AAEC SYMPOSIUM

ON

URANIUM PROCESSING

PAPER II

CONVENTIONAL PROCESSES TO PRODUCE YELLOW CAKE

by

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1. INTRODUCTION

The term 'conventional' applied to this industry is an unfortunate choice of adjectives, as any implication that the industry is hidebound would be false. However, 'traditional' is also hardly adequate to describe processes which were developed only in the last 20 to 25 years. Prior to the discovery of nuclear fission, uranium metal was a curiosity and its compounds were produced only in small quantities for special purposes in the glass and ceramic industry, and mainly as by-products in the production of radium. The sources were equally restricted - the relatively rich pitchblende deposits of Shinkolobwe (the Belgian Congo), the Great Bear Lake (Canada) and Joachimstal (Czechoslovakia). Radium Hill davidite in South Australia was also processed intermittently for radium between 1908 and the early 1920s.

The first treatment processes used to extract uranium and applied, in fact, to produce the material for the original military devices, utilised direct precipitation, usually in more than one stage, to produce a relatively crude concentrate. Nitric acid solution and ether solvent treatment based on laboratory and analytical procedures was developed for purification purposes. Direct precipitation was extended to the recovery of uranium from relatively dilute solutions, but it was the development of the use of anion exchange resins in the late 1940s which really set the stage for large-scale economic exploitation of low-grade ores, the first commercial plant being installed in South Africa in 1952 (Lower 1951, Arden 1956, Taverner 1956).

Between that time and the mid- to late-fifties, when the alkyl hydrogen phosphate and amine solvents were applied to solvent extraction from sulphuric acid leach liquors, commercial processes were developed and these processes have changed only in detail to this day. Papers such as Ellis (1955) Brown et al. (1954) represent pioneering work in solvent extraction. In such a brief historical summary, the alkaline leach process using sodium carbonate should not be overlooked, as it was developed in a very early stage; in fact, it pre-dated modern acid recovery circuits in its commercial application at Beaverlodge in Canada (Thunaes 1958).

To undertake a detailed bibliographic review would be a monumental task and is neither the objective nor the intention of this paper. However, for those who are new in this field, the following references will lead any worker into the literature on uranium with little danger of missing any publication of significance.

Clegg and Foley (1958) although dated, is an excellent starting point. The authors of the various chapters were all men of considerable experience in their particular aspects of the practice of processing uranium ores and the bibliographies in the various chapters provide an excellent summary of pertinent literature up to the end of 1957, when most of the processes used in practice had already been developed and applied.

Merritt (1971) is a more recent survey and gives an excellent cover of American practice with particular attention to changes in the industry during the late 1960s. Another useful text is Wilkinson (1962 Vol. 1).

The United Nations and the International Atomic Energy Agency have held several conferences whose proceedings cover most of the technology developed (IAEA 1967, 1970; United Nations 1956, 1958).

Australian practice has been described at two symposia; AAEC (1958) and Berkman et al. (1968). A review of Australian practice has also appeared, collated by Fitzgerald and Hartley (1965).

2. RELEVANCE OF MINERALOGY

The operations involved in processing uranium ores can be subdivided into two major parts (Figure 1), that depending upon the mineralogy of the ore and the quantity of ore to be treated, and that depending on the quantity of uranium and the quality of the product. The common denominator of the two parts is ore grade.

The mineralogy of the ore is the most important quality controlling the process conditions required to produce the primary or 'pregnant' leach liquor. For this reason, practice from one operation can seldom be transferred directly to another. A knowledge of the mineralogy of the ore is most important to permit prediction of the likely response of the ore to subsequent operations and therefore to narrow the choice of the primary processes. The mineralogy of uranium and the behaviour of uranium minerals in processing is discussed in detail by various authors. Frondel et al. (1967) and Frondel (1958) are excellent references for uranium mineralogy, and George (1958) gives one account of the mineralogy of uranium as it relates to hydrometallurgical processing.

For brevity, and risking over-generalisation, two major classifications are suggested here, the first being subdivided into two sections, namely:

1. Ores in which the main uranium-containing minerals are taken into solution with sufficient ease that the uranium can be extracted economically from most ores, although the details of the treatment are determined as much by gangue mineralogy as by uranium mineralogy.
   a. Ores containing uraninite or pitchblende with much uranium in the 4-valency state and hence requiring an oxidant.

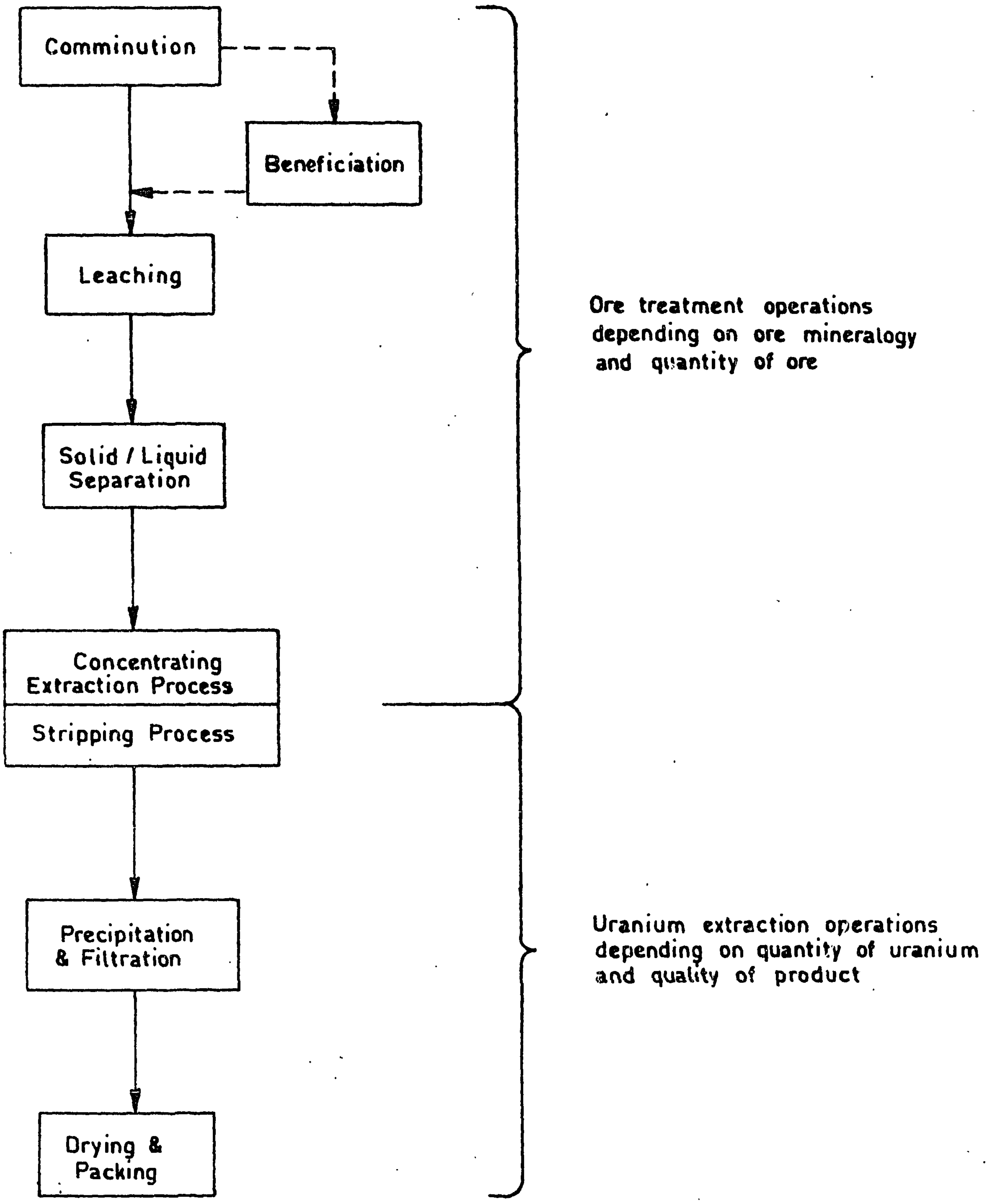


FIGURE 1. SCHEMATIC FLOWSHEET

b. Ores containing 'secondary' minerals such as gummite, becquerelite, autunite, saleeite, torbernite, uranophane, carnotite, etc. with uranium in the hexavalent state and hence requiring no oxidant.

2. Ores in which the uranium mineral requires such severe conditions for dissolution that the mineralogy of the associated gangue usually determines whether the ore can be processed economically at all. These are ores containing a predominance of the 'multiple oxide' type of uranium mineral (niobates, tantalates, titanates and zircon, etc.). The most important economic mineral in this class is brannerite. Davidite ores such as occurred at Radium Hill are also in this category

Fortunately most of the world's uranium occurs in ores of (1a + b). A notable exception is the Blind River ore, which contains a significant quantity of brannerite.

The mineralogy of the gangue has a profound effect on the economics of recovering uranium from its ores. Quartz is a non-reactive mineral and the fact that it is a major component in two of the largest uranium ore bodies (South Africa and Blind River) contributes (by default of other reactive minerals) in no small measure to the economic viability of these ores. The Westmoreland deposit in north-western Queensland also has uranium ore as uraninite and secondary minerals associated predominantly with quartz conglomerates and sandstone.

Carbonate minerals consume acid at the pH required for the dissolution of uranium minerals, and their presence as a major component has usually been the determining factor in choosing alkaline or sodium carbonate leaching, where this method has been adopted. Figure 2 gives an indication of the effect of carbonate on the economics of acid leaching.

Phosphate, particularly in the form of apatite, causes several difficulties. Firstly, it is also an acid consumer at relatively low acidities. Secondly, phosphate ions complex ferric ions and interfere with the usual role of the ferric ion as an electron transfer carrier between the oxidant and quadrivalent uranium. Thirdly, in the subsequent processing, phosphate can lead to reprecipitation unless a relatively low pH is maintained throughout. This was found to be particularly troublesome in treating some of the Palette ore at Moline (Murray and Fisher 1968).

These two components are major deterrents in the development of an economic process for treating Anderson's lode and similar ores which occur in the Mount Isa region, although the peculiarity of the uranium mineral is also significant.

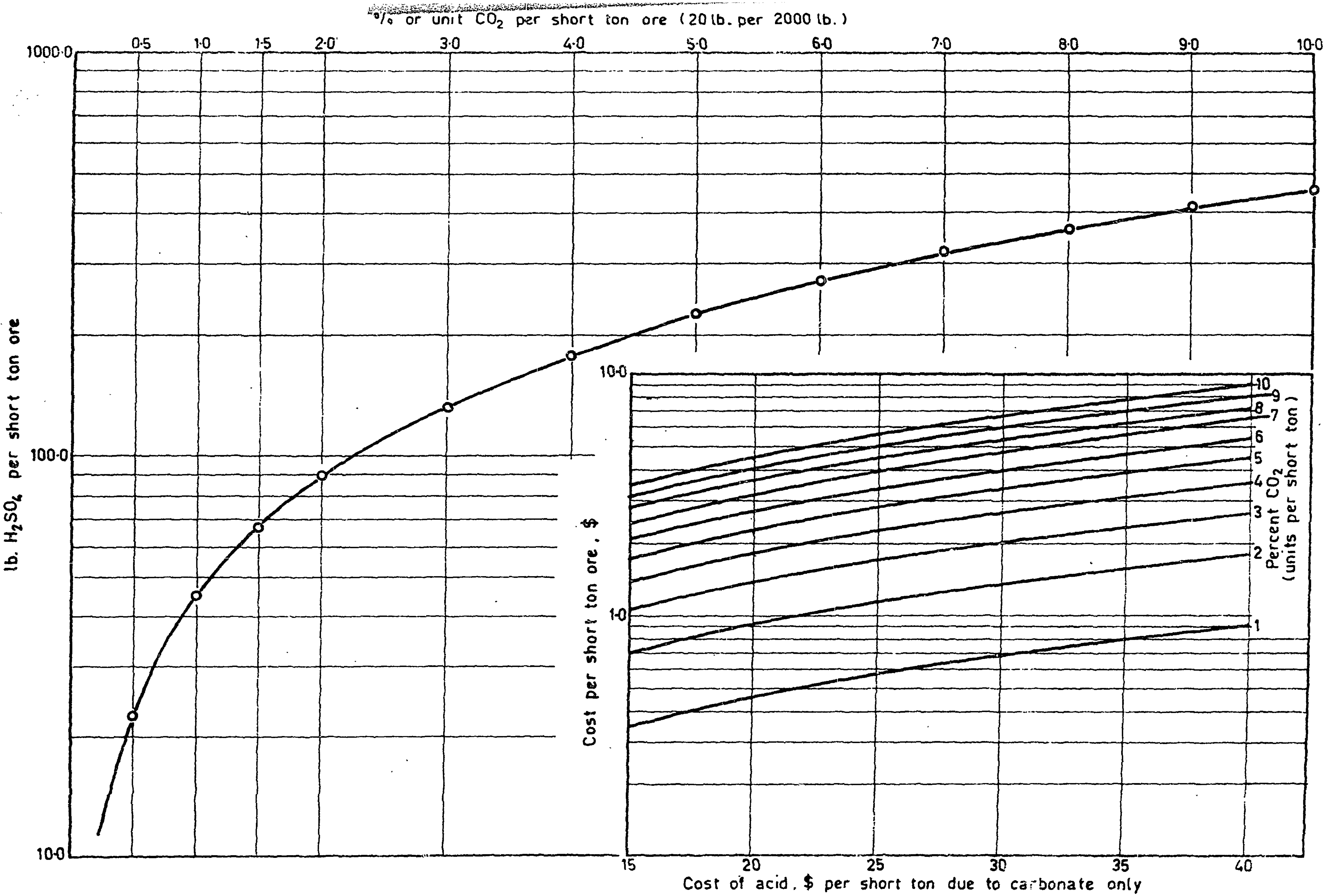


FIGURE 2. EFFECT OF CO_2 CONTENT ON ACID CONSUMPTION

Of the silicates, the primary rock-forming minerals are not sufficiently reactive to anticipate difficulties unless the uranium mineral itself requires highly acid conditions. The secondary silicates, such as chlorite and clay minerals, dissolve in part even in dilute acid leaching and contribute most of the alumina and silica and much of the iron to the solution. However, their tendency to slime can lead to more serious difficulties than their contribution to the acid consumption. These minerals certainly play the major role in determining the characteristics and the cost of the solid/liquid separation stage. This was a major problem with the Rum Jungle ores (Dyson's ore in particular).

