

URANIUM FUEL AS BYPRODUCT OF PHOSPHATE FERTILIZER PRODUCTION

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ABSTRACT

The world has substantial unconventional energy resources in phosphate rock deposits and sea water which contain vast amounts of dilute uranium.

The South Mediterranean region, as a remnant of the ancient Tethys Sea, is endowed with large supplies of uranium fuel that is embedded in the phosphate rock being processed into fertilizer. Establishing a phosphate fertilizer industry that uses the appropriate processes would allow extraction of the uranium as a byproduct.

Uranium from phosphorites constitutes a large and long term resource base compared with the short-lived high concentration ores which have been depleted in the deposits exploited for export such as at the Gabon Republic.

An increased price of U_3O_8 would make its extraction from phosphate rocks potentially economical. What makes this feasible is that the fuel cost is a minor part of the nuclear electricity price, making it possible to exploit higher cost ores, particularly for the purpose of long term energy independence and security for countries desiring to produce future nuclear electricity and desalted water.

In addition, the development and implementation of more efficient extraction methods such as the liquid membrane approach may also make it more economical. This would turn the region along the ancient Tethys Sea shores into a future nuclear energy fuel source as well as a food energy source as fertilizer for the world.

The extraction of uranium as a byproduct in the wet phosphoric acid production process is discussed. The Liquid Membrane (LM) technology, even though not industrially developed, is identified as possessing the potential to efficiently separate and concentrate uranium from process phosphoric acid and is thought to be superior to the solvent extraction methods.

1. INTRODUCTION

The world today depends on phosphate rocks as a source of phosphorous fertilizer to enhance soil productivity in addition to potassium and nitrogen fertilizers in modern farming. Purified food grade phosphoric acid is used as an ingredient in food staples and soft drinks. The main sources of phosphate fertilizer have been Florida in the USA, Morocco, Jordan and Kazakhstan. World demand growth for phosphate exceeded the supply in 2007 and the trend is expected to continue through 2012 based on the world population increasing by 1.1 billion within 12 years. Excluding China, the global phosphoric acid capacity has declined from 2003 to 2007 by close to 1.5 million tons of phosphoric pentoxide.

The average uranium content in phosphate rock is low at 50-200 parts per million (ppm) or 0.005-0.020 percent. For comparison, some Canadian commercial rich ores have up to 15 percent or 150,000 ppm in uranium. Yet some low concentration ores are being mined in countries that are short in the high grade ores. For instance, mines at Jaduguda, India have just 0.06 percent or 600 ppm, and at Andhra Pradesh, India at 0.3 percent or 3,000 ppm. Since the fuel cost is a small component of the total cost nuclear electricity, countries that seek energy independence and secure energy supplies find it imperative to use their domestic uranium resources, even at low uranium concentrations in the ore deposits.

The world uranium resources in phosphate rocks are estimated at 9×10^6 metric tonnes (mt) of Uranium (U). In most situations, it is left in the produced fertilizer as a radioactive contaminant; necessitating health physics and radiation protection measures to protect its handlers.

Phosphogypsum accumulates as a waste product from the production of phosphoric acid containing traces of uranium and its daughter radioactive decay products such as radium and needs handling as a low level radioactive waste stream. Typical activities are 4 Becquerels (Bq) or 0.32 mg of U^{238} and 1 Bq or Ra^{226} per gram of P_2O_5 . With the appropriate extraction methods, uranium could be produced as a byproduct of the wet process phosphoric acid production process.

Over the period 1998-2008 about 30 percent of the world nuclear fuel demand was met by dismantling nuclear devices and from Russia's stockpile of high enriched uranium that was being diluted to low enriched uranium for power reactors use. The "High Enriched Uranium Agreement" also called the "Megatons to Megawatts" program between the USA and Russia terminates by 2013. Accordingly, a prospect exists of the disappearance of 30 million pounds of uranium from the supply lines. The forecast production for the Cigar Lake mine project by the Cameco Company in Canada is 18 million lbs/year, leaving a substantial shortfall of 12 million lbs/year. The last frontier for a major find is in Australia. Accordingly, sovereign investment funds from China and India have been reported as stockpiling uranium, affecting the demand side of the equation, suggesting a potential price rise above the level of \$40/lb of U_3O_8 .

A possible resource for phosphates and uranium is introduced as the ancient Tethys Sea along the present day Southern Mediterranean Sea with uranium 20 times cheaper to find than oil in terms of the finding cost share of the sale price [1].

This is a different geology than in the American West where prospectors equipped with Geiger counters found and mined high concentration small size deposits in a previously wet forest, glacier and water flow environment. There, the uranium tended to concentrate in petrified wood in deposits sometimes just the size of a large tree.

The price of spot uranium as yellow cake, the oxide of uranium U_3O_8 , fluctuated up to a maximum price of \$138 in 2007 per pound (lb)

from \$45 in 2006 and \$10 in 2002, on strong demand from the nuclear industry given high oil prices and a global effort to clamp down on carbon dioxide emissions blamed for climate change. A few pundits speculated about its price rising to the \$200 per pound range even though the price retreated in 2010 to the \$40 per lb level after the USA Department of Energy (USDOE) sold into the uranium market enriched uranium as UF₆ from its stockpile to the USA Enrichment Corporation (USEC) to internally finance cleanup projects. Hedge funds were forced to liquidate their speculative holdings as a result of the 2008-2009 financial crisis. There appears also that a distinct positive correlation exists with the price of other energy supplies, particularly petroleum, natural gas and coal.

An increased price of U₃O₈ would make its extraction from phosphate rocks potentially economical. What makes this feasible is that the fuel cost is a minor part of the nuclear electricity price, making it possible to exploit higher cost ores, particularly for the purpose of energy independence and security for countries desiring to produce nuclear electricity. In addition, the development and implementation of more efficient extraction methods such as the liquid membrane approach may also make it more economical. This would turn the region along the ancient Tethys Sea shores into a future nuclear energy fuel source as well as a food energy source as fertilizer for the world.

Uranium has come of age on the back of the world's expanded energy requirements, and the acceptance of nuclear reactors as a safe and relatively clean source of power. Nuclear power capacity is expected to rise to 519 gigawatts electric (GWe) by 2030 from 370 GWe in 2006, according to the International Energy Agency (IEA) forecasts.

The USA as of 2010 had 104 operating nuclear power plants generating 100,683 MWe or about 101 GWe of electricity per year; accounting for about 19.66 percent of the USA's electrical energy use [2].

2. PEAK OIL, NO PEAK URANIUM

The world much touted nuclear renaissance raises concerns about future uranium supplies. The Chinese nuclear expansion program could strain the uranium supplies since its production is below its domestic needs. India's nuclear reactors are running below capacity for lack of domestic uranium supplies. The UK, USA, Middle East are planning new nuclear installed capacity.

The International Atomic Energy Agency, IAEA estimates the global annual consumption at 69,100 tons against a global production from mining of just 43,000 tons. The discrepancy is temporarily satisfied by supplies of Highly Enriched Uranium, HEU from about 12,000 dismantled nuclear devices. A supply crunch is expected by 2013, assuming no fuel recycling, no introduction of U²³⁸-Pu²³⁹ fast reactors and no introduction of the Th²³²-U²³³ fuel cycle.

A lack of uranium supplies situation could lead to a forced shutdown of existing plants in countries without sufficient secondary uranium (tailings re-enrichment, fuel reprocessing, dismantled warheads, civilian and military reserves and surplus stocks) and primary mining resources and enrichment capabilities, jeopardizing the hope of a nuclear renaissance and replacement of the depleting fossil supplies. "Uranium supply shortfalls could develop if production facilities are not implemented in a timely manner [3]." Consequently, any country envisaging future nuclear power plants is well advised to secure guaranteed domestic or external uranium fuel supplies for at least the 40 years project time in which it will invest a capital cost of about \$ 5-10 billion per 1,000 MWe of installed capacity.

Each GWe of installed nuclear capacity needs 500 tonnes of uranium for the first load, and 170 tonnes of natural uranium equivalent of the fissile isotopes U²³⁵ and Pu²³⁹ per year for the next years. The uranium demand is expected to increase from 65,000 tonnes in 2008 to 90,000 tonnes by 2015. Of the 31 countries operating nuclear power plants only three: Canada, South Africa and Russia are self sufficient in their uranium needs.

Secondary uranium resources have lately provided the fuel for about 1/3 of the world's nuclear power production. These secondary supplies are expected to become exhausted by 2013; a serious unsustainable situation.

The secondary resources include:

- a) Fissile U²³⁵ produced from the re-enrichment of previously depleted U tailings.
- b) Fuel produced from recycled reactor fuel and surplus military plutonium.
- c) Accumulated civilian and military stocks of natural uranium, weapons-grade U²³⁵ and Pu²³⁹.

