

LEACHING AND SOLVENT EXTRACTION AT MARY KATHLEEN URANIUM LTD.

By

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ABSTRACT

Mary Kathleen Uranium Ltd. recommenced operations in early 1976 following a twelve year period of care and maintenance. Several sections of the plant were modified or completely changed for the second operation. The most important change was the replacement of ion exchange with solvent extraction as the means of purifying and upgrading uranium rich solutions.

Most of the problems experienced in the solvent extraction system originate from the leach liquor which has a strong tendency to form stable emulsions. This has been countered by some careful control of leaching conditions and by closer observation of operations in the solvent extraction area. Most problems have now been resolved and plant recoveries are quite satisfactory.

INTRODUCTION

Mary Kathleen Uranium Ltd. first commenced the mining and milling of uranium ores in 1958. This operation ran successfully until 1963 when the lack of sales contracts forced the closure of the mine. The treatment plant was kept on a care and maintenance basis until the end of 1974 when the recommissioning commenced. Several alterations were made to the flowsheet and its various items of equipment before the re-opening of the treatment plant, the most

significant changes having occurred in the uranium extraction sections. These include: the use of a parallel cyclone wash circuit for coarse solids and a thickener wash circuit for fine solids in the liquid-solid separation section; the replacement of the pregnant liquor pre-coat filters with four sand clarifiers; the replacement of the ion exchange process with a solvent extraction section; the use of anhydrous ammonia in the precipitation section in place of caustic magnesia.

A flowsheet of the extraction section of Mary Kathleen is shown in Figure 1.

LEACHING

The leaching section consists of eight 3.6 m diameter by 6.1 m deep vessels arranged in two sets of parallel banks of four vessels in series. Feed to the leaching section is divided equally between the two banks in a simple pulp splitter box. There is provision to add water into this box to control leach temperature. Pulp flows from one vessel to the next via an overflow spout directly opposite the incoming feed. Bypass launders are available so any vessel may be emptied for maintenance. Each vessel has a conical bottom fitted with a dump valve.

Each vessel is agitated by two stage mixer turbine agitators driven by 37.3 kW motors through Falk triple reduction gear boxes.

All components in contact with the leach pulp are rubber lined to resist abrasion and corrosion.

Sulphuric acid, produced in another section of the treatment plant, is added at 98.5 percent