Iron oxides, particularly goethite and haematite, dissolve completely or in part and in general are beneficial in their contribution of ferric ions to the system.

The behaviour of sulphides is not easy to predict as their reactivity to dilute acids and the general environment of the dissolution medium is variable. However, in general, the presence of iron sulphides suggests that more oxidants may be required, and as a corollary may lead to higher acid consumption. In addition their presence may indicate that the ore will be subject to rapid weathering and 'natural' leaching on stockpiles, etc.

At Mary Kathleen, the gangue minerals containing the uraninite are the basic rare earth minerals allanite and stillwellite. The increase in the rate of dissolution of these minerals over the pH range 2.0 to 1.0 was a major factor affecting the conditions used for leaching this ore (Couche and Hartley 1958, Hartley 1968).

3. ORE TREATMENT OPERATIONS

Although the operations are considered to start with the comminution processes, for control purposes the interface between mine and mill sometimes calls for selective control and ore bedding and blending. Mary Kathleen was a notable example which required selective blasting followed by the use of Geiger counters for bench sorting and subsequent truck monitoring for despatch to waste and ore stockpiles. The truck 'discriminator' consisted of an arch below which the truck could be driven, and on which were mounted six Geiger tubes whose integrated signal was used to determine the stockpile to which the load was despatched (Wreford 1965). Blending was an essential part of the treatment at Moline, where twelve ore bodies, spread over a distance of eleven miles, were mined and transported.

All of the Rum Jungle ores (White's, Dyson's and Rum Jungle Creek South) were subject to significant natural leaching, requiring precautions to be taken (Fitzgerald and Hartley 1965). Advantage can be taken when this characteristic exists, to win some of the uranium from low-grade materials by heap leaching and by natural mine leaching. Both techniques have been applied overseas (Mashbir 1964, George and Ross 1967, Anderson and Ritchie 1968, MacGregor 1964, Thunaes 1967, Downes 1967, Sugier 1967, De Lacerda 1967).

4. COMMINUTION

Compared to the grinding often required to release minerals for physical beneficiation by such processes as flotation, acid leaching does not usually require very fine grinding, diffusion through and dissolution of gangue being sufficient to give high recoveries at relatively coarse sizes. However, grinding to an upper size passing 60 mesh (250 µm) is advisable for ease of pumping and handling through the subsequent leaching and solid/liquid separation circuits. Alkaline sodium carbonate leaching is more sensitive to grinding, presumably because the gangue minerals are generally inert to this media.

The comminution plants for crushing and grinding do not differ from those employed in other metallurgical processes. The largest mill in Australia, Mary Kathleen, used conventional three-stage crushing, followed by an open-circuit rod mill and two closed-circuit ball mills, to reduce the ore to 65% minus 200 mesh (75 µm)(Wreford 1965, Harris et al. 1961). Rum Jungle treated ores with a high proportion of relatively soft, highly sheared shaley slates, schists and similar rocks and used two-stage crushing followed by open-circuit rod milling (Fitzgerald and Hartley 1965, Allman et al. 1968). Open-circuit rod milling was also used in the small Rock Hole mine treating ore not dissimilar to the recently discovered ores of Nabarlek, Jim-Jim and Ranger. However, a small proportion of harder material can lead to problems in maintaining satisfactory operation when large tonnages are being treated, and the Mary Kathleen circuit would usually be preferred for larger operations.

Between 22 and 27% of the capital cost of the treatment plant is in the comminution section (for grades of up to say 10 lb of U_3O_8 per ton of ore). This section is also the greatest power consumer. Table I is taken from Mary Kathleen experience, where a relatively large power draw was also taken by the leaching section.

In addition, 3 lb of steel per ton of ore was used for rods and balls. By comparison at Rum Jungle, the ore required only 5 to 6 kWh per ton for comminution and 0.5 lb of steel per ton. Between 10 and 20% of the treatment cost is usually in this section, which is second only to that involved in leaching.

TABLE I - POWER CONSUMPTION IN PROCESSING MARY KATHLEEN ORE

Section	kWh/ton Ore
Primary crushing	0.47
Secondary crushing	2.05
Ore sorting	0.24
Grinding (ore)	10.45
Grinding (manganese dioxide)	0.26
Leaching	3.73
CCD	1.57
Tailings disposal	0.63
Clarification	0.42
Ion exchange	0.52
Precipitation	1.02
Product drying	0.27
Vacuum (filters in both clarification and precipitation)	1.75
Total	23.38

The crushing plant is essentially a materials-handling operation and considerable operating benefits will result from the careful study of the handling characteristics of the ore, when wet and dry, and the lay-out and machinery installed in this section of the plant. Control to the secondary and tertiary crushers by optimising power draw, and attention to design for good housekeeping and materials to maximise the life of screens, chutes and crusher liners, will all effect significant operating economies with little if any increase in capital.

Autogenous milling has been adopted at Utah's Shirley Basin mill (Ritchie 1971) where a major advantage is its ability to handle wet ore, which can be troublesome or impossible through the conventional crushing, screening and conveying systems. A pilot study using an autogenous 6 by 2 Hardinge mill has been described (Zivanovic et al. 1971). Pebble milling has been shown to demonstrate savings and has been adopted in a number of mills at Elliot Lake (Roach 1958, Roach et al. 1964).

5. PHYSICAL BENEFICIATION

Physical beneficiation before chemical treatment offers the following potential economic advantages:

a. Capital savings in the ore treatment section of the plant (Figure 1). This is particularly pertinent to ores containing less than about 0.25% U_3O_8.

b. Transportation of up-graded concentrate to a distant treatment plant is possible.

c. A significant increase in the uranium-producing capacity of the plant can be effected with minimal extra capital costs.

d. Reagent consumption in the leaching section and general operating charges per pound of U_3O_8 can be reduced by effectively increasing the grade fed to the ore treatment section of the plant.

e. In the extreme case of (d) the amount of reagent consuming gangue materials (such as carbonates and phosphates) can be reduced sufficiently to make the uranium extraction economically viable.

Some consideration should always be given to the possibility and likely economics of beneficiation procedures. These can be obtained from basic mineralogy (with particular regard to uranium distribution and its association with the gangue mineral) to suggest those parts of the ore which must be rejected to obtain a barren or low uranium fraction, or concentrated to produce a rich uranium fraction.

The high-grade uranium ores produced for radium in the early days, were concentrated by simple gravity methods, using jigs and tables similar to those used for cassiterite. The Eldorado Mining and Refining Company gravity plant was probably the best known (Behan 1956) and was operated until 1960. A small gravity plant, using hand-sorting, a jig and a table, was used to produce 100 tons of pitchblende concentrate (approximately \$1.4 million worth of U_3O_8) from the El Sherana mines in the South Alligator area of Australia, and two large lumps - one of 1,875 and the other 1,250 lb weight - are noteworthy (Murray and Fisher 1968).

The Radium Hill ore of South Australia was concentrated by heavy media separation (ferrosilicon suspension), followed by flotation. The overall recovery of the uranium, which occurred in the davidite mineral was 86.4%, and the concentration ratio was 5.4 : 1, producing a concentrate of approximately 1% U_3O_8 for shipment to the Port Pirie treatment plant (Rodgers 1958, Armstrong 1965). The ore could not have been treated without this prior concentration step.

Radiometric sorting was used at Mary Kathleen to effect a significant rejection of barren garnet and in part allanite rock, from the plus 3-inch feed after the primary crusher. Up to 22,000 tons of waste was rejected per month and a 30% increase in feed grade was achieved. The success of the method was particularly dependent on the unique U_3O_8 distribution through the size range which existed in the feed. Thus about 33% by weight of the plus 3-inch material contained less than 0.04% U_3O_8, virtually none contained 0.04 to 0.1%, and about 66% by weight contained more than 0.1% U_3O_8. A cut-off of 0.07% therefore discriminated ore from waste very easily (Harris and Steele 1960, Wreford 1965).

The heavy-media cyclone has been extensively exploited in South Africa. Its advantages are in particular the ability to treat large quantities in a relatively small physical plant, the ability to control the spigot density within fine limits (0.005 sp.gr.) and the ability to treat material down to 0.5 mm size. A plant has been installed at Vaal Reefs Exploration and Mining Co. Ltd., South Africa, to treat uranium ore. Twenty-five per cent of the feed to the cyclone is bypassed (as overflow) to the gold plant at less than 0.001% U_3O_8.

Techniques, developed in Australia in association with beach sand heavy-mineral concentration, have been utilised to treat the tailings from the large copper plant of Palabora Mining Co. Tailings (about 60,000 tons per day) in six separate streams are deslimed and treated by Reichert cones, spirals, magnets and tables to produce a concentrate of uranium mineral together with magnetite. A significant proportion of chalcopyrite is also scavenged from the tailings.

I am not aware of any published information on these plants, and readers are referred to general references in the introduction to this paper for descriptions of other overseas beneficiation operations.

6. LEACHING

Uranium can be taken into solution by acid or by alkaline carbonate solutions. In sulphuric acid solution a number of complex anions are formed, typified by:

$$UO_2(SO_4)_2^{2-} \text{ and } UO_2(SO_4)_3^{4-}$$

while in carbonate solutions, the main complex anion is:

$$UO_2(CO_3)_3^{4-}$$

The chemistry of the solution of hexavalent uranium oxide or compounds is more or less an acid/base dissolution, the protons combining with the oxygen or the anion associated with the UO_2^{2+}. Thus, for the oxide, the following equations apply:

Proton Reaction: $UO_3 + 2H^+ \longrightarrow UO_2^{2+} + H_2O$ ...(1)

and either

'Acid' Sulphate: $UO_2^{2+} + 3SO_4^{2-} \longrightarrow UO_2(SO_4)_3^{4-}$ ...(2)

or 'Alkaline' Carbonate: $UO_2^{2+} + 3CO_3^{2-} \longrightarrow UO_2(CO_3)_3^{4-}$ ...(3)

For Reaction (2), the hydrogen ion in (1) comes from the sulphuric acid and for Reaction (3) it is supplied by bicarbonate which must be present. If the uranium is present in the tetravalent form, as in UO_2, such as it is in part in uraninite, it does not dissolve in dilute sulphuric acid nor in carbonate solutions at perceptible rates, and requires oxidising to the hexavalent form:

$$UO_2 - 2e \longrightarrow UO_2^{2+} \qquad ...(4)$$

The oxidation reaction can be quite complex, rapid oxidation in acid medium being achieved mainly by the presence of ferric ions in solution:

$$UO_2 + 2Fe^{3+} \longrightarrow UO_2^{2+} + 2Fe^{2+} \qquad ...(5)$$

and hydrogen ions are not required. However, to maintain the dissolution of the UO_2, the Fe^{3+} must be renewed by subsequent oxidation of the Fe^{2+} formed in (5), and this reaction uses hydrogen ions. Thus, if manganese dioxide is used (pyrolusite) the following applies:

$$2Fe^{2+} + MnO_2 + 4H^+ \longrightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O \qquad ...(6)$$

The role of the ferric ion in the acid dissolution of UO_2 is most important. It acts essentially as an electron transfer 'catalyst'. Neither oxygen, manganese dioxide nor chlorate ions, for example, are effective in oxidising UO_2 at practical rates under normal conditions of temperature and pressure (Rhees 1962, Arden 1959). The ferric ion is thought to act by adsorption on the mineral surface. Ferric ions, of course, cannot be maintained in an alkaline carbonate solution and it is the lack of such a catalyst which is largely responsible for the very different conditions required in carbonate leaching, as compared to acid leaching. Carbonate leaching calls for more severe conditions of pressure and temperature, often a longer leaching time, and finer grind size to effect the oxidation of the UO_2. Cupric ions act as an oxidant in these solutions and can be added as cupric ammonium solutions (Magno and De Sesa 1957, Clifford et al. 1956).

