



## URANIUM RECOVERY FROM PHOSPHATE FERTILIZER IN THE FORM OF A HIGH PURITY COMPOUND

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### Abstract

Uranium recovery from phosphate fertilizer industry is based on a one cycle extraction-stripping process. The process was experimented on both sulfuric and nitric acid attack of phosphate rock when uranium is dissolved in phosphoric acid (WPA) or phosphonitric (PN) solution respectively. The WPA and PN solution must be clarified. In the first alternative by ageing and settling and in the second by settling in the presence of flocculant. The organic components must be removed on active carbon for WPA only since in the case of nitric attack calcined phosphates are used. In both alternatives uranium is extracted from aqueous acidic solutions in the same time with the rare earths (REE), by di(2-ethylhexyl) phosphate (DEPA) as basic extractants, eventually in the presence of octylphosphine oxide (TOPO) as synergic agent. The stripping process is carried out in two stages: in the first stage REE are stripped and precipitated by HF or  $\text{NH}_4\text{F} + \text{H}_2\text{SO}_4$  and in the second stage uranium as U(VI) is stripped by the same reagents but in the presence of Fe(II) as reductant for U(VI) to U(IV) inextractible species. Tetravalent uranium is also precipitated as green cake either  $\text{UF}_4 \cdot x\text{H}_2\text{O}$  or  $(\text{NH}_4)_7\text{U}_6\text{F}_{31}$  as dependent on reagents HF or  $\text{NH}_4\text{F} + \text{H}_2\text{SO}_4$ . Uranium stripping is possible for PN solution only if  $\text{HNO}_3$  partially extracted is previously washed out by a urea solution. The green cake washed and filtered is dissolved in nitric acid in presence of  $\text{Al}(\text{OH})_3$  as complexant for F. The filtered nitric solution is adjusted to 3-5 mol/L  $\text{HNO}_3$  and extracted by 20% TBP when uranium is transferred to the organic phase which after scrubbing is stripped in the classic way with acidulated ( $\text{HNO}_3$ ) demineralized water. Uranium is precipitated as diuranate of high purity. Rare earths left in the aqueous raffinate are extracted by pure TBP from 8-10 mol/L  $\text{HNO}_3$  medium. The stripping process takes place with acidulated water. Rare earths are precipitated as hydroxides.

In the previous papers [1,2,3,4] a one cycle extraction - stripping process was described for uranium recovery from phosphate fertiliser industry in Romania (Fig.1).

There are 8 industrial plants in Romania processing each 330,000 t/yr phosphates, mostly of sedimentary origin, therefore a total of approx. 3 millions t/yr. The average content of uranium in sedimentary phosphates is 0.012% U or at total capacity 300 t/y recoverable uranium.

Four plants processing phosphates in Romania are based on sulphuric acid attack (dihydrate process) resulting as intermediate phosphoric acid (WPA) which contains more than 90% of uranium of the rock in the dissolved form as U (VI).

The rest of the four plants of identical capacity are processing calcined phosphates by nitric acid attack resulting a mixture of phosphoric and nitric acids so called phosphonitric (P.N.) solution containing all uranium in dissolved form from the rock.

In the first alternative WPA is filtered and separated of calcium sulphate in the second P.N. solution filtered is cooled to separate calcium nitrate leaving uranium unaffected. Both solutions still have solids which must be eliminated in a solvent extraction system. In the case of WPA the clarification process is carried out by ageing and settling but for P.N. solution a settling process is required and is possible only in the presence of flocculant of certain type efficient at low temperatures, which are characteristic for P.N. solutions.

