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
UO_3 Plant	1952 - 1972 and 1984 - 1993

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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 -

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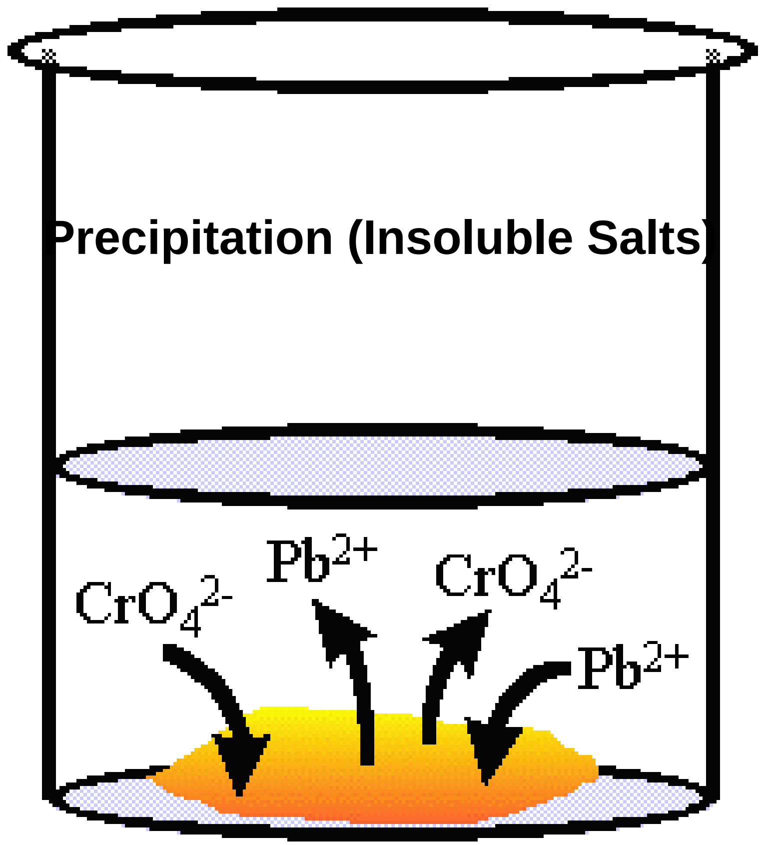
Selected Chemical properties of various oxidation # for actinides

Oxidation #	F^{-1}	$(PO_4)^{-3}$	$(SO_4)^{-2}$
+2 +3	PPT PPT	PPT PPT	Partial PPT PPT
+4	PPT	PPT	PPT
+5 +6	Soluble Soluble	Soluble 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

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

1) $K_2Cr_2O_7$
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 ($Pu^{+4} \rightarrow Pu^{+3}$):

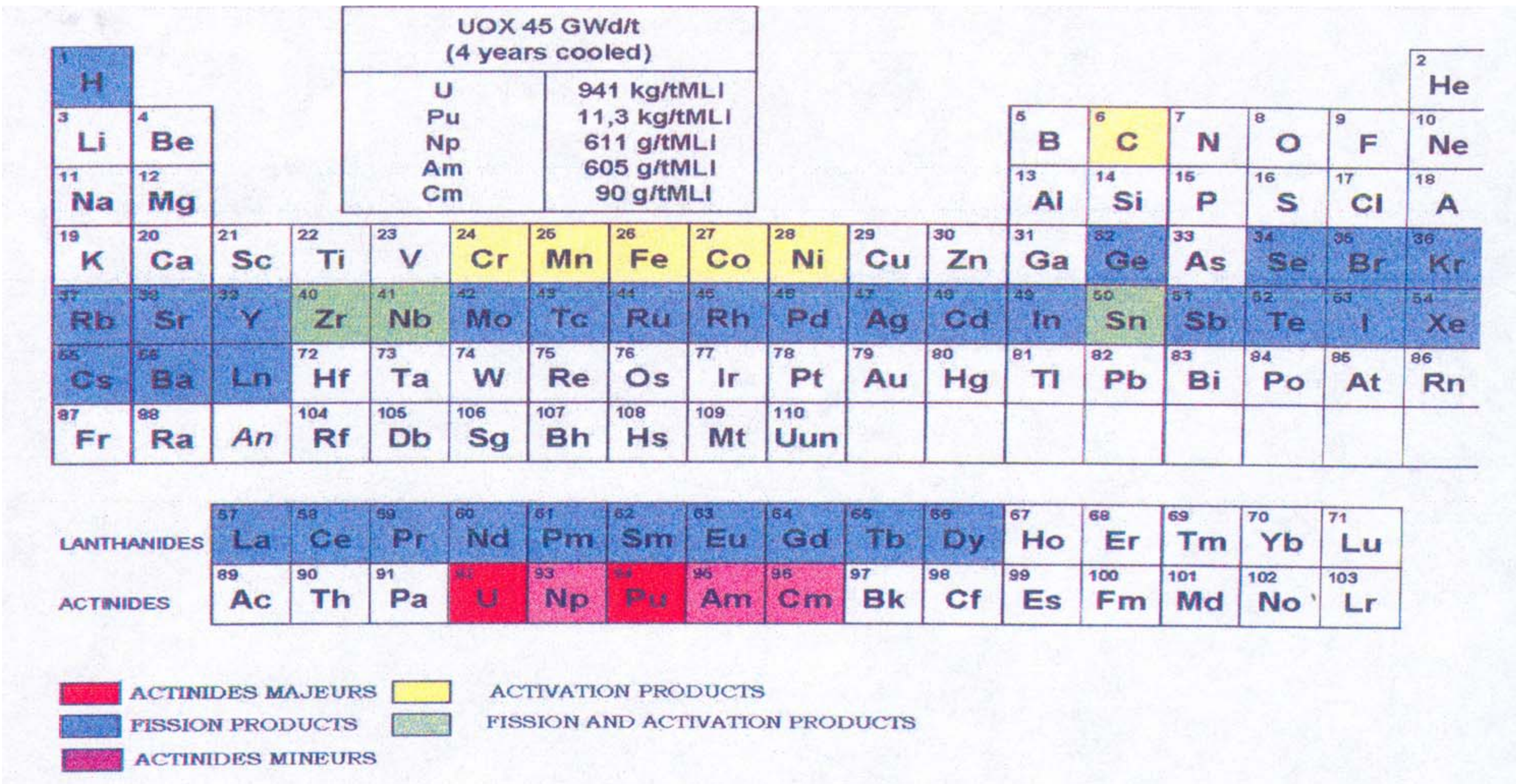
1) Zn metal
2) Fe^{+2}
3) NaI (I^{-1})
4) $NH_2OH.HNO_3$ (hydroxylamine nitrate)
5) Ti^{+3} & U^{+4}