This review was originally intended to deal with alkaline carbonate and acid leaching practices. The former has been omitted because another paper (Butler 1972) deals specifically with carbonate leaching practice. Suffice it to say, that alkaline carbonate leaching is considered only when the acid-consuming carbonate gangue minerals are present in excessive quantities, probably when the ore contains somewhere between 2 to 4% CO_2 or more, depending upon the cost of acid (refer Figure 2).

The variables affecting the leaching of the ore in sulphuric acid are: the mineralogy, grind size, acidity, oxidant addition, temperature and pulp density, and a systematic experimental programme should examine each of these for any particular ore using mineralogy as a base guide.

As was indicated previously, the mineralogy plays such a dominating role in determining processing conditions, that a generalisation of operating practice is hardly possible. A few comparisons between Australian practices will serve to illustrate.

The need to beneficiate the Radium Hill ore to prepare a concentrate for leaching has been described. This concentrate contained the uranium in davidite - a highly refractory mineral. 840 lb of acid to a ton of concentrate were added as 98% acid to a 61% solid slurry. The heat of solution of the acid brought the mixture to the boil and this condition was maintained for 10 hours by steam injection, in vessels fitted with sealed agitators and lined with acid-proof brick. Such conditions are fortunately not often required. Details of this operation have been described by Almond (1958) and will not be discussed further.

The leaching conditions at Mary Kathleen can be compared with those at the other three Australian plants which operated. There were features of MK which particularly highlight the effect of ore mineralogy on the choice of the process conditions.

Physically, the MK ore produced a gritty, non-plastic pulp and had a high specific gravity (3.6), so that the slurry had relatively little viscosity, whereas Rum Jungle ores (in particular Dyson's ore) were somewhat notorious for their clay-like character, giving relatively high viscosity slurries, which were not easy to thicken or filter. The South Alligator ores were also in this sense similar to the Rum Jungle ores, although they did not prove to be particularly difficult to thicken. With the coarse grinds employed in each case (particularly the open circuit grind at Rum Jungle) difficulties were encountered in handling all of these pulps if adequate pumping velocities were not maintained, but much greater problems could have arisen with the Mary Kathleen ore. Hence conventional rod mill, close circuit ball milling was adopted to ensure a minimum of plus 250 µm material. Also the power required for air agitation was shown in pilot plant work in pachucas to be little less than for mechanical agitation to maintain adequate suspension.

Another reason for the choice of mechanical agitation in the leaching section at Mary Kathleen, compared to the relatively gentle pachuca action at Rum Jungle, was to effect very rapid blending of acid. This was essential to achieve control of pH to within close limits throughout the total leaching vessel. The main gangue minerals containing the uraninite were highly reactive in acid at a pH of about 1.5 and less, but adequate rates of leaching could not be achieved for uraninite, unless the pH could be maintained much of the time at about 1.7. The reactivity of the gangue to acid is illustrated by Figure 3 (Hartley 1968) which shows the rapid increase in pH when the acid addition was stopped at various stages in the leaching. In many plants throughout the world pH was used to observe and control acidity, and thus effect a marginal economic saving and achieve a terminal pH satisfactory for the extraction operation, without recourse to neutralising agents. At Mary Kathleen, however, pH control was mandatory if good leaching was to be achieved without gross dissolution of gangue with its resulting problems (Couche and Hartley 1958, Hartley 1968).

In ores containing brannerite or 'metamict' zircon such as Blind River and some of the ores in Australia around the Mount Isa area, a relatively high acidity (of the order of 0.5 to 1.0 normal) must be maintained throughout the leaching period to obtain satisfactory dissolution rates for these minerals. In the absence of reactive gangue (such as at Blind River) little acid is actually consumed by the leaching reaction. However, this means that considerable excess acid is left in the resulting liquor, so that neutralisation is required to adjust the pH to the 1.5 to 1.7 range normally used in the extraction circuit. A two-stage leaching procedure has been adopted in some Canadian plants, to make effective use of this free acid by contacting the liquor with fresh ore before separating for extraction (Robb et al. 1963).

The need for an oxidant and the oxidation mechanism has already been discussed. Sodium chlorate is used by some mills in Canada and the United States, but in Australia manganese dioxide in the form of pyrolusite has been the cheapest form available. It can be added in part at the mill, but customarily it is added during the leach and its addition is controlled by

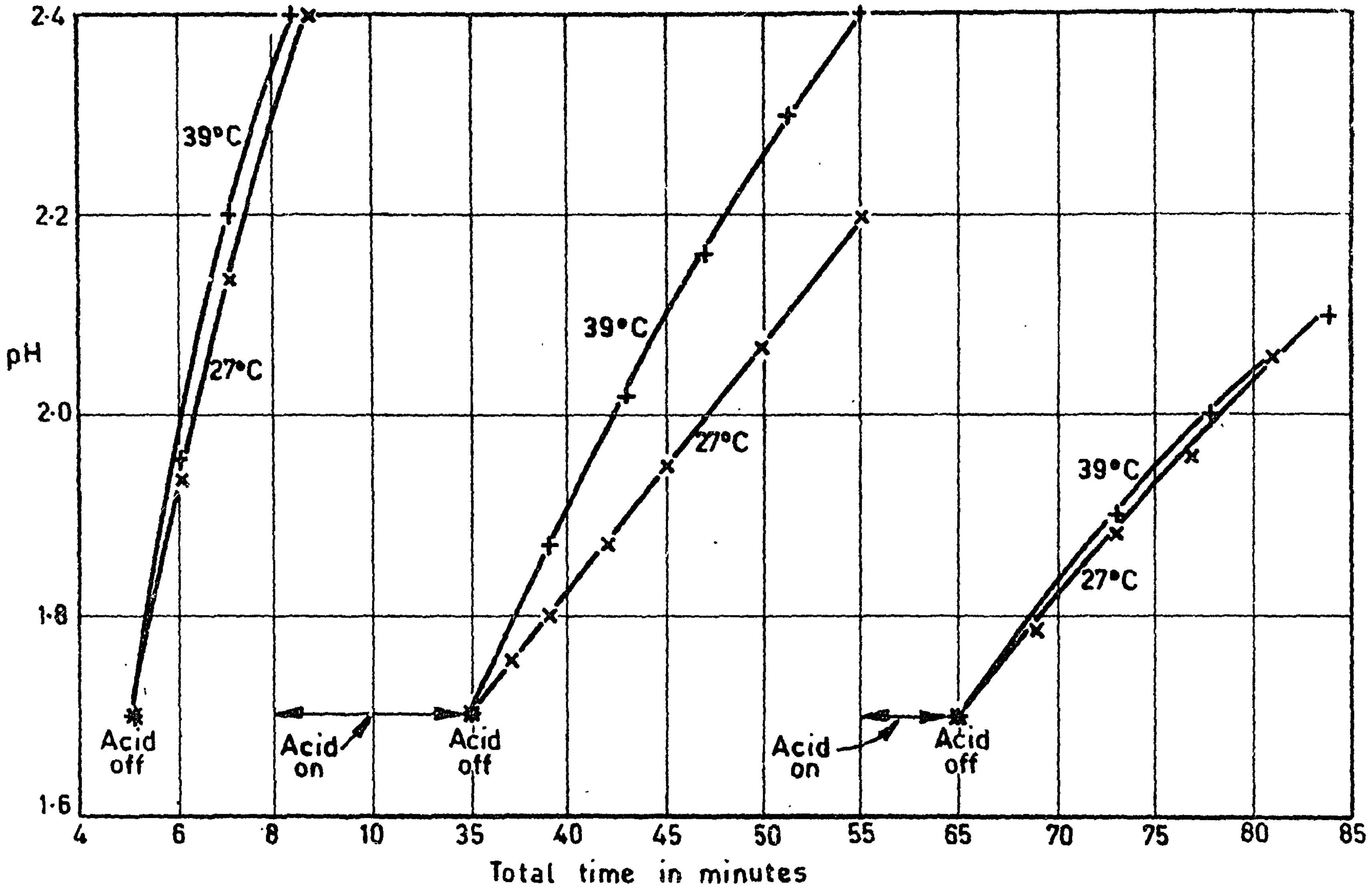


FIGURE 3. CHANGE IN pH WITH TIME

60% Solids; Temperature 27°C and 39°C

continuous measurement of the redox potential which is maintained below -350 mV, preferably between -400 and -500 mV. Ferric iron, must be present, and its concentration should never be less than 0.5 g/litre. The ratio of ferric to ferrous iron has been found to affect the dissolution of the UO_2; however, whether redox potential or this ratio is used to control the oxidising condition of the leach, the particular figure used for one ore cannot necessarily be transferred to another. The reason undoubtedly lies in the mechanism of the catalytic effect of the ferric iron in transferring electrons from the pyrolusite to the UO_2. Since it appears to be dependent on adsorption of the ferric ions on the UO_2 surface, the surface area available and the number of competing ions in the liquor will affect the result (Laxen 1964).

The pulp density is maintained at as high a figure as can be handled and between 50 and 60% solids by weight is common.

Although temperature affects the rate of dissolution in acid, heat is not often required for leaching of ores other than the compound oxide types (brannerite, davidite, etc.). In some cases, Mary Kathleen being a particular example, there is advantage in removing heat from the system to limit the attack on the gangue minerals. In undertaking experimental work on leaching, it is always as well to remember that the ambient temperature in the commercial leaching circuit could be quite different from that in the laboratory. In the Northern Territory, temperatures are frequently significantly higher than those in the south. In addition, the heating effect of the grinding, and the heat of dilution of the acid which is added to the pulp, must be taken into account. Therefore, leaching experiments should be conducted in the laboratory at the temperature which might be expected to be achieved on the plant, if one is not to be faced with unexpected results on the plant operation. At Mary Kathleen, the acid was first diluted to 50% and then cooled before adding to the leach, to remove most of the heat of dilution of the acid and avoid excessive attack on the allanite (Hartley 1968).

Of the order of 50% of the treatment costs can be involved in the leaching operation. Therefore, a detailed experimental study, which should include a range of samples from the ore body, can effect considerable savings during future operations.

7. SOLID LIQUID SEPARATION

There are two operations involved: the separation and washing of the gross amount of the leach residue from the leach or pregnant liquor, and the clarification of the pregnant liquor.

Multiple stages of filters are used in South Africa for the primary separation and washing of the leach residue, and also in some Canadian plants. Counter-current decantation (CCD) in thickeners is favoured in the USA and Australia. The choice of filters or CCD depends upon such factors as the grade of ore and the ease of filtration without blinding. Thickening is less susceptible to variations in the ore but the solids from each stage contain more liquor, so a greater dilution results, and more water is required. Space may be at a premium, particularly in sub-zero climatic conditions (as in Canada) so favouring filters. Operating and maintenance costs of filters are usually high, but personal preference also plays a part in the decision.

Filters were originally installed at Rum Jungle, but were replaced by CCD, which was used in all the other four uranium plants in Australia. Poor washing efficiency at this stage can lead to a greater economic loss than at any other stage in the plant.

Flocculants are almost universally used to improve the settling rate of the solids. It is not unusual to be able to reduce the area required for the thickener by a factor of four and more, by the use of these reagents. Mary Kathleen was the first CCD plant actually designed to use the synthetic polyacrylamide flocculants. Table II compares Australian statistics in CCD plants.

TABLE II: SUMMARY OF AUSTRALIAN CCD PLANTS

Plant and Throughput (ton/day)	Number and Diam. (ft)	Area (ft^2/ton/day)	Flocculant and Amount (lb/ton Solids)
Rum Jungle (400)	1 x 100 3 x 75	20 12	Guar Gum Total 0.27
Mary Kathleen (1200)	5 x 75	4	Separan NP10 No.1 0.090 No.2 0.026 No.3 0.010 No.4 0.010 No.5 0.010
			Total 0.146
Subsequently changed to Superfloc 16:			Total 0.047
Moline (100)	4 x 25	5	Separan 0.3 total
Rock Hole (15)	5 x 10	5	Superfloc 16 0.21 total
Port Pirie (100)	2 x 100 2 x 80	80 50	Glue + Separan 2.0 + 0.02 total

The area figures for Rum Jungle do not reflect any shortcomings in the performance of guar gum so much as the notoriously poor settling characteristics of the ore.

