DEVELOPMENT OF INNOVATIVE PROCESSES FOR THE SEPARATION OF HIGH PURITY URANIUM FROM PHOSPHORIC ACID

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Phosphoric acid is processed in large volumes by Indian industries, into fertilizers and detergent phosphates. A major proportion of this acid contains uranium in significant concentration. Phosphates have long been recognized to be an important secondary source of uranium and indigenous development of processes of separation, has been an important area of R&D at BARC [1]. The key step in the separation flowsheet is solvent extraction. In India, the major proportion of phosphoric acid is in the concentrated form, generally called the ‘Merchant Grade’ Acid (MGA). The phosphate content of MGA, expressed as P₂O₅ weight percentage is ~ 55.

Typical analysis is given in Table 1. Viscosity of MGA is high, in the range of 20-50 centipoise. Depending on the nature of phosphoric acid, a particular type of solvent is needed. BARC has recently developed a novel solvent extraction process based on Di-Nonyl Phenyl Phosphoric Acid (DNPPA) which has been patented [2]. Another process has been developed and patented using currently available indigenous industrial solvents for extraction from ~28% P₂O₅ weak acid (WPA) [3]. The salient details of these two processes are described in this paper, after giving a general description of the overall separation flow sheet. Some recent R&D work is summarized in the concluding part of the paper. More details are available in the published references [4-9].

Process Flow sheet for Uranium Separation from Phosphoric Acid

The overall flowsheet for separation of uranium from WPA or MGA is schematically shown in Fig. 1. It involves four types of operations, which can be described as pre-treatment, solvent extraction, ‘yellow cake’ recovery and post-treatment.

Pre-treatment of phosphoric acid involves cooling of the acid as a first step. The efficiency of separation is improved as a result of cooling since the subsequent solvent extraction is an exothermic equilibrium process. The phosphoric acid as produced in industries is often hot. Hence cooling to a temperature of ~30°C is carried out. A flash cooling system with high recycle ratio is preferred, since solids are present in the phosphoric acid. Solids are generated as a result of cooling, since the lowering of temperature results in supersaturation of the aqueous phase, with reference to many dissolved salts.

Table 1: Typical analysis of concentrated ‘merchant grade’ phosphoric acid (MGA)
Fig. 1: Overall flowsheet for uranium separation from phosphoric acid
For smaller duties, spiral coolers can be used. The next step in pre-treatment is separation of suspended solids. This is achieved by clariflocculation with high molecular weight polymeric flocculants. Several indigenously produced flocculants have been successfully tested and product acid with <300 ppm solids was obtained, in both lab-scale and pilot-scale tests. Our studies show that polymeric flocculants also serve to separate a significant amount of humic material from the acid. While gravity clariflocculators are suitable for weak acid, concentrated MGA needs amplification of the gravity force in machines, such as solid bowl centrifuges. The concentrated acid is far more viscous than weaker acid and hence solid-liquid separation becomes more difficult. Separation of solids serves to ensure trouble-free down-stream operations of carbon treatment and solvent extraction. Solid separation by filtration is difficult to achieve for the viscous MGA and although it is feasible for weaker acid, it is industrially an expensive option. The third step of pre-treatment, after cooling and solid separation, is separation of the contained humic matter. Phosphoric acid produced from naturally occurring rocks, invariably contains humic matter, that can interfere with the solvent extraction. Hence, this separation is essential. It is most efficiently achieved by adsorption of humic material on activated carbon, used in the form of granules that have been packed into a series of columns. A view of such a facility is shown in Fig. 2. Pilot plant continuous test-work has been carried out, both with weak and concentrated phosphoric acids. Various grades of indigenous carbons have been tested and in particular the material prepared from coconut shells has been found to be eminently suitable. In fact, such carbons are exported from India. Tests have shown that performance of Indian carbons is superior to that of imported materials. Several cycles of column adsorption, washing and re-generation with NaOH solution have been carried out. The acid obtained from activated carbon pre-treatment, is a green acid. A cheaper option to activated carbon, involves the use of activated clays. We have evaluated a number of indigenous clays in once-through mode based on filtration. Depending on specific local conditions in a host plant, this option can be feasible. The clean green acid is subjected to the next step of pre-treatment, that involves oxidation with air or gaseous oxygen, followed by finishing with aqueous hydrogen peroxide. This step of oxidation serves to convert all the uranium from tetravalent to hexavalent state, the form which is necessary for the two innovative processes as given in the patents.