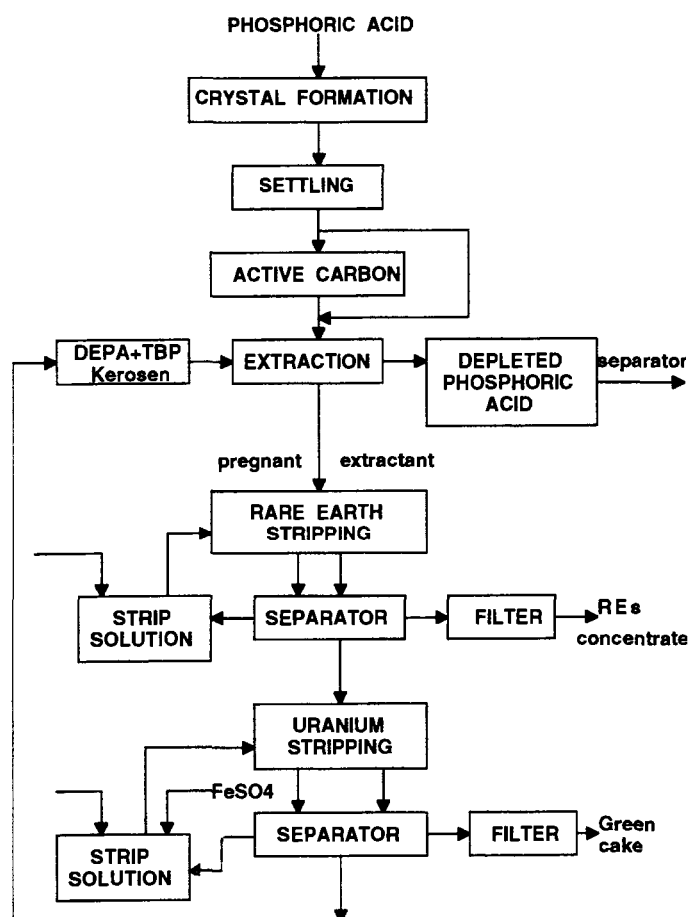


FIG. 1. One cycle extraction stripping flowsheet sulfuric attack

The clarified WPA acid usually has organic components content. In the case of green acid the organic components contents is low and need no extra treatment but for yellow or brown acid the high content of organics require a further treatment to eliminate these components, a process which in this paper was carried out on active carbon. A suitable regeneration and treatment of column led to a high efficiency and long life span of carbon. Uranium retention on active carbon may attain several percent for high content of organics.

Extraction process takes place in a multistage mixer-settler extractor using as basic extractant di (2-ethylhexyl) phosphate (DEPA) used at 1.2 mol/L concentration in kerosene. It may also be used in presence of 0.2 mol/L tri-n-butyl phosphate (TBP) or tri-n-octyl phosphine oxide. In the last case the best synergic mixture is 0.6 mol/L DEPA+0.1 mol/L TOPO [5,6] (See Fig.2).

