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# AUSTRALIAN ATOMIC ENERGY COMMISSION

## RESEARCH ESTABLISHMENT
## LUCAS HEIGHTS

PAPERS PRESENTED TO THE

AAEC SYMPOSIUM

ON

# URANIUM PROCESSING

LUCAS HEIGHTS

20 - 21 JULY 1972

Published September 1972

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[II] BIBLIOGRAPHIES; COST; CRUSHING; GANGUE; GRINDING; ION EXCHANGE; LEACHING; MINERALOGY; OPERATION; ORE ENRICHMENT; PRECIPITATION; PRODUCTION; REVIEWS; SOLVENT EXTRACTION; URANINITES; URANIUM; URANIUM CONCENTRATES; URANIUM MINERALS; U308

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[IV] AUTORADIOGRAPHY; GANGUE; LEACHING; MINERALOGY; ORE ENRICHMENT; QUANTITATIVE CHEMICAL ANALYSIS; QUANTITY RATIO; URANIUM MINERALS; URANIUM ORES; U308

[V] BRANNERITE; GANGUE; LEACHING; MINERALOGY; ORE ENRICHMENT; PH VALUE; PRECIPITATION; SOLVENT EXTRACTION; SULFURIC ACID; TEMPERATURE DEPENDENCE; URANINITES; URANIUM ORES; U308

[VI] COST; COUNTER CURRENT; CRUSHING; FLOWSHEETS; GRINDING; ION EXCHANGE; LEACHING; MARY KATHLEEN MINES; ORE ENRICHMENT; PLANNING; PRECIPITATION; SOLVENT EXTRACTION; URANIUM CONCENTRATES; U308

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[VIII] ADU; DENITRATION; FLOWSHEETS; FLUIDIZED BED REACTORS; FLUORINATION; FLUORINE; ORE CONCENTRATES; PRODUCTION; PURIFICATION; REVIEWS; SOLVENT EXTRACTION; URANIUM DIOXIDE; URANIUM HEXAFLUORIDE; URANIUM TETRAFLUORIDE; URANIUM TRIOXIDE; U308

[IX] CAPITAL; COST; ECONOMICS; FLOWSHEETS; FLUORINATION; INVESTMENT; LEACHING; OPERATION; PLANNING; PRODUCTION; PURIFICATION; SITE SELECTION; SOLVENT EXTRACTION; TRANSPORT; URANIUM CONCENTRATES; URANIUM HEXAFLUORIDE; WASTE DISPOSAL

[X] AUSTRALIA; ECONOMICS; ENRICHED URANIUM; MARKET; POWER REACTORS; PRODUCTION; TRADE; TRANSPORT; URANIUM HEXAFLUORIDE; U308

# FOREWORD

These Proceedings contain the papers presented at a two-day Symposium on Uranium Processing held at the Research Establishment of the Australian Atomic Energy Commission on July 20 and 21, 1972.

Although the Symposium was organised by the Commission, about three quarters of the participants came from other organisations, and of these the majority were representatives from industry.

The main purpose of the Symposium was to assist industry in its thinking and planning for the future by presentation of papers on the principles and 'state of the art' in the field of uranium processing, and by providing a forum for discussion.

The success of the meeting thus depended heavily on participation by industry and other organisations. The Commission was gratified by the response, and wishes to thank those responsible in industry and the other organisations involved for their assistance. In particular, the success of the sessions dealing with processing at the minesite was largely due to the considerable efforts put forward by authors from the Australian Mineral Development Laboratories and from industry.

This was the second Symposium organised by the Commission in collaboration with the uranium industry. The first, on radiological safety and environmental matters, was held in November 1971. The success of these meetings reflects the current interest in uranium, and the future importance of uranium resources and processing in Australia.

This importance arises not only because our uranium reserves have a high intrinsic value. They are a large asset in terms of money, but even larger in terms of energy. Theoretically, one ton of uranium, if totally consumed, is equivalent to about 3 million tons of high grade black coal. Although present day reactors can liberate only about one per cent of the energy inherent in uranium, late in this century Fast Breeder Reactors will begin to come into service around the world, and they should be able to utilise at least two-thirds of it - thus one ton of uranium will be equivalent to about two million tons of black coal. The energy inherent in our uranium reserves is thus considerably higher than that in all of our coal.

By the end of this century it is expected that about 60 per cent of the non-Communist world's power generation will be based on nuclear stations. The cumulative needs for uranium will exceed two million tons by that time - about twice the known reserves recoverable economically. More must be found. We do not know how much there is in Australia - at least 100,000 tons, probably much more. Australia thus has the potential to be major world supplier; our position with uranium appears to be similar to that applying with bauxite, coal, natural gas, and iron ore. A major question for the future is how far we should process our uranium in Australia, and presentation and discussion of the various processing steps was one major object of this Symposium.

The future potential of our uranium resources is ironical to some people at present, because of the depressed state of the market; currently uranium is hard to sell. By the 1980s the position should be quite different. There are two aspects of the 'silver lining' to the present clouds. One, current prices and sales are not such as to encourage exploration in many areas overseas, and this leads to better prospects for those who have material available for the 1980s. Two, the temporary lull in demand gives us time to think and to plan for the most favourable development of the industry; time is on our side. It is to be hoped that this Symposium made some worth-while contributions to this thinking and planning.

The subjects covered did not include the enrichment of uranium, which is a complex and difficult field; time would not have allowed a meaningful coverage within the Symposium. Until quite recently, because of security restrictions overseas, there was very little information available on the processes used for enrichment. Only within the past year has this begun to change, and the Commission is currently studying the various technologies and their possible implications for Australia quite intensively. For example we are engaged in a joint study with France on gaseous diffusion technology, and several of us have been to the United States recently for discussion on the possible use of their technology outside of the USA. All these studies are preliminary and we hope that eventually their results will be of considerable help to Australian industry, should it emerge that the enrichment process looks attractive for Australia, and we also hope that there is interest among companies to pursue detailed assessment of the prospects.

In conclusion, may I emphasise the objectives of the Symposium - they were educational, not promotional. Under the Atomic Energy Act the Commission is

charged with a responsibility to be a centre of knowledge and 'expertise' on Atomic Energy. Papers presented at this Symposium by AAEC staff were intended to assist industry in its deliberations. There is a considerable amount of expertise available within the Commission on uranium as a nuclear fuel - on the characteristics of nuclear reactors, the requirements, the performance, and the nature of their fuels, and of nuclear fuel cycles, including the various refining and manufacturing process steps. Since the end uses and the requirements at intermediate stages of any product have effects throughout its production, the Commission's knowledge can provide useful advice and guidance, and we hope this will continue to be put to good use. There should be much to be gained on both sides by collaboration between government, science and industry; the Commission hopes that industry finds meetings such as this useful, and that resultant 'feedback' from industry concerning its problems will provide guidance to the Commission on its own future programme.

K. F. ALDER

COMMISSIONER FOR DEVELOPMENT, AAEC

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ON

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PAPER I

# REVIEW OF NUCLEAR FUEL CYCLES AND WORLD TRENDS

by

G. L. MILES

CHIEF, NUCLEAR DEVELOPMENT DIVISION, AAEC

## 1. INTRODUCTION

In providing background to subsequent presentations describing the problems of uranium ore processing and the provision of specific intermediate compounds, this paper considers uranium as a fuel industry, examines trends in demand for and supply of uranium in its various forms, and suggests areas of possible Australian involvement.

### 1.1 The Fuel Cycle

The nuclear power reactor replacing the boiler of conventional fossil-fuelled power stations, has several characteristics which greatly complicate the use of uranium as a fuel. These include :

1. The fission process cannot proceed to completion - only a proportion of the fissile fuel (uranium-235) is consumed; on the other hand, a proportion of the uranium-238 is converted to plutonium-239 which itself is partly fissioned and converted to other isotopes.
2. The performance of a reactor and in particular, its specific power, is a function of the concentration of uranium-235 in the fuel. The use of natural uranium places severe restrictions on the reactor designer in terms of choice of constructional materials, moderator and coolant. The use of enriched uranium assists flexibility in design and results in lower capital costs.
3. The fission products accumulating as the fuel is 'burned' must be removed before the uranium and plutonium are recovered and reconstituted.

The concentration of uranium-235 used varies with the type of power reactor. The original UK and French gas cooled graphite moderated 'magnox' reactors, and the Canadian heavy water moderated reactors, use natural uranium which contains 0.71% of $^{235}U$. However, the majority of the world's power reactors, both built and projected, use uranium enriched to between 2 and 3% $^{235}U$. These include both the light water moderated and cooled reactors (PWR's and BWR's) and the advanced gas cooled reactors (AGR). An exception is the class of fast reactors currently being developed. These are fuelled either with plutonium or highly enriched (greater than 25%) uranium-235. There are of course also many smaller research reactors which

require a high concentration of uranium-235, such as the Commission's reactor HIFAR. To summarise, however, nearly all the uranium currently being marketed is destined to be passed through the enrichment process to produce a product containing a few percent of uranium-235. This in turn must eventually be recycled.

Figures 1-6 illustrate in simplified form the various stages of the nuclear fuel cycle based on uranium.

## 2. URANIUM AS A FUEL

Many general statements are made about uranium as a fuel - for example, complete burn-up of the $^{235}U$ in a tonne of natural uranium has an energy equivalent of 21,400 short tons of 13,000 Btu/lb coal. The next part of this paper examines the relationship between uranium requirements and electrical power production. There is no shortage of estimates of future uranium demands, based on published national programmes, estimates of trends in power consumption and individual industrial proposals. The Australian Atomic Energy Commission, in common with parallel organisations in other countries, maintains a constant survey of such information with regular review and updating of material. This is much more than an exercise in transcription, when allowance is made for such factors as demands for particular types of reactor, plutonium recycle and future introduction of fast reactors.

Figure 7 illustrates some of this material. The broad picture which emerges is one of reasonable consistency in the various national and international estimates of future world requirements, with the major uncertainties appearing after the next 15 years. Some current problems of safety analysis and licensing and of pressures from environmentalists have resulted in specific delays, particularly in the USA, and naturally the accompanying publicity reflects on the validity of long-term predictions. While these delays have been frustrating for the utilities and the reactor vendors, they are occurring at a time when the rate of expansion of the nuclear industry is taxing the resources of construction companies in the USA. Further, the present safety-environmental debate will provide a firmer foundation for future commitment to nuclear power. It is to be regretted that other more noxious industries developed in the past without similar public concern.

Many observers believe that similar and increasing examination and criticism of fossil fuelled power stations, and reassurance concerning the

safety of nuclear stations, will lead before very long to a swing in public attitudes which will intensify the demand for nuclear power. Certainly the estimates presented in Figure 7 could prove to be very conservative.

Quantitatively, a typical light water power reactor plant generating for example 1000 MW(e), would require for its fuelling an initial inventory of 103 tonnes of enriched uranium together with replacement fuel at 28.9 tonnes/year. Eventually, recycling of the spent fuel would reduce the annual demand by about 17% and if plutonium is recycled and not reserved for eventual use in fast reactors, by a further 10%. This means that the average annual requirement per 1000 MW(e) adjusted for initial inventory is about 25.7 tonnes of 3% enriched uranium.

To fuel this requires an input from the mines to the fuel cycle of about 153 tonnes of uranium per year (200 short tons $U_3O_8$). Incidentally, if the gaseous diffusion process is used, the annual power consumption to achieve the enrichment of this fuel is at the rate of about 28 MW(e). However, this is not the full story, because unlike the original fossil fuel, the nuclear fuel is not fully burned - if all the uranium (including the $^{238}U$ could eventually be fissioned (using conversion in a fast reactor to plutonium) the electrical power which would be produced from 153 tonnes of uranium would be of the order of 400 thousand MW years.

Figure 8 translates the nuclear power estimates into estimates of world demand for uranium (as yellow cake) in relation to current reserves.

Figures 9 and 10 illustrate the distribution of demand in terms of major users.

## 3. UPGRADING OF URANIUM

The proposition that local upgrading of Australian mineral products is economically and presumably socially desirable has been popularly accepted, almost as an article of faith. It is instructive to examine, at least broadly, the possible implications of this philosophy for the uranium industry.

Uranium as mined typically occurs as a low grade ore, usually less than 1%, which cannot be concentrated by simple beneficiation. Mine site processing is therefore essential to produce the uranium in an economically transportable form. Traditionally this form has been a crude oxide $U_3O_8$ (yellow cake) although during this Symposium one or two alternatives will be mentioned.

The average price of yellow cake is around $6 per lb $U_3O_8$, i.e. $15.6 per kg, expressed as contained elemental uranium or $2.2 per g of contained uranium-235.

This yellow cake must then be converted to uranium hexafluoride (possibly through a separate $UF_4$ intermediate process). The cost of this conversion is about $2.5 per kg of contained uranium - the capital investment required being around $3.6 per kg U/year, depending on the scale of the operation. This brings the cost of the uranium up to about $18.1 per kg total U or $2.5 per g contained $^{235}U$.

The next upgrading step is uranium enrichment, which is peculiar in that it involves the rejection of about 85% of the total uranium and around one-third of the original uranium-235. Figure 3 illustrates this. The cost of a 3% enriched product as hexafluoride is about $230 per kg total weight of enriched uranium. Of this cost 45% derives from the original feed material, and the rest represents the cost of the separative work performed by the enrichment plant. The capital involvement in the enrichment stage amounts to about $88 per kg U/year of the original feed material.

The next step in the fuel cycle, fuel element fabrication, in which the $UF_6$ is converted to ceramic oxide form, canned and assembled to precise mechanical standards, yields a product (in the case of light water reactor fuel) priced at about $310 per kg total (enriched) uranium, or $10.3 per g of contained $^{235}U$. The capital involvement in this stage amounts to about $45 per kg U/year of the enriched fuel or $7.5 per kg U/year in the original product mined.

Finally, after use in the reactor, the 'spent' fuel must be reprocessed to recover the (somewhat depleted) uranium and plutonium and separate out the fission products. The cost of this step amounts to about $35 per kg of uranium fuel, or $4.4 per g of contained $^{235}U$ if no credit is allowed for the recovered plutonium. The capital cost involvement in this stage is relatively high, depending upon scale and is typically around $50 per kg per year total uranium processed, which corresponds to $8.3 per kg U/year originally mined.

Figure 11 illustrates the value added in the various process stages, expressed in terms of the orginal ore, together with the associated capital involvement. Figure 12 illustrates the value added in terms of employment and compares the potential of the uranium industry with three other major industries.

## 4. URANIUM HEXAFLUORIDE PRODUCTION IN RELATION TO ENRICHMENT IN AUSTRALIA

Subsequent papers in this Symposium consider in detail the economics of hexafluoride production, however it is appropriate to consider here some of the factors which complicate the planning of Australian conversion plant.

### 4.1 Timing

The construction of uranium hexafluoride plant could be timed to coincide with the bringing into production of uranium fields in the South Alligator River district. This would be several years before the likely date of commissioning of a uranium enrichment plant. There would, however, be some advantages in the earlier introduction of the technology, both in relation to marketing and in establishing confidence in the process operation.

### 4.2 Scale

The scale of operation which would arise from present production plans would initially be less than 5,000 tonnes/year of uranium hexafluoride. However, an enrichment plant would require production on a scale of 15-20,000 tonnes/year.

### 4.3 Siting

Selection of a site for an 'export based' plant would involve optimisation of transport, plant and operating costs, which could point to a location at, for example, a port adjacent to the uranium mines. On the other hand, if a large enrichment plant is to be built in Australia, the economies in locating the conversion plant adjacent to the enrichment plant are likely to be substantial. Direct piping of the product from conversion plant to enrichment plant would eliminate the use of relatively small and heavy transport containers. Fortunately, it is unlikely that the site selected for an enrichment plant would be unsuitable for chemical plant construction or badly placed in relation to port facilities.

### 4.4 Process Selection

Both process selection for the conversion plant and the determination of the mine-site product should logically arise from an optimisation study of transport and process costs relevant to the production scale. For example, it might pay to produce a crude product at the various mine sites and carry out additional purification at the central conversion plant. This approach is made difficult by the fact that planning of production of yellow cake is proceeding ahead of the later upgrading steps. Uniformity of product from

different producers would also be difficult to achieve when different types or ore and consequently, different leaching processes, are involved.

## 5. CONCLUSION

The purpose of this Symposium is to provide an opportunity for exchange of information on uranium processing and to present defferent points of view. The technical and subsequent upgrading are complex. The best solutions, both industrially and nationally, will only be achieved by early recognition of the importance of mutual consultation, both between governmental organisations and industry, and within the industry itself.

## 6. ACKNOWLEDGEMENT

The assistance of members of the Nuclear Development Division in the preparation of this paper is gratefully acknowledged, particularly the contributions of M.R. Richmond and J.M. Silver.

## 7. REFERENCES

Boxer, L. W., Haussermann, W., Cameron, J., Roberts, J. T. (1971) - Uranium Resources, Production and Demand. Paper 678, Fourth International Conference on Peaceful Uses of Atomic Energy, Geneva.

National Petroleum Council (1971) - U.S. Energy Outlook; an Initial Appraisal 1971-1985. Prepared by the NPC Committee on U.S. Energy Outlook. Washington.

Nininger, R. D. (1970) - The World Uranium Picture. In Mining Year Book 1970, Colorado Mining Association. Denver, U.S.A.

Silver, J. M., and Richmond, M. R. (1972) - Uranium Fuel - Predictions of Requirements and Resources. Unpublished A.A.E.C. Report.

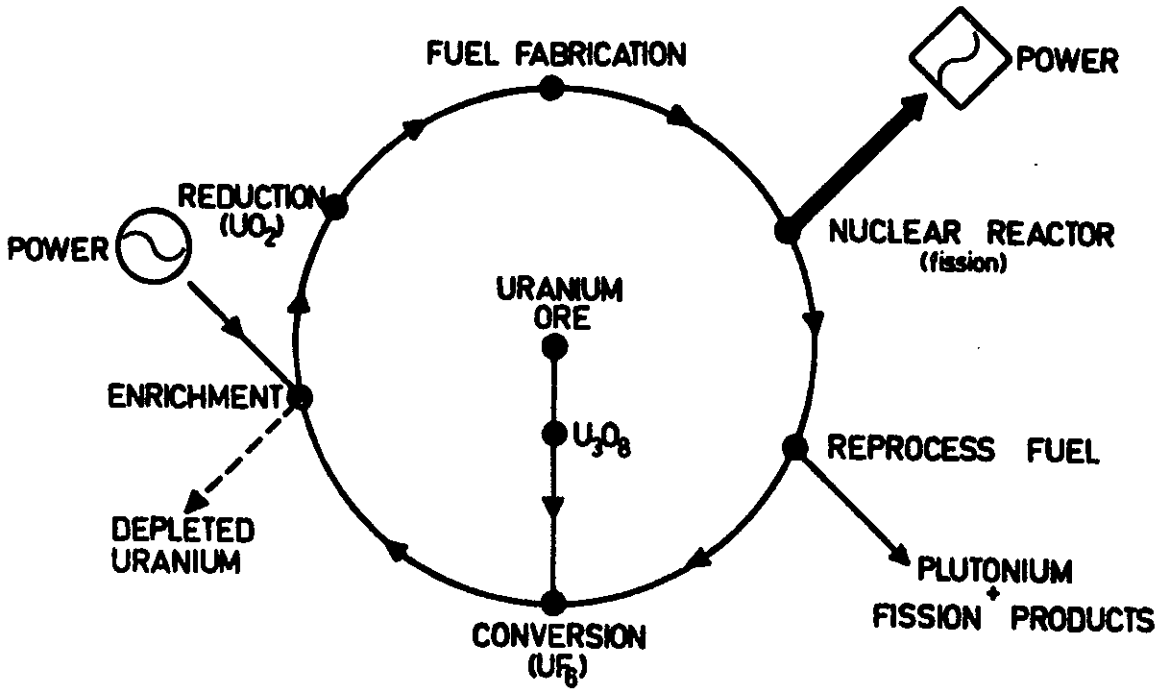


FIGURE 1. NUCLEAR FUEL CYCLE

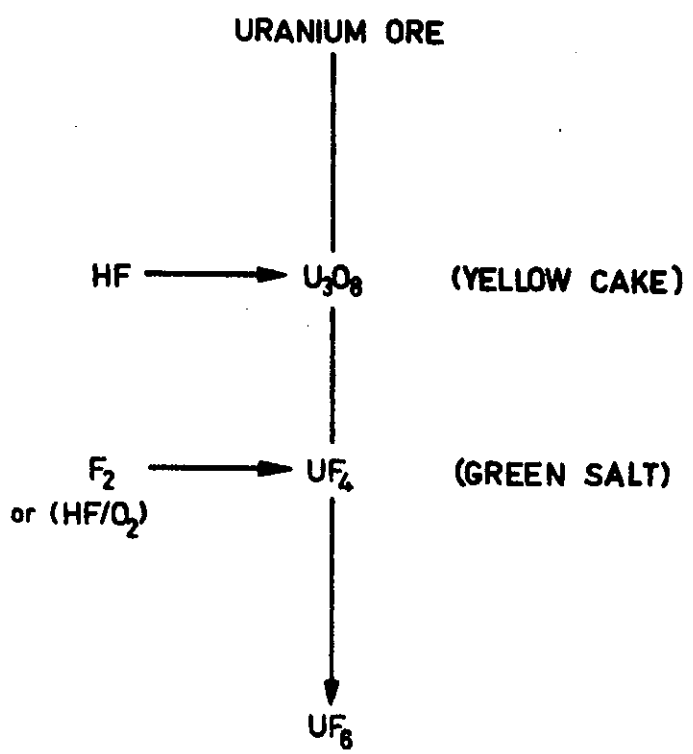


FIGURE 2. URANIUM HEXAFLUORIDE PRODUCTION

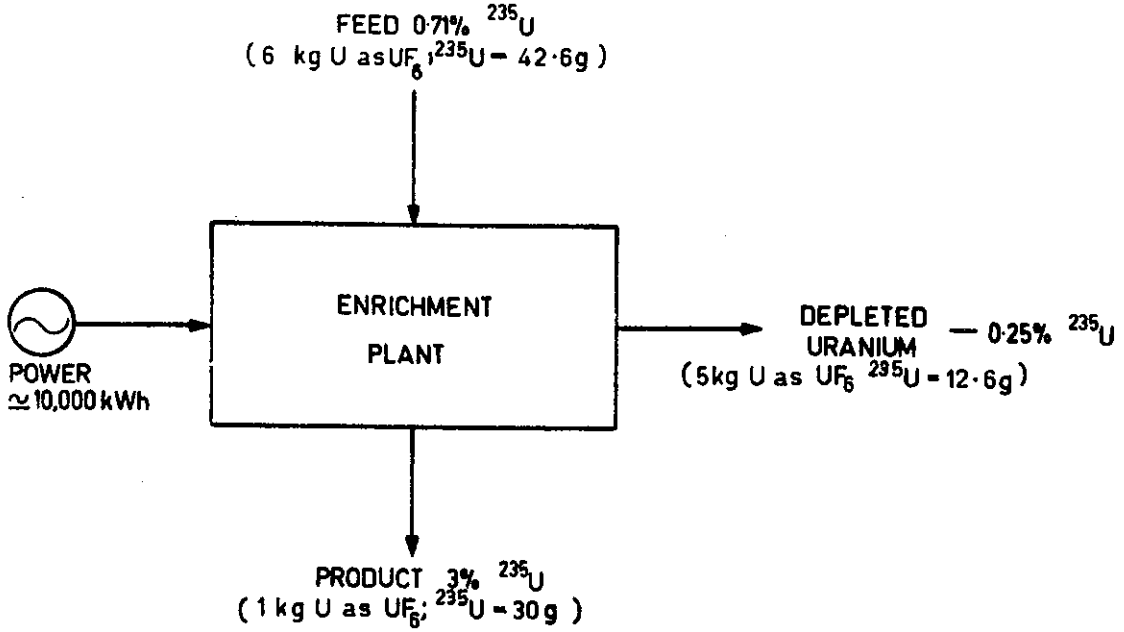


**FIGURE 3. ENRICHMENT (DIFFUSION PROCESS)**

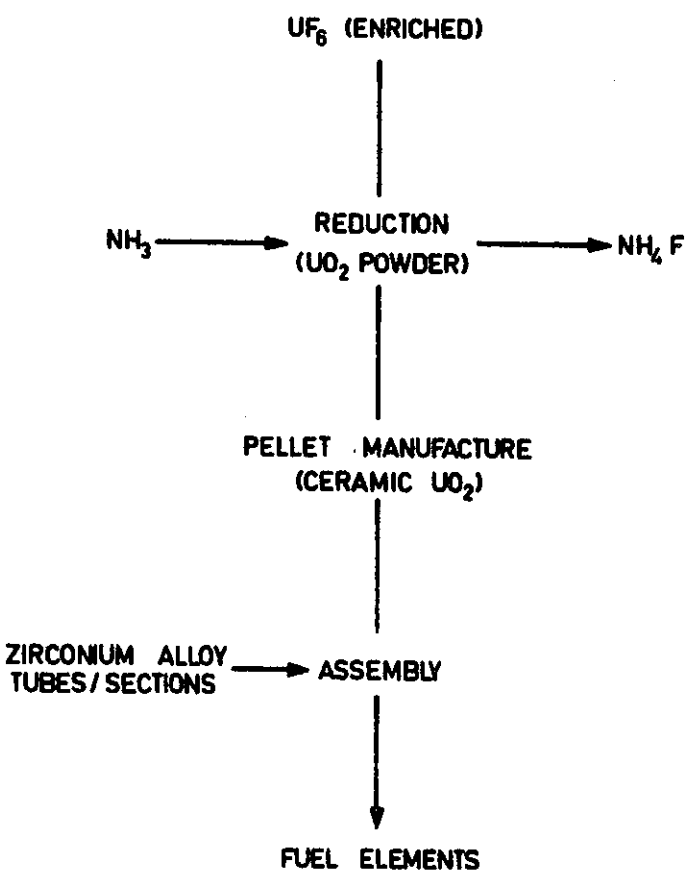


**FIGURE 4. FUEL FABRICATION**

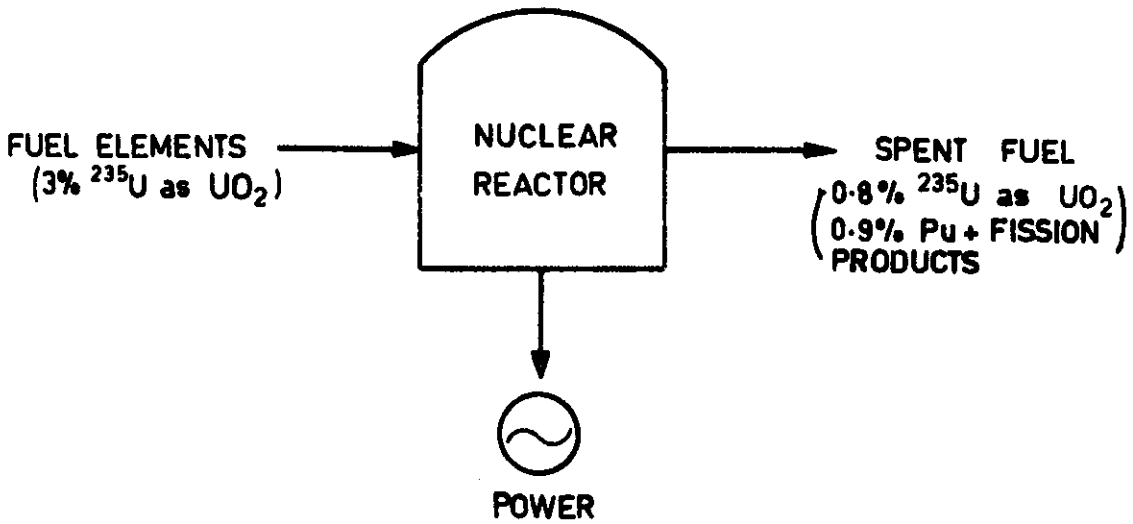


FIGURE 5. NUCLEAR REACTOR

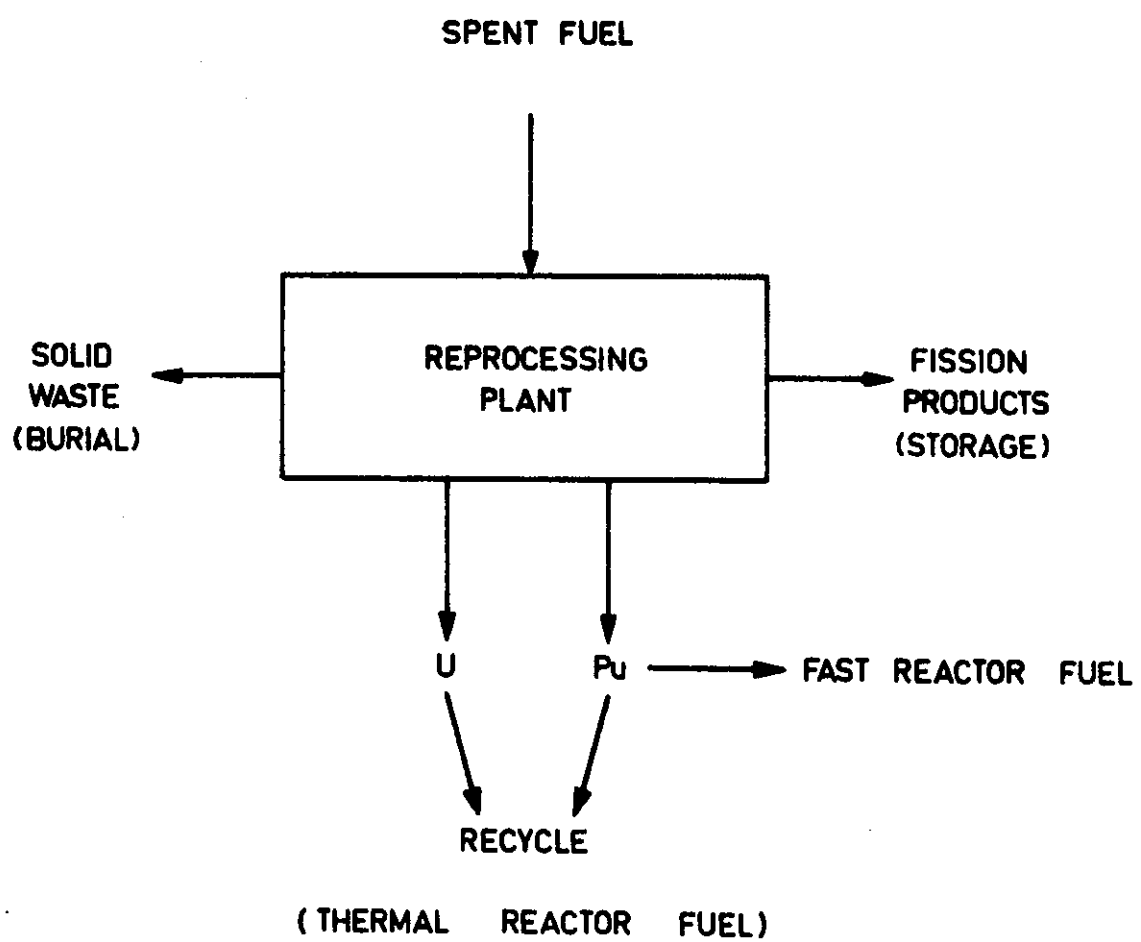


FIGURE 6. FUEL REPROCESSING

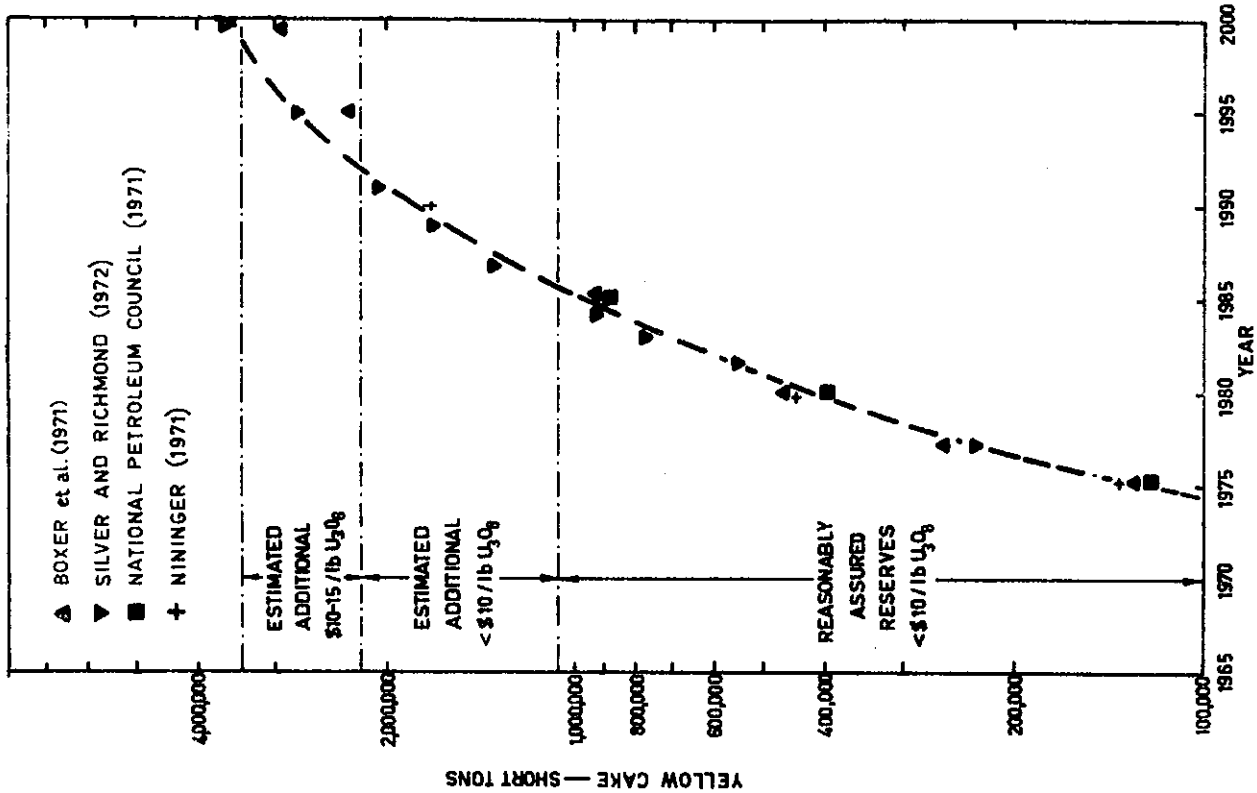


FIGURE 8. CUMULATIVE REQUIREMENTS AND SUPPLY OF YELLOW CAKE

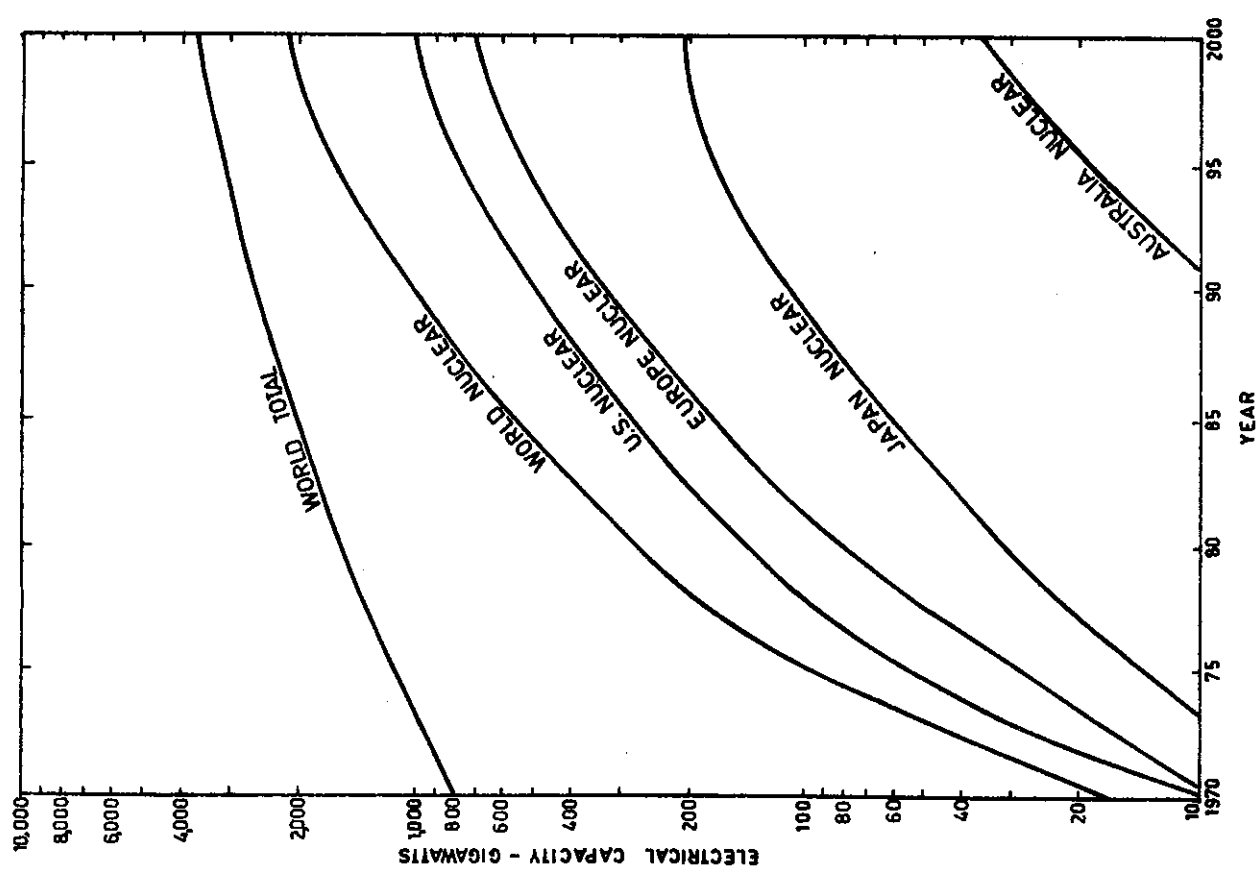


FIGURE 7. GROWTH OF NUCLEAR POWER

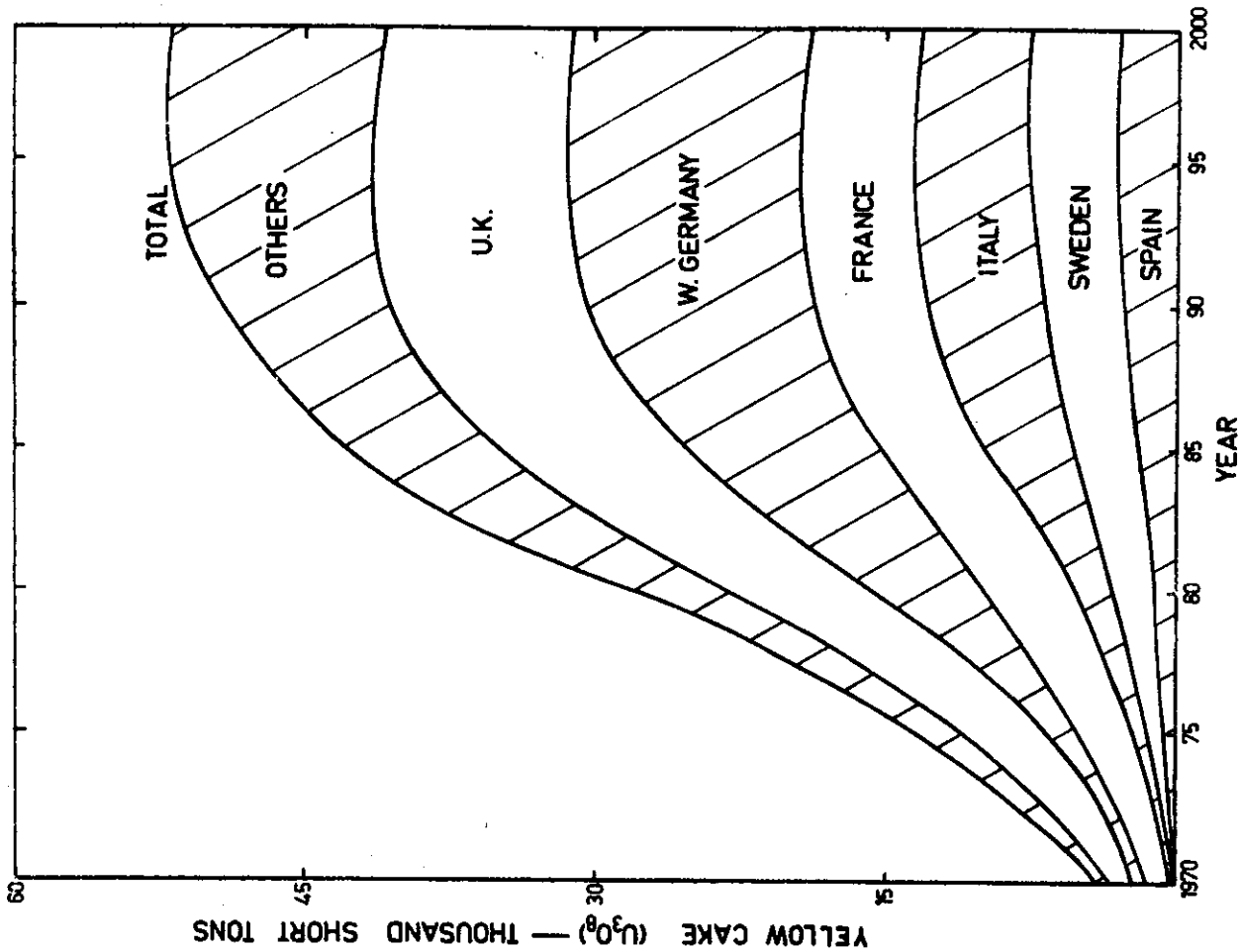


FIGURE 10. EUROPEAN YELLOW CAKE REQUIREMENTS

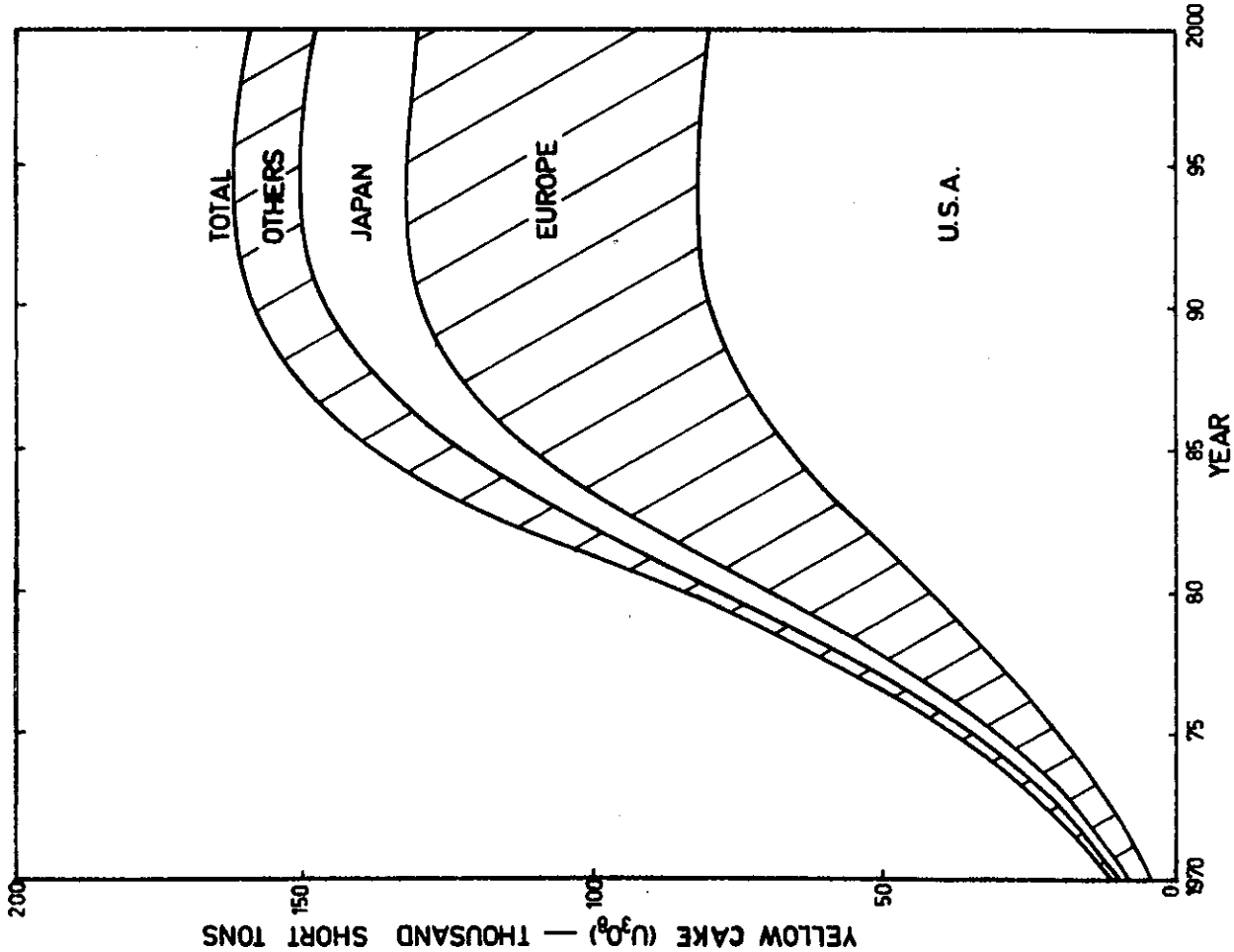


FIGURE 9. WORLD YELLOW CAKE REQUIREMENTS

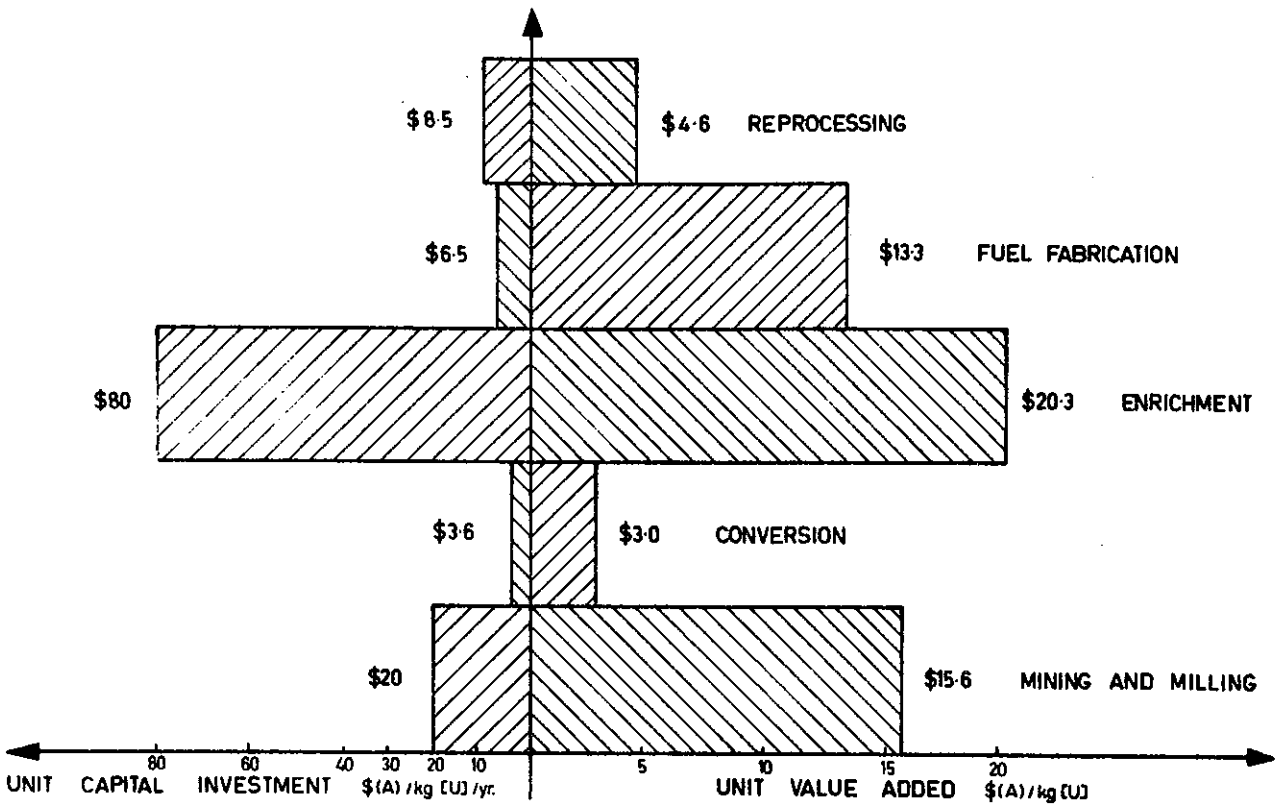


FIGURE 11. SHOWING RELATIVE ADDED VALUES AND UNIT CAPITAL COSTS WITHIN THE NUCLEAR FUEL CYCLE

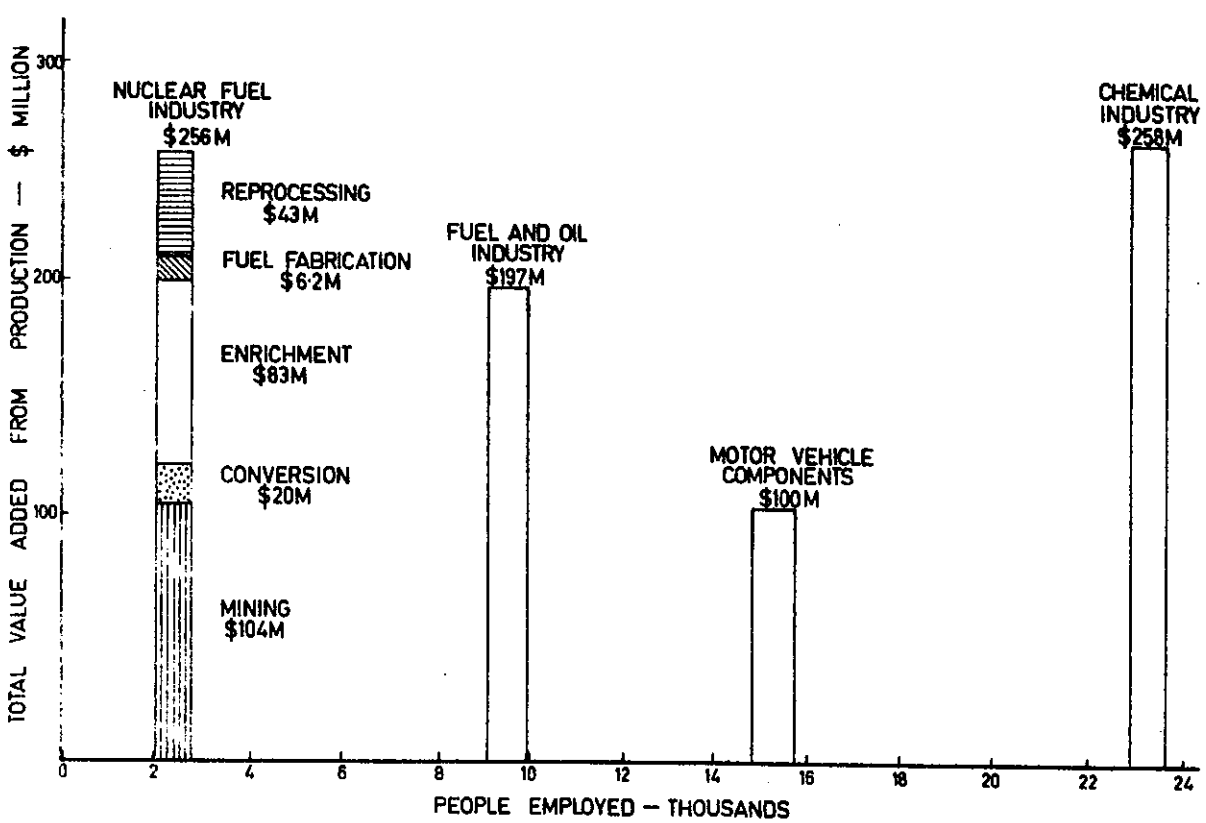


FIGURE 12. VALUE ADDED Vs. EMPLOYMENT FOR SEVERAL INDUSTRIAL SECTORS

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.

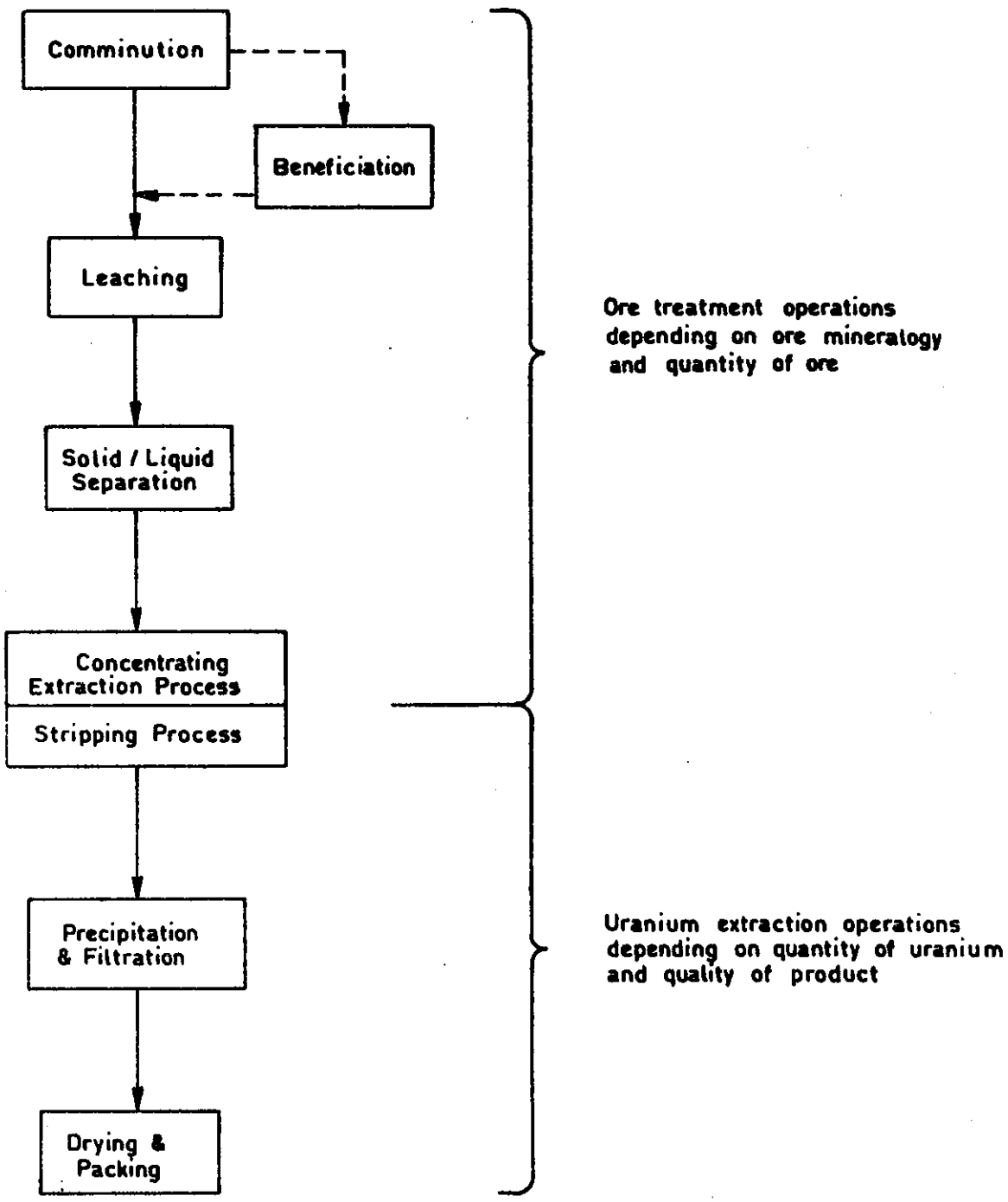



FIGURE 1. SCHEMATIC FLOWSHEET

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.

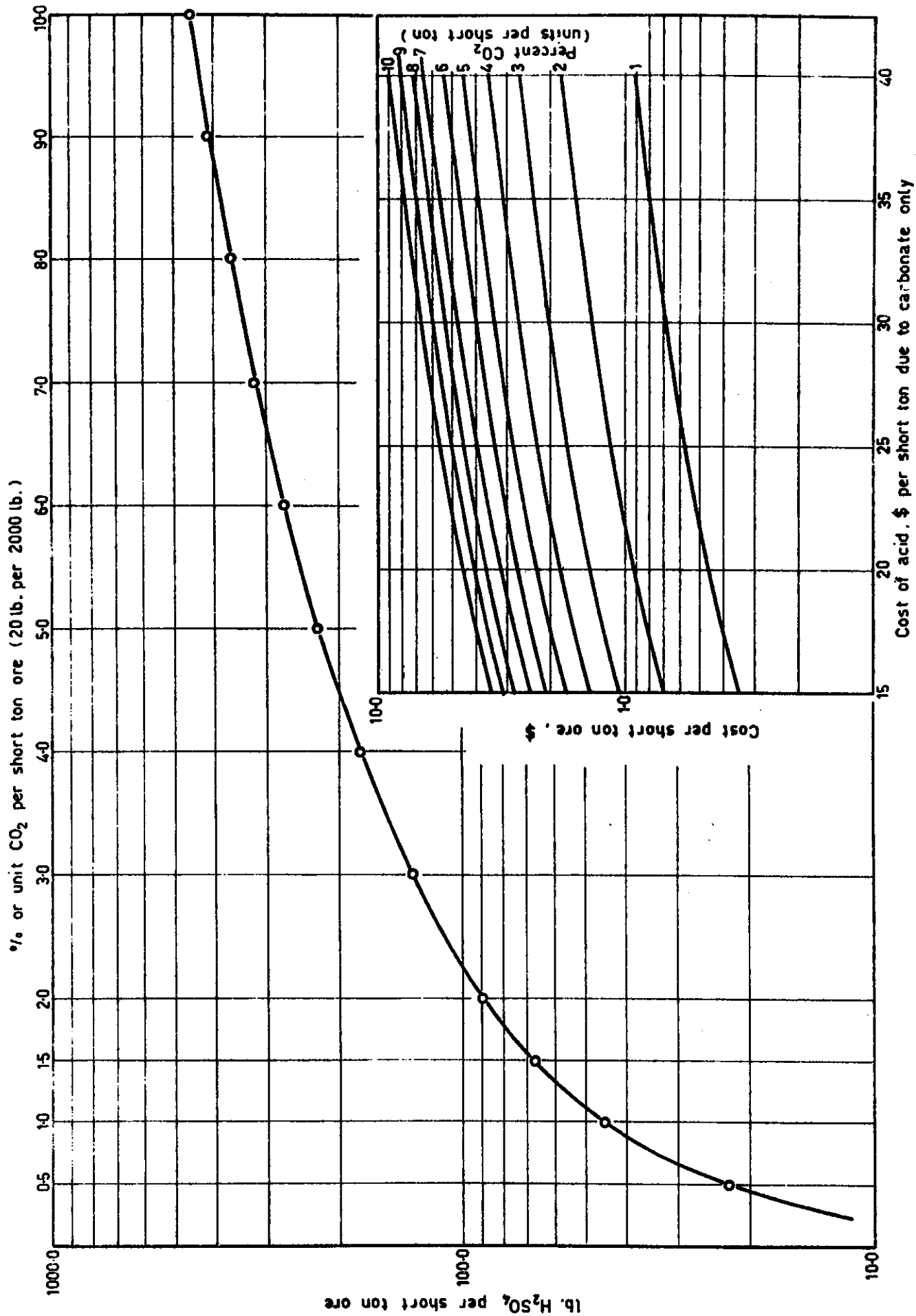



FIGURE 2. EFFECT OF $CO_2$ CONTENT ON ACID CONSUMPTION

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

and either

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

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

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:

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

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

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

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:

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

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

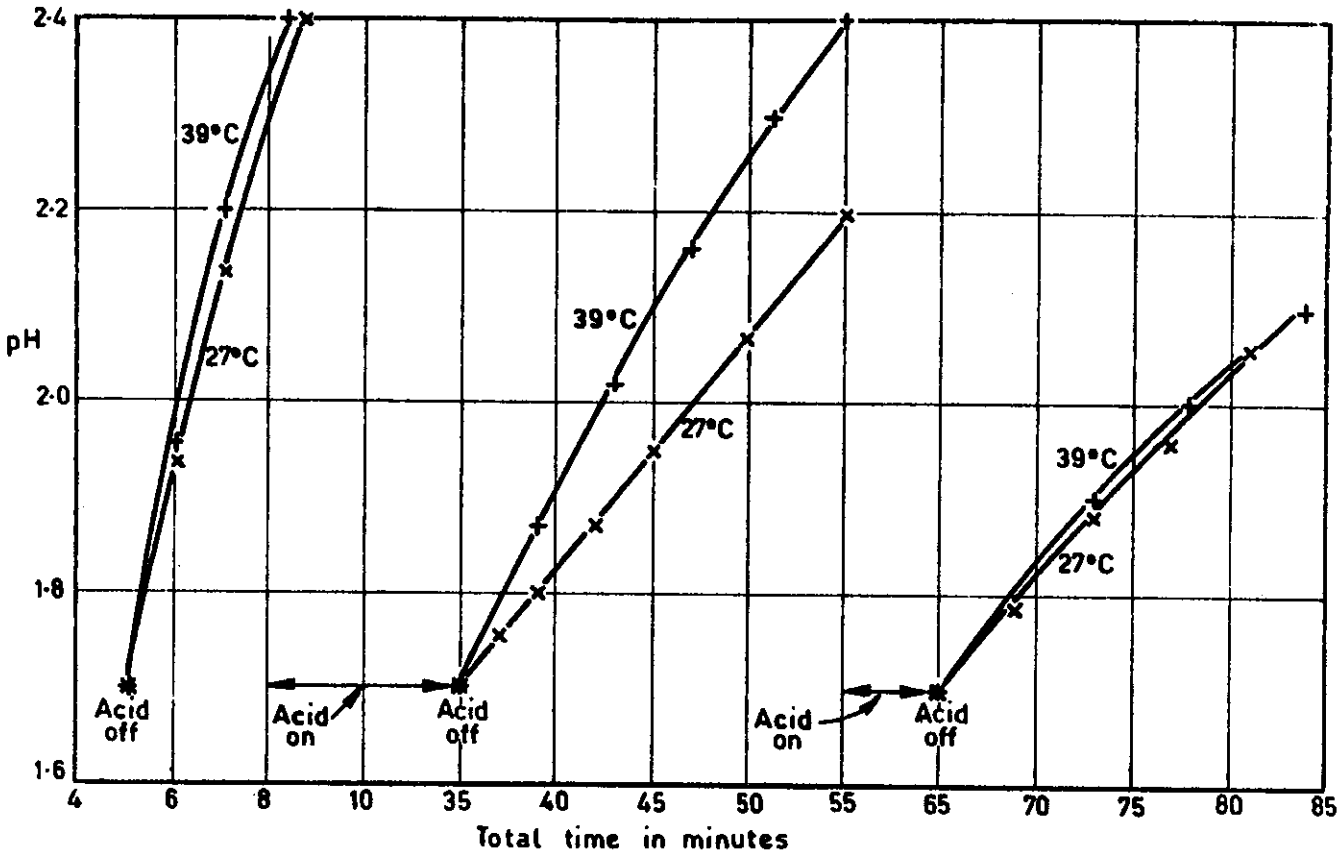



**FIGURE 3. CHANGE IN pH WITH TIME**

**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<br>3 x 75 | 20<br>12 | Guar Gum<br>Total 0.27 |
| Mary Kathleen (1200) | 5 x 75 | 4 | Separan NP10<br>No.1 0.090<br>No.2 0.026<br>No.3 0.010<br>No.4 0.010<br>No.5 0.010<br>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<br>0.21 total |
| Port Pirie (100) | 2 x 100<br>2 x 80 | 80<br>50 | Glue + Separan<br>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.