Solvent extraction of uranium from phosphoric acid by the two processes, has several features in common, that are described herein. An important feature is the concept of a dual cycle flowsheet. In the first cycle, uranium is first extracted and then stripped into a small stream of concentrated acid. As a result of this first cycle operation, uranium concentration increases by a factor of 50-100. This cycle is optimized for high recovery with as few stages of contacting as technically needed, in order to reduce plant inventory and lower capital and operating costs. A common feature of the two patented processes,
is the use of MGA as stripping agent at 55-60°C under reducing conditions, achieved by the using metallic iron. Both conditions of raising the temperature and use of MGA (instead of weak acid) aid in efficiency of operation. In the second cycle of solvent extraction, the purity of uranium with respect to co-extracted impurities such as iron, rare earths and phosphate is achieved, by incorporating a set of scrubbing stages in the flowsheet. For both the patented processes, selection of a suitable scrubbing medium is a key feature of the innovation. In addition to this, the outlet scrub stream provides a potential source of by-products such as rare earths. In the second cycle, the medium used for stripping of purified uranium extract is alkaline solution of ammonium or sodium carbonate. The uranium bearing aqueous alkaline solution is further processed by precipitation of uranyl peroxide. The peroxide precipitation is a common feature of the two patented processes that yields a ‘yellow cake’ which is far superior to the Magnesium Diuranate (MDU) industrially produced for decades in the country. A view of samples of uranium peroxide from phosphates, diuranates and trioxide obtained from the peroxide is shown in Fig. 3.

The barren phosphoric acid from the solvent extraction battery is returned to the mother phosphate industry after ‘post-treatment’. This involves separation of traces of solvent from the aqueous phase, with the twin objectives of: a) Solvent recovery for techno-economic operation and b) ensuring the return acid does not contain any contaminants that can interfere with the subsequent acid processing in the host industry. This step of post–treatment is carried out in a series of equipment consisting of lamellar coalescer, dissolved air floatation, counter-current diluent washing and activated carbon adsorption. The final acid is pre-heated before return, if required by the host plant. Similarly the solids that had been separated as a part of pre-treatment, are mixed with return acid, if needed by host plant, to ensure downstream operation of production of fertilizer granules is unaffected.

Next the specific innovative details of the two processes, which have been developed to meet two different indigenous requirements are described.

**DNPPA-TOPO Solvent Extraction Process for uranium recovery from MGA.**

This process was developed specifically in the context of indigenous industry, which uses concentrated acid (MGA) from various sources in large volumes. In fact, the largest phosphatic plants in the country use MGA as the source material rather than the weaker acid. Even plants that rely on weak acid as source material, have the option of switching over to purchased MGA in the event of non-availability of weak acid. Large volumes of the MGA handled in the industry enable economy of scale. An additional conclusion derived from the data collected by BARC is that, MGA sources are richer in...
uranium content, on an average, as compared to weaker acid – even when comparison is based on U/P ratio rather than concentration in ppm. The reason for this, lies in the observed higher uranium content of the rocks used for MGA, than those used for WPA.

A survey of the literature revealed that world-wide uranium recovery has been attempted only from the weaker phosphoric acid, in view of the difficulty of extraction, which is in turn related to the complexation of ionic species of uranium into less extractable form, as the acidity increases. Limited studies that have been reported [11] on the separation of uranium from concentrated acid, have involved the extraction of tetravalent uranium by a mixture of mono-ester and di-ester forms of phenyl phosphoric acid. Such processes suffer from the disadvantages that considerable amount of other impurities such as iron and rare earths are co-extracted, the stripping of uranium involves corrosive acids such as HF, the solvent system is unstable and overall recovery uneconomic. In fact, an earlier study from BARC had reported results in this direction [12] which in itself was a significant scientific advance, that phenyl phosphoric acids could be used as feasible extractants.