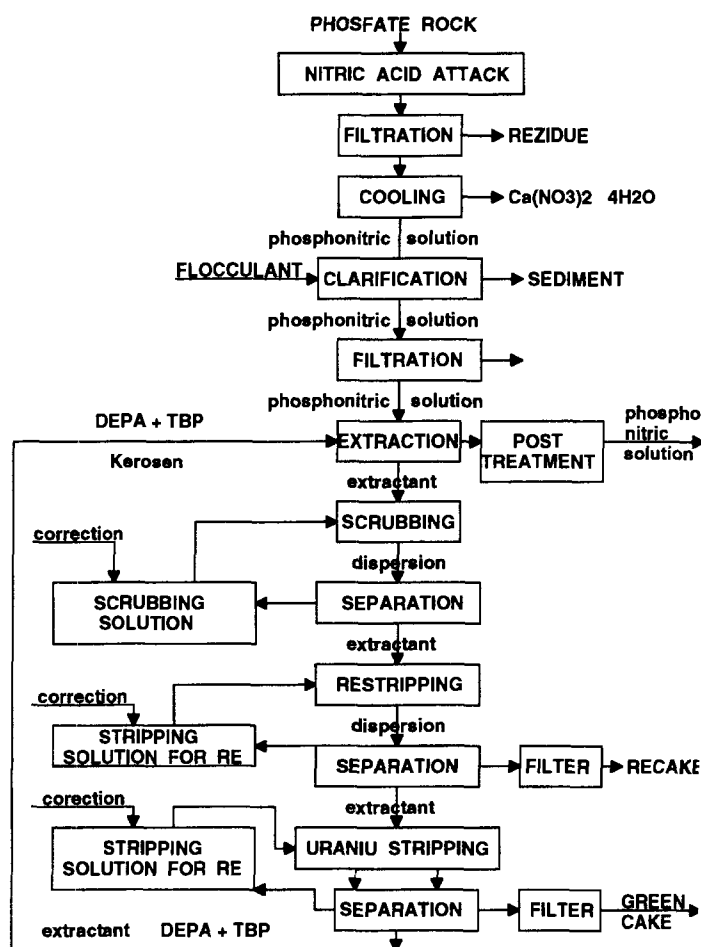


FIG.2. Uranium and rare earth recovery from phosphonitric solution

The synergic mixture with TOPO for U (VI) led to an important enhancement with much higher distribution coefficients permitting the use of extractant / aqueous ratio 1:2 with all favourable consequences resulted.

During the extraction process uranium extracted as U (VI) is attended by rare earth elements (REE). The REE are precipitated as hydroxides of high purity (See Fig.3).

The extractant mentioned was stable therefore no change in distribution coefficients, IR. spectra, potentiometric titration was noticed.

The pregnant extractant leaving the extractor is sent to the stripping stages. The depleted raffinate (WPA or P.N. solution) is sent to a separator in order to achieve an advanced recovery of extractant entrained. This process is important in the alternative of P.N. solution where a final treatment on active carbon might be required to avoid an eventual fire hazard resulted in the end fertiliser product due to the presence of organic extractant.

The first stripping stage consisted of a mixer where the extractant and stripping reagents are introduced. The chemical reagent is either 15% HF or 15% F as  $\text{NH}_4\text{F} + 2 \text{ mol/L H}_2\text{SO}_4$ .

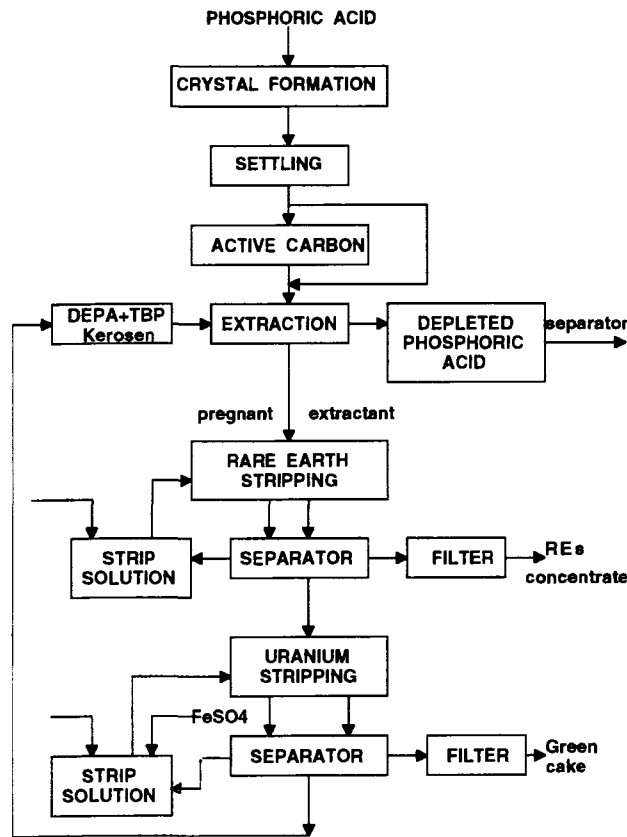


FIG.3. Uranium and RE separate extraction and stripping process

At this stage REE and some impurities are stripped and precipitated. The fine dispersion of the mixer is continuously discharged in a separator where the three existent phases are separated. The solid product from the bottom is unloaded on the filter. The aqueous reagent via hydraulic tubes is sent to a storage tank and is recirculated.

The extractant with U(VI) unaffected via overflow is discharged to uranium stripping stage of similar construction with previous equipment met at REE stripping.

In the mixer the same time with pregnant extractant, the stripping reagent is also introduced. The stripping reagent consisted of: 15% HF + 2-4 g/L Fe (II) or 15% F<sup>-</sup> as NH<sub>4</sub>F + 2 mol/L H<sub>2</sub>SO<sub>4</sub> + 2-4 g/l Fe (II). The stripping reagents have a strong reduction capacity for U (VI) which will be transformed to U(IV) inextractible species. The redox potential involved is even lower than in the phosphoric medium [7].