Effective repulping agitators are required between stages together with good density control in the underflow to achieve optimum performance in the washing circuit. In determining the number of stages of CCD, the incremental weight of the uranium recovered is the important factor rather than the per cent recovery. The usual wash ratio (that is, the ratio of wash liquor or pregnant liquor volume to the underflow liquor volume) is between 5 and 6, with between 15 and 20% by weight of solids in the feed to the thickeners, and between 50 and 60% in the underflow.

The pregnant liquor must be polished by clarification before going to the extraction circuit, either ion exchange or solvent extraction. A variety of equipment has been used, ranging from pressure leaf pre-coat filters to continuous rotary drum vacuum pre-coat filters. Gravity sand filters have commonly been used in South Africa, where very large volumes are clarified and labour for cleaning is relatively cheap. Pressure sand filters have proved successful in Australia, being used at Rum Jungle and the South Alligator River plants. There is a danger of upsetting the solution balance should the thickeners overflow very cloudy liquors, because of the more frequent need to backwash. Continuous vacuum pre-coat drum filters such as were used at Port Pirie and at Mary Kathleen are excellent, giving a very clear filtrate and having the flexibility of being able to handle more solids. Although the operating costs are higher than for sand filters, the extra costs can be taken up by reducing the flocculant to the CCD, deliberately permitting more slimes to go to the clarifier.

8. URANIUM EXTRACTION OPERATIONS

The pregnant liquor contains a complex mixture of cations and anions, as well as the uranium in a sulphate solution of pH usually between 1.5 and 2. The composition of the liquor depends on its origin, the ore minerals, but there is always a proportion of aluminium and iron, usually some silica and a small amount of many other elements. Mary Kathleen contained a significant component of rare earths and of phosphate, and an exceptionally large amount of silica (1.5 to 3.0 g/litre). Rum Jungle liquors contained copper in sufficient quantity to justify recovery by cementation and Radium Hill liquors, which were exceptionally concentrated because of the very aggressive leaching conditions (iron of 16 g/litre and higher, for example) also contained rare earths, scandium, titanium and a significant amount of vanadium. At concentrations of between about 0.5 and 1.5 g/litre, uranium is therefore a minor constituent, considering the molecular weight involved. Thus the molar concentration of UO_2^{2+} is seldom more than 0.005 in solutions which are typically greater than 0.15 molar in SO_4^{2-}, up to 0.3 molar being not uncommon.

A highly selective process is therefore required to prepare a high-grade uranium product from such solutions.

Three main processes have been used: selective direct precipitation, ion exchange, and solvent extraction.

The following species can be present in the sulphate solution:

UO_2^{2+}, UO_2SO_4, $UO_2OHSO_4^-$, $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$.

In the range of concentration and pH usually existing in process solutions, $UO_2(SO_4)_3^{4-}$ is the dominant species. The characteristics of these ions, such as multivalence and low solvation, favour the adsorbate in ion exchangeable systems, and advantage is taken of this in the use of solid resin ion exchangers and liquid solvent ion exchangers. General reactions of the following type take place:

1. Quaternary amine - anion exchange - most resins are of this type, e.g. resin in chloride form:

$$4R_4NCl + UO_2(SO_4)_3^{4-} \rightleftharpoons (R_4N)_4UO_2(SO_4)_3 + 4Cl^- \qquad ...(7)$$

2. Tertiary amine - anion exchange - most solvent systems use this type, e.g. a solvent in a chloride form:

$$4R_3NHCl + UO_2(SO_4)_3^{4-} \rightleftharpoons (R_3NH)_4UO_2(SO_4)_3 + 4Cl^- \qquad ...(8)$$

3. Alkyl phosphate - cation exchange - some solvent systems are of this type:

$$2R_2HPO_4 + UO_2^{2+} \rightleftharpoons (R_2PO_4)_2UO_2 + 2H^+ \qquad ...(9)$$

No cation exchange system has been used with solid resins. In the industry, the resin system is called ion exchange (IX) and the liquid solvent system is called solvent extraction (SX) and will thus be referred to.

Both IX and SX consist of two parts. In the first part, pregnant liquor is contacted with organic phase to transfer the uranium relatively selectively, into the organic phase. This is termed the adsorption stage in IX and the extraction stage in the SX. In the second part, the organic phase is contacted with an aqueous solution of such a nature that it strips the uranium back into a high-grade, relatively pure, uranium solution. In IX this is termed the elution, and in SX the stripping stage.

9. FEATURES OF THE IX PROCESS

In the 'conventional' process, the resin does not move. It is contained in a series of columns through which the various aqueous solutions are passed. The IX process depends upon the characteristics of the resin and the characteristics of the pregnant solution.

Ion exchange resins for uranium adsorption are strong base (quaternary) amine type resins, which appear as relatively rigid, spherical beads, the matrix of which is a polystyrene (Robinson et al. 1958, Grinstead et al. 1955, Preuss and Kunin 1955, Helfferich 1962). The major characteristics of the resin affecting the process are the chemical capacity, the rate of exchange and its sensitivity to ions other than uranium.

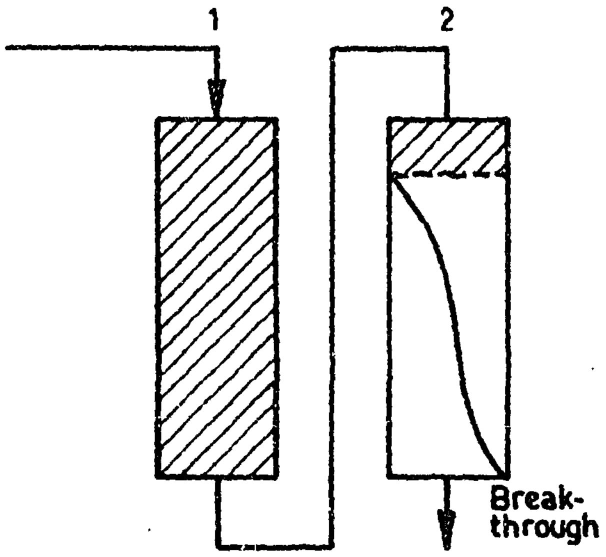
The chemical capacity is usually measured in terms of milli-equivalents of exchangeable ions per gram of dry resin or per ml of 'wet settled resin'. The latter is a less exact measure but more meaningful when related to the volume of resin in the column. The capacity of resins available on the market varies between 3.5 and 4.5 milli-equivalents per gram, or 1.2 to 1.4 per ml of 'wet settled resin'. The rate of loading and of elution is most important, as also is the sensitivity of the resin to various foreign ions in the solution.

These three characteristics determine the operating capacity of the resin, which is defined as the weight of uranium processed per cubic foot of resin per unit of time. The following procedure was adopted in determining operating design capacity and choice of resin at Mary Kathleen, and illustrates the importance of the rate effect.

When the pregnant liquor passes through the column, the resin at the top adsorbs uranium and becomes 'saturated' or fully loaded first. The liquor is depleted in uranium, so that further down the column the liquor has no uranium (is 'barren') and the resin, of course, has no uranium. A concentration profile is therefore established as shown by Figure 4, which gives the concentration of uranium in the effluent sampled after it passed through the resin. Point A marked 'breakthrough' is usually taken as a concentration of U_3O_8 equivalent to 2% of the concentration of the head or pregnant liquor. In practice, when breakthrough occurs, a second column is brought into line. When the 'leading' column effluent reaches Point B, the resin is not adsorbing any more uranium and has reached 'saturation' under the particular conditions operating. Ideally, this should coincide with breakthrough on the 'trailing' or second column. Usual practice is to control on breakthrough of the trailing column, and design so that the resin column is rather deeper than required to contain the concentration profile, thus ensuring that the leading column is fully loaded. This column is then taken off line for elution, and column 3 is brought in as the trailing column. The inset to Figure 4 shows this system schematically.

To prepare design data and choose the most suitable resin, experiments were conducted to determine the volume of liquor to breakthrough, and the volume between breakthrough and saturation at various flowrates of pregnant liquor. A plot then gave the optimum retention time and the volume of resin required. Figure 5 illustrates the type of plot for two different resins.

The resins were then eluted using 1.0 molar sodium chloride in 0.05



END OF ADSORPTION STAGE COLUMNS 1-2
Showing schematic profile of liquor concentration in Col. 2
Column 1 now goes to elution stage.
Column 3 comes on adsorption

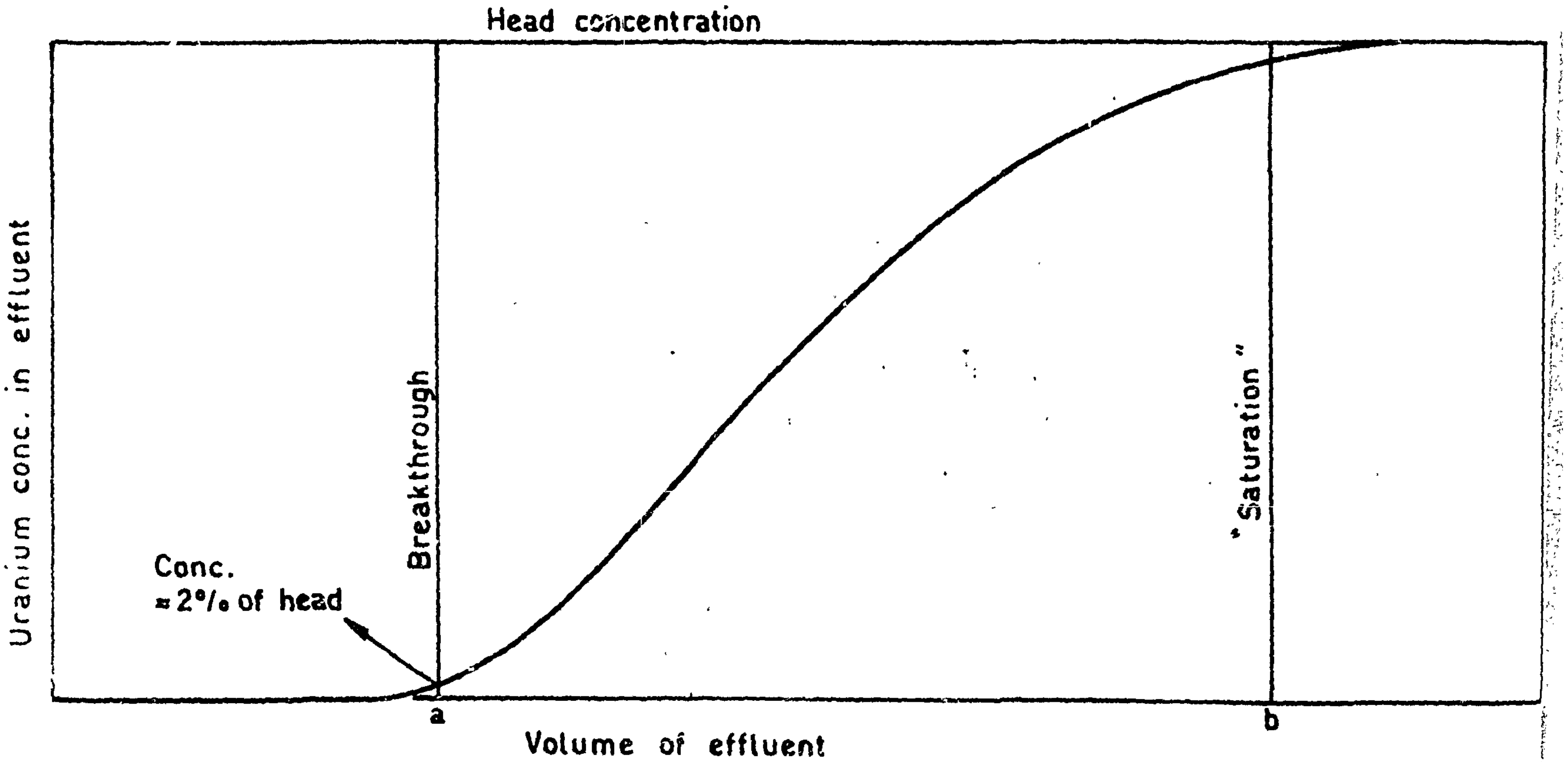
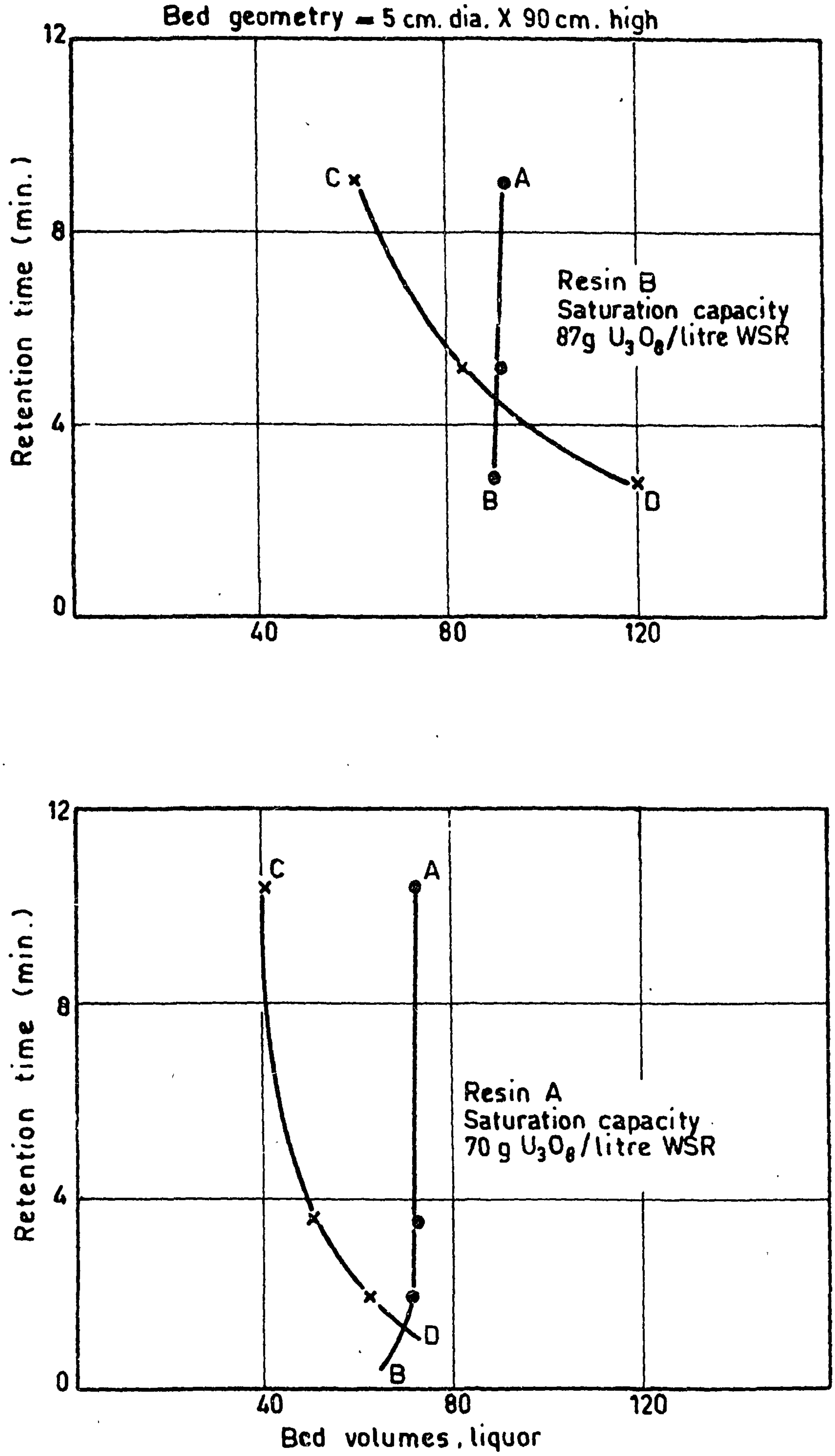


