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Who Did What in Solvent Extraction A Demonstrated & Proven Technology for Uranium Recovery from Phosphoric Acid

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There and Back Again 2.5

Who Did What in Solvent Extraction A Demonstrated & Proven Technology for Uranium Recovery from Phosphoric Acid

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Beneficiation of Phosphates VII

Melbourne, Australia

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There and Back Again 2.5

- History
- What we Know!
- Present!
- Future!!

History….Two.5 Waves

History....The Waves

- Started in 1950s, ended early 1960s – Emphasis on Military Stockpiling
- Started late 1970s, ended 1990s – Nuclear Power
- 2010s? – Nuclear Renaissance/ Era of Resource Conservation and Sustainability, Carbon Dioxide Mitigation
- Renewed Interest in Uranium Supply.

P_2O_5
A Potential Major Source for Uranium

- Phosphate Deposits Contain Uranium
  - Nature and Value of Deposits are in a Phase of Extreme Transition

- Uranium Recovery is a Well-Tested Additional Opportunity in Phosphoric Acid Production
  - Range: 0.1-7 Kg/Tonne of P_2O_5
  - Typically: 0.3-0.6 Kg U per Tonne P_2O_5
  - Price: Volatile, but in 2007, U_3O_8 Reached $300/KG
  - Currently About $90/Kg on Spot Market and $150/Kg for Some Long Term Contracts

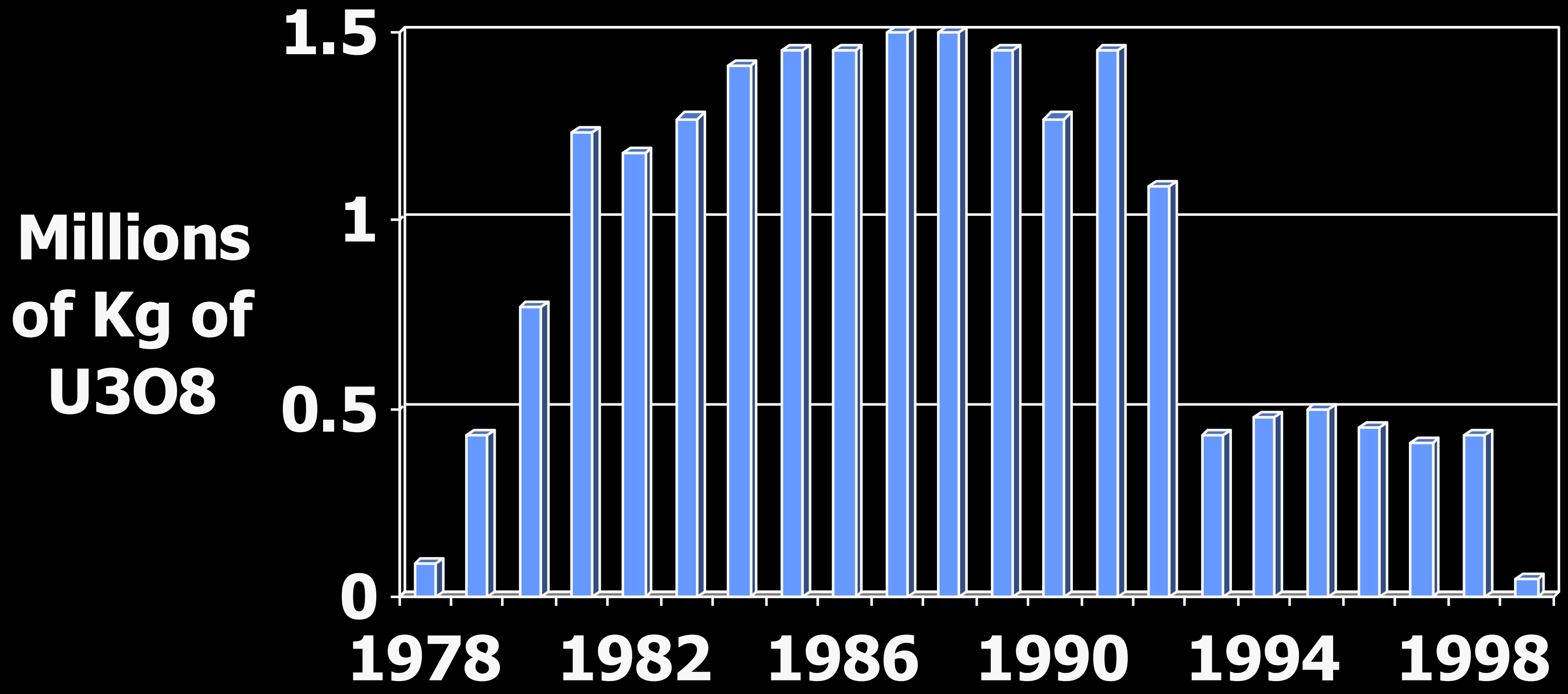
History of Uranium Recovery .. First Wave

