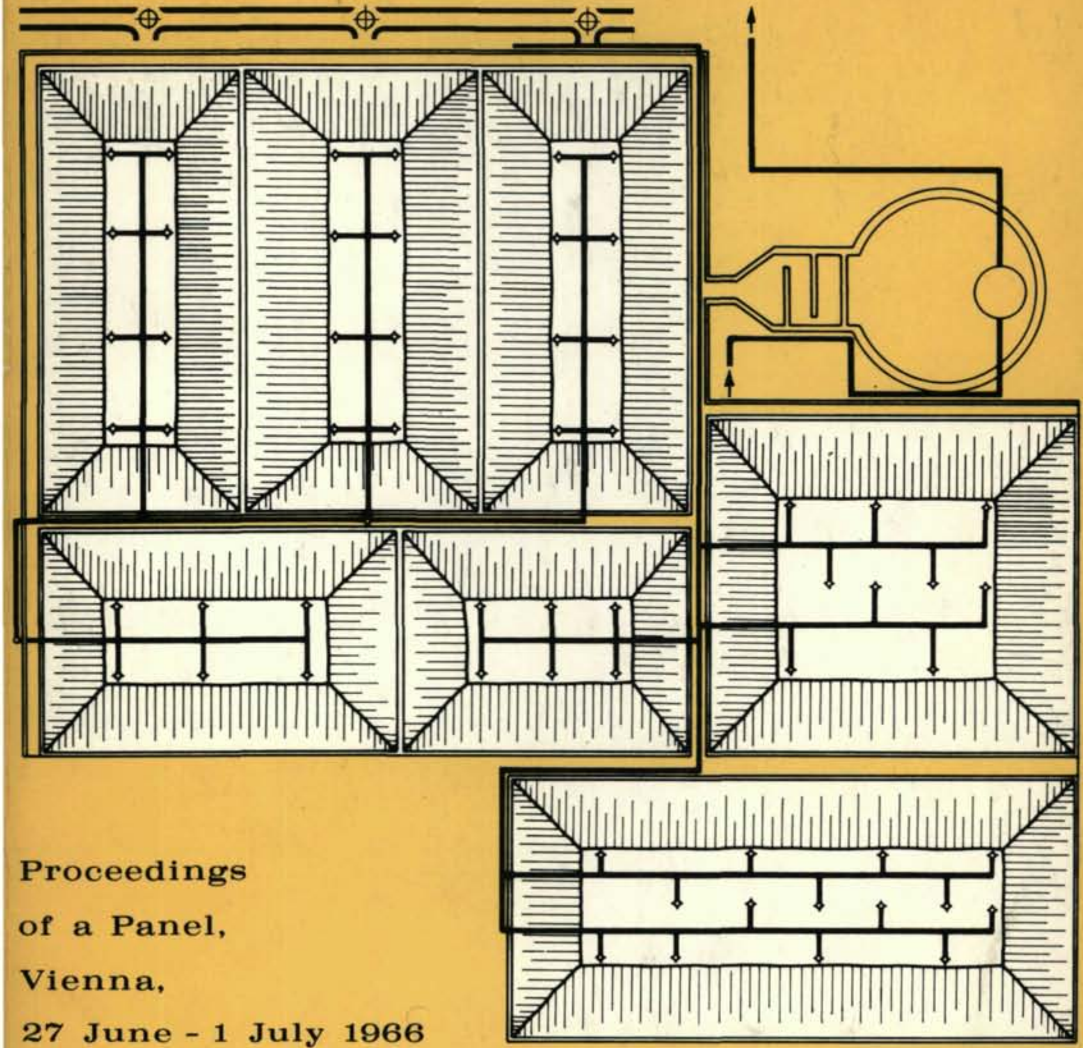

Proceedings
of a Panel,
Vienna,
27 June - 1 July 1966

# Processing of Low-Grade Uranium Ores

INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1967

# PROCESSING OF LOW-GRADE URANIUM ORES

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June 1967

PANEL PROCEEDINGS SERIES

# PROCESSING OF LOW-GRADE URANIUM ORES

PROCEEDINGS OF A PANEL
HELD IN VIENNA, 27 JUNE - 1 JULY 1966

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 1967

PROCESSING OF LOW-GRADE URANIUM ORES
(Panel Proceedings Series)

ABSTRACT. Proceedings of a panel convened by the IAEA in Vienna, 27 June - 1 July 1966. The 22 specialists from 15 countries and one international organization who attended the meeting were asked to give an appraisal of the current situation with regard to the processing of low-grade uranium ores and make recommendations for a possible IAEA programme of activities. This publication covers the work of the panel.

Contents: Status reports (13 reports); Technical reports (13 reports); Summaries of discussions; Recommendations of the panel.

Each report is in its original language (16 English, 4 French, 2 Russian and 4 Spanish) and each technical report is preceded by an abstract in English and one in the original language if this is not English. The summaries of discussions and the panel recommendations are in English.

(247 pp., 16 x 24 cm, paper-bound, 62 figures)
(1967) Price: US $5.00; £1.15.4

PROCESSING OF LOW-GRADE URANIUM ORES
IAEA, VIENNA, 1967
STI/PUB/146

# FOREWORD

The rapid development of nuclear power — the total capacity is now about 9000 MW(e) — is expected to lead to a great increase in the demand for uranium. This in turn will make it necessary to extract uranium from ores of lower grade than are usable at present. Since the resources of these ores are at least ten times as great as those of ores from which uranium can be extracted at current costs, the processing of such low-grade ores is of particular interest to many countries.

Realizing the importance of this problem, the International Atomic Energy Agency convened a panel of experts from 27 June to 1 July 1966 at its headquarters in Vienna. A total of 22 specialists from 15 countries and one international organization took part in this meeting, which was asked to give an appraisal of the current status in this field and make recommendations for a possible Agency programme.

This publication covers the Panel's work and includes 26 papers and reports, a summary of the technical discussions and the Panel's recommendations. There are a number of status reports covering recent work in various countries. The technical papers are devoted primarily to preconcentration of ores, solubilization of uranium from ores and recovery of uranium from solutions and slurries. The contributions revealed impressive advances in processing techniques made over the past few years which may enable substantial reductions to be made in the cost of extraction from ores.

It is hoped that the proceedings will be of interest to engineers and scientists working on uranium and other non-ferrous ore processing.

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## COMMERCIAL PRODUCTION

During the period 1954-59, five plants for the production of uranium chemical concentrates (yellowcake) were constructed in Australia. Only one of these is in operation at the present time, but two more have been kept on a 'care-and-maintenance' basis pending revival of the market for uranium. The other two were disbanded after completion of contract production. Brief details of each of the plants are given below.

### Rum Jungle

Commissioned in 1954, this plant was built to produce about 200 short tons of uranium oxide per year from ores grading 5 - 8 lb $U_3O_8$/ton[1]. More recently, the availability of ore with more favourable treatment characteristics has giver the plant a greater production potential but, in present circumstances, production has not been expanded. The main ore type mined in the area is finely divided pitchblende in carbonaceous slate; some secondary minerals also occur. As in the case of the other commercial producers, the mineralization occurs in rocks of Precambrian age. One of the Rum Jungle uranium deposits contained economic copper mineralization, so a base metal flotation circuit and a cementation copper unit were also provided in the plant. Until 1962, uranium ore treatment was carried out by acid leaching followed by ion exchange and magnesia precipitation. In that year, the ion exchange unit was replaced by a solvent extraction circuit. This change made possible the production of a higher grade product containing about 90% $U_3O_8$, compared with 60-70% $U_3O_8$ by the ion exchange process. It also resulted in economies in plant operation.

### Radium Hill/Port Pirie

The Port Pirie plant, which commenced operations in 1955, was capable of producing up to about 175 short tons of uranium oxide per year. Davidite ore was mined at Radium Hill and pre-concentrated at the mine site by heavy medium separation and flotation. The resulting concentrates were then railed to the treatment plant at Port Pirie. Due to the refractory nature of the ore mineral, leaching had to be carried out at boiling point with strong sulphuric acid. The uranium was then recovered by ion exchange and magnesia precipitation. Both the physical and chemical concentration plants were dismantled after completion of

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[1] All tons are long tons of 2240 lb unless otherwise stated.

deliveries under the sale contract, due partly to lack of further proven ore reserves, and partly to the inherently costly nature of the treatment process.

### Mary Kathleen

The Mary Kathleen plant was completed in 1958. An electronic sorting unit was installed in 1960 to reduce the amount of waste material fed to the mill. The plant can produce about 1000 short tons of uranium oxide per year when working at full capacity. The Mary Kathleen ore consists of a garnet-rich rock containing microscopic grains of pitchblende in allanite. The treatment process comprises acid leaching, ion exchange and magnesia precipitation.

### South Alligator River Area

There were two small uranium treatment plants in this general area. One had a production capacity of the order of 140 short tons of uranium oxide per year, while the output of the other was about 55 short tons per year. Both plants were of the acid leach/solvent extraction/magnesia precipitation type. The larger one treated a variety of ores from a number of deposits. The ore types ranged from massive pitchblende mineralization to ores consisting entirely of secondary uranium minerals. These different ores were blended to achieve an average head feed grade of 7-9 lb/ton, except in 1963 when the average grade of ore treated was 15.2 lb/ton. The smaller plant treated high-grade ore from the Rockhole mine which averaged about 1% $U_3O_8$.

## ACID CONSUMPTION

A most important element in the cost of chemical treatment of Australian ores has been the quantity of concentrated sulphuric acid which must be added to accomplish a satisfactory recovery in the leaching stage. Because of the remote location of both Rum Jungle and Mary Kathleen, sulphuric acid manufacturing plants had to be constructed at each site. The South Alligator companies purchased their acid requirements from Rum Jungle. The average acid consumptions of the various ores treated to date are shown in Table I. Actual acid addition in all plants except Radium Hill was governed by pH requirements. At Radium Hill, the treatment process called for a fixed addition of 840 lb of concentrated acid per ton of ore. Retention time in the leaching stage ranged from 2½ h for Rum Jungle Creek South ore to 20 h for South Alligator Uranium N.L.'s high-grade ore. At Radium Hill leaching was carried out at boiling point for 10 h.

## METALLURGICAL RESEARCH

In addition to test work associated with the operations of the production plants, considerable research effort in Australia was devoted to ores not amenable to treatment by the processes used in the existing

TABLE I. CONSUMPTION OF SULPHURIC ACID FOR AUSTRALIAN ORES

| Ore | Acid addition (lb/ton) |
|---|---|
| Rum Jungle | |
| (a) White's ore | 260 |
| (b) Dyson's ore | 315 |
| (c) Rum Jungle Creek South ore | 155 |
| Radium Hill | 840 |
| Mary Kathleen | 157 |
| South Alligator (2) | 80 |

plants. Despite this research, satisfactory treatment processes are still not available for a number of different ore types found in Australia. Worthwhile reserves of several of these ore types are known to exist.

The main lines of investigation undertaken and the results obtained are summarized in the paper 'Uranium Processing Research in Australia' in section II of these Proceedings.

## DEFINITION OF LOW-GRADE ORE

A low-grade ore might be defined as an ore which cannot be treated economically for the recovery of its uranium content in an existing plant (either alone or in conjunction with higher grade material) and which would not, under present economic conditions, support the erection of a new plant.

When mining an orebody, it is necessary to adopt a cut-off grade such that the average grade of the material supplied to the mill is sufficiently high to make the operation economically viable. For example, at Rum Jungle the cut-off grade has normally been set at 2 lb $U_3O_8$/ton because this cut-off has resulted in an average mill feed grade of 6 lb/ton or better. As the ore in all four uranium orebodies mined in this area was won by open-cut methods, material with a uranium content below the cut-off grade was recovered at practically no extra cost and stockpiled. This stockpiled 'low-grade ore' averages about 1.5 lb/ton and could not be treated economically in the Rum Jungle plant. It may, however, be possible to recover the uranium in it by bacterial leaching if natural leaching in the monsoonal climate does not extract too great a percentage of the uranium values in the meantime.

As most Australian uranium orebodies exploited to date have been worked by open-cut methods, little low-grade ore has been left in the ground. The situation would, of course, be likely to change significantly with a larger proportion of producers using underground mining methods.

In addition to ore which is below the cut-off grade for an associated treatment plant, other occurrences of uranium mineralization may not be economic for one or more of the following reasons: (a) insufficient tonnage, (b) grade too low, (c) too expensive to mine (e.g. at too great depth or in bad ground conditions), (d) ore is refractory (too difficult or too expensive to treat).

As mentioned above, low-grade ore may occur in deposits which have proved to be economic to exploit, or in deposits which have not proved to be economic to exploit. In general, it could be said that there is a complete spectrum of occurrences ranging from rocks containing only a few parts per million of uranium through to high-grade ores from which uranium can be recovered at costs of production as low as US $2-3/lb.

In Australia there has been no attempt to investigate in detail discoveries of uranium mineralization in what might be called the 'very low-grade' category. The Rum Jungle and Mary Kathleen plants were the only ones available for the custom treatment of outside ores. It was well known that these plants had been designed to treat ore grading 6 lb $U_3O_8$/ton and 4 lb/ton respectively and it was therefore generally recognized by prospectors that a grade of 4-5 lb/ton would probably be necessary for economic exploitation, either by custom treatment in an existing plant or as a new producer. Certainly, mineralization appearing to have an average grade of 2 lb/ton or less was discounted as a possible source of commercial production.

It also became known early in the search for uranium in Australia that certain ore types were not amenable to treatment by the processes used commercially at the time.

Although the Radium Hill/Port Pirie operation was based on treatment of davidite ore, the Port Pirie plant was not able to accept custom ores. In any case, such ores, or physical concentrates made from them, could not have been transported economically over long distances to the Port Pirie plant. Thus, although a number of davidite-type deposits were found in South Australia, New South Wales and Queensland, very little development work was carried out on these prospects.

As well as the davidite-type ores, there were a number of other ore types which proved to be not amenable to standard treatment processes. Some deposits of this type were of reasonable grade and offered significant tonnages of ore. The most notable example is Anderson's Lode in Queensland. Reserves proven to a depth of 1000 ft in this deposit total 2280 short tons $U_3O_8$ contained in 1 200 000 tons of ore grading 3.8 lb/ton. The mineralization consists of an extremely finely divided uranium mineral in an altered calcareous greywacke.

## ANDERSON'S LODE

An intensive programme of research into possible methods of treating this ore was carried out by the Department of Mining and Metallurgical Engineering, University of Queensland. Early tests had shown that, under normal acid leaching conditions, acid consumption would be of the order of 800 lb/ton for a recovery of 84%; if carbonate leaching were used, recovery would be only about 50%.

Later tests using carbonate leaching showed that multi-stage, counter-current leaching improved recoveries, but that temperatures of over 104°C were required. Even under these conditions, it was apparent that it would be difficult to achieve an extraction significantly greater than 63% overall in the leaching stage.

With two-stage acid leaching, the highest extraction obtained was 79%. Tests showed that 20% of the uranium in the ore was so finely divided that it was not exposed to acid attack even after very fine grinding.

As more drill core samples became available, it was noticed that, where the carbonate content of the ore increased, there was a much greater than equivalent increase in acid consumption. Further, analyses showed that the fraction of ore within the $U_3O_8$ grade range 0-0.1% contained approximately 20% of the ore, 38% of the carbonate and 6% of the uranium. This suggested the possibility of developing a flotation process for the separation and concentration of the carbonate minerals in the ore.

For a flotation stage to be successful, it was necessary to ensure that the tails would be sufficiently low in carbonate to permit direct acid leaching. It was also desirable that the concentrate should contain as little uranium as possible, because it was envisaged that it would be subjected to carbonate leaching, with its attendant lower recovery. However, even if the carbonate fraction were rejected, the average loss of $U_3O_8$ per ton of ore treated would be only 0.23 lb.

Certain long chain fatty acids showed promise as flotation reagents but, when the recovery was satisfactory, the degree of concentration was not sufficiently high. Resuls using a depressant and cleaning stages were more satisfactory and concentration ratios of 4-5 to 1 were obtained.

To test the laboratory results, a pilot plant was set up. With single-stage leaching, extraction of uranium increased with increasing acid addition up to 200-250 lb/ton. Above this range, acid addition up to 350-400 lb/ton caused no increase in uranium extraction. It was concluded that single-stage leaching could not give recoveries greater than 62% without the use of an excessive amount of acid. Two-stage leaching at a minimum leaching temperature of 45°C resulted in a significant improvement in recovery. At plant scale, it was considered reasonable to predict an extraction efficiency of 65-70% at an acid consumption of 190-240 lb/ton. For cost estimating purposes a recovery of 66% at 210 lb/ton acid addition was assumed.

To carry out multi-stage leaching in an industrial plant, resin-in-pulp, solvent-in-pulp or counter-current decantation could be used for extraction of uranium between leaching stages. In the particular case of Anderson's Lode, however, multi-stage leaching would have to be carried out at elevated temperatures. Counter-current decantation would therefore be excessively expensive due to the necessity to reheat the pulp between leaching stages.

Considerable experimental work was carried out on the solvent-in-pulp process. The results obtained were quite promising but considerable further developmental work would be required before a commercial plant could be designed. (Further details are given in the paper 'Uranium Processing Research in Australia'.)

Another possibility in a plant designed to treat Anderson's Lode ore might be an electronic sorting unit to reject ore containing less than 0.1% $U_3O_8$. This fraction, as mentioned previously, would contain 38% of the carbonate content and 6% of the uranium content of the ore, and could be stockpiled for later treatment by carbonate leaching. If electronic sorting proved feasible, it would not then be necessary to incorporate a flotation circuit in the plant.

Despite the considerable research effort summarized above, a treatment process which would ensure reasonable recovery of uranium from the Anderson's Lode deposit at a cost which would enable the product to be sold at US $8-10/lb has not been developed. Thus, over 2000 short tons of uranium oxide in this deposit are not economically available at the present time. In addition, there are other orebodies in the Mt.Isa district known to be of similar type, including particularly the Skal Lode. The reserves available in the Skal Lode are not known with certainty, but are probably considerably in excess of 650 short tons $U_3O_8$. Other deposits, which appear to be smaller, also occur.

## PRESENT AUSTRALIAN POSITION

From Australia's point of view, it would be of considerable advantage to have available economic processing techniques which would enable uranium to be recovered from those ores of reasonable grade which must at present be regarded as uneconomic. These include, particularly, carbonate-rich ores in which the uranium exists in a finely divided state and is not amenable to carbonate leaching, and refractory ores containing minerals such as davidite, absite (thorian brannerite), etc. With reserves of uranium in these types of ores amounting to thousands of tons, no metallurgical research effort has to date been directed at possible future processing of very low-grade ores containing 1-2 lb $U_3O_8$/ton or less.

On geological grounds, there would seem to be good prospects for further discoveries of medium- to high-grade ores in Australia. If such discoveries are not forthcoming when the search for uranium is renewed to meet the steadily growing demands of the nuclear power industry, attention will have to be directed towards occurrences of low-grade ores.

Several low-grade deposits, possibly of quite large dimensions, are known at the present time but their treatment characteristics are unknown. For example, the mineralization in one such deposit is known to consist mainly of thorogummite. No work has been done on the treatment characteristics of mineralization of this type.

# STATUS REPORT FROM CANADA

A. THUNAES
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OTTAWA, CANADA

The Canadian production of uranium increased in a spectacular manner during the period 1955-1959 from 1000 to 15 500 tons $U_3O_8$ per year. Since 1959 the production has declined to the 1966 level of 3900 tons $U_3O_8$ per year; stretch-out of contracts and government stockpiling programmes has made the decline gradual, and is maintaining the current rate of production until 1970 [1, 2].

Nineteen mills were in operation during the period of peak production but only three are operating today. Ten mills were shut down and dismantled because of exhaustion of ore bodies or because the operation was uneconomical; six mills are maintained in stand-by condition. The total daily capacity of mills in operation or standing by is about 28 000 tons ore, but some of these mills would not be reopened unless an appreciable increase in uranium price occurs [3].

The tide of uranium demand is about ready to turn and prospecting for uranium is very active this year, particularly in the Elliot Lake and Beaverlodge areas. The estimates for uranium demand in 1975-1980 are such that new ore will have to be found and developed, and new treatment plants must be built. The new ore that is found will likely be of lower grade or more expensive to mine than most of the current proven reserves in Canada [3, 4] and the most efficient methods of treatment will be needed to avoid excessive increases in production costs.

This seems an opportune time to review Canadian milling of uranium ore, the improvements that have been made and development work towards further improvements.

## URANIUM MILLING PLANTS

Three principal leaching systems have been in use, the choice of process being made to suit the ore type [5]:

(a) Sulphuric acid leaching of pitchblende ores at controlled pH level 1.5-1.8 for 24 h at ambient temperature; sodium chlorate oxidant; recovery of uranium from solution by ion exchange or solvent extraction. Seven mills were employing this process but are not active at present [6]. One mill may eventually reopen, the others were shut down because of lack of ore. Total capacity 7700 tons per day.

(b) Sulphuric acid leaching of brannerite ores with free acid at 5%, long retention time, higher temperatures, recovery from solution by ion exchange. All mills in the Elliot Lake district are treating brannerite ores and 90% of known Canadian reserves of uranium is this type [7]. Total capacity installed was 35 000 tons ore per day from eleven mills but only seven mills are operating or maintained on a stand-by basis.

(c) Sodium carbonate leaching of pitchblende ore, with recovery from solution as sodium diuranate. The only mill of this type is the Eldorado mill at Beaverlodge which is operating at 1500 tons or 75% capacity [8].

## VARIATION IN MILLING PRACTICE AND IMPROVEMENTS MADE IN PROCESSING SINCE THE ORIGINAL INSTALLATION

In the rush to reach production, the many large mills in the Elliot Lake area were built and brought into production with only a limited amount of laboratory and pilot plant testing. This testing was done at the Mines Branch Laboratories where capacities for pilot plant throughput was of the order of one ton per day; due to demand for testing facilities, the duration of pilot plant testing of each ore was short [9].

The mills treating pitchblende ores had the benefit of quite extensive pilot plant testing of acid and alkaline leaching systems for Port Radium and Beaverlodge ores.

While all milling results from the start of operation showed gratifying results, many refinements and cost saving changes have been made as operating experience was gained. Some of these changes are noted below; they have contributed to reduction in processing cost in spite of increase in labour rates and unit costs of supplies.

(a) Grinding costs were reduced by changes from ball to pebble grinding at mills in the Elliot Lake district [10]. Besides a saving in cost of grinding steel, the lesser amount of abraded steel in the pulp appeared to lower the consumption of oxidizing agents. The mills in the Bancroft district had pebble grinding in the original installations. Autogenous grinding of coarse ore was recently (1965) installed in the Beaverlodge mill. Canadian uranium ores are hard, and grinding costs correspondingly high, so savings in this section are important.

(b) Equipment has been improved both as regards design and material. Most mills that were installed with mechanical agitators in the leaching section have converted to pachuca-type leaching, lower maintenance costs have resulted and a slight saving in reagents. In the Beaverlodge plant pachucas have replaced autoclaves for similar reasons.

Significant changes have been made towards more corrosion resistant and durable materials for tank linings, piping, filter cloths and pumps. Even in alkaline leaching corrosion was a major problem until remedies were found [11].

(c) Automatic controls were used to some extent in the first Canadian uranium leaching plant at Port Radium, particularly for control of acidity. All plants now have automatic controls in some areas, such as for grinding, density and level control, acidity, temperature and emf range.

(d) Electronic sorting of waste from coarse ore, which had been developed and tested in the early period of Canadian uranium research [12], was improved and installed for plant operation at the Bicroft mill in 1958. A second sorting plant has operated since 1962 in the Beaverlodge plant in northern Saskatchewan [13].

Electronic sorting is practical for +3 inch ore; provided the uranium is not too uniformly distributed with ore, useful savings can be made.

Many changes have been made to the actual chemical and physical process conditions of the uranium ore processing since the original plant installation, and alternative or additional processing steps have been introduced. Among the more important changes are the following:

(1) In some Elliot Lake leaching plants two-stage leaching was introduced [14]. In this system the high acid leach liquor (5% $H_2SO_4$) was

separated by filtration and returned to leach new ore in a low acid system and the resultant pregnant solution was of lower acidity, requiring less pH adjustment for ion exchange. Appreciable acid savings resulted.

(2) Higher pulp densities, with consequent longer contact time, and higher temperatures, have become common practice in Elliot Lake mills; this change has improved extraction from 90-92% to near 95% [7].

(3) In the Port Radium leaching plant from 1958 to the mine shutdown in 1960 solvent extraction was used for recovery of uranium from solution. This was the first solvent extraction plant employing tertiary amines, and the results were excellent as regards costs and recovery [15].

In the Beaverlodge mill, which is the only Canadian plant based on sodium carbonate leaching, a number of process changes have been made since the original installation [16].

(4) Flotation of sulphides for separate treatment in a small acid leaching circuit as a means of saving expensive reagents.

(5) Change from autoclave to pachuca-type leaching with consequent savings in maintenance and reagents.

(6) Evaporation of the solution before precipitation to save reagents and to reduce soluble loss to a minimum. A fairly high content of sodium bicarbonate must be present in solutions during leaching in order to extract uranium at a satisfactory rate from Beaverlodge ore. The removal of some bicarbonate before precipitation saves reagents for precipitation. Evaporation of water from leach solution permits the use of a corresponding amount of wash water to filtration without bleeding of solution; this reduces soluble loss of sodium carbonate and uranium to a very low level.

(7) Lime is used as a partial replacement for caustic soda to reduce consumption of the more expensive reagent. Another benefit of this system is removal of ionium which is an objectionable impurity in the precipitate.

(8) Oxygen has been used as replacement for air as an oxidizing agent since 1965. The use of oxygen greatly reduces the volume of exhaust gases and thereby reduces heating costs. Further reduction in heating costs have been made by pulp-to-pulp or gas-to-pulp heat exchangers.

(9) In all uranium plants thickening and filtration have been improved by the use of better flocculating reagents in a more efficient way.

(10) Underground leaching of uranium ores is a relatively recent development in Canada, having been initiated in late 1962 [17]. At present, several mines in the Elliot Lake area are recovering uranium from mine water, obtained by washing down stopes and sprinkling of low-grade heaps or ore in a systematic manner. The water is pumped to the surface for recovery of uranium. The dissolution of uranium is apparently accelerated by the presence of bacteria that produce ferric sulphate and acid from sulphides, but optimum conditions for bacterial leaching have not been aimed at. The combined annual production from these operations is now in excess of 500 000 lb $U_3O_8$.

(11) By-products, such as thorium and yttrium, are now recovered from ion exchange barren solution in the Elliot Lake area [18]. The production of readily recovered thorium and yttrium is already a factor in overall costs and production could be greatly expanded if the demand warrants this in the future.

(12) One plant has been established by Rio Algom Mines for production of nuclear grade $UO_2$ from ion exchange eluate. This plant commenced operation in 1966.

## CANADIAN DEVELOPMENT WORK IN URANIUM PROCESSING OF POSSIBLE INTEREST TO FUTURE OPERATION

After the great rush to place the many uranium mills in operation and towards the latter part of the nineteen fifties, metallurgical development work for most companies was aimed at solving day-to-day problems in processing, establishment of optimum process conditions and introducing improvements or additions to the original flowsheets as mentioned earlier. The milling plants were established and paid for, but contracts for sale of uranium were of short duration. Consequently, the management of many companies were not too interested in spending money on long-term metallurgical development work.

In spite of the unfavourable short-time outlook for uranium sales, research and development on uranium ore processing did continue to a significant extent at the laboratories of the Mines Branch, Eldorado Mining and Refining, Rio Algom Mines and others. In 1959, The Canadian Uranium Producers Metallurgial Committee was formed for the purpose of exchanging information on research in uranium ore treatment, discussing results and recommending new projects. The CUPMC has been, and is, a valuable clearing house for information on all uranium development, except in isolated cases where commercial secrecy applies.

Some of the more interesting development work that has been done, and is in progress, is mentioned below:

(a) Flotation of uranium ores for the purpose of pre-concentration has been the subject of considerable laboratory and pilot plant development work [19, 20]. Three main types of Canadian uranium ores have been of economic importance: (i) the Elliot Lake type which contains brannerite with some pitchblende or uraninite in a quartz conglomerate associated with pyrite; (ii) pitchblende in hydrothermal veins, generally finely dispersed and closely associated with chlorite and calcite; and (iii) pegmatitic ore containing uraninite and uranothorianite.

Testwork on flotation of brannerite ores and of pegmatitic ores has shown promising results, and this will be covered in a paper presented to the Panel (see section II). Attempts to concentrate uranium from pitchblende ores of the hydrothermal type have been less successful; testwork in laboratory and pilot plants has shown, however, that acid consuming minerals can be separated rather successfully from the bulk of the ore, giving two products for separate leaching by acid and sodium carbonate solutions. This approach may be of interest for some future plants.

(b) Pre-concentration by gravity concentration methods has been tested quite extensively and may yet have its place in future treatment of Canadian ores, particularly ores of lower grade.

Conventional heavy media separation of crushed ore is well established in the milling of base metal ores, and has been tested on some uranium ores. In recent years, the heavy media separation in cyclone systems has been improved to a point where ore down to 65 mesh can be treated and results are close to the theoretical separation obtainable by heavy liquid separation in the laboratory [21].

A recent Canadian development is the 'Compound Water Cyclone' which operates with automatic control of the vortex and does not employ a heavy media. This most promising system will soon be tested for concentration of uranium ores [22, 23].

(c) The Jones Wet Magnetic Separator has been tested for concentration of some Canadian uranium ores and very interesting results have been obtained as regards recovery and ratio of concentration [24]. Additional testwork is planned; recent manufacture of large units with capacities up to 30 tons per hour has been reported.

(d) Bacterial leaching of uranium from ores has been studied quite extensively in Canada, particularly at the Mines Branch Laboratories [25]. A paper outlining research work in this field will be presented to the Panel (see section II). At this stage it is evident that bacterial leaching should be considered in conjunction with pre-concentration; these two low cost systems should complement each other, bacterial leaching being applied to rejects from pre-concentration.

(e) Solvent extraction from acid leach slurry has been a subject for research in many countries, including Canada. Eldorado has developed a system which appears practical and pilot plant testing was commenced last year in the Beaverlodge mill. The pulp used for testing is the acid slurry from leaching of pyrite flotation concentrate. A second pilot plant run is now underway and results should be available in two or three months.

(f) Production of sulphuric acid from pyrite or sulphur without a conventional plant for acid manufacture has been tested quite extensively. Some systems involve production of acid in the pulp with simultaneous leaching of uranium either at elevated or atmospheric pressures. Other systems tested have aimed at producing acid from a pyrite concentrate, the resulting strong acid pulp being returned to leaching of the main ore. Leaching of uranium ore by introduction of $SO_2$ and air has been successfully accomplished in the laboratory and small pilot plants; many variations have been tried and for certain types of ore the methods are of interest. Finally, the production of relatively strong sulphuric acid by auto-oxidation in aqueous solutions with $SO_2$ and air was developed to a significantly higher efficiency.

(g) Recovery of uranium from ores by chloride volatilization has been tested to a limited degree in the Eldorado Laboratory. While recoveries of uranium were satisfactory, the regeneration of reagent, or a more selective volatilization process, is required in order to make the system economically attractive [26].

## FUTURE TREATMENT OF LOW-GRADE URANIUM ORES IN CANADA

In the foreseeable future – say for 20 to 25 years – the uranium ores that will be treated in Canada will likely be of the same three main types as those that have been mined to date. However, as the need for additional reserves will increase, it seems likely that these ores will be of lower grade.

As the demand for production increases new plants will be needed, and sections may be added to existing mills in order to apply pre-concentration and bacterial leaching for increased capacity.

The many cost saving changes that have found their way into operation, and others that have been developed through the testing stage, will help to prevent runaway prices for uranium in 10 to 15 years.

## REFERENCES

[1] ELDORADO MINING AND REFINING LTD., Uranium in Canada (1964).

[2] POPOFF, D.R., Uranium, Can.nucl. Tech. 5 (1966) 21-25.

[3] ROSCOE, S.M., "Unexplored uranium and thorium resources in Canada", Geological Survey of Canada, Economic Geology Ser. 16, 2nd ed. (1962) paper 66-12.

[4] LANG, A.H., GRIFFITH, J.W., STEACY, H.R., "Canadian deposits of uranium and thorium" Geological Survey of Canada, Economic Geology Ser. 16, 2nd ed. (1962).

[5] THUNAES, A., Canadian practice in uranium recovery plants, Can. Min. J. (June 1956).

[6] DEPT MINES AND TECHNICAL SURVEYS, Canada, Development of the Port Radium Leaching Process, Tech. paper 13 (1955).

[7] EHRLICH, R.P., "Uranium mills in the Blind River area", Uranium Ore Processing, (CLEGG, J.W., FOLEY, D., Eds) Adison Wesley Publishing Corp. (1958).

[8] THUNAES, A., "Development of the Beaverlodge Mill", Uranium Ore Processing, (CLEGG, J.W., FOLEY, D., Eds) Adison Wesley Publishing Corp. (1958) 306-23.

[9] SMITH, H.W., BULL, W.R., Uranium ore research, Can. Min. J. (June 1956).

[10] ROACH, A.G., ANDERSON, A.C., EHRLICH, R.P., "Conversion to ore pebble grinding", Presented at Int. Mineral Processing Congr., New York, 23 Sep. 1964.

[11] COLBORNE, G.F., ALLEN, A.R., THUNAES, A., Controlling serious corrosion pitting of process tanks, Corrosion 17 12 (1961) 20-24.

[12] BETTENS, A.H., LAPOINTE, C.M., Electronic Sorting of Low-grade Ores, Dept Mines and Technical Surveys, Canada, Tech. paper 10 (1955).

[13] COLBORNE, G.F., Electronic sorting at Beaverlodge, Can. Min. metall. Bull. (Aug. 1963).

[14] ROBB, N., OPRATKO, V., PRICE, L.S., Milliken's two stage sulphuric acid leaching process for uranium, Can. Inst. Min. Metall. Bull. 56 (June 1963) 614.

[15] TREMBLAY, R., BRAMWELL, P., Eldorado's solvent extraction plant at Port Radium NWT, Trans. Can. Inst. Min. Metall. LXII (1959) 44-53.

[16] THUNAES, A., COLBORNE, G.F., "Auxiliary processes in the Beaverlodge uranium leaching plant", Presented at A.I.M.E. meeting, Dallas, Texas, 1963.

[17] MacGREGOR, R.A., "Recovery of $U_3O_8$ by underground leaching at Stanrock Uranium Mines Ltd.", Presented at Can. Inst. Min. Metall. meeting, Montreal, Quebec, 13-15 Apr. 1964.

[18] VERMEULEN, L.W., Recovery of thorium from uranium solutions, J. Metals (Jan 1966).

[19] HONEYWELL, W.R., KAIMAN, S., Flotation of uranium from Lake Elliot ores, Trans. Can. Inst. Min. Metall. LXIX (1966) 99-107.

[20] HONEYWELL, W.R., HARRISON, V.F., Two stage flotation treatment of uranium ore from Faraday Uranium Mines Ltd., Trans. Can. Inst. Min. Metall. LXVI (1963) 280-84.

[21] LILGE, E.O., Hydroclone fundamentals, Trans. Instn Min. Metall. 71 6 (1961-62).

[22] WYMAN, R.A., STONE, W.J.D., HARTMAN, H.F., Illustrative Application of the Jones Wet Magnetic Separator, Dept Mines and Technical Surveys, Canada, Tech. Bull. 36 (1962).

[23] VISMAN, J., Bulk processing of fine materials by compound water cyclones, Can. Inst. Min. Metall. Bull. (Mar. 1966).

[24] STONE, W.J.D., "Effect of variable adjustments on separation in Jones Magnetic Separator" A.I.M.E. preprint 63B303.

[25] HARRISON, V.F., GOW, W.A., IVARSON, K.C., Leaching of uranium from Elliot Lake ore in the presence of bacteria, Can. Min. J. 87 (1966) 64-67.

[26] LACHANCE, G.R., Gas Phase Chlorination of Beaverlodge Ores using Carbon Tetrachloride, Eldorado Mining and Refining Ltd., rep. T60-24.

# STATUS REPORT FROM CZECHOSLOVAKIA

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## INTRODUCTION

The present paper deals with the fundamental problems and the main routes followed in processing low-grade uranium ores in CSSR. In this connection it may be useful to discuss the definition of low-grade ore.

In our country this term is applied to uraniferous material with a very low content of uranium (of the order of 0.01%) whose treatment causes no particular difficulty. However, the same term is also used to designate those materials whose processibility lies on the verge of economic profitability. In our view, this classification of an ore using two independent criteria (i.e. uranium content and processing economy) is useful from the standpoint of technology. The treatment of both such ore types is as a rule carried out by specific technological processes.