Common Oxidation States

In HNO_3/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



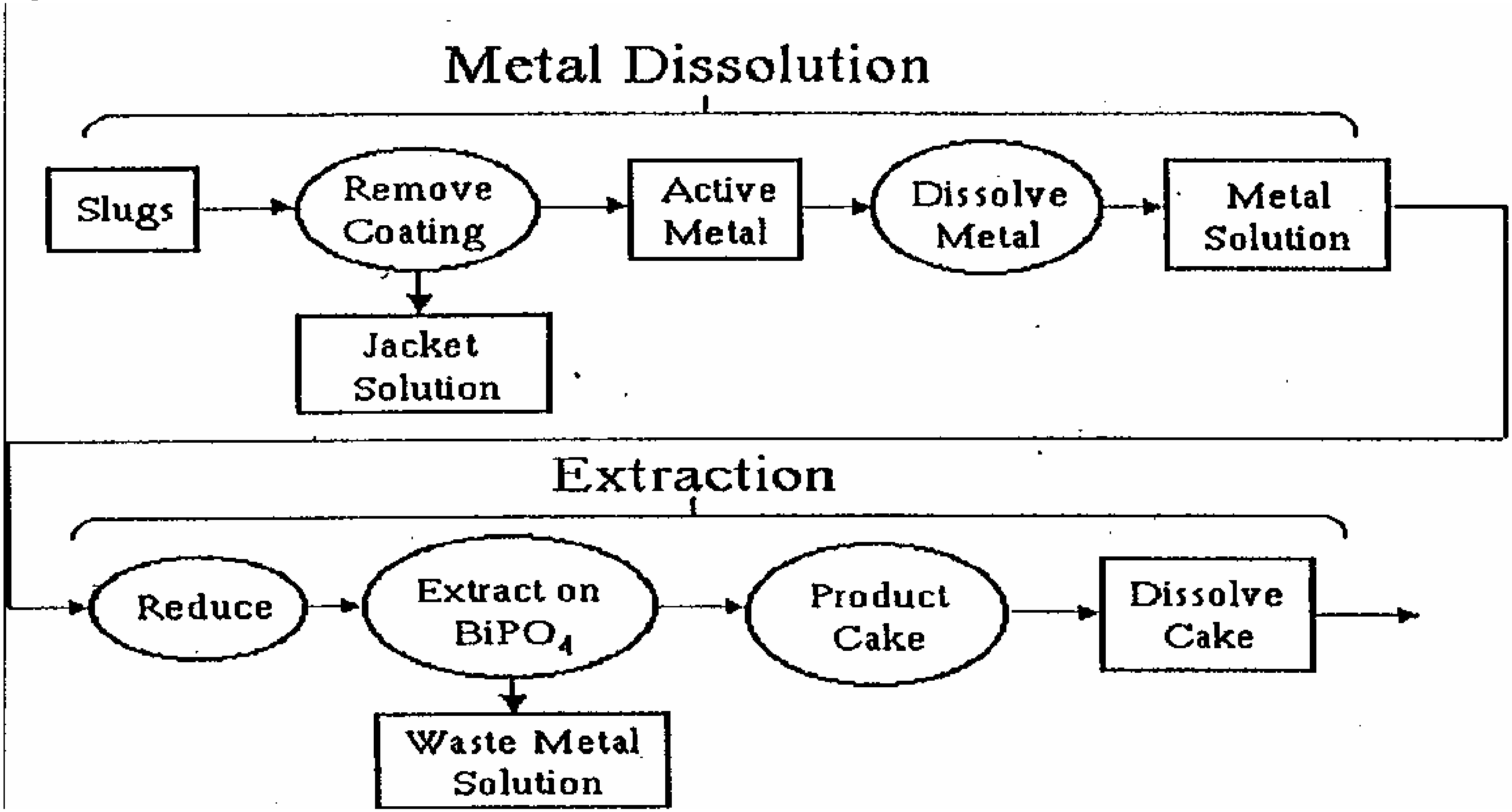
Carrier usage

- For ^{90}Sr 138 Ci = 1 gram
- Separations are most easily accomplished when performed on a kilogram-scale, e.g., .0015 Kg Zr^{+4} / 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_2SO_4	SO_4^{-2}	0.397
$NaNO_2$	reducing Agent	0.091
$BiONO_3$	Bi^{+3} (ppt)	0.063
H_3PO_4	PO_4^{-4} (ppt)	0.985
$NaBiO_3$	Bi^{+3} (ppt)	0.016
$Na_2Cr_2O_7$	strong oxidant	0.0073
$(NH_4)_2Ce(NO_3)_6$	Ce^{+4} (strong oxidant)	0.0015
H_2O_2	oxidant	0.014
