

Technologies for Uranium Recovery from Phosphoric Acid

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1.0 Abstract

The rapid increase in uranium oxide (U_3O_8) prices over the last few years, and the changing fundamentals in the world's uranium supply/demand balance have re-kindled the interest in extraction of uranium from phosphoric acid.

This paper examines different technologies that can be used to extract uranium oxide (U_3O_8) from phosphoric acid streams:

- Solvent extraction (SX) techniques modified and updated from those used in previous SX processes developed in the 1970's and 1980's.
- Advanced Technology (AT) techniques that offer simpler processing techniques, lesser equipment requirements, and lower capital and operating costs compared with SX.

The paper will briefly describe how each of the processes work, and ascribe comparative order of magnitude capital and operating costs to each process based on a hypothetical uranium content in a typical phosphoric acid stream, for a standard size phosphoric acid unit. Comparative economics will also be developed for each of these cases. Finally, a recommended test program encompassing all three processes will be recommended for those who may be interested in pursuing commercial development.

2.0 The Uranium Industry

Before getting in the specifics of uranium extraction from phosphoric acid, it is helpful to describe the uranium industry itself in some greater detail. This review will include how uranium is processed into nuclear fuel, nuclear fuel terminology, and some of the parameters and statistics associated with uranium supply and demand.

2.1 The Nuclear Fuel Cycle

Uranium is obtained by mining uranium containing ore known as pitchblende. The primary chemical form of the mineral concentrate that is recovered by modern mining and beneficiation techniques is triuranium octoxide (U_3O_8), known as yellowcake. In the mining process, ore is first crushed and ground to a fine powder to produce "pulped" ore. This is further processed with concentrated acid, alkaline, or peroxide solutions to leach out the uranium. Yellowcake is what remains after filtering and drying. In most cases, yellowcake produced by most modern mills is not yellow, but brown or black. The name comes from the color and texture of the concentrates produced by early mining operations.

Next the yellowcake is converted into uranium hexafluoride (UF_6) gas. This is a complex chemical process by which yellowcake is dissolved in nitric acid to yield uranyl nitrate $UO_2(NO_3)_2$. The uranyl nitrate is then treated with ammonia to produce ammonium diuranate $(NH_4)_2U_2O_7$. Reduction with hydrogen gives UO_2 , which is converted with hydrofluoric acid (HF) to uranium tetrafluoride, UF_4 . Oxidation with fluorine finally yields UF_6 .

Now the uranium must be “enriched” to get it into a form that can be used by a nuclear power plant. In its natural form, uranium occurs in two atomic states, U^{238} and U^{235} . The U^{238} form is stable and non-fissionable, while the U^{235} form can be broken down by neutron bombardment into two lighter elements, which is the essence of the nuclear fission reaction that releases large amounts of heat. The greater majority of natural uranium is as the U^{238} isotope, comprising 99.289% of all uranium atoms. Only 0.711% of naturally occurring uranium is as the U^{235} isotope. Enrichment is accomplished by separating the heavier U^{238} isotopes from the lighter U^{235} isotopes in the UF_6 gas by using either gaseous diffusion or gas centrifuges. A level of 4-5% U^{235} is required in order to be used as fuel for a typical nuclear power plant. By contrast, weapons grade uranium has levels of 90% or greater U^{235} and requires a far more complex enrichment process.

Then enriched UF_6 is converted into uranium dioxide (UO_2) powder, which is formed into cylindrical pellets, then sealed in metal fuel rods and bundled into fuel assemblies. The fuel assemblies are loaded into nuclear reactors where the U^{235} atoms fission, producing heat to create steam which is used to generate electricity.

The entire process is summarized in Figure 1.