- First Plant was Built in 1952 in Joliet Illinois. It Precipitated the Uranium as a Phosphate
- Two Plants were Built in 1955 & 1957 in Florida. These Used a Solvent Extraction Process (Octyl Pyro Phosphoric Acid)
- All Three Plants Operated until the Early 60s, when the Low Cost Production of Uranium from Western Mines Depressed the Price

History of Uranium Recovery .. Second Wave

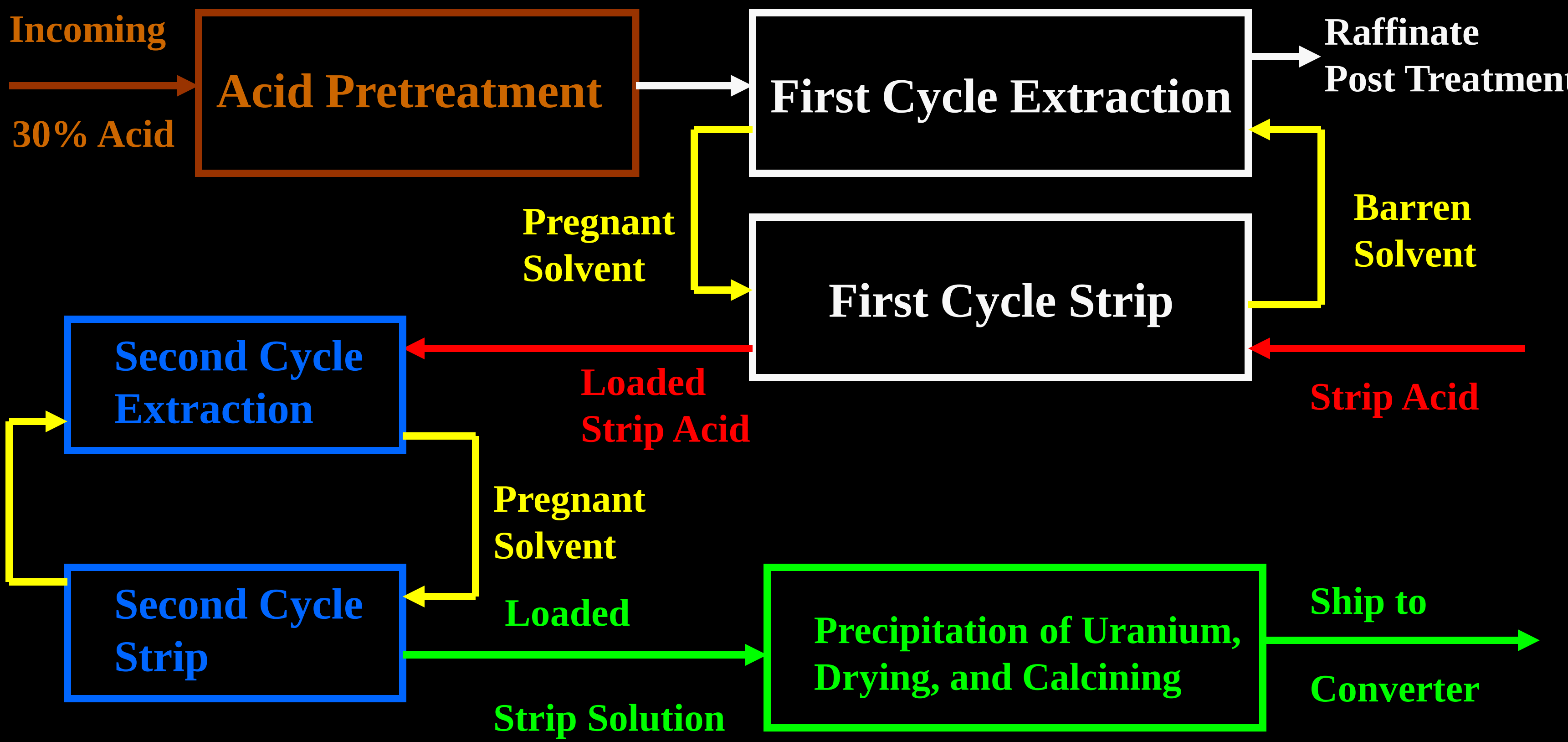
- The Price of Uranium Increased Dramatically in the 1970s
- Eight new Plants were Built in the United States for the Recovery of Uranium From Phosphoric Acid
- Six were in Florida and Two were in Louisiana
- Plants were also Built in Canada, Spain, Israel, Belgium, Iran, Iraq, China and Taiwan