The U (IV) in presence of F<sup>-</sup> is precipitated as dependent on reagents used: UF<sub>4</sub>xH<sub>2</sub>O, (NH<sub>4</sub>)<sub>7</sub>U<sub>6</sub>F<sub>31</sub>.

The fine dispersion from the mixer is discharged to the separator where the solid product is separated at the bottom and is unloaded on the filter, obtaining so called "green cake".

The aqueous reagent eventually corrected in the recirculation tank is reintroduced at stripping stage of uranium. The separated depleted extractant is recirculated at extraction stage without any further treatment.

This flowsheet is valid in the case of WPA. In the case of P.N. solutions during the extraction process some  $\text{HNO}_3$  ( $\text{HNO}_2$ ) is also extracted. The presence of  $\text{HNO}_3$  ( $\text{HNO}_2$ ) seriously interferes in the stripping stage of uranium. The divalent iron is oxidised to Fe(III) leading to an increase of redox potential of the system, uranium as U(VI) being left unaffected and thus cancelling the stripping effect. In order to avoid this behaviour, the extractant is previously scrubbed with urea solution when  $\text{HNO}_3$  is eliminated as urea nitrate. For this process a similar mixer-separator unit is used.

The whole system is based and regulated by gravity flow reducing at minimum the power requirements.

The data obtained in the pilot plant processing 5-7  $\text{m}^3/\text{h}$  WPA have permitted to estimate the operation costs at \$ 30/Kg U.

This cost is difficult to be attained by any other process and the green cake resulted in our process, calcined at  $400^\circ\text{C}$  in nitrogen media led to anhydrous  $\text{UF}_4$ . This was fluorinated to obtain  $\text{UF}_6$  of high purity because no other existent impurity produced volatile fluorides.

Starting with this process three uranium recovery plants were built in Romania adjacent to three fertiliser plants processing phosphate rock by sulphuric attack (dihydrate).

Since our nuclear power plants are based on CANDU reactors a further study was required in order to obtain in a wet process an uranium compound of high purity.

For this purpose the green cake of 30-50% U has been used to feed a purification plant.

The process studied in this paper started with dissolution of green cake which is not a simple process. The dissolution in nitric acid is only feasible in the presence of a complexing agent for  $\text{F}^-$ . Any kind of aluminium salt, even in solid form is suitable for this process. The most convenient to use is aluminium hydroxide. The dissolution process is fast in 33%  $\text{HNO}_3$  and in the presence of aluminium hydroxide.

The nitric solution is filtered and adjusted at 3-5 mol/L  $\text{HNO}_3$ .

A similar behaviour is envisaged for REE which were not completely removed at the stripping stage and some are present in the green cake. There is also the possibility to strip both uranium and REE in the same product.

Uranium is extracted from nitric solution with 15-25% TBP in kerosene using a 5-7 step mixer settler extractor. The REE and the rest of impurities are left in the aqueous raffinate. For this purpose it is required to saturate as much as possible the TBP in uranium.

The stripping process of pregnant extractant is also carried out in 7 step mixer settler (extractor) using as stripping reagent 0.1 mol/L  $\text{HNO}_3$  aqueous solution.

Uranium is precipitated as a diuranate or with perhidrol as peroxide when the product is of nuclear purity.

The aqueous nitric raffinate is adjusted to 8-10 mol/L  $\text{HNO}_3$  and the REE are extracted in pure TBP. At high nitric acid concentration and in pure TBP the distribution coefficients for REE are high. Several extraction steps are required as in case of stripping process carried out with 0.1 mol/L  $\text{HNO}_3$ .

The REE are precipitated as hydroxides of high purity.

The total operation costs of a product of nuclear purity starting from the green cake is estimated at \$ 17/Kg U and from the WPA \$ 47/ Kg U.

The one cycle extraction stripping process described in this paper is different of ORNL two cycle extraction-stripping process [8] since uranium is obtained as a green cake and REE are also recovered especially from WPA where yttrium is predominant, more than 90%. There is also the advantage of obtaining UF<sub>6</sub> directly from the green cake.

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