Consequently, low-grade uranium ores can be divided into two groups:

(1) Ores with a low uranium content. To this category belong in our country uraniferous materials which originate as a by-product of technological processes used in processing other materials. This is primarily gangue and tailings of various physical or physico-chemical pretreatment operations to which the ore is subjected at the mining site. Mention should be made in this connection of mine waters, which represent a useful complementary source of uranium despite their low uranium content (of the order of milligrams per litre).

(2) Ores whose economical treatment is problematic. To this category belong deposits of conventional ore types with a uranium content on the limit of profitable treatment. Also, those deposits containing atypical materials possessing such properties which impair the economy of their treatment. This includes ores with a considerable amount of components which are difficult to separate and which at the same time consume the leaching agents. Finally, it covers uranium-bearing materials in refractory forms which are difficult to dissolve and also some special materials, such as lignites, uranium-bearing shales, loams, etc. The profitable treatment of these and similar materials usually requires a considerably higher uranium content, or isolation of additional valuable by-products.

## A SHORT SUMMARY PRESENTING THE EXPERIENCE GAINED IN PROCESSING LOW-GRADE ORES OF THE FIRST CATEGORY

Materials belonging to both categories occur in our country and this paper deals with the processing of ores belonging to the first category, since our knowledge of the materials belonging to the second one is limited to the sedimentary deposits in tertiary formations which form the subject of our second paper (see section II).

On the industrial scale, the following materials are processed at present: tailings from radiometric concentration; tailing ponds from gravitational concentration; and mine waters.

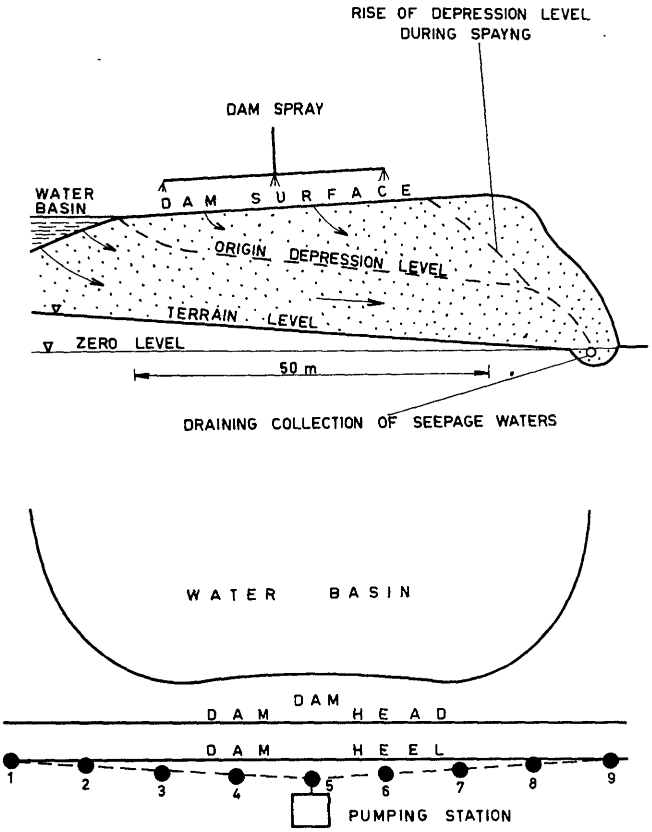

FIG. 1. Diagram of seepage and water withdrawal from the tailings pond: 1, 2 etc. individual shafts for seepage water.

## Tailings from Radiometric Concentration

Heap leaching with sprayed sodium carbonate solution is used with subsequent sorption of uranium on strongly basic resins, chloride elution and other conventional operations which are carried out in existing hydrometallurgical installations. The need for good filtration of the material sometimes requires de-sliming before further treatment. This can be done economically only in some cases. The technological procedure is usually performed directly at the mining sites. In the processing of tailings, less than 30 mm with uranium content of 0.02 to 0.03%, yields of 40 to 50% were obtained after leaching periods of 3 to 6 months.

## Tailing Ponds from Graviational Concentration

Deposits of tailings from the gravitational concentration plant for carbonate ore containing pitchblende are being processed as follows: the seepage waters from the pond dam (see Fig. 1) containing originally about 5 mg U/litre enriched on filtering through the dam body to approximately 15 mg U/litre. It should be stressed that this enrichment occurs at pH values of approximately 7, i.e. without the addition of leaching agents. An analysis of this effect indicates that this kind of leaching has far more in common with geochemical reactions than with the dissolution of uranium from uranium-bearing ores as normally envisaged. The seepage waters are drained by a collecting system running along the dam and pumped from a basin to a sorption unit with a strongly basic resin.

To extract also the metal from the part of the dam lying above the depression line proper, the dam top is sprayed. Proper precautions are taken against the possible weakening of the dam by the rise in the depression level. Preliminary data indicate that the daily production of uranium is equal to about 0.1% of the total uranium contained in the dam material.

## Mine waters

Mine waters from the operating mines containing 2-5 mg U/litre are processed. At the mining site, only the sorption unit is operated, the resin being regenerated in a plant serving these stations. On regeneration, the resin is again transported to the site and recharged. The sorption units are in continuous operation.

These operations are highly economical. Uranium is produced at 30 to 50% of the costs necessary for the treatment of the normal so-called rich ores. Moreover, these costs should not be considered as final and their gradual lowering can be expected.

## OUTLINE OF THE PROGRAMME FOR LOW-GRADE ORE PROCESSING IN 1966-1970

The chief aims for this period are as follows:

(1) To investigate various combinations of physical and physicochemical methods for ore pretreatment with processes of extractive uranium metallurgy from various intermediate products and tailings. In this connection, the existing methods for thickening and liquid-solid separation, as well as for the separation of individual ore components, should be improved or new and original technical solutions found. This applies to conventional ores as well as to uranium-bearing materials containing coal and loam, which are dealt with in our second paper, in section II.

(2) To extend the present knowledge of the technologically and economically important properties of the main Czechoslovak ores. In addition, the processes taking place during individual operations of particular importance should be studied and the existing equipment designs improved.

For the analysis of the various alternatives, mathematical methods and methods of mathematical statistics for optimalization will be applied as fully as possible.

(3) To design, build and test a mobile ion exchange unit of the building set type. This should be done in two alternative forms, the first destined for sites adjacent to a hydro-metallurgical plant, the second for more distant sites. In the first case, simple units without resin regeneration will be used. The columns with the spent resin will be substituted by columns with regenerated resin. The resin will be then processed in the nearest hydro-metallurgical plant. In the other case, the basic ion exchange resin in the columns will be regenerated by a sodium chloride solution. The diuranate concentrate will then be precipitated and filtered.

These units will be used to process waters from flooded unused mines as well as from operating mines, and for the processing of leaching solutions from heap leaching at the gangue depots and tailing ponds

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# RAPPORT SUR L'ETAT D'AVANCEMENT DES TRAVAUX EN FRANCE

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Les minerais d'uranium traités dans les usines de concentration en France proviennent de districts uranifères appartenant aux massifs hercyniens essentiellement granitiques. Leurs teneurs en uranium sont relativement faibles, comprises pour la plupart entre 0,9 et 2‰. Les gisements se présentent sous forme de filons et d'amas ou stockwerks.

Les districts uranifères actuellement exploités par le Commissariat à l'énergie atomique sont situés au Forez, à la Crouzille dans le Nord Limousin et en Vendée; ils sont situés dans l'une et l'autre branche de l'édifice hercynien du massif central français.

Les minéralisations de ces gîtes comprennent, en particulier:

a) de la pechblende et des sulfures de fer, parmi lesquels l'association pyrite-marcassite est constante dans la calcédoine;
b) de la fluorine;
c) parfois du quartz du type enfumé et des sulfures: pyrite, galène, chalcopyrite, blende, ces derniers en très petite quantité.

La minéralisation uranifère se répartit en deux classes:

a) uranium sous forme tétravalente, pechblende;
b) uranium sous forme hexavalente, comme l'autunite, la chalcolite et les gummites.

Les minerais d'uranium mis en exploitation en France étaient traités en 1953 dans la seule usine existante à cette époque, à l'usine du Bouchet située dans la région parisienne, c'est-à-dire à environ 400 km des centres miniers.

Il était nécessaire, comme pour les minerais des métaux non ferreux, de procéder sur place à un enrichissement par voie physique. Mais, contrairement à ce qui se passe habituellement dans la métallurgie des métaux non ferreux, il n'était pas possible et il n'est encore pas possible de concentrer les minerais d'uranium exploités en France intégralement par voie physique sans consentir une perte en métal importante; d'autre part, les taux de concentration obtenus restent faibles.

La nécessité de produire de l'uranium en 1953 et l'espoir de retraiter ultérieurement les pseudos stériles faisaient qu'à cette époque cette perte n'était pas un obstacle à l'application de ce procédé, le but essentiel de l'opération étant de produire un préconcentré pouvant être traité à l'usine du Bouchet par la méthode d'attaque nitrique, complexion au carbonate de soude et décomplexion sulfurique.

Les besoins immédiats en uranium étant satisfaits, il devint nécessaire de mettre au point des procédés par voie chimique pour extraire le métal sur place à partir de ces minerais, avec un rendement élevé, le transformant en un nouveau composé encore impur mais cependant suffisamment concentré pour pouvoir supporter les frais de transport jusqu'à l'usine de raffinage.

Ces études ont été réalisées par les équipes de chercheurs du Département de chimie et de la Direction des productions du Commissariat à l'énergie atomique, cel'es de la Société de potasse et engrais chimiques et, enfin, par les etablissements Kuhlmann.

Ces derniers, comme nous le verrons au cours de la description des installations industrielles, ont réalisé en particulier les études qui ont abouti à la construction des usines de la Société industrielle des minerais de l'ouest en Vendée, à la Crouzille et au Forez.

Si économiquement la concentration intégrale par voie physique n'a pas pu être appliquée, les chercheurs du Commissariat à l'énergie atomique ont mis au point des méthodes de préconcentration physique qui ont permis, avec de faibles dépenses et un excellent rendement, d'éliminer des stériles du tout-venant à traiter, donc de réduire le tonnage de minerai devant subir les opérations coûteuses de broyage et d'attaque sulfurique.

Deux voies ont été explorées: la séparation granulométrique d'une part, le triage radiométrique d'autre part.

Certains minerais présentent la particularité d'avoir des teneurs en uranium nettement plus élevées dans les produits fins que dans les gros. Une simple opération de criblage permet d'éliminer les grosses granulométries stériles. En 1954, une installation pilote de préconcentration basée sur ce principe avait été réalisée à Bauzot et avait donné des résultats intéressants.

Les teneurs en U des gros éliminés restaient cependant relativement trop élevées, par suite de la présence de fines particules riches en uranium les enrobant et la présence de quelques gros morceaux minéralisés. Cette installation fut arrêtée après épuisement du gisement.

Par la suite, le Commissariat à l'énergie atomique a mis au point un procédé de triage radiométrique en continu sur bande en fonction de la radioactivité, qui est en réalité une amélioration du procédé précédent.

En effet, pour éviter toute interférence des fines riches en uranium enrobant le minerai, on procède d'abord à un lavage sur le crible de séparation granulométrique et par conséquent on récupère cet uranium; pour éviter les pertes dues aux grains minéralisés, ils sont classés en continu sur la bande en fonction de leur activité spécifique.

Une installation basée sur ce principe, que nous décrirons au cours de cet exposé, a été montée dans l'atelier de préparation des minerais de la Division de la Crouzille et donne d'excellents résultats. En France, c'est la seule méthode de préconcentration physique utilisée au niveau des usines de traitement.

Actuellement, les minerais français provenant des exploitations du Commissariat et ceux provenant des exploitants privés après concassage ou concassage et broyage ou concassage et triage radiométrique dans les ateliers de préparation du Commissariat, sont concentrés dans les trois usines de Bessines, sur la division de la Crouzille, de l'Ecarpière sur la division de Vendée et du Forez sur la division du Forez.

Les deux premières usines appartiennent à la Société Industrielle des Minerais de l'Ouest (SIMO) qui est une société anonyme à capitaux du Commissariat à l'énergie atomique, de la Caisse des dépôts et consignations et des Etablissements Kuhlmann.

Les procédés utilisés par la SIMO ont été mis au point en laboratoire et en atelier pilote par les Etablissements Kuhlmann en liaison avec le Commissariat à l'énergie atomique. Les Etablissements Kuhlmann ont également été chargés de la réalisation de ces usines.

La troisième usine, celle du Forez, a été également construite par les Etablissements Kuhlmann; elle appartient au Commissariat à l'énergie atomique et est gérée par la SIMO.

A ces usines de traitement des minerais métropolitains s'ajoutent l'usine de Gueugnon du Commissariat, qui retraite les préconcentrés chimiques uranifères produits à Mounana (Gabon) par la Compagnie des mines d'uranium de Franceville, et l'usine d'uranothorianite du Bouchet, qui traite les concentrés physiques d'uranothorianite importés de Madagascar.

Nous ne décrirons, dans cet exposé, que les trois usines de traitement des minerais français: celles de l'Ecarpière, de Bessines et du Forez dont la situation géographique est indiquée sur la figure 1.

Les dates de démarrage et les capacités nominales de ces usines sont données dans le tableau suivant:

| | Dates de démarrage | Capacité | |
|---|---|---|---|
| | | Minerai en T | Uranium en T |
| Ecarpière | Mars 1957 | 300 000 | 300 |
| Bessines | Juillet 1958 | 600 000 | 900 |
| Forez | 1960 | 180 000 | 330 |
| Capacité totale | | 1 080 000 | 1 530 |

Ces trois usines, comme nous l'avons indiqué ci-dessus, sont alimentées en minerais à partir d'ateliers de préparation exploités par le Commissariat.

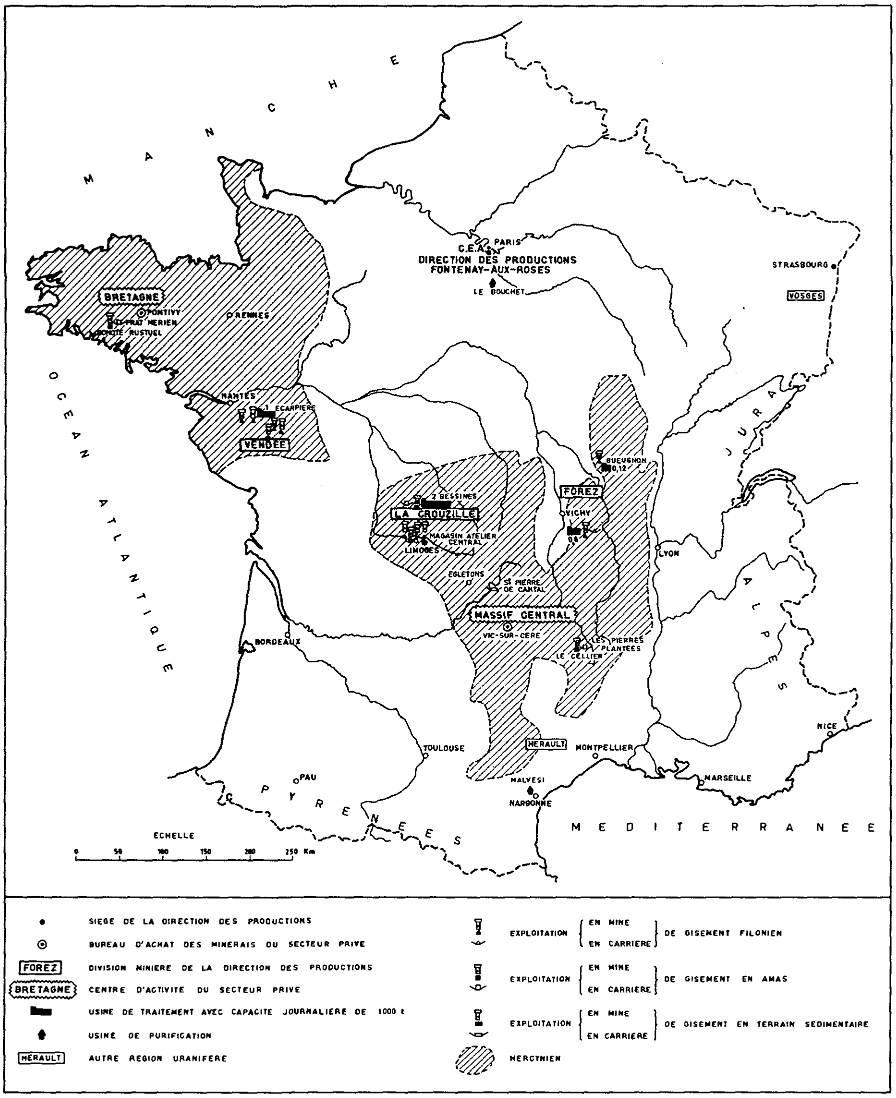

FIG. 1. L'uranium en France.

L'usine de l'Ecarpière est alimentée en minerai simplement concassé à 70 mm.

L'usine de Bessines reçoit du minerai concassé à 70 mm et une pulpe de granulométrie inférieure à 0,8 mm. Cette pulpe provient du débourbage indispensable du minerai avant passage de celui-ci sur les cribles et sur les bandes de triage radiométrique.

L'atelier de triage radiométrique (figure 2) s'inscrit dans l'atelier de préparation des minerais et comprend principalement deux bandes transporteuses d'un débit moyen de 50 t/h. Ces bandes reçoivent le minerai à granulométrie supérieure à 50 mm sur lequel s'effectue l'opération de triage.

En moyenne, le triage radiométrique permet d'éliminer 16 à 20% du poids de minerai entrant à l'atelier de préparation. La teneur moyenne des stériles ainsi éliminés est de 0,10‰ en uranium et le rendement métal de l'opération est de 99 à 99,5%.

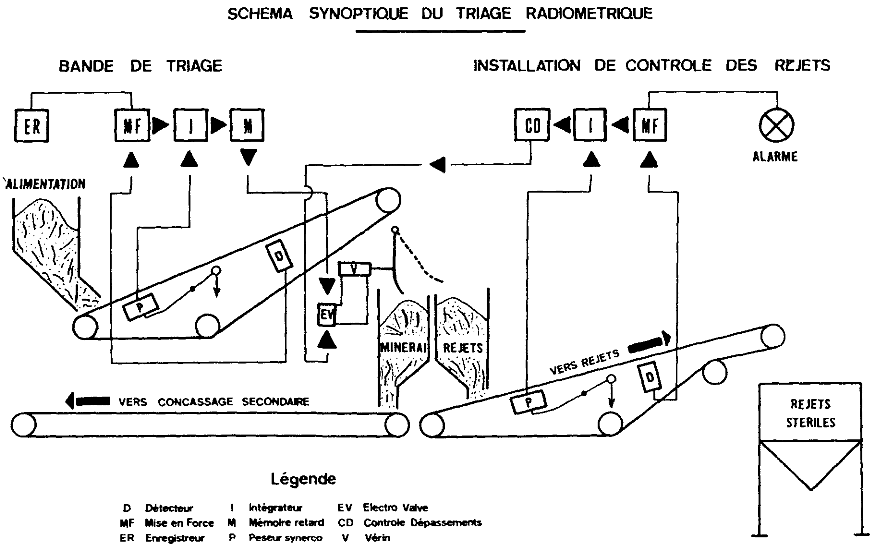

FIG. 2. Atelier de préparation des minerais de Bessines.

L'usine du Forez est alimentée en minerai broyé à 450 $\mu$m par l'atelier de préparation du Commissariat.

Dans les trois usines exploitées par la SIMO, l'attaque des minerais s'effectue à chaud par l'acide sulfurique avec oxydation par le chlorate de soude. Les figures 3, 4 et 5 montrent les grandes lignes des procédés utilisés à l'Ecarpière, Bessines et au Forez.

A l'Ecarpière comme au Forez, l'attaque de la totalité du minerai se réalise dans un seul circuit; a Bessines, deux circuits d'attaque sont utilisés.

Les fines inférieures à 150 $\mu$m sont, comme à l'Ecarpière et au Forez, attaquées dans des cuves agitées et chauffées. Les sables de granulométrie comprise entre 150 $\mu$m et 1 mm sont attaqués dans des tambours tournants.

La séparation sables et fines s'effectue dans un hydroclasseur et un classificateur installés sur le circuit fermé du broyeur à barres. Grâce à cette méthode, on obtient des solutions relativement concentrées en uranium provenant du circuit des tambours tournants et des solutions relativement pauvres provenant du circuit des fines lixiviées en cuves caoutchoutées.

Les deux usines de l'Ecarpière et de Bessines procèdent au lavage des stériles par contre-courant dans des épaississeurs classiques pour les fines et à contre-courant dans des classificateurs de drainage pour les sables. A l'usine du Forez, le lavage des stériles est effectué sur filtre à tambour à deux étages.

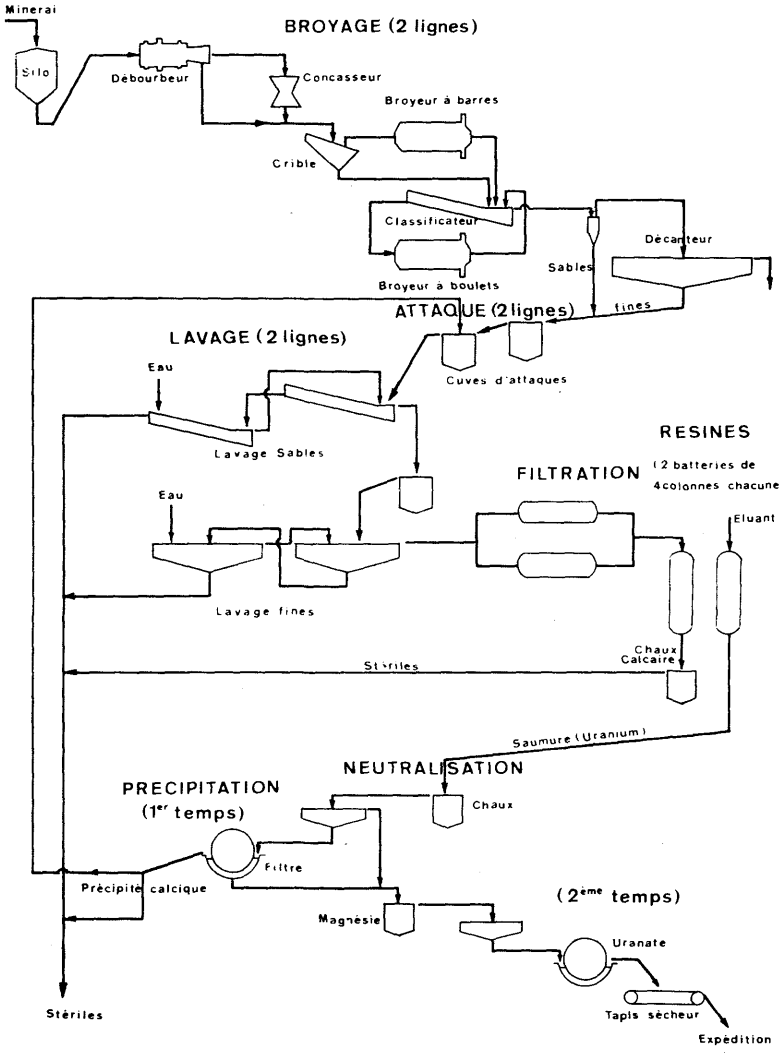

FIG. 3. Schéma général de traitement des minerais à l'usine de l'Ecarpière.

Le traitement des liqueurs de lixiviation s'effectue à l'Ecarpière et à Bessines sur résines échangeuses d'ions avec élution chlorure de sodium et acide sulfurique et précipitation de l'uranium contenu dans les liqueurs d'élution par de la magnésie.

Avant précipitation par la magnésie, on procède à une précipitation par la chaux jusqu'à pH 3 afin de réduire l'acidité et d'éliminer les impuretés. Le gâteau calcique ainsi obtenu qui contient un peu d'uranium est recyclé dans les cuves d'attaque. L'uranate de magnésie obtenu est filtré sur filtre à tambour, séché et expédié vers les usines de raffinage. La teneur moyenne en U% est de 68 à 72 sur sec.

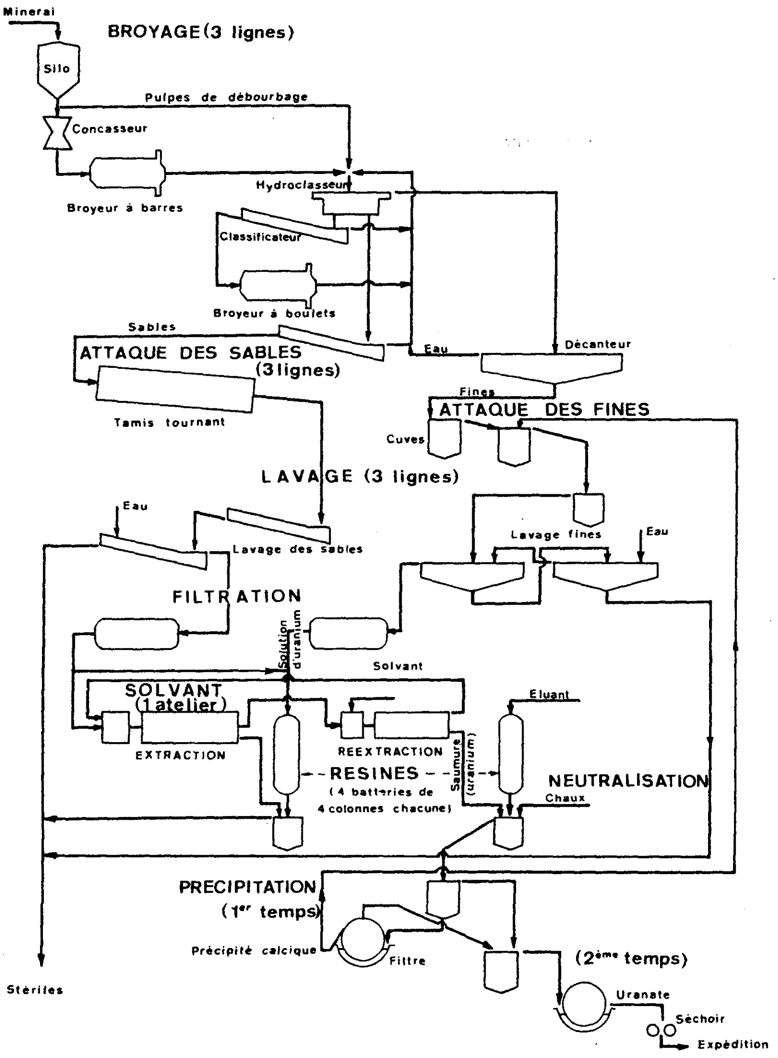

FIG. 4. Schéma général de traitement des minerais à l'usine de Bessines.

De plus, à Bessines un atelier de purification par solvants aminés est installé mais il est actuellement inemployé.

A l'usine de Forez, le procédé de traitement des liqueurs sulfuriques est un procédé original français qui permet d'obtenir comme concentré final très pur du nitrate d'uranyle en solution titrant 400 g d'uranium par litre.

Comme l'indique le schéma 5, il consiste essentiellement en une précipitation à la chaux des liqueurs d'attaque en deux temps: un premier temps à pH 2,5 à 3 pour éliminer le fer et l'acidité excédentaire, un deuxième temps à pH 6 à 7 pour obtenir un uranate de chaux impur à 18 ou 25% d'uranium.

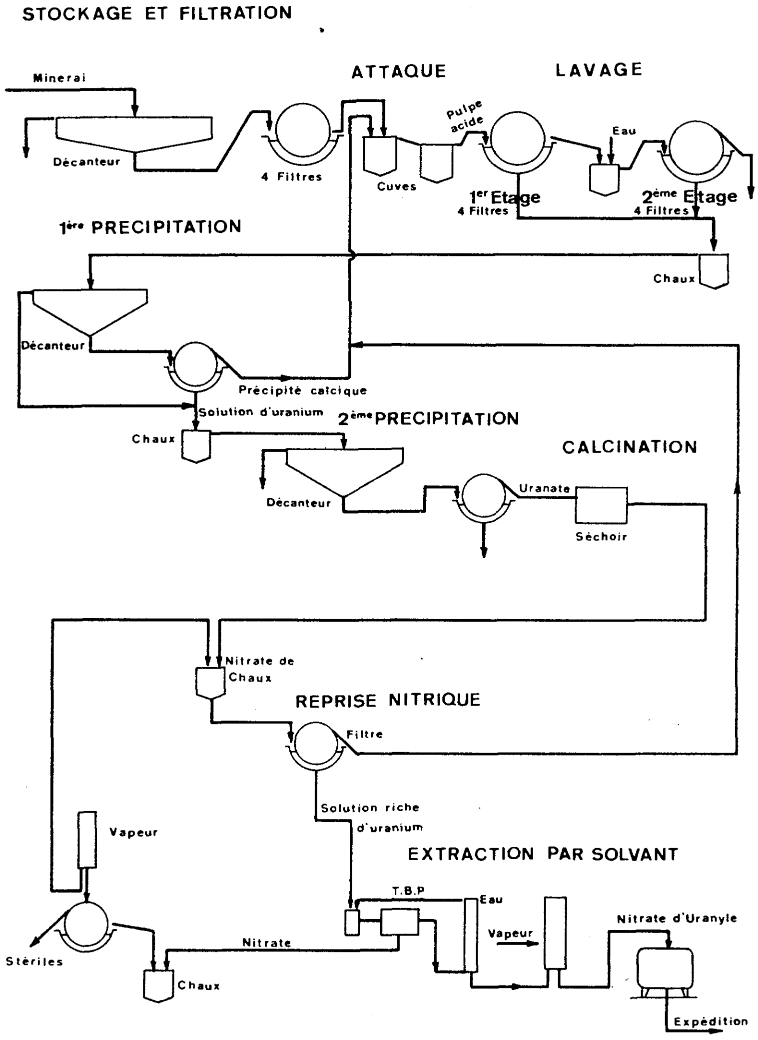

FIG. 5. Schéma général de traitement des minerais à l'usine du Forez.

Cet uranate, après séchage, est repris par de l'acide sulfurique et une solution de nitrate de chaux afin de faire passer l'uranium en solution sous forme de sulfate d'uranyle d'abord, puis sous forme de nitrate d'uranyle, ce qui permet après filtration de l'insoluble constitué en majeure partie par du sulfate de chaux, de traiter les solutions uranifères sur TBP.

L'uranium fixé sur TBP est réextrait par de l'eau déminéralisée et la liqueur de nitrate d'uranyle obtenue titrant 90 à 100 g d'U/l est concentrée par évaporation jusqu'à 400 g d'U/l. Ce nitrate d'uranyle est ensuite chargé dans des conteneurs et expédié vers les usines de raffinage.

Les liqueurs désuraniées après passage sur TBP qui contiennent du nitrate de chaux et des impuretés sont traitées par de la chaux pour éliminer les hydroxydes de fer et d'alumine, puis, après filtration, concentrées par évaporation afin de réintroduire dans le circuit de reprise de l'uranate de chaux le nitrate de chaux nécessaire à la transformation du sulfate d'uranyle en nitrate d'uranyle.

Les trois usines que nous venons de décrire marchent régulièrement depuis leur mise en service avec d'excellents résultats économiques et techniques. Les rendements globaux sont à peu près identiques et varient entre 95 et 96%. Le but qui avait été primitivement fixé a été atteint, mais n'y a-t-il plus de progrès possibles?

En dehors bien sur des améliorations de détail dans les procédés actuellement utilisés, améliorations qui ne sont pas spectaculaires mais qui sont constantes dans la vie de nos usines et qui ont permis et permettront encore de réduire les prix de revient et, dans tous les cas, de compenser les hausses normales des prix des matières premières et de la main d'œuvre, trois voies prometteuses sont à notre avis encore ouvertes aux chercheurs:

- La première est celle de la préconcentration physique et même encore celle de la concentration physique. Les chercheurs du Commissariat à l'énergie atomique poursuivent les études dans ce domaine qui, en réalité, n'a jamais été abandonné par nos laboratoires.
- La deuxième voie où des économies certaines pourraient être réalisées est la mise au point de procédés fournissant, à partir des concentrés actuels ou avant précipitation de ces concentrés et afin d'éviter une nouvelle phase de purification dans les usines métallurgiques, des composés d'uranium d'une grande pureté. On a essayé aussi des procédés de fabrication conduisant par exemple au tétrafluorure d'uranium ou à l'oxyde pouvant être produit directement avec de faibles dépenses supplémentaires dans les usines de concentration. Les équipes de chercheurs de la SIMO étudient ces problèmes dont la solution peut présenter, comme nous l'avons dit, un intérêt économique important.
- La troisième voie est celle qui consiste à la mise au point des méthodes de traitement par lixiviation naturelle, soit des minerais en tas, déjà largement utilisée dans certains pays, soit des minerais in situ. Ces méthodes de traitement font l'objet en France d'études d'applications au stade semi-industriel. Elles peuvent permettre de récupérer à un prix raisonnable l'uranium contenu dans les minerais inframarginaux qui ne pourraient pas être traités économiquement en usine et peuvent également être utilisées pour le traitement de minerais à faible teneur produits dans des petits gisements trop éloignés d'une usine existante.

On poursuit également, dans les sièges miniers du Commissariat, la mise au point des méthodes de lixiviation des minerais in situ, par arrosage avec des solutions acides de panneaux non exploitables par les méthodes classiques. Elles permettent, dans certains cas, la récupération de tonnages appréciables d'uranium.

Nous noterons en particulier à ce sujet les résultats obtenus dans un de nos sièges où grâce à une sélection des eaux de drainage des travaux miniers naturellement minéralisées et à l'arrosage acide de certains panneaux déjà exploités, nous arrivons à récupérer 30 $m^3/h$ environ d'eaux titrant en moyenne 100 g d'U/$m^3$, soit 20 à 24 t d'U/an.

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# STATUS REPORT FROM INDIA

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The Energy Survey Committee of India, in its report to the Government, has estimated that the energy requirements in the year 1985/86 would be $290 \times 10^9$ kWh, i.e. eight times the present requirement, and in the year 2000 it would be $820 \times 10^9$ kWh, which is about 22 times the present requirement. The hydropotential that can be developed during the next 20 years is estimated to be of the order of $150 \times 10^9$ kWh and hence the difference of about $140 \times 10^9$ kWh will have to be obtained from either fossil or nuclear fuel. This would mean installating a generation capacity of about 26 000 MW in the next 20 years. To conserve the limited fossil fuel reserves, it has been estimated that about 70% of this capacity, i.e. about 18 000 MW, should form the nuclear component. This will be about 25% of the total energy requirements by 1985/86. The uranium requirements to meet this growth will be about 10 000 tonnes by 1985/86 which, from the point of view of our resources, is a substantial quantity.

The most important uranium deposits are located in South Bihar in the Singhbhum Thrust belt, which is well known for its copper, apatite magnetite and kyanite deposits. On the basis of their uranium contents, these ores can be classified into two broad categories – one with low copper and high uranium contents and the other with high copper and low uranium contents. Another source of uranium in India is monazite. Some particulars about these deposits are given in Table I.

Facilities for the recovery of byproduct uranium from monazite already exist in the country. But its production from this source, conditioned as it is by the limited demand for thorium, cannot be very large.

Both the categories of the ores from the Singhbhum belt can be considered as low grade. Uranium from the ores in category (B) can be recovered, in the present state of knowledge, only as a byproduct of the copper industry.

In the case of ores in the category (A), attempts have been made to recover uranium from the ore deposits at Jadugoda, assaying 0.06–0.07% $U_3O_8$, first on the laboratory and then on a pilot plant scale. Based on this work, a mill, capable of treating 1000 tonnes of ore per day, is being set up at Jadugoda and is expected to go into production during 1966. It is hoped that the operation of this mill will provide an impetus and expericence towards concerted and determined efforts to develop methods which will cut down costs of treating ores from the thrust belt. A brief

TABLE I. SOURCES OF URANIUM

| Location | Typical analysis (%) | Proved and inferred reserves (t $U_3O_8$) |
|---|---|---|
| Singhbhum Thrust Belt, Bihar - Jadugoda, Narwapahar and Bhatin. | | |
| (A) low copper content | $U_3O_8$, 0.04-0.08 | |
| | CuO, 0.05-0.07 | |
| | NiO, 0.20-0.30 | 16 000 |
| (B) high copper content | $U_3O_8$, 0.01-0.03 | |
| | CuO, 1.00-2.00 | |
| | NiO, 0.10-0.20 | 17 000 |
| South Western Coast and Ranchi plateau in Bihar-monazite deposits | $U_3O_8$, 0.25-0.35 | |
| | $ThO_2$, 8.50-9.50 | 15 000 |
| | Total $U_3O_8$ reserves | 48 000 |

TABLE II. JADUGODA ORE ANALYSIS

| | % |
|---|---|
| $U_3O_8$ | 0.07 |
| $SiO_2$ | 66 |
| $Fe_2O_3$ | 17.8 |
| NiO | 0.25 |
| CuO | 0.01 |
| CaO | 1.4 |
| MgO | 1.9 |
| $P_2O_5$ | 1 |
| S | 0.3 |

outline of the work done on Jadugoda ore and the process that was finally selected is given below.