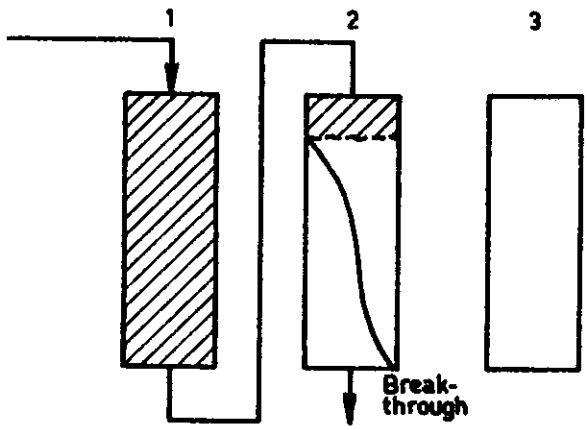
The chemical capacity is usually measured in terms of milli-equivalents of exchangeable ions per gram of dry resin or per ml of 'wet settled resin'. The latter is a less exact measure but more meaningful when related to the volume of resin in the column. The capacity of resins available on the market 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

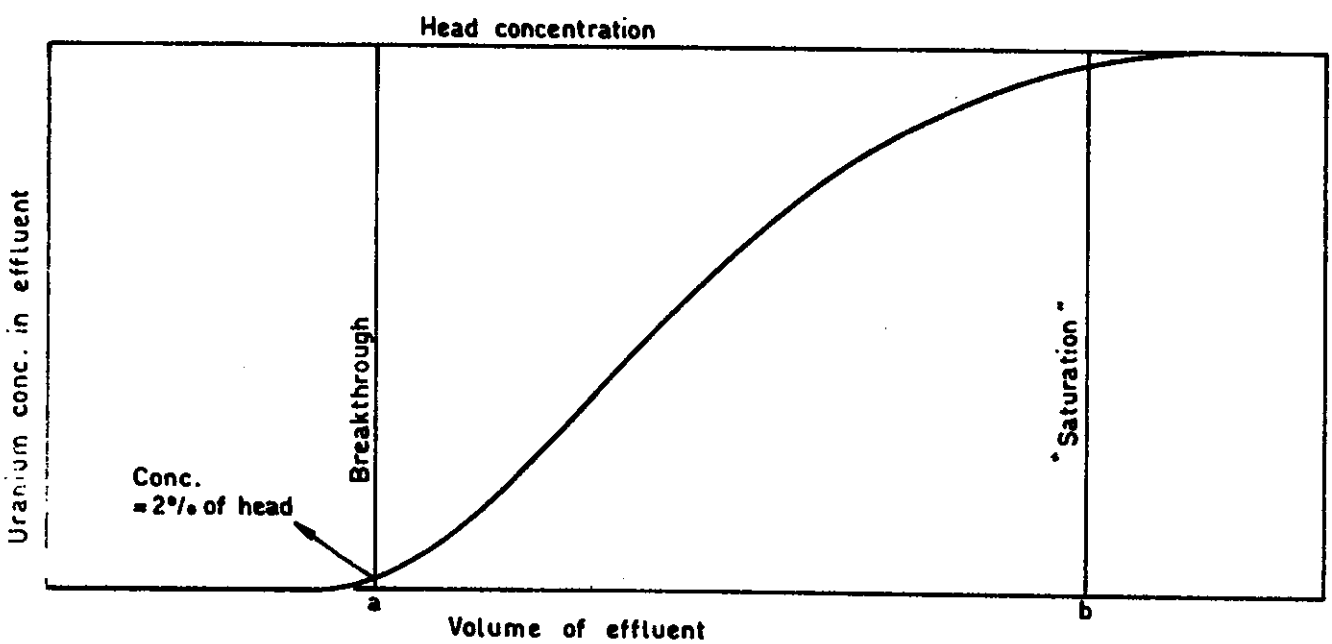



**FIGURE 4. ION EXCHANGE CONCENTRATION PROFILE**

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

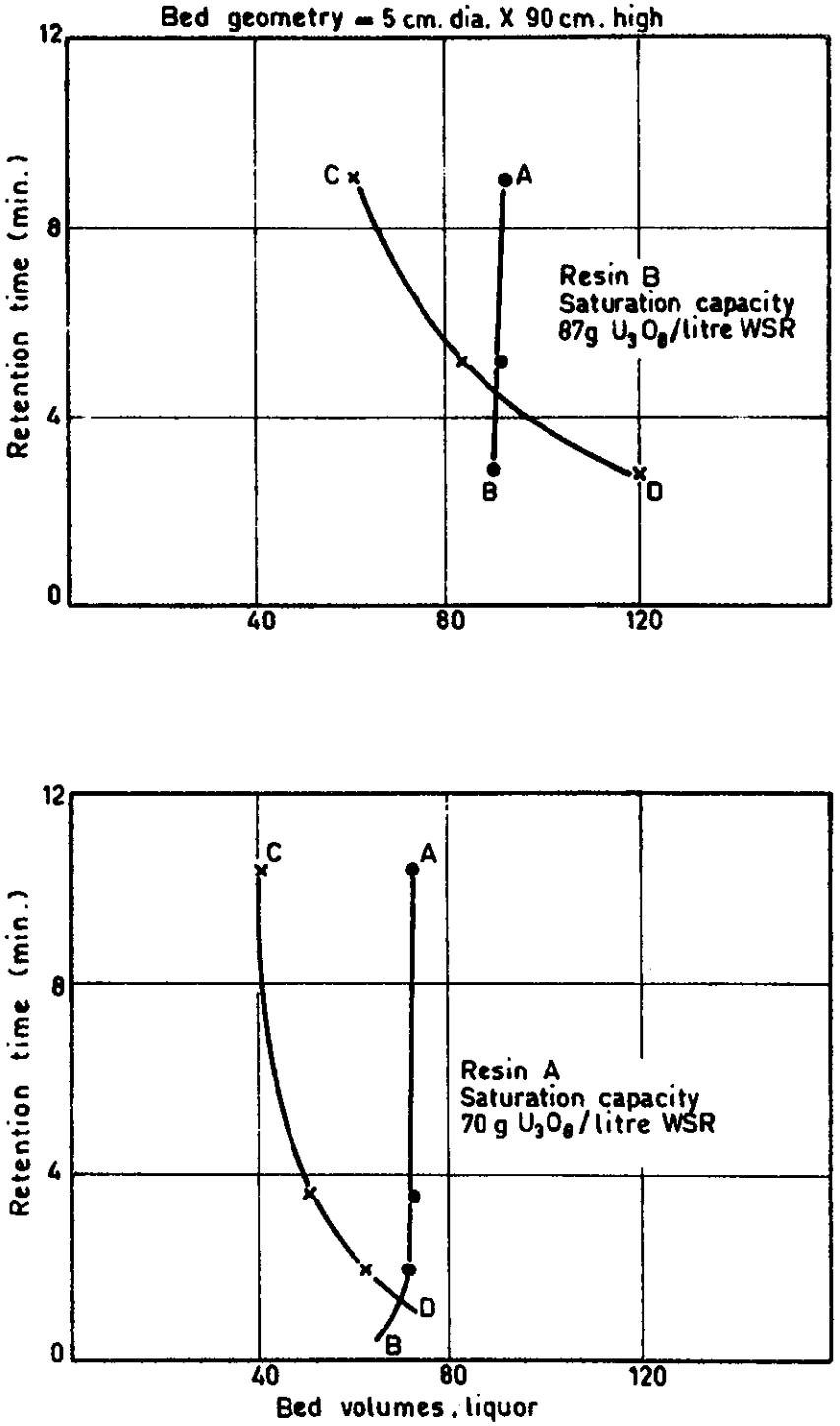



FIGURE 5. DETERMINATION OF RETENTION TIME AND RESIN VOLUME

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.

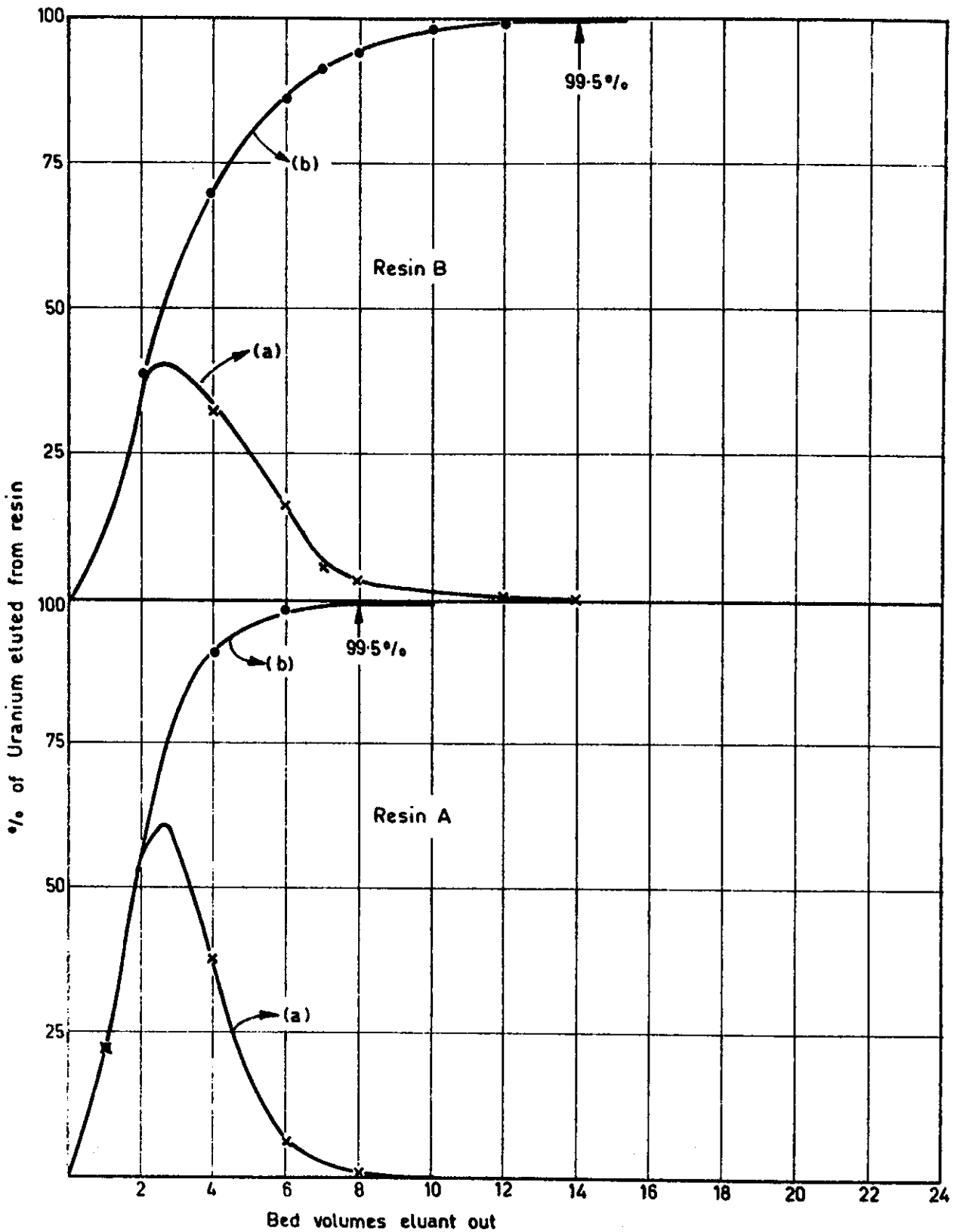



FIGURE 6. ELUTION CURVES

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

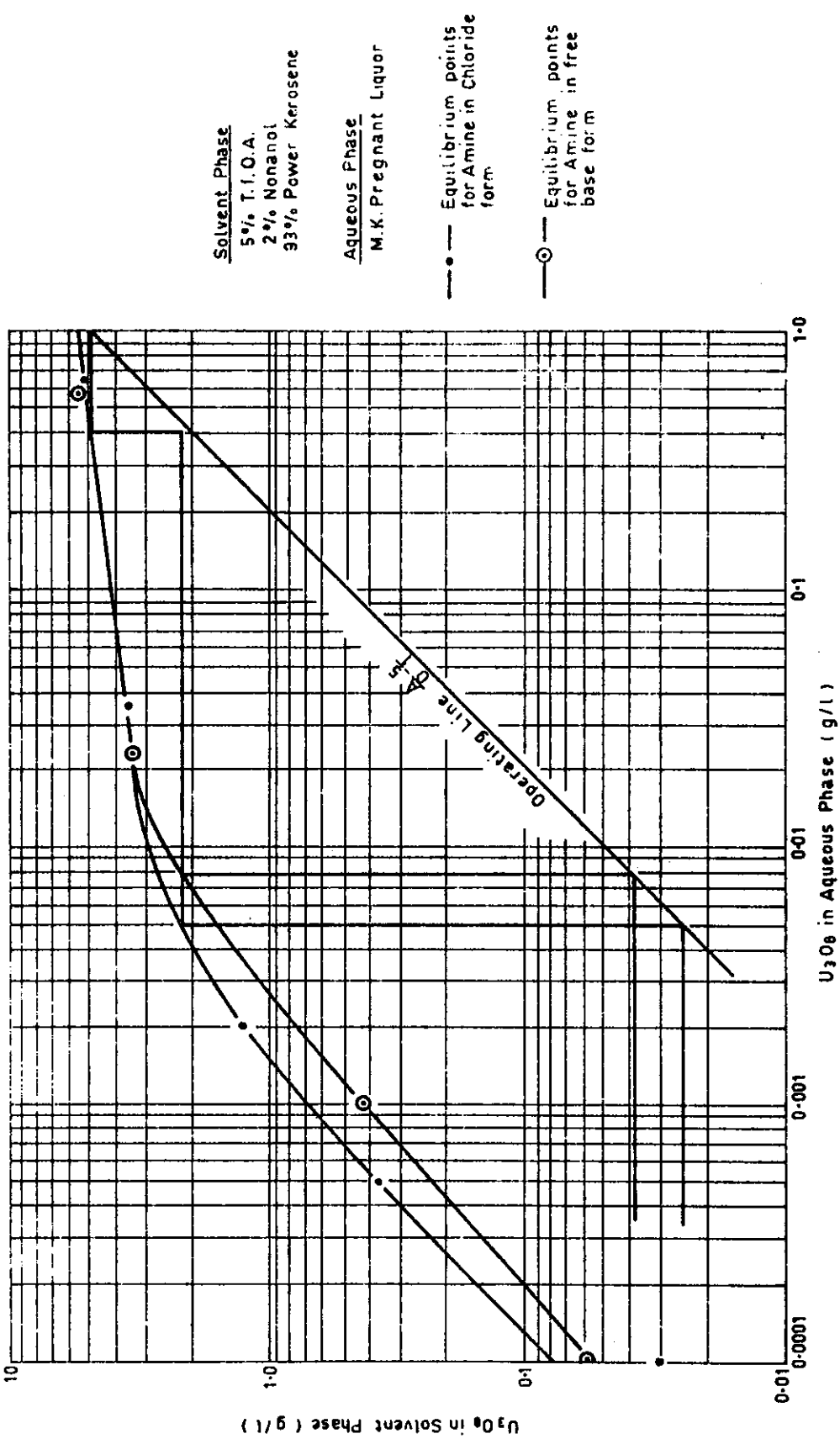
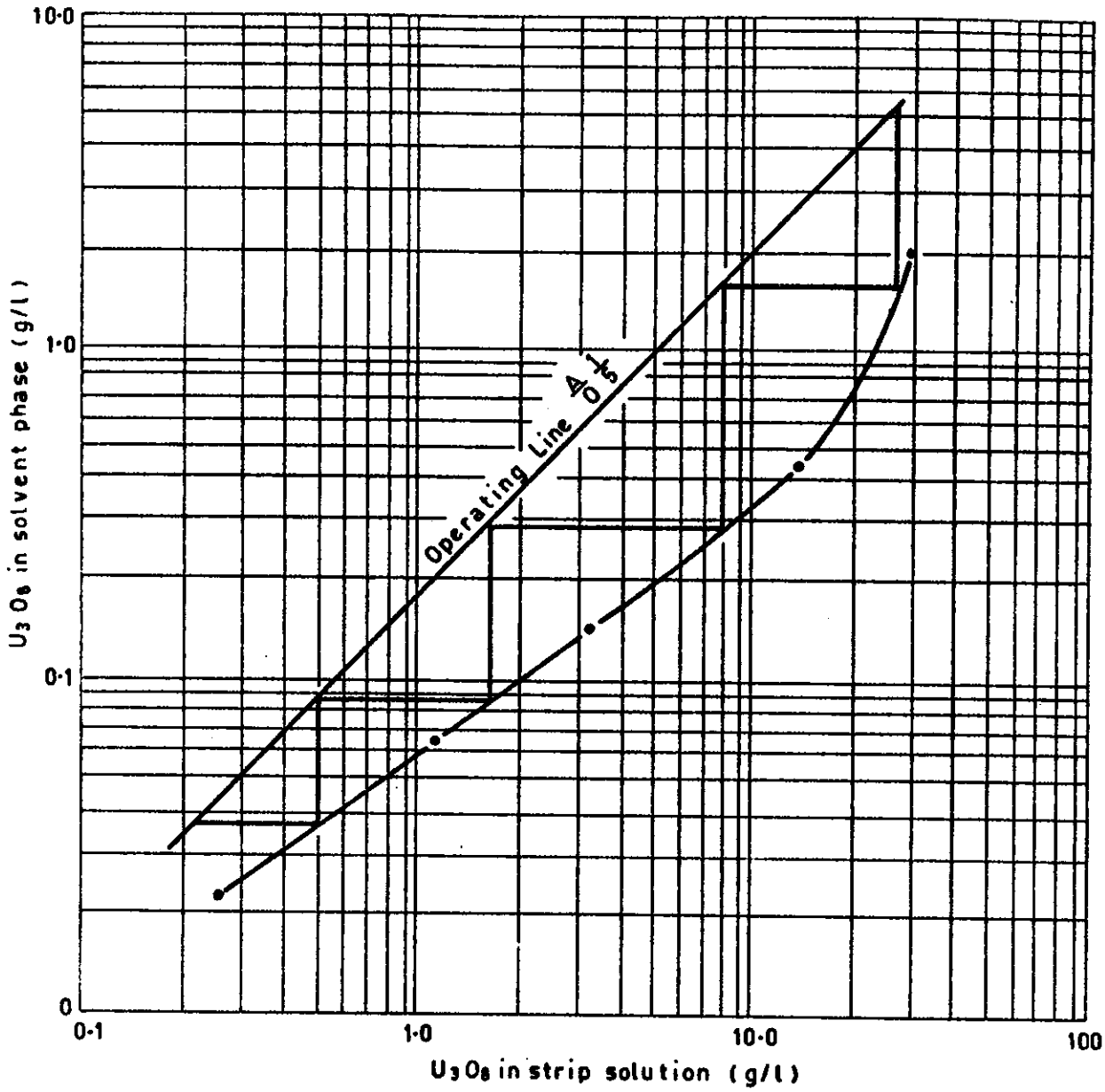



FIGURE 7. EXTRACTION ISOTHERMS




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

**Strip Solution**
58g. NaCl / litre
pH. - 6·5

**FIGURE 8. STRIPPING ISOTHERM**

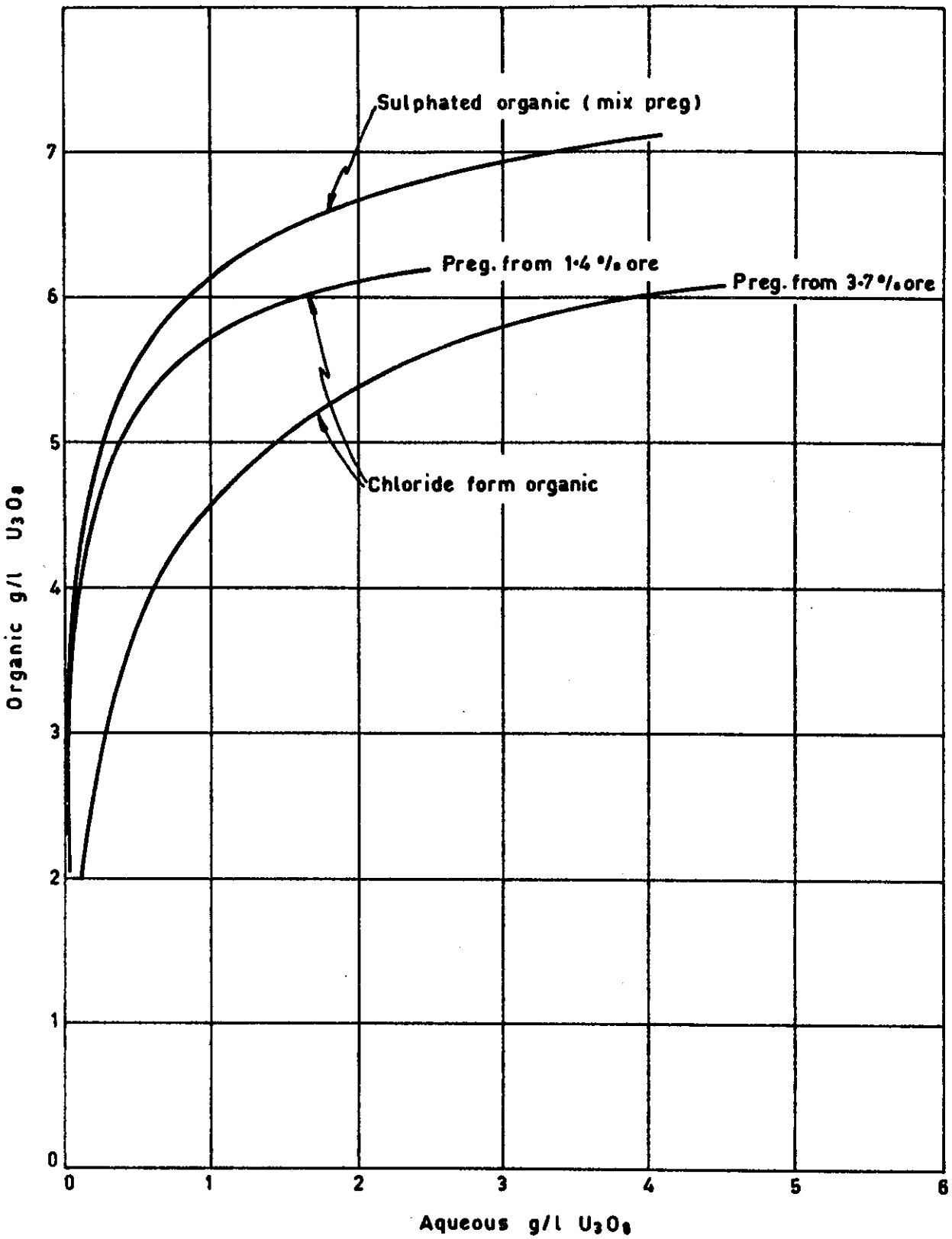



FIGURE 9. SOLVENT EXTRACTION EQUILIBRIUM DATA

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

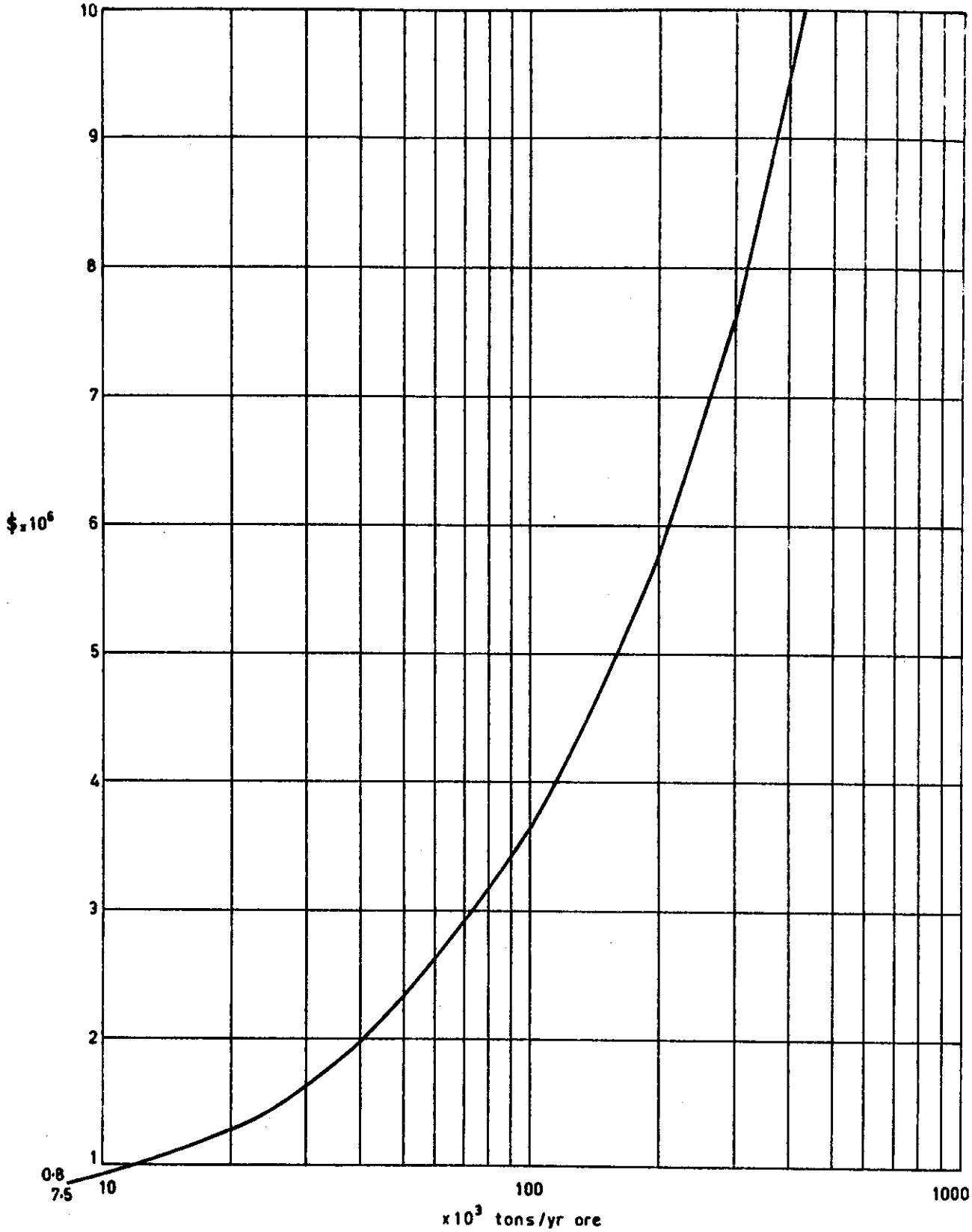



**FIGURE 10. CAPITAL COST FOR ORE TREATMENT SECTION.**
**Comminution, Leaching, CCD, Clarification, Extraction, Power Plant, Service Bldgs. and Mine not included.**

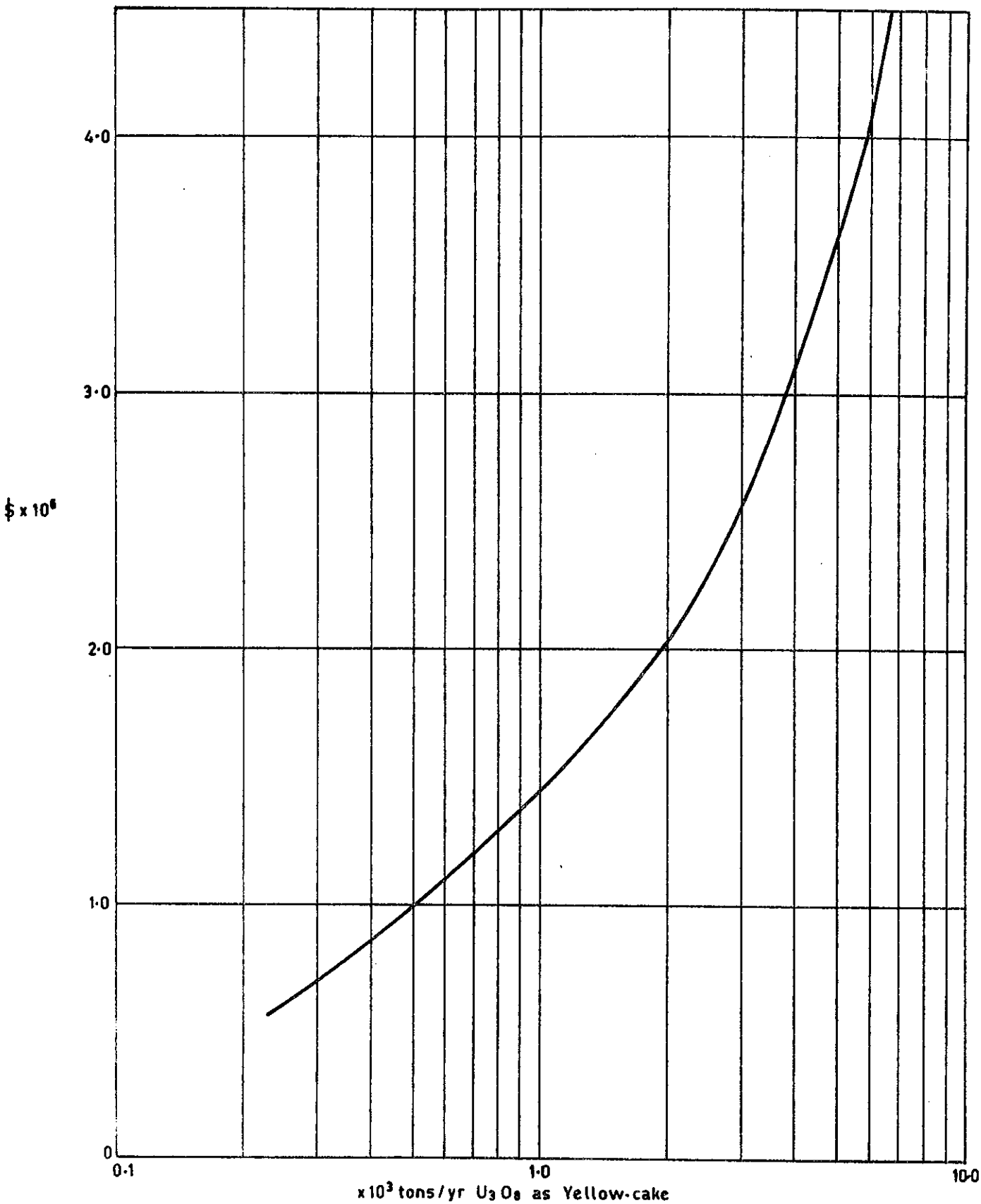



FIGURE 11. CAPITAL COST FOR URANIUM EXTRACTION SECTION.
Stripping, Precipitation, Filtration, Drying and Packing.

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.

16. REFERENCES

AAEC (1958) - Proceedings of a Symposium on the Peaceful Uses of Atomic Energy, Sydney, June 2-6 1958. Melbourne University Press.

Allman, M.B., Harris, J.A. and Bayly, M.G. (1968) - Treatment of Rum Jungle Uranium ore. In Berkman et al. (1968) p. 90-124.

Almond, J.N. (1958) - Treatment of Radium Hill concentrates for the recovery of uranium. In AAEC (1958) p. 67-74.

Anderson, J.S. and Ritchie, M.I. (1968) - Solution mining of uranium. Min. Congress J. 54 (1) 20-23.

Arden, T.V. (1956) - The concentration of uranium from low-grade ores. Ind. Chemist 32 202.

Arden, T.V. (1959) - The analysis and recovery of uranium from low-grade ores. AERE-R2862.

Armstrong, A.T. (1965) - Port Pirie treatment plant. In Fitzgerald and Hartley (1965) p. 224-5.

Barlow, T. (1965) - Rum Jungle.Ibid. p. 211-16.

Behan, R.L. (1956) - The Eldorado gravity plant, Port Radium N.W. Territory. Trans. Can. Inst. Min. and Met. 59 154-161.

Bellingham, A.I. (1961) - The application of solvent extraction in the recovery of uranium from El Sherana ore. Proc. Aust. Inst. Min. and Met. 198 86-112.

Berkman, D.A., Cuthbert, R.H. and Harris, J.A. (Editors) (1968) - Papers delivered to the Symposium on Uranium in Australia, Rum Jungle, Northern Territory June 16-21 1968. Published by Aust. Inst. of Min. and Met.

Blake, C.A. jr., Blaes, C.F. jr., Brown, K.B., Coleman, C.F. and White, J.C. (1958) - Solvent extraction of Uranium and other metals by acidic and neutral organophosphorous compounds. In United Nations (1958) Vol. 28 p. 289-97.

Bridges, D.W. and Rosenbaum, J.B. (1962) - Metallurgical applications of solvent extraction. Fundamentals of process. U.S. Bur. Mines, I.C. 8139.

Brown, K.B., Coleman, C.S., Crouse, D.J., Denis, J.O., and Moore, J.G. (1954) - The use of amines as extractants for Uranium from acidic sulphate liquors. AECD-4142.

Butler, R.D. (1972) - Carbonate leaching of Uranium ores - a review. Paper presented to this symposium.

Clegg, J.W. and Foley, D.D. (Editors) (1958) - Uranium ore processing. Addison - Wesley Pub. Co. Inc., Reading, Mass.

Clifford, W.E., Larkin, E.E. and Smith, E.M. (1956) - Catalysis of air and hypochlorite oxidation of Uranium compounds in carbonate leach solution. RMO-2621.

Couche, R.E. and Hartley, F.R. (1958) - Features of the development of chemical processing for Mary Kathleen Ores. In AAEC (1958) p. 75-85.

De Lacerda, J. (1967) - Treatment of Uranium ores by natural leaching in Portugal. In IAEA (1967) p.101-18.

Downes, K.W. (1967) - Recent developments in the treatment of Uranium ores from the Elliot Lake District. Ibid. p. 79-88.

Ellis, D.A. (1955) - Recovery of Uranium from Colorado Plateau ores by solvent extraction. DOW-131.

Faure, A. and seven co-authors (1966) - The production of high purity Uranium at a South African gold mine. J. Sth. Afr. Inst. Min. and Met. 66 319-41.

Faure, A. and Tunley, T.H. (1970) - Uranium recovery by liquid-liquid extraction in South Africa. In IAEA (1970) p. 241-51.

Fisher, W.J. (1968) - Mining practice in the South Alligator Valley. In Berkman et al. (1968) p. 57-89.

Fitzgerald, M.L. and Hartley, F.R. (Collaters) (1965) - 'Uranium'. Proc. 8th Commonwealth Mining and Metallurgical Congress. Vol. 3, Ch. 9, Aust. Inst. Min. and Met., Melbourne.

Frondel, C. (1958) - Systematic mineralogy of Uranium and Thorium. U.S. Geol. Survey Bull. 1064.

Frondel, J.W., Fleischer, M. and Jones, R.S. (1967) - Glossary of Uranium and Thorium-bearing minerals, 4th Ed. U.S. Geol. Survey Bull. 1250.

George, D.R. (1958) - Mineralogy of Uranium as it relates to hydrometallurgical processing. In Clegg and Foley (1958) Ch. 4 p. 89-102.

George, D.R. and Ross, J.R. (1967) - New developments in the recovery of Uranium by ion exchange. Paper presented to Uranium Symposium of Am. Inst. Metallurgical Engineers, Utah.

George, D.R. and Ross, J.R. (1967) - Recovery of Uranium from Uranium mine waters and Copper ore leaching solutions. In IAEA (1967) p. 227-34.

Grinstead, R.R., Ellis, D.A. and Olsen, R.S. (1956) - Recovery of Uranium from Sulfuric acid and Carbonate leach liquors by anion exchange. In United Nations (1956) Vol. 8, 552-9.

Hancher, C.W. (1959) - Comparing fixed and moving bed ion exchange techniques. Eng. Mining J. 160 80-83.

Harris, J.W., Boag, J. and Hemmingway, P. (1961) - Some technical aspects of treatment operations at Mary Kathleen Uranium Ltd. Proc. Aust. Inst. Min. and Met. 198 207-226.

Harris, J.W. and Steele, E.A.R., (1960) - Radiometric sorting at Mary Kathleen Uranium Ltd. Paper presented to Annual Conf. Aust. Inst. Min. and Met. August 1960.

Hartley, F.R. (1968) - Treatment of Mary Kathleen Uranium ore - a review. In Berkman et al. (1968) p. 138-160.

Hartley, F.R. and Lawrie, D.W. (1955) - Report RD 17. South Aust. Dept. Mines.

Helfferich, F. (1962) - Ion Exchange. McGraw Hill, New York.

Herwig, G.L., Stewart, R.M., Swinton, E.A. and Weiss, D.E. (1958) - The 'jigged bed' ion exchange pilot plant for Uranium extraction. In AAEC (1958) p. 86-98.

Higgins, I.R. (1955) - Mechanical features of the Higgins continuous ion exchange column. ORNL-1907.

Hollis, R.F. and McArthur, C.K. (1956) - The resin-in-pulp process for the recovery of Uranium. In United Nations (1956) Vol. 8, 54-63.

IAEA (1967) - Proceedings of a Panel on the Processing of low-grade ores, Vienna, 27 June - 1 July 1966. IAEA Vienna. STI/PUB-146.

IAEA (1970) - Proceedings of a Symposium on the Recovery of Uranium from its Ores and Other Sources, Sao Paulo, Brazil 17-21 August 1970. IAEA Vienna. STI/PUB-262.

Laxen, P.A. (1964) - Factors in the dissolution of Uranium from South African ores and observations on the nature of the undissolved Uranium. Proc. Int. Symp. on Unit Processes in Hydrometallurgy, Dallas, Texas, February 24-28 1963. Metallurgical Society Conf. series, Vol. 24 p. 143-156. Gordon and Breach, New York.

Laxen, P.A. (1965) - Leaching fundamentals. Report No. 2 - the dissolution of Uranium minerals from South African ores in acid solutions. SAAEB Report PEL-121, Vol. 5, p. 434-5.

Lentz, K.W. and Temple, F.T. (1959) - Union Carbide's operations at Maybell, Colorado. Paper presented to Annual meeting of Amer. Inst. Min. Met. and Pet. Engineers, San Francisco, February 1959.

Lower, G.W. (1951) - Systematic ion exchange studies. AECD-4113.

MacGregor, R.A. (1966) - Recovery of $U_3O_8$ by underground leaching at Stanrock Uranium Mines Ltd. Can. Inst. Min. and Met. Bull. 59 583.

Magno, P.J. and De Sesa, M.A. (1957) - Oxidants in carbonate leaching of uraniferous ores. WIN-86.

Mashbir, D.J. (1964) - Heap leaching of low-grade Uranium ore. Mining Congress J. 50 (12), 50-54.

Merritt, R.E. (1971) - Extractive Metallurgy of Uranium. TID-25711.

Meyburgh, B.G. (1970) - Design, erection and operation of the Purlex Plant at Buffelsfontein Gold Mining Co. Ltd. J. Sth. Afr. Inst. Min. and Met. 71 (3) 55.

Murray, R.J. and Fisher, W.J. (1968) - The treatment of South Alligator Valley Uranium ores. In Berkman et al. (1968) p. 125-137.

Preuss, A. and Kunin, R. (1956) - A general survey of the types and characteristics of ion exchange resins used in Uranium recovery. In United Nations (1956) Vol. 8. 45-48.

Rhees, R.G. (1962) - EMF values - what they are - what they mean. Paper presented to Amer. Potash and Chemical Corp. Symp. on Sodium Chlorate in Uranium Refining.

Ritchie, M.I. (1970) - Utah Construction and Mining Company's unique Shirley Basin Uranium mill. In IAEA (1970) p. 147-56.

Roach, R.J. (1958) Pebble milling, its application and performance at Faraday Uranium Mines. Paper presented to Annual meeting of Amer. Inst. Min. Met. and Pet. Engineers, February 1958.

Roach, A.G., Anderson, A.C., Ehrlich, R.P. (1964) - Conversion to ore pebble grinding. Paper presented to Int. Mineral Processing Congress. New York. 23 Sept. 1964.

Robb, N., Opratko, V., and Price, L.S. (1963) - Milliken's two-stage sulphuric acid leaching process for Uranium. Can. Inst. Min. and Met. Bull. 56 614.

Robinson, R.E., Velthuis, R.G. and Pinkney, E.T. (1958) - An analysis of the characteristics of anion exchange resins suitable for the Uranium recovery from acid leach liquors. In United Nations (1958) Vol. 3 p. 415-26.

Rodgers, T.A. (1958) - The location, mining and concentration of Uranium ores at Radium Hill, South Australia. In AAEC (1958) p. 44-52.

Sugier, P. (1967) - Recovery of Uranium in mine waters. In IAEA (1967) p. 96-100.

Taverner, L. (1956) - An historical review of the events and developments culminating in the construction of plants for the recovery of Uranium from Gold ore residues. J. Sth. Af. Inst. Min. and Met. 57 (4) 125-143.

Thunaes A. (1958) - Development of the Beaverlodge Mill. In Clegg and Foley (1958) p. 306-23.

Thunaes, A. (1967) - Status report from Canada. In IAEA (1967) p. 9-14.

United Nations (1956) - Proceedings of 1st International Conference on the Peaceful Uses of Atomic Energy, Geneva, 8-20 August 1955. United Nations, New York. 16 Vols.

United Nations (1958) - Proceedings of 2nd International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1-13 September 1958. United Nations, Geneva. 33 Vols.

Wilkinson, W.D. (1962) - Uranium Metallurgy, Vol. 1 - Uranium Process Metallurgy. Interscience Publishers.

Wreford, P.M. (1965) - Mary Kathleen Uranium Limited. In Fitzgerald and Hartley (1965) Ch. 9.

Zivanovic, V., Vracar, N., Milic, D. et al. (1970) - Development in the treatment of Uranium ores from the Gorenja Vas Area. In IAEA (1970) p. 43-56.

AAEC SYMPOSIUM

ON

URANIUM PROCESSING

PAPER III

# CARBONATE LEACHING OF URANIUM ORES

## A REVIEW

by

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## 1. INTRODUCTION

The recent discovery of extensive deposits containing uranium mineralisation in a shallow calcrete environment in Western Australia has directed attention to the possible application of carbonate leaching as an alternative to the acid leaching process used at all plants operated to date in Australia.

Only sketchy information on mineralisation is available for publication at this stage, but the ores are of secondary origin and apparently contain carnotite and other oxidised minerals, with uranium/vanadium ratios ranging from 1:1 to 10:1. The mineralisation is associated with calcite and pyrite is absent. One published report has indicated an average grade of 3 lb $U_3O_8$/long ton* (Liddy 1972).

This paper reviews the standard practice in Canada and the United States with special references to the Beaverlodge plant in Canada, with which the author was associated some years ago. Apart from the question of its application to carbonate-bearing ores, carbonate leaching could have special significance in the West Australian environment because of its closed-circuit operation. This minimises the fresh-water intake requirements and reduces pollution problems as a negligible quantity of dissolved chemicals is discharged from the plant.

## 2. THE SELECTION OF CARBONATE LEACHING

The presence of carbonate minerals in sufficient quantity to cause acid consumptions of more than 150-200 lb/ton is likely to be the deciding factor in favour of using a carbonate leach. This is equivalent to a calcite content in the ore of 7%-9% (Gow and Ritcey 1969).

Much higher acid consumptions (~250-350 lb/ton) may be acceptable where a high vanadium content warrants its recovery in addition to the uranium. Vanadium cannot be efficiently recovered by a sodium carbonate leach, except after salt roasting which produces water-soluble sodium vanadate and sodium uranyl vanadate. A high calcium carbonate content in the ore interferes with the effectiveness of salt roasting (Merritt 1971).

Modern practice, adopted in four American mills recovering both uranium and vanadium from carnotite ores with U/V ratios of between 1:3 and 1:5, is to use high acid concentrations in two-stage countercurrent leaching circuits.

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* As other data in this paper are derived from Canadian or American sources, the term 'ton' refers to the short ton of 2,000 lb and '$' refers to the American or Canadian dollar.

Recoveries of the order of 95% of the uranium and 75% of the vanadium are achieved, with both products being of approximately equal value. Recovery of vanadium from carnotite ores has not been a prime consideration in the design of plants in the United States where the U/V ratio has been 1:1 or higher in uranium content.

## 3. CHEMISTRY OF CARBONATE LEACHING PROCESS

The basis of the process is the formation of the stable 'uranyl tricarbonate' complex ion, in which form the uranium passes into solution. To be able to dissolve in carbonate solution, the uranium must be present in the hexavalent (uranyl) state and it is necessary, therefore, first to oxidise tetravalent (uranous) minerals.

The dissolution may be represented by the following equations:

(a) In the case of oxidised minerals - such as carnotite, $K_2O \cdot 2UO_3 \cdot V_2O_5$

$$UO_3 + 3CO_3^{=} + H_2O = \left[UO_2(CO_3)_3\right]^{4-} + 2OH^- \quad ...(1)$$

(b) In the case of primary minerals - such as uraninite, $(UO_2)_nUO_3$

$$UO_2 + \tfrac{1}{2}O_2 + 3CO_3^{=} + H_2O = \left[UO_2(CO_3)_3\right]^{4-} + 2OH^- \quad ...(2)$$

The dissolution reaction produces hydroxyl ion and is reversible. For maximum dissolution, the hydroxyl ion must be removed and this is normally achieved by neutralisation with bicarbonate ion.

$$HCO_3^- + OH^- = CO_3^{=} + H_2O \quad ...(3)$$

Precipitation is achieved by first neutralising the excess bicarbonate ion and adding sufficient caustic soda to precipitate sodium diuranate, essentially reversing equation (1) above:

$$2\left[UO_2(CO_3)_3\right]^{4-} + 6OH^- + 2Na^+ = Na_2U_2O_7 + 6CO_3^{=} + 3H_2O \quad ...(4)$$

This occurs at a pH of approximately 11. It should be noted that precipitation may also be achieved by acidifying to pH 6 and this has been used commercially on liquors containing both vanadium and uranium. Several other precipitation methods have been investigated. Hydrogen reduction appears attractive, but requires high temperatures and pressures to achieve satisfactory precipitation rates.

Ion exchange processes have been developed for the selective recovery of uranium from carbonate leach solutions. Solvent extraction has not proved economically attractive, but resin-in-pulp extraction (with a quaternary ammonium resin) is used at one plant.

The barren liquor after precipitation with caustic soda will contain excess sodium hydroxide, sodium carbonate and some residual uranium. The excess caustic is converted to carbonate and bicarbonate by contacting with carbon dioxide, thereby regenerating the leach liquor for re-cycling.

$$2OH^- + CO_2 = CO_3^= + H_2O \quad ...(5)$$

$$CO_3^= + H_2O + CO_2 = 2HCO_3^- \quad ...(6)$$

In the leaching stage, sodium carbonate is consumed by sulphide minerals, commonly pyrite, and by gypsum, producing sodium sulphate. At higher temperatures and pressures, it may also react with silica and alumina (Merritt 1971, McClaine et al. 1956, Stephens and MacDonald 1956, Thunaes et al. 1957).

## 4. FACTORS AFFECTING LEACHING RATE

### 4.1 Oxidation

Under carbonate leaching conditions, effective oxidation of tetravalent uranium can be achieved by molecular oxygen. The rate of oxidation is proportional to the square root of the oxygen partial pressure and can be increased, therefore, by operating with oxygen-enriched air or under high total pressure conditions.

Although more rapid oxidation and improved recoveries can be achieved under alkaline conditions with chemical oxidants (e.g., potassium permanganate) or with air in the presence of an oxidation catalyst (e.g., cupric-ammonia complex), economic conditions generally favour the use of air or oxygen, with relatively long leaching times (Merritt 1971).

### 4.2 Temperature

Elevated temperatures are necessary to achieve acceptable reaction rates which almost double for each ten-degree rise in temperature between 60°C and 100°C. It must be noted that oxygen solubility (i.e., partial pressure) falls with increasing temperature under constant pressure conditions and, therefore, a combination of elevated temperature and high pressure gives the highest dissolution rate. Temperatures over 70°C must be used to achieve acceptable air oxidation rates for tetravalent uranium minerals (Forward et al. 1953).

### 4.3 Reagent Concentration

Leach solutions contain a mixture of sodium carbonate and bicarbonate, each of which dissolves uranium. The rate of dissolution increases with increasing reagent concentration. Some bicarbonate is necessary to prevent re-precipitation of dissolved uranium, but excess bicarbonate consumes caustic

soda in the precipitation stage. The carbonate concentration is dictated by economic considerations such as soluble losses. Normal concentrations (in circuit feed) are 30 - 60 g/litre $Na_2Co_3$ and 5 - 15 g/litre $NaHCo_3$.

4.4 Particle Size

The rate of chemical reaction is controlled by the specific surface available. In carbonate leaching, a high specific surface area is necessary to achieve acceptable leaching rates and grinding to 70% - 80% passing 200 mesh is common. A few sandstone ores, where the uranium is present in interstitial cementing material, give good extractions at comparatively coarse grinds (Stephens and MacDonald 1956).

## 5. ELDORADO BEAVERLODGE OPERATION

### 5.1 Introduction

The Eldorado Nuclear mill at Beaverlodge is the only Canadian operation using an alkaline leaching process (Harding et al. 1960, Thunaes and Colborne 1964, Colborne 1963, Marshall 1962). It has a semi-isolated location, north of Lake Athabasca in the far north of Saskatchewan. The processing plant has been in continuous operation since 1953 when a 500 ton/day pressure leaching circuit was started up. It was enlarged to 750 ton/day in 1955 and 2,000 ton/day capacity in 1957 by the addition of atmospheric leach pachucas. The autoclave section was shut down in 1963 and the plant is currently operated on a reduced tonnage of approximately 900 ton/day.

The current flow-sheet utilises autogenous grinding in carbonate solution, flotation to remove pyrite, atmospheric carbonate leaching, liquid-solid separation by two stages of filtration, precipitation of the product with caustic soda and re-generation of the barren liquor. The small quantity of pyrite concentrate is acid-leached in a batch system. A flow-sheet is shown in Figure 1. Recovery has averaged approximately 90% of the $U_3O_8$.

### 5.2 Ore

Uranium occurs as the mineral pitchblende in a series of vein-type deposits in association with calcite, chlorite and haematite. Calcite content averages in excess of 8%. Pyrite and chalcopyrite are present with an average sulphur content of 0.5%, but ranging up to several per cent in some sections. The ore is very hard with a Bond Work Index of 20. The average grade of current reserves is 0.24% $U_3O_8$.

### 5.3 Ore Sorting

Because of the nature of the orebodies - fracture fillings associated

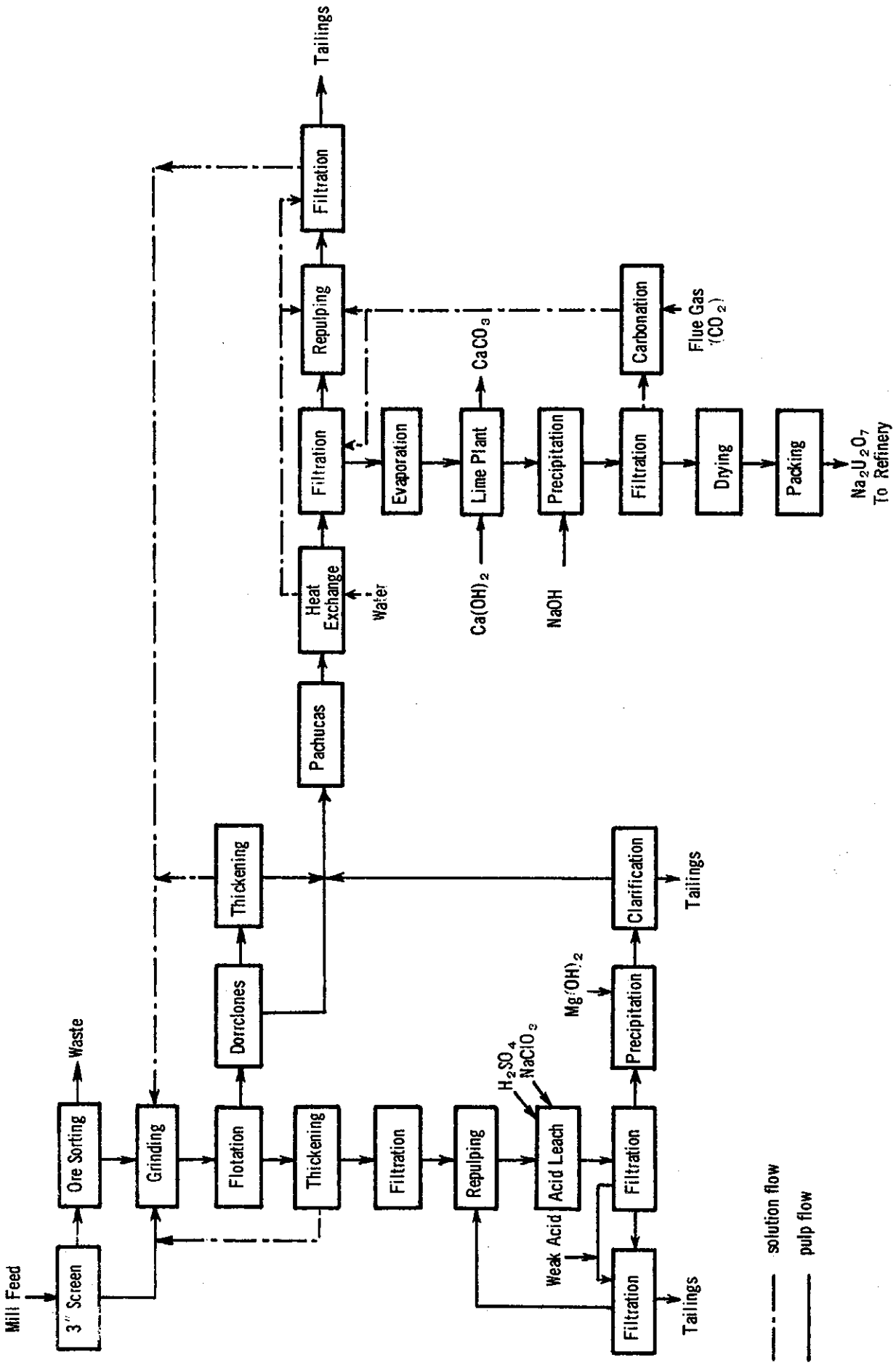


FIGURE 1. ELDORADO NUCLEAR BEAVERLODGE MILL FLOWSHEET

with a major fault system - there is a sharp demarcation between barren country rock and the mineralised vein material. This feature permits upgrading by electronic ore sorting (Colborne 1963).

The ore sorting plant has been shut down since 1964 partly due to a change in run-of-mine ore sizing, and partly due to the planned cut-back in production resulting in adequate capacity to process the entire mine output. Run-of-mine ore is crushed to a maximum size of about 6" underground and is screened at 3" ahead of the coarse ore bin.

The oversize (3 - 6"), which constitutes about 35% of the ore feed, passes to 4 K and H Ore Sorters, where approximately half is rejected. Each sorter handles 20 tons of rock per hour. Thus, 17% of the feed is rejected as coarse waste with a loss of 2% of the uranium value. The sorting units result in a net operating cost saving of about 20 cents per ton of ore mined.

5.4 Comminution

Crushing was formerly by a conventional two-stage circuit to approximately 1/2-inch sizing. The crushing plant is now largely by-passed and run-of-mine ore is fed directly to a 19' x 12' Nordberg semi-autogenous mill with central peripheral discharge. The run-of-mine ore is too fine for good autogenous grinding and it has been necessary to add a light charge of 6" balls to the mill to prevent the build-up of small rock (Lendrom 1970).

The pump from the autogenous mill is classified on a stationary sloping B - Z screen with 35 mesh deck, the oversize material being re-circulated. The minus 35 mesh ore is cycloned to remove minus 200 mesh material before passing to two conventional ball mills, operating in parallel in closed circuit with rake classifiers. This secondary grinding reduces the ore to 70% passing 200 mesh which is necessary for good extraction.

It is of particular interest to note that all grinding is done in the mill-leaching solution with a mean S.G. of 1.13 and temperature about 40°C. This results in equipment capacities considerably below those required for grinding in a water media (Harding et al. 1960).

5.5 Flotation

To decrease reagent consumption, pyrite is removed from the carbonate pulp by flotation prior to leaching. Approximately 90% of the pyrite content is removed to give a leach circuit feed assaying 0.06% S. Essentially, all the sulphur passing through the pachucas reacts with sodium carbonate to produce sulphate and bicarbonate, consuming 3.3 pounds of soda ash per pound

of sulphur (Thunaes and Colborne 1964).

Isopropyl xanthate is used as a collector. A frother has been found to be unnecessary. The rougher concentrate is subjected to three stages of cleaning to give a product assaying 25 - 30% S. The concentrate, after thickening and wash filtration, is subjected to acid leaching. Uranium is precipitated from the acid pregnant solution with magnesium hydroxide and the impure precipitate returned to the alkaline leaching circuit.

Operation of the flotation-acid leach section costs 25 - 30 cents/ton. By eliminating an average of 0.50% sulphide sulphur, the reagent saving has been $1.80 per ton for a net saving of about $1.50 per ton.

5.6 Leaching

The sulphide flotation tailings slurry is thickened to 50 - 55% solids before entering the pachuca circuit. Thickening is achieved by a combination of cyclones and thickeners, the latter operating on the cyclone overflow only. Flocculants are added to the thickener feed.

There are four parallel banks of six pachucas per bank. Each pachuca is 18 feet in diameter and approximately 50 feet high, with a 60-degree cone bottom. When first installed, agitation was achieved by a central air lift, with oxidising air introduced through eight separate diffusers. The pachucas have recently been modified to mechanical agitation, with gaseous oxygen being fed through two diffusers. Heat is provided by steam coils. No chemical oxidants are used in the leaching circuit.

Temperature is held above 80°C. Retention time is approximately 96 hours. The change from the use of air as a means both of oxidation and of agitation, has resulted in a major reduction of heat losses and improved extractions on refractory ores.

5.7 Filtration

On leaving the pachuca circuit, the leached pump passes to the filtration circuit via a concentric pipe heat exchanger which reduces the pulp temperature from 80°C to 50°C and transfers heat to the residue wash water. The leached residues are separated by two-stage filtration utilising string discharge drum filters. Washing on the first stage is with fresh leach liquor, whilst repulping and second-stage washing use hot water. Soluble losses average 1% of the uranium feed.

5.8 Steam Stripping and Lime Addition

After clarification, part of the pregnant solution passes through steam

stripping and lime addition before precipitation with caustic soda. The primary purpose of these units is to remove bicarbonate ion from the solution prior to precipitation and thereby reduce the consumption of caustic soda in precipitation. A secondary objective of the steam-stripping plant is to remove water in order to control circuit solution volumes. By removing water at this point, additional water can be introduced at the second-stage filter wash, thereby reducing dissolved uranium losses.

The steam-stripping process is essentially two-stage evaporation with the second-stage steam going to the pachuca heating coils at 10 - 20 psig. The capacity of the plant is 350 tons evaporated water per day. Two - three lb NaOH per ton of ore are saved by the 350 tons/day reduction in pregnant solution volume. In addition, approximately 14,000 lb per day of bicarbonate are converted to carbonate, saving 4 lb sodium hydroxide per ton of ore. Net savings attributed to the plant amount to 45 - 50 cents per ton.

The lime addition plant reduces the sodium bicarbonate content of the liquor from 12 - 14 g/litre to 3 - 5 g/litre by reaction with lime. (The bicarbonate level must not be reduced below 2 g/litre or premature uranium precipitation may occur.) Calcium carbonate is precipitated according to the reaction:

$$2\ NaHCO_3 + Ca(OH)_2 = CaCO_3 + Na_2CO_3 + H_2O$$

and is removed by settlement in a thickener, the overflow passing to precipitation. The lime sludge is fed into the pachuca leaching circuit. The lime plant results in a net saving of 50 cents/ton.

