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ABSTRACT

Nuclear purity uranyl nitrate solutions were produced from Rum Jungle yellow cake by dissolution in nitric acid and purification by solvent extraction with 20 vol.% tributyl phosphate in kerosene using pump-mix mixer-settler contactors. The design of the equipment, experimental studies and operating experience are described.

Dissolution of yellow cake and recycled uranium oxide materials was readily carried out in a 100 ℓ dissolver to give solutions containing 300 gU ℓ^{-1} and 0.5 to 4 $\mathfrak{M}$ nitric acid. Filtration of silica from this solution prior to solvent extraction was not necessary in this work for yellow cake containing 0.25 per cent silica.

A low acid flowsheet for uranium purification was developed in which the nitric acid consumption was reduced by 76 per cent and the throughput of the mixer-settler units was increased by 67 per cent compared with the initial design flowsheet. Nine extraction and seven scrubbing stages were used with a feed solution containing 300 gU ℓ^{-1} and 1.0 $\mathfrak{M}$ nitric acid and with a portion of the product recycled as scrub solution. The loaded organic phase was stripped in 16 stages with 0.05 $\mathfrak{M}$ nitric acid heated to 60° C to give a 120 gU ℓ^{-1} product. The uranium concentration in the raffinate was < 0.04 g ℓ^{-1}, corresponding to ~ 0.01 per cent of the feed.

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AQUEOUS SOLUTIONS; DISSOLUTION; FILTRATION; FLOWSHEETS; FUEL FABRICATION PLANTS; INDUSTRIAL PLANTS; NITRIC ACID; OPERATION; PRODUCTION; PURIFICATION; SOLVENT EXTRACTION; SPECIFICATIONS; TBP; URANIUM DIOXIDE

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1. INTRODUCTION

As part of the Australian Atomic Energy Commission's program to investigate all aspects of the production of fuel elements for uranium dioxide (UO_2) fuelled, water–cooled power reactors, pilot plant facilities were established for the production of nuclear grade natural uranium dioxide powder from Australian ore concentrates (Alfredson 1972). The objectives of this research and development work were to establish the necessary technology using conventional techniques and to make improvements in processes and equipment where possible.

This report describes the development of processes for the production of nuclear purity uranyl nitrate solutions from Rum Jungle uranium ore concentrates (yellow cake). The well established route for uranium refining, involving dissolution in nitric acid and purification by solvent extraction using tributyl phosphate, was adopted. Dissolution of yellow cake was carried out in a batch dissolver and mixer-settlers were chosen as the solvent extraction equipment because of previous experience with these units. The design of the equipment, development of process flowsheets, including a low acid solvent extraction process, and operating experience are described.

2. DISSOLUTION

The dissolution step was designed to process yellow cake as well as recycled uranium materials (ammonium diuranate (ADU), UO_2 powders and pellets, *etc*.), and to permit dilution and adjustment of acidity of the solutions. In general, a dissolver product solution containing 300 gU ℓ^{-1} and 0.5 to 4 M nitric acid was used as the feed for the solvent extraction processes.

2.1 Design of the Dissolver

An existing 100-litre dissolver constructed of AISI 321 stainless steel was used in this work. The dissolver was heated *via* steam coils and the contents were agitated by sparging with air. A reflux condenser mounted on top of the dissolver served to minimise loss of nitric acid fumes from the dissolver and,in conjunction with air sparging, to recover some of the nitrogen oxide off-gases produced in dissolution; for example

$$U_3O_8 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + 2NO_2 + 4H_2O \quad (1)$$

$$UO_2 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O \quad (2)$$

$$2UO_2 + 6HNO_3 \rightarrow 2UO_2(NO_3)_2 + NO + NO_2 + 3H_2O \quad (3)$$

$$3UO_2 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + 2NO + 4H_2O \quad (4)$$

It also allowed the removal of the exothermic heat of dissolution. The off-gases from the condenser were scrubbed with 10 wt.% sodium carbonate, or hydroxide solution in a packed column, before being discharged through de-entrainment separators to the building ventilation system. Detailed design features of the dissolver are summarised in Table 1. Figure 1 is a general view of this equipment and Figure 2 is a detailed equipment flowsheet of the dissolver system.

Steam pressure to the dissolver was limited to less than 0.2 MPa (gauge) by means of pressure regulating and relief valves so that the surface temperature of the steam coils could not approach 135 °C during the occasional boiling down of uranyl nitrate solutions possibly containing tributyl phosphate solvent. Above this temperature, explosions have been observed (Colven, Nichols and Siddall 1953). The dissolver was designed for operation at atmospheric pressure and was protected by a pressure control device set to vent at 1.25 kPa.

2.2 Operational Experience

For about 4 years, uranium materials containing approximately 3 Mg uranium were dissolved successfully in batches of up to 25 kg of contained uranium without any operational problems. Yellow cake and ADU were found to dissolve satisfactorily by adding all the required acid over a quarter of an hour, then heating the reactor to about 100 °C, giving a total dissolution time of half an hour. The heat of dissolution was not sufficient to maintain the required temperature and steam heating was needed. Dissolution of UO_2 powder was strongly exothermic; the required acid was added to a preheated (80 °C) slurry in 0.5 ℓ lots over a total of four hours until dissolution was complete. With UO_2 pellets, some UO_2 remained undissolved even after twelve hours.

The presence of silica in mixer-settlers tends to retard the rate of disengagement of the mixed phase in the settlers, can result in enhanced carryover of phases and reduced decontamination between stages, and may require a reduction in throughput to maintain hydraulic stability. The silica precipitates slowly from acid solutions to form a gel which is difficult to filter (Mason and Smith 1965). Late precipitation of silica gel in the mixer- settlers can also lead to blockages of ports (Littlechild 1967). These problems can be minimised by heating the dissolver solution at above 95 °C for at least two hours; this treatment causes the silica to precipitate quickly (Tunley and Hart 1965) and modifies the gelatinous precipitate to a semi-crystalline form which is more readily filtered (Mason and Smith 1965). A digestion of four hours at 100 °C was used as a standard process.

Approximately one mol of sodium hydroxide was consumed per mol of uranium in scrubbing the off gases during the dissolution of UO_2. By comparison, only 0.3 mol of sodium hydroxide per mol of uranium was required during the dissolution of ADU or yellow cake.

3. FILTRATION

In other countries there are various opinions on the need to filter the dissolver solution prior to solvent extraction. The UKAEA practice is to filter all solutions on a precoated, rotary drum vacuum filter (Littlechild 1967), whereas French plants decant the clear liquor and filter the settled liquors on a rotary drum vacuum filter (Decrop *et al.* 1958). Producers in the United States (Thayer 1958) and Canada (Burger and Jardine 1958) do not filter their solutions.

The UKAEA filtration practice has been reported in detail (Mason and Smith 1965) and is based on concentrates varying from 0.7 to 4.0% silica which are blended to produce a solution of 1.8% silica on a uranium basis. The Rum Jungle concentrates used in the present work contained only approximately 0.25% silica on a uranium basis.

No difficulties were encountered in our pump-mix mixer-settler units because of the presence of silica in the feed, although blockages of the flowmeter and valve used to control the feed rate did occur initially when a gravity feed system was employed. A piston-type metering pump was installed in place of the flowmeter and valve and operated satisfactorily. Brief tests with a solid bowl centrifuge indicated that the silica could be removed readily if required.

4. DESIGN OF SOLVENT EXTRACTION FLOWSHEETS

4.1 Concentration of Solvent

Tributyl phosphate (TBP) is widely used for the purification of uranyl nitrate because of its low mutual solubility with an aqueous phase and its relatively high selectivity for uranyl nitrate, which it extracts as an undissociated molecule. However, as pure TBP has a fairly high viscosity and a density very similar to the densities of the aqueous solutions encountered in uranium purification, it is normally used in an inert diluent, often a paraffinic fraction, such as 'odourless' kerosene or 'odourless' mineral spirits ('odourless' meaning aromatic-free). The

extraction properties of TBP seem to be very little affected by the particular diluent chosen (Apelblat and Faraggi 1966).

The concentration of TBP chosen for uranyl nitrate purification varies among processing plants in the range 20 to 40 volume per cent, the former being favoured in the United Kingdom (Page *et al.* 1960) and the latter in France (Decrop *et al.* 1958). Above about 35 per cent, the density of the extract can become greater than that of the feed solution and phase inversion can occur in the solvent extraction equipment. In general terms, as the solvent is made more dilute, larger volumes of liquid must be handled to attain a specified extraction capacity, and hence costs increase (Harrington and Ruehle 1959). However, dilution allows a greater difference in the density of the phases, improved rates of disengagement in the settlers and a higher organic to aqueous flow ratio in the stripping section of the plant, increasing the ultimate uranium concentration in the product.

A low TBP concentration also has the advantage of increasing the difference between the partition coefficients of the uranium and impurity elements (Wood and Williams 1958). Harrington and Ruehle (1959) reported that equipment and operating costs are approximately constant in the range 22 to 30 per cent TBP. In this work, 20 volume per cent TBP in odourless kerosene was chosen as the solvent, following the UKAEA practice (Page *et al.* 1960).

4.2 Equilibrium Data

The equilibrium data for uranium distribution at 25 °C, which were used for flowsheet calculations in this work, are shown in Figure 3 and are based on the work of Apelblat and Faraggi (1966). The nitric acid concentrations for the equilibrium lines refer to the concentrations in the aqueous phase. Uranium distribution is sensitive to acid concentration, especially at low uranium concentrations.

The effect of temperature on the uranium equilibrium data is most marked at low acid concentrations (Rozen *et al.* 1962, Harrington and Ruehle 1959). Figure 4 shows this effect using data from Rozen *et al.* for typical uranium stripping conditions (0.05 M HNO_3). The results of equilibrium measurements made during this work (Table 2) in the temperature range 16.5 to 29.5 °C are shown in Figure 5. The interpolated (dashed) line corresponds to a temperature of 25 °C and agrees with the data in Figure 3 for zero acid concentration within 5 per cent. An increase in temperature decreases the extraction of uranium into the solvent phase, thus enhancing the efficiency of the stripping stages. Conversely, the efficiency of the extraction cycle is diminished by an increase in temperature, though this effect is not nearly so marked as in the stripping stages, and it is desirable to maintain the temperature of the extraction stages as low as practicable.

Equilibrium data for nitric acid distribution as a function of uranium concentration (Wood and Williams, 1958) are shown in Figure 6. Similar data have been presented by Rozen *et al.* (1962), Apelblat and Faraggi (1966) and other workers. The nitric acid concentration in the organic phase decreases with increasing uranium concentration in the aqueous phase and is not much affected by the acid concentration in the aqueous phase, except at low uranium concentrations (< 10 g ℓ^{-1}). Interpolation on Figure 6, for values of uranium concentration not shown, is almost linear (Wood and Williams 1958).

4.3 High Acid Flowsheet

Initially, a high acid solvent extraction flowsheet was employed in the experimental program: a feed solution containing 300 gU ℓ^{-1} and 4 M free nitric acid was selected, the loaded solvent was scrubbed with 1 M HNO_3, and the purified uranium was stripped from the solvent using dilute nitric acid solution. Stripping was carried out initially with 0.01 M HNO_3 but this was later changed to 0.05 M HNO_3, as discussed in Section 6.1.

The required number of ideal stages was calculated by the McCabe-Thiele method allowing for the co-extraction of uranium and nitric acid by the method of Wood and Williams (1958). Initially, the calculations were made assuming the extraction stages operated nominally at 3 M HNO_3, the scrubbing stages at 1 M HNO_3 and the stripping stages at 0.0 M HNO_3 (Figure 3). Assuming a 'pinch' (see below) at a uranium concentration in the aqueous phase of ~ 100 g ℓ^{-1}, three ideal stages of extraction were required to reduce the uranium concentration in the raffinate to less than 0.05 g ℓ^{-1}, and six ideal stages were required to strip the loaded organic (60 gU ℓ^{-1}) to less than 0.1 gU ℓ^{-1}. For efficient and stable operation in the scrubbing stages, a 'pinch' must be obtained, that is the equilibrium and operating lines should cross or be tangential. Under these conditions, changes in the flowrates of the aqueous and organic phases or in the number of stages have little effect on the uranium concentration in the loaded organic, but improved decontamination from impurities can be obtained. Figure 3 does not show a pinch, but when the co-extraction of nitric acid is allowed for, a pinch is obtained just above the feed stage.

As stated above, Figure 3 takes no account of changes in acidity along the contactor due to the co-extraction of nitric acid as well as uranium, nor of changes in volume owing to the transfer of uranium from one phase to the other. The latter is of the order of 5 per cent (Wood and Williams 1958) and is usually neglected. Figure 6 shows McCabe-Thiele calculations for nitric acid extraction, based on the uranium concentrations calculated from Figure 3. The nitric acid concentration in the extraction stages exceeds the concentration in the feed solution, particularly close to the feed stage, and enhances uranium extraction. The McCabe-Thiele calculations for uranium extraction were repeated using the nitric acid concentrations calculated in Figure 6. The required numbers of ideal stages for extraction and stripping were unchanged compared with Figure 3, but a pinch was obtained in the scrubbing section after approximately three ideal stages.

Figure 7 summarises the calculated high acid flowsheet.

4.4 Low Acid Flowsheet

Essentially all of the free acid in the feed solution, and that added in the scrubbing stages, is discharged in the raffinate waste stream and must be recovered for an economic large-scale operation. Littlechild (1967) reported briefly a modified flowsheet, in use in the UKAEA, in which the acid scrub was replaced by recycling part of the purified product and reducing the scrub volume. This increased the uranium concentration in the scrubbing stages and in the loaded organic and enabled a more concentrated product (100 gU ℓ^{-1}) containing less free acid (< 0.1 M HNO_3) to be produced. Increasing the uranium saturation of the solvent is advantageous in increasing the decontamination factor for impurity elements (Lang and Krieg 1959). The use of uranyl nitrate product as scrub solution also increased the throughput of the UKAEA purification and evaporation plants and reduced corrosion of the evaporators.

The effect on uranium extraction of free acid concentrations in the feed and of uranyl nitrate scrub solution was examined in this work. The distribution coefficient for uranium is sensitive to acid concentration in the aqueous phase, especially at low uranium concentrations (see Figure 3). Some free acid is essential in the feed solution if low uranium values (< 0.05 gU ℓ^{-1}) in the raffinate are to be achieved when the recycled organic contains up to 0.1 gU ℓ^{-1} because of the inflection in the equilibrium curves, particularly at nitric acid concentrations less than 1.0 M. McCabe-Thiele calculations of the number of ideal extraction stages to produce a uranium concentration less than 0.05 g ℓ^{-1} in the raffinate, gave five stages for free acid concentrations in the feed of both 1.0 and 3.0 M.