The inventive work covered by our patented processes, adopted a different approach, based on extraction of hexavalent uranium by a synergistic mixture of acidic organo-phosphorus compound, with a neutral synergist molecule. Such a system enables reductive stripping, adoption of dual cycle approach which yields high purity uranium, leads to minimum contamination of phosphoric acid as is desired by host fertilizer plant, avoids corrosive chemicals and has the flexibility of being integrated into a host plant, handling both weak and concentrated phosphoric acids.

In order to meet the above objective, the solvent used had to be of high purity, another point of departure from earlier work in this field, at BARC. Based on accumulated experience and literature survey, DNPPA was selected as the acidic extractant and TOPO as the synergist. Since DNPPA is not commercially available, it was synthesized by us in the laboratory. A mixture of di- and mono-esters of nonylphenyl phosphoric acid was obtained by reacting p-nonyl phenol with phosphorous oxy-chloride in the presence of pyridine in the mole ratio of 2:1:2. The reaction mixture was hydrolyzed with excess of 6 M HCl at 80°C for 12 h. The di-ester and mono-ester were separated by extraction from benzene solution with 70% methanol. The unreacted nonyl phenol and neutral compounds, were separated by loading the benzene layer with neodymium (Nd) and precipitating the Nd-diester salt, in excess acetone. Di-ester was obtained by dissolving the salt in benzene and stripping with oxalic acid. The concentrations of mono and di-esters were determined by potentiometric titration with alkali in ethanol medium. Pure DNPPA was found to be a pale yellow liquid with a density of 1.03, refractive index of 1.513, having acid number of 105.53 and molecular weight of 502.

The extraction ability of the solvent thus obtained was evaluated by contacting with synthetic phosphoric acid spiked with uranium. As shown in Table 2, the synergistic phenomenon is established by the fact, that the extraction power (measured by the distribution ratio D which is the ratio of equilibrium concentrations of uranium in the extracted organic phase to the aqueous phase) for the mixture is higher than that of DNPPA or TOPO alone. Next, the comparison of using DNPPA instead of D2EHPA which is conventional in weak acid extractions is shown in Table 3. The extraction power is increased 3-4 times when DNPPA replaces D2EHPA in the organic phase. This conclusion is based on molar comparison. Recognizing the higher molecular weight of DNPPA than that of D2EHPA, results are different when comparison is on the basis of weight. Next, the mole ratio of DNPPA to TOPO in the organic phase was varied and it was found that the optimum mole ratio is [DNPPA]/[TOPO] = 2:1 as against the optimum ratio of 4:1 for the D2EHPA – TOPO mixture. This shows that the nature of extracted species is different and there is no a priori rule for optimization. Next, at constant mole ratio, the DNPPA...
concentration was varied. Results are shown in Table 4. The increase in D value is found to follow a power law with an exponent of 0.6. It may be noted that DNPPA is a highly viscous extractant and the minimum necessary concentration in a diluent, is to be used. A further comparison of extraction of U-VI by 0.6 DNPPA + 0.3 M TOPO, with that of U-IV by 0.1 M DNPPA + 0.1 M MNPPA, showed comparable efficacy of separation, without the disadvantages associated with the extraction of tetravalent uranium, as discussed earlier.

Encouraged by the results of single-stage equilibrium extraction, tests were carried out in counter-current stages at aqueous to organic phase ratio of 1.5 and over 90% extraction of uranium was obtained in eight stages of separation. Next the reductive stripping was carried out using 12M H₃PO₄ with 10 g Fe²⁺/L at organic to aqueous ratio of 20 and temperature of 60°C. In five counter-current stages, with a loaded organic feed of 0.11g U₃O₈/L, a pregnant aqueous solution containing > 2g U₃O₈/L was obtained.

