



# Recovery of Uranium from Phosphoric Acid by Ion Exchange

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IAEA Technical Meeting – Uranium from Unconventional Resources

## Outline of this presentation

- Introduction to phosphate rock processing
- Uranium department in WPA
- Why Ion exchange technology
- Understanding the mechanism for uranium extraction by IX
- Conclusions
- Important targets for processing

## Uranium Content in Phosphate Rocks

Phosphate Rocks	P <sub>2</sub> O <sub>5</sub> content (%)	U content (ppm)	RE content (%)
USA - Florida	31	180	0.5
Morocco - Khouribga	30	115	0.15
Morocco -Safi	33	155	0.4
Egypt - Abu Tartur		25	0.1
Russia - Kola	38	10	0.9
S. Africa - Phalaborwa			0.5 - 1

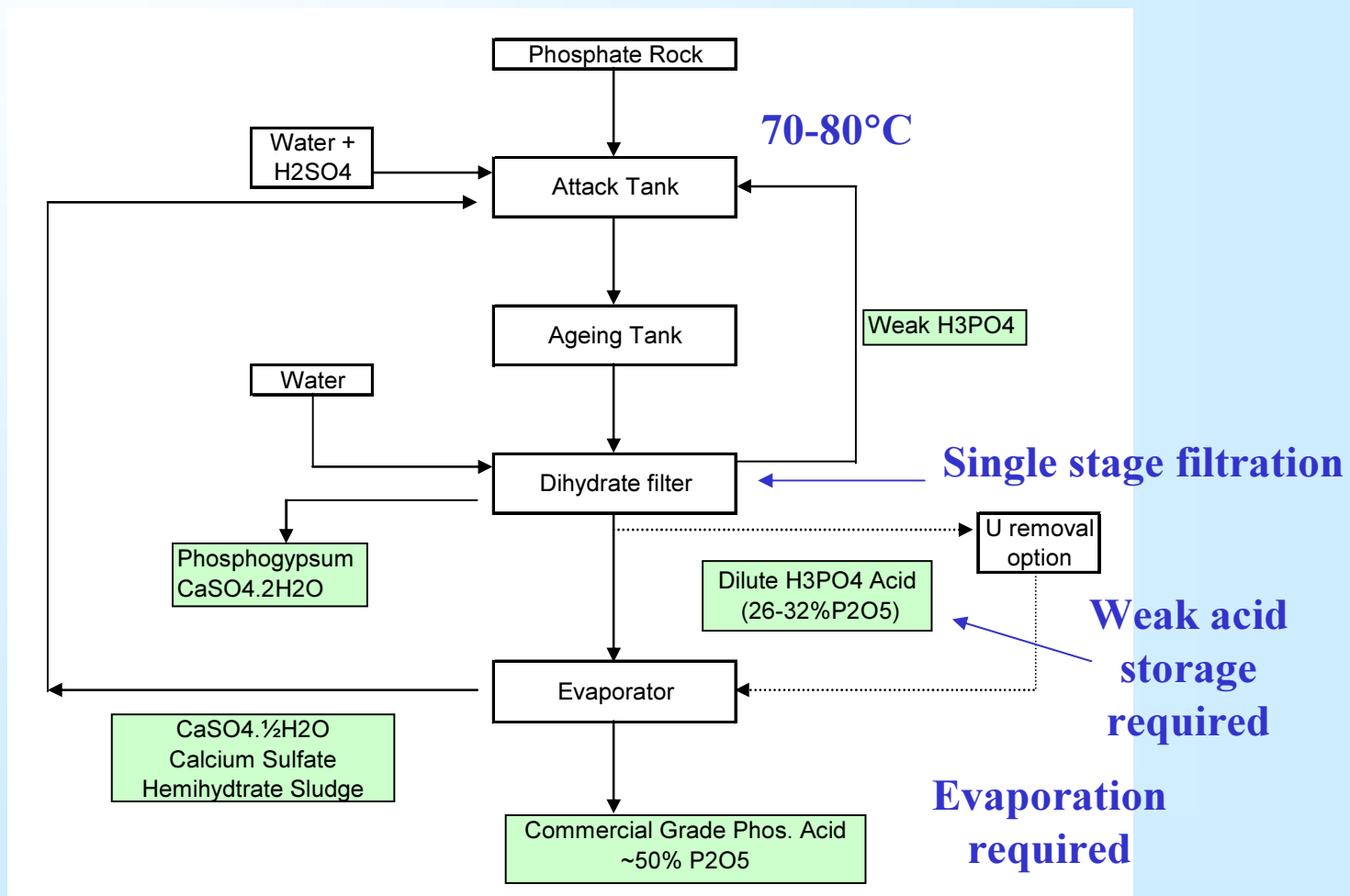
## Typical Composition of Phosphate Rock

$P_2O_5$	29-38 %	U	100 -200 ppm
$Fe_2O_3$	0.2-1 %	REO	0.1-1 %
$Al_2O_3$	0.1-1 %	Cl	0.01-0.7 %
CaO	48-52 %	$K_2O$	0.1-0.4 %
MgO	0.2-0.8 %	F	3.3-4.3 %
$SiO_2$	0.2-5 %	Organic Carbon	0-0.4 %

## Phosphoric Acid Production

- Sulphuric acid attack for phosphoric acid production
  - Conventional, widely used ~ 90%
  - Uranium reports with the phosphoric acid and/or gypsum depending on process conditions
  - Uranium has been recovered in industrial scale
- Nitrate route for fertiliser production
  - Commercial process – not widely used ~10%
  - Uranium only present as impurity
- Chloride route
  - Niche market for high grade phosphoric acid

# Dihydrate Process



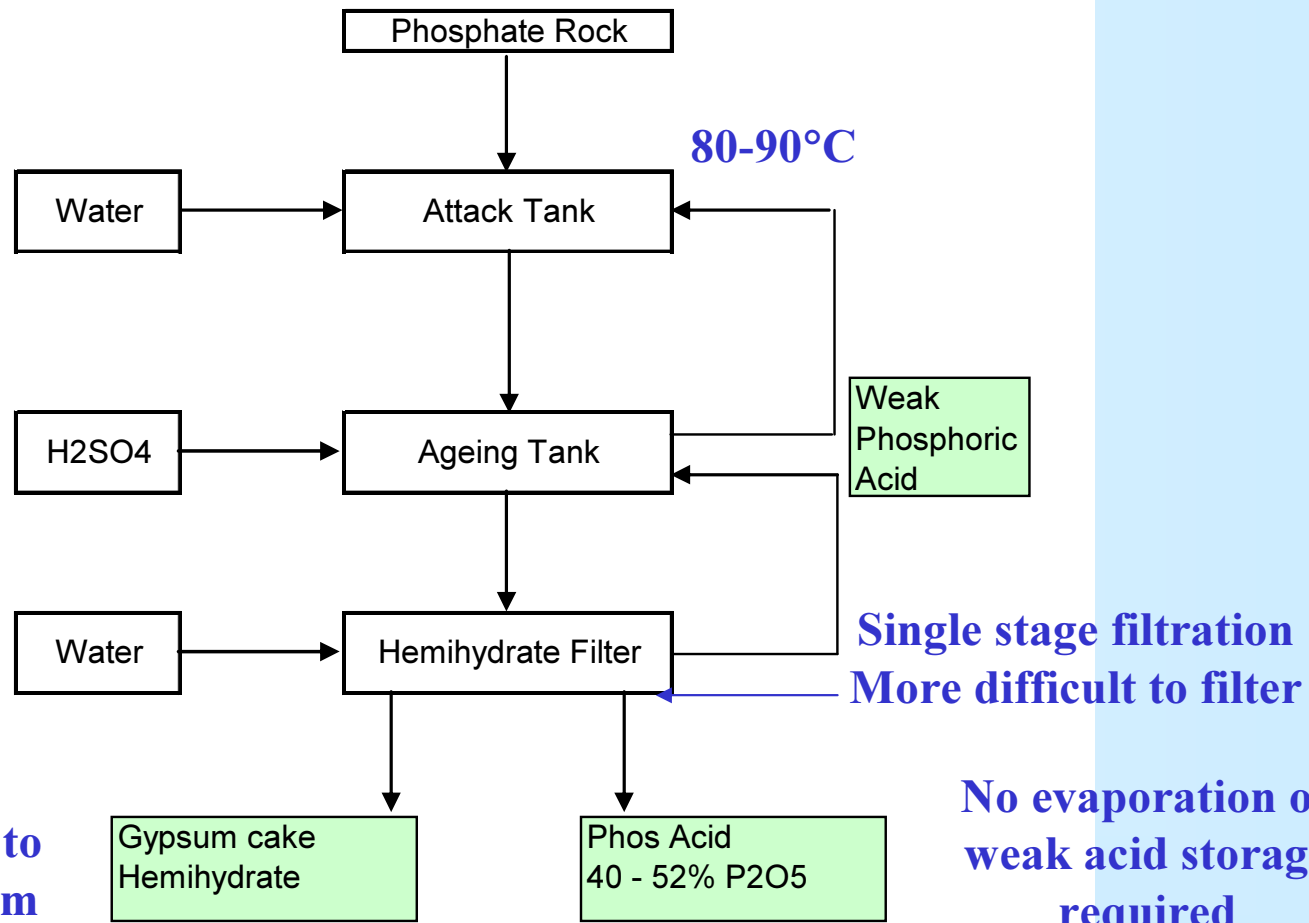
## Uranium Dissolution

- Phosphate rock hosts U(IV)
- ORP affects U dissolution
- Reducing conditions direct U to the gypsum
- Oxidising conditions promote dissolution