With 0.5 M acid in the feed solution and a uranium concentration of 0.1 g ℓ^{-1} in the recycled organic phase, a uranium concentration in the raffinate of 0.05 g ℓ^{-1} cannot be obtained because of a pinch in the extraction stages. If the recycled organic contains only 0.05 g ℓ^{-1}, approximately seven theoretical extraction stages are required to give a uranium concentration in the raffinate of 0.05 g ℓ^{-1}. Figure 8 illustrates these calculations for 0.5 M free acid in the

feed and uranyl nitrate solution (100 gU ℓ^{-1}) as the scrub solution (co-extraction of nitric acid is neglected). The acid concentrations in the extraction and scrubbing stages were assumed to be 0.5 and 0.0 M respectively.

With a uranium concentration in the loaded organic of 70 g ℓ^{-1}, approximately 12 ideal stages are required to give a 100 g ℓ^{-1} product and reduce the uranium concentration in the stripped organic to less than 0.05 g ℓ^{-1}. Figure 9 summarises this calculated low acid flowsheet in which the feed solution contains only 0.5 M free acid, portion of the product solution (100 gU ℓ^{-1}) is recycled as scrub liquor and approximately 7, 5 and 12 ideal stages are required for extraction, scrubbing and stripping respectively.

Experimental difficulties were encountered in reducing the uranium concentration in the recycled organic to these low levels in the 16-stage stripping unit (see Section 6.2). However, increasing temperature enhances the efficiency of stripping. At 60°C, six stripping stages can give a uranium product containing 120 gU ℓ^{-1} from a loaded organic containing 70 gU ℓ^{-1} and a recycled organic stream containing < 0.1 gU ℓ^{-1} (Figure 4).

Cavendish and Leist (1970) reported a somewhat similar flowsheet using a feed solution containing 400 gU ℓ^{-1}, 0.5 M free nitric acid, and 0.5 M ammonium nitrate. The ammonium nitrate provided as much salting strength (displacement of uranium from the aqueous to the solvent phase) as 2.5 M nitric acid.

5. SOLVENT EXTRACTION EQUIPMENT AND PROCEDURE

An equipment flowsheet for the purification of uranyl nitrate by solvent extraction is shown in Figure 10.

5.1 Design of Mixer–Settlers

Two identical, general purpose 16-stage mixer-settler units were used, one for extraction and scrubbing and one for stripping. The design of the mixer-settler units is shown in Figure 11 and a general view of the equipment in Figure 12. The mixer-settlers were of the pump-mix design based on the original KAPL work (Coplan *et al.* 1954) and incorporating some of the developments of Baillie and Cairns (1958, 1960) and Cairns *et al.* (1967). The units were constructed of AISI Type 321 stainless steel, with Perspex windows and polytetrafluorethylene gaskets. The feed point in the extraction/scrubbing unit could be varied from the sixth to the tenth stage.

Each mixer was 63 mm x 63 mm x 93 mm deep and each settler was 63 mm x 203 mm x 165 mm deep, corresponding to design residence times of 30 seconds in the mixer and 180 seconds in the settler. These parameters corresponded to a total phase flowrate of 47 ℓ h^{-1} in the stripping unit, equivalent to a throughput of 1.5 kgU h^{-1} on the basis of the flowsheet in Figure 7. The cross-sectional area of the settler was based on a settling rate of approximately 1 mm s^{-1}. The residence times are shorter and the settling rate faster than those specified by Cairns *et al.* (1967), but the residence times are at least twice those quoted by Coplan *et al.* (1954) for this type of unit.

Agitation in the mixing chambers was effected by centrifugal pump-mix impellers fitted with additional mixing blades (Figure 13). The agitators in each unit were driven by an electronically controlled d.c. motor through a gear train; this allowed impeller speeds from approximately 2 to 30 rev s^{-1}.

The level of the aqueous phase in the final stage of each unit was controlled with an adjustable, external overflow weir. The solvent phase overflowed a fixed outlet weir in the final stage of each unit and was fed by gravity from the scrubbing section in the stripping unit. Phase separators were provided on all outlet streams in an attempt to remove secondary haze by allowing some further settling; those on solvent streams were 136 mm diameter with a working depth of 95 mm,

and those on aqueous streams were 74 mm diameter with a working depth of 76 mm. The de-entrained aqueous phase was removed intermittently from the separators by means of a drain valve. In particular, with heated stripping stages, about 0.1 vol.% water was separated from the stripped solvent.

The organic extractant, scrub and strip solutions were fed by gravity from head tanks and the flowrates were controlled by needle valves and flowmeters. The uranium feed solution was supplied through a positive displacement metering pump. Gravity feeding and flow control *via* the needle valve and flowmeter method was unsatisfactory owing to the presence of small amounts of silica in the feed and the relatively low flowrates for this equipment.

The uranyl nitrate product solution was pumped intermittently from a 150 ℓ delay tank to storage tanks (total capacity 1500 ℓ). The raffinate solution was stored in a 200 ℓ tank and pumped to waste after analysis for uranium. The stripped organic solution was stored in a 150 ℓ tank except during solvent washing operations (see Section 5.2).

5.2 Solvent Washing Equipment

Both the tributyl phosphate (TBP) extractant and the kerosene diluent are subject to hydrolysis and degradation owing to the strong acid conditions in the extraction section. The tributyl phosphate hydrolyses slowly to di- and mono-butyl phosphates and the kerosene forms carboxylic acids and nitrated products, with some degradation of the larger molecules (Moore 1955). If these impurities are allowed to accumulate in the solvent, the uranium retention in the solvent after stripping and the tendency to emulsification and entrainment increase, reducing the efficiency of the process and the quality of the product. The established method of washing with a 5 per cent solution of sodium carbonate, followed by a dilute nitric acid wash to prevent carry-over of the sodium carbonate into the extraction section, was used to remove these impurities (Harrington and Ruehle 1959, Littlechild 1967, Cavendish and Leist 1970). The hydrolysis products readily dissolve in the carbonate solution, as does uranium which forms the soluble $UO_2(CO_3)_3^{4-}$ complex (Harrington and Ruehle 1959). However, the kerosene degradation products are rather more intractable (Littlechild 1967).

The solvent was pumped to a head tank from where it flowed by gravity through two glass columns each 100 mm diameter x 1.7 m long, packed to a height of 0.9 m with 10 mm Raschig rings, and returned to the feed tank (Figure 10). In a simple arrangement, the two columns contained sufficient static 5 wt.% sodium carbonate and 0.1 $\mathbb{M}$ nitric acid solution respectively, to maintain the organic-aqueous interface between the top of the packing and the solvent outlet. The vent on the first column was 0.9 m high and allowed a head of solvent to be developed which was sufficient for the pressure drop in the second column. In a production plant, countercurrent operation would be used.

The columns were designed to have a throughput of 70 $cm^3\ s^{-1}$ on the basis of the Crawford and Wilke (1951) correlation for packed extraction columns. The continuous aqueous phase velocity was assumed to be zero. In practice, the solvent flowrate to the first column was controlled at approximately 40 $cm^3\ s^{-1}$ using a needle valve, and the solvent then overflowed to the second column. This flowrate was found to be close to the throughput for flooding in the carbonate column.

5.3 Product Washing Equipment

The solubility of tributyl phosphate in water is 0.39 $g\ \ell^{-1}$ at 25 °C (Harrington and Ruehle 1959) and, although it is reduced in the presence of uranyl nitrate, the uranyl nitrate product solution does contain some TBP. Secondary haze droplets of solvent are also carried into the product and settle very slowly. A simple arrangement with a glass column 76 mm diameter x 1.5 m high and packed to a height of 1.2 m with 10 mm diameter Raschig rings, containing a static continuous phase of kerosene, was used in some *ad hoc* experiments to remove as

much TBP as possible (Figure 10). The flowrate of uranyl nitrate product solution to the top of the column was controlled by a needle valve at approximately 30 $cm^3\ s^{-1}$ and discharged from the bottom of the column to a further product storage tank. In a production plant, countercurrent operation would be used.

5.4 Operating Experience

All equipment was initially assembled, and leak and operational testing was carried out using kerosene and water. The most important factor influencing operation of the mixer-settlers was the height of the impellers. Raising the impeller decreased the flow of aqueous phase from the previous stage and hence raised the interface level in that stage and *vice versa*. Each impeller was individually adjusted during operation of the unit until the level of the interface was approximately the same throughout the unit. No attempt was made to find the maximum throughput, but the units were operated with water and kerosene flowrates of 40 and 54 $\ell\ h^{-1}$ respectively, a total flowrate which was twice the design throughput. Subsequently, Royston and Burwell (1973) examined the hydrodynamic characteristics of these mixer-settler units in more detail.

Operation of the mixer-settlers was generally stable during uranium processing, although some early difficulties were experienced. Once the units were operating with uranium solutions, it was necessary to readjust the heights of the impellers to obtain stable operation. This was associated with problems of maintaining the required interface level in the final product stage of the stripping unit, overflowing of the demister unit between the scrubbing and stripping units and flooding (filling to overflowing) of some stages of the stripping unit.

The choice of impeller speed was a compromise between increasing mass transfer efficiency on the one hand and emulsion stability and secondary haze formation on the other. It was found that an impeller speed of 12 rev s^{-1} was satisfactory for the extraction and scrubbing unit, but that increasing the speed above 10 rev s^{-1} in the stripping unit tended to enhance the formation of stable emulsions and make the unit more liable to flooding and unstable operation. The units were, therefore, operated at 12 and 10 rev s^{-1} respectively.

For process control, simple, rapid methods of analysis were desirable. A gamma absorptiometer (Yates and May 1970) was used to analyse uranium solutions in the range 10 to 400 g ℓ^{-1}. Gamma-ray excited X-ray fluorescence was investigated for analysis in the range 0.05 to 10 g ℓ^{-1} (Ryan *et al.* 1974).

Occasional blockages occurred within the mixer-settlers due to foreign objects dropping into the units. Perspex covers were fitted to the boxes to prevent this occurrence. The stage in which the blockage occurred could be cleaned by covering the appropriate mixed-phase ports and syphoning out the liquids in the stage.

After the first two years' operation, the units were stripped down for thorough cleaning and maintenance. The equipment was generally in good condition, though some bearings in the gear train drive above the extraction unit had been affected by acid fumes and required replacement. Considerable amounts of crud were present in the units, but no significant effect on the operation or unit efficiency was observed.

Some problems were encountered on cold days with the crystallisation of uranyl nitrate hexahydrate from uranium feed solutions, particularly when high free acid concentrations were used. Crystallisation in the metering pump was encountered on several occasions and this was overcome by heating the feed solution and metering pump to about 25 °C.

The solvent and product washing columns performed satisfactorily and no detailed tests were carried out to determine their efficiency. There was no deterioration in the quality of the solvent during four years of intermittent operation. The sodium carbonate solution became yellow in use, but this colour probably indicated that degradation products were being removed from the solvent. Quite strongly coloured sodium carbonate solutions from the washing column were analysed

for uranium and shown to contain less than 1 g ℓ^{-1}. When the yellow colour became strong (usually after processing about 400 ℓ of solvent), the washing was stopped, the carbonate solution ($\sim$ 10 ℓ) was drained from the column, and the column was refilled with fresh solution. The nitric acid solution was changed less frequently, usually about every fourth time that the carbonate solution was changed.

A single *ad hoc* test on the product washing column indicated that the TBP concentration was reduced from 256 mg ℓ^{-1} to 78 mg ℓ^{-1}. Bench-scale batch experiments indicated that fresh kerosene could wash approximately 100 times its own volume of uranyl nitrate solution and remain as effective in removing TBP at the end of this washing as at the beginning.

6. INVESTIGATION OF SOLVENT EXTRACTION PROCESSES

6.1 High Acid Flowsheet

The high acid flowsheet (Figure 7) was initially operated with a feedrate of 5 ℓ h^{-1} (1.5 kgU h^{-1}); this was subsequently increased to 6 ℓ h^{-1} with a corresponding increase in the other streams (Runs 1 to 10 in Table 3). Note that the numbers of actual stages used in practice were at least twice the numbers of ideal stages calculated in Section 4.3, *i.e.* 6 extraction, 10 scrubbing and 16 stripping stages. The uranium concentration in the loaded organic was generally maintained at $\sim$ 60 g ℓ^{-1} and the uranium concentration in the raffinate was typically $\sim$ 50 mg ℓ^{-1}. The uranium concentration in the uranium product was maintained at 70 g ℓ^{-1} and the stripped organic solvent typically contained < 0.5 gU ℓ^{-1} and was recycled without further treatment, although it exceeded the design value in the calculated flowsheet.

Spectrographic analysis of the uranium product gave reasonably consistent results (Table 4) which were generally within the limits of the stringent Canadian specification for uranium dioxide powder (Chalder 1961). Comparison of the analyses for typical feed and product solutions indicates a substantial decontamination of the uranium during solvent extraction. Three elements – cadmium, copper and nickel – were difficult to maintain below the specification limits. Copper and nickel concentrations were in the ranges 10 – 70 and 5 – 55 μg g^{-1}, compared with the specification limits of 10 and 20 μg g^{-1} respectively. These high concentrations were attributed to contamination of the units by copper and stainless steel particles from a working area above and were reduced after covers were fitted to the mixer-settler units. Boron and cadmium concentrations were generally less than the analytical limits of detection at that point in the experimental program but these limits were above the specification requirements. Improvements in analytical methods towards the end of this series of runs gave results which indicated the boron concentrations were below the specification limit (0.3 μg g^{-1}) but the cadmium concentrations were above the specification limit (0.2 μg g^{-1}).

An early problem was encountered with this flowsheet, namely the appearance of an interfacial crud. This was a white material, presumably a stable emulsion, which may have been caused by the addition of some unsintered UO_2 pellets which contained 'Sterotex' (a proprietary vegetable fat product used as a binder/lubricant in pressing) during preparation of the dissolver feed solution. Spectrographic analysis failed to reveal any inorganic material and treatment with nitric acid eliminated the crud. It was shown in tests with a two-stage mixer-settler system, that trace quantities of Sterotex could cause stable emulsions. The crud was extremely troublesome to remove and despite cleaning of the mixer–settler units and complete replacement of the solvent it reappeared in the next run. Finally, after increasing the acidity of the strip solution from 0.01 $\mathfrak{M}$ to 0.05 $\mathfrak{M}$, the crud gradually disappeared.

