Nuclear Process & Radio-Analytical Chemistry

Class Notes – Section 3.2

PUREX Process

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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

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

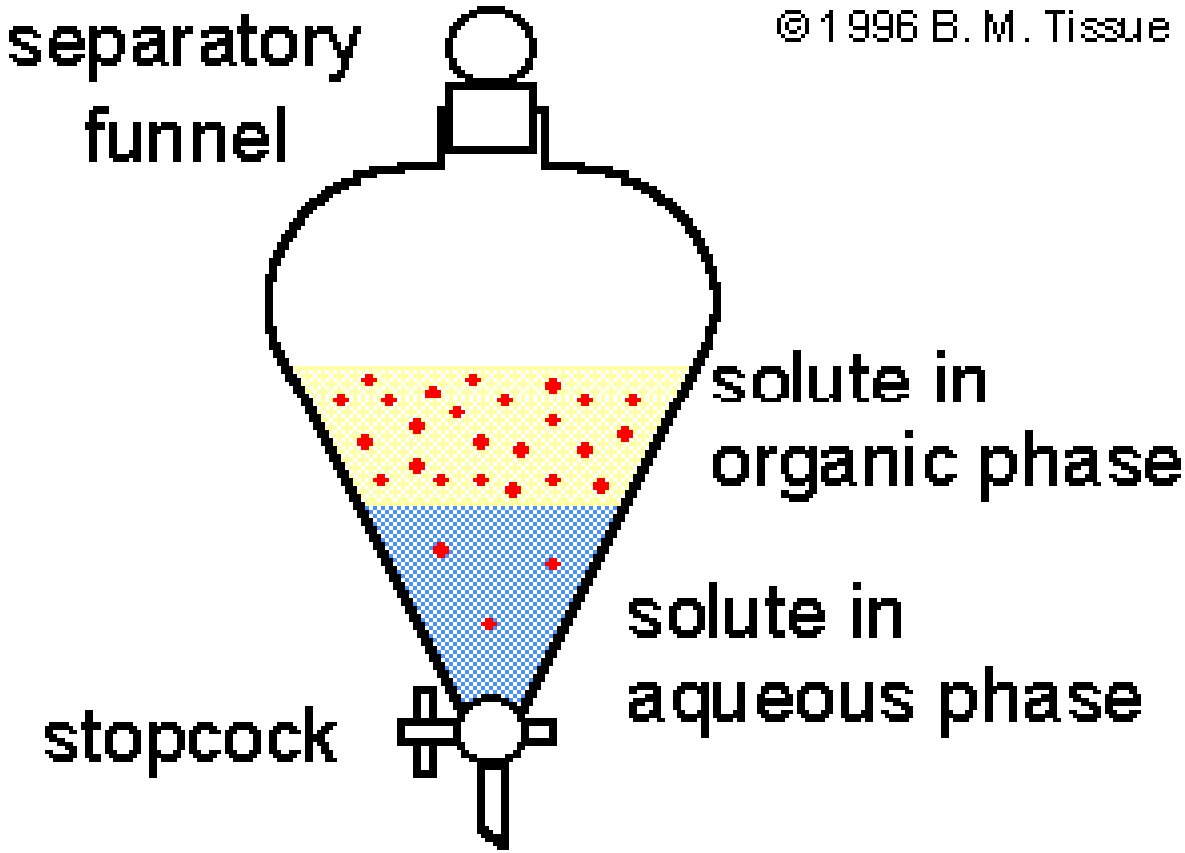
In HNO_3/HNO_2 solution, majority of each actinide will be shown the following oxidation states:

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

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



PUREX Process

PUREX is a liquid-liquid solvent extraction process that:

1) **Separates Uranium and Plutonium from fission products in dissolved, irradiated reactor fuel; and then**
2) **Separate Uranium from Plutonium.**

Solvent extraction is accomplished using tributyl phosphate (TBP) dissolved in a hydrocarbon diluent (NPH) at a concentration of 30 volume % TBP.

