OPERATING EXPERIENCE IN THE REFINING OF URANIUM BY SOLVENT EXTRACTION USING MIXER-SETTLER

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Uranium purification at Uranium Metal Plant is carried out using solvent extraction process. Equipment used is mixer-settler. The process includes extraction, scrubbing, stripping and solvent processing. Operating experience in these stages is discussed. Effect of silica in feed, fluoride level, solvent quality and entrainment levels are discussed. Experience has shown stripping capacity is limited by low specific settling rate of used solvent with diminer-alised water at ambient temperature. Efforts have been made to study these factors in detail. A new stripping and solvent processing unit has been designed. A slurry extractor is being fabricated for over-coming silica problem. Improvements in instrumentation and control are discussed.

I. INTRODUCTION

Uranium Metal Plant is using solvent extraction process for the purification of crude uranyl nitrate solution as an intermediate step in production of nuclear grade uranium ingots. Magnesium diuranate (MDU) received from U.C.I.L. and scrap powders generated during processing at U.M.P. and A.F.D. are dissolved in nitric acid for feed preparation. The production process of MDU has been described earlier(1). The MDU cake contains appreciable silica which affects subsequent processing in solvent extraction. The scrap powders are relatively pure and pose less problems.

II. SOLVENT EXTRACTION PROCESS

The process flow-sheet is shown in Figure 1. The solvent used is tri-n-butyl phosphate (TBP) diluted to 30% v/v in kerosene. The slurry after dissolution is filtered and analysed. Feed solution to extraction contains about 225 g/l of uranium and has free acidity (FA) of 2 N. The uranium is selectively extracted into solvent phase in 7 stage mixer-settler battery. The organic to aqueous (O/A) ratio is maintained at 2:1 and 80-90% saturation of solvent is achieved.

The loaded solvent containing traces of aqueous entrainment and co-extracted impurities is scrubbed with 0.5 N nitric acid at O/A ratio of 10/1. The pure extract is
stripped with demineralised water (DMW) to transfer uranium to the aqueous phase. The phase ratio is controlled at \( \frac{O/A}{2/3} \).

The lean solvent, free of uranium, however, contains hydrolysis products of TBP and degradation products of kerosene. These are removed by washing with soda ash solution. The solvent is re-acidified and recycled.

The equipment used for solvent extraction was initially pulsed columns. During expansion of UMP a decision was taken to switch-over to mixer-settlers for simplicity, design reliability and flexibility in operation. The mixer-settlers used are similar to the units in use at ZOP, NFC.

III. COMMISSIONING EXPERIENCE

During commissioning it was found that the aqueous level in settler of stripping unit used to build-up and flood the unit. As a remedial measure, the aqueous baffles height in stripping unit was reduced from 10 cm. to 2 cm. In addition, inter-phase controllers were redesigned. However, the flooding of aqueous phase still persisted. The design was re-examined and model simulations carried out at different available density data. It was found that it is difficult to maintain adequate inter-phase levels without increasing depth of the unit to 1 metre. The specific settling rate with the used solvent was found to be 2 - 2.5 m³/hr/m² as against design value of 4 m³/hr/m². As a compromise for efficient operation, it was decided to derate the whole unit.

IV. OPERATING EXPERIENCE

4.1 Silica Accumulation: The feed to solvent extraction process obtained after filtration of MDU slurry generally contains about 0.5 gpl SiO₂. This silica slowly accumulates in the extraction battery and it becomes necessary to clean the unit once in a month. This involves draining the entire hold-up and filtration. Spillage and solvent losses, besides demand on manpower, are high. Often, due to mal-functioning in filtration, the silica level goes very high in the feed and immediately the ports get choked and flooding occurs. Several flocculants and filter-aids were tested in lab-scale but without much improvement. The type and quality of filter cloth used was found to have strong effect on the clarity of feed solution. Rotary pre-coat vacuum filtration for silica control was not attempted due to limitations of space and the problem of processing pre-coat cake.