Optimisation of the operation of the mixer-settlers with the high acid flowsheet was attempted with the aim of maximising the uranium throughput, subject to the product purity being within the limits of the Canadian specification for uranium dioxide powder, but was not successful and the study was terminated (Lackey 1973).

6.2 Low Acid Flowsheet

Operation with the low acid flowsheet was initially started by using the high acid flowsheet (with 3 M free acid in the uranium feed) and then changing the scrub solution to purified uranyl nitrate with a concentration of about 70 to 90 gU ℓ^{-1}. This change-over was similar to that described by Littlechild (1967). The flowrate of the scrub solution was decreased over a period of about five hours until the required flowrate was obtained. As the loaded organic concentration increased, the strip flowrate was adjusted to bring the product concentration up to the desired 100 gU ℓ^{-1}. As more concentrated uranyl nitrate solutions became available, the scrub solution concentration was increased. About ten hours of operation at a feed flowrate of 6 ℓ h^{-1} were necessary before the concentrations throughout the scrub section were close to the anticipated values and about 20 hours of operation elapsed before stable operation was achieved.

By recycling product solution to the scrubbing stages, as described in Section 4.4, the uranium concentration in the loaded organic increased from 60 g ℓ^{-1} (with the high acid flowsheet) to 70 g ℓ^{-1}. However, the uranium concentration in the raffinate increased to ~1 g ℓ^{-1} and this was offset by increasing the number of extraction stages from six to eight, thus reducing the number of scrubbing stages to eight. The uranium concentration in the product solution was increased from 70 g ℓ^{-1} to 90 – 100 g ℓ^{-1}, corresponding to the increase in the uranium concentration in the loaded organic from 60 g ℓ^{-1} to 70 g ℓ^{-1} .

Two aspects of the operation of the low acid flowsheet were investigated: the acid consumption and the throughput of the mixer-settler units. The effect of free acid concentration in the feed on uranium extraction was investigated in a series of experiments using 0.5, 1.0, 1.5 M and 3 M free acid (Runs 20 to 48 in Table 3). In most cases, 9 actual extraction and 7 scrubbing stages were used. The uranium concentration in the raffinates increased with a reduction in the free acid in the feed solution. For example, with 0.5 M free acid in the feed (see Figure 9 for calculated flowsheet), the raffinate typically contained up to 0.5 gU ℓ^{-1}, a factor of ten greater than the design value. These increased uranium concentrations in the raffinates were caused largely by incomplete removal of uranium from the organic phase in the stripping stages as discussed in Section 4.4. Although 12 ideal stages are required to strip a 70 gU ℓ^{-1} loaded organic and give a 100 gU ℓ^{-1} product and a stripped organic containing < 0.05 gU ℓ^{-1}, in practice a product containing 90 – 100 gU ℓ^{-1} was obtained in 16 actual stages and it was generally difficult to reduce the uranium concentration in the recycled organic to < 1 gU ℓ^{-1} (Runs 25 to 28 in Table 3).

This problem was overcome by heating the dilute nitric acid solution used for stripping to ~ 60°C to take advantage of the increased efficiency of stripping at higher temperatures (Section 4.4). The temperatures in the stripping stages varied from 60 to 30°C. Under these conditions, the uranium concentration in the product was increased to 120 g ℓ^{-1} while the uranium concentration in the stripped organic was maintained at less than 0.005 g ℓ^{-1} (Runs 33 to 42 in Table 3). With recycled extractant containing so little uranium, uranium concentrations in the raffinate were generally reduced to < 0.2 (Runs 29 to 34) and < 0.02 g ℓ^{-1} (Runs 36 to 43) for 0.5 and 1.0 – 1.5 M free acid in the feed respectively. A free acid concentration in the feed of 1 M HNO_3 was adopted for subsequent operations to ensure low uranium concentrations in the raffinate.

The mixer-settler units described in Section 5.1 were designed for a throughput of 1.5 kgU h^{-1}, corresponding to a total phase flowrate in the stripping section of 47 ℓ h^{-1}. For this flowrate the above modifications in the flowsheet increased the throughput to 2.1 kgU h^{-1}. Royston and Burwell (1973) showed that, from a hydrodynamic viewpoint, operation of these mixer-settlers should be practicable with total phase flowrates up to 75 ℓ h^{-1} before flooding occurred. In a series of experiments (Runs 43 to 48 in Table 3) using a feed solution containing 300 gU ℓ^{-1} and 1 M HNO_3 (requiring five theoretical extraction stages – Section 4.4), the uranium throughput was increased to 2.7 kg h^{-1}, corresponding to a total phase flowrate of 64 ℓ h^{-1} in the stripping section. At uranium throughputs up to 2.5 kg h^{-1}, the product solution was maintained at 118 – 120 gU ℓ^{-1} and the stripped organic contained < 0.08 gU ℓ^{-1} (Runs 43, 45). Uranium losses in the raffinate were < 0.04 gU ℓ^{-1}, corresponding to ~ 0.01% of the uranium feed. At higher throughputs,

uranium losses in the raffinate were unacceptable (in the range 1 – 2 gU ℓ^{-1} for throughputs of 2.7 kgU h^{-1}) but the uranium concentrations in the stripped organic generally remained at a satisfactory level (< 0.3 gU ℓ^{-1}). The effect of increasing the throughput was to reduce the mass transfer efficiency of the mixer-settler stages to ~ 50 per cent, and this rather than flooding constituted the operating limit.

The final low acid flowsheet which was adopted in this work is shown in Figure 14. In subsequent operations producing nuclear purity uranyl nitrate solutions for other research programs, the mixer-settlers were operated with this flowsheet at a throughput of 2.5 kgU h^{-1}, to process approximately 1.5 Mg uranium. These conditions correspond to a reduction of 76 per cent in nitric acid consumption and an increase of 67 per cent in throughput of uranium compared with the original design flowsheet (Figure 7) and throughput.

The purity of the uranyl nitrate product solution obtained with low acid flowsheets was generally within the limits of the Canadian specification (Chalder 1961) and was not affected by the changes in the flowsheet and throughput (Table 4). However, cadmium was difficult to maintain below the specification limits of 0.2 μg g^{-1} and varied from 0.1 to 0.8 μg g^{-1}. Contamination of the product by corrosion products of cadmium-plated structural components above the mixer-settler units and associated cadmium-plated nuts and bolts was suspected as the cause of this problem. The concentrations of rare earths were below the detectable limits of 0.5 μg g^{-1} for samarium and 0.05 μg g^{-1} for europium, gadolinium and dysprosium.

7. CONCLUSIONS

Nuclear purity uranyl nitrate solutions containing 3 Mg uranium were produced from Australian yellow cake and recycled materials on the pilot plant scale by the established route involving dissolution in nitric acid and purification by solvent extraction with 20 vol.% tributyl phosphate in kerosene using mixer-settler contactors.

Dissolution of yellow cake and recycled uranium oxide materials was readily carried out in a 100 ℓ dissolver to give solutions containing 300 gU ℓ^{-1} and 0.5 to 4 M free acid. Filtration of silica from this solution prior to solvent extraction was not necessary for yellow cake containing 0.25 per cent silica.

A low acid flowsheet for uranium purification, which represents a substantial improvement over previous flowsheets, was derived theoretically and tested experimentally. With nine extraction and seven scrubbing stages, the consumption of nitric acid was minimised by reducing the free acid concentration in the feed to 1.0 M and recycling portion of the product solution to the scrubbing stages. The loaded organic phase containing 70 gU ℓ^{-1} was stripped in 16 stages with 0.05 M nitric acid heated to 60 °C to give uranyl nitrate product solutions with concentrations up to 120 gU ℓ^{-1}. The uranium concentration in the raffinate was less than 0.04 gU ℓ^{-1}, corresponding to a loss of ~ 0.01 per cent of the feed, and the recycled organic contained less than 0.08 gU ℓ^{-1}. The throughput of the mixer-settler units was also increased to 2.5 kgU h^{-1} compared with the design value of 1.5 kgU h^{-1}.

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TABLE 1

DESIGN DATA FOR DISSOLVER SYSTEM

DISSOLVER

Nominal Volume : 100 ℓ

Construction:

Material : Stainless Steel Type AISI 321
Height : 816 mm
Internal diameter : 460 mm
Thickness : 3 mm

Heating Coils:

Heat transfer area : 0.37 m^2
Coil diameter : 38 mm o.d. x 3 mm wall thickness
Coil position : 3 coils at 200 mm i.d.
2 coils at 356 mm i.d.
Concentric

REFLUX CONDENSER

Material : Stainless Steel Type AISI 321
Tube dimensions : 19 tubes, 32 mm o.d. x 3 mm wall thickness
Heat transfer area : 1.4 m^2
Cooling water flow: 400 ℓ h^{-1}

PACKED SCRUBBER

Material : Stainless Steel Type AISI 321
Diameter : 102 mm
Height (packed) : 2130 mm
Packing : 13 x 13 mm Raschig rings

DE-ENTRAINER

Material : Stainless Steel AISI 321
Diameter : 127 mm
Height : 203 mm
Rough Filter : 13 x 13 mm Glass Raschig rings
Fine Filter : 3 x 0.8 mm mesh screens

TABLE 2

EQUILIBRIUM DATA FOR 20 vol.% TRIBUTYL PHOSPHATE/KEROSENE – URANYL NITRATE–NITRIC ACID–WATER SYSTEM (Lackey 1973)

Temperature	16.5 ± 0.5°C		21.0 ± 1°C		21.0 ± 1°C		29.5 ± 1°C	
Acid Normality (aqueous phase)	0.0		0.0		1.0		0.0	
	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous	Organic
Concentration ($gU\ \ell^{-1}$)	16.9	5.6	52.7	31.5	51.2	54.5	19.6	4.9
	18.6	6.6	71.3	42.0	61.8	61.0	24.4	7.8
	24.6	11.2	80.8	49.2	68.2	60.0	24.2	8.0
	33.6	18.3	116.5	62.2	75.3	65.2	27.1	9.8
	35.0	19.6	127.0	63.0	90.0	67.8	33.4	14.2
	42.7	26.2	130.0	64.5	108.3	70.0	38.6	17.6
	43.8	26.4	131.8	63.5	111.3	67.4	51.6	25.8
	45.8	28.2	145.3	67.0	144.5	74.0	51.4	26.3
	53.1	33.9	150.4	68.8	146.5	73.0	58.6	30.4
	66.1	41.0	162.5	70.0	147.0	72.0	71.6	38.4
	69.4	43.3	175.5	70.5	166.5	74.0	101.3	51.2
			186.0	73.5	179.2	75.0		
			192.5	74.0	200.0	74.8		
			215.5	76.5	216.0	75.5		
			223.5	76.5	253.0	78.0		
			252.6	77.5				
			301.0	78.8				
			307.5	79.0				

TABLE 3

SUMMARY OF EXPERIMENTAL RESULTS

Run No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Feed – Material *	YC	YC+R	YC+R	YC	YC	YC+R	YC	YC+R	YC+R	YC+R	YC+R	YC+R	YC+R	YC	R	YC+R
– Uranium concentration (g ℓ^{-1})	300	259	268	304	267	330	267	304	306	348	336	320	320	308	341	330
– Nitric acid concentration (M)	n.a.	n.a.	3.9	4.2	3.8	3.9	3.7	4.2	4.0	3.8	3.2	3.2	3.2	3.0	2.92	3.2
– Number of extraction stages	6	6	6	6	6	6	6	6	6	8	7	6	8	8	8	8
– Feed flowrate F(ℓ h^{-1})	5.0	7.5	5.8	5.0	5.8	6.0	6.5	5.4	5.0	5.0	5.4	5.0	6.0	6.0	6.0	6.0
– Organic flowrate O(ℓ h^{-1})	25	25	25	31.4	30.4	30	30	30	25	25	30.2	23.2	28.3	28.3	32.0	28.6
– (F + Sc)/O	0.30	0.25	0.33	0.24	0.28	0.30	0.30	0.30	0.30	0.30	0.27	0.30	0.29	0.29	0.25	0.28
– Uranium concentration in raffinate (mg ℓ^{-1})	25–43	35–102	54	48–2300	3–57	n.a.	43–1500	n.a.	n.a.	91–760	17	735	n.a.	1390	n.a.	n.a.
Scrub – Uranium concentration (g ℓ^{-1})	–	–	–	–	–	–	–	–	–	–	70	90	97	95	100	100
– Nitric acid concentration (M)	1.0	1.0	1.0	1.04	1.0	1.0	1.0	1.0	1.0	1.15	1.1	n.a.	n.a.	n.a.	0.075	n.a.
– Number of scrubbing stages	10	10	10	10	10	10	10	10	10	8	9	10	8	8	8	8
– Scrub liquor flowrate Sc(ℓ h^{-1})	2.5	2.5	2.5	2.6	2.6	3.0	2.5	2.6	2.6	2.5	2.7	2.0	2.1	2.1	2.0	2.0
– Sc/O	0.10	0.10	0.10	0.08	0.09	0.10	0.08	0.08	0.10	0.10	0.09	0.09	0.07	0.07	0.06	0.07
– Uranium concentration in loaded organic (g ℓ^{-1})	52–70	53–72	53–70	45–50	44–54	44–61	52–63	30–69	49–72	47–63	54–70	62–72	57–69	65–70	67–75	58–69
Strip – Nitric acid concentration (M)	0.011	0.005	0.005	0.007	0.005	0.01	0.01	0.01	0.05	0.045	0.06	0.05	0.05	0.05	0.05	0.05
– Strip liquor flowrate St(ℓ h^{-1})	20	18	18	20	19	24	20	24	21	21.5	23	> 17	20.1	20.1	22.5	19.8
– St/O	0.80	0.72	0.72	0.64	0.63	0.80	0.67	0.80	0.84	0.86	0.76	0.73	0.71	0.71	0.70	0.69
– Uranium concentration in product (g ℓ^{-1})	56–77	61–83	72–83	63–72	67–81	54–88	64–81	45–85	49–81	47–75	54–89	75–101	75–100	95–104	90–106	84–99
– Uranium concentration in stripped organic (mg ℓ^{-1})	150–160	7–107	5300	3–31	9–31	n.a.	77–250	n.a.	n.a.	30–660	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
– Heated (Yes / No)	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No	No
COMMENTS			Crud					Feed uneven		Flood-ing in extn. stage	Started UN scrub	Feed rate variable	Block-age in parts of extn. stages			

