Recovery of Uranium from Phosphoric Acid*

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During the production of phosphate fertilizer material the raw phosphate rock or apatite which contains uranium is treated with sulfuric acid to produce an intermediate product called wet-process phosphoric acid or 30% \( \text{P}_2\text{O}_5 \) acid and waste product, gypsum. About 5 tons of gypsum is produced for each ton of \( \text{P}_2\text{O}_5 \) and this greyish white material is stored in large piles next to the phosphoric acid plant while the wet-process phosphoric acid is evaporated to a more concentrated form for conversion to fertilizer.

The uranium is recovered from the phosphoric acid by either a single cycle or two cycle so-called solvent extraction technique. This is a process in which the uranium is selectively extracted into an organic solution and then stripped back into a second water-containing stream and is concentrated later. Usually there are included pretreatment and posttreatment steps along with the first cycle solvent extraction circuit.

There are at least three solvent extraction processes available for recovering the uranium; (1) the pyro process in which a long chain alcohol (e.g. capryl alcohol) is reacted with phosphorous pentoxide (\( \text{P}_2\text{O}_5 \)) on site to prepare the extractant, (2) the DEPA-TOPO process which uses a mixture of di-2ethylhexyl phosphoric acid (DEPA) and trioctylphosphine oxide (TOPO) and (3) the OPAP process which uses octylphenyl acid phosphate as the extractant. All of these materials are dissolved in a kerosene type diluent or extender. You might look for drums with the names, capryl, D2EHPA, TOPO or OPAP printed on them.
This slide shows a typical flowsheet of the two cycle process and consists of pretreatment to clean up the acid, first and second cycle solvent extraction circuits and uranium refining. The uranium laden phosphoric acid is pumped into a large clarifier unit to remove solids and then through towers of activated carbon to remove organic matter. Depending on the process used, the acid may be treated with hydrogen peroxide (H₂O₂) to oxidize the uranium or passed through a bath of scrap iron or iron filings to reduce the uranium. Here you might look for drums labeled H₂O₂ or see iron scrap laying around. In most cases the solution will also be pumped through a couple of heat exchangers to cool the acid. After cleaning and cooling, the acid is pumped into a series of 4 to 5 mixer-settler units countercurrent to a stream of solvent which extracts the uranium from the acid. Uranium is then stripped from the solvent in another 3 to 4 mixer-settler units. This step concentrates the uranium by a factor of 50-100 and this aqueous strip solution is pumped to the second cycle. The solvent goes round and round in the first cycle circuit as it is cycled between extraction and stripping units. The main phosphoric acid stream (or raffinate), after removal of the uranium, is pumped to a large hold-up tank and then through an air flotation unit to remove entrained solvent before returning the acid to the acid plant for evaporation. The strip solution is then pumped to an oxidation tank for oxidation of the uranium. There may be a tank of H₂O₂ in the vicinity. The oxidized solution is pumped to the second cycle for further treatment or may be pumped to a tank truck so it can be carried to the central recovery facility.

The second cycle, when compared to the first cycle, is a very small scale operation consisting of an extraction circuit with 3 pilot-plant size mixer-settler units, a scrub section with 2 mixer-settler units and a carbonate
strip circuit with 2 mixer-settler units. You might look for drums or tanks of ammonia and carbon dioxide. A yellow uranium product is recovered from this circuit. This material is calcined by heating to 600-800°C to remove carbon dioxide and ammonia and form uranium oxide. Special precautions will be taken in this area to prevent the spread of the radioactive powder and radiation symbols will be present.

Now, let's take a look at some of the individual units.

This next slide shows a mixer-settler unit, one of the key components of a solvent extraction process.

SLIDE

Each unit is considered to be a stage. These units may range from 10 ft wide by 20 ft long to 20 ft by 50 ft or larger. Usually, there will be 7 to 9 units or stages in a row. The mixers will be on alternate ends of adjoining stages. In some cases round mixers and settlers may be used.

Another important piece of equipment, a gravity thickener will probably be present. This slide shows a schematic drawing of such a unit.

SLIDE

They usually run about 100 ft in diameter and are used in pretreatment for clarification of the acid.

One other piece of equipment worth noting is the air flotation unit used in posttreatment to clean up the acid before return to the acid plant. This is shown in the next slide.

