-align: center;"> U Pu Np Am Cm </td> <td style="text-align: center;"> 941 kg/tMLI 11,3 kg/tMLI 611 g/tMLI 605 g/tMLI 90 g/tMLI </td> </tr> </table>																		UOX 45 Gwd/t (4 years cooled)		U Pu Np Am Cm	941 kg/tMLI 11,3 kg/tMLI 611 g/tMLI 605 g/tMLI 90 g/tMLI
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U Pu Np Am Cm	941 kg/tMLI 11,3 kg/tMLI 611 g/tMLI 605 g/tMLI 90 g/tMLI																				
1 H																	2 He				
3 Li	4 Be															5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg															13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr				
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe				
55 Cs	56 Ba	Ln	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn				
87 Fr	88 Ra	An	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun												

LANTHANIDES	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
ACTINIDES	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

- ACTINIDES MAJEURS
- ACTIVATION PRODUCTS
- FISSION PRODUCTS
- FISSION AND ACTIVATION PRODUCTS
- ACTINIDES MINEURS



Carrier usage

- For ^{90}Sr $138 \text{ Ci} = 1 \text{ gram}$
- Separations are most easily accomplished when performed on a kilogram-scale, e.g., $.0015 \text{ Kg Zr}^{+4} / \text{Kg U}$ for M^{+4}
- In many cases, the carrier is an on-radioactive isotope of the analyte
- Some carriers are stable isotopes of chemically similar elements
- It is often necessary to add holdback carriers to analytical mixtures to prevent unwanted radionuclides from being carried in a chemical process

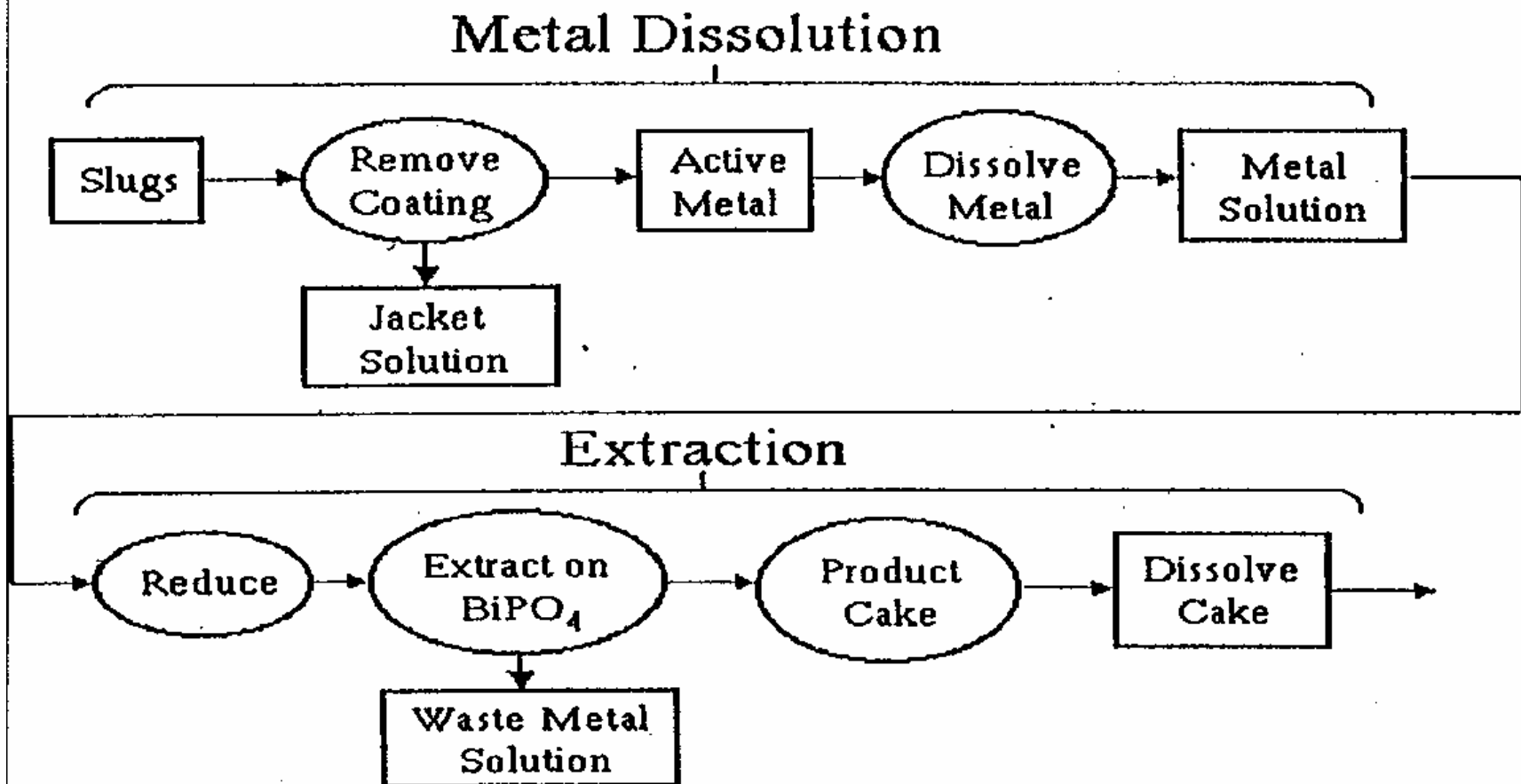
Chemical Usage in the Bismuth Phosphate Process