$(NH_4)_2SiF_6$	?	0.116
$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$	Hold back Carrier (M^{+2})	0.210
$La(NO_3)_3 \cdot 2NH_4NO_3 \cdot 2H_2O$	La^{+3} (M^{+3})	0.0112
$H_2C_2O_4 \cdot 2H_2O$	$Pu(C_2O_4)_2$ ≡ ppt	0.0041
HF	LaF_3 ≡ ppt	0.0052
KOH	dissolution reagent	0.122
$KMnO_4$	strong oxidant	0.0087
$(NH_4)_2SO_4$	ligand for UO_2^{+2}	0.0005
$(NH_4)_2SO_3$	reducing Agent	0.0001
$ZrO(NO_3)_2$	hold back carrier (M^{+4})	0.0015

$BiPO_4$ Process



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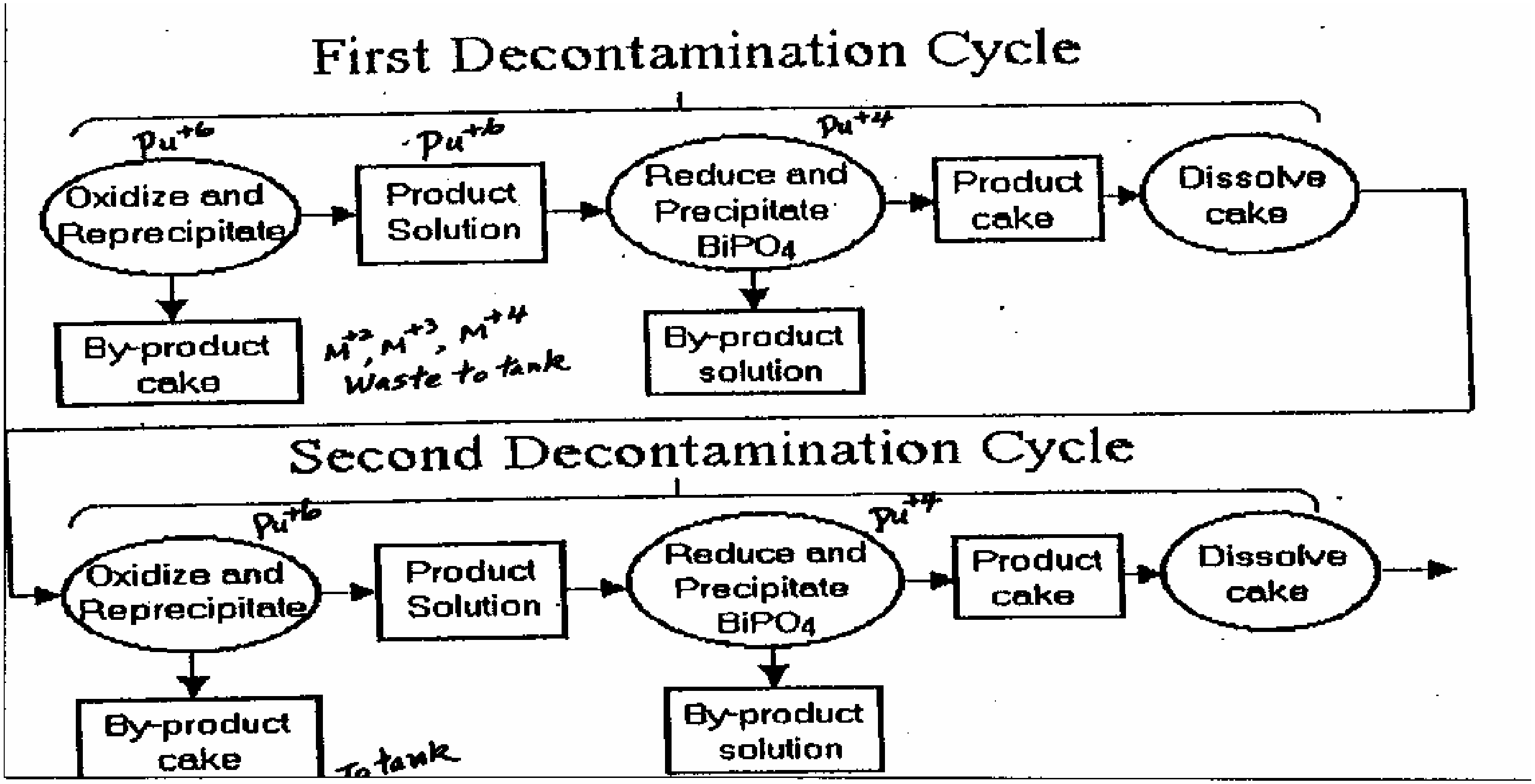
$BiPO_4$ Process