The process chosen is a conventional one with acid leaching of ground ore, followed by two stages of filtration, ion exchange in fixed beds with elution by salt solution and recovery by magnesia in a two-stage precipitation system. Chemical analysis of a typical Jadugoda ore sample is given in Table II.

In the early stages considerable difficulty was encountered with the ore in acid leaching. Maximum recovery of uranium (90-95%) was obtained only with an acid consumption of about 90 kg sulphuric acid per tonne of ore. About 7 kg of manganese dioxide was used for oxidation. The resultant leach liquor contained up to 10 g/litre of $P_2O_5$ and 70 g/litre of sulphate and the pH was less than 1.0. The acid requirement alone meant an expenditure of about $4.0 per tonne of ore. Several methods were tried, therefore, to bring down acid consumption and produce a leach liquor which could be used directly for ion exchange, without partial neutralization. These methods were: (i) a two-stage leach process, where the strong leach solution containing the dissolved uranium and unused reagents was advanced to the neutralizing stage of leaching; and (ii) leaching with addition of ferric salt. In both the methods, reduction in acid consumption was not appreciable. However, after undertaking a detailed study of the leaching behaviour of apatite, it was apparent that its dissolution in sulphuric acid was dependent not only on the acid concentration, but also on the concentration of ferric ions and the temperature used for leaching. For a given concentration of ferric ion (in the range 1-5 g/litre) and pH (in the range 1.4-2.0), a higher temperature was more favourable for preventing apatite dissolution. This fact greatly helped us in fixing the final conditions of leaching, which are given below.

The ground ore (about 55%-200 mesh (B.S.S.) is leached at 60% solids and 1.5-1.6 pH at 45-50°C. After about one hour ground pyrolusite, 4.5-5.0 kg/ton, is added for oxidation and the leaching continued for four hours. At the end of this period acid addition is stopped and pH allowed to rise to about 1.8 over a period of 7 to 8 hours. During this stage some ferric phosphate is precipitated. Under these conditions the acid consumption is about 25 kg per tonne of ore, which is equivalent to $1.10 per tonne of ore, and about 90 to 95% of the uranium is leached. The dissolution of apatite, iron and other impurities is very much reduced.

The leach liquor obtained thus has a pH of 1.8, an emf of -450 mV and the following composition:

| | |
|---|---|
| $U_3O_8$ | 0.6 g/litre |
| Fe (total) | 3.5 g/litre |
| $SiO_2$ | 1-1.5 g/litre |
| $SO_4$ | 25 g/litre |
| $P_2O_5$ | 0.5 g/litre |
| $Mn^{++}$ | 3-3.5 g/litre |

This liquor can be used directly for uranium recovery by ion exchange.

Considerable work has also been done on a laboratory scale in the recovery of uranium from ores falling into category (B). One of the sources of uranium in this category is the tailings of the Indian Copper Corporation (ICC) Plant, which is situated at a distance of about 12 km east of Jadugoda. About 1300 tonnes of tailings, assaying about 0.011% $U_3O_8$, are discarded every day. In spite of several favourable factors such as no cost on exploration, mining, crushing and grinding, we have not been able to develop a method which will enable us to recover uranium from this source in $5-10 per lb $U_3O_8$ range.

Efforts to upgrade this material by physical beneficiation techniques did not yield the desired results. Studies were then conducted using extractive metallurgical techniques and some of the results obtained are summarized below.

Studies in uranium leaching from these tailings showed that about 80% of uranium could be recovered using 25 kg $H_2SO_4$ and 4 kg $MnO_4$ per tonne at 55°C in about 4 hours time. The composition of a typical leach solution is as follows:

| Constituent | Concentration (g/litre) |
|---|---|
| $U_3O_8$ | 0.102 |
| $Fe^{++}$ | 2.4 |
| $Fe^{+++}$ | 1.8 |
| $P_2O_5$ | 0.3 |
| $SO_4$ | 24.5 |
| $SiO_2$ | 2.0 |
| $S_4O_6$ | 14.0 |

A saturation loading of 31 g $U_3O_8$ per litre of wet settled resin was obtained with the above solution.

To reduce processing costs, studies on percolation leaching methods have been undertaken. The work is in progress and a few of the main observations are as follows. Due to fine grind the percolation rate is rather poor and requires 48 hours for one solution displacement for a stack of 2.5 metre height. The rate is likely to reduce further when we think of large-scale operations. The above rates were obtained with columns up to 30 cm diam. In this method the acid consumption is reduced by about 5 kg per tonne of ore; however, the recovery of uranium is also reduced by about 5%. Detailed cost calculations and some large-scale work which is now being undertaken will prove whether or not the percolation leaching method would be more advantageous than the conventional method of leaching. Preliminary calculations have shown that uranium from these tailings can be recovered in the range of $15-20 per pound $U_3O_8$.

During preliminary studies on percolation leaching it was noted that when tap water was allowed to percolate through a three-year old and a one-year old sample of tailings, about 80% and 63% of uranium was leached out from the two samples respectively. The leaching was mainly due to the breaking down of the sulphides present in the tailings with the generation of sulphuric acid and ferric sulphate, both beneficial for uranium leaching. It was, however, found that from a fresh sample of the tailings practically no uranium could be leached by water percolation. The breaking down of the sulphides could be due to the action of bacteria. To accelerate the process of sulphides decomposition some preliminary work on bacterial leaching has been started.

Extensive deposits of this category of ore are available in and around Jadugoda. A copper plant with a capacity of about 5000 tonnes ore per day is likely to be set up within the next 5 years in the region. The tailings of this plant are expected to behave in a manner similar to the ICC tailings and as such any improvement in the process now achieved will have a significant bearing on our future plans.

The other direction in which we have put in some effort is that of physical beneficiation. A large number of ore samples have been tried on laboratory scale using gravity method (wet tabling) and flotation. In some cases good results have been obtained. Recent tests on Jadugoda ore by flotation, using an amine (Primene T) and petroleum sulphonate, have shown an enrichment ratio of 2.0 with an overall uranium recovery of about 95%. While detailed cost calculations and other implications on the design of the mill have not been ascertained, prima facie the results obtained seem to be encouraging and worth detailed investigation.

# RAPPORT SUR L'ETAT D'AVANCEMENT DES TRAVAUX AU PORTUGAL

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Les principales études effectuées jusqu'à maintenant au Portugal ont eu pour but la mise au point de deux types de traitement des minerais d'uranium:

- Lixiviation classique par agitation du minerai finement broyé dans une solution sulfurique;
- Lixiviation du type «heap leaching» dans laquelle le minerai, à peine concassé, est entassé puis arrosé avec une solution sulfurique.

Des essais de lixiviation classique ont été effectués avec les échantillons de minerais portugais dont on disposait. Le plus souvent, la dissolution de l'uranium est facile et la consommation d'acide faible.

Les efforts ont été orientés dans le sens d'une lixiviation du type «heap leaching». Au Portugal, le procédé a été utilisé à l'échelle pilote; il a été décrit en détail dans une communication présentée à la troisième Conférence internationale sur l'Utilisation de l'énergie atomique à des fins pacifiques (Genève, 1964).

L'objectif poursuivi était le traitement économique du minerai à proximité des petits gisements, ce qui permet d'éviter les frais de transport. Les résultats de l'étude des aspects économiques et techniques et ceux des essais effectués en laboratoire ont conduit au choix du procédé dont le schéma est donné au tableau I.

Le minerai, entassé à côté de la mine, est arrosé avec une solution d'acide sulfurique à 5% environ, puis avec de l'eau. Sur les autres tas de minerai on recycle les liqueurs encore acides provenant des traitements antérieurs. On arrive ainsi à réduire la consommation de réactifs.

Avec le procédé indiqué et dans le cas d'un minerai bien étudié en laboratoire, la durée du cycle total de traitement, y compris la charge et la décharge des tas, est de 14 j et le rendement d'extraction de l'uranium de l'ordre de 80%.

TABLEAU I. PROCEDE DE TRAITEMENT DU MINERAI D'URANIUM

Minerai
Broyage jusqu'à 1/2 pouce
Arrosage avec une solution sulfurique
Arrosage avec de l'eau
Liqueur
Ajustage du pH
Echange d'ions
Précipitation
Uranate
Séchage
Concentré ~75% $U_3O_8$

L'installation a une capacité d'environ 15 t de $U_3O_8$ par an. L'équipement est aisément transportable d'une mine à l'autre.

Ce procédé présente l'avantage d'être rapide et de n'exiger qu'un équipement réduit, car il permet d'éliminer les opérations les plus volumineuses inhérentes aux installations classiques de traitement chimique, telles que le broyage fin, la lixiviation classique et la séparation solide-liquide. Néanmoins, le rendement d'extraction de l'uranium est inférieur à celui du procédé classique; on croit qu'il convient particulièrement aux minerais secondaires, lorsque le minéral est bien exposé mais la teneur en argile faible. L'application économique de ce procédé aux minerais pauvres est conditionnée surtout par la consommation d'acide sulfurique et les frais de charge et de décharge des tas.

Dans les cas où les minerais présentent une tendance à l'imperméabilisation, divers procédés ont été essayés:

- Mélange avec d'autres minerais.
- Séparation préalable des fines et leur traitement dans des installations classiques. Dans de nombreux cas les fines sont plus riches en uranium que les gros du minerai. Au laboratoire on est arrivé à des résultats très intéressants sur ce procédé. On n'a pas encore eu la possibilité de faire des essais à l'échelle pilote dans des conditions convenables.
- Immersion du minerai en solution sulfurique avec introduction de la liqueur par la partie inférieure des bassins. Dans certains cas on a abouti à de bons résultats au laboratoire et à l'échelle pilote.

On a examiné la possibilité d'appliquer ce procédé à différents minerais. On a pour cela essayé d'imprégner le minerai d'une solution d'acide sulfurique, puis d'entraîner l'uranium solubilisé en l'arrosant avec de l'eau ou une solution sulfurique très diluée.

On a constaté encore qu'en utilisant les effluents acides des résines échangeuses d'ions il était possible de récupérer de l'uranium contenu dans les minerais résiduels après traitement. On est parvenu à retirer 50% de l'uranium existant dans ces résidus. Le coût de ce procédé est très réduit.

Bien que ces effluents acides n'aient pas encore été utilisés pour traiter des minerais pauvres, ces essais sur les résidus permettent d'envisager la possibilité de le faire. Il faudrait cependant qu'une installation de lixiviation acide et d'échange d'ions ou d'extraction par solvants existe à proximité de ces minerais.

En ce moment, on étudie également la lixiviation de minerais en lit statique par l'eau et par des solutions à différentes concentrations en acide sulfurique, qui présente une certaine similitude avec la lixiviation par capillarité en usage en France; on a cependant adopté des débits plus importants pour permettre des traitements plus rapides.

On envisage la possibilité de développer ces techniques ainsi que la lixiviation par l'eau avec ou sans addition de réactifs solides, pour le traitement des minerais pauvres.

Pour réduire les frais de préparation physique et, par conséquent, traiter économiquement des minerais pauvres, des essais ont été effectués en vue d'évaluer l'influence de la granulométrie sur la dissolution de l'uranium et d'autres éléments.

On a étudié le traitement d'un échantillon de minerai phosphaté de l'Angola, dont la teneur en uranium était d'environ 0,05% de $U_3O_8$. On a utilisé sans difficulté le procédé classique de lixiviation par l'acide sulfurique et d'extraction par des esters phosphoriques. Cependant, l'économie de la récupération de l'uranium de ces minerais dépend entièrement de la possibilité de valorisation de l'acide phosphorique.

# STATUS REPORT FROM SOUTH AFRICA

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## INTRODUCTION

Most of the research work on the processing of uranium ores in South Africa is being conducted by the Extraction Metallurgy Division of the S.A. Atomic Energy Board. Nevertheless, a considerable amount of applied research has been done by the different mining groups concerned with the operation of uranium plants, and also by the Transvaal and

Orange Free State Chamber of Mines research laboratories. There is, however, very close collaboration between the various research groups and the Atomic Energy Board and the main research described below is conducted on a collaborative basis.

## ORES BEING TREATED

All the ores being treated in South Africa are probably in the category of low-grade ores containing approximately 250 grams $U_3O_8$ per tonne. However, the uranium processing plants have the big advantage of treating a material which has already been mined, crushed and finely ground for gold extraction, since in all cases the ores being treated contain both gold and uranium. In fact, the economics of uranium extraction, and thus the reserves of uranium ore, are intimately related to the economy of gold mining operations. The uranium present is in the form of uraninite (either primary uraninite or secondary uraninite) intimately associated with the gold in the so-called conglomerates.

Because of this association of gold and uranium it has been possible to utilize extraction techniques which would probably be considered too costly if used for ores containing similar concentrations of uranium alone.

## PRESENT PROCESSING TECHNIQUES

In all cases the uranium plants use an acid leaching process (using $H_2SO_4$ and $MnO_2$ as reagents) followed by ion exchange treatment of the leach solutions produced. The ion exchange eluates are treated first with CaO to precipitate iron, after which the uranium is precipitated with ammonia to give a product which after calcination contains approximately 90% $U_3O_8$.

Initially all plants treated the residue from the gold recovery plants. Fairly recently, however, several plants have converted to a 'reversed leach' procedure in which the uranium is extracted first, followed by gold extraction by cyanidation. The essential advantage of this reversed leach is to eliminate the formation of cobalt-cyanide complexes which act as severe resin poisons.

There have been modifications to the standard leach and at one plant a 'ferric leach' process has been adopted. In this modification a portion of the uranium-free leach solution (after ion exchange) is rejected and sulphuric acid and ferric ions are regenerated by the introduction of $SO_2$ and oxygen to this solution.

## RESEARCH WORK IN PROGRESS

### Fundamental work on leaching mechanisms

This work is being conducted by the staff of the National Institute for Metallurgy (the home of the Extraction Metallurgy Division of the Atomic Energy Board) and was first commenced to explain the poor uranium dissolutions obtained on some of the South Africa ores. Originally it was believed that the undissolved uranium remaining after leaching was present in the form of a 'refractory' mineral (such as uranothorianite) but as the investigation progressed, it became quite clear that this explanation was incorrect.

Later work showed that there existed distinct differences in the leachability of primary uraninite as compared with secondary uraninite. The secondary uraninite, although of essentially the same chemical and crystalline form, and generally of a smaller particle size, dissolved in acid-oxidizing solutions at a very much slower rate than the primary uraninite. Invariably, by virtue of the fact that the secondary uraninite had been dissolved and redeposited by geological processes, it occurred in regions of the orebody where there were increased concentrations of impurities such as phosphate, zirconium, etc. It was further shown that the addition of such impurities to the leach solution decreased the rate of dissolution very significantly and it appeared resonably certain that the poor leachability of certain ores was not due to the pressure of refractory minerals, but rather due to the association of the uraninite with impurities such as phosphate, zirconium, etc.

Further work was conducted on a more fundamental basis in an attempt to explain how these impurities affected the rate of dissolution, and this work in turn led to an attempt to postulate the detailed reaction mechanism and the important factors influencing the kinetics of the reaction. This work is by no means completed but several interesting results have been obtained.

Although, of course, an oxidant must be present in the leach solution, the rate of dissolution bears no relationship to the redox potential of the system being used. In fact, tests with different oxidants have indicated that the effectiveness of an oxidant in uraninite leaching is closely related to the rate at which these species react in homogeneous solution which has been shown to be a characteristic of the electronic structure of the ions involved.

It has also been shown that the mechanism of dissolution involves the adsorption of complexes, such as $[Fe(OH)_2]^+$, on the surface of the mineral and can be influenced considerably by a competitive adsorbtion of non-active ions. It is possible that in this way the interference of phosphate can be explained. However, the investigation is not complete and further work is proceeding.

## Combined gold-uranium leaching

Work is also being undertaken on the possibility of dissolving both gold and uranium simultaneously. Such a process would have obvious economic advantages since the two separate stages of filtration and washing would be eliminated. It is hoped that in addition it would be possible to treat material of a much lower uranium content than could be treated by the conventional process.

The essential feature of this work is the use of alkaline leach solutions containing sodium carbonate and bicarbonate, a suitable oxidant and cyanide ions.

From the point of view of gold extraction, the process is exactly analogous to the conventional cyanide process using lime and sodium cyanide, except that the alkali-lime is replaced by sodium carbonate.

The latter reagent, being very much more costly than lime, requires that special attention be devoted to the recovery and recycling of the leach solutions and this aspect is an important part of the research programme.

Sodium carbonate-bicarbonate solutions are also solvents for uraninite if a suitable oxidant is present but, unlike the gold dissolution process, the dissolved oxygen in solution at normal temperatures is not effective as such an oxidant. By conducting a leach at elevated temperatures and high oxygen pressures, uraninite will dissolve, but the capital cost of the equipment necessary and cost of heating the vast tonnages of low-grade solution make the use of high pressures and temperatures uneconomic.

Attention has therefore been focussed on finding a suitable oxidant to permit dissolution of the uraninite at ambient temperatures. Oxidants such as the permanganate ion or hypochlorite ion are too costly and the most promising reagent is a copper cyanide complex. The oxidized cupri-cyanide complex is an effective oxidant for uraninite, and after reaction, the reduced form, a cupro-cyanide complex, can be reoxidized to the original form by dissolved oxygen in the leach solutions. Thus, the complex acts as a catalyst and only relatively small amounts need be used. The possibility also exists of recovering the residual copper from the leach solutions.

This work is still at an early stage. The exact nature of the active copper cyanide complex has not been established, nor have the details of the recovery of sodium carbonate and bicarbonate systems been established. Precipitation of gold or zinc dust appears to be feasible and recovery of the uranyl carbonate complex should present no great problem. The process appears to have a potential advantage in that the reagent consumptions are considerably lower in an alkaline circuit than in an acid circuit.

### Research on solvent extraction process

Most of the research activities in South Africa have been devoted to the development of a solvent extraction process to be used either in addition to or as a replacement for the ion exchange process. A detailed technical paper on the Bufflex process is presented as a separate paper (see section II). In this process the solvent extraction operation is introduced after the ion-exchange process, the main objective being to produce a more highly refined final product. In fact, a product very close to acceptable nuclear grade specifications has been achieved.

The most recent work is directed towards replacing the ion exchange process with a solvent extraction process. The same solvent is used as in the Bufflex process (Alamine 336) and the chemical processes are essentially the same. However, in this case the main emphasis is on the design of large-scale low-cost plants (particularly mixer-settlers for solvent extraction) and reduction of solvent losses. Preliminary tests on a pilot plant scale have indicated that the most important cost factor is the amine losses in the discarded solutions and this appears to be approximately the same as resin replacement costs.

## OTHER MISCELLANEOUS TESTWORK

A very limited amount of work is being conducted on the recovery of uranothorianite from the Phalaborwa Carbonatite deposit, the main emphasis being on ore-dressing techniques. A considerable amount of work is being conducted on refining processes with particular emphasis on developing low-cost processes which can take advantage of the high purity characteristics of the material produced by the Bufflex process. Some work is also being conducted on recovery of other valuable constituents in the ores being processed.

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# INFORME SOBRE LA SITUACION ACTUAL EN ESPAÑA

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## 1. MINERALES

De acuerdo con el programa español de reactores nucleares las necesidades de uranio se estiman entre 1400 y 1600 t hasta 1970 y entre 11 000 y 14 000 t hasta 1980 [1].

En el estado de prospección actual se cuenta [2] con unas reservas de 11 000 t $U_3O_8$ con costes entre 5 y 10 \$/lb $U_3O_8$, 40 000 t con costes de 10 a 15 \$/lb $U_3O_8$ y unas 250 000 t con unos posibles costes entre 15 y 30 \$/lb $U_3O_8$.

Las reservas para explotación próxima (con leyes 0,1-0,2% $U_3O_8$) están formadas por yacimientos en rocas graníticas (40%) y el resto en rocas metamórficas (pizarras), localizadas en el oeste de España. Las reservas a más largo plazo están constituidas por lignitos y formaciones sedimentarias (estratos del mioceno central, sedimentos del este de España y cuarcitas de Sierra Morena).

## 2. TRATAMIENTO DE MINERALES A ESCALA INDUSTRIAL

En España la única fábrica existente de tratamiento de minerales de uranio está situada en Andújar (Jaén). Tiene una capacidad de 200 t/d. Emplea un circuito de lixiviación ácida-cambio de ion-precipitación. Los estudios de los procedimientos los realizó la propia Junta de Energía Nuclear (JEN) que también hizo el proyecto y montaje. Se puso en marcha a finales de 1959, y excepto una reducción en la producción en el año 1963 ha funcionado todo el tiempo a su capacidad de diseño tratando 60-70 000 t/a de mineral con leyes medias de 0,1 al 0,12% $U_3O_8$.

Los minerales tratados han sido fundamentalmente graníticos. Procedieron de pequeñas minas de la región y de labores de investigación en otras zonas. En total se han tratado minerales de más de 20 orígenes distintos. Las leyes y características fueron muy diversas y, en ocasiones, los minerales eran bastante pobres en uranio, 700 ppm, los cuales, en compensación, ofrecían leyes altas en cobre (5-8% Cu).

El funcionamiento de la fábrica se puede considerar normal, con solubilizaciones de uranio en ataque comprendidas entre el 85 y el 95%. Del resto del circuito cabe señalar la operación de cambio de ion que vino afectada por el tipo y ley del mineral y por las condiciones y resultados de ataque; se tuvieron capacidades para las resinas comprendidas entre 120 g $U_3O_8$/l de resina, para líquidos altos en fosfatos, y 30 g $U_3O_8$/l para las soluciones muy impuras de tratamiento de minerales de cobre.

En el tratamiento de minerales de uranio y cobre se ha recuperado éste en un doble circuito de flotación y cementación con un rendimiento global del 85% aproximadamente. Las principales dificultades se encontraron en la flotación del cobre de los estériles de lixiviación y lavado.

Se espera que la fábrica funcione todavía unos tres años, pasados los cuales la mayoría del equipo se trasladará a una nueva planta en una zona del oeste de España. En el terreno y edificaciones actuales la JEN montará otras instalaciones.

Se ha estudiado el tratamiento de minerales de pizarras y actualmente está en vías de realización el proyecto de una planta para 1000 t/d de mineral, que se instalará en la zona de Salamanca.

También existen proyectos para la próxima realización de instalaciones de lixiviación estática y unidades móviles de cambio de ion y extracción con aminas.

## 3. INVESTIGACION

### 3.1. Medios

La investigación sobre el tratamiento de los minerales españoles de uranio se realiza en los propios laboratorios de la JEN en Madrid. Una pequeña fracción (5%), especialmente sobre problemas específicos, se hace mediante contrato con las universidades. Para algunas operaciones en particular, por ejemplo molienda, también se han establecido contactos con los fabricantes de material.

Sobre problemas de interés inmediato marginal y de aplicación práctica remota la JEN concede becas a los licenciados para que trabajen en sus laboratorios y preparen sus tesis doctorales.

Los laboratorios de la JEN están bastante completos y tienen equipo para la realización de ensayos discontinuos de concentración física, hidrometalúrgica y de tostación. La planta piloto, que se montó en 1954, ha sido reformada recientemente a los efectos de reducir su capacidad a 1-2 t/d, y prever la máxima flexibilidad para la realización de circuitos diferentes.

El personal de la JEN que se dedica a trabajos de investigación y desarrollo comprende unos 15 técnicos superiores y 45 auxiliares. Para el desarrollo de los trabajos, aparte la nómina de personal, la JEN viene a asignar de 4 a 5 millones de pesetas por año.

## 3.2. Temas

En concentración física los trabajos se han dirigido fundamentalmente a la eliminación de los elementos consumidores de ácido por flotación con ácidos grasos y depresión del uranio con ácidos orgánicos de bajo peso molecular, así como a la recuperación de subproductos. También se está estudiando la separación de limonitas uraníferas de difícil ataque, a partir de minerales de pizarras. Con varios minerales se ha ensayado el estrío electrónico. Algunos particulares realizan la concentración física de monacitas.

Las experiencias por vía seca se han limitado a ensayos de tostación, fundamentalmente sobre lignitos.

Se está dedicando gran atención a la lixiviación en lecho estático, tanto en lo que se refiere al diagnóstico de las posibles pérdidas como a su posible explotación industrial. Para lo primero se han montado técnicas y dispositivos diversos, incluidos equipos de funcionamiento automático según programas preestablecidos.

Con miras a la explotación industrial se investiga la lixiviación con agua, la adición de piritas y el empleo de bacterias. Este último estudio se realiza en cooperación con el Instituto de Fermentaciones Industriales del Consejo Superior de Investigaciones Científicas, que está aislando las especies que se encuentran en las aguas de las minas españolas y en los efluentes de las eras de lixiviación natural. También se están ensayando algunas cepas de bacterias ferroxidantes y tioxidantes, importadas de Estados Unidos (American Type Culture Collection y Kennecot Copper Co.).

Se han estudiado muchos minerales por ataque con ácido sulfúrico, en lecho estático, según se puede ver en una comunicación técnica presentada a este grupo de trabajo. Creemos que los resultados son alentadores para el beneficio de minas pequeñas o del material marginal que vaya a quedar al pie de la mina o cantera.

El ataque convencional del mineral molido, es la operación que recibe más atención. Las técnicas están normalizadas y se reciben muchas muestras para su estudio. Se utilizan planteos estadísticos que comprenden por lo general cuatro variables: dosis de ácido, temperatura, tiempo y oxidante a dos o tres niveles. Los diseños se simplifican cuando se trata de obtener solamente información complementaria a los trabajos de investigación geológica. En la separación sólido-líquido se considera, fundamentalmente, el espesamineto y el empleo de floculantes.

En el estudio del cambio de ion se siguen las directrices: a) técnica normal de empleo de columnas, como servicio a la fábrica en funcionamiento; b) empleo de esta misma técnica para los líquidos de lixiviación estática, en pequeñas unidades móviles que trabajen a boca mina; c) recuperación del uranio de aguas de mina, pues las hay con pH 2,5-3,0 y unos 20 mg $U_3O_8$/l; d) sistema de columnas con elución sulfúrica, seguido de la extracción del uranio con aminas y ácidos alquilfosfóricos y e) elución nítrica similar a la que se usa en Andújar seguida de eliminación de sulfatos, extracción con TBP y precipitación de uranato amónico; los estudios sobre esta vía se están llevando de forma paralela para resinas y aminas.

En extracción con disolventes la investigación se centra en: a) tratamiento de los líquidos normales de lixiviación, intentando extender el empleo de las aminas a líquidos diluidos; la planta piloto (50 $m^3$/d) anexa a la fábrica de Andújar ha tratado líquidos de hasta 200 mg $U_3O_8$/l; b) aplicación de la extracción con aminas a la recuperación del uranio de circuitos de lixiviación estática a boca mina, mediante pequeñas unidades; c) recuperación de subproductos (cobre y vanadio) por extracción con LIX-64 y aminas o D2EHPA y d) extracción de uranio a partir de líquidos de ataque alcalino utilizando bases de amonio cuaternario (CDMBA, Armil).

Otros métodos de recuperar el uranio de soluciones diluidas ha sido su fijación sobre orujo de aceitunas y turbas. Se han estudiado las capacidades de cambio. Algunos tipos españoles de turbas llegan a cargar de 1 a 1,5 meq/g y se van a ensayar en escala piloto. La recuperación del uranio a partir de estos productos será tema de futura investigación.

### 3.3. Proyectos

A continuación se enumeran algunos de los proyectos específicos sobre lixiviación y extracción en desarrollo e independientes de las investigaciones de tipo general:

a) Estudios de los nuevos yacimientos que se descubren y que se enviarán a la fábrica de Andújar.
b) Ensayos con nuevas muestras de pizarras, complementarias al proyecto de la fábrica de tratamiento de pizarras.
c) Tratamiento de los lignitos radiactivos de la zona de Calaf.
d) Conjunto de dos instalaciones de lixiviación estática a boca mina con una unidad de cambio de ion, con capacidad equivalente a 30 t/d.
e) Instalación de lixiviación estática-extracción para mineral marginal de pizarras que funcionará a título de instalación piloto a boca mina y que supondrá 1500 t/mes.

## 4. COOPERACION

Limitándonos a las actividades más o menos continuadas se pueden señalar:

Los contactos regulares con Francia y Portugal sobre el tema de la lixiviación estática de minerales de uranio.

La presencia frecuente de becarios hispanoamericanos en los laboratorios del Centro Nacional de Energía Nuclear Juan Vigón, en Madrid.

Los estudios de minerales radiactivos privados, de cuyo tratamiento se encarga la JEN o para los cuales sus propietarios están considerando la posibilidad de construcción de una planta.

La preocupación por la formación de personal se manifiesta en el sentido ya indicado de concesión de becas para hacer tesis doctorales, así como en las facilidades que se dan a los estudiantes de ingeniería para la realización de sus prácticas y memorias de fin de carrera. Para el personal auxiliar se organizan frecuentemente cursos de capacitación.

## 5. PROGRAMA

Para resumir, podemos decir que:

1. España está interesada en la valorización de sus reservas radiactivas, para lo cual está realizando una intensa labor de prospección

e investigación geológica y tratando de que los particulares se sumen a la misma.

2. Trata de hallar las técnicas adecuadas para el tratamiento de sus minerales, primero mediante los métodos convencionales y procurando luego mejorarlos.

3. Tiene prevista la continuación de la explotación de su fábrica de Andújar (200 t/d) y el montaje inmediato de pequeñas instalaciones a boca mina que en conjunto podrían suponer 100 t/d de mineral adicional.

4. Para un futuro próximo tiene previsto el montaje de una planta de 1000 t/d de pizarras con ley media del 0,11% $U_3O_8$; en su construcción y funcionamiento trata de interesar al capital privado.

5. Realizará investigaciones de interés general sobre las diversas técnicas indicadas en los párrafos 3.2 y 3.3.

## REFERENCIAS

[1] ANTOÑANZAS, J.L., FUSTEL, E., GUTIERREZ JODRA, L., HERNANDEZ VARELA, J.L., RODRIGUEZ, M.L., MARTIN DELGADO, J., SUAREZ FEITO, J., Contribución española al cuestionario I, Combustibles, II Congreso de Foratom, Frankfurt (1965).

[2] OECD, World Uranium and Thorium Resources, ENEA (Agosto 1965).

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# STATUS REPORT FROM SWEDEN

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## INTRODUCTION

The Ministry of Education was authorized in November 1945 to appoint a commission to study the organization of nuclear energy research. In April 1947 this commission, the Swedish Atomic Energy Commission, proposed the formation of a semi-state-owned company to be a central body for applied research work and development in the nuclear energy field in Sweden.

In November 1947 the Atomic Energy Company (AB Atomenergi) had its statutory meeting. The State owns 4/7 of the share capital and the remaining 3/7 is owned by 71 private and municipal share-holders. Except for a part of the stock capital, all investments and running costs of the company have been financed by the Government. The company is in practice answerable to the Department of Commerce which has an advisory body, the Atomic Energy Board. AB Atomenergi is responsible for Government-financed research on the industrial applications of nuclear energy, the milling of uranium ores and refining of uranium.

The total number of employees is at present about 1400, 800 of which work at the company's research establishment Studsvik about 120 km south of Stockholm.

As early as 1945 the Research Institute of the Swedish National Defence started work in the field of uranium processing. Similar work was also started quite early by the Boliden Mining Company, the Swedish Shale Oil Company and Wargöns AB. After the establishment of AB Atomenergi, all work in the uranium processing field was transferred to this company. In fact one of the main reasons for the formation of AB Atomenergi was the need for Swedish uranium production as there was no possibility of importing uranium at that time.

As a result of research and development in uranium processing a pilot plant at Kvarntorp near Örebro in central Sweden started milling a low-grade uranium ore (shale) in 1953. The capacity of this plant was 5-10 tons of uranium a year. A uranium mill at Ranstad in south-west Sweden, near Skövde, with a capacity of 120 tons of uranium a year started production on a reduced scale in the middle of 1965.

## LEGAL ASPECTS OF URANIUM MINING IN SWEDEN

A special atomic energy law (Atomic Energy Act) came into force in 1956 and a special law regarding uranium mining was passed in 1960.

In Sweden anyone is allowed to prospect for uranium (and thorium) anywhere provided that this does not infringe upon the rights of the landowner. If anyone wishes to make a closer examination, he can come to an agreement with the landowner. If such an agreement cannot be reached, the prospector can apply for a special permit from a government authority. If several persons apply for a permit for the same area, the authority has to pay special attention to the claims of that person who discovered the deposit. The special investigation permit is issued for a maximum of three years at a time.

The right to mine uranium-bearing minerals is subject to the issue of a special concession by the Government. Before granting such a concession, the authorities have to decide whether or not state interests are served by the issue of such a concession. If several persons seek a concession for the same area, the Government will decide which person is best suited to receive a concession. A concession may not be transferred to another person without the permission of the Government. Once granted, a concession can be recalled by the Government if the owner of the concession fails to comply with the conditions under which the concession was issued or if there are other very strong reasons. Otherwise, once granted, a concession is permanent. The holder of the concession must pay compensation to the owner of the property.

## GEOLOGICAL CONDITIONS

The Swedish bedrock mainly consists of gneisses and granites from the Precambrian. The deposits formed during the Cambrian, the Ordovician, and the Silurian have mostly been eroded except for some places where they have been protected through displacement or by an impervious blanket of diabase (dolerite). The Cambro-Silurian deposits have layers of sandstone above the Precambrian bedrock, followed by layers of shales, limestone and clay slate. Sedimentary rocks from periods after the Silurian are only to be found in Skåne (Scania). The mountain-range in the West is a Caledonian mountain system raised in late Silurian to early Devonian times and is composed of metamorphic rocks including igneous rocks as well as sedimentary (mainly Cambro-Silurian) rocks. At the border of the mountain-range there are Cambro-Silurian deposits which are not metamorphosed.

## URANIUM PROSPECTING

The search for uranium for nuclear energy purposes was started in 1945 by the Atomic Energy Committee. AB Atomenergi has provided capital for uranium exploration since the start of the company and in 1954 a prospecting division was formed within the company. Uranium prospecting reached its maximum during the years 1955–1958 due to increased interest by the Swedish Government. In addition to AB Atomenergi, a lot of other companies and 'weekend' prospectors took part in uranium prospecting. Since 1960 almost all uranium prospecting has been carried out by AB Atomenergi.

The introductory part of a prospecting campaign consists of radiological surveys on a regional basis by the aid of airborne and car-borne instruments. Anomalies discovered are subsequently investigated on the ground with Geiger or scintillation instruments. Those anomalies considered promising enough for further investigation are studied by magnetic and electric methods and by diamond core drilling, etc.

The results of the uranium prospecting programme are briefly as follows [1-3]. No high-grade ore deposits worth mining have been found but there are very large low-grade uranium deposits.

## DESCRIPTION OF SWEDEN'S LOW-GRADE URANIUM DEPOSITS

The most important and well-known uranium deposits are those in the alum shales. Uranium content reaching 100 g/t ore more is found in the strata beginning with the Olenus in the upper Cambrian and ending with the Dictyonema and the Ceratopyge in the region between Cambrian and Ordovician.

The Olenus shale is regionally distributed into nearly all Cambro-Silurian districts in Sweden, i.e. in the provinces of Scania, Öland, Västergötland, Närke and Norrland. Two districts are, however, of special interest, namely the Billingen-Falbygden district in Västergötland and the province of Närke, where uranium contents between 200 and 400 g/t are found. The stratum richest in uranium is the Peltura Scarabaeoides zone, which also contains a coal-like substance (kolm) in the form of lenses. Kolm has a uranium content of about 3000 g/t and its contribution to the total uranium content in the richest part of the Peltura Scarabaeoides zone is between 5 and 10%.

The occurrence of uranium in alum shales has been known for more than 60 years. At the start of the atomic energy programme in Sweden it was believed that the richest uranium deposit was at Kvarntorp in Närke. Later extensive drilling programmes made by the Geological Survey of Sweden on behalf of AB Atomenergi showed that the Billingen-Falbygden district had much larger and richer deposits of uranium than Närke. The uranium resources in the two districts are summarized in Table I [4].