A major advantage of the steam stripping and lime plant is that they have reduced the caustic addition requirements, bringing it into balance with the sodium ion removed from the circuit in the yellow cake and as the minor solution loss occurring with the washed tailings. Thus a solution bleed is no longer necessary to maintain a balance.

5.9 Precipitation

Pregnant solution is precipitated with caustic soda. Sufficient caustic is added to ensure an excess of 6 g/litre and the temperature is held at about 50°C. Precipitation takes place in a series of six agitators. Retention time is 10 - 12 hours. Pregnant solution entering the circuit contains an average of 2 - 3 g/litre $U_3O_8$. Barren solution after precipitation averages 0.1 g/litre. A 'reseeding cone' is included in the circuit to recycle fine

precipitate to the head of the precipitation tanks. This results in a coarser particle size, and improved filtration.

The yellow cake slurry is filtered in standard filter presses. The cake discharged from the presses is re-pulped and pumped into a steam-heated twin-screw Holoflite drier. The average composition of the drummed precipitate is:

| | |
|---|---|
| $U_3O_8$: | 72 - 77% |
| $H_2O$ : | 2 - 4% |
| $V_2O_5$: | 0.5 - 0.7% |
| $SO_4^=$: | 0.4 - 0.5% |
| $Cl^-$ : | 0.02 - 0.05% |

5.10 Solution Regeneration

The carbonate process is a closed-circuit operation. It is, therefore, necessary to maintain close control on water and chemical balances. The advantages of the steam-stripping and lime unit operations in removing water and controlling sodium hydroxide addition have already been pointed out.

Carbonation of the caustic barren solution is achieved by blowing flue gas from the boilers and power-house installation through two packed towers. The barren solution flows countercurrent to the gases through the towers, converting 6 g/litre caustic soda content to about 3 g/litre sodium bicarbonate.

Sulphate ion generated by the oxidation of pyrite has built up to very high levels (50 - 60 g/litre, sodium sulphate) without adversely affecting leaching rates or product quality. Sulphate ion level is controlled by solution losses with the tailings and by removal in the yellow cake (Clegg and Foley 1958).

5.11 Corrosion

Corrosion proved to be an unexpected major problem as alkaline sodium sulphate-carbonate-bicarbonate solutions had not been considered corrosive to plain carbon steel from which the process tanks were fabricated. Severe pitting corrosion was found beneath caked solids at the froth line and below the pulp surface in leaching vessels after a relatively short period of operation (Colborne et al. 1961). Undoubtedly, the major pitting was due to differential aeration cells (soil-type corrosion) being set up under caked solids. Their activity was probably greatly enhanced by the high solution

conductivity, the presence of oxygen consumers in the deposited solids and the cementing action of iron oxides produced by the corrosion.

However, it was established that the mud deposits are not required to initiate corrosion, but arise subsequently, aggravating the situation. Severe corrosion was shown to take place in clear solutions at pHs of 9.5 and less, but is insignificant when the pH is over 9.7. Arising from this, action was taken to operate at a minimum pH of 9.5 in the leaching circuit and this has greatly reduced corrosion. Additionally, a programme of repair and protection was undertaken. Epoxy tank linings have been found to perform very satisfactorily.

5.12 Reagent Consumption

Sodium hydroxide consumption has been reduced to 10 lb/ton with 7 - 8 lb/ton of lime. These are the only reagents used in the carbonate-leaching section of the plant (Ross and Guglielmin 1968).

Reagent consumption in the acid circuit is:

| | lb/ton of Concentrate | lb/ton of Mill Feed |
|---|---|---|
| Sulphuric Acid | 100 | 2 |
| Sodium Chlorate | 3 | 0.06 |
| Magnesium Hydroxide | 15 | 0.3 |

Overall power consumption is 30 - 35 kWh/ton and water usage 550 gallons/ton, with no re-cycling of tailings pond water.

## 6. COMPARISON OF ALKALINE LEACHING PLANTS

There are three alkaline leach plants operating in the United States (1970 data):

- Moab Mill (Atlas Corporation) - 900 ton/day (plus 400 ton/day acid circuit).
- Cotter Corporation Mill - 400 ton/day.
- United Nuclear-Homestake Mill - 3,500 ton/day.

Detailed descriptions of these three plants are given by Merritt (1971).

A comparison of practice at the four plants follows:

One plant (Cotter) operates on hydrothermal vein-type ore similar to the Beaverlodge ore. The other two operate on sandstone ores where the uranium occurs in association with vanadium as coatings and interstitial filling in

the sandstone and, thus, a relatively-coarse grind (to 65 mesh) is adequate to liberate the uranium for dissolution. Crushing and grinding practices tend to be conventional, except for the Beaverlodge autogenous mill.

All plants, except the United-Homestake plant, provide facilities for the flotation of sulphides before leaching. All plants grind and float in leach solution. Leaching is by autoclaves in the Moab and United-Homestake plant, and by pachucas in the Cotter Mill. Increased capacity has been added to the United-Homestake autoclaves by adding pachucas and to the Cotter pachucas by adding autoclaves. Generally speaking, autoclaves operated at 50 - 80 psig and 95° - 120°C give a slightly improved recovery in about 20% of the leaching time required by pachucas operating at 70° - 80°C. Beaverlodge experience indicates a net cost saving in favour of pachucas of about 45 cents per ton of ore based on the technology of the mid-1950s (Thunaes and Colborne 1964). Advances in pressure-leaching techniques could alter this assessment.

In all cases, air or oxygen has been used as the oxidant. The Moab Mill uses a copper-ammonium complex as an oxidation catalyst and this was formerly used at the United-Homestake Mill when processing refractory ore. The addition of three pachucas provided additional air and residence time to achieve the same results as the catalyst. From this, it would appear that the use of the copper-ammonium catalyst results in a 10% - 20% reduction in leaching time. The copper-ammonium catalyst is not effective in atmospheric leaching due to the rapid volatilisation of ammonia from the solution.

Various combinations of filters and thickeners are used for separating and washing the leached residue. The problem of slimes has resulted in the use of Esperanza classifiers at the Moab Mill to separate a sand fraction from the slime fraction, followed by resin-in-pulp recovery of the uranium values. All other plants employ caustic soda precipitation. The Moab Mill resin-in-pulp process uses a strong base anionic resin, Dowex 21K.

In two of the American mills, yellow cake is re-processed to give a purer product. At the Cotter Corporation Mill where the caustic-precipitated product is too high in sodium content, the yellow cake is dissolved in sulphuric acid and re-precipitated with ammonia. At the United-Homestake Mill, the yellow cake is roasted with soda ash to solubilise the vanadium content which is removed by water leaching.

## 7. CARBONATE LEACHING COSTS

It is somewhat difficult to draw reliable conclusions on the subject of

costs from the sketchy and varied information available. The following general remarks are offered as a guide:

(a) The capital cost of a carbonate leach plant is likely to be about 10% - 20% higher than an acid leach plant of the same capacity (Ross and Guglielmin 1968).

(b) The capital cost of two carbonate leach plants built in 1958 were -

| | | |
|---|---|---|
| 1,500 ton/day (Homestake) | - | $6,000.00 per ton/day capacity. |
| 200 ton/day (Cotter) | - | $9,000.00 per ton/day capacity. |

To arrive at a 1972 costing basis, these capital costs should be increased by 40% - 50%.

(c) Beaverlodge milling costs in 1960 were $4.80 per ton or $1.22 per pound of $U_3O_8$ produced (Harding et al. 1960).

The breakdown of these costs was as follows :

| | |
|---|---|
| Labour | 26.5% |
| Supplies | 16.3% |
| Reagents | 30.7% |
| Power | 9.3% |
| Air | 3.7% |
| Process and Building Heat | 11.7% |
| Other Distributables | 1.8% |

## 8. ACKNOWLEDGEMENTS

The carbonate leaching process at Beaverlodge has been refined over the years by the team work of many skilled engineers, with whom the author was proud to be associated for a period. In particular, thanks are due to Mr. G.F. Colborne, of Eldorado Nuclear Ltd., whose critical reading of the manuscript has been greatly appreciated.

## 9. REFERENCES

Clegg, J.W. and Foley, D.D. (1958) - Uranium Ore Processing. Addison-Wesley Pub. Co. Inc., Reading, Mass.

Colborne, G.F., Allan, A.R., Thunaes A., (1961) - Crash repair program to control serious pitting corrosion on process tanks. Corrosion, 17 (12) 20-24.

Colborne, G.F. (1963) - Electronic ore sorting at Beaver Lodge. Can. Inst. Min. and Met. Bull. 56 (616) 664-68.

Forward, F.A. and Halpern, J. and Peters, E. (1953) - Studies in the carbonate leaching of Uranium Ores. Can. Inst. Min. and Met. Bull. 46 (498) 634-47.

Gow, W.A. and Ritcey, G.M. (1969) - The treatment of Canadian Uranium Ores - a review. Can. Inst. Min. and Met. Bull. 62 (692) 1330-39.

Harding, J.W., Pedersen, O.E. and Schinkel, R. (1960) - Eldorado Beaverlodge Operation. Can. Mining J. 81 (6) 75-149.

Lendrum, F.C. (1970) - Developments in Canadian uranium mining practice. AIME J. of Metals 22 (7) 52-56.

Liddy, J.C. (1972) - The uranium potential of Australia. Australian Mining 64 (5) 24-33.

McClaine, L.A., Bullwinkel, E.P. and Huggins, J.C. (1956) - The carbonate chemistry of uranium : theory and applications. Proc. 1st Int. Conf. on Peaceful Uses of Atomic Energy. Geneva 8-20 August 1955, Vol.8 p26-37. United Nations New York.

Marshall, K. (1962) - Eldorado's lime plant. Can. Mining J. 83 (1) 31-33.

Merritt, R.C. (1971) - The extractive metallurgy of uranium. TID-25711.

Ross, A.H. and Guglielmin (1968) - Milling technology of uranium ores. Trans. Amer. Nucl. Soc. 11 121-2.

Stephens, F.M. and MacDonald, R.J. (1956) - Alkaline leaching of Uranium ores. Proc. 1st Int. Conf. on Peaceful Uses of Atomic Energy. Geneva 8-20 August 1955, Vol. 8. p18-25. United Nations, New York.

Thunaes, A. (Editor) (1957) - Milling of uranium ores (15 contributors) Proc. 6th Commonwealth Mining and Metallurgical Congress, Vol. 3, Ch.9, p331-60. Can. Inst. Min. and Met.

Thunaes, A. and Colborne, G.F. (1964) - Auxiliary processes in the Beaverlodge Uranium Plant. In "Unit Processes in Hydrometallurgy". Gordon and Breach Science Publishers 683-96.

AAEC SYMPOSIUM

ON

URANIUM PROCESSING

PAPER IV

# THE APPLICATION OF MINERALOGY TO URANIUM ORE PROCESSING

by

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## 1. INTRODUCTION

A typical uranium ore is composed of a small proportion of one or more uraniferous minerals distributed in a large proportion of non-uraniferous minerals, most of which are of no commercial value (gangue), but some of which (e.g. gold, vanadium, copper sulphides) may be commercially recovered. In many cases uranium is the sole element of interest but in some cases uraniferous ores have been mined for other metals prior to the development of the uranium industry (the vanadiferous "Colorado Plateau-type" ores of the U.S.A., and the gold-bearing conglomerates of South Africa being two notable examples). The nature of the minerals present in a uranium ore directly determines the response of the ore to physical beneficiation and chemical extraction and it is the purpose of this paper to review the relation between mineralogy and ore processing and to indicate where mineralogical investigation can assist the metallurgist.

A typical uranium processing flowsheet is illustrated in Figure 1 (Smith and White 1969). Beginning with the mined ore this involves coarse crushing, fine grinding using wet rod and pebble mills, leaching of the uranium using acid or alkaline solutions, washing and filtering, extracting the uranium from the clear liquor by ion exchange or solvent extraction, stripping the uranium from the resin or solvent, precipitating the uranium as an insoluble compound, and filtering the compound followed by drying or roasting to give 'yellow cake' ($\simeq$80% $U_3O_8$). Variations in this generalised treatment are indicated in Figure 1. These include physical beneficiation of the ore prior to leaching and direct extraction of the uranium from the pulp (Smith and White 1969).

Mineralogical investigation has its main application in the earlier stages of the process outlined above, but problems can arise in the later stages (e.g. poisoning of resins) which are dependent on the ore mineralogy and which can be forecast on the basis of prior mineralogical information. Detailed mineralogical study of the head ore can determine the proportions of the various uranium and gangue minerals present, the distribution of uranium between the different minerals, the liberation characteristics of the uranium minerals and gangue, and the physical and chemical properties of the individual minerals. On the basis of this information, it is possible to indicate the following :

(a) the likely response of the ore to physical beneficiation
(b) whether acid or alkaline leaching is preferable
(c) the likely conditions necessary for leaching

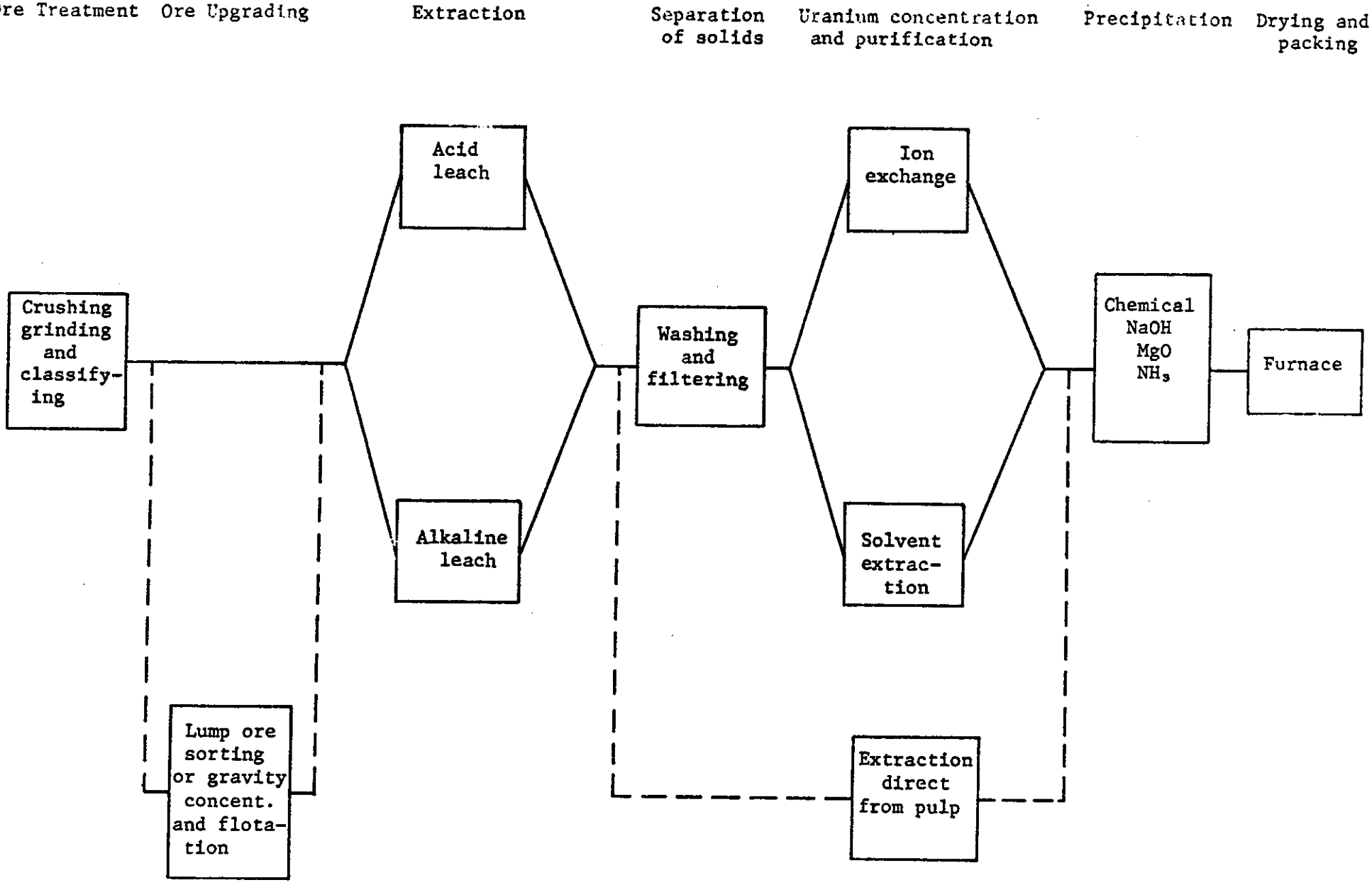



FIGURE 1. TYPICAL URANIUM ORE PROCESSING FLOWSHEET
(after Smith and White 1969)

(d) the cause of high reagent consumption during leaching and ways in which this may be reduced

(e) whether problems are likely to arise in thickening and filtration.

Detailed mineralogical study of the tailings from physical beneficiation or leaching can identify the nature of the unrecovered uranium and indicate ways in which recovery might be improved. Similarly, investigation of concentrates from physical beneficiation can determine the cause of low concentrate grade and suggest ways in which the grade might be improved.

There is thus wide scope for the mineralogist to assist the metallurgist in developing and optimising uranium processing operations and this is confirmed by numerous publications on this subject from organisations in Australia, Canada, South Africa and the U.S.A.

## 2. METHODS OF STUDY

### 2.1 Mineral Identification

The first, basic requirement of any mineralogical investigation, whether of drill-core, beneficiation product or leach residue, is to identify the minerals present. The identification should naturally include the various uraniferous minerals and other minerals of potential value, but it should also include the gangue minerals as these may have a profound effect on the response of the ore to physical beneficiation or leaching. Numerous texts on methods of mineral identification have been written and it is not proposed to consider these methods in detail here.

Autoradiography (Yagoda 1949) can be used to locate radioactive minerals in solid rocks and ores and in polished sections of grains (e.g. leach residues). This technique is fairly simple and normally involves placing the flat surface of the solid material or polished section in contact with a photographic film or nuclear-type film for a period of up to several weeks. At the end of this time the film is developed and the distribution of radioactivity in the sample surface is indicated by blackened areas on the film (negative), the degree of blackening being related to the intensity of the radioactivity (Figure 2). Having located the sites of radioactivity these can then be investigated to determine their nature. This subsequent investigation can involve a variety of different techniques including microscopic examination in reflected or transmitted polarised light, X-ray diffraction analysis, electron-probe microanalysis and chemical analysis.

Microscopic examination gives information not only on the uranium mineral

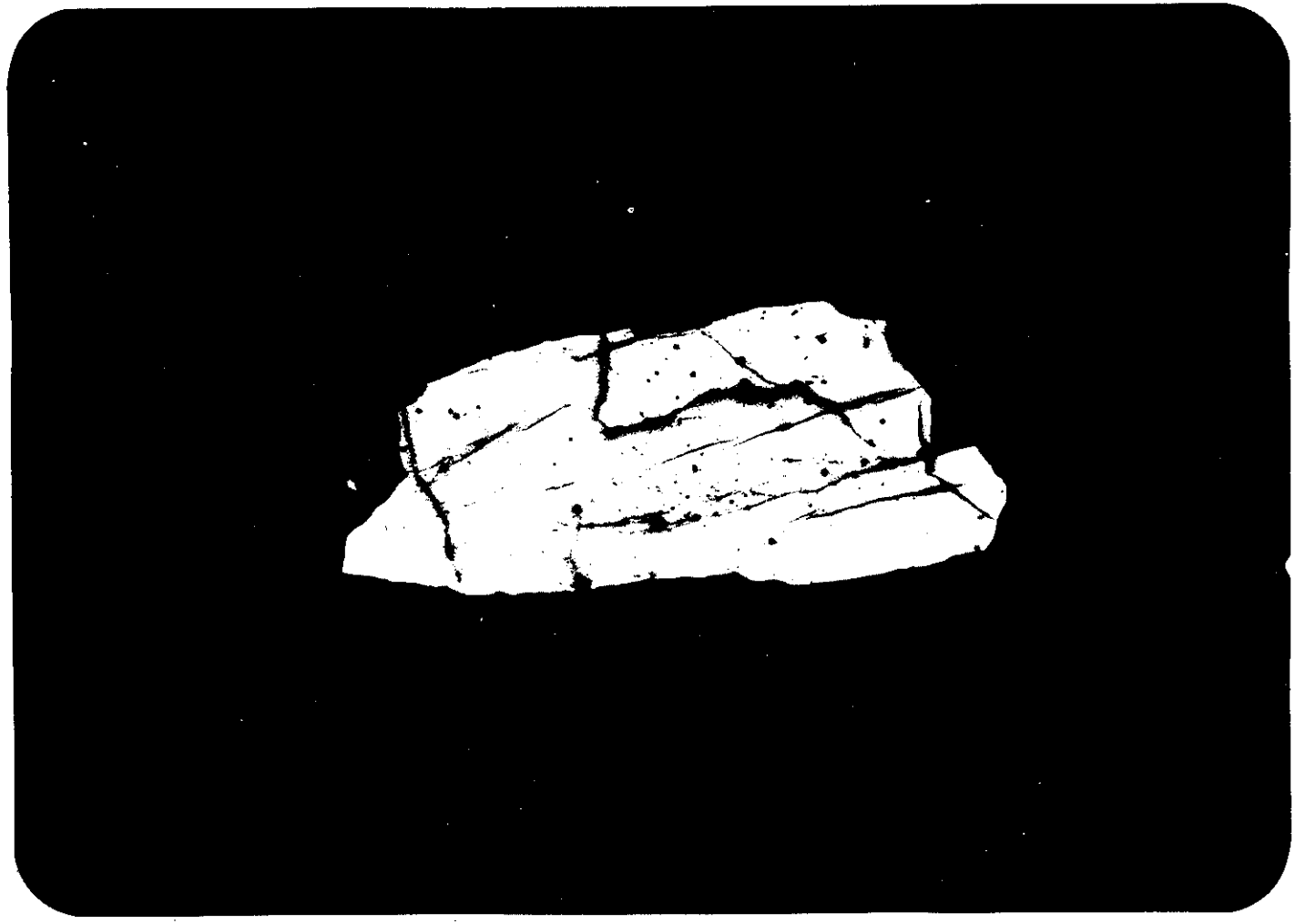


FIGURE 2. AUTORADIOGRAPH OF A WEATHERED GRANITIC ROCK CONTAINING DISSEMINATIONS AND FRACTURE INFILLINGS OF META-AUTUNITE ($Ca-U-P-H_2O$)

species present but also on their textural relations with other minerals. However, it is commonly difficult to identify uranium minerals conclusively by microscopy alone, even making use of the characteristic fluorescence colour in ultra-violet light which many secondary uranium minerals exhibit (Volborth 1958); in such cases it may be possible to extract a small amount of the material of interest and carry out an X-ray diffraction analysis. The X-ray diffraction pattern obtained from the material is compared with reference data (e.g. the card index of the Joint Committee on Powder Diffraction Standards) and in many cases this provides a conclusive identification. However, certain difficulties can arise when two minerals which have a solid solution relationship (e.g. meta-autunite ($Ca\text{-}U\text{-}P\text{-}H_2O$) and meta-uranocircite ($Ba\text{-}U\text{-}P\text{-}H_2O$)) do not differ significantly in diffraction pattern, or where a mineral is metamict.

Metamict minerals (Pabst 1952) are those in which bombardment by alpha particles from the contained uranium, thorium and their decay products produces structural disarrangement with a consequent loss of X-ray diffraction pattern (i.e. they are X-ray amorphous). However, a characteristic X-ray pattern (not necessarily the same as that of the original mineral) can often be restored by heat treatment, thereby enabling the mineral to be identified (Lima da Faria 1964).

Electron-probe microanalysis, with its capability of qualitatively or quantitatively analysing a point as small as 1μm in diameter on a polished mineral surface, has wide application in identifying uraniferous minerals and also in determining their uranium content (Figure 3). It is particularly useful in identifying minerals which occur in grains which are too small for convenient optical or X-ray diffraction identification (less than about 0.05 mm in diameter) and in determining the distribution and content of uranium in slightly uraniferous minerals (e.g. monazite or zircon).

2.2 Modal Analysis

Following mineral identification it is generally necessary to determine quantitatively or semi-quantitatively the proportions of the uranium minerals present in a particular ore or beneficiation product (i.e. modal analysis). Such information is used, in combination with information on the uranium contents of the minerals, to determine the distribution of uranium between the various sources. Knowledge of the proportions of acid-consuming gangue such as carbonates, chlorite, apatite, etc., present in an ore will indicate whether acid leaching of the whole ore is likely to be economically feasible or

## KEY TO FIGURE 3

Electron-probe scanning photograph of an intergrowth of pitchblende, chlorite, galena and chalcopyrite in Nabarlek uranium ore. The width of the field corresponds to 0.1 mm. In (a) the white areas correspond to regions of low atomic number whereas in (b) - (f) the white areas denote concentrations of the particular elements.

(a) Absorbed electron image. Black - pitchblende; grey - chalcopyrite; white - chlorite.

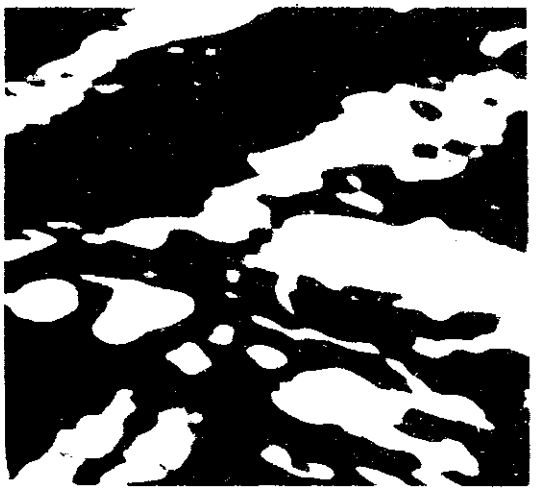
(b) Uranium distribution. The high concentrations of uranium are due to pitchblende.

(c) Lead distribution. The high concentrations of lead are due to galena grains and there is a general lower level of lead (in solid solution) in the pitchblende (cf. the uranium distribution (b)).

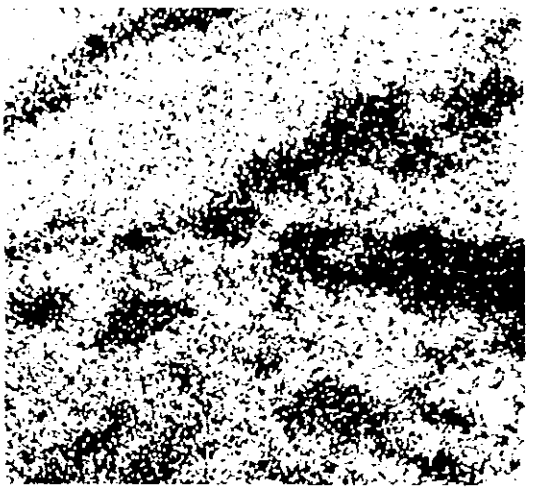
(d) Silicon distribution. The high concentrations of silicon correspond to the mineral chlorite.

(e) Sulphur distribution. The high concentrations of sulphur are due to chalcopyrite and galena.

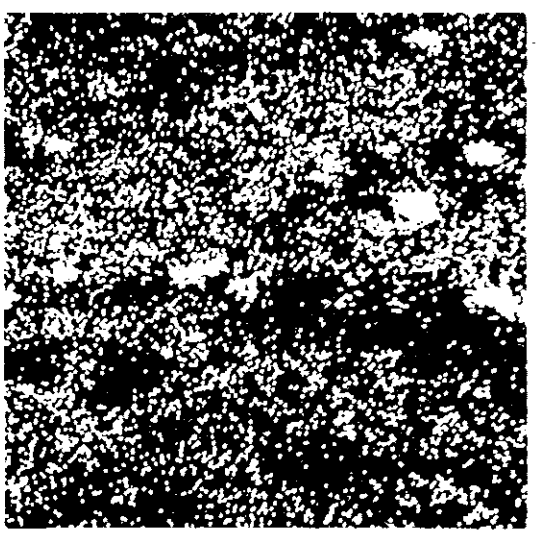
(f) Copper distribution. The high concentration of copper is due to chalcopyrite.



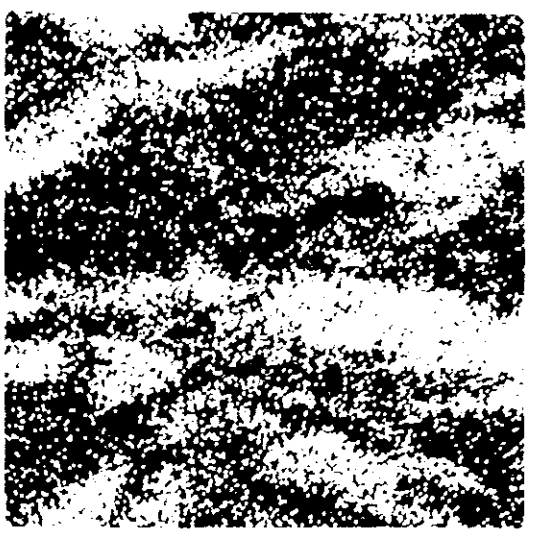
a. A.E.I.



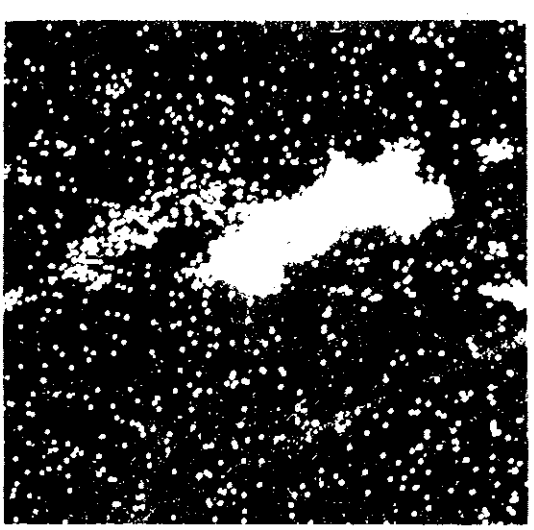
b. U



c. Pb



d. Si



e. S

f. Cu

**FIGURE 3**

whether some form of pre-treatment to remove these minerals may be necessary. Similarly, knowledge of the proportion of alkali-consuming minerals such as sulphides will indicate whether alkaline leaching of the whole ore is likely to be economically feasible or whether sulphide flotation prior to leaching may be necessary. Information on the proportion of clay in an ore can indicate at an early stage whether thickening and filtration problems are to be expected.

There are several methods available for the determination of the modal analysis of a material and these may be used individually or in combination. The methods include grain-counting, point-counting, mineral separation and chemical analysis (Muller, Henley and Benjamin 1969, Henley 1972).

Grain-counting is a relatively simple method of microscopic analysis. In this procedure closely sized fractions of the material are spread on a millimetre grid (to avoid grains being counted more than once) and the individual minerals are identified and counted using a stereo-binocular microscope. In the event that the minerals cannot be distinguished easily under a stereo-binocular microscope, the grains are spread on a glass slide and the minerals are identified and counted using a transmitted polarised light microscope. The resulting number percentages for each mineral are converted to weight percentages using the known or measured densities of the minerals.

Point-counting is a microscopic method of modal analysis widely used by geologists and mineralogists. It involves identifying and counting each mineral occurring under a number of points distributed over a random plane of section through a material. Such a plane may be a polished or thin section and the points are generated by the automatic movement of a mechanical stage or by an eyepiece graticule. The number percentage for each mineral is directly related to its volume percentage in the sample and the volume percentages obtained are converted to weight percentages using the known or measured densities of the minerals.

A third method of modal analysis is based on the complete separation and weighing of the fully liberated minerals in a small representative sample using such procedures as heavy liquid, magnetic or electrostatic separation. The heavy liquid density gradient column is particularly useful where the minerals have a specific gravity of less than about 4.3 and it is effective for particle sizes down to 0.01 mm (Muller and Burton 1965, Muller, Henley and Benjamin 1969).

Chemical analysis can be used in certain instances to derive the proportions of particular minerals. This applies especially to elements which are

known to be present in one mineral (e.g. Zr in zircon), and where an element is present in more than one mineral (e.g. U in uraninite and brannerite) it is not usually possibly to use the chemical analysis in this way. However, it is possible to check the accuracy of a modal analysis by comparing calculated elemental contents with the chemical analysis.

2.3 Specific Mineral Properties

Although the physical and chemical properties of many minerals are reasonably constant, in certain cases a mineral may have a wide range in these properties and it may then be necessary to determine precisely some of these properties so that due account may be taken of them when planning a metallurgical process. For example, the mineral uraninite can show wide variation in its degree of oxidation, thorium content, crystallite size and reaction to acids (Heinrich 1958, Liebenberg and Taverner 1958), and these variations may have a significant bearing on the effectiveness of any beneficiation or extraction process. Similarly, other minerals associated with uranium ores may show variations in physical and chemical properties. In some cases there appears to be a lack of definitive information on certain mineral properties, for example, the magnetic susceptibility of the uranium minerals (Hartman and Wyman 1969).

Data on the chemical composition of minerals in situ in a sample can generally be obtained by electron-probe microanalysis but in the case of physical properties it is usually necessary to prepare a small pure sample of the mineral of interest. There are many techniques available for the small-scale preparation of pure mineral samples, including the use of heavy liquids, low and high intensity magnetic separation, electrostatic and high tension separation, the micro-panner, the super-panner, elutriation, flotation and hand-picking (Zussman 1967). A discussion of these techniques and the methods available for determination of specific mineral properties is outside the scope of this paper, but it may be noted in passing that in the process of separation and purification much useful information may be obtained on the physical properties of the minerals which are relevant to commercial separation.

2.4 Liberation and Associations

Knowledge of the proportions and properties of the minerals present in an ore is not generally sufficient on its own to enable the response of the ore to various physical beneficiation and chemical extraction procedures to be forecast. To do this, information is required on the liberation

characteristics and associations of the minerals. However, with all these data available it is possible for the mineralogist to indicate the optimum grind necessary for various treatment procedures, the likely response of the ore to gravity, magnetic, electrostatic and (to a lesser extent) flotation methods of separation, the response of the ore to leaching, and likely concentrate grades and losses in tailings.

In addition, knowledge of the liberation characteristics and associations of the uranium minerals in tailings or leach residues can indicate the causes of uranium loss and whether any possibility exists for recovering this uranium economically. An indication of the probable liberation size of a mineral in an ore may be obtained by determining its grain-size distribution by normal microscopic techniques. However, this gives approximate results only and does not take into account the breakage characteristics of the ore.

There are several methods available for determining liberation characteristics more accurately than by the above method and all of these involve assessment of size fractions of ore which has been crushed and ground. In the first method samples of each size fraction are introduced into separate density gradient columns and the sharpness of the individual mineral bands assessed (Muller and Burton 1965). In such columns liberated mineral grains settle to a level corresponding to their own density and form bands whereas composite grains, with intermediate density, occur between the main mineral bands. With progressively decreasing grain size and hence increasing liberation the proportion of intermediate-density particles decreases and the mineral bands become progressively sharper (Figure 4). Visual inspection of the sharpness of the bands can often give a clear indication of the liberation size of the minerals but a more accurate procedure for the determination of uranium liberation is to separate the bands and the intermediate-density particles and analyse them for uranium (Table 1). From these data and from microscopic examination of the products the amount of uranium locked with each mineral can be determined and the overall liberation assessed. The method is normally applicable to particle sizes in the range >5 mm to 0.01 mm and over the density range 1 - 4.3 g/ml.

The second method is analogous to the first in that it uses heavy liquids to separate liberated mineral grains from composite grains, but it differs in that information is normally obtained on the economic minerals only (Muller, Henley and Benjamin 1969, Henley 1970a). It is normally applicable over the size range >15 cm - 0.01 mm and the density range 1 - 4.3 g/ml. Samples of

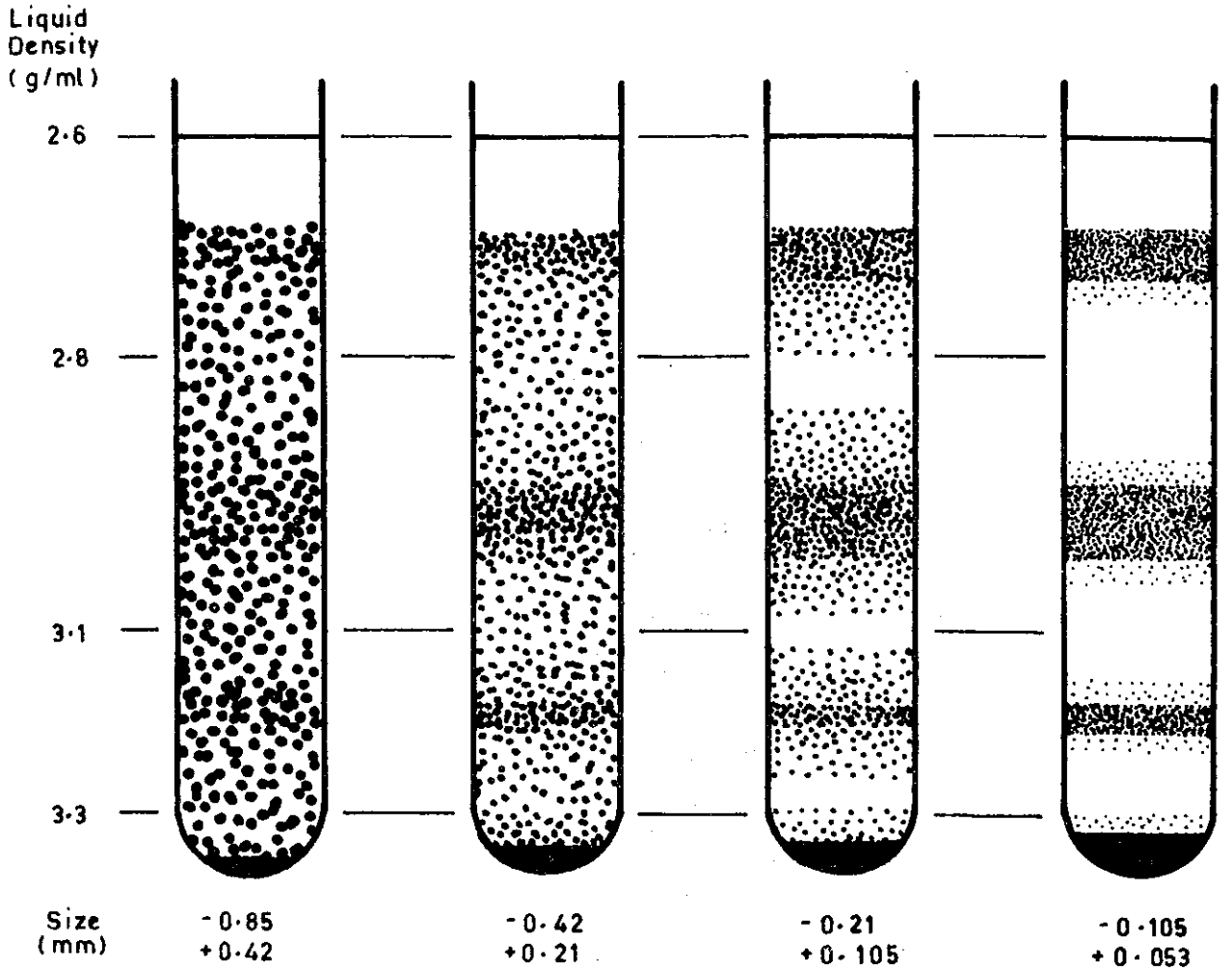



**FIGURE 4. DENSITY GRADIENT SEPARATION OF SIZE FRACTIONS OF A URANIUM ORE ILLUSTRATING INCREASING MINERAL LIBERATION WITH DECREASING GRAIN SIZE**

TABLE 1 DISTRIBUTION OF $U_3O_8$ IN DENSITY GRADIENT SEPARATION PRODUCTS OF A URANIUM ORE, ILLUSTRATING THE INCREASING LIBERATION OF URANIUM WITH DECREASING GRAIN SIZE

| Density Product (g/ml) | $U_3O_8$ Distn. (%) within Size Fraction (mm) | | | | Main Mineral(s) Present at Liberation |
|---|---|---|---|---|---|
| | -0.85 +0.42 | -0.42 +0.21 | -0.21 +0.105 | -0.105 +0.053 | |
| 2.6-2.8 | 24 | 8 | 2 | 1 | Quartz |
| 2.8-3.1 | 36 | 34 | 20 | 3 | Dolomite |
| 3.1-3.3 | 30 | 36 | 16 | 4 | Fluorite |
| >3.3 | 10 | 22 | 62 | 92 | Sulphides Uraninite |
| | 100 | 100 | 100 | 100 | |

The data presented in this table show that with decreasing size (and increasing liberation) progressively more of the uranium within a size fraction concentrates in the >3.3 g/ml density product. The data may be compared with the visual appearance of the density gradients shown in Figure 4.

each size fraction of the ground ore are separated in liquids of selected densities such that, at complete liberation, uranium minerals report into a certain density product whereas the gangue minerals report into other density products. The various density products and the unseparated slimes are weighed and assayed for uranium (and possibly other elements or radicals of interest, e.g. $CO_3$) and the distribution of uranium with size and density is calculated. In each size fraction the proportion of uranium reporting into the density product appropriate for the gangue minerals is a quantitative measure of the proportion of uranium locked with gangue at that size. With decreasing particle size progressively more uranium reports into its appropriate density product until below a certain size the percentage uranium distribution becomes constant, at which size the uranium minerals are effectively liberated from gangue. In addition to determining the overall mineral liberation and the mineral liberation in each size fraction, information on preferential grinding can be obtained from the calculated assays of the size fractions. A typical example of this type of liberation analysis is given in Table 2 and Figure 5. The method can also be used to simulate heavy medium separation and the optimum weight and uranium rejection at various sizes and densities can be determined prior to actual heavy medium separation.

When other heavy minerals (e.g. sulphides) are also present it may not be possible to determine completely the liberation characteristics of the uranium minerals by the use of heavy liquids alone. In such cases it is possible to determine the liberation characteristics by quantitative microscopic counting techniques. Polished sections are prepared of the heavy liquid separation products, or of the unseparated size fractions, and between 300 and 1,000 grains are assessed by an areal estimation technique (Gaudin 1939, Muller, Henley and Benjamin 1969) or by a point-counting technique. In the areal estimation technique the composition of each grain is estimated in terms of its component minerals (e.g. 100% uraninite, 70% uraninite/30% galena, etc.), whereas in the point-counting technique each point falling on a grain is classified by the mineral under the point and the other minerals in the grain; the data in each case are summated to give the proportions of each mineral which are liberated and locked, and if locked, the other minerals with which they are intergrown.

The areal estimation and point-counting techniques are approximately equivalent and both, in addition to giving information on liberation characteristics, can also give a quantitative mineralogical analysis (modal analysis) of the material examined. However, the point-counting method is considered to

TABLE 2 HEAVY LIQUID SEPARATION/ASSAY DATA FOR VARIOUS SIZE FRACTIONS OF A URANIUM ORE COMPOSED OF QUARTZ (DENSITY 2.65 g/ml), CHLORITE (DENSITY 2.9 g/ml), URANINITE (DENSITY 9.5 g/ml), SULPHIDES AND MAGNETITE (DENSITY 5 - 7.5 g/ml)*

| Size Fraction (mm) | Density (g/ml) | Weight % | $U_3O_8$ | |
|---|---|---|---|---|
| | | | Assay % | Distribution % |
| +1.68 | < 2.8 | 98.4 | 0.42 | 52.9 |
| | 2.8 - 4.2 | 1.6 | 23.0 | 47.1 |
| | > 4.2 | - | - | - |
| | | 100.0 | (0.78) | 100.0 |
| -1.68+0.85 | < 2.8 | 97.8 | 0.37 | 45.5 |
| | 2.8 - 4.2 | 1.9 | 20.0 | 47.8 |
| | > 4.2 | 0.1 | 53.0 | 6.7 |
| | | 100.0 | (0.80) | 100.0 |
| -0.85+0.42 | < 2.8 | 96.9 | 0.30 | 34.7 |
| | 2.8 - 4.2 | 2.5 | 9.0 | 26.9 |
| | > 4.2 | 0.6 | 53.6 | 38.4 |
| | | 100.0 | (0.83) | 100.0 |
| -0.42+0.21 | < 2.8 | 95.2 | 0.11 | 12.0 |
| | 2.8 - 4.2 | 3.5 | 3.32 | 13.4 |
| | > 4.2 | 1.2 | 54.0 | 74.6 |
| | | 100.0 | (0.87) | 100.0 |
| -0.21+0.105 | < 2.8 | 93.5 | 0.06 | 4.8 |
| | 2.8 - 4.2 | 4.5 | 1.44 | 5.2 |
| | > 4.2 | 2.0 | 55.4 | 90.0 |
| | | 100.0 | (1.25) | 100.0 |
| -0.105+0.053 | < 2.8 | 91.3 | 0.05 | 2.8 |
| | 2.8 - 4.2 | 6.0 | 1.09 | 4.0 |
| | > 4.2 | 2.7 | 56.7 | 93.2 |
| | | 100.0 | (1.64) | 100.0 |

* These data are plotted in Figure 5

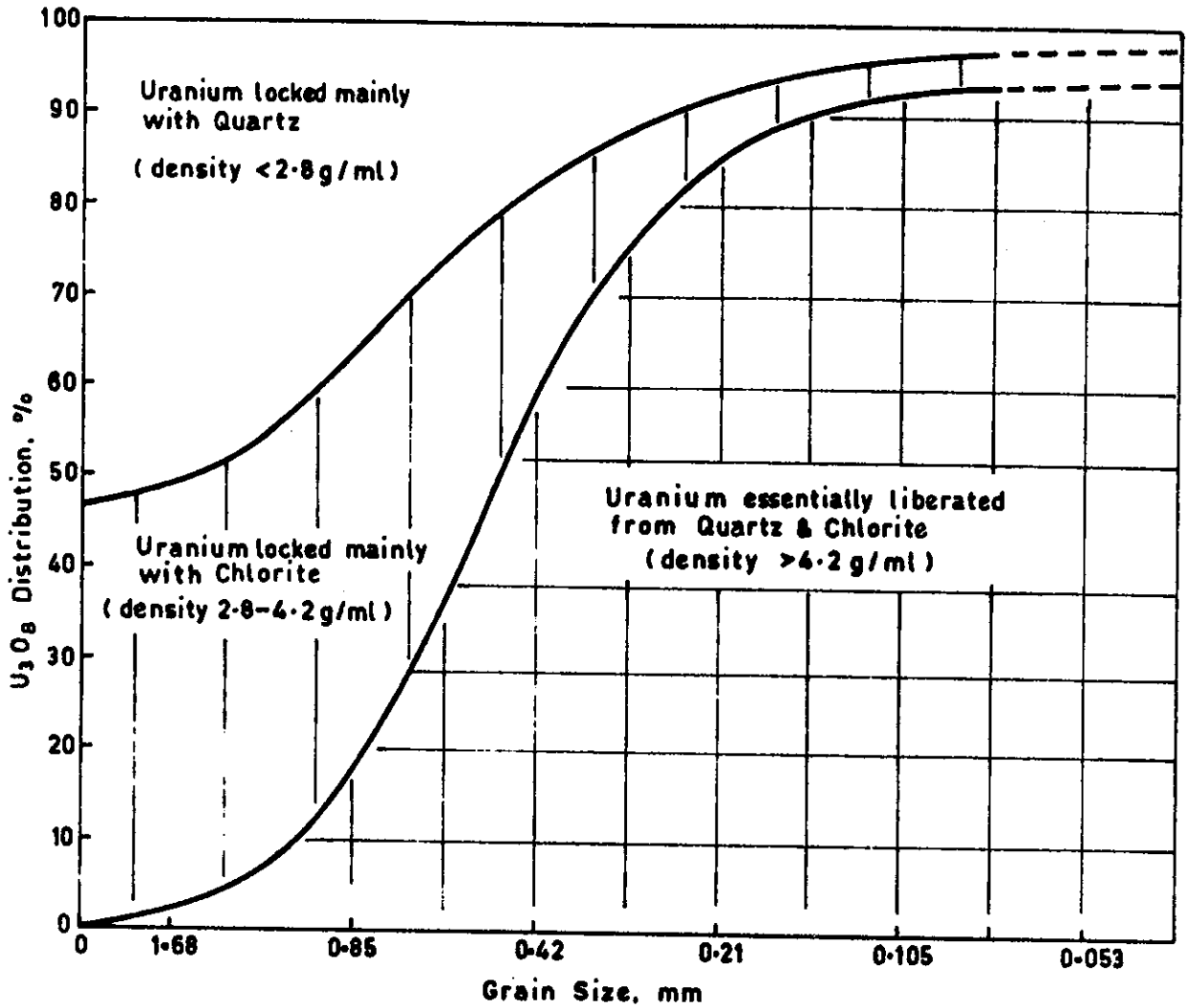



FIGURE 5. GRAPHICAL REPRESENTATION OF URANIUM LIBERATION.
Based on the data in Table 2

be generally preferable because it can be used on widely sized or unsized material (whereas the material must be closely sized for the areal estimation method), it is not dependent on grain shape (as is the areal estimation method), it does not involve visual estimation of mineral proportions (as does the areal estimation method) and hence gives a more accurate modal analysis than the areal estimation method. A typical output is given in Table 3 to illustrate the nature of the information provided. From this type of study it is possible to determine the degree of locking of the uranium minerals with each other and with other minerals in various size ranges, to indicate likely losses of uranium into, for example, a sulphide flotation concentrate, or to indicate whether regrinding is necessary to expose the uranium minerals to leach solutions.

TABLE 3 LIBERATION DATA FOR URANINITE OBTAINED BY POINT-COUNTING THE >4.2 g/ml HEAVY PRODUCTS OF SIZE FRACTIONS OF A URANIUM ORE

| Size Fraction (mm) | % Liberated | % Locked in Binary Composites with | | | % Locked in Ternary(+) Grains* | Total |
|---|---|---|---|---|---|---|
| | | Galena | Chalcopyrite | Magnetite | | |
| +1.68 | ← No Heavy Product Obtained → | | | | | |
| -1.68+0.85 | 38 | 24 | 5 | 11 | 22 | 100 |
| -0.85+0.42 | 71 | 14 | 4 | 3 | 8 | 100 |
| -0.42+0.21 | 87 | 7 | 3 | 2 | 1 | 100 |
| -0.21+0.105 | 95 | 3 | 1 | 1 | - | 100 |
| -0.105+0.053 | 98 | 2 | - | - | - | 100 |

* Grains composed of three or more minerals.

The data presented in this table show that uraninite is well liberated at sizes below 0.85 mm and that the bulk of the locked uraninite occurs in composite grains with galena. At all sizes only a small proportion of uraninite is locked with chalcopyrite or magnetite and below 0.85mm only a small proportion of the uraninite is locked with two or more minerals in ternary (+) grains.

Where magnetic minerals such as chlorite, garnet, magnetite etc., are present in an ore it may be more appropriate to use magnetic separation rather than heavy liquid separation as a means of determining liberation characteristics. In this case, instead of separating size fractions of the ore in heavy liquids, the size fractions may be separated in a Frantz-type magnetic separator at selected current (intensity) settings. Alternatively, the

products of heavy liquid separation may be separated magnetically but in either case information can be obtained on mineral liberation and also on the magnetic response of the various minerals.

## 3. APPLICATIONS

To illustrate the application of quantitative mineralogical data to uranium ore processing the following examples are given. They are drawn from both published and unpublished Amdel investigations and have been chosen to demonstrate the relevance of mineralogical investigations to various aspects of the typical uranium processing flowsheet (Figure 1). Three examples only are given but for other examples the reader is referred to papers by Liebenberg (1956, 1970) and Liebenberg and Taverner (1958).

### 3.1 Mary Kathleen Uranium Ore

Mineralogy played a critical role in the development of a flowsheet for the Mary Kathleen uranium plant. Allanite, apatite and garnet are the main components of the ore zone and small amounts of the mineral stillwellite (a lanthanon borosilicate) together with a variety of other minerals are also present. The uranium mineral in the primary ore is uraninite, present mainly as ovoidal grains 0.1 - 0.01 mm in diameter with some grains up to 2 - 3 mm in diameter and generally enclosed within a halo of silica or iron sulphide which separates it from the host minerals. Uraninite is found in greatest concentration in either allanite or stillwellite, with subordinate amounts in apatite. The form of the haloes is more complex in the zone of weathering. In the deepest, less weathered zone, the leached uraninite nucleus is encased in concentric shells of uranophane (Ca-U-Si-$H_2O$) and silica. At shallow depths and at the surface the uraninite is completely replaced by gummite which penetrates the silica and uranophane shells along radial expansion cracks (Whittle 1960).

The mineralogy suggested that a high acid consumption with high phosphate content in the liquor would result from acid leaching. Consequently, alkaline leaching was attempted but gave extractions of uranium of only 70 - 75% at 70°C (Couche and Hartley 1958).

Acid leaching tests on relatively pure samples of the various minerals were then carried out to determine the optimum leaching conditions of each mineral and finally an acid leaching circuit was adopted which incorporated automatic pH control to prevent the dissolution of large amounts of allanite, stillwellite and apatite while at the same time giving satisfactory extraction of uranium (Couche and Hartley 1958, Hartley 1968).

Mineralogy was used consistently throughout the development to guide the testwork and determine causes of poor extraction. It has also been used more recently to assess the potential of heavy medium cyclone separation to reject acid-consuming carbonate-gangue from the ore (Weir 1969). In this latter work a density gradient column with liquid densities varying between 4.17 and 3.26 over a length of 10 cm was used to determine whether liberated carbonates potentially separable from the heavier silicates were present. This density column investigation indicated that rejection of carbonate from the ore by heavy medium cycloning was feasible and subsequent testwork confirmed this (D'Rozario and Canning 1970).

3.2 Valhalla Uranium Ore

Mineralogical investigation of a suite of ore samples from Queensland Mines Ltd's Valhalla leases, 30 miles north of Mt Isa, was undertaken prior to beneficiation and leaching studies (Kelly 1970). The host rocks to the mineralisation are metamorphosed tuffs and the main constituent minerals were identified as albite, sodic pyroxene, sodic amphibole, carbonates (dolomite and calcite) and quartz. Traces of apatite, magnetite, haematite, ilmenite, pyrite and chalcopyrite were also present.

Uranium was found to be present in two contrasting minerals - brannerite and a zircon-type mineral. The brannerite was identified by electron-probe analysis (it contained major U and Ti with minor Ca, Si and Fe), and occurred as grains generally smaller than 0.025 mm and commonly within the size range 0.001 - 0.005 mm. It was closely associated with fine-grained sodic pyroxene. The zircon-type mineral was not specifically identified but it was found, by electron-probe analysis, to contain major Zr and Si and minor ($\simeq$7%) U. This mineral (which was metamict) occurred in a variety of matrices; individual grains were mainly less than 0.03 mm in size with some grains ranging up to 0.1 mm. Density gradient separation of two size-fractions of the ore were carried out and the products assayed for uranium and carbonate (Table 4).

The mineralogical results suggested that :

(i) Liberation of the uranium minerals from gangue would require very fine grinding.

(ii) Physical beneficiation would not be effective in upgrading the uranium content of the ore without unacceptable losses of uranium in tailings.

(iii) Without prior rejection of carbonates by physical beneficiation the high carbonate content would make acid leaching of the ore economically doubtful.

(iv) Alkaline leaching of the ore would give low uranium recoveries due to the fine grain-size and nature of the uranium minerals.

(v) Acid leaching of the ore would require high concentrations and temperatures of acid to dissolve the brannerite and zircon-type mineral.

(vi) Poor uranium extractions could be expected from the zircon-type mineral even at high concentrations and temperatures of acid due to its probable refractory nature.

TABLE 4 DENSITY GRADIENT SEPARATION RESULTS ON TWO SIZE FRACTIONS OF VALHALLA ORE

| Size Fraction (mm) | Density Range (g/ml) | Wt.% | $U_3O_8$ | | $CO_2$ | |
|---|---|---|---|---|---|---|
| | | | Assay % | Distn.% | Assay % | Distn.% |
| -0.71 | <2.90 | 65.0 | 0.05 | 27.6 | 8.55 | 62.9 |
| +0.25 | 2.90 - 3.08 | 23.0 | 0.17 | 32.8 | 10.90 | 28.0 |
| | 3.08 - 3.21 | 4.0 | 0.31 | 10.4 | 9.05 | 4.0 |
| | >3.21 | 7.1 | 0.49 | 29.2 | 6.45 | 5.1 |
| | | 100.0 | (0.12) | 100.0 | (8.96) | 100.0 |
| -0.18 | <2.90 | 49.8 | 0.04 | 15.9 | 7.70 | 41.6 |
| +0.063 | 2.90 - 3.08 | 35.1 | 0.15 | 41.9 | 13.00 | 49.5 |
| | 3.08 - 3.21 | 8.6 | 0.32 | 21.8 | 6.20 | 5.8 |
| | >3.21 | 6.6 | 0.39 | 20.4 | 4.35 | 3.1 |
| | | 100.0 | (0.13) | 100.0 | (9.21) | 100.0 |

In contrast to the data in Table 1, these data show that (a) there is virtually no preferential grinding of the uranium minerals (calculated assays of size fractions are similar), (b) there is negligible (less than 5%) liberation of uranium in the two size fractions, the uranium being distributed throughout the density range.

Subsequent beneficiation and leaching tests on the Valhalla ore (Canning 1971, Goldney, Canning and Gooden 1972) confirmed all of these predictions except the last. Leaching tests on a sample of drill-core material containing mainly brannerite and on a sample containing mainly zircon-type mineral both gave similar recoveries (80 - 85%). The explanation for this probably lies in the metamict nature of the zircon-type mineral, the mineral being considerably more reactive than normal crystalline zircon and presumably containing $(OH)_4$ substituting for $SiO_4$ (Frondel 1953).

3.3 Nabarlek Leach Residues

An example of the application of mineralogy to determine the cause of uranium losses in leach residues is provided by work carried out on leach residues of Queensland Mines Ltd's Nabarlek (Northern Territory) uranium ore.

The primary mineralisation at Nabarlek consists of disseminated and massive pitchblende in a muscovite-chlorite schist (Figure 2). Near the surface the pitchblende has altered to various secondary uranium minerals which include curite ($Pb\text{-}U\text{-}H_2O$), rutherfordine ($U\text{-}CO_3$), kasolite ($Pb\text{-}U\text{-}Si\text{-}H_2O$) and sklodowskite ($Mg\text{-}U\text{-}Si\text{-}H_2O$).

Leaching tests on primary and secondary ores from Nabarlek have been carried out and are reported in Goldney, Canning and Gooden (1972). It was found that there were significant differences in the conditions required for satisfactory acid leaching of the two ore types, but that the leach residue in each case contained approximately the same amount of uranium ($\sim 0.05\%$ $U_3O_8$). A detailed mineralogical investigation was therefore carried out on the leach residues to determine the nature of the unrecovered uranium.

X-ray diffraction analysis indicated that chlorite and muscovite were the main constituents of each residue. Autoradiographs showed that discrete uranium minerals were very rare, a general haze being produced on the film characteristic of a uniform dispersion of uranium at low levels in the silicates. Electron-probe analysis failed to detect uranium in the residue at a detection limit of 0.2% $U_3O_8$. To determine the location of the uranium more precisely, the residues were wet sieved at 0.037 mm (400 mesh BS) and the +0.037 mm fractions were run through a Frantz magnetic separator to obtain separate fractions rich in chlorite and muscovite respectively. The products from the magnetic separation were then centrifuged in methylene iodide (density 3.3 g/ml) to concentrate any discrete heavy uranium-rich minerals and the 'sinks' and 'floats', together with the unseparated -0.037 mm fraction were assayed for $U_3O_8$. The distribution of weight and $U_3O_8$ between the various products is given in Table 5, from which the following can be deduced:

(i) Uranium is more abundant in the -0.037 mm fractions than in the +0.037 mm fractions.

(ii) In the +0.037 mm fractions of the primary ore residue uranium is enriched in the muscovite (<3.3 g/ml non-magnetics - 0.045% $U_3O_8$) relative to the chlorite (<3.3 g/ml magnetics - 0.018% $U_3O_8$) whereas in the secondary ore residue the reverse is the case (muscovite - 0.021% $U_3O_8$; chlorite - 0.077% $U_3O_8$).

(iii) Only a small proportion of the total uranium in the +0.037 mm fraction of each residue reports into the 'sinks' product (22% in the primary ore residue, 7% in the secondary ore residue).

TABLE 5 DISTRIBUTION OF WEIGHT AND URANIUM IN NABARLEK LEACH RESIDUES

| Size Fraction (mm) | Density Product (g/ml) | Magnetic Product | $U_3O_8$ Assay % | In Size Fraction | | In Total Sample | |
|---|---|---|---|---|---|---|---|
| | | | | Weight % | $U_3O_8$ Distn.% | Weight % | $U_3O_8$ Distn.% |
| **(a) Primary Ore Residue** | | | | | | | |
| +0.037 | <3.3 | Mags. | 0.018 | 52.9 | 24.4 | 29.5 | 10.8 |
| | <3.3 | Non-Mags. | 0.045 | 46.4 | 53.6 | 25.8 | 23.6 |
| | >3.3 | Mags+Non-Mags. | 1.211 | 0.7 | 22.0 | 0.4 | 9.7 |
| | Sub-Total | | 0.039 | 100.0 | 100.0 | 55.7 | 44.1 |
| -0.037 | Sub-Total | | 0.062 | | | 44.3 | 55.9 |
| Total | | | (0.049) | | | 100.0 | 100.0 |
| **(b) Secondary Ore Residue** | | | | | | | |
| +0.037 | <3.3 | Mags. | 0.077 | 22.6 | 48.4 | 10.0 | 14.7 |
| | <3.3 | Non-Mags. | 0.021 | 75.8 | 44.2 | 33.6 | 13.3 |
| | >3.3 | Mags+Non-Mags. | 0.168 | 1.6 | 7.4 | 0.7 | 2.2 |
| | Sub-Total | | 0.036 | 100.0 | 100.0 | 44.3 | 30.2 |
| -0.037 | Sub-Total | | 0.066 | | | 55.7 | 69.8 |
| Total | | | (0.051) | | | 100.0 | 100.0 |

As a result of this work it was apparent that a large proportion of the uranium was associated with the micaceous silicates. It was thought that this uranium might have been adsorbed onto the surfaces of these minerals during leaching and it was reasoned that if this were the case then there should be a progressive increase in the uranium content of these minerals with decreasing grain size (and hence increasing surface area available for adsorption). To test this hypothesis new samples of leach residue were sized and cyclosized into +0.045, -0.045 +0.010 and -0.010 mm fractions which were then assayed for uranium and the distribution of weight and uranium calculated (Table 6). The mineralogy of the size fractions was determined by X-ray diffraction and this confirmed that chlorite and muscovite were the dominant minerals throughout the size range.