Uranium Recovered From Phosphoric Acid in the USA



Total U_3O_8 Recovered Approximately 20 Million Kgs

Flow Sheets of Recent U.S.A. Plants



Flow Sheets of Recent U.S.A. Plants

- All Plants Extracted Uranium from Acid Produced by Di-Hydrate Processes (27-28% P_2O_5 Plus 1.5-3% Sulfate)
- All Acids were Produced from Central Florida Rock
- U_3O_8 Content of All Acids was About 0.5 Kg/Tonne P_2O_5
- All Used a Solvent Extraction Process
- The Processes were Developed by Westinghouse, IMC (3 Plants), Uranium Recovery Corp., Freeport (2 Plants), and Gardinier

On Stream Factor and Recovery

- Westinghouse Plant Operated With 98+ % On Stream Factor and 92+% U_3O_8 Recovery
  - Turn Around After 2 Years and Down for Mechanical Problems Only
- IMC Plants Operated at 92% On Stream Factor and 96% U_3O_8 Recovery
  - Down Weekly for Line Scrubs and Yearly Turn Around)
- Freeport Plants Operated at 92% On Stream Factor and 95% U_3O_8 Recovery
  - (Down Weekly for Line Scrubs and Yearly Turn Around)
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Annual U_3O_8 Capacity

- IMC New Wales Plant Produced as Much as 591,000 Kg/Yr U_3O_8.
  - CF Plant City Module Produced as Much as 409,000 Kg/Yr U_3O_8.
  - One CF Plant Closed Down After Less than 3 Years of Operation
- Freeport Plants Produced as Much as 482,000 Kg/Yr U_3O_8. (Combined)

Plant / Design	Freeport	Gardinier	IMC	Uranium Recovery Corp.	Westinghouse
Pretreatment Cooling	No cooling	2-stage flash cooling - 32°C	Spiral coolers cool - 49°C	No cooling	Flash cool - 38°C
Solids Removal	Flocculant added before clarification	Filtered using pressure leaf filters	Clay /flocculant added before clarification	Flocculant added before clarification	Flocculant added before clarification
Further Pretreatment	None	None	Colour removal - activated C	None	None
Oxidation State Change	Oxidised with oxygen	Reduced with scrap Fe	Oxidised with H_2O_2. Later O_2	Reduced using ferro-silicon	Oxidised using nitric acid
First Cycle Solvent	DEHPA/TOPO	Octyl pyro-phosphoric acid (OPPA)	DEHPA/TOPO	Octyl pyro-phosphoric acid (OPPA)	DEHPA/TOPO
Mixer Settler Design	Low profile rectangular pumper-mixer settlers	Rectangular pumper-mixer settlers	Circular mixer settlers	Deep-cone bottom settlers	Low profile rectangular pumper-mixer settlers
First Cycle Strip Solution	31% P_2O_5 acid plus iron	15% HF precipitated U as green salt	31% P_2O_5 acid plus sulphuric acid and iron	40% P_2O_5 acid plus hydrogen peroxide	27% P_2O_5 acid plus iron
Second Cycle Oxidation State Change	Oxidised with oxygen	Dissolved in nitric acid	Oxidised with H_2O_2. Later used oxygen	No oxidation change required	Oxidised using nitric acid
Second Cycle Solvent	DEHPA/TOPO	TBP	DEHPA/TOPO	DEHPA/TOPO	DEHPA/TOPO
Uranium Precipitate Form	Ammonium diuranate	Ammonium diuranate	Uranyl peroxide	Ammonium uranyl tricarbonate	Ammonium uranyl tricarbonate