The alum shales are fine-grained (1-10 $\mu$m), bituminous black shales with a density of about 2.1 to 2.3 t/m$^3$. Their composition is a mixture of bituminous substance (kerogen) together with quartz, illite, feldspar, kaolinite, pyrite and calcite. The uranium is present in a very dispersed condition and has not yet been traced to any given mineral.

TABLE I. URANIUM RESOURCES

| Area | Ore ($10^6$ t) | Uranium (%) | Uranium ($10^6$ t) |
|---|---|---|---|
| Västergötland | 3000 | 0.03 | 0.9 |
| Närke | 700 | >0.02 | 0.15 |

A zone rich in phosphorite and uranium was found at Tåsjö at the border of the mountain range by the prospecting division of AB Atomenergi in 1958. The zone is situated in lower Ordovician. The shale of this zone has quite a different character from the alum shales described above. The uranium-rich zone some metres thick has a uranium content between 200 and 1000 g/t. The Tåsjö deposit, however, has only been investigated to a very limited extent.

## EXTRACTION OF URANIUM FROM ALUM SHALE

When AB Atomenergi was founded in 1947 there was no possibility of importing uranium and the only known deposits were the shales in Närke and Västergötland. As mentioned above, we still do not have any richer uranium deposits. Most of our work on uranium processing has thus of necessity been made with alum shale as source material, and only this work will be described in this paper.

During the first years we were doubtful whether it would be technically possible to extract uranium from such a poor ore as shale. Therefore, our work at first was concentrated upon the treatment of kolm. The following exposition will deal with both kolm and shale.

### Mining

At Kvarntorp the shale was quarried by opencast mining. At Ranstad the same method will be used for the first period of about 15-30 years but later on underground mining will be employed [5].

## Physical concentration

There have been two reasons for physical beneficiation:

(1) To separate kolm from shale
(2) To separate shale from limestone

In 1946 trials were made in laboratory to separate kolm and shale by use of a sink and float method. A pilot plant using a magnetite slurry with a density of 1.9 t/m$^3$ was set up at Kvarntorp in January 1949 and was operated until January 1954.

The same process, i.e. heavy-media-separation (HMS) with the aid of a magnetite slurry, was tried when the need arose of separating shale from limestone. The process worked well in spite of the fact that the density of the magnetite slurry had to be kept as high as 2.3 t/m$^3$. The high purity of Swedish magnetite made this possible.

The HMS process was put into operation in 1953 at the pilot uranium extraction plant at Kvarntorp [6]. The same process is also used at the newly started uranium mill at Ranstad [7]. The HMS process works well for shale plus 6 mm. For shale minus 6 mm it is possible to use hydrocyclones for the separation from limestone.. At present this process is not used for economic reasons.

## Roasting before leaching

To facilitate the leaching process roasting has been tried. The first trials were made in 1946. Pure oxidating roasting was tried as well as sulphatizing [8] or chloridizing roasting. The pure oxidating roasting process has turned out to be the most promising. Laboratory and pilot-plant work has shown the possibility of getting a 10-15% higher yield of uranium when leaching roasted shale than when using the percolation leach process described below. The roasting must be carried out at low temperatures (600-700°C, preferably 600) under careful control which is possible with the use of fluidized-bed ovens (however, this has at present only been demonstrated for small-scale work). After roasting, the particles of about 6 mm size easily break down to a very fine-grained mass when stirred with water, i.e. they disintegrate to give the original small mineral grains (50%, 5 $\mu$m). Roasting is thus a substitute for a fine grinding step. Furthermore, the roasting process also produces heat for steam and electric power, and sulphur dioxide which is converted to sulphuric acid. The roasted and leached residue (which is a sort of clay) is very suitable for the production of light-weight aggregate, tiles, pozzolana etc.

## Weathering storage

It has been found very beneficial at Ranstad to give the shale an intermediate storage outdoors [7]. Because of this storage (maturing) a higher yield of uranium is achieved in the leaching step. The difference in yield between unstored shale and shale stored for some weeks is more than 10%. The maturing effect is quite small for shale from Närke and was not used at Kvarntorp.

## Leaching

In the first years a variety of methods were tried in leaching uranium from shale (and kolm). Both alkaline and acid leaching was tried and agitation leach as well as percolation leach. Depending on the problems encountered in the separation of pregnant liquor from the solid residue and in the disposal of this residue, the percolation leach technique on a basis of unroasted shale was soon preferred for future development work. This is also the method used today at the new uranium mill at Ranstad (which can treat around 850 000 tons of ore per year).

TABLE II. ANALYSIS OF SHALE, LEACH RESIDUE AND LEACH LIQUOR

| | Shale (%) | Leach residue (%) | Leach liquor (g/l) |
|---|---|---|---|
| $SiO_2$ | 44.9 | 45.5 | 0.8 |
| $Al_2O_3$ | 12.3 | 12.0 | 18.0 |
| $Fe_2O_3$ | 8.7 | 7.1 | 14.0 |
| CaO | 1.5 | 1.2 | 1.1 |
| MgO | 0.8 | 0.7 | 4.8 |
| $Na_2O$ | 0.3 | 0.3 | 0.8 |
| $K_2O$ | 4.8 | 4.7 | 5.2 |
| S | 6.9 | 6.4 | - |
| $SO_4$ | - | - | 100 |
| P | 0.08 | 0.01 | 1.7 |
| As | 0.008 | 0.007 | 0.12 |
| U | 0.03 | 0.008 | 0.6 |
| $C_{org}$ | 15.5 | 15.5 | - |

The preferred leaching medium for the first years was a circulating solution of ferric chloride. However, the final choice for the pilot plant at Kvarntorp was a non-circulating solution of sulphuric acid. The same medium is also used at the Ranstad plant.

Among other leaching methods tested are pressure leaching [9] and the use of circulating sulphuric acid leach liquor through auto-oxidation of sulphur dioxide in this liquor. The final percolation leach process with sulphuric acid solution as leaching medium is described in the technical paper delivered to this Panel [7].

## Recovery of uranium from leach liquor

The leach liquor from the leaching of shale is rather impure as is seen in Table II. At first precipitation by adding hydroxide followed by digestion with sodium or ammonium carbonate solution was tried. However, in 1950 the uranous phosphate precipitation process was developed [6, 10]. The process was used both for ferric chloride and sulphuric acid leach liquors. The method was used at Kvarntorp between 1953 and 1957.

The search for better methods led to a process for selective adsorption of uranium as a negative uranyl sulphate complex [11] from sulphate leach liquors by the aid of strong anion exchangers [12]. This method was developed in Sweden as early as 1952 and a pilot plant was erected at Kvarntorp in 1954 [6]. A commercial ion exchange equipment was installed at Kvarntorp at the end of 1957.

At Kvarntorp an acidified ammonium nitrate solution was used for the elution of uranium. In the planning of the Ranstad mill it became obvious that this elution agent could not be used because of water pollution problems. As described [7] several possibilities were considered for the concentration step, among these extraction with alkylamines and dialkyl-phosphoric acid. The final choice was a combination of ion exchange and extraction with dialkyl-phosphoric acid (the Eluex process). Today we are trying to develop this method into a process which will give uranium oxide of nuclear grade without further purification.

## Recovery of uranium from eluate solutions

At Kvarntorp precipitation of uranium from the eluate was made in two steps. By adjusting the pH value to about 3.5 with limestone most of the impurities were separated from the uranium. In the filtrate from this step uranium was precipitated by aid of ammonia and after filtration and washing dried and sent to the refinery.

At Ranstad a continuous precipitation process is used after the extraction process. Uranium is precipitated from the re-extraction solution (sodium carbonate) with sodium hydroxide at elevated temperature. By careful control of pH and agitation an easily settling precipitate is obtained. The precipitate is washed in a thickener and dried without filtration in a dryer that treats the precipitate in a very mild way in order to conserve the particle size of the precipitate, thereby giving the dried concentrate in the form of a free-flowing powder.

## Waste treatment

Two types of waste are obtained from the processing of uranium shale; the leaching residue and the barren solution from the ion exchange step. The waste treatment procedures were developed very early and are described in more detail in the technical paper to this Panel [7].

The leaching residue is transported to a low level area and then the neutralized sludge from the treatment of the barren leach solution with limestone is pumped upon the leaching residue. The waste water from the waste disposal area is collected and further treated before being pumped to recipients.

## THE ECONOMY OF SWEDISH URANIUM PROCESSING

Up to 1955 the yearly cost for prospecting and research and development work on uranium processing (including refining processes) was about 1 million kr ($ 200 000). Between 1955 and 1965 the average yearly cost for the same purposes has been about 2 million kr ($ 400 000).

The Kvarntorp plant required an investment of 10 million kr ($ 2 million). The total operating cost (including investment) between the start in 1953 and the closing of the plant in 1963 was 30 million kr ($ 6 million). During this period a total of 62 tons of uranium were produced (part of which was produced from imported material).

The results of uranium production at Ranstad are given in the technical paper to this Panel [7]. According to this account, on the basis of one year of operation (testing period) the yearly cost per kilogram uranium in 1966-1967 at full capacity (120 t U/yr) will be 136-148 kr ($ 10-11 per lb $U_3O_8$), not including amortization charges.

Combining the present Ranstad plant with a by-product plant based on roasting of the leach residue [7] would lower the production cost per kilogram uranium considerably but still give a cost above the present world market price.

At a future very large exploitation of the Billingen shale the total production cost (including amortization) probably will be between 160 and 190 kr/kg U ($ 12-14 per lb $U_3O_8$).

## REFERENCES

[1] SVENKE, E., "The occurrence of uranium and thorium in Sweden", Proc. UN Int. Conf. PUAE 6 (1956) 198.

[2] MÅRTENSSON, C., WELIN, E., "Uranium mineralisation in iron ores of Central Sweden", Proc. 2nd UN Int. Conf. PUAE 2 (1958) 560.

[3] WELIN, E., Uranium mineralizations and age relationships in the precambrian bedrock of central and southeastern Sweden. Geol. Fören. Stockholm förh. 88 (1966) 34-67.

[4] World Uranium and Thorium Resources, OECD-ENEA survey, Paris (Aug. 1965).

[5] JANELID, I., OLSSON, G., The Janol method – a new mining concept, Engng Min. J. 160 7 (1959).

[6] SVENKE, E., "Recovery of uranium from uranium bearing alum sahle", Proc. UN Int. Conf. PUAE 8 (1956) 90.

[7] PETERSON, A., "Ranstad - a new uranium-processing plant", these Proceedings.

[8] SVENKE, E., GELIN, R., WELIN, E., "Preparation of uranium and thorium compounds from their ores", Chemical Processing of Reactor Fuels, Academic Press, New York (1961) 21-22.

[9] PETERSON, A., GELIN, R., "Some tests on pressure leaching of Swedish alum shale", Compte-rendu du colloque sur les traitements des Minerais d'Uranium Saclay (1956) 107-12.

[10] STRANDELL, E., An investigation of conditions for precipitation of uranium (IV) orthophosphate, Acta Chem. Scand. 11 (1957) 105.

[11] PETERSON, A., Studies on the hydrolysis of metal ions – The uranyl ion $UO_2^{2+}$, in $Na_2SO_4$ medium, Acta Chem. Scand. 15 (1961) 117.

[12] ARNFELT, A.-L., A rapid method for the determination of uranium, Acta Chem. Scand. 9 (1955) 1484.

# ДОКЛАД О СОСТОЯНИИ ВОПРОСА В СССР

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ГОСУДАРСТВЕННЫЙ КОМИТЕТ ПО ИСПОЛЬЗОВАНИЮ
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## ВВЕДЕНИЕ

Урановая промышленность по переработке бедных урановых руд в СССР была создана в последние годы. В результате работ научно-исследовательских институтов и предприятий в развитии указанной отрасли промышленности был обеспечен быстрый технический прогресс, который позволил резко повысить производительность, сократить расход реагентов, упростить технологические схемы и снизить себестоимость продукции.

В настоящее время базой для урановой промышленности в том числе и бедных урановых руд в СССР являются месторождения с различным содержанием ценных компонентов (урана, фосфора, молибдена, редкоземельных элементов, тория, железа и др.).

## I. ОБОГАЩЕНИЕ БЕДНЫХ УРАНОВЫХ РУД

Впредь под ними мы будем понимать только бедные руды. Урановые руды отличаются исключительным разнообразием вещественного состава. В большинстве случаев уран в рудах представлен не одним, а несколькими минеральными образованиями с различными физико-химическими свойствами. Среди них имеются в различных соотношениях как собственно урановые минералы, так и многообразные минералы – носители урана.

В связи с этим в процессе обогащения урановых руд решаются две главные задачи: удаление из добытой горной массы основного количества пустых проб, что позволяет вовлекать в эксплуатацию все более бедные руды; разделение остального материала на такие продукты, которые по своему минеральному составу наиболее благоприятны для последующих операций общей технологической схемы, что дает возможность снизить себестоимость гидрометаллургических операций и облегчить комплексное использование сырья.

### Методы обогащения урановых руд

Вещественный состав урановых руд предопределяет необходимость гибкого использования различных методов обогащения и тщательного согласования операций обогащения и гидрометаллургии.

Радиометрическая сепарация. При большом разнообразии физико-химических свойств урансодержащих минералов все они обладают одним общим свойством – радиоактивностью.

Сущность процесса радиометрического обогащения, основанного на измерении интенсивности радиоактивных излучений, заключается в автоматизированном разделении рудной массы на продукты с кондиционным и отвальным содержанием урана.

Имеются три разновидности процесса радиометрической сепарации: порционный, поточный и кусковой.

Начальные стадии радиометрического обогащения рационально согласовываются с технологией горных работ.

Вся добытая горная масса в процессе ее транспортировки в вагонетках или других стандартных емкостях проходит (под землей, или на поверхности) через радиометрические контрольные станции (РКС).

С помошью РКС осуществляется учет добытого металла, удаление основной массы пустой породы в отвал и разделение руды по содержанию урана на сорта, если это необходимо.

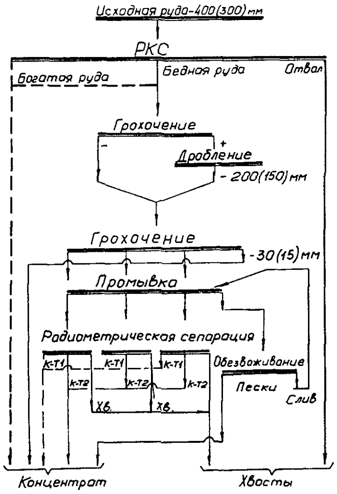

Рис. 1. Типовая схема радиометрической обогатительной фабрики.

За счет массовости измерений и высокой чувствительности приборов радиометрические контрольные станции обеспечивают приемлемую точность определений при большой производительности.

При достаточно высокой контрастности руды промежуточные сорта ее, выделенные на РКС, представляют собой лишь грубый концентрат, в котором имеются значительные количества пустой породы. Они направляются на вторую стадию радиометрического обогащения обычно в кусковом (иногда в поточном) режиме.

Вторая стадия обогащения включает необходимые подготовительные операции: дробление до крупности − 200 (− 150) мм, грохочение на 3 − 4 класса, промывку тех классов, которые подвергаются радиометрической сепарации, и обезвоживание. Класс крупностью − 30 (− 15) мм, как правило, радиометрическому обогащению не подвергается.

На второй стадии радиометрического обогащения наибольшее распространение получил универсальный ленточный многоканальный сепаратор. Узел измерения сепаратора состоит из унифицированного блок-экрана, в который устанавливаются детекторы излучения. Блок-экран одновременно служит головным барабаном ленточного конвейера.

Конструкция блок-экрана позволяет максимально приблизить датчик радиометра к рудным кускам, выбрать угол наклона датчиков и установить требуемое число параллельно работающих каналов (от 2 до 6).

Разделяющие шиберы имеют электромагнитный привод. Конструкция шиберов блочная и позволяет регулировать их положение относительно траектории движения кусков. Имеется защитный экран, позволяющий уменьшить и интенсивность фонового излучения.

Производительность ленточных сепараторов, в зависимости от крупности перерабатываемого класса и числа используемых каналов, составляет от 6 до 40 – 50 т/час.

На рис.1. показана принципиальная схема радиометрического обогащения. Технологические показатели радиометрической сепарации могут колебаться в широких пределах, в зависимости от природных качеств руды (контрастность, гранулометрический состав и др.), совершенства применяемой аппаратуры и правильности технологических приемов. Выход отвальных хвостов достигает 70 – 80% от веса сортируемых классов.

В зависимости от вещественного состава руд и других факторов, радиометрическое обогащение можно применять как единственный обогатительный процесс или в сочетании с другими способами обогащения.

Гравитационное обогащение. Для руд жильного типа с преимущественно настурановой минерализацией радиометрическая сепарация хорошо комбинируется с гравитационными методами обогащения – отсадкой, концентрацией на столах и обогащением в тяжелых суспензиях.

Особенно эффективным (при благоприятном вещественном составе руды) является суспензионное гидроциклонирование, применяемое к материалам крупностью от 15 (20) до 1 – 2 мм.

Флотация. Как способ извлечения урановых минералов флотация не оправдала ранее возлагавшихся на нее надежд. Сложность схем, как правило, не оправдывалась экономическими показателями. Однако флотация применяется для выделения имеющихся в руде (радиометрических или гравитационных концентратах) сульфидных минералов и разделения руды или концентратов на карбонатный или силикатный продукты.

Целесообразность флотационного выделения сульфидов связана или с необходимостью комплексного использования сырья (извлечение кобальта, никеля, молибдена и др.) или с рациональной подготовкой материала к содовому выщелачиванию и последующей сорбции урана. В последнем случае измельчение и флотацию можно вести с использованием оборотных карбонатных растворов. При этом снижается расход реагентов, достигается более полное извлечение сульфидов и уменьшается содержание политионатов и сульфатов в пульпе, поступающей на сорбцию.

При кислотной гидрометаллургической схеме, применяемой при переработке сырья, содержащего карбонатные минералы, возникают непроизводительные расходы химикатов, поэтому выделение карбонатов в отдельный продукт для содового выщелачивания или для нейтрализации кислых пульп может быть целесообразным.

## II. ГИДРОМЕТАЛЛУРГИЧЕСКАЯ ПЕРЕРАБОТКА РУД

### 1. Выщелачивание урана из руд

Кислотное выщелачивание. При выщелачивании урана из силикатных и алюмосиликатных руд с невысоким содержанием карбонатов основным является метод избирательного выщелачивания раствором серной кислоты с окислителями (пиролюзит, хлораты натрия и калия). Этот метод характеризуется низкой кислотностью (pH = 0,3 ÷ 2,0), низкой температурой (20 – 60 °С), но сравнительно большой продолжительностью (12 – 24 час). Для него требуется более тонкое измельчение руды. Благодаря этому снижается расход кислоты и окислителя и получаются растворы с меньшим содержанием примесей, что значительно улучшает все последующие процессы (сорбцию и экстракцию).

Теоретические исследования показали, что при сернокислотном выщелачивании большую роль в окислении четырехвалентного урана играют ионы трехвалентного железа. Систематические исследования поведения урановых минералов и сопутствующих минералов пустой породы при сернокислотном выщелачивании урановых руд с добавкой различных окислителей позволили определить характер действия окислителей. Были выявлены преимущества природного пиролюзита как наиболее дешевого и эффективного окислителя, обеспечивающего высокое извлечение урана.

Дозировка кислоты и окислителя при избирательном выщелачивании полностью автоматизирована (по значениям величин pH и окислительно-восстановительного потенциала).

Использование при выщелачивании серной кислоты и природного пиролюзита позволило ликвидировать проблему очистки выхлопных газов, облегчило очистку и обезвреживание сточных вод и обеспечило возможность полной механизации и автоматизации процесса выщелачивания. Существенное значение в снижении расходов на выщелачивание имела также замена чанов с механическим перемешиванием пульпы на чаны типа пачука большого объема (до 300 – 500м$^3$) с пневматическим перемешиванием (сокращение расхода электроэнергии и затрат на ремонт и обслуживание). Дальнейшим развитием метода избирательного выщелачивания явилась разработка метода сорбционного выщелачивания, при котором избирательное выщелачивание и сорбционное извлечение урана из пульпы анионообменной смолой совмещены в одном процессе. Это обеспечивает снижение расхода реагентов, сокращение и упрощение всей технологической схемы извлечения урана из руды.

Перспективен и метод кислотного автоклавного выщелачивания урановых руд. Применение автоклавов позволяет интенсифицировать процесс выщелачивания, комплексно и с минимальными затратами на реагенты перерабытывать сульфидсодержащие руды. При этом достигается высокий процент извлечения урана и ряда сопутствующих ценных компонентов и снижается переход в раствор примесей.

Другим направлением использования автоклавов является высокотемпературный гидролиз, который можно применить для очистки растворов и регенерации реагентов.

Представляет интерес возможность совмещения в одном аппарате процессов выщелачивания и бесшарового измельчения (измельчение в кислой среде). При этом растворяется до 50 – 80% урана и одновременно интенсифицируется сам процесс измельчения (скорость увеличивается в 1,5 – 2 раза), так как разрушение частиц руды происходит также и химическим путем.

Дешевым и простым является метод бактериального выщелачивания урановых руд, при котором растворение урановых минералов происходит за счет серной кислоты и сульфата окиси железа, образующихся при бактериальном окислении пирита. В случае пиритсодержащих руд выщелачивание можно производить без химических реагентов; для алюмосиликатных руд с низким содержанием серы требуется добавка небольшого количества пирита.

Наряду с ураном при бактериальном выщелачивании в значительной степени извлекаются и другие ценные компоненты, такие, как молибден и торий. Метод кучного бактериального выщелачивания перспективен для извлечения урана из забалансовых руд попутной добычи, хвостов радиометрической сортировки, а также для руд некоторых месторождений с ограниченными запасами урана, но благоприятными условиями добычи. Бактериальное выщелачивание находит применение и в подземных условиях.

Существенным этапом в деле совершенствования технологии переработки урановых руд, а также увеличения полноты использования имеющихся в недрах запасов урана явилась разработка методов подземного выщелачивания. Разработаны и нашли практическое применение методы подземного выщелачивания для извлечения урана из руд месторождений с твердыми скальными породами и из руд осадочных месторождений.

В первом случае выщелачивание производится в подземных блоках, в которых магазинируется руда, предварительно раздробленная взрывами. Блоки орошаются раствором серной кислоты. Во втором случае раствор серной кислоты подается с поверхности в пласт через одни скважины, а урансодержащий раствор выводится из пласта через другие скважины, оборудованные аэролифтными насосами.

Карбонатное выщелачивание. Основным вопросом содового выщелачивания является окисление четырехвалентного урана в карбонатном растворе. Наиболее дешевый окислитель – кислород воздуха. Работа по усовершенствованию процессов карбонатного выщелачивания проводилась в направлении улучшения условий окисления в открытых аппаратах путем тонкого диспергирования воздуха и подбором катализаторов и применения автоклавов.

Определены оптимальные условия использования таких катализаторов окисления, как медно-аммиачный комплекс, феррацианиды, соединения двух- и четырехвалентного марганца, халькопирит и др.

Наибольшая интенсификация процессов карбонатного выщелачивания достигается при использовании в качестве окислителей кислорода или воздуха под давлением. Повышение температуры до 120 – 130°С позволяет достичь высокого извлечения урана даже из весьма упорных руд.

Для проведения автоклавного карбонатного выщелачивания разработаны конструкции многокамерных горизонтальных автоклавов объемом 30 и 120 $м^3$ (рис.2) и однокамерных вертикальных автоклавов объемом до 50 $м^3$.

При карбонатном выщелачивании весьма эффективно решается вопрос о попутном извлечении такого ценного компонента, как молибден, часто встречающегося в урановых рудах.

## 2. Сорбционное извлечение урана и сопутствующих элементов

В начале развития урановой промышленности проблема извлечения урана из кислых и карбонатных пульп после выщелачивания решалась на базе фильтрационных схем (кислотно-содовых и содово-кислотных), требующих высоких затрат труда, реагентов и материалов.

Открытие в конце сороковых годов явления комплексообразования уранил-иона с карбоксильными группами некоторых слабокислых катионообменников дало возможность уже в начале пятидесятых годов организовать производство и применение МБ механически прочных, дешевых и селективных катионитов для сорбционного извлечения урана из пульпы.

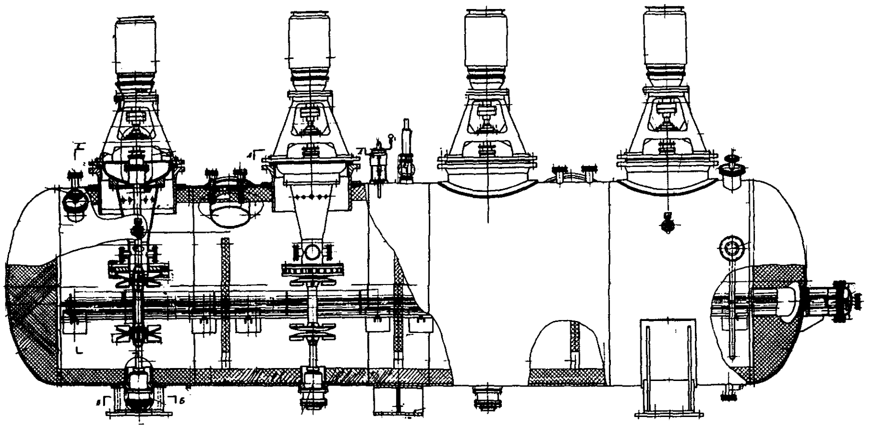

Рис. 2. Автоклав для выщелачивания бедных урановых руд.

Некоторые недостатки карбоксильных катионитов (сравнительно замедленная кинетика сорбции и необходимость проведения процесса при относительно низких концентрациях иона водорода) на данном этапе развития сорбционных процессов вполне окупались высокой их механической прочностью и низкой стоимостью.

Высокий экономический эффект от внедрения процессов сорбции из пульп в значительной мере был связан с разработкой максимально простых и эффективных методов их аппаратурного оформления. Если первое время использовалось разнообразное оборудование (чаны с механическим перемешиванием, колонны со взвешенным слоем ионита) и полунепрерывные методы работы, то с конца пятидесятых годов всеобщее распространение получил непрерывный метод сорбции в аппаратах специальной конструкции с пневматическим перемешиванием.

Указанный метод отличается высокой универсальностью, пригоден для переработки пульп с содержанием твердого до 50 – 60% в том числе 3 – 5% частиц крупностью +0,15 мм. В настоящее время созданы и эксплуатируются аппараты объемом от десятков до сотен кубических метров, что позволяет свести к минимуму количество технологических ниток (рис.3).

Разработанная система аппаратурного оформления не имеет движущихся частей и конструкций, легко автоматизируется простейшими средствами и отличается хорошей устойчивостью в работе. Специальная самотечная транспортировка ионита обеспечивает сравнительно низкие потери его за счет механического износа, а возможность работы на пульпах высокой плотности позволяет достичь высокой удельной производительности.

Следующий этап развития методов сорбции из пульп был связан с разработкой синтеза и организацией промышленного производства высокопрочных анионообменников различной основности и назначения.

В отличие от карбоксильных катионитов аниониты более чувствительны к содержанию в пульпе таких примесей, как нитраты, хлориды, политионаты и т.д. Однако высокая кинетика сорбции (сильноосновных анионитов) и возможность использования анионитов для извлечения урана как из кислых, так и из карбонатных сред в ряде случаев обусловливают их более предпочтительное применение.

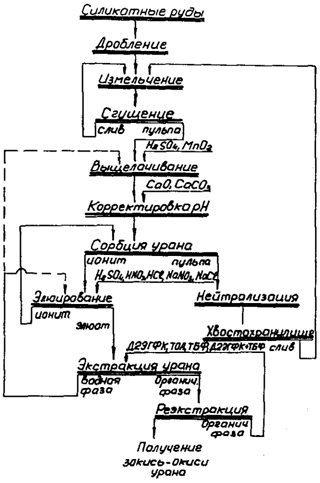

Рис. 3. Типичная схема переработки силикатной бедной урановой руды.

Преимущества анионитов особенно проявляются при переработке глинистых и каустобиолитовых руд, т.е. руд со значительной сорбционной способностью.

Исследования карбонатного и кислотного выщелачивания урана из различных руд показали, что скорость этого процесса, а также извлечение и расход реагентов зависят от скорости диффузии продуктов растворения урановых минералов в объем растворения и от ряда вторичных факторов (обратного соосаждения и осаждения, окклюзии и сорбции рудным остатком). Введение ионита в пульпу непосредственно при выщелачивании обеспечивает не только снятие диффузионных ограничений скорости процесса, но и сводит к минимуму отрицательное влияние вторичных факторов. Это позволяет осуществлять процесс выщелачивания при меньших концентрациях растворителя, иметь более высокую сорбционную емкость и интенсифицировать процесс за счет совмещения операций сорбции и выщелачивания.

Одновременно с дальнейшим усовершенствованием процессов сорбции урана из пульп большое внимание уделялось сорбционным схемам попутного извлечения ценных компонентов, встречающихся в урановых рудах.

## III. ЭКСТРАКЦИОННОЕ ИЗВЛЕЧЕНИЕ УРАНА

Экстракционная переработка технологических растворов применяется почти на всех сырьевых урановых заводах. Все более широкое применение экстракция получает также в гидрометаллургической переработке руд цветных и редких металлов.

В урановой технологии большое распространение имеют схемы, сочетающие сорбционное извлечение и концентрирование металла из рудных пульп с последующей экстракционной перечисткой десорбционных растворов для получения готовой продукции.

Из поставляемых промышленностью Советского Союза экстрагентов наибольшее распространение имеют: трибутилфосфат (ТБФ), используемый главным образом на аффинажных операциях, кислые алкилфосфаты (ди-(2-этилгексил) фосфорная кислота), алкилфосфонаты (диизоамиловый и октиловый эфиры метилфосфоновой кислоты) и алкиламины. Последние широко используются при перечистке сернокислых десорбционных регенератов, получаемых по схеме, совмещающей сорбцию и экстракцию.

В области аппаратурного оформления экстракционных схем продолжаются работы по созданию высокопроизводительных экстракторов применительно к специфике отдельных технологических процессов. Одним из этих аппаратов является усовершенствованный смеситель-отстойник ящичного типа с гидравлическими затворами в каждой камере, обеспечивающими независимость работы ступеней и возможность проведения процесса в широком диапазоне соотношения фаз.

Смесительно-отстойные экстракторы используются почти на всех сырьевых урановых заводах, работающих по экстракционным схемам для бедных руд. Для переработки больших объемов технологических растворов целесообразно использовать смесительноотстойные экстракторы цилиндрического типа с интенсифицированным разделением фаз.

Экстракция осуществляется в каскаде одноступенчатых аппаратов, устанавливаемых на одной отметке, без специальных промежуточных перекачивающих устройств.

Дальнейшим усовершенствованием экстракционных аппаратов является разработка экстракторов центробежного типа. Особое внимание при конструировании таких аппаратов обращается на возможность обработки систем, содержащих некоторое количество твердых взвесей.

Весьма эффективным представляется использование в экстракционных схемах центробежных сепараторов (тарельчатого типа) как для очистки двухфазных систем, так и для разделения трехфазных систем.

Одним из перспективных направлений дальнейшего развития экстракционной технологии является разработка методов неводного экстракционного выщелачивания и извлечения урана из рудных пульп различной плотности. Основное затруднение при промышленном использовании этих методов связано с большими безвозвратными потерями экстрагентов с твердой частью пульпы. Эти затруднения могут быть в значительной мере преодолены за счет использования относительно недорогих и легко регенерируемых экстрагентов, а также применения специальных конструкций экстракторов. Представляет также интерес осуществление процесса экстракции из пульп в аппаратах с пленочным режимом массообмена. К таким аппаратам относятся известные пленочно-дисковые контакторы.

Экстракционные схемы и их аппаратурное оформление характеризуются большой компактностью и обеспечивают возможность полной автоматизации процессов с сокращением до минимума обслуживающего персонала.

## IV. КОНТРОЛЬ И УПРАВЛЕНИЕ ТЕХНОЛОГИЧЕСКИМИ ПРОЦЕССАМИ

Особенностями переработки урановых руд являются большие масштабы производства и комплексное использование сырья. Эти факторы выдвигают серьезные задачи перед системами автоматического контроля и регулирования основных параметров технологических процессов. Одновременно возникает задача оптимального управления как отдельными технологическими процессами, так и всем производством с целью уменьшения потерь реагентов, энергии и др.

Автоматические системы контроля и регулирования отдельных технологических процессов базируются на контроле технологических параметров: концентрации урана, кислоты, окислителя, расхода пульпы, температуры среды и т.д. Системы регулирования строятся по принципу стабилизации этих параметров.

Для контроля содержания урана в рудах и технологических продуктах гидрометаллургического производства применяются следующие методы: гамма-абсорбционный, дифференциальный гамма-спектральный, гамма-рентгеноспектральный и рентгеноспектральный.

Из этих методов второй и четвертый обладают высокой селективностью по отношению к соседним с ураном тяжелым элементам. Кроме того, для контроля урана в растворе применяются спектрофотометрические методы:

а) по собственному поглощению света;

б) с предварительной химической подготовкой раствора;

в) с предварительной химической подготовкой раствора и экстракцией.

Контроль концентраций свободной кислоты в процессе разложения сырья производится измерением электропроводности технологических растворов.

Автоматическое регулирование кислотности пульп исключает грубые нарушения кислотного режима разложения, увеличивает процент извлечения ценных компонентов, сокращает расход реагентов и уменьшает количество обслуживающего персонала.

Чтобы не допустить реакцию окисления азотистой кислотой пирита, находящегося в руде, необходимо контролировать и регулировать окислительно-восстановительный потенциал раствора. Такой контроль осуществляется с помощью платинового и каломельного электродов, высокоомных преобразователей и регулирующих приборов.

В тех случаях, когда разложение сырья производится при концентрациях кислот 10 ÷ 15 г/л, контроль и регулирование кислотности осуществляются pH-метрами со стеклянными электродами. Точность регулирования достигает ±0,2 pH. Контроль расхода урановых и других технологических пульп и растворов производится при помощи электромагнитных, щелевых и других типов расходомеров.

В процессах сорбции при переработке руд контролируются такие параметры, как уровень сорбента в регенерационных колоннах, количество сорбента в пучках, pH пульпы. При одновременном контроле потоков и концентрации урана по аппаратам система управления позволяет вести процесс сорбции при малых потерях реагентов.

В процессах экстракции регулируется соотношение расходов уран-содержащего неорганического раствора и органического экстрагента с целью получения насыщенного ураном экстракта и бедного рафината.

Управление всеми процесами переработки руд осуществляется с местных и центральных щитов. С местных щитов производится дистанционное управление электрическими, пневматическими исполнительными механизмами и приводами. Здесь же располагаются измерительные регистрирующие приборы и регуляторы отдельных процессов, мнемосхемы, аппаратура программного управления, блокировки, приборы световой и звуковой аварийной сигнализации.

В ряде случаев значения основных технологических параметров выносятся на приборы центрального щита. Наличие центральных щитов позволяет более оперативно управлять работой цехов.

К приборам, расположенным на щитах, можно подключать входные устройства вычислительных машин, предназначенных для переработки информации о технологических процессах.

Все в бóльших масштабах проводится разработка и внедрение методов оптимального управления как отдельными технологическими процессами, так и всем производством. При этом особое внимание обращается на оптимизацию технологических режимов и аппаратурного оформления технологических схем.

Основными методами оптимального управления, которые находят применение, являются статистические, основанные на математической статистике и теории статистических решений, а также методы математического моделирования на основе физико-химических закономерностей и методы поиска экстремума непосредственно в ходе технологического процесса.

Применение описанного выше комплекса систем автоматического контроля и управления обеспечивает получение оптимальных технико-экономических показателей процесса с минимальными затратами ручного труда.

# STATUS REPORT FROM THE UNITED KINGDOM

A.A. NORTH
WARREN SPRING LABORATORY,
STEVENAGE, HERTS.,
ENGLAND

The invitation to present this status report could have been taken literally as a request for information on experience gained in the actual processing of low-grade uranium ores in the United Kingdom, in which case there would have been very little to report; however, the invitation naturally was considered to be a request for a report on the experience gained by the United Kingdom of the processing of uranium ores. Low-grade uranium ores are not treated in the United Kingdom simply because the country does not possess any known significant deposits of uranium ore. It is of interest to record the fact that during the nineteenth century mesothermal vein deposits associated with Hercynian granite were worked at South Terras, Cornwall, and ore that contained approximately 100 tons of uranium oxide was exported to Germany. Now only some 20 tons of contained uranium oxide remain at South Terras; also in Cornwall there is a small number of other vein deposits that each hold about five tons of uranium. Small lodes of uranium ore have been located in the southern uplands of Scotland; in North Wales lower palaeozoic black shales have only as much as 50 to 80 parts per million of uranium oxide, and a slightly lower grade carbonaceous shale is found near the base of the millstone grit that occurs in the north of England. Thus the experience gained by the United Kingdom has been of the treatment of uranium ores that occur abroad.

