Uranium from Phosphates: Rethinking Beneficiation

Patrick Zhang
Research Director
Florida Industrial & Phosphate Research Institute
Florida Polytechnic University
jzhang@flpoly.org

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The Alarming Trend of World Consumption of Materials and Energy

**Material use**
- Construction minerals
- Ores and industrial minerals
- Fossil energy carriers
- Biomass

**Energy**
- Modern renewable electricity: wind, solar, geothermal, etc.
- Hydro
- Nuclear
- Natural gas
- Oil
- Coal
- Biomass and biofuels

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The Alarming Trend of CO$_2$ Concentration in the Atmosphere
The Alarming Number of Undernourished People

Figure 1 – Trend in number of undernourished people, 1970-2010

Source: FAO, 2011.
The Alarming Trends Call for:

• Low-carbon energy production – U from phosphate
• More efficient food production – more P
• More efficient recovery of P from ore
• Rethinking phosphate beneficiation
Three Aspects of CX, Sustainable Development of Mineral Resources

- Environmental
- Economic
- Governmental

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Environmental Aspects

- Promote responsible stewardship of natural resources and the environment, including remediation of past damage
- Minimize waste and environmental damage throughout the whole supply chain
- Exercise prudence where impacts are unknown or uncertain
- Operate within ecological limits and protect critical natural capital
Economic Aspects

- Maximize human well-being
- Ensure efficient use of all resources, natural and otherwise, by maximizing returns
- Seek to identify and internalize environmental and social costs
- Maintain and enhance the conditions for viable enterprise
Governance Aspects

- Ensure transparency by providing all stakeholders with access to relevant and accurate information.
- Ensure accountability for decisions and actions.
- Encourage cooperation in order to build trust and shared goals and values.
- Ensure that decisions are made at the appropriate level as close as possible to and with the people and communities most directly affected.
Production of Ammonium Phosphates

Demands for Phosphoric Acid

- The first wet-acid plant built in Germany in 1870
- The first wet-acid plant in the U.S. in 1890
- Thermal processes (using either blast furnace or electric furnace) dominated during the early phosphate booming years
- Since 1950, the wet acid process has quickly overtaken the thermal method
- Diammonium phosphate (DAP)

\[ \text{H}_3\text{PO}_4 + 2\text{NH}_3 = (\text{NH}_4)_2\text{HPO}_4 \]
World Phosphate Rock Consumption by Category

- Wet acid: 71%
- SSP: 13.50%
- Others (animal feed, FMP, MKP, TSP, NPK, NP): 10%
- Thermal phosphorus: 5%
- Direct application: 0.50%
“Wet Process” Phosphoric Acid Production and Phosphogypsum (PG)

(fluorapatite) $\text{Ca}_{10}\text{F}_2(\text{PO}_4)_6 + 10\text{H}_2\text{SO}_4 + 10n\text{H}_2\text{O} \rightarrow 10\text{CaSO}_4\cdot n\text{H}_2\text{O} \text{ (PG)} + 6\text{H}_3\text{PO}_4 + 2\text{HF}$

- Di-hydrate process, $n=2$
- Hemi-hydrate process, $n=1/2$
- Anhydrite, $n=0$

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Phase Diagram of PG in Phos. Acid

Temperature (°C)

Concentration $P_2O_5$ (w%)
Comprehensive Recovery: Treating Phosphate as an Energy Mineral

- Well known fact: phosphate is a crop nutrient (providing energy for plants) mineral, key to production of food that provides energy for mankind

- Less known truth: phosphate is also a energy mineral
  - Uranium (nuclear energy)
  - Rare earths (green energy)
  - Thorium (green nuclear energy)

Phosphate powers the world!
## Average Uranium and Thorium Contents (ppm) in Selected Phosphate Ores