ORP (mV)	% U Leached
240	70
290	80
510	96
850	98

Ref: Gupta & Singh – Uranium  
Resource Processing – Secondary  
Resources

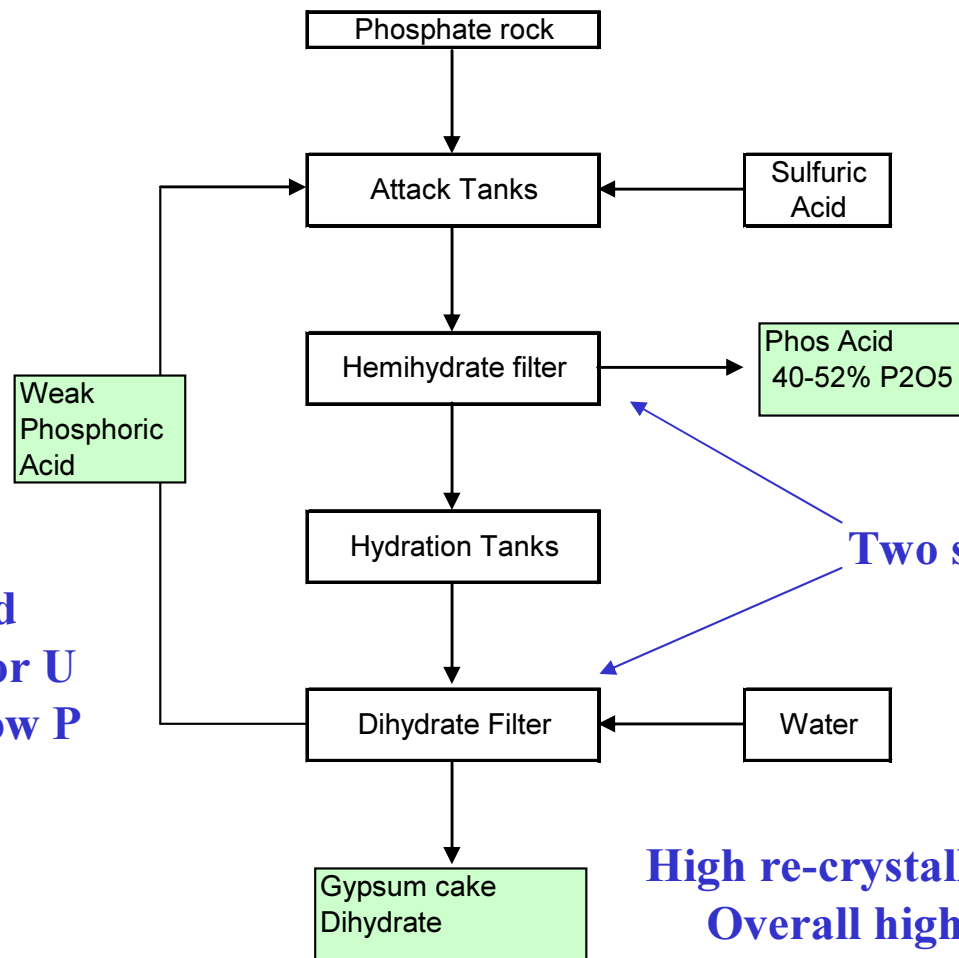
## Hemihydrate Process



Uranium tends to report to gypsum

No evaporation or weak acid storage required

## Hemihydrate-Dihydrate Process



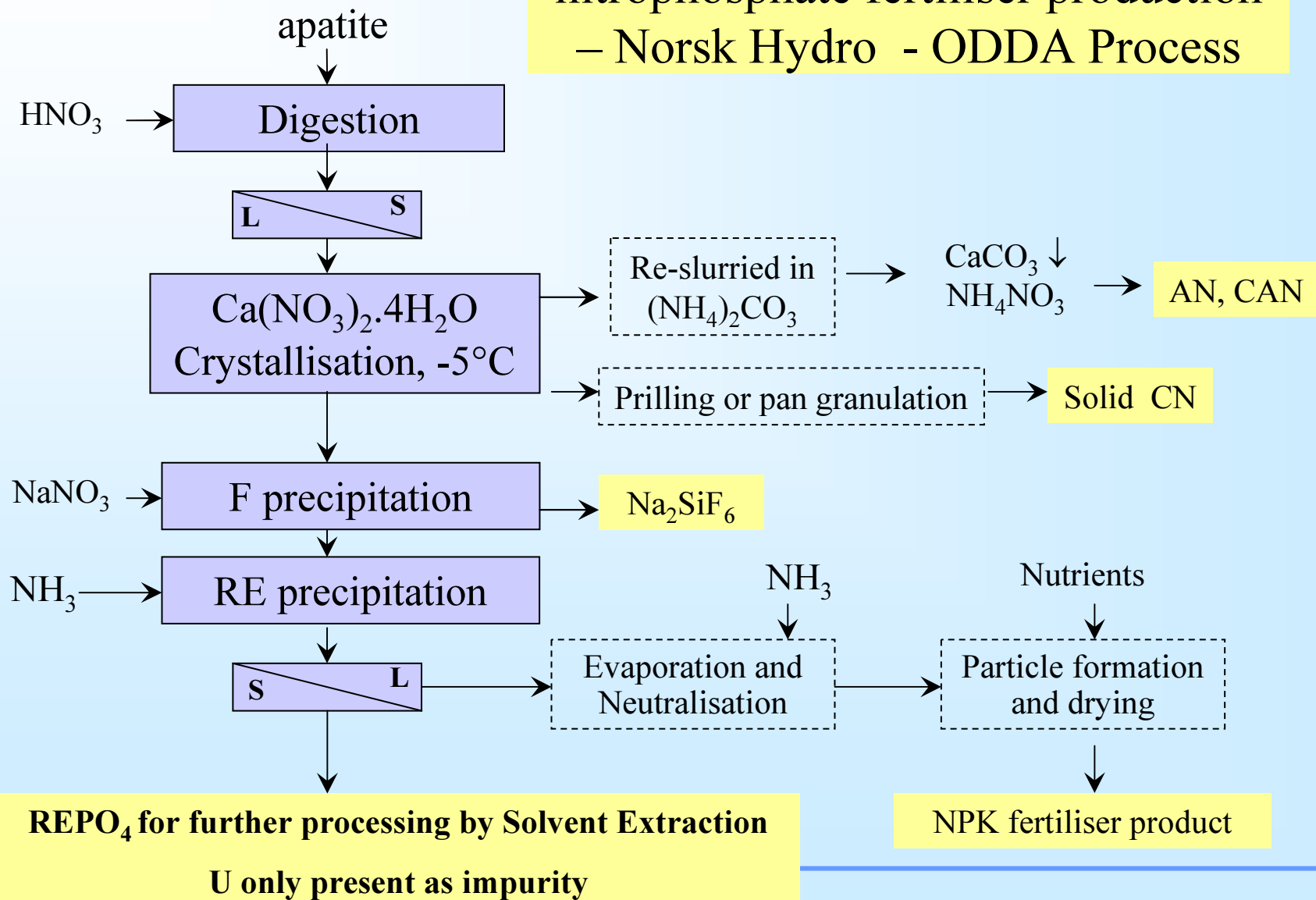
**Very good  
conditions for U  
recovery – low P**

**No evaporation or  
weak acid storage  
required**

**Two stage filtration**

**High re-crystallisation volume  
Overall high capital cost**

Recovery of RE integrated into  
nitrophosphate fertiliser production  
– Norsk Hydro - ODDA Process



## Uranium Recovery from Phosphoric Acid

- Solvent Extraction
  - Only technology that has been commercialised
  - OPPA Process
  - MOPPA/DOPPA
  - DEHPA/TOPO
  - Two Cycles of extraction and stripping
- Ion Exchange
  - Pilot stage
  - Suggestion of impregnated resin using DEHPA/TOPO but low loadings
- Precipitation
  - Has been used commercially but required free acid adjustment

## Pre and Post Treatment associated with Solvent Extraction

- Oxidation/Reduction
  - Reduction for OPPA and MOPPA/DOPPA Processes
  - Oxidation for DEHPA/TOPO
- Cooling
  - SX requires 40°C
- Filtration
  - Removal of suspended solids
- Organic Removal
  - Activated Carbon
  - Clay Treatment
- Post-Treatment
  - Removal/recovery of entrained solvent