In the United Kingdom, laboratory and pilot plant work on the processing of low-grade uranium ores has been in progress for twenty years. In 1946 the organization which later became the United Kingdom Atomic Energy Authority placed a contract with the Department of Scientific and Industrial Research (D.S.I.R.) to undertake work on the development of analytical techniques for uranium and for the development of chemical processing methods for the recovery of uranium at its National Chemical Laboratory at Teddington, Middlesex. In 1964, this work and personnel engaged upon it were transferred to another station of D.S.I.R., the Warren Spring Laboratory, Stevenage, Hertfordshire, where a mineral engineering group had been in existence since the formation of the Laboratory in 1958. This group was formed in part by the transfer of the Mineral Dressing Group of the Chemical Engineering Division of the Atomic Energy Research Establishment, Harwell. The last administrative change occurred in 1965 when the Warren Spring Laboratory was transferred to the new Ministry of Technology which also assumed parliamentary responsibility for the United Kingdom Atomic Energy Authority.

To give in detail the experience gained over a period of twenty years by research, development and process design teams that maintained close contacts with the producers of uranium concentrates in Africa, Australia, Canada, Portugal and the United States of America is obviously beyond the scope of this review; particularly as trends have not always been governed by consideration of technical feasibility but by economic factors. The outline of the experience bulges heavily in the area that covers the leaching of ores of uranium with sulphuric acid or with carbonate solutions, for either lixiviant the role played by oxidants received a considerable amount of attention. The phenomenon of natural leaching of uranium ores as the result of attack from ferric sulphate and sulphuric acid produced by the action of air and rainwater on pyrite was examined and the important contribution of the autotrophic bacteria Ferrobacillus ferro-oxidans, Thiobacillus ferro-oxidans and Thiobacillus thio-oxidans to the leaching processes was demonstrated.

Very early work on the recovery of uranium from leach liquors was concerned with the selective precipitation of uranium, but this type of work soon gave way to the investigation of the recovery of uranium by means of the use of anion-exchange resins. It was very appropriate for this work to be done at Teddington because the first synthetic ion-exchange resins were prepared at the Chemical Research Laboratory, Teddington, by B.A. Adams and E.L. Holmes in 1935. The poisoning of ion-exchange resin by thiocyanates, polythionates, sulphur, silica, cobalt cyanides and molybdenum compounds was investigated. In particular the study of poisoning by silica was protracted, and new anion-exchange resins for the recovery of uranium from siliceous liquors were developed. The new weak-base resins prepared by the amination of polyvinylchloride beads reject silica more completely than conventional strong-base polystyrene resins and so do not exhibit a gradual deterioration in performance due to the cumulative retention of silica.

On the advent of liquid ion-exchangers a number of alkyl and aryl esters of phosphoric acid and alkylamines were evaluated for their potential use as extractants for the recovery of uranium from leach liquors by solvent extraction processes, and a few such process design studies were completed. Further experience of the conventional type of solvent extraction process development work stemmed from investigations of the recovery of thorium from uranium-barren liquors and of beryllium from leach liquors. The recovery of uranium by solvent extraction direct from leached ore slurries was accomplished by means of a specially designed rotary-film disc contactor wherein neither phase was truly dispersed in the other since this avoided the creation of solid-stabilized emulsions.

Unfortunately this brief summary of experience of chemical processing of uranium ores does not permit a detailed account of invaluable contributions made to the geological and mineralogical aspects of the United Kingdom's programme by the Atomic Energy Division of the Institute of Geological Sciences and by the Mineral Dressing Group (q.v.), where the physical pretreatment of ores was studied. It is also regretted that it is impossible to catalogue the vast experience acquired by the manufacturers of equipment for mineral and chemical processing plants.

It is desirable to stray beyond the confines provided implicitly by the title of this review to refer to research work conducted in the United Kingdom on the recovery of uranium from sea water. For this work, undertaken principally by the Atomic Energy Research Establishment, Harwell, organic and inorganic absorbents (e.g. precipitated titanium hydroxide) were developed for the extraction of uranium from sea water; an account of this process has been given by Davies, R.V. et al., Nature, Lond. 203 (1964) 1110. A description of the recent progress of the work, currently being written up for publication, is unfortunately not available at the present time. The work is continuing on a further phase of the study which may take a year or two; when this is completed a forecast of the future potential of the process will be attempted.

Before describing the status of current research and development work on or pertinent to the processing of low-grade uranium ores it is desirable to give some indication of present environments. The United Kingdom Atomic Energy Authority is fully aware of the responsibility that it carries to ensure the availability of adequate supplies of fissile and fertile material. The present supply position, however, is one of emergence from there being a glut of uranium, and furthermore the Authority has confidence in its fast reactor programme. (The construction at Dounreay of a prototype fast reactor with a designed electrical output of

250 MW (600 MW(th)) is due to commence this year and the reactor should be in operation by 1971.) It is not surprising, therefore, that the current programme of the Mineral Science and Technology Division of the Warren Spring Laboratory is not dominated by work on the processing of low-grade uranium ores. The investigation of natural leaching of low-grade uranium ores is being continued, but for this study the emphasis is on improving the production of lixiviants from pyrite and from sulphur. The extraction of uranium from pure sulphate solutions is being studied incidentally as part of a basic investigation into the mechanism and kinetics of the solvent extraction of metals, this work utilizes a rotary-film disc contactor. In general the wide-ranging programme of research is not tied to any particular metal, but is concerned with a range of unit processes which are commonly encountered in mineral processing operations, including those devoted to the recovery of uranium, for example study of the control and automation of processing plants.

# STATUS REPORT FROM THE UNITED STATES OF AMERICA

R.H. KENNEDY
UNITED STATES ATOMIC ENERGY COMMISSION,
WASHINGTON, D.C., UNITED STATES OF AMERICA

The US uranium production rate has been dropping gradually from a high of 17 760 tons in fiscal year 1961 to a level of about 10 400 tons in fiscal year 1966. As of 1 January 1966, there were 17 uranium mills in operation in the USA compared with a maximum of 26 during 1961, the peak production year. Uranium procurement contracts between the USAEC and companies operating 11 mills have been extended through calendar year 1970. The USAEC contracts for the other six mills are scheduled to expire 31 December 1966. Some of these mills, however, have substantial private orders for production of uranium for nuclear power plants and will continue to operate after completion of deliveries under USAEC contracts. No new uranium mills have been brought into production since 1962. Under these circumstances the emphasis in process development activities in recent years has tended toward improvements that could be incorporated within the general framework of the existing plants.

Some major flowsheet changes have been made, however. For example, two of the ore-processing plants have shifted from acid leaching to sodium carbonate leach in order to provide the flexibility to process an increasing proportion of ores of high limestone content in the tributary areas. Several mills employing ion exchange as the primary step for recovery of uranium from solution have added an 'Eluex' solvent extraction step on the ion exchange eluate. This process not only results in a high-grade final product, but also eliminates several metallurgical problems formerly caused by the chloride and nitrate eluants. Such changes together with numerous minor improvements have gradually reduced production cost and increased recoveries.

The domestic uranium milling companies have generally had reserves of normal-grade ores well in excess of the amounts required to fulfil the requirements for their contracts with the USAEC. Therefore, there has been little incentive to undertake the processing of lower grade ores. However, there have been occasional circumstances in which the uranium in low-grade or marginal materials could be recovered at costs competitive with the costs of conventional ore mining and treatment. The procedures which are employed in treating these materials are given in the technical papers which were prepared for this meeting (see section II).

The USAEC conducted a vigorous research programme in uranium ore processing technology from about 1947 through 1958. This work was carried out by many different types of organizations including USAEC laboratories, other government agencies, universities, and private companies. Research activities were also closely co-ordinated with the work of laboratories in several other countries.

TABLE I. LEACHING AND RECOVERY METHODS

| Leach process | Primary recovery process | | Number of plants employing unit operations |
|---|---|---|---|
| Sodium carbonate | Hydroxide precipitation | | 2 |
| | Resin-in-pulp (basket) | | 1 |
| Sulphuric acid | Solvent extraction | | 6 |
| | Alkyl phosphates | 3 | |
| | Alkyl amines | 3 | |
| | Ion exchange | | 8 |
| | Column ion exchange | 3 | |
| | Resin-in-pulp (basket) | 2 | |
| | Continuous resin-in-pulp | 3 | |

Every uranium processing plant in the United States now employs one or more unit operations developed as a result of this USAEC research programme. In addition most of the mills in other countries from which the USAEC has purchased uranium have also benefitted materially from this process development work. Metallurgical performance has been improved to the point that 95% or higher recovery of the metal values in the ores are commonly achieved, an improvement of 20% or more over recoveries by earlier processing methods. At the same time, the unit productivity of labour has increased several fold.

Table I shows the leaching and recovery methods in use at the present time. Three of the plants employing resin-in-pulp as the primary recovery process use a solvent extraction operation (Eluex) on the ion exchange eluate.

Announced plans for installed generating capacity by the end of 1970 are in excess of 10 000 MW, and the projection for 1980 is 80 000 to 110 000 MW. The amount of uranium needed to support such a programme through 1980 would be about 170 000 tons. The annual requirement by 1980 would be at a level of about 27 000 tons. To meet this projected growth in requirements, a rapid build-up in mining and milling activity will be needed over the next few years, involving eventually a new generation of mines and mills.

The new mills can be expected to incorporate any improved techniques that may be developed before the time design is decided upon and construction is started. In addition, improvements in uranium ore processing technology can also help to increase the available ore reserves. Further attention is needed to the problems of treatment of low-grade resources which have received little attention in the past. It is likely that the USAEC will resume a somewhat more active role in ore processing research and development work than it has had in recent years. We are interested in gaining a better understanding of the basic reaction mechanisms in hydro metallurgical operations which would permit better process control. Uranium ore processing technology has improved greatly over the last fifteen years. Nevertheless it is a field in which much further promising research work could be done.

# STATUS REPORT FROM YUGOSLAVIA

B. BUNJI
INSTITUTE FOR TECHNOLOGY OF NUCLEAR AND OTHER
RAW MATERIALS,
BELGRADE, YUGOSLAVIA

The greater part of our activities is connected with the problem of extracting uranium from low-grade ores. In this paper, a brief review of the most important recent developments will be presented.

In this connection, it may be useful to determine the definition of low-grade ores. This term can be applied to ore from which the uranium content cannot be extracted under normal economic conditions. Thus this term can be applied to uranium-bearing material with a uranium content of no more than 0.05%. But, in general, it could be said that there is a very large range of uranium content where uranium extraction may not be economic for such different reasons as; (a) the size or other facts in connection with the orebodies themselves; (b) refractory ore; or (c) other local conditions.

During research on the treatment of low-grade ore from the deposit at Gabrovnica (Stara Planina, Yugoslavia) it became apparent that an alkaline leaching process would have to be carried out. The treatment of this granitic type of ore causes no particular difficulties. The required temperature is about 90°C. The retention time in the leaching stage is from 4 to 12 hours. Sodium carbonate consumption is not higher than 15 kg/t of ore. Pachuca-type leaching shows satisfactory maintenance and processing costs.

At Kalna uranium precipitation by means of hydrogen pressure reduction has been developed, and is being developed and investigated in full-scale operation. Details of the process were published in Geneva in 1963. On the basis of the experience gained from full-scale operation, many refinements and cost-saving changes have been made. A normal steel wire screen used as a catalyst carrier shows a very good improvement over free-moving $UO_2$ as catalyst. In large-scale operation (200 t/d), after the precipitation of uranium the barren solution content is about 1 g U/$m^3$. The content of the pregnant solution is of the order of 300 - 600 g/$m^3$. Recycling the barren solution has resulted in important savings on reagent.

The overall economy compared under local conditions with ion-exchange or solvent extraction is in favour of the reduction process.

Some research work on heap leaching and leaching in situ is included in our activities. In connection with the conditions at Kalna it was possible to carry out large-scale heap leaching and leaching in situ. The former was carried out on waste rocks with a uranium content below the cut-off grade.

To avoid solution losses, the surface area from the heap pile is covered with thin plastic sheets. Good drainage from the bottom is obtained by using perforated 10-in. asbestos-concrete pipes. The technique of construction of the heap pile is as usual, and mostly depends on local conditions. The heap leach pile is about 12 m high. The solution retention time is about 8 days.

The barren solution from the reduction plant or mine water with a uranium content in the range of 2 to 6 g/$m^3$ is used for the heap leaching. The pregnant solution is returned into the processing plant.

Because the heap leach pile obtained is practically without any charge, the operating and the construction costs of the heap pile need only be in balance with the value of the recovered uranium.

Investigation of bacterial leaching has shown some influence on the leaching rate. The bacteria belonging to the Thiobacillus-Ferrobacillus group were obtained from mine water, selected and cultivated. It seems that the concentration of bacteria has some influence on the extraction time and percentage of extracted uranium,and it can be said that the application of bacteria in heap leaching and leaching in situ will in the future be one of the most effective methods of uranium extraction from ore that is below cut-off grade.

# TECHNICAL REPORTS

# URANIUM PROCESSING RESEARCH IN AUSTRALIA

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## Abstract

URANIUM PROCESSING RESEARCH IN AUSTRALIA. Uranium processing research in Australia has included studies of flotation, magnetic separation, gravity separation, heavy medium separation, atmospheric leaching, multi-stage leaching, alkali leaching, solar heating of leach pulps, jigged-bed resin-in-pulp and solvent-in-pulp extraction. Brief details of the results obtained are given. In general, it can be said that gravity, magnetic and flotation methods are of limited usefulness in the treatment of Australian uranium ores. Alkali leaching seldom gives satisfactory recoveries and multi-stage leaching is expensive. Jigged-bed resin-in-pulp and packed tower solvent-in-pulp extraction systems both show promise, but plant-scale development work is required. Bacterial leaching may be useful in the case of certain low-grade ores. The main difficulties to be overcome, either singly or in combination, in the case of Australian uranium ores not currently considered economically exploitable, are the extremely finely divided state of the uranium mineral, the refractory nature of the uranium mineral and adverse effects due to the gangue minerals present. With respect to known low-grade ores, it would be possible in only a few cases to achieve satisfactory recovery of uranium at reasonable cost by standard treatment methods.

## INTRODUCTION

As in most other countries, direct acid leaching of ore pulp followed by ion exchange separation and precipitation of uranate concentrates was the metallurgical process used initially in Australia for the treatment of uranium ores. Details of this process are widely known and will not be discussed further in this paper.

During the 1950's, when there was rapid development of the uranium industry in Australia, research was carried out into a number of other possible treatment processes. Although the results of much of this work have been recorded in the literature, some of the publications concerned are not widely available. It is therefore considered useful to present the following summary of the major lines of investigation undertaken and the results obtained.

## FLOTATION

The physical concentration plant at Radium Hill, South Australia, was the only uranium treatment plant in Australia which utilized flotation. In this plant flotation was used to clean the davidite concentrates obtained by heavy medium separation. A pilot-scale unit was constructed first to test the process. In addition to heavy medium concentrates, a portion of the minus 10 mesh (0.0660 in.) fraction of the ore was also included in the feed to the flotation cells. The overall results obtained on treatment of 3096 tons[1] of feed were as follows:

| | |
|---|---|
| Grade of feed | 7.2 lb $U_3O_8$/ton |
| Grade of concentrate | 18.3 lb $U_3O_8$/ton |
| Recovery in section | 85% [1] |

In the industrial plant, six banks of four-cell flotation units were arranged as rougher and cleaner units. Reagents added per ton of flotation feed were as follows:

| | |
|---|---|
| Linseed fatty acids | 2.5 lb |
| Fuel oil | 10.0 lb |
| Peltogen | 1.5 lb |
| Settling agent | 0.01 lb |
| Cresylic acid | 0.5 lb |

Recovery in the section was 92% with a concentration ratio of 3 : 1 [2].

Considerable research effort was devoted to the possibility of using the flotation method for pre-concentration of Australian uranium ores. However, the very finely divided state of at least a portion of the uranium-bearing mineral in most of the known ores resulted in flotation recoveries not comparable with those obtained by direct leaching of the ore as mined.

The Commonwealth Scientific and Industrial Research Organization (C.S.I.R.O.) conducted a comprehensive series of investigations on a synthetic pitchblende ore and on two grades of natural pitchblende ore from the Rockhole mine, South Alligator River area, N.T.

In view of the inconclusive nature of the results of pitchblende flotation reported in the literature, it was decided to investigate first the flotation of this mineral from a synthetic ore made up of clean, free pitchblende and quartz. The various types of reagents for which success had been claimed in the literature were tested on this synthetic ore in a laboratory flotation cell. Of all the collectors tested, sodium oleate gave the best results. With this reagent flotation was selective and rapid in the pH range 6.0 - 7.0 and the recovery obtained (97.5%) was close to the maximum obtainable by any concentrating operation. Soaps of other fatty acids did not show the same selectivity and results were not improved by the addition of several commonly used gangue depressants. A wide range of other surface active agents were tested, including resin soaps, alkyl-aryl sulphonates, ester sulphonates, amide sulphonates, anionic sulphates, anionic phosphates, sulphydric collectors and cationic collectors. Only two of these — an ester sulphonate and a resin soap — were found to be collectors for pitchblende, and they were not as effective as sodium oleate.

The fact that some of the reagents tested did not function with the success recorded in the literature may have been due to the fact that the pitchblende tested by other workers occurred in composite particles with other minerals, particularly iron-containing minerals. The reagents concerned may well function as effective collectors of pitchblende in these circumstances.

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[1] All tons are long tons of 2240 lb unless otherwise stated.

Further tests with sodium oleate on the effect of variations in feed assay showed that the grade of the final concentrate varied with the feed assay and that the rate of recovery of pitchblende increased from 83.2% at 0.01% $U_3O_8$ to 95.1% at 0.69% $U_3O_8$ and then dropped slightly to 93.8% at 3.12% $U_3O_8$. It was also shown that recovery was fairly high over a wide range of size fractions with the exception of the coarsest material (over 211 μm) where the particles were presumably too heavy to be readily buoyed up by bubbles of the size produced in the laboratory flotation cell used. The maximum recovery (97.3%) was reached in the region 30 - 40 μm; at 3.5 μm recovery was still 62.6%.

The work then proceeded on a sample of pitchblende ore from the Rockhole mine assaying 0.78% $U_3O_8$. Ore of such high grade was selected to ensure that the investigation could be conducted on material containing a proportion of liberated pitchblende so that the effects characteristic of the mineral itself could be distinguished from those dependent upon the degree of liberation, which tend to mask all other effects in the treatment of very low-grade ores.

Several of the most successful collectors found in the work on the synthetic ore were tested. For ore deslimed at 10 μm equivalent pitchblende size, a combination of a tall oil fatty acid and an ester sulphonate was found to give 81.1% recovery after two stages of flotation. However, this represented a recovery of only about 45% of the original ore due to the fact that the slime contained as much pitchblende as the concentrate. The grade of the slime was too low for it to be combined with the concentrate, so flotation tests were carried out on ore deslimed at various sizes down to 1 μm. With three-stage flotation the recoveries increased from 49.9% at 10 μm to 68.6% at 1 μm. Although the concentrate grade did not alter significantly, the assay of the slime increased from 0.85% $U_3O_8$ to 1.18%. The product obtained by combining the concentrate with the slime therefore increased in grade as the desliming size was reduced, although overall uranium recovery was fairly constant at about 92% in 57% of the original weight until the 1 μm desliming size where recovery dropped slightly to 87.2%.

In the case of undeslimed ore, the efficiency of flotation was greatly reduced. Only 39.5% of the uranium could be recovered in 27.3% of the original weight.

A further series of tests was carried out on ore deslimed at 1 μm to see if results could be improved. These involved increased grinding time, increased collector additions and addition of gangue depressants. The effect of desliming before grinding was also investigated. As the results of these tests tended to approach each other in the vicinity of 70% overall recovery irrespective of the flotation conditions, it appeared that the degree of liberation of pitchblende, rather than the test conditions, was the factor controlling the final recovery obtainable. Stage grinding was therefore employed to reduce the size of the flotation feed to minus 200 mesh (0.0030 in.). This enabled the recovery to be increased to a maximum of 81.3%. Because it appeared that the final 20% or so of the pitchblende particles were locked up in composite particles, a typical flotation tailing containing 0.26% $U_3O_8$ was sized and the size fractions separated in tetrabromoethane. Most of the valuable mineral remained in the float products and the constant assay of these in the size ranges from 200 mesh down to 10 μm indicated that the association of the minerals was very fine and that little liberation could be expected by further grinding.

The conclusion that about 20% of the pitchblende was in a very fine state of association with the gangue was supported by the study of autoradiographs which showed that areas of gangue in which no pitchblende was visible under the microscope gave evidence of very finely dispersed radioactive material.

Attempts were made to improve results with undeslimed ores to a point where they were approximately equal to the best results obtainable on deslimed ore (81.3% recovery in a concentrate containing 2.41% $U_3O_8$ and 26.6% of the original weight). Emulsions containing kerosene appeared promising but supplies of the ore grading 0.78% $U_3O_8$ had been exhausted and the further test work was carried out on higher grade ore assaying 1.25% $U_3O_8$.

For comparison purposes the higher grade ore was deslimed and tested under the conditions which gave the optimum result with the lower grade ore. The result in this case was a recovery of 81% of the total uranium in a concentrate containing 5.4% $U_3O_8$ and 18.7% of the original weight.

The most satisfactory reagent combination for undeslimed higher grade ore was a mixture containing a collector/emulsifier (sodium oleate or sulphonated whale oil), a fatty acid (palmitic acid) and kerosene in the proportion 1 : 1 : 1.2. Gangue depressants had little effect. The best result achieved was the recovery of 80.4% of the uranium in a concentrate containing 5.46% $U_3O_8$ and 18.4% of the original weight.

For all the flotation tests, the assay of the tailing was in the range 0.2 - 0.3% $U_3O_8$. These tailings did not represent products which could be discarded and flotation could not therefore be regarded as an alternative treatment method to leaching, where the tailing assay can be reduced to a much lower figure [3].

The C.S.I.R.O. also carried out flotation tests on three samples of Rum Jungle Creek South uranium ore assaying 0.08, 0.15 and 0.25% $U_3O_8$. The ore, comprising finely divided pitchblende in slate, was tested with various combinations of reagents. In any one combination the reagents used were: (a) a surface active agent soluble in water; (b) a surface active agent only slightly soluble in water (a fatty acid); and (c) a hydrocarbon oil (usually kerosene). The most selective separation was achieved with a sodium alkyl sulphate, an unsaturated fatty acid and kerosene. There was no improvement when different grinding times were used or when the ore was stage ground. The response of the three samples was such that up to about 60% of the uranium could be recovered in a concentrate in which the enrichment ratio was 1.3 to 1.4. The results were consistent with fine dissemination of a large proportion of the valuable mineral and consequent limitation of the extent to which concentration by flotation would be possible [4].

Testing at the University of Queensland of torbernite/clay ore from the Milo deposit showed that recoveries of over 90% of the uranium were possible with torbernite up to 52 mesh (0.0116 in.) in size although flotation at the coarser sizes was slower. The preliminary experimental work suggested that an average recovery of 80 - 85% $U_3O_8$ would be possible in concentrate grading 20 - 30% $U_3O_8$.

Test work was also carried out at the University of Queensland on ore from the Flat Tyre deposit, but even when the ore was finely ground (50% minus 10 μm) there was little difference between the uranium content of the concentrate and the tailings.

Experiments with a more theoretical bias were carried out at the University of Melbourne to investigate the flotation behaviour of small particles of pitchblende by means of the bubble pick-up technique. The reagents tested, under varying conditions of pH and temperature, were diethyldithiocarbamate and dodecylamine [5].

## MAGNETIC SEPARATION

Laboratory studies carried out by the South Australian Department of Mines on the davidite ore from the Radium Hill deposit showed that magnetic separation might offer a possible treatment method. Because of the lack of water at Radium Hill and the urgent necessity to produce concentrate in ton lots for testing, it was decided to install a pilot scale magnetic separation machine with a capacity of 1 to 2 tons of concentrate per day.

During the period of operation, 1015 tons were treated with the following results:

| | |
|---|---|
| Ore grade | 4.08 lb $U_3O_8$/ton |
| Concentrate grade | 16.1 lb $U_3O_8$/ton |
| Recovery | 60% |

The grade of concentrate produced was almost directly proportional to the grade of feed, but recovery was largely governed by the moisture content of the feed. No difficulties were encountered with dry ore from surface dumps, but with ore from underground, extraction fell rapidly when the moisture content of the ore exceeded 2% [1, 5, 6].

At a later stage, following the installation of a heavy medium separation unit for plus 10 mesh ore, the minus 10 mesh fraction of the ore was fed to the magnetic section. These fines contained most of the moisture present in the ore delivered from the mine and the results obtained were very poor, viz:

| | |
|---|---|
| Feed | 127 tons at 2.3 lb $U_3O_8$/ton |
| Concentrates | 14.2 tons at 6.4 lb $U_3O_8$/ton |
| Recovery | 31% [1] |

In connection with the operations of the United Uranium N. L. in the South Alligator River area, N. T., the C. S. I. R. O. tested a sample of uranium table concentrate assaying 36% $U_3O_8$ by magnetic separation to endeavour to remove the principal gangue minerals — haematite, limonite and pyrite — and produce a concentrate meeting the specification minimum of 50% $U_3O_8$ content.

The tests were carried out on the concentrate as received, and also after roasting. The purpose of roasting was to convert the haematite into magnetite and so improve the efficiency of magnetic separation. Sized and unsized feed was tested in each case. Concentrates of over

50% grade were obtained without roasting after the feed was split into two or more size fractions but sizing was not necessary to produce concentrates of this grade when roasting at 550°C preceded magnetic separation. Despite the fact that roasting improved the grade of concentrate obtainable, this was not due to an improvement in the magnetic results but rather to calcination of carbonate minerals and dehydration [7].

The C.S.I.R.O. also tested a sample of ore from Milestone, N.T., containing 0.96% $U_3O_8$ as pitchblende in haematite. This material had been rejected after hand sorting of the highest grade ore for shipment to the Rum Jungle plant. It was found that 62% of the uranium could be recovered in 1.9% of the original weight by a combination of gravity and magnetic concentration after crushing to 14 mesh (0.0474 in.). A further 12% could be recovered in a middling with an assay of about twice the head value but this middling would not respond well to retreatment. The reject material would still contain 0.3% $U_3O_8$. The inclusion of the magnetic concentration step resulted in worthwhile up-grading of the table concentrate with relatively little loss of available uranium – 92% of the uranium in the table concentrate was recovered in about 48% of the weight [8].

Magnetic separation tests were carried out on ores from Mary Kathleen, Anderson's Lode, Skal and Flat Tyre deposits in the Mt. Isa district, Queensland, but without success. The Flat Tyre ore, in particular, contained a considerable quantity of magnetite and an attempt was made to remove this by wet magnetic separation. However, no effective concentration of the uranium was possible [9 - 11].

## GRAVITY SEPARATION

Gravity separation was used on a plant scale by only one Australian uranium producer. This producer (United Uranium N.L.) worked a number of small, rich uranium deposits in the South Alligator River area, N.T., and at one stage held a contract for delivery of pitchblende concentrates with a minimum $U_3O_8$ content of 50%. Tests carried out by the South Australian Mines Department showed that, after initial hand sorting of massive pitchblende, satisfactory concentrates could be recovered from the remainder of the high-grade ore from the El Sherana deposit using a jig and gravity table concentration plant. This plant produced 167.8 short tons of pitchblende concentrates and 4600 tons of residues assaying 0.7% $U_3O_8$ [12]. (Later on, the Company constructed a chemical treatment plant of the usual kind.)

Ore from the Milestone deposit, N.T., consisting of pitchblende in haematite and containing 0.96% $U_3O_8$ was tested by the C.S.I.R.O. to see if it could be concentrated by gravity methods because of the small size of the deposit and its very remote location. As mentioned in the section on magnetic concentration, it was found necessary to subject the gravity concentrate to magnetic treatment to obtain the best result. Overall, it was found possible to recover 62% of the uranium in 1.9% of the original weight. With ore from the same deposit containing 14.8% $U_3O_8$, 60% of the uranium was recovered in 20% of the original weight in a simple tabling test after reduction to minus 35 mesh (0.0164 in.). A further 23% was recovered in a high-grade middling. However, the tailing was still of high grade, viz. 2.3% $U_3O_8$ [8, 13].

Attempts were made to concentrate ore from the Milo deposit, Queensland, by gravity separation. This ore consisted of torbernite flakes in clayey material. Some concentration was achieved but tailing losses were high. This was due partly to the platey shape of the grains of torbernite which tended to slide down the concentrating deck and be carried into the tails.

All other attempts to use gravity separation methods proved unsuccessful. For example, the C.S.I.R.O. tested ore from Mary Kathleen, Anderson's Lode and the Skal Lease in the Mt. Isa district, Queensland, but very little separation could be effected. Work at the University of Queensland showed that no effective concentration of the very finely divided uranium mineral present was possible in the case of ore from the Flat Tyre deposit [9 - 11].

## HEAVY MEDIUM SEPARATION

Visual examination of ore from the Radium Hill deposit, South Australia, showed that much of the uranium-bearing mineral (davidite) occurred as quite large grains associated with quartz and biotite. Laboratory experiments demonstrated that the heavy medium separation process was suitable for Radium Hill ore in the size range 0.25 - 1 in. More than half the ore could be rejected as a residue and the remaining concentrate could then be further cleaned by flotation. Pilot-scale equipment was installed at the mine to check the laboratory results. In Table I the laboratory and pilot-scale results are compared.

TABLE I. COMPARISON OF LABORATORY ESTIMATES AND PILOT PLANT RESULTS

| | Laboratory estimate | Pilot plant results |
|---|---|---|
| Feed | 5.2 lb $U_3O_8$/ton | 2.04 lb $U_3O_8$/ton |
| Concentrate | 15.6 lb $U_3O_8$/ton | 7.53 lb $U_3O_8$/ton |
| Recovery | 90% | 87% [1] |

Following the pilot-scale testing, a full-scale plant was constructed at Radium Hill. Run-of-mine ore was crushed to 1 in. and, after washing and screening, plus 10 mesh material was delivered to a heavy medium separation unit using an aqueous ferrosilicon suspension having a specific gravity of 2.83. Approximately 91% of the uranium was recovered in the heavy medium concentrate; the ratio of concentration was 3.6 : 1. A specific gravity differential of 0.10 - 0.15 was maintained between the top and bottom of the separation vessel to ensure well defined sink and float products. Consumption of ferrosilicon was 0.38 lb/ton of plus 10 mesh material treated [5].

## RADIOMETRIC SORTING

The occurrence of ore-grade mineralization in the Mary Kathleen deposit in Queensland is highly irregular and therefore it was necessary to employ very strict selective mining practices to maintain a satisfactory grade of ore to the mill. Despite the great care exercised in the mine, it became apparent at an early stage that the ore fed to the mill contained an appreciable tonnage of waste or very low-grade material.

Gravity and flotation methods of pre-concentration proved unsuccessful. Visual hand sorting was also considered but, although some waste rock could be readily recognized, the size of an adequate hand-sorting plant and the low efficiency of such a plant were not economically attractive.

Close investigation of the uranium values in the +3-in. fraction of the discharge from the primary jaw crusher showed that there was a considerable concentration of weight in the assay range less than 0.04% $U_3O_8$, very little in the range 0.04 - 0.10%, and good concentration of weight in the assay range above 0.10%. These results showed that the grade of ore delivered to the mill was controlled by the amount of waste present rather than by the presence of lower grade ore. Test work indicated a 50% rejection of plus 3-in. material, equivalent to discard of 30 - 33% of run-of-mine ore [14].

Four electronic sorter units were installed in parallel, giving a total sorting capacity of 160 ton/h. Rejection achieved in practice was of the order of 31% of the initial crusher feed, i.e. 31% of the ore as delivered from the mine [15].

## LEACHING INVESTIGATIONS

During the course of investigations into possible treatment processes for Australian uranium ores, variations in the normal acid leaching procedures were tested. In addition, alkaline leaching and multi-stage leaching were also tried in particular cases.

The tests quoted in Table II, which were carried out under Mary Kathleen leaching conditions at pH 1.7, show the unsuitability of normal acid leaching in the case of many Queensland ores.

During research on treatment of certain of these Queensland ores it became apparent that in any satisfactory flow sheet the leaching process would have to be carried out at elevated temperatures. In the case of Anderson's Lode, the temperature required would be approximately 140°F for acid leaching, or 230 - 300°F for carbonate leaching. The possibility of using solar radiation to heat the leach pulps was therefore investigated.

In the case of acid leaching of Anderson's Lode ore, at a throughput of 500 ton/d, an absorber area of 80 000 $ft^2$ would be required assuming a solar radiation of 2000 $Btu/ft^2$ of absorber area per day and a conversion efficiency of 50%. These assumptions are probably conservative and the absorber area required might well be significantly less than the figure quoted.

Although preliminary investigations only have been carried out to date, solar heating appears to offer considerable promise for cost saving where leach pulps must be heated above ambient temperatures.

TABLE II. ACID LEACHING TEST RESULTS

| Name of lease | Sample grade (% $U_3O_8$) | Acid consumption (lb/ton) | Recovery (%) |
|---|---|---|---|
| Mighty Glare | 0.165 | 65 | 51 |
| Dalveen | 0.101 | 50 | 37 |
| Carol | 0.075 | 410 | 22 |
| Lucky Dot | 0.355 | 275 | 13 |
| Big Dip | 0.54 | 655 | 9 |
| Leftover | 0.155 | 360 | 5 |
| Duke | 0.895 | 555 | 2 |
| Batman | 0.19 | 570 | 0 |
| Future | 0.11 | 330 | 0 |

Laboratory and field tests have been carried out to determine the degree of atmospheric leaching of uranium ores left exposed in the monsoonal wet season of North Australia.

As a laboratory test, South Alligator River area pitchblende was crushed to minus 10 mesh and contacted with distilled water, both alone and in the presence of pyrite. After seven days, concentrations of uranium in excess of 1000 ppm were recorded. After two months, the water in contact with pitchblende alone showed a uranium concentration of 3800 ppm, while the water in contact with the pitchblende/pyrite mixture showed a uranium concentration of 6500 ppm.

It has been demonstrated on several occasions that heaps of ores containing pitchblende or secondary uranium minerals may lose up to 30%, and even more, of their uranium content in a single wet season if left exposed.

Tests have been carried out by the Australian Mineral Development Laboratories on the possibility of heap leaching of low-grade Rum Jungle ores. These tests, which were discontinued before leaching was complete, proved that heap leaching would probably be technically feasible, but further testing under actual operating conditions would be necessary to assess the economics of the process. Recirculation of the leach liquors would probably not be possible due to build-up of the concentration of phosphate.

Little work has been done to date in Australia on the role of bacteria in heap leaching of uranium ores but recently some experiments have been commenced at the University of New South Wales. Results are not yet available.

## RESIN-IN-PULP

During the period 1954 - 57, the C.S.I.R.O. developed a high efficiency jigged-bed ion exchange extraction unit for uranium recovery. Slimes at a pulp density between 20 and 30%, depending on the characteristics of the ore, were pumped upwards through a column containing a floating bed of a special coarse-size ion exchange resin held against a screen across the top of the column by the flow of pulp. Blockage of the bed and the screen were prevented by a slow, gentle pulsation applied to the flow of pulp. To reduce the size of the plant the operation was made continuous. Eluted resin was fed to the top of the column, and uranium-loaded resin was taken from the base of the bed, washed and eluted in a separate system [5]. (The loaded resin, being heavier than unloaded resin, sinks to the bottom of the bed.)

A 4-ft diameter adsorber in counter-current series with an elution vessel 2 ft 6 in. in diameter and 12 ft high was constructed at Rum Jungle, N. T., for full-scale test work on ore from Dyson's mine, which contained a high percentage of clay and was difficult to settle or filter. The 4-ft prototype unit was capable of producing 480 lb of uranium oxide per day from a pulp flow of 25 gal/min at a concentration of 1.3 g $U_3O_8$/litre. Although the full-scale unit performed quite well, unpredictable blockages occurred in the adsorber section and further development of the unit would be necessary before it could be considered suitable for industrial use.

In general, the easier an ore is to treat by conventional methods, the easier it could be handled by the jigged-bed process, but the margin for possible savings would be less. For a slimy, viscous ore, the savings in pulp preparation would be high and in the ion exchange step the cost of the jigged-bed process would be only slightly higher than that of the conventional process [16, 17].

