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Uranium from Phosphates

(Updated May 2020)

- Rock phosphate deposits contain many million tonnes of uranium, which may be extracted as a by-product of making fertilisers.
- Some 20,000 tonnes of uranium has already been obtained from these rock phosphate deposits, but the process became uneconomic in the 1990s.
- Higher uranium prices and process refinements have changed the economic situation.

In addition to the 6.1 million tonnes of uranium in known recoverable resources, there are substantial amounts comprising what is known as 'unconventional resources'. The main unconventional resource for uranium is rock phosphate, or phosphorite, and some 20,000 tU has been recovered as a by-product of agricultural phosphate production to the 1990s, but it then became uneconomic. Estimates of the amount available range from 9 to 22 million tonnes of uranium. The World Distribution of Uranium Deposits (UDEPO) database tabulates 14 million tonnes, though the 2018 *Red Book* tabulates only about 8 million tonnes.

With uranium as a minor by-product of phosphates, the potential supply is tied to the economics of phosphate production, as well as uranium price, coupled with the environmental benefits of removing uranium from the waste stream and/or product. World phosphorous pentoxide (P_2O_5) production capacity is about 50 million tonnes per year according to PhosEnergy, 9.5 Mt in North America, 9.4 Mt in Africa and 19.2 Mt in Asia. About 250 Mt/yr of rock phosphate is mined.

From 1981 to 1992 US production from central Florida's phosphate deposits as by-product averaged just over 1000 tU per year, comprising up to 20% of US total, then fell away sharply and finished in 1998 as it became uneconomic.

Cameco and Uranium Equities aimed to set up a demonstration plant in the USA using a refined process – PhosEnergy – and estimate that some 7700 tU could be recovered annually as by-product from phosphate production, including 2300 tU/yr in the USA. The prefeasibility study on the PhosEnergy process completed early in 2015 confirmed its potential as a low-cost process, at about \$21/lb. However, the capital costs in a weak uranium market do not encourage investment yet, and developments are on hold.

Phosphate rock production for fertilizer in 2019, million tonnes

Algeria	1.2
Australia	2.7
Brazil	5.3
China	110
Egypt	5.0
Israel	3.5
Jordan	8.0
Morocco & W. Sahara	36
Peru	3.7
Russia	14

Other countries World total in 2019	14.5 240 Mt
USA	23
Tunisia	3.0
Syria	2.0
South Africa	1.9
Saudi Arabia	6.2

Source: USGS 20201

Phosphate rock (phosphorite) is a marine sedimentary rock which contains $18-40\% P_2O_5$, as well as some uranium and all its decay products, often 70 to 200 ppmU, and sometimes up to 800 ppm. The main mineral in the phosphate rock is apatite, and most commonly, fluorapatite – $Ca_5(PO_4)_3F$ or $Ca_{10}(PO_4)_6(F,OH)_2$. This is insoluble, so cannot directly be used as a fertiliser (unless in very acid soils) so must first be processed. This is normally in a wet process phosphoric acid (WPA) plant where it is first dissolved in sulphuric acid. About 2-4% fluorine is usually present. There are about 400 plants using this wet process worldwide, with capacity of some 50 million tonnes P_2O_5 per year.

Some phosphate deposits – about 4% of total known – are igneous, created by magmatic extrusion as an alkaline chimney. The main mineral is apatite, with some fluorapatite.

When phosphate rock is treated with sulphuric acid in sub stoichiometric quantity, normal superphosphate is formed. If more sulphuric acid is added, a mixture of phosphoric acid and gypsum (calcium sulphate) is obtained. After the gypsum is filtered out, the resultant phosphoric acid can be treated to recover uranium.

The basic reaction is:

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O ==> 2H_3PO_4 + 3CaSO_4 \cdot 2H_2O - exothermic$$

An improved higher-temperature process produces hemihydrate: CaSO₄.1/2H₂O

Fluorides need to be controlled as gases and in effluents (HF, fluorosilicic acid) and about half the fluorine reports with the gypsum. In the process a lot of crud is generated, and this was disposed of with gypsum tailings, despite its low-level radioactivity.