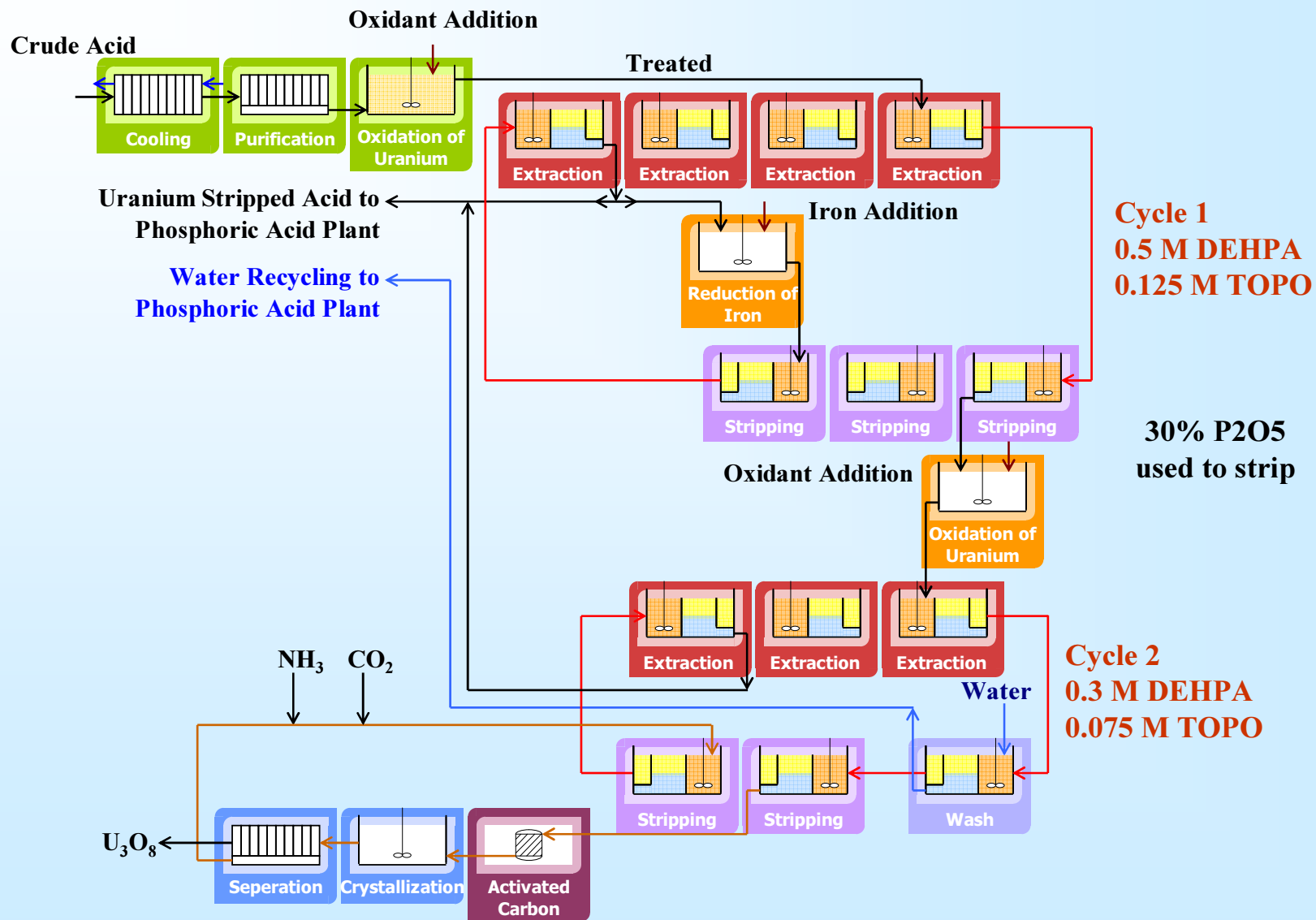
## SX OPPA Process

- Extraction with dioctyl pyrophosphoric acid
  - Strongly extracts U(IV)
  - Reagent is not stable and has to be produced on site
- Stripping requires HF
  - U also ppt (impure product)
  - Hydrolysis of the solvent is an issue
  - Re-dissolution of Uranium
- 2<sup>nd</sup> Cycle
  - Re-dissolution of U in nitric
  - Conventional TBP extraction, water strip and ppt ADU

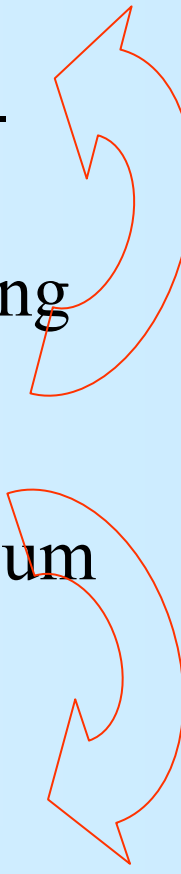
## SX MOPPA/DOPPA Process

- Extraction with mono and dioctyl phenylphosphoric acid
  - Extracts mainly U(IV) – feed needs to be reduced
- Stripping uses concentrated P<sub>2</sub>O<sub>5</sub> (40-50%)
  - U needs to be oxidised for stripping
  - Dilution to 30% P<sub>2</sub>O<sub>5</sub> is required before 2<sup>nd</sup> cycle
- 2<sup>nd</sup> Cycle
  - Same reagent
    - Requires U as U(IV) – need to reduce strip solution
    - Stripping with HF
  - DEHPA/TOPO
    - Requires U as U(VI)
    - Stripping with ammonium carbonate

# SX DEPA-TOPO Process



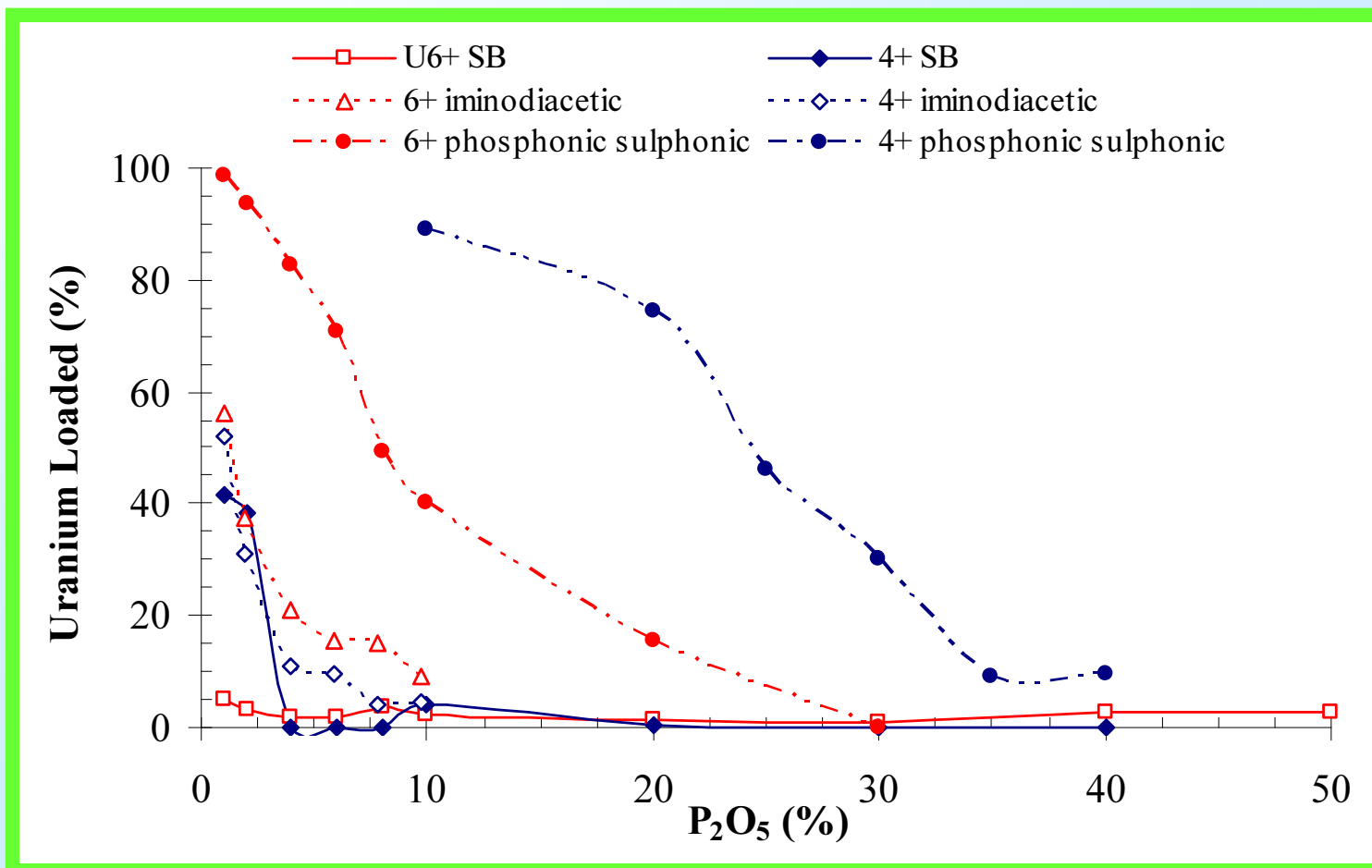
# Objectives of Alternative Process

- Reduce requirement for pre-treatment and post-treatment
  - Improve operability of the process by introducing an alternate uranium concentration process
    - Ion exchange technology
  - Use conventional uranium technology for uranium purification and concentration
  - Aim to reduce capital and operating costs
- 

## Advantages of Ion Exchange Technology

- IX is better suited for feed liquors  $< 300$  mg/L U
- IX processes tend to have lower capital and operating costs compared to SX at low feed concentrations
- Maybe more tolerant to higher temperature (max 80°C)
- Maybe more tolerant organic acids in the feed
- Eliminate requirement for post-treatment of phosphoric acid
- Fluidised bed ion exchange systems are tolerant to solids – reduced need for clarification