Chemical

Usage, mass/mass U

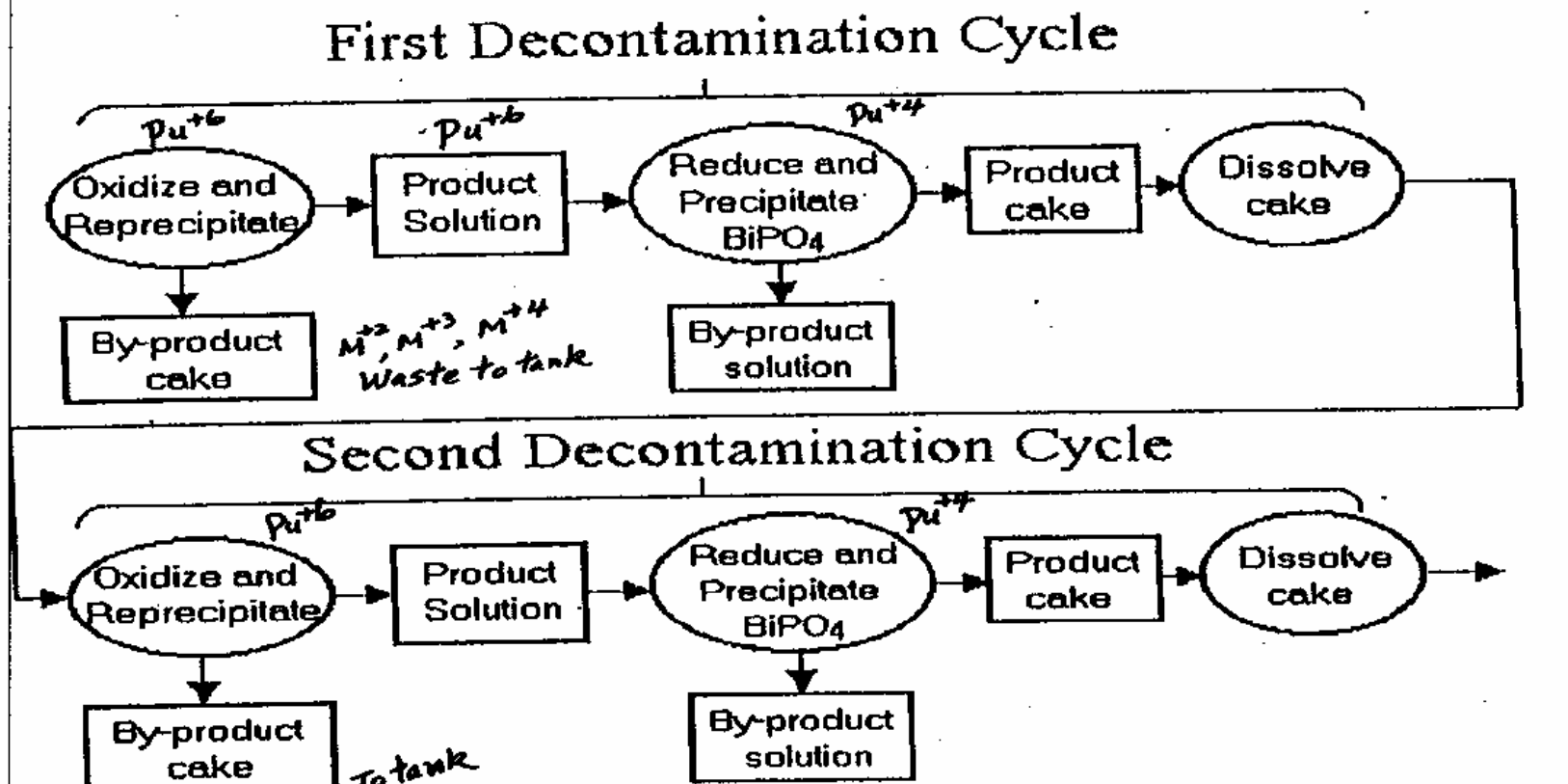
HNO ₃	dissolution reagent	3.00
H ₂ SO ₄	SO ₄ ⁻²	0.397
NaNO ₂	reducing Agent	0.091
BiONO ₃	Bi ⁺³ (ppt)	0.063
H ₃ PO ₄	PO ₄ ⁻⁴ (ppt)	0.985
NaBiO ₃	Bi ⁺³ (ppt)	0.016
Na ₂ Cr ₂ O ₇	strong oxidant	0.0073
(NH ₄) ₂ Ce(NO ₃) ₆	Ce ⁺⁴ (strong oxidant)	0.0015
H ₂ O ₂	oxidant	0.014
(NH ₄) ₂ SiF ₆	?	0.116
FeSO ₄ ·(NH ₄) ₂ SO ₄ ·6H ₂ O	Hold-back Carrier (M ⁺²)	0.210
La(NO ₃) ₃ ·2NH ₄ NO ₃ ·2H ₂ O	La ⁺³ (M ⁺³)	0.0112
H ₂ C ₂ O ₄ ·2H ₂ O	Pu(C ₂ O ₄) ₂ ≡ ppt	0.0041
HF	LaF ₃ ≡ ppt	0.0052
KOH	dissolution reagent	0.122
KMnO ₄	strong oxidant	0.0087
(NH ₄) ₂ SO ₄	ligand for UO ₂ ⁺²	0.0005
(NH ₄) ₂ SO ₃	reducing Agent	0.0001
ZrO(NO ₃) ₂	hold back Carrier (M ⁺⁴)	0.0015