* YC = Yellow Cake, R = Recycled uranium oxide materials n.a. = not available

TABLE 3 (continued)

Run No.	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
Feed – Material *	YC+R	R	R	YC	YC	YC	R	R	R	R	R	YC	YC	R	YC	R
– Uranium concentration (g ℓ^{-1})	310	300	300	278	300	295	302	302	291	300	296	300	311	306	315	293
– Nitric acid concentration (M)	3.2	3.0	3.0	0.75	0.55	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.6	0.5
– Number of extraction stages	8	6	6	6	7	7	7	7	9	9	9	9	9	9	9	9
– Feed flowrate F($\ell\ h^{-1}$)	6.0	6.0	6.0	6.1	6.4	4.95	5.14	6.1	5.4	5.8	5.9	5.9	5.7	5.7	5.2	6.0
– Organic flowrate O($\ell\ h^{-1}$)	26.5	25	25	26	30	29	29	30	27	28	29	28	29	27	29	29.5
– (F + Sc) / O	0.30	0.32	0.32	0.31	0.28	0.23	0.25	0.25	0.26	0.26	0.26	0.28	0.26	0.28	0.25	0.27
– Uranium concentration in raffinate (mg ℓ^{-1})	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.2–0.6	0.16–0.44	0.06	0.3–0.8	0.17	0.05–0.13	n.a.	0.09–0.1
Scrub – Uranium concentration (g ℓ^{-1})	100	n.a.	80	n.a.	n.a.	n.a.	90	91	100	95	94	92	92	92	n.a.	n.a.
– Nitric acid concentration (M)	–	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
– Number of scrubbing stages	8	10	10	10	9	9	9	9	7	7	7	7	7	7	7	7
– Scrub liquor flowrate Sc($\ell\ h^{-1}$)	2.0	2.0	2.0	2.0	2.0	1.86	2.0	1.5	1.75	1.4	1.59	1.84	1.82	1.8	2.0	2.0
– Sc / O	0.08	0.08	0.08	0.08	0.07	0.06	0.07	0.05	0.06	0.05	0.05	0.07	0.06	0.07	0.07	0.07
– Uranium concentration in loaded organic (g ℓ^{-1})	65–73	65–75	70	n.a.	70–73	59–60	58–60	54–64	60–62	62–71	62–66	64–67	65–67	62–66	61	52–62
Strip – Nitric acid concentration (M)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
– Strip liquor flowrate St($\ell\ h^{-1}$)	18.5	18	18	18	21	20	21	18.5	18	19	19	18.5	19	19.5	20.0	20.0
– St / O	0.70	0.72	0.72	0.69	0.70	0.69	0.72	0.62	0.67	0.68	0.66	0.66	0.65	0.72	0.69	0.68
– Uranium concentration in product (g ℓ^{-1})	73–95	99	96	81	94	82	91	92	89	92	92	95	93	89	93	107
– Uranium concentration in stripped organic (mg ℓ^{-1})	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	1.5–1.9	1.8–2.1	1.0	0.3–0.6	0.08–0.12	0.07–0.09	n.a.	0.1–0.2
– Heated (Yes / No)	No	No	No	No	No	No	No	No	No	No	No	No	Yes	Yes	Yes	Yes
COMMENTS																

TABLE 3 (continued)

Run No.	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48
Feed – Material *	R	R	YC	YC	YC	R	R	R	YC	YC	R	R	R	R	R	R
– Uranium concentration (g ℓ^{-1})	300	306	290	298	300	305	298	300	290	306	300	308	308	305	305	305
– Nitric acid concentration (M)	0.5	0.5	1.4	1.5	1.5	1.5	1.5	1.5	1.0	1.0	1.1	1.2	1.2	1.0	1.0	1.0
– Number of extraction stages	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9
– Feed flowrate F(ℓ h^{-1})	6.3	6.1	5.7	6.6	5.7	6.5	5.5	6.4	7.0	7.0	8.0	9.0	8.25	8.8	7.6	8.5
– Organic flowrate O(ℓ h^{-1})	29.5	30	29.5	30	29.5	29	29.5	31	31	30	34	40	38	40	34.5	38
– (F + Sc) /O	0.28	0.26	0.26	0.28	0.26	0.29	0.25	0.27	0.27	0.29	0.30	0.29	0.29	0.27	0.28	0.28
– Uranium concentration in raffinate (mg ℓ^{-1})	0.06–0.29	0.03–0.08	n.a.	0.007–0.009	0.015	0.02–0.1	n.a.	n.a.	n.a.	0.012–0.023	0.022–0.034	0.12–1.8	0.037	1.4	0.17	1.06
Scrub – Uranium concentration (g ℓ^{-1})	104	104	105	100	105	105	100	n.a.	100	100	98	100	100	100	100	100
– Nitric acid concentration (M)	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
– Number of scrubbing stages	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7	7
– Scrub liquor flowrate Sc(ℓ h^{-1})	1.82	1.8	~2.0	1.9	~2.0	1.9	~2.0	1.95	1.5	1.76	2.33	2.75	2.67	2.0	2.14	2.0
– Sc /O	0.06	0.06	0.07	0.06	0.07	0.07	0.07	0.06	0.05	0.06	0.07	0.07	0.07	0.05	0.06	0.05
– Uranium concentration in loaded organic (g ℓ^{-1})	58–60	62–64	57–62	60–63	56–65	59–64	52–62	60	60–67	70	70	67	65	67	67	67
Strip – Nitric acid concentration (M)	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
– Strip liquor flowrate St(ℓ h^{-1})	17.5	18	18	17.2	18	17	18	17	17.5	17	20	24	24		20	21
– St /O	0.59	0.60	0.61	0.57	0.60	0.57	0.61	0.55								
– Uranium concentration in product (g ℓ^{-1})	102	106	102	104	104	107	107	106	108	110	118	115	119	119	119	120
– Uranium concentration in stripped organic (mg ℓ^{-1})	0.005–0.008	0.002	n.a.	0.0004–0.003	0.0005	0.0002	n.a.	n.a.	n.a.	0.003–0.012	0.014–0.085	0.013–0.03	0.003	0.3	0.25	0.54
– Heated (yes /No)	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
COMMENTS																

* YC = Yellow Cake, R = Recycled uranium oxide materials n.a. = not available

TABLE 4

SUMMARY OF SPECTROGRAPHIC ANALYSES OF URANIUM PRODUCT SOLUTIONS
($\mu g\ g^{-1}$ U basis)

Element	Canadian Specification	Typical Rum Jungle Feed Solution	Run No. 1	2	4	6	7	8	9	10	11	12	13	14	15	16	17	30	42	45
Ag	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.1	3	0.4	0.1	0.3	<0.1	1	0.3	<0.1	0.2	1
Al	25	25	<10	<10	20	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	n.d.	10	<10
B	0.3	<1	<1	<1	<1	<1	<1	<0.1	<1	<0.1	0.15	0.2	<0.1	<0.1	<0.1	<0.1	0.15	0.2	0.2	0.3
C	200	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ca	50	1000	n.d.	n.d.	n.d.	n.d.	n.d.	35	n.d.	<10	20	10	n.d.	n.d.	2	15	10	35	2	n.d.
Cd	0.2	<10	<10	<10	<10	<10	<10	0.5	<10	0.3	0.4	0.8	0.2	0.2	0.2	0.6	0.6	0.5	0.1	0.4
Co	100	<10	<1	<10	<10	<10	<10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cr	15	5	<10	<10	<10	<10	<10	<5	<10	10	10	<10	<10	<10	10	20	10	10	<10	<5
Cu	10	50	10	12	70	10	20	45	15	10	10	20	3	2	7	45	7	12	n.d.	6
Dy	0.15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
F	50	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Fe	50	3000	30	25	30	<10	125	20	40	15	40	10	10	10	25	20	10	20	20	50
Gd	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mg	10	500	<10	<10	<10	<10	1	10	3	4	8	1	5	<1	3	10	1	10	20	10
Mn	5	5	n.d.	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1	<1	<1	<1	<1	2	n.d.
Mo	2	<10	<2	<2	<2	<2	<2	<0.5	<2	<0.5	<0.5	<0.5	<0.5	0.5	<0.5	<0.5	<0.5	<0.5	1	<1
Na	100	35,000	<50	<20	80	40	<20	<20	50	20	50	<20	<20	<20	<20	<20	<20	<20	<20	<10
Ni	20	100	25	7	n.d.	5	50	35	55	7	<3	<3	5	5	<3	<3	<3	<3	3	5
Pb	100	75	17	5	6	5	4	n.d.	16	10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Si	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	15	80	30	20	30	65	30	10	25	15	50
V	100	<5	<1	<1	<1	<1	<1	<3	<1	<3	<3	<3	<3	<3	<3	<3	<3	n.d.	<1	<5
Zn	100	200	100	25	40	20	75	40	90	15	<15	<15	<15	<15	<15	<15	<15	<15	20	10