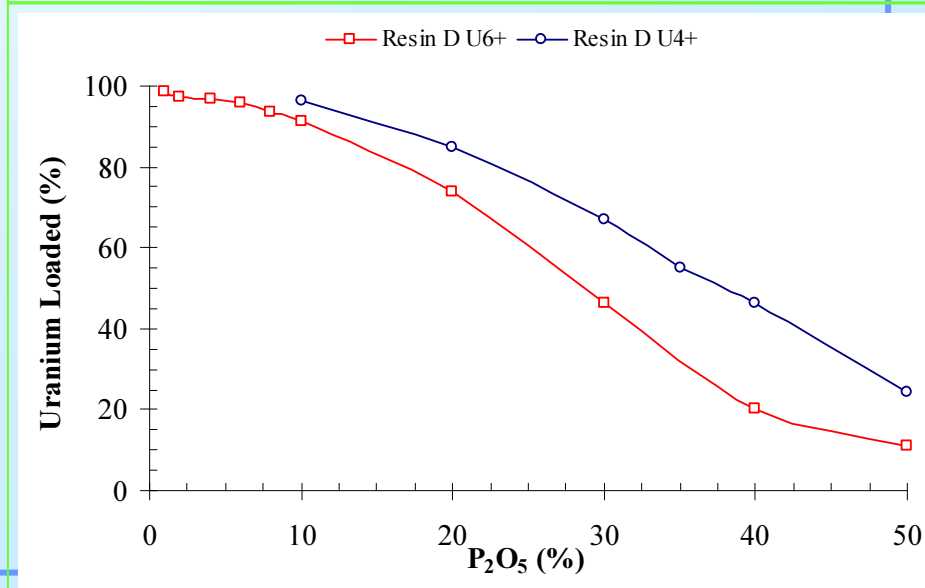
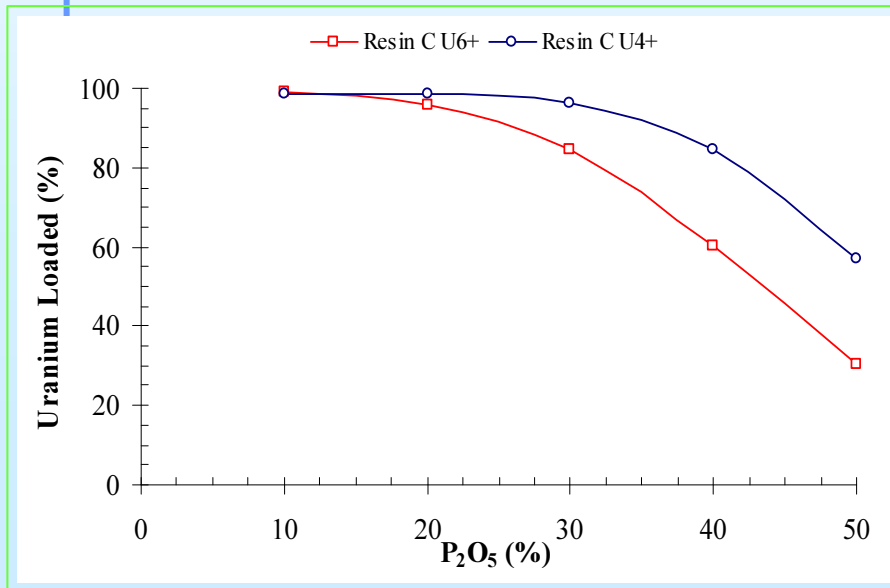
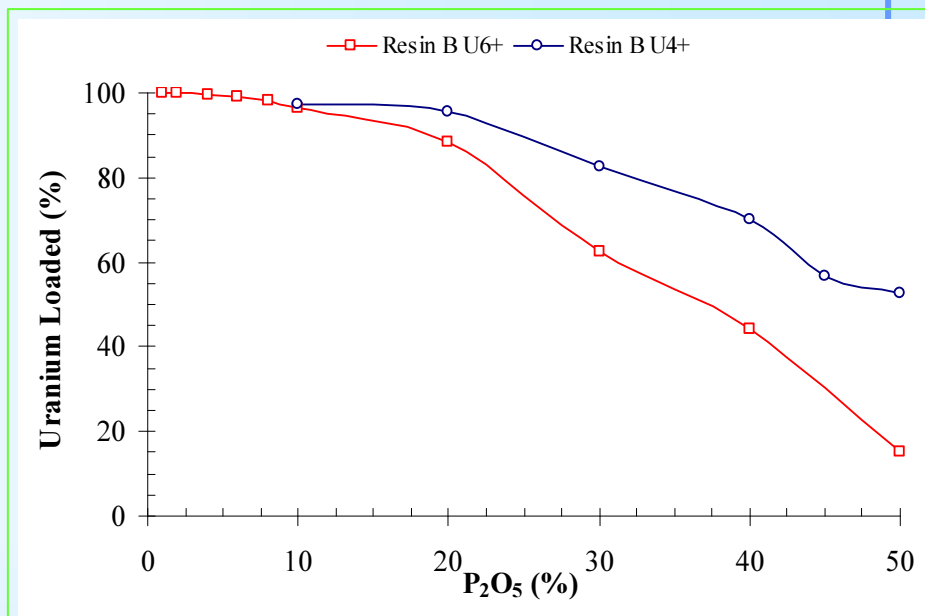
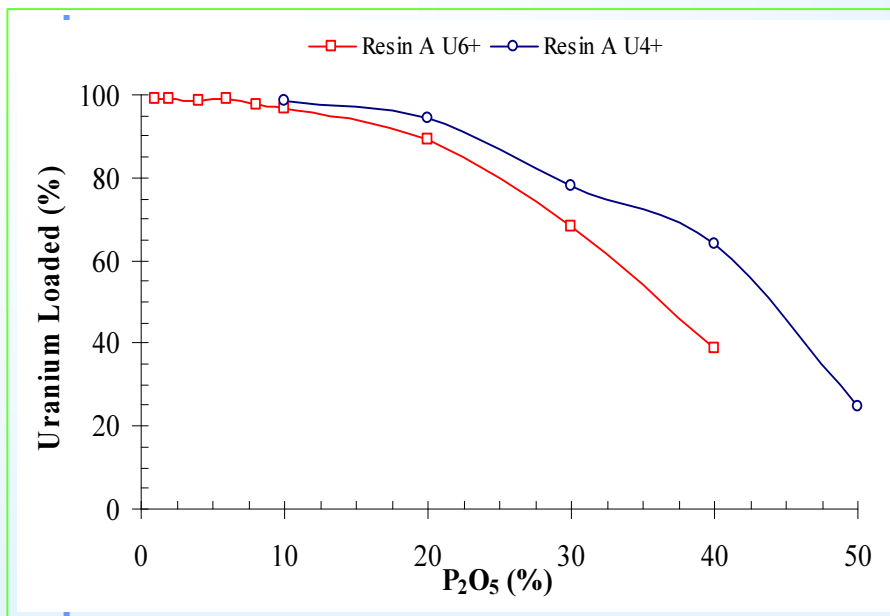
## Screening Resin with Synthetic Solutions Extraction of Uranium 6+ and 4+



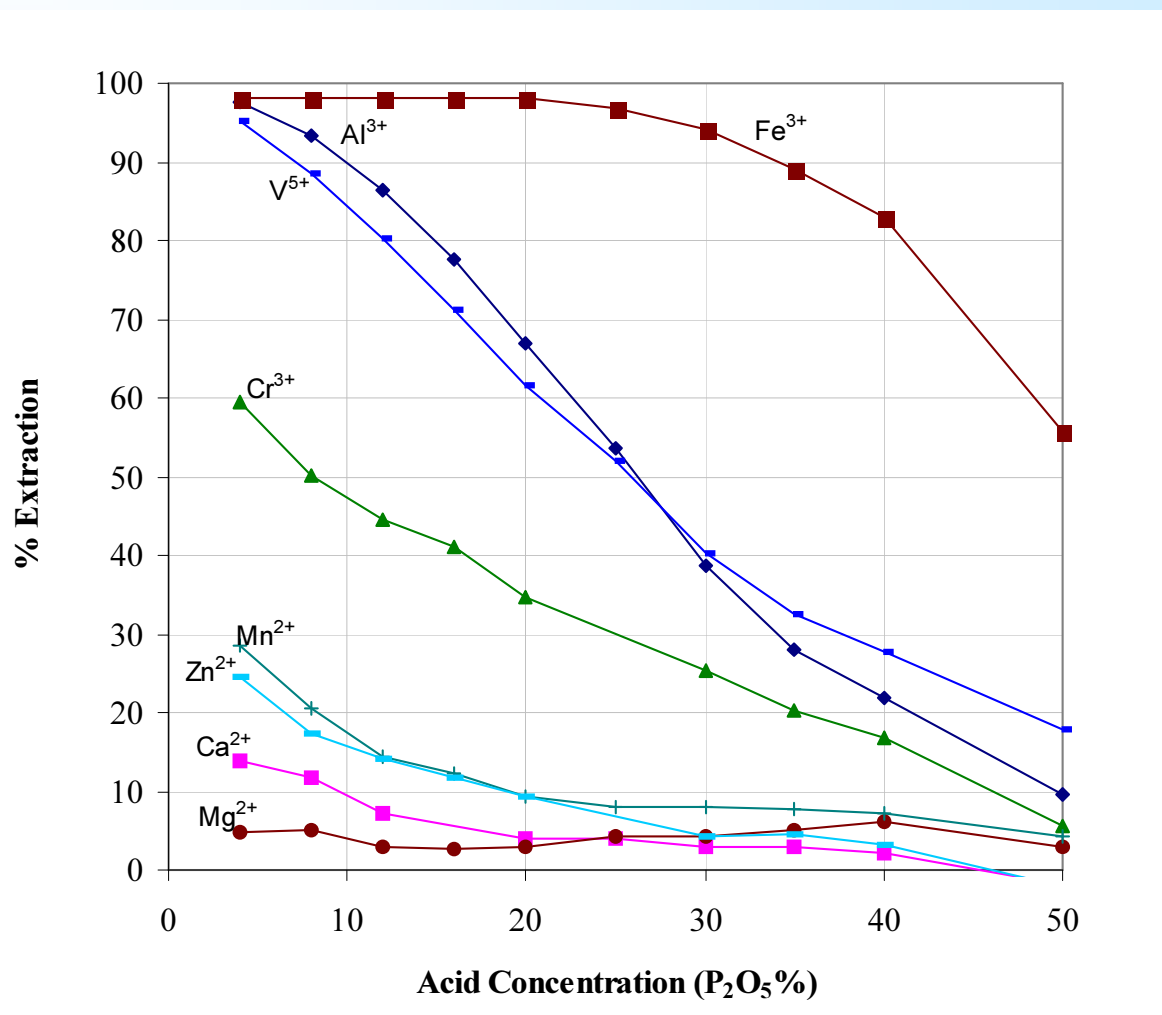
## Aminophosphonic Resins

Resin Name	Ionic Form (supplied)	Moisture content (%)	Specification capacity (eq/L)	Maximum Operating Temp (°C)	Particle Size (mm)
Lewatit TP260	(Na)	58-62%	2.3		0.500 - 0.600
Purolite S940	(Na)	55-65%	2.0	90	0.425 - 0.850
Amberlite IRC747	(Na)	64-69%	1.75	80	0.520 - 0.660
Duolite C467	(Na)	65-70%	1.0	80	0.500 - 0.700