BiPO₄ Process

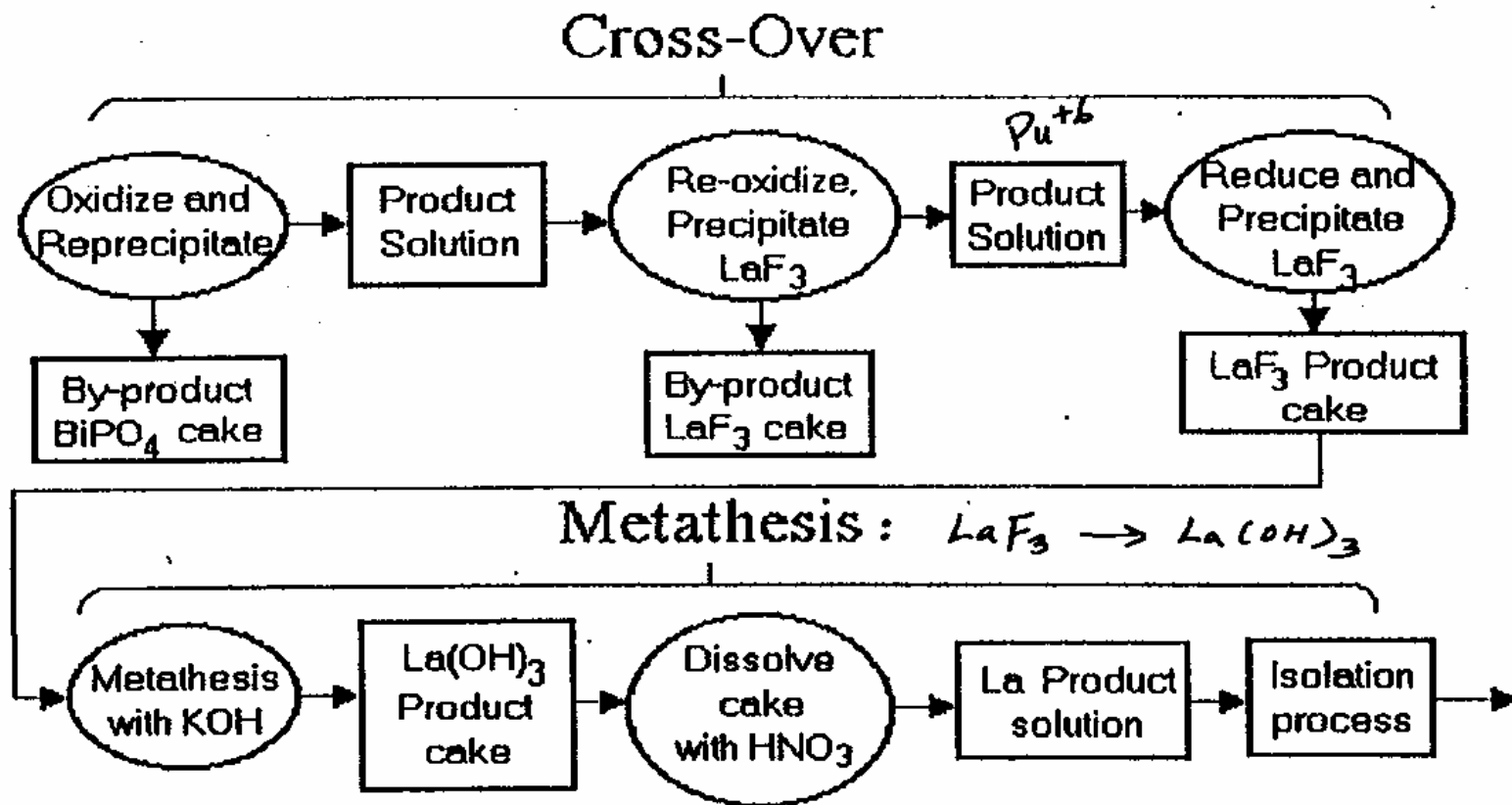


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