Whereas one can speak about peak fossil fuels such as oil or natural gas, there is no peak for uranium. It is not a depletable energy source derived from decaying biological organisms deriving from stored solar energy, such as petroleum, coal and natural gas whose deposits are finite in size. Uranium is abundant in the Earth's crust and can be located everywhere in rock formations, in sediments as well as in sea water.

There exist 4.7 x 10⁶ metric tonnes (mt) of uranium ore reserves that are economically extractable globally. The International Atomic Energy Agency (IAEA) reports an 85 years supply of uranium at current rates of consumption and extractable at a cost of \$130/kg or less using current technology.

Another 35 x 10⁶ mt are classified as mineral resources or reasonable prospects for eventual economic extraction. These would come from unconventional sources such as phosphate rocks.

An additional 4.6 x 10⁹ mt of uranium are estimated to be in sea water and could be extracted using ion exchange methods.

At the time when the ore bodies with high uranium concentrations are depleted, the uranium's price is expected to increase. However, we shall not run out of it. The lower the concentration of uranium in the Earth's crust, the greater the quantity that exists that can be extracted. In mineral extraction, a concentration drop by a factor of 1/10 yields 300 times more of a given resource.

The sustainability criterion for uranium as a fuel is that the energy yield should exceed the energy used in its extraction:

$$\begin{aligned} E_{out} &> E_{extraction} \\ \frac{E_{out}}{E_{extraction}} &> 1 \end{aligned} \quad (1)$$

which constitutes an energy breakeven condition.

As the price of easily extractable uranium increases, fast neutron spectrum breeder reactors would become economical, using just 1/60th of the uranium current reactors use for the same amount of electrical energy produced.

Thermal neutron spectrum breeding using the even more abundant thorium can also be used. The IAEA suggests that the supply can be extended to 2,500 years if fast breeders technology is adopted. This smoothly paves the way to a timely introduction of fusion energy or other potential forms of energy sources for future generations.

3. URANIUM FUEL BURNUP AND CONSUMPTION

The fission process releases about 200 MeV per fission event of which 10 MeV, or 5 percent, are in the form of antineutrinos whose energy is not extractable.

For a reactor generating a thermal power of P MWth, the fission rate of an extractable fission energy yield of 190 [MeV/fission], is given by:

$$\begin{aligned} \frac{d(\text{fissions})}{dt} &= P [\text{MW}_{\text{th}} \frac{10^6 \text{W}_{\text{th}}}{\text{MW}_{\text{th}}} \frac{1 \text{Joule}}{\text{W}_{\text{th}} \cdot \text{sec}} \frac{\text{MeV}}{1.6 \times 10^{-13} \text{Joule}} \frac{\text{fissions}}{190 \text{ MeV}} \frac{24.60.60 \text{sec}}{\text{day}}] \\ &= 2.7 \times 10^{21} P \left[\frac{\text{fissions}}{\text{day}} \right] \end{aligned}$$

This fission rate can be expressed in terms of Avogadro's law as:

$$\begin{aligned} \frac{d(\text{fissions})}{dt} &= \frac{g[\text{grams/day}]}{M} A_v \\ \text{where: } M &= 235 \text{amu}, A_v = \text{Avogadro's number} \end{aligned}$$

The fuel burnup rate is "g" and is given by:

$$\begin{aligned} g &= \frac{M}{A_v} \frac{d(\text{fissions})}{dt} \\ &= 2.84 \times 10^{21} \frac{235}{0.6021 \times 10^{24}} P \left[\frac{\text{fissions}}{\text{day}} \right] \\ &= 1.11 P \left[\frac{\text{gm}}{\text{day}} \right] \end{aligned} \quad (2)$$

One MWth of power burns up 1.11 gm of U²³⁵ per day. If a reactor operates at 3,000 MWth, its fuel burnup is 3,015 grams or 3.330 kgs of fissile U²³⁵ per day.

Not all the fissile nuclei undergo fission to produce power. A fraction of them undergo a radiative capture process, in which a neutron is absorbed with the emission of a gamma photon, without fissioning. Thus we can define the fuel consumption rate as a function of its microscopic radiative capture cross section σ_c and its microscopic fission cross section σ_f as:

$$\begin{aligned} \text{consumption rate} &= \frac{\sigma_c + \sigma_f}{\sigma_f} \text{burnup rate} \\ &= 1.11 \left(1 + \frac{\sigma_c}{\sigma_f} \right) P \\ &= 1.11 (1 + \alpha) P \end{aligned} \quad (3)$$

The ratio of microscopic capture to fission cross sections is:

$$\alpha = \frac{\sigma_c}{\sigma_f} = \frac{99}{582} = 0.17, \text{ for thermal fissions in U}^{235}$$

Thus the fuel consumption rate is about 1.11 x (1+0.17) = 1.30 grams per MWth per day for U²³⁵.

To estimate the total fuel consumption in the USA reactors, the thermal power generation is related to the electrical power through the thermal efficiency of the plant as:

$$P_e [\text{MWe}] = \eta_{\text{th}} P_{\text{th}} [\text{MWth}] \quad (4)$$

At a thermal efficiency of 30 percent, the yearly consumption of fissile U²³⁵ in the USA with 104 operational reactors of 1,000 MWe capacity each is:

$$\begin{aligned} &104 [\text{reactors}] \times 1,000 \left[\frac{\text{MWe}}{\text{reactor}} \right] \times \frac{100}{30} \left[\frac{\text{MWth}}{\text{MWe}} \right] \times 1.30 \left[\frac{\text{gm U}^{235}}{\text{MWth} \cdot \text{day}} \right] \\ &\times \frac{1}{1,000} \left[\frac{\text{kg U}^{235}}{\text{gm U}^{235}} \right] \times 365 \left[\frac{\text{days}}{\text{year}} \right] \times \frac{1}{1,000} \left[\frac{\text{mt U}^{235}}{\text{kg U}^{235}} \right] \\ &= 164.49 \left[\frac{\text{mt U}^{235}}{\text{year}} \right] \end{aligned}$$

Considering that natural uranium contains 0.72 percent of the uranium isotope, the total yearly consumption of the natural uranium metal would amount to:

$$164.49 \left[\frac{\text{mt U}^{235}}{\text{year}} \right] \times \frac{100}{0.72} \left[\frac{\text{t U}}{\text{t U}^{235}} \right] = 22,845.8 \left[\frac{\text{mt U}}{\text{year}} \right]$$

Thus, just about 23 thousand metric tonnes (mt) of natural uranium metal, ignoring process losses, need to be extracted per year to supply the whole operational fleet of 104 operational USA nuclear power plants. The share of each reactor is 22,845.8 / 104 = 219.67 mt of natural uranium per year.

The high specific energy of uranium or energy produced per unit mass presents a unique advantage compared with other fuels in terms of mining, transportation and manufacturing safety as well as waste disposal.

4. URANIUM RESOURCES

About 30 percent of the known recoverable global uranium oxide resources are found in Australia, followed by Kazakhstan (17 percent), Canada (12 percent), South Africa (8 percent), Namibia (6 percent), and Russia, Brazil and the USA, each with about 4 percent of the world production.

The uranium resources are classified into "conventional" and "non-conventional" resources. The conventional resources are further categorized into "Reasonably Assured Resources," RAR and the believed-to-exist "Inferred Resources," IR [2].

The RAR and IR categories are further subdivided according to the assumed exploitation cost in USA dollars. These cost categories are given as < 40 \$/kg, < 80 \$/kg, and < 130 \$/kg.

The non-conventional resources are split into "Undiscovered Resources," UR, further separated into "Undiscovered Prognosticated Resources," UPR with assumed cost ranges of < 80 \$/kg and < 130 \$/kg, and "Undiscovered Speculative Resources" USR.

The USR numbers are given for an estimated exploitation cost of < 130 \$/kg and also for a category with an unknown cost.

In the twentieth century, the USA was the world leading uranium producer until it was surpassed by Canada and Australia. In 2007, Canada accounted for 23 percent and Australia for 21 percent of global production, with the USA at 4 percent. Africa is becoming a new frontier in uranium production with Namibia 7 percent, Niger 8 percent, and South Africa 1 percent. Exploration and new mine development is ongoing in Botswana, Tanzania and Nigeria.

The federal, provincial and local governments in Australia have all unilaterally and forcefully banned the development of any new uranium mines, even though existing mines continue operation. The French company Areva was not successful in receiving approval to build a new

uranium mine in Australia. It has mining activities in the Niger Republic and received exploration licenses in other countries such as Jordan.

Canadian producer Cameco rates as the first world producer of uranium oxide, followed by French Areva, and then Energy Resources of Australia (68 percent owned by Rio Tinto, which produces some 6,000 tons per year.