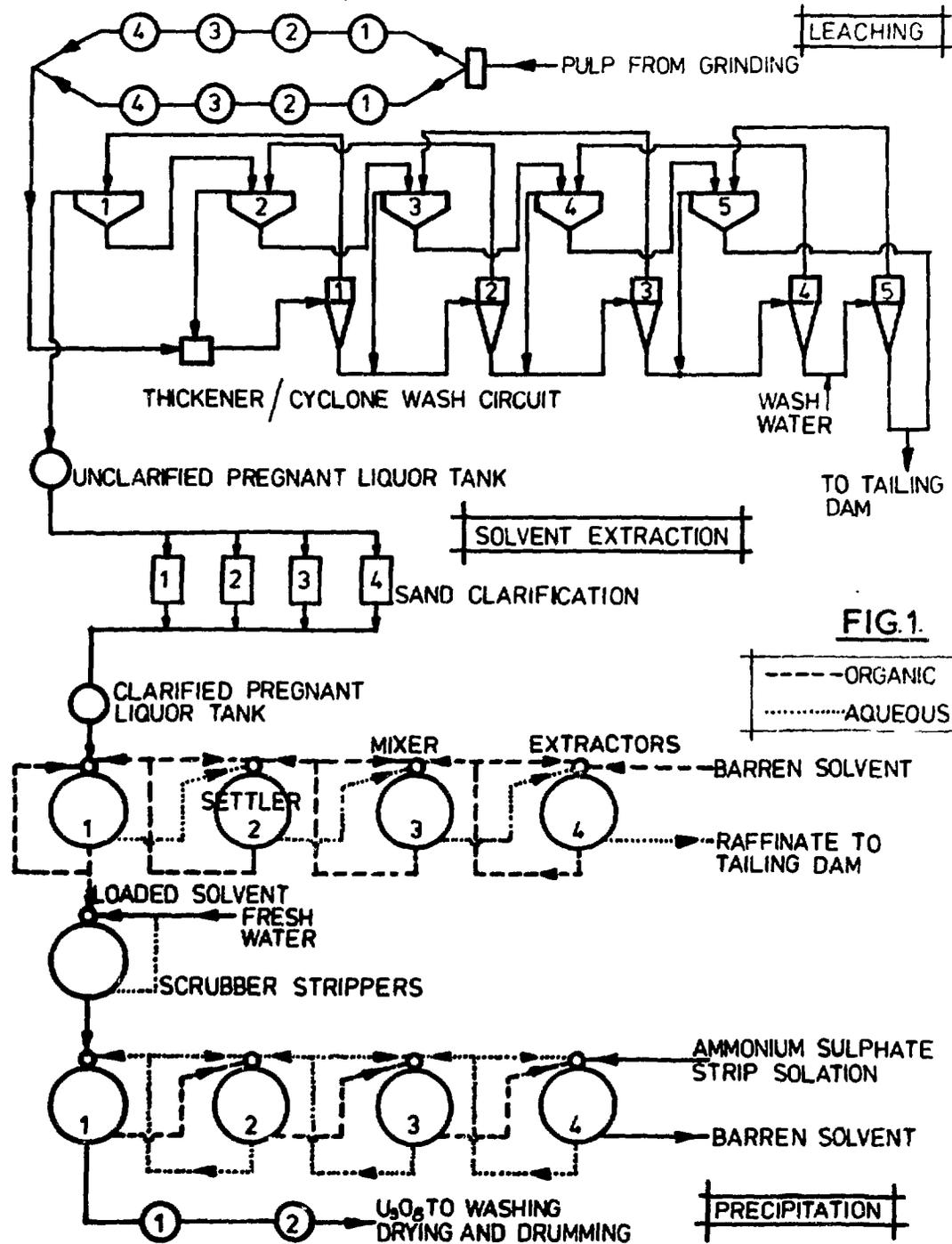
PLANT METALLURGIST

MARY KATHLEEN URANIUM LTD.

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FLWSHEET FOR LEACHING, L.S.S. AND SOLVENT EXTRACTION SECTIONS



strength to each vessel through automatic valves fitted with Viton diaphragms. Each automatic valve has a manual by-pass system. Acid is added to the pulp by simple drop pipes extending one metre into the pulp. Redox potential in the leach pulp is maintained by the addition of pyrolusite (containing 50 - 54 percent MnO₂) in the grinding circuit.

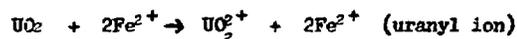
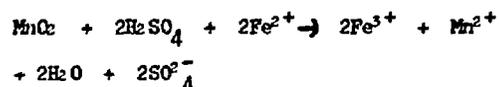
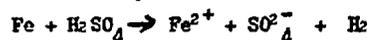
Instruments in the leaching section currently measure pH in each vessel and redox in the second and third vessels of both banks.

Provision has been made for the inclusion of two extra leaching vessels one for each bank. These vessels are larger being 4.6 m diameter and 5.2 m deep and are flat bottomed vessels. They will become the final leach vessel in each bank.

CHEMISTRY

Uranium is present in the ore in the mineral uraninite finely disseminated in allanite. The uranium is present partly in the tetravalent state and this must be oxidised to the hexavalent state before dissolution occurs. Pyrolusite (approximately 50 - 54 percent MnO₂) is added to the leach vessels for this purpose. The pyrolusite upon dissolution in the leach liquor, oxidises iron present in solution, either dissolved from the ore or introduced by wear of grinding media, to produce ferric ions. This in turn oxidises the uranium from the tetravalent to the soluble hexavalent state. The ferric ions are reduced to ferrous ions in this reaction.

Briefly the chemical reactions are :



A more complete description of this process can be found in Merritt (1971).

OPERATIONAL PROCEDURE

Several variables control the rate of leaching and the ultimate leach recoveries.

Redox potential

The control of an adequate redox potential is the key to maximum leach recoveries. Values above 400 mV must be held otherwise a substantial decrease in leaching rate will be experienced. Data collected so far indicated that there is little benefit in leach efficiency in increasing the redox potential above 500 mV.