The strip solution collected in the first cycle was used as feed, after dilution and oxidation of uranium, for a second cycle. The extractant used in the second cycle was 0.3 M D2EHPA + 0.075 M TOPO. However, the phase ratio was increased in view of the dilute feed and the extract was scrubbed with dilute sulfuric acid. From the loaded organic phase, uranium was stripped with 1 M ammonium carbonate solution. The strip solution was filtered to remove traces of iron precipitate. The uranyl tri-carbonate solution contained excess ammonium carbonate and pH was found to be 8.3. Uranium precipitation was carried out using a solution of 40% H₂O₂. The neutralization was carried out with sulfuric acid. In a pH range of 3-4, the uranium precipitation was complete (>99%). The pale yellow uranium peroxide (UO₄.xH₂O) was filtered, washed, dried and calcined to obtain black UO₃ powder of >99% purity. Thus the entire process was proven.

An important feature of the solvent for industrial use involves stability of the solvent. In order to establish this, the solvent was contacted with feed acid for 15 days. After this period, the extraction behaviour was compared with that of freshly prepared solvent and found identical. Similarly cyclic stability tests were conducted. These involved repeated extraction and stripping. Both the composition and the phase separation behaviour were studied. It was found, that over 50 cycles could be carried out without any significant change. It was also found that low monoester content of <1% was important for stability.
The studies were also carried out using other synergistic reagents such as di-butyl butyl phosphonate (DBBP) and lower concentration of extractants when contacting with weak phosphoric acid. In all cases satisfactory extraction with DNPPA based systems was achieved which was superior to the D2EHPA based extractants.

**D2EHPA – TBP Solvent Extraction Process for Weak Phosphoric Acid**

While the technical superiority of the DNPPA-TOPO process is established, its large scale industrial application is constrained by the non-availability of both the components in tonnage scale. Thus industrial exploitation of technology is presently limited to weaker phosphoric acid for which D2EHPA is adequate and BARC has proved the know how for its indigenous manufacture. But in this case difficulties were encountered in the availability of TOPO and an indigenous option was urgently needed. Hence, we developed an alternate process based on indigenously available solvents D2EHPA and TBP in a short span of less than one year.

A literature search revealed, that very limited work on the D2EHPA-TBP for uranium extraction from phosphoric acid, had been carried out. The only process reported \[13\] involved the use of HF for stripping and resulted in a crude uranium product that was contaminated with rare earths. Besides, there were several inconsistencies in the data. Hence, systematic parallel investigations were carried out by us incorporating innovative approaches to overcome the limitations of known processes. In particular it was found, that a suitable scrubbing stage in second cycle of two-cycle process, coupled with uranyl peroxide precipitation, yielded a product of high purity. The process was tested at several labs as well as pilot plant tests were carried out, using freshly produced phosphoric acid at industrial sites in the country. Composition of various acids is given in Table 5.

The synergism between the extraction of uranium by D2EHPA and by TBP is weaker than that of D2EHPA and TOPO. However it is significant as shown by the results given in Table 6. This significant increase translates into a very significant increase in recovery, when the effect is multiplied in a counter-current cascade. This was verified on a number of phosphoric acids and results are given in the patent.

It is shown that depending on the feed acid characteristics, over 90% uranium can be extracted in 6-8 stages operating at $-30^\circ$C using 1.5 M D2EHPA + 0.2 M TBP. The extraction is to be applied for weak phosphoric acid only, since as shown by the data given in Table 7, the extraction power sharply decreases

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**Table 5: Analysis of weak phosphoric acids (WPA)**
with the acid concentration. The behaviour of rare
earths, which are present in the phosphoric acid in
concentrations often higher than uranium, is equally
important. With yttrium, as a representative element,
the behaviour is shown in Table 8. This data also shows
that using concentrated phosphoric acid in the
subsequent stripping operation, both uranium and rare
earths should get transferred from the organic phase to
the aqueous phase. In the first cycle of operation, this
ensures that there is no build-up of these elements in
the recycled organic. However in the second cycle, the
separation of co-extracted uranium and rare earths into
two different streams is desirable for product purity. This
separation is achieved by scrubbing. Sulphuric acid is a
very suitable scrubbing agent in the environment of a
phosphatic fertilizer plant. Using this agent, the effect
of acid concentration is shown in Table 9. Thus efficient
scrubbing is feasible by adjusting the aqueous acidity.