n.d. – not determined

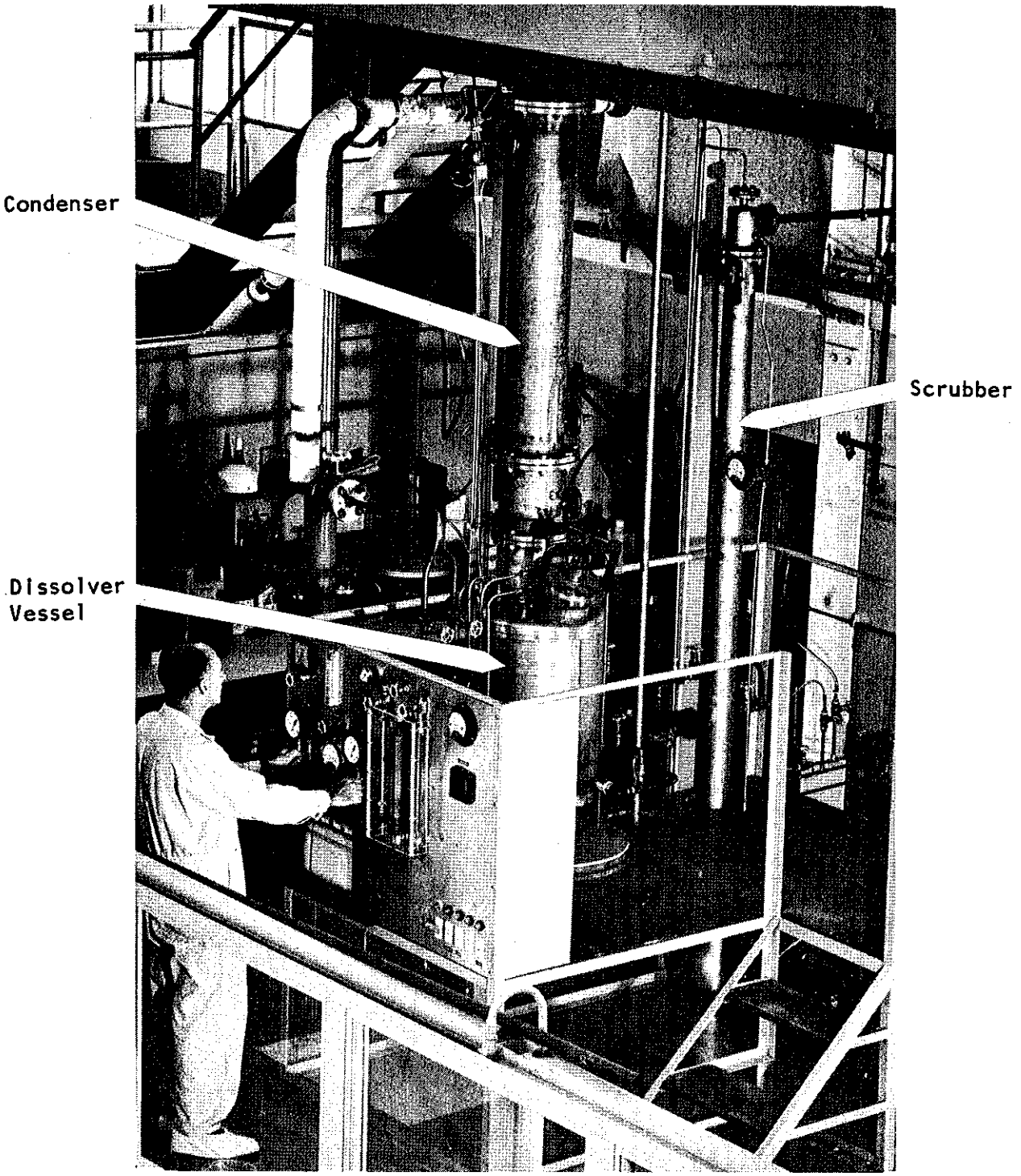


FIGURE 1. GENERAL VIEW OF DISSOLVER

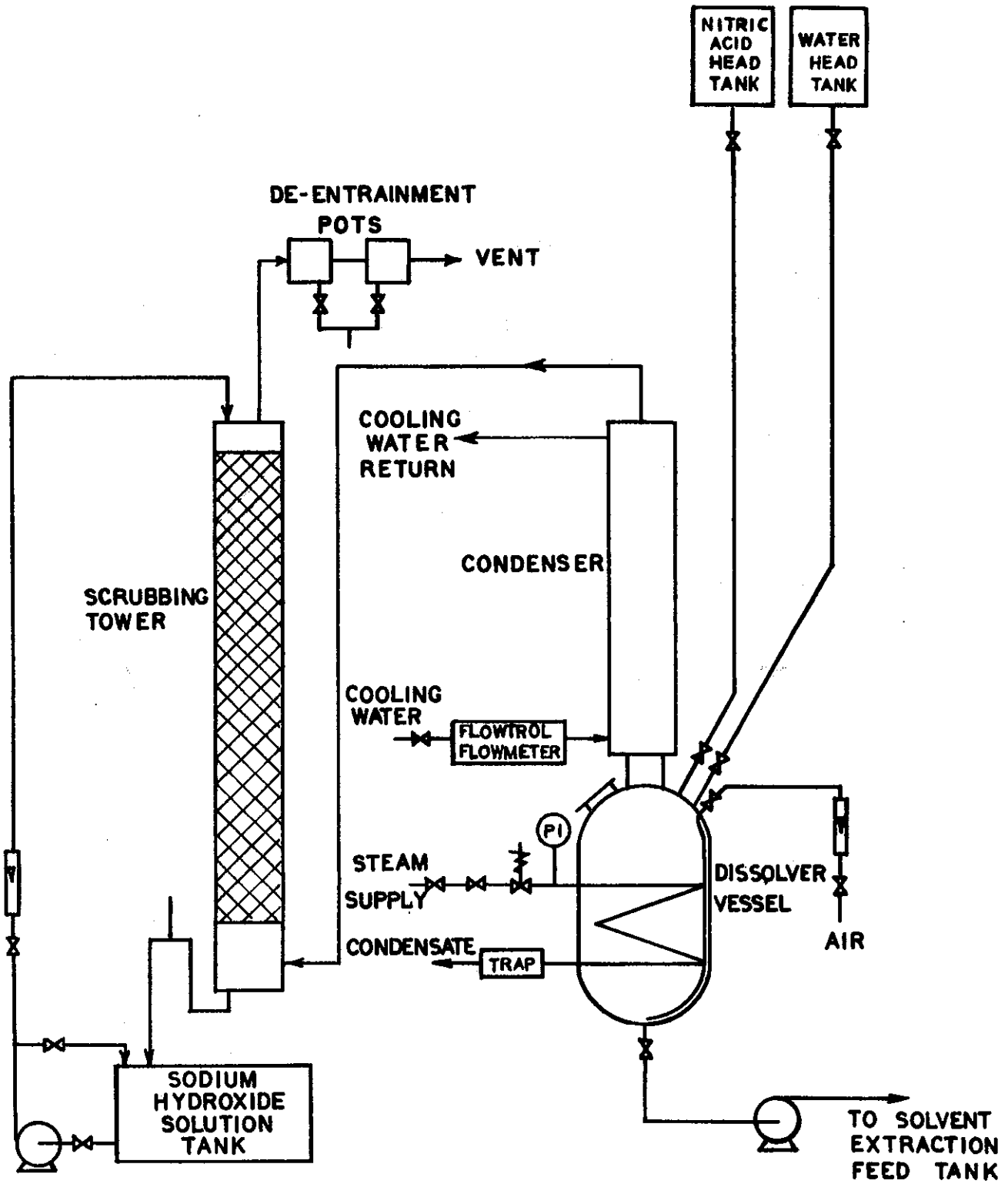


FIGURE 2. EQUIPMENT FLOWSHEET FOR DISSOLVER SYSTEM

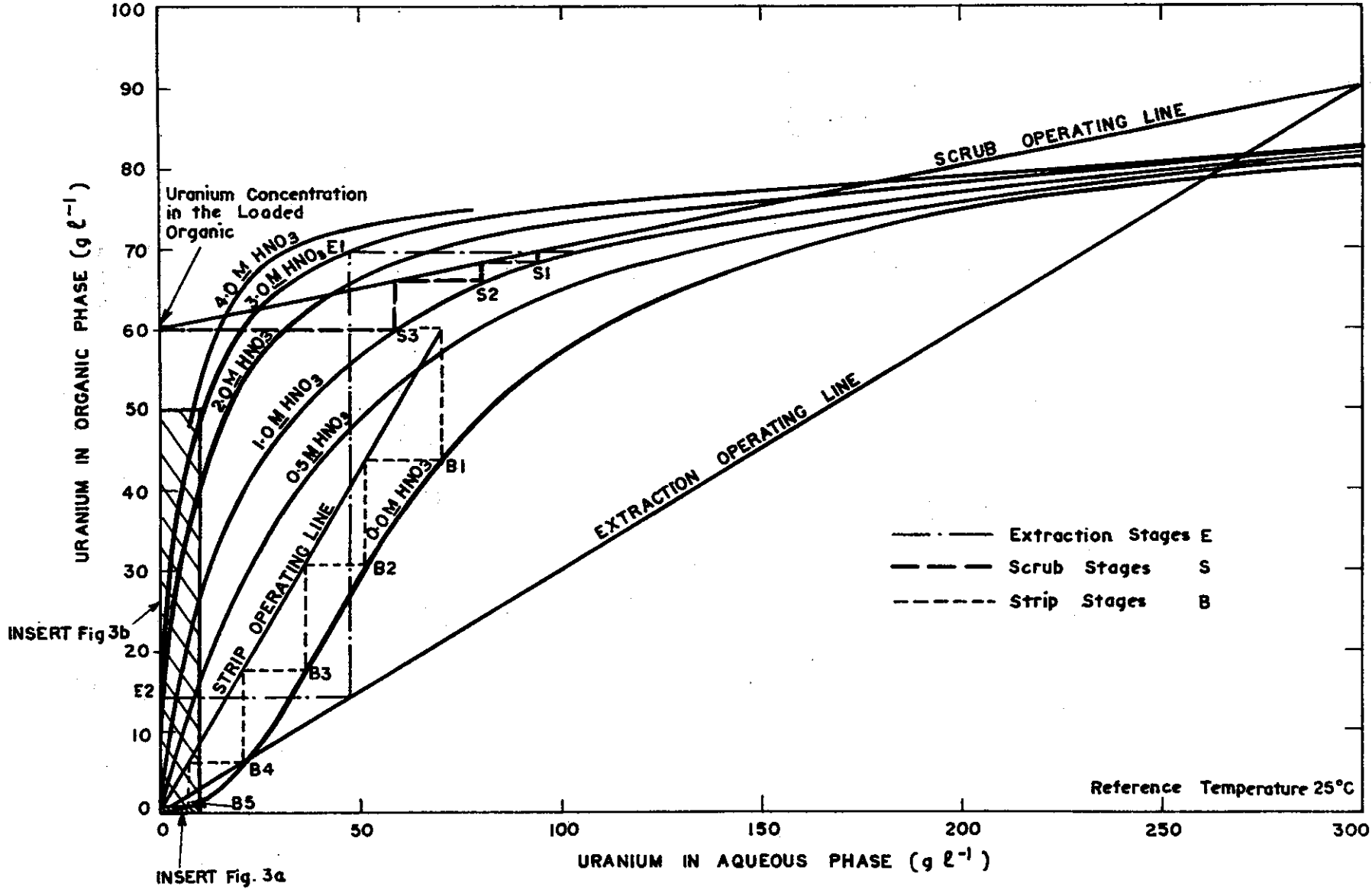
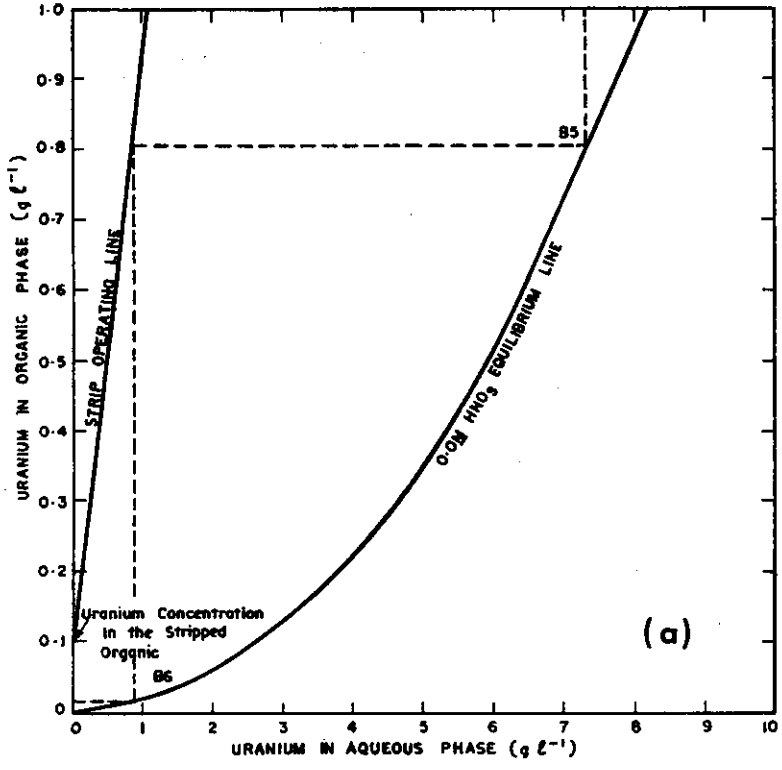


FIGURE 3. URANIUM DISTRIBUTION DATA, 20 vol. % TRIBUTYL PHOSPHATE/KEROSENE-URANYL NITRATE-NITRIC ACID-WATER SYSTEM (after Apelblat & Faraggi 1966)



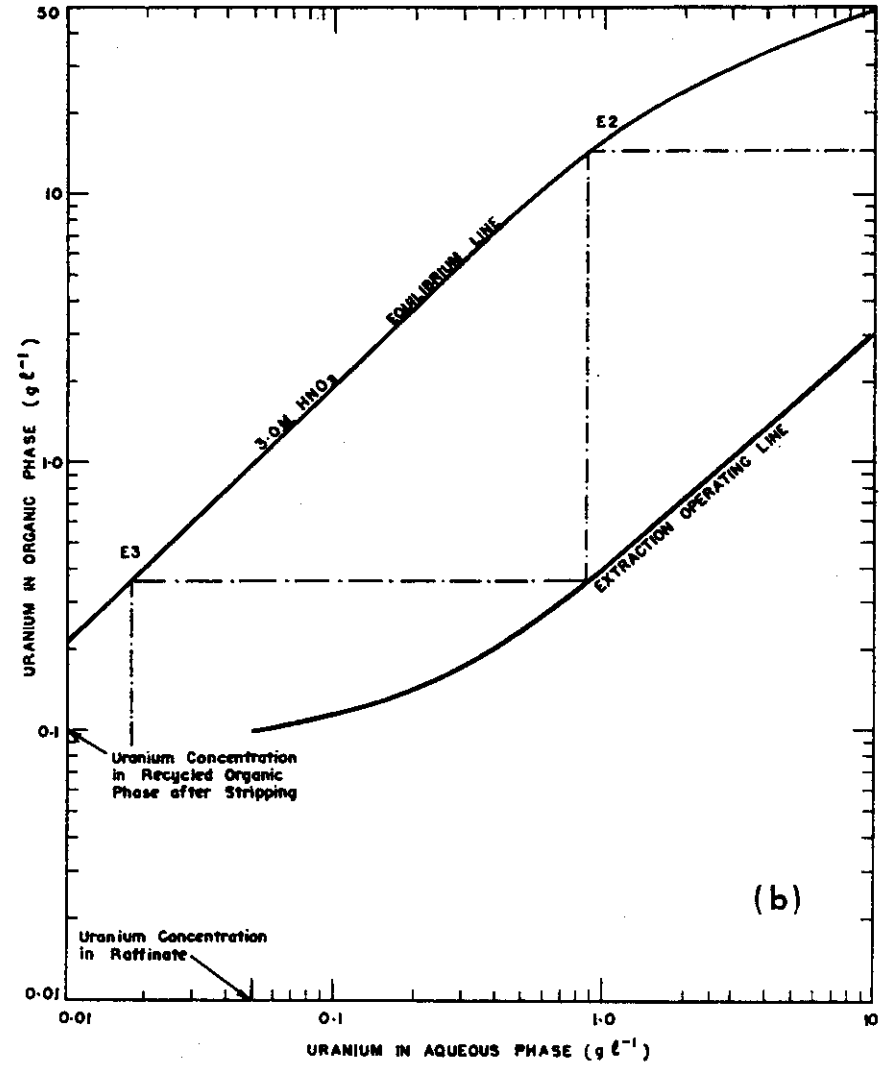


FIGURE 3. INSERTS a AND b

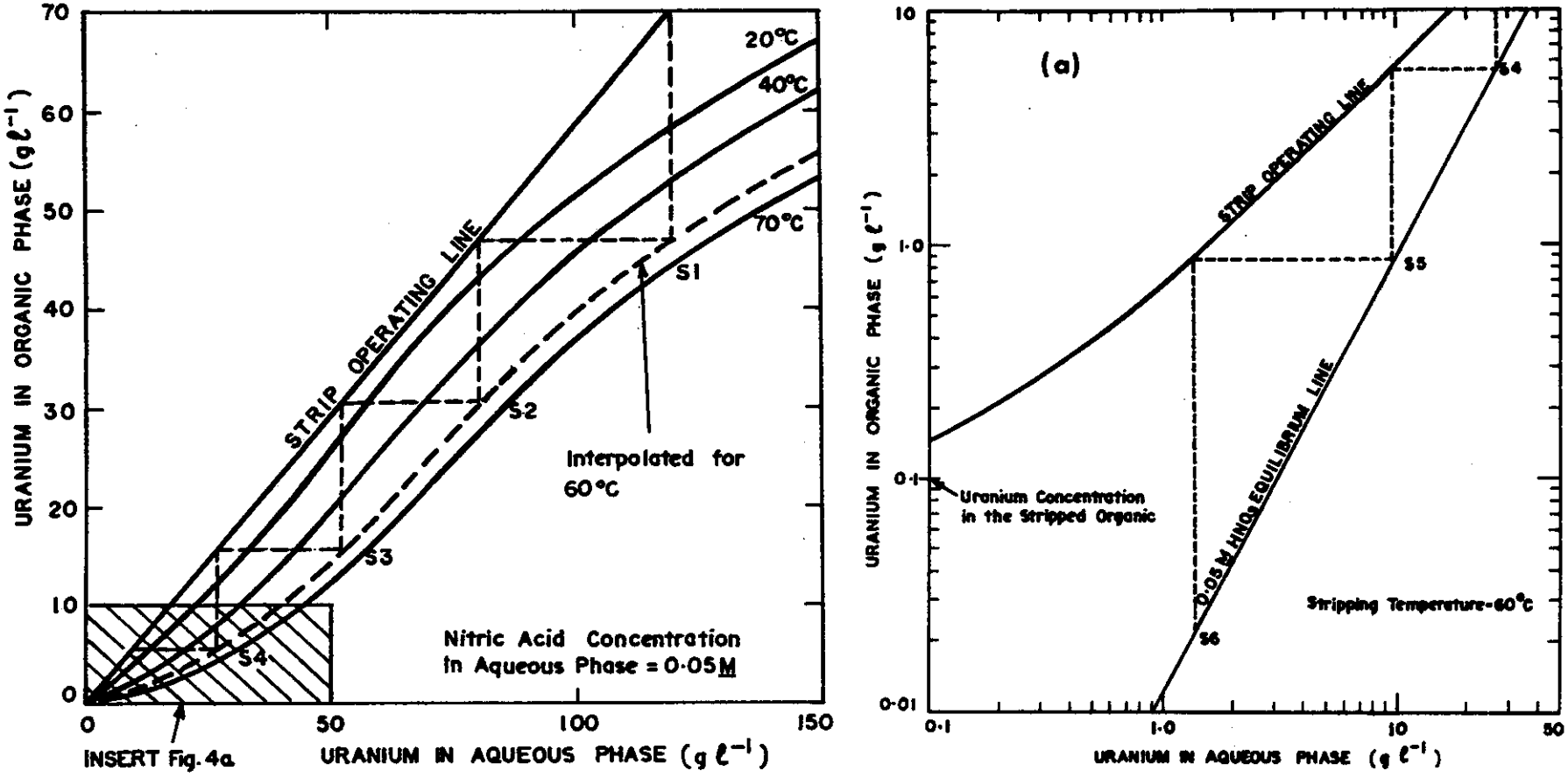


FIGURE 4. EFFECT OF TEMPERATURE ON URANIUM DISTRIBUTION DATA
(after Rozen et al. 1962)