<table>
<thead>
<tr>
<th>Sample</th>
<th>No. of sample</th>
<th>U</th>
<th>Th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Florida, USA pebble, 1926-1935</td>
<td>11</td>
<td>208</td>
<td>14</td>
</tr>
<tr>
<td>Florida, USA pebble, 1946-1955</td>
<td>14</td>
<td>148</td>
<td>13</td>
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<tr>
<td>Florida, USA pebble, 1959-1964</td>
<td>12</td>
<td>127</td>
<td>17</td>
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<tr>
<td>Florida, USA Pebble, 1994</td>
<td>3</td>
<td>95</td>
<td>--</td>
</tr>
<tr>
<td>North Carolina, USA, 1957-1964</td>
<td>3</td>
<td>79</td>
<td>9</td>
</tr>
<tr>
<td>Utah, USA, 1936-1961</td>
<td>9</td>
<td>128</td>
<td>7</td>
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<tr>
<td>Idaho, USA</td>
<td>5</td>
<td>151</td>
<td>8</td>
</tr>
<tr>
<td>Peru, washed rock, 1961-1964</td>
<td>7</td>
<td>106</td>
<td>8</td>
</tr>
<tr>
<td>Morocco, 1937-1943</td>
<td>5</td>
<td>141</td>
<td>8</td>
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<tr>
<td>Tunisia,1927-1955</td>
<td>6</td>
<td>48</td>
<td>23</td>
</tr>
<tr>
<td>Jordan, 1956-1963</td>
<td>6</td>
<td>48</td>
<td>0</td>
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<tr>
<td>Egypt, 1936-1937</td>
<td>6</td>
<td>122</td>
<td>6</td>
</tr>
<tr>
<td>Senegal</td>
<td>6</td>
<td>107</td>
<td>17</td>
</tr>
</tbody>
</table>
### Uranium in Selected Phosphate Rock and Phosphoric Acid Samples (ppm)

<table>
<thead>
<tr>
<th>Location</th>
<th>$\text{U}_3\text{O}_8$ in Rock</th>
<th>$\text{U}_3\text{O}_8$ in Phosphoric Acid (30% $\text{P}_2\text{O}_5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algeria</td>
<td>110-140</td>
<td>130</td>
</tr>
<tr>
<td>Brazil</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Israel</td>
<td>50-150</td>
<td>165</td>
</tr>
<tr>
<td>Jordan</td>
<td>120-150</td>
<td>165</td>
</tr>
<tr>
<td>Morocco</td>
<td>90-140</td>
<td>140</td>
</tr>
<tr>
<td>Tunisia</td>
<td>50-100</td>
<td>80</td>
</tr>
<tr>
<td>Florida</td>
<td>150-180</td>
<td>190</td>
</tr>
</tbody>
</table>
Uranium in Phosphate: Basic Facts

- Concentration ranging from 50 to 200 ppm, averaging +100 ppm
- Worldwide annual U unrecovered from phosphate totaling 18 million kg (based on 180Mt rock production)
- Worldwide total U resources topping 29 billion kg (based on total phosphate resources of 290 billion tons)
Uranium in Phosphate Accounting for 88% of the World’s Unconventional U

Source: Harikrishnan Tulsidas, IAEA, 2012
Fate of Uranium in the Wet Acid & Fertilizer Manufacturing Processes

- 80-90% in phosphoric acid
- 10-20% in phosphogypsum (PG)
  - About 10% in dihydrate PG
  - Up to 20% in hemihydrate PG
- Nearly all the U in the acid ends up in fertilizers
Recovery of Uranium from Phos. Acid

- Industrially proven in numerous plants and twice in the history
- No mining costs
- Easy to permit
- Saving a resource otherwise forever lost
- Other elements of value (Th and REE) can be recovered from the same liquid
Form of Uranium in Phosphoric Acid

- In sedimentary-type U exists in isomorphous substitution for Ca
- In igneous phosphate U is associated with thorium (232Th) and rare earths
Techniques for Uranium Extraction from Phosphoric Acid

• Solvent extraction (SX), the industrially proven process
• Ion exchange (IX), the intensively investigated method with many promises
• Precipitation, the “abandoned” process?
Solvent Extraction Based Technologies for U Recovery from Phosphoric Acid in Sulfate Media

• DEPA-TOPO (also DEHPA-TOPO, D2EHPA-TOPO) uses di(2-ethylhexyl) phosphoric acid and trioctyl phosphine oxide as extractants (ORNL process)

• OPAP uses octyl phenyl acid phosphate as extractant (ORNL process)

• OPPA uses octyl pyro phosphoric acid as extractant (Dow process)
# Three Major SX Systems