As of 2007, five operating uranium mines existed in the USA, with 3 in Texas, one in Wyoming and one in Northern Nebraska as shown in Table 1. The state of Texas has a positive attitude towards uranium mining, and energy production in general, with an advantageous

regulatory framework that streamlines the permit process using in situ leaching of uranium. Texas, being an "Agreement State," means that the USA Nuclear Regulatory Commission (NRC) has delegated its authority to the state regulatory agencies such as the Texas Commission on Environmental Quality (TCEQ), and companies deal directly with the state agencies in Texas rather than with the federal government's NRC. Most of the uranium mining operations in the USA and Kazakhstan use in situ leach methods, also designated as In Situ Recovery (ISR) methods.

Table I
Uranium concentrates production in the USA, 2007

Mine	Location	Company	Production 2005 [10 ⁶ lb U ₃ O ₈]	Production 2006 [10 ⁶ lb U ₃ O ₈]
Smith Ranch/Highland	Wyoming	Power Resources, Cameco	1.3	2.0
Crow Butte	Nebraska	Crow Butte Resources, Cameco	0.8	0.7
Vasquez	South Texas	Uranium Resources	0.3	0.2
Kingsville Dome	South Texas	Uranium Resources	-	0.1
Alta Mesa	South Texas	Alta Mesa	0.3	1.0
Total USA production			2.7	4.0

Uranium in the Colorado Plateau in the USA has an average grade of 0.25 percent or 2,500 ppm uranium in addition to 1.7 percent vanadium within the Uravan Mineral Belt. Goliad County, Texas has an average grade of 0.076 percent (760 ppm) uranium oxide in sandstone deposits permeated by groundwater suggesting in situ leaching methods where water treated with carbon dioxide is injected into the deposit. The leachate is pumped and passed over ion exchange resins to extract the dissolved uranium.

Phosphate rocks containing just 120 ppm in U have been used as a source of uranium in the USA. The fertilizer industry produces large quantities of wet process phosphoric acid solution containing 0.1-0.2 gram/liter (g/l) of uranium, which represent a significant potential source of uranium.

A two cycle process can be used for the recovery of uranium from these phosphoric acid solutions by extraction with di(2-ethyl-hexyl)-phosphoric-acid (Depa) plus tri-octyl-phosphine-oxide (Topo) in an aliphatic diluent. Later studies simplified the solution chemistry of the process by replacing the first extraction cycle with the commercial solvent mixture, mono- and di-octyl-phenyl-phosphoric-acid or octyl-phenyl-acid-phosphate (Opap).

5. TETHYS SEA

The Tethys (Pronounced as: Tee this) Sea, an ancestor of the present day Mediterranean Sea, was a primeval shallow body of water that separated the landmass of the ancient mega continent of Laurasia in the north, from its counterpart Gondwanaland in the south along the north continental shelves of the Arabo-African Craton. It existed during the early Mesozoic Era separating Europe from Asia and Africa, at a period extending from 540-245 to 66.4

million years ago when the Mediterranean Sea and its margins was the site of this large Tethys Sea. This sea extended across the Middle East and North Africa and had a strong westerly current that flowed through an area from Turkey to Morocco.

In Greek mythology, Gaea was the goddess of the Earth, descended directly from Chaos. Uranus, god of the sea, was Gaea's son by her own father. Gaea bore to her own son Uranus many offspring including the twelve Titans, the three Cyclopes, who ruled thunder and lightning, and the three Centimani; each possessing 100 hands. Gaea and Uranus also had a daughter, Tethys, who married her own brother Oceanus, who was one of the Titans.

The Greek poet Homer portrayed Oceanus as a great river surrounding the ancient world, and Hesiod related that from Oceanus and Tethys sprang all the rivers. When the Austrian Geologist Eduard Suess in 1893 extended Neumayr's concept of a Mediterranean sea extending from Mexico via the Alps to the Himalayas, separating a northern continent, Angaraland, from a southern continent Gondwanaland, he recalled the Greek myth and called this equatorial seaway Tethys, daughter of Gaea.

Tethys was considered as mother of the chief rivers of the ancient universe, such as the Nile, the Alpheus, the Maeander, and about three thousand daughters called the Oceanids or sea nymphs. Tethys, along with her husband Oceanus, ruled the seas before Poseidon. During the war against the Titans, Tethys raised Rhea as her god child. Tethys is sometimes confused with Thetis, the wife of Peleus and mother of Achilles. Hera was not pleased with the placement of Callisto and Arcas in the sky, as the constellations Ursa Major and Ursa Minor, so she asked her nurse, Tethys, to help. Tethys, a marine goddess, cursed the constellations to forever circle the sky

and never drop below the horizon, hence explaining why they are circumpolar.



Figure 1. Mosaic showing Poseidon, Okeanus and Tethys, a titaness goddess of the sea. Poseidon drives a chariot drawn by two Hippokampoi or fish tailed horses across the sea. Poseidon wields a trident in his hand and beneath him are the old sea gods: Okeanus and Tethys sitting wrapped in the tail of a sea serpent. Source: Gaziantep Museum, Turkey.

If the Tethys Sea had survived to the present day where Africa and Eurasia converge there would be no need for the Suez Canal to connect the West to the East.

By 10 million years ago, the tectonic plate collisions sealed off the eastern Mediterranean, trapping small remnants of ocean floor in the Black and Caspian Seas. Mountain barriers in the Balkans sealed off a large inland sea, which became brackish as salt water was flushed out by river water.

About 6 million years ago, Spain and Africa collided, raising a mountain barrier and sealing off the western end of the Mediterranean. River inflow was not enough to maintain the level of the Mediterranean, which dried out. Since the rivers flowing to the Mediterranean can cut below the Atlantic sea level, the Atlantic sea water eventually started flowing in, cutting the Strait of Gibraltar and filling out the previously dried Mediterranean.

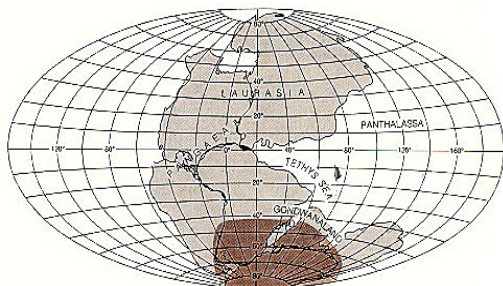


Figure 2. The ancient landmass Pangaea or 'All lands,' 200 million years ago. Panthalassa or 'All seas' evolved into the Pacific Ocean, and the present Mediterranean Sea is a remnant of the Tethys. A single continental glacier flowed over the south polar regions of Gondwanaland in the Permian time, before the breakup of the continents [4].

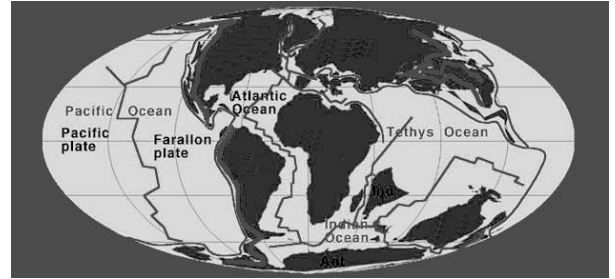


Figure 3. The Tethys Ocean, 80 million years ago [4].

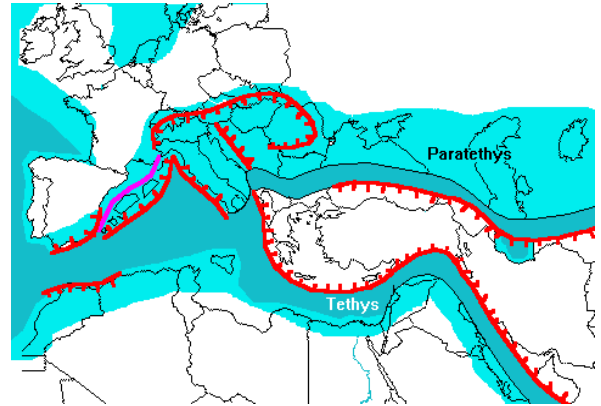


Figure 4. The Tethys Sea location 20 million years ago compared with the present day Mediterranean coast lines [4].

The Arabian tectonic plate broke away from Africa, with the tilting of the Arabian Plate causing petroleum to migrate up the tilted layers in the Gulf region and the deformation creating oil traps.

At the Tethys Sea, the remains of decayed organisms, mainly plankton, plants, and animals in this sea, formed the existing sedimentary series containing shales, dolomites and limestones. Through a process of diagenesis the Tethys Sea organic mix content turned into a phosphate rock deposits province that is the largest in the world.

A number of exploitable wide scale phosphate deposits are located along this belt, including the deposits in Iraq, Syria, Jordan, Saudi Arabia, Egypt, Israel, Tunisia, Algeria, and Morocco. The phosphorites were deposited in the southern edges of the Tethys Sea. Some deposits may still have remained unidentified.