FIGURE 4. ION EXCHANGE CONCENTRATION PROFILE



AB = Volume to breakthrough
CD = Volume between breakthrough and saturation
Bed volume = Volume of wet settled resin in the column
Retention time = $\frac{\text{Void volume}}{\text{Volumetric flow rate}}$
Bed geometry = 5 cm. dia. X 90 cm. high

FIGURE 5. DETERMINATION OF RETENTION TIME AND RESIN VOLUME

molar sulphuric acid, the eluant commonly used in Australia for ion exchange operations. The reaction of the eluant is for the chloride ion to displace the $UO_2(SO_4)_3^{4-}$ complex, thus reversing Reaction (7) above, the acid being required to prevent any precipitation. The elution concentration profile is quite different from the absorption, since a loaded stationary phase is being stripped with the flowing aqueous phase. The uranium concentration rapidly increases in the eluate, then tails off, as the resin approaches the fully stripped condition. Figure 6 illustrates this profile for the two resins concerned.

The marked difference in the rates is shown by these figures. This was done for three different resins, and computations, using the figures obtained, gave the results summarised in Table III. Note that the resin with the lowest saturation capacity was much superior, due to the faster rates of loading and elution.

TABLE III: OPERATING CHARACTERISTICS FOR ION EXCHANGE RESINS

	Retention Time		
	1.5 min Resin A	3.3 min Resin B	4.2 min Resin C
Saturation uranium loading (g U_3O_8/litre resin)	70	87	78
Vol. of liquor treated/cycle (bed volumes)	72	90	78
Cycle time: $\frac{\text{Vol. treated/cycle}}{\text{flowrate}}$ (minutes)	270	742	819
U_3O_8 produced (g U_3O_8/litre resin/col/hr)	15.5	7.0	5.7
Eluant required (litres/litre resin/cycle)	6.61	12.6	15.7
= (mℓ/g U_3O_8 produced)	94	145	201

A major disadvantage of conventional ion exchange is the fact that the concentration of the eluate varies, as shown in Figure 6 (curves a). The practice adopted is to split the elution into two main fractions, the first (high grade) going to precipitation; the second fraction then becomes the first fraction in the next elution. This makes more effective use of the chloride, and sends high-grade solution to the precipitation circuit.

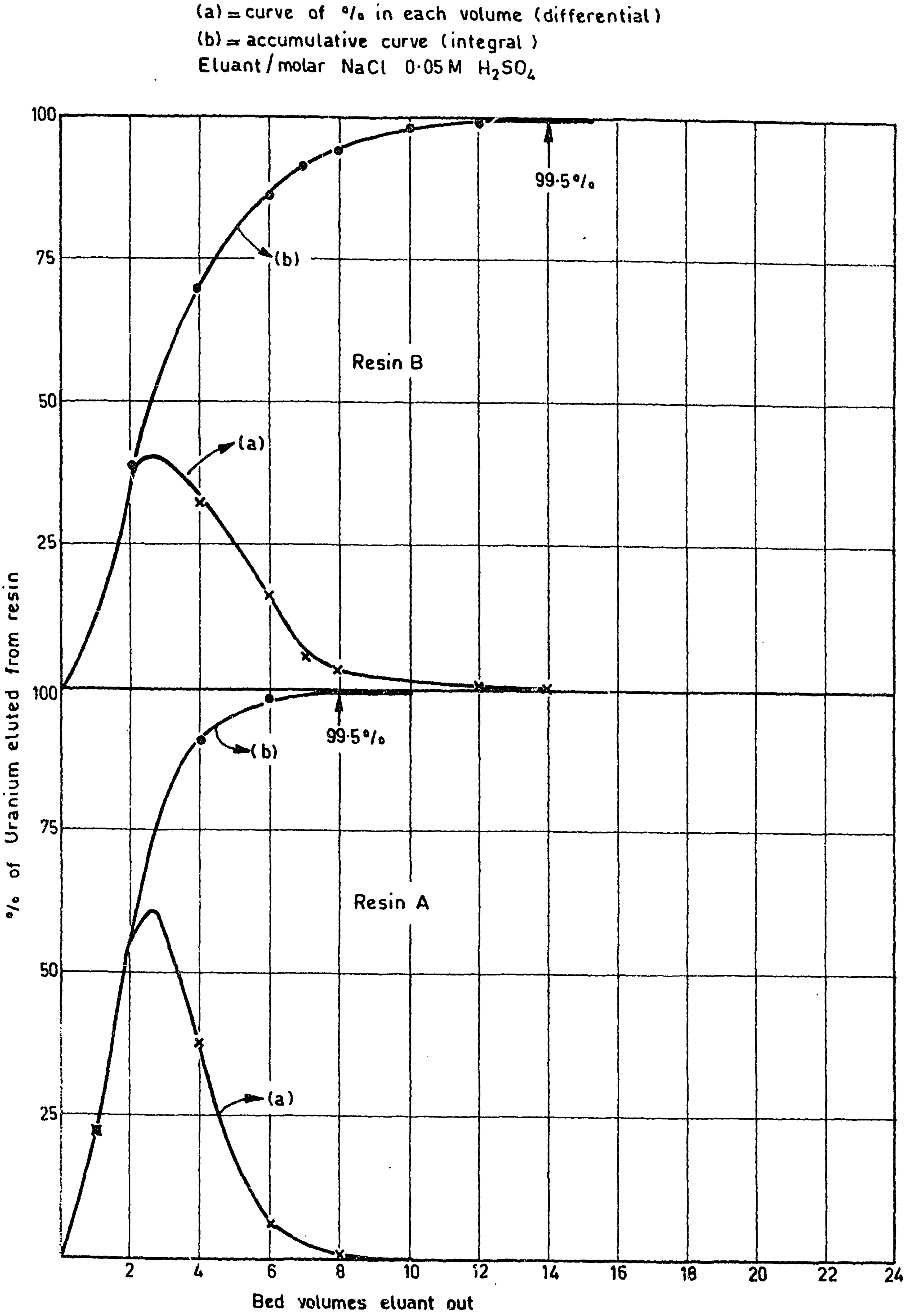


FIGURE 6. ELUTION CURVES

The resin must be washed and various liquors displaced from the bed between each stage. Sometimes special cuts are made to separate fractions of the eluate containing contaminants or to control the sulphate build-up in the eluant. Thus a fairly complex cycle of operations is involved with an extensive tank farm to deliver and receive a number of fractions. The cycles are controlled automatically by time switching of valves after a manual changeover of the adsorptions at breakthrough. At Mary Kathleen, where lanthanons and sulphate were controlled in the elution cycle, there were eleven stages altogether, with seven in the elution cycle (Hartley 1968, Harris et al. 1961).

Since the formation of the divalent complex $UO_2(SO_4)_2^{2-}$ is favoured by higher pH, it is preferable to increase the pH of the pregnant liquor (and thus achieve higher loadings). However, iron also forms sulphate anion complexes whose concentrations increase considerably with pHs above 2. Also, precipitation must be avoided, and consequently the pregnant liquor pH going to ion exchange is usually about 1.7 or sometimes as low as 1.5, if iron is particularly troublesome. Much the same applies to solvent extraction.

Some components in the pregnant liquor can poison the resin by irreversible absorption. Titanium and silica were troublesome at Port Pirie and Mary Kathleen, respectively. These two components undergo a polymerisation in the resin, and so lead to 'mechanical' blockage, that is, they slow down the rate of diffusion rather than affecting the absolute chemical capacity of the resin. Methods of combating these 'poisons' are described in the literature (Harris et al. 1961, Hartley 1968, Hartley and Lawrie 1955). Reference to the literature will give information on other types of poisons encountered in South Africa and elsewhere.

Although sodium chloride eluant was used in each of the three ion exchange plants in Australia (i.e. Port Pirie, Rum Jungle and Mary Kathleen), nitrate eluant is used in South Africa and sulphuric acid has also been used in conjunction with the 'Eluex' process in which the eluate is treated by solvent extraction to obtain a purer product (refer to Merritt (1971) for a more detailed review of ion exchange processing).

Moving bed resin systems have been developed to overcome the cumbersome multi-stage cycle; to enable the plant to accept solids (resin-in-pulp); to maintain 'steady state' concentration in the various feed and product streams; and to reduce resin inventory (George and Ross 1967, Higgins 1955, Hancher 1959, Herwig et al. 1958).

Resin-in-pulp plants using baskets and modifications of the Infilco CST exchanger system are operated in the United States (Hollis and McArthur 1956, Lentz and Temple 1959). The latter system is probably the closest analogy that the solid phase ion exchange system has to the liquid SX counter-current system.

10. FEATURES OF THE SX PROCESS

The chief advantage of SX over IX is the fact that both phases move counter-currently and the system is more or less in steady state, continuously producing 'barren' from the extraction section and high-grade strip solution from the other section, the solvent acting as a transfer medium for the uranium from one stream to the other.

Solvents typically have compositions as follows:

'Base Exchange'		by Volume
Carrier,	kerosene	90 to 93%
Extractant,	amine such as tricapryl amine (alamine 336)	4 to 5% (a little over 0.1 M)
Modifier,	Nonanol	2 to 5%

In some South African operations aromatic hydrocarbons have replaced the alcohol modifier although higher concentrations are required (up to 35%). The modifier improves phase disengagement.

'Cation Exchange'		
Carrier,	kerosene	90 to 93%
Extractant,	Alkyl phosphate such as di-2-ethyl hexyl phosphoric acid	5%
Modifier,	Organic phosphate such as T.B.P.	3 to 5%

Here the modifier has a marked synergistic effect on the uranium extraction (Blake et al. 1959) and greatly improves the solubility of the sodium salt formed during stripping.

The amines rapidly superseded the alkyl phosphate solvents although several plants in the United States still use phosphates, particularly where vanadium is also extracted. Only the amines have been used in Australia. They are considerably more selective than the phosphates and do not require sodium carbonate for effective stripping.

Various types of equipment can be used (Clegg and Foley 1958) but the mixer-settler has become almost universally adopted and was used in the three Australian plants.