TABLE 6 SIZE/ASSAY ANALYSIS OF NABARLEK LEACH RESIDUES

(a) Primary Ore Residue

| Size Fraction (mm) | Weight % | $U_3O_8$ Assay % |
|---|---|---|
| +0.045 | 51.1 | 0.045 |
| -0.045+0.010 | 17.6 | 0.075 * |
| -0.010 | 31.3 | 0.055 |
| | 100.0 | (0.053) |

* 0.065% of the 0.075% $U_3O_8$ is due to uranium in chlorite and muscovite, the remainder being due to heavy uranium-rich minerals.

(b) Secondary Ore Residue

| Size Fraction (mm) | Weight % | $U_3O_8$ Assay % |
|---|---|---|
| +0.045 | 61.0 | 0.040 |
| -0.045+0.010 | 7.4 | 0.085 ** |
| -0.010 | 31.6 | 0.070 |
| | 100.0 | (0.052) |

** 0.080% of the 0.085% $U_3O_8$ is due to uranium in chlorite and muscovite, the remainder being due to heavy uranium-rich minerals.

The results of this investigation indicated that there was only a slight increase in uranium content with decreasing grain size and suggested that the uranium was relatively uniformly dispersed at low levels throughout the micaceous minerals rather than being adsorbed onto the surface. The question remains unanswered as to whether the uranium was introduced into the micaceous minerals during leaching or whether it was introduced during the original mineralisation. However, in view of the similarity in uranium contents of the micaceous silicates in both the primary and secondary leach residues, it is suggested that the uranium was introduced during leaching, since it could be expected that if introduction of uranium into micaceous silicates had taken place during mineralisation, the extended contact between the micaceous

silicates and uranyl ions released during supergene alteration would have enriched the micaceous minerals in the secondary ore relative to those in the primary ore. That enrichment of micaceous minerals in cations can readily occur under near surface conditions of supergene alteration is indicated by the known occurrence under such conditions of muscovite carrying over 1% copper (Henley 1970b) and chlorite containing several percent nickel.

## 4. CONCLUSIONS

This paper has attempted briefly to review the methods used by the applied mineralogist in his investigation of uranium ores and to illustrate the relevance of mineralogy to various aspects of the physical beneficiation and chemical extraction of uranium ores. It is the belief of the authors that mineralogy has a vital role to play in metallurgical studies, not only those concerned with uranium ores, and that much abortive and expensive metallurgical testwork can be avoided by appropriate mineralogical assessment of ores, beneficiation products, leach residues, etc.

In the course of preparing this paper it has become clear that there are two particular areas where intensive mineralogical investigation is warranted at the present time, apart from investigations of individual ores and their treatment products. The first is in the characterisation of specific physical and chemical features of uranium minerals, particularly those relevant to possible physical beneficiation procedures (e.g. density, magnetic susceptibility, conductivity, fluorescence, radioactivity, flotation properties) which may be expected to be applied increasingly in the future (Smith and White 1969). Although a considerable amount of data has been accumulated on certain mineral properties (e.g. density) there is a dearth of quantitative data on others; Hartman and Wyman (1969) for instance, report that they are unaware of any data on the magnetic susceptibilities of uranium minerals.

The second area of interest is the detailed investigation of leach-residues to determine the nature of the unleached uranium. It seems possible that in many cases uranium may enter the lattices of gangue minerals during leaching, the Nabarlek leach residues perhaps being one such example. This particularly applies to clays and other minerals of high cation exchange capacity (for example, it is known that copper can be lost from leaching circuits by absorption into montmorillonite) but under the conditions which characterise many acid leaching circuits (low pH, elevated temperature, and presence of uranyl ions) it is probable that uranium can substitute to a small extent in the lattices of minerals of relatively low cation exchange capacity.

It could be expected that significant advances in the physical beneficiation and chemical extraction of uranium ores would derive from an investigation of these two relatively neglected areas.

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## 6. REFERENCES

Canning, R.G. (1971). Leaching studies. Unpublished Amdel Report (No. 792).

Clegg, J.W. and Foley, D.D. (Eds) (1958). Uranium ore processing. Addison-Wesley Publishing Company Inc., Reading, Massachusetts.

Couche, R.A. and Hartley, F.R. (1958). Features of the development of chemical processing for Mary Kathleen ores. In Australian Atomic Energy Commission Symposium, Australian Atomic Energy Commission, 75-85.

D'Rozario, H.L. and Canning, R.G. (1970). Heavy media separation of Mary Kathleen uranium ore. Unpublished Amdel Report (No 678).

Frondel, C. (1953). Hydroxyl substitution in thorite and zircon. Amer. Mineral., 38, 1007-1018.

Gaudin, A.M. (1939). Principles of mineral dressing. McGraw-Hill, New York and London, 85-89.

Goldney, L.H., Canning, R.G. and Gooden, J.E.A. (1972). Extraction investigations with some Australian uranium ores. Paper presented to this Symposium.

Hartley, F.R. (1968). Treatment of Mary Kathleen uranium ore - a review. In Symposium "Uranium in Australia". Australian Institute of Mining and Metallurgy (Rum Jungle Branch).

Hartman, F.H. and Wyman, R.A. (1969). Concentration of uranium minerals from Canadian ores by magnetic means. Mines Branch Tech. Bull. T.B. 118, Dept. of Energy, Mines and Resources, Ottawa.

Heinrich, E.W. (1958). Mineralogy and geology of radioactive raw materials. McGraw-Hill, New York.

Henley, K.J. (1970a). Mineralogical assessment of a churn-drill core from an alluvial tin deposit. Proc. Aust. Inst. Min. Metall., 236, 43-57.

Henley, K.J. (1970b). Cupriferous sericite from the Sar Cheshmeh porphyry copper ore, Kerman Province. Iran. Mineral. Mag., 37, 945-947.

Henley, K.J. (1972). The quantitative mineralogical evaluation of alluvial ores. Amdel Bull. (in press).

Kelly, A. (1970). Mineralogical studies. Unpublished Amdel Report (No. 685).

Liebenberg, W.R. (1956). A mineralogical approach to the development of the uranium extraction processes practised on the Witwatersrand. Journ. South African Inst. Min. Metall., 57, 153-208.

Liebenberg, W.R. (1970). Mineralogy and the metallurgist. Minerals Sci. Engng., 2 (4), 3-23.

Liebenberg, W.R. and Taverner, L. (1958). Mineralogical studies related to the uranium recovery and extraction processes practised on the Witwatersrand with special reference to acid leaching. Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy, 3, 296-302.

Lima da Faria, J. (1964). Identification of metamict minerals by X-ray powder photographs. Estudos, ensaios e documentos No 112. Junta de investigacoes do Ultramar, Lisboa, Portugal.

Muller, L.D. and Burton, C.J. (1965). The heavy liquid density gradient and its application in ore dressing mineralogy. Eighth Commonwealth Min. and Metall. Congr., Australia and New Zealand, 6, 1151-1163.

Muller, L.D., Henley, K.J. and Benjamin, R.E.K. (1969). Applied mineralogy in tin ore beneficiation. In 'A second technical conference on tin'. Edited by W. Fox, International Tin Council. 2, 559-600.

Pabst, A. (1952). The metamict state. Amer. Mineral., 37, 137-157.

Smith, S.E. and White, P.A. (1969). Review of uranium ore processing research. Canad. Min. Journ., 90 (5), 71-74.

Volborth, A. (1958). Identification tables for uranium and thorium minerals. Econ. Geol., 53, 300-308.

Weir, L. (1969). Flotation of Mary Kathleen ore. Unpublished Amdel Report (No 634).

Whittle, A.W.G. (1960). Contact mineralization phenomena at the Mary Kathleen uranium deposit. Neues Jahrb. Mineral. Abh., 94, 798-830.

Yagoda, H. (1949). Radioactive measurements with nuclear emulsions. John Wiley and Sons Inc., New York.

Zussman, J. (Ed) (1967). Physical methods in determinative mineralogy. Academic Press Inc. (London) Ltd., London.

AAEC SYMPOSIUM

ON

URANIUM PROCESSING

PAPER V

# EXTRACTION INVESTIGATIONS WITH SOME AUSTRALIAN URANIUM ORES

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## 1. INTRODUCTION

Laboratory extraction investigations with three Australian uranium ores are described. These ores have been selected from those investigated by Amdel over the past few years because the companies concerned have approved the publication of the results of the work carried out for them, and while all are amenable to acid leaching, they represent an interesting variety.

Nabarlek ore is high-grade and the greater part of the uranium is present as easily-leachable pitchblende. The two ores from the Mount Painter area are both low-grade and the lower-grade of the two responds to preconcentration. The greater part of the uranium is present as uraninite which leaches readily. The Valhalla ore, however, is both low-grade and chemically more refractory, the greater part of the uranium occurring as brannerite with a smaller proportion in a zircon-type mineral.

For all these ores treatment flowsheets have been prepared and process design and costing carried out, in varying depth. Because of limited space, as well as client confidentiality, this paper is confined to experimental results.

## 2. EXPERIMENTAL WORK AND RESULTS

### 2.1 Nabarlek

The Nabarlek deposit is located in the Northern Territory 130 miles east of Darwin. The estimated $U_3O_8$ reserves are "10,500 short tons in the ground contained in ore of an average grade of 47 lb $U_3O_8$ per short ton" (Queensland Mines Limited Annual Report 1971.) In ore grade this is one of the richest known deposits in the world. Queensland Mines Limited commissioned Amdel in August 1971 to establish the process conditions required to produce a high grade yellow cake product from this ore and to give preliminary estimates of capital and operating costs for conventional processing methods.

Two representative composite samples were prepared from diamond drill cores. The secondary or upper level ore sample contained 1.5% $U_3O_8$ (30 lb $U_3O_8$/short ton) while the primary ore sample was of higher grade averaging 3.7% $U_3O_8$ (74 lb $U_3O_8$/short ton). The demarcation between secondary and primary ores closely follows the water table which is 60 to 70 feet below the surface.

#### 2.1.1 Mineralogy

The ore body at Nabarlek consists of massive and disseminated pitchblende, which near the surface has partly altered to various secondary uranium minerals. The host rock to the mineralisation is a chlorite (Mg-Fe-Al silicate) -

muscovite (K-Al silicate) schist. The secondary minerals identified include curite ($PbO.8UO_3.4H_2O$), rutherfordine $\{(UO_2)CO_3\}$, kasolite $\{Pb(UO_2)(SiO_3)(OH)_2\}$ and sklodowskite $\{Mg(UO_2)_2(SiO_3)_2(OH)_2.6H_2O\}$ but these are believed to contain only a minor proportion of the total uranium in the ore-body.

2.1.2 Leaching

A leaching programme was conducted to determine satisfactory conditions for uranium extraction from both secondary and primary ores. The variables considered included grind size, solids concentration, temperature, acidity, time and oxidant requirements.

The effect of grind size on rates of extraction was studied by leaching slurries of ore, ground to the nominal sizings of 30%, 50% and 75% minus 200 mesh BSS (0.075 mm), with sulphuric acid at pH 1.0 in the presence of excess oxidant. The extraction rates, shown in Figure 1, indicated that fine grinding was not necessary for high uranium extractions, particularly with the secondary ore. A nominal grind size of 50% minus 200 mesh BSS is satisfactory for both ore types.

The specific gravity of both ore samples is 2.8 but slurries of the two samples with the same solids weight composition exhibited different viscosity characteristics. However, agitation and leaching of both ore samples was satisfactory with slurries of solids concentration 60% (W/W). Only a minor increase in extraction rates was obtained at lower solids concentrations.

Leaching temperature had a significant effect on extraction rates; for example, with secondary ore the $U_3O_8$ extracted after 24 hours was 86% at 20°C, increasing to 95% at 45°C but with a considerable increase in acid consumption mainly due to increased gangue attack. However, in this case, the increase in acid addition is definitely warranted economically.

Acid concentration during leaching has a marked effect on the rate of uranium extraction. Both samples were leached with sulphuric acid at controlled pH's of 2.0, 1.5 and 1.0, and the resulting extraction rates and acid consumptions are shown in Figures 2 (secondary ore) and 3 (primary ore). High acid concentrations (pH 1.0) gave high extraction rates but with excessive acid consumption, particularly for the primary ore. Extraction rates decreased at intermediate acid concentrations (pH 1.5) but high leaching efficiencies were still obtained by extending the leaching time. Under these conditions there was a marked decrease in acid consumption, particularly significant with the primary ore. At low acid concentrations (pH 2.0) the acid requirement was further decreased but with a loss of secondary ore leaching efficiency, even with extended time.

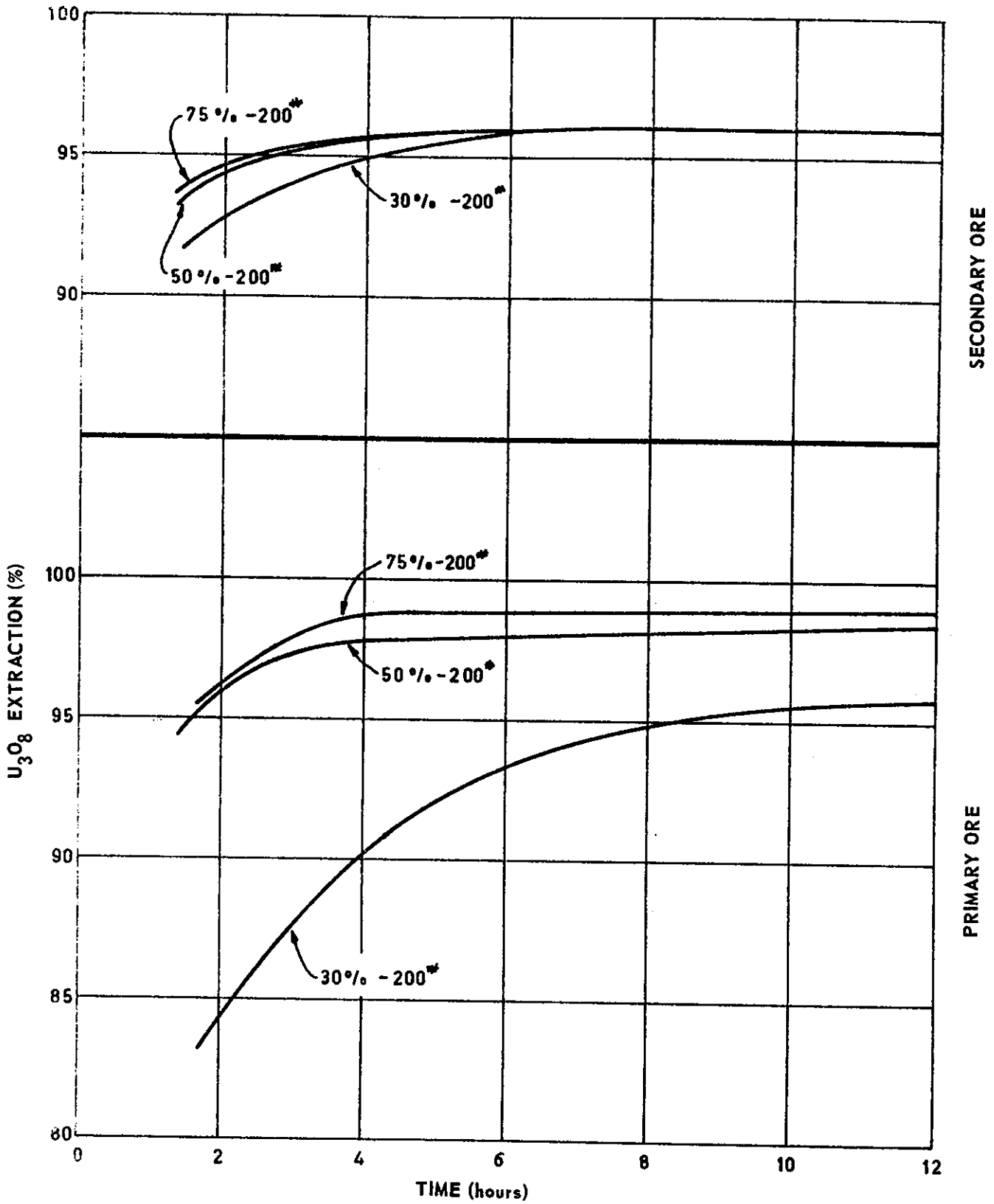


FIGURE 1. NABARLEK ORE - EXTRACTION RATES v. SOLIDS SIZE

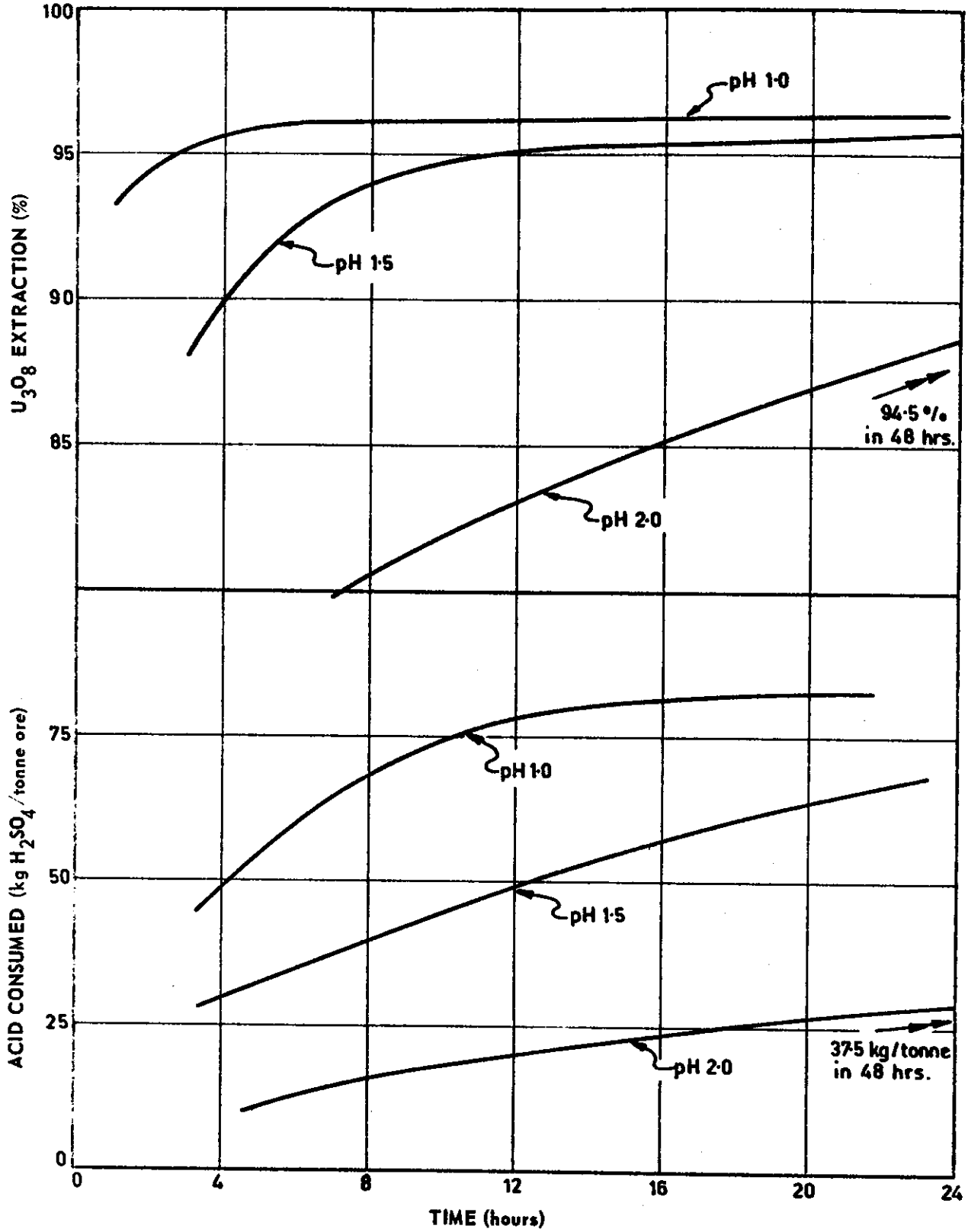


**FIGURE 2. NABARLEK SECONDARY ORE EXTRACTION RATES v. ACID CONSUMPTION**

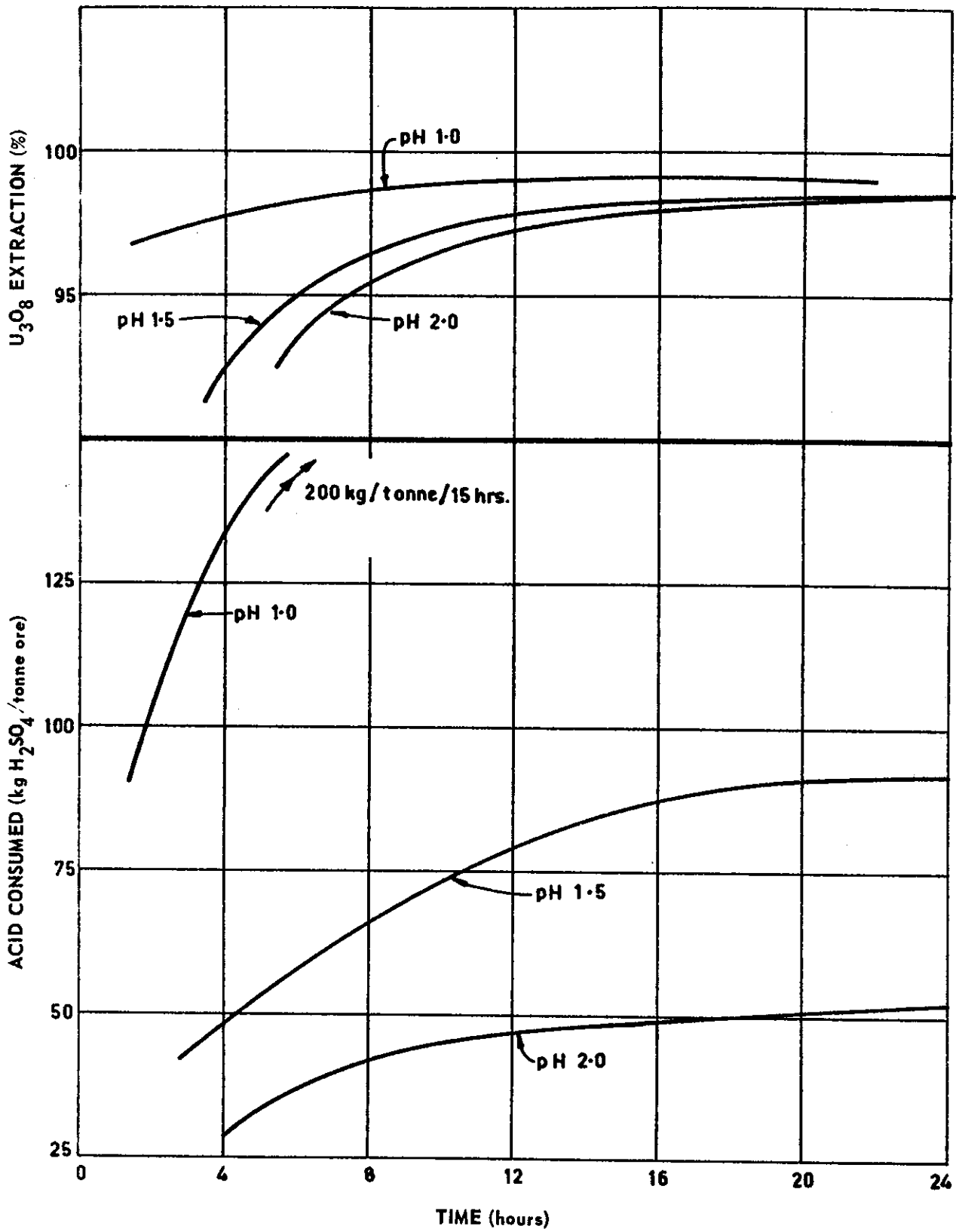


FIGURE 3. NABARLEK PRIMARY ORE
EXTRACTION RATES v. ACID CONSUMPTION

Oxidising conditions are normally required for the dissolution of pitchblende in acid solutions, and the essentially unoxidised primary ore required oxidant additions in the range 7.5-10 kg $MnO_2$/tonne ore for high leaching efficiency. With nil oxidant the $U_3O_8$ extraction was only 90% in 24 hours but with oxidant addition this was increased to over 98% in sixteen hours. The secondary ore minerals were either oxidised, or alternatively sufficient ferric iron was present to provide oxidant for any unoxidised minerals, and no additional oxidant was required for leaching.

2.1.3 Solids-liquid separation

Preliminary filtration tests on leached slurries did not give encouraging results and emphasis was placed on obtaining data for the design of a counter-current decantation circuit. Both types of ore responded well to flocculation although the secondary ore required additions in the range 0.1 to 0.15 kg flocculant/tonne solids compared with 0.05 to 0.075 kg/tonne for the primary ore. With the different ore characteristics, an underflow density of only 50% W/W solids was obtained with the secondary ore but 60% W/W solids was obtainable with the primary ore, in continuous raking tests. The primary ore had a faster settling rate as shown in Figure 4.

2.1.4 Solvent extraction and product precipitation

The relatively high grade pregnant liquors obtained from the leaching of Nabarlek ores were particularly amenable to solvent extraction with tertiary amines, producing high purity strip liquors for product precipitation.

Because of the high $U_3O_8$ concentration in the pregnant liquor, the ratio of recycle solvent to aqueous phase was relatively high. With solvent in the chloride form from the stripping circuit, the chloride exchanged to the aqueous phase in the subsequent extraction process depressed uranium extraction, but by prior sulphation of the solvent, high extraction efficiencies were maintained. By substituting ammonium sulphate as strip solution, with subsequent ammonia precipitation from the high grade strip, solvent sulphation would not be required.

Precipitation conditions were not studied in detail but with sodium hydroxide precipitation product grades up to 94% $U_3O_8$ were obtained after calcination at 750°C.

2.1.5 Discussion

Extremely fine grinding of the ore is not required for subsequent high leaching efficiencies and a grind giving approximately 50% passing 200 mesh BSS is acceptable for both types of ore. A coarser grind is satisfactory for secondary ore leaching but could cause physical difficulties in subsequent

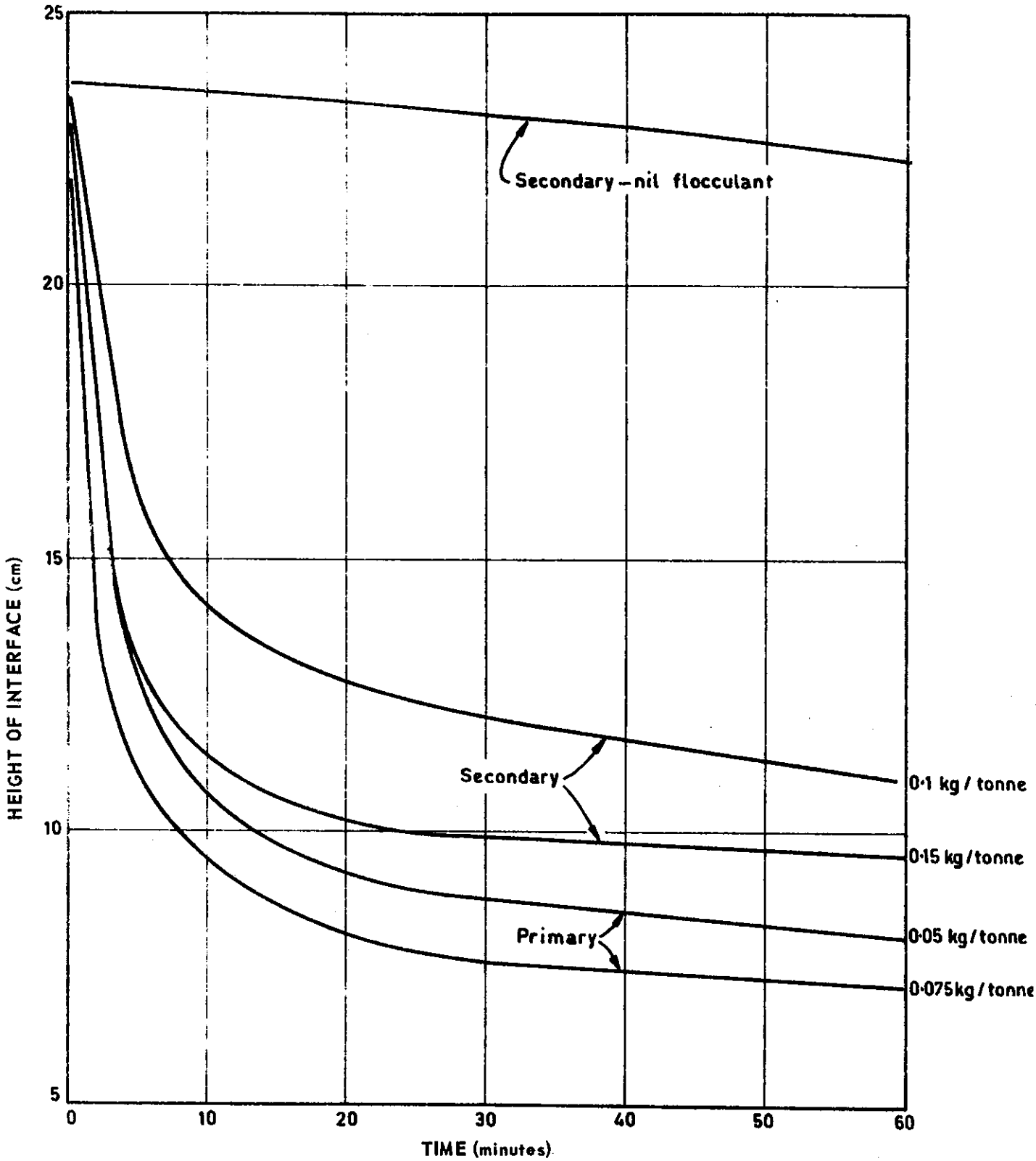


FIGURE 4. LEACHED NABARLEK SECONDARY AND PRIMARY ORES SETTLING RATES

slurry handling operations, particularly in the C.C.D. circuit.

Close control of the acid concentration in the leaching circuit is required to avoid excessive gangue attack with consequent high acid consumption. Leaching near pH 1.5 for 16 to 24 hours is required for high extractions and moderate acid requirements for mixtures of secondary and primary ores. For straight secondary ore the acidity can be higher (nearer pH 1.0) and the leaching time reduced. With straight primary ore the acidity can be lower (nearer pH 2.0) resulting in a significant decrease in the acid requirement. The full leaching time is required under this condition. The slower settling rate of the secondary ore is the limiting factor for thickener design but with suitable flocculant additions the thickener area can be reduced to 0.4 $m^2$/tonne solids/24 hours.

Refinements to the solvent extraction, precipitation and calcination conditions, which were not studied in detail, could give a product grade in excess of 94% $U_3O_8$.

2.2 Armchair Creek and Streitberg Ridge

These two deposits in the vicinity of Mount Painter, Northern Flinders Ranges, South Australia, have been investigated by the Exoil NL-Transoil NL partnership. The Australian Mineral Industry - 1968 Review reports that "in June 1969 reserves were stated as 2 million tons assaying 2 lb $U_3O_8$ per ton" (0.1% $U_3O_8$).

The extraction work was carried out at Amdel from late 1968 through 1969, in two stages. The initial stage was carried out on 9 kg of Armchair Creek ore assaying 0.08% $U_3O_8$ and 40 kg of Streitberg Ridge ore assaying 0.065% $U_3O_8$, both obtained by bulking selected footages from two drill cores, based on assay data. The second stage used 900 kg of Armchair Creek ore assaying 0.1% $U_3O_8$ and 1300 kg of Streitberg Ridge ore assaying 0.055% $U_3O_8$, both obtained from 4-inch drill cores by selecting footages on the basis of gamma logs of the holes.

2.2.1 Mineralogy

Microscopic, autoradiographic and electron-probe examination of samples from the initial Armchair Creek cores showed that the uranium occurred as uraninite (sometimes associated with pyrite), and as pitchblende in microspherulites in the matrix and between tabular haematite crystals. There was also a trace of uranium in the monazite, and radioactivity was found in occurrences of a yellow clay thought to be a breakdown product of brannerite.

A similar examination of the initial Streitberg Ridge cores showed that

the principal form of the uranium was a uraninite, euhedral and corroded, the grains ranging from 0.5 to 4 mm. There was also a small proportion of uraniferous ilmenite (possibly davidite). There was some meta-autunite and some uranium in allanite.

In both cases the host rock was a hydrothermally-altered breccia which was once granitic but much of the potash feldspar had been replaced by a mixture of chlorite and chloritic clay. The main possibility for physical preconcentration appeared to be recovery of the uraninite, and the indications were that since the proportion of the uranium present as uraninite appeared to be higher in the Streitberg Ridge material, the latter would probably be more amenable to preconcentration.

2.2.2 Physical beneficiation

Initial preconcentration tests included heavy liquid separation at specific gravities 2.96 and 3.31, superpanning, flotation, magnetic and high tension separation, heavy-medium cyclone separation of plus 30-mesh (0.50 mm) material and spiralling. Figure 5 summarises the results obtained. Heavy medium cyclone concentration appeared the most useful method and 30 kg batches of the second-stage samples were therefore treated in the Fraser and Chalmers pilot unit. Figure 6 shows the separation curves based on these tests, in which the plus 30-mesh ore was treated and the minus 30-mesh ore combined with the underflow (uranium concentrate) for subsequent processing. Spiral concentration of the minus 30-mesh fraction was also carried out.

2.2.3 Leaching

Concomitantly with the physical beneficiation studies leaching tests were carried out on head ore and concentrates. The procedure was to mix a weighed portion of the ore or concentrate with an equal weight of water and stir mechanically throughout the leaching period. Sulphuric acid was added to maintain the selected pH, and manganese dioxide was added to maintain a redox potential, measured with respect to a saturated calomel electrode, of at least 400 mV.

The large number of tests carried out to investigate systematically all variables showed that by grinding Armchair Creek ore as fine as minus 100 mesh a leaching efficiency of 85% could be achieved with an acid consumption of 35 kg per kg of $U_3O_8$ extracted. Leaching of a combined HM cyclone and spiral concentrate consumed slightly less acid (30 kg per kg of $U_3O_8$ extracted) for a leaching efficiency of 87%, but due to uranium losses in beneficiation the overall extraction was only 65%. There was thus no justification for preconcentrating Armchair Creek ore.

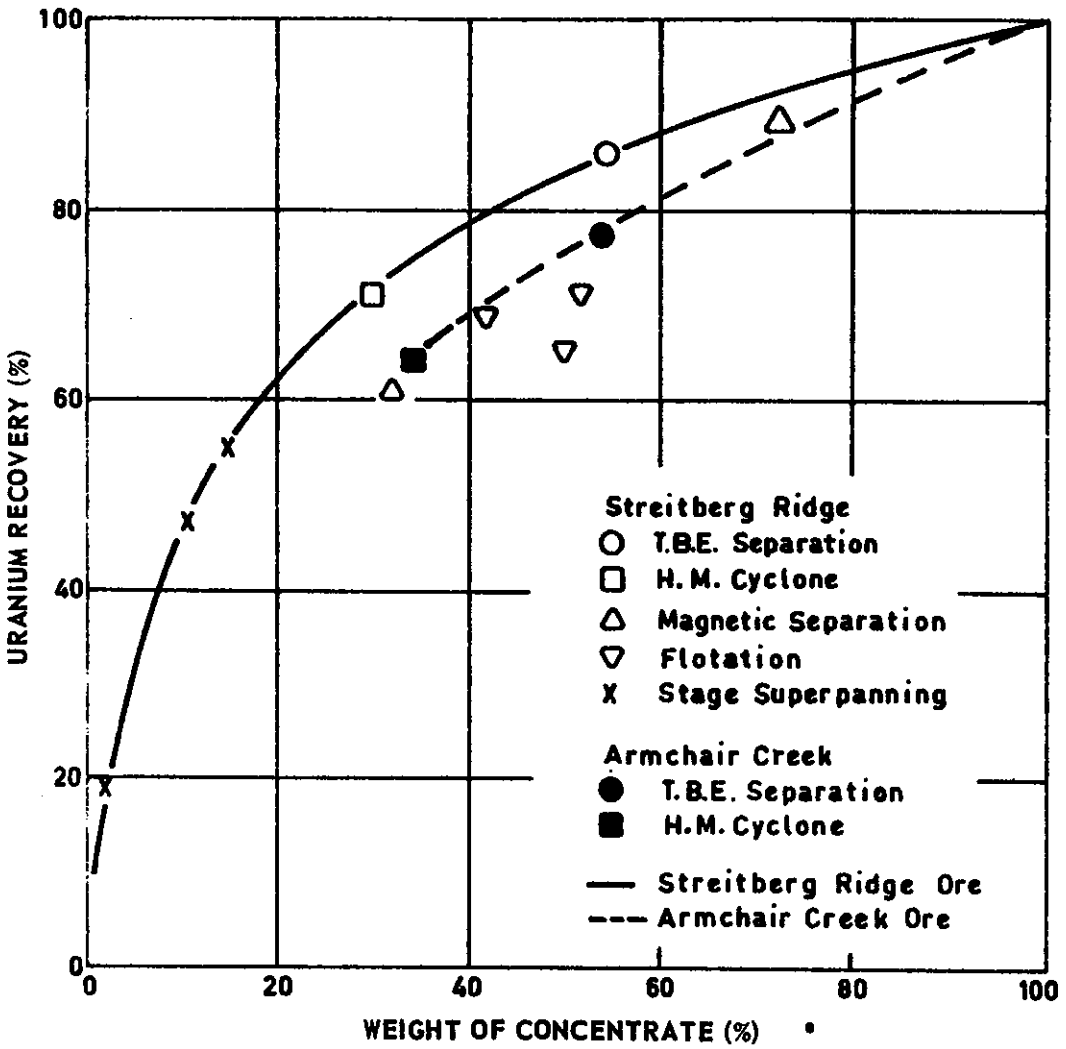


FIGURE 5. SUMMARY OF BEST INITIAL-STAGE BENEFICIATION RESULTS

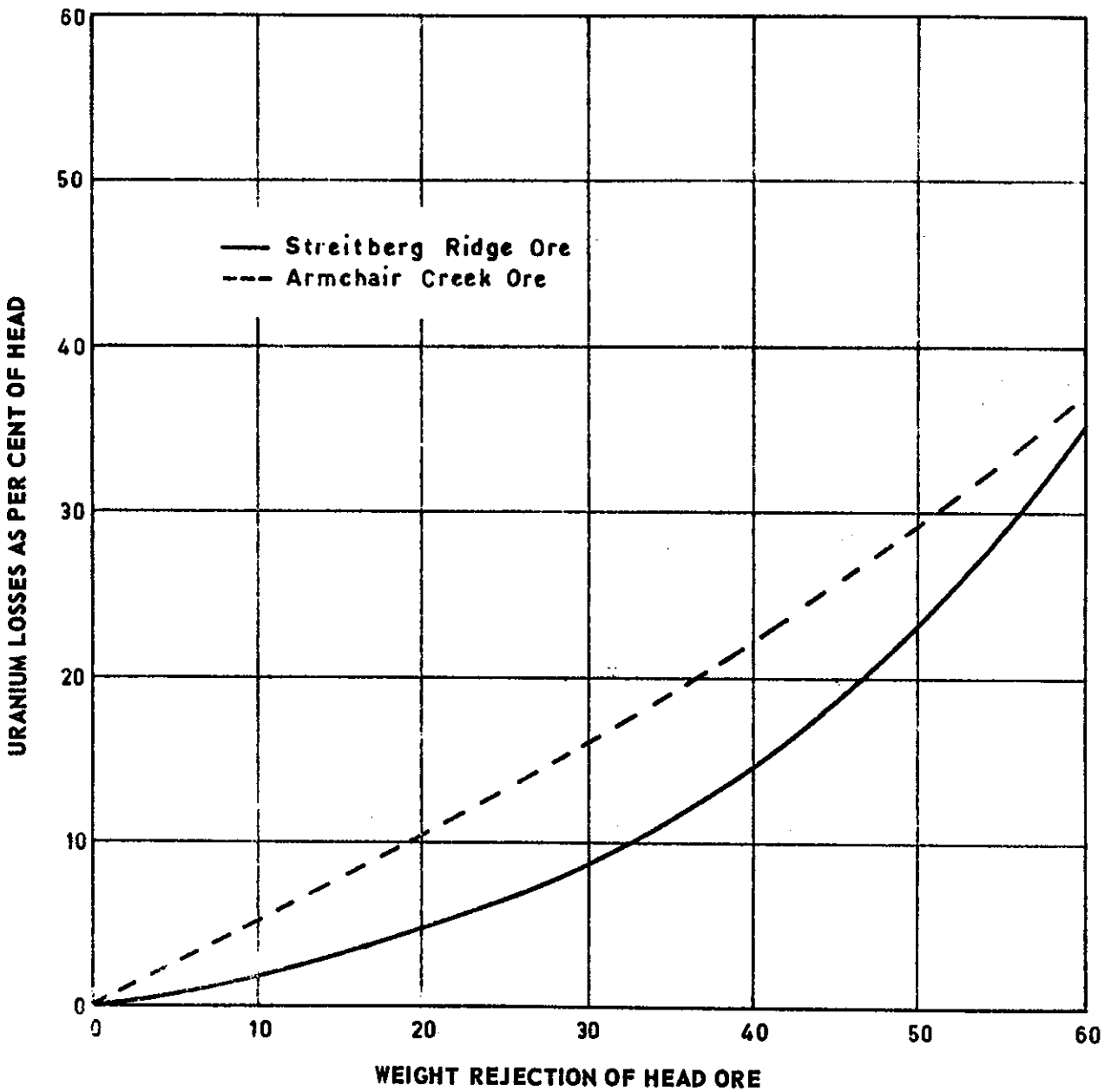


FIGURE 6. PILOT HEAVY-MEDIUM CYCLONE TREATMENT

Streitberg Ridge ore behaved very differently. At minus 100 mesh with other conditions optimised the head ore consumed 185 kg acid per kg of $U_3O_8$ extracted, for a uranium extraction of 69.5%. A combined HM cyclone and spiral concentrate under the same conditions consumed only 60 kg acid per kg of $U_3O_8$ extracted for a uranium leaching efficiency of 75% (overall extraction of uranium from ore of 53%). This result reflects a very useful rejection of acid-consuming gangue in preconcentration. Further reduction in acid consumption to 50 kg acid per kg of $U_3O_8$ extracted was possible for negligible loss of uranium by using a coarser grind (72 mesh BSS, 0.210 mm).

Satisfactory leaching conditions for the two ores were pH 1.7 (optimum possibly higher), 20°C, 5 hours, continuous agitation. Oxidant consumption was minimal.

2.3 Valhalla

2.3.1 Background

The low-grade Valhalla deposit is favourably situated approximately 30 miles north of Mount Isa, Queensland. The size of the deposit and its favourable location prompted Queensland Mines Limited to commission Amdel to carry out preliminary mineralogical and processing studies during 1969 and 1970 in order to gain some insight to plan drilling targets. For beneficiation and leaching studies composite samples were prepared by Amdel from samples of drill-hole cuttings and the composite sample QVI, used for the main leaching study, contained 0.16% $U_3O_8$ and 9.2% $CO_2$.

2.3.2 Mineralogy

Mineralogical study, including semi-quantitative electron-probe microanalysis of drill-core samples, established that two main species of uranium minerals were present either separately or together, one being a brannerite containing more than 50% uranium oxide, and the other a metamict zircon-type mineral containing approximately 7-8% uranium oxide. In the samples examined brannerite apparently accounted for most of the uranium present. This was confirmed by a comparison of chemical analyses of sample QVI and of a specimen drill-core sample selected mineralogically as containing only the zircon-type mineralisation. Calculations showed that in sample QVI the zircon-type mineral accounted for approximately 20% of the uranium present. The zircon-type sample contained 0.97% $U_3O_8$ and 5.1% Zr by chemical analysis. Assuming no other impurities in the zircon and no other uranium or zirconium minerals present in the sample, these assays are equivalent to a zircon-type mineral containing 8.5% $U_3O_8$, compared to 7-8% $U_3O_8$ determined by electron-probe microanalysis.

Major gangue minerals identified in the mineralised zone of the drill core from which the sample QVI was obtained, were albite, dolomite, quartz, sodic pyroxene, and sodic amphibole, the proportions varying considerably even over short intervals. The significant impurity for acid leaching of the ore was dolomite which, together with a trace of calcite, accounted for 9.2% $CO_2$ in composite sample QVI. It was apparent therefore that some form of physical beneficiation was desirable to separate at least part of the dolomite prior to acid leaching of the ore.

2.3.3 Physical beneficiation

No significant concentration of uranium minerals or separation of dolomite from uranium minerals was obtained by size fractionation, gravity separation, or magnetic separation. The most promising results were obtained by froth flotation of carbonate minerals, leaving uranium minerals in the tailing. Flotation products were prepared in which the carbonate levels were reduced from 9% to as low as 3% $CO_2$ and with a small upgrading of uranium. However, uranium recoveries were not as high as was considered desirable, due to the extremely fine grain size and poor liberation characteristics of the uranium minerals.

2.3.4 Leaching

Brannerite ores are known to require stronger leaching conditions than ores containing uraninite or secondary uranium minerals, and this was confirmed in the present studies. Nevertheless, from whole ore composite sample QVI, over 80% extraction of uranium could be obtained with sulphuric acid leaching at 50°C with continuous agitation over a period of 50 hours, provided the ore was finely ground to minus 240 mesh BSS (0.063 mm) and the free acidity of the leach liquor was maintained at 0.5N or higher throughout the leaching period. Similar results could be achieved in shorter times using higher free acidity levels and/or higher temperatures. The addition of oxidant, either as $MnO_2$ or as a soluble ferric salt increased the rate of leaching significantly under most conditions and also increased the final leaching efficiency to some extent. The effect of the addition of oxidant was more significant at the lower free acidity levels. More detailed studies would be required to establish the optimum quantity and form of oxidant for a given set of leaching conditions. Finer grinding of the ore to minus 350 mesh BSS (0.045 mm) resulted in a small improvement in leaching rate and in final extraction in tests at 50°C, but had no effect in tests at 70°C. It was concluded that finer grinding would not be worthwhile, and in fact the optimum grind size could well be coarser than the minus 240 mesh BSS size used in these tests.

Rates of leaching at various levels of free acidity are shown graphically in Figure 7 which also includes a typical acid consumption curve. Despite the maintenance of a relatively high level of free acidity throughout the leach, very little consumption of acid occurred after the initial rapid reaction with carbonate minerals. However, leaching of uranium continued over a long period.

A prime object of these preliminary leaching investigations was to establish a 'standard' leaching procedure suitable for leachability tests on samples from different parts of the ore body. The conditions chosen were not expected to yield maximum possible extractions, nor were they necessarily the economic optimum, but they were designed for comparison of the behaviour of the various ore samples. A leaching time of 30 hours was chosen partly for convenience (allowing commencement and completion of tests during normal working hours on successive days, with continuous agitation unattended overnight) and partly because the leaching rate curves generally showed a tailing-off after approximately 30 hours.

'Standard' leaching conditions were:

| | |
|---|---|
| Grind size of ore: | -240 mesh BSS (0.063 mm) |
| Constant free acidity: | 0.5N (25 g $H_2SO_4$/litre) |
| Oxidant: | 10 kg $MnO_2$ per tonne of ore and 3 g $Fe^{3+}$ per litre (as ferric sulphate). |
| Temperature: | 50°C. |
| Time: | 30 hours. |

Procedure:

The ore, $MnO_2$, and ferric sulphate were slurried with water and heated to 50°C. With continuous agitation, sulphuric acid was added until the reaction with carbonate minerals was complete, as judged by the pH remaining constant in the range 2 to 3 over a period of 10 minutes or more without further addition of acid. Sufficient additional acid was then added to make the liquor 0.5N (25 g $H_2SO_4$ per litre), and agitation was continued at 50°C for 30 hours. The free acidity level was checked by titration of samples withdrawn at suitable intervals and additional acid was added as required to maintain 0.5N free acidity. At the end of the period, leached solids were filtered, washed, and dried for assay.

Table 1 shows the results of 'standard' leaching tests on a range of samples, namely whole ore composite (QVI), flotation products A and B, brannerite and zircon-type ores (selected mineralogical specimens), and a sample of

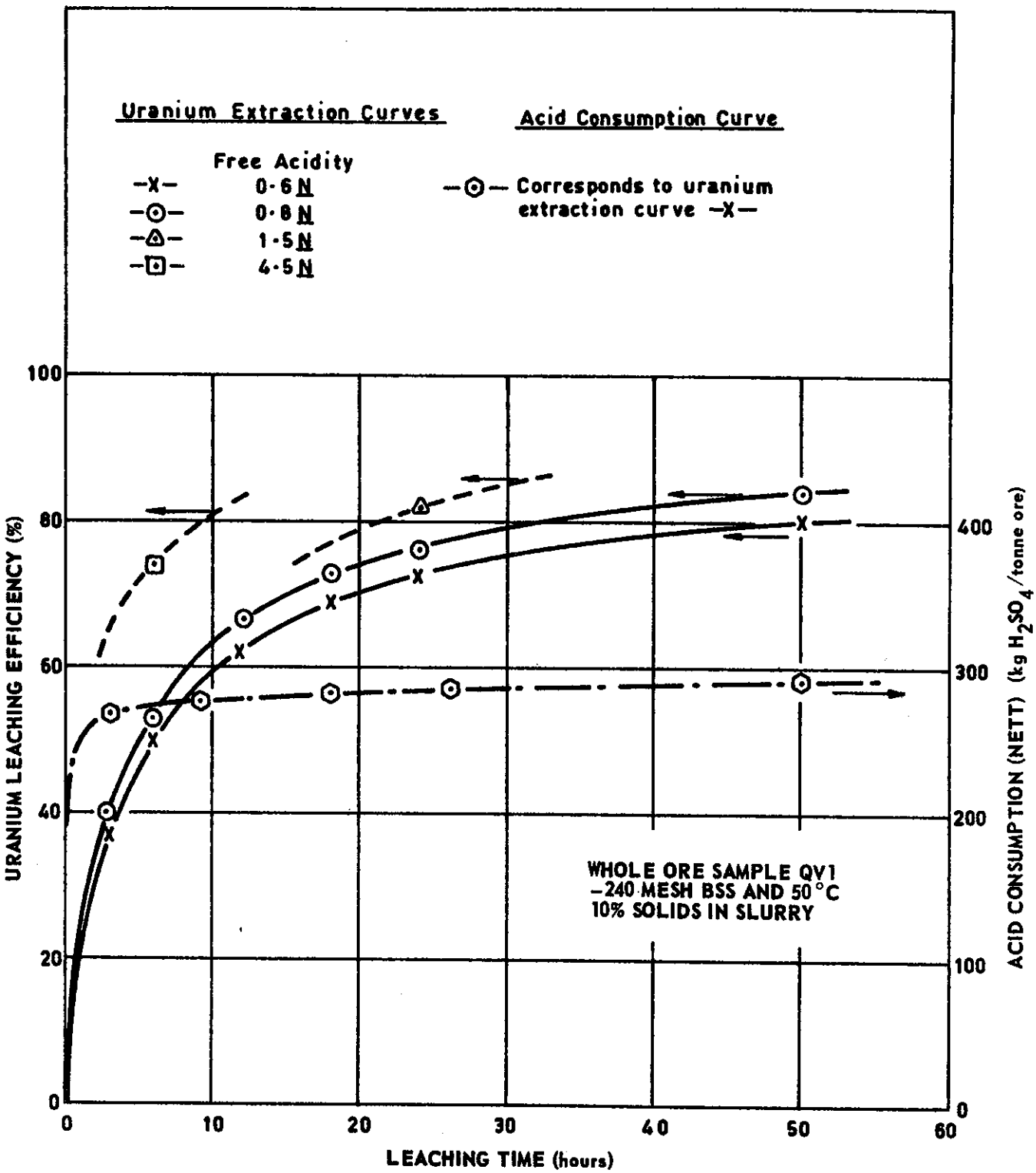


FIGURE 7. SULPHURIC ACID LEACHING OF VALHALLA ORE. EFFECT OF FREE ACIDITY LEVEL ON RATE OF LEACHING.

TABLE 1: SULPHURIC ACID LEACHING OF VALHALLA ORES

"Standard" Leaching Conditions, approximately 10% solids in slurry.

| Sample Type | Whole Ore | Flotation Product | | Selected Drill-Core | | Weathered |
|---|---|---|---|---|---|---|
| Designation | QV1 | A | B | Brannerite | Zircon | Zone |
| Head Assay | | | | | | |
| $U_3O_8$% | 0.16 | 0.18 | 0.18 | 0.69 | 0.97 | 0.048 |
| $CO_2$% | 9.2 | 3.1 | 5.0 | n.d. | n.d. | n.d. |
| Zr% | 0.21 | n.d. | n.d. | n.d. | 5.1 | n.d. |
| Uranium Leaching Efficiency, % | 82 | 66 | 68 | 85 | 83 | 3.4 |
| Acid Consumption (nett) | | | | | | |
| kg $H_2SO_4$ per tonne of ore | 225 | 155 | 185 | 95 | 200 | n.d. |
| kg $H_2SO_4$ per kg of $U_3O_8$ dissolved | 170 | 130 | 150 | 16 | 25 | n.d. |

n.d. - not determined.

weathered zone ore. It is interesting to note that the zircon-type ore was leached almost as efficiently as the brannerite ore, thus the presence of the zircon-type mineral is no problem as far as leaching is concerned. The sample of weathered zone ore proved to contain uranium in a highly refractory form and it was apparent that the weathered ore would not be amenable to leaching.

Nitric acid leaching of the whole ore (QVI) was tested as an alternative to sulphuric acid plus oxidant. Although similar extractions were obtained it was apparent that the sulphuric acid leach would be much cheaper.

Alkaline leaching of sample QVI was also tested as a possible means of overcoming the problems caused by carbonate minerals. Leaching minus 350 mesh BSS ore at 50°C for 50 hours with a leach solution containing 50 g $Na_2CO_3$ and 50 g $NaHCO_3$ per litre resulted in a uranium extraction of 24%. A similar leach at 20°C resulted in 18% extraction of uranium. Higher temperature alkaline leaching should be systematically investigated, though a single leach at 100°C on a random Valhalla sample was quite ineffective.

## 3. DISCUSSION

These investigations on Valhalla ores were of particular interest in that no brannerite ores have yet been treated commercially in Australia. The presence of a proportion of the uranium in the unusual zircon-type mineralisation was also a challenge and its successful leaching, to almost the same extent as brannerite ore, was contrary to early expectations in this work, but simplified processing considerations.

The major processing problem remains one of reducing acid consumption by separation of at least part of the dolomite contained in the ore. The leaching and uranium recovery stages should present no major problems provided acid consumption by carbonates can be cut significantly. The requirement of maintaining a relatively high free acidity during leaching would call for a two stage counter-current leaching system with intermediate solids separation. The free acid remaining in the leach liquor at the end of the main leach would thus be neutralised by the carbonate content of the ore in the fresh ore leaching stage.

It should be emphasised that this work on Valhalla ore was preliminary in nature, and that more detailed studies of both physical beneficiation and chemical processing will be required if commercial development of the deposit is considered. With the results obtained to date, and assuming that the ore body is typified by composite sample QVI, it is unlikely that processing of the ore will be economic unless a substantial separation of dolomite from

uranium minerals can be obtained by some form of physical beneficiation before leaching.

## 4. ACKNOWLEDGEMENTS

A number of other Amdel staff members were responsible for portions of the work described, including Dr K. Henley, Dr R. Davy, A. Kelly (mineralogy), H. D'Rozario, J. Dixon (physical beneficiation), J.D. Hayton and G.B. Warburton (leaching).

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AAEC SYMPOSIUM

ON

URANIUM PROCESSING

PAPER VI

# PLANNED CHANGES IN THE MARY KATHLEEN TREATMENT PLANT FOR FUTURE OPERATIONS

by

M. G. BAILLIE

J. A. THOMAS

MARY KATHLEEN URANIUM LTD.

## 1. INTRODUCTION

In the early 1950s a world wide uranium boom occurred, followed by an enthusiastic search for economic ore bodies in many parts of the world, including Australia. As a result of this activity a significant uranium occurrence was located at Mary Kathleen in July 1954. Extensive geological mapping, diamond drilling and metallurgical research followed. These activities proved that the ore body was economic and its development for production was commenced.

With a contract for the supply of yellow cake to the U.K.A.E.A. finalised in March 1956, construction of mine installations, the treatment plant and support facilities was commenced. The plant was in operation by June 1958 and continued production till 1963, during which time a total of 2,900,000 tons of ore were treated for a production of 9,000,000 lb of $U_3O_8$ as yellow cake. Since shutdown the plant and facilities have been maintained on a care and maintenance basis so that reopening can be achieved with the minimum of costly repair. Even though a large proportion of the treatment plant equipment and the buildings are exposed to the wind, rain and sun, the deterioration has been minimal, mainly as a result of the very dry air conditions which prevail nearly all year round.

Over the last few years there has been an increase in the use of nuclear power for electricity generation, and Mary Kathleen Uranium Ltd. has been able to secure contracts sufficient to justify reopening. On the basis of currently held sales contracts, it is planned to reopen the plant for production of yellow cake in late 1974. This will require the recommissioning of the original plant and installation of new equipment to begin at the end of this year.

It is envisaged that there will be a number of process changes and additions. The capacity of the plant will also be increased so that an output of two million pounds per year of $U_3O_8$ can be maintained with the future mill feed despite the fact that it will be of lower grade than during the previous operation. A number of process changes, discussion of which forms the basis of this paper, are also envisaged in order that operating costs can be reduced.

## 2. THE ORIGINAL FLOWSHEET

The existing treatment plant was based on a standard acid leach - fixed bed ion exchange recovery process. The flowsheet was not particularly unusual for its period although the concept of four stage continuous leaching with pH

and oxidation potential control was certainly advanced.

The basic process steps, which are illustrated in Figure 1, are as follows:

1. Primary crushing
2. Ore sorting
3. Secondary and tertiary crushing
4. Fine grinding
5. Leaching
6. Countercurrent decantation
7. Clarification
8. Ion exchange
9. Precipitation
10. Drying

As a number of these steps will be modified or replaced, it is useful to examine some of them as they existed previously so that the alterations can be more readily understood.

2.1 Primary Crushing and Sorting

Uranium bearing mineralisation is distinctly separate from barren minerals within the ore body. This permitted selective mining which upgraded the feed to the mill. The ore was trucked in 15 ton capacity rear dump trucks to the 48" x 60" Allis Chalmers primary jaw crusher. After crushing, the ore was screened at three inches, the oversize being conveyed to the ore sorter feed bins and the undersize to the surge bin ahead of the secondary and tertiary crushers. The plus three inch ore was fed to four radiometric ore sorters by vibrating grizzly feeders. As it left the feeder the ore dropped onto a rotating cone with a helical scroll. This caused the rocks to line up in single file for discharge onto a conveyor belt moving at about 180 feet per minute. As the rocks moved on the belt a mechanism positioned them in a straight line for final presentation to the discriminating apparatus.