The Tethys Sea phosphate deposits belong to the Late Cretaceous Early Eocene at 90-45 million years before present (bp). To this belt also belong the Colombian and the Venezuelan phosphate deposits in South America which formed in the same paleogeographic system.

The paleo latitude of this entire area lied within 8-15 degrees North, together with the creation of a circumglobal East to West equatorial oceanic circulation, and a northward Ekman offshore transport of surface waters arising from the easterly winds. This resulted in upwelling of nutrient rich waters onto the southern Tethys shelves. The high productivity regime which was established in this area at different Cretaceous Eocene time intervals led to the deposition of an organic and phosphorous rich sequence formed by carbonates, phosphorites and biosiliceous sediments.

Components other than phosphorous control the marketability of the phosphorites. A higher $\text{CaO/P}_2\text{O}_5$ ratio causes higher sulfuric acid consumption during phosphoric acid production, high levels of

Mg cause binding of the filters, silica as SiO_2 causes filtration problems, Na and K results in equipment scaling, organic matter causes foaming during phosphoric acid manufacture, Cl causes excessive corrosion, and high levels of toxic elements such as Cd, Se and As would make the phosphorite unsuitable for fertilizer production.

6. WADI AL HITAN, VALLEY OF THE WHALES, FAYOUM, EGYPT

The Fayoum province in Egypt area contains some of the best preserved paleontological sites in the world one of which is the Valley of the Whales, or in Arabic, Wadi Al Hitan. It is a remote valley in the Egyptian Western Desert about 150 kilometers southwest of Cairo. The valley is located near the Al Katrani mountain range, a well known and valuable geological site for its rare vertebrate fossils and mega fossils.

Evidence indicates that the basin of Wadi Al Hitan was submerged in water some 40 to 50 million years ago and was part of the Tethys Sea. The Tethys Sea has retreated north and over the years deposited thick sediments of sandstone and limestone visible in rock formations in Wadi Al Hitan. The Valley of the Whales, also known as the Zeuglodon Valley, lies within the boundaries of the Wadi Al Rayan Protected Area (WRPA), about eighty kilometers from Fayoum City. It was created in 1989, and lies in the vicinity of a series of natural hot springs and two lakes created in the 1970s from excess drainage agricultural water channeled from the nearby Lake Qarun.



Figure 5. Valley of the Whales, Wadi Al Hitan or the Zeuglodon Valley, Fayoum, Egypt, as part of the ancient Tethys Sea [5]

As the ancient Tethys Sea receded between 250 and 35 million years ago, over 400 skeletons of ancient water life dating over 40 million years have been identified in what used to be an ancient shoreline. The number of identified species grows as research is carried out in this area which was designated in 2005 as a World Heritage Site by the UNESCO.

7. DEPLETION OF COLD WAR URANIUM²³⁵ STOCKPILES

The “Megatons for Megawatts” program was planned to reduce the Highly Enriched Uranium (HEU) at above 90 percent weight enrichment in the U^{235} isotope in thousands of nuclear warheads into Low Enriched Uranium (LEU) useful to power plants at the 3-5

percent in U^{235} enrichment level. The program was sponsored by the USA and Russia and started in 1994 and is expected to end in 2013. It called for Russia to convert 500 metric tonnes of uranium from nuclear warheads to low enriched uranium for use at commercial nuclear power plants in the USA. As of the end of 2008, 352 metric tonnes of HEU, the equivalent of 14, 900 warheads were processed into 10,213 metric tonnes of LEU.

In an agreement in September 2000 between the USA and Russia, both countries agreed to convert 34 tonnes each into Mixed Oxide (MOX) fuel at the rate of at least 2 tonnes per year. During the lifetime of the agreement this adds 600 tons of natural uranium to the secondary supply.

It has turned 250 metric tonnes of HEU from about 10,000 nuclear warheads into LEU usable for energy generation. These massive supplies of uranium that were built up during 50 years of the Cold War arms race are starting to run low. By the year 2013 the agreement will terminate and Russia and the USA will quit supplying LEU to nuclear power plants in the USA. These will then be in need for new supplies of LEU.

As a result of this program, uranium mining dropped in popularity. Each ton of converted uranium removed 2,000 tons of yellow cake demand. Hundreds of tons were converted in addition to uranium drawn down from old military stockpiles, and dumping back into the market yellow cake mined decades earlier, taking out the breath out of 40 percent of what was left of the uranium market.

8. INELASTIC URANIUM DEMAND

Uranium demand is highly inelastic. High uranium demand is poorly correlated to its price and high uranium prices have little impact on the finances of nuclear electrical utilities. Uranium demand inelasticity results from the large amounts of energy per unit mass it can potentially produce, making the fuel cost a minor part of the cost of electricity compared with the capital cost and the operation and maintenance cost. A nuclear power plant cost, like a hydroelectric power plant, is dominated by the capital cost, and not the fuel cost. In fact the fuel cost constitutes just 7.08 percent of the nuclear power generation cost at \$85/lb of uranium.

With an energy cost of nuclear electricity at \$60/MWe.hr, the fuel cost is just: $\$60 \times 0.0708 = \$4.248/\text{MWe.hr}$. Uranium can reach \$200/lb adding an extra cost of \$2.05/MWe.hr to the fuel cost without much concern to the utilities which can charge their customers an extra $\$2.05 / \$60 = 3.42$ percent to their utility rates. Even \$1,000 per pound of yellowcake would impact a delivered kilowatt-hour no more than if natural gas rose from the current \$7 per 1,000 cubic feet to \$12 per 1,000 cubic feet.

The uranium fuel cost in nuclear electrical power generation being a minor component, a 50 percent increase in the fuel cost would affect the cost of electricity to the tune of 3 percent. This would lead to a more significant increase in coal of 21 percent, and in natural gas of 38 percent.

In fact it can be proven that a large percentage increase in the cost of an input when the input is a small part of the overall cost, does not affect the fact that it is still a small contribution to the overall cost. As an example, in the passive smoking context, a large percentage increase in a miniscule risk still leaves the risk in the miniscule category.

The 104 nuclear power plants in the USA are using about 55 million lbs of U_3O_8 per year.

9. URANIUM SUPPLY AND DEMAND

The USA consumes 25 percent of the world's oil and natural gas and 33 percent of the world's uranium supply. It accounts for only 4 percent of the global uranium production. Just 25 years ago, the USA produced four times more uranium than it used.

By the end of 2008, there were 4 uranium mills located in the USA with a total capacity of 6,150 short tons of ore per day. Only

one mill was operating, with a capacity of 2,000 short tons of ore per day. There were 9 uranium in-situ leaching operations using ion exchange media with a total capacity of 12 million pounds of U₃O₈ per year. Four in-situ leaching plants were operating, with a combined capacity of 8.5 million pounds of U₃O₈ per year.

Table II
World Uranium production and resources.

Country	Production 10 ⁶ lbs U ₃ O ₈ 2006	Percentage 2006	Percentage* 2008	Resource [mt]	Resource [percent]
Canada	26	26	21	423,000	8
Australia	20	19	19	1,243,000	23
Commonwealth of Independent States (CIS)/China	18	18	-	546,000	10
Russia	-	-	8		
South Africa	18	17	-	435,000	8
Niger	-	-	7		
Namibia	-	-	10		
Kazakhstan	14	13	19	817,000	15
Uzbekistan	-	-	5		
USA	4	4	4	342	6
Other	3	3	7		
Total	103	100	100		

* Source: Cameco.

France, with a population of 50 million, generates 76.18 percent of its electricity from nuclear power and produces no uranium. It uses up 15 percent of the world's uranium supply.

Japan, Germany, South Korea, and the UK jointly consume 24 percent of the uranium supply and combine to produce 0.196 percent of the world's annual uranium production. Western countries consume 72 percent of the world's uranium but contribute about 4 percent of the global supply.

With oil prices on the rise with reserves depletion and global warming becoming the latest ecological concern, nuclear energy is enjoying a comeback as a green form of energy. It is presently the world's third largest source of electricity following coal and hydroelectric power.

Table III
World Electricity Generation. Source: World Nuclear Association.

Electricity Source	Percentage
Coal	40
Hydroelectric	19
Nuclear	16
Natural Gas	15
Oil	10
Total	100

There are 400 uranium exploration and production companies. However, the largest uranium resources in the world have barely been tapped. Australia, which sits atop 24 percent of the world's known uranium reserves, limited the number of uranium mines to three in 1982 and this constraint is still in effect. Demand for uranium is outstripping its supply. In 2005, the latest year for which complete data are available, 68,000 tons of raw uranium ore were consumed but only 39,000 tons were produced. That is a substantial 43 percent gap between supply and demand.