In fact high values have a marked detrimental effect as they cause overleaching. This produces an excess of slime difficult to handle in liquid-solid separation and high levels of dissolved impurities, noticeably in silica, potentially harmful to solvent extraction.

The correct addition of pyrolusite has been difficult to maintain due to long lag times between addition of pyrolusite and the measurement of redox potential. Also the control of feedrate has been a problem as the particle size is large and feedrates are low.

pH

The leaching pH is controlled by the addition of 98.5 percent sulphuric acid. The pH is reduced stagewise to restrict acid consumption and the set points currently used are 2.2, 2.0, 1.8 and 1.8 for the four vessels respectively. Lowering set points below these values does not appear to improve leaching rate recovery and is detrimental in that it increases acid consumption and generates over-leached fine material.

The redox measurement of each vessel is pH dependent. If the pH rises above the set point the redox value decreases, probably due to a reduction in the dissolution rate of the pyrolusite.

Regular cleaning of pH probes and acid drop lines is required because of rapid deposition of calcium sulphate.

Pulp Density

The discharge density of the pulp from the grinding circuit is controlled to about 50 percent solids. For higher densities, temperatures become excessive and overleaching occurs. Also, as densities approach 60 percent solids reaction rates decrease with increasing pulp viscosity.

Low densities are detrimental because of

1. shorter particle residence time in the leach vessels;
2. a reduction in leach rate due to lower leach temperatures, and
3. a low density feed to the liquid-solid separation circuit reduces the washing efficiency.

Temperature

In the leach vessels, heat is released by the dilution of concentrated sulphuric acid in water. According to the quantity of water present, or pulp density the temperature may range from near ambient upwards to as high as 90°C. In practice the temperature is controlled in the range 45 - 60°C by water addition to the pulp. This avoids the problems of overleaching whilst maintaining the leaching rate as high as possible.

Residence Time

Residence time in the leach vessels is determined by the pulp density and mill tonnages. Typically for a 70 tph mill tonnage producing a 50 percent solids pulp the residence time in the leach vessels is four hours. Provided redox values are sufficient, i.e., 400 mV and pH values are correct almost total leaching can occur within one hour.

Particle Size

The reduction in average particle size has not produced any significant effect on leach recoveries for sizes finer than 212 micrometres. The average grind sizing is 55 percent minus 75 micrometres.

LIQUID-SOLID SEPARATION

Liquid solid separation is carried out using a five stage countercurrent washing cyclone circuit operating in parallel with a five stage countercurrent thickener circuit. An initial split of fine and coarse particles is made in the No. 1 cyclone and fine particles then pass through the thickener circuit whilst the coarse particles are washed in the remaining cyclones. Wash water enters the circuit through No. 5 cyclone feed and then passes alternatively between cyclone and thickener in decreasing order. The overflow from No. 1 thickener passes to the solvent extraction section for clarification. The wash water is acidified to pH 2.0 in order to improve settling properties of the fine material. Raffinate from the solvent extraction section can be used for wash water. Its use is restricted because it contains some solvent carry-over which adversely affects any natural rubber lined components of the circuit. Also some impurities such as phosphate and silica in solution can cause problems in solvent extraction if they are continuously recycled.

Pulp densities of the thickener underflows are maintained between 50 - 55 percent solids and of the cyclones underflows between 65 - 70 percent solids.

All thickeners, cyclones and auxiliary components are rubber lined.

Thickener underflow pulp is transferred with VMR 6 Dorrco diaphragm pumps with a Warman repulper between each stage.

Each cyclone is fed by a 6/4 Warman pump.

The underflow from No. 5 cyclone and No. 5 thickener are combined and pumped to the tailings dam.

The aqueous feed to solvent extraction usually contains 0.5 g/l U_3O_8 at a flowrate of 2400 lpm.

SOLVENT EXTRACTIONEQUIPMENTSand Clarification

The pregnant liquor which overflows No. 1 thickener passes to an unclarified pregnant liquor storage tank 7.3 m diameter x 4.5 m high. The liquor is pumped from here to the sand clarification columns for removal of suspended solids. There are four columns each 2.4 m diameter and 4 m high and containing a 1.8 m deep bed of sand retained by layers of graded gravel. Three columns are used for clarification whilst the fourth is either back washing or on standby. The liquor is split equally between the three clarifiers and passes downwards through the bed. When the differential pressure between the top and bottom of the bed exceeds 70 kPa the column is removed from service for backwashing. The column is drained, filled with water, air agitated, and backflushed with water. The bed is then reconsolidated, and finally refilled ready for use.