When the particles reached the end of the belt they were discharged and fell past a light source/photo electric cell combination. From the variation in the intensity of the light, the area of the rock was measured. Still falling freely, the particle then passed a scintillation detector which measured the rock's radioactivity. The area and radioactivity signals were then compared. If the area signal was bigger than expected in relation to the radioactivity measurement for an ore particle of cut-off grade, the particle

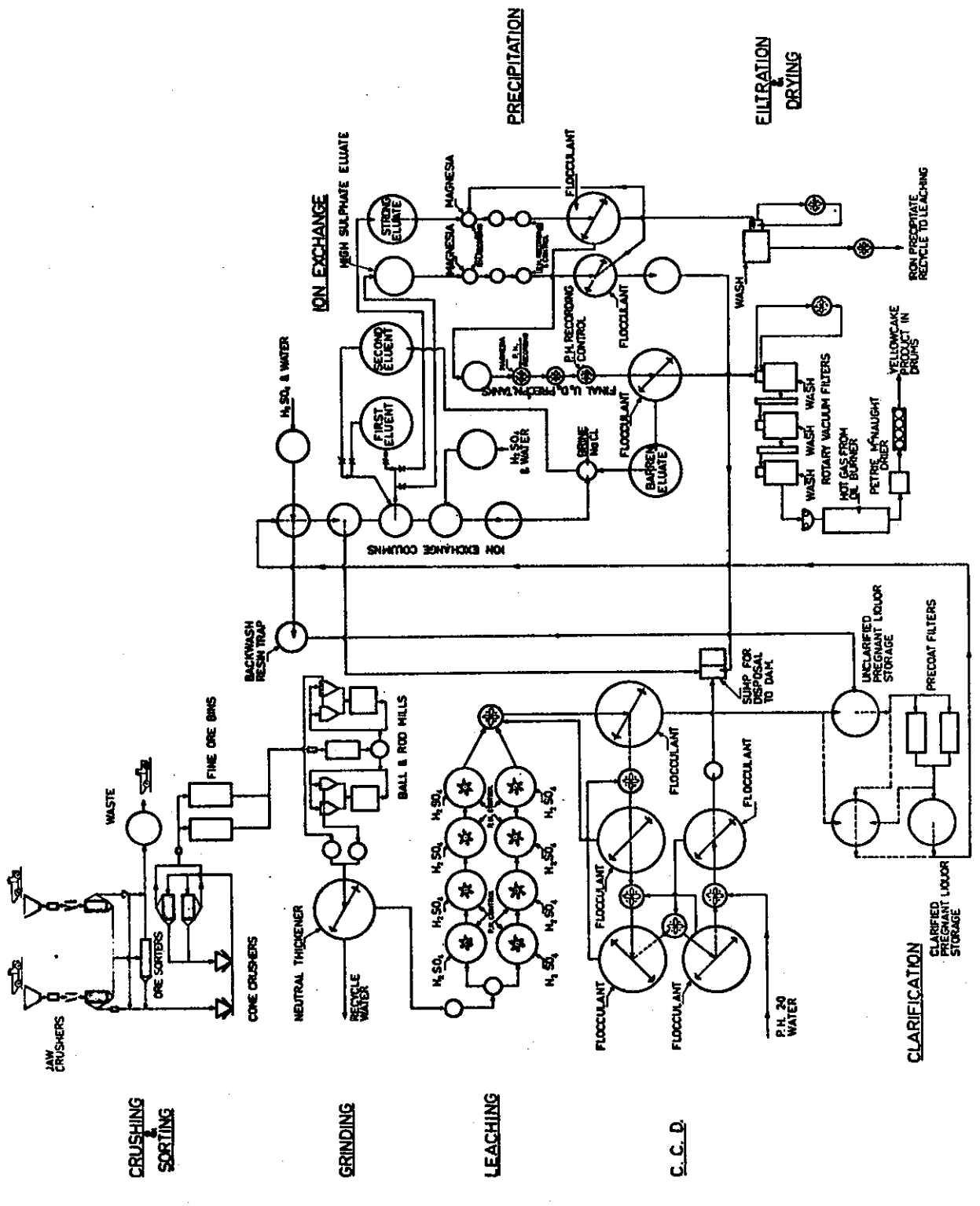


FIGURE 1. ORIGINAL TREATMENT PLANT FLOWSHEET MARY KATHLEEN

was judged as waste. The electronic circuitry then activated three solenoid valves linked to air blast valves causing 90 psi compressed air to blast the waste particle aside at the correctly timed instant.

If the area signal indicated that the radioactivity measured was above the level for the cut-off grade set, the particle was allowed to fall freely onto the ore conveyor from which it was delivered with the minus three inch ore to the fine crushing surge bin.

2.2 Clarification

After the pregnant liquor overflowed from the No. 1 thickener in the countercurrent decantation circuit it was normally relatively clear (100 ppm solids). However, in order that the resin would not become contaminated, especially under surge conditions, when the pregnant liquor became excessively loaded with solids, the liquor was fed to a pair of rotary drum precoat filters, each with a surface area of 400 square feet. The precoat material was a mixture of two diatomaceous earth products. Occasionally the load was too great for the precoat filters and unclarified liquor was allowed into the ion exchange circuit without any apparent harmful effects.

2.3 Ion Exchange, Precipitation and Drying

After the pregnant liquor was clarified it was pumped to the ion exchange circuit consisting of three sets of four eight foot diameter columns, each loaded with 300 cubic feet of Deacidite FF resin, where absorption by ion exchange took place. Subsequently, a series of elution cycles were practised resulting in two concentrated uranium eluates relatively free of rare earths. (Rare earths were the contaminants of primary concern.) Elution was performed with return eluent made up to one molar sodium chloride and 0.1 normal sulphuric acid. This return eluent was recycled after precipitation of uranium from the normal eluate. The first major portion of the liquor produced during elution was separated and termed the high sulphate eluate. Since it was relatively low in chloride it was used as the sulphate bleed for the circuit after uranium precipitation. The second major portion, called the normal eluate, was higher in chloride, but lower in uranium and sulphate.

The high-sulphate eluate was neutralised to pH 7.0 with caustic magnesia resulting in the precipitation of iron and uranium. This precipitate was then pumped to the normal eluate precipitation circuit and mixed with normal eluate. Caustic magnesia was again added to precipitate the iron at pH 3.5. The resultant solution, containing most of the uranium was then neutralised

to pH 7.0 with super grade caustic magnesia (low in silica) to precipitate uranium. The yellow cake precipitate was thickened, filtered and washed on three successive rotary drum filters. The final filter cake was then dried at about 350°F in an oil fired conveyer type drier.

## 3. THE MODIFIED FLOWSHEET

Since the treatment plant operated at Mary Kathleen previously, a number of important developments have been tested and proven in other operating uranium mills and at Mary Kathleen as part of the development program. Where relevant, developments which would enable plant operating costs to be reduced have been incorporated into the proposed new flowsheet, which is shown in Figure 2.

### 3.1 Ore Sorting

As has been already stated, sorting was carried out on the plus three inch ore after primary crushing. The maximum throughput was approximately 35 short tons per hour per sorter, with four sorters installed. Once the throughput was increased the sorting efficiency began to decrease.

Theoretically, the maximum capacity of a sorter installation is set by the inherent reaction frequency of the sensing head and attendant mechanical apparatus such as the blast valves. The maximum counting frequency under ideal conditions is believed to be six rocks per second.

With a maximum counting rate of six particles per second the spacing of particles on the belt from centre to centre for a belt speed of 180 ft/min would be six inches. For example five inch diameter particles would be spaced one inch apart and so on. During previous operation the optimum practical figure was about 4.5 rocks per second, taking into account the concentrate grade and recovery.

The need to depart from the ideal situation arises from two main factors.

1. A rock particle of high grade can influence the radioactivity reading for a waste particle thus resulting in it being accepted as ore. This situation is at its worst when a large ore particle precedes or follows a small waste particle.
2. The large range of particle sizes present in plus three inch ore can lead to a situation where the particle spacing becomes very difficult to control at an optimum figure (e.g. 7" rocks would overlap). The efficiency of blasting is affected

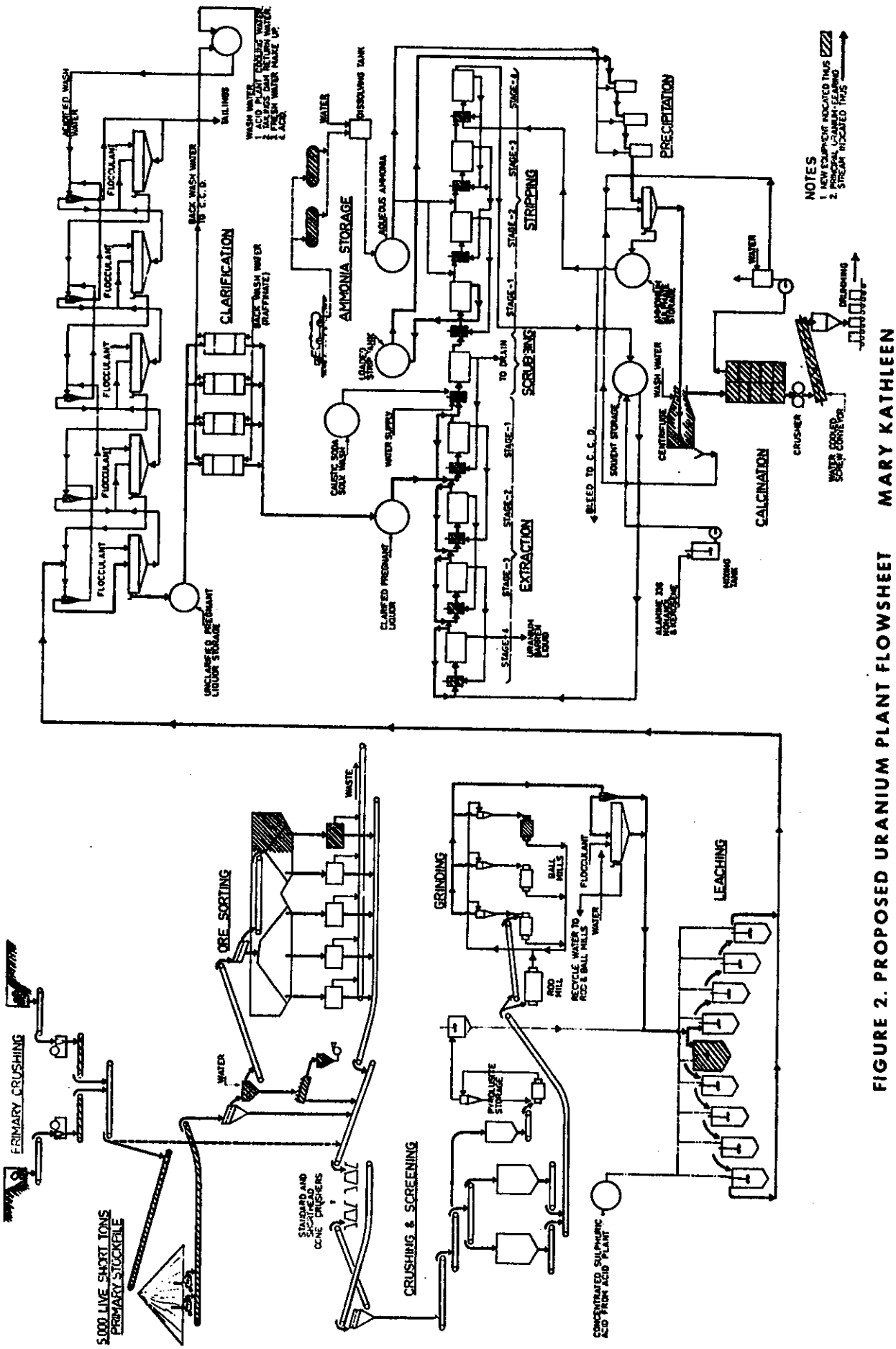


FIGURE 2. PROPOSED URANIUM PLANT FLOWSHEET MARY KATHLEEN

under these conditions.

To lessen these problems, and at the same time increase the sorting installation capacity, it is planned to screen the ore sorter feed into at least two size ranges. Advantage will be taken of this increased capacity to present a slightly lower minimum feed size to the sorters. Therefore a greater overall beneficiation of the ore will be achieved with the same sorting equipment.

Whereas the maximum practical throughput for +3" ore as a single fraction was previously about 140 short tons per hour, for +3" ore split into two size fractions the throughput, as calculated from experimental test runs, should be increased by 15% for similar recoveries and grades. Initially, two screen sizes, -10" + 4½" and -4½" + 2¾", will be fed to the sorters. This will allow a balanced feed with two sorters being used for the coarser fraction and three sorters for the finer fraction. The fifth sorter will be a new one required in any event to handle the higher throughput needed to counteract decreasing feed grades.

The new fifth sorter will perform the same function as the others but its electronic circuitry will be built of solid state components as distinct from the older valve type construction. It is believed that this will lead to substantially better performance with lower maintenance costs. If this does occur, the other sorters will progressively be equipped with solid state components.

3.2 Sand Clarification

With a uranium solvent extraction process, the need for a clear pregnant feed liquor is greater than for ion exchange. A maximum solids content in the feed liquor of 20 ppm is expected to be acceptable. However, since

- on occasion during previous operation, the precoat filters were overloaded
- the pregnant liquor throughput will be increased, and,
- the operating cost for the precoat filters was relatively high at nearly 3¢/lb $U_3O_8$ produced,

the possibility of replacing the precoat filters with pressure sand clarification columns was examined.

As explained below, the decision to replace the ion exchange plant with a solvent extraction system has been made. Thus it will be possible to convert some of the 12 ion exchange columns to pressure sand clarifiers. The

economics of the alternatives of reusing the precoat filters, or installing pressure sand clarifiers using the existing ion exchange columns were compared by developing comparative cost figures. This demonstrated that pressure sand clarification would be superior.

Basically, pressure sand clarifiers can be operated on either the downflow or the upflow principle. There are a number of different bed types available, apart from plain graded sand, which can take advantage of the different principles of operation. For example, if three materials of different specific gravity such as coal, garnet and silica sand are used in a bed then downflow operation can be used while minimising the harmful effects of clogging of the top bed layers as occurs with graded silica sand alone.

The final decision on the type of pressure sand clarifier has not been made but the leaning is towards the downflow type through a graded sand bed similar to that used at the Rum Jungle plant. Previous work at Amdel has also indicated that this method would be suitable for Mary Kathleen pregnant liquors.

### 3.3 Solvent Extraction, Precipitation and Calcination

When considering the choice between ion exchange and solvent extraction in a completely new application, a number of variations on these basic alternatives must be examined. If the resin-in-pulp process is applicable to the particular ore, then it is generally the cheapest route capital wise because there is a large saving as a result of the elimination of the solid-liquid separation circuit. However, solvent extraction generally results in a lower capital cost than fixed bed ion exchange. Relative operating costs often favour solvent extraction, but the degree of advantage is highly dependent on location.

The economic comparison between ion exchange and solvent extraction for Mary Kathleen was based on using the existing ion exchange plant with a new charge of a recently available tertiary amine resin. The original resin has deteriorated and lost too much of its loading capacity to be serviceable under full load conditions. This was compared with the alternative of modifying suitable equipment associated with the ion exchange plant to provide facilities for solvent extraction. Thus it should be emphasised that the comparison of solvent extraction in preference to ion exchange is based entirely on conditions peculiar to Mary Kathleen.

The evaluation showed that in spite of the higher capital expenditure necessary for the solvent extraction plant, the reduction in annual operating costs more than compensated for this and justifies the installation of a solvent extraction plant in the Mary Kathleen situation. The proposed solvent extraction method, as shown in Figure 3, is basically the Purlex process. It involves extraction of the uranium from the clarified pregnant liquor using a tertiary amine solvent in a kerosene diluent. A small percentage (3%) of a fatty alcohol (nonanol) is also included in the kerosene to help with phase disengagement.

After countercurrent extraction in four stages, the solvent will be scrubbed with water in a single stage to reduce the level of impurities such as rare earths. Stripping will then take place in four stages using ammonium sulphate, with pH control being maintained on stages 2 and 3 using 5% aqueous ammonia solution. Intermittent scrubbing of the solvent with sodium carbonate will also be performed. The loaded aqueous strip solution will finally be adjusted to pH 7.5 in three stages with ammonia to precipitate uranium. The yellow cake precipitate will then be thickened to about 30% solids and pumped to a centrifuge where a cake of about 60-70% solids will be produced. This cake will be calcined at 500$^{o}$C in a multiple hearth drier.

A number of the decisions related to the selection of various alternatives in this final section of the treatment plant flowsheet are integrally related. Ammonia was chosen for stripping pH adjustment and for yellow cake precipitation because it is basically cheaper than other alkali reagents for these operations, and it also enables a very high grade product to be produced by calcination, thus reducing the cost of transport per unit of contained $U_3O_8$. Ammonia is driven off in the calcination step whereas the sodium and the magnesium in their respective diuranate yellow cake precipitates remain after calcination. In addition, it is worth noting that, because of the geographical location of Mary Kathleen, an important factor in the selection of ammonia as a more economical reagent than caustic soda or calcined magnesia, is its low molecular weight and hence the reduced freight costs associated with using it.

A comparative list of operating requirements and costs is shown in Table 1 for:

(i) an ion exchange process based on previous experience at Mary Kathleen and recent experimental results with modern weak basic tertiary amine resins, and

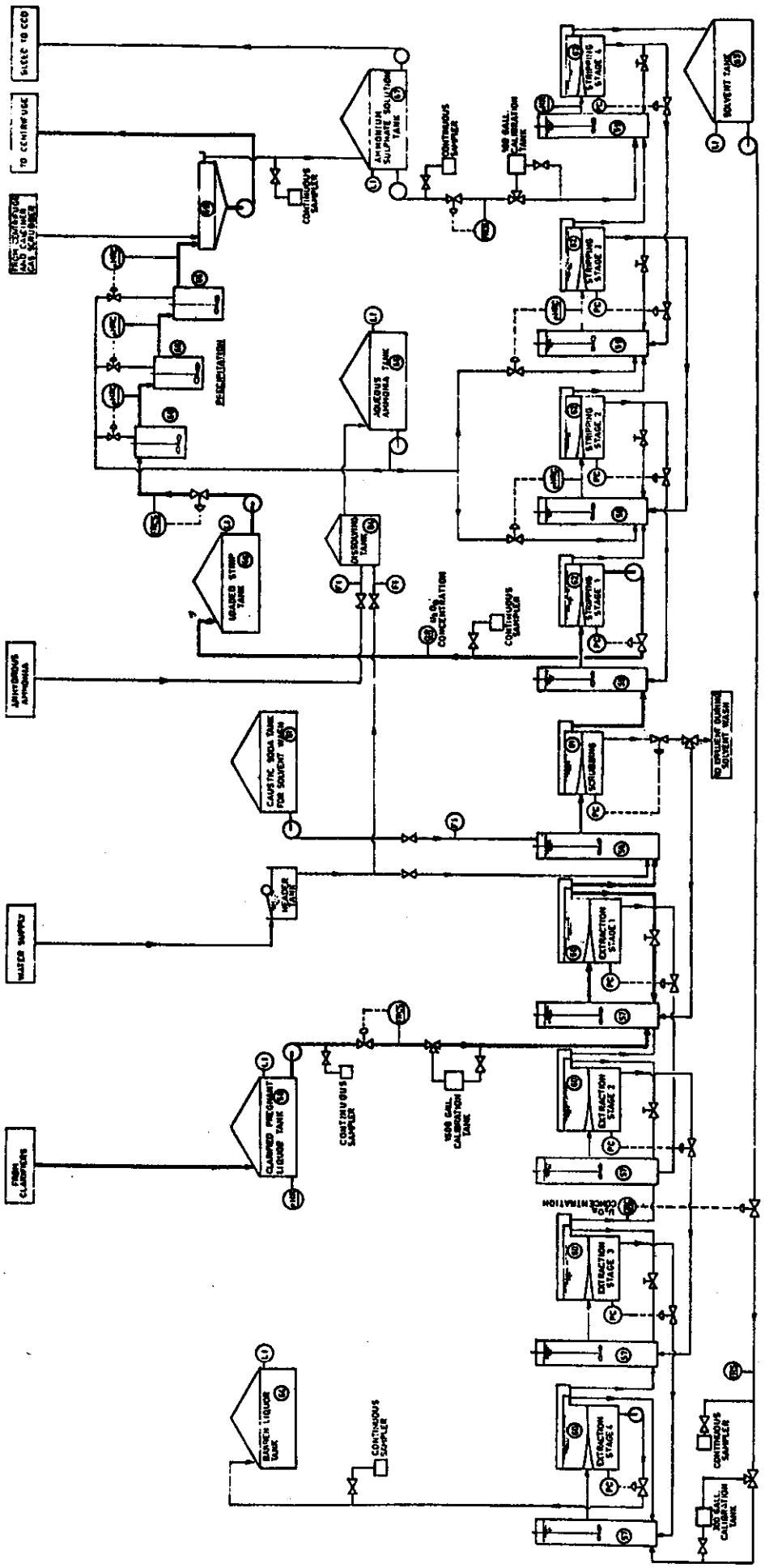


FIGURE 3. SOLVENT EXTRACTION PLANT DETAIL FLOWSHEET MARY KATHLEEN

(ii) the proposed solvent extraction plant.

Precipitation is also allowed for in these requirements.

The effect of the high cost of transporting raw materials to Mary Kathleen has a strong influence on the economics of ion exchange, which uses a larger weight of raw materials in process. Weight can be more important at Mary Kathleen than basic chemical cost. Sodium chloride is an extreme example of this situation. It is also expected that some labour reduction will be possible with the solvent extraction plant.

A solid bowl scroll discharge type centrifuge has been chosen as the replacement for the three stage filtration system for the final yellow cake product. Though the economics are only marginally in favour of the centrifuge there are other qualitative factors which make the choice decisive. One important feature is the elimination of possible contamination of the working area by the enclosed operation of the centrifuge. Another is its ability to handle a slimy precipitate.

### 3.4 Additional Modifications

As well as the alternations already described several other changes to the circuit will be made. The countercurrent decantation circuit (CCD) consisting of five 75' diameter thickeners was previously close to capacity during the final months of operation. Since the ore throughput will increase it is anticipated that the CCD circuit could become overloaded. Therefore a cyclone will be installed to scalp off the heavier and coarser particles of leached ore and only allow the finer and lighter material to reach the thickeners. Coarser material will be washed in a further series of cyclones.

In keeping with the policy of eliminating as much waste as possible, wash water for the CCD circuit will be made up partly by recycle from the liquor dam. At the same time some soluble uranium will be recovered which would otherwise be lost. This raffinate, which has a pH around 2.0, will also be utilised in the heap leaching of waste and low grade ore before recycle, producing some additional uranium and permitting acid to be recovered from the raffinate.

## 4. CONCLUSION

We hope that this brief discussion of the bases for proposed changes in the Mary Kathleen flowsheet will help to illustrate the need for a unique approach to any new uranium processing requirement and the need for constant review of the situation even after the initial choice is made.

TABLE 1

COMPARATIVE OPERATING REQUIREMENTS AND COSTS

| | Solvent Extraction | | Ion Exchange | |
|---|---|---|---|---|
| | Usage lb/lb $U_3O_8$ produced | Cost ¢/lb $U_3O_8$ produced | Usage lb/lb $U_3O_8$ produced | Cost ¢/lb $U_3O_8$ produced |
| **Raw Materials** | | | | |
| Kerosene | 0.133 | 0.41 | | |
| Amine | 0.008 | 0.60 | | |
| Nonanol | 0.070 | 1.46 | | |
| Sulphuric Acid | | | 0.164 | 0.15 |
| Sodium Chloride | | | 2.2 | 4.32 |
| Caustic Soda | | | 0.192 | 1.36 |
| Ammonia | 0.435 | 2.96 | 0.18 | 1.22 |
| Resin | | | $3.38 \times 10^{-4}$ ft$^3$ | 1.76 |
| Sub Total | | 5.43 | | 8.81 |
| Labour | 2 men/shift + 1 man day shift | 2.57 | 3 men/shift 2 men day shift | 3.99 |
| Operating Supplies | 10% of labour | 0.26 | 10% of labour | 0.40 |
| **Utilities** | | | | |
| Water | $1.2 \times 10^7$ gal/yr | 0.02 | $6.7 \times 10^6$ gal/yr | 0.01 |
| Electricity | $1.18 \times 10^6$ kWh/yr | 1.30 | $1.02 \times 10^6$ kWh/yr | 1.12 |
| GRAND TOTAL | | 9.58 | | 14.33 |

NOTE: Costs are in 1972 terms.

AAEC SYMPOSIUM

ON

URANIUM PROCESSING

PAPER VII

# POSSIBLE TRENDS AND METHODS FOR THE PRODUCTION OF HIGH-PURITY PRODUCTS

by

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## 1. INTRODUCTION

The usual product from uranium mills throughout the world has been, up to the present, a semi-refined product known as uranium ore concentrate or yellow cake, containing greater than about 65 wt.% uranium. The yellow cake is shipped to refineries for conversion into 'nuclear purity' natural uranium dioxide ($UO_2$), uranium hexafluoride ($UF_6$) or uranium metal. The $UF_6$ from the refinery is then sent to a gaseous diffusion plant to produce enriched $UF_6$, and this is finally converted into enriched 'nuclear purity' $UO_2$ or uranium metal and fabricated into fuel elements.

In principle, the integration of mining, milling and refining offers the potential of simplification of the overall process by eliminating the precipitation of yellow cake from the leach liquor, drying, and packaging at the mill, and its dissolution at the refinery. The direct operating cost of the three operations above at the mill is 7-11¢/lb of uranium in the yellow cake and this represents about 10% of the total direct milling cost in a medium size mill in the USA or Canada (Ross and Guglielmin 1968). It has sometimes been suggested that refining at the mill site could give the mining company advantages in establishing flexibility in the marketing of their products. Much work and thought has been devoted to the production at the mill site of nuclear purity yellow cake or uranium tetrafluoride ($UF_4$), which is the key intermediate in the route to $UF_6$.

However, there are many technical, economic, and marketing factors which must be considered in evaluating the advisability of producing a refined product at a mill. These will be discussed after a brief review is given of the main processes which have been published for the production of high-purity yellow cake and $UF_4$. The production of $UF_6$ from these intermediates is discussed by Alfredson (1972).

## 2. SPECIFICATIONS OF PURITY

Uranium ore concentrate or yellow cake must usually conform to certain specifications before it is accepted by a refinery for further processing. Penalties are often applied which reflect the increase in refining costs because of higher than normal levels of impurities in the mill product. There are many specifications for 'nuclear purity' uranium products drawn up in different countries for various uses. In general, they follow the same pattern in specifying low levels of elements which have high capture cross-sections for neutrons, or of anions which are known to affect the normal processes adversely. In the USA, the specification depends upon whether the material is sent

to a USAEC plant or to a commercial plant, e.g. Allied Chemical Corporation or Kerr-McGee Corporation. If the material is sent to a commercial plant, the refining operation may involve a more stringent specification, which in turn may require a change in the final steps in the milling process to avoid penalty charges. Typical uranium ore concentrate specifications for both markets are given in Table I (Merritt 1971).

The final product from a refinery is usually of 'nuclear purity', and again the specification may be very different in different countries and for different products, e.g. $UO_2$ or $UF_6$. One of the most stringent specifications is the Canadian one for $UO_2$(Chalder 1961), and this is compared in Table I with the specifications for uranium concentrates. The Canadian specification will be used as a standard with which to compare the products of the various processes described below.

## 3. PROCESSES FOR THE PRODUCTION OF HIGH-PURITY YELLOW CAKE AT A MILL

The three main stages in the production of a normal mill grade uranium ore concentrate are (a) production of a leach liquor from the ore by acid or alkaline leaching, (b) purification of this by an ion exchange or solvent extraction process, and (c) precipitation of the yellow cake with ammonia, magnesia or some other reagent. The mill-grade product is then usually sent to a refinery where it is dissolved in nitric acid and purified by solvent extraction with tributylphosphate to give a nuclear purity uranyl nitrate solution for conversion to a variety of products.

### 3.1 Purification in Alkaline Leach Processes

Alkaline leaching of uranium ores gives greater selectivity for uranium in comparison with acid leaching, and in some mills a satisfactory uranium ore concentrate for further refining has been produced by direct precipitation from the leach liquor, e.g. at the Eldorado Nuclear Mill at Beaverlodge, Canada (Butler 1972). In the three carbonate leaching plants in the USA in 1970, further purification was necessary to obtain a satisfactory product. At the Atlas Corporation mill at Moab, Utah, a resin-in-pulp process was used to purify the uranium, and the product was said to meet the USAEC specification, but to have vanadium, molybdenum, and sodium contents close to the limits for the commercial market (Merritt 1971). At the Cotter Corporation mill at Canon City, Colorado, the initial precipitate with caustic soda has to be redissolved in sulphuric acid and reprecipitated with ammonia to obtain a product with a sufficiently low sodium content. The United Nuclear-Homestake Partners mill, New Mexico, has to roast the initial yellow cake precipitate with soda ash to solubilise the 5-6% $V_2O_5$, and then leach the calcine with water to obtain a

TABLE I. COMPARISON OF REFINERY SPECIFICATIONS FOR URANIUM CONCENTRATE AND THE CANADIAN SPECIFICATION FOR NUCLEAR PURITY URANIUM DIOXIDE

| Constituent | Specification Limit without Surcharge % of U content, or ppm based on U in brackets | | Canadian Specification for $UO_2$ Powder ppm based on U |
|---|---|---|---|
| | USAEC | Allied Chem. | |
| Uranium | 65.0 min | 65.0 min | (73.0% min) |
| Iron | - | 1.54 | 50 |
| Molybdenum | 0.69 | 0.15(1500) | 2 |
| Boron | 0.23 | 0.15(1500) | 0.3 |
| Cadmium | - | - | 0.2 |
| Chromium | - | - | 15 |
| Copper | - | - | 10 |
| Manganese | - | - | 5 |
| Nickel | - | - | 20 |
| Vanadium | 1.26 | 0.23 | - |
| Silicon | - | - | 30 |
| Arsenic | 2.30 | 1.06 | - |
| Thorium | 2.30 | - | - |
| Aluminium | - | - | 25 |
| Magnesium | - | - | 40 |
| Sodium | - | 0.78 | - |
| Potassium | - | 4.60 | - |
| Dysprosium | 0.017(170) | - | 0.15 |
| Gadolinium | 0.017(170) | - | 0.10 |
| Sulphate | 11.5 | 12.3 | - |
| Phosphate | 4.6 | 1.1 | - |
| Carbonate | 4.6 | 2.0 | - |

final product with 0.2-0.8% $V_2O_5$, and 7.5% Na. If a lower sodium content is required the product is redissolved in acid and reprecipitated.

Very little work has been reported on processes for obtaining high-purity yellow cake from alkaline leach liquors. No satisfactory solvent extraction process has yet been devised for processing carbonate leach liquors.

### 3.2 Purification in Acid Leach Processes

The majority of mills have used sulphuric acid to leach the uranium ore, e.g. 13 out of 16 mills in the USA in 1967 (Merritt 1971). Ion exchange (IX) and solvent extraction (SX) have both been used very effectively in many countries in recent years for the primary purification stage, e.g. IX in eight mills, and SX in 14 mills in the US in 1967 (some mills used both processes). The primary aim of almost all of these mills was to produce a concentrate or yellow cake conforming to a USAEC or similar specification.

Several processes have been developed to produce a yellow cake of higher than normal purity at the mill from a sulphate leach liquor by using a two-stage system, e.g. IX followed by SX, or by optimising the extraction, scrubbing and stripping operations in an SX process. The various alternatives are compared in Figure 1 with the processes used to produce normal mill grade product, and are described briefly below.

The two most frequently used SX processes in the USA for the production of normal grade uranium products at the mill are the Amex Process and the Dapex Process (seven mills and three mills respectively in 1967).

#### 3.2.1 Amex Process

In this process a long-chain amine in a kerosene diluent is used to extract uranium from a clarified leach liquor containing about 1-2 g $U_3O_8$/litre, and the uranium is stripped from the loaded solvent with ammonium sulphate, sodium chloride or sodium carbonate solution.

#### 3.2.2 Dapex Process

In this process di-2-ethylhexylphosphoric acid in a kerosene diluent (usually with a small amount of tributylphosphate added) is used to extract the uranium from the leach liquor, and the uranium is stripped from the loaded solvent with sodium carbonate solution.

A purer concentrate can be produced directly from both the Amex and the Dapex processes by stripping the loaded solvent with ammonium carbonate saturated with uranium. This method gives a precipitate of ammonium uranyl

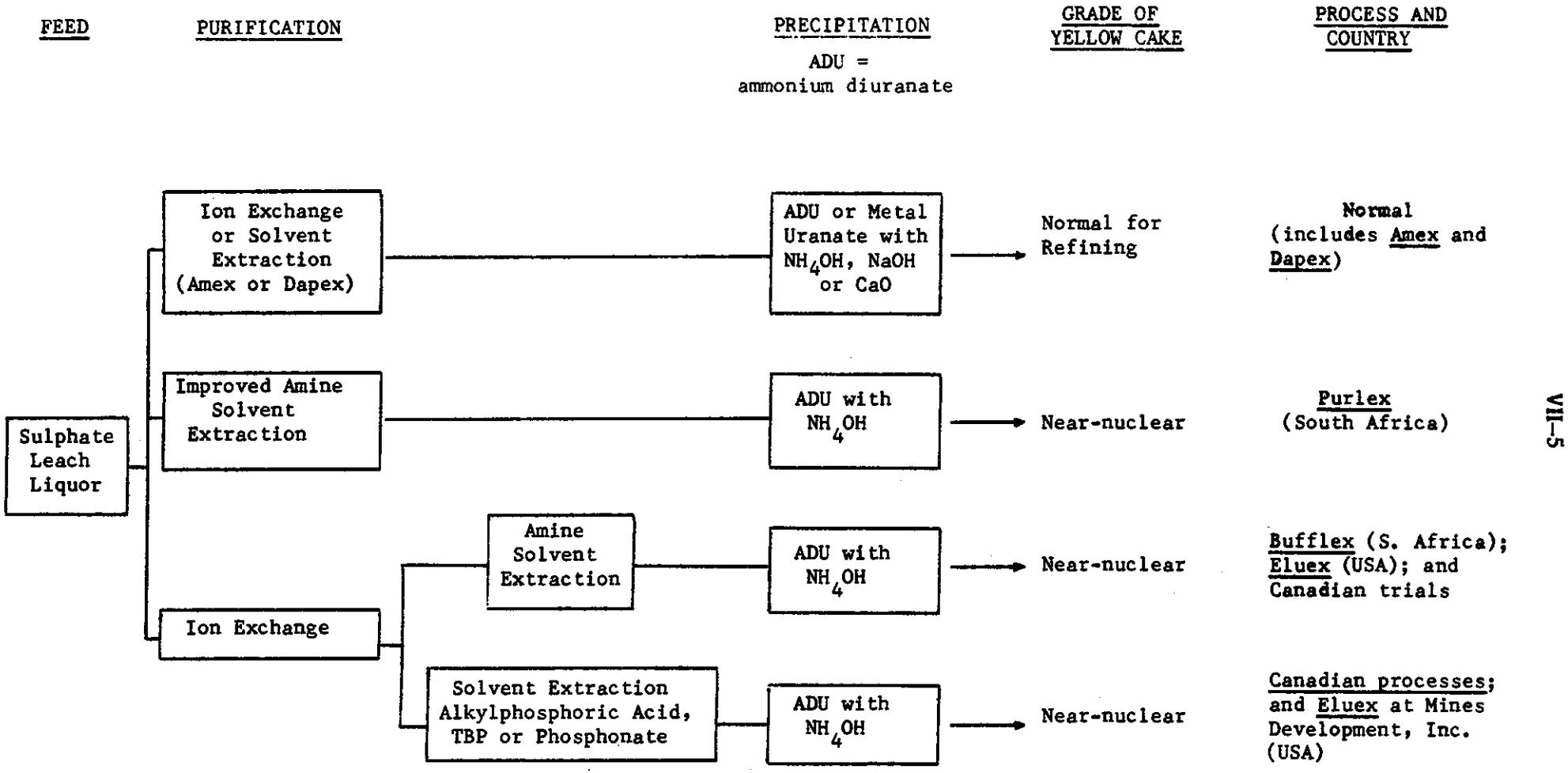


**FIGURE 1. PROCESSES FOR THE PRODUCTION OF HIGH-PURITY YELLOW CAKE**

tricarbonate (AUT) directly and the product is low in sodium, molybdenum and vanadium. The cost was claimed to be less than that of the conventional process with a sodium carbonate stripping stage and the product (after calcination at 500°C) contained 95-97% $U_3O_8$ and less than 0.03% Mo, but it was not of nuclear purity (Merritt 1971).

### 3.2.3 Eluex Process (USA)

This was used in four US mills in 1967. The uranium is first loaded from the sulphate leach liquor onto an ion exchange bed (or a resin-in-pulp system is used) and eluted with sulphuric acid. It is then solvent extracted with an amine (as in the previously described Amex process) or an alkylphosphoric acid (as in the Dapex process). The uranium is stripped from the loaded solvent with a solution of ammonium sulphate (as in the Amex process) or with ammonium carbonate (as in the Dapex process). The combinations of stages used in the four US mills are given in Table II.

TABLE II. URANIUM MILLS USING THE ELUEX PROCESS IN THE USA

| Mill | Capacity ton ore/day | Process Stages |
|---|---|---|
| Federal-American Partners (Wyoming) | 950 | Ion exchange columns; amine extraction |
| Mines Development Inc. (South Dakota) | 500 | Resin-in-pulp; alkyl-phosphoric acid extraction |
| Utah Const. and Mining (Utah) | 1,200 | Moving bed ion exchange; amine extraction |
| Western Nuclear Inc. (Wyoming) | 1,200 | Resin-in-pulp; amine extraction |

This process is claimed to have several advantages (Merritt 1971):

(i) Nitrates and chlorides are not used. This permits more of the tailings solutions to be recirculated, and eliminates pollution problems associated with nitrates.

(ii) No neutralisation, or other adjustment, is required on the solvent extraction feed, and make-up acid need

be added only to compensate for actual consumption in the IX and SX circuits.

(iii) A large saving in reagent costs is possible by substituting sulphuric acid for the more expensive nitrates or chlorides. In conjunction with ammonium sulphate stripping and ammonia precipitation, chemical costs in this process are about half those required for earlier processes.

(iv) A purer product is obtained compared with the use of either an IX or a SX process on its own. However, the product is not of nuclear purity, and recent modifications of the basic process (e.g. in Canada, see below) have had difficulty in meeting the specification for molybdenum and rare-earth elements.

### 3.2.4 Canadian processes

In 1961 the Canadians published work on three solvent extraction processes similar to the Eluex process and designed to follow an initial ion exchange process to produce high-purity yellow cake:

(i) tributylphosphate extraction from a nitrate eluate from the ion exchange columns, followed by a water strip;

(ii) dibutyl butyl phosphonate extraction from a nitrate eluate, followed by an ammonium sulphate strip;

(iii) amine extraction from a sulphate eluate, followed by an ammonium sulphate strip.

The ammonium diuranate products from the tests in small pilot plants did not fully meet the tight Canadian specification, mainly with respect to a few heavy elements, e.g. molybdenum, copper, rare-earths. The conclusions were that all three processes were technically feasible with the amine process being the most attractive with a saving in reagent costs of 10¢/lb $U_3O_8$. The phosphonate process had a small additional cost of 3¢/lb $U_3O_8$, and the TBP process a large additional cost of 17¢/lb $U_3O_8$, compared with the normal two-stage precipitation process used on the eluate from the primary ion exchange process.

### 3.2.5 Bufflex Process

In this South African version of the Eluex Process, the leach liquor is first loaded onto an ion exchange column and stripped with sulphuric acid. The uranium is then solvent extracted with an amine, Alamine 336, scrubbed with water or dilute ammonia solution, and stripped with ammonium sulphate. In

1966, the operating cost of the process was claimed (Faure 1966) to be cheaper by at least 5¢/lb $U_3O_8$ compared with the conventional ion exchange process, but a detailed estimate of the capital cost of the respective plants was not made.

This process has now been superseded in South Africa by the Purlex Process, in which the ion exchange step is not required, and plants constructed recently have been claimed to give a greater saving in operating costs (Meyburgh 1970). However, this saving is offset by a reduction in the purity of the product, because the Bufflex process gave significantly lower amounts of cobalt, iron, molybdenum, silicon and zirconium than does the Purlex process. The Bufflex process did not, however, give a product of nuclear purity.

### 3.2.6 Purlex Process

This process is similar in many respects to the Amex solvent extraction process as practised in the USA. An amine, Alamine 336, is used to extract the uranium directly from a sulphate leach liquor, typically containing 0.3 g U/litre and 16 to 20 g sulphate/litre. The loaded solvent is scrubbed with sulphuric acid and then with an ammonium sulphate solution to remove impurities such as iron, arsenic and silica. The product is finally stripped from the loaded organic phase with ammonium sulphate solution assisted by hydrolysis with ammonium hydroxide solution. This process was previously considered not to be practicable because the treatment of a large volume of low grade liquor would lead to an unacceptable loss of solvent, e.g. compared with the Bufflex Process which was fed with a more concentrated uranium solution from an ion exchange stage.

The purity of the final yellow cake product was found (Meyburgh 1970) to vary widely and the average concentrations of several significant elements, e.g. boron, molybdenum, iron and silicon, were well outside the Canadian specification for nuclear purity, and even outside the less stringent South African Atomic Energy Board specification (Faure 1966) for some elements. Nevertheless, a plant was commissioned in 1968 at Buffelsfontein to treat 1,600 gal/min of leach liquor for an annual production of 780 short tons $U_3O_8$. The saving in operating costs estimated from pilot plant operations was claimed to be 21¢/lb $U_3O_8$ produced compared with the conventional ion exchange process used previously, and 8¢/lb $U_3O_8$ compared with the Bufflex Process.

Further work was under way in 1970 to reduce solvent losses to the minimum set by a solubility of about 4 ppm, to improve the purity of the product (although it is believed that a satisfactory $UF_4$ can be made from the present

product), and to reduce the fire hazard of the flammable solvent mixture.

The solvent extraction process proposed (Baillie and Thomas 1972) for the future operations at the Mary Kathleen plant is basically the Purlex Process, with four stages of amine extraction, one stage of water scrubbing, and four stages of stripping with ammonium sulphate (two of these stages having ammonia addition). The operating cost estimate indicates a saving of 5.65¢/lb $U_3O_8$ at a throughput of 1,000 tons $U_3O_8$/year compared with the ion exchange process used previously.

## 4. PROCESSES FOR THE PRODUCTION OF HIGH-PURITY $UF_4$

Uranium tetrafluoride ($UF_4$ or green salt) is a key intermediate in the production of $UF_6$ for enrichment, and has also been used in the past for the production of uranium metal. It can be produced in high purity by either a 'dry' or a 'wet' route.

In the 'dry' route, the yellow cake or ore concentrate is treated, usually by dissolution in nitric acid and solvent extraction with tributylphosphate, to make a solution of uranyl nitrate of nuclear purity. The uranyl nitrate is converted into uranium trioxide by precipitation of pure yellow cake and calcination, or by evaporation and thermal denitration. The resulting $UO_3$ is reduced to $UO_2$ with hydrogen and hydrofluorinated to $UF_4$ with anhydrous hydrogen fluoride. These reactions need to be closely controlled, and require relatively expensive raw materials, and it is not generally considered to be possible to use the dry route to make $UF_4$ at a remote mill site. It has therefore only been used at a central refinery.

Several different processes based on a 'wet' route have been used, or suggested, in various countries (Table III). Some of these have been developed specifically for use at a mill site. Each of them is briefly described below.

### 4.1 Excer Process

In 1956 workers at the Oak Ridge National Laboratory developed a method, known as the Excer process, for producing uranium tetrafluoride from aqueous solutions (Higgins et al. 1958). In this process, ion exchangers were used to prepare purified concentrated aqueous solutions of uranyl chloride directly from sulphuric acid leach liquors, sulphate or chloride concentrates, or nitrate concentrates from solvent extraction processes. A chloride medium was preferred to a sulphate one, because of the low decontamination factor for sulphur across the final precipitation stage. The uranium in solution was then reduced either chemically, with metallic iron, or electrolytically, and the

TABLE III. AQUEOUS PROCESSES FOR THE PRODUCTION OF HIGH-PURITY $UF_4$

| Process | Country of Development | Date | Outline* |
|---|---|---|---|
| Excer | USA | 1956 | (a) Ion exchange; chloride conversion; water strip; chemical or electrolytic reduction; precipitation;<br>(b) later version: anion exchange; sulphate elution; iron reduction; anion exchange; sulphate elution; cation exchange; chloride elution; precipitation. |
| Winlo | USA | 1958 | Amine extraction; chloride conversion; reduction-precipitation with $SO_2$/copper/HF |
| Dow | USA | 1958 | Ion exchange, amine or phosphate extraction; iron or electrolytic reduction; second stage SX; precipitation. |
| "French" | France | 1964 | Ammonium uranium fluoride precipitation with $SO_2$ and fluoride. |
| SIMO | France | 1970 | Uranyl nitrate feed; sulphate conversion; electrolytic reduction; precipitation. |
| PNC | Japan | 1970 | Amine extraction; chloride conversion; electrolytic reduction; precipitation. |

* All of the processes end with the dehydration of a $UF_4$ hydrate (except the "French" process)

uranium was precipitated by the addition of hydrofluoric acid to the heated solution. The green salt was collected and dried. The advantages of the Excer process were claimed to be its adaptability, the reduction of the number of operations required, and the good decontamination achieved because there are two purification stages, viz. the ion exchange stage and the precipitation stage.

### 4.2 Winlo Process

In this process, developed in 1958 at the laboratories of the National Lead Company of Ohio (Allen et al.1958, Cseplo and Fogel 1964), liquid ion exchangers were substituted for solid ion exchange resins in the concentration and purification step, and a catalytic reduction stage was used to produce the uranium(IV) solution. The uranium in the leach liquor was solvent extracted using a tertiary-amine and stripped from the organic solvent with hydrochloric acid to produce an aqueous solution of uranyl chloride. The uranium was then reduced in solution using sulphur dioxide gas with copper(II) as a catalyst. In the chloride medium, sulphur dioxide reduced the copper(II) to copper(I) ions which in turn reduced the uranium. The reduction was carried out at elevated temperature, in the presence of fluoride ions, and the tetrafluoride was precipitated as the uranium was reduced. The originators of the process claimed a denser product was obtained than that from the Excer process.

### 4.3 Dow Processes

Investigators at the laboratories of the Dow Chemical Company reported a variety of methods for obtaining high-purity uranium tetrafluoride from aqueous solutions (Long et al.1958). They employed alkyl phosphates, amines or ion exchange resins for the recovery of the uranium from the sulphate leach liquor. The uranium in the stripped solutions was reduced chemically (with iron) or electrolytically, and the solution of tetravalent uranium was further purified with an amine or alkylphosphate before precipitation of the tetrafluoride.

### 4.4 SIMO Process

This process was developed in France, and was installed at the Eurochemic reprocessing plant at Mol, by a combine of several European companies and institutes and uses a uranyl nitrate feed solution (Weinhold 1970). Conversion to the sulphate form was achieved by heating the uranyl nitrate with concentrated sulphuric acid at approximately 120°C, and this was followed by electrolytic reduction and precipitation at 95°C.

### 4.5 PNC Process

The Power Reactor and Nuclear Fuel Development Corporation of Japan recently announced the development of the PNC process (Takada et al.1971). This process combines features from both the Excer and Winlo processes. Uranium is recovered from the sulphate leach liquor by extraction with tri-n-octylamine (TNOA). Whilst still in the organic phase, the uranium is converted from a sulphate to a chloride species by washing with 8M HCl (chloride conversion step as with the Amex process). The chloride species is then stripped from the organic phase with 0.05M HCl, electrolytically reduced, and hydrofluoric acid is added to precipitate the uranium as the tetrafluoride. The $UF_4$ hydrate is dried at 350°C under nitrogen gas. The amine solvent and the chloride are recycled. The process gains over the Winlo process in that no foreign substances are added in the reduction stage.

The PNC process has been tested on a pilot plant scale up to the purified uranyl chloride stage at the Ningyo-Toge Mine in Japan using uranium ores containing 0.03-0.15% $U_3O_8$. The uranyl chloride solution was then converted to $UF_4$ at the Tokai Pilot Refinery. The product was claimed to be of reactor grade (or nuclear purity) and the production cost ($2.68/lb $U_3O_8$*) to be lower than that of the conventional processes which go through a yellow cake stage (see section 6.3).

### 4.6 French Process

In this process (Robinson et al.1964), a double fluoride, $UF_4.NH_4F$, is precipitated by sulphur dioxide from a solution containing ammonium fluoride, uranyl nitrate, and formic acid at about 80°C. Uranous ions, formed by reduction of hexavalent uranium by nascent hyposulphurous acid, combine with the alkali fluoride to precipitate the unhydrated uranous ammonium salt, which is decomposed by heating to $UF_4$ in a fluidised bed. The process has the disadvantage of the need for pure reagents to avoid contamination of the product. It was estimated to be more expensive in overall manufacturing costs than the equivalent 'dry way' process (MacMillan et al.1965).

## 5. PROCESSES FOR THE PRODUCTION OF OTHER HIGH-PURITY PRODUCTS

Processes have been used or proposed for the production of uranyl nitrate, uranium peroxide, and uranium dioxide of high purity at a mill. These are briefly reviewed below.

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*All costs in this paper are expressed in US dollars.

### 5.1 SIMO Process

This process is operated by the Societe Industrielle des Minerais de l'Ouest at the "Le Forez" plant, near Vichy in France. The plant was commissioned in 1960 and was designed to process a specific ore from the Black Woods deposit near the plant, although small tonnages of other ores have been blended with it on occasions. The process uses sulphuric acid leaching, precipitation in two stages with lime, calcination to crude yellow cake (15-30% U), dissolution in nitric acid, and solvent extraction with tributylphosphate to give a high-purity uranyl nitrate product at a capacity of 330 tons U/annum. No details of the purity have been published but it is claimed that it can be nuclear purity if desired (SIMO 1970).

### 5.2 Uranium Peroxide Processes

The selective precipitation of uranium as the peroxide has been applied in refinery processes since the mid-1940s, and has been studied for possible use in ore treatment plants in South Africa and Canada (Merritt 1971). Its use in a milling process was reported by the Climax Uranium Company in Colorado. They obtained a product which met the yellow cake specification for shipment to a refinery at a cost somewhat greater than that of more conventional processes. However, the extra cost was more than offset by the savings in penalty charges which might otherwise have been imposed by the refinery for excessive levels of impurities.

### 5.3 Yugoslav $UO_2$ Process

Uranium can be precipitated from carbonate solution by hydrogen reduction with the advantage that nearly quantitative recovery can be obtained and the barren solution can be recycled to the leaching stage. The method was first investigated in Canada (Forward 1953) in the early 1950s for the treatment of low-grade liquors.

More recently it has been studied on a pilot plant scale in Yugoslavia (Bunji and Zogovic 1958). Solutions containing 0.6 g U/litre were treated successfully at a cost reported to be lower than that for concentration by ion exchange followed by a conventional precipitation process. The reduction and precipitation of the uranium are accomplished by treating the carbonate solution with hydrogen under pressure at up to 200°C in the presence of a catalyst. In later work it was found that finely-precipitated $UO_2$ was a suitable catalyst, with obvious advantages. The disadvantages of the process are the need to operate with hydrogen under pressure (10 atmospheres), and temperature

(200°C), and the accompanying high capital cost and maintenance cost of the equipment. The product is not of nuclear purity, but is of much higher purity (in the absence of large amounts of vanadium) than the usual yellow cake.

## 6. ECONOMIC AND MARKETING FACTORS

### 6.1 Production of Normal Purity Yellow Cake

The total cost of producing uranium ore concentrate or yellow cake of normal purity for further purification in a central refinery includes the costs of mining, ore haulage, and milling. Typical production costs are given in Table IV for open pit operations in the USA up to 1966, but adjusted to 1970 by Merritt (1971), based on 95% recovery of uranium from a 0.25% $U_3O_8$ ore (5 lb $U_3O_8$/ton). Costs for underground mining were about 9% higher.

TABLE IV. TYPICAL PRODUCTION COSTS

| | 200 ton ore/day plant | | 1000 ton ore/day plant | |
|---|---|---|---|---|
| | $/ton | $/lb $U_3O_8$ | $/ton | $/lb $U_3O_8$ |
| Mining | 12.00 | 2.53 | 11.50 | 2.42 |
| Ore Hauling | 2.00 | 0.42 | 2.00 | 0.42 |
| Mill Operating | 9.75 | 2.05 | 5.72 | 1.20 |
| Mill Amortisation* | 2.78 | 0.59 | 1.64 | 0.35 |
| TOTAL | 26.53 | 5.59 | 20.86 | 4.39 |

*based on 10-year amortisation period and mill construction costs of $2M for a 200 ton ore/day plant and $5.9M for a 1000 ton ore/day plant

In an Australian situation in, for example, the Northern Territory, it is likely that a higher feed grade of ore than 5 lb $U_3O_8$/ton would be available, which would decrease the milling cost component/lb $U_3O_8$ significantly, but the cost of the mill and infrastructure would be considerably higher, which would increase the mill amortisation component.

The direct operating costs of the milling stage were summarised by Ross

and Guglielmin (1968) for several mills in the USA and Canada. The range was from \$0.88/lb $U_3O_8$ for 2000-3500 tons ore/day of 4 lb $U_3O_8$/ton grade at Ambrosia Lake, New Mexico, to \$1.59/lb $U_3O_8$ for 1000 tons ore/day of 2.2 lb $U_3O_8$/ton grade at Bancroft, Ontario. Between 30 and 55% of these costs were for chemicals and grinding media.

With this background of costs, the savings claimed for processes giving higher-purity products can be judged qualitatively, although it is difficult to determine what has been included or excluded in much of the published information.

6.2 Production of High-Purity Yellow Cake at a Mill

Several processes have been used (e.g. Eluex, Purlex) or suggested (Canadian) to produce a yellow cake concentrate of higher than normal purity, but not one of these processes has clearly achieved a product of nuclear purity at a mill. However, the higher purity has generally been achieved at a lower cost than by the conventional ion exchange or solvent extraction processes used in early plants. The savings in operating costs claimed over the conventional ion exchange process are summarised in Table V.

TABLE V. SUMMARY OF ESTIMATED SAVINGS IN DIRECT OPERATING COSTS FOR IMPROVED PROCESSES

| Improved Process | Saving ¢/lb $U_3O_8$ |
|---|---|
| Eluex (USA) (Merritt 1971) | 20-30 |
| Bufflex (South Africa) (Faure 1966) | 5 |
| Purlex (South Africa) (Meyburgh 1970) | 21 |
| Canadian (IX + Amine SX) (Simard et al.1961) | 10 |
| Purlex (Mary Kathleen proposed plant) (Baillie and Thomas 1972) | 5.65 |

The savings given for the Eluex Process are calculated by assuming a 50% saving in the cost of chemicals, which represents 40% of the average direct milling cost of \$0.88-1.59/lb $U_3O_8$. However, higher capital and therefore financial costs for IX + SX circuits, compared with only an IX circuit, will partly offset this saving.

These savings can be compared with

(a) the range or normal operating costs quoted above of \$0.88-1.59/lb $U_3O_8$ for plants of greater than 1,000 tons ore/day capacity, and

(b) the saving of 7-11¢/lb $U_3O_8$ to be expected (Ross and Guglielmin 1968) from integrating milling and refining by eliminating the precipitation of yellow cake, drying, and packaging (if this were possible).

It is apparent that the Eluex Process, or the South African Purlex version, is the most attractive, and explains why a number of plants based on this process are being planned or are under construction in South Africa at mines where the ore reserves and the life of the mine justify the capital expenditure. It is interesting that the cost savings quoted in South Africa (Meyburgh 1970) refer to a large plant capacity of 8,300 tons ore/day, but because the grade is only 0.5 lb $U_3O_8$/ton, this corresponds to only 780 short tons $U_3O_8$/year.

The lower cost saving estimated for the Mary Kathleen plant is possibly due to the effect of the remote location with the higher cost of transport of raw materials, etc. The comparable throughput is 2,000,000 lb $U_3O_8$/year or 1,000 short tons $U_3O_8$/year.

### 6.3 Production of High-Purity $UF_4$ at a Mill

Published information on the wet processes for the production of $UF_4$ at a mill is mostly of a technical nature and refers to laboratory work, or small pilot plants. The only process for which a recent estimate is available (Takada et al.1971) is the PNC process which has been demonstrated to give nuclear purity $UF_4$ from low-grade leach liquor on a pilot plant scale. The production cost from ore to $UF_4$ was estimated by scaling up pilot plant information as \$2.68/lb $U_3O_8$, made up of 27% for depreciation and 73% for direct operating costs, for a plant treating 1,000 tons ore/day of 0.12% $U_3O_8$ grade (2.4 lb $U_3O_8$/ton). The above scale of production is only 360 tons $U_3O_8$/year (308 tonne U/year). This is much lower than the likely production rate of future uranium mills in Australia, which are also likely to have feed grades of ore containing much higher than 2.4 lb $U_3O_8$/ton.

The production cost of normal grade yellow cake at a mill can be estimated (Merritt 1971) as a function of throughput in tons ore/day, feed grade in lbs $U_3O_8$/ton, and various assumptions on the financial costs. One can then estimate the cost of all of the stages in going from ore to $UF_6$ delivered to

an enrichment plant. However, it is not possible to do this at present with published information on the PNC process (or on any other wet process for the production of $UF_4$) and therefore a meaningful comparison cannot be made of the normal yellow cake route with the PNC route.

It appears that the production of nuclear purity $UF_4$ at a mill is technically feasible but it is likely that the PNC process will only show an overall cost-saving (for ore to $UF_6$) if the $UF_6$ conversion plant is specially designed to take the $UF_4$ feed, and not uranium ore concentrate (UOC) feed. The operator of an existing conversion plant designed for a UOC feed is unlikely to be able to offer a customer a large saving in toll conversion costs if nuclear purity $UF_4$ is supplied instead of UOC (probably only 14¢/lb U on a cost of $1.31/lb U for toll conversion to $UF_6$) (Costello 1972).

There are several possible disadvantages for a mill operator in producing nuclear purity $UF_4$ for export rather than normal-grade yellow cake:

(i) At present, refining capacity in North America, in the UK, and in Europe, appears to be adequate for the next few years. A new refinery using a USAEC flowsheet with a capacity of 5,000-10,000 tons UOC/year has commenced operation (USAEC 1971) in Oklahoma for the Kerr-McGee Corporation, and Eldorado Nuclear Limited have indicated their intention of adding to their Port Hope Plant to convert UOC to $UF_6$ (Ross and Guglielmin 1968). British Nuclear Fuels Ltd in the UK are planning to add a second unit to convert $UF_4$ to $UF_6$ at their Springfields plant and are likely to expand the capacity of the earlier stages of their refinery operations.

(ii) Refineries usually have a minimum capacity of 2,500-5,000 tons U/year, and this is larger than most individual mills. It represents a considerable economic advantage of larger scale for the refinery compared with a small mill.

(iii) A remote mill site is usually at a disadvantage compared with a central refinery in the costs of chemicals, power and labour.

(iv) It is likely that further development will be needed to guarantee the routine production of nuclear purity $UF_4$ on a large scale at a mill compared with an established process for producing normal-grade yellow cake.

The conclusion from the above comments is that, to be economically attractive, a new mill would have to have a long-term guaranteed market for its nuclear purity $UF_4$ product, probably to a special conversion plant designed to accept $UF_4$ and convert it to $UF_6$ at minimum capital cost and operating cost. Otherwise the mill operator would be better advised to produce high-quality yellow cake for export to a wide range of possible refineries.

## 7. POSSIBLE TRENDS

The trend over the last few years has been for uranium mills to use improved solvent extraction processes based on amines to obtain high-purity (but not nuclear purity) yellow cake. They are thus able to obtain or predict a saving in direct operating costs over conventional ion exchange processes while still obtaining a high-quality product. The yellow cake product is easy to export at present and fits readily into the overall conversion process to $UF_6$ or to uranium metal and natural ceramic-grade $UO_2$.

The production of nuclear purity $UF_4$ appears to be technically feasible at a mill, but may require further development work to guarantee routine production at this purity on a large scale. The $UF_4$ production at a mill would almost certainly have to be closely coupled to a specially designed conversion plant to optimise the costs of the overall route.

There is a continuing effort to improve the early stages of the overall process of ore to $UF_6$, and further cost savings are likely to be obtained in the stages of ore crushing, grinding, leaching, solid-liquid separation and purification.

Examples of the possible savings in grinding and leaching stages are:

(a) the recently published (Garrett and Smith 1970) development work in the UKAEA on the use of high concentrations of sulphuric acid to leach uranium ores (similar to some earlier pug-leaching processes). This process reduces the amount of grinding required, and the cost of liquid-solid separation after leaching, and also gives coarser tailings which can be separated and contained more readily. A preliminary capital cost estimate for a 3,000 ton ore/day plant for Elliot Lake ore was \$8M, compared with \$12M for a conventional plant. This is equivalent to a financial saving of \$0.26/lb $U_3O_8$ when amortised over seven years. The saving in direct operating costs was estimated to be about \$0.10/lb $U_3O_8$,

giving an overall reduction of \$0.36/lb $U_3O_8$. This is a substantial fraction of the overall production cost of \$1.53/lb $U_3O_8$ given for the Elliot Lake Plant in Canada (Ross and Guglielmin 1968).

(b) Conventional crushing and fine grinding have been eliminated at the new 1,200 ton ore/day Shirley Basin Plant of the Utah Construction and Mining Company in Wyoming, USA (Ritchie 1971). Run-of-the-mine ore is fed to a special cascade mill to be ground in water and classified in a closed circuit. This stage gives a 60% solids pulp which is leached continuously in pachucas and the product is fed to an ion exchange plant. A 50% saving in operating costs up to the ion exchange plant is claimed.

Although solvent extraction processes are popular at present, ion exchange resin-in-pulp processes are being used, or are being recommended seriously, to achieve reductions in both capital and operating costs over the solvent extraction processes for the purification of the leach liquor. The following examples are given:

(a) the recent work in the UKAEA (Garrett and Smith 1970) indicated that a resin-in-pulp process designed for Elliot Lake ore would save about \$0.06/lb $U_3O_8$ compared with solvent extraction if conventional resins were used, or a slightly higher saving if the new weak-base resins were used.

(b) The US Bureau of Mines calculated (Rosenbaum and George 1971) that an ion exchange resin-in-pulp plant of 2,000 ton ore/day capacity would have a 27% lower capital cost than a conventional solvent extraction plant, and a 20% lower operating cost (a saving of at least \$0.20/lb $U_3O_8$).

(c) Two mills in the USA are using resin-in-pulp circuits successfully in the first stage of Eluex Processes in which the second stage of purification is solvent extraction (Merritt 1971).

(d) The National Institute for Metallurgy in South Africa concluded in 1971 that "continuous ion exchange should be chosen in preference to Purlex-type liquid-liquid extraction for most new uranium plants". They obtained

greater than 99.5% extraction of uranium from unclarified pregnant liquor with a resin inventory less than a third of that using the old fixed-bed ion exchange plants.