As of 2007, the world does not have enough enriched uranium to supply the 435 nuclear reactors used to generate 17 percent of the world's electricity, let alone enough to supply the 28 reactors under construction. By 2013, 48 new plants will be completed. More than 200 new reactors are either planned or under construction worldwide. China plans 100 new or proposed plants, Russia 58 and the USA 28 new applications exist by 2009. Each 1,000 MWe plant requires 600 metric tonnes (mt) of U₃O₈ at startup then needs 200 mt/year thereafter.

The projected production from mining sources and the corresponding demand in the uranium supplies shown in Table IV show a shortfall that, if materialized, would make the extraction of uranium from phosphate rocks sources necessary to bridge the gap.

10. ORIGIN OF PHOSPHORITE DEPOSITS

The world phosphorite deposits were formed on the continental shelves of ancient shallow marine environments. The deposition process is thought to have involved the mixing of upwelling deep cold seawater rich in the apatite mineral and warm ocean currents or

warm shallow shelf waters. They contain syn-sedimentary stratiform disseminated uranium in fine-grained apatite.

Table IV

Projected uranium production and demand in million pounds of yellow cake. Source: Clifton Farrell, Nuclear Energy Institute.

	USA [10 ⁶ lbs U ₃ O ₈]	World [10 ⁶ lbs U ₃ O ₈]
Demand		
2006	57	180
2025	75	(230-300)
Production		
2006	4	110
2025	(10-20)	(170-200)
Shortfall		
2006	-53	-70
2025	-(55-65)	-(30-130)

Apatite is three different minerals depending on the predominance of either fluorine, chlorine or the hydroxyl group. These ions can freely substitute in the crystal lattice and all three are usually present in every specimen although some specimens have been close to 100 percent in one or the other. The names of these minerals are Fluorapatite, Chlorapatite and Hydroxylapatite. The three are usually considered together due to the difficulty in distinguishing them in hand samples using ordinary methods.

Apatite is the mineral that makes up the teeth in all vertebrate animals as well as their bones. The name apatite comes from a Greek word meaning "to deceive" in reference to its similarity to other more valuable minerals such as olivine, peridot and beryl. Apatite is widely distributed in all rock types; igneous, sedimentary and metamorphic, in the form of small disseminated grains or cryptocrystalline fragments. Large well formed crystals though can be found in certain contact metamorphic rocks.

Since cold water can dissolve more CO₂ and apatite than warm water, PO₄ averages 0.3 ppm in cold water compared with only 0.003-0.010 ppm in warm shallow water. As the deep apatite saturated water is warmed up, CO₂ is degassed and the pH value rises. Apatite is less soluble in alkaline water, so calcium phosphate precipitates from the supersaturated waters.

If the upwelling process is sustained for a long time, the phosphorite deposit may become thick. They range from Precambrian to recent in age and appear to have formed at various times and places within 40 degrees of latitude north or south of the paleoequator.

11. DEPOSITS TYPES

Phosphorite deposits are low grade but large uranium resources which can be recovered as a byproduct of phosphate production.

Examples include New Wales Florida pebble phosphate and Uncle Sam in the USA, Gantour in Morocco and Al Abiad in Jordan.

Organic phosphate deposits, including argillaceous marine sediments enriched in fish remains that are uraniferous include the Melovoe deposit in Kazakhstan).

Apatite is the main mineral that is a source of phosphorous. It is Calcium (Fluoro, Chloro, Hydroxyl) Phosphate: Ca₅(PO₄)₃(F, Cl, OH).

There exist several types of phosphorite deposits [2]:

1: Bedded phosphorite deposits

These were deposited in distal continental shelf environments where upwelling phosphate enriched seawater provided a renewable source of phosphorus and where upwelling uranium enriched water flooded the phosphorite accumulations. These environments had very slow rates of deposition. An example is the Phosphoria Formation in Idaho, USA.

The bedded phosphorite deposits are composed of bedded fluor-carbonate apatite, which occurs as oolites, pisolites, pellets and laminae and as phosphatic fossil fragments mixed with clay-rich and carbonaceous fine-grained detritus. They typically grade into black shales in a basinward direction and into chert beds in a landward direction and are over and underlain by pyritic chert, mudstone and black shale.

The average grades in bedded Phosphorite deposits are 50- 300 ppm, with layers locally enriched to 600 ppm.

2: Nodular phosphorite deposits

These were deposited nearer to the shores shore in shallower water than the bedded ones. They consist of reworked phosphatic pebbly sandstones with nodules and sand sized fluor-carbonate apatite mixed with clay minerals and marine sands.

Exposure of the apatite particles to uranium bearing seawater during marine transgressions leads to a variation of nodular phosphorite deposits referred to as land pebble phosphorite.

They are interbedded with marine sands and shallow water carbonates and evaporites. An example is the Land Pebble district in Florida, USA in the Pliocene Bone Valley Formation containing fluor-carbonate apatite nodules and grains that are enriched up to 30 percent P₂O₅ and 500 ppm uranium. Weathering has produced a unit in the Bone Valley Formation in which the apatite is further enriched locally to several thousand ppm of uranium.

The nodular phosphorite deposits typically average 10-20 percent P₂O₅ and 20-80 ppm uranium.

3: Continental phosphorite deposits

In these deposits, uranium occurs within fluorapatites in the basal formations and is concentrated in secondary minerals such as autunite and torbernite in the surficial formations.

The only known continental phosphorite deposit is at Bakouma in the Central African Republic with resources of 17,000 t U at an average grade of 0.24 percent. The mineralization at Bakouma occurs in 10 lenses of various sizes of 500-6400 t U, and different grades of 0.18-0.32 percent.

12. PHOSPHORITES OCCURRENCE

The marine phosphorite deposits have a broad regional extent. The bedded phosphorite deposits of the Phosphoria Formation extend over an area of several thousand square kilometers. The Mead Peak Phosphatic Shale Member, its main member, varies in thickness from 60-50 m and averages 11-12 percent P₂O₅. The upper and lower 1-3 m average 25-35 percent P. The uranium content is also higher.

The land pebble lower Bone Valley Formation in Florida covers an area of about 2,500 square kilometers. The mineralized beds are 5-7 meters in thickness. The total resources of this district are about

420,000 t U. The average grade of the land pebble mineralization is 150 ppm U.

13. ENRICHMENT IN URANIUM

The uranium enrichment in marine phosphorite deposits is thought to have occurred through the extraction of uranium from seawater and syngenetic incorporation into cryptocrystalline fluorcarbonate apatite. The slow rate of deposition that characterizes bedded phosphates permitted longer exposure of the apatite grains, which in turn allowed uranium from seawater to replace Ca in the apatite.

Bedded phosphorite deposits are characterized by the absence of carbonate beds. The low concentration of CO₂ +2 ions that must have characterized the marine waters in phosphorite depositional environments allowed uranium to remain in solution and to interact with the apatite.

As an example, the phosphorite deposits in Morocco range from the Upper Cretaceous to the Eocene in age. The Eocene age Khouribga deposit is 5 m thick and contains up to 36 percent P₂O₅ with uranium values of 150 ppm U and local enrichment in some layers to 500–600 ppm. The phosphate consists of 0.1-0.2 mm diameter grains of F-collophanite enclosed in a clayey and calcareous matrix that is locally impregnated with opal.

The phosphate grains often have quartz or zircon grains at their centers, which served as the nucleus of phosphate precipitation.

Zircon, is zirconium silicate occurs often with some hafnium, uranium, thorium and yttrium, (Zr, Hf, U, Th, Y)SiO₄, is the mineral for the production of zirconium used in the cladding of fuel elements in nuclear reactors. Zirconium or zargun is named from the Persian, “zar” for gold and “gun” for like, meaning “like gold.” The zircon ore contain trace amounts of uranium and can be detected by its radioactivity.

14. URANIUM IN PHOSPHATE ROCKS

The average uranium content in phosphate rock worldwide is about 50-200 ppm. Marine phosphorite deposits contain 6-120 ppm, and organic phosphorite deposits up to 600 ppm.

Table V
Estimated world uranium resources in phosphate rock.

Source	Country	Uranium resource in phosphate rock 10 ⁶ t U
Marine phosphorite		
	Morocco	6.9
	USA	1.2
	Mexico	0.15
	Jordan	0.1
	Others	0.65
Organic phosphorite		
	Kazakhstan, Russia	0.12
Total		9.12

Phosphate rocks used for fertilizer contain trace amounts uranium and thorium. The specific activity in the ores can reach 0.9-1.8 Bq/g. The phosphogypsum waste stream yields about an activity of 1 Bq/g, and up to 3 Bq/g in the superphosphate product. The phosphogypsum contains significant quantities of the daughter nuclides in the uranium²³⁸ decay chain including the Ra²²⁶, Pb²¹⁰ and Po²¹⁰ isotopes. In the USA, 50 x 10⁶ t/year of phosphate rock were produced at some time, and state figures averaged up to 10 Bq/g of total activity.