Figure 1- Nuclear Fuel Cycle – From Mine to Reactor

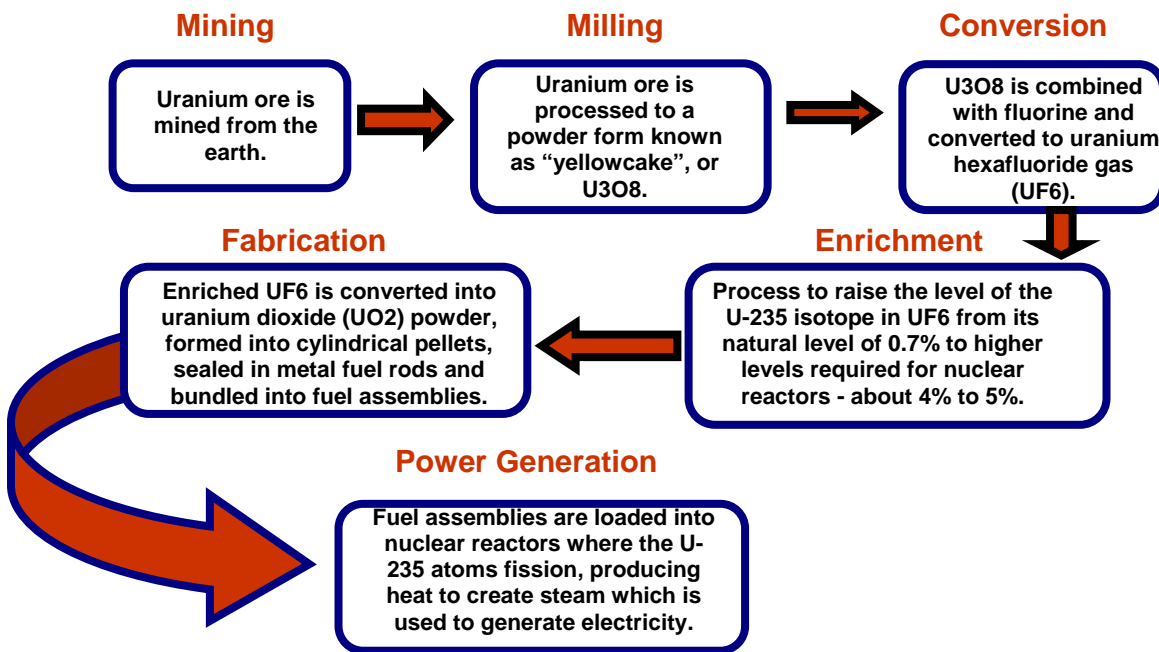


Table 1 illustrates some of the major terms used in the uranium industry.

Table 1 – Nuclear Fuel Terms

Natural Uranium	U ²³⁵ isotope = 0.711%
Enriched Uranium	U ²³⁵ isotope > 0.711%
Depleted Uranium	U ²³⁵ isotope < 0.711%
U ₃ O ₈	Yellowcake, Concentrates
UF ₆	Natural uranium in the form of hexafluoride
LEU	Low Enriched Uranium – U ²³⁵ isotope >0.711% and <20%. Typically 4%-5%
HEU	Highly Enriched Uranium – U ²³⁵ isotope > 20%. Typically weapons' grade at 90%+

2.2 Uranium Supply

Nuclear power is expected to be an important part of the worldwide energy mix at least for the next 50 years, and by most projections well beyond. That is, of course, provided an adequate supply of uranium is available to sustain the nominal growth rate for nuclear power of 2 to 3.5% per year that is projected by some analysts ⁽¹⁾.

Uranium supply is broadly classified into two categories: primary and secondary.

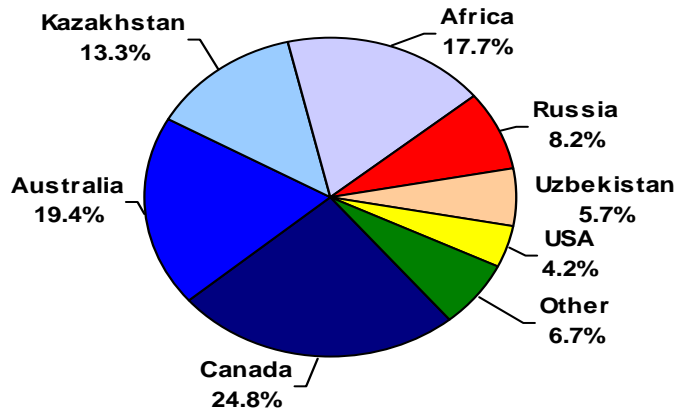
- Primary supply includes all newly mined and processed uranium. It also includes uranium that would be extracted as a by-product of other mineral production (e.g. uranium extracted from phosphoric acid). Mined uranium production in 2007 was about 112 million lb U₃O₈ [42 500 tonne U]⁽²⁾. This is only 62% of global demand of around 180 million lb U₃O₈ [68 000 tonne U]⁽²⁾. Currently there is no known uranium extracted from phosphoric acid, as the last of these plants shut down in 1999.
- Secondary supply is uranium held in inventory in one form or another. This category includes highly enriched uranium (HEU) from ex-military weapons, natural and low enriched uranium (LEU) held in civil and government inventories, recycled uranium and plutonium from spent fuel as mixed oxide fuel (MOX), reprocessed spent uranium fuel (RepU) and reenrichment of depleted uranium tails (tails).