There are a number of design criteria, including:

a. The number of mixer-settler stages required in the extraction section to achieve near complete extraction of uranium into the organic phase.

b. The number of stages required in the stripping section to achieve a uranium concentration in the solvent sufficiently low to return to the extraction.

c. The phase ratio (aqueous phase:organic phase volumes) which is required in each section to achieve efficient utilisation of the organic solvent and the concentration ratio required across the plant.

d. The retention time required in the mixer to achieve equilibrium in each stage.

e. The agitation required to effect satisfactory transfer rates.

f. Constraints on agitation to avoid formation of secondary dispersion, which can lead to high solvent loss because of long coalescence time.

g. The area or volume required in the settler to permit complete phase separation.

The principles of the solvent extraction process are well described by Bridges and Rosenbaum (1962). In practice, the estimation of (a) (b) and (c) above is relatively simple from laboratory shake-out experiments designed to determine the distribution isotherm of the uranium between the aqueous and the solvent phase. A McCabe-Thiele diagram is constructed to estimate the number of stages required in the extraction and stripping sections. The operating line is drawn with a slope equivalent to the phase ratio, which is selected. This ratio is normally selected to obtain a concentration in the organic between 3.5 and 6 g U_3O_8/litre and to achieve a barren raffinate concentration of 0.002 g U_3O_8/litre or less from the extraction circuit. The phase ratio in the stripping section is usually equivalent to A/O of 0.25 to 0.2 giving strip solution concentrations of between 15 and 30 g U_3O_8/litre. The isotherm plots are best drawn on log-log co-ordinates to identify more accurately the critical parts near the barren end of the raffinate. Figures 7 and 8 show typical McCabe-Thiele diagrams for the extraction and stripping of a sample of Mary Kathleen pregnant liquor.

The free base solvent is not quite as good as the chloride form, but the difference is inconsequential. However, if the concentration of uranium in the pregnant liquor becomes too high the phase ratio A/O is so low that the chloride displaced from the solvent becomes sufficiently concentrated in the aqueous phase to affect the extraction isotherm significantly. Figure 9

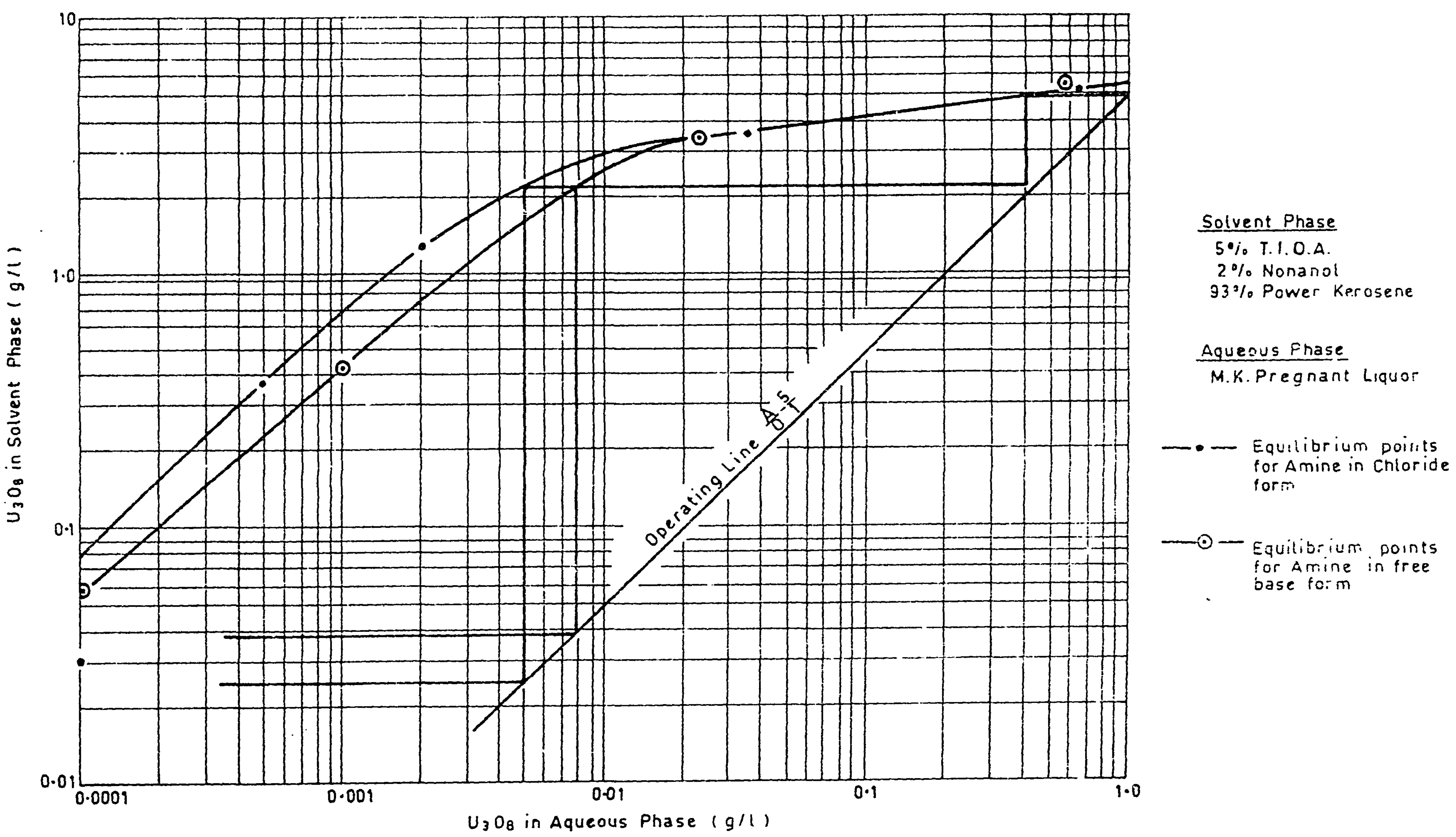
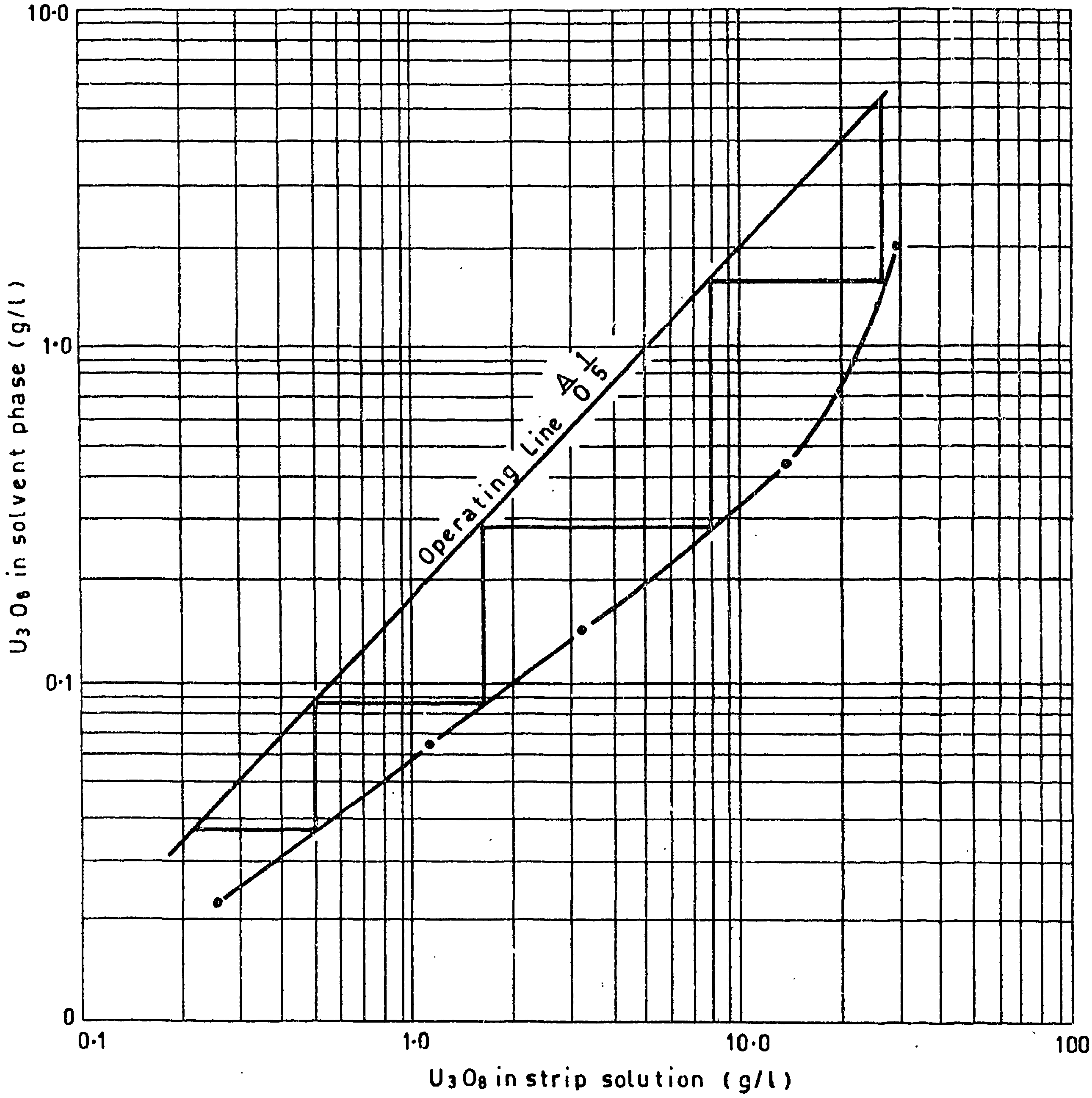


FIGURE 7. EXTRACTION ISOTHERMS



Solvent Phase

5% T.I.O.A.
2% Nonanol
93% Power kerosene
loaded from M.K. liquor

Strip Solution

58 g. NaCl / litre
pH. - 6·5

FIGURE 8. STRIPPING ISOTHERM

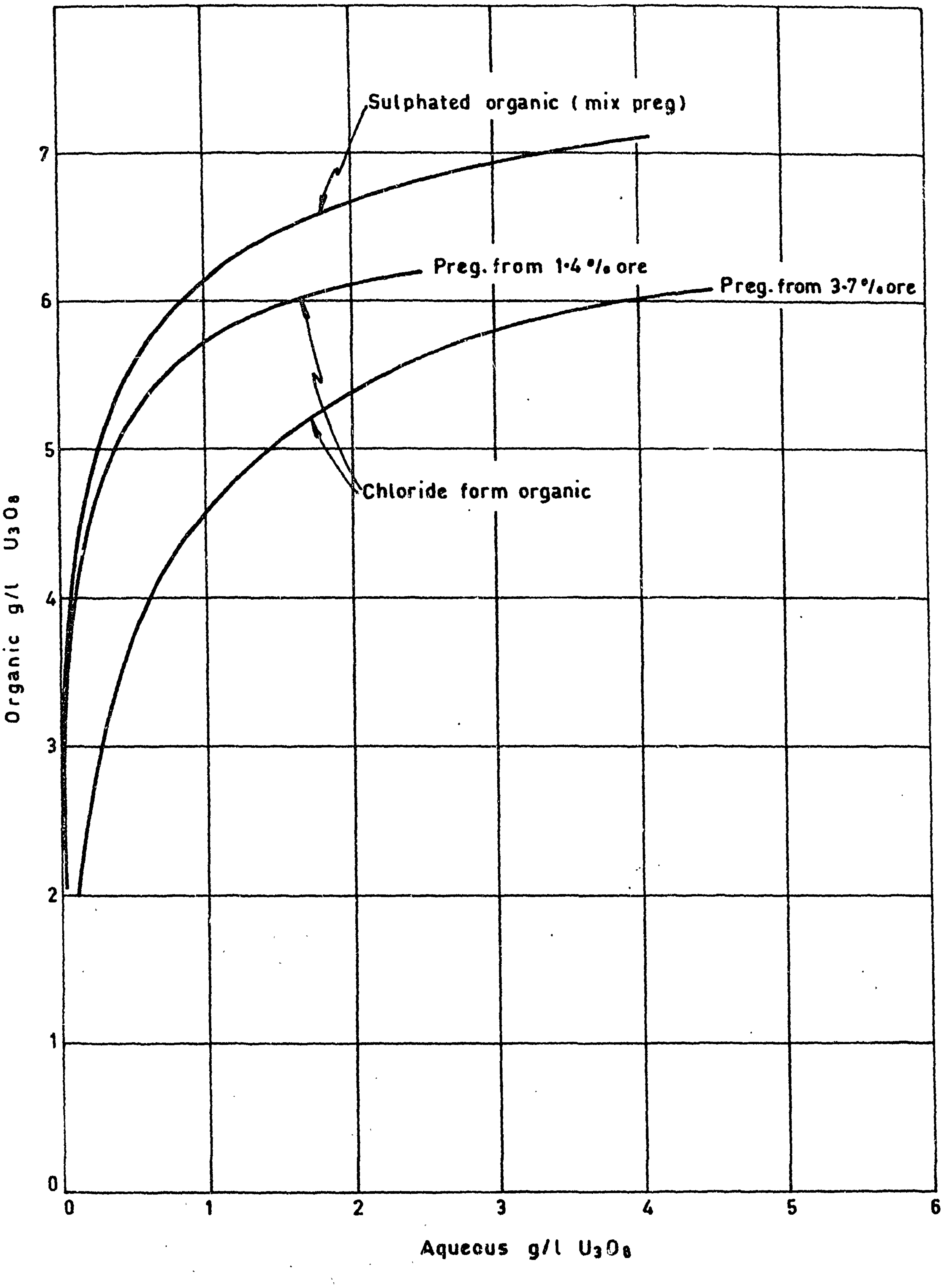


FIGURE 9. SOLVENT EXTRACTION EQUILIBRIUM DATA

illustrates this effect for two pregnant liquors produced from samples of Nabarlek ores of approximately 1.4 and 3.1% U_3O_8. If chloride stripping is used under these circumstances, the solvent may require sulphating in a separate stage, using sulphuric acid before returning to the extraction circuit.

