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## Evaluation of the opportunity of production of uranium from phosphorite ore

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### INTRODUCTION

The bulk of the unconventional uranium resources worldwide is associated with phosphorite ores. Despite the ongoing depression in the world uranium markets, intense research is underway in various countries with an objective of developing cost-effective ways of uranium recovery from non-conventional resources. The world phosphorous pentoxide ( $P_2O_5$ ) per year is about 50 Mt, including 9,5 Mt in North America, 9,4 Mt in Africa and 19,2 Mt in Asia. Up to 15 400 tU is contained in phosphorite ores mined worldwide each year, while practically no uranium production has been reported. The value of uranium produced as a minor by-product during the phosphate fertilizer production is negligible when compared to value of the main product (phosphate fertilizers). Hence, the phosphate fertilizers market acts as a determining factor of how much uranium contained in the phosphate resources can be produced, and of its production cost parameters which are closely tied to the fertilizer production economy.

### DESCRIPTION

According to the traditional technology, uranium is recovered from wet-process phosphoric acid using SX-based flowcharts, with octylpyrophosphoric acid (OPPA), di(2-ethylhexyl)phosphoric acid coupled with tri-octylphosphinic oxide (DHEPA-TOPO), and octylphenylphosphoric acid (OPAP) used as extractants. The preliminary reduction of U(VI) to U(IV) is traditionally performed by adding iron powder (specific consumption of the iron powder being 8 kg/m<sup>3</sup> of the source solution).

In 2009, Urtek LLC developed an alternative uranium recovery technology from phosphorites named PhosEnergy and successively piloted it in Australia and the US. The novel technology features ordinary IX sorption of uranium from the wet-process phosphoric acid followed by its desorption and yellowcake production using traditional methods.

Wet-process phosphoric acid (20–40 %  $H_3PO_4$ ) coming directly from the phosphorite sulfuric acid treatment is used as the uranium source for the PhosEnergy process. The uranium sorption is combined with its oxidation from U(IV) to U(VI). The phosphoric acid, thus purified of uranium, is then returned to the main process stream. The PhosEnergy process can be essentially described as the decontamination of the wet-process phosphoric acid of U and V without any waste or refuse forming.

In the former USSR lean complex phosphate-type ores of Melovoye and Tasmurun deposits were mined for uranium. The ores of those deposits are represented by exotic uranium-rare metal-phosphate-containing bone detritus hosted by Maikop (Oligocene–Early Miocene) clays originating from outer deep sea depressions of the vast marine paleobasin of Eastern Paratetis. Skeletal detritus of various marine paleofauna in which the original bone tissue was replaced by francolite—a phosphate mineral—is uniformly distributed throughout the ore mass. Both U and REEs are contained in the crystalline structure of francolite partially replacing calcium ions of the lattice, with the other valuable elements concentrated in pyrite also contained in the ores.

The yttrium-group REE grade in the ores is uniquely high, totalling about 30–35 % of the overall REE grade. The uranium reserves of Melovoye deposit—the largest ore deposit of the Transcaspian uranium region (Kazakhstan)—were put at 44 000 tU.

The uranium recovery from the lean ores (<0,05 % U) was conducted by means of the hydraulic separation of the bone concentrate and the subsequent production of phosphate fertilisers from it during which process not only uranium but also valuable minor by-products were recovered (thorium, REE, scandium, sulfur) [3].

The above-mentioned francolite concentrate produced by the hydraulic separation pre-concentration process consisted mainly of francolite with minor admixture of residual clay and pyrite. On the average, the concentrate contained ca. 25% P<sub>2</sub>O<sub>5</sub>, up to 1% Ln<sub>2</sub>O<sub>3</sub>, 0,2% U and up to 0,04 % Sc. The dissolution of the concentrate was performed by using sulfuric acid or a sulfuric acid-nitric acid mix taken stoichiometrically against the CaO contents in the concentrate [1].

The recovery of uranium from the resulting acid digestion solutions was conducted via SX with the final product being U<sub>3</sub>O<sub>8</sub>. During the SX process, iron and scandium are co-extracted into the organic phase while both phosphorus and REE remained in the raffinate. Following the stripping of uranium from the organic phase, the stripping of scandium was made with 99,9 % Sc<sub>2</sub>O<sub>3</sub> finally produced as a by-product [1, 2].