In 2007 secondary supply covered about 38% of demand. However, because supplies from inventory will continue to decline, the contribution from various secondary sources is projected to drop to between 4 and 6% of demand by 2025, and the percentage will continue to decline thereafter.

The role of primary supply will have to expand as the contribution from secondary supply diminishes.

Figure 2 shows the distribution of mined (primary) uranium production in 2006. Currently the major producers of mined uranium are Canada, Australia and Kazakhstan. Total production in that year was 102 million lbs as U₃O₈.

Figure 2 – World Uranium Mined Production in 2006⁽³⁾



The World Nuclear Association (WNA) in its 2007 report forecasts that mined production will increase to 171 million lb as U₃O₈ by the year 2020⁽³⁾. The three leading producers should continue to be Canada, Australia and Kazakhstan, with Australia and Canada having about 25% each and Kazakhstan around 20% of total world mined production.

2.3 Uranium Demand

The top ten nuclear generating countries in 2006 are shown in the Table 2 below.

Table 2 – Top 10 Nuclear Generating Countries – 2006⁽¹⁾⁽³⁾

Country	Electricity Generated Trillion Wh
United States	787
France	429
Japan	292
Germany	159
Russia	144
South Korea	141
China (incl Taiwan)	93
Canada	92
Ukraine	85
United Kingdom	69

In 2007 there were 438 operating nuclear reactors. By 2030, The WNA is predicting an increase to 523 in its Reference Case and 748 in its Upper Case ⁽³⁾. New plants are expected in China (23-29), Russia and Eastern Europe (22-30), India (10-14), Japan (10-13), U.S. (8-12), South Africa (8-14), and South Korea (8+). The majority of these plants are expected to be larger than 1,000 MW.

According to WNA, the demand for uranium is expected to grow by 2 to 3.5% per year over the next 20-30 years. Demand will be accelerated by the response to:

- High fossil fuel prices
- Climate change

At these growth rates, uranium demand is expected to be 255 to 335 million lb/y U₃O₈ [97 to 127 000 t U] by 2025. Using the more conservative low demand growth rate, and factoring in the reduction in secondary supply sources expected, primary production will have to increase to about 245 million lb/y. This is more than double current primary production levels. This can be seen in Table 3, which ignores changes in inventory.

Table 3 – Uranium Supply/Demand 2007 to 2025⁽²⁾⁽³⁾

	2007	2025
U₃O₈ Demand - Million lb	180	255
U₃O₈ Supply – Million lb		
Primary	112	245
Secondary	68	10
Total	180	255

This supply/demand scenario portends well for recovering uranium from phosphoric acid, as it is questionable if mined production can increase by the required amount in this timeframe. This should ensure that prices of U₃O₈ should stay relatively high into the future.

One other point is worth noting. The world produced 34.2 million tonnes of P₂O₅ acid in 2006 according to statistics from IFA. Not all of this acid was produced by the wet process method. However, assuming that it was and that all of the world's phosphoric acid plants were equipped with uranium extraction facilities (none are currently); the maximum quantity of U₃O₈ that could be extracted assuming a liberal 100 ppm of U₃O₈ in the filter acid is about 25 million lb/y. This is only a fraction of the new primary supply that will be required over the next 15-20 years. One can conclude from this that production of uranium from phosphoric acid would not significantly impact global uranium supply factors.

3.0 Phosphate Rock Contains Uranium

Phosphate rock contains uranium in various concentrations. Generally igneous rocks contain lower levels than sedimentary rocks. The table below shows reported concentrations of uranium in phosphate rock in various parts of the world.