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Capital Costs

- Westinghouse Total Capital Cost was Less Than $20,000,000. *(About 20% of the Equipment was Not Used or Eliminated)*
- IMC Total Capital Cost was About $200,000,000 (3 Plants), *(At Least 30% of the Equipment was Eventually Eliminated*)
- URC Total Capital Cost was About $30,000,000
- Freeport Total Capital Cost was $40,000,000 for Uncle Sam and $30,000,000 for Faustina. *(About 10% of the Equipment was Eventually Eliminated)*
- The Gardinier Capital Cost was About $25,000,000

Cash Costs / Kg

- Westinghouse Total Cash Cost (Including Royalty, Cost of Acid Dilution, Losses and Reheat) was About $37/Kg U_3O_8 *($24/Kg w/o Royalty etc)*
- IMC (New Wales) Cash Operating Costs (No Royalty, Dilution, Reheat or Loss Cost) was About $24/Kg U_3O_8
- URC Total Cash Cost (Including Royalty, Cost of Acid Dilution and Acid Losses) was About $100/Kg U_3O_8 *(Low Throughput and Operating Factor)*
- Freeport Cash Operating Costs (No Royalty, Dilution, Reheat or Loss Cost) was About $26/Kg U_3O_8
- Gardinier Cash Operating Cost was About $40/Kg U_3O_8

Present

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Really

The Future Wave 0.5?

Opportunities to Reduce Cost of "Next Generation" Plants

- Each of the Previous Plants had its Strong Points and Weak Points
- Combining the Best of Each will Reduce Both Capital and Operating Costs

Opportunities to Reduce Cost of "Next Generation" Plants

- **Some had 5 First Cycle Stages of Extraction, Whereas Others had 4.**

- **Some had 5 First Cycle Stages of Strip, Whereas Others Had 3.**

- **Pretreatment Costs Varied by More than a Factor of Ten: ($0.50->$9.00/Kg U_3O_8)**

Opportunities to Reduce Cost of "Next Generation" Plants

- **Solvent Losses Varied by Over a factor of Three: (\$4->\$12/Kg U_3O_8)**
- **Total of Solvent Loss Cost and Pretreatment Cost Varied by Over a Factor of Three: (\$5.70->\$17.00/Kg U_3O_8)**
- **Average Solvent Raffinate Concentrations Ranged From: 5 ppm to 100 ppm**
- **Solvent Loss Due to Settler Cleanings Ranged from < 0.1 to > 0.5 Kg/tonne P2O5 Processed**

Opportunities to Reduce Cost of "Next Generation" Plants

- **Oxidation Cost Ranged from $0.10 to $1.65/Tonne P2O5**
- **The Ratio of Fe+2/Fe Added Ranged from Less Than 2 to over 3**
- **Second Cycle Operating Costs Were Similar, but One had a Significantly Lower Capital Cost and had Much Simpler Chemistry.**

Opportunities to Reduce Cost of "Next Generation" Plants

- **P2O5 Losses Ranged from <0.1% to ~1%**
- **Acid Dilution Ranged from Nil to >1%**
- **Strip Coefficients Ranged from 15 to 150**
- **Some Plants had Negative Impact on Fertilizer Production, Some Had Positive Impact**

Opportunities to Reduce Cost of "Next Generation" Plants

- During the Operation of the Plants, Studies were Conducted to Understand the Reasons for these Differences
- Most were and are Well Understood
- Most Significantly, the Causes of Crud Were Determined
- Taking Advantage of this Understanding will Significantly Reduce Both the Capital and Operating Costs of the "Next Generation" Plants
- Reductions as Much as 40% in Both Capital and Operating Costs Are Expected

What if we do the Best of the Best, & Avoid the Worst and the Failures.