A decision is now taken to replace the mixer-settler battery for extraction by a slurry extractor to overcome the silica problem.
4.2 Settling Rate in Stripping: The settling rate in stripping unit was found to be the limiting factor in capacity. At high flows, coalescence was incomplete, back-mixing occurred across stages, and concentration gradients were poor. Investigations were carried out to improve the rate by increasing temperature and aqueous phase acidity. Batch coalescence times were measured. It was found at 50°C, the coalescence time was less than half its value at 30°C. Similarly, use of 0.5 M nitric acid instead of DM water for stripping, reduced the coalescence time without increasing uranium concentration in the lean solvent. Based on these results, stripping is now carried out with 0.05 N acid.

4.3 Solvent Quality: Freshly prepared solvent gives high phase separation rate. As the solvent is recycled, the solvent quality degrades and phase separation time increases. This is independent of DBP and U concentration. For example, a fresh solvent yields complete batch coalescence in 1 min, solvent used for about a year requires 5 min for separation and a "rejected" lot (used over 2 years) does not yield separation even in 15 minutes. Hence a regular check on solvent quality is kept by an empirical batch test.

4.4 Solvent Entrainment Loss: Solvent is lost by entrainment into raffinate stream, alkali wash stream and pure solution stream from stripper. The physical solubility loss is comparatively lower. Studies have shown that alkali wash has maximum entrainment (9 - 15 ml/l) while raffinate loss varies 0.7 to 2 ml/l. The entrainment with pure solution is 0.5 to 3 ml/l, most of which is recovered by providing an intermediate hold-up tank for coalescence.

4.5 Product Purity: The overall performance has been very good, with less than 5% of total processed batches having high impurity level. The higher level is found to correlate with high impurity in feed itself resulting from recycle of raffinate cakes to dissolution. However, even for impure batches, the UO3 obtained was pure when EDTA was added during precipitation. No product solution was required to be recycled to starting stage, as was the case with pulse columns. In fact, an evaporator obtained to facilitate this recycle has been rendered redundant.

4.6 Fluoride Level: The fluoride content of the feed in some batches has been found to be high (over 1 gm/l). This creates severe corrosion problem in extraction battery, where some agitators have shown stress-corrosion cracking at weld joints of impeller to shaft. To avoid this problem, the fluoride-bearing solutions are processed separately in polypropylene mixer-settler.

4.7 Extraction from Fluoride Solutions: When magnesium fluoride is processed by acid leaching solution containing 10 - 15 g U/l, 1 - 3 g F/l and 7 gm Mg/l is obtained. This is highly corrosive. Recovery of uranium from this solution is best achieved by solvent extraction. A 5 stage mixer-settler battery operating at overall phase ratio of
O/A = 1/4 has been in operation for last 3 years. Internal recycle from settler to mixer is provided to maintain mixer ratio of O/A = 1.5/1 for efficient operation. The unit is made of polypropylene and transfer pumps of magnetic drive type are used. The extract containing 40-60 g U/l is fed to scrubbing battery of main unit. To ensure raffinate level of 0.5 gpl of U, it is necessary to restrict loading to 65-70 gpl, maintain FA of 2-2.5 N, and ensure that lean solvent has less than 2.5 g U/l.

4.8 Knit-mesh packing: A dual material woven stainless steel and polypropylene knitted mesh, packing has been installed in stripper. This has reduced emulsion band width by a factor of 2 and reduced entrainment losses by a factor of 5.

V. DEVELOPMENT AND DESIGN STUDIES

6.1 New Stripping Unit: Both batch and continuous single stage testing with used solvent was carried out under various conditions. The data is used for design of high capacity stripping unit. The settler flux of 2.5 m³/hr/m², top shrouded six-blade turbine mixer, hydraulically independent stages with internal recirculation are some of the salient features. This unit is under fabrication at Central Workshop of BARC.

5.2 New Solvent Processing Unit: Matching the capacity of new stripping unit, a high capacity alkali and acid washing mixer-settler battery has been designed and is under fabrication at Central Workshop, BARC.

In addition laboratory scale test-work has shown that distillation of solvent in 40°C - 130°C can improve solvent quality with reference to phase separation. The residue obtained (5% by volume) is thick viscous black liquid which causes emulsion formation.

5.3 Slurry Extractor: Mixer-settler battery for extraction is being replaced by a ‘slurry extractor’ developed in Nuclear Fuel Complex (4). The design has been made compact and modular for meeting site-specific constraints. The design of slurry extractor requires close control over phase-ratios, flow-rates and inter-phase level. An automatic control system is under development jointly with Reactor Control Division of B.A.R.C.
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