Table 4 – Uranium Content of Selected World Phosphate Rock⁽⁴⁾

Country	Deposit	U (ppm)		
Algeria	Djebel Onk	25		
	Djebel Kouif	100		
Australia	Duchess	80	to	92
China	Undifferentiated	10	to	39
Egypt	Abu Tartur	40	to	120
Israel	Arad	150		
Jordan	Shidyia	46		
Morocco	Bucraa	70	to	80
	Khourigba	80	to	120
Peru	Sechura	47	to	80
Saudia Arabia		25	to	85
Senegal	Taiba	64	to	70
Syria	Khneifiss	75		
Tanzania	Minjingu	390		
Togo		77	to	110
Tunisia		12	to	88
USA	Central Florida	59		200
	North Florida	50		143
	Idaho	60		141
	North Carolina	41		93

Not a well publicized fact is that uranium is retained in phosphate fertilizer products unless it is separately extracted. Future environmental awareness and regulations could require that phosphate producers remove the uranium from the fertilizer, which, as unlikely as this scenario may sound in today's world, would guarantee another supply source, albeit an involuntary one.

4.0 Uranium Can Be Recovered From Phosphoric Acid

Wet process phosphoric acid (WPPA) is the major means of producing phosphoric acid in the world today. Uranium in the form of U_3O_8 can be recovered from the weak filter phosphoric acid (25-30% P_2O_5) produced in WPPA. Filter acid is fed to a separate extraction circuit for removal and concentration of the uranium. After extraction, the uranium-depleted phosphoric acid can then be returned for evaporation and conversion to concentrated phosphate fertilizers (for example DAP, MAP), MGA or technical grade acid.

Alternatively, if technical grade acid or tech phosphates are already being produced, uranium can be recovered from the raffinate waste stream, or a precipitated impurity solid stream, as it tends to concentrate in this material.

The phosphoric acid recovery circuit can be installed and located in a separate portion of an existing phosphoric acid facility, so as not to disrupt the existing operation while being constructed. It can then be “plugged in” at the appropriate time after completion with minimum production disruptions. With the proper design and project execution, the uranium recovery circuit will not hinder the overall throughput of the phosphoric acid/downstream products plants.

There were two previous waves of construction of uranium recovery plants. See Table 5. The first commercial plant to recover uranium from phosphoric acid (by precipitation in a sodium phosphate solution) was built in Illinois in 1952. In 1955 IMC built a commercial plant based on solvent extraction in Florida, and another was built by US Phosphoric Products (later to become Gardiner).

Table 5 – Past Uranium From Phosphoric Acid Projects

Company		Process	Capacity t/y		Start	Close
			P ₂ O ₅ lb/y	U ₃ O ₈		
Blockson	IL	Precipitation	100,000	80,000	1952	1961
IMC	FL	OPPA	100,000	80,000	1955	1961
IMC	FL	DEPA-TOPO	1,700,000	1,360,000	1980	1992
US Phosphoric Products (Gardiner)	FL	OPPA	200,000	160,000	1955	1961
		Revised	450,000	360,000	1979	1982
URC/WR Grace	FL	OPAP	330,000	264,000	1976	1980
WMC/Farmland	FL	DEPA-TOPO	450,000	360,000	1978	1981
Freeport/Agrico/IMC	LA	DEPA-TOPO	950,000	760,000	1978	1998
Freeport/Agrico/IMC	LA	DEPA-TOPO	540,000	432,000	1980	1998
CFI	FL	DEPA-TOPO	950,000	760,000	1980	1992
CFI	FL	DEPA-TOPO	600,000	480,000	1980	1985
ESI/Western Coop	Canada	OPAP	110,000	88,000	1980	1981
		DEPA-TOPO				
Chemie Rupel	Belgium	DEPA-TOPO	140,000	112,000	1980	1998
China Phosphate	Taiwan	DEPA-TOPO	33,000	26,400	1981	1985
SOM	Iraq	DEPA-TOPO	90,000	72,000	1984	1991

The 1970s saw a rapid increase in fossil fuel prices, resulting in a resurgent nuclear energy program in the US and a consequent rise in uranium prices. Uranium prices peaked at over \$40/lb in mid 1978. As a result a wave of uranium extraction plants were built in the late 1970s to early 1980s, and most were based on long term contracts with utilities having nuclear power plants.