## SOLVENT EXTRACTION

The first uranium chemical treatment plants used the ion exchange process for the recovery of uranium from leach liquors. The rapid growth in the use of solvent extraction resulted from the development of extractants enabling high distribution coefficients to be obtained from sulphate solutions. Capital cost is lower than in the case of the ion exchange process and solvent extraction also offers the advantages of a simple continuous process with improved selectivity.

The cut-off point between ion exchange and solvent extraction in uranium recovery is difficult to determine because it depends on a number of factors, such as the uranium content of the liquor, the effect of other metal ions present and also local conditions not related to the plant itself. Normally, solvent extraction would be more suitable for small volumes of comparatively rich liquor. Large quantities of low-grade liquor can be more economically treated by ion exchange. Stream pollution can also create serious problems in the case of plants using solvent extraction [17].

The first plant in Australia to use solvent extraction on an industrial scale was that of United Uranium N. L., at Moline, N. T. It employed mixer-settlers, and comprised four stages of extraction, three stages of chloride stripping and one stage of secondary carbonate stripping. The solvent was a 5% solution of tri(iso-octyl)amine in kerosene modified with 4% of a long chain alcohol; the stripping reagent was a molar solution of sodium chloride. It was necessary to remove continuously the build-up of molybdenum, which was present in the leach liquor at a concentration of 1 ppm, by giving 10% of the stripped solvent a 'clean-up wash' by contacting it with sodium carbonate solution. The performance and control of the industrial plant proved satisfactory. 99.7% of the uranium was recovered for the loss of 0.3 gal of kerosene and 0.4 lb of amine per 1000 gal of liquor treated [18].

Later, solvent extraction was used by South Alligator Uranium N.L. in the South Alligator River area, and at Rum Jungle.

## SOLVENT EXTRACTION-IN-PULP

As mentioned previously, severe difficulties were encountered in the endeavour to develop suitable treatment processes for a number of ores occurring in the Mt. Isa district of Queensland. Comprehensive investigations on the ore from Anderson's Lode showed that the most promising treatment process would require several stages of acid leaching at 60°C with extraction of uranium between stages. Although the extraction steps between stages could be carried out using counter-current decantation and conventional solvent extraction, this would involve an economically unacceptable loss of heat between the leaching stages. It was apparent, therefore, that it would be necessary to try and develop a solvent-in-pulp extraction method. An investigation of possible solvent-in-pulp systems was therefore carried out by the Department of Mining and Metallurgical Engineering, University of Queensland. As all attempts to use mixer-settlers and pulse columns had resulted in the formation of excessive quantities of emulsion and consequent high solvent losses, experiments were carried out using packed towers filled with regular grid packings.

The original experimental tower was 4-in. square by 6 ft high. Later a 12-ft tower with the same cross-sectional area was constructed. The solvent used consisted of a 5% solution of di-2-ethyl-hexyl phosphoric acid in kerosene, modified with 5% of tri-butyl phosphate. With a feed rate of 4 litre/min of leached pulp to the larger tower, 96.8% of the uranium was recovered for losses of 1.35 litre of kerosene, 0.095 litre of di-2-ethyl-hexyl phosphoric acid and 0.155 litre of tri-butyl phosphate per metric ton of solids treated.

The results were promising but considerable further developmental work would be required before a commercial plant could be designed.

## CONCLUSIONS

As a result of the work outlined above, it can be said that, in general, gravity, magnetic and flotation methods are of limited usefulness in the treatment of known Australian uranium ores. Alkali leaching seldom gives satisfactory recoveries and multi-stage leaching is expensive. Jigged-bed resin-in-pulp and packed tower solvent-in-pulp extraction systems both show promise, but plant-scale development work is required. Bacterial leaching may be useful in the future in the case of certain low-grade ores. The main difficulties to be overcome, either singly or in combination, in the case of Australian uranium ores not currently considered economically exploitable, are the extremely finely divided state of the uranium mineral, the refractory nature of the uranium mineral and adverse effects due to the gangue minerals present. With respect to known low-grade ores, it would be possible in only a few cases to achieve satisfactory recovery of uranium at reasonable cost by standard treatment methods.

## REFERENCES

[1] DEPARTMENT OF MINES, South Australia, Mining Review for Half-year ended 30th June, 1954, No.100, 112-30.

[2] Atom. Energy, Sydney 4 4 (1961); reprinted in Ref.14.

[3] TRAHAR, W.J., "Flotation of pitchblende from a synthetic ore and from ores of the South Alligator River district, Northern Territory", Ore Dressing Investigations, C.S.I.R.O. and Mining Dept., Univ. Melbourne rep. 603 (Sep.1960).

[4] TRAHAR, W.J.,, "Flotation of uranium ores from Rum Jungle Creek South", Ore Dressing Investigations, C.S.I.R.O. and Mining Dept., Univ. Melbourne rep. 614 (June 1961).

[5] Australian Atomic Energy Symposium 1958, Melbourne Univ. Press.

[6] DEPARTMENT OF MINES, South Australia, Mining Review for Half-year ended 31st December, 1952, No.97, 168 - 71.

[7] HUDSON, S.B., "Magnetic concentration of a uranium table concentrate from El Sherana, Northern Territory, Australia", Ore Dressing Investigations, C.S.I.R.O. and Mining Dept., Univ. Melbourne rep. 582 (Apr.1958).

[8] TRAHAR, W.J., "Concentration of a uranium ore from Milestone, N.T.", Ore Dressing Investigations, C.S.I.R.O. and Mining Dept., Univ. Melbourne rep. 582 (Aug.1959).

[9] BLASKETT, K.S., "Preliminary concentration tests on uranium ore from the Mary Kathleen lease, Mt. Isa District, Queensland", Ore Dressing Investigations, C.S.I.R.O. and Mining Dept., Univ. Melbourne rep. 503 (May 1955).

[10] BLASKETT, K.S., "Preliminary concentration tests on uranium ore from Anderson's Lode, Mt. Isa District, Queensland", Ore Dressing Investigations, C.S.I.R.O. and Mining Dept., Univ. Melbourne rep. 502 (May 1955).

[11] BLASKETT, K.S., "Preliminary concentration tests on uranium ore from the Skal Prospect, Mt. Isa District, Queensland", Ore Dressin Investigations, C.S.I.R.O. and Mining Dept., Univ. Melbourne rep. 501 (May 1955).

[12] Uranium Mines No Liability, Ann. rep. 1956.

[13] CARR, J.S., TRAHAR, W.J., "Table concentration of a uranium ore from the Calvert Hills District, Northern Territory", Ore Dressing Investigations, C.S.I.R.O. and Mining Dept., Univ. Melbourne rep. 528 (Mar.1957).

[14] AUSTRALIAN ATOMIC ENERGY COMMISSION, Uranium in Australia (1962).

[15] MARY KATHLEEN URANIUM Ltd., Ann. rep. 1963.

[16] ARDEN, T.V., DAVIS, J.B., HERWIG, G.L., STEWART, R.M., SWINTON, E.A., WEISS, D.E., "Extraction of uranium from acid leach pulps by jigged-bed ion exchange", Proc. 2nd UN Int. Conf. PUAE 3 (1958) 396-414.

[17] ARDEN, T.V., Ion exchange processes in the atomic industry, Proc. Australas. Inst. Min. Metall. 198 (1961) 153-206.

[18] BELLINGHAM, A.I., The application of solvent extraction to the recovery of uranium from El Sherana ore, Proc. Australas. Inst. Min. Metall. 198 (1961) 86-112.

# RECENT DEVELOPMENTS IN THE TREATMENT OF URANIUM ORES FROM THE ELLIOT LAKE DISTRICT

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## Abstract

RECENT DEVELOPMENTS IN THE TREATMENT OF URANIUM ORES FROM THE ELLIOT LAKE DISTRICT. A summary of the results obtained during investigations on the treatment of uranium ores from the Elliot Lake district in the laboratories of the Mines Branch, and of developments in operating procedures introduced in the uranium mills in the Elliot Lake district, is presented.

Concentration of Elliot Lake ore on a pilot-plant scale by a combined gravity-flotation procedure yielded a 90% recovery of uranium at a ratio of concentration of 2.4 to 1.0. The mineralogical composition of the ore, the flow sheet used and the reagents employed are described. An approximate cost estimate indicates that, although the capacity of an existing uranium leaching plant would be doubled by introducing the procedure, the production cost per pound of $U_3O_8$ would not be affected. Bacterial leaching of Elliot Lake ore on a laboratory scale yielded, under favourable conditions, extractions of 90 per cent in 5 weeks, and of 95 per cent in 15 weeks. The conditions that were found to influence the leaching results are outlined, and the effects of the leaching solutions are discussed. The purification of ion exchange eluates by liquid-liquid extraction, using tri-n-butyl phosphate, dibutyl butylphosphonate and tri-capryl amine in a continuous process, yielded solutions from which refined ammonium diuranate was precipitated using gaseous ammonia. The effectiveness of the three extractants is discussed, and the effects of the procedures employed on the production costs per pound of $U_3O_8$ is estimated. Some improvements in operating procedures introduced in the Elliot Lake district uranium mills are briefly described, and their effects on the operations are indicated. Present methods of controlling radiological pollution of drainage waters by uranium mill tailings are outlined.

## INTRODUCTION

Although uranium was first mined in Canada in 1933 at Port Radium in the North West Territories, only gravity concentrates were chemically treated at that time, a nitric acid leaching process being employed. When the importance and value of uranium became clear as a result of war-time developments, a method for treating the comparatively low-grade mine tailings was sought, and in 1947, as a result of collaboration between the Mines Branch and Eldorado Mining and Refining Ltd., the dilute sulphuric acid process for uranium extraction was developed in the Mines Branch laboratories. When it was demonstrated that this process, with minor modifications, was effective when used on Elliot Lake ores, all the mills in the Elliot Lake district adopted it. Encouraged by government contracts for the purchase of uranium concentrates, the mining companies in the Elliot Lake district brought their mines and mills into production as quickly as possible, the last one coming into operation in 1958.

In outline the process consists of three steps; a dilute sulphuric acid leach of the whole ore, followed by ion exchange to concentrate and purify the uranium and then treatment of the ion exchange eluate with ammonia, caustic soda or magnesia to precipitate a uranium salt.

Although only three of the original eleven uranium mills are now in operation, research and development work on uranium ore treatment has been pursued almost continuously both in the Mines Branch laboratories at Ottawa and in the operating plants. In this paper a brief review of the most significant recent developments will be presented. The first three parts of the paper will discuss laboratory and pilot plants work on Elliot Lake ores that was conducted in the Mines Branch laboratories; these ores have received our principal attention since they comprise over 90% of the known Canadian reserves of uranium. The fourth and last part of the paper will discuss developments in uranium ore treatment procedures that have been made by the mining companies at Elliot Lake.

## DEVELOPMENTS IN THE MINES BRANCH LABORATORIES

### I. Flotation concentration of Elliot Lake uranium ores [1]

The Elliot Lake ores are essentially a quartz-pebble conglomerate, with the uranium minerals occurring in the matrix. The ratio of pebbles to matrix is approximately 2 to 1. The matrix consists principally of quartz, sericite, feldspar, chlorite, pyrite, pyrrhotite, and the uranium-containing minerals brannerite, uraninite and monazite, with minor amounts of thucholite, coffinite, pitchblende and uranothorite. The intergrowths and the fine dissemination of the uranium minerals present serious problems when one attempts to make a reasonable recovery of uranium, without carrying with the uranium substantial quantities of gangue minerals.

These ores when ground produce moderate amounts of slimes, the amounts depending on the fineness of grind. In the investigation it was found that the slimes interfered with the flotation, and thus it was necessary to deslime before further treatment. Since the slimes contained uranium in about the same concentration as did the original ore, the slimes could not be discarded, but were eventually added to the concentrate.

The paper referred to describes both an all-flotation procedure and a combined gravity-flotation procedure. The combined procedure gave the best results; it was operated continuously at the rate of 500 lb/h, and consisted in its final form of the following steps:

(1) Grind in ball mill to 55% minus 200 mesh

(2) Pass the ground product over a Humphrey spiral to obtain three products: (a) slimes, which became part of the final concentrate, (b) a heavy material which became part of the final concentrate, and (c) a middlings, which went to flotation

(3) Dewater in a cone

(4) Condition and float with Acintol FA-1 as collector, cresylic acid and kerosene as frothers, sodium carbonate as pH regulator, and sodium silicate and gelatin as gangue depressants, to produce a concentrate which became part of the final concentrate, and a tailing

(5) Pass the flotation tailing over a Humphrey spiral to produce (a) a heavy material which was added to the final concentrate, and (b) a final tailing.

The ore fed to this circuit contained 0.16% $U_3O_8$. At a ratio of concentration of 2.4:1, recovery of uranium in the final concentrate was 90%, the concentrate containing 0.35% $U_3O_8$ (calculated) and the tailing 0.028% $U_3O_8$. At a ratio of concentration of 3.3:1, recovery of uranium in the final concentrate was 85.6%, the concentrate containing 0.46% $U_3O_8$ (calculated) and the tailing 0.031% $U_3O_8$.

The paper from which these results are taken contains a calculation showing that using mining and milling costs appropriate to Canadian conditions and valuing uranium at \$5.00/lb $U_3O_8$, the value of the uranium lost in the concentration procedure described exceeds the saving to be obtained by employing the process. However, it has been suggested that it would be preferable to value the uranium lost in the concentration procedure at the cost of replacing it from the mine. On this basis, assuming mining costs of \$4.50 per ton, crushing and grinding at \$0.70 per ton, concentration at \$0.70 per ton and hydrometallurgy (leaching and recovery) at \$2.80 per ton, with an extraction of 94% from either whole ore or concentrate, the following costs per pound of $U_3O_8$ produced can be calculated:

| Procedure | Cost (\$/lb $U_3O_8$) |
|---|---|
| Leaching whole ore | \$2.66 |
| Concentration, ratio of concentration 2.4:1, recovery 90%, | \$2.61 |
| Concentration, ratio of concentration 3.3:1, recovery 85.6% | \$2.62 |

While this is an approximate calculation only, it suggests that the production costs of $U_3O_8$ from Elliot Lake ores would not be reduced by introducing the concentration procedure described.

Although these results do not promise any reduction in production costs of $U_3O_8$ by using the combined gravity-flotation process, the results do indicate that the size of future uranium leaching plants might be reduced to something less than one half that of the present leaching plants. In addition, it must be remembered that the calculation given above provides for the mining, crushing and grinding costs of the uranium in the concentration plant tailings. If a low-cost means of recovering this 10% of the uranium can be found, an overall economic advantage in employing the gravity-flotation procedure might result. A method that may turn out to be low in cost is discussed in the next section of this paper.

## II. The application of bacterial leaching to Elliot Lake ores [2]

When Elliot Lake uranium ores are crushed and brought into contact with air and water in the presence of bacteria belonging to the Ferrobacillus-Thiobacillus group, the sulphides in the ore are oxidized to form ferric sulphate and sulphuric acid. These reagents are effective in leaching the uranium from the ore, extractions of from 50% to over 90% having been obtained in our laboratory investigations. The principal variable affecting the leaching action is the particle size of the material being treated; there is some reason to believe that extractions approximating 90% would be obtained using coarse ore, if sufficient time were allowed.

The bacterial strains used in this work are indigenous to the Elliot Lake mines, and were obtained from mine waters. They are thus adapted to conditions resulting from the interaction of ore, moisture and air. Our experiments did not disclose any tendency for their activity to be inhibited by the presence of uranium or other heavy metals at the concentrations that were developed in the leaching solutions, nor by acidities down to pH 1.3.

In our investigation the bacteria-bearing solutions were brought into contact with the ore by percolation leaching, and for this to be effective the slimes had to be removed. The finest ore tested was minus 14 mesh plus 20 mesh; from this material, experiments showed that 90% of the uranium was extracted in 5 weeks, and over 95% in 15 weeks. The next coarsest fraction tested was minus 8 mesh plus 14 mesh; from this material, experiments showed that, on the average, approximately 90% of the uranium was extracted in 15 weeks. The next coarsest fraction tested was minus 4 mesh plus 8 mesh; from this material, experiments showed that, on the average, approximately 77% of the uranium was extracted in 15 weeks. The coarsest fraction tested was minus 1 inch plus 4 mesh; from this material, experiments showed that, on the average, approximately 50% of the uranium was extracted in 15 weeks.

While the rate of uranium extraction was markedly reduced as the particle size of the ore being leached increased, it is notable that, even with the minus 1 inch plus 4 mesh fraction, the uranium was still being extracted, although slowly, at the end of the fifteenth week. Indeed, an experiment with this coarse fraction was continued for thirty weeks, by which time the extraction had risen to 75%, and was still rising. It is obvious that bacterial leaching not only extracted exposed uranium, but was capable of penetrating into particles of ores.

When the percentage of uranium extracted was plotted against the logarithm of the leaching time, it was found possible to represent the results by straight lines, showing that the rate of uranium extraction decreased logarithmically. This logarithmic relationship appeared to hold for all sizes of material tested. These results suggest that it may be difficult to set a limit on the size of material that can be effectively treated by bacterial leaching, provided sufficient leaching time is allowed.

While bacterial leaching of Elliot Lake ore took place spontaneously when ore, air, water and bacteria were brought together, the leaching rate of the coarser sizes was increased when ferrous sulphate, ammonium sulphate and potassium orthophosphate, up to concentrations of 1.0 g Fe/litre, 3.0 g $(NH_4)_2SO_4$/litre and 0.5 g $K_2H\ PO_4$/litre, were added to the water. The details of these additions and their effects are described in Ref. [2]. The consumption of these reagents would probably be much reduced if the leaching solutions could be recycled after being stripped of uranium. However, we have not so far experimented with recycled stripped solutions for bacterial leaching.

Flotation tailings and float products from sink-float investigations were also investigated for their amenability to bacterial leaching. The flotation tailings were deslimed first, 6% by weight of pyrite was added to replace the sulphides removed by flotation, and ammonium sulphate, potassium orthophosphate and ferric sulphate were added to the water employed; under these conditions 90% of the uranium was extracted in eleven weeks. The float product did not respond so well, as only 42% of the uranium was extracted in 29 weeks. This slow extraction is partly because the material was coarser than the flotation tailings, having been crushed to minus 4 mesh, and probably partly because it contained only 1.2% of pyrite, so that the leaching solutions did not develop the desirable concentrations of iron and sulphuric acid.

Mineralogical examination of residues from bacterial leaching indicated that uraninite, brannerite and thucholite were attacked by the leaching solutions, whereas monazite and coffinite were unattacked. The examination confirmed a result that had been deduced from the leaching experiments, namely that the leaching action was able to penetrate into the ore particles.

## III. Treatment of uranium leaching plant solutions by liquid-liquid extraction [3]

All the uranium leaching plants based on Elliot Lake ores used, or are using, sulphuric acid leaching followed by ion exchange. The ion exchange resin is eluted with a nitric acid-nitrate mixture, the eluate being treated with lime to pH 3.0 to precipitate most of the iron and sulphate, and then with ammonia to precipitate ammonium diuranate relatively free of iron, thorium, phosphates or halides. This diuranate is shipped to a refinery for further processing.

In the Canadian refinery of Eldorado Mining and Refining Ltd., the ammonium diuranate is dissolved in nitric acid and the uranyl nitrate is extracted with 25% tri-n-butyl phosphate (TBP) in kerosene, followed by stripping with water. The water strip is then treated with ammonia to precipitate refined ammonium diuranate.

It is evident that, if the ion exchange eluates could be effectively purified, the treatment with ammonia would precipitate a refined ammonium diuranate directly, and that this would eliminate the precipitation, drying and the packaging of the unrefined ammonium diuranate. Accordingly, an investigation was made of the feasibility, cost and adaptability of three liquid-liquid extraction processes as applied to ion exchange eluates. The eluates, with the one exception noted below, were obtained from two leaching plants operating in the Elliot Lake district.

In the purification of nitrate eluates the principal process variables are the acidity, the nitrate content, and the sulphate content. These variables are controllable in the plant by controlling the additions of lime to the eluate prior to liquid-liquid extraction, and also by making adjustments to the composition of the eluting solution before recycling it to ion exchange. In this investigation, only conditions that could be realized in practice at reasonable cost were studied as a continuous process. The circuit was operated for from six to seven solvent replacements. The nitrate eluates contained 15 g $U_3O_8$/litre, and were reduced to 0.1 g $U_3O_8$/litre, a concentration that would permit efficient elution when the eluate was recycled.

Using TBP as a solvent, it was noted that the distribution coefficient was improved as the nitric acid content of the eluate was raised, and also as the sulphate content was lowered. The conditions chosen for continuous operation were $HNO_3$ 1.2 N, total $NO_3^-$ 3.1 N, $SO_4^{2-}$ 0.5 N. Under these conditions five extraction stages were necessary to reduce the content of the eluate to 0.1 g $U_3O_8$/litre. Stripping was effected with water, and required only four stages.

Two alkylphosphonates were also considered as solvents, dibutyl butyl-phosphonate (DBBP) and di-2 ethylhexyl 2 ethylhexyl phosphonate (DEEP). Both of these solvents exhibit satisfactory distribution coefficients at much lower nitric acid levels than does TBP, and these distribution coefficients are not greatly disturbed by changes in sulphate levels. Of the two solvents DBBP was chosen for investigation in continuous operation, because its capacity is almost double that of DEEP and its extraction coefficient at low concentration is about 2½ times higher.

Using DBBP, with conditions adjusted to $HNO_3$ 0.4 N, total $NO_3^-$ 0.2 N and $SO_4^{2-}$ N, only four extraction stages were necessary to reduce the content of the eluate to 0.1 g $U_3O_8$/litre. On the other hand, water was a relatively poor stripping agent. Effective stripping was obtained, however, in four stages, using an 8% solution of ammonium sulphate.

Sulphuric acid can be used in place of nitric acid as an eluant for uranium. Its disadvantage with respect to nitric acid is that it does not produce an eluate with as high a content of uranium. However, it has two advantages over nitric acid, in that it is cheaper and in that the barren sulphuric acid can be used in the leaching operation, replacing fresh sulphuric acid. In view of these advantages, it was decided to prepare some sulphuric acid eluate in the Mines Branch pilot plant, using Elliot Lake ore as a source of uranium, and to investigate the use of tri-capryl amine (TCP) as a solvent.

Using TCP and an eluate containing 5.47 g $U_3O_8$/litre and 0.95 M $H_2SO_4$, only three extraction stages were necessary to reduce the eluate to less than 0.2 g $U_3O_8$/litre, an acceptable figure if the barren eluate is to be sent to the leaching operation. For effective stripping a 15% solution of ammonium sulphate and four stages were needed, with the pH in the stripping section controlled close to a value of 7.0.

Following these extraction and stripping investigations, the ammonium diuranate was precipitated from the stripping solutions with gaseous ammonia to study the effects of pH, temperature and ammonia gas dilution on the filtering and washing of the ammonium diuranate and on its subsequent reduction and sintering to $UO_2$. Details of these procedures are given in the paper referred to. The purity of the refined ammonium diuranate was comparable to, or closely met, refinery specifications, except that when refining with TBP the thorium was 100 ppm instead of the specification of 50 ppm, and that when refining with TCA the molybdenum was 200 ppm instead of the specification of 1 ppm.

The continuous operation of the refining procedures enabled reagent consumptions and costs to be calculated for the three processes. These have been calculated as costs over and above the cost of producing crude ammonium diuranate. These are as follows:

| Refining process | Reagent cost ($/lb $U_3O_8$) |
|---|---|
| TBP | 0.21 |
| DBBP | 0.03 |
| TCA | -0.11 |

The reagent cost for TCA is shown as a negative cost, that is, as a saving. This results from the fact that the sulphuric acid used for the elution, which would eventually be used in the leaching process, replaces all the nitric acid and lime used in the current process producing crude ammonium diuranate. Solvent losses were not determined for TBP, but amounted to 0.006 lb/lb $U_3O_8$ for DBBP, and were too low to determine for TCA.

This investigation was intended to provide a basis for development work by individual uranium-producing companies. The work indicates (1) that refining with TBP would be the most expensive, and that the refined ammonium diuranate may be above specifications with respect to thorium; (2) that refining with DBBP would add little to current costs, and would yield the purest product; and (3) that refining with TCA is the most economical, but that molybdenum might present a problem. It should also be noted that refining with TCA would be done in an open circuit, which would prevent the build-up of impurities, and that it obviates the necessity for disposal of nitrate-bearing solutions. However, the uranium content of the refining circuit is much lower than with the other extractants, hence the volumes of the solutions handled would be larger.

## DEVELOPMENTS BY THE ELLIOT LAKE MINING COMPANIES

### I. Improvements in the conventional acid leaching process

The basic process as originally laid out, has withstood the test of time. However the operators of the mills have introduced improvements that in sum, have resulted in a substantial reduction in operating costs. Some of the more significant of these improvements are listed below:

(1) Pebble grinding has replaced grinding with steel in the fine grinding mills, the original ball mills having been either lengthened or replaced. This conversion has reduced grinding costs, and in addition, because grinding steel consumes reagents in the leaching operation, has reduced leaching costs.

(2) The leaching temperature has been raised to 70°C and the pulp density in the leaching pachucas has been raised to 75% solids. The effect of these changes has been to reduce the consumption of sulphuric acid per ton of ore treated. The increased pulp density is obtained by filtering a part of the feed to the leaching pachucas.

(3) At one plant, now shut down because of lack of markets for uranium, sulphuric acid consumption per ton of ore treated was reduced by two-stage leaching. In this circuit, fresh ore was leached in the first stage by strong acid solution from the second stage, to produce a

weakly acid pregnant solution. In the second stage the first stage residue was re-leached with fresh acid to produce a residue for discard and a strong acid solution for the first stage. This circuit provided the best utilization of the sulphuric acid, but filtration costs were higher than when single stage leaching was used.

(4) Rubber-lined pachucas have replaced wooden air-lift agitators, which has made possible the higher leaching temperature. In addition, part of the final leach slurry is recycled back to the head of the leaching circuit. The use of pachucas and the recycling of the final leach slurry has eliminated the need for sodium chlorate addition to the leaching operation, since enough ferric iron is now formed during the leaching to oxidize the tetravalent uranium to the hexavalent state.

(5) In the original process uranium was precipitated from the ion exchange eluate by sodium hydroxide or magnesium oxide. At the present time anhydrous ammonia is used, which is easier to handle and yields a higher grade product, raising the grade of the precipitate about 5% to over 80% $U_3O_8$. The production of refined ammonium diuranate as proposed in Ref. [3] is under way at one uranium mill and is being considered at another.

(6) Alhtough no Canadian uranium mill has made any serious attempt fully to automate its operations, acid strength and temperature of the leaching operations have been put under automatic control, and the oxidation potential in the leaching operation is monitored continuously by instruments. The ion exchange operations are controlled by automatic timing devices.

## II. Investigations on bacterial leaching and its applications

The first work on bacterial leaching of Elliot Lake uranium ores was done in 1961 by Rio Algom Mines Ltd., and has been described by Fisher [4]. The first routine production of uranium from underground by bacterial leaching was initiated by Stanrock Uranium Mines Ltd. early in 1963 and has been described by MacGregor [5]. The Mines Branch laboratory investigations began in 1963, and are continuing. All these programmes have been pursued almost entirely independently, and the results are generally, although not completely, concordant.

The shapes of the extraction-time curves obtained by Rio Algom are different from ours, in that Rio Algom found a rate which at first increased, then decreased, and finally increased again, with time, while our curves showed a steadily decreasing rate. Rio Algom found that the use of nutrients was generally beneficial, whereas we found nutrients to be beneficial only on the coarser sized material. With respect to the production of uranium by underground leaching, Stanrock found that the use of nutrients did not improve their recovery of uranium, while Rio Algom found that it did. Stanrock and Rio Algom agree that substantial volumes of high-pressure water are necessary to dissolve uranium that has been rendered soluble by bacterial action.

Rio Algom and Stanrock agree that the principal advantages from bacterial leaching result when such leaching is conducted in conjunction with conventional mining operations, with the conventional operations carrying the costs of pumping, servicing, and overhead. Rio Algom concluded, however, that bacterial leaching could be conducted independently of other operations in a closed-down mine to recover uranium at what is described as a 'competitive cost'. Since Stanrock is now recovering all its uranium by bacterial leaching, this last conclusion appears to be a sound one.

An interesting aspect of these bacterial leaching operations, which consist simply of periodically washing the walls and floors of the stopes with water using a hose held in the hand, is that the recovery of uranium has not fallen off with time. It is obvious that the leaching action is penetrating into the rock, and one wonders how deeply this penetration will go, and at what rate. Time and careful observation will throw light on these questions; in the meantime the details of the process are obscured by two facts. One fact is that there is a good deal of loose, broken muck in the mines, of widely differing sizes, so that the surface area responsible for generating the soluble uranium is unknown. The second fact is that at Stanrock Uranium Mines Ltd. where production of uranium by bacterial action has been carried on for over three years, a continual scaling away of material from the walls is observable, exposing new surfaces. Stanrock is a deep mine, and some operators attribute this scaling principally to rock pressures. However, the oxidation of iron sulphide to sulphates must generate an increase in volume, and the rock may be being broken up even when the rock pressures do not result in obvious scaling. More detailed observations are needed to clarify these points.

For the immediate future, developments in the application of bacterial leaching at Elliot Lake will depend principally on economic factors. Those mines that have ample or surplus conventional leaching equipment will probably continue conventional mining and leaching, coupled with a stope washing programme underground to supplement uranium production. Those mines that wish to expand beyond their present leaching capacity, or that have to replace present leaching equipment, will seriously consider pre-concentration coupled with bacterial leaching of the concentration tails, the bacterial leaching probably to be done underground. At the present time such a combined process appears to be quite feasible technically. However, the problem of obtaining adequate ventilation particularly in winter time, without reducing the temperatures in the mines to the point where bacterial action is negligible, the problem of handling the concentration tails, and the problem of obtaining adequate contact between solids to be leached and leaching solutions, will have to be solved. These are problems that are primarily for the mining companies to solve, and until they are solved, the economics of bacterial leaching as a primary uranium recovery process will remain largely conjectural.

## III. Control over the radiological content of uranium mill effluents

Control over the radiological content of uranium mill effluents, which is an important aspect of uranium mill operation, now appears to be adequate in the Elliot Lake district. Although at no time have hazards to human health existed in Elliot Lake, about three years ago it became clear that simple neutralization of the mill effluents with lime would not be sufficient protection over the long term, and the provincial authorities, which have control over these matters, requested that an improved technique be introduced. The procedure that appears to be the best at the present time is to discharge the neutralized solids and liquids together into a large settling pond, so that the overflow is always clear. At the overflow, which is held at a pH of 8.0, 0.02 lb of barium chloride per ton of effluent is added, and the effluent is sent to a second settling pond, again large enough so that the overflow is always clear. It has been found that this procedure yields a final overflow containing from 3 to 4 pCi/litre, often less.

The Mines Branch was not involved in the problem of radiological control, but it is my understanding that the procedure described was originally developed in the United States of America. I also understand that the provincial authorities are satisfied with the results being obtained.

## REFERENCES

[1] HONEYWELL, W.R., KAIMAN, S., Flotation of uranium from Elliot Lake ores, Can.Inst.Min. Metall.Bull.59, (1966) 347.

[2] HARRISON, V.F., GOW, W.A., HUGHSON, M.R., "Factors influencing the application of bacterial leaching to a Canadian uranium ore", Presented at Ninety-Fifth Ann.Meeting American Institute of Mining, Metallurgical and Petroleum Engineers, New York City, 1966.

[3] SIMARD, R., GILMORE, A.J., McNAMARA, V.M., PARSONS, H.W., SMITH, H.W., Treatment of uranium leach plant solutions by liquid-liquid extraction to produce high purity uranium products, Can.J.chem.Engng 39 (1961) 229.

[4] FISHER, J.R., Bacterial leaching of Elliot Lake uranium ore, Can.Inst.Min.Metall.Bull. 59 (1966) 588.

[5] MacGREGOR, R.A., Recovery of $U_3O_8$ by underground leaching, Can.Inst.Min.Metall.Bull. 59 (1966) 583.

# PROCESSING URANIUM-BEARING MATERIALS CONTAINING COAL AND LOAM

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## Abstract

PROCESSING URANIUM-BEARING MATERIALS CONTAINING COAL AND LOAM. Among the ores which are classified as low-grade in the CSSR are mixtures of coal and bentonitic loam of tertiary origin, containing approximately 0.1% U and with a moisture content at times well above 20-30%. The uranium is held mainly by the carbonaceous component. Conventional processing of these materials presents various difficulties which are not easily overcome. During leaching the pulp thickens and frequently becomes pasty, due to the presence of montmorillonites. Further complications arise from the high sorption capacity of the materials (again primarily due to montmorillonites) and poor sedimentation of the viscous pulps. In addition, the materials are highly refractory to the leaching agents.

The paper presents experience gained in solving the problems of processing these ores. The following basic routes were explored: (1) separation of the carbonaceous and loamy components: The organic component appears to be the main activity carrier. Processing the concentrated material upon separation of the inactive or less active loam may not only remove the thixotropic behaviour but also substantially reduce the cost of the ore treatment; (2) 'liquifying' the pulps or preventing the thickening of the pulp by addition of suitable agents; (3) joint acid or carbonate processing of the materials in question with current ore types; (4) removal or suppression of thixotropic behaviour by thermal pretreatment of the material; and (5) application of the 'acid cure' method. The first method appears to be the most effective, but it presents considerable difficulties due to the extreme dispersion of the carbonaceous phase and further research is being carried out. Methods 2 and 3 proved to be unacceptable. Method 4, which includes roasting at 300-400°C, is now being operated on an industrial scale. The final method has also shown definite advantages for particular deposits of high montmorillonite content material.

## INTRODUCTION

The development of technological procedures for the treatment of sedimentary uranium-bearing deposits of tertiary origin is currently being given considerable attention in our country. The ore from these deposits is classified under the second category, as defined in our other paper (see section I), i.e. its economic processing by normal technological procedures is problematic, if not impossible.

## DESCRIPTION OF THE MATERIAL

The deposits in question consist mainly of a mixture of coal and loam with admixtures of some minerals. The particle size is fine, mostly below 2 mm. The coarser fraction above 2 mm is formed mainly by fragments of tufitic minerals, quartz, and brown coal. The majority of the material is less than 0.05 mm in size and is formed by minerals of the loam, mostly montmorillonite and kaolinite. In addition, volcanic dust and ashes together with finely divided organic matter are found. The material has 20 - 30% humidity and the mean uranium concentration is

0. 1%. The uranium content is in direct correlation to the content of organic carbon. The main portion of uranium accompanies the finely divided organic matter in the loam, or is contained in the coal. Macroscopic or microscopic observation has discovered no uranium mineral. Only in X-ray analyses were lines found denoting the presence of uraninite. The nature of the uranium bond is not clear at the present time. Evidently, some organic bonds (e. g. uranium humates) and sorption on organic or loamy materials can be considered. Other minerals found were sulphides, hematite and hydrated ion oxides, also hydromicas in minor quantities.

Table I shows the chemical composition and indicates the probable range of content of individual components in the material from the locality under consideration.

TABLE I. APPROXIMATE CHEMICAL COMPOSITION OF THE MATERIAL

| Component | Content (%) | Component | Content (%) |
|---|---|---|---|
| $Al_2O_3$ | 10 - 15 | $SiO_2$ | 40 - 55 |
| $Fe_2O_3$ | 10 - 13 | S total | 3 - 8 |
| $TiO_2$ | 2 - 4 | S combustible | 2 - 7 |
| MnO | 0. 03 - 0. 1 | $P_2O_5$ | 0. 3 - 0. 7 |
| CaO | 1. 5 - 4 | $CO_2$ | 0. 3 - 1. 5 |
| MgO | 0. 5 - 2. 5 | C organic | 5 - 10 |
| $K_2O$ | 0. 7 - 1. 1 | $H_2O$ bound | 4 - 6 |
| $Na_2O$ | 0. 3 - 0. 6 | loss on ignition | 10 - 30 |

In accordance with the variable chemical composition, the material exhibits a lesser or greater variability of its properties. This applies not only to the material from a single deposit, but also to the deposits as such. In the latter case these differences have a fundamental technological importance. At present we are thus compelled to distinguish between at least two types of deposits, which are denoted in this paper as types A and B. Material B, compared to Material A, contains a considerably higher amount of montmorillonite and has a higher ratio of montmorillonite to kaolinite (up to 9 : 1 as compared to 1 : 1). Also, the uranium compounds in type B are distinctly more refractory to the leaching agents under otherwise identical conditions. This may be explained by the following hypothesis: in contrast to the deposits of type A, the basalt formation erupted to the surface of the earth and covered deposit B with solidifying magma. The material of the deposit thus might be subjected to high temperatures under reducing conditions, due to the presence of organic matter.