Processing gives rise to measurable radiation doses to the handlers necessitating occupational health physics protection measures.

Phosphate rocks containing up to 120 ppm U have been used as a source of uranium fuel. If uranium is produced as a byproduct, the presence of Cd must be avoided as a contaminant since it is a strong neutron absorber and would make the uranium unsuitable for use as nuclear fuel.

The recovery of uranium and phosphorous from phosphorous uraniferous ore bodies is based on a combination of physical and chemical processes. These include the use of flotation to concentrate the phosphate bearing uranium ore, followed by the chemical dissolution of the concentrate by the wet phosphoric acid process for the solvent extraction of uranium and the purification of the phosphoric acid P₂O₅. The major part of the heavy metals such as Cd, U, Ni, Pb, Zn, Cr, and Cu are first solubilized using sulfuric acid, producing a 28-32 percent concentrate of P₂O₅. Special attention must be devoted to Cd as a toxic element, as well as uranium which raises environmental concerns [3].

Phosphoric acid is an important intermediate in the fertilizer industry, the manufacture of detergents, water treatment chemicals, bread leavening agents, and animal feed supplements.

15. WORLD RESOURCES

Worldwide phosphate deposits potentially total 22 million t U, but proven resource estimates are 7-7.2 million t U.

Phosphate related resources in Morocco alone total 6.53 million t U or 93 percent of the worldwide total. Other countries with significant phosphate related resources include Brazil, Egypt, Jordan, Saudi Arabia, Mexico, Israel, Syria and the USA.

About 690 t U were recovered from processing Moroccan phosphate rock in Belgium; at least 18,200 t U were recovered in the USA. Around 1980 there were 8 plants recovering uranium from phosphoric acid manufacturing in the USA and 6 000 t U were recovered from processing marine organic deposits as fish bones in Kazakhstan.

A small amount of uranium was also recovered in Canada from processing USA phosphate rock.

Recovery of uranium from marine phosphorite deposits uses well established technology, which has been used in Belgium and the USA as recently as 1999, respectively. The uranium produced as a by-product of phosphoric acid production in Belgium from processed phosphate rock imported from Morocco, was controlled by Prayon-Rupel Technologies, S.A. The Uncle Sam uranium production facility, the last operating plant in the USA, had a production capacity of about 300 t U per year, is owned by IMC-Agrico Company.

16. PHOSPHATE DEPOSITS IN SAUDI ARABIA AND JORDAN

North West Saudi Arabia and Jordan, as part of the ancient Tethys Sea is host to the largest undeveloped phosphate rocks deposits with their uranium content in the world. Limestones, cherts and phosphate rocks, known as the Turayf Group were geologically formed in flat lying surfaces over large expanses. Earth movements that were associated with the formation of the Red Sea have preserved the phosphate bearing beds in a series of grabens or down faulted basins.

According to Khalid Toukan, Jordan has an estimated 1.2 billion tonnes or 1.3 billion tons of phosphate reserves. This is in addition to other higher concentration uranium ore reserves. Director of the Natural resources Authority (NRA) Maher Hijazin reported that the estimated uranium reserves in the kingdom are 80,000 tons in four desert regions and the reserve quantities of natural phosphate are estimated at 140,000 tons, considered as commercial quantities. The economically exploitable ores appear to be 1/10 of the estimated reserves.

The phosphorite deposits in Jordan exist at Al Abiad, Al Hassa, Eshidia, Ruseita and Siwaqa; all dormant except for the latter with a resource base of 25,000-50,000 t U [2].

It is estimated that Jordan's phosphate reserves contain 100,000 tonnes of uranium, and other uranic ores contain 80,000 tonnes. This would account for about 2 percent of the world's uranium reserves.

In Saudi Arabia, the Turayf Group is composed of three formations: Urn Wu'al, Mira and Al Jalameed. Figure 6 shows an open trench at the Al Jalameed deposit with a 9.5 m thick overburden of dolomitic limestone in North West Saudi Arabia. The top of the Thaniyat phosphorite member contains calcareous compact to semi friable phosphorite with a 25 percent P₂O₅ concentration.



Figure 6. Al Jalameed phosphorite deposit [4].

The Turayf Group possesses a phosphate horizon at its base that ranges from 2-40 meters in thickness. These deposits were first discovered in 1965 from the bore holes drilled alongside the Trans Arabian pipeline. Other deposits include the Thaniyat Turayf and As Sanam. These deposits are extensive with a substantial potential for commercial development.

The Saudi Arabian phosphates are expected to replace the declining Florida, USA, production which has been decreasing. Development is planned by the Maaden, or Minerals in Arabic, mining company. A railroad coupling to the industrial Gulf port of Al Jubail is planned. The availability of ammonia, sulfur and energy there would facilitate value addition through the manufacture of fertilizers rather than the export of the mineral ores.

At Al Jalameed, 213 x 10⁶ metric tonnes of reserves underlying a mining area of 18 km² have been identified with good beneficiation characteristics. The phosphorite is 17 meters thick depending on the palaeo topography with an average thickness of 6.5 meters.

The upper phosphate horizon with a stripping ratio of 2:1 is of commercial interest in contrast to the middle and lower members with stripping ratios larger than 5:1. Initially, the phosphate content was about 10 percent. Through weathering and de-dolomitization and calcite leaching it has been upgraded to 15-32 percent with an average of 21 percent. The phosphorite has a mining cut off of 15 percent P₂O₅.

If we assume a uranium oxide U₃O₈ content of 200 ppm, the uranium oxide reserves at Al Jalameed amounts to:

$$213 \times 10^6 \times 200 \times 10^{-6} = 42,600 \text{ mt.}$$

The 3 million tons per year phosphate project cost is estimated at \$3.5-5.6 billion, with the mine costing \$400 million, and the 1,000 miles long railroad link \$1.2 billion to ship the ore from Northern Saudi Arabia to the port city of Al Jubail. Energy would be provided by a fuel oil fired turbine generators with an installed capacity of 28 MW. The underlying Tawil aquifer could provide a sustainable water flow of 13 x 10⁶ m³/year for process needs. Potable fresh water would be produced by a Reverse Osmosis (RO) plant. Completion is projected by 2012.

The deposits would use drilling and blasting with the overburden removed by drag lines and front loaders and loaded on 85 t trucks to a semi mobile crushing station. A fine grained slurry would be produced by the milling process. Flotation using a wax type reagent would be used to float the dolomite and calcite from the phosphorite producing 4.5x10⁶ t/year of concentrate averaging 32.5 percent P₂O₅ from 11.2 x 10⁶ t/year of mined ore.

Even though not extracted as a byproduct, the concentrate would contain a potential uranium oxide content of:

$$4.5 \times 10^6 \times 200 \times 10^{-6} = 900 \frac{\text{t}}{\text{year}}$$

The mine produced concentrates would be transported to the industrial port city of Al Jubail using a railroad link. There, a plant producing 10⁶ t/year of Di-Ammonium Phosphate (DAP) using imported phosphoric acid uses a sulfuric acid, ammonia and granulation plants to convert the concentrate to DAP. The 4.5 x 10⁶ t/year of concentrate would be converted into 2.9 x 10⁶ t/year of DAP.

17. SYRIAN PHOSPHATE

There are reports that Syria has conducted research to examine the feasibility of exploiting phosphate rock to recover uranium.

The country is rich in phosphate sediments deposits and produces around one fifth of the phosphate rock mined in the entire Middle East.

According to statistics, in 2001, Syria mined over 2.04 million tons of phosphate. A food-grade phosphoric acid micro-pilot plant is already operating at the city of Homs under IAEA safeguards provisions.

18. MOROCCAN PHOSPHATES

The Office Cherifien Des Phosphates (OCP), a Moroccan state owned agency formed in 1920, is solely responsible for the Benguérir, Khouribga and Youssoufia mines in central Morocco. The country's large measured phosphorite resources of 85,000 Mt are

hosted in upper cretaceous, palaeocene and Eocene sediments, and sequences comprising clays, marls, limestones and cherts contain several phosphate rich beds. Mineable phosphate rich beds range from one to three meters in thickness and grades from 22-28 percent in P₂O₅.

Morocco produces more than 23 million tons of ore per year. The OCP and the French Company Areva plan to launch a joint study into the feasibility of an industrial site producing uranium from phosphoric acid. OCP, which is the world's largest exporter of phosphate in all forms, sells 95 percent of its production on external markets. As an international player, it is achieving an annual turnover of \$1.3 billion.

