Uranium Extraction from Wet Process Phosphoric Acid, The Third Time Around

Joe Guida
Doug Royster
Regis Stana

History of Uranium Recovery from Phosphoric Acid
First Time

- First Plant was Built in 1952 in Joilet 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 60’s, when the Low Cost Production of Uranium from Western Mines Depressed the Price
History of Uranium Recovery from Phosphoric Acid
Second Time

- The Price of Uranium Increased Dramatically in the 1970’s
- 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 and Taiwan
Flow Sheets of Recent U.S.A. Plants

- All Plants Extracted Uranium from Acid Produced by Dihydrate Processes (27-28% P₂O₅ Plus 1.5-3% Sulfate).
- All Acids were Produced from Central Florida Rock.
- U₃O₈ Content of All Acids was About 1.0 lb/Ton P₂O₅.
- All Used a Solvent Extraction Process.
- The Processes were Developed by Westinghouse, IMC (3 Plants), Uranium Recovery Corp., Freeport (2 Plants), and Gardinier.
Flow Sheets of Recent U.S.A. Plants

• Pretreatment
  – Westinghouse Flash Cooled to 100 °F, Clarified with Flocculent and Reheated to 104 °F
  – IMC Used Spiral Coolers to Cool to 120 °F, Added Clay and Flocculent before Clarification, then Passed Acid Through Carbon Columns (Abandoned after 6 Years)

Flow Sheets of Recent U.S.A. Plants

• Pretreatment (Contd)
  – URC Did Not Cool, and Clarified Only
  – Freeport Did Not Cool, but Added a Flocculent and Clarified
  – Gardinier Cooled the Acid to 90 °F Using 2 Stage Flash coolers and Clarified the Acid. The Acid was Reduced with Scap Iron and then Filtered Using Pressure Leaf Filters
Flow Sheets of Recent U.S.A. Plants

- **Oxidation Change**
  - Westinghouse Used Nitric Acid to Oxidize Acid (and Uranium)
  - IMC Used Hydrogen Peroxide (Later Changed to Oxygen) to Oxidize Acid (and Uranium)
  - URC Used Ferro Silicon to Reduce Acid (and Uranium)
  - Freeport Used Oxygen to Oxidize Acid (and Uranium)
  - Gardinier Used Iron to Reduce the Acid

Flow Sheets of Recent U.S.A. Plants

- **Uranium Extraction**
  - Westinghouse Used DEPA/TOPO as Extractant
  - IMC Used DEPA/TOPO as Extractant
  - URC Used Octyl Pyro Phosphoric Acid as Extractant
  - Freeport Used DEPA/TOPO as Extractant
  - Gardinier Used Octyl Pyro Phosphoric Acid as the Extractant
Flow Sheets of Recent U.S.A. Plants

- Mixer Settler Design
  - Westinghouse Used Holms and Narver Low Profile Pumper/Mixers/Rectangular Settlers
  - IMC Used Circular Mixers and Settlers
  - URC Used Deep Cone Bottom Tank Mixers and Settlers
  - Freeport Used Low Profile Pumper/Mixers & Racked Rectangular Mixer/Settlers
  - Gardinier Used Rectangular Mixer/Settlers

Flow Sheets of Recent U.S.A. Plants

- When Any Organic Solvent is Mixed with Wet Process Phosphoric Acid, a Third Interfacial Phase is Formed that is Termed “Crud” or “Gunk”.
- It Must be Removed from the Settlers or it will Interfere with the Performance of the Settler
- “Crud” Contains About 50% Solvent, so the Solvent Must be Recovered
Flow Sheets of Recent U.S.A. Plants

- Crud Removal
  - Westinghouse Continuously Over Flowed Crud from First Settler and Intermittently Pumped from the Rest
  - IMC Pumped Crud From All Circular Settlers
  - URC Batch Overflowed Crud From Settlers
  - Freeport Used Interface Drag Devices to Pull Crud Out of Settlers
  - The Crud Removal System For Gardinier Consisted of Pumping and Pressure Leaf Filtration

