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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

29th March to 3rd April, 2015
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.
P₂O₅
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 P₂O₅
  – Typically: 0.3-0.6 Kg U per Tonne P₂O₅
  – Price: Volatile, but in 2007, U₃O₈ 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 $\text{U}_3\text{O}_8$ Recovered Approximately 20 Million Kgs
Flow Sheets of Recent U.S.A. Plants

- Incoming 30% Acid
- Acid Pretreatment
  - First Cycle Extraction
  - First Cycle Strip
  - Second Cycle Extraction
  - Second Cycle Strip
- Loaded Strip Acid
- Pregnant Solvent
- Precipitation of Uranium, Drying, and Calcining
- Ship to Converter
- Raffinate Post Treatment
- Barren Solvent
- Strip Acid
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)
Annual $\text{U}_3\text{O}_8$ Capacity

- IMC New Wales Plant Produced as Much as 591,000 Kg/Yr $\text{U}_3\text{O}_8$.
  - CF Plant City Module Produced as Much as 409,000 Kg/Yr $\text{U}_3\text{O}_8$.
  - One CF Plant Closed Down After Less than 3 Years of Operation

- Freeport Plants Produced as Much as 482,000 Kg/Yr $\text{U}_3\text{O}_8$. (Combined)
<table>
<thead>
<tr>
<th>Plant / Design</th>
<th>Freeport</th>
<th>Gardinier</th>
<th>IMC</th>
<th>Uranium Recovery Corp.</th>
<th>Westinghouse</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pretreatment Cooling</strong></td>
<td>No cooling</td>
<td>2-stage flash cooling - 32°C</td>
<td>Spiral coolers cool - 49°C</td>
<td>No cooling</td>
<td>Flash cool - 38°C</td>
</tr>
<tr>
<td><strong>Solids Removal</strong></td>
<td>Flocculant added before clarification</td>
<td>Filtered using pressure leaf filters</td>
<td>Clay/flocculant added before clarification</td>
<td>Flocculant added before clarification</td>
<td>Flocculant added before clarification</td>
</tr>
<tr>
<td><strong>Further Pretreatment</strong></td>
<td>None</td>
<td>None</td>
<td>Colour removal - activated C</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td><strong>Oxidation State Change</strong></td>
<td>Oxidised with oxygen</td>
<td>Reduced with scrap Fe and H₂O₂. Later used oxygen</td>
<td>Oxidised with H₂O₂ and iron</td>
<td>Reduced using ferro-silicon</td>
<td>Oxidised using nitric acid</td>
</tr>
<tr>
<td><strong>First Cycle Solvent</strong></td>
<td>DEHPA/TOPO</td>
<td>Octyl pyrophosphoric acid (OPPA)</td>
<td>DEHPA/TOPO</td>
<td>Octyl pyrophosphoric acid (OPPA)</td>
<td>DEHPA/TOPO</td>
</tr>
<tr>
<td><strong>Mixer Settler Design</strong></td>
<td>Low profile rectangular pumper-mixer settlers</td>
<td>Rectangular pumper-mixer settlers</td>
<td>Circular mixer settlers</td>
<td>Deep-cone bottom settlers</td>
<td>Low profile rectangular pumper-mixer settlers</td>
</tr>
<tr>
<td><strong>First Cycle Strip Solution</strong></td>
<td>31% P₂O₅ acid plus iron</td>
<td>15% HF precipitated U as green salt</td>
<td>31% P₂O₅ acid plus sulphuric acid and iron</td>
<td>40% P₂O₅ acid plus hydrogen peroxide</td>
<td>27% P₂O₅ acid plus iron</td>
</tr>
<tr>
<td><strong>Second Cycle Oxidation State Change</strong></td>
<td>Oxidised with oxygen</td>
<td>Dissolved in nitric acid</td>
<td>Oxidised with H₂O₂ and iron</td>
<td>No oxidation change required</td>
<td>Oxidised using nitric acid</td>
</tr>
<tr>
<td><strong>Second Cycle Solvent</strong></td>
<td>DEHPA/TOPO</td>
<td>TBP</td>
<td>DEHPA/TOPO</td>
<td>DEHPA/TOPO</td>
<td>DEHPA/TOPO</td>
</tr>
<tr>
<td><strong>Uranium Precipitate Form</strong></td>
<td>Ammonium diuranate</td>
<td>Ammonium diuranate</td>
<td>Uranyl peroxide</td>
<td>Ammonium uranyl tricarbonate</td>
<td>Ammonium uranyl tricarbonate</td>
</tr>
</tbody>
</table>
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 U₃O₈ ($24/Kg w/o Royalty etc)

- IMC (New Wales) Cash Operating Costs (No Royalty, Dilution, Reheat or Loss Cost) was About $24/Kg U₃O₈

- URC Total Cash Cost (Including Royalty, Cost of Acid Dilution and Acid Losses) was About $100/Kg U₃O₈ (Low Throughput and Operating Factor)

- Freeport Cash Operating Costs (No Royalty, Dilution, Reheat or Loss Cost) was About $26/Kg U₃O₈

- Gardinier Cash Operating Cost was About $40/Kg U₃O₈
Present

“Really”

“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 U₃O₈)
Opportunities to Reduce Cost of “Next Generation” Plants

- Solvent Losses Varied by Over a factor of Three: ($4-\rightarrow$12/Kg $\text{U}_3\text{O}_8$)

- Total of Solvent Loss Cost and Pretreatment Cost Varied by Over a Factor of Three: ($5.70-\rightarrow$17.00/Kg $\text{U}_3\text{O}_8$)

- 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 # U₃O₈/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$_3$O$_8$/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 U₃O₈
- 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 U₃O₈/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.
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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