However, further developments in solvent extraction processes using a solvent-in-pulp system are likely. Solvent losses have in the past been the main disadvantage of this system. Some early work was done in Australia by Byerlee (1969) who used packed towers. Ritcey (1971) at the Canadian Department of Energy, Mines and Resources, has recently obtained low solvent losses, e.g. 0.1 lb/ton dry feed, by using sieve-plate pulsed columns and this compares favourably with conventional solvent extraction circuits. He estimated cost savings of \$0.08/lb $U_3O_8$ for solvent extraction from a slurry, over ion exchange from a slurry, and \$0.20/lb $U_3O_8$ over solvent extraction from a clarified leach solution, because of the large savings due to eliminating the liquid-solid separation stage. These estimates refer to a 3,000 ton ore/day plant with an Elliot Lake ore of 0.1% $U_3O_8$.

The conclusion from the several examples given above is that significant further savings can be made in the stages from ore to purified uranium solution, and that these improved processes are likely to benefit a plant to produce either high-quality yellow cake or nuclear purity $UF_4$. These trends are to be welcomed in principle and keenly awaited in practice.

## 8. REFERENCES

Alfredson, P.G. (1972) - Review of methods and technology for the production of Uranium Hexafluoride. Paper presented to this Symposium.

Allen, R.J., Petrow, H.G., Whitman, A. (1958) - Preparation of dense, metal grade Uranium Tetrafluoride from uraniferous ores. Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva. Vol. 4, 121-124, United Nations, Geneva.

Baillie, M.G. and Thomas, J.A. (1972) - Planned changes in the Mary Kathleen treatment plant for future operations. Paper presented to this Symposium.

Bunji, B. and Zogovic, B. (1958) - Reduction of Uranium from carbonate solutions with Hydrogen using $UO_2$ as catalyst. Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva. Vol. 3, 350-55, United Nations, Geneva.

Butler, R.D. (1972) - Carbonate leaching of Uranium ores - a review. Paper presented to this Symposium.

Byerlee, H.W. (1969) - The solvent extraction of Uranium from slurries. Paper

presented to Annual Conf. of the Australasian Institute of Mining and Metallurgy, Sydney, August, 1969.

Chalder, G.H. (1961) - Uranium Dioxide powder for the manufacture of high density sintered pellets. AECL-1327 (Issue 1).

Costello, J.M. (1972) - Capital and operating costs for the production of Uranium Hexafluoride. Paper presented to this Symposium.

Cseplo, S. and Fogel, C.C. (1964) - Pilot plant production of Uranium Tetrafluoride by the Winlo aqueous precipitation method. NLCO-901.

Faure, A. (1966) - The production of high purity Uranium at a South African gold mine. J. Sth Afr. Inst. Min. and Met. 6 319-341.

Forward, F.A., Halpern, J. and Peters, E. (1953) - Studies in the carbonate leaching of Uranium ores. Can. Min. and Met. Bull. 46 (498) 634.

Garrett, K.H. and Smith, S.E. (1972) - Some recent developments in the extraction of Uranium from its ores. Paper presented at a Symposium on Chemical Engineering Developments in Mineral Processes, London, March 1972. See also Proc. Symp. on the Recovery of Uranium from its ores and other sources. Sao Paulo, Brazil, August, 1970. IAEA Vienna STI/PUB-262, 3-16.

Higgins, I.R., Neill, W.J., and McNeese, L.E. (1958) - The Excer process: an aqueous method for production of pure Uranium Tetrafluoride from crude Uranium sources. Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva. Vol. 4, 113-17. United Nations, Geneva.

Long, R.S., Ellis, D.A. and Magner, J.E. (1958) - Improved methods for the preparation of high-purity Uranium salts. Proc. 2nd Int. Conf. on Peaceful Uses of Atomic Energy, Geneva. Vol. 4, 118-120. United Nations, Geneva.

Macmillan, I.C., Paynter, J.C. and Geertsma, J.C. (1965) - Fluorox process: conversion of Uranyl Fluoride ($UO_2F_2$) to Uranium Tetrafluoride ($UF_4$). South African Atomic Energy Bd. PEL-121, Vol. 2, 161.

Merritt, R.C. (1971) - The extractive metallurgy of Uranium. TID-25711.

Meyburgh, B.G. (1970) - Design, erection and operation of a Purlex plant at Buffelsfontein Gold Mining Company Ltd. J. Sth Afr. Inst. Min. and Met. 71 (3) 55-56.

National Institute of Metallurgy, South Africa (1971) - Annual Report, 23.

Ritchie, M.I. (1971) - Utah Construction and Mining Company's unique Shirley Basin Uranium Mill. Proc. Symp. on the Recovery of uranium from its ores and other sources. Sao Paulo, Brazil, August, 1970. IAEA Vienna STI/PUB-262, 147-56.

Ritcey, G.M. (1971) - Solvent-in-pulp processing using sieve plate pulse columns. Chemistry and Industry, No. 45 (1971) 1294-1299.

Robinson, R.E., Geertsma, J.C., Muir, C.W.A. and Peratides, G. (1964) Laboratory and pilot tests on the production of Ammonium Uranous Fluoride in refining operations. Proc. 3rd Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva 31st August - 9th September 1964, Vol. 12, 281.

Rosenbaum, J.B. and George, D.R. (1971) - Cost reductions in ion exchange processing of Uranium ores. Proc. Symp. on the Recovery of Uranium from its ores and other sources, Sao Paulo, Brazil, August, 1970. IAEA Vienna STI/PUB-262, 297-309.

Ross, A.H. and Guglielmin, L.G. (1968) - Milling technology of Uranium ores. Nuclear Applications 5 311-18. See also Trans. Amer. Nucl. Soc. 11 121-2.

Simard, R., Gilmore, A.J., McNamara, V.M., Parsons, H.W. and Smith, H.W.(1961)- Treatment of Uranium leach plant solutions by liquid-liquid extraction to produce high purity Uranium products. Can. J. Chem. Eng. 39 (6) 229-34.

SIMO (1970) - Societe Industrielle des Minerais de l'Ouest - boulevard de l'Amiral-Bruix, Paris; Brochure.

Takada. S., Amanuna, T. and Fukuda, G. (1971) - Uranium processing pilot mill at the Nihgyo-Toge Mine. Proc. Symp. on the Recovery of Uranium from its ores and other sources, Sao Paulo, Brazil, August, 1970. IAEA Vienna STI/PUB-262. 97.

Weingold, G., (1970) - Conversion of Uranyl Nitrate to Uranium Tetrafluoride. Kerntechnik 12 338-40.

AAEC SYMPOSIUM

ON

URANIUM PROCESSING

PAPER VIII

# REVIEW OF METHODS AND TECHNOLOGY FOR THE PRODUCTION OF URANIUM HEXAFLUORIDE

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## 1. INTRODUCTION

Most types of nuclear power reactors use enriched uranium dioxide fuel and consequently most uranium concentrates (yellow cake) are converted to uranium hexafluoride ($UF_6$) as the feed material for enrichment in gaseous diffusion plants. As a potential large producer of uranium, it will be in Australia's interest ultimately to sell uranium hexafluoride overseas in addition to yellow cake.

This paper describes the properties of uranium hexafluoride and the main flowsheets used industrially for its production. The processes and the technology of their associated equipment are reviewed, including some alternatives which have potential for future development.

## 2. PROPERTIES OF URANIUM HEXAFLUORIDE

Uranium hexafluoride is a colourless, crystalline solid which sublimes without melting at ambient temperature and pressure. At room temperature it has a vapour pressure of 16 kPa (120 mmHg). Because the triple point occurs at only 64.02°C and 152 kPa (1134 mmHg), uranium hexafluoride is readily handled as a solid, liquid or gas. Selected physical properties of uranium hexafluoride are summarised in Table 1.

Uranium hexafluoride is a highly reactive substance and will spontaneously ignite most organic materials at room temperature. It reacts vigorously with water vapour forming uranyl fluoride and hydrogen fluoride. Uranium hexafluoride reacts with most metals but nickel, copper and aluminium and their alloys are relatively resistant to corrosion. Mild steel is satisfactory at ambient temperature and is used, for example, for the construction of the typical USAEC 10-ton storage containers (USAEC 1968).

The USAEC specification for natural uranium hexafluoride is shown in Table 2.

## 3. PROCESSES FOR CONVERSION OF YELLOW CAKE TO URANIUM HEXAFLUORIDE

Three main processes have been developed and are currently used for the production of uranium hexafluoride as shown in Figure 1.

In process A, the yellow cake is dissolved in nitric acid and the uranium is recovered and purified by a solvent extraction process. Ammonium diuranate (ADU) is precipitated with ammonia from the purified uranyl nitrate solution, filtered, dried, and calcined in air to uranium trioxide ($UO_3$). This is reacted with hydrogen to form uranium dioxide ($UO_2$) and fluorinated first with hydrogen fluoride to form uranium tetrafluoride ($UF_4$) then with

TABLE 1

SELECTED PHYSICAL PROPERTIES OF URANIUM HEXAFLUORIDE

(after Katz and Seaborg 1957)

| Property | Value | Temperature °C |
|---|---|---|
| Triple Point | 64.01 ± 0.05°C, 1134 mm Hg | - |
| Density, solid | 5.060 ± 0.005 g/cm$^3$ | 25 |
| Density, liquid | 3.595 g/cm$^3$ | 70 |
| Viscosity, liquid | 0.91 cp | 70 |
| Viscosity, gas | 0.01999 cp | 80 |
| Surface tension | 16.8 ± 0.3 dyne/cm | 70 |
| Thermal conductivity, gas | 1.0 x 10$^{-5}$ cal/sec cm$^2$(°C/cm) | 5 |
| Heat of vaporisation | 6.82 kcal/mole | 64.02 |
| Heat of sublimation | 12.02 kcal/mole | 0 |

Vapour pressure data for uranium hexafluoride were correlated by the following equations by Oliver et al. (1953) -

$$\log p_{mm} = 6.38363 + 0.0075377t - 942.76/(t + 183.416) \quad (0\text{-}64^\circ C)$$

$$\log p_{mm} = 6.99464 - 1126.288/(t + 221.963) \quad (64\text{-}116^\circ C)$$

$$\log p_{mm} = 7.69069 - 1683.165/(t + 302.148) \quad (116\text{-}230^\circ C)$$

TABLE 2

USAEC SPECIFICATION - NATURAL URANIUM HEXAFLUORIDE

| | |
|---|---|
| Maximum vapour pressure of filled container at 200°F (93.3°C) | 75 psi (0.517 MPa) |
| Minimum weight percent of $UF_6$ in material | 99.5 |
| Maximum mol percent of hydrocarbons, chlorocarbons, and partially substituted halohydrocarbons | 0.01 |
| Maximum number of parts of elements indicated per million parts of total uranium: | |
| Antimony | 1 |
| Bromine | 5 |
| Chlorine | 100 |
| Niobium | 1 |
| Phosphorus | 50 |
| Ruthenium | 1 |
| Silicon | 100 |
| Tantalum | 1 |
| Titanium | 1 |
| Total number of parts of elements forming non-volatile fluorides (having a vapour pressure of one atmosphere or less at 300°C) per million parts of total uranium e.g. aluminium, barium, bismuth, cadmium, calcium, chromium, copper, iron, lead, lithium, magnesium, manganese, nickel, potassium, silver, sodium, strontium, thorium, tin, zinc and zirconium | 300 |
| Maximum number of parts of elements or isotopes indicated per million parts of U-235: | |
| Chromium | 1500 |
| Molybdenum | 200 |
| Tungsten | 200 |
| Vanadium | 200 |
| Uranium-233 | 500 |
| Uranium-232 | 0.110 |
| Maximum thermal neutron absorption of total impurity elements as equivalent parts of boron per million parts of total uranium | 8 |

fluorine to form uranium hexafluoride ($UF_6$).

In process B, the purified uranyl nitrate solution from solvent extraction is concentrated by evaporation to molten uranyl nitrate hexahydrate (UNH), thermally decomposed to $UO_3$ and then converted in turn to $UO_2$, $UF_4$ and $UF_6$. In process C, yellow cake is initially treated to size the material and make it suitable for fluidised bed operation and possibly to remove some of the contained sodium, then reduced with hydrogen to $UO_2$, and fluorinated to $UF_4$ using hydrogen fluoride. A major portion of the impurities in the original yellow cake is eliminated during these steps. The crude $UF_4$ is then converted to $UF_6$ and most of the impurities forming non-volatile compounds are rejected as solid ash. The residual impurities in the $UF_6$ are removed by fractional distillation.

Process A is used by COMURHEX at its Malvesi Plant in France (Blanvillain 1964) and was used in the first uranium plant at the United Kingdom Atomic Energy Authority's Springfields works for the production of $UF_4$ for reduction to metal (Hinton 1955). It is also the process most widely used for the production of sinterable natural uranium dioxide powder for the fabrication of fuel pellets. The process has been investigated and demonstrated on the pilot plant scale by the Australian Atomic Energy Commission and improvements were made at several stages (Alfredson 1970, 1972). Process B is used by British Nuclear Fuels Limited at Springfields (Alexander et al. 1960, Page et al. 1960, Hawthorn et al. 1960), by Kerr McGee Corporation at its Sequoyah plant in the United States (Kerr McGee Corp. 1971), by Eldorado Nuclear Ltd at its Port Hope refinery in Canada (Berry 1969), and at the uranium feed materials plants operated for the USAEC (Harrington and Ruehle 1959, Powell 1958, Smiley 1961, Thayer 1958). Process C is used by the Allied Chemical Corporation in its plant at Metropolis, Illinois (Ruch et al. 1960, Sutton et al. 1966).

Processes A and B are similar in that they both use a head-end purification step to obtain uranyl nitrate solution of the required purity whereas, in process C, complete purification is not obtained until the uranium hexafluoride has been produced. Processes A and B therefore have the ability to produce nuclear purity intermediate products, e.g. $UO_2$ for pellet fabrication and $UF_4$ for reduction to metal, if required. Process C avoids the generation of nitrate waste solutions which must be recycled for acid recovery and/or waste treatment.

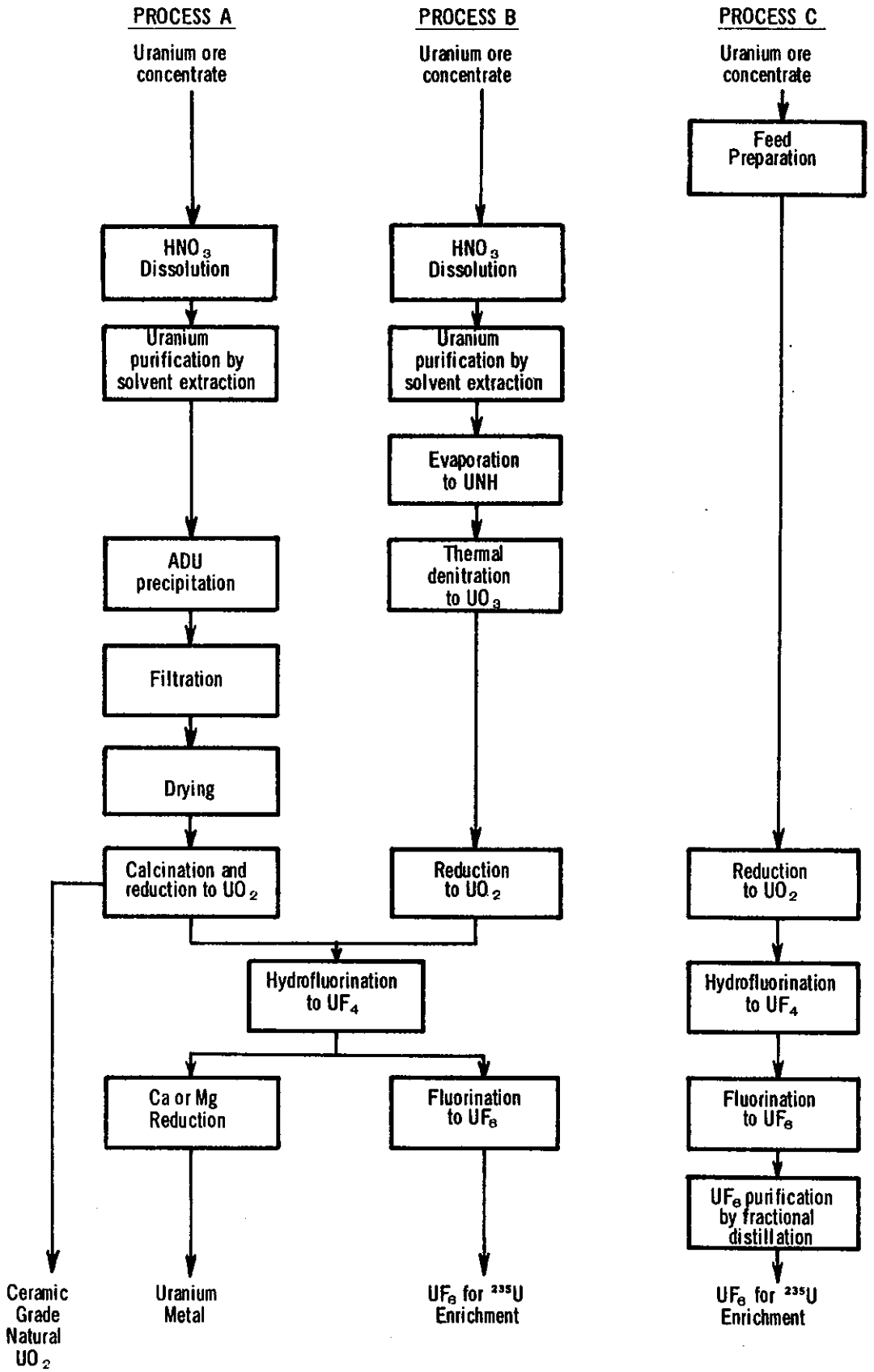


FIGURE 1. PROCESSES FOR PRODUCTION OF NUCLEAR GRADE URANIUM MATERIALS FROM ORE CONCENTRATES

In process A, uranyl nitrate is denitrated chemically to $UO_3$ by the precipitation and calcination of ADU and the nitrate cannot be readily recovered as nitric acid for further use. In process B, uranyl nitrate is decomposed to $UO_3$ by heating and the nitrogen oxide off-gases are recovered and re-used. All three flowsheets use the same chemical steps for the reduction of $UO_3$ (or $U_3O_8$) to $UO_2$ and its subsequent fluorination to $UF_6$.

In the following Sections, the process steps are described briefly and the various alternative items of equipment for each step are discussed. In addition, some alternative processes which have been developed for the production of uranium tetrafluoride and its conversion to uranium hexafluoride are outlined.

## 4. PROCESS STEPS AND EQUIPMENT ALTERNATIVES

### 4.1 Dissolution of Yellow Cake

The yellow cake (typically containing >60% $U_3O_8$) is received in drums, weighed, sampled and blended. It dissolves readily in nitric acid and both batch and continuous operating dissolvers are used. Generally, a product solution containing 300-450 gU/l and 0.5-3M nitric acid is required.

Yellow cake may contain several wt % silica, some of which dissolves and may subsequently cause emulsion problems during solvent extraction. The insoluble silica is in a gelatinous form which is difficult to remove by filtration. These problems can be minimised by "ageing" the dissolver solution at 95°C for 2 hours to convert the silica to a more readily filterable form (Page et al. 1960). Typical residence times of up to 8 hours are used with continuous dissolvers which often comprise several stages in series to minimise by-passing in the system. Agitated cylindrical tanks (sometimes baffled) of stainless steel are used. The off-gases are generally scrubbed with water to absorb and condense nitric oxide gases for recycling and subsequently scrubbed with caustic solution before being discharged to the atmosphere.

Practice varies concerning the need to remove silica from the dissolver solution prior to solvent extraction. At the BNFL Springfields plant (Page et al. 1960) and the COMURHEX Malvesi Plant (Blanvillain 1964), the silica is removed by rotary drum vacuum filters using precoat methods whereas most other plants do not filter out the silica.

### 4.2 Solvent Extraction

Purification of the uranium is accomplished by solvent extraction using a solvent containing tributyl phosphate (TBP) in an aliphatic diluent. Concentrations of TBP in the range 20 to 40 vol % have been adopted with odourless kerosene (implying aromatic-free) or hexane as an inert diluent (Harrington and Ruehle, 1959). A typical modern solvent extraction flowsheet is shown in Figure 2. The feed solution is contacted initially with the solvent which preferentially extracts the uranium. The loaded organic is contacted with a portion of the product solution to scrub out any impurities which may have extracted along with the uranium and the purified uranium is then stripped from the solvent using slightly acidified water at $\sim 60^{\circ}C$ to give a product solution containing 100-140 gU/l and $<0.05M$ $HNO_3$.

The recycled organic solvent is washed in turn with sodium carbonate solution and nitric acid to remove any degradation products from the solvent and minimise the buildup of uranium in the solvent. The impurities in the original feed solution are discharged in the raffinate which may be recycled for nitric acid recovery and is then neutralised with lime.

Both mixer-settlers (Page et al. 1960) and pulsed columns (e.g. Thayer 1958, Burger and Jardine 1958) have been used for counter-current contacting of the organic and aqueous phases. Pulsed columns have the advantage of a smaller holdup, are more responsive to control and require less floor area than mixer-settlers. However their disadvantages are that they require much greater height in the process building (typically 15 metres) and a reliable pulsing unit is essential.

### 4.3 Denitration via ADU Precipitation

The uranium in the product solution from solvent extraction is precipitated as ADU using ammonia gas or ammonium hydroxide solution at about $80^{\circ}C$. A simple agitated tank of stainless steel is used. The ADU is filtered on rotary drum vacuum filters, dried in a continuous band drier and then calcined to $UO_3$ in a second band drier heated to $\sim 400^{\circ}C$ by a counter-current flow of hot air (Blanvillain 1964). Precipitation at relatively high pH is used so that hard $UO_3$ agglomerates are obtained which are suitable for the French moving-bed reactors used in subsequent steps. The reactivity of this $UO_3$ is greater than that produced via thermal denitration.

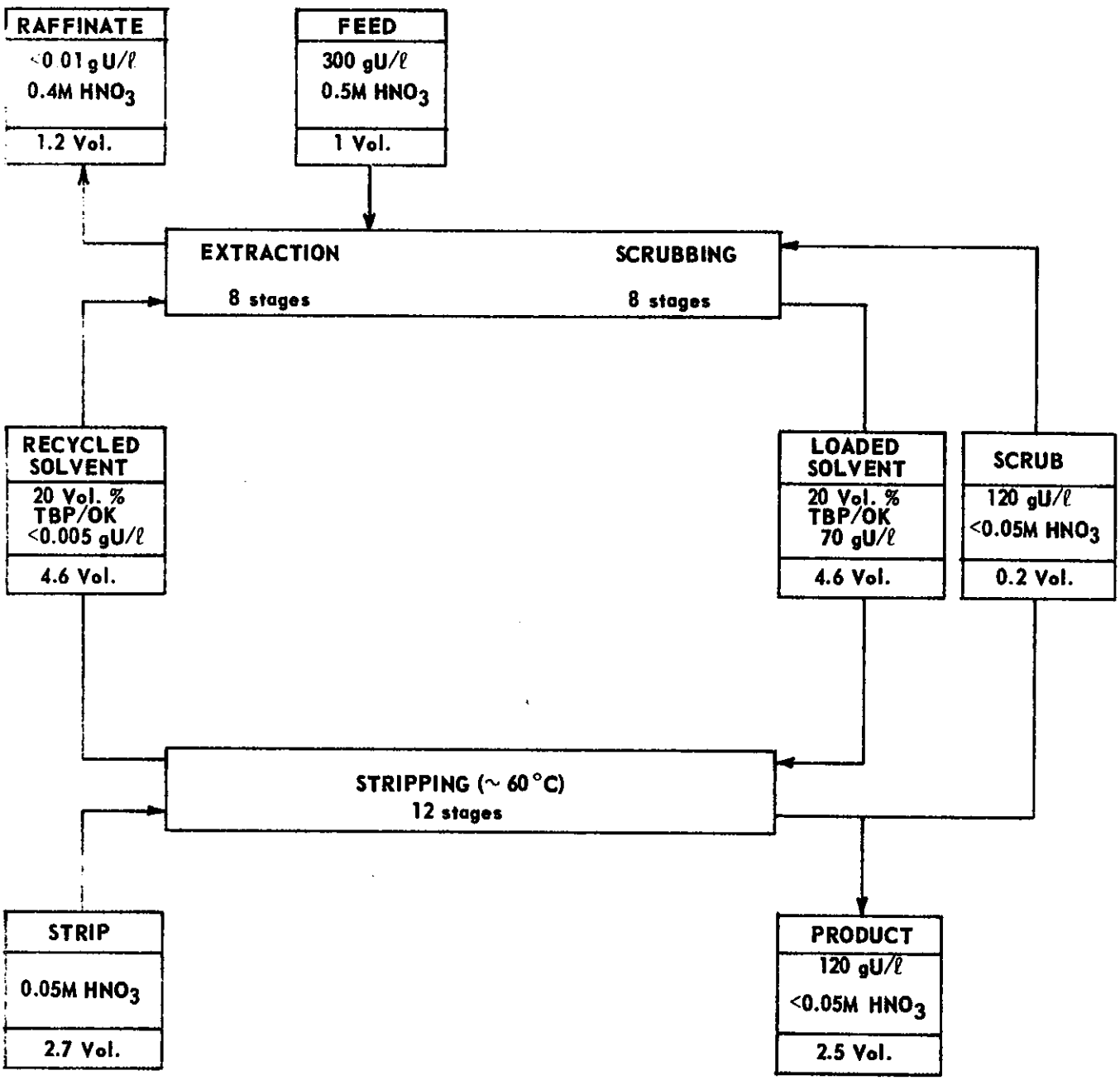


FIGURE 2 TYPICAL MODERN SOLVENT EXTRACTION FLOWSHEET FOR URANIUM PURIFICATION
[Based on data of Alfredson (1972)]

4.4 Thermal Denitration

The uranium product solution from solvent extraction is concentrated by multiple effect evaporation to approximately 1000 gU/l, corresponding to molten uranyl nitrate hexahydrate (UNH). In the United States and Canada, denitration is carried out in direct gas-fired or electrically-heated stirred pots, of stainless steel, which operate on a batch basis. Typical production pots are 1.7 m diameter x 1.1 m deep, hold a charge of 1.1 $m^3$, and operate on an 8-hour cycle. The $UO_3$ product is broken up manually and pneumatically removed from the pot denitrator. The off-gases pass to a nitric acid recovery system. The disadvantages of pot denitration include high maintenance and labour costs.

Stirred bed denitrators were also developed in the United States. The UNH was charged into a bed of $UO_3$ particles contained in a heated agitated trough such that the bed temperature was ~300°C. A production unit (Figure 3), 0.66 m wide (with a rounded bottom) x 3.66 m long had a capacity* of 3270 tonnes of contained uranium per year (Smiley 1961).

Fluidised bed denitrators are used in the BNFL Springfields plant (Hawthorn et al. 1960) and were also investigated on the plant-scale in the United States (Robinson and Todd, 1966). The molten UNH is continuously atomised through horizontal two-fluid nozzles into a bed of $UO_3$ particles fluidised with air or steam and maintained at 300-350°C, and the product overflows through a discharge pipe (Figure 4).

The heat required for the endothermic denitration reaction is provided by internal bayonet heaters and external heating. The off-gases are filtered through porous stainless steel filter elements to remove any entrained $UO_3$ particles and then passed to a nitric acid recovery system.

The physical properties of the $UO_3$ particles obtained by these three methods are quite different and much effort has been expended in trying to relate their physical properties to their reactivity towards reduction and hydrofluorination (Harrington and Ruehle 1959). Much of the product from stirred pot denitrators is a very fine powder (-325 mesh) with good reactivity. The product from stirred bed and fluidised bed denitrators consists of coarse, free-flowing particles with low reactivity which can be increased by the

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* Assumes continuous operation for 300 days/year.

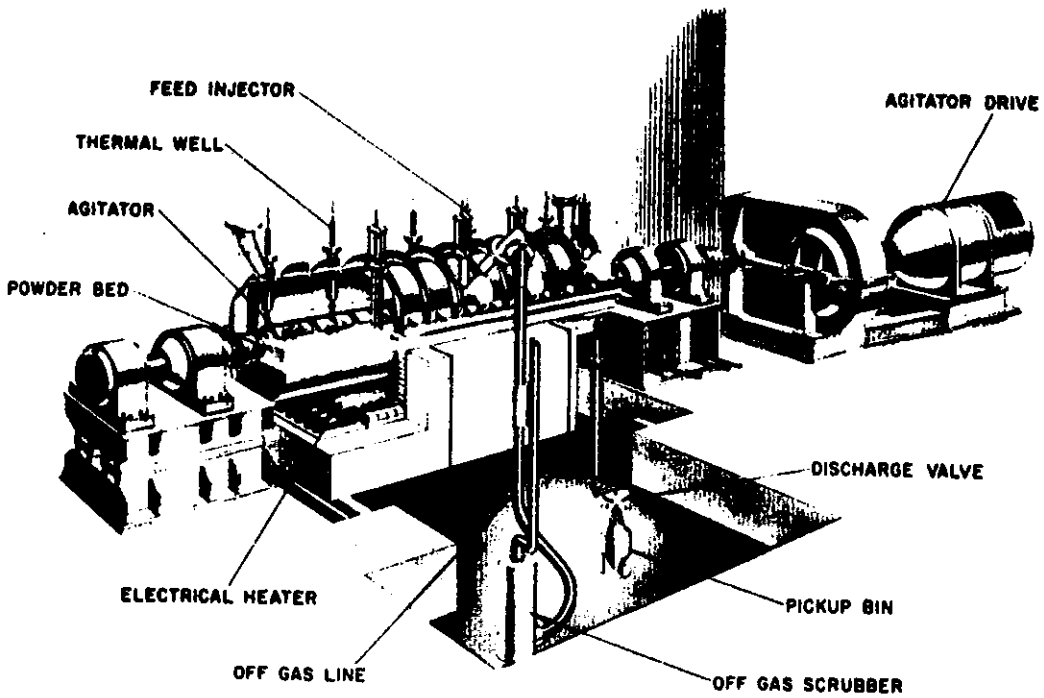



**FIGURE 3 CONTINUOUS STIRRED BED DENITRATOR**
**(after Smiley, 1961)**

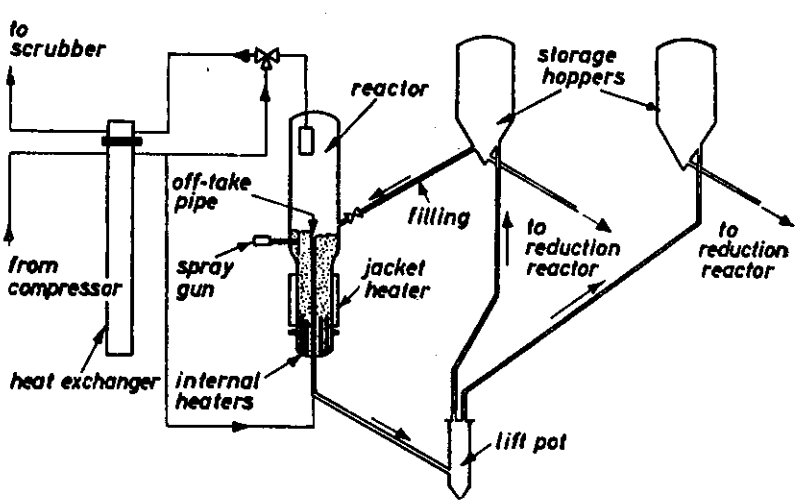



**FIGURE 4 CONTINUOUS FLUIDISED BED DENITRATOR**
**(after Hawthorn et al., 1960)**

addition of small quantities of sulphuric acid to the UNH before denitration (Smiley 1961).

4.5 Reduction of $UO_3$ to $UO_2$

Batch reduction processes in which the powder was held in trays in heated muffle furnaces were used in the early plants. Around the early 1950's, continuous processing techniques were developed which utilised vibratory-tray, stirred-bed and moving bed reactors. The combination of poor heat transfer characteristics and the exothermic nature of the reaction limited the capacity of these types of reactors. High bed temperatures must be avoided because partial sintering of the powder may occur with a reduction in the surface area of the $UO_2$ product. The $UO_2$ is then relatively unreactive in the hydrofluorination step and acceptable conversions can only be obtained at comparatively low rates (Smiley 1961). Fluidised bed reactors were developed in both the United States (Powell 1958, Smiley 1961) and the United Kingdom (Hawthorn et al. 1960) to overcome these problems but moving bed reactors are used in Canada (Berry 1961, Melvanin 1958) and France (Haegi et al. 1968).

The USAEC uranium conversion plants use continuous, two-stage, fluidised bed units (Powell 1958, Smiley 1961) and these have apparently also been adopted by Kerr McGee Corp. (1971). Allied Chemical Co. uses a continuous single-stage unit (Sutton et al. 1966) and batch-operated fluidised bed reactors are used by BNFL (Hawthorn et al. 1960). The standard USAEC units (Figure 5) have an inside diameter of 0.34 m tapering to 0.25 m over the bottom 0.46 m of the reactor, a 1.4 m bed depth and are constructed of stainless steel. The $UO_3$ is charged to the first stage near the top of the bed and partially reduced oxide overflows into the second stage. The beds are fluidised with cracked ammonia and the outlet gases and $UO_2$ product are discharged to a product hopper where the gases are filtered through porous stainless steel filters and burned. Capacities of ~2900 tonnes U/year are obtained at reactor temperatures of 540-570°C using feed material obtained from pot denitration (Smiley 1961). The Allied Chemicals reduction reactor is 0.94 m diameter at the distributor plate increasing to 1.37 m approximately 1.8 m above this plate. Throughput rates as high as 10,000 tonnes U/year have been sustained at temperatures above 550°C with 99% conversion of yellow cake to $UO_2$ (Sutton et al. 1966).

In the COMURHEX plant at Malvesi, reduction and hydrofluorination are carried out sequentially in a moving bed reactor known as an "LC furnace"

(Haegi et al. 1968) shown in Figure 6. ADU-derived $UO_3$ is fed to the top of the reactor and contacted with cracked ammonia at about 700°C. Reduction is essentially complete over a distance of about 1 m. Hydrofluorination occurs further down the furnace and is described in Section 4.7.

In the Canadian plant, $UO_3$ produced by pot denitration is hydrated, pelletised through the use of a casting belt, dried, cured and classified before being fed to the moving bed reactor. Pellets with a maximum dimension in the range 0.3 to 1.3 mm are required (Melvanin 1958). Dehydration occurs in the top zone of the furnace, followed by reduction at 550°C with cracked ammonia which flows countercurrent to the pellets (Berry 1969).

4.6 Hydrofluorination of $UO_2$ to $UF_4$

The equipment developed for this step has closely followed that of the previous reduction step. However the hydrofluorination reaction is generally more difficult to handle because the reaction is reversible at practical operating temperatures and approximately twice as exothermic as the reduction reaction. The $UF_4$ product and even partly reacted materials sinter at relatively low temperatures and operational difficulties due to bed caking and reduced reactivity are encountered.

Batch-tray reactors were used in early production plants but subsequently horizontal stirred-bed, moving bed and fluidised bed reactors were developed. Virtually all the $UF_4$ manufactured in the USAEC plants has been produced in horizontal stirred-bed (screw) reactors (Figure 7). A typical bank of reactors consists of three horizontal reactors, each 0.4 m diameter x 6.1 m long, arranged one above the other. Uranium dioxide is fed to the top reactor and moved through the reactor by a motor-driven, spiral ribbon blade assembly, then falls to the second and finally to the third. Preheated anhydrous HF (at least 10% in excess of stoichiometric requirements) is fed at the discharge end of the bottom reactor and flows countercurrent to the movement of the solids. Within the reactors, temperature zones are controlled from about 290°C at the $UO_2$ inlet to about 540°C at the $UF_4$ discharge (Powell 1958). Off-gases are condensed, distilled and recycled to the process. Throughput rates (with pot calcined oxide reduced in fluidised-bed reactors) of up to 3500 tonnes U/year with 94-95% conversion to $UF_4$ were reported by Smiley (1961).

Attempts to use conventional fluidised-bed reactors with the fine, reactive oxide powders produced via pot denitration were unsuccessful due to

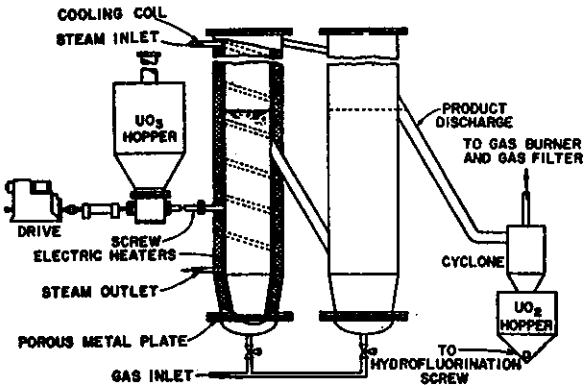
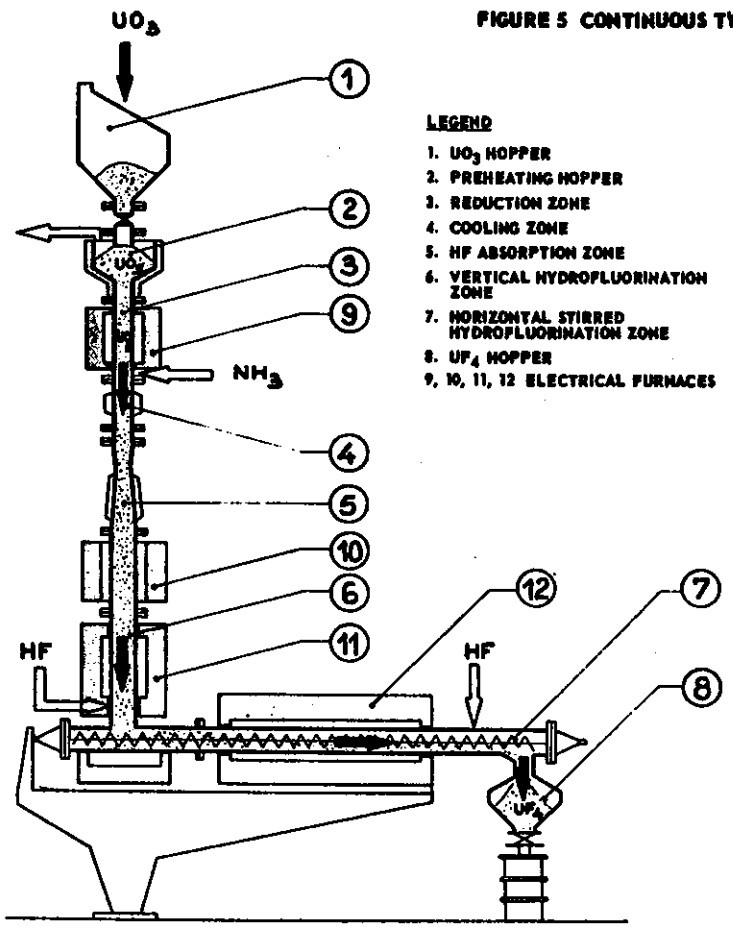



FIGURE 5 CONTINUOUS TWO-STAGE FLUIDISED BED REDUCTION SYSTEM (after Smiley 1961)




LEGEND

1. $UO_3$ HOPPER
2. PREHEATING HOPPER
3. REDUCTION ZONE
4. COOLING ZONE
5. HF ABSORPTION ZONE
6. VERTICAL HYDROFLUORINATION ZONE
7. HORIZONTAL STIRRED HYDROFLUORINATION ZONE
8. $UF_4$ HOPPER
9, 10, 11, 12 ELECTRICAL FURNACES

FIGURE 6 CONTINUOUS MOVING BED REACTOR (LC FURNACE) FOR REDUCTION AND HYDROFLUORINATION (after Hoegi et al. 1968)

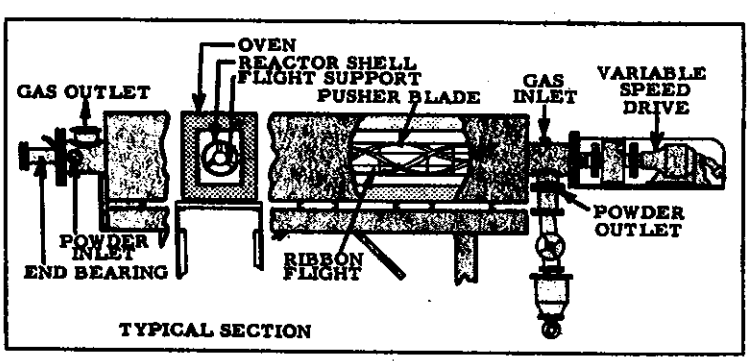



FIGURE 7 CONTINUOUS STIRRED BED REACTOR FOR HYDROFLUORINATION (after Thayer, 1958)

caking of the bed but a two-stage stirred fluidised-bed reactor was developed successfully at the Paducah Gaseous Diffusion Plant (Brater et al. 1966). Two 0.76 m diameter reactors, with a bed depth of ~1.8 m, had production rates equivalent to 4600-6500 tonnes U/year with greater than 95% conversion of $UO_2$ to $UF_4$. The first and second stages were controlled at temperatures of 330 and 500°C respectively (Brater et al. 1966).

No difficulties are encountered with the fluidisation of coarse free-flowing particles produced via fluid-bed denitration or by pretreatment of yellow cake to obtain a sized feed material. The BNFL Springfields plant uses batch-operated fluidised-bed reactors whereas the Allied Chemical Co. uses continuous two-stage fluidised-bed reactors. The off-gases are filtered with porous sintered metal filters, condensed and recycled after distillation.

In the COMURHEX plant, reaction with hydrogen fluoride takes place in the "LC furnace" beneath the reduction zone (Figure 6). Anhydrous HF is fed to the bottom of the moving bed reactor and at the $UF_4$ exit. A temperature gradient is maintained in the direction of flow of the HF, decreasing from 550°C at the bottom of the moving bed to 150°C at the top of the fluorination zone. Only the stoichiometric amount of HF is required which greatly simplifies the need for off-gas treatment. The standard LC furnace has a throughput equivalent to 350 tonnes U/year (Haegi et al. 1968). The Eldorado Port Hope refinery uses a separate moving bed reactor for the hydrofluorination reaction with countercurrent flow of gas and solids (Berry 1969).

### 4.7 Fluorination of $UF_4$ to $UF_6$

Two types of reactors are used for the reaction of $UF_4$ with fluorine to form uranium hexafluoride: flame reactors (Figure 8) and fluidised bed reactors (Figure 9). The former were developed in the United States (Powell 1958, Smiley and Brater 1958, Smiley 1961) and are used in all plants in the United States (except by Allied Chemical Co), Canada (Kerr McGee 1971) and France (Level 1964, 1969). Fluidised-bed reactors are used by Allied Chemical Co (Ruch et al. 1960) and by BNFL at Springfields (Rogan 1970).

Flame reactors are typically constructed of 8-inch (0.2 m) diameter Schedule 40 monel pipe, approximately 3.3 m long with cooling coils wrapped along the entire length. Fine $UF_4$ powder is dispersed at the top of the reactor and reacts with a co-current flow of preheated fluorine as it falls in the column. The reaction is highly exothermic and cooling of the outer wall is essential to maintain the surface temperature below 500°C. Most of

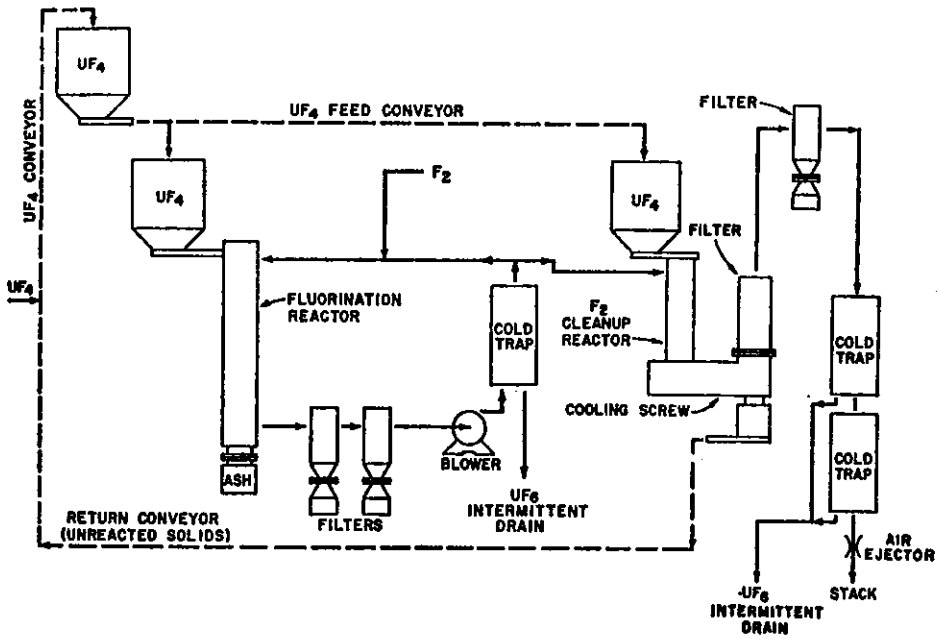



**FIGURE 8 FLAME REACTOR SYSTEM FOR $UF_6$ PRODUCTION (after Smiley, 1961)**

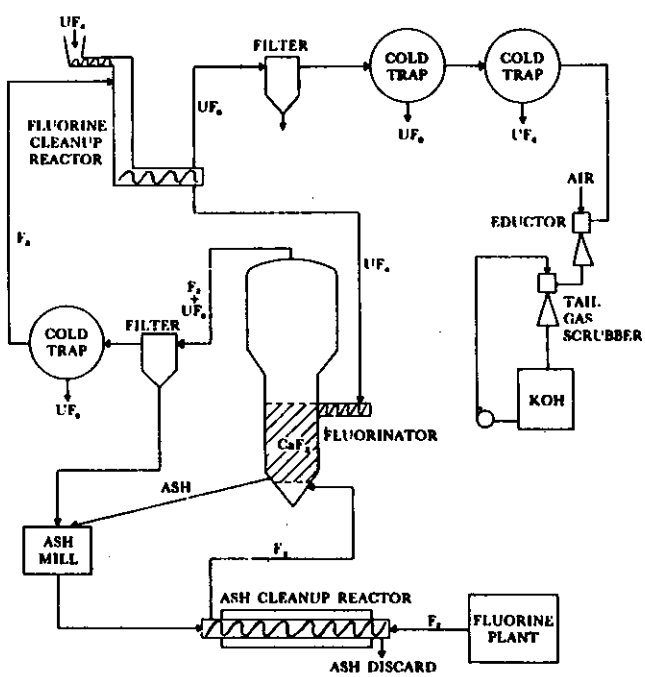



**FIGURE 9 FLUIDISED BED REACTOR SYSTEM FOR $UF_6$ PRODUCTION (after Ruch et al., 1960)**

the reaction takes place in the top one metre of the reactor. The optimum processing rate of the flame reactor has been reported as 2100 tonnes U/year (Smiley 1961).

The off-gases are cooled and then filtered through porous monel or nickel filters before the uranium hexafluoride product is condensed in a series of refrigerated cold traps in the temperature range -10°C to -40°C. When the condensers are full, the uranium hexafluoride is liquified by heating and drained into storage cylinders. Approximately 10-20% excess fluorine is fed to the flame reactor and must be recovered for economic operation. The unreacted fluorine is recovered by further reaction with an excess of $UF_4$ in separate modified flame reactors (Powell 1958), fluidised bed reactors (Pedigo et al. 1966) or tray reactors (Level 1964). The unfluorinated ash from the primary flame reactor is crushed and blended with further $UF_4$ and also fed to this backup reactor. The residual off-gases are scrubbed with caustic solution before being discharged.

In fluidised bed fluorination reactors, a bed of inert material such as calcium fluoride is maintained as the heat transfer medium with a minimum amount of $UF_4$ present to avoid caking in the bed. The reactors are constructed of monel and operate at approximately 500°C. A single fluidised bed reactor, 1-1.5 m diameter may have a throughput of 3000-5000 tonnes U/year.

Off-gases from the fluidised bed reactor are treated similarly to those for the flame reactor although larger volumes are involved. A portion of the bed material from the reactor is also removed to prevent the buildup in the bed of radioactive daughter products of uranium, and in the Allied Chemicals plant to eliminate nonvolatile impurities such as sodium fluoride which forms complexes with uranium hexafluoride. These have relatively low melting points and may cause caking in the bed. This material is treated in a screw reactor located in the fluorine line to recover residual uranium (Figure 9).

### 4.8 Fluorine Production

Fluorine is produced by the electrolysis of anhydrous hydrofluoric acid dissolved in molten salt electrolyte KF.2HF at ~90°C. The standard USAEC production cell (Figure 10) produces 4 kg fluorine per hour when operating at 6000A and 9 to 12 V (Huber et al. 1958). It consists of a monel bath divided into two compartments by cooling tubes. Each compartment contains

one anode assembly and one cathode assembly (Figure 11). The anode assembly consists of eight pairs of carbon anodes bolted to support bars. The cathode surrounds the anode assembly and is fabricated from steel plate. In each compartment a monel skirt is welded to the cover of the cell bath and immersed in the electrolyte to provide separate gas chambers for the anode and cathode assemblies and to prevent explosive reaction between the hydrogen and fluorine evolved. Diaphragms, fabricated from monel mesh, are welded to the skirts and extend to the bottom of the anodes and cathodes. Conductor posts for the anode and cathode assemblies penetrate the cell cover through insulated packing glands. Off-gas connections and hydrogen fluoride feed lines are also welded to the cover. The cell is surrounded by a water-jacket which, together with the internal cooling tubes, provides for heating or cooling the electrolyte.

Similar designs are used by other producers although in some cases the bath is fabricated from mild steel rather than monel and the bath itself is used as the cathode instead of having separate internal cathodes (Kirk and Othmer 1966, Bergeret 1965, Level 1969).

Hydrogen fluoride (as liquid or gas) is fed to the cell to maintain the required composition and depth of electrolyte. The fluorine and hydrogen off-gases, containing up to 10 vol % hydrogen fluoride, are passed to surge tanks to minimise pressure fluctuations in the plant, then to entrainment separators to remove electrolyte mist, and to condensers at -50 to -70°C to reduce the hydrogen fluoride concentration to 2-3 vol %. The condensed hydrofluoric acid is recycled. The hydrogen stream is scrubbed with caustic solution and discharged to atmosphere or burned.

The lifetime of the USAEC cells is typically $50 \times 10^6$ ampere-hours, corresponding to approximately a year's operation, and is limited by corrosion of the metal components of the anode assembly and a buildup of a sludge of impurities in the bottom of the bath. A maintenance facility is provided in a fluorine plant for systematic disassembly, cleaning and rebuilding of cells during the life of the plant.

### 4.9 Purification of $UF_6$ by Distillation

After fluorination, the uranium hexafluoride product from the Allied Chemicals Co. process still contains impurities which are either more volatile than $UF_6$, e.g. molybdenum hexafluoride ($MoF_6$) and vanadium oxyfluoride ($VOF_3$), or less volatile e.g. some molybdenum oxyfluorides. These impurities are separated in two monel distillation columns operating at about 0.7 MPa (90 psig)

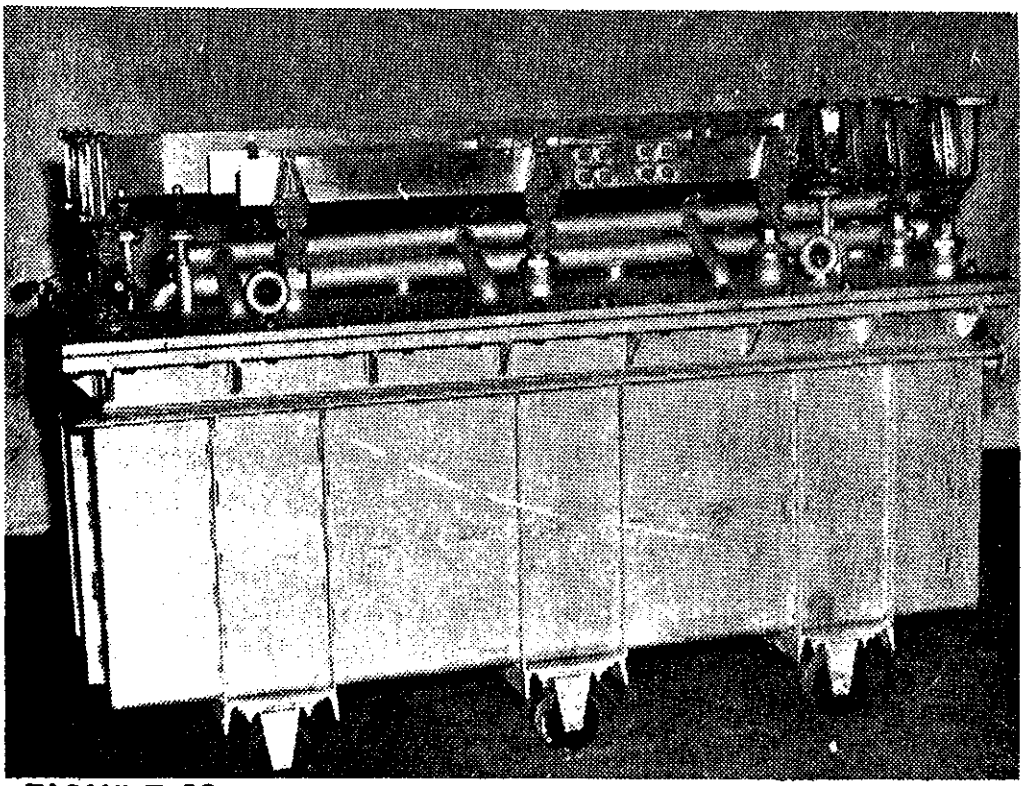


**FIGURE 10 USAEC FLUORINE PRODUCTION CELL**
**(after Huber et al., 1958)**

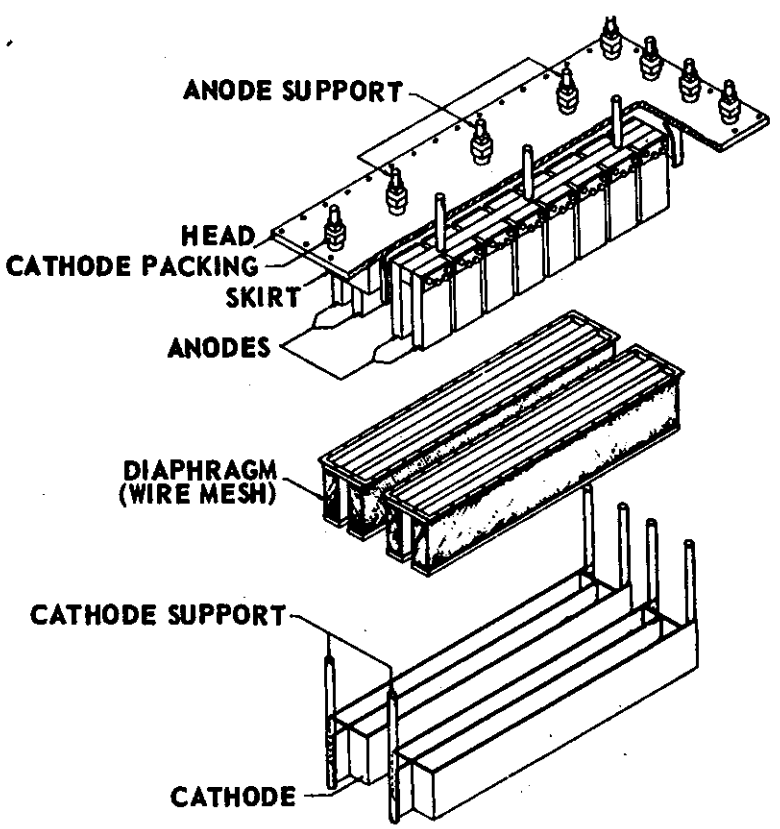



**FIGURE 11 HEAD ASSEMBLY FOR FLUORINE CELL**
**(after Huber et al. 1958)**

and 100°C. The high and low boiling fractions from distillation are treated to recover contained uranium by wet processing methods. According to Ruch et al. (1960), these residues represent only 1-2% of the total throughput.

## 5. ALTERNATIVE PROCESSES FOR THE PRODUCTION OF $UF_4$ AND $UF_6$

The processes for the production of $UF_4$ at a refinery which have been described so far involve high temperature gas-solid reactions ("dryway methods") for the reduction and fluorination steps. There has been considerable interest in the production of $UF_4$ by wet methods, especially associated with uranium ore processing plants. These methods are reviewed in another paper at this Symposium (Hardy 1972) and include the Excer, Winlo, French, Simo and PNC processes. In general, they would require conversion from a nitrate to a chloride or sulphate solution (depending on the particular process), reduction from hexavalent to tetravalent state by electrolytic or chemical methods, precipitation of $UF_4.3/4H_2O$ followed by drying and dehydration to $UF_4$.

Wet processing methods are attractive in that additional purification is available during conversion to the tetrafluoride and the processing conditions (temperature, corrosion etc) are generally less severe than for dryway methods. The first of these reasons is perhaps not of much significance where a TBP solvent extraction purification step is used since this has been shown to be quite adequate to meet the required purity levels.

Fluorination of $UF_4$ to $UF_6$ can also be achieved with reactants other than elemental fluorine, e.g. chlorine trifluoride and bromine pentafluoride, but since their preparation requires the use of fluorine there is no advantage in their use. However $UF_6$ can be produced by the oxidation of $UF_4$ with air or oxygen at 800°C (Fluorox process)

$$2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2$$

The uranyl fluoride byproduct is recycled by reduction and hydrofluorination to $UF_4$. The Fluorox process has been investigated on the pilot plant scale in the United States (Scott et al. 1964) and South Africa (Geertsma et al. 1965) using both fluidised bed reactors and moving bed reactors, but the severe corrosion rates encountered under the reaction conditions have limited this development.

## 6. CONCLUDING REMARKS

Determination of the optimum chemical process and equipment flowsheets for the production of $UF_6$ is obviously complex and must be assessed carefully for any particular application. Processes A and B, which use headend purification, have the ability to handle a wide range of yellow cake concentrates and to produce nuclear purity intermediate products, but generate substantial volumes of nitrate waste solutions which must be recycled for acid recovery and subjected to waste treatment. By contrast, process C is best suited to yellow cake which has a low sodium content e.g. as prepared via acid leaching. Higher grade concentrates are preferable since the amount of hydrogen, hydrogen fluoride and fluorine consumed in reaction with these impurities is reduced.

The French workers have developed their moving bed reactors (LC furnace) as a very efficient means of taking advantage of the high reactivity of $UO_3$ and $UO_2$ powders derived from ADU. With process B, fluidised bed reactors appear to have advantages over other gas-solids reactors for future applications. In general, fluidised bed reactors are of simple design, are amenable to continuous operation and offer good heat transfer and gas-solids contacting for all the dryway gas-solids reactions. Their application in the Allied Chemicals plant using process C is a key factor in the success of that operation. Nevertheless, wet processing methods for $UF_4$ production at the ore treatment plant or in the refinery and conversion plant will continue to attract attention for future development.

## 7. REFERENCES

Alexander, R.C., Shortis, L.P. and Turner, C.J.(1960) - The second uranium plant at Springfields. Trans. Inst. Chem. Eng. 38 (4) 177-183.

Alfredson, P.G. (1970) - The production of nuclear grade Uranium Dioxide powders from Australian ores. Proc. Aust. Inst. Min. Metall. No.233, 61-68.

Alfredson, P.G. (1972) - Pilot plant development of processes for the production of nuclear grade Uranium Dioxide. Paper presented to the Aust. Chem. Eng. Conf. on "Development and Innovation for Australian Process Industries", Newcastle, N.S.W., August 17-18, 1972.

Bergeret, M. (1965) - Usine chimique de Pierrelatte.Energie Nucléaire 7 (2), 99-93. [AAEC LIB/TRANS 252]

Berry, R.M. (1969) - Eldorado's Port Hope Refinery, 1969. Can. Inst. Min. Metall. Bull. 62 (690) 1093-99.

Blanvillain, M. (1964) - Le raffinage de l'uranium à l'usine de Malvesi. Bull. Inf. Sci. Tech. No. 80 69-85. [AAEC LIB/TRANS 175]

Brater, D.C., Castro, D.L., Dean, L.A., Pashley, J.H., Smiley, S.H. (1966) - Development and production experience with mechanically agitated fluid beds as applied to hydrofluorination of fine Uranium Oxide powders. Chem. Eng. Prog. Symp. Series 62 (65) 1-11.

Geertsma, J.C., MacMillan, I., Paynter, J.C., Van Rensburg J. (1965) - A discussion on the programme of the Extraction Metallurgy Division. 1st to 3rd December, 1965. S. Afr. Atomic Energy Board, PEL121, Vol.II.

Haegi, W., Verot, L. and Muller, J. (1968) - Réalisations industrielles pour la fabrication de tétrafluorure d'uranium par la procédé francais de "réduction-fluororation" en "lit-coulant" (fours L.C.) Energie Nucléaire 10 (3) 1-8. [AAEC LIB/TRANS 262]

Hardy, C.J. (1972) - Possible trends and methods for the production of high-purity products. Paper presented to this Symposium.

Harrington, C.D. and Ruehle, A.E. (Eds) (1959) - Uranium Production Technology, D. Van Nostrand Co. Inc., Princeton.

Hawthorn, E., Shortis, L.P. and Lloyd, J.E. (1960) - The fluidised solids dry way process for the production of Uranium Tetrafluoride at Springfields. Trans. Inst. Chem. Eng. 38 (4) 197-207.

Hinton C. (1955) - Some aspects of chemical processes ancillary to atomic energy - manufacture of Uranium metal from ore. Trans. Inst. Chem. Eng. 33 (1) 45-51.

Huber, A.P., Dykstra, J., Thompson, B.H. (1958) - Multi-ton production of Fluorine for manufacture of Uranium Hexafluoride. Proc. 2nd Int. Conf. on Peaceful Uses of Atomic Energy 4 172-180.

Katz, J.J. and Seaborg, G.T. (1957) - The Chemistry of the Actinide Elements. Methuen and Co. Ltd, London.

Kerr McGhee Corp. (1971) - Sequoyah Uranium Hexafluoride production plant. Environmental report. USAEC Docket 40-8027-4.