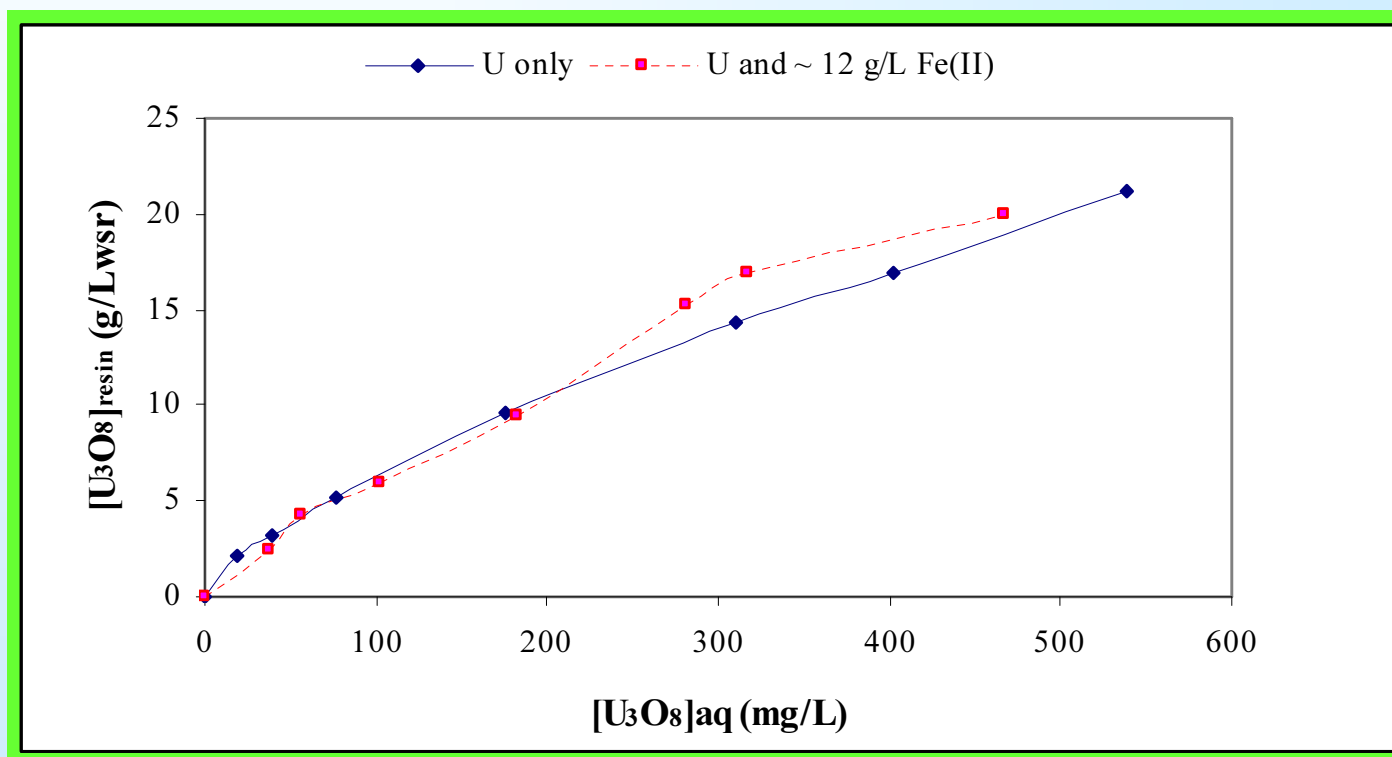
# Extraction of Uranium with Aminophosphonic Resins



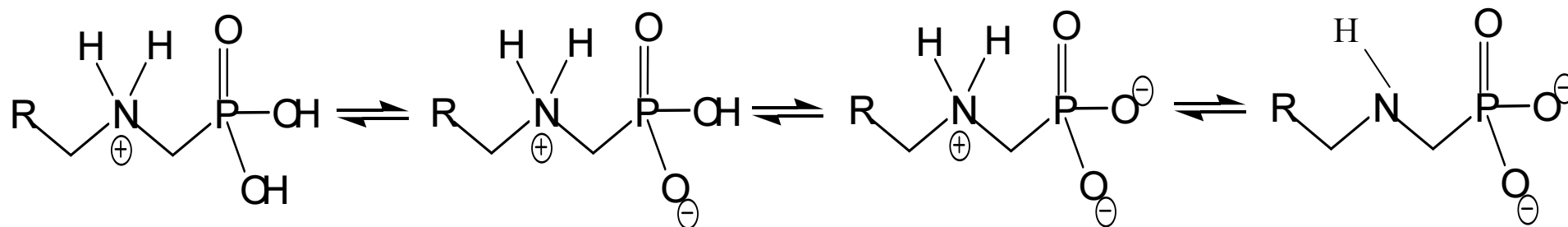
## Screening resins with synthetic liquors Extraction of other metal ions – Resin A



## Equilibrium Loading from Synthetic Solution Impact of Fe(II)



## How do Aminophosphonic Resins Extract Ions from Solution?



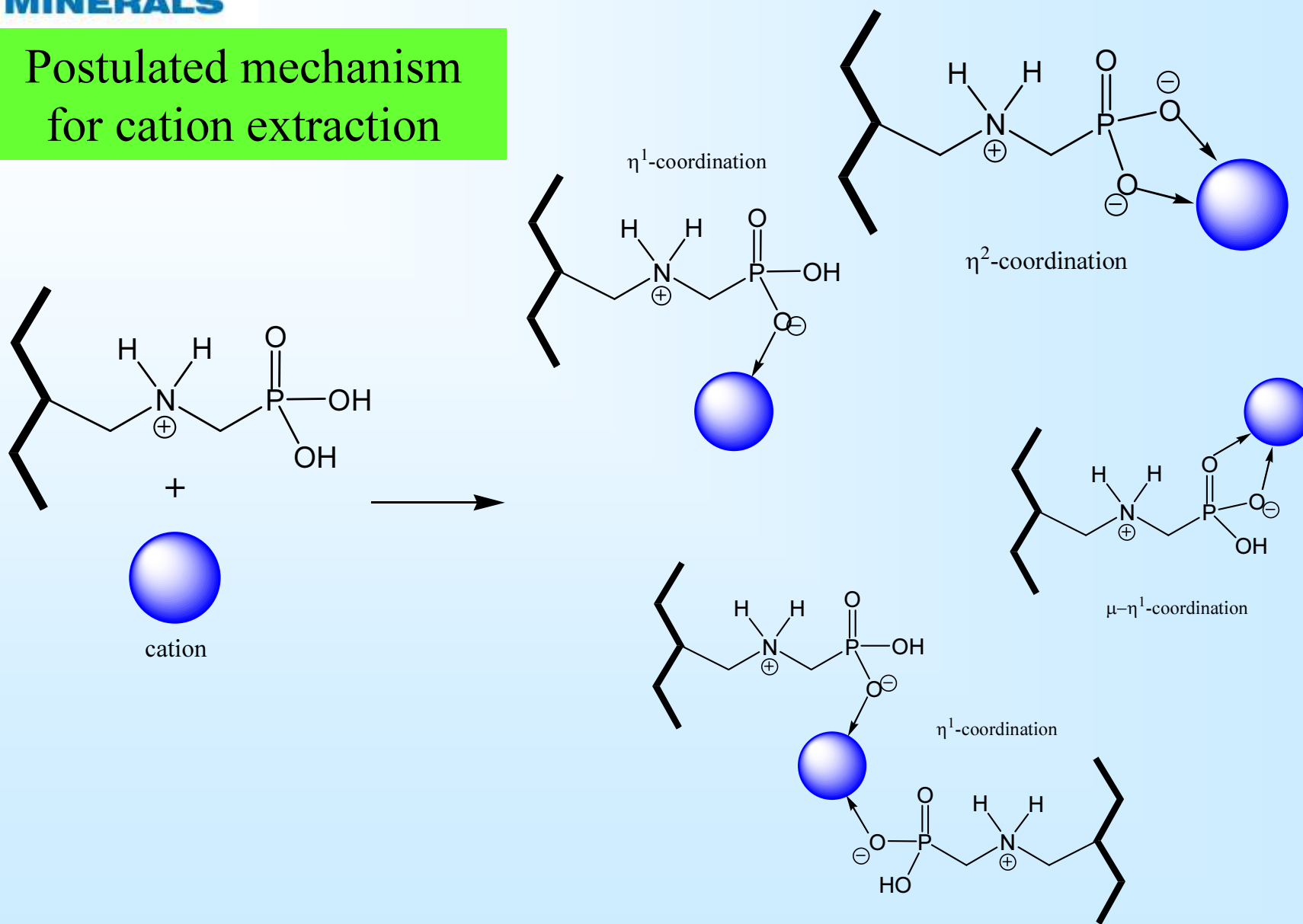
pH ~1.5

pH ~5.3

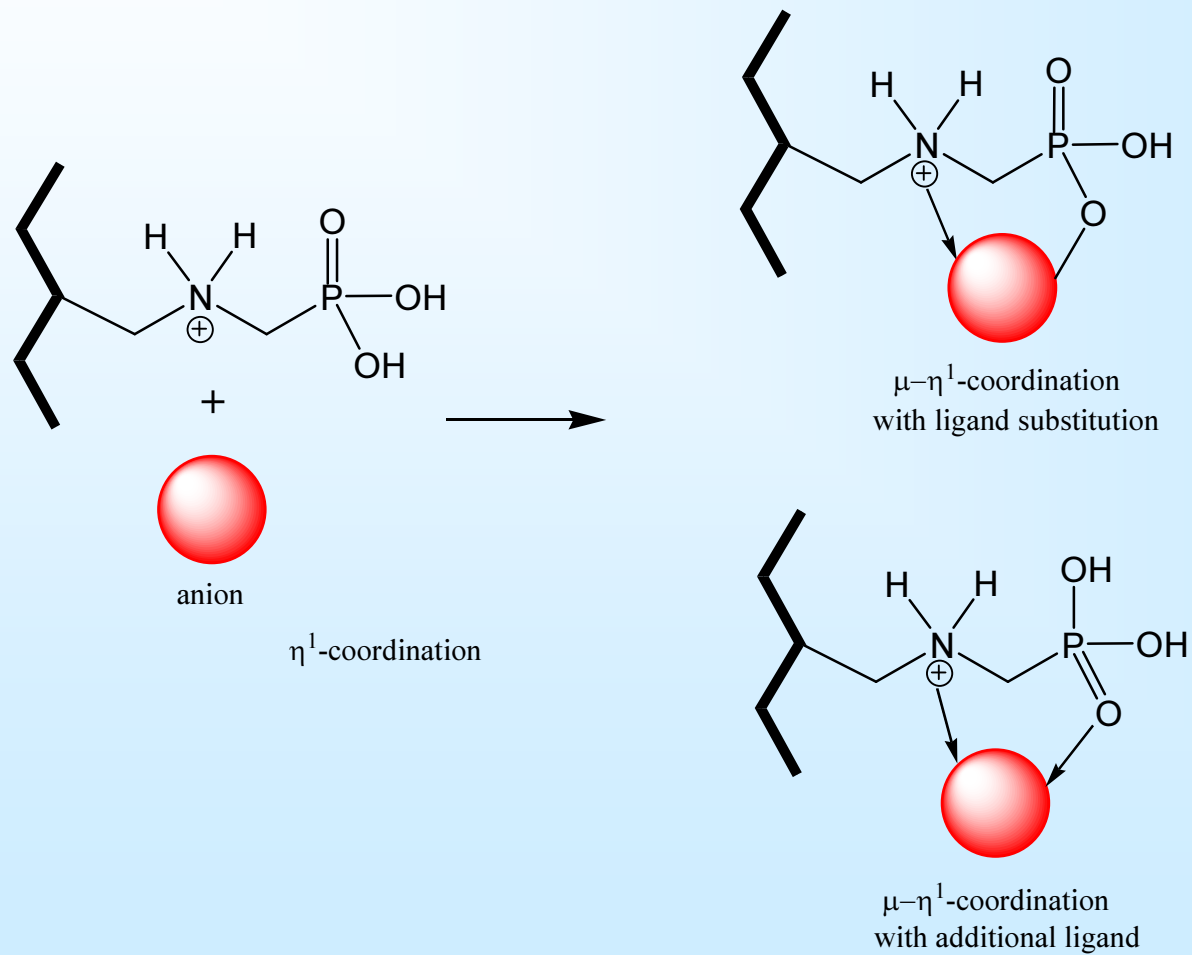
pH ~11

Ref: Nesterenko et al (1999)