Morocco is the largest phosphate exporter in the world, and ever since the world's fourth largest phosphate deposit was discovered at Bou Craa in the Western Sahara in 1963, Morocco has shown interest in it. When the colonizing power, Spain, withdrew from the territory in 1975, Morocco annexed the northern 2/3 of the Western Sahara, including the phosphate mines. In return for relinquishing its colony, Spain retained a 35 percent interest in the Bou Craa phosphate mine; Morocco's share was 65 percent. Morocco essentially relinquished the southern 1/3 of the territory to Mauritania, which has since renounced its claim after being targeted by the Polisario rebel group raids for years. The Western Saharans object to not being consulted on these actions leading to a lingering source of conflict.

To control the phosphate deposits there would give Morocco a near monopoly over the non-Communist world's phosphate reserves given the world demand for phosphate to make fertilizer.

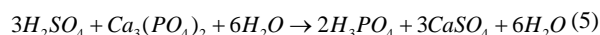
Uranium is more lucrative. Toshiba-Westinghouse and a few other companies, including International Mineral and Chemical, Freeport Mineral Corporation and Gardinier, Inc., have developed the technology for extracting uranium from the phosphoric acid in phosphates. This new industry has been centered in Florida, the site of 80 percent of the USA phosphate deposits, the other 20 percent are found largely in Idaho and North Carolina.

The uranium-from-phosphate extraction technology was first developed by the USA Atomic Energy Commission (AEC) in the 1950s. U₃O₈ is extracted from the phosphate and converted into UF₆, then enriched, and eventually manufactured by firms like Toshiba-Westinghouse and General Electric into the pellets for the fuel rods in nuclear power reactors. Toshiba-Westinghouse's uranium subsidiary, Wyoming Mineral, has joined IMC, Freeport and Gardinier in exploiting this technology in Florida's "Bone Valley," the region south of the cities of Orlando and Tampa.

19. WET PHOSPHORIC ACID PROCESS

In the wet phosphoric acid production process, the phosphate concentrate slurry is dissolved in a strong acid, usually sulfuric acid H₂SO₄, producing green phosphoric acid H₃PO₄, with the sulfur from the sulfuric acid combining with the calcium phosphate concentrate

to produce phosphogypsum or calcium sulfate as a waste product, which is separated by filters:

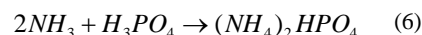


The calcium sulfate obtained depends on the process used and appears in different forms such as anhydrous: CaSO₄, hemihydrate: CaSO₄.1/2H₂O, or dihydrate: CaSO₄.2H₂O.

The dihydrate and hemihydrate-dihydrate processes result in phosphoric acid containing 27-29 percent P₂O₅. Concentration using evaporation leads to a commercial product with 52-54 percent P₂O₅.

20. DIAMMONIUM PHOSPHATE (DAP) FERTILIZER PRODUCTION

The phosphoric acid is treated with ammonia produced from natural gas to produce the diammonium phosphate or DAP final product.



The reaction produces a soft solid which is dried and granulated to a size around 3 mm, and is adjusted to reach the industry standard composition of 18-40-0 in N-P-K.

In addition to its use as a fertilizer, DAP is also used as a fire retardant, a yeast nutrient, and an additive in cigarettes manufacture.

21. URANIUM RECOVERY

Three main industrial processes have been developed for the extraction of uranium from phosphoric acid:

1. The di-octyl-pyro-phosphoric-acid, or Oppa process.
2. The di-(2-ethyl-hexyl-phosphoric)-acid tri-octyl-phosphine-oxide, or Depa-Topo process.
3. A mixture of mono-octyl-phenyl-phosphoric-acid and di-octyl-phenyl-phosphoric-acid, or Opap process.

The Depa-Topo process has been the favored one in industry. It possesses the following characteristics:

1. It is very selective towards uranium,
2. Its solubility in phosphoric acid is minimal,
3. The process is relatively chemically stable,
4. It extracts the U(VI) valency which is the naturally predominant valency in phosphoric acid compared with the other U(IV) valency. The oxidation process could be completed through the addition of oxidizing agents such as H₂O₄ prior to the extraction, resulting in no contamination of the phosphoric acid by the reducing agents.

Table VI
Main facilities where uranium was extracted from the wet phosphoric acid process [4].

	Plant Capacity [t U / year]	Process
Farmland, Pierce, Florida.	173	Depa-Topo
Freeport minerals, Uncle Sam,	265	Depa-Topo

Louisiana.		
Agrico, Donaldsonville, Louisiana.	162	Depa-Topo
IMC, New Wales, Florida.	289	Depa-Topo
CF industries, Bartow, Florida.	254	Depa-Topo
CF industries, Plant City, Florida.	231	Depa-Topo
WR Grace, Bartow, Florida.	127	Opap
Gardiner, East Tampa, Florida.	163	Opap
Western Corp, Calgary, Canada.	42	Opap
Prayon, Puurs, Engis, Belgium.	57	Depa-Topo
China phosphate, Taiwan.	10	Depa-Topo

The solvent extraction process includes elaborate pre and post treatment operations.

The pre-treatment of the acid is as important as the final extraction process. It involves:

1. Total elimination of the acid's solid phase,
2. Soluble and insoluble organic matter elimination,
3. Low temperature de-supersaturation over an extended time period.

The post-treatment involves a tripping operation to eliminate the traces of the extractant and diluent solvents remaining in the acid.

22. LIQUID MEMBRANE (LM) URANIUM EXTRACTION

The Liquid Membrane (LM) technology, even though not industrially developed, offers the potential to efficiently separate and concentrate uranium from process phosphoric acid and is thought to be superior to the solvent extraction systems.

The LM technique utilizes emulsion technology to extract, concentrate, and recover components of dilute solutions. Globules of oil and water emulsion are dispersed into a third phase containing the material to be recovered. The process involves the creation of an emulsion whose globules are then dispersed into the third external aqueous phase. Each globule contains many small internal droplets. The internal droplets of the emulsion are typically quite small in size of 1-10 microns (μm) in diameter. Transport of the metal ions occurs from the external aqueous solution across the oil membrane of the globule into the internal aqueous small droplets, extracting and concentrating it.

For the extraction of metals, the emulsion is usually oil external since the feed streams are frequently aqueous. Individual metal ions or complexes species are extracted through the "oil membrane" into the internal aqueous droplets of the emulsion for later disposal or recovery.

This concept can also be used for encapsulation and controlled release if desired. The liquid membranes are stabilized by surfactant molecules which line up at the interfaces between the membrane and the aqueous phases. A reagent could be encapsulated in the internal phase either for controlled release or for reacting with the permeates. The process is tailor made for specific applications using suitable surfactants and reagents.

The methodology is advocated as having a sufficient return on capital even under depressed uranium prices to allow extraction of uranium in phosphoric acid plants. Additional improvements in the process can be achieved such as the elimination of the filtration in the feed pretreatment and operation at a temperature of 70 degrees C,

reducing the extraction process to two stages. This improvement in the operating margin can make the liquid membrane process the lowest cost technology for the extraction of uranium from the Wet Process Phosphoric Acid (WPPA) process. When the demand of uranium is increased, new uranium extraction plants would be well advised to adopt the Liquid Membrane approach [4].

23. TRANSPORT MECHANISMS

Two facilitated transport mechanisms are involved in liquid membrane transport. The first is based on reaction with the internal phase, and the second is based on reaction both in the membrane and the internal phase.

Liquid membranes simultaneously extract at the external interface and strip at the internal interface. This process of simultaneous extraction and stripping results in fast separation and needs only a small amount of extracting agents in the membrane phase.

High degrees of separation can be achieved with liquid membranes. For instance, the concentration of chromate in waste water could be reduced in continuous runs from 100 to 1 ppm. A small amount of liquid emulsion is used and is recycled and reused continuously for 31 hours. At this time the internal phase would have a chromatic concentration of 182,000 ppm. The concentration ratio between the internal phase and external phase is in this case 182,000 : 1.

24. REACTION WITH INTERNAL PHASE

In this process liquid membranes can remove organic bases and compounds such as ammonia (NH_3) from their aqueous solutions. The compounds permeate from the external phase to the internal phase because of their appreciable solubility in the membrane phase. Once in the internal phase, the compounds interact with the encapsulated chemical reagents to form products that are not soluble in the membrane, and hence they are held inside.

For instance, ammonia in the un-ionized form is soluble in the oil membrane will permeate into the internal phase where it reacts with encapsulated sulfuric acid to form the ammonium ion, NH_4^+ which has no solubility in the membrane phase and is therefore held inside. H_2SO_4 at a high concentration can be encapsulated in the internal phase to build a high concentration of NH_3 in this phase.

Similarly, organic acids and compounds such as H_2S can be removed because of their solubility in the membrane phase. A base, such as NaOH , could be encapsulated in the internal phase to neutralize the acidic permeates and trap them inside.

This approach is unsuitable for uranium extraction.