<table>
<thead>
<tr>
<th>Process</th>
<th>Extractant</th>
<th>Formular</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPPA</td>
<td>Octyl pyrophosphoric acid Dissolving $\text{P}_2\text{O}_5$ in octyl alcohol in the absence of moisture and below 15°C</td>
<td>where $R$ is $\text{CH}_3.(\text{CH}_2)_6.\text{CH}_2$-</td>
</tr>
<tr>
<td>D2EHPA/TOPO</td>
<td>A mixture of di(2-thylhexyl) phosphoric acid and trioctyl phosphine oxide, ${\text{H}_3\text{C}(\text{CH}_2)_7}_3\text{P}=$</td>
<td>where $R$ is $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_3.\text{CH}_2.\text{CH}_3$</td>
</tr>
<tr>
<td>DEPA/TOPO</td>
<td>A mixture of di(2-thylhexyl) phosphoric acid and trioctyl phosphine oxide, ${\text{H}_3\text{C}(\text{CH}_2)_7}_3\text{P}=$</td>
<td>where $R$ is $\text{CH}_3.\text{CH}_2.\text{CH}_2.\text{CH}_3.\text{CH}_2.\text{CH}_3$</td>
</tr>
<tr>
<td>OPAP process</td>
<td>A mixture of mono and di-octylphenyl phosphoric acids and tributyl phosphate, $(\text{C}_4\text{H}_9\text{O})_3\text{P}=${</td>
<td>Where $R$ is</td>
</tr>
</tbody>
</table>
The Synergic Effect of TOPO

- Organic Phase: 0.18 M D2EHPA-TOPO-NDD
  Aqueous Phase: Pure 5.3 M H₃PO₄, 0.2 g U/liter

- Organic Phase: 0.5 M D2EHPA-TOPO--NDD--
  Aqueous Phase: Tech. phosphoric acid

URANIUM EXTRACTION COEFFICIENT, $E$

TOPO CONCENTRATION (M)
DEPA/TOPO Based Process: Pretreatment

- **Cooling**
  - To precipitate $\text{Na}_2\text{SiF}_6$ and $\text{CaSO}_4$ and improve SX efficiency

- **Flocculation-filtration**
  - To remove precipitates

- **Absorption with activated carbon or sand**
  - To remove organics

- **Oxidation (with H}_2\text{O}_2, \text{O}_2, \text{or Fe}^{+2})**
  - To convert all U to hexavalent form

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DEPA/TOPO Based Process: Two-cycle Extraction

• First cycle
  - In a counter-current mixer/settler system, clarified acid is contacted with DEPA-TOPO solvent dissolved in kerosene; U is transferred to the organic phase. Lean phosphoric acid is returned to the phosphoric acid plant.

• First cycle stripping
  - The organic phase containing uranium in the U$^{6+}$ state is reduced to the U$^{4+}$ state; it is then contacted with more concentrated phosphoric acid in a second mixer/settler system. Here the U is stripped from the relatively large volume of organic solvent and transferred to the smaller volume of a stripping acid.
DEPA/TOPO Based Process: Two-cycle Extraction

• Second cycle extraction
  ➢ The loaded primary stripping acid is oxidized to convert uranium back to the $\text{U}^{6+}$ state. The strip acid is then contacted with DEPA-TOPO solvent in a mixer/settler system, where concentrated U is transferred to the solvent phase and further concentration takes place to form “pregnant secondary organic”.

• Second cycle stripping
  ➢ The pregnant secondary organic containing the U is contacted with an alkaline solution in a mixer/settler system. Here the U is stripped from the organic solvent and transferred to the alkaline solution in a more concentrated form. The secondary strip solution is treated to neutralize the alkali and produce an acidic uranium solution.
DEPA/TOPO Based Process: Oxidizing & Refining

• The acid uranium solution is oxidized:
  – with hydrogen peroxide to form uranyl peroxide UO$_4$·nH$_2$O
  – with ammonia to form ammonium diuranate (ADU), (NH$_4$)$_2$U$_2$O$_7$
  – with to ammonium carbonate (or ammonia+CO$_2$) to form ammonium uranyl tricarbonate (AUT), (NH$_4$)$_4$U$_2$O$_7$(CO$_3$)$_3$