## PROCESSING OF THE MATERIALS BY CONVENTIONAL METHODS

In the usual uranium ore treatment, characterized by leaching the ore in the pulp form, both types of material pose the following problems to the technologist:

(a) Pulps from both materials become increasingly viscous during carbonate or acid leaching and frequently become completely pasty in the reactor.

(b) The ore is highly resistant to the leaching agents.

(c) Considerable difficulties are encountered during transport and mechanical processing (crushing, milling, sedimentation, classification).

(d) High sorption ability for the dissolved uranium is shown by the material.

(e) Requirements for conducting the process on an optimum level are very difficult to meet in view of the large variability of the properties of the material from different lots.

These features of ore behaviour are more marked with material B. Analysing the causes, we find that (a) and (d) are due to the presence of montmorillonite components of the loam, whereas (c) is due to the high humidity and high clay content. The high resistance to the leaching agents is evidently caused by the structure of the uranium bonding with the material, the nature of which is as yet unknown.

The severe thickening of the pulp from these materials during leaching is of primary importance, since it considerably limits the use of normal technological procedures. Consequently, attempts were made to suppress this property by suitable means. This was done:

(1) By simple dilution of the pulp, or by addition of suitable agents to enhance the 'fluidity' of the pulp

(2) By joint processing of these materials with standard ores.

In the first case, the desired 'liquefaction' and, simultaneously, the necessary conditions for the leaching are achieved only at forbidding costs for the chemicals required. Moreover, the sedimentation and filtration properties of these pulps are bad and thus no recirculation of the solutions is possible, e. g. in acid leaching the required suppression of thixotropic behaviour was attained only at 20% solids in the pulp, while in carbonate leaching it was necessary to keep the amount of the solid phase still further below this value.

In the laboratory, ammonium and sodium nitrate, ammonium rhodanide and sodium fluoride were active in suppressing the thickening of the pulp but only at amounts of 50 to 200 kg/ton.

Laboratory tests of joint processing have indicated that a proper mixture of the tertiary material and standard ores at normal pulp densities (45-50% solid phase) shows no pseudoplastic behaviour. It was found that the amount of the materials in the mixture may not exceed a limit of 25% in acid, and 15% in carbonate leaching. This was confirmed on a plant scale. Simultaneously, other difficulties became apparent: the material often stuck to the transport belts and blocked the crushers, and a thick foam was formed in the first reactors of the acid leach cascade. In the carbonate process, the yield also fell considerably.

These problems, and the danger of the pulp thickening in the course of the process (if the maximum allowable ratio of the two mixture components were exceeded), led to further work in this direction being discontinued.

## OTHER TECHNOLOGICAL METHODS INVESTIGATED

The failure to solve the problems of pulp thickening encountered during the standard technological treatment led us to seek specific procedures to solve the problems outlined above. The routes which were studied are:

(1) Separation of uranium-bearing organic components from the loamy substance causing the thickening of the pulp.
(2) Thermal pretreatment of the material to enable it to be processed by normal procedures.
(3) Acid curing of the raw or dried material with subsequent application of the resin-in-pulp method.

The aim of the first alternative is evident. The use of procedures currently practised in the ceramic and coal industries was investigated. Gravitational, electrophoretic, flotation and radiometric classification, together with various washing methods were studied. In addition, pneumatic, electrostatic, magnetic, and radiometric classification after thermal treatment at 300-400°C was tried. All these methods showed little success, mainly due to the extremely fine division of the uraniferous organic matter in the remaining material. Almost equal uranium content of individual fractions according to particle size or specific gravity was found. All separation procedures are hampered by the high content of fines below 0. 05 mm which have approximately the same uranium content as the original material.

Separation of the materials will be tried in the nearest future using the prototype of a special centrifuge designed to handle clayey material of extremely fine size.

The second alternative aimed at suppression of the pseudoplasticity in the pulp. The thermal treatment leads to gradual liberation of the interstitial water in the montmorillonite materials. This in turn partly or wholy removes the thixotropic behaviour. In addition, improvement could be expected in materials handling operations and sedimentation. These assumptions proved correct both on the laboratory and on the plant scale. Moreover, a decrease in the sorption ability of the material was found. A negative factor is the lowering of the leaching yield which correlates with rise in the mean temperature of the thermal treatment.

Plant-scale operations for treatment of type A material were made. The material is roasted at a temperature of 300-400°C in a rotary kiln heated by heavy oil. The flow of gas and material is concurrent. The shell of the kiln has flights which split the material and improve the heat transfer. A perforated-plate tower for scrubbing the fines from the stack gas with water is included in the thermal treatment plant. The material leaving the kiln is crushed and sieved and then transported by rail to a mill where it is subjected to the conventional acid processing. As a high sulphuric acid concentration must be maintained throughout the leaching stage, the pulp leaving the leaching agitators is introduced into the leaching stage of standard ore where its high residual acidity is utilized. The flow sheets of the process are shown in Figs 1 and 2.

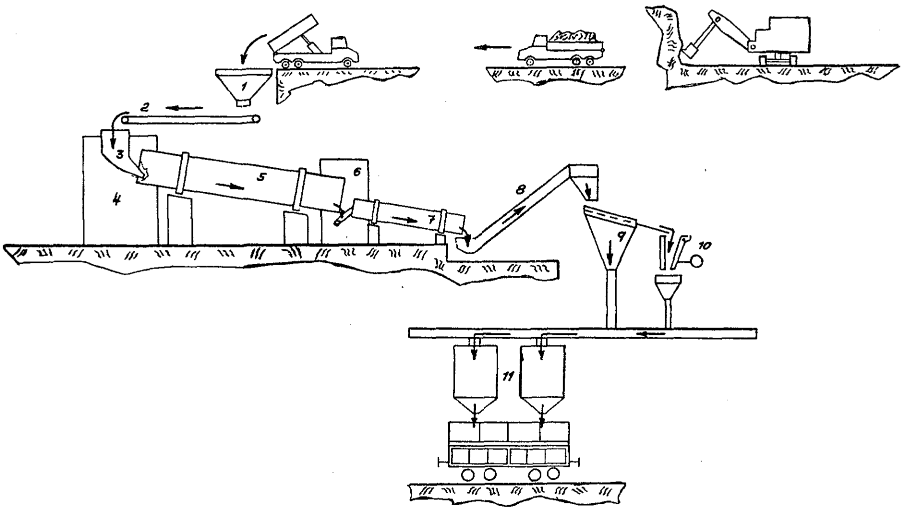

FIG. 1. Flow sheet of the thermal pretreatment and crushing
1. Chute; 2. Transport belt; 3. Chute; 4. Combustion chamber; 5. Rotary kiln;
6. Perforated-plate scrubber; 7. Cooling and spraying drum; 8. Transport belt with chute;
9. 10-mm sieve; 10. Jaw crusher; 11. Bunker chute.

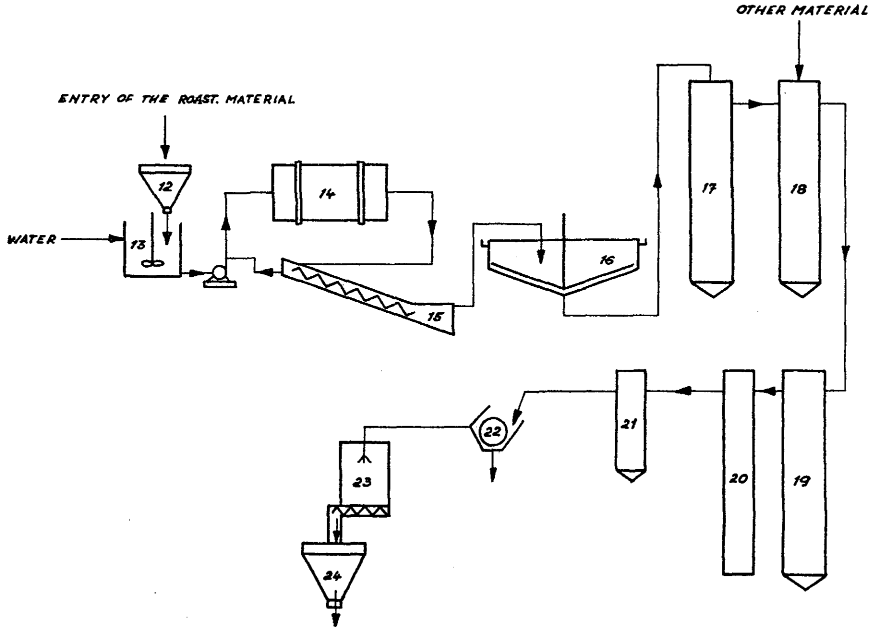

FIG. 2. Flow sheet of the technological process
12. Chute; 13. Repulper; 14. Ball-mill; 15. Spiral classifier; 16. Thickener;
17. Leaching I (original material); 18. Leaching II (joint); 19. Sorption; 20. Elution;
21. Precipitation; 22. Filtration; 23. Drying; 24. Bunker chute.

The possibility of application of this technological procedure to type B material was investigated in the laboratory and at the plant. The operation proved to be unprofitable since the temperature of 450 to 500°C required to cope with the pseudoplastic behaviour of this material has in turn considerably reduced the yield of uranium in comparison with type A material. Simultaneously, the acid consumption was considerably increased. The uranium yield even from type B raw material is 10-20% lower than from type A material under identical leaching conditions.

The acid cure method was envisaged primarily for the treatment of type B material, or as a universal procedure for both types, should this method prove to be economically more feasible.

TABLE II. THE MAIN PARAMETERS AND COSTS PER UNIT PRODUCTION FOR BOTH FLOWSHEETS INVESTIGATED

| | Flowsheet I Thermal pretreatment | | Flowsheet II Acid cure | |
|---|---|---|---|---|
| | Ore A | Ore B | Ore A | Ore B |
| Roasting - Temperature | 300-400°C | 450-500°C | drying | drying |
| Crushing - Particle size | -10 mm | -10 mm | -4 mm | -4 mm |
| Milling - Particle size | -0.15 mm | -0.15 mm | - | - |
| Thickening - Weight of solids | 40% | 40% | - | - |
| Flocculant consumption | 350 g/t | 350 g/t | - | - |
| Leaching - Temperature | 60-70°C | 60-70°C | - | - |
| Oxidizing agent ($HNO_3$) | - | - | 30 kg/t | 30 kg/t |
| Time | 4 h | 4 h | curing 24 h | curing 24 h |
| Residual concn. $H_2SO_4$ | 50 g/litre | 50 g/litre | - | - |
| Residual concn. after joint leaching | 8-10 g/litre | 8-10 g/litre | - | - |
| $H_2SO_4$ consumption | 105 kg/t | 160 kg/t | 100 kg/t | 100 kg/t |
| Leaching yield | 85% | 65% | 90% | 75% |
| Pulp neutralization - | | | | |
| Lime consumption | 50 kg/t | 70 kg/t | 50 kg/t | 50 kg/t |
| Processing costs per unit production | 100% | 147% | 94.2% | 102% |

Laboratory and bench-scale investigation indicated that on acid curing the pulp exhibits no thixotropic behaviour if it is not heated in the following stages. Furthermore it was found that the acid consumption remains the same for material A, while the yield of uranium is increased. The latter applies also to material B, where the consumption of acid is materially lowered. The calculations shown in Table II indicate that an economically feasible process for both materials may thus have been found.

At the present time, the following two flow-sheets for both types of material are being investigated:

(I) Thermal pretreatment application

The flowsheet consists of the following operations: open-cast mining – roasting – crushing – transport to the mill – milling – thickening – leaching – joint leaching with normal ore (residual acidity utilization) – sorption on strongly basic anionic exchange resin – elution – concentrate precipitation – drying.

(II) Acid curing

This flowsheet includes: open-cast mining – drying – crushing – transport to the mill – mixing with the acid – curing – repulping – classification of coarser fractions with countercurrent washing – sorption from the pulp on strongly basic anionic exchange resin – elution – precipitation of the concentrate – drying.

Table II presents the main technological parameters and costs per unit concentrate production. The table omits those operations which have the same parameters. The cost is given in per cent of the cost of flowsheet I, now used in the plant to process type A material. Under the economic conditions prevailing at the present time, the cost of 105% is very nearly the limit of economic operation.

## CONCLUSION

The problems discussed form an important part of the task to be fulfilled in our country if low-grade ores are to be processed. It should be clear that, above all, new economically more effective ways for pretreatment of the ore must be sought and found. We also think that in this search the conventional technological approach, which as a rule does not yield all the necessary information, must be substituted by a considerably deeper scientific and economic analysis of individual process stages from the standpoint of chemical engineering science. At the same time, mathematical methods and methods of mathematical statistics for optimization must be applied to guarantee profitable operation of the ore treatment process.

# RECUPERATION DE L'URANIUM DANS LES EAUX DES MINES

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RECOVERY OF URANIUM IN MINE WATERS. In a brief introductory survey the author indicates the date on which leaching was first observed in the CEA mines and lists the main factors necessary for, or favourable to, the solubilization of uranium in mines. Information is given on the various sources of this type at present identified in France and the methods used to recover uranium in mines situated near ore-concentration plants. An explanation is given for the use of the calcium precipitation technique in connection with waters produced in mines not situated near ore-concentration plants.

Data are given on the results of laboratory tests carried out on waters containing uranium, together with a description of an industrial-scale facility built in consequence of these tests. Details are given of the statistical results obtained. The author concludes by outlining the programme which will be implemented in the near future with a view to increasing the tonnage of uranium produced by in situ leaching and indicates that the CEA engineers are very optimistic about the prospects of this new low-cost method of producing uranium.

RECUPERATION DE L'URANIUM DANS LES EAUX DE MINES. Après un bref rappel historique précisant la date de constatation du phénomène de lixiviation dans les mines d'uranium du Commissariat et un rapide inventaire des principales conditions nécessaires ou favorisant la solubilisation de l'uranium dans les mines, l'auteur indique les différentes sources actuellement reconnues en France et les méthodes utilisées pour récupérer l'uranium dans les mines situées près d'une usine de concentration des minerais. Il donne ensuite les raisons motivant le choix du procédé de précipitation calcique pour les eaux produites dans des mines éloignées des usines de concentration des minerais.

Les résultats d'essais de laboratoire effectués sur des eaux chargées en uranium sont donnés et l'installation industrielle réalisée à la suite de ces essais est décrite; les résultats statistiques obtenus sont détaillés. En conclusion de son exposé, l'auteur trace les grandes lignes du programme d'action prévu dans l'immédiat pour accroître le tonnage d'uranium produit à partir de la lixiviation in situ et indique que c'est avec beaucoup d'espoir de réussite que les ingénieurs du Commissariat à l'énergie atomique abordent cette nouvelle voie très prometteuse de production d'uranium à bas prix.

## HISTORIQUE ET INTRODUCTION

En France, la présence d'uranium dans les eaux des mines a été constatée à partir de 1959 dans le gisement des Sagnes, dans le Limousin.

La solubilisation de l'uranium peut être provoquée par de nombreux facteurs, parmi lesquels nous citerons: les gaz en solution, les sels, les bactéries, les substances organiques, etc. Les solutions provenant du lessivage naturel des sulfures de fer constituent également un milieu particulièrement favorable à la solubilisation de l'uranium.

Actuellement trois mines du Commissariat à l'énergie atomique produisent des eaux d'exhaure contenant de l'uranium: ce sont les mines de Fanay dans le Limousin, de l'Ecarpière et de la Chapelle Largeau en Vendée.

Bien entendu, toutes les eaux de drainage de ces mines ne sont pas uranifères mais un inventaire et une classification des diverses venues d'eau en fonction de leurs teneurs en uranium nous ont permis de réaliser, au fond de chacune de ces mines, un circuit d'exhaure pratiquement stérile et un circuit d'exhaure uranifère.

La classification des venues d'eau en fonction de la teneur en uranium a pu être réalisée grâce à l'utilisation sur place d'une méthode de dosage colorimétrique rapide mise au point par les services du CEA.

A l'Ecarpière, la production d'eau uranifère est de l'ordre de 20 à 30 $m^3/h$ titrant en moyenne 100 mg d'uranium par litre. Nous pensons, en 1966, récupérer 18 à 25 tonnes de métal.

A la Chapelle Largeau, le poids de métal récupéré en 1966 sera de l'ordre de 4 t. Les débits horaires sont de 5 $m^3/h$ et la teneur moyenne en U de 100 mg/l. A Fanay, actuellement en cours d'équipement, nous pensons récupérer en 1967 un poids de métal de l'ordre de 20 à 25 t.

Le traitement des eaux uranifères de la mine de l'Ecarpière, par suite de la proximité de l'usine chimique, n'a posé aucun problème particulier. Il nous a suffi, en effet, de pomper ces eaux directement dans l'usine où nous les traitons par passage après clarification et acidification sur des colonnes de résines installées spécialement pour effectuer ce travail.

Dans les mines de la Chapelle Largeau et de Fanay, distantes des usines chimiques de 40 km pour la première et 20 km pour la seconde, la question du choix du procédé à adopter pour la récupération de l'uranium s'est posée.

Il nous fallait adopter un procédé relativement simple, pouvant être conduit par du personnel non spécialisé avec des dépenses comparables à celles du procédé de récupération par résines échangeuses d'ions.

Nous avons donc pensé au procédé de traitement des eaux uranifères par neutralisation par la chaux. Le but de cette neutralisation étant de produire un préconcentré calcique à teneur suffisamment élevée permettant son transport sans trop de frais à l'usine chimique pour le retraiter par redissolution sulfurique et passage sur résines.

Des essais de traitement des eaux minéralisées par ce procédé ont été réalisés au laboratoire du Service d'études de concentration de la Direction des productions. Ces essais avaient pour but de confirmer la validité de la méthode dans ce cas particulier et de fixer les paramètres nécessaires à la réalisation d'une installation industrielle.

## RESULTATS DES ESSAIS

L'échantillon d'eau étudié répondait à l'analyse suivante:

| | |
|---|---|
| U | 100 mg/l |
| $Fe^{2+}$ | traces |
| $Fe^{3+}$ | 53 mg/l |
| $Al^{3+}$ | 25 mg/l |
| $PO_4^{3-}$ | traces |
| $SiO_2$ | 66 mg/l |
| $SO_4$ | 1890 mg/l |
| pH | 2, 90 |
| EH | 530 mV |

Les études ont porté sur trois points:

a) neutralisation proprement dite par un lait de chaux à 200 g de chaux/l;
b) décantation à l'aide d'une solution de séparan NP/10 à 1‰ ;
c) reprise sulfurique de l'uranate de chaux produit.

Nous indiquons en suivant les résultats obtenus:

| | | |
|---|---|---|
| Neutralisation | pH après neutralisation | 7 |
| | Durée de l'opération | 1 h |
| | U ‰ dans la solution à pH 7 | 1 mg/l |
| | Chaux consommée | 700 g/$m^3$ d'eau d'exhaure |
| Décantation | Séparan consommé | 5 g/$m^3$ d'eau d'exhaure |
| | Vitesse de décantation | 2 m/h |
| | Concentration en solide de la pulpe décantée après 24h | 30 g/l |
| | Teneur en U du précipité obtenu sur sec | 15% |
| Reprise sulfurique | Acide sulfurique consommé | 9 kg/kg d'uranium |
| | Durée de l'opération | 1 h |
| | pH terminal | 1, 2 |
| | Rendement de l'opération | 99, 8% |

Les résultats des essais ayant confirmé la possibilité de traitement des eaux uranifères par neutralisation par la chaux, nous avons étudié la réalisation d'une installation capable de traiter 5 $m^3$/h sur le siège minier de la Chapelle Largeau.

## DESCRIPTION DE L'INSTALLATION

Les débits et les caractéristiques des divers appareils utilisés sont indiqués sur le schéma de marche de la figure 1.

Les eaux pompées de la mine sont reçues dans un bassin de stockage de 50 $m^3$ afin de donner une certaine autonomie à la station de pompage du fond de la mine et à la station de traitement des eaux. A partir de ce bassin, les eaux sont pompées en continu et circulent dans deux cuves de neutralisation.

La première cuve reçoit directement le lait de chaux, qui est préparé une fois par jour, à un débit réglé automatiquement à l'aide d'un pH mètre régulateur. Les électrodes sont installées au déversement de la deuxième cuve de neutralisation.

La solution de séparan préparée également une fois par jour est ajoutée au débit nécessaire dans la goulotte de déversement par trop plein de la deuxième cuve de neutralisation dans l'épaississeur de 7 m de diamètre.

La surverse de l'épaississeur stérile est rejetée à la rivière, sans crainte de pollution des eaux. La sousverse est reprise par pompe puis alimente par gravité un filtre-presse sous une dénivellation de 2, 50 m environ.

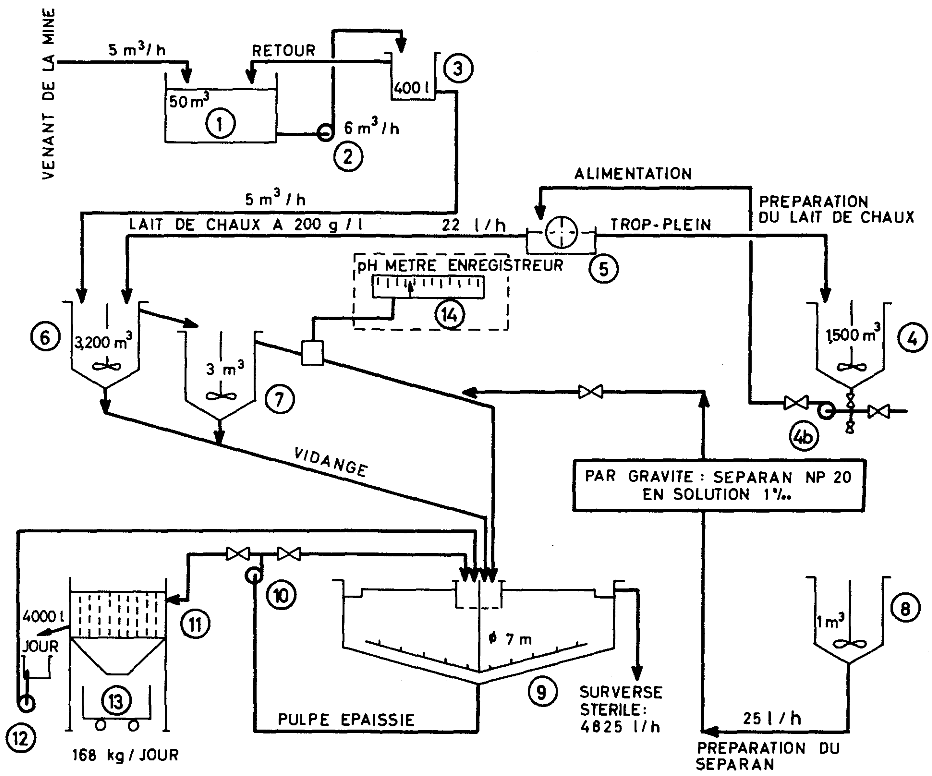

Fig. 1. Traitement des eaux minéralisées dans l'installation de la Chapelle Largeau.

1. Bassin de 50 m$^3$.
2. 1 pompe inox. 5 m$^3$/h.
3. Cuve à débit constant de 400 litres.
4. 1 conditionneur à lait de chaux de 1, 5 m$^3$.
4. bis. Pompe « Délasco ».
5. 1 distributeur à lait de chaux type godets Minerais et Métaux.
6. 1 cuve inox. de 3, 200 m$^3$ avec agitateur.
7. 1 cuve en acier ordinaire de 3 m$^3$ avec agitateur.
8. 1 cuve préparation floculant de 1 m$^3$ avec agitateur.
9. 1 épaississeur de 7 m de diam.
10. 1 pompe Dorrco de 2 pouces.
11. Filtre « Liogier ».
12. Pompe « Plastilac ».
13. Cuve de stockage des uranates.
14. pHmètre enregistreur.

## RESULTATS STATISTIQUES DE LA MARCHE INDUSTRIELLE

| | |
|---|---|
| Débit horaire | 5 $m^3/h$ |
| pH avant neutralisation | 3 |
| Teneur en U des eaux uranifères | 100 mg/l |
| Chaux consommée | 500 $g/m^3$ |
| pH après neutralisation | 8 à 9 |
| Séparan consommé | 3 $g/m^3$ |
| Teneur en U de la surverse | 1 mg/l |
| Poids de précipité par litre à la sousverse de l'épaississeur | 35 g/l |
| Teneur en U du précipité | 12% |
| Teneur en humidité du précipité filtré | 80% |

Les résultats obtenus industriellement ont confirmé les essais de laboratoire et actuellement nous sommes en train de réaliser à Fanay une installation de ce type, d'une capacité horaire de 40 $m^3/h$.

## CONCLUSION

En France, comme nous venons de le voir, les tonnages d'uranium pouvant être récupérés à partir des eaux de drainage uranifères des mines sont importants.

Compte tenu de la valeur du métal et des dépenses relativement faibles à engager pour récupérer l'uranium, l'économie de l'opération est remarquablement intéressante.

Nos efforts se sont limités, jusqu'à présent, à l'inventaire des venues d'eau naturellement uranifères et à la mise en place dans nos mines les plus favorisées de stations de traitement de ces eaux minéralisées.

Dans un deuxième stade, nos efforts vont porter vers l'accélération du processus de solubilisation in situ, soit sur des panneaux déjà exploités, soit sur des panneaux minéralisés mais inexploitables économiquement par les méthodes minières classiques.

Une voie très prometteuse s'ouvre devant nous et nous l'abordons actuellement avec beaucoup d'espoir de réussite.

# TRAITEMENT PAR LIXIVIATION NATURELLE DES MINERAIS URANIFERES PORTUGAIS

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TREATMENT OF URANIUM ORES BY NATURAL LEACHING IN PORTUGAL. The technique described for treating uranium ores by natural leaching has been developed as a result of research carried out in Portugal with a view to determining and eliminating the causes of uranium migration in ores stored in the open.

With the natural leaching method, which has been successfully applied to primary uranium ores, the ore is piled up on a waterproof surface and sprayed intermittently with mine water. Pyrite and ferrous sulphate are used as solid reagents and are mixed with the ore in amounts averaging 0. 4% and 0. 2% respectively.

Over 70 000 tons of ore with a $U_3O_8$ content of between 0. 076 and 0. 150% have been treated at five natural leaching plants. The average recovery in these operations was between 57. 7 and 85. 9%. The average cost was US $3. 31/lb $U_3O_8$.

TRAITEMENT PAR LIXIVIATION NATURELLE DES MINERAIS URANIFERES PORTUGAIS. Le traitement des minerais uranifères par lixiviation naturelle est le fruit des recherches effectuées au Portugal dans le but de déterminer et d'éliminer les causes de la migration de l'uranium contenu dans les minerais emmagasinés à ciel ouvert.

La méthode de lixiviation naturelle, appliquée avec succès aux minéraux primaires d'uranium, consiste essentiellement en l'arrosage intermittent, avec l'eau des mines, du minerai entassé sur des aires imperméabilisées. On utilise comme réactifs solides la pyrite et le sulfate ferreux mélangés avec le minerai à raison de 0, 4% et 0, 2% respectivement en moyenne.

Plus de 70 000 t de minerai, dont les teneurs en $U_3O_8$ étaient comprises entre 0, 076% et 0, 150%, ont été traitées dans cinq installations de lixiviation naturelle où on a obtenu des récupérations moyennes oscillant entre 57, 7% et 85, 9%, pour le prix de revient moyen de 3, 31 dollars par livre de $U_3O_8$.

## 1. INTRODUCTION

La méthode de traitement des minerais uranifères par lixiviation naturelle a été mise au point, au Portugal, par les techniciens de la Companhia Portuguesa de Radium, Ld$^{\underline{a}}$ (CPR, Ld$^{\underline{a}}$), qui se sont appuyés sur les études et essais effectués au Chemical Research Laboratory (CRL) de Teddington (Angleterre), principalement pendant la phase expérimentale.

Cette méthode est le fruit des recherches effectuées en vue de déterminer et d'éliminer les causes de la migration de l'uranium contenu dans les minerais stockés à l'air libre. Elle a été appliquée par la CPR, Ld$^{\underline{a}}$ à l'échelle industrielle dans plusieurs mines de 1953 à 1962, et ensuite par la Junta de Energia Nuclear (JEN) dans les établissements de la mine de Urgeiriça.

Les minerais soumis à la lixiviation naturelle proviennent tous de filons renfermant des minéraux primaires et secondaires d'uranium, contenus dans les granites de la province de Beira Alta.

L'idée d'appliquer la lixiviation naturelle au traitement des minerais uranifères a pris corps lorsqu'on s'est rendu compte que les minerais primaires, après exposition prolongée aux intempéries, avaient perdu un pourcentage élevé d'uranium [1].

Après avoir constaté cette fuite, les techniciens de la CPR, Ldª ont reçu l'ordre [2] de procéder à l'examen des points suivants:

- Migration de l'uranium dans les conditions naturelles
- Prévention de cette migration
- Développement de méthodes fondées sur l'utilisation de cette migration comme moyen pratique de lixiviation.

Les recherches sur la prévention de la migration ont été abandonnées à la suite de quelques expériences [3] menées sur des tas de minerais recouverts de chaux, qui n'ont pas permis d'éviter les pertes d'uranium.

Le développement de méthodes fondées sur la lixiviation naturelle a, par suite, acquis plus d'importance, et tous les essais se sont poursuivis dans ce sens.

Les recherches ont été effectuées dans une installation constituée par sept réservoirs de 2,0 × 2,0 × 1,5 m, d'une capacité de 9 t (fig. 1).

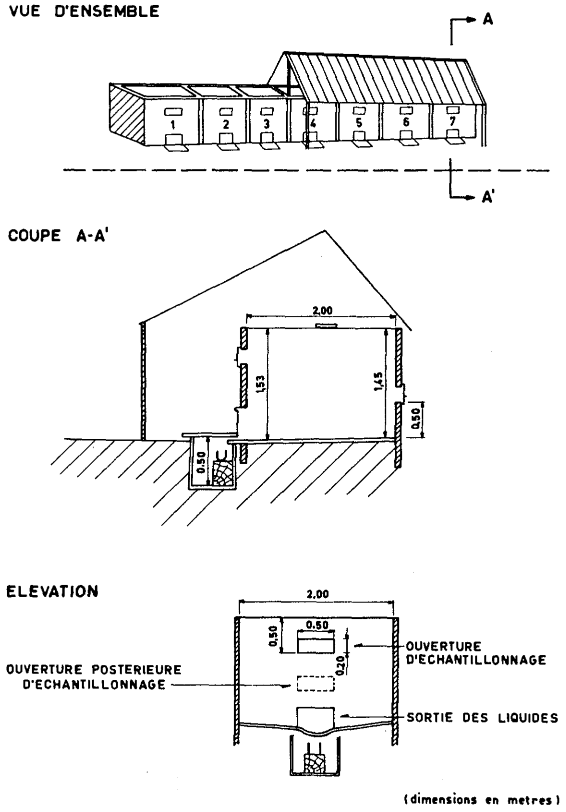

FIG. 1. Installation expérimentale de lixiviation naturelle.

Les essais consistaient à remplir les réservoirs de minerais provenant de différentes mines et de granulométrie variable; trois de ces réservoirs étaient exposés à l'action du temps tandis que les quatre autres étaient soumis à des arrosages systématiques.

Plus tard, quand il a été nécessaire d'effectuer un grand nombre d'expériences pour comparer plusieurs méthodes et réactifs, les essais ont dû être faits à l'abri des intempéries, dans des tuyaux en grès d'une capacité de 150 kg de minerai concassé à -1/2 pouce, chaque récipient étant arrosé avec 500 litres d'eau par jour.

Les essais en laboratoire et à l'échelle pilote et les enseignements qu'on a pu tirer de l'application industrielle de la méthode ont permis de déterminer les facteurs dont dépendait le rendement de la lixiviation naturelle des minerais d'uranium portugais.

## 2. FACTEURS PRINCIPAUX INFLUENCANT LA LIXIVIATION NATURELLE

### 2.1. Type de minerai

Comme on pouvait s'y attendre, les essais ont confirmé que le rendement de la lixiviation dépend des caractéristiques minéralogiques, chimiques et physiques du minerai, ce qui ressort du tableau I où sont indiquées les quantités cumulées, en pourcentage de la teneur initiale en uranium, extraites des minerais soumis à l'action exclusive de la pluie, pendant une période de quatre ans.

Ces chiffres montrent bien que le rendement de la lixiviation dépend des caractéristiques mentionnées et, en particulier, que les minerais secondaires ne subissent pas de perte appréciable quand ils sont exposés à l'action de la pluie.

Ainsi surgit la première limitation, d'ailleurs confirmée par la pratique industrielle, du champ d'application de la lixiviation naturelle: elle ne peut pas être appliquée avec succès au traitement des minerais secondaires d'uranium.

### 2.2. Présence de pyrite dans le minerai

Les essais en laboratoire et à l'échelle pilote ont montré que la présence de pyrite est indispensable pour déclencher et entretenir les réactions qui donnent lieu à la lixiviation naturelle des minerais d'uranium. Ces réactions sont probablement produites par l'altération de la pyrite qui, au contact de l'eau et de l'oxygène de l'air, donnerait du sulfate ferrique et de l'acide sulfurique, le sulfate constituant l'agent oxydant qui pourrait permettre le passage de l'uranium tétravalent, peu soluble dans l'acide sulfurique dilué, à l'uranium hexavalent, facilement soluble [4].

L'action lixiviante de la pyrite peut encore être accrue par l'adjonction de sulfate ferreux qui, en quantités inférieures à 1% du minerai à traiter, accélère l'extraction de l'uranium.

Bien que la pyrite joue un rôle essentiel dans le mécanisme de la lixiviation naturelle, sa capacité de réaction dépend de son type minéralogique; ainsi on a constaté parfois que, dans certains minerais qui en contenaient, la lixiviation ne se déclenchait pas. C'est le cas [5] par exemple d'un minerai primaire de la mine de Bica, où la lixiviation ne s'est pas faite malgré la présence de pyrite dans le tout venant; cependant ce même minerai, après avoir été mélangé avec de la pyrite d'une autre provenance, a donné les taux d'extraction suivants:

Après 6 mois, 42% de l'uranium initial
Après 12 mois, 56% de l'uranium initial
Après 18 mois, 60% de l'uranium initial

TABLEAU I. QUANTITES D'URANIUM EXTRAITES DE MINERAIS SOUMIS A L'ACTION EXCLUSIVE DE LA PLUIE

| Minerai | | Durée du traitement (années) | Extraction totale (%) |
|---|---|---|---|
| Provenance | Type | | |
| Rosmaneira | Primaire avec des pyrites visibles | 1 | 41 |
| | | 2 | 61 |
| | | 3 | 69 |
| | | 4 | 71 |
| Reboleiro | Primaire avec des pyrites visibles | 1 | Traces |
| | | 2 | 6 |
| | | 3 | 8 |
| | | 4 | 30 |
| Reboleiro | Secondaire sans pyrites visibles | 1 | Traces |
| | | 2 | Traces |
| | | 3 | Traces |
| | | 4 | Traces |
| Reboleiro | Secondaire avec des pyrites additionnées | 1 | 27 |

L'action de la pyrite dépend aussi en grande partie de la granulométrie de broyage et du degré d'altération au moment où commence le traitement par lixiviation naturelle. La granulométrie doit être la plus fine possible, sans toutefois nuire à la circulation de l'air et de l'eau dans le tas de minerai.

Les résultats des essais entrepris pour déterminer l'influence de la pyrite et du sulfate ferreux sur la lixiviation des minerais d'uranium sont donnés par les courbes des figures 2 et 3.

La figure 2 donne les courbes d'extraction de trois minerais différents – de Rosmaneira, de Urgeiriça et de Bica; les deux premiers ont été traités seulement avec la pyrite du tout venant tandis qu'au dernier a été ajoutée de la pyrite d'une autre origine, parce que celle qu'il contenait n'était pas oxydable [1, 5]. Sur ces courbes d'extraction on peut distinguer trois phases:

a) Phase initiale d'extraction lente, d'une durée de deux mois environ;
b) Phase intermédiaire de courte durée, mais avec une vitesse d'extraction plus grande;
c) Phase finale d'extraction lente et de vitesse décroissante.