Postulated mechanism  
for cation extraction



Postulated mechanism  
for anion extraction



## Modelling of Speciation Chemistry of Uranium in 30% P<sub>2</sub>O<sub>5</sub>

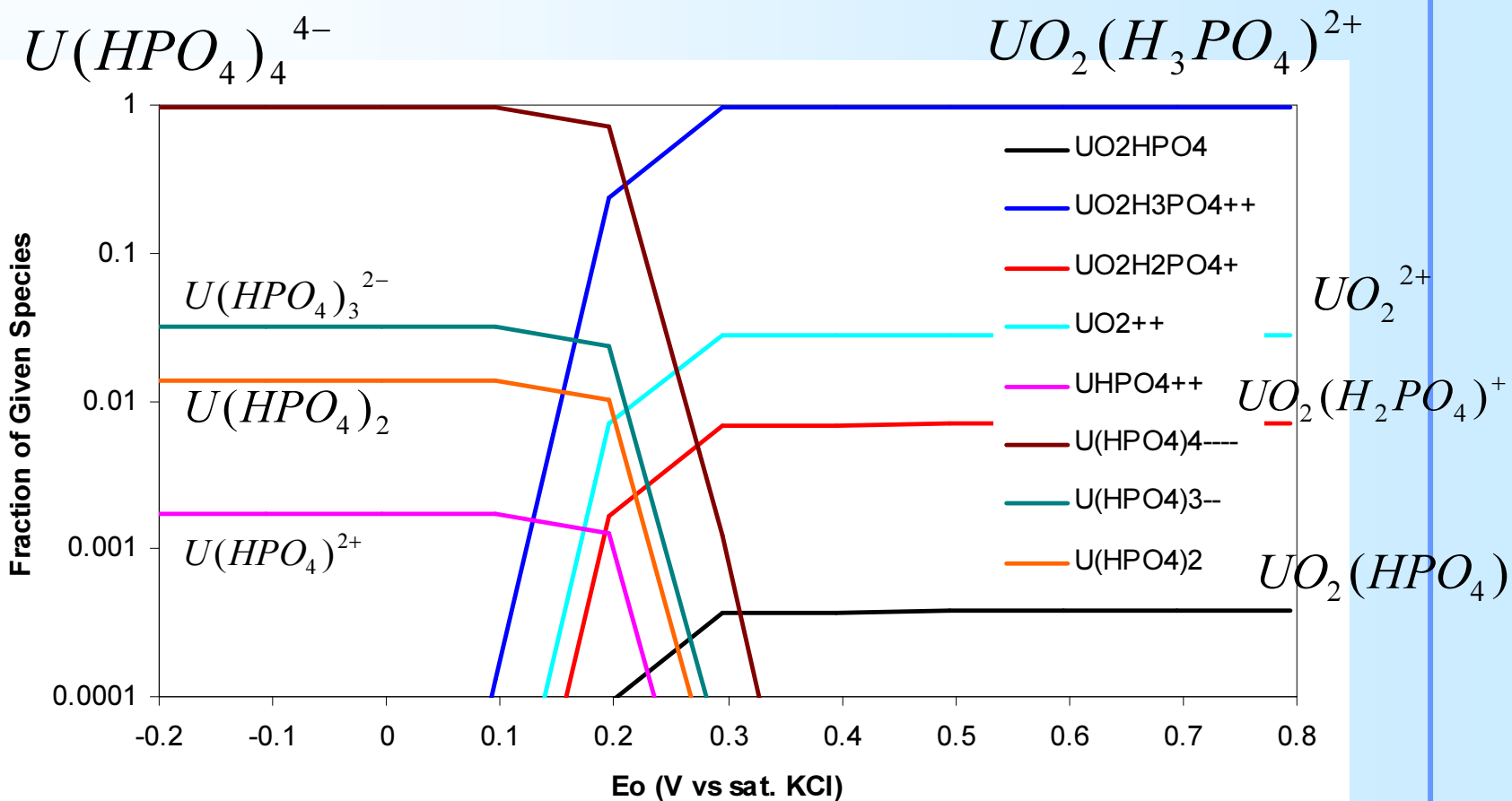
- Use geochemical modelling package
- Activity model based on effective concentration of model species
- Activity corrections based on Debye-Huckel method (applicable to 0.1 Molal)
- Extension to 0.5 Molal based on Davies Equation
- Backed by extensive thermodynamic databases
- Models included 45 aqueous species and 25 minerals
- Baseline model included 2.2 g/L Fe, 0.2 g/L U, 5 M H<sub>3</sub>PO<sub>4</sub>

Typical output from  
program

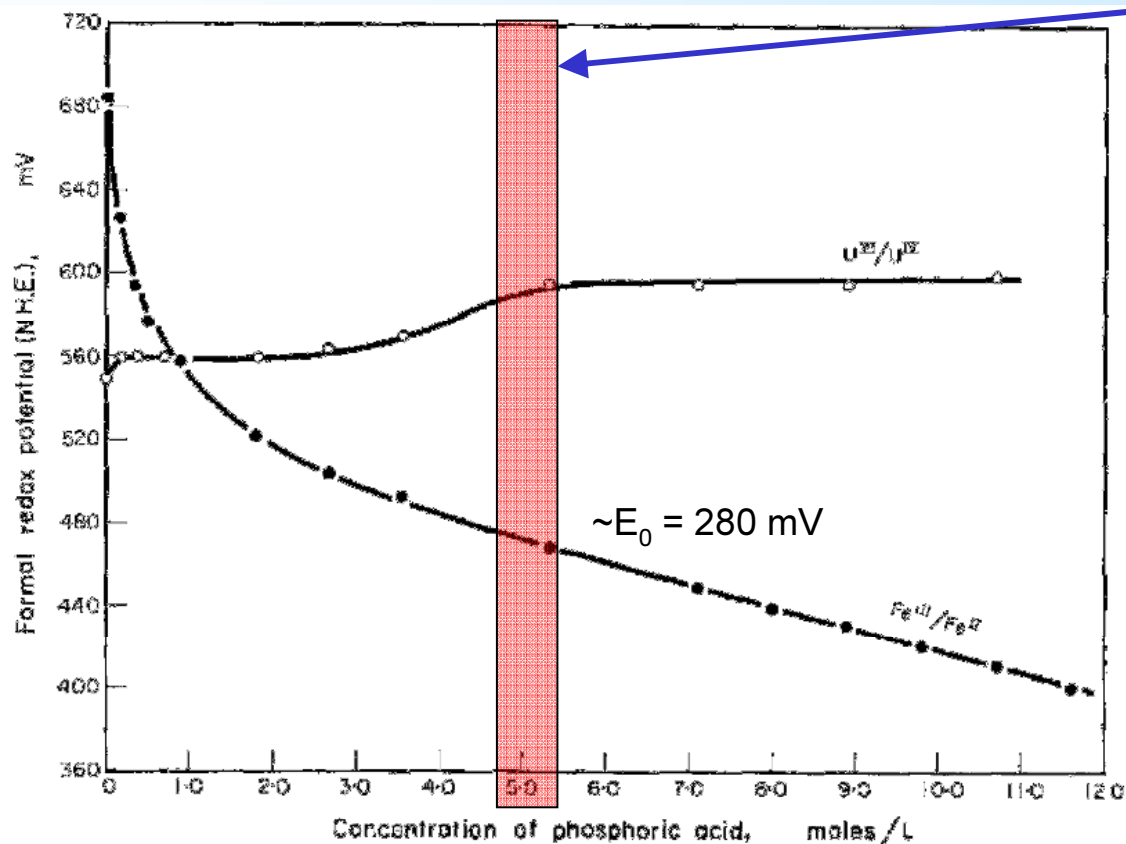
Geochemist Workbench V 8.0  
Bethke, C.M, University of Illinois,  
Urbana, Illinois