By the 1980s, there were eight commercial plants in the US, and one each in Canada, Belgium, Taiwan and Iraq. All these plants were based on solvent extraction technology. By 1999, all had been shut down and dismantled.

5.0 Conventional Uranium Solvent Extraction (SX) Technologies

Much of the development work on solvent extraction was done by the US Government-owned Oak Ridge National Laboratory (ORNL) in Tennessee.

There were essentially three different solvent processes used.

- OPAP Process - U reduction by iron; extraction with octyl pyrophosphoric acid + kerosene. This was used by IMC and US Phosphoric Products (later Gardinier).
- 2 Stage DEPA-TOPO Process – Most popular and efficient SX process. This was used by IMC/Prayon, Freeport, Wyoming Mineral Corp (WMC).
- OPAP Process. Octyl phenyl acid phosphate (OPAP) was used in the first cycle and DEPA-TOPO in the second cycle. This was used by UNC Recovery Corp., (URC) and Earth Sciences, Inc. (ESI).

All SX processes generally have the same unit operations. The following process description is particular to the 2 stage DEPA-TOPO process (see Figure 3):

Acid Pre-treatment – phosphoric acid from the filter (at 25-30% P_2O_5) is cooled, decolorized, and then clarified to remove solids.

Primary SX extraction – clarified acid is contacted with DEPA-TOPO solvent dissolved in kerosene in a counter-current mixer/settler system, where U is transferred to the solvent phase (“pregnant organic”). Lean phosphoric acid is returned to the phosphoric acid plant.

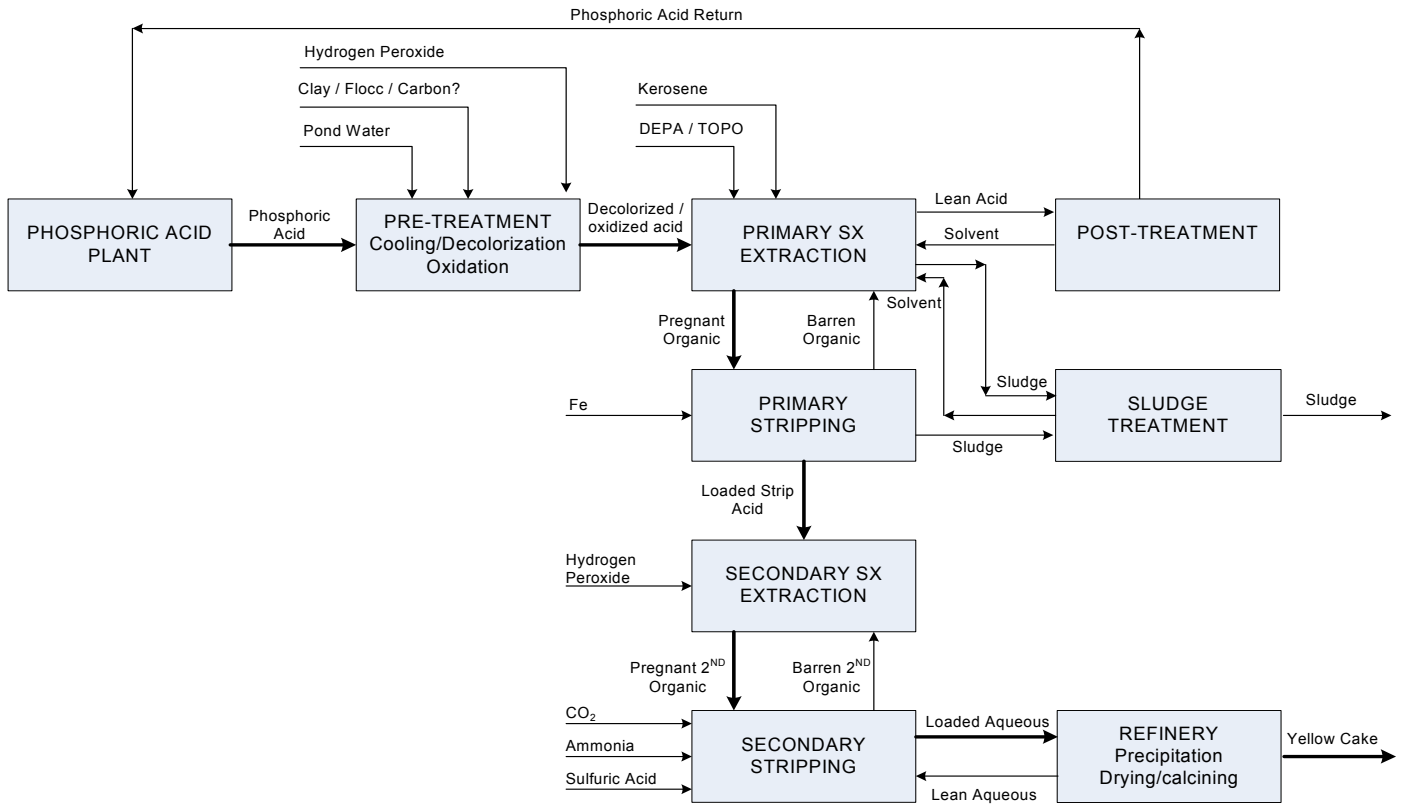
Primary SX stripping – the pregnant organic containing uranium in the U^{6+} state is treated with a reducing agent to convert it to the U^{4+} state; it is then contacted with more concentrated phosphoric acid in another mixer/settler system. Here the U is stripped from a large volume of organic solvent and transferred to a smaller volume of strip acid (loaded primary strip acid). Significant uranium concentration factors are achieved during this step.