25. REACTION WITH INTERNAL PHASE AND MEMBRANE

This is used to remove ionic species which are not themselves very soluble in the membrane phase. This is used to recover uranium ions from phosphoric solutions such as in the Wet Process Phosphoric Acid, WPPA.

In this case ionic compounds can first react with specially chosen reagents in the membrane phase to form a membrane soluble complex. Another reaction at the internal phase boundary decomplexes the product of the first reaction and deposits it in the internal phase.

For instance, a cation carrier in the membrane phase complexes with Cu ions and moves them across the membrane to the internal

side, where the complex is decomposed because of an ion exchange reaction with sulfuric acid. The complex will release the copper and carry hydrogen ions back to the external side where the hydrogen ions will be replaced by copper ions and the whole cycle of ion exchange reactions will start again. In the case of anions such as chromates, a specific anion carrier is needed in the membrane and a stripping reagent in the internal phase.

26. ADVANTAGES OF LIQUID MEMBRANES

Liquid membranes offer technical and economic advantages over biological treatment, ion exchange and solvent extraction in the separation field for metals recovery and waste water applications.

A comparison between the solvent Extraction and liquid membrane processes is shown in Table VII.

Table VII
Comparison of the Solvent Extraction and the Liquid Membrane processes.

	Solvent Extraction	Liquid Membrane
Feed pretreatment steps	Oxidation Solids removal Cooling Soluble organics Removal	Oxidation Solids removal
Extraction and stripping stages	Eight stages	Three stages, maximum Coalescer Emulsifier
DEHPA/TOPO secondary extraction		
Concentration	1	1/5
Crude make	1	1/4 - 1/5
Feed to organic ratio	1:1	18:1

27. SUPPORTED LIQUID MEMBRANE (SLM) PROCESS

As a variant of the Liquid Membrane process is the Supported Liquid Membrane (SLM) to separate of hexavalent uranium (VI) from the phosphoric acid medium.

In this approach, tri-*n*-octyl phosphine oxide (TOPO)/*n*-dodecane is used as a carrier and ammonium carbonate as a receiving phase for the separation of uranium (VI) from phosphoric acid.

Flat sheets type hydrophobic microporous membranes of poly-tetra-fluoro-ethylene (PTFE) are used in the process as a support. The porosity of the membranes is 84 percent.

There is very little transport from pure phosphoric acid of Uranium (VI). The process is sensitive to its controlling parameters such as feed acidity of the phosphoric acid, the carrier concentration, and the stripping agents used. The transport increases significantly if 2 M nitric acid is added to the feed phase. More than 90 percent uranium (VI) is recovered in 360 minutes using 0.5 M TOPO/*n*-dodecane as carrier and 1.89 M ammonium carbonate as stripping phase from a mixture of 0.001 M H₃PO₄ as a feed.

Lower concentrations of phosphoric acid with 2M HNO₃ and higher concentrations of the carrier are found to be the most optimal condition for the maximum transport of uranium (VI) from its low concentration source levels such as commercial phosphoric acid [2].

28. MINING COSTS AND REVENUE

In situ leaching is one of the most profitable methods of uranium mining. A mining facility producing approximately one million pounds of U₃O₈ per year would require a capital expenditure of \$8 million for 125 closely spaced injection wells, 100 producing wells and 60 monitoring sites.

The cost of the plant to process and dry the uranium into yellow cake would cost another \$10 million. The total cost would be about 8 + 10 = \$18 million bringing in an annual revenue at \$90 per lb of U₃O₈ of \$90 million, for an amortization time of 18 / 90 = 0.2 year.

29. TECHNICAL CONSIDERATIONS

The investment in a uranium recovery process from phosphoric acid can be justified as a part of a larger strategy for securing a dependable and independent fuel supply for a nuclear electricity or a desalination project.

The construction of nuclear power as well as desalination plants entails a long construction time and a large capital cost investment. However, once under operation, the electricity and fresh water costs would be about half that of a fossil fuel approach [4].

With the expected future increase in the price of fossil fuels, a country with phosphate resources could opt for the uranium recovery

approach to secure energy independence in an environmentally benign way.

A uranium recovery facility requires about 2 years for setup and should be planned concurrently with any power reactor project which requires a setup time of no less than 6-10 years.

30. DISCUSSION

The conventional world-wide uranium resources are estimated as 5.5 million tons. Out of these, 3.3 million tons are assigned to the reasonably assured category, and 2.2 million tons are associated with the not yet discovered but assumed to exist inferred resources. The actual known exploitable resources are much smaller.

The “economic-geological hypothesis” asserts that a doubling of the uranium price would increase the amount of exploitable uranium resources by a factor larger than 2.

The “energy-physical” opposing argument by M. K. Hubbert to David Nissen from the Exxon Company is: “There is a different and more fundamental cost that is independent of the monetary price. That is the energy cost of exploration and production. So long as oil is used as a source of energy, when the energy cost of recovering a barrel of oil becomes greater than the energy content of the oil, production will cease no matter what the monetary price may be.” Instead of the monetary price, this argument depends on the “energy breakeven condition” or the “Energy Return On Energy Invested” or EROEI principle.

Nations starting nuclear power programs face the consideration of their long term sustainability. This implies the need for the availability of local resources. Dependence on foreign suppliers would eventually pose supply constraints and the surrender of a degree of dependency in exchange for a dependable fuel supply for their electrical generation capacity. The world high grade uranium resources appear insufficient for an expanded global nuclear power program. The current light water reactors cycle primarily burns the U^{235} isotope and can last only from 40 to 50 years.

The resource base can be expanded by the exploitation of the lower grade ores such as from phosphate rocks. The world average uranium content in phosphate rock is 50 - 200 ppm. Marine phosphorite deposits contain averages of 6 - 120 ppm, and organic phosphorite deposits up to 600 ppm.

The world has 15 billion mt of proven phosphate rock reserves, which could last for 100 years. There are another 35 billion tons of lower-grade and unexplored phosphate reserves, which are potentially economically feasible.

Worldwide, there are approximately 400 wet-process phosphoric acid plants in operation. Eight plants for the recovery of uranium from phosphoric acid have been built and operated in the United States since 1976: Florida: 6, Louisiana: 2. Plants have also been built in Canada, Spain, Belgium, Syria, Israel, and Taiwan.

For the long term, sustainability depends on the introduction of nuclear fuel recycling technology, fast breeder technology as a substitute to the “once-through” U-Pu²³⁹ fuel cycle, the adoption of the thermal breeding Th-U²³³ fuel cycle and the eventual development of fusion energy. With the world developing substitutes for petroleum, it will also develop substitutes to the unsustainable light water reactors technology before its limited supplies of U^{235} follow oil down the depletion path.

APPENDIX I

The top countries that produce 95 percent of the world’s total phosphate rock are: USA, Morocco, China, Russia, Tunisia, Jordan, Brazil, Israel, the Republic of South Africa, Syria, Senegal, Australia, India, Togo, Egypt and Algeria. Moroccan reserves account for around 50 percent of the world total. With phosphate consumption growth at 1-2 percent per year, global phosphate reserves would last for centuries. However, the depletion of the most economically exploitable reserves occurs within 100-130 years.

Table A1
World Phosphate Resources.

Country	Reserves [percent]	Potential Reserves [percent]
USA	4-10	7-13
China	2-25	2-10
Russia	3	7-10
Morocco	46-53	63
Jordan	2-3	1-3
Tunisia	1	1
South Africa	9-22	3-22
Brazil	1-3	1-2
Iraq	1	3
Peru	1	
Total P_2O_5 [billion tons]	3.6-8.0	11-22

APPENDIX II

PHOSPHATE PRODUCTS

About 95 percent of the world’s total phosphate rock production is used in agriculture as fertilizers, pesticides and animal feeds. Around 93 percent of the phosphate rock produced is used to produce mineral fertilizers including Di-ammonium Phosphate, DAP, Mono-ammonium Phosphate, MAP, triple Superphosphate, TSP, Single Super Phosphate, SSP, phosphoric acid, and animal feed.

Five percent of the production is used in non-agricultural products. Phosphorus Trichloride, PCl_3 is mostly used to produce organophosphate insecticides and the glyphosate herbicide (Roundup). Half of the 500,000 tons/year PCl_3 is used to produce organophosphate insecticides; the other half is used for glyphosate herbicide production.

The production of Red Phosphorus amounts to 10,000 tonnes per year and it is for the production of flame retardants, semiconductors, fireworks and matches.

The commercial use of food-grade phosphates amounts to hundreds of thousands of tons. It is used in soft drinks, in treating fish filets and freshly processed poultry, as sodium pyrophosphates in baking mixtures as an acidulant, and in potato processing.

Phosphorus compounds are found in several household applications: high grade detergents, cleaning agents, tooth-paste, and flame retardants for clothing, carpets, and curtains.

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