Following the recovery of uranium and the valuable by-products the acid technology solutions containing both phosphate and the residual sulfuric acid were further treated to produce a granulated complex ammophos-type fertiliser containing in excess of 50 % of N and P<sub>2</sub>O<sub>5</sub>. The fertiliser production process consisted of the ammonisation of the source solution followed by further concentration for which countercurrent multiple-effect evaporation scheme was employed. The resulting concentrated slurry was then granulated, dried, chipped and classified before packaging and shipping [1].

The final products of the ore processing, along with the fertilisers, were U<sub>3</sub>O<sub>8</sub>, REE oxides and Sc<sub>2</sub>O<sub>3</sub>. The total percentage recovery of the target elements stood as follows: U - 93%, REE - 54%, Sc - 70%, P<sub>2</sub>O<sub>5</sub> - 85,5% from the respective source ore grades.

The technology described above was implemented in 1969 at Almaz Production Association (Lermontov town) and had been used with some minor adjustments until 1991. The processing of the ore concentrates sourced from Melovoye deposit had been conducted at a plant in Dneprodzerzhinsk until 1989.

The Yergeninsky uranium ore district situated in the Republic of Kalmykia is a Russian Federation analog of Melovoye deposit. It comprises 13 uranium deposits hosted in Oligocenic to Early Miocenic clay sediments of the Maikop series, featuring the above-mentioned complex uranium-phosphate-rare earth ores. The resource estimate for these as represented by the author calculations is 59 000 tU, 84 620 t P and 260 000 t REE. The Shargadyk deposit is the most extensively studied one of the Yergeninsky ore district.

The resources of the deposit to be commercialized are uranium, phosphates and REE. The main ore constituent is fossilized bone detritus (15 –45 % of the bulk ore) which contains the uranium and the REE resources. The detritus is associated with varying proportions of minor ferric sulfide, clay and carbonate constituents. It is essentially a calcium phosphate-based mineral matter mineralogically very similar to hydroxylised carbonated fluorapatite, containing some minor organic impurities.

In 2015 –2016, a pilot plant run was conducted at the Shargadyk deposit to test the possibility of the target metal recovery from the ores by heap leaching. The sulfuric acid solution leaching of the agglomerated ore was successfully tested. The source ore was crushed to 100 % –20 mm and then agglomerated before the leaching. The resulting ore agglomerate was placed into percolation columns measuring 1 m in diameter and 5 m in height. During the ensuing sulfuric acid percolation leaching U, REE, Ni, Co along with P<sub>2</sub>O<sub>5</sub> became dissolved for subsequent separation and recovery of individual products from the resulting solutions using ion exchange sorption (IX) and selective precipitation. The results obtained during the pilot plant run were a sufficient ground to recommend the heap leach processing of Shargadyk deposit ores occurring at the depth of up to 120 m., which can easily be mined using the open-pit method.

The prospective process flowchart tested and streamlined during the pilot plant operation comprises the following stages and operations:

1. Ore preparation (mining, crushing, agglomeration, heap stacking):
  - Ore delivery to the heap leach site using dump trucks combined with the simultaneous transporting of the leached ore for dumping to old excavated parts of the open pit (up to 1500 t/day);
  - The ore crushing to 100 % –20 mm (up to 100 t/hr);
  - The agglomeration of the crushed ore with concentrated sulfuric acid and sodium silicate to be added into the process. The agglomerate is to be produced in a pipe-type agglomerator. The ore throughput rate: up to 100t/hr;
  - The stacking and formation of the ore heaps using a heap stacker with the subsequent pipelining at the rate of one heap (84 000 t of the agglomerated ore) every 2 months (up to 1500 t ore per day).
2. The heap leaching of the ore heaps comprising the following operations:
  - The three-stage heap leaching at the rate of 6 ore heaps per annum (84 000 t of the agglomerated ore each). Two ore heaps are to be leached at a time to produce the heap leach solutions at the mean rate of 230 m<sup>3</sup>/hr with the collection of the drainage into the collector ponds.
  - The heap leach solutions are to be collected into 5 collector ponds as follows:

2 individual collector ponds No.1 and 2 ( $V = 25\ 000\ m^3$  each) are to receive Stage 1 heap leach solutions (one to serve as a drainage reception unit, the other –as an evaporation pond). Collector pond No.3 ( $V = 5\ 000\ m^3$ ) is to receive Stage 2 heap leach solutions, collector pond No.4 ( $V = 5\ 000\ m^3$ ) is to receive Stage 3 heap leach solutions. One collector pond ( $V = 10\ 000\ m^3$ ) is to be used for collecting the barren solutions to be pumped back to the irrigation.