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
H3PO4	5.060	3.298e+005	1.1720	0.7730
H+	1.307	875.9	0.7480	-0.0100
H2PO4-	0.05770	3722.	0.7480	-1.3650
U(HPO4)4----	0.0008020	331.8	0.0096	-5.1137
UO2H3PO4++	0.0002511	61.48	0.3130	-4.1046
U(HPO4)3--	2.510e-005	8.782	0.3130	-5.1048
U(HPO4)2 (aq)	1.055e-005	3.018	1.1720	-4.9078
UO2++	7.360e-006	1.322	0.3130	-5.6376
UO2H2PO4+	1.752e-006	0.4277	0.7480	-5.8826
UHPO4++	1.363e-006	0.3029	0.3130	-6.3698
UO2HPO4 (aq)	9.561e-008	0.02328	1.1720	-6.9506
U++++	1.358e-008	0.002151	0.0096	-9.8849
HPO4--	8.944e-009	0.0005710	0.3130	-8.5530
UOH+++	3.526e-010	5.982e-005	0.0733	-10.5878
UO2OH+	1.579e-011	3.014e-006	0.7480	-10.9278
(UO2)2OH+++	1.317e-013	4.881e-008	0.0733	-14.0154
UO2PO4-	6.318e-014	1.534e-008	0.7480	-13.3256
OH-	1.227e-014	1.388e-010	0.7480	-14.0372
(UO2)2(OH)2++	3.379e-017	1.290e-011	0.3130	-16.9757
UO2(OH)2 (aq)	1.156e-018	2.338e-013	1.1720	-17.8681
PO4---	1.649e-020	1.041e-015	0.0733	-20.9180
U(OH)4 (aq)	7.679e-021	1.563e-015	1.1720	-20.0458
UO2(OH)3-	1.312e-026	2.801e-021	0.7480	-26.0083
(UO2)3(OH)4++	3.394e-029	1.983e-023	0.3130	-28.9737
(UO2)3(OH)5+	2.898e-033	1.726e-027	0.7480	-32.6640
UO2(OH)4--	2.023e-038	4.549e-033	0.3130	-38.1985
(UO2)4(OH)7+	2.478e-045	1.976e-039	0.7480	-44.7320
(UO2)3(OH)7-	5.391e-050	3.332e-044	0.7480	-49.3944
O2(aq)	6.888e-060	1.466e-055	1.1720	-59.0930
Mineral saturation states				
	log Q/K		log Q/K	
U(HPO4)2:4H2O	-0.3577	UO2(OH)2 (beta)	-11.3297	
UO2HPO4	-2.3406	Schoepite	-11.7623	
H-Autunite	-5.2001	Gummite	-13.3396	
Uraninite	-5.2760	UO3	-13.3678	
UO2 (am)	-8.4453	U4O9	-23.2680	
(UO2)3(PO4)2	-9.3488	U3O8	-23.9324	
Gases				
	fugacity	log fug.		
O2 (g)	7.899e-057	-56.102		

# Predicted Uranium Speciation



# Impact of H<sub>3</sub>PO<sub>4</sub> on Fe<sup>3+</sup>/Fe<sup>2+</sup> reduction potential



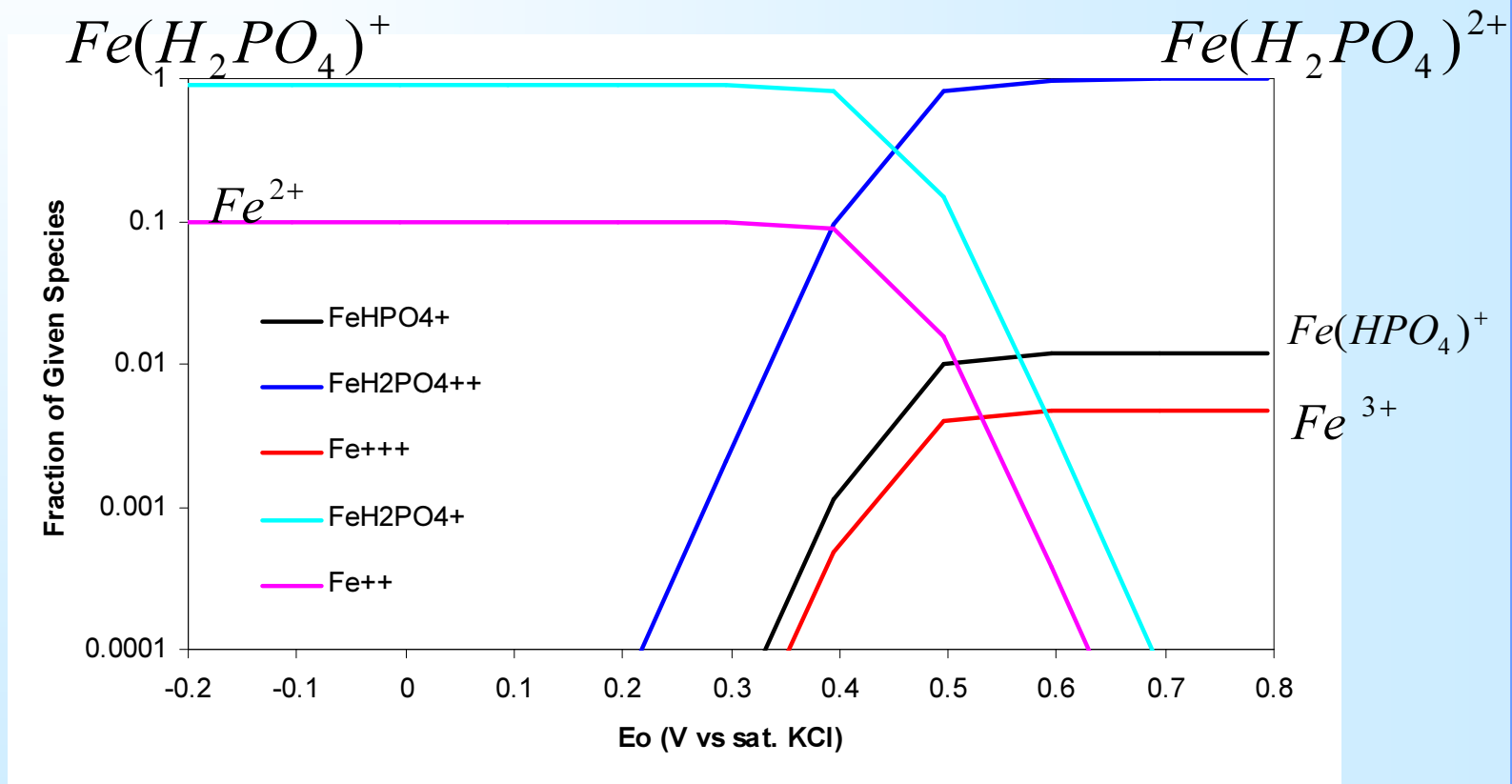
30% P<sub>2</sub>O<sub>5</sub>

FIG. 1--Formal redox potentials of U<sup>VI</sup>/U<sup>IV</sup> and Fe<sup>III</sup>/Fe<sup>II</sup> couples in a phosphoric acid medium.

Ref: Gopala  
et al (1962)