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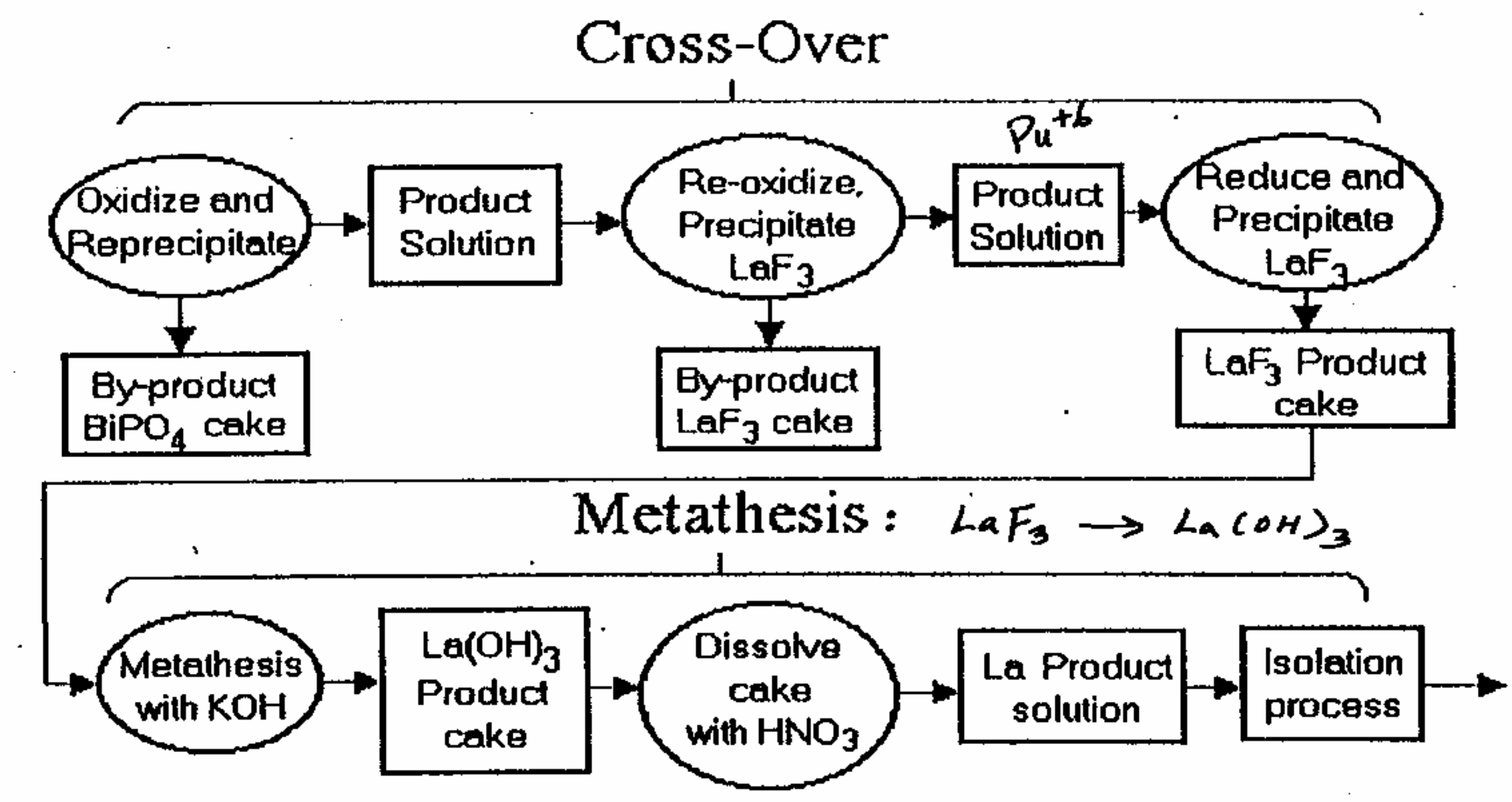