SLIDE

Finally, let's take a look at an actual uranium extraction facility at a phosphoric acid plant in the last slide --
A cluster of 10 mixer-settler units can be seen in the foreground. Unfortunately, the other units are lost in the background.

In conclusion, because of miscellaneous tanks, miles of piping, etc. it may be very difficult to pick out a uranium recovery facility. Mixer-settlers will probably be the easiest equipment to spot. Secondly, chemical names and symbols may give a clue. For this reason the next slide shows a list of the major chemicals that may be expected.
Simplified Flowsheet for Wet-Process $\text{H}_3\text{PO}_4$ Production

- **Phosphate Rock**: $\text{Ca}_3\text{F} (\text{PO}_4)_2$
- **Beneficiation Grinding**
- **Dissolution**: $\text{H}_2\text{SO}_4$
- **Calcination**
- **Filtration**: (30-32% $\text{P}_2\text{O}_5$)
- **Evaporation**: ($54\% \text{P}_2\text{O}_5$)
- **Merchant Acid**
- **Organic Matter**
- **Waste**
- **Black Acid**
- **Green Acid**: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
- **Gypsum**
- **High Analysis Liquid Fertilizers**
- **MAP**
- **DAP**
- **Triple Super Phosphate**

ORNL-DWG. 76-2800
FIRST OR CONCENTRATION CYCLE

WET-PROCESS PHOSPHORIC ACID PLANT
1000 tons \( P_2O_5 \) / day
1000 lb \( U_3O_8 \) / day

FILTER ACID
32% \( P_2O_5 \)
400 gal/min
0.0017 lb \( U_3O_8 \)/gal

PRETREATMENT

URANIUM EXTRACTION

POST TREATMENT

EXTRACTANT
~200 gal/min

URANIUM STRIPPING

URANIUM PRODUCT
SOLUTION 32% \( P_2O_5 \)
~8 gal/min
0.09 lb \( U_3O_8 \)/gal
to SECOND CYCLE

32% \( P_2O_5 \)
< 100 ppm ORGANIC

~8 gal/min
ORNL DWG 79-178

URANIUM RECOVERY PROCESS

ACID CLEANUP & TREATMENT

Recycled Organic (Uranium-free)

Primary Solvent Extraction Circuit

Pretreated Phosphoric Acid (Uranium-loaded)
Strip Acid (Uranium-loaded)

Secondary Solvent Extraction Circuit

Secondary Strip Circuit

Secondary Strip Solution (Uranium-loaded)

Secondary Strip Solution (Uranium-free)

Yellow-Cake Product

URANIUM REFINING SYSTEM

Phosphoric Acid from Existing Plant

Carbon Columns

Yellow-Cake Slurry

Uranium Precipitation

Scrubber

Drying

Storage & Shipping
TORQUE INDICATOR, OVERLOAD ALARM, MOTOR CUTOUT

MECHANISM SUPPORT

LONG ARMS

BLADES

DRIVE UNIT

GEAR MOTOR

SHORT ARMS (OPTIONAL)

LIFTING DEVICE

OVERFLOW WEIR

FEED LAUNDER

VERTICAL SHAFT

ARM

FEED WELL

DISCHARGE CONE

CONESCRAPER

BLADES
<table>
<thead>
<tr>
<th>Chemical</th>
<th>Symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid</td>
<td>$\text{H}_3\text{PO}_4$, $\text{P}_2\text{O}_5$</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>$\text{H}_2\text{SO}_4$</td>
</tr>
<tr>
<td>Gypsum</td>
<td>$\text{CaSO}_4\cdot\text{2H}_2\text{O}$</td>
</tr>
<tr>
<td>Uranium</td>
<td>$\text{U}$, $\text{U}_3\text{O}_8$, yellow cake</td>
</tr>
<tr>
<td>Iron</td>
<td>$\text{Fe}$</td>
</tr>
<tr>
<td>Hydrogen peroxide</td>
<td>$\text{H}_2\text{O}_2$</td>
</tr>
<tr>
<td>Ammonia</td>
<td>$\text{NH}_3$</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>$\text{CO}_2$</td>
</tr>
<tr>
<td>Di-2ethylhexyl phosphoric acid</td>
<td>$\text{D}_2\text{EHPA}$</td>
</tr>
<tr>
<td>Triocetylphosphine oxide</td>
<td>$\text{TOPO}$</td>
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