The solids removed by backflushing are currently sent to tailings.

The clarified liquor is then sent to a clarified pregnant liquor storage tank which is 7.3 m diameter x 4.5 m high.

Extraction

The extraction of the uranium from the pregnant liquor now takes place in four mixer settler units. The pregnant liquor or aqueous phase is contacted with a solvent or organic phase which flows countercurrent to the aqueous phase. The solvent has three components : a tertiary amine, Adogen 364 from Ashland Chemicals, which has the ability to selectively extract uranium from aqueous solution; Nonanol, a long chain alcohol which is added as a modifier to prevent the formation of third phase amine salts and to improve phase separation, home heating oil which is used as a carrier for the tertiary amine.

The proportions are : Adogen 364 4%
Nonanol 7%
Home heating 92%
Oil

The solvent is contacted with the clarified pregnant liquor in a series of mixers each 1.7 m diameter by 1.8 m high and constructed of stainless steel. All interstage transfer of aqueous and organic phases is carried out by the mixer impellers which are a type of shrouded turbine and provide both pumping and mixing of the phases to be contacted. These units are driven by 11.0 kW motors with Reeves variable speed drives connected to 20 to 1 reduction gearboxes.

Three streams enter each extractor mixer :

1. interstage solvent phase,
2. interstage aqueous phase,
3. recycle solvent phase.

Following contact in the mixer the aqueous solvent emulsion overflows to a fibre glass lined settler of 9.7 m diameter by 4.5 m. Isophthalic resins are used in the fibre glass linings. Wooden baffles are placed in this mixer to evenly distribute flow patterns across the settler. In the settler the solvent and aqueous phases disengage and aqueous and solvent bands emerge. Typically solvent layers of 0.4 m are present with aqueous layers of 4.0 m

The separated phases then overflow internal weirs inside the settlers. The aqueous phase then passes to the next mixer whilst the solvent phases flows to an external weir. Each external weir has two compartments. The first compartment contains the inlet flow from the internal weir and an outlet for the recycle solvent line to the mixer of that same vessel. Any solvent not required for recycle overflows a fixed weir into a second compartment where it is transferred to the next stage of the process.

All transfer lines are fitted with valves for regulation of flows.

Levels inside the settler can also be

adjusted by the change of internal weir heights. This method is very useful for the control of solvent depths in the settlers.

Sight-glasses are provided on all vessels to give indication of the relative heights of aqueous and solvent layers.

Typical flowrates are 2400 lpm of aqueous and 400 lpm of solvent, these flows giving an effective sixfold upgrading of the uranium concentration. The loaded solvent contains between 3 - 5 g/l U_3O_8 . Recycle solvent flowrates are of the order of 3200 lpm. Recycle of solvent is necessary to improve the phase ratios of solvent to aqueous in the mixer to greater than 1.3/1. This ratio must be maintained to keep the mixer operating on a solvent continuous phase, i.e., an emulsion of aqueous droplets contained in a continuous solvent phase. If the mixer "flips" or changes to an aqueous continuous phase the resultant emulsion will be very stable and will not disengage quickly enough in the settler.

The aqueous solution which has passed through four extractors is now termed raffinate and this liquor is pumped to the tailing's dam. Raffinate may be recycled as wash water in the wash circuit if necessary. The raffinate normally contains 0.003 g/l U_3O_8 .

Each mixer is fitted with a conductivity mixer.

The pH of the incoming pregnant liquor is adjusted to 1.7. Too low a pH decreases the extraction coefficient of the solvent whilst too high a pH can cause problems with slow settling emulsions.

The loaded solvent then passes to a scrubber tank 4.5 m diameter by 4.5 m. Here the solution is contacted with a fresh water flow of 100 lpm and a recycle aqueous flow sufficient for scrubber mixer to operate on aqueous continuous phase. This removes the majority of entrained aqueous impurities from the solvent as the solvent phase is now

disengaging from a solvent aqueous emulsion and the chances of entrainment are considerably reduced. Excess aqueous phase is returned to the first extractor.