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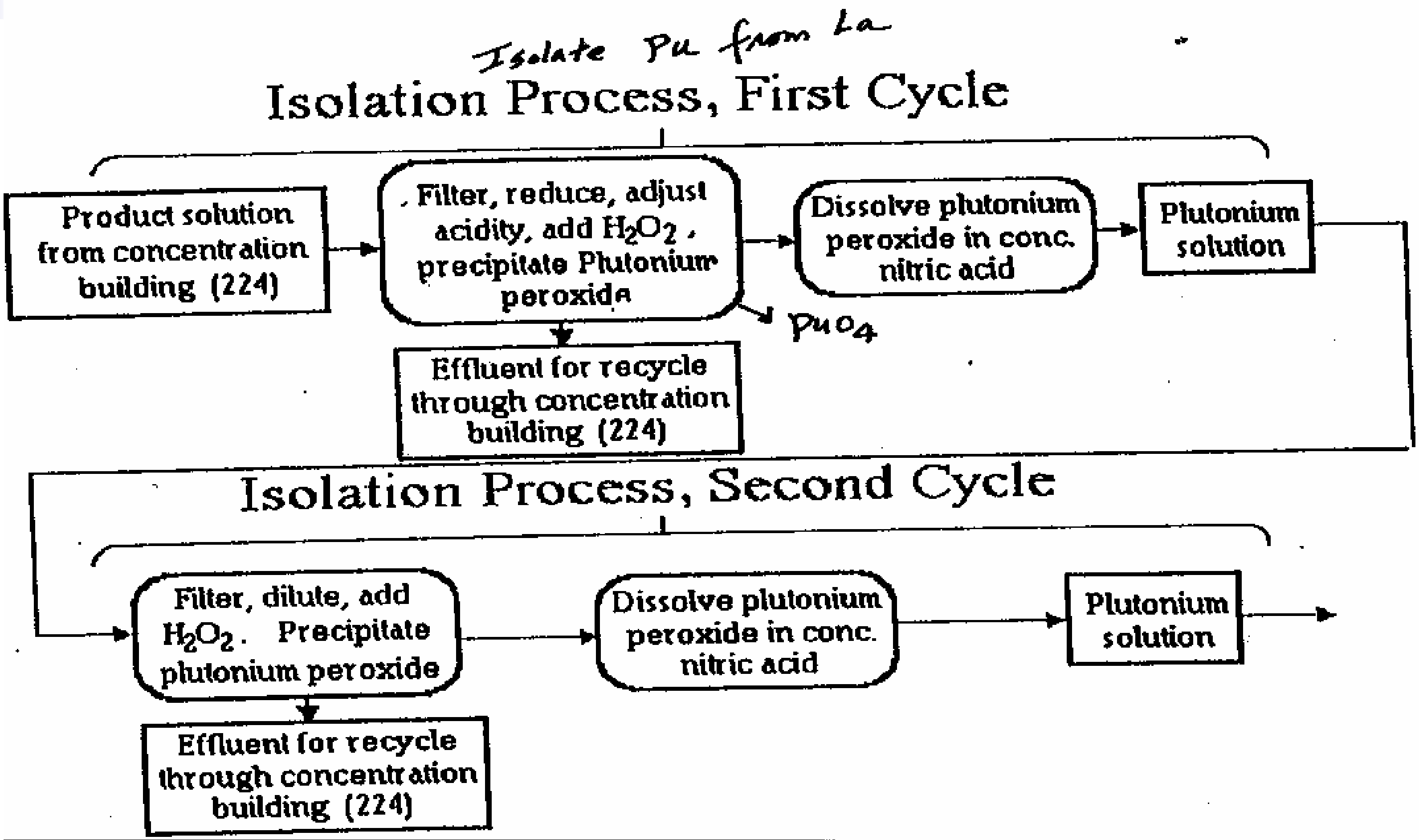