Stripping can also be effected by pH control between 3.5 and 6.5 across the stripping circuit, using ammonia in an ammonium sulphate solution. This technique was developed in South Africa for the 'Bufflex' and 'Purlex' processes, now operated by several plants in that country (Faure et al. 1966, Faure and Tunley 1970, Meyburgh 1970). Such a process is capable of producing very high-grade oxide. Naturally the problem of sulphating the solvent does not arise in this situation. Another advantage is that the barrens or water from treated barrens does not accumulate an undue concentration of chloride, and hence can be recycled into the plant without danger of interfering with the extraction circuit.

The solvent loss is essentially related to the volume of aqueous phase passing through the extraction circuit, provided the plant is well designed. On a well-designed plant the loss is quite modest, as is illustrated by the following figures from Australian plants:

Reagent	Plant	lb/lb U_3O_8
Amine	Moline (Alamine 336)	0.019
	South Alligator (TIOA)	0.012
	Rum Jungle (Alamine 336)	0.004
Modifier	Moline (Nonanol)	0.015
	South Alligator (Nonanol)	0.02
	Rum Jungle (Nonanol)	0.071
Kerosene	Moline	0.1 (approx)
	Rum Jungle	0.017 gal/lb U_3O_8

None the less, the cost of solvent replacement remains the greatest single contribution to the cost of running a solvent extraction plant and poor design can lead to serious results if large solvent losses occur. Criteria (d) (e) (f) and (g) above are associated more closely with the mechanical design and the control of solvent loss, but they are also strongly dependent on the characteristics of the metal being extracted and the solvent system itself, and care should be taken not to infer that a design suitable for one system will necessarily be satisfactory for another.

Uranium is extracted very quickly by amine solvents when the aqueous phase is suitably dispersed in the organic phase, a fraction of a minute of contact being adequate. In relatively small capacity plants the difference in cost in increasing the size of the tank and agitator is small, and one minute is usually allowed for the retention time of the total flow in designing the size of the mixer. Closer tolerances are required in the larger South African plants where half a minute is used as the design criteria. Stripping is somewhat slower and retention times of 1.5 to 3 minutes are usually allowed. However, because the aqueous flow is very much less than that in an extraction circuit and because there is no organic recycle, the mixers in the stripping circuit are usually quite small.

Published systematic work on agitator design for this purpose is scarce. During the design of the Australian SX plants in the South Alligator valley, Bellingham (1961) studied the development of secondary dispersion and other factors and concluded that the scale up of turbine agitators was satisfactory if n^3d^2 was less than 20, where n = revolutions per second and d was equal to turbine diameter in feet (this becomes 1.9 if d is in metres). Equal power per unit volume is then applied with this criterion.

This criterion has been used in all Australian plants and has greatly influenced overseas designs (Faure and Tunley 1971).

To avoid high solvent losses, the mixer must be operated with the aqueous phase dispersed in a continuous organic phase. Since the aqueous to organic ratio in the extraction circuit is 5:1 or higher, a large recycle of organic is required from the settlers back to their respective mixers. For this reason in small capacity plants (flowrates of combined flows of up to 200 - 300 gallons per minute) the internal mixer is very suitable, permitting easy gravity overflow recycle of solvent. However in large plants such as in South Africa it is essential to reduce the depth of the settler, to minimise solvent inventory and reduce overall capital cost. South African plants run settlers of 35 ft diameter with an overall solution depth of only 28 inches. The mixer must then be outside and a pump arrangement is used to ensure automatic recycle of the correct amount of solvent. This problem does not arise in the stripping circuit, where the aqueous to organic ratio is less than 1.0. Rectangular or 'box' mixer settler designs save space and usually incorporate a pump-type mixer and automatic recycle.

The design for phase disengagement in the settlers is sometimes based on area, particularly in the extraction plant where design varies between 1 and 2 gallons per minute per square foot based on dispersed phase flowrate. Some prefer to use retention time, particularly in the stripping circuit. Primary phase disengagement is usually complete within 30 seconds and secondary disengagement within 90 to 120 seconds. Baffling of settlers has been introduced to reduce the total volume required but permit adequate retention times for secondary phase dispersion.

Crud formation at the interface is a potential hazard but effective clarification will usually ensure that this is not serious. Silica can polymerise and stabilise interface crud and fungus formation has proved a problem on some South African plants. A few metals, notably molybdenum, form complexes with amines which are not stripped by acid solution and a simple small stage is often introduced to accept some solvent for cleaning with sodium carbonate to remove molybdenum.

11. PRECIPITATION PROCESS

As referred to in the early part of the paper, Figure 1 shows two major divisions of the total treatment process. In the first part although a choice of process equipment is open to the operator relatively independently, the process conditions are dictated by the characteristics of the ore.

From the elution or stripping stages to the end of the process, the choice of the basic process flowsheet can be decided by the operator based on the following considerations:

a. Cost of reagents for stripping and precipitation.
b. Product specifications for the market.
c. Whether the effluent will be recycled (note comment on chlorides above).
d. Policy of the Company towards designing a plant capable of producing higher grade for future markets.

Likewise, although one cannot change from IX to SX without a major operation, changes can be made to reagent systems and various other stages with little effort or expenditure. The original source of the uranium (the ore) will influence this part of the process only in so far as additional stages or changes in detail may be required to cope with any impurity or 'poison' elements which are totally or partly transferred from the treatment liquor by the solvent or ion exchange resin (Fe^{3+}, Mo, SiO_2). Thus for the elution of ion exchange resin there is a choice of nitrate or chloride eluants or we can consider sulphuric acid followed by solvent extraction. Use of chloride means additional care in washing the product as it is an undesirable impurity in the final yellow cake (specifications vary from 0.15 to about 0.3%, total halogens based on contained U_3O_8). However, in Australia chloride supplied in the form of salt is so much cheaper than a nitrate source that it was chosen by all five operating plants. For amine solvent extraction there is a choice of a chloride strip or an ammonium sulphate/ammonia strip (nitrate can be used but there is evidence that it leads to solvent degradation (Faure 1966)). The choice again will depend on the product specification and the cost of the reagents and, as mentioned above, whether the effluent from the plant is to be recycled when chloride accumulation should be avoided. The three SX plants in Australia used chloride stripping solution, but future plants designed for solvent extraction would certainly be wise to allow for the use of the ammonia/ammonium sulphate system, as there is a continuous trend in the market towards higher grade yellow cake.

Turning to the process for precipitating the yellow cake from the high-grade solution, again there is a choice of reagents: ammonia, magnesia or sodium hydroxide.

Ion exchange resins are not as selective as amine solvents and the eluates contain significantly more ferric iron. This can be removed in a first stage of precipitation by neutralising the solution to a pH of approximately 3.5. This procedure was used at Mary Kathleen and Port Pirie. In the latter plant, calcium carbonate was used as the reagent thus effectively neutralising most of the free acid with a cheap reagent and also removing much of the sulphate from the return eluant (Almond 1958). A low grade of magnesia was used at Mary Kathleen. The precipitate from the first stage was thickened, filtered, washed and then returned to the head of the leaching circuit to recover any co-precipitated uranium.

For the precipitation of the uranium yellow cake the pH is then taken to 7.0. Ammonia has been used for this stage almost exclusively in South Africa and widely in the USA and Canada. Sodium hydroxide is also used in the USA and Canada, and was used in the later period of operation at Rum Jungle. Magnesia, however, was the most widely used reagent in Australia, being used in all plants except for the later part of the Rum Jungle operation.

The chemistry of uranium precipitation is quite complex and a range of compounds have been postulated, a number of which have been demonstrated to form during the precipitation process. These compounds range from simple hydroxides to basic sulphates of various compositions to metal uranates and double sodium uranium basic sulphates, of various compositions. The formation of these compounds is dependent on the pH, the time the solution is held at a certain pH, the temperature and the concentration of the various compounding ions in solutions. A study of the precipitation conditions for magnesia was carried out by Port Pirie workers (unpublished) and a study of the precipitation of uranium by magnesia and sodium hydroxide in particular has been published by Allman et al. (1968).

In a three-stage continuous precipitation circuit at Port Pirie, using high-grade caustic magnesia slurry, the precipitating temperature was between 85 and 90°C. Products approaching 90% U_3O_8 were produced consistently during the final years of operation of that plant. Continuous precipitation was also used successfully at Mary Kathleen where 'super' grade magnesia was specified (less than 0.7% SiO_2). Very good steady-state control can be maintained by continuous system and 'seeding' is automatic. Caustic soda requires much greater care to avoid problems with the physical nature of the product, but with the understanding gained from their research work, Rum Jungle operators demonstrated the method using this reagent, and claim sufficient advantages to have abandoned the use of magnesia. That plant used batch precipitation, which was also used at Moline and South Alligator. Ammonia is used almost exclusively in South Africa and widely in America for the precipitation of the yellow cake. If ammonium sulphate/ammonia stripping is used, one would naturally use ammonia for the precipitation stage. Again, to obtain a consistently coarse grained, high-grade product it is important to control the rate of precipitation and to precipitate from warm to hot solutions.

12. FINAL YELLOW CAKE PROCESSING

For these stages of the operation there is also a range of choices. For small plants batch filters such as plate and frame, pressure filters and tray driers are satisfactory and were used at South Alligator. However, for plants of the size normally contemplated for the future, continuous filters are preferred. It is necessary to provide for two stages of filtration with intermediate repulping as well as washing on the filter. Roll or belt discharge is preferred, the product being relatively clay-like in nature and tending to slime and blind the cloth using ordinary knife discharge.

Continuous driers are also normally used, the type most commonly seen uses a continuous stainless steel belt or set of stainless steel pallets on to which the yellow cake is extruded to pass into the drier. South Africa's central plant operated by the Nuclear Fuel Corporation, receives the yellow cake from all the operating plants for the final filtration, drying and packing operations.

Up to the early 1960s drying temperatures were limited so that only the free water was removed. It is now customary, however, partially to calcine the product at temperatures between 400° and 800°C. This has the advantage of producing a denser product. Thus the weight packed in drums at Mary Kathleen using low-temperature drying averaged about 640 lb per drum whilst at Rum Jungle in the later years, using 450°C as the operating temperature, approximately 800 lb were packed in a drum. In addition some of the impurities can be calcined out of the product.

13. TAILINGS DISPOSAL

Common practice is to combine the leach residue with the barren raffinates and other discard solutions and pump them to the tailings disposal site. In Australia tailings were not treated but were sent to areas for impounding. At Port Pirie a farm of tailings dams was constructed to impound the total effluent, the solids gradually filling the dams and the liquor flowing on and gradually evaporating. Later work on scandium recovery indicated by sampling that these dams had successfully impounded and contained the total effluent. At Mary Kathleen a treatment plant was designed to neutralise the tailings but this was never installed. Instead a large area was fenced at the head of which a tailings dam was constructed for collecting the solid. The liquor overflowed into the larger low-lying area for evaporation.

In general the liquid effluent can be satisfactorily treated in this way if local conditions allow. There are no highly toxic materials present except perhaps traces of the tertiary amines. However, the high sulphate level is obnoxious and any impounding area must be fenced to prevent accidental ingestion by stock.

If the effluent is to be released to streams, neutralisation with lime together with the addition of small amounts of barium is essential to reduce the sulphate level, neutralise the acid and precipitate the trace amounts of soluble radium salts. There is no official legislation as yet in Australia but guidelines are provided by reference to overseas leglislation and publications. Merritt (1971) gives a general review of US practice.

14. CAPITAL AND OPERATING COSTS

Very little has been published outside of press statements and company reports on the capital costs of the uranium plants built in Australia. The author was associated with four of these plants during the stage of estimating and installation from 1952 to 1960. Escalating the information available from these projects to the present day and utilising data from other metallurgical plant costs in Australia, Figures 10 and 11 have been prepared. Again the operation has been divided into two main sections, as the cost of one part is dependent on the amount of ore treated and the other on the quantity of uranium produced. A total estimate for a complete plant can be derived knowing the grade and the production target.