PUREX Process

PROCESS CHEMISTRY BASIS FOT THE PUREX SOLVENT EXTRACTION FLOWSHEET

$(UO_2)^{+2} + 2NO_3^- (Aq.) + 2TBP \rightleftharpoons UO_2(NO_3)_2.(TBP)_2 (Org.)$

$Pu^{+4} (Aq.) + 4NO_3^- (Aq.) + 2TBP (Org.) \rightleftharpoons Pu(NO_3)_4.(TBP)_2 (Org.)$

$Pu^{+3} (Aq.) + 3NO_3^- (Aq.) + 3TBP (Org.) \rightleftharpoons Pu(NO_3)_3.(TBP)_3 (Org.)$

$PuO_2^{+2} + 2NO_3^- (Aq.) + 2TBP (Org.) \rightleftharpoons PuO_2(NO_3)_2.(TBP)_2 (Org.)$

$Zr^{+4} + 4NO_3 (Aq.) + 2TBP (Org.) \rightleftharpoons Zr(NO_3)_4.(TBP)_2 (Org.)$

$Ru(NO)(NO_3)_3 (Aq.) + xTBP (Org.) \rightleftharpoons Ru(NO)(NO_3)_3.(TBP)_x (Org.)$

$H^+ + NO_3^- (Aq.) + TBP (Org) \rightleftharpoons HNO_3.TBP (Org.)$

$M^{3+} + 3NO_3 (Aq.) + 3TBP (Org) \rightleftharpoons M(NO_3)_3.3TBP$

$Pu^{4+} + Fe^{++} \rightleftharpoons Pu^{3+} + Fe^{3+}$

PUREX Process

EFFECT OF NITRIC ACID ON DISTRIBUTION COEFFICIENTS for URANIUM AND PLUTONIUM (in 20% TBP in hydrocarbon)

	Distribution Coefficient	
Metal or Radical	1 M HNO3	6 M HNO3
UO_2^{++}	5	30
PuO_2^{++}	0.7	3
Pu^{4+}	1.3	20
Pu^{3+}	0.015	0.01

PUREX Process

BEHAVIOR OF FISSION PRODUCTS IN EXTRACTION OF URANIUM FROM FISSION PRODUCTS
[15 vol% TBP]

	DECONTAMINATION FACTOR		
	EXTRACTING SECTION	SCRUB SECTION	OVERALL
GROSS BETA	330	30	9.8 E3
RUTHENIUM	106	5	530
CERIUM	1.4 E3	380	5.3 E5
ZIRCONIUM	71	210	1.5 E4
NIOBIUM	1.5 E3	5.6	8.3 E3

PUREX Process

IRRADIATED FUEL ELEMENT CHEMICAL DECLADDING

ALUMINUM JACKET REMOVAL

$$8Al + 5NaOH + 3NaNO_3 + 2H_2O \longrightarrow 8NaAlO_2 + 3NH_3 \quad (1)$$

$$2Al + 2NaOH + 3NaNO_3 \longrightarrow 2NaAlO_3 + 3NaNO_2 + H_2O \quad (2)$$

$$2Al + NaOH + NaNO_2 + H_2O \longrightarrow 2NaAlO_2 + NH_3 \quad (3)$$

ZIRCALOY JACKET REMOVAL

$$Zr + 6NH_4F + 0.47\ NH_4NO_3 \longrightarrow (NH_4)_2ZrF_6 + 4.94NH_3\ (g) + 0.12H_2\ (g) + 1.41H_2O \quad (4)$$

$$Sn + 6NH_4F + 0.47\ NH_4NO_3 \longrightarrow (NH_4)_2SnF_6 + 4.94NH_3\ (g) + 0.12H_2\ (g) + 1.41H_2O \quad (5)$$

$$Pu + 6NH_4F + 0.47\ NH_4NO_3 \longrightarrow (NH_4)_2PuF_6 + 4.94NH_3\ (g) + 0.12H_2\ (g) + 1.41H_2O \quad (6)$$

$$U + 6NH_4F + 0.47\ NH_4NO_3 \longrightarrow (NH_4)_2UF_6 + 4.94NH_3\ (g) + 0.12H_2\ (g) + 1.41H_2O \quad (7)$$

Metathesis

$$(NH_4)_2UF_6\ (s) + 6KOH \longrightarrow UO_2{\cdot}2H_2O + 6KF + 2NH_3\ (g) + H_2O \quad (8)$$

$$(NH_4)_2PuF_6\ (s) + 6KOH \longrightarrow PuO_2{\cdot}2H_2O + 6KF + 2NH_3\ (g) + H_2O \quad (9)$$