- Crud Processing
  - Westinghouse Used Centrifuge (Abandoned) and Pre Coat Vacuum Drum Filter
  - IMC Initially Used Plate and Frame Filters and then Pre Coat Vacuum Drum Filter
  - URC Used Centrifuges and Pre Coat Vacuum Drum Filter
  - Freeport Used Chemical Treatment, a Patented Centrifuge Separation, and a Crud Maker System
  - The Crud Processing System for Gardinier was a Pressure Leaf Filter
Flow Sheets of Recent U.S.A. Plants

• First Cycle Stripping
  – Westinghouse Used 27% $P_2O_5$ Acid Reduced with Scrap Iron Plus Powdered Iron Within Stages
  – IMC Used 31% $P_2O_5$ Acid Plus Sulfuric with Iron Ball Towers for Each Stage for Reduction
  – URC Used 40% $P_2O_5$ Acid Plus Peroxide
  – Freeport Used a Boosted Strength 31% $P_2O_5$ Acid With Iron Ball Towers for Each Stage for Reduction
  – Gardinier Stripped the Solvent Using 15% HF

Flow Sheets of Recent U.S.A. Plants

• Second Cycle Oxidation
  – Westinghouse Used Nitric Acid to Oxidize Acid (and Uranium)
  – IMC Used Hydrogen Peroxide (Later Changed to Oxygen) to Oxidize Acid (and Uranium)
  – URC First Cycle Acid Was Already Oxidized
  – Freeport Used Oxygen to Oxidize Acid (and Uranium)
  – The Gardinier Process Did not Require Oxidation
Flow Sheets of Recent U.S.A. Plants

- Second Cycles
  - All Plants (Except Gardinier Which Used TBP) Used DEPA/TOPO in Second Cycle with Rectangular Mixer Settlers for Extraction and Strip
  - All Used Ammonium Carbonate for Stripping
  - Each Precipitated the Uranium as an Ammonium Compound
  - All Calcined to a Black Oxide and Shipped in 55 Gallon Drums

Operating Experience with Plants

- Westinghouse Plant Operated With 98+ % On Stream Factor and 92+% U₃O₈ Recovery
  - Turn Around After 2 Years and Down for Mechanical Problems Only
  - Organic Advance was Being Increased to Increase Recovery to 96% when Price of Uranium Dropped and Plant Closed
- IMC Plants Operated at 92% On Stream Factor and 96% U₃O₈ Recovery (Down Weekly for Line Scrubs and Yearly Turn Around)
Operating Experience with Plants

- URC Plant Operated at Less Than 60% On Stream Factor and Less than 80% Recovery (Lots of Mechanical Problems and Problems with Crud Build Up)
- Freeport Plants Operated at 92% On Stream Factor and 95% U₃O₈ Recovery (Down Weekly for Line Scrubs and Yearly Turn Around)
- The Gardinier Plant Obtained About 90% Recovery

Operating Experience with Plants

- Westinghouse Plant Produced Over 300,000 lbs/Yr U₃O₈.
- IMC New Wales Plant Produced as Much as 1,300,000 lbs/Yr U₃O₈. CF Plant City Module Produced as Much as 900,000 lbs/Yr U₃O₈. One CF Plant Closed Down After Less than 3 Years of Operation
- URC Plant Produced About 100,000 lbs/Yr U₃O₈.
- Freeport Plants Produced as Much as 1,060,000 lbs/Yr U₃O₈. (Combined)
- The Gardinier Plant Had a Design Production of 400,000 lbs/Yr U₃O₈.
Economics of Previous Plants