Kirk, R.E. and Othmer, D.F. (Eds) (1966) - Encyclopaedia of Chemical Technology Vol. 9, p.510-16. Interscience Publishers.

Level, A. (1964) - Pierrelatte - les usines chimiques. Préparation de l'hexafluorure d'uranium. Energie Nucléaire 6 (4) 225-32. [AAEC LIB/TRANS 251]

Level, A. (1969) - la chimie industrielle du fluor. Chemie et Industrie - Génie Chimique 102 (8) 1077-82. [AAEC LIB/TRANS 260]

Melvanin, F.W. (1958) - Canadian development work with moving-bed reactors for reduction of Uranium Trioxide and hydrofluorination to Uranium Tetrafluoride for subsequent production of metal. Proc. 2nd Int. Conf. on Peaceful Uses of Atomic Energy 4 133-38.

Oliver, G.D., Milton, H.T., Grisard, J.W. (1953) - The vapor pressure and critical constants of Uranium Hexafluoride. J. Am. Chem. Soc. 75 (12) 2827-29.

Page, H., Shortis, L.P., Dukes, J.A. (1960) - The processing of Uranium ore concentrates and recycle residues to purified Uranyl Nitrate solution at Springfields. Trans. Inst. Chem. Eng. 38 (4) 184-96.

Pedigo, R., King, C.R., Dean, L.A., Owen, J.E., Bernstein, S. (1966) - Fluidized bed recovery of Fluorine in manufacture of $UF_6$. Chem. Eng. Progr. Symp. Series, Vol. 62, No. 65, 12-19.

Powell, C.A. (1958) - Current manufacturing processes used in the United States for mass production of $UF_6$ from purified $UO_3$. Proc. 2nd Int. Conf. on Peaceful Uses of Atomic Energy 4 165-71.

Robinson, S.N. and Todd, J.E. (1966) - Plant-scale fluid-bed denitrator. MCW-1509.

Rogan, H. (1970) - Fuel manufacturing technology and production facilities at Springfields. Paper presented to 4th Foratom Congress held at Stockholm September 21-23, 1970. British Nuclear Forum - Session IV : Fuel Manufacturing p.1-8.

Ruch, W.C., Peterson, D.A., Gaskill, E.A., Tepp, H.G. (1960) - Production of pure Uranium Hexafluoride from ore concentrate. Chem. Eng. Prog. Symp. Series. Vol. 56, No. 28. 35-41.

Scott, C.D., Adams, J.B. and Bresee, J.C. (1964) - Production of Uranium Hexafluoride in a fluidized bed reactor by reaction of Uranium Tetrafluoride with oxygen. Ind. Eng. Chem. Process Des. Dev. 3 (3) 266-270.

Smiley, S.H. (1961) - Gas-solids reactors in Uranium processing: a critical review. Progress in Nuclear Energy, Series IV, Technology, Engineering and Safety (Ed. C.M. Nicholls), Vol. 4, 191-278 Pergamon London.

Sutton, A.H., Bishop, J.C., Cohen, M.H., Stahman, K.J. (1966) - Reduction and hydrofluorination of Uranium concentrates by fluid bed techniques. Chem. Eng. Progr. Symp. Series, Vol. 62, No. 65, 20-30.

Thayer, H.E. (1958) - The newest United States uranium processing plant. Proc. 2nd Int. Conf. on Peaceful Uses of Atomic Energy 4 22-29.

USAEC (1968) - Uranium Hexafluoride handling procedures and containing criteria. ORO-651 Revision 2. November 1968.

AAEC SYMPOSIUM

ON

URANIUM PROCESSING

PAPER IX

# CAPITAL AND OPERATING COSTS FOR THE PRODUCTION OF URANIUM HEXAFLUORIDE

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## 1. INTRODUCTION

This paper derives the approximate capital investment and unit reprocessing cost for the conversion of uranium ore concentrates to uranium hexafluoride. The cost is derived for plants of nominal annual capacity 3,000 and 10,000 tonnes of uranium.

## 2. PROCESS DESCRIPTION

The main line process costed is similar to that employed by British Nuclear Fuels Ltd. (Alexander et al. 1960, Hawthorn et al. 1960, Page et al. 1960, Littlechild 1967), Kerr-McGee Corporation (Kerr-McGee 1971) and Eldorado Nuclear Ltd. (Berry 1969). It is a continuous process involving head end purification of uranium ore concentrates prior to hexafluoride conversion. This process was selected because of its inherent flexibility to accept all grades of ore concentrate.

### 2.1 Chemical Flowsheet

Figure 1 shows the chemical flowsheet for the main line process. The uranic content of ore concentrates is leached into nitric acid solution, insoluble siliceous solids removed by filtration, and the uranyl nitrate purified by solvent extraction; the pure nitrate solution is evaporated, thermally denitrated to uranium trioxide and reduced to uranium dioxide; this is hydrofluorinated with anhydrous hydrofluoric acid to produce uranium tetrafluoride, which is reacted with elemental fluorine to yield uranium hexafluoride. Ancillary processes include recovery of nitric acid and hydrofluoric acid from effluent streams for recycle, and treatment of effluents for disposal.

### 2.2 Process Equipment

#### 2.2.1 Leaching of ore concentrates (Figure 2)

Ore concentrates received from the mine sites are sampled and received into bulk storage hoppers. The concentrate is metered by screw feeder into an enclosed cylindrical leacher, fabricated from stainless steel, and divided into compartments through which the feed slurry flows in sequence. Each compartment is heated and stirred. The leacher is fed with strong, fresh and recovered nitric acid, dilute acid from recovery cycles, and water. The uranyl nitrate product is aged and filtered from insoluble silaceous residues. Nitric acid is recovered from leached off-gases.

#### 2.2.2 Purification by solvent extraction (Figure 2)

The impure uranyl nitrate solution is fed into a series of multistage mixer-settlers operated counter-currently with tributyl phosphate in kerosene as solvent. Uranium is extracted into solvent solution in 8 stages, scrubbed

from extracted impurities (8 stages), and stripped into aqueous nitric acid solution (12 stages). The aqueous raffinate from extraction is routed to nitric acid recovery and effluent treatment.

2.2.3 Evaporation and denitration (Figure 3)

The pure uranyl nitrate solution from solvent extraction is concentrated to the molten hexahydrate state ($UO_2(NO_3)_2 \cdot 6H_2O$) in a multiple effect evaporator (selected for steam economy). The concentrate is conditioned and injected into an electrically heated bed of uranium trioxide ($UO_3$) fluidised with air. Uranyl nitrate hexahydrate is decomposed into $UO_3$, nitrogen oxides and steam. Nitric acid is recovered from off-gases.

2.2.4 Reduction and hydrofluorination (Figure 4)

Uranium trioxide is metered continuously into the first of two beds of uranium dioxide ($UO_2$) series. The beds are fluidised with nitrogen, and reduction to $UO_2$ is achieved by a feed of cracked ammonia.

Uranium dioxide is hydrofluorinated to uranium tetrafluoride ($UF_4$) in two series connected beds containing $UF_4$, fluidised with nitrogen. Partial hydrofluorination is effected in the first reactor with dilute hydrofluoric acid vapour from HF recovery, and completed in the second reactor with anhydrous hydrofluoric acid vapour. Excess hydrofluoric acid is recovered from the reactor off-gases.

2.2.5 Fluorination (Figures 5 and 6)

Uranium tetrafluoride is metered continuously into a bed of calcium fluoride, fluidised with nitrogen, and fed with fluorine gas generated from electrolytic cells. The gaseous product uranium hexafluoride ($UF_6$) is condensed from the off-gas stream in a series of cold traps.

The inlet fluorine is fed counter-current to the solid waste underflow from the reactor to effect recovery of uranium. The exhaust gases from the reactor pass counter-current to the inlet uranium tetrafluoride to effect recovery of unreacted fluorine.

Feed fluorine is manufactured by electrolysis of fused potassium hydrogen fluoride (KHF) and anhydrous hydrofluoric acid (AHF) in a bath fabricated from Monel. Plant controls are centralised and integrated into the overall hexafluoride manufacturing system.

2.2.6 Recovery streams (Figures 7 and 8)

Nitric acid is recovered from process off-gas and acid effluent streams. Aqueous raffinate from solvent extraction is flash evaporated; the nitric

acid overheads together with condensate from leaching and thermal denitration are fractionally distilled to produce strong nitric acid for recycle.

Hydrofluoric acid is recovered from the hydrofluorination off-gases by fractional distillation to the $HF-H_2O$ azeotrope, which is recycled to hydrofluorination.

2.2.7 Waste disposal (Figure 9)

Waste streams consist mainly of strong nitric acid-salt streams from solvent extraction, strong hydrofluoric acid-salt streams from fluorine generation (both of relatively small volume), and weak acid overheads of large volume arising from fractional distillation. The salt streams are neutralised separately and evaporated in spray driers. Overheads from the driers are discharged together with neutralised fractionator overheads.

2.3 Conceptual Plant Layout (Figures 10, 11, 12)

Conceptual plant layouts for a capacity of 10,000 tonne U/year have been based on duplicate lines of leaching-filtration solvent extraction equipment, each line of 5,000 tonne U/year capacity, allied to three evaporation and fluidised bed 'dry-way' equipment lines each of 3,000 + tonne U/year.

Conceptual layout of plant to convert ore concentrate to uranium tetrafluoride is shown in Figure 10, fluorine cells and fluorination equipment in Figure 11, and an overall schematic site plan of the conversion complex in Figure 12.

## 3. PRELIMINARY COST ESTIMATE

### 3.1 General

The approximate capital investment and unit manufacturing costs for the conversion process described has been determined for plants of nominal capacity 3,000 and 10,000 tonne U/year, representing a range of capacity from the minimum likely to be economic to a capacity comparable with overseas conversion facilities. The latter capacity is of the order of size required to support an Australian enrichment facility.

Capital costs have been derived primarily from an assessment made in South Africa (Paynter and Geertsma 1965) of fixed capital costs for the unit operations of leaching, solvent extraction, reduction, hydrofluorination and fluorination including fluorine generation, at a capacity of 400 short ton/year. The cost of major plant items, pipework and instrumentation, has been deduced from a fixed capital cost breakdown, and updated to 1972 prices.

The effect of plant scale on cost has been derived from the South African

and other data for plants producing $UF_4$ and $UF_6$ at capacities between 400 and 3,000 tonne U/year; the indices have been used to calculate the effect of scale on costs of larger plant.

The cost of land, buildings, prices of process chemicals and labour have been assessed separately for conditions in Australia. Overall capital costs have been compared with available data.

3.2 Assumptions in the Cost Estimate

The following assumptions have been made:

(a) Plant Capacity

3,000 and 10,000 tonne U/year steady state operation at 100% utilisation. The plant equipment required for the 10,000 tonne U/year facility is in general assumed to consist of multiples of that in the 3,000 tonne U/year facility, effecting economy of scale where possible in common services and equipment.

(b) Annual Operating Period

7 day week, 300 days/year.

(c) Pre-operational Period

6 months at annual cost for labour, consumables and services.

(d) Losses and Inventory of Ore Concentrate

Excluded from production estimate; a 0.5% uranium loss has been costed for the commissioning period.

The plant is assumed to operate on a 'toll conversion' basis, i.e. to sell the conversion service to customers who provide their own yellow cake; as such no allowance is made in the production cost for material losses (0.5%) or inventory. This would not exclude the direct sale of hexafluoride (i.e. yellow cake plus conversion) from the plant; 'toll conversion' is, however, the normal basis on which similar plants operate overseas.

(e) Financial

Debt-Equity ratio 50%; equipment and installation depreciated over 10 years; other capital depreciated over 15 years; no residual value for establishment.

8.75% interest on debt capital; 12% return to equity (after tax); taxation rate of 0.475 on equity.

Interest during construction assumed equivalent to 1 year at 8.75% on debt component.

## 3.3 Reference Costs

### 3.3.1 Plant equipment

The South African data (Paynter et al. 1965) on Fixed Capital Costs for the unit operations in a 400 short ton/year plant have been used to derive the cost of plant equipment applying the following ground rules :

(a) Average cost of physical plant items
(equipment + pipework + instrumentation)
= 0.456 x Fixed Capital Cost.

(b) Buildings + civil work = 20% of physical plant cost up to production of $UF_4$.
Buildings + civil work = 35% of physical plant cost for fluorine generation and $UF_6$ production.

(c) Scaling factors of 0.67 and 0.81 between plant capacities of 400-1,000 tonne U/year and 1,000-3,000 + tonne U/year respectively.

The estimates have been updated to a 1972 basis assuming annual escalation factors of 4% and 6.5% for the periods 1965-1970 and 1970-1972 respectively, and scaled up to capacities of 3,000 and 10,000 tonne U/year.

### 3.3.2 Process chemicals

The major process feeds are listed in Table 1 together with their costs per tonne U on a Sydney basis for the two scales of hexafluoride production. The major cost in process chemicals is incurred in the supply of anhydrous hydrofluoric acid.

### 3.3.3 Transport of raw materials

A conversion plant sited at Townsville was selected for assessment of transport costs. Ore concentrates have been assumed to be transported 1,500 miles at an average cost of 6c/ton mile, equivalent to 9c/kg U. Process chemicals (assumed transported from Brisbane and Sydney) incurred a total cost of 10c/kg U.

### 3.3.4 Utilities

The capital cost and annual operating cost of major plant services are listed in Tables 2 and 3 respectively, together with estimates of service capacity, annual demand, and unit rates assumed (Peters and Timmerhans 1968, Buchanan and Sinclair 1966).

### 3.3.5 Maintenance materials

An allocation of 2% per year of the fixed capital cost has been made to cover maintenance requirements.

3.3.6 Labour

Table 4 shows a projected staffing and wage structure for the three capacities of plant considered. Plants of 10,000 tonne U/year capacity are envisaged as replication of part of the process units of a 3,000 tonne U/year facility. Centralisation of control stations has been assumed for the larger facility, and an appropriate economy of scale in labour has been allowed.

3.4 Capital Summary

Table 5 summarises the capital required for the plants including land, buildings, equipment, fees (design and installation), and pre-operational capital. Equipment and associated installation costs have been depreciated over 10 years and the balance of fixed capital over 15 years. The plant is assumed to have no residual value; operating capital is recovered at the end of the 15 year period.

Fixed capital costs of about $\$A13 \times 10^6$ and $\$A33 \times 10^6$ are indicated for conversion capacities of 3,000 and 10,000 tonne U/year.

Figure 13 compares capital costs derived in this manner with those from American (Nuclear Industry, 1970), UK (private communication, July 1972), Canadian (Williams 1970), and French (private communication, July 1972) sources. In general allowing for the differences in ground rules which apply to each estimate the derived capital costs are reasonably in agreement.

Further information on the capital cost of equipment, particularly fluid beds, fluorine cells and ancillary equipment will be necessary before the confidence in these estimates can be determined for Australian conditions. A clarification of the responsibility for inventory between the customer and the operators of the hexafluoride and yellow cake plants will also be necessary; the present estimates of capital and operating costs exclude all inventory charges of ore concentrate or $UF_6$.

3.5 Annual Operating Charges

Table 6 summarises the annual operating cost for plant operation, and the unit manufacturing cost has been calculated from these costs and the plant throughput. The cost includes a 10% contingency on annual charges; this high level has been adopted in view of the many assumptions on which this exercise is based.

Unit Toll Conversion charges, inclusive of transport and insurance of hexafluoride to the Oak Ridge enrichment plant (about $US 0.64/kg U) are estimated at $A2.91 and 2.53 per kg U for capacities of 3,000 and 10,000

tonne U/year respectively. The conversion cost, exclusive of $UF_6$ transport charges are $A2.27 and $A1.89 per kg U for the above plant capacities.

3.6 Analysis of Costs of Conversion

Table 7 presents an analysis of the factors in the unit cost of $UF_6$ production, expressed both as percentages and actual costs.

Costs arising from capital investment (depreciation, loan interest, equity repayment and taxation) account for about 44% of the cost of conversion.

The major process chemical cost (13-15%) is incurred by hydrofluoric acid, with about 5% contributed by use of nitric acid.

Labour charges amount to about 7-11% of the total conversion cost.

3.7 Comparison of total cost of conversion to a utility purchasing uranium ore concentrate

Table 8 puts into perspective the total costs which a purchaser of uranium ore concentrate would incur by conversion in an Australian plant, or in a plant in the USA. On present toll conversion rates quoted by Allied Chemical Corporation, for example, the purchasing utility would incur a total charge of about $A2.98/kg U for $UF_6$ delivered to Oak Ridge enrichment plant, compared with an estimated total cost (manufacture and transport) of $A2.62-3.00 for conversion in an Australian plant and delivery to Oak Ridge.

## 4. POSSIBLE LOCATIONS AND CO-ORDINATION WITH OTHER FACILITIES

The assessment previously presented has assumed a non-associated plant at an east coast location (Townsville) for estimation of transport costs. The possible advantages of locating a hexafluoride conversion plant either adjacent to the mining operations in the Northern Territory or associated with an enrichment plant have also been assessed. The major conclusions are as follows :

(a) Location of the hexafluoride plant adjacent to the mines could result in a direct operating penalty of 12-15 cents per kg U due to additional costs of transport, relative to locations at Darwin or on the eastern coast. The mines' locations are also not favoured because of the lack of infrastructure (power, services, labour).

(b) Location of the conversion and enrichment plants on the same site, and sale of enriched hexafluoride, would allow significant economies in inventory and transport, tentatively assessed at 15-20 cents per kg U (natural).

(c) A joint location would also facilitate the recovery and recycling of fluorine, thereby effecting further economies. (The 'depleted' uranium hexafluoride from the enrichment plant would be converted to uranium dioxide - which is more readily stored than hexafluoride - and the fluorine recovered as hydrofluoric acid for re-use in the conversion plant. The economics of this operation are still being examined but they appear to be favourable).

(d) In the longer term, shipment of the enriched uranium as oxide (rather than hexafluoride) could be accepted commercial practice; a joint location would facilitate this reconversion to oxide.

(e) As the outputs suggested, a hexafluoride plant would justify the establishment of a 'captive' plant for manufacture of sulphuric and hydrofluoric acid (and for recovery of dilute acid in the event of fluorine recycle); this might stimulate the development of fluorite deposits in Australia, and reduce the operating cost from supply and transport of hydrofluoric acid. A combined captive plant installation costing about $A2-2.5 \times 10^6$ is estimated for support of a conversion plant of 10,000 tonne U/year.

## 5. CONCLUSIONS

1. Plants for the conversion of uranium ore concentrates to hexafluoride at capacities of 3,000 and 10,000 tonne U/year would require fixed capital investments of about $A13 \times 10^6$ and $A33 \times 10^6$ respectively. These costs exclude supporting industries and other development; captive hydrofluoric and sulphuric acid plants may cost a further $A2-2.5 \times 10^6$.

2. Plants of 3,000 and 10,000 tonne U/year capacity could supply toll conversion services for costs of $A2.91/kg U and $A2.53/kg U respectively, inclusive of transport charges for delivery of hexafluoride at Oak Ridge enrichment plant.

3. The total cost to a utility purchasing Australian ore concentrate for conversion and delivery to Oak Ridge enrichment plant is estimated at $A2.62-3.00/kg U for conversion in an Australian plant, compared with $A2.98/kg U for conversion in the USA.

## 6. ACKNOWLEDGEMENTS

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## 7. REFERENCES

Alexander, R.C., Shortis, L.P., Turner, C.J. (1960) - The Second Uranium Plant at Springfields. Brit. Nucl. En. Conf. J. 5 (4) 264.

Berry, R.M. (1969) - Eldorado's Port Hope Refinery 1969. Can. Mining and Metallurgical Bull. 62, 1093.

Buchanan, R.H., and Sinclair, C.G. (Editors) (1966) - Costs and Economics of the Australian Process Industries. West Publishing Corporation.

Hawthorn, E., Shortis, L.P., Lloyd, J.E. (1960) - The Fluidised Solids Dryway Process for the Production of Uranium Tetrafluoride at Springfields. Brit. Nucl. En. Conf. J. 5 (4) 285.

Kerr-McGee (1971) - Sequoiah Uranium Hexafluoride Production Plant. Kerr-McGee Corporation. Docket 408027-2.

Littlechild, J.E. (1967) - Operational Development of a Uranium Ore Solution and Extraction Plant. I. Chem. Eng. Symp. Series No. 26.

NUCLEAR INDUSTRY (1970) - Kerr-McGee Adds to U.S. Commercial $U_3O_8$ - $UF_6$ Conversion Capacity - No author cited. Nuc. Ind. 17 (5) 25.

Page, H., Shortis, L.P., Dukes, J.A. (1960) - The Processing of Uranium Ore Concentrates and Recycle Residues to Purified Uranyl Nitrate Solution at Springfields. Brit. Nucl. En. Conf. J. 5 (4) 272.

Paynter, J.C., and Geertsma, J.C. (1965) - Design of a 400 ton/annum Uranium Refining Plant. PEL-121 Volumes 1 and 2, Atomic Energy Board, South Africa.

Peters, M.S., and Timmerhaus, K.D. (1968) - Plant Design and Economics for Chemical Engineers. McGraw-Hill Co.

Williams, R.M., (1970) - Uranium. Can. Mining Journal Feb. 1970, p.120.

TABLE 1

COST OF PROCESS FEEDS

| Feed Material | Usage tonne/tonne U | Plant Capacity (tonne U/year) | | | |
|---|---|---|---|---|---|
| | | 3,000 | | 10,000 | |
| | | $A/tonne Material Cost | $A/tonne U | $A/tonne Material Cost | $A/tonne U |
| 60% $HNO_3$ | 0.828 | 118.0 | 97.7 | 118.0 | 97.7 |
| TBP/Kerosene | 0.01/0.02 | | 5.0 | | 5.0 |
| $NH_3$ anhydrous | 0.048 | 162.5 | 7.7 | 152.5 | 7.2 |
| HF anhydrous | 0.57 | 530.0 | 302.0 | 500.0 | 285.0 |
| KHF | 0.01 | 673.0 | 6.7 | 673.0 | 6.7 |
| Lime | 0.5 | 16.0 | 8.0 | 16.0 | 8.0 |
| $N_2$ | ~1500 $ft^3$/tonne | $A3/1000 $ft^3$ | 3.9 | $A3/1000 $ft^3$ | 3.9 |
| Miscellaneous | | | 3.2 | | 3.2 |
| Total Materials Cost ($A/tonne U) | | | 434.2 | | 416.7 |

TABLE 2

SERVICES - CAPITAL COST OF INSTALLATION

| Service | Cost Basis | Plant Capacity (tonne U/year) | | | |
|---|---|---|---|---|---|
| | | 3,000 | | 10,000 | |
| | | Capacity | $A | Capacity | $A |
| Electricity | $A100/kVA | 2,250 kVA | 225,000 | 7,510 kVA | 751,000 |
| | +$A1.0/ft$^2$ | 83,300 ft$^2$ | 83,300 | 136,425 ft$^2$ | 136,425 |
| Water | $A 20/gph | 13,542 gph | 270,840 | 45,140 gph | 902,800 |
| Plumbing | $A 1/ft$^2$ | | 83,300 | | 136,425 |
| Steam | (Peters and Timmerhaus 1968) | 17,250 lb/hr | 21,200 | 57,500 lb/hr | 106,000 |
| Compressed Air | (Peters and Timmerhaus 1968) | 800 m$^3$/hr | 10,000 | 2,666 m$^3$/hr | 30,000 |
| Total Capital Cost ($A) | | | 693,640 | | 2,062,650 |

TABLE 3

SERVICES - ANNUAL OPERATING COSTS

| Service | Rate Assumed | Plant Capacity (tonne U/year) | | | |
|---|---|---|---|---|---|
| | | 3,000 | | 10,000 | |
| | | Annual Demand | $A | Annual Demand | $A |
| Electricity | 2c/kWh | $16.2 \times 10^6$ kWh | 324,000 | $54 \times 10^6$ kWh | 1,080,000 |
| Water | $A0.4/1000 gal | $97.5 \times 10^6$ gal | 39,000 | $325 \times 10^6$ gal | 130,000 |
| Steam | $A1.0/1000 lb | $124.2 \times 10^6$ lb | 124,000 | $414 \times 10^6$ lb | 414,000 |
| Compressed Air (included in Elect. Cost.) | | | | | |
| Annual Cost ($A) | | | 487,200 | | 1,624,000 |

TABLE 4

LABOUR RATES AND ANNUAL COSTS

| Classification | Rate $A/year | Plant Capacity (tonne U/year) | | | |
|---|---|---|---|---|---|
| | | 3,000 | | 10,000 | |
| | | No. | $A/year | No. | $A/year |
| Superintendent | 12,794 | 1 | 12,794 | 1 | 12,794 |
| Production Manager | 11,451 | 1 | 11,451 | 1 | 11,451 |
| Production Engineer | 10,182 | 1 | 10,182 | 1 | 10,182 |
| Accountant | 6,819 | 1 | 6,819 | 1 | 6,819 |
| Assistant Accountant | 5,293 | 1 | 5,293 | 1 | 5,293 |
| Production Clerk | 4,340 | 4 | 17,360 | 6 | 26,040 |
| Typist | 3,086 | 4 | 12,344 | 6 | 18,516 |
| Storeman and Tank Farm* | 4,796 | 5 | 23,980 | 7 | 33,572 |
| Health Physics* | 5,337 | 5 | 26,685 | 6 | 32,022 |
| Medical Staff (Nurse) | 4,000 | 1 | 4,000 | 1 | 4,000 |
| Security* | 5,427 | 5 | 27,135 | 5 | 27,135 |
| Analytical Services* | 5,337 | 5 | 26,685 | 6 | 32,022 |
| Technical Staff | 8,570 | 2 | 17,140 | 3 | 25,710 |
| Shift Supervisor* | 11,200 | 5 | 56,000 | 9 | 100,800 |
| Maintenance Foreman | 5,096 | 1 | 5,096 | 2 | 10,192 |
| Maintenance Staff | 3,947 | 10 | 39,470 | 16 | 63,152 |
| Instrument Mechanic | 4,288 | 1 | 4,288 | 3 | 12,864 |
| Process Operator* | | | | | |
| 1) Digestion and Solvent Extraction | 5,337 | 11 | 58,707 | 22 | 117,414 |
| 2) Denitration | 5,337 | 5 | 26,585 | 10 | 53,370 |
| 3) Reduction and Hydro-fluorination | 5,337 | 11 | 58,707 | 22 | 117,414 |
| 4) Direct Fluorination | 5,337 | 27 | 144,099 | 54 | 288,198 |
| Sub-Totals | | | 594,820 | | 1,008,960 |
| + 18% Statutory overheads (pension fund, workers compensation, long service leave)<br>+ 4.5% Training<br>+ 2.5% Payroll Tax | | | 148,705 | | 252,240 |
| Total $A/year | | | 743,525 | | 1,261,200 |

* Operators employed on shift roster; the rate is inclusive of shift allowance.

## TABLE 5

## CAPITAL SUMMARY

| Item | | | Plant Capacity (tonne U/year) 3,000 $A | 10,000 $A |
|---|---|---|---|---|
| 1. | SITE AND SITE DEVELOPMENT | | 3,000 | 10,000 |
| | 1.1 Land $6,000/Acre : 30 acres | | 180,000 | 180,000 |
| | 1.2 Land Services $8,000/Acre | | 240,000 | 240,000 |
| | 1.3 Process Buildings | 35% of 2.1.5 and 2.1.6 | 854,000 | 2,263,000 |
| | | 20% of 2.1 and 2.2 excluding 2.1.5 and 2.1.6 | 540,000 | 1,421,000 |
| | 1.4 Process Services | | 694,000 | 2,063,000 |
| 2. | EQUIPMENT | | | |
| | 2.1 Process Equipment | | | |
| | 2.1.1 Dissolver/Solvent Extraction | | 523,000 | 1,386,000 |
| | 2.1.2 Denitration | | 348,000 | 924,000 |
| | 2.1.3 Reduction<br>2.1.4 $UF_4$ conversion | | 697,000 | 1,847,000 |
| | 2.1.5 $UF_6$ conversion | | 1,255,000 | 3,325,000 |
| | 2.1.6 Fluorine production | | 1,184,000 | 3,141,000 |
| | 2.1.7 Fluorine recovery | | 340,000 | 907,000 |
| | 2.1.8 Waste recovery | | 567,000 | 1,474,000 |
| | 2.2 Contingency on equipment 5% | | 227,000 | 567,000 |
| 3. | FEES AND SERVICES | | | |
| | 3.1 Architect/Layout | 10% of 1.2 and 1.3 and 1.4 | 232,000 | 599,000 |
| | 3.2 Engineering Design | 15% of 2 | 771,000 | 2,036,000 |
| | 3.3 Procurement | 5% of 2 | 257,000 | 679,000 |
| | 3.4 Installation | 35% of 2 | 1,799,000 | 4,750,000 |
| | 3.5 Insurance/services | 1% of 1 and 2 | 76,000 | 197,000 |
| 4. | PRE OPERATIONAL COSTS | | | |
| | 4.1 Interest on Capital | 1 year at 8.75% on debt Component (50% fixed capital) | 561,000 | 1,468,000 |
| | 4.2 Labour | 6 months annual cost | 371,000 | 632,000 |
| | 4.3 Consumables | 6 months annual cost | 784,000 | 2,410,000 |
| | 4.4 Services | 6 months annual cost | 244,000 | 812,000 |
| | 4.5 Losses | 0.5% of throughput during commissioning | 75,000 | 250,000 |
| 5. | TOTAL FIXED CAPITAL | | 12,819,000 | 33,562,000 |
| 6. | OPERATING CAPITAL | | | |
| | 6.1 Work in hand | 1 month's supply of process chemicals | 109,000 | 347,000 |
| | 6.2 Stores and Spares | 10% of 2 | 514,000 | 1,357,000 |
| | 6.3 Funds | 10% of annual operating costs | 700,000 | 1,800,000 |
| 7. | TOTAL CAPITAL | | 14,142,000 | 37,081,000 |
| | 7.1 10 Year Capital | (2.1 + 2.2 + 3.4) | 6,940,000 | 18,321,000 |
| | 7.2 15 Year Capital | (7 - 6 - 7.1) | 5,897,000 | 15,256,000 |
| | 7.3 Returned Capital | | 1,323,000 | 3,504,000 |

TABLE 6

ANNUAL EXPENDITURES AND UNIT MANUFACTURING COST

| Item | Plant Capacity (tonne U/year) | | | |
|---|---|---|---|---|
| | 3,000 | | 10,000 | |
| | $A/kg U | $A/year | $A/kg U | $A/year |
| 1. Manufacturing Costs | | | | |
| 1.1 Depreciation - (8.75% interest yield) | | | | |
| (a) 10 Year Capital (.083) | 0.19 | 576,000 | 0.15 | 1,521,000 |
| (b) 15 Year Capital (.050) | 0.10 | 293,000 | 0.08 | 763,000 |
| 1.2 Labour | 0.25 | 743,000 | 0.13 | 1,261,000 |
| 1.3 Consumables | | | | |
| (a) Process chemicals | 0.43 | 1,303,000 | 0.42 | 4,161,000 |
| (b) Maintenance (2% fixed capital) | 0.09 | 255,000 | 0.07 | 669,000 |
| 1.4 Services | 0.16 | 487,000 | 0.16 | 1,624,000 |
| 1.5 Fees (1% Fixed Capital) | 0.04 | 127,000 | 0.03 | 334,000 |
| 1.6 Contingency (10% of above) | 0.12 | 372,000 | 0.11 | 1,193,000 |
| 1.7 Unit Manufacturing Cost | 1.38 | | 1.15 | |
| 2. Sampling and Transport Costs | | | | |
| 2.1 Yellow cake sampling | 0.06 | | 0.06 | |
| 2.2 Transport of process chemicals | 0.10 | | 0.10 | |
| 2.3 Transport and Insurance of $UF_6$ to Oak Ridge | 0.64 | | 0.64 | |
| 3. Financial Expenditures | | | | |
| 3.1 Interest payment of debt capital (8.75% of 50% of total capital) | 0.20 | 615,000 | 0.16 | 1,616,000 |
| 3.2 Return to equity (12% of 50% total capital) | 0.28 | 843,000 | 0.22 | 2,216,000 |
| 3.3 Implied taxation (3.2 x 0.475/1-0.475) | 0.25 | 763,000 | 0.20 | 2,005,000 |
| 4. Unit Cost of Toll Conversion (including sampling charges) | 2.27 | | 1.89 | |
| 5. Unit Cost of Toll Conversion (including $UF_6$ transport to Oak Ridge) | 2.91 | | 2.53 | |

TABLE 7

FACTORS IN THE UNIT TOLL CONVERSION COST OF $UF_6$ PRODUCTION

| Item | Plant Capacity (tonne U/a) | | | |
|---|---|---|---|---|
| | 3,000 | | 10,000 | |
| | % | $A/kg U | % | $A/kg U |
| Depreciation - Buildings and Equipment | 12.4 | 0.28 | 12.2 | 0.23 |
| Labour | 11.0 | 0.25 | 6.9 | 0.13 |
| Nitric Acid | 4.8 | 0.11 | 5.3 | 0.10 |
| Hydrofluoric Acid | 13.2 | 0.30 | 15.2 | 0.29 |
| Other Chemicals | 1.7 | 0.04 | 1.6 | 0.03 |
| Maintenance Materials | 4.0 | 0.09 | 3.7 | 0.07 |
| Services | 7.1 | 0.16 | 8.5 | 0.16 |
| Fees | 1.7 | 0.04 | 1.6 | 0.03 |
| Contingency | 5.3 | 0.12 | 5.8 | 0.11 |
| Sampling of Ore Concentrate and Transport Costs of Process Chemicals | 7.1 | 0.16 | 8.5 | 0.16 |
| Interest on Debt | 8.8 | 0.20 | 8.5 | 0.16 |
| Return to Equity at 12% | 11.9 | 0.27 | 11.6 | 0.22 |
| Tax on Gross Profit | 11.0 | 0.25 | 10.6 | 0.20 |
| | 100.0 | 2.27 | 100.0 | 1.89 |

TABLE 8

COMPARISON OF CONVERSION OPTIONS

Option 1

Purchase of Australian ore concentrate, transport and conversion in an Australian hexafluoride plant, with shipping and rail transport of $UF_6$ to a US enrichment plant.

| | Plant Capacity (tonne U/year) | |
|---|---|---|
| | 3,000 $A/kg U | 10,000 $A/kg U |
| Cost of transport of ore concentrate 1,500 miles at 6c/ton mile | 0.09 | 0.09 |
| Cost of sampling and conversion to $UF_6$ | 2.27 | 1.89 |
| Cost of transport of $UF_6$ to Oak Ridge enrichment plant | 0.64 | 0.64 |
| Total | 3.00 | 2.62 |

Option 2

Purchase of Australian ore concentrate, transport and shipping to USA and conversion in a US plant with transport of $UF_6$ to a U.S. enrichment plant.

| | $A/kg U |
|---|---|
| Cost of transport of ore concentrate | 0.50 |
| Cost of sampling ore concentrate | 0.06 |
| US conversion charge ($US 1.31/lb U) (includes transport charge to enrichment plant) | 2.42 |
| Total | 2.98 |