BiPO₄ Process

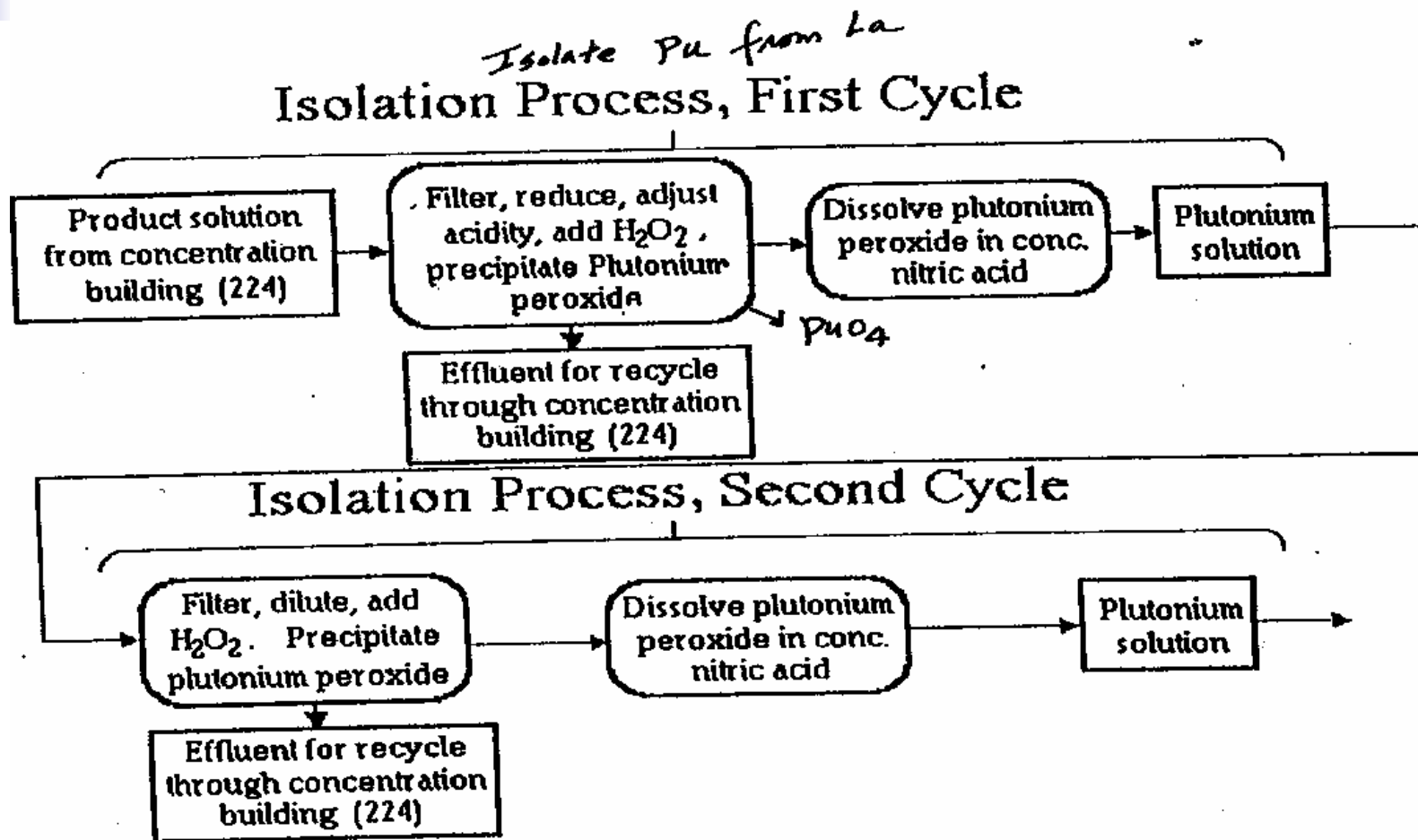


BiPO₄ Process