Strip Circuit

The clean loaded solvent is now ready for stripping. The extraction process can now be reversed as impurities have now been removed in the raffinate. The loaded solvent is now contacted with a 100 - 120 g/l solution of ammonia sulphate in a four stage countercurrent circuit with the pH being adjusted to 4.4 in two stages. This strips uranium from the solvent and loads the ammonia sulphate solution to produce a high grade strip liquor which is suitable for direct precipitation of ammonium diuranate at pH 7.5.

The strip circuit consists of four vessels each of the same design as the extractor mixer settlers but smaller, the settlers being 4.5 m diameter by 4.5 m. Flow between vessels uses the same system of internal and external weirs with the exception that no recycle is required for the first strip vessel. The remaining three strip vessels have aqueous recycle to allow the mixers to operate on aqueous continuous phase. The first vessel operates organic continuous in order to reduce organic carryover to the precipitation section whilst the other strip vessels operate aqueous continuous because this allows easier pH control and measurement.

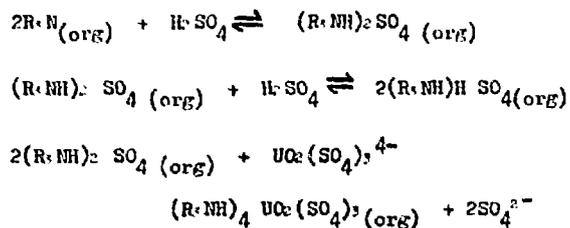
The pH is adjusted in the second and third stages to 4.0 and 4.4 respectively by the addition of a 5 percent aqueous ammonia solution.

The ammonia concentration is measured by the temperature differential between the water and aqueous ammonia solution.

Chemistry

Uranium can be extracted from sulphate leach liquors as a sulphate anion by high molecular weight tri-alkyl tertiary amines. Formation of the amine sulphate and bi-sulphate salts and typical extraction reactions are

shown as follows :



The ability of the solvent to extract uranium from aqueous solutions is determined by the extraction co-efficient for the given conditions. This is a measure of the overall driving force of the reaction and is analogous to the equilibrium constant of an ordinary chemical reaction. The extraction co-efficient varies with the aqueous and organic uranium concentrations and the manner in which it does this determines the number of stages and efficiency of each stage.

Uranium can be stripped from amines by a variety of stripping agents including nitrates, chlorides, sulphates, carbonates, hydroxides, dilute acids and by a controlled pH stripping with ammonium sulphate solution.

More detailed accounts of the chemistry of solvent extraction can be found in Merritt (1971).

OPERATIONAL PROCEDURE

Interface Levels

The key to the efficient operation of the solvent extraction system at Mary Kathleen is to maintain steady state conditions within mixers and settlers. Correct settings of mixer speeds, flow rates, interface levels as regulated by weir heights and recycle flows are all important to keep the system balanced. Uneven flow surges of either aqueous or organic phases through the system can cause temporary flooding, inefficient extraction, increased solvent losses and worst of all, the formation of very stable emulsions or crud.

The equilibrium position of the interface in a settler is controlled by the difference in

densities between the two phases and by the difference in the levels of the two internal overflow weirs. Effective weir heights include the flow crest over the weir. The interface adjusts to the position where hydrostatic pressures are balanced. The depth of the solvent layer when at equilibrium, is approximately five times the difference in effective weir heights and any change in weir height differences results in five times that change to the interface position. This happens when a significant change is made in the flowrate of one phase. This causes a change in flow crest height over the weir and thus alters the effective difference in weir heights. Similarly the flooding of a weir box can cause major changes to interface equilibrium positions. Because a shift of interface involves large volumes it takes some time to reach new equilibrium positions, meanwhile it causes surges of interstage flow rates and the subsequent compounding of problems in other settlers.

Crud Formation

A solvent must be capable of rapid and complete separation from the aqueous phase before any solvent extraction system is feasible. Any tendency for the formation of stable emulsions or crud must be avoided to prevent high solvent losses and, in the extreme, the shutdown of the section for a total clean out. When crud does form the loss of solvent stocks can be very rapid and a major replenishment of inventory could be necessary.