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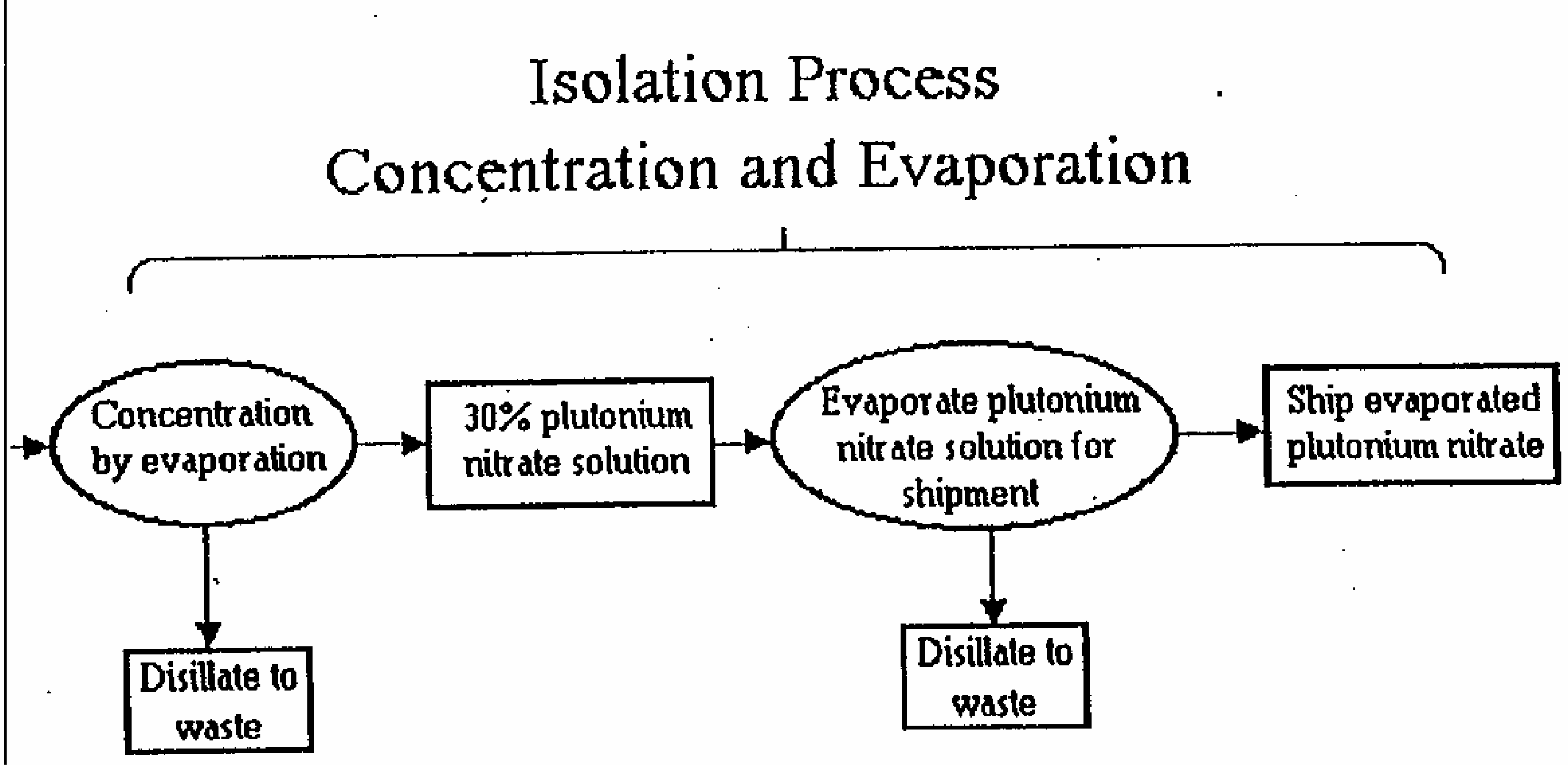

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