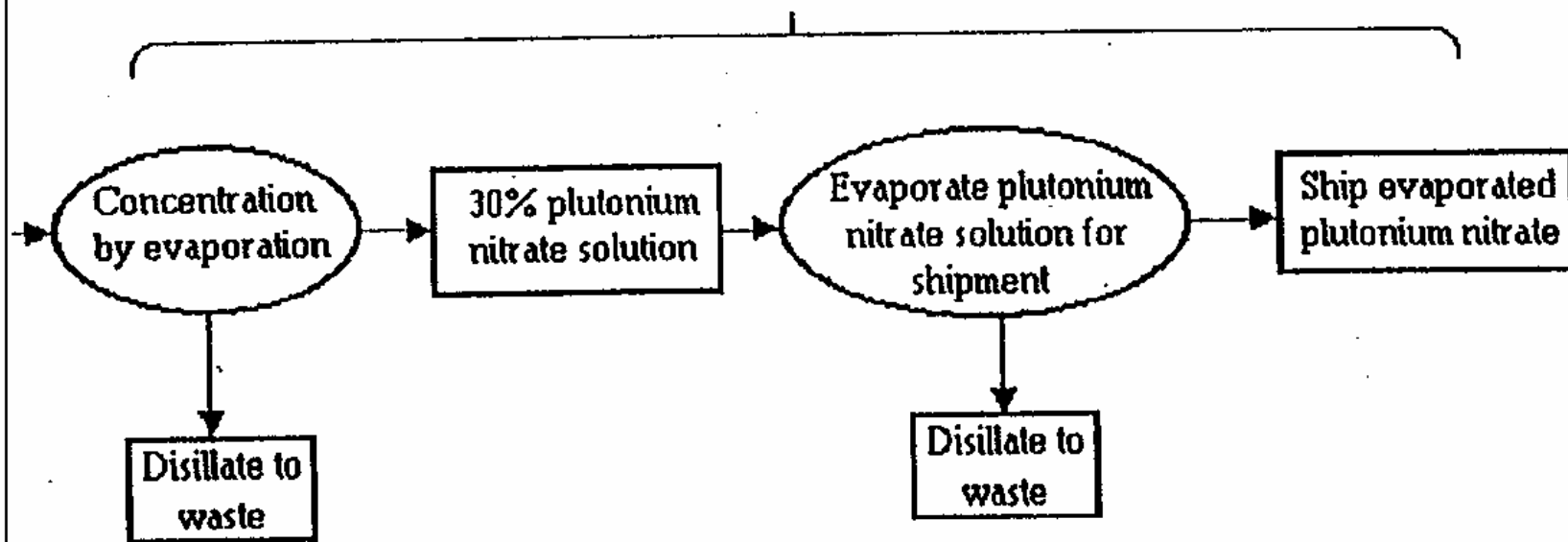
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BiPO₄ Process