Crud normally appears as a light brown, porridge like substance at the aqueous - solvent interface. It consists of aqueous and solvent phases combined with any fine solids and precipitates contained in the pregnant liquor.

Crud formation is particularly enhanced by the presence of any fine solids in solution, solids which have not been removed by sand clarification. This condition particularly applies to the amine type extractant commonly

used in uranium solvent extraction plants. Feed solutions should contain less than 50 ppm suspended solids but even at this level very fine quantities of crud will form with corresponding extra losses of solvent.

The rate of crud formation is considerably increased if certain impurities are present in the liquor. At Mary Kathleen the most troublesome impurity is dissolved silica and concentrations of 3 g/l normally lead to massive crud formations. Under normal conditions dissolved silica levels rarely exceed 1 g/l but when overleaching occurs silica levels rapidly increase and the problem is complicated by the presence of very fine solids in overleached liquors. Once silica concentrations exceed 3 g/l the section virtually cannot be operated as any mixing of solvent and aqueous phases forms crud and the solvent band diminishes. Once crud begins to be recycled with the solvent the rate of formation and the stability of the crud both increase rapidly. The section must be shutdown long before this happens and any high silica concentration liquor removed from the circuit.

Phase disengagement is also influenced by the emulsion type, that is, whether the emulsion is a dispersion of organic droplets in a continuous water phase or a dispersion of water in a continuous organic phase.

These phases are known as aqueous continuous and organic continuous respectively. At Mary Kathleen phase disengagement in the extractor circuit is much faster from the organic continuous phase as this type of emulsion is less affected by dissolved silica. Concentrations as low as 0.7 g/l silica have been known to cause stable emulsions in aqueous continuous systems.

Recycling techniques are used to ensure correct emulsion type in the settlers mixers. Sufficient solvent is recycled to keep the organic to aqueous ratio at or above 1.3 to 1.

Typically for an aqueous flowrate of 2400 lpm and a solvent flowrate of 400 lpm a solvent recycle of at least 2720 lpm would be required.

When the feed solution contains fine suspended solids or high silica concentrations the organic to aqueous ratio in the extractors should be increased to as high as 2 to 1 to prevent the mixer from flipping to the wrong phase. When a mixer flips after a period of steady operation this usually indicates a deterioration in the quality of the feed liquor.

Other factors to affect crud formation are mixer speeds and high pH levels. High mixer speeds can cause increased shear which produces a finer dispersion of each phase in the other. This may promote crud formation and greater entrainment losses. Within the small range of mixer speeds available at Mary Kathleen no effect of mixer speeds has been apparent. High pH values are also known to promote crud formation and poor extraction. So far this problem has not been apparent.

Because leach liquors at Mary Kathleen are susceptible to crud formation solvent losses are higher than in some other operations. Total evaporation and entrainment losses are around 400 ppm for normal conditions.

Design Problems

The circuit when designed did not make sufficient allowance for the crud formation properties of the local leach liquors. There is little ability to increase recycle flows to a level which is necessary for dirty liquors. This has resulted in the mixers being operated at or near maximum speeds constantly. This has led to frequent mixer breakdowns, and, as no bypass system is available, resulted in section shutdowns.

Also no provision was made for the removal of crud from the circuit. Crud is now pushed from extractor to extractor until it collected in the scrub vessel. From here it is dumped into a bund area and pumped to a crud storage vessel.

This procedure requires the crud to pass through as many as four mixers with the resultant formation of more crud on each pass.

PRECIPITATION

The aqueous liquor overflowing the first strip vessel is termed high grade strip liquor and is pumped directly to a two stage precipitation circuit. Anhydrous ammonia is added to these vessels to adjust the pH to 7.0 and 7.8 in the first and second stage respectively. With the increase in pH the uranium in solution precipitates as ammonium diuranate $(NH_4)_2U_2O_7$.

CONCLUSION

Following early teething problems the leaching, liquid-solid separation and solvent extraction sections are now operating quite satisfactorily. With increased throughput it

has become necessary to keep a closer control over certain variables to maintain maximum plant efficiency. In the leaching section the emphasis is on holding correct pH and redox values. In the solvent extraction section it is important to receive clear feed liquors, to maintain correct phase continuity and to hold correct pH readings in the strip circuit.

ACKNOWLEDGEMENT

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REFERENCE

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