After the gypsum precipitation stage, triple superphosphate is obtained by reacting the phosphoric acid with further phosphate rock. Otherwise, various ammonium phosphate fertilizers can be produced by reacting the phosphoric acid with ammonia.

The uranium is normally recovered from the phosphoric acid (H_3PO_4 – bearing about 28% P_2O_5) by some form of solvent extraction (SX). Kamorphos is developing a simpler version of this.

PhosEnergy, an ion exchange (IX) process, represents a step-change refinement of the old processes. It was announced in 2009, offering uranium recovery costs of \$25-30 /lb U_3O_8 , compared with historical costs of double this. A demonstration plant was built in Adelaide, South Australia, and shipped to the USA to operate at a US fertilizer producer, where it was commissioned in May 2012. The test campaign with four trials on two feed sources was successful, showing recoveries of over 92% at \$20-25/lb operating cost, and with Cameco very fully involved. Full evaluation of the project operation with an engineering study was reported in March 2013, and \$18/lb operating cost with capital cost of \$156 million for a base case 400 t/yr U_3O_8 plant were quoted. Cameco reaffirmed its commitment in subscribing a further \$4 million. PhosEnergy (25.79%) and Cameco (74.21%) are progressing the project in the USA through Urtek.

The PhosEnergy process involves pre-treatment of 27% phosphoric acid feed, which is loaded onto the ion exchanger where uranium ions are adsorbed. The phosphoric acid is displaced from the ion exchange column and returned to the main process stream, and the uranium is eluted with aqueous ammonium carbonate. In a secondary ion exchange, ammonium uranyl carbonate from the primary elution is concentrated and purified, then eluted with a salt/bicarbonate mixture. (The secondary IX uranium recovery is much the same as that in Cameco's US ISL operations, so potential synergy.) The process achieves 95% U recovery, leaving no radwaste, with improved acid quality for the main plant, for \$120 million bolt-on plant cost. The 2015 prefeasibility study estimated that a 0.44 Mt/yr phosphate plant capable of producing 155 tU/yr would operate at \$21/lb U₃O₈, but the capital cost would be high relative to conventional uranium plants.

Continuous onsite PhosEnergy demonstration plant operation at the site of an existing US phosphate producer took place over ten weeks to May 2014 with consistent recoveries of over 92% from the filter-grade acid stream. The product was shipped to a licensed uranium mill in Wyoming where it was converted into saleable product. This phase will underpin a definitive feasibility study (DFS) and be the basis for a full-scale commercial facility, which might be constructed and commissioned within three years of the commencement of a DFS.

In 2019 PhosEnergy and Cameco decided to curtail "unnecessary expenditure on the PhosEnergy process" due to low uranium prices.

As well as the PhosEnergy project, Cameco was involved independently through its subsidiary Nukem with CF Industries in developing a facility to recover about 400 tU/yr from Florida phosphates.

In the USA eight plants for the recovery of uranium from phosphoric acid have been built and operated since the 1970s (six in Florida, two in Louisiana). Plants have also been built in Canada, Spain, Belgium (for Moroccan phosphate), Israel, and Taiwan.

In Brazil where uranium is essentially a co-product with phosphate, the Santa Quitéria joint venture between the government company, Indústrias Nucleares do Brasil (INB), and Galvani phosphates, has a prime customer in the form of Eletrobras, owner of the national nuclear power operator, Eletronuclear. This project based on the Santa Quiteria and Itataia mines will produce both uranium concentrate and diammonium phosphate (DAP) in a single integrated process. The mine was expected to produce 970 tU/yr from 2015, and ramp up to 1270 tU per year in 2017 as by-product or co-product of phosphate. Reserves are 76,000 tU at 0.08% U, though resources are reported as 140,000 tU at Santa Quiteria and 80,000 tU at Itataia, grading 0.054% U in P₂O₅.