BiPO₄ Process

Isolation Process Concentration and Evaporation



BiPO₄ Process

Slugs (irradiated fuel)

metal dissolution

Reduction (NaNO₂ / HNO₃)
 BiONO₃ + H₃PO₄

aqn
 M⁺⁴, M⁺⁵, M⁺⁶, M⁺⁷
 (Th⁺⁴, U⁺⁶, Np⁺⁵)

ppt (BiPO₄)
 M⁺², M⁺³, M⁺⁴
 (Pu⁺⁴)

Dissolve ppt with strong oxidant
 oxidize Pu⁺⁴ → Pu⁺⁶

Ⓐ

aqn
 M⁺⁴, M⁺⁵, M⁺⁶
 (Pu⁺⁶)

ppt
 M⁺², M⁺³, M⁺⁴

Reduce with NO₂⁻
 BiONO₃ + H₃PO₄

aqn

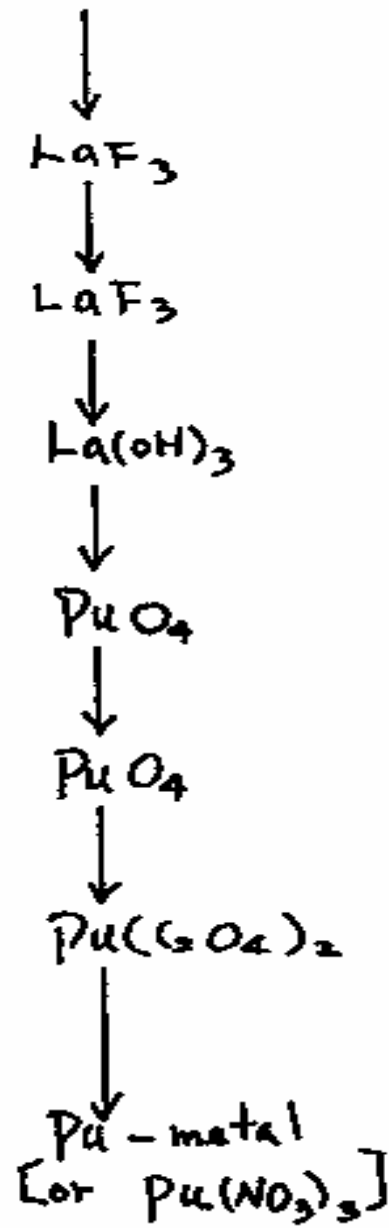
ppt
 (Pu⁺⁴)