- A New Optimal Complete Flow Scheme
- Recent FEED Study Done………………..
- Say a facility of 900,000 # U_3O_8/Yr, (450,000 Kg/yr).
  Capital ~$150MM
  Operating Cost < $20/#, < $40/Kg

- Looks Very Good Indeed!!!

Risks

- Most Fertilizer Producers are Concerned with the Effect the Uranium Recovery Plant Will Have on Their Operations
  - P_2O_5 Losses
  - Effect on Rubber Lined Equipment
  - Acid Dilution
  - Acid Reheat
  - Product Grade of Fertilizer Products
- All These were Found to be Minimal or Positive in the Better Designed and Operated Plants

What if We Go Bigger!!

- Using a New Optimal Complete Flow Scheme
- Say a facility of 1,000,000 Kg U_3O_8/Yr, 2,200,000 #/yr.
- What Would Design be?

1,000,000 Kg U_3O_8/Yr, 2,200,000 #/yr

- What Pre-Treatment to Use?
- Columns or Mixer/settlers?
- Secondary Extraction/ Stripping
- Many Other Opportunities

What Pre-Treatment

- This Area Has Very Significant Impact on Operational and Capital Costs.
- Note: Prior Focus on Differing Pre-Treatment Philosophies in 80’s!!
- A Preferred Method was used in the FEED study, and Would be In Future Recovery Projects.

Columns or Mixer/Settlers

- Prior FEED Study @ 1MM#/yr Had:
  - 4 M/S FS Extractors, 24 x 4.9 x 1.2m
  - 3 M/S FS Strippers,   21 x 4.6 x 1.2m

- So for 1MMKg/Yr:-
  - Two Trains of M/S Required, 14 units
    - Allows any M/S to be taken Out of Service
    - Little impact on recovery as other units operating.
    - Recovery 96.97%

Columns or Mixer/Settlers

- Columns Size Now Restricted to about 100,000 Kg/Yr U_3O_8
- Thus Need at Least 10 Extraction Columns
- And Need at Least 5 Stripping Columns
- Say 5 Trains needed, 2Ex, 1 Str, but More Costly and Less Flexible Than M/S's.

- Recovery Comparable to M/S's….~97%

Secondary Extraction/ Stripping

- Focus on Chemistry in secondary circuit and refinery.
- Use Chemistry to Minimize Capital Cost.
- Use Chemistry to Simplify the Operational Criteria.
- Some Circuits Were Complex, others Very Simple.

1,000,000 Kg U_3O_8/Yr, 2,200,000 #/yr

- Best of the Best:-
- Using New Optimal Complete Flow Scheme
- Operating Cost < $18/#, < $36/Kg
- Should be a Winner!!

Enhance the Uranium Level

- Enhance the uranium content of the acid that is produced by the phosphoric acid plant.
- Yes. Very Interesting Twist!!!

Waste

- As We Speak, the Phosphate Industry is “Throwing Away” Enough Uranium every Four Days to Fuel a Nuclear Power Plant for a Year!

What About Hemi or 40% Clarified Acid?

- Octyl Phenol Phosphoric Acid Solvent has Been Demonstrated to Work Effectively in Lab
- Operating and Capital Costs will be about the Same per Pound as Central Florida
- Piloting Will be Required for any New Solvent or Acid Strength, and of course New Technology.
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Uranium from Phosphates

- So How Much Uranium Can We Recover?
  - 0 Kg
- If We Procrastinate

- Been There
- Done That
- Like to do it Again, but Better!!
- Thank You
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