### 3. The pregnant solution processing.

- The IX sorption of nickel and cobalt to Lewatit TP 207 ionite to produce the Ni-Co concentrate.
- The IX sorption of uranium to Lewatit K 1000 ionite to produce the U concentrate.
- Adding magnesia ( $MgO$ ) to the pregnant solution from the above operation to produce three separate phosphate precipitates of Fe, REE and Mg.
- The sintering of the iron and REE phosphate products (10 t/hr) with sodium carbonate (5 t/hr) in a natural gas-heated tube kiln at 7000C.
- Hot water leaching of sodium phosphate from the sintering product followed by the precipitation of secondary magnesium phosphate with sodium sulfate solution as a by-product.
- The addition of sulfuric acid solution to the precipitates of the primary and secondary magnesium phosphate to produce a solution containing phosphoric acid and magnesium sulfate.
- Adding lime to the above solution to produce a superphosphate precipitate and a magnesium sulfate solution. The rinsed residue of the hot water leaching of sodium phosphate from the sintering product is to be leached with 50 g/l  $H_2SO_4$  for REE; the solution is to be treated with oxalic acid to produce the REE oxalate concentrate containing ca. 50% REE (3 kg of the concentrate/t ore); the oxalic acid leaching residue is then to be calcined to produce ferric cake (43 kg of the cake/t ore), containing 180 g/t Sc and 45%  $Fe_2O_3$ .
- The evaporation of the post-precipitation solutions to produce magnesium sulfate and sodium sulfate products (5 t/hr each) by crystallization.

The marketable products of the project are: superphosphate ( $P_2O_5$  grade 27 %, according to Russian technical specifications (TY 2182-003-56937109-2002), uranium concentrate (ammonium polyuranate, grade no less than 60 % U according to Russian technical specifications TY –95.2822.2002), a 50 % nickel-cobalt hydroxide mix concentrate (Ni –37 %, Co –13 %), a mixed hydroxide-oxalate REE concentrate, containing ca. 50 % REE+Y. Marketable side products obtained during the utilisation of the leaching chemicals are sodium sulfate, technical grade (grade 2 according to Russian Federation state standard GOST 6318-77), magnesium sulfate heptahydrate (GOST 4523-77), construction-grade sand (GOST 8736-2014).

The summary recovery rates for the key elements have been confirmed to be as follows: U –84 %, Ni –76 %, Co –61 %,  $\Sigma$  REE+Y - 63 %,  $P_2O_5$  –77 %, with the respective average content values in the dewatered source ore: U –0,035 %, Ni –0,05 %, Co –0,02 %,  $\Sigma$  REE+Y - 0,28 %,  $P_2O_5$  –11 %.

The solid wastes of the project are ore processing tailings (mainly phosphogypsum), which are to be used as a backfill for the ore pit upon depletion, and the ferric residue containing 180 g/t Sc to be stored on-site for the recovery of scandium in the future.

The value breakdown for the final products of the proposed heap leach plant looks as follows: superphosphate (53 %), followed by uranium concentrate (17,6 %), sodium sulfate (10,8 %) and the REE concentrate (9,6 %).

### DISCUSSION AND CONCLUSION

The feasibility analysis was calculated proceeding from the discount rates set at 10 % and 15 %. The ore resources of the projected plant are sufficient for the 39 years of operation. The planning horizon used was assumed to equal 17 years.

The feasibility analysis conducted backs up the potential commercial profitability of the development and exploitation of the Shargadyk deposit resources. In case the discount rate is set at 10 %, the NPV (net present value) is to total RUR 2661,4 million, the yield index –1,2, the internal rate of return (IRR) stands at 14,4 %, the discounted payback period is 9,5 years while the discounted budget efficiency totals RUR 4607,1 million.

The main conclusions from the above pilot plant test results:

–In the market scenario, the recovery of uranium and the associated metals from Shargadyk complex phosphate ore deposit will be considered only when it is economically viable to do so.

–The development of the Shargadyk deposit of complex uranium-phosphate-rare earth ores looks commercially profitable.

The development project displays fairly high commercial and internal financial efficiency values in case the discount rate stands at 10%, yet the efficiency looks to be problematic in case the discount rate of 15 % is adopted.

### REFERENCES

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