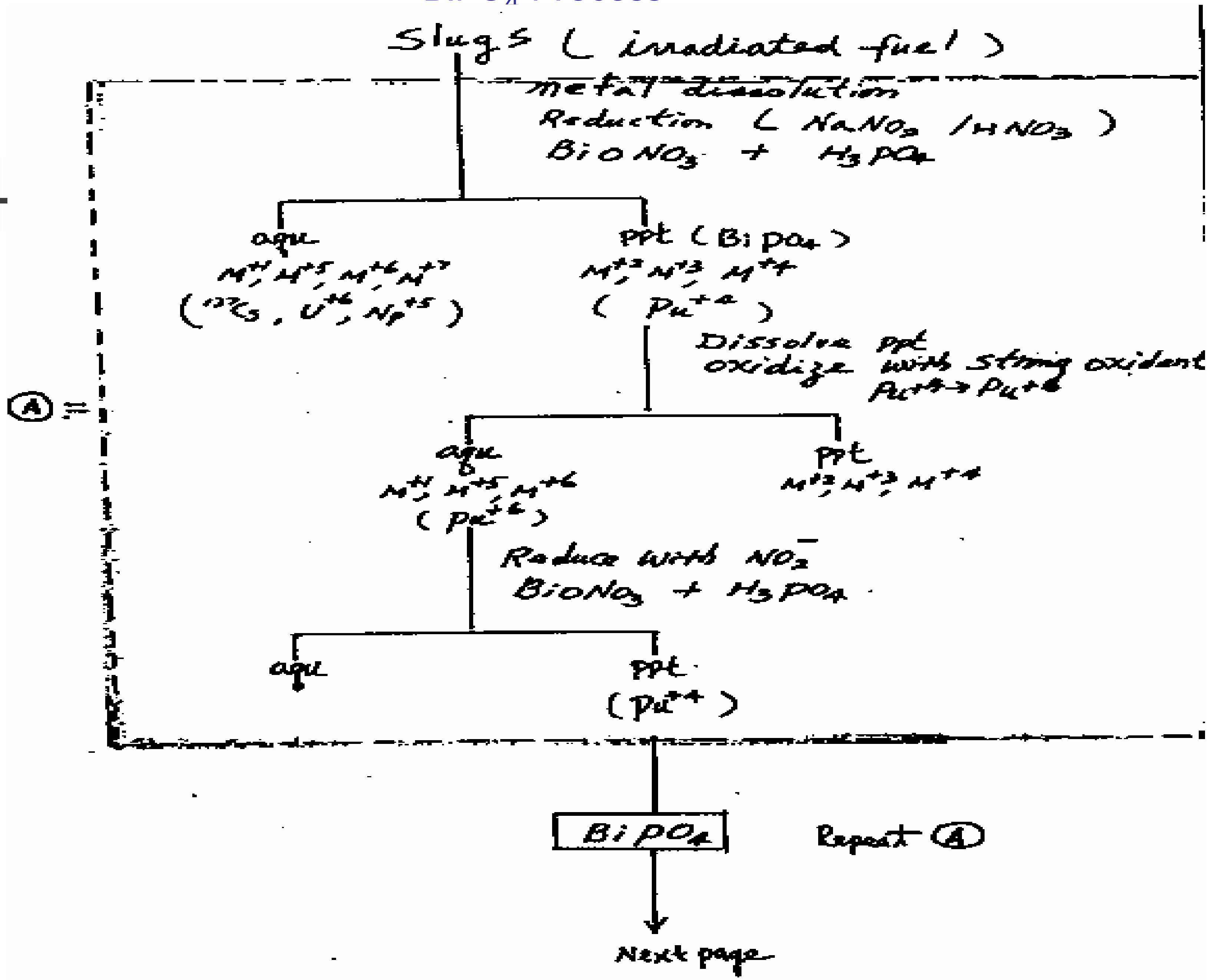
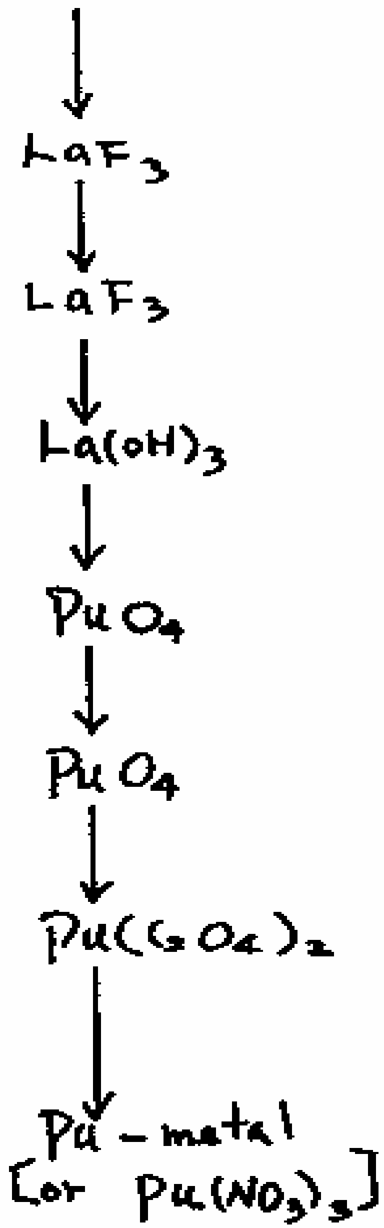
$BiPO_4$ Process