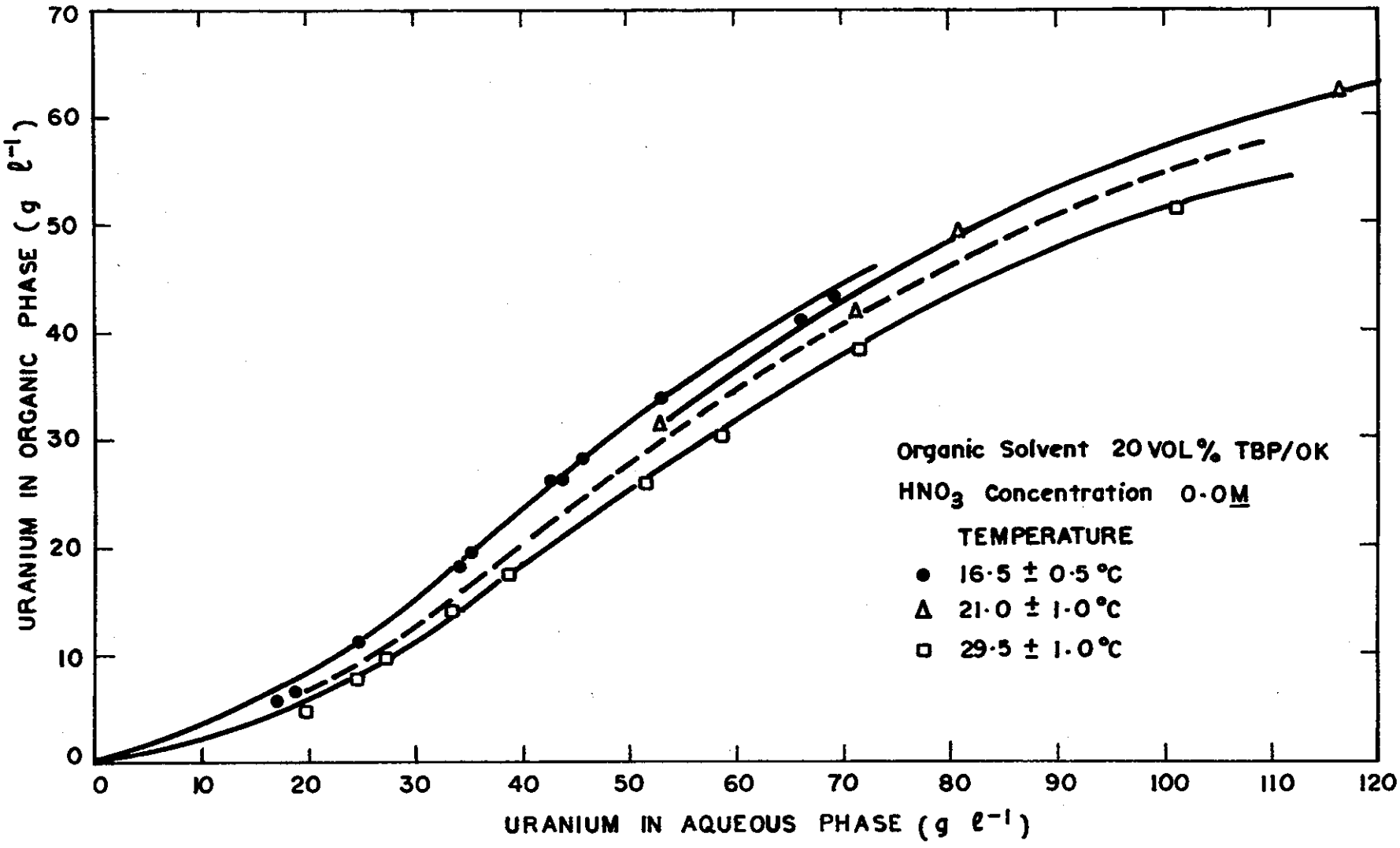


FIGURE 5. EFFECT OF TEMPERATURE ON URANIUM DISTRIBUTION DATA (Lackey 1973)

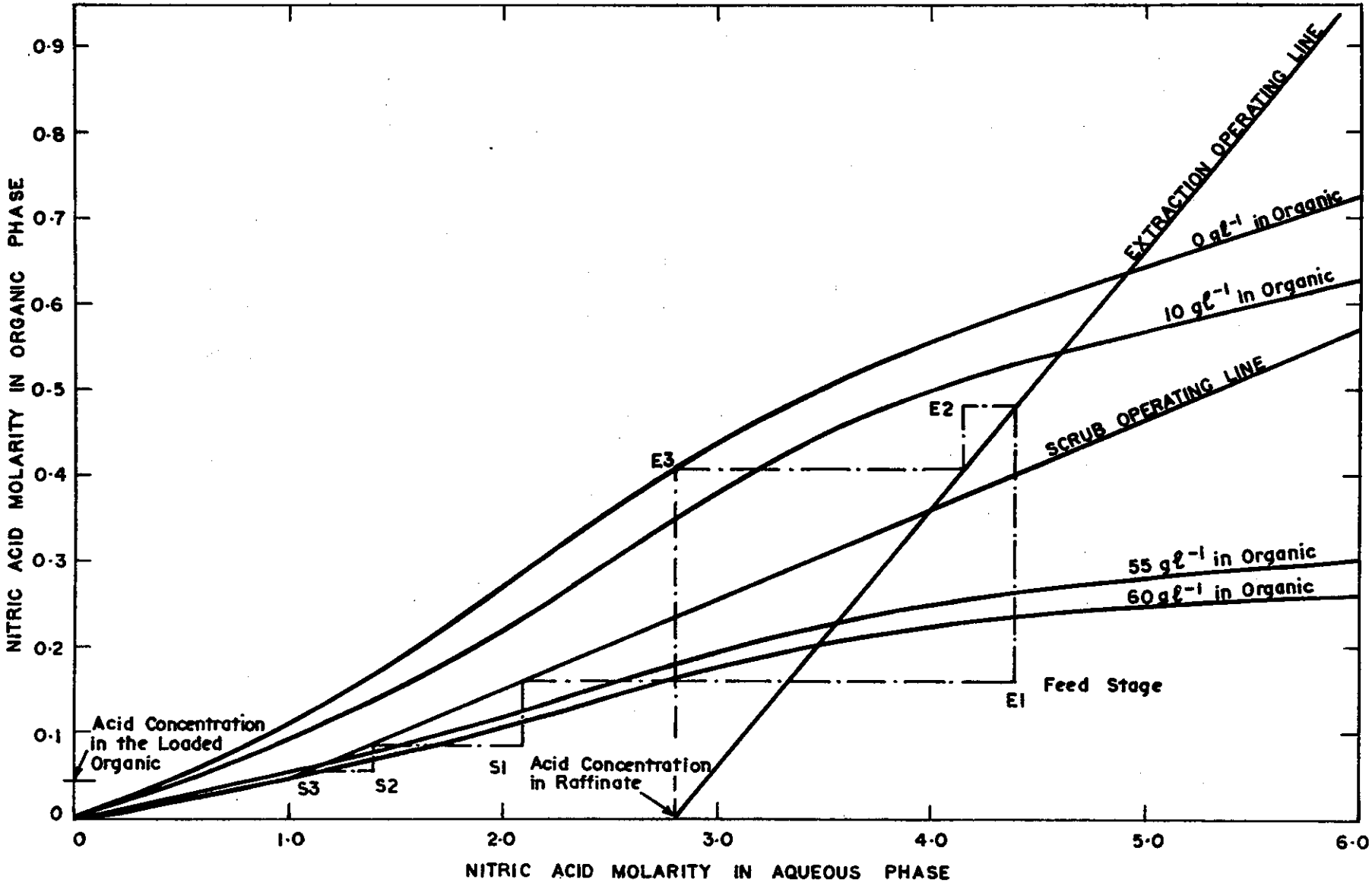


FIGURE 6. NITRIC ACID DISTRIBUTION DATA, 20 vol. % TRIBUTYL PHOSPHATE/KEROSENE-URANYL NITRATE-NITRIC ACID-WATER SYSTEM (after Wood and Williams 1958)