Secondary SX extraction – the loaded primary strip acid is oxidized to convert uranium back to the 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”.

Secondary SX 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.

Refining –The acid uranium solution is reacted with hydrogen peroxide to precipitate a uranyl peroxide salt (UO_2), which is then thickened, washed, dried, and calcined to produce U_3O_8 “yellowcake”.

Figure 3 – Typical SX Process Flow Diagram



6.0 Advanced Technologies (AT) for Extracting Uranium

Any solvent extraction based uranium recovery process has inherent disadvantages, particularly the carrier for the solvent itself. Large equipment is required in multiple banks of mixer-settlers..

The Advanced Technologies (AT) pioneered by K-Technologies, Inc. are based on a continuous liquid – solid contacting system as opposed to the multi-layer SX processes which are based on a liquid – liquid contacting system. The AT processes offer the following improvements versus SX:

- Elimination of kerosene carrier.
- Fewer process steps and simpler processes within the steps, resulting in fewer equipment items.
- Higher overall uranium recoveries.
- Lower capital and operating costs.

Exact descriptions of the processes are proprietary, but the generalized process steps can be summarized as follows:

Acid Pre-treatment – same as in SX, but the degree of decolorization and solids removal will not be as great as required for SX. The exact parameters would be established by test work.

Primary extraction - clarified acid is contacted with a solid state system in a continuous contacting system. U is transferred from the phosphoric acid to the extractant. Lean phosphoric acid is returned to the phosphoric acid plant. No solvent treatment is required.

Primary stripping – in a different section of the same contacting system the U contained in the extractant is stripped through a low volume stripping solution. The extractant part of the same contacting system is then returned to extraction service.

Secondary extraction/stripping – is a greatly simplified system for strip solution treatment to get the uranium in the alkali form. The alkali strip solution is then treated to neutralize the alkali and produce an acidic uranium solution.

Refining –The acid uranium solution is reacted with hydrogen peroxide to precipitate a uranyl peroxide salt (UO_2), which is then thickened, washed, dried and calcined to produce U_3O_8 “yellowcake”.

7.0 Major Differences Between SX and AT Processes

There are significant differences and advantages offered by the AT processes versus SX. The major ones can be summarized in Table 6.