PUREX Process

FUEL DISSOLUTION

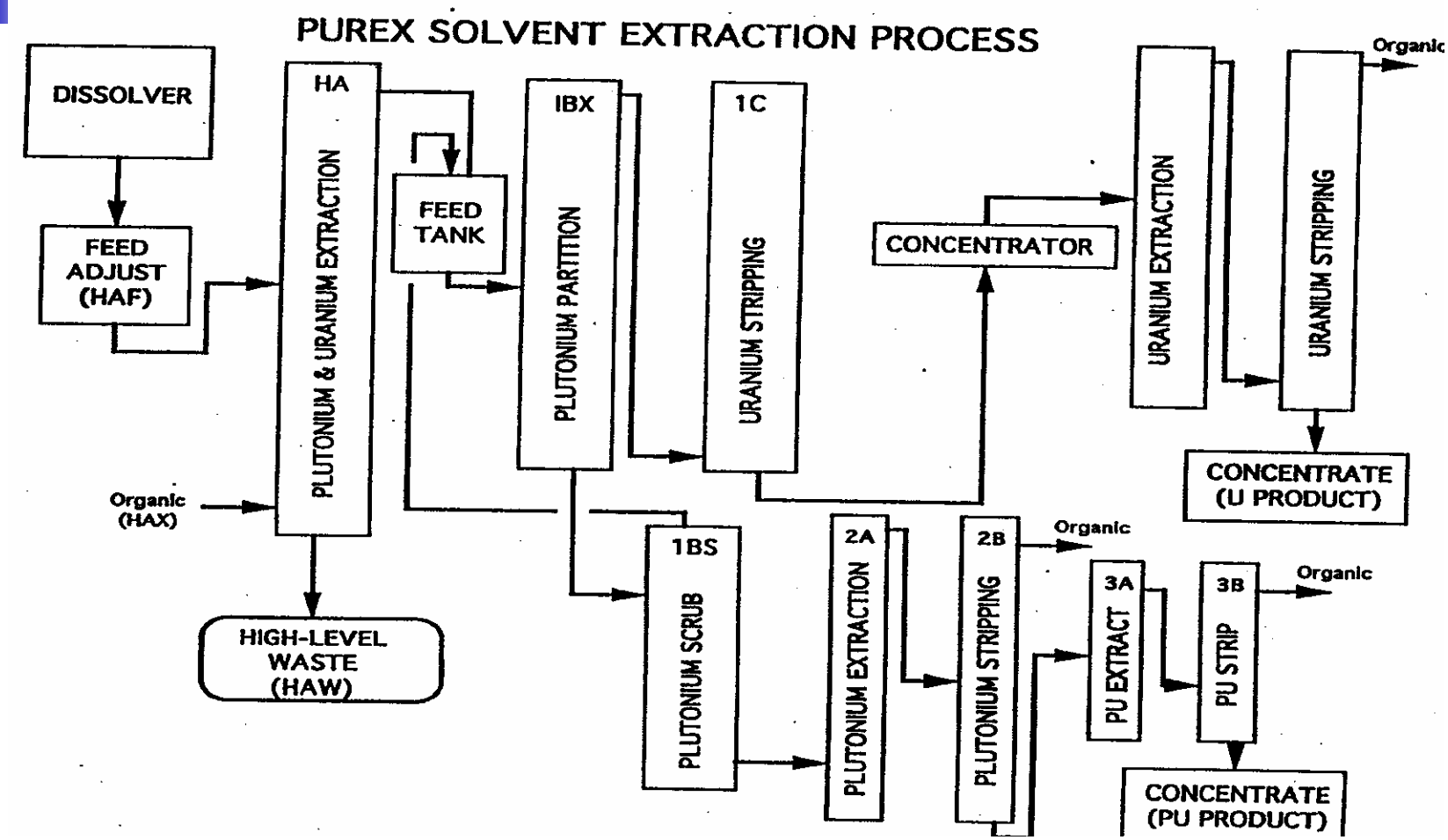
$$U + 3.8\ HNO_3 + 0.15O_2 \longrightarrow UO_2(NO_3)_2 + 1.8NO + 1.9H_2O \quad (1)$$

$$Pu + 7.6HNO_3 + 0.1O_2 \longrightarrow Pu(NO_3)_4 + 3.6NO_2 + 3.8H_2O \quad (2)$$

$$UO_2{\cdot}2H_2O + 3.8HNO_3 + .05O_2 \longrightarrow UO_2(NO_3)_2 + 3.9H_2O + 1.8NO_2 \quad (3)$$

$$PuO_2{\cdot}2H_2O + 4HNO_3 \longrightarrow Pu(NO_3)_4 + 4H_2O \quad (4)$$

PUREX Process



PUREX Process