These figures have been derived for a five-stage CCD wash plant in the

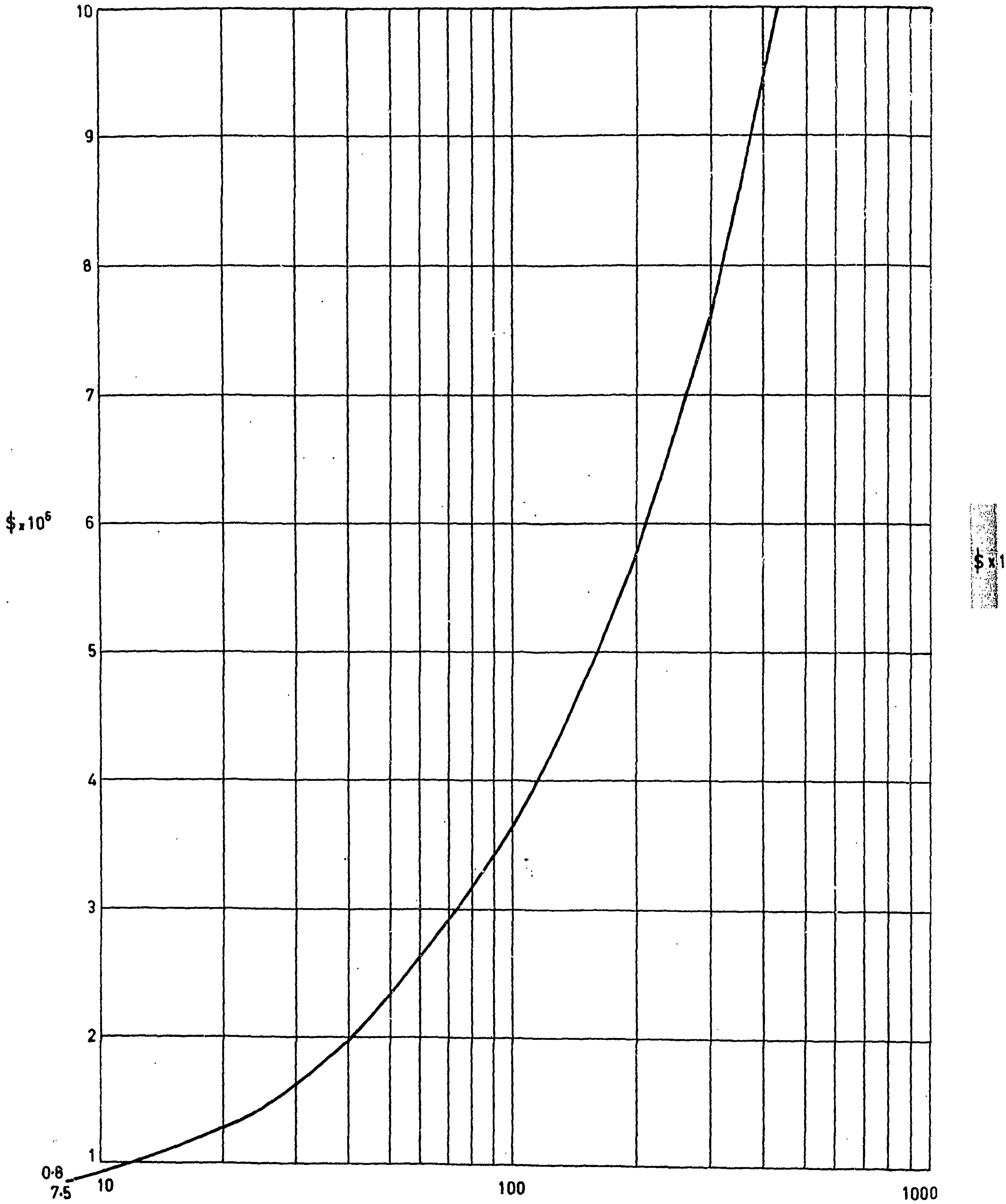


FIGURE 10. CAPITAL COST FOR ORE TREATMENT SECTION.
Comminution, Leaching, CCD, Clarification, Extraction, Power Plant, Service Bldgs. and Mine not included.

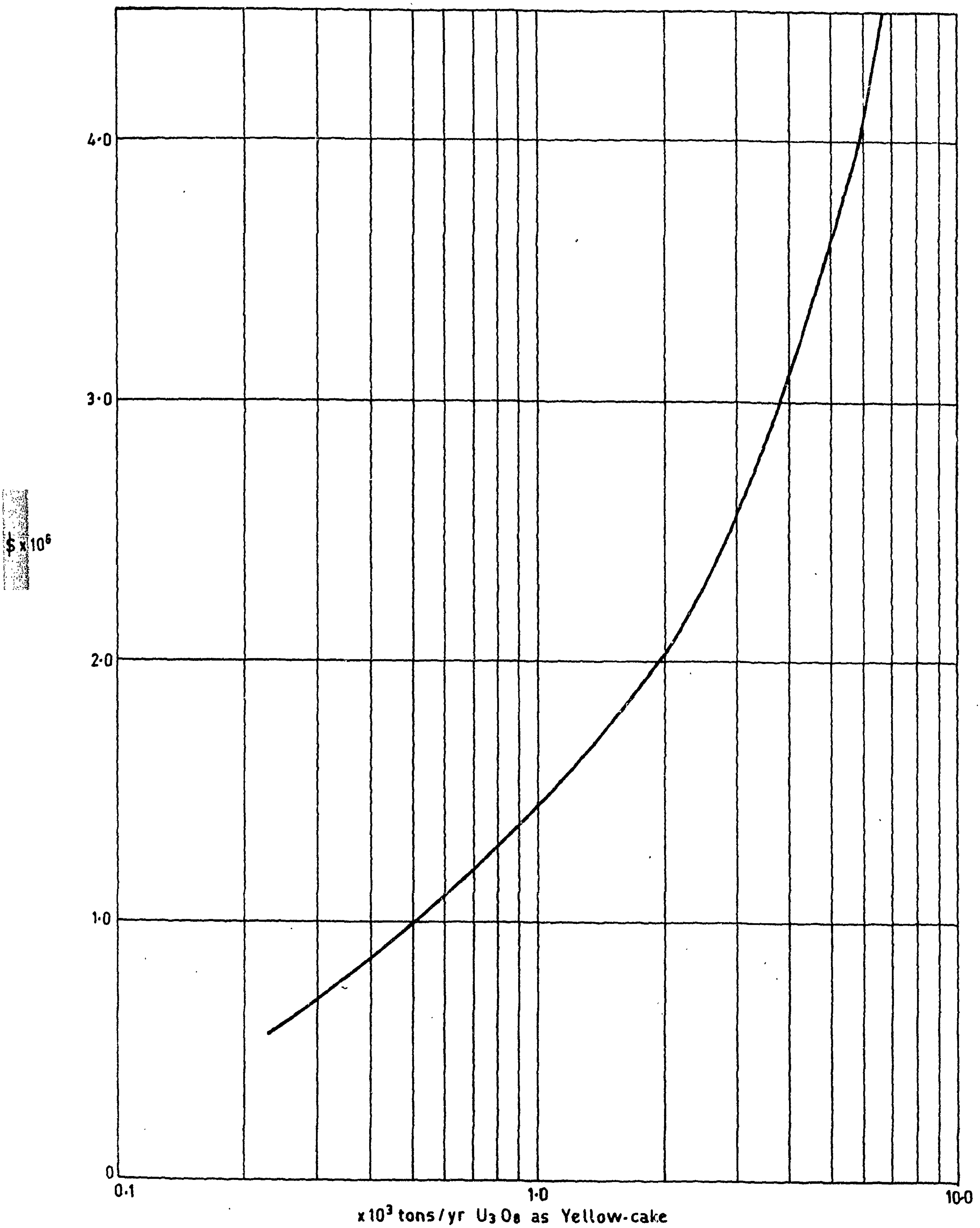


FIGURE 11. CAPITAL COST FOR URANIUM EXTRACTION SECTION. Stripping, Precipitation, Filtration, Drying and Packing.

TABLE IV : SUMMARY OF REAGENTS AND SERVICES REQUIRED FOR TREATMENT PLANT

1. Those which can be equated to the tons of ore treated.

Ore Treatment Section, Reagents and Power

Reagent	Unit Cost(a)	Per Ton of Ore		
		Amount		Cost, $
Water	50¢/1,000 gal	660 gal		0.33
Steel	$240/ton	3 lb		0.36
Acid	$ 35/ton(b)	120 lb		2.10
Oxidant	$200/ton	5 lb		0.50
Flocculant	$1.15/lb	0.2 lb		0.23
Precoat	$180/ton	0.40 lb		0.03
Solvent:				
Kerosene	30¢/gal	0.12 gal	0.036	
Amine	$1.00 lb	0.046 lb	0.046	
Nonanol	$2.50/gal	0.04 gal	0.100	
			0.182	0.18
Power	4¢/kWh	20.0 kWh		0.80
				4.53

(a) Includes freight into store remote site.

(b) Includes capital charges for acid plant.

Therefore, if 7.5 lb U_3O_8 are extracted, cost per lb U_3O_8 would be $0.60.

2. Those dependent on the quantity of uranium extracted. This exercise assumes that sodium chloride stripping solution is used and precipitation is effected with caustic soda.

Extraction Section, Reagents and Power

Reagent	Unit Cost	Per Pound of U_3O_8	
		Amount	Cost, $
Salt	$ 40/ton	1.5 lb	0.030
Acid	$ 35/ton	0.3 lb	0.005
Caustic Soda	$250/ton	0.5 lb	0.063
Sodium Carbonate	$180/ton	0.15 lb	0.014
Oil	$ 30/ton	2.7 lb	0.040
Product Containers	$ 15 each	3 drums/ton	0.023
Power	4¢/kWh	0.4 kWh	0.016
			0.191

Say $0.19 per lb U_3O_8.

ore treatment section, and for solvent extraction to be used in the extraction plant. However, the order of magnitude will not vary greatly if alternatives to these processes are used.

Information for American plants has been surveyed by Merritt (1971). There is a relatively wide range shown for the capital costs of mills built in the USA and Canada, but it is difficult to determine what has been included in these costs.

Concerning operating costs, readers are also referred to Merritt, and to the various papers describing Australian practice given in the bibliography of this paper, for information concerning the reagent consumption and similar factors affecting operating costs. For this paper costs have been developed for a typical, although hypothetical operation, based on the following assumptions. The ore is assumed to contain 0.4% U_3O_8, which on treatment yields 7.5 lb of U_3O_8 per ton. Uranium is in the form of uraninite and no highly acid-consuming minerals are present. Average behaviour is assumed for solid/liquid separation. Assume that acid consumption is equivalent to 120 lb sulphuric acid per ton of ore and that 5 lb of MnO_2 per ton of ore are required.

Costs have again been examined for the two major parts of the operation; that related to the tons of ore treated, and that related to the quantity of uranium extracted (Table IV). The grade chosen for this study falls within the range of what I might term the 'conventional grades' (since we are talking of 'conventional' processes), which are being treated in various parts of the world. For higher grade ores, the costs per ton in the ore treatment section can be significantly affected by the quantity of uranium. For example, the amount of water used per ton of ore could be significantly greater and the amount of uranium mineral itself will have a significant incremental effect on the amount of acid and oxidant required.

The major cost per pound of U_3O_8 is obviously that incurred in the treatment of the ore, in particular the cost of the leaching operation.

In addition to these costs there are labour, maintenance, plant and management overheads, general overheads such as payroll, property tax, insurance, general operating supplies and sampling handling and control. These are listed below and related only to costs per ton of ore as the breakdown between the two would not be particularly significant. The following costs are of the order applying to the range of tonnage of ore shown.

Other Operating Costs	$/ton Ore	
Tons of ore per year	50,000	400,000
Operating Labour	3.3	0.50
Repairs and Maintenance	4.5	1.50
Plant overhead (admin and management services, etc.)	4.0	0.75
Payroll overhead	0.6	0.10
	12.4	2.85

For the grade of ore in question this amounts to between $1.65 and $0.38 per pound of U_3O_8.

Therefore the total operating costs for the treatment of the ore are of the order of $2.44 to $1.17 per pound of U_3O_8 for ore of this particular grade. To this cost must be added mining costs, capital charges and realisation charges remembering that capital charges must cover total capital investment (exploration, mine capital, mill and infrastructure capital).

While costs will change with any process change in the Extraction Section, they will be incrementally small compared with the differences which can be effected by attention to detail in the ore treatment section, particularly to the leaching operation where the cost of acid and oxidant are most significant.

Also as mentioned earlier, excessive soluble losses in the solid/liquid separation section (here CCD) must be avoided.

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