Table 6 – Major Differences in SX and AT Uranium Extraction Processes

	SX	AT
Acid pretreatment	√	√ (but less)
Extraction state	Liquid-liquid	Liquid-solid
Primary extractant	DEPA-TOPO liquid	Solid state
Kerosene needed	√	No
Interfacial sludge (crud)	√	Reduced or eliminated
Secondary extraction/ stripping system	√	Eliminated (or greatly reduced)
Contacting equipment	Multiple mixer/settlers	Single continuous unit
U_3O_8 refinery	√	√
Equipment requirements	More	Less

8.0 Capital and Operating Cost Comparison

Table 7 provides order of magnitude capital and operating costs for two theoretical phosphoric acid plants:

- A smaller plant that produces 400,000 tonnes/y of P₂O₅ acid.
- A large plant that produces 2,000,000 tonnes/y of P₂O₅ acid.

For each of the two plants, estimates are provided for retrofitting these plants with a conventional SX system using DEPA-TOPO solvent, and the other using one of the AT systems. The filter phosphoric acid (28% P₂O₅) at each plant is assumed to contain 120 ppm U₃O₈, with uranium recovery assumed to be 90% for both processes, even though the AT should yield higher recovery rates (92-93%).

Table 7 – Capital and Operating Cost Comparisons Between SX and AT

	SX		AT	
P ₂ O ₅ Production t/y	400,000	2,000,000	400,000	2,000,000
U ₃ O ₈ Production lb/y	340,000	1,700,000	340,000	1,700,000
Capex (ISBL) US \$ million	\$55 - 65	\$275 - 295	\$40 - 50	\$190 - 210
Cash operating cost \$/lb	\$34 - 36	\$28 - 30	\$30 - 32	\$24 - 26

9.0 Economic Comparison

For each of the two sized plants described in the forgoing section, economic analyses have been performed using a cash flow model for each technology with two methods of financing, i.e. 100% equity and 50% debt/50% equity.

The major assumptions for these analyses are as follows:

- Project development/construction schedule – 3 years
- Project operating life – 15 years
- Capex and Opex – midpoint of above table
- U₃O₈ selling price (long term contract basis) - \$70/lb
- Depreciation/amortization – 15 years straight line

- Income tax rate – 30%
- Debt financing parameters:
 - Loan amortization – 7 years mortgage style
 - Interest rate – 8.5%
 - Interest capitalized during construction

The results are summarized in Tables 8 and 9:

Table 8 – Economics for Smaller Phosphoric Acid Plant

Economics for Production of 340,000 lb/y of U₃O₈		
	SX	AT
Sales - US \$ million/y	\$24	\$24
Net Income - \$ million/y		
• 100% equity	\$6	\$7
• 50% /50% debt/equity	\$5	\$7
Cash Flow - \$ million/y		
• 100% equity	\$8	\$9
• 50% /50% debt/equity	\$6	\$7
IRR		
• 100% equity	9.9%	15.8%
• 50% /50% debt/equity	11.0%	19.8%

Table 9 – Economics for Larger Phosphoric Acid Plant

Economics for Production of 1,700,000 lb/y of U₃O₈		
	SX	AT
Sales - US \$ million/y	\$119	\$119
Net Income - \$ million/y		
• 100% equity	\$36	\$44
• 50% /50% debt/equity	\$33	\$42
Cash Flow - \$ million/y		
• 100% equity	\$48	\$52
• 50% /50% debt/equity	\$36	\$43
IRR		
• 100% equity	13.0%	20.5%
• 50% /50% debt/equity	15.6%	27.1%