• Thicken, wash, dry, and calcine the above products to produce U$_3$O$_8$ – yellow cake
History of U Recovery from Phos. Acid

• 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 60s, when the low cost production of uranium from western mines depressed the price.
• 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 in Florida and two in Louisiana

• Plants were also built in Canada, Spain, Israel, Belgium, and Iraq
<table>
<thead>
<tr>
<th>Acid Producer</th>
<th>Uranium Producer</th>
<th>Location</th>
<th>Capacity $P_2O_5$ (tons/year)</th>
<th>Capacity $U_3O_8$ (lbs/year)</th>
<th>Process</th>
<th>Operating Period</th>
</tr>
</thead>
<tbody>
<tr>
<td>Farmland</td>
<td>Wyoming Minerals</td>
<td>Pierce, FL</td>
<td>450,000</td>
<td>400,000</td>
<td>WMC, DEPA-TOPO</td>
<td>1978 – 1981</td>
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<tr>
<td>Freeport</td>
<td>Freeport Minerals Co.</td>
<td>Uncle Sam, LA</td>
<td>675,000</td>
<td>690,000</td>
<td>FMC, DEPA-TOPO</td>
<td>1978 - 1999</td>
</tr>
<tr>
<td>Agrico</td>
<td>Freeport Minerals Co.</td>
<td>Donaldsonville, LA</td>
<td>360,000</td>
<td>420,000</td>
<td>FMC, DEPA-TOPO</td>
<td>1981 - 1998</td>
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<tr>
<td>IMC</td>
<td>IMC</td>
<td>New Wales, FL</td>
<td>1,000,000</td>
<td>800,000</td>
<td>IMC, DEPA-TOPO</td>
<td>1980 - 1992</td>
</tr>
<tr>
<td>CF Industries</td>
<td>IMC</td>
<td>Bartow, FL</td>
<td>720,000</td>
<td>600,000</td>
<td>IMC, DEPA-TOPO</td>
<td>1981 - 1985</td>
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<tr>
<td>CF Industries</td>
<td>IMC</td>
<td>Plant City, FL</td>
<td>680,000</td>
<td>600,000</td>
<td>IMC, DEPA-TOPO</td>
<td>1980 - 1992</td>
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<tr>
<td>Gardinier</td>
<td>Gardinier</td>
<td>East Tampa, FL</td>
<td>500,000</td>
<td>420,000</td>
<td>Gardinier, OPPA</td>
<td>1979 – 1982</td>
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<tr>
<td>Western Coop. Fertilizer</td>
<td>Earth Sciences</td>
<td>Calgary, Alberta, Canada</td>
<td>144,000</td>
<td>120,000</td>
<td>ESI, OPAP</td>
<td>1981 – 1987</td>
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<tr>
<td>Chemie Rupel</td>
<td>Umipray</td>
<td>Purrs, Belgium</td>
<td>100,000</td>
<td>150,000</td>
<td>IMC – Prayon, DEPA-TOPO</td>
<td>1980 - 1998</td>
</tr>
</tbody>
</table>
Uranium Recovered from Phosphoric Acid in the USA

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Westinghouse Plant at Farmland Industries

First Stage Mixer Settlers
IMC Plant at New Wales
Flow Sheets of Recent USA Plants

Incoming 30% Acid

Acid Pretreatment

First Cycle Extraction

First Cycle Strip

Pregnant Solvent

Loaded Strip Acid

Precipitation of Uranium, Drying, and Calcining

Strip Solution

Second Cycle Extraction

Second Cycle Strip

Pregnant Solvent

Loaded

Strip Acid

Raffinate Post Treatment

Barren Solvent

Ship to Converter

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Characteristics of Recent USA Plants

• All plants extracted uranium from acid produced by Dihydrate processes (27-28% P₂O₅, 1.5-3% sulfate)
• All acids were produced from central Florida rock
• U₃O₈ content of all acids was about 0.5 Kg/ton P₂O₅
• All used a solvent extraction process
• The processes were developed by Westinghouse, IMC (3 Plants), Uranium Recovery Corp., Freeport (2 Plants), Oak Ridge Lab, and Gardinier
Processing Steps of Recent USA Plants