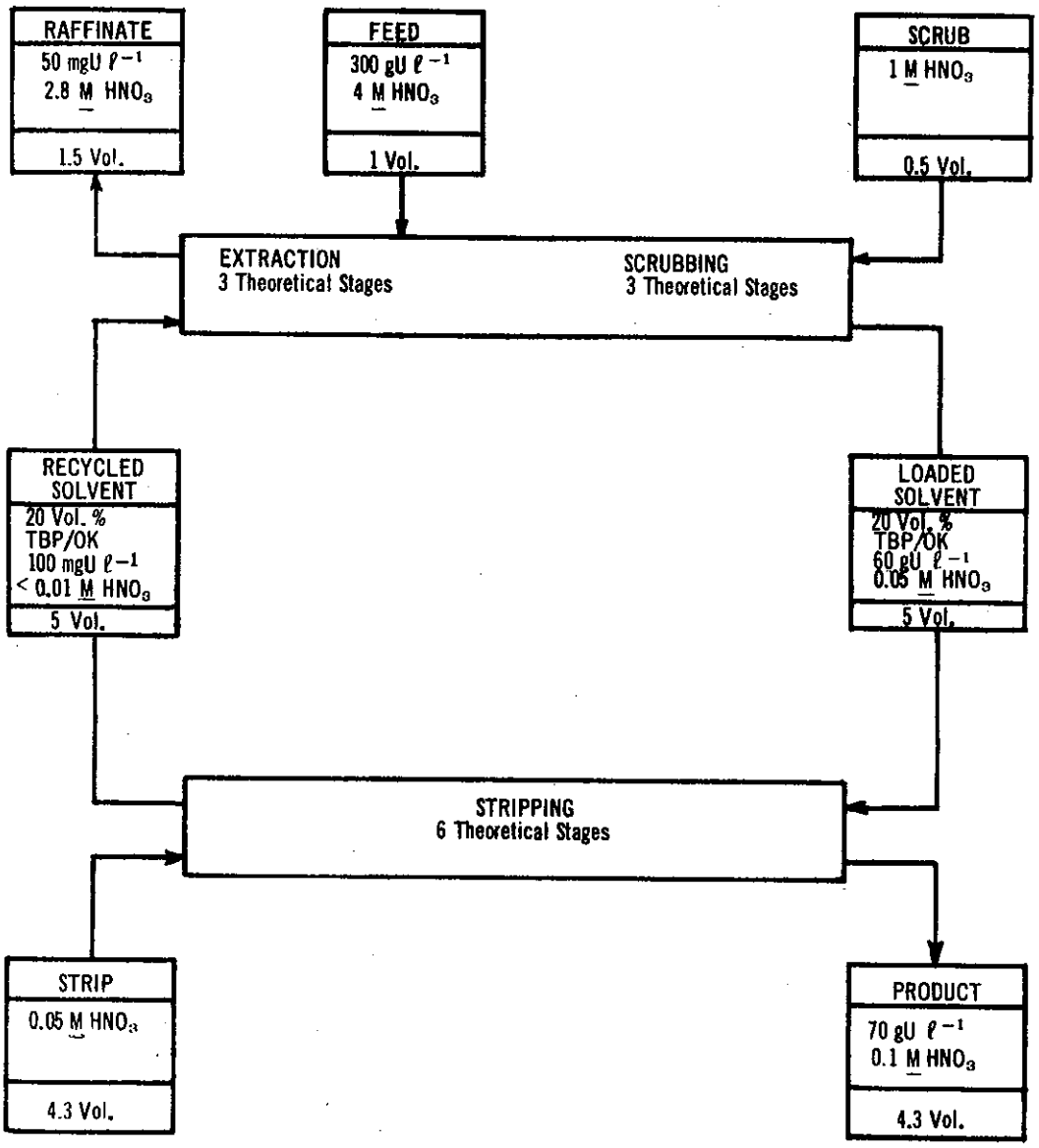


FIGURE 7. CALCULATED HIGH ACID SOLVENT EXTRACTION FLOWSHEET

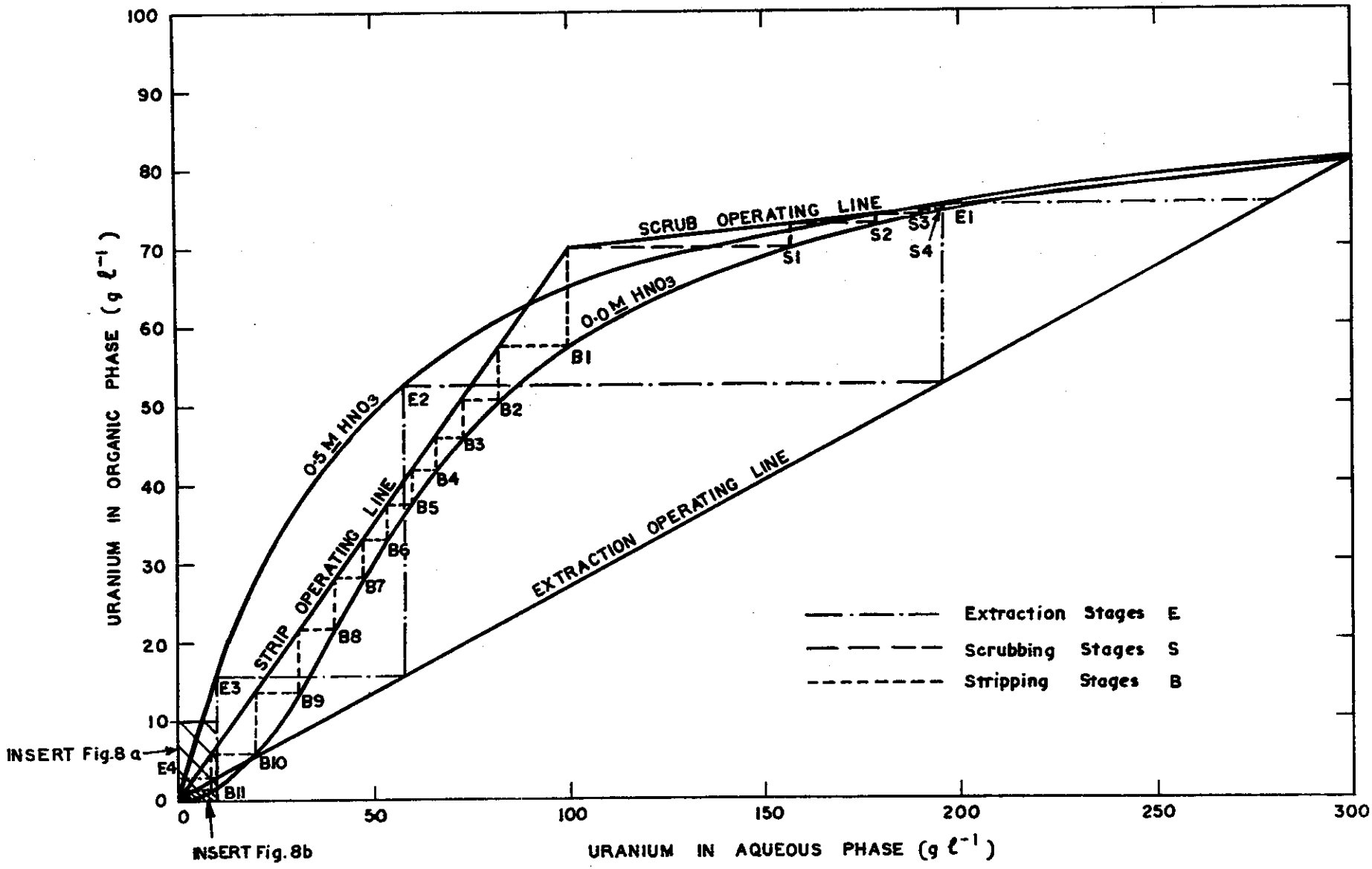


FIGURE 8. McCABE-THIELE URANIUM CALCULATIONS FOR LOW ACID FLOWSHEET

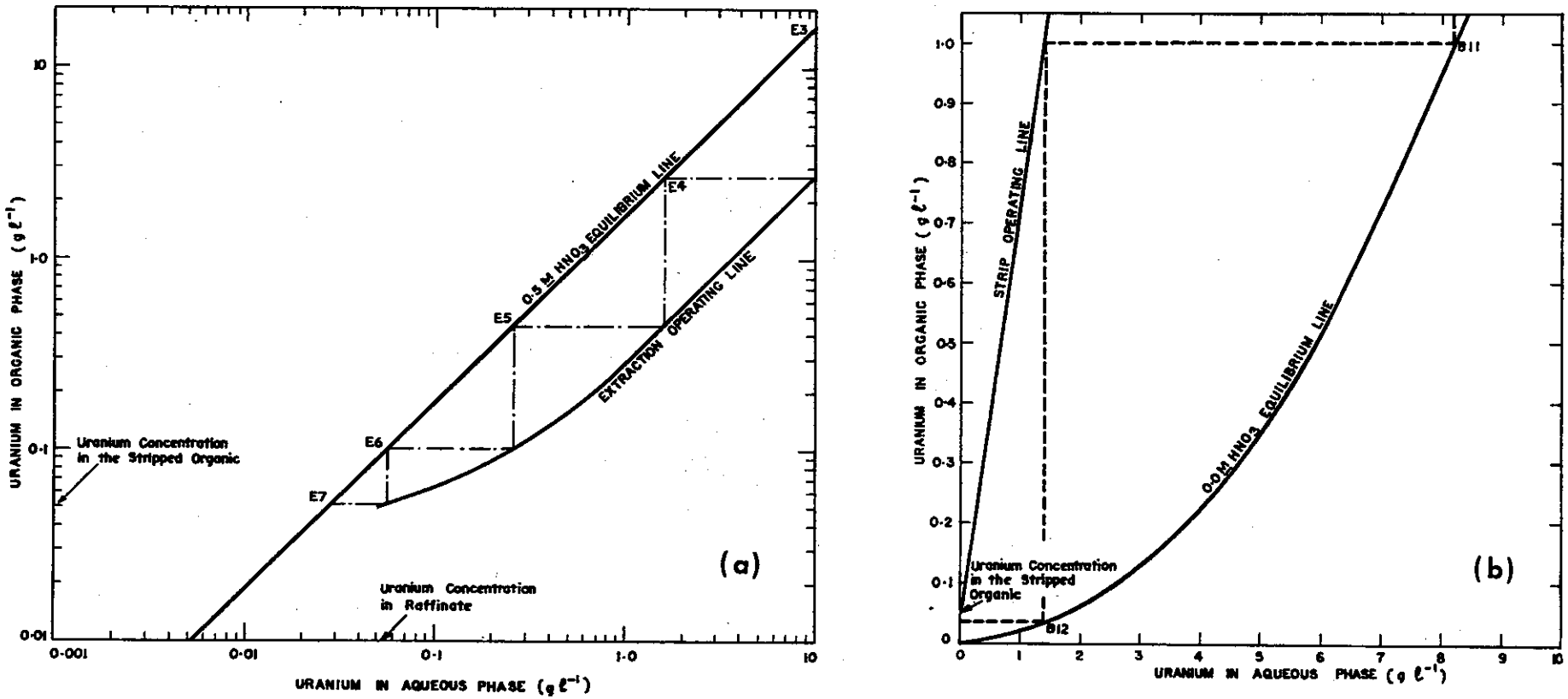


FIGURE 8. INSERTS a AND b

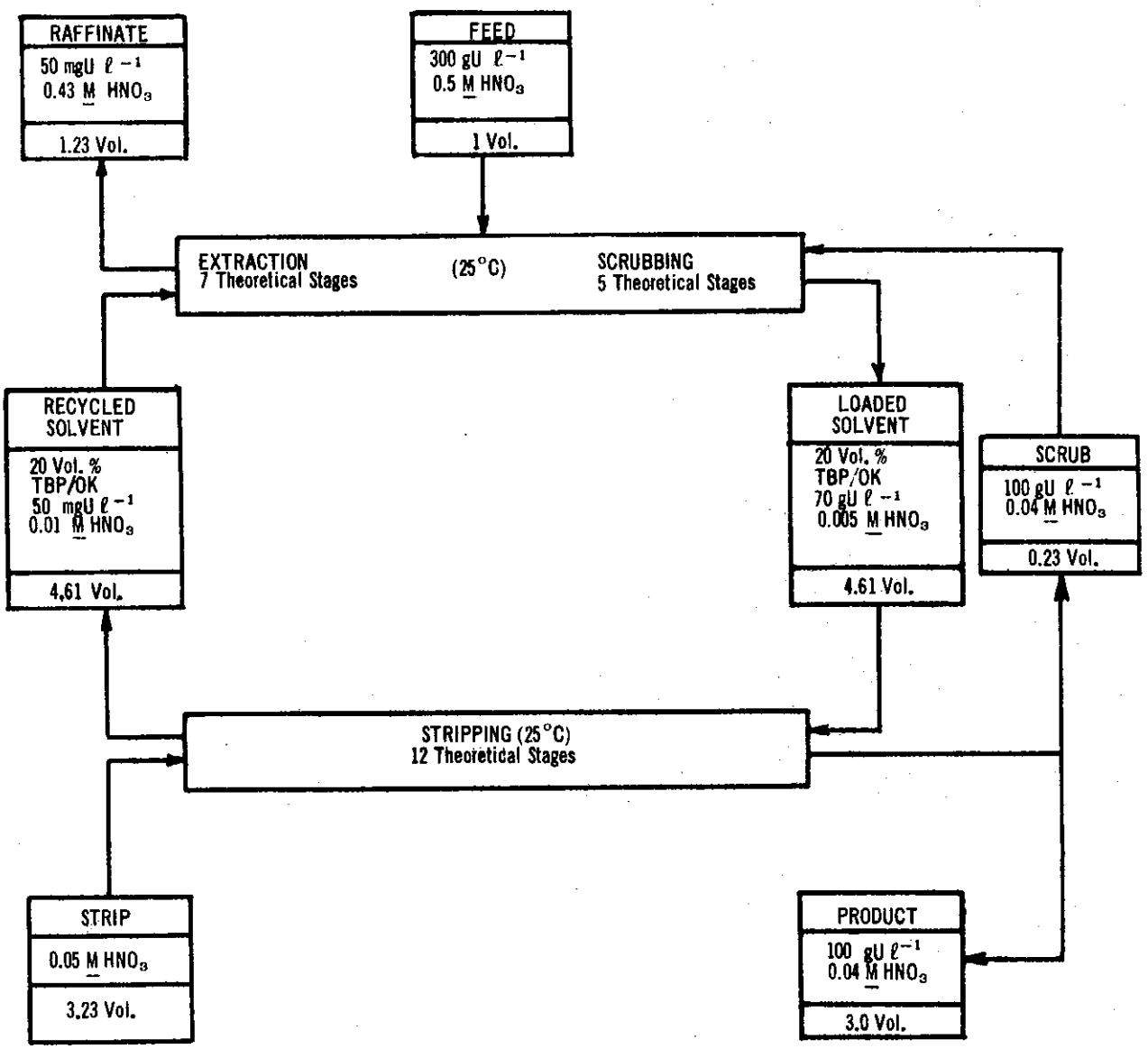


FIGURE 9. CALCULATED LOW ACID SOLVENT EXTRACTION FLOWSHEET

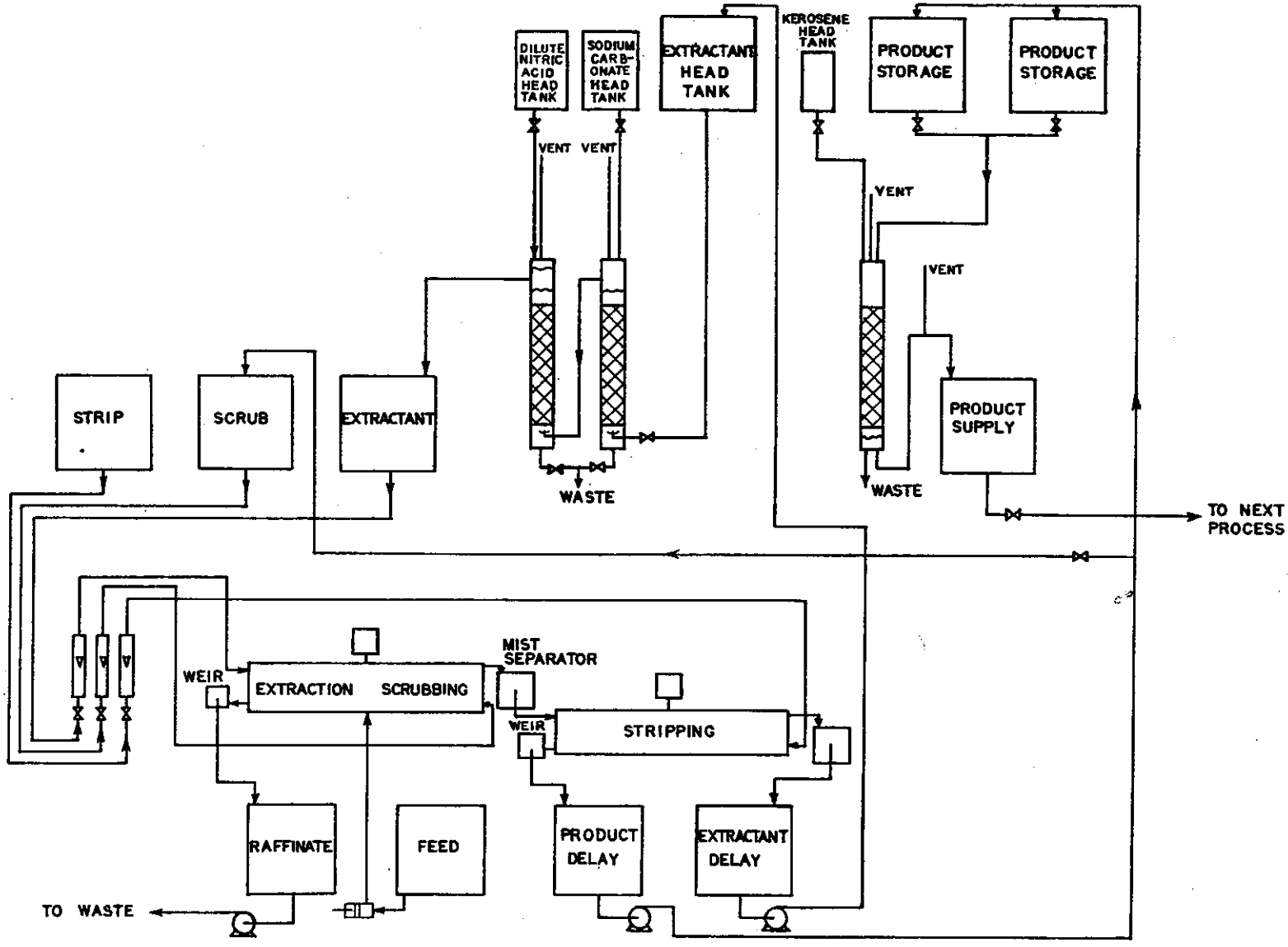