- 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

Economics of Previous Plants

- Westinghouse Total Cash Cost (Including Royalty, Cost of Acid Dilution, Losses and Reheat) was About $17/Lb U₃O₈ ($11/Lb w/o Royalty etc)
- IMC (New Wales) Cash Operating Costs (No Royalty, Dilution, Reheat or Loss Cost) was About $11/Lb U₃O₈
- URC Total Cash Cost (Including Royalty, Cost of Acid Dilution and Acid Losses) was About $45/Lb U₃O₈
  (Low Throughput and Operating Factor)
- Freeport Cash Operating Costs (No Royalty, Dilution, Reheat or Loss Cost) was About $12/Lb U₃O₈
- Gardinier Cash Operating Cost was About $18/Lb U₃O₈
Opportunities to Reduce Cost of “Next Generation” Plant

• Each of the Previous Plants had it’s Strong Points and Weak Points.
• Combining the Best of Each can Reduce Both Capital and Operating Costs

Opportunities to Reduce Cost of “Next Generation” Plant

• For Example
  – Solvent Losses Varied by over a factor of three
  – Pretreatment Costs Varied by More than a Factor of Three.
  – The Total of Solvent Loss Cost and Pretretment Varied by Over a Factor of Three
  – Freeport and Westinghouse Required 5 First Cycle Stages of Extraction Whereas IMC Only Required 4
  – Freeport Required 5 First Cycle Stages of Strip, Whereas IMC and Westinghouse Only Required 3.
  – Second Cycle Operating Costs Were Similar, but One had a Significantly Lower Capital Cost
Opportunities to Reduce Cost of “Next Generation” Plant

• For Example
  – Average Solvent Concentrations in the Raffinate Ranged From 5 ppm to 100 ppm
  – P₂O₅ Losses Ranged from <0.1% to ~1%
  – Strip Coefficients Ranged from 15 to 150
  – Solvent Loss Due to Settler Cleanings Ranged from <.05 to >.2 lb/ton P₂O₅ Processed
  – Some Equipment Remains From the Original Plants and is Still Operating.

Opportunities to Reduce Cost of “Next Generation” Plant

• During the Operation of the Plants, Studies were Conducted to Understand the Reasons for these Differences
• Most are Well Understood
• Taking Advantage of this Understanding can Significantly Reduce Both the Capital and Operating Costs of the “Next Generation” Plants.

Uranium Recovery from Phosphates
Estimates of Current Operating Costs
Third Time

• Current Operating Costs Will be Higher Due to:
  – Lower Uranium Content of Rock
    (1.0 Lb/Ton Previously to Estimated 0.8-0.9 Lb/Ton for Next 10 Years)
  – Somewhat Higher Solvent Cost
  – Higher Electricity Cost
  – Higher Labor Cost (Can be Offset with Automatic Controls)
  – Total Cash Operating Costs Should be Less than $20/lb
  – + Regulations ??? $

Estimates of Current Capital Costs

• Capital Costs (Adjusted for Inflation) Should Be Lower than Previous Plants, but Highly Dependent on Flow Sheet Adopted
What About North Florida, North Carolina and Western US Operations?

- Uranium Content is about Half
- But Much of the Acid is Produce By Hemi Process (~40% Acid)
- Uranium Content on g/l is Similar to Central Florida
- Octyl Phenol Phosphoric Acid Solvent has Been Demonstrated to Work Effectively in Lab with Phosphoric Acid up to 54%
- Operating and Capital Costs will be about the Same per Pound as Central Florida (But less Pounds Produced)
- Piloting is Probably Required

Other Opportunities

- New Solvents
  - Octyl-Phenol-Phosphoric Acid
    - Lower Cost
    - Higher Extraction Coefficient
- New Contactors
  - Columns
- New Technology
  - Ion Exchange
  - Ultrafiltration
  - Micro-emulsions
  - Chelating Agents
  - Computer Controls
Will the Third Time be the Last!

- It May be the Last Time for the US Plants!
- Let’s Get it Right!

US Plants and Trends

Only 1 Plant by 2020!