• Pretreatment
  – Westinghouse: Flash cooled acid to 100\(^\circ\) F (38\(^\circ\) C), clarified with flocculent, and reheated to 104\(^\circ\) F (40\(^\circ\) C)
  – IMC: Used spiral coolers to cool acid to 120\(^\circ\) F (49\(^\circ\) C), added clay and flocculent before clarification, then passed acid through carbon columns (Abandoned after 6 Years)
• Pretreatment (Contd.)
  – URC: Did not cool but clarified only
  – Freeport: Did not cool, but added a flocculent and clarified
  – Gardinier: Cooled the acid to 90°F (32°C) using 2-stage flash coolers and clarified the acid. The acid was then reduced with scrap iron and then filtered
Oxidation/Reduction

- Westinghouse: Used nitric acid to oxidize the acid (and Uranium)
- IMC: Used hydrogen peroxide (later changed to oxygen) as the oxidant
- URC: Used ferro silicon to reduce the acid (and Uranium)
- Freeport: Used oxygen as the oxidant
- Gardinier: Used iron to reduce the acid
Processing Steps of Recent USA Plants

- **Uranium Extraction**
  - Westinghouse: Used DEPA/TOPO as extractant
  - IMC: Used DEPA/TOPO as extractant
  - URC: Used Octyl Pyro Phosphoric Acid (OPPA) as extractant
  - Freeport: Used DEPA/TOPO as extractant
  - Gardinier: Used Octyl Pyro Phosphoric Acid (OPPA) as extractant
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
When any organic solvent is mixed with Wet Process Phosphoric Acid, a third interfacial phase is formed that is termed “Crud” or “Gunk”, which is also common in other SX systems. It Must be removed from the settlers or it will interfere with the performance of the settler. The “Crud” contains about 50% solvent, so the solvent must be recovered.
Processing Steps of Recent USA Plants

- **Crud Removal**
  - Westinghouse continuously overflowed 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
Processing Steps of Recent USA Plants

- **Crud Processing**
  - Westinghouse used centrifuge (abandoned later) 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
Processing Steps of Recent USA Plants

- **First Cycle Stripping**
  - Westinghouse used 27\% \( \text{P}_2\text{O}_5 \) acid reduced with scrap iron plus powdered iron within stages
  - IMC used 31\% \( \text{P}_2\text{O}_5 \) acid plus sulfuric with iron ball towers for each stage for reduction
  - URC used 40\% \( \text{P}_2\text{O}_5 \) acid plus peroxide
  - Freeport used a boosted strength 31\% \( \text{P}_2\text{O}_5 \) acid with iron ball towers for each stage for reduction
  - Gardinier stripped the solvent using 15\% HF
Processing Steps of Recent USA 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
Processing Steps of Recent USA Plants

• Second Cycles
  – All plants (except Gardinier) 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 US 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 US 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% \( \text{U}_3\text{O}_8 \) recovery (down weekly for line scrubs and yearly turn around)
- The Gardinier plant obtained about 90% recovery
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 $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
Estimates of Current Operating Costs
Third Wave

• Current operating costs will be higher due to:
  – Lower uranium content of rock (for Central Florida plants) (0.50 Kg/Tonne previously to estimated 0.40-0.45 Kg/Tonne 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 $40/Kg
Estimates of Current Capital Costs

• Capital costs (Adjusted for Inflation) should be lower than previous plants, but highly dependent on flow sheet adopted
U Recovery from Concentrated Phos. Acid from Hemihydrate Process

- Solvent DEPHA + TOPO proved to be effective.
- Both the technical and economic feasibility demonstrated for uranium recovery from hemihydrate acid (40-45% P$_2$O$_5$) were demonstrated.
Solvent Extraction Based Technologies for U Recovery from Phosphoric Acid via Nitric Acid Digestion

• Tributyl phosphate (TBP)
• Tertiary amyl alcohol
Advantages of the Nitrate Route

- No phosphogypsum problem
- Suitable for in-situ or heap leaching of low grade phosphate ores
- Better for REE recovery
- More complete REE dissolution by nitric acid
- Both extractants capable of picking up REE while extracting U
Recovery of Uranium from Phos. Acid Challenges