BiPO₄

Repeat Ⓐ

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BiPO₄ Process

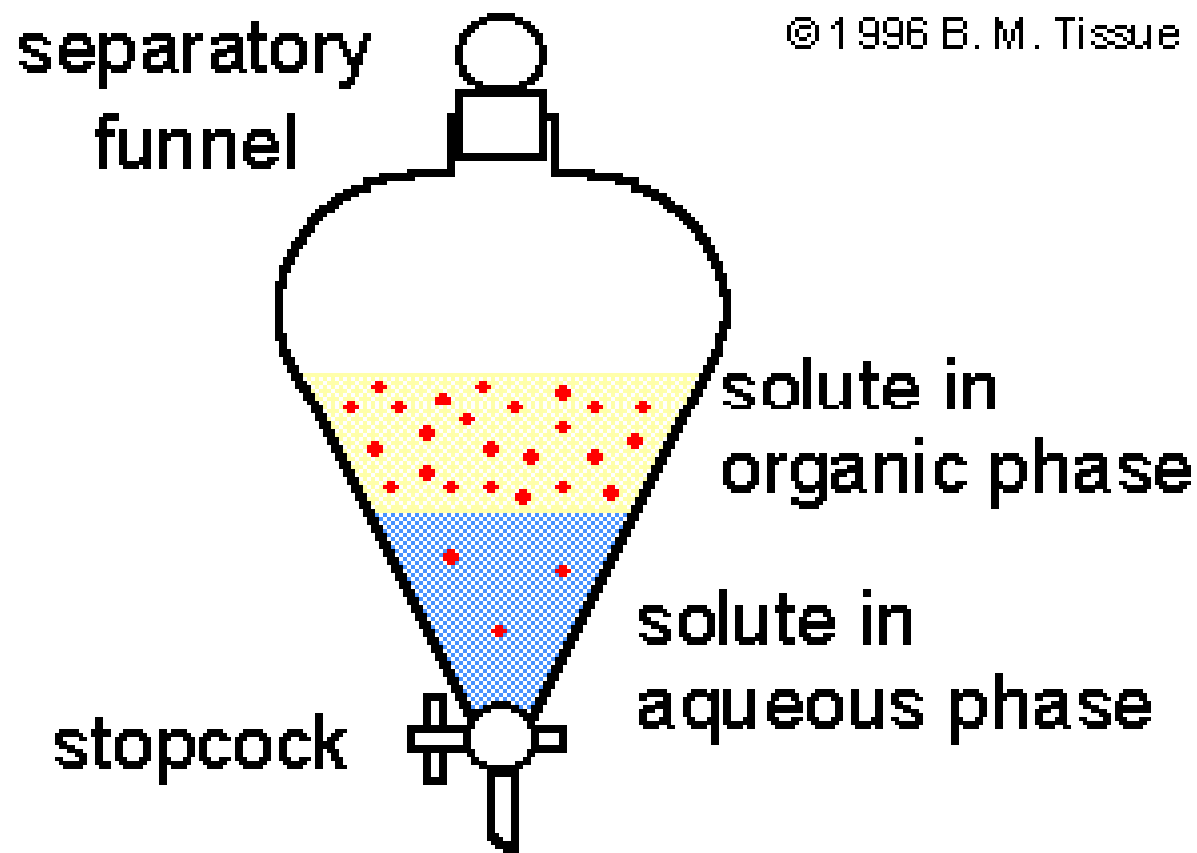




Solvent Extraction Behavior for Oxidation # of actinide

Oxidation #	Hexone	Tri-butyl Phosphate	Aliphatic Amine
+3	Non-extract	Non-extract	Non-extract
+4	Non-extract	extract	extract
+6	extract	extract	extract

Solvent Extraction



(3.1)