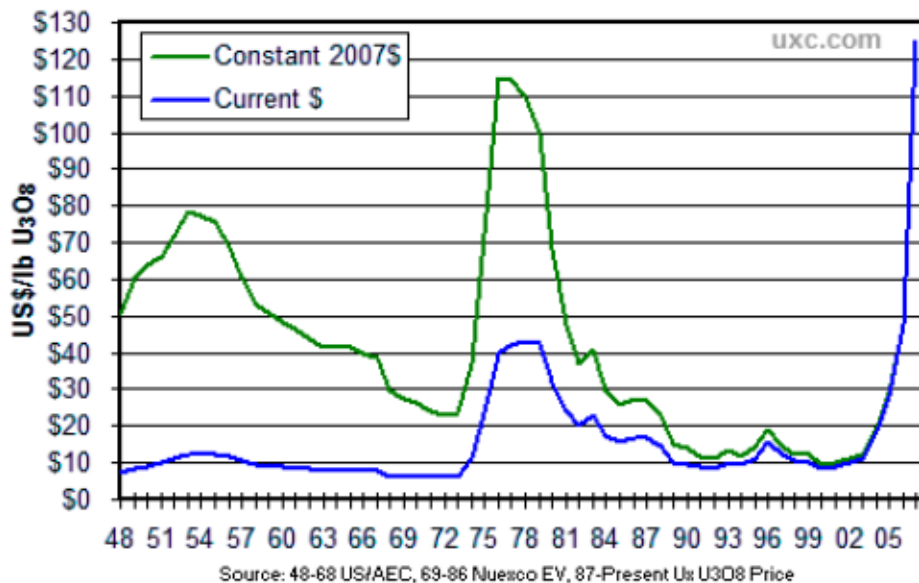
It can be seen that the AT scenario yields much better economics for either size plant compared with SX. This is to be expected as the AT saves about 30% on capital costs and some 13% on cash operating costs. Also as expected, the larger plant shows better economics in all cases compared with the smaller facility, primarily due to the advantages of scale. The AT internal rates of return (IRR) range from 16-27%, and are attractive for all cases examined for all financing alternatives. On the other hand, only the leveraged case for the larger plant puts the SX technology over the 15% IRR threshold required by many companies to justify a project.

10.0 Conclusions

Production of uranium from phosphoric acid was accomplished on a fairly large scale by the early 1980s. This was due primarily to the rapid increase in uranium demand necessitated by the growth in nuclear power plants in the 1970s in answer to the energy crisis during that decade. Prices of yellowcake rose to over \$40/lb in the late 1970s, equivalent to nearly \$120/lb in 2007 dollars. All uranium extraction plants that were built utilized conventional SX processes, mostly using DEPA-TOPO as the solvent. Figure 4 illustrates a history of spot uranium prices over the last 60 years.

Figure 4 – History of U3O8 Spot Prices 1948-2007

Constant 2007 US\$ vs. Current US\$ Spot U₃O₈ Prices



Following the moratorium on building new nuclear plants after accidents at Three Mile Island (1979) and Chernobyl (1986), and due to large releases of uranium stockpiles after the breakup of the Soviet Union in the early to late 1990s, prices for yellowcake plummeted to single digits. The result was that it became uneconomic to operate

existing uranium extraction facilities, and by 1999, all had closed after their long-term contracts with the utilities expired.

However, since about the middle of the current decade, demand for uranium has begun to accelerate again. This is due to a drive to build a new generation of nuclear power plants in emerging markets like China, Russia and India, where energy demand is rapidly increasing. Also the political push to reduce greenhouse gases from conventional carbon based fuels is causing many developed economies to consider adding more nuclear plants. At the same time, traditional secondary supply sources from various stockpiles around the world are beginning to decline, and mined production is not increasing at a rate that some feel is enough to satisfy increasing world demand for yellowcake.

The result has been a rapid acceleration in prices of U_3O_8 over the last few years. This has been exacerbated by the entrance of speculators and hedge funds into the market. Spot prices reached as high as \$136/lb in mid 2007, but have since backed off to \$60-70/lb currently (May 2008). Most experts feel that prices will stay relatively high and trend even higher in the next decade, as some 135 million lb/y of new primary supply will be needed just to meet the low WNA demand growth estimate by 2025. This is about 120% of current world mine production.

These changes in the uranium industry bode well for a need to once again resume the practice of extracting uranium from phosphoric acid. The SX process route is proven technology that can be used for the next generation of these plants. However, there are competing AT processes that can simplify process steps, increase uranium recoveries, lessen equipment requirements, and most importantly considerably reduce new plant capital and operating costs. This should lead to a high return on investment for these AT uranium extraction facilities.

These new AT technologies are available through Jacobs Engineering Group and its technology partner, K-Technologies, Inc. This partnership can work closely with interested phosphate producers who are considering installing uranium extraction facilities. The first steps would be to outline and execute a specific development program under appropriate confidentiality agreements. Such a program can be accomplished in phases and would involve a desk study, laboratory and pilot plant test work, leading to a preliminary design engineering package for a commercial facility.

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