- Fluctuating uranium prices
- Unfavorable public perception and political atmosphere about nuclear power due to the accident in Japan
- Industry fatigue
- Industry becoming more risk averse
Rethinking Phosphate Beneficiation in Consideration of Uranium Recovery

- Expanding beneficiation beyond phosphate rock production
- Including rare earths recovery
REE in Phosphate Rock

- Rare earths constitute 0.01 to 0.1% of the apatite, averaging 300 ppm
- About 200 million tons of phosphate rock processed annually
- REE may be recovered together with uranium
Rare Earth Elements in the Phosphate Deposits of the Tethys

- The Tethys covering Algeria, Egypt, Iran, Iraq, Jordan, Libya, Morocco, Syria, and Tunisia
- Phosphate deposits totaling 90 billion tons
- Averaging 300 ppm REE
- Containing 2.1 billion tons of REE resources
- Representing 15,000 years of current world consumption of 14,000 tons per year!
Recovery of REE from Phosphate Challenges

- No industrially proven process?
- No successful, significant scale pilot testing
- Only 30% REE in the acidulation feed reports to phosphoric acid
- A significant amount (79% in rock product) reports to large volume of phosphogypsum
Recovery of REE from Phosphate Opportunities

- Global interest in diversifying REE supplies
- Newly established US Critical Materials Institute
- Possibility of enriching REE in the liquid phase
Recovery of REE from Phosphoric Acid

- One of the solvents, di-2-ethylhexyl phosphoric acid (D2EHPA), for extracting uranium from phosphoric acid was found to be effective for extracting REE from phosphoric acid.
- Technical feasibility has been demonstrated.
Recovery of REE from Phosphoric Acid (continued)

- Research showed that REE leaching efficiency into the phosphoric acid phase could be increased to 75% by three methods:
  - lowering leaching temperature
  - reducing the solid/liquid ratio in the reactor
  - adding surfactant to enhance gypsum crystal growth thus reducing REE adsorption

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Recovery of REE from Phosphate: The Florida Case Study

- A significant amount of REE-containing concentrate can be obtained from flotation tailings by simple gravity separation.
- REE in waste clay may be concentrated
- Dihydrate process is relatively easy to modify to increase REE dissolution
- More relative heavy rare earths in Florida phosphate

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### REEs in US Phosphate Could Meet Much of World Demand for REE

<table>
<thead>
<tr>
<th>REE</th>
<th>MT/y</th>
<th>Value(^1), $/y</th>
<th>Fraction of 2013 global supply(^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yttrium</td>
<td>7500</td>
<td>88 million</td>
<td>180%</td>
</tr>
<tr>
<td>Neodymium</td>
<td>6000</td>
<td>450 million</td>
<td>42%</td>
</tr>
<tr>
<td>Dysprosium</td>
<td>860</td>
<td>280 million</td>
<td>130%</td>
</tr>
<tr>
<td>Europium</td>
<td>210</td>
<td>170 million</td>
<td>83%</td>
</tr>
<tr>
<td>Terbium</td>
<td>110</td>
<td>67 million</td>
<td>72%</td>
</tr>
</tbody>
</table>

\(^1\) Value in $/y for 2013

\(^2\) Fraction of 2013 global supply

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Florida Industrial and Phosphate Research Institute
REE Distribution in Phosphate Mining and Processing Streams – Florida Case Study

- Phosphate ore (matrix)
- Dissolution
  - Phosphate rock product
  - Sulfuric acid
- Filtration
  - Phosphogypsum (~38% of REE)
- Acid plant
- Sand tailings (~10% of REE)
- Waste clay (~40% of REE)
- Clay pond
- PG Stack
- Phosphoric Acid (~12% of REE)
Conclusions

• Comprehensive recovery of U, REE and Th would transform phosphate into an energy mineral.
• The Third Wave plant for U recovery from phosphoric acid would be based on the DEPA/TOPO process incorporating lessons learned from previous operations.
• Further pilot testing is necessary for 3 reasons:
  1. Optimizing pretreatment
  2. Evaluating new equipment and unit operations
  3. Finding the best system for strong phosphoric acid
Acknowledge

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