REDOX Process

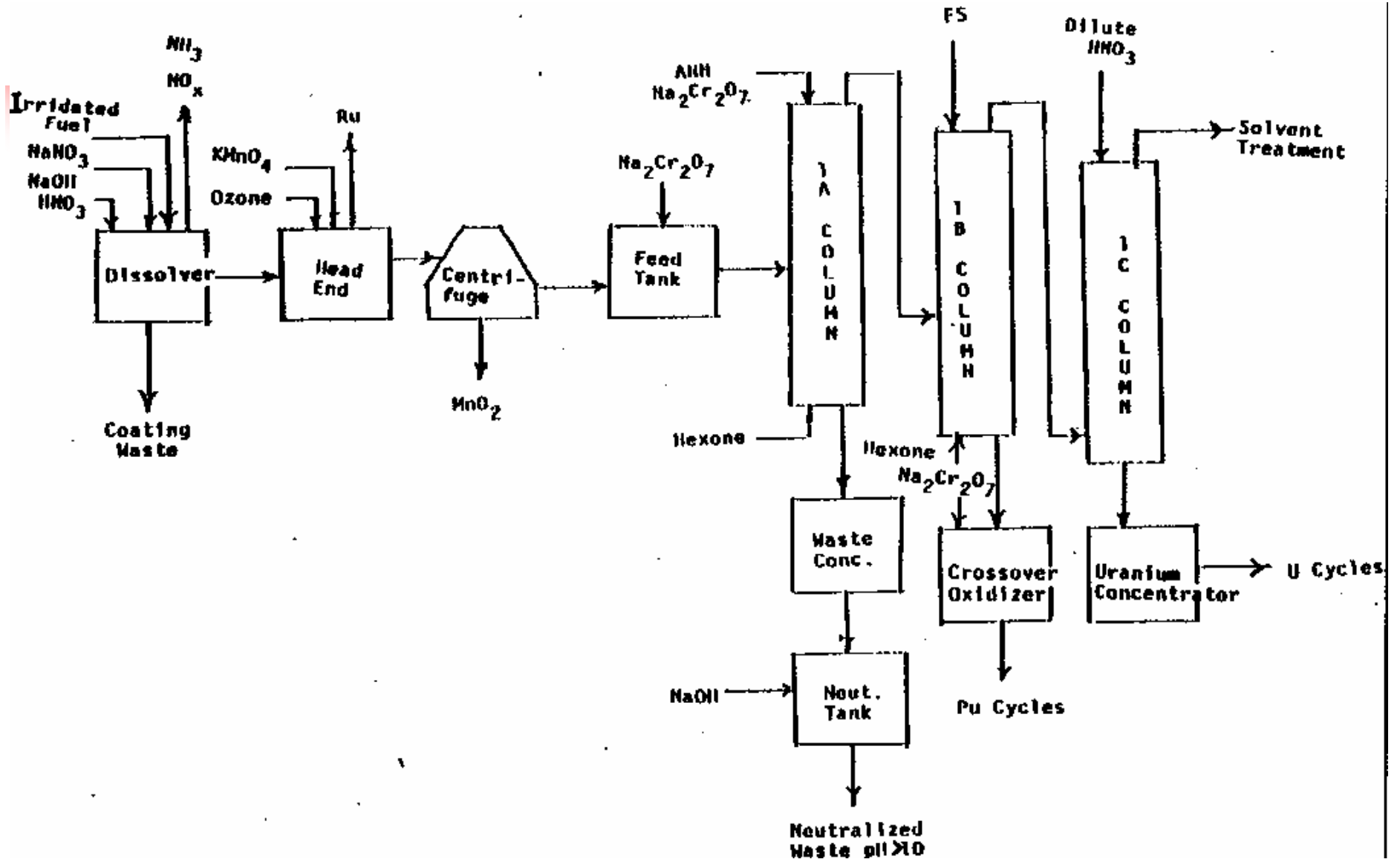
- Extract Pu & U from other actinides and FP
- Hexone can only extract M^{+6} (e.g., Pu^{+6} & U^{+6})
- Need salting agents & higher concentration of $[H^+]$
- $[H^+]$ must be high enough to prevent hydrolysis



REDOX Process

- Organic phase goes into 1B
- FS = Ferrous Sulfamate = $\text{Fe}_3(\text{NH}_2\text{SO}_3)_2$
FS will reduce Np^{+6} & $\text{Pu}^{+6} \rightarrow \text{Np}^{+4}$ & Pu^{+4} ; but not $\text{U}^{+6} \rightarrow \text{U}^{+4}$
- Pu Cycle \rightarrow Extract with Hexone twice
- ANN = long chain hydrocarbon diluent

REDOX Process



(3.1)

REDOX Process