Morocco has by far the largest known resources of uranium in phosphate rock.

The economic benefit of recovering uranium from WPA phosphoric acid streams will be both in the value of the uranium and in reduced regulatory demands on disposal of low-level radioactive wastes arising from the WPA process. Estimated uranium production costs will put the new process in the lowest quartile of new uranium production.

USA

The country has reserves of 1400 Mt phosphates containing about 170,000 tU. At 9.6 Mt/yr P2O5 production, this would yield 2300-2680 tU/yr by-product. Nukem and CF Industries were planning a 430 tU/yr uranium recovery operation at CF's Plant City.

Jordan

The country has reserves of 1500 Mt phosphates containing up to 140,000 tU. At 676,000 t/yr P205 production the uranium potential is 135 tU/yr. The government is putting out the Qatrana phosphorites for tender to develop, containing 52 Mt phosphate and 22,000 tU with vanadium.

Morocco

The country has reserves of 50 billion tonnes of phosphates containing about 6.9 MtU. At 4.8 Mt/yr P2O5 production, this would yield 960 tU/yr by-product. There is some expectation of 1900 tU/yr production from 2017.

Egypt

The country has reserves of 100 Mt phosphates containing about 40,000 tU at 50-200 ppm U.

Tunisia

The country has reserves of 100 Mt phosphates containing about 50,000 tU. At 1.6 Mt/yr P2O5 production, this would yield 265 tU/yr by-product.

Central African Republic

Areva's Bakouma deposit has inferred resources of 36,475 tU at 0.02% reported at the end of 2013 in a continental phosphate deposit grading up to 1.27% U.

India

A commercial-scale uranium extraction plant for recovering uranium from fertilizer-grade phosphoric acid is being set up at Paradeep in Odisha, at Indian Farmers Fertiliser Cooperative Limited's (IFFCO's) phosphatic fertilizers complex. A second project for extracting uranium and other rare earth elements from wet phosphoric acid (WPA) is planned for Paradeep Phosphates Limited (PPL), a privatized fertilizer enterprise. The government has declared the proposed Rare Material Recovery (RMR) Plant as strategic.

New Zealand

There was a proposal to mine phosphate from the sea bed on the Chatham Rise, offshore east of the South Island. An average of 240 ppm uranium occurs in the phosphates, which would be dredged then processed onshore at the rate of about 1.5 million

tonnes per year for about 35 years. In February 2015 the NZ Environment Protection Authority refused permission for the
Chatham Rock Phosphate Ltd project.

Notes & references

Notes

a. The PhosEnergy process was being developed by Uranium Equities Limited (UEQ) through a US registered company, <u>Urtek LLC</u>. Cameco secured rights to earn up to a 73% interest in the technology, and initially paid \$12.5 million of the \$16.5 million required for this to UEQ and a further \$4.5 million for the founder's 10%. UEQ subsequently agreed to pay Cameco a share of that 10%, to hold 27% of the rights for the process. Cameco paid a further \$4 million in March 2013 to reach 73% share. At the end of 2019 Cameco held 74.21% of Urtek, Phosenergy 25.79%. On the basis of its earlier 70% interest, Cameco agreed to provide funding for a minimum of 50% of UEQ's portion of capital expenditure for the construction of the first commercial plant, repayable out of earnings. Cameco and UEQ are seeking commercial arrangements with phosphate producers where the process would provide a technical solution for the recovery of uranium from phosphates. The capital required to install the process would be in exchange for off-take from the facility. [Back]

References

1. National Minerals Information Center, U.S. Geological Survey, Phosphate Rock Statistics and Information, <u>2020 phosphate</u> <u>rock annual summary</u> [Back]

General sources

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Tulsidas, H. *et al*, 2014, <u>Uranium Extraction from Phosphates</u>

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