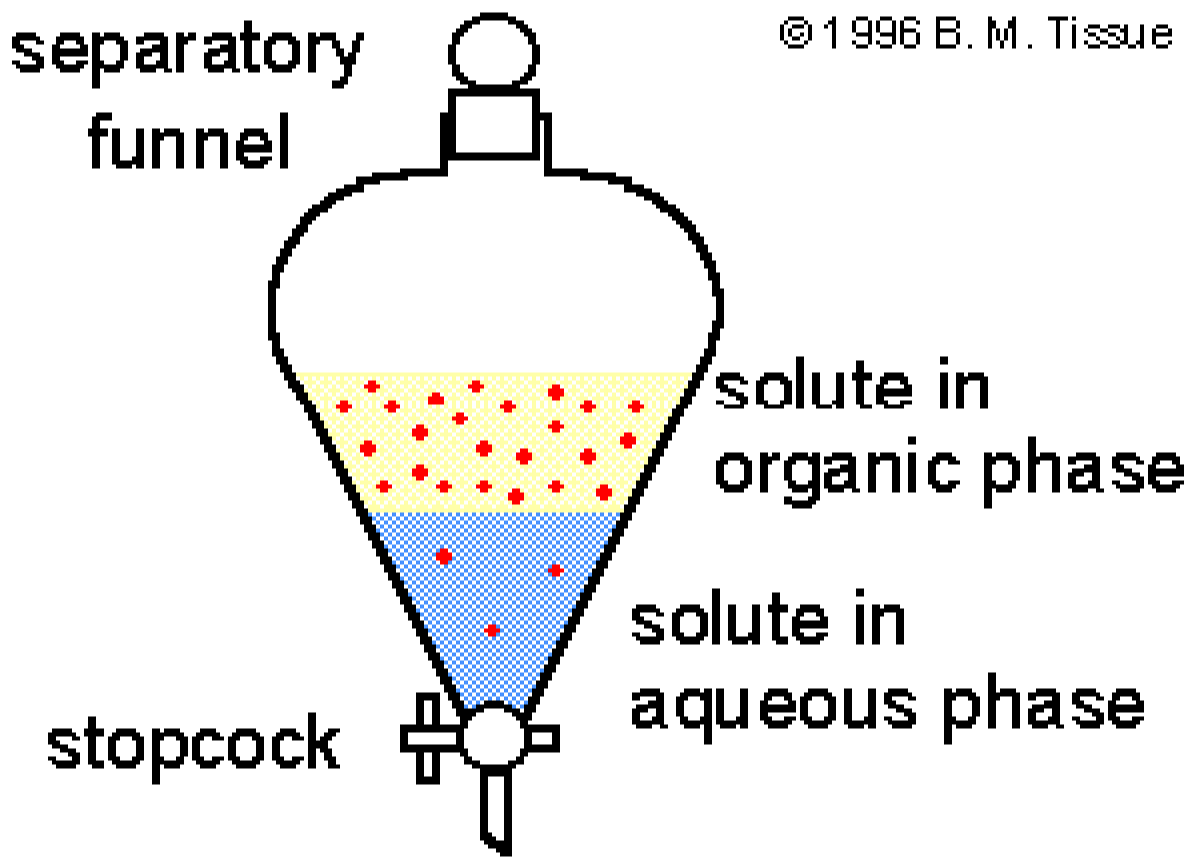
$BiPO_4$ Process



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



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REDOX Process

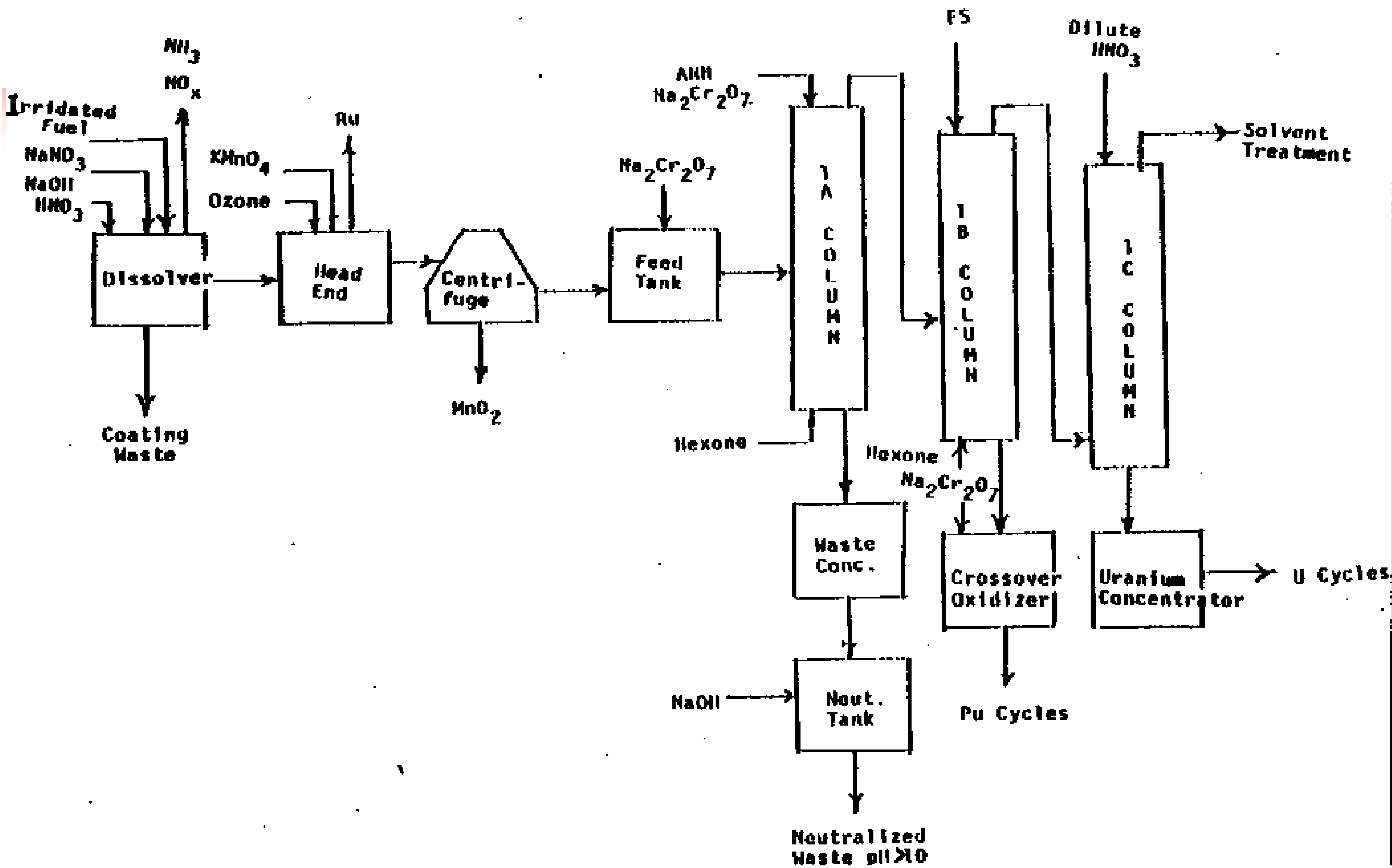
- Extract Pu & U from other actinides and FP
- Hexone can only extract M^{+6} (e.g., Pu^{+6} & U^{+6})
- Need salting agents & higher concentration of $[H^+]$
- $[H^+]$ must be high enough to prevent hydrolysis

REDOX Process

- Organic phase goes into 1B
- FS = Ferrous Sulfamate = $Fe_3(NH_2SO_3)_2$

  FS will reduce Np^{+6} & Pu^{+6} → Np^{+4} & Pu^{+4}; but not U^{+6} → U^{+4}
- Pu Cycle → Extract with Hexone twice
- ANN = long chain hydrocarbon diluent

REDOX Process



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REDOX Process