$$E_H = E_0 + \sim 205 \text{ mV}$$

# Predicted Iron Speciation





General E-chem  
Setup

Rotating disc electrode

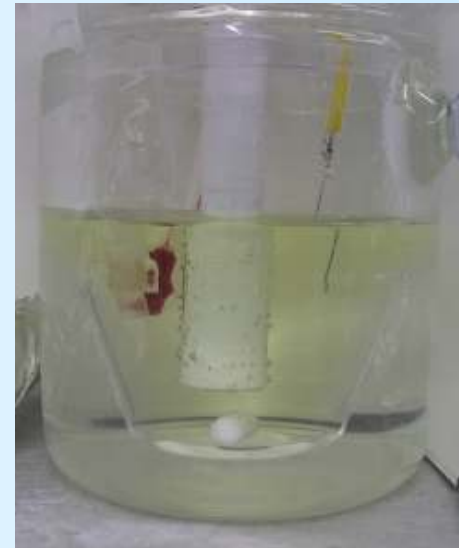
Solartron 1840

EIS interface

2 g/L Fe, 0 mg/L U



2 g/L Fe, 100 mg/L U



2 g/L Fe, 200 mg/L U

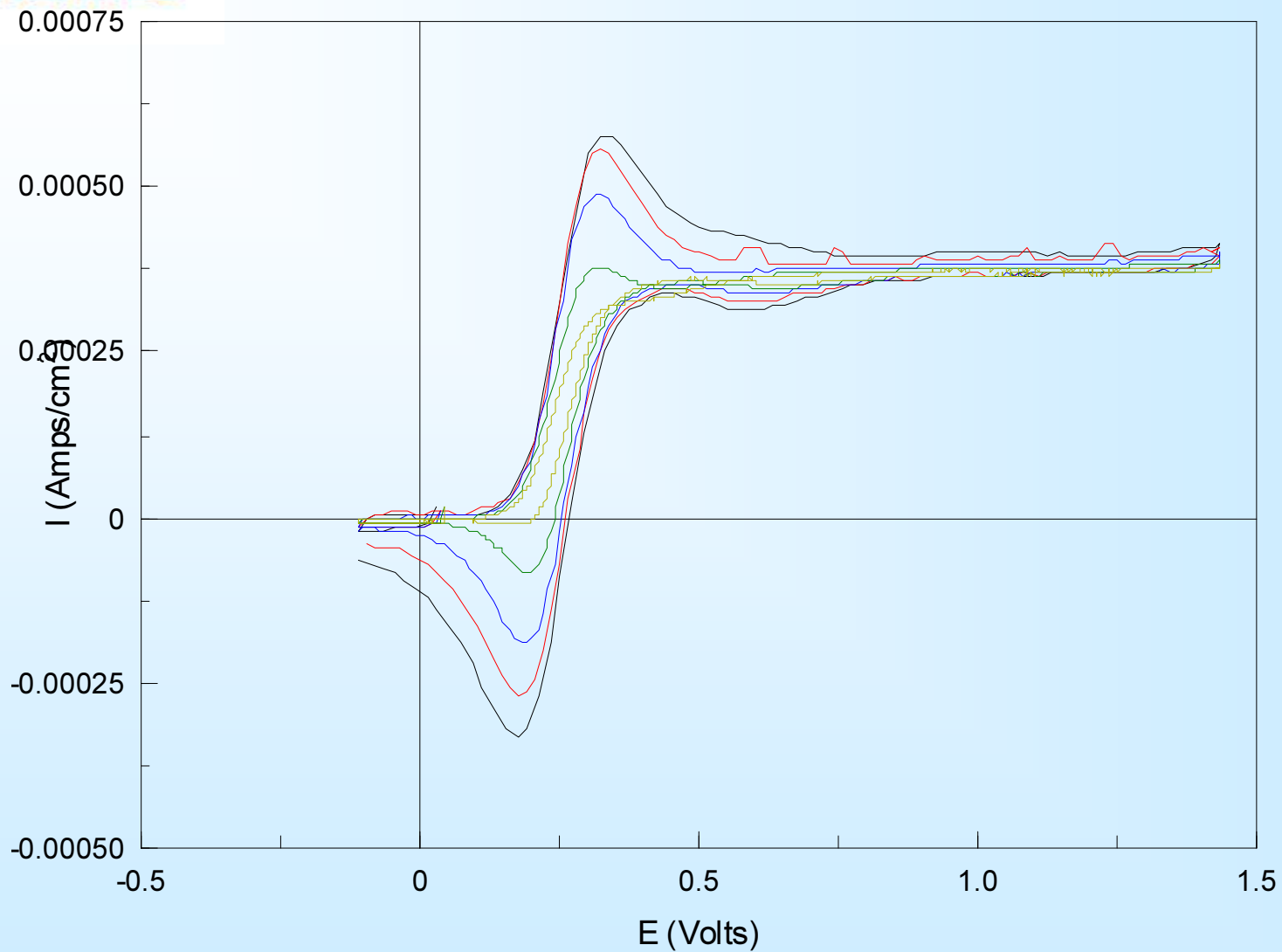


2 g/L Fe, 600 mg/L U



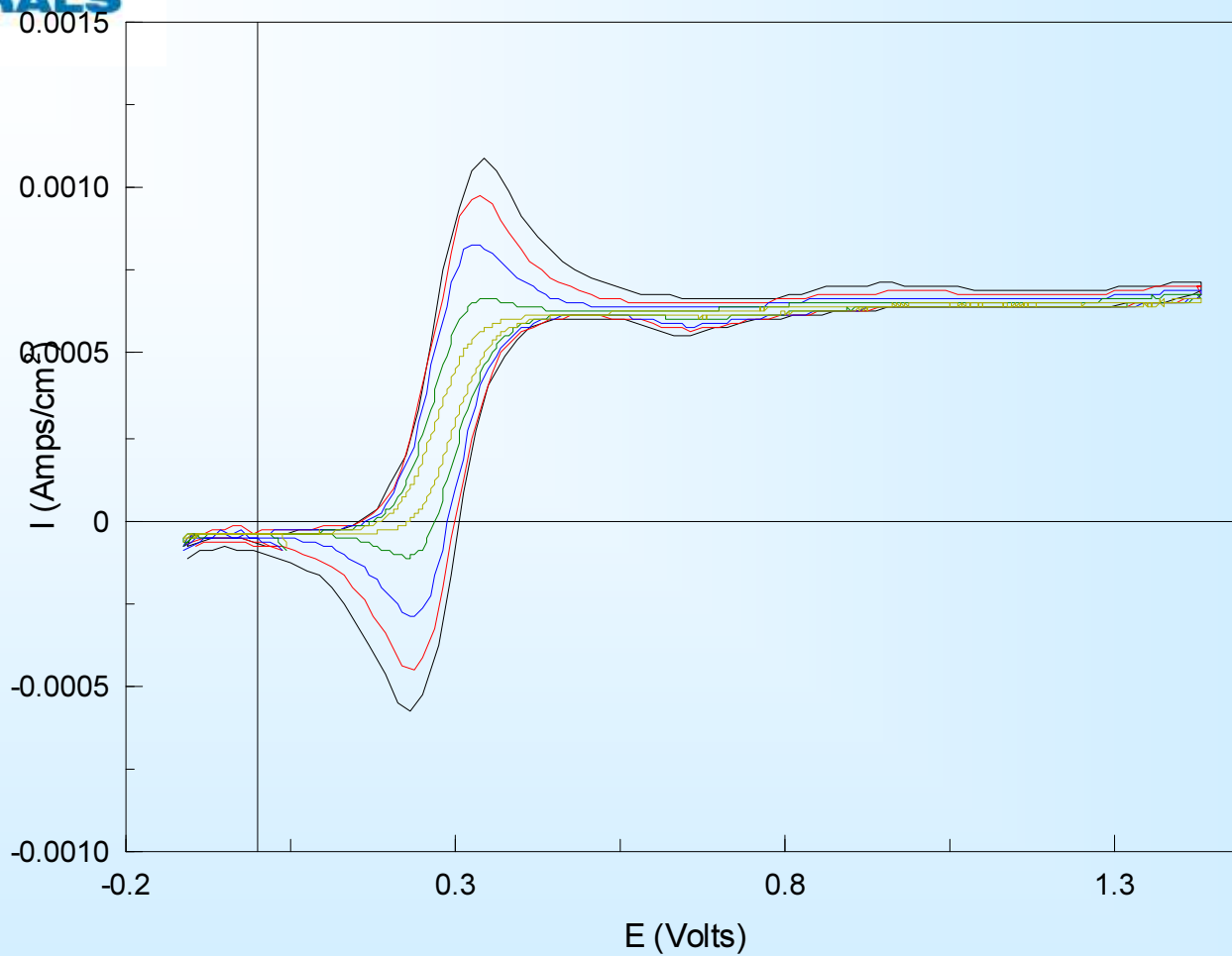
2 g/L Fe, 1200 mg/L U





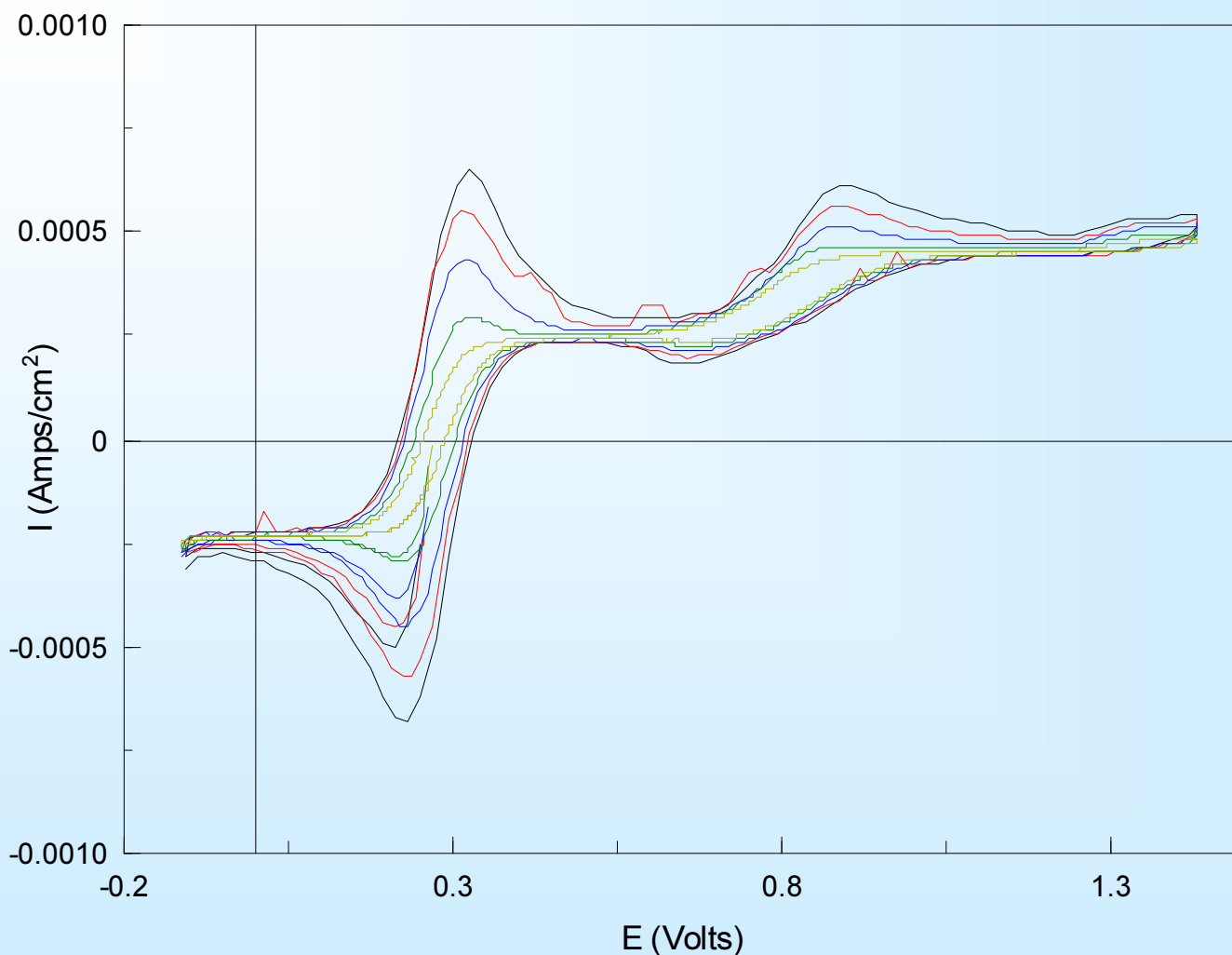
Reductive (~0.2 V) and oxidative waves (0.3 V) clearly present

$\text{H}_3\text{PO}_4 \sim 5.3 \text{ M}$  with 2 g/L Fe and 200 mg/L U



Features from both Fe and U redox profiles present  
U redox couple 'swamped' by Fe but still present

$H_3PO_4$  ~5.3 M with 2 g/L Fe and 1800 mg/L U



Increased U shows U redox couple much better

Shape of redcutive wave for U is due to precipitation of U/Phosphate at these concentrations

Fe redox couple lies below that of U as predicted by literature

## Conclusions

- Extraction of uranium with aminophosphonic resins is a good option for an IX process
  - Both U(IV) and U(VI) are extracted at 30% P<sub>2</sub>O<sub>5</sub>
  - Loading is adequate
- Speciation studies indicate that U(IV) is predominantly anionic and U(VI) is predominantly cationic
- Confirmed reversal of U and Fe redox potentials in phosphoric acid compared to sulphate systems
- Studies are ongoing to determine the extraction mechanism in synthetic solutions and how other impurities present in WPA especially Fe, impact on uranium extraction

## Important Targets for Processing

- Work with real WPA solutions
- Require high U extraction
- Control of impurities
- Develop U recovery from IX eluate
- Mini-Pilot Plant Trials of integrated process with resin recycle

# THANK YOU

ANSTO OPAL Research Reactor