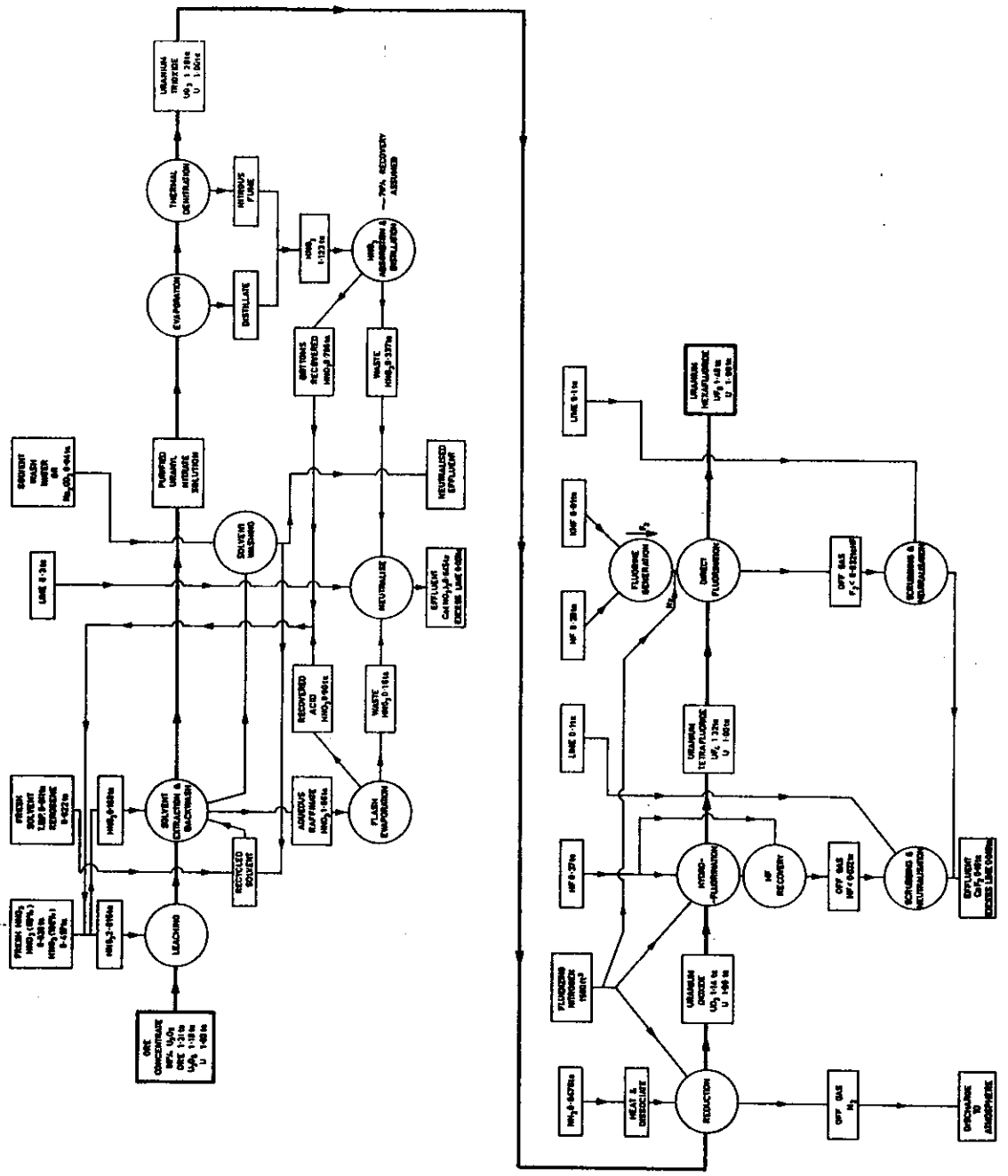

FIGURE 1. MATERIALS FLOWSHEET FOR CONVERSION OF ORE CONCENTRATE TO $UF_6$

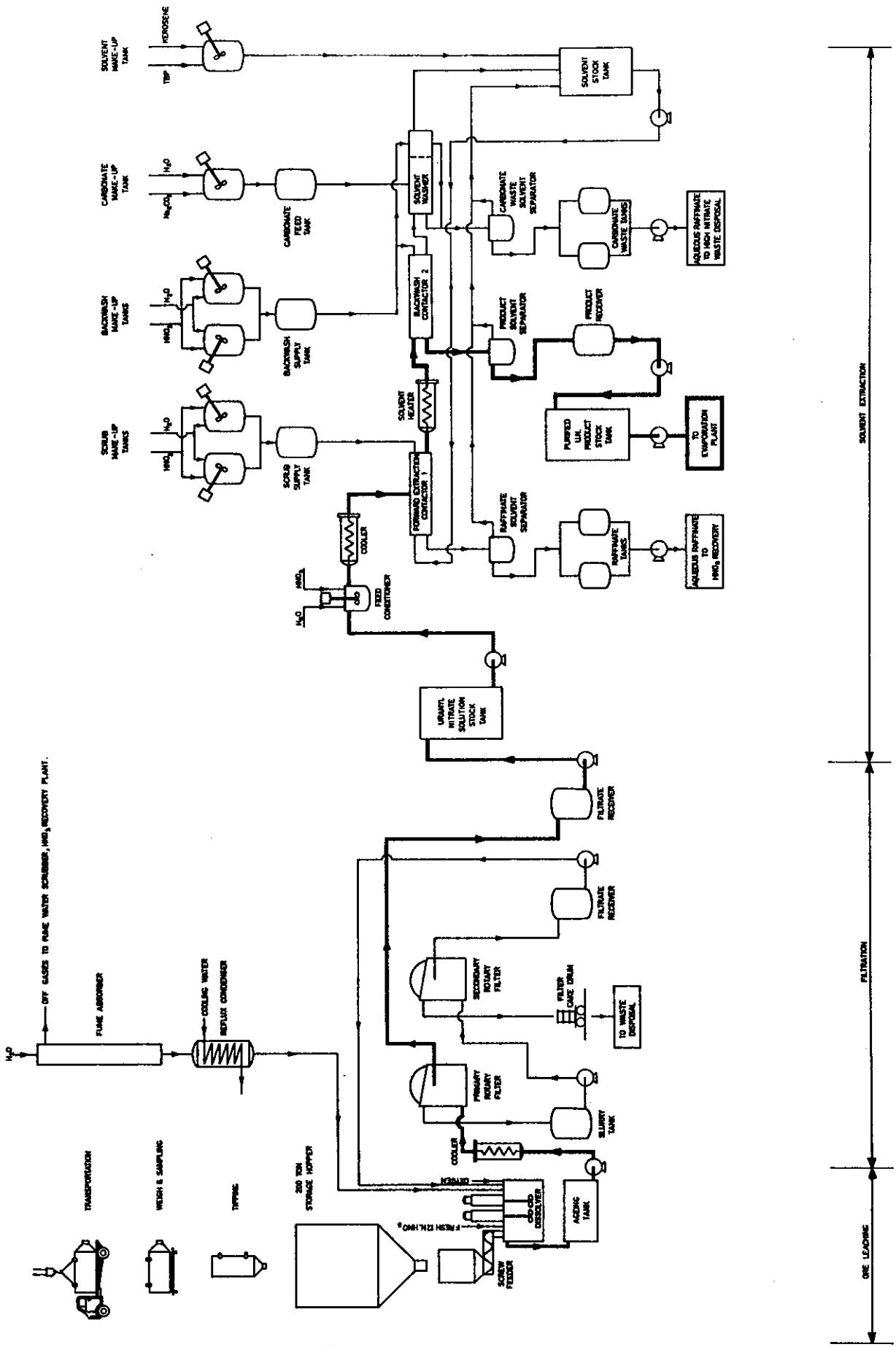


FIGURE 2. FLOW DIAGRAM: ORE LEACHING, FILTRATION AND SOLVENT EXTRACTION

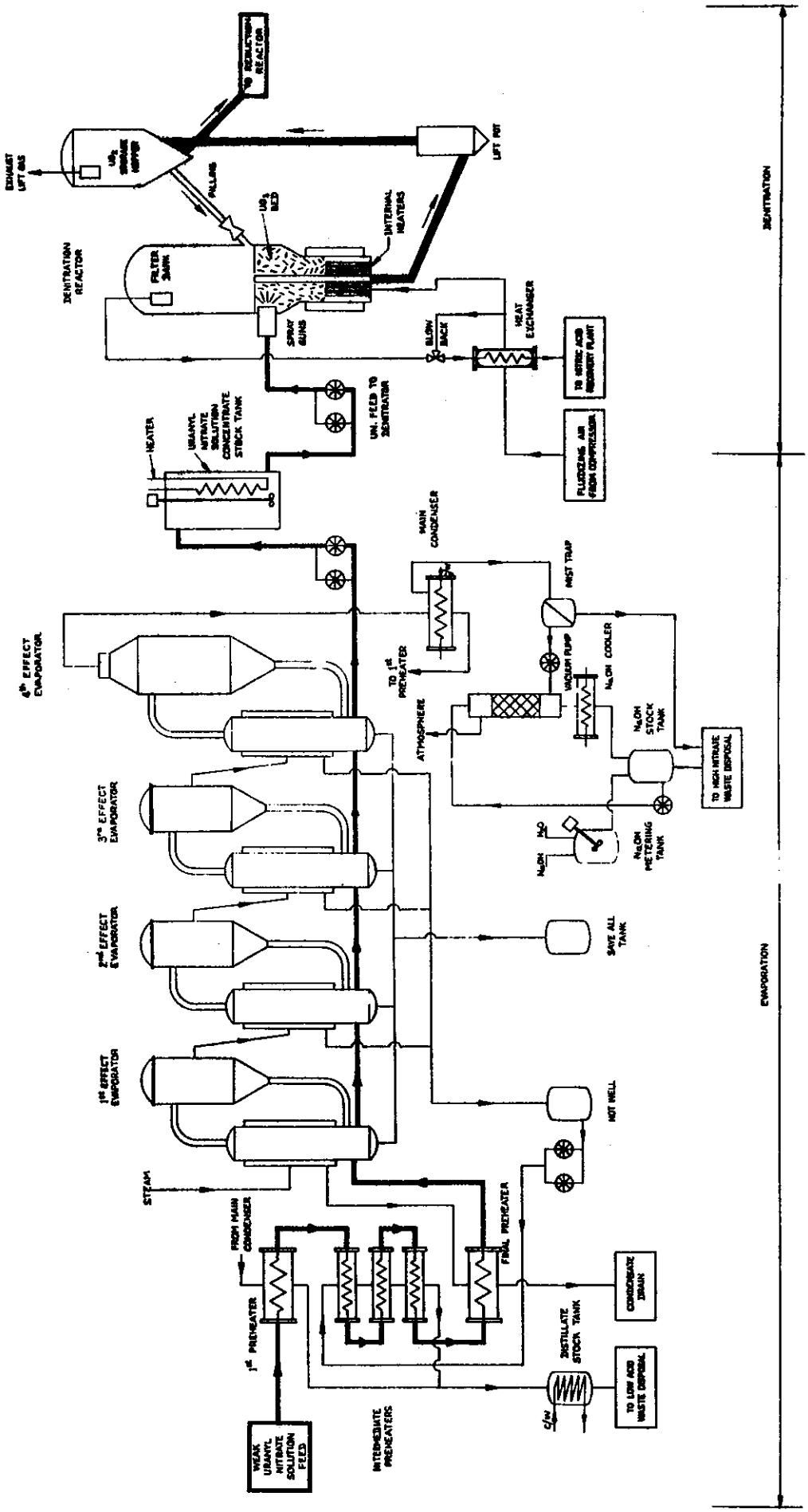


FIGURE 3. FLOW DIAGRAM: EVAPORATION AND THERMAL DENITRATION

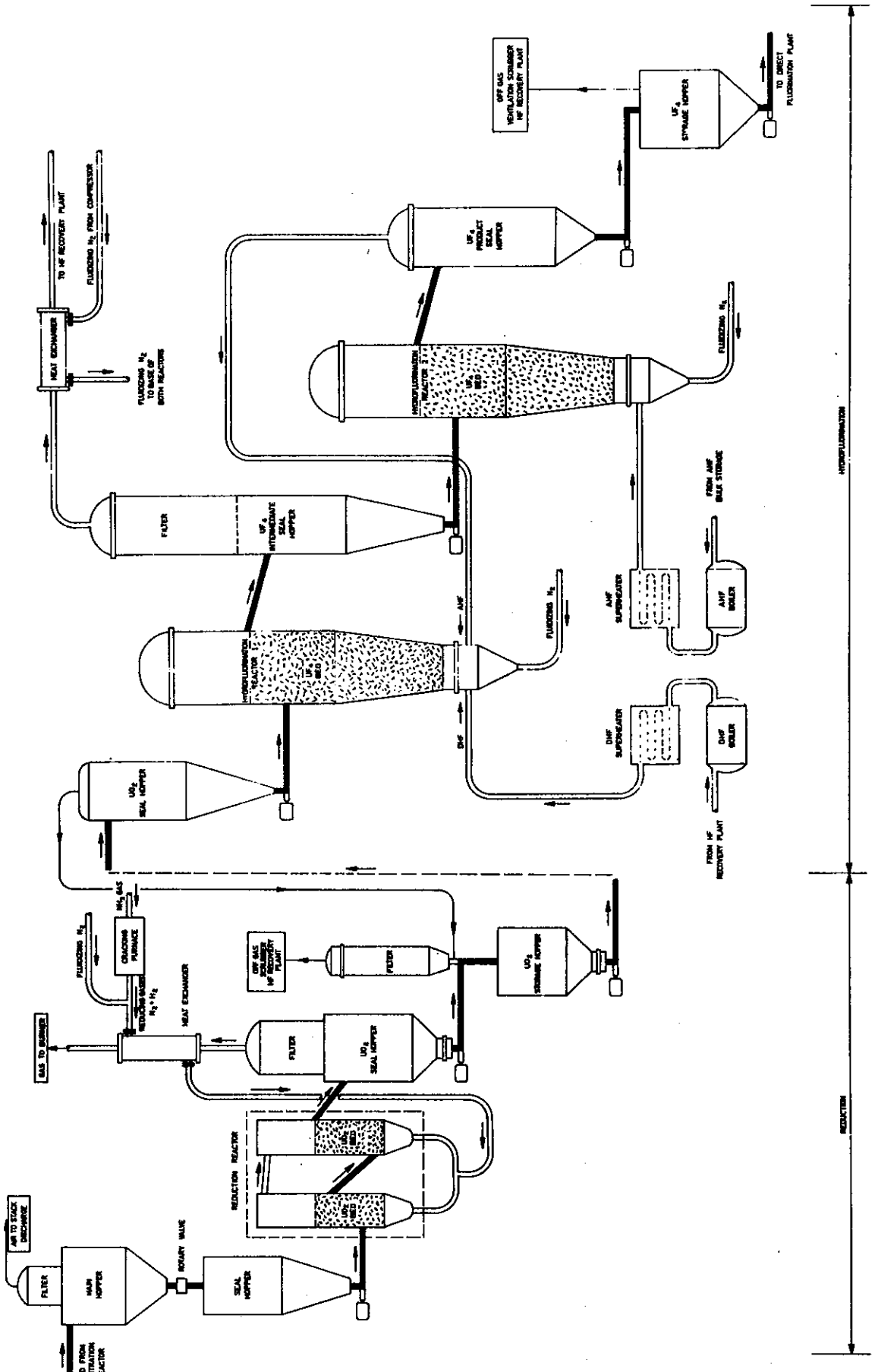


FIGURE 4. FLOW DIAGRAM: REDUCTION AND HYDROFLUORINATION

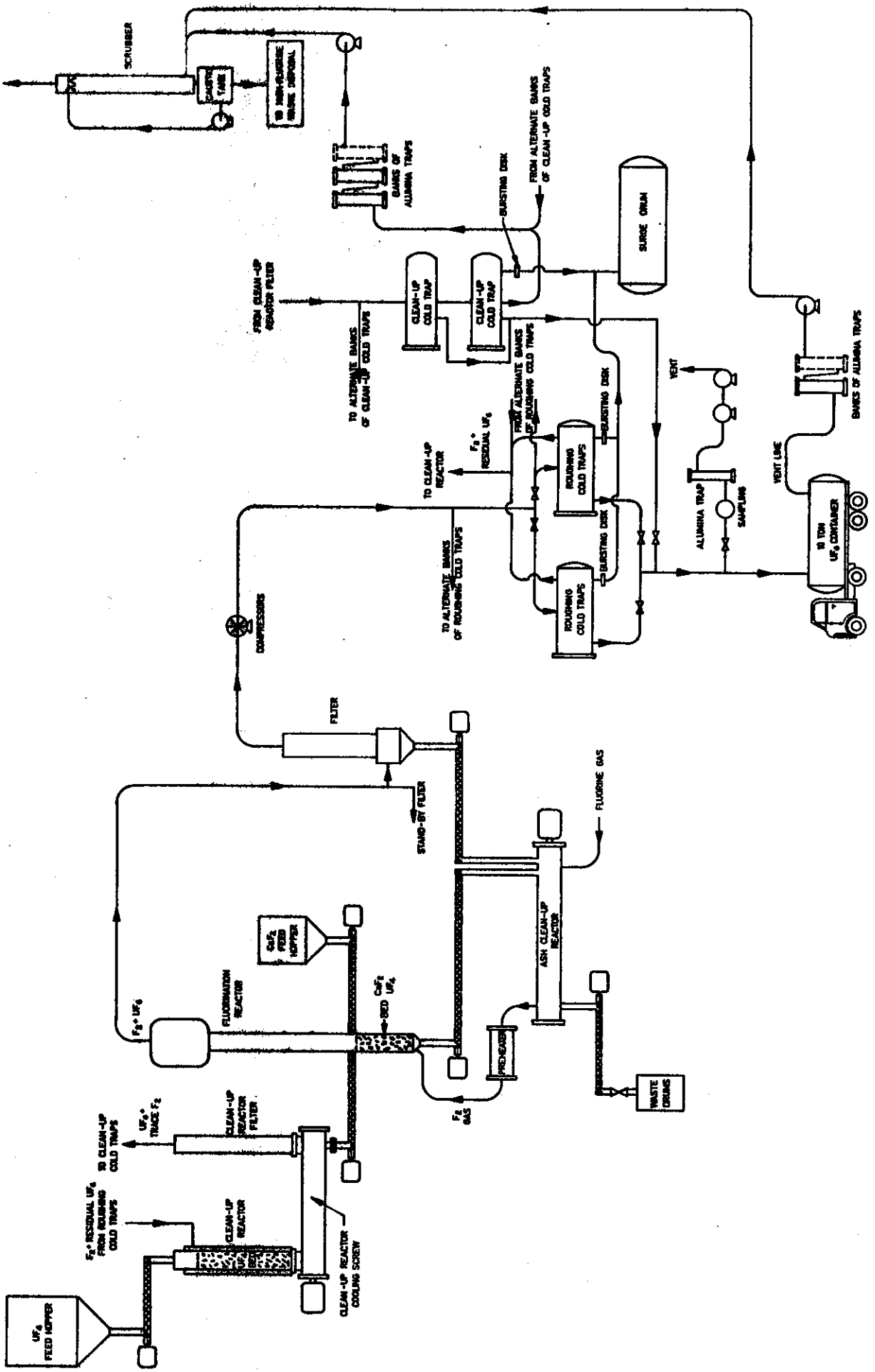


FIGURE 5. FLUORINATION FLOW DIAGRAM

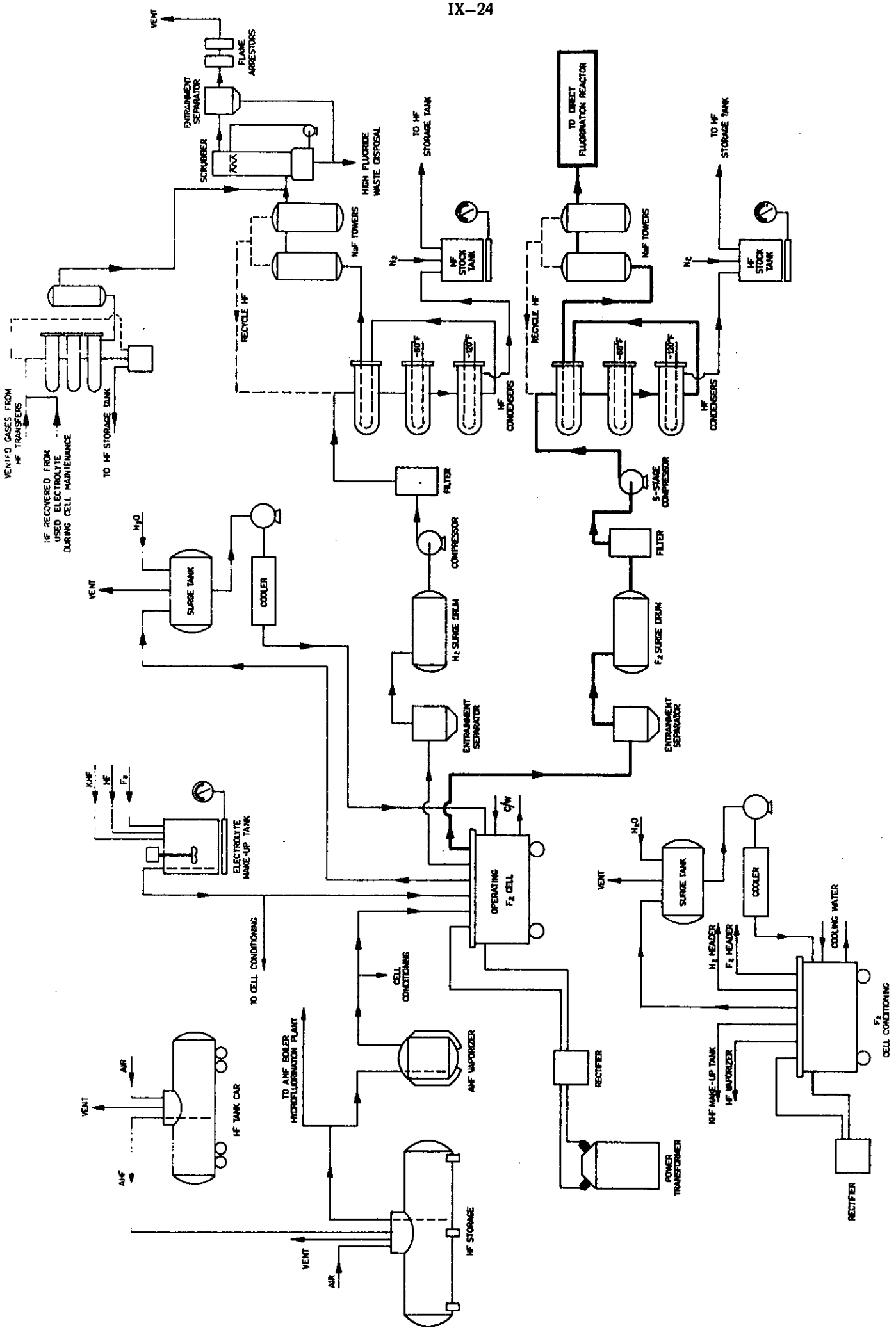


FIGURE 6. FLUORINE GENERATING PLANT

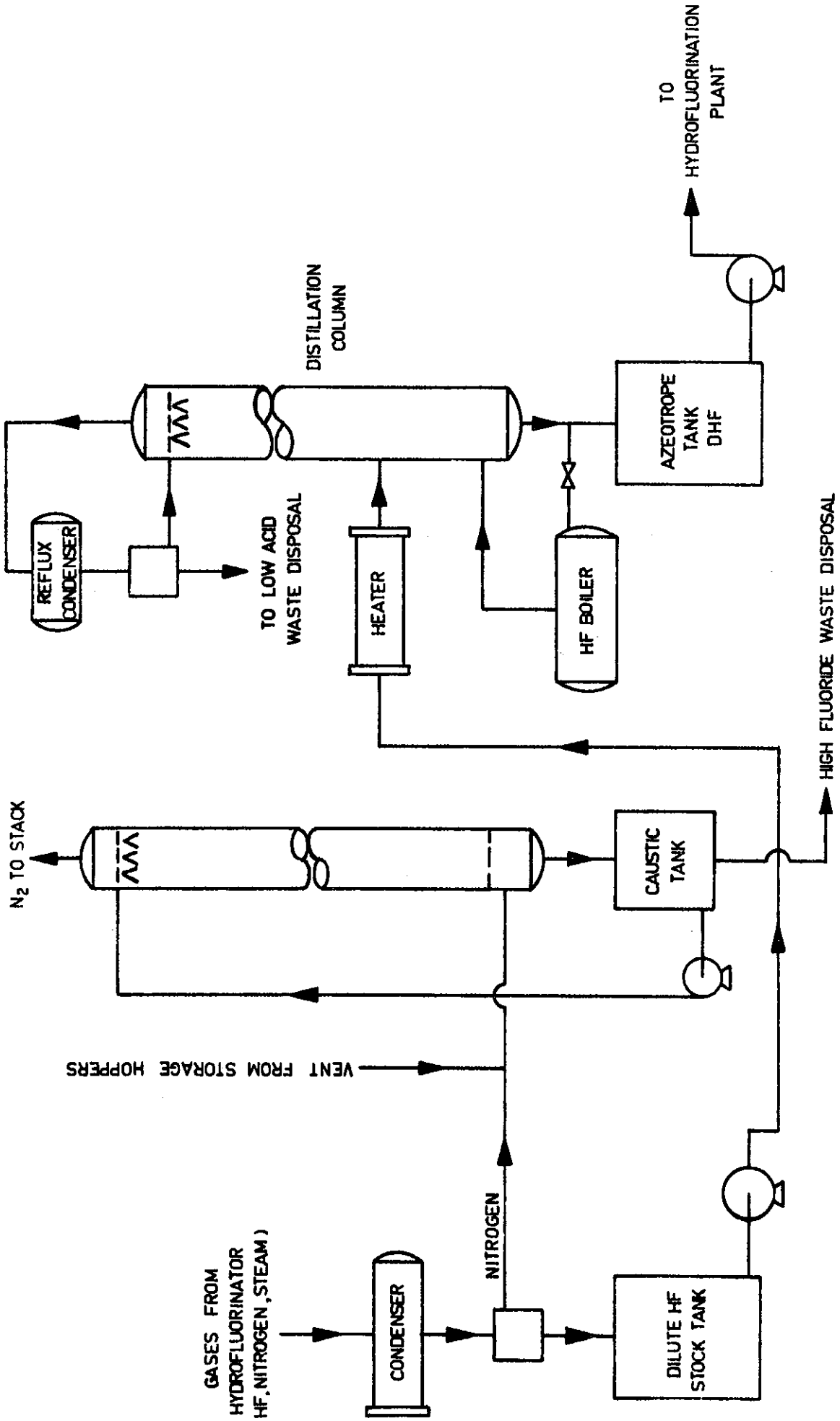


FIGURE 7. HF RECOVERY PLANT

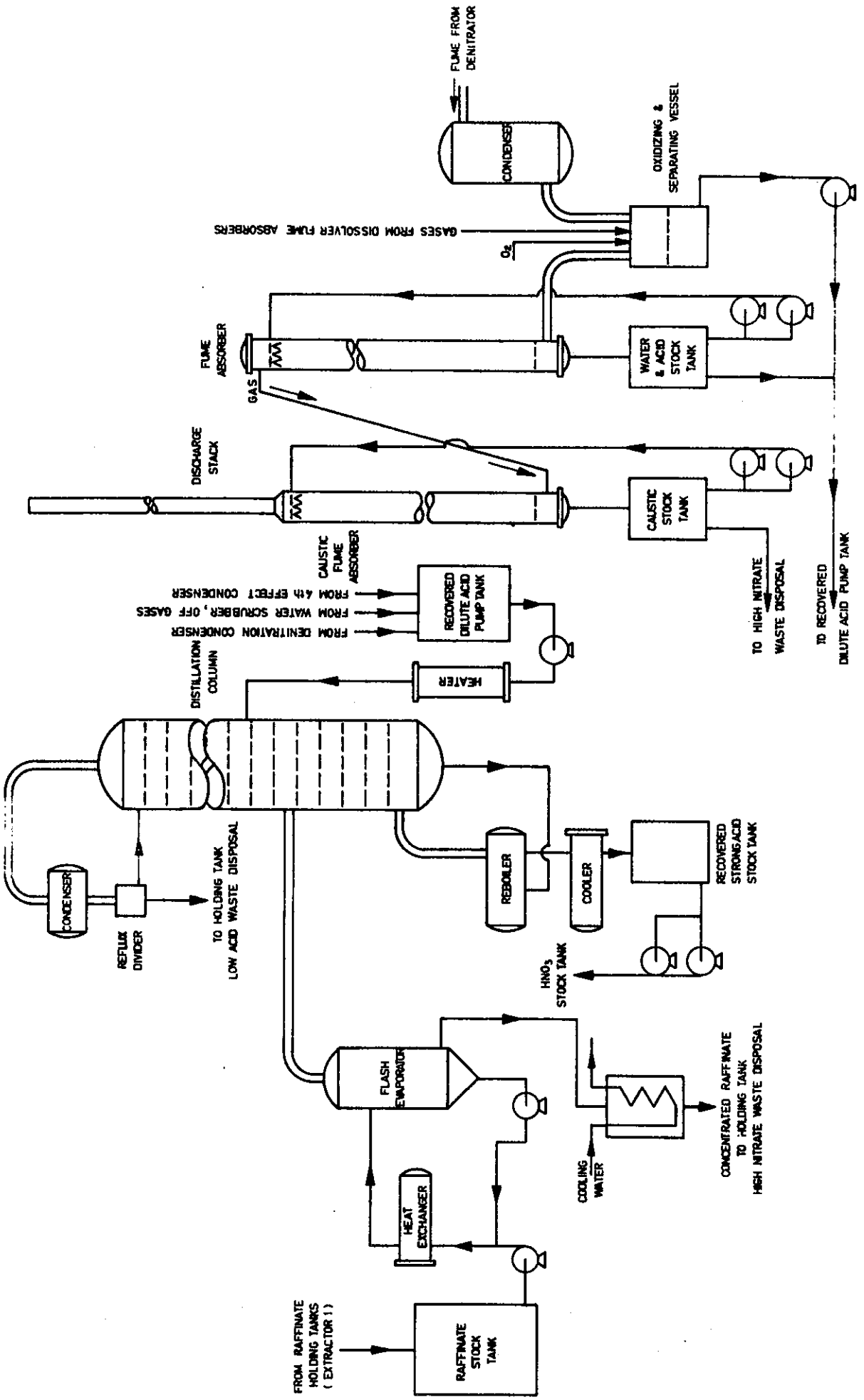


FIGURE 8. NITRIC ACID RECOVERY

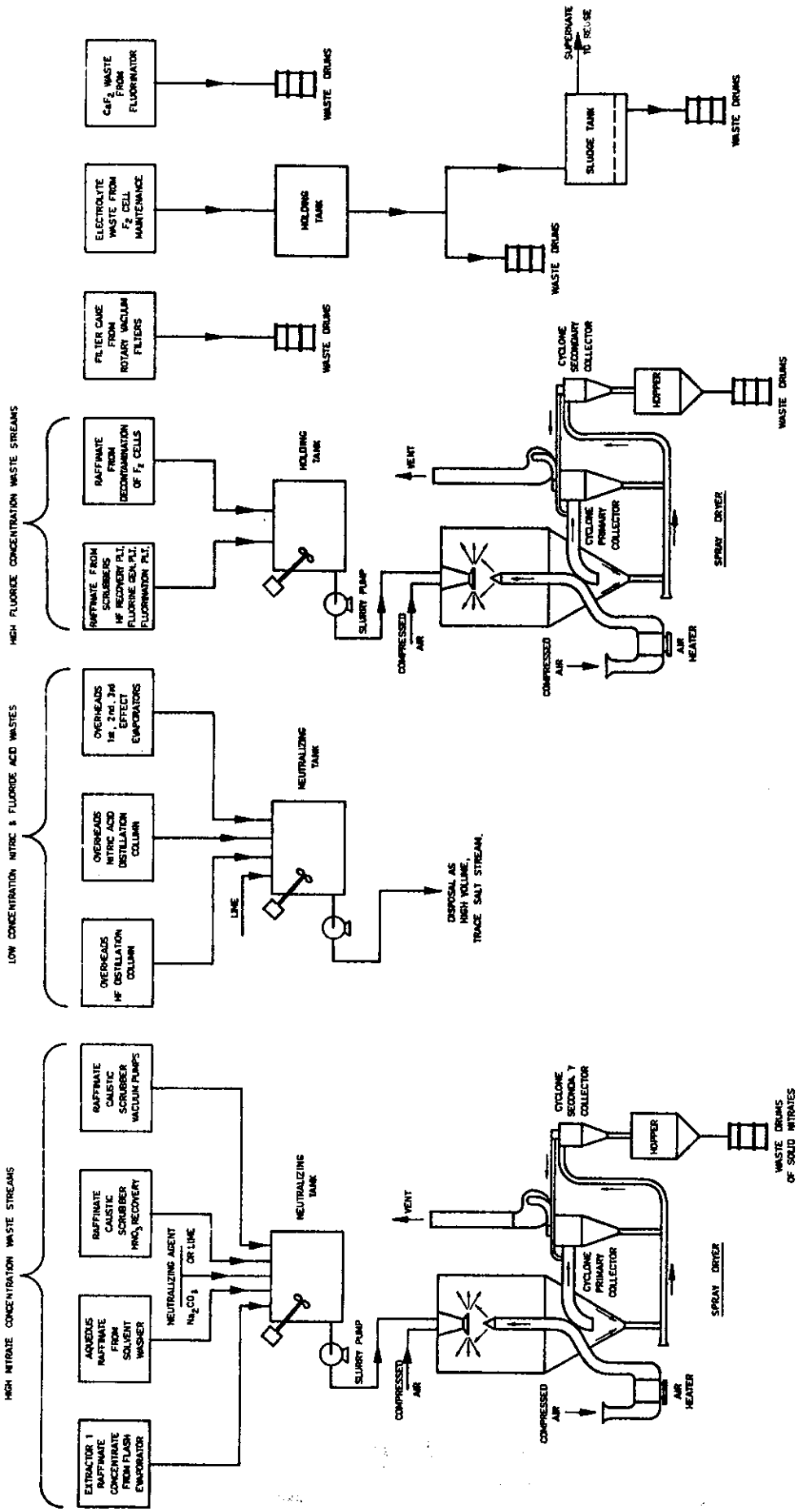


FIGURE 9. WASTE DISPOSAL FLOWSHEET

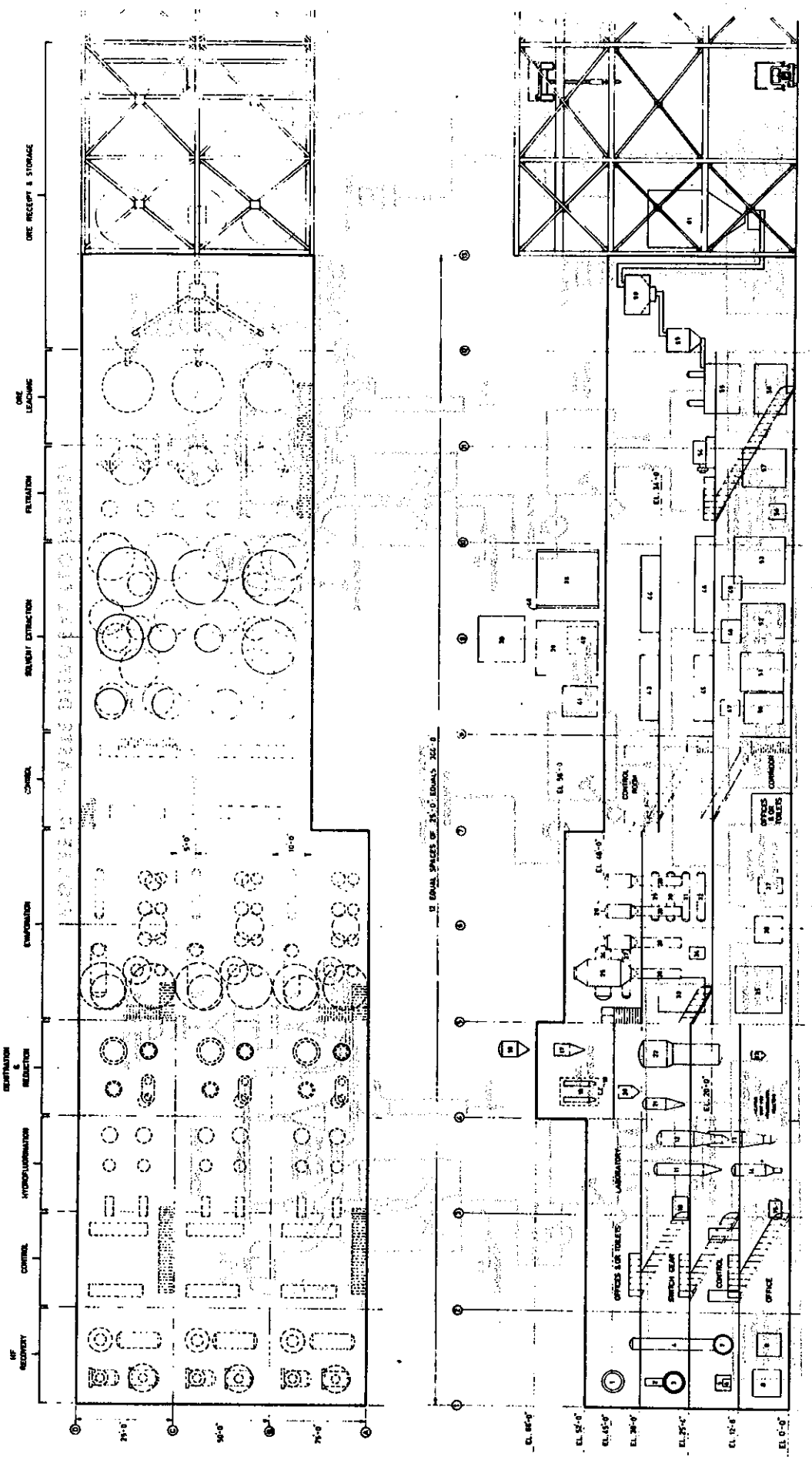


FIGURE 10. CONCEPTUAL LAYOUT $UF_6$ PLANT

KEY TO FIGURE 10

| Item | Description | Item | Description | Item | Description |
|---|---|---|---|---|---|
| 1 | Reflux Condenser | 21 | $UO_2$ Seal Hopper | 42 | Scrub Supply |
| 2 | Caustic Fume Absorber | 22 | Denitration Reactor | 43 | Scrubber Container |
| 3 | Condenser | 23 | Lift Pot | 44 | Forward Contactor No. 1 |
| 4 | Distillation Column | 24 | Main Condenser | 45 | Solvent Washer |
| 5 | Caustic Tank | 25 | 4th Effect Evaporator | 46 | Backwash Contactor No. 2 |
| 6 | Separator | 26 | 1st, 2nd and 3rd Effect Evaporators | 47 | Carbonate Solvent Separator |
| 7 | HF Boiler | 27 | Partial Preheater/Condenser | 48 | Product Solvent Separator |
| 8 | Dilute HF Stock Tank | 28 | Condensers | 49 | Raffinate Solvent Separator |
| 9 | Azeotrope Tank | 29 | 1st Preheater | 50 | Carbonate Waste Tanks |
| 10 | AHF and DHF Superheater | 30 | 2nd Preheater | 51 | Solvent Stock Tank |
| 11 | $UF_4$ Intermediate Seal Hopper | 31 | 3rd Preheater | 52 | Product Receiver |
| 12 | Hydrofluorination Reactor No. 1 | 32 | 4th Preheater | 53 | Raffinate Storage Tanks |
| 13 | Hydrofluorination Reactor No. 2 | 33 | Concentrate Stock Tank | 54 | Rotary Vacuum Filter |
| 14 | Product Seal Hopper | 34 | Mist Trap | 55 | Dissolver |
| 15 | AHF and DHF Boilers | 35 | Distillate Stock Tanks | 56 | Filtrate Receiver Tanks |
| 16 | Hopper | 36 | Save-all Drain Tank | 57 | Reslurry Tanks |
| 17 | Seal Hopper | 37 | Hot Well | 58 | Dissolver Holding Tanks |
| 18 | Reduction Reactors | 38 | Nitric Acid Stock Tank | 59 | Dissolver Feed Hopper |
| 19 | $UO_2$ Seal Hopper | 39 | Backwash Supply | 60 | Yellow Cake, Distribution Hopper |
| 20 | $UO_2$ Storage Hopper | 40 | Solvent Head Tank | 61 | Yellow Cake, Main Storage Hopper |
| | | 41 | Carbonate Supply | | |

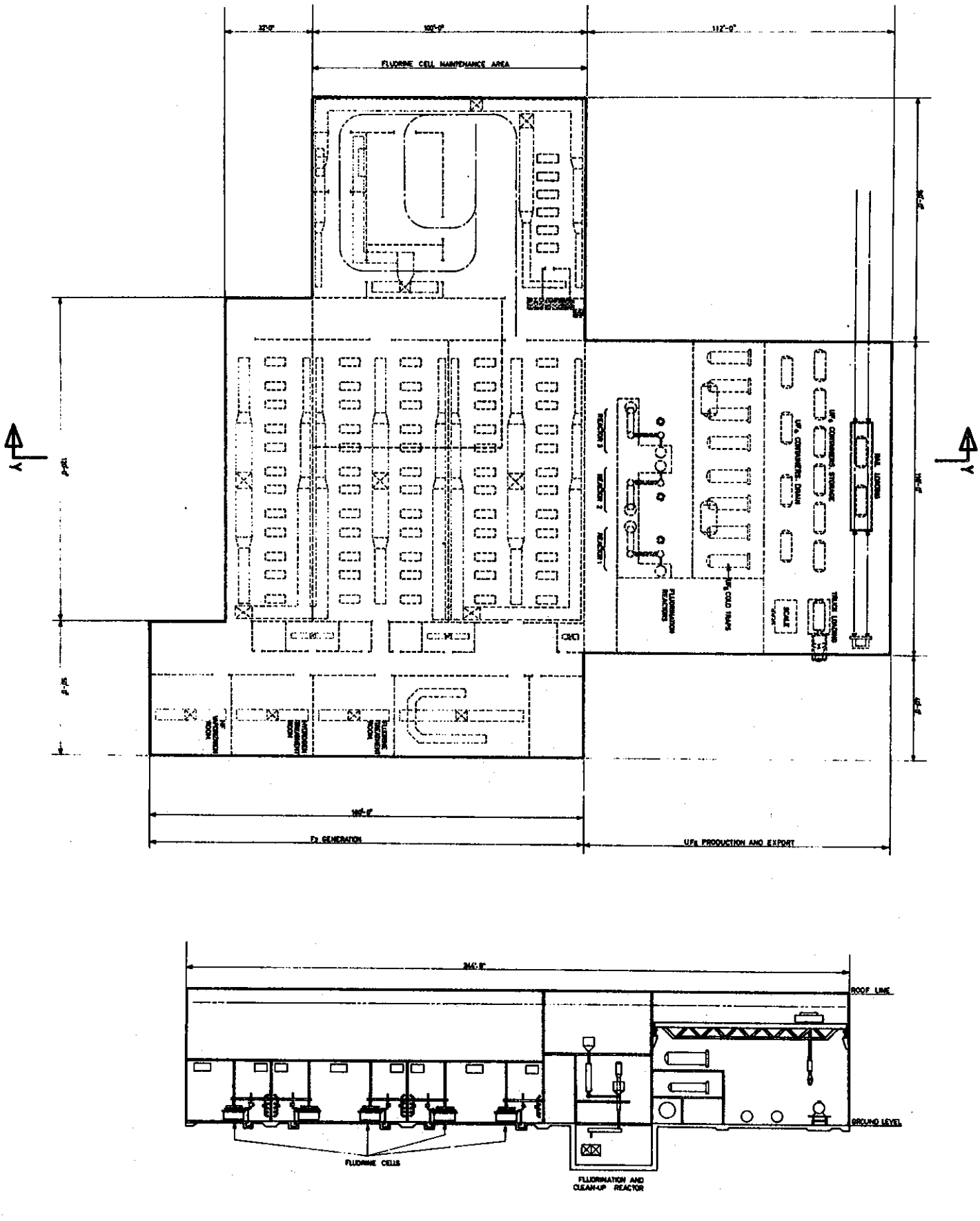


FIGURE 11. CONCEPTUAL LAYOUT $UF_6$ PLANT

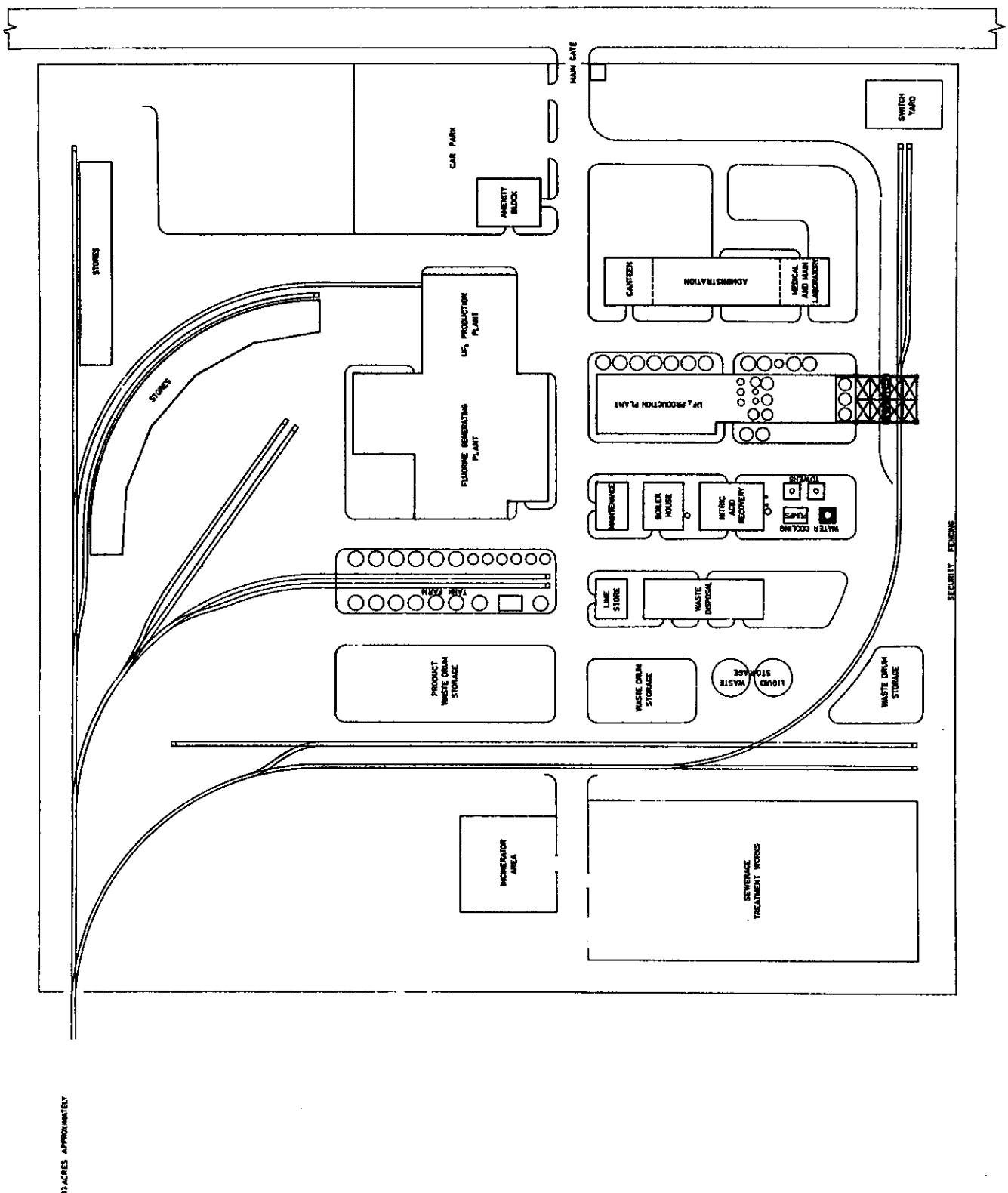


FIGURE 12. CONCEPTUAL SITE PLAN

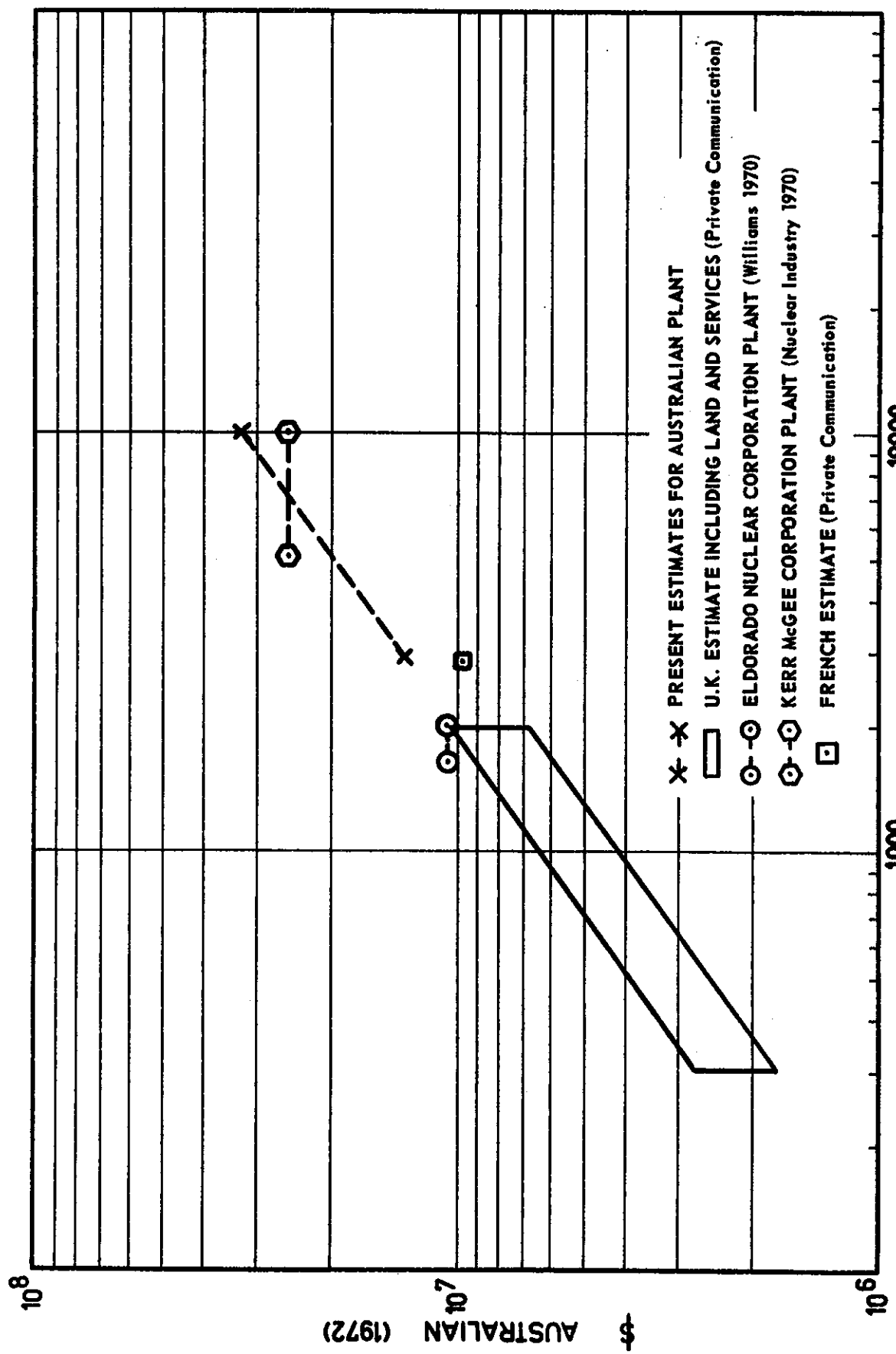


FIGURE 13. COMPARATIVE FIXED CAPITAL COSTS FOR CONVERSION OF YELLOWCAKE TO $UF_6$

AAEC SYMPOSIUM

ON

URANIUM PROCESSING

PAPER X

# THE MARKET FOR AUSTRALIAN CONVERSION SERVICES

by

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## 1. INTRODUCTION

The current and foreseeable nuclear power and enrichment technologies dictate a continuing need for uranium oxide concentrate ($U_3O_8$) or yellow cake and its conversion to uranium hexafluoride ($UF_6$). This paper describes the variables affecting the growth of this need on a world-wide scale together with an analysis of the current and expected $UF_6$ conversion industry.

The paper first establishes world requirements for $U_3O_8$ and $UF_6$. The major variables affecting these estimates are:

(i) the proportion of world demand for electric energy supplied by nuclear power;

(ii) the types of nuclear reactors adopted;

(iii) the 'tails' concentration of enrichment plants;

(iv) the rate and mode of plutonium utilisation in thermal reactors.

The paper then assesses the market penetration which an Australian conversion plant could obtain in competition with overseas plants. This is strongly dependent on:

(a) alternative market suppliers;

(b) Australia's past trading performance;

(c) the relative production economics of $UF_6$;

(d) Australia's future position covering both $U_3O_8$ and enriched uranium production.

## 2. WORLD URANIUM MARKET

### 2.1 The Growth of Nuclear Power

The Western world's present nuclear power stations are capable of generating about 25 GW(e) and a further 180 GW(e) are committed or under construction. Thus the nuclear proportion of electrical capacity can be predicted to 1985 in some detail on a country-by-country basis with good agreement between several national and international authorities (WASH 1139 1971, ENEA/IAEA 1970, Spinrad 1971). Beyond this period, the nuclear proportion is more speculative, but we assume it increases to 60%-70% of the world's total generating capacity by the year 2000. Our long-term

estimates of generating capacity suggest that a decrease will occur in the present steady exponential rate of increase in electrical consumption. Thus, the world's total generating capacity in the year 2000 is predicted to be 3800 GW(e) (four times the present value) and nuclear capacity is predicted to increase to about 2200 GW(e). Figure 1 shows the world's annual nuclear capacity from 1970-2000 based on the aggregate of country-by-country estimates.

### 2.2 Yellow Cake ($U_3O_8$) Requirements

Several estimates of world annual requirements for $U_3O_8$ have been published and these are shown in Figure 2. It is generally assumed that the Light Water Reactors (LWR) developed in the U.S. will dominate all major nuclear programmes to the year 1985. The estimates are in good agreement to this date and show world requirements increasing from about 18,000 short tons $U_3O_8$* in 1972 to about 135,000 short tons $U_3O_8$ in 1985. For the decade 1975-1985 the average annual growth rate will be 12%.

Beyond the early 1980s, the annual $U_3O_8$ requirements are significantly influenced by the rate of nuclear power growth and the further effects of 'tails assay', plutonium recycle, and fast breeder reactor development.

### 2.3 Uranium Hexafluoride ($UF_6$) Requirements

The greater part of all mined uranium will be converted into $UF_6$ for enrichment and subsequent reduction into uranium dioxide ($UO_2$) fuel for the LWR system. Thus the $U_3O_8$ and $UF_6$ requirements will be closely related and world $UF_6$ requirements will increase from about 13,000 tonnes U in 1972 to about 100,000 tonnes U in 1985, averaging an annual growth rate of 12% over the decade 1975-1985.

### 2.4 Tails Assay

Concurrent with the enriched $UF_6$ product from enrichment plants there is a depleted $UF_6$ residue discharged as 'tails'. The 'tails assay' from the present USAEC enrichment facilities was optimised at 0.2% $^{235}U$, but the growing requirements for enrichment services and the planned reduction of the present U.S. uranium stockpile has caused a re-optimisation of tails assay to 0.275% $^{235}U$. This latter assay reduces the requirements for enrichment services by about 16% with a corresponding increase in $U_3O_8$ and

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* 1 tonne U = 1.3 short tons $U_3O_8$

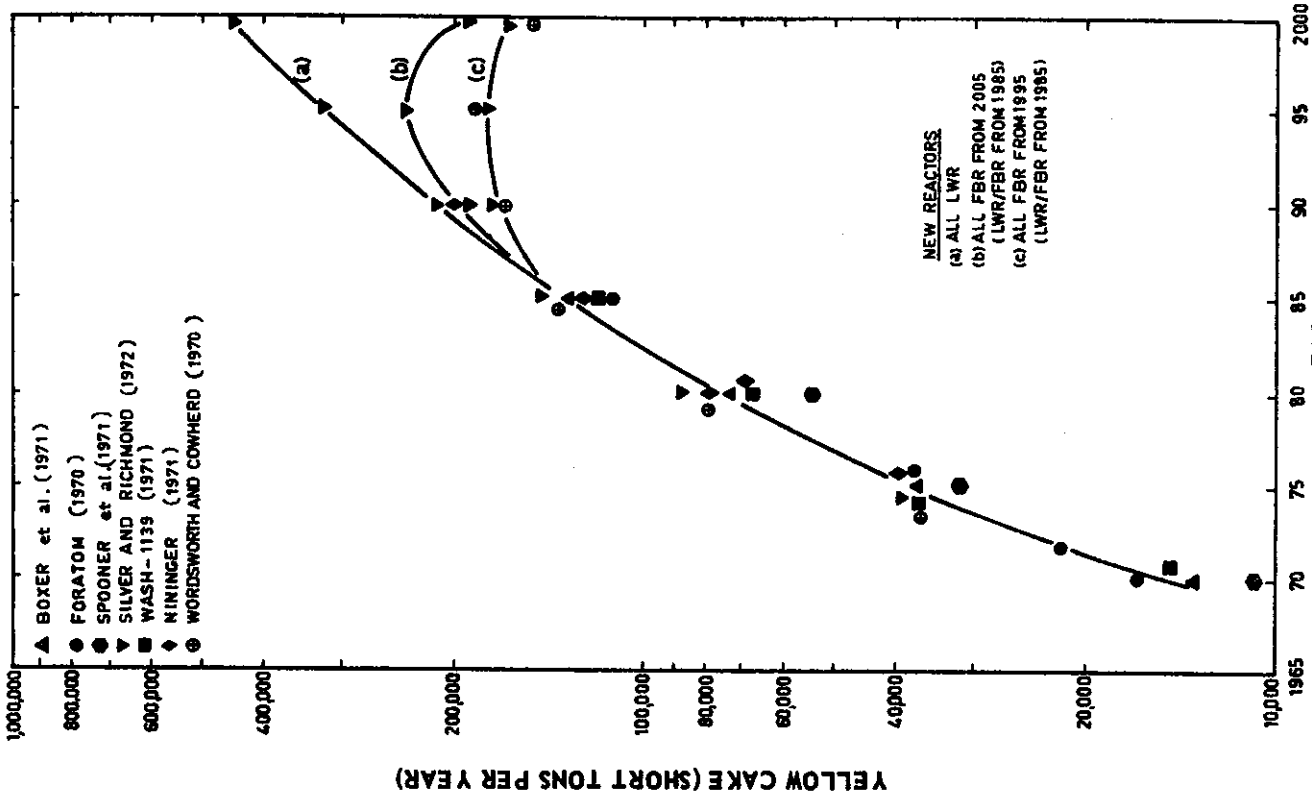


FIGURE 2. WORLD YELLOW CAKE REQUIREMENTS

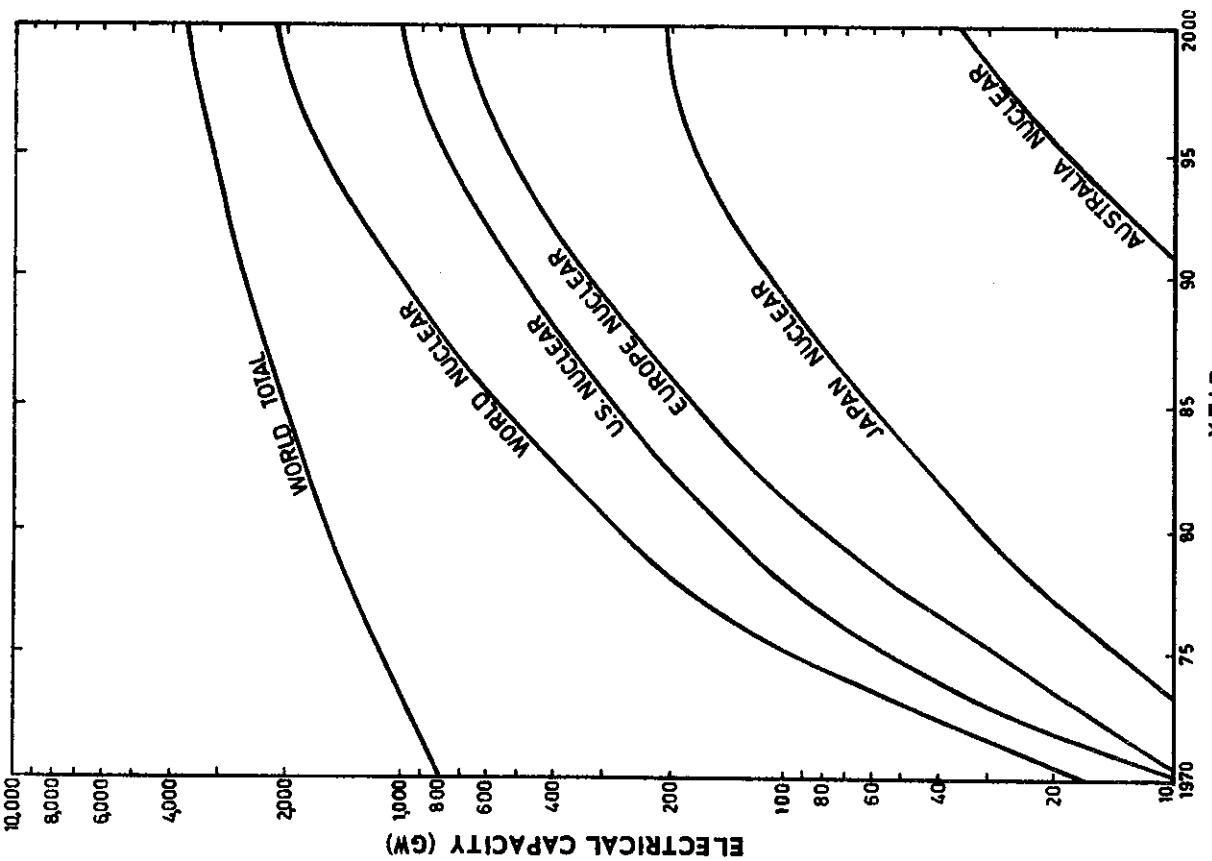


FIGURE 1. GROWTH OF NUCLEAR POWER

$UF_6$ requirements. Since the extra $U_3O_8$ will come from the USAEC stockpile and its conversion to $UF_6$ will be provided by USAEC facilities, this programme will have a strong depressing effect on $U_3O_8$ and $UF_6$ requirements until the stockpile is eliminated in the early 1980s.

2.5 Plutonium Recycle

The requirements for $U_3O_8$ and $UF_6$ can be further reduced by the use of plutonium recovered from the reprocessing of spent LWR fuel in place of enriched uranium. Each kilogram of plutonium recycled in a LWR is equivalent to about 0.2 short tons of $U_3O_8$. If all the plutonium produced from LWR's was recycled, it would reduce the annual uranium and conversion requirements by about 6% in 1980 and 10% in 1985.

2.6 Fast Breeder Reactors (FBR)

One of the most promising long term solutions to the eventual depletion of the world's uranium resources is the development of the FBR in which plutonium is the nuclear fuel. The initial plutonium fuel for the FBR will be recovered from the spent fuel discharged from the earlier reactor types including natural uranium fuelled reactors. The FBR will then breed sufficient plutonium to be self-sufficient for fuel and even produce a surplus to fuel the later FBR's installed to satisfy the predicted continued increase in power requirements. Beyond 1985, the FBR could become a significant alternative reactor type and be installed in competition during the period 1985-1995, after which mainly FBR's would be installed. The rate of FBR introduction will be subject to its economic viability and the quantity of plutonium available from the reprocessing of spent fuel.

Figure 3 shows the range in long-term requirements for $UF_6$ assuming:

(i) a maximum rate of FBR introduction after 1985,

(ii) no FBR introduction before 2000.

It is most likely that the long-term requirements will be related to the introduction of the FBR over a period of 15 years beginning in 1985.

These assumptions are considered by the authors to provide the 'most likely' limits of demand.

## 3. MARKET ECONOMICS

### 3.1 Present and Future Overseas Conversion Plants

The current world $UF_6$ production capacity of about 25,000 tonnes U per year is supplied by five plants. On existing conditions the considerable world over-capacity from these plants will continue until about 1975. Table 1 lists the plants, their present and projected capacities, and their exportable surplus.

TABLE 1

URANIUM HEXAFLUORIDE PRODUCTION CAPABILITY

| PLANT | TONNES U PER YEAR | | | |
|---|---|---|---|---|
| | CAPABILITY | | EXPORT SURPLUS | |
| | 1972 | 1975 | 1972 | 1975 |
| 1. Allied Chemical (US) | 13000 | 13000 | 13500 | 6500 |
| 2. Kerr McGee (US) | 4500 | 9000 | | |
| 3. British Nuclear Fuels Ltd. (UK) | 3000 | 5000 | 2200 | 3400 |
| 4. COMURHEX (France) | 3000 | 6000 | 2800 | 4500 |
| 5. Eldorado Nuclear (Can.) | 1600 | 3800 | 2000 | 3800 |
| Total | 25100 | 36800 | | |
| World Requirements | 13000 | 29000 | | |

There have been in the past two main underlying factors leading to the installation of conversion plants.

(a) Established local demand. Four of the present conversion plants are located within countries with a significant nuclear programme over the past decade, e.g. U.S., U.K. and France. Future plants may therefore be built in West Germany and Japan to convert local $U_3O_8$ requirements into $UF_6$ for local or overseas enrichment.

(b) Established Suppliers of $U_3O_8$. Canada is a major supplier of $U_3O_8$ and has a $UF_6$ plant but no $UF_6$ requirement. (The Canadian nuclear programme is based on Heavy Water Reactors fuelled with

natural uranium dioxide.) Thus South African and Australian $U_3O_8$ suppliers are also potential $UF_6$ producers particularly as it is possible $UF_6$ could replace $U_3O_8$ as the form in which uranium is normally traded.

Presumably the above two factors will remain dominant, particularly as those countries with a large nuclear industry also contain the sophisticated chemical industry necessary for the development of conversion facilities. The high growth rate and low barriers to market entry characterised by the conversion industry are likely to attract new producers. This probable continuation of the present level of over-capacity situation could be partially reduced by the completion of the U.S. stockpile reduction programme in 1980. There will then be a sharp increase in both $U_3O_8$ and $UF_6$ demand. However, in the long term, it is likely that the conversion service market will be 'tight' from the sellers' viewpoint.

3.2 Australian Penetration of World Market

The long term market for $UF_6$ is shown in Figure 4. It can be seen that the U.S. represents about 50% of the market, Europe 30%, Japan 10% and 'Others' 10%.

A market/trade analysis was carried out for the export of $UF_6$ by an examination of Australia's present and projected performance in international trade, particularly in the area of upgraded raw materials. This analysis was modified for some countries to allow for the presence of indigenous conversion plants. The provision of significant conversion services to these countries depends upon establishing a favoured position relative to the local plant. This may be:

(i) if the Australian producer offered a lower price;

(ii) if Australian conversion gave savings in transport, inventory and administrative charges, particularly if enrichment was to be provided within Australia.

Sales to the U.S. can be considered as a special case. The U.S. market is very large, but it is assumed that the U.S. will continue to be self-sufficient in uranium. The rapid growth could however, remove the present U.S. embargo on uranium imports and allow spot purchases or medium term contracts in the form of $UF_6$.

A possible 5% share of this market represents 1500 tonnes U in 1980 and 2500 tonnes U in 1985.

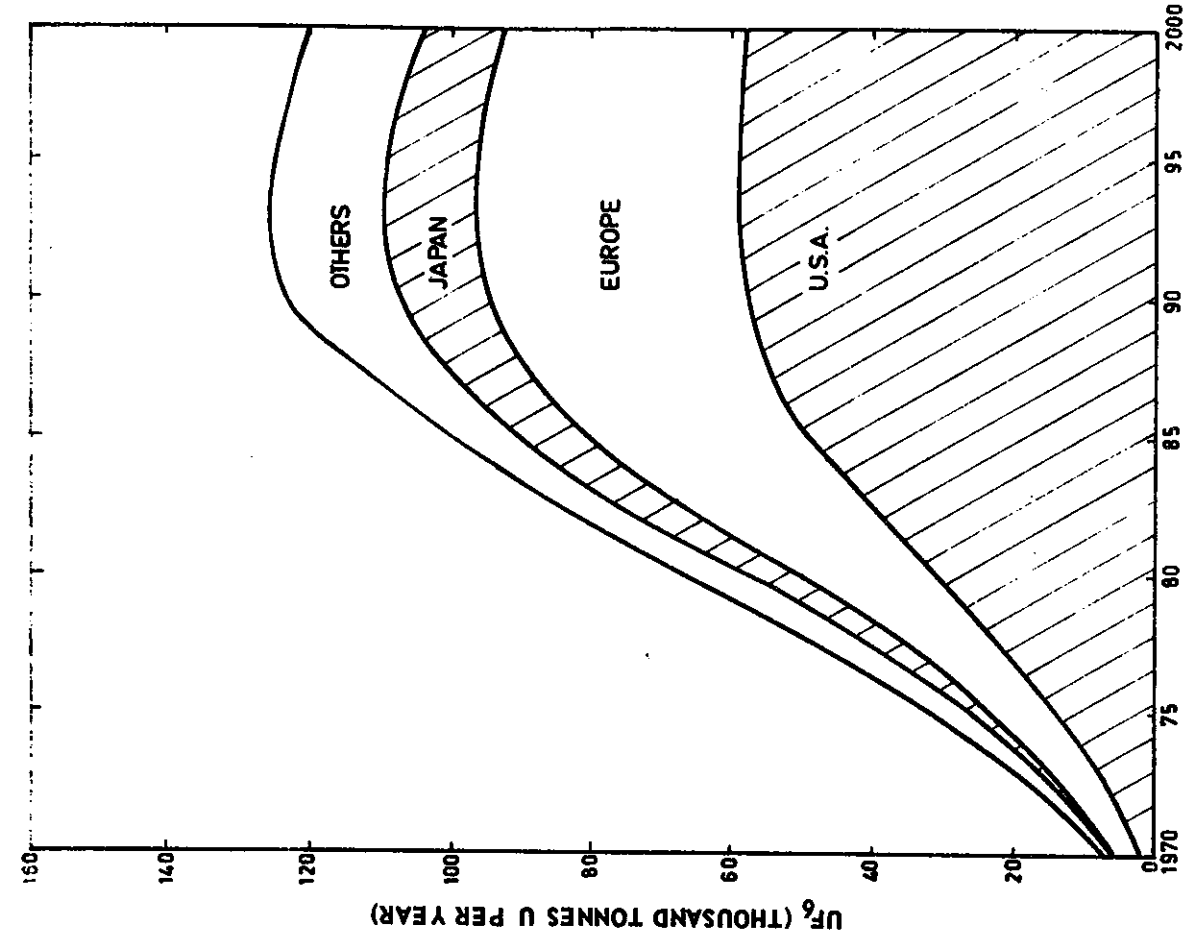


FIGURE 4. WORLD URANIUM HEXAFLUORIDE MARKET

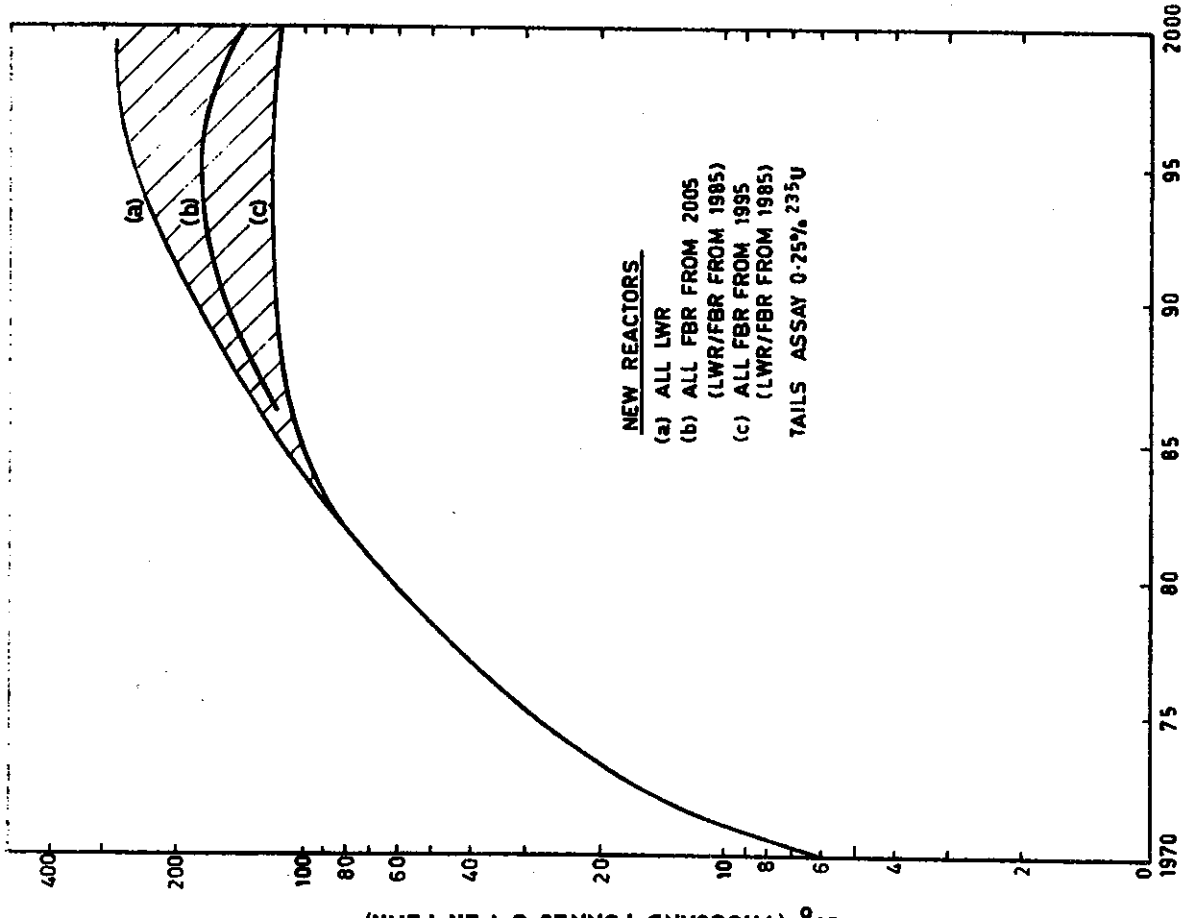


FIGURE 3. WORLD URANIUM HEXAFLUORIDE REQUIREMENTS

Tables 2 and 3 summarise the predicted overall market penetration for both long and short term sales.

TABLE 2

LONG-TERM $UF_6$ SALES

| COUNTRY | Australian Share of Imports (%) | AMOUNT - tonne U | | | |
|---|---|---|---|---|---|
| | | 1980 | | 1985 | |
| | | Low | High | Low | High |
| U.K. | 15/30 | 200 | 400 | 350 | 700 |
| W. Germany | 15/30 | 230 | 460 | 350 | 700 |
| Japan | 30/40 | 900 | 1200 | 2000 | 2700 |
| Italy | 10/20 | 120 | 240 | 350 | 700 |
| 'Other' - Europe | 10/20 | 450 | 900 | 700 | 1400 |
| Australia | 100 | 200 | 300 | 800 | 800 |
| | Total Sale | 2100 | 3500 | 4550 | 7000 |
| | Average Sale | 2800 | | 5800 | |

TABLE 3

SPOT AND MEDIUM-TERM SALES

| COUNTRY | Australian Share of Imports (%) | AMOUNT - Tonne U | | | |
|---|---|---|---|---|---|
| | | 1980 | | 1985 | |
| | | Low | High | Low | High |
| Europe | 15/30 | 300 | 600 | 500 | 1000 |
| 'Other' - World | 15/30 | 300 | 600 | 750 | 1500 |
| U.S. | 10/30 | 200 | 600 | 500 | 1500 |
| | Total Sale | 800 | 1800 | 1750 | 4000 |
| | Average Sale | 1300 | | 2900 | |

The manner in which the predicted world requirements for conversion services would be supplied was also examined by a scenario writing method. A feasible solution was the one considered the 'best-fit' for the available information concerning

(i) the country-by-country requirements;

(ii) the probable new market suppliers;

(iii) the probable expansion of existing plants;

(iv) the attitudes of potential customers for conversion services.

Table 4 shows the conclusions reached from this method.

TABLE 4

FEASIBLE AUSTRALIAN ENTRY INTO WORLD $UF_6$ MARKET

| | CAPACITY (tonne U per year) | | | AUSTRALIAN SALES (tonne U) | | |
|---|---|---|---|---|---|---|
| | 1975 | 1980 | 1985 | 1975 | 1980 | 1985 |
| U.S. | 22000 | 35000 | 50000 | - | 250 | 500 |
| W. Europe | 10000 | 15000 | 25000 | - | 2000 | 4000 |
| Japan | - | - | 5000 | - | 1000 | 2200 |
| South Africa | - | 5000 | 10000 | - | - | - |
| Canada | 3800 | 6000 | 10000 | - | - | - |
| 'Others' | - | - | - | - | 450 | 1000 |
| Australia | - | 5000 | 10000 | - | 300 | 800 |
| Totals | 35800 | 66000 | 110000 | - | 4000 | 8500 |
| World Requirements | 29000 | 64000 | 100000 | | | |

The two approaches give supporting evidence that total annual sales for an Australian conversion plant would average 4000 tonnes U in 1980 and 8500 tonnes U in 1985.

### 3.3 Relative Conversion Selling Costs

Neglecting the special case where enrichment is carried out in Australia, the marketing success of an Australian conversion plant largely rests on the ability of the plant to provide conversion services at prices comparable to those prevailing in the world market. Table 5 gives some recent prices by present producers. The production economics of an Australian conversion plant are examined by Costello (1972). It is clear that the Australian plant would not possess any characteristics that could reduce production costs below American or European plants. The most important factors affecting production costs are the scale of operations, chemical costs and capital charges. Australian conversion costs will therefore be similar to the probable overseas costs.

TABLE 5

TOLL CONVERSION CHARGES

| PLANT | $ US per kilogram U | | | |
|---|---|---|---|---|
| | 1965 | 1970 | 1971 | 1972 |
| 1. Allied Chemicals | 2.29 | 2.63 | 2.75 | 2.86 |
| 2. Kerr McGee | - | 2.74* | 2.74* | NA |
| 3. Eldorado Nuclear | - | - | - | 2.88* |
| 4. BNFL | - | as above or lower* | | |
| 5. COMURHEX | - | as above or lower* | | |

* Includes $U_3O_8$ sampling and $UF_6$ transport to Oak Ridge.

For most buyers of Australian uranium, conversion within Australia could provide savings in transport and inventory costs, relative to effecting conversion in their own country. These savings occur from the direct shipment of $UF_6$ from Australia to the U.S. enrichment plants rather than shipment of $U_3O_8$ to Europe or Japan for conversion and then shipment of $UF_6$ to the U.S. for enrichment. The perennial Australian problem of transport diseconomics could be expected to play a lesser role. The cost of $UF_6$ transport from Australia will be offset for the purchaser of Australian uranium by the transport cost for the equivalent quantity of $U_3O_8$.

A recent USAEC publication (ORO-685, 1972) suggests that $UF_6$ transport costs are:

| Transport | | Natural $UF_6$ |
|---|---|---|
| Rail | 1000 miles | $US 0.15 per kg U |
| Sea | 5000 miles | $US 0.31 per kg U |

Our estimate of $U_3O_8$ transport costs are:-

| Transport | | $U_3O_8$ |
|---|---|---|
| Road | 1500 miles | $A 0.10 per kg U |
| Sea | 5000 miles | $A 0.30 per kg U |

Table 6 lists all relative transport costs associated with some of the purchase strategies. These are conversion in: (i) Europe, (ii) Japan, (iii) U.S.A., and (iv) Australia. In each case enrichment is assumed to be carried out at Oak Ridge, U.S.A.

TABLE 6

RELATIVE TRANSPORT COSTS

($/kg U)

| TRANSPORT | Conversion Site | | | Australian Conversion |
|---|---|---|---|---|
| | Europe | Japan | U.S. | |
| Aust. $U_3O_8$ to | 0.45 | 0.30 | 0.50 | 0.10 |
| $UF_6$ to Oak Ridge | 0.30 | 0.64 | 0.15 | 0.64 |
| Total $ | 0.75 | 0.94 | 0.65 | 0.74 |

Finally, Table 7 gives the likely conversion charge an Australian producer would offer. It therefore becomes apparent that even if present U.S. prices are artificially high (due to the monopolistic situation) an Australian producer should be able to achieve a rough cost parity with his overseas competitors, provided that his plant is big enough. The economics of scale as suggested by Costello (1972) are significant; the cost/output relationship is given by:

$$C_A = C_N \left( \frac{O_A}{O_N} \right)^{-0.16}$$

where $C_A$ is the production cost for a plant of output $O_A$

$C_N$ is the production cost for a normalised plant of output $O_N$.

This indicates that a 50% increase in a plant of size 3000 tonnes U per year will lead to a 7% decrease in manufacturing cost.

The USAEC (WASH 1082, 1968) from the design of a 5000 tonne U per year plant, predicted conversion charges to have a similar relationship:

$$C_A = C_N \left( \frac{O_A}{O_N} \right)^{-0.32}$$

The larger exponent (-0.32) may relate to the replication of equipment of larger unit size and leads to a greater cost reduction. A minimum plant size of 5000 tonnes U per year is therefore suggested.

TABLE 7

COMPARISON OF CONVERSION OPTIONS

Option 1

Purchase of Australian ore concentrate, transport and conversion in an Australian hexafluoride plant, with shipping and rail transport of $UF_6$ to a U.S. enrichment plant.

| | Conversion Plant Capacity | |
|---|---|---|
| | 3,000 tonne/year $A/kg U | 10,000 tonne/year $A/kg U |
| Cost of transport of ore concentrate 1500 miles at 6¢/ton mile | 0.09 | 0.09 |
| Cost of sampling and conversion to $UF_6$ | 2.27 | 1.89 |
| Cost of transport of $UF_6$ to Oak Ridge enrichment plant | 0.64 | 0.64 |
| Total | 3.00 | 2.62 |

Option 2

Purchase of Australian ore concentrate, transport and shipping to U.S.A. and conversion in a U.S. plant with transport of $UF_6$ to a U.S. enrichment plant.

| | $A/kg U |
|---|---|
| Cost of transport of ore concentrate | 0.50 |
| Cost of sampling ore concentrate | 0.06 |
| U.S. conversion charge (1.31 $US/lb U) (includes transport charge to enrichment plant) | 2.42 |
| Total | 2.98 |

3.4 Conversion as a Fuel Cost

To place conversion service in perspective with regard to the total costs for nuclear fuel, it is necessary to examine the other fuel cost components.

There are three main costs in the manufacture of fuel for an LWR. These are:

(i) Uranium, purchased as $U_3O_8$ ($US 7 per pound)

(ii) Enrichment services ($US 32 per kg S.W.U.*)

(iii) Fabrication ($US 80 per kg U).

Assuming the above average values for these costs, then each of the three components represent about 30% of the total fuel cost. In this context, conversion services represent about 6% of the total cost of nuclear fuel. Thus, significant reductions in the cost of conversion services can have only a minor effect on the final cost of fuel to the power utility.

### 3.5 The Effect of an Australian Enrichment Plant

The analysis of market penetration refers to the export of uranium as $UF_6$ for enrichment overseas. If a major enrichment plant is built in Australia, the local production of $UF_6$ would be an essential part of the project.

An enrichment plant of 6000 tonnes SW capacity requires about 10,000 tonnes U per year as $UF_6$, while a 10,000 tonnes SW plant requires 16,000 tonnes U. In this latter case one large conversion plant could be built near and scaled to the requirements of the enrichment plant or two plants may be built and surplus capacity exported for enrichment overseas. As significant extra transport costs are involved, it is highly unlikely that purchasers of Australian enrichment services and yellow cake ($U_3O_8$) would use non-Australian conversion facilities.

## 4. AUSTRALIAN CONVERSION PLANT ESTABLISHMENT

### 4.1 Timing of Market Entry

The earliest period for the establishment of an Australian plant is between 1978-80 when the world $UF_6$ market will be expanding at a rate of 5000 tonnes U per year. If conversion services were contracted in conjunction with Australian sales of $U_3O_8$ to Japan and Europe, then a new plant could enter and expand its output with the growing market.

### 4.2 Plant Size

The market penetration analysis suggests that conversion sales could be 4000 tonnes U in 1980 rising to 8500 tonnes U in 1985. The initial plant capacity could therefore be 5000 tonnes U per year and expand to 10,000 tonnes U per year over a period of 5-7 years, dependent on market growth.

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* SW - Separative Work, a measure of the 'work' done in the enrichment of uranium. Units are quoted as 'kilograms' or 'tonnes'.

To this figure may be added the derived demand from an Australian enrichment plant.

### 4.3 Plant Profitability

The production costs for conversion services presented by Costello (1972) relate to a 12% return to equity capital and assume the plant operates continuously at design output. Table 8 shows the effect on profitability when the plant is operating at reduced outputs. The break-even point is shown to be 50% of design output. This low figure is largely due to the high level of variable costs, particularly in the form of HF and consequently allows a producer greater flexibility in his market entry strategy.

TABLE 8

PROFIT v. OUTPUT

| PLANT OUTPUT<br>100% = 10,000 tonnes U | PROFIT<br>(%) | SELLING COST<br>$A |
|---|---|---|
| 100% | 12.0 | 2.53 |
| 95% | 10.8 | " |
| 90% | 9.5 | " |
| 70% | 4.5 | " |
| 50% | Break even | " |

## 5. CONCLUSIONS

1. The total potential market for uranium converted to $UF_6$ is estimated as:
   29,000 tonnes U in 1975
   64,000 tonnes U in 1980
   100,000 tonnes U in 1985.

2. Market analysis suggests the possible market penetration by an Australian conversion plant as:
   4,000 tonnes U in 1980
   8,500 tonnes U in 1985.

3. Establishment of an Australian enrichment plant in the early 1980s would significantly increase this market penetration so that sales could increase to between 10-20,000 tonnes U in 1985.

4. The suggested minimum plant size is 5,000 tonnes U per year.

## 6. REFERENCES

Boxer, L.W., Haussermann, W., Cameron, J., Roberts, J.T. (1971) - Uranium Resources, Production and Demand. Paper 678, Fourth International Conference on Peaceful Uses of Atomic Energy, Geneva.

Costello, J.M. (1972) - Capital and Operating Costs for the Production of Uranium Hexafluoride. Paper presented to this Symposium.

ENEA/IAEA (1970) - Uranium, Resources, Production and Demand. Joint report by ENEA and IAEA. OECD, Paris.

FORATOM (1970) - Industrial Aspects of the Nuclear Fuel Cycle in Europe. Papers and documents from the Fourth Foratom Congress, Stockholm, 21-23 September, 1970. Four volumes.

Nininger, R.D. (1970) - The World Uranium Picture. In Mining Year Book 1970, Colorado Mining Association, Denver, U.S.A.

ORO-685 (1972) - Data on New Gaseous Diffusion Plants. Prepared for the Oak Ridge Operations Office, USAEC.

Silver, J.M. and Richmond, M.R. (1972) - Uranium Fuel — Predictions of Requirements and Resources. Unpublished AAEC Report.

Spinrad, B.I. (1971) - The Role of Nuclear Power in Meeting World Energy Needs. Proc. Symp. 'Environmental Aspects of Nuclear Power Stations', New York, 10-14 August, 1970.

Spooner, J., Lord, B., Kennedy, A., Williams, L. (Editors) (1971) - The Mining Journal - Annual Review 1971.

WASH 1082 (1968) - Civilian Nuclear Power — Current Status and Future Technical and Economic Potential of Light Water Reactors. Prepared for the Division of Reactor Development and Technology, USAEC.

WASH 1139 (1971) - Forecast of Growth of Nuclear Power. Prepared by the Division of Operations Analysis and Forecasting, USAEC.

Wordsworth, A.D., and Cowherd, S.J. (1970) - Factors Affecting the Cost of Nuclear Fuels and the Selection of Reactor Fuel Cycles in the Developing Countries. Symposium on Nuclear Energy Costs and Economic Development, Istanbul, October, 1969.