FIGURE 10. EQUIPMENT FLOWSHEET FOR SOLVENT EXTRACTION

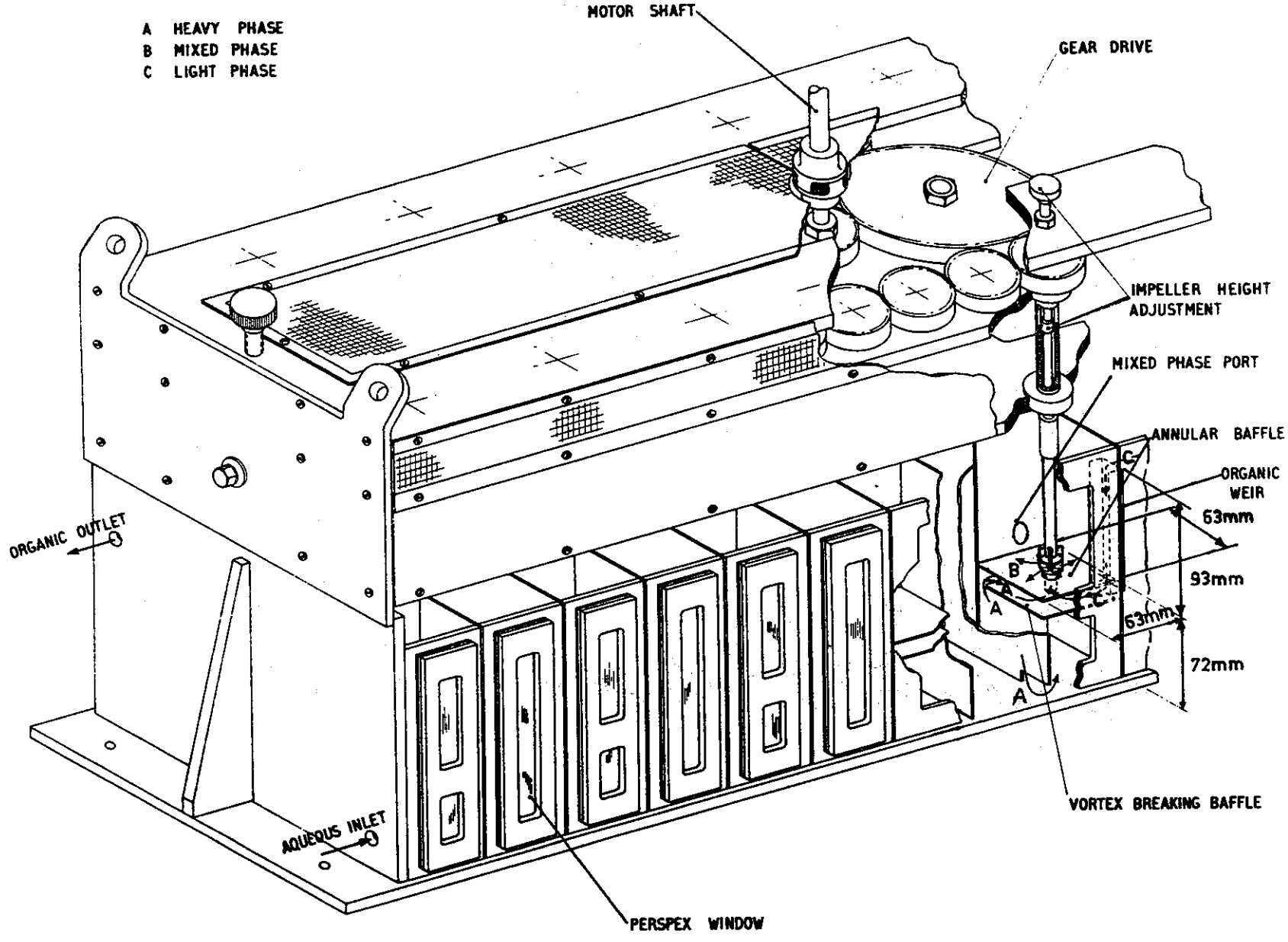


FIGURE 11. SIXTEEN STAGE MIXER-SETTLER UNIT

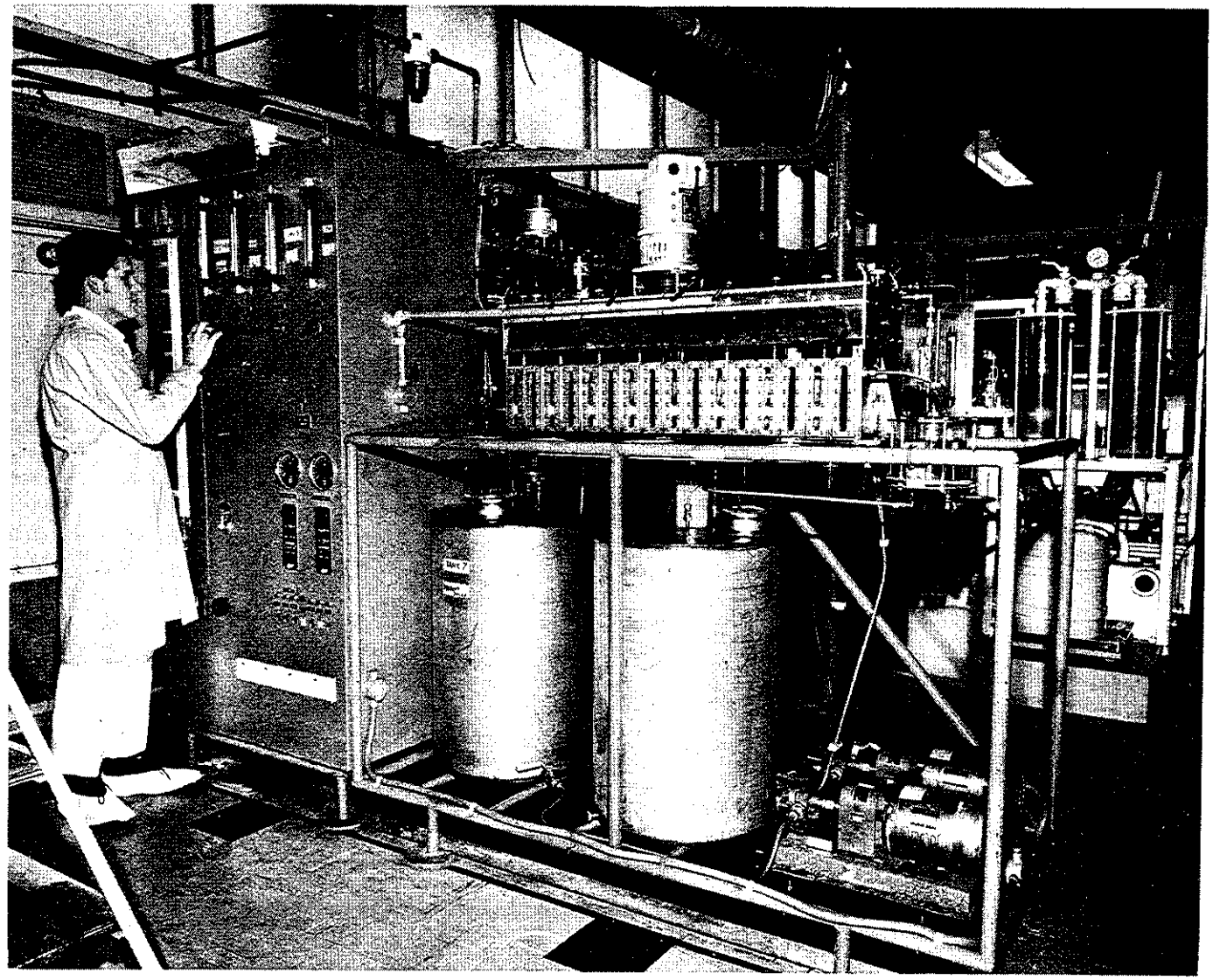


FIGURE 12. PILOT PLANT MIXER-SETTLER EQUIPMENT

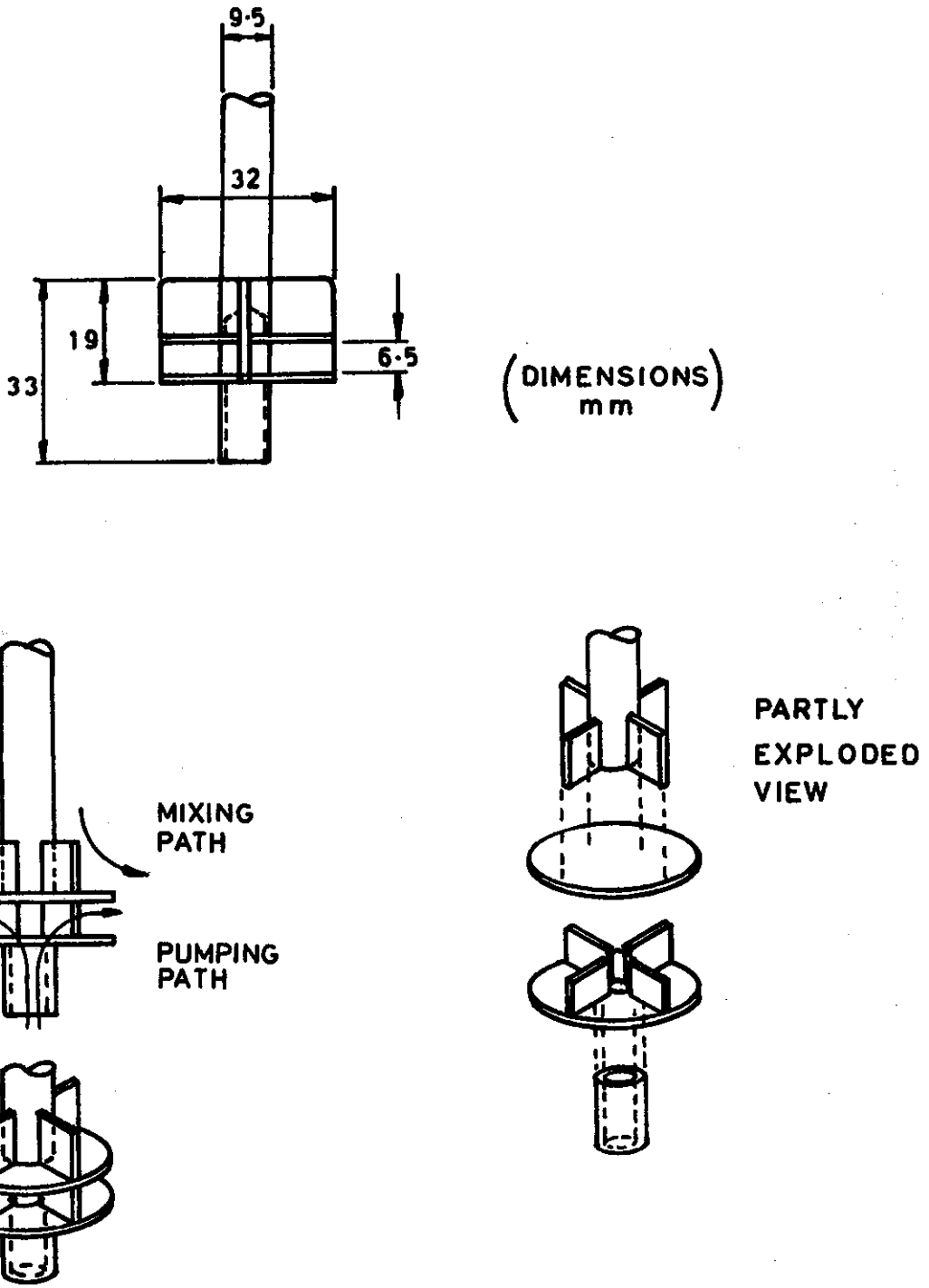


FIGURE 13. DESIGN OF IMPELLER IN MIXER-SETTLER UNITS

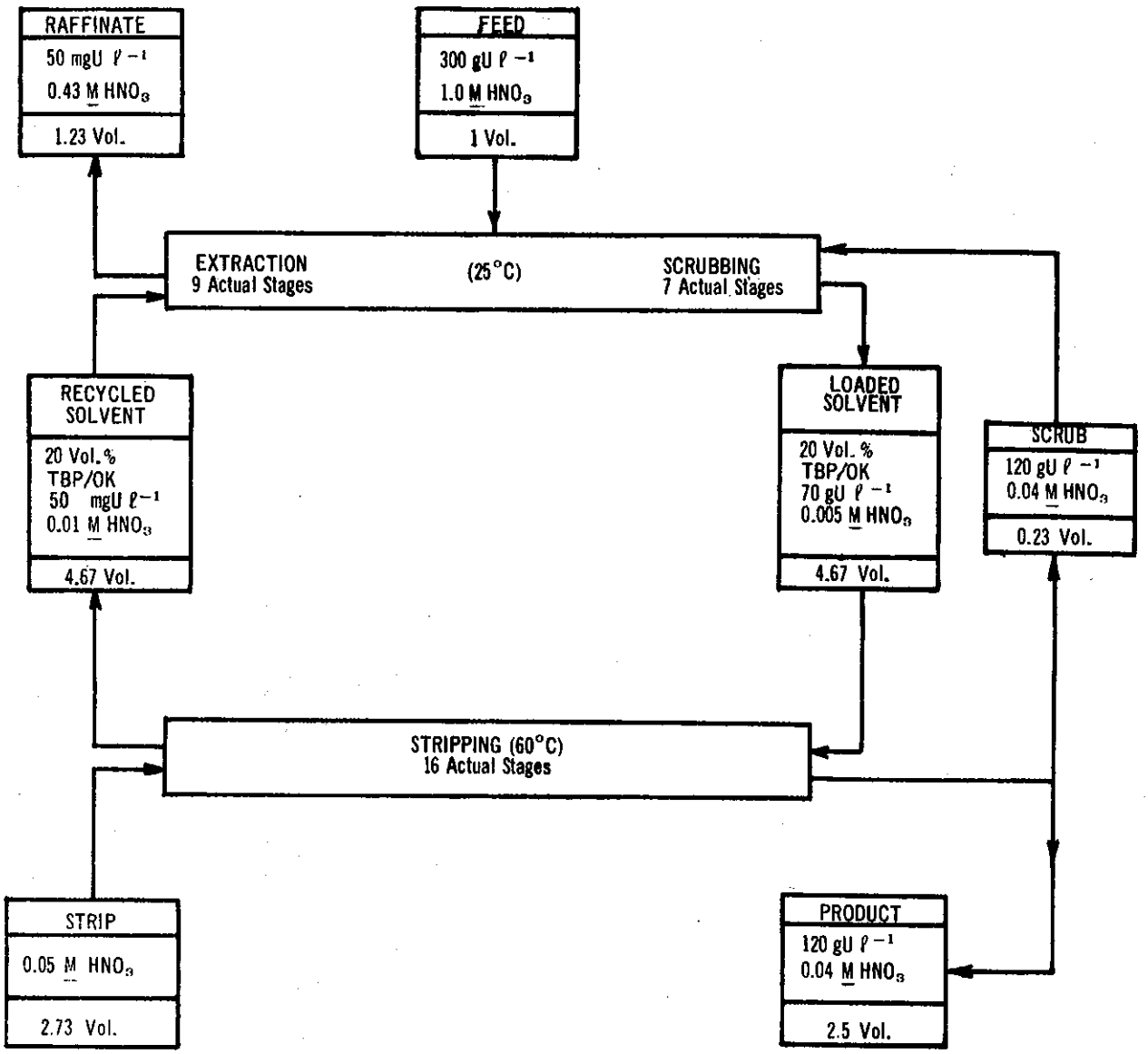


FIGURE 14. RECOMMENDED LOW ACID SOLVENT EXTRACTION FLOWSHEET