The precipitation of uranium after the process of
dual cycle extraction, is illustrated by the experimental
data described hereinafter, for a typical fertilizer acid.
Five litres of the combined solution resulting from
alkaline carbonate strip of second cycle, containing
22.01 g/l uranium, was mixed at room temperature
of 29°C with 0.4 l of 12.5 M NaOH solution.
This raised the pH to 12 and precipitated sodium
diuranate. The precipitate was filtered and slurried
in one litre of water and then 250 ml of 4 M sulfuric acid was added to it and the precipitate was dissolved. The insolubles were filtered out and the pH of the clear filtrate solution was adjusted to 3.5 using 80 ml of 12.5 M NaOH. After pH adjustment, 100 ml of H2O2 was added. This precipitated uranyl peroxide. It was filtered and the filter cake was washed with 1500 ml of acidic water. The 1300 ml filtrate and 150 ml washing analyzed 2 and 1 ppm uranium respectively. The air-dried cake weighed 168 gm with uranium content of 67% by wt. With respect to uranium in the feed acid for extraction and that in the stripping acid, this represented an overall recovery of 90.7% by wt. The purity of the uranium prepared was > 99.9 % by wt. The uranium peroxide filter cake, after washing was dried at 200°C for 1 hr, to obtain a uranium trioxide product. Analysis of a number of samples is given in Table 10.

The stability of the D2EHPA-TBP solvent was also tested in a manner similar to that for DNPPA-TOPO. The results showed that D2EHPA-TBP is a very stable solvent under the processing conditions.

Recent advances

The R&D work in the field of uranium separation from phosphoric acid by REDS, BARC has led to industrial activity by the sister units of BARC [14] and currently two of the engineers are on project deputation. The research has led to setting up of large-scale (60m³/h) pump-mix unit [15]. The pictorial details of a pilot scale (10m³/h) unit at Trombay are shown in Fig. 4. Another technological innovation is the duplex mixer design as shown in Fig. 5. The process R&D has spanned to cover uranium recovery from partially neutralized and diluted acid (PNDA) [16] as well as the ‘hemi-hydrate’ (HH) acid by the 1.5 M D2EHPA + 0.375 M TOPO process[17]. The DNPPA extractant has also been studied for uranium separation from acid leach solution from ore processing [18]. An oxalate scrubbing has been tested for incorporating in the two patented processes described in this publication [19]. This variation has the potential to enable rare earths separation as a by-product of uranium from phosphoric acid. In view of the proven advantages of uranyl peroxide-derived yellow cake over magnesium diurate (MDU), which has lower purity and more importantly it leads to the ‘silica problem’ in subsequent refining. Hence the R&D work was extended to precipitation of uranium from the ion exchange product solution [20]. The peroxide precipitation process has been industrially demonstrated at UCIL for incorporation in their yellow cake production. The stability of the uranyl peroxide and effervescence during subsequent dissolution in refining process have been factors of concern. Research has shown, that by drying

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part of Plan projects, include R&D related to dissolved and entrained solvent recovery as well as rare earths by-product recovery. Rare earth elements such as Dy$_2$O$_3$ are of interest in nuclear reactors such as AHWR while gadolinium oxide is used in PHWRs.

the uranyl peroxide at a suitable temperature and heating rate, stable UO$_3$ is obtained. This is illustrated by the data of Fig. 6. The oxide product is a very stable pure form of uranium obtained from the secondary phosphatic sources. The data on these and related aspects has been compiled [21-23]. Current areas of research in REDS, as

References

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