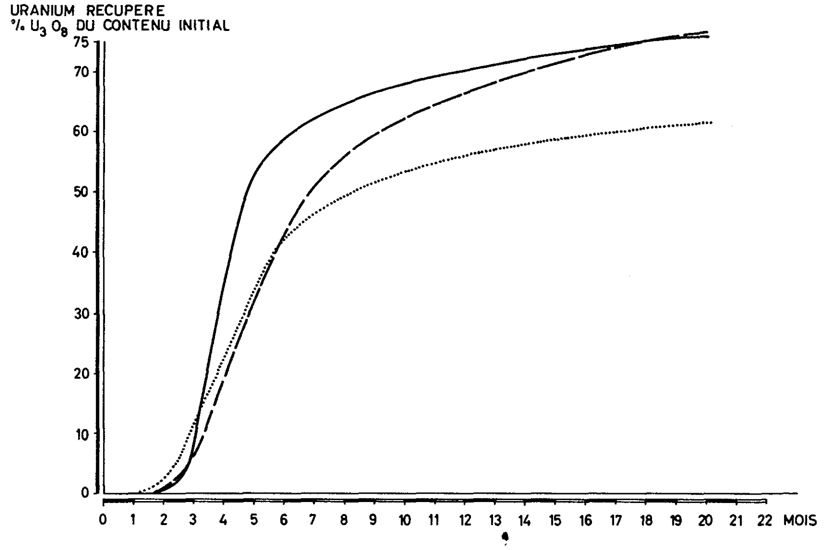

FIG. 2. Minerais à faible teneur en uranium: rendement d'extraction (essais à grande échelle).

________ Minerai de Rosmaneira
_ _ _ _ _ Minerai de Urgeiriça
.......... Minerai de Bica (pyrite)

Etant donné que la plus grande partie de l'uranium récupérable est extraite dans un court laps de temps, qui correspond à la phase b), on aura tout intérêt, lors de l'application industrielle de la méthode, à réduire la phase a) et à prolonger le plus possible la phase b), de façon à obtenir une récupération raisonnable avant la phase c) qui pourra ainsi être abandonnée.

A cette fin, on a fait une série d'essais avec du minerai de Urgeiriça additionné de pyrite et de sulfate ferreux ou de pyrolusite. Les résultats obtenus sont représentés à la figure 3; ils montrent que l'extraction n'a pas été influencée par la pyrolusite, mais qu'elle a été accélérée par la pyrite et par le sulfate ferreux, principalement dans le cas où ces deux réactifs avaient été ajoutés au minerai.

## 2.3. Granulométrie de broyage et hauteur des tas de minerai

Les essais effectués ont mis en évidence l'influence de la granulométrie de broyage sur la récupération de l'uranium, comme on peut le voir sur le tableau II où sont donnés, pour des minerais de plusieurs origines, les pourcentages d'uranium extrait pour chaque granulométrie au bout de 21 mois de traitement. Ces chiffres montrent clairement que le rendement d'extraction augmente lorsque la granulométrie diminue; cependant, on ne peut pas descendre au-dessous d'une valeur déterminée à partir de laquelle la circulation de l'eau et de l'air dans le minerai devient difficile, ce qui a un effet nuisible sur l'extraction.

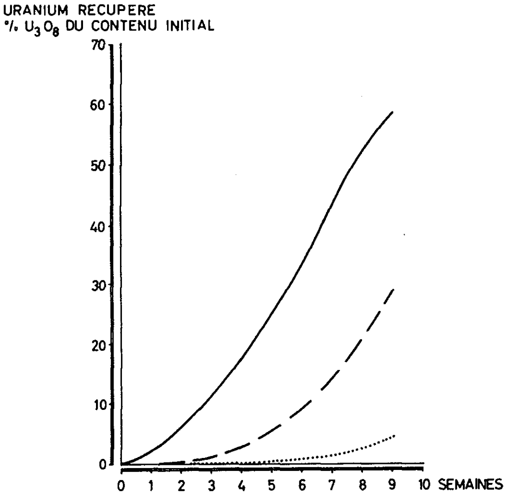

FIG. 3. Minerais à faible teneur en uranium: rendement d'extraction (essais à petite échelle).

——————— + 5 kg de pyrite, 10 kg de sulfate ferreux
– – – – – + 10 kg de pyrite
.......... + 5 kg de pyrite, 10 kg de pyrolusite

## TABLEAU II. TAUX D'EXTRACTION (%) EN FONCTION DE LA GRANULOMETRIE

| Provenance du minerai | Granulométrie | | |
|---|---|---|---|
| | +1" | -1"/+1/4" | - 1/4" |
| Urgeiriça | 37 | 69 | 87 |
| Rosmaneira | 57 | 56 | 76 |
| Bica | 0 | 51 | 66 |

Dans la pratique on a adopté la granulométrie - 1" pour tous les minerais soumis à la lixiviation naturelle, et -1/2" dans quelques cas particuliers. Cependant, on a vérifié le degré d'imperméabilité des tas de minerai chaque fois que celui-ci contenait un haut pourcentage de grains fins ou qu'il était argileux.

La hauteur des tas de minerai exerce aussi une influence sur le rendement de la lixiviation; il doit exister un rapport optimal entre la granulométrie et la hauteur des tas. Etant donné que les informations disponibles étaient insuffisantes pour nous permettre de fixer ce rapport, nous avons adopté pour les applications industrielles une hauteur de 2 m pour les tas de minerai ayant les granulométries indiquées ci-dessus, cette hauteur pouvant toutefois atteindre 6 m dans le cas des tas placés à flanc de coteau, donc sur une base inclinée.

### 2.4. Alternance de périodes humides et sèches

Quand la lixiviation naturelle a été appliquée à l'échelle industrielle, on a constaté que, pour obtenir une extraction d'uranium satisfaisante, les tas de minerai devaient passer alternativement par des périodes sèches et humides, les arrosages ne pouvant pas être continus.

La périodicité des arrosages a été fixée d'une manière empirique, en fonction surtout de la pluviosité, mais le régime préféré en temps sec a été celui des arrosages quotidiens d'une durée de 3 à 4 h, soit en une fois, soit par périodes de 1 à 2 h échelonnées au cours de la journée.

### 2.5. Température

Tant les essais de laboratoire [6] que les essais à l'échelle industrielle ont prouvé l'influence de la température sur les réactions de lixiviation; celles-ci sont intensifiées par l'élévation de la température jusqu'à une limite supérieure de 40°C environ, mais elles cessent au-dessus de cette valeur, en raison peut-être de la diminution ou même de la cessation de l'activité des bactéries oxydantes.

Il existe aussi une limite inférieure de température au-dessous de laquelle les réactions de lixiviation s'effectuent lentement ou sont pratiquement nulles.

Le fonctionnement des installations industrielles de traitement par lixiviation naturelle est toujours influencé par la baisse de la température de l'air en hiver, comme le montre l'exemple donné à la figure 4 où l'on voit les concentrations des liqueurs produites par cinq tas de minerai de Urgeiriça traités dans ces installations entre août 1964 et avril 1965; ce graphique donne également les températures moyennes de l'air observées au cours de la même période.

Dans la pratique, comme dans les installations de lixiviation naturelle, le minerai reste toujours exposé aux intempéries et on ne peut guère éviter l'effet gênant des températures basses. On ne peut que fixer la date du commencement du traitement de façon à faire coïncider la période des températures favorables avec la phase b).

### 2.6. Bactéries oxydantes

Des recherches faites avant 1957 sur des minerais d'uranium portugais au Chemical Research Laboratory de Teddington ont montré que certains types de bactéries influençaient la lixiviation de l'uranium [6]. Le service de microbiologie de ce laboratoire a identifié *Thiobacillus thio-oxidans* et *Ferrobacillus ferro-oxidans* dans les minerais de Urgeiriça et de Bica, et *Thiobacillus thioporus* dans des minerais de Valinhos.

On a préparé des cultures des deux premières espèces isolées avec lesquelles ont été ensemencés des échantillons de minerais des trois mines citées, qui ont ensuite été soumis à des essais de lixiviation avec de la pyrite et du sulfate ferreux; à des fins de comparaison on a préparé en même temps des échantillons stérilisés.

D'une façon générale, les extractions obtenues dans le cas des échantillons inoculés ont été supérieures à celles des échantillons stérilisés, ce qui faisait penser que les espèces présentes de bactéries favorisaient la lixiviation des minerais étudiés. Cependant, les résultats n'ont pas été totalement concluants.

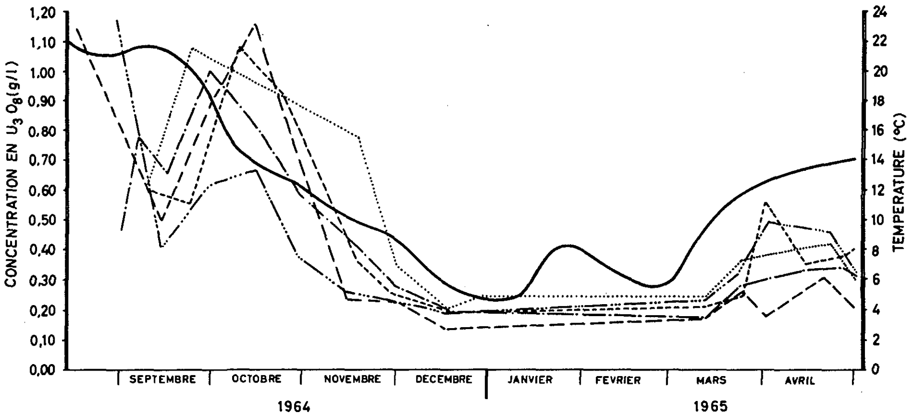

FIG. 4. Concentration des liqueurs et température moyenne de l'air.

———— Température moyenne de l'air
— — — — — Tas n° 1
—·· —·· — Tas n° 2
—·—·—·— Tas n° 3
- - - - - Tas n° 4
········· Tas n° 5

## 3. APPLICATIONS INDUSTRIELLES DE LA LIXIVIATION NATURELLE

La méthode de lixiviation naturelle des minerais d'uranium a été appliquée à l'échelle industrielle dans le but de traiter des minerais qui auraient été rejetés comme stériles en raison de leur teneur trop basse pour être compatible avec les conditions techniquo-économiques de l'usine de traitement classique existant au Portugal. Ainsi, les minerais pouvant être traités par lixiviation naturelle ont été considérés d'abord comme des produits sans valeur pour la gestion et, à partir de 1957, comme des sous-produits n'ayant d'autre valeur que celle relative aux dépenses afférentes à l'extraction de la mine.

Selon le critère ci-dessus, étaient destinés à la lixiviation naturelle tous les minerais qui, à la sortie de la mine, avaient une teneur en $U_3O_8$ inférieure à 0,15%, limite qui, depuis 1962, a été abaissée à 0,12%;

## TABLEAU III. FONCTIONNEMENT DES INSTALLATIONS DE LIXIVIATION

| Installation | Alimentation | | Réactifs (kg/t) | | Durée du traitement (mois) | Teneur en $U_3O_8$ du résidu (%) | Récupération (%) |
|---|---|---|---|---|---|---|---|
| | Tonnes humides | (%) $U_3O_8$ | Pyrite | Sulfate ferreux | | | |
| Bica | 22172 | 0,134 | 4,0 | 1,4 | 20,5 | 0,057 | 57,7 |
| Rosmaneira | 6380 | 0,150 | 4,0 | 1,8 | 17 | 0,058 | 61,6 |
| Urgeiriça | 24760 | 0,076 | 3,7 | 2,9 | 13 | 0,019 | 75,0 |
| Vale de Arca | 4755 | 0,109 | 5,3 | 2,1 | 18 | 0,031 | 71,6 |
| Valinhos | 12365 | 0,093 | 8,0 | 5,8 | 18 | 0,014 | 85,9 |

le tableau III donne les teneurs moyennes pour chaque installation. Le schéma du traitement de ces minerais est le suivant:

- Criblage à - 1''
- Addition de pyrite et de sulfate ferreux
- Déversement du minerai sur des aires ou dans des réservoirs imperméabilisés, en tas de 2 à 6 m de hauteur
- Arrosage intermittent des tas
- Récolte des liqueurs produites
- Précipitation par la magnésie de l'uranium contenu dans les liqueurs, ou envoi des liqueurs à l'usine de traitement lorsque celle-ci est proche.

Ce schéma a été appliqué dans des installations construites spécialement, qui sont décrites ci-après ainsi que leur fonctionnement et les résultats obtenus.

## 3.1. Caractéristiques des installations

Les installations de lixiviation naturelle sont constituées par les aires où est déposé le minerai, le réservoir où sont recueillies les liqueurs résultant des arrosages, et, dans les installations qui ne se trouvent pas à proximité de l'usine du traitement, l'atelier de précipitation des liqueurs.

Les aires de stockage du minerai ont été construites de la manière la plus simple; on a cherché à éviter les mouvements de terrain et à profiter autant que possible de la pente pour obtenir une disposition en cascade, de façon à rendre inutile l'usage de pompes. Les aires sont constituées par une plate-forme en béton imperméabilisée avec du Flintkote n° 5 Shell, et par des parois latérales sans fonction de soutènement, qui servent seulement à retenir les liqueurs (raison pour laquelle elles sont enduites du même produit que le fond).

Dans les régions peu accidentées, par exemple Urgeiriça, les réservoirs sont tous sur le même plan; ils reposent sur une couche de pierres (fig. 5); la figure 6 montre le cas d'une installation située au flanc d'un coteau, où les aires ont été construites en gradins, pour éviter de grandes excavations. Presque tout le fond repose sur du granite; seules les parties altérées sont enlevées et imperméabilisées avec du Flintkote.

Les ateliers de précipitation sont de simples bâtiments démontables (fig. 7) où se trouvent placés les cuves de précipitation des liqueurs et un dispositif de filtrage des concentrés obtenus.

On a construit cinq installations de lixiviation (tableau IV), elles consistent en 21 aires de stockage d'une surface totale de 9346 m$^2$.

Le prix de revient des aires a varié entre 106, 90 escudos/m$^2$ pour les installations sur des endroits plats, et 251, 60 escudos/m$^2$ pour celles situées à flanc de coteau. Le prix de revient moyen des cinq installations a été de 164, 40 escudos/m$^2$.

## 3.2. Fonctionnement des installations

### 3.2.1. Constitution des tas de minerai

Dans chaque installation on mélange les minerais provenant de la mine à laquelle elle appartient avec des minerais des mines les plus proches et, dans certains cas (Urgeiriça et Valinhos), on les mélange de plus avec des sables de l'usine de traitement chimique de Urgeiriça, qui améliorent la lixiviation grâce à leur bas pH et apportent encore quelques résidus d'uranium.

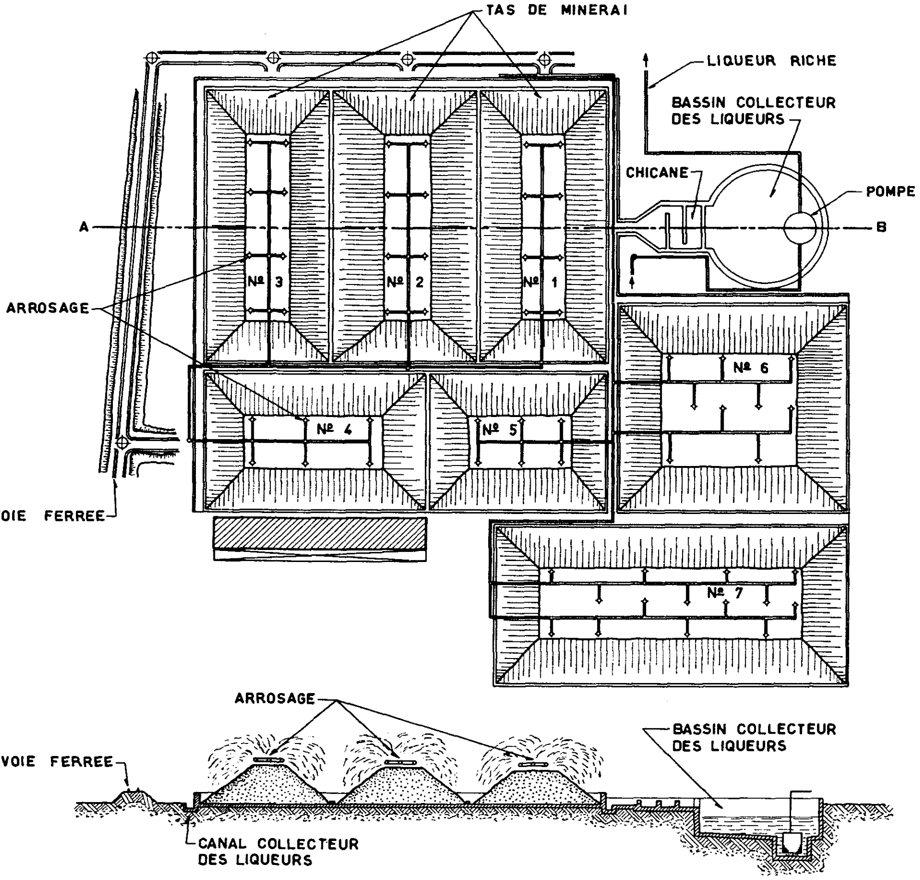

FIG. 5. Installation d'Urgeiriça.

Le minerai de chaque mine, ou chaque type particulier de minerai provenant de la même mine, est étudié au préalable pour déterminer les pourcentages de pyrite et de sulfate ferreux nécessaires à une bonne extraction. A la sortie de la mine, le minerai est criblé à -1", il reçoit les apports estimés nécessaires, puis il est déversé dans les réservoirs de lixiviation. On peut voir au tableau III les quantités moyennes de réactifs utilisées dans chaque installation.

Dans l'installation de Urgeiriça, on essaie maintenant de constituer les tas sans cribler le minerai à 1"; à la fin du traitement, on détermine la quantité de gros qui sont alors, selon leur teneur, broyés et réintroduits dans les réservoirs de lixiviation naturelle ou envoyés à l'usine du traitement chimique.

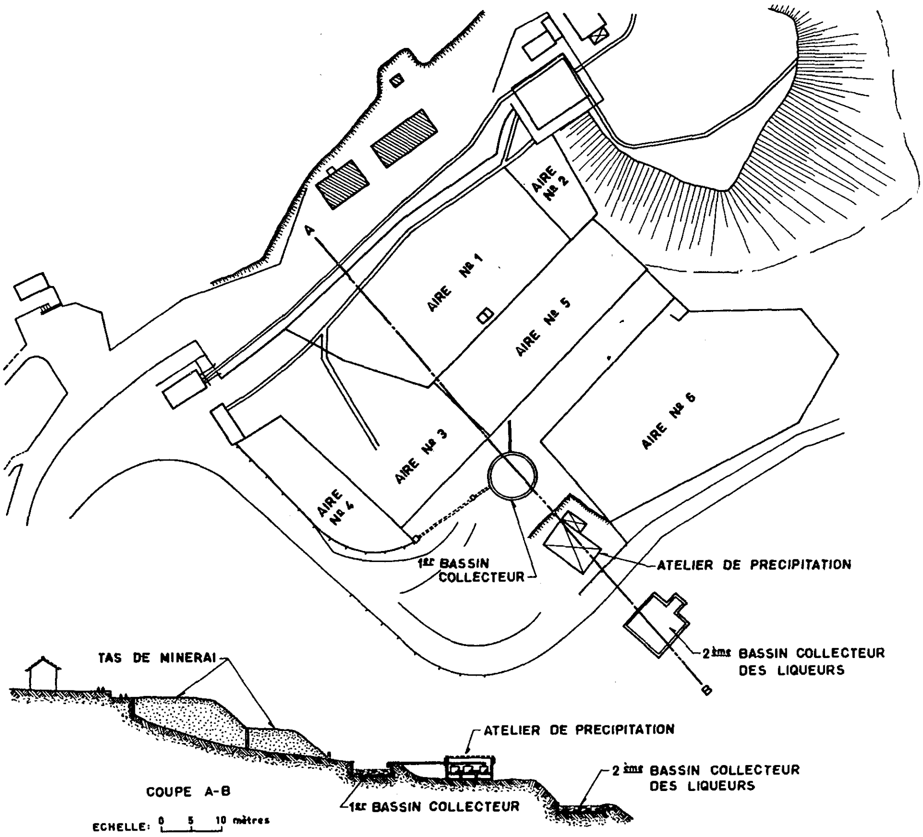

FIG. 6. Installation de Bica.

Le minerai est placé dans les réservoirs en tas d'une hauteur minimale de 2 m; cette hauteur est dépassée dans les installations où les aires sont disposées en gradins, selon l'inclinaison de la base et la largeur des tas.

L'installation d'arrosage, placée directement à la surface supérieure des tas, consiste en une tuyauterie principale de $1\frac{1}{2}''$ avec des ramifications perpendiculaires de $\frac{1}{2}''$ où se trouvent les tourniquets d'aspersion. L'installation est alimentée à partir d'un dépôt élevé, généralement avec de l'eau des mines.

Teneur moyenne

Initialement on ne destinait à la lixiviation naturelle que des minerais dont la teneur en $U_3O_8$ était comprise entre 0,15% et 0,05%; à partir de

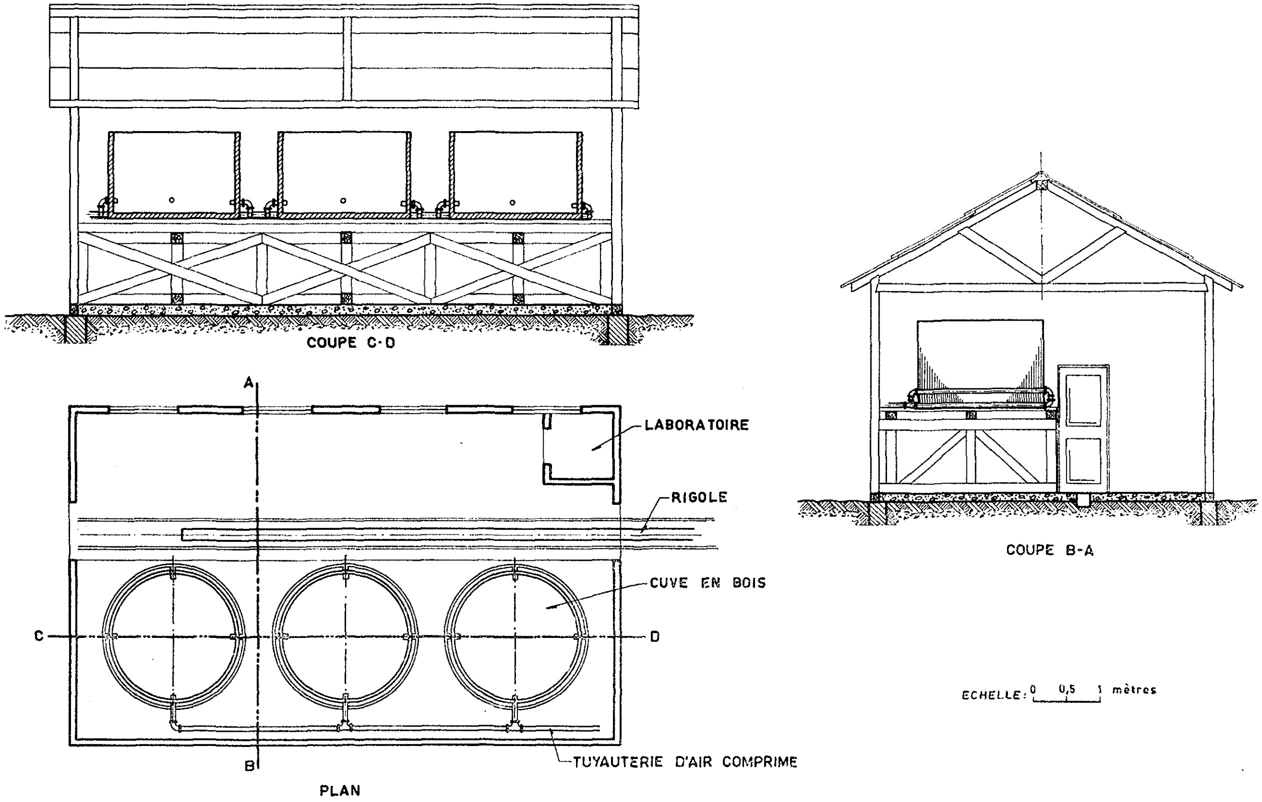

FIG. 7. Atelier de précipitation.

TABLEAU IV. CARACTERISTIQUES DES INSTALLATIONS DE LIXIVIATION

| Installation | Aires | |
|---|---|---|
| | Nombre | Surface ($m^2$) |
| Urgeiriça | 10 | 2252 |
| Rosmaneira | 1 | 600 |
| Bica | 6 | 3720 |
| Valinhos | 2 | 1619 |
| Vale de Arca | 2 | 1115 |

TABLEAU V. POURCENTAGES DE MINERAIS TRAITES PAR CHAQUE METHODE

| Année | Lixiviation naturelle | Usine de traitement |
|---|---|---|
| 1953 à 1962 | 14 | 86 |
| 1963 | 27 | 73 |
| 1964 | 11 | 89 |
| 1965 | 4 | 96 |

1962, pour mieux tirer profit des réserves des mines en exploitation, la limite supérieure a été abaissée à 0,12% (tableau III). Cet abaissement de la teneur supérieure a réduit l'importance de la méthode, les quantités de minerais traités par lixiviation naturelle devenant de plus en plus petites par rapport à celles qui sont envoyées à l'usine de traitement chimique de Urgeiriça (tableau V). (Les chiffres pour 1963 sont sans intérêt, car ils se rapportent à une année où n'ont été effectués dans les mines que des travaux de reconnaissance et de traçage.)

### 3.2.2. Traitement

On commence l'arrosage systématique des tas de minerai en utilisant l'eau de la mine; cette eau présente l'avantage de contenir un peu d'uranium en solution et, généralement, d'être elle-même acide.

La fréquence et la durée des arrosages dépendent de la pluviosité; on les règle de façon à produire des liqueurs ayant des concentrations en uranium convenables. Généralement les arrosages sont quotidiens et d'une durée totale de 3 à 4 heures (un ou plusieurs arrosages); les débits de liqueurs ainsi obtenus oscillent entre 1 et 1, 5 litres/h par $m^2$ d'aire de traitement.

On contrôle le processus de lixiviation en prélevant des échantillons, soit du minerai des tas (avec un tube-sonde de 200 × 5 cm), soit des liqueurs produites par chaque tas. On détermine la teneur moyenne en $U_3O_8$ des échantillons pour calculer le taux d'extraction obtenu; dans le cas des liqueurs, on détermine le pH, les concentrations en $U_3O_8$ et $Fe^{3+}$ et le rapport $Fe^{3+}/U_3O_8$.

On ajuste la fréquence et la durée des arrosages ou la quantité du sulfate ferreux selon les résultats obtenus. Lorsque cela se révèle nécessaire, on répand du sulfate ferreux sur les tas pour accélérer la lixiviation.

### Liqueurs produites

Les liqueurs sont recueillies dans un réservoir et échantillonnées, pour déterminer le pH, les concentrations en $U_3O_8$ et $Fe^{3+}$ et le rapport $Fe^{3+}/U_3O_8$ (tableau VI).

Les liqueurs peuvent ensuite suivre deux chemins différents:

- Dans le cas des installations de lixiviation proches de l'usine de traitement chimique, elles sont pompées et introduites dans le circuit en un point qui dépend de leur concentration en $U_3O_8$.
- Dans le cas des mines éloignées de l'usine de traitement chimique, elles sont envoyées à l'atelier de précipitation de l'installation.

Dans les ateliers de précipitation, les liqueurs sont pompées dans des réservoirs en bois où on leur ajoute du lait de magnésie jusqu'à ce que le pH atteigne une valeur de 6, 3. Le liquide est agité par de l'air comprimé pendant 30 min, après quoi on corrige le pH si cela est nécessaire, on ajoute le floculant Separan NP 10 et on laisse décanter le précipité, qui est ensuite filtré, mis dans des bidons et envoyé à l'usine de traitement chimique de Urgeiriça, où il est séché et emballé.

On peut voir au tableau VI les teneurs moyennes des concentrés obtenus dans les trois installations de lixiviation naturelle où s'effectue la précipitation directe des liqueurs par la magnésie (Bica, Rosmaneira et Vale de Arca).

### Durée du traitement et récupération finale

Quand on a commencé à appliquer la lixiviation naturelle à l'échelle industrielle, on a fixé la durée du traitement à 12 mois au maximum, pour maintenir les frais d'amortissement et d'exploitation dans des limites raisonnables. Dans la pratique, on a constaté qu'il n'était pas possible d'effectuer la lixiviation dans le temps fixé (voir les durées moyennes de traitement données au tableau III pour chaque installation). Cette durée excessive du temps de traitement constitue donc une autre limitation de la méthode. Pour la rendre applicable à d'autres types de minerais plus pauvres, il semble qu'on doive prendre deux mesures:

## TABLEAU VI. LIQUEURS ET CONCENTRES OBTENUS PAR LIXIVIATION NATURELLE

| Installation | Liqueurs | | | | Concentrés |
|---|---|---|---|---|---|
| | pH | $U_3O_8$ (g/l) | $Fe^{3+}$ (g/l) | $\frac{Fe^{3+}}{U_3O_8}$ | $U_3O_8$ (%) |
| Bica | 2,82 | 0,57 | 0,33 | 0,58 | 12,9 |
| Rosmaneira | 2,45 | 0,81 | 0,59 | 0,73 | 8,9 |
| Urgeiriça | 2,98 | 0,31 | 0,65 | 2,10 | - [a] |
| Vale de Arca | 2,63 | 0,46 | 0,62 | 1,35 | 9,0 |
| Valinhos | 3,70 | 0,28 | 0,48 | 1,71 | - [a] |

[a] Les liqueurs des installations de Urgeiriça et de Valinhos sont pompées vers l'usine de traitement chimique.

- Rejeter le minerai des réservoirs quand il entre dans la phase c) (fig. 2), ce qui implique par conséquent une perte appréciable d'uranium;
- Augmenter le nombre et la taille des réservoirs, avec pour conséquence une élévation des frais d'amortissement.

TABLEAU VII. PRIX DE REVIENT DU TRAITEMENT PAR LIXIVIATION NATURELLE EN ESCUDOS/kg $U_3O_8$

| Poste | Installation | | | | |
|---|---|---|---|---|---|
| | Bica | Rosmaneira | Urgeiriça | Vale de Arca | Valinhos |
| Main d'oeuvre | 34,22 | 73,41 | 16,71 | 43,22 | 24,49 |
| Ateliers | 2,01 | 5,25 | 5,54 | 4,77 | 8,00 |
| Laboratoire | 16,04 | 26,39 | 18,73 | 19,45 | 14,33 |
| Réactifs | 32,46 | 35,60 | 3,55 | 28,37 | 18,02 |
| Matériaux divers | 9,16 | 16,20 | 6,37 | 11,11 | 10,70 |
| Traitement à Urgeiriça | 7,45 | 3,93 | 19,77 | 14,29 | 28,49 |
| Transport | 3,63 | 9,04 | 2,96 | 5,47 | 7,43 |
| Divers | 0,66 | 5,53 | 0,98 | 2,27 | 4,04 |
| Dépréciation | 33,70 | 41,73 | 31,50 | 44,15 | 51,63 |
| Frais totaux | 139,44 | 217,08 | 106,11 | 173,10 | 167,13 |

Les récupérations totales obtenues en fin de traitement sont données au tableau III, ainsi que les teneurs des résidus à partir desquelles elles ont été calculées.

On constate que l'on a atteint des récupérations raisonnables principalement à Urgeiriça et à Valinhos, où elles ont été respectivement de 75% et 85,9%. Dans le cas de Bica, la récupération n'a été que de 57,7%, ce qu'on attribue à la haute teneur en carbonates du minerai. Il faut noter qu'au cours de la dernière année d'activité de cette mine il a été nécessaire d'effectuer des arrosages avec de l'acide sulfurique N/10 pour réussir la lixiviation du minerai placé sur les aires.

### 3.2.3. Production et frais

A la fin de 1965 la production de $U_3O_8$ dans les différentes installations de lixiviation naturelle a atteint le total de 44 206 kg, répartis de la manière suivante:

| | |
|---|---|
| Bica | 15 362 kg |
| Rosmaneira | 4 813 kg |
| Urgeiriça | 12 531 kg |
| Vale de Arca | 2 761 kg |
| Valinhos | 8 739 kg |

Les prix de revient ventilés du traitement par lixiviation naturelle se rapportant à cette production figurent sur le tableau VII. Si l'on tient compte de la valeur du minerai, les prix de revient sont les suivants:

| | Escudos/kg $U_3O_8$ | Dollars/livre $U_3O_8$ |
|---|---|---|
| Bica | 210, 22 | 3, 21 |
| Rosmaneira | 378, 28 | 5, 95 |
| Urgeiriça | 141, 64 | 2, 20 |
| Vale de Arca | 403, 40 | 6, 35 |
| Valinhos | 189, 67 | 2, 98 |

Le prix de revient moyen pondéré tenant compte de la valeur du minerai est, pour les cinq installations, de 210,77 escudos/kg $U_3O_8$, soit 3, 31 dollars/livre $U_3O_8$.

Ce prix de revient est assez bas, mais on doit remarquer que, selon le critère de gestion adopté, le minerai destiné à la lixiviation naturelle est considéré comme un sous-produit de l'exploitation des mines; dans le calcul de sa valeur on ne considère pourtant que les dépenses afférentes à l'extraction et au transport à la surface.

## REFERENCES

[1] BYRNE, J.S., Natural Leaching.

[2] Correspondance échangée entre la CPR, Ldª et le CRL.

[3] Rapports de travail de la CPR, Ldª.

[4] WELLS, R.A., Observations on Natural Leaching.

[5] RAMOS, A.G., Lixiviação Natural de Minérios de Urânio Portugueses (1963).

[6] WELLS, R.A., MILLER, R.P., NAPIER, E., Natural Leaching of Uranium Ores, Part I, Preliminary Tests on Portuguese Ores;
AUDSLEY, A., DABORN, G.R., Natural Leaching of Uranium Ores, Part II, Study of the Experimental Variables.

# PRODUCTION OF HIGH-PURITY URANIUM AT A SOUTH AFRICAN GOLD MINE *

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## Abstract

PRODUCTION OF HIGH-PURITY URANIUM AT A SOUTH AFRICAN GOLD MINE. The chemistry of the Bufflex solvent-extraction process is described. Uranium is extracted by a tertiary amine solvent, from which the impurities are removed by means of dilute ammonia, and the uranium is stripped by an ammonium sulphate strip. In the pilot plant, these processes are carried out in mixer-settlers. Details of pumps, flow controllers, and materials of construction are given. The operation of the extraction, scrub, strip, precipitation and thickening, and regeneration sections is described. Comparative tests on the elution of ion-exchange resin with 10% sulphuric acid, and with nitrate, are described. The results of resin analyses and plant tests are given. A breakdown of the costs of reagents in the Bufflex process, compared with the conventional process, is given. It is concluded that a solvent-extraction process treating the sulphuric acid eluate from ion-exchange columns is technically feasible. As regards the resin itself, elution with 10% sulphuric acid is satisfactory. There is more polythionate build-up than with nitrate elution, and the capacity of the resin is slightly lower, but the difference is small. The operating cost of the Bufflex process is cheaper by at least 5 ¢/lb $U_3O_8$ produced. The product satisfies the most stringent specification for nuclear-grade uranium, except as regards cobalt, molybdenum, silicon, and hafnium.

## 1. INTRODUCTION

A co-operative research programme was undertaken by the Atomic Energy Board and Buffelsfontein Gold Mining Company Ltd. to investigate the production of nuclear-grade uranium by a combination of the sulphuric acid elution and solvent-extraction processes. It was decided that a fairly large pilot plant would be needed for this purpose, since polythionate build-up on ion exchange resin could be a serious problem, and this could only be tested satisfactorily on a set of large columns. One of the six sets of columns of the Buffelsfontein uranium plant was set aside for this purpose, since it was more economical and convenient than building a new set.

## 2. THE SOLVENT-EXTRACTION PROCESS

Solvent extraction can be defined, for the present purposes, as the extraction of a metal from an aqueous solution by an immiscible organic solvent, and the subsequent stripping (or back-extraction into aqueous solution) of the metal from the organic solvent.

In this 'Bufflex' process, uranium is extracted by amine sulphates from the sulphate solution obtained by eluting the ion-exchange columns with sulphuric acid. Chemically this is very similar to the ion-exchange

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* The work on which this report is based was carried out by the Extraction Metallurgy Division of the South African Energy Board.

process, except that, where ion exchange utilizes the strongly basic quaternary ammonium groups, the Bufflex process uses the weakly basic trialkyl amines. The solvent is Alamine 336, which is mainly a mixture of tridecyl and trioctyl amines. This is used as a 5% solution in lighting paraffin, to which 2% isodecanol is added. The paraffin serves to lower the viscosity of the amine, and the isodecanol maintains the amine sulphate in solution, thereby preventing the so-called third phase formation.

The extraction process can be represented by the equation

$$UO_2(SO_4)_2^{2-} + \underline{2(R_3NH)_2SO_4} \rightleftharpoons (R_3NH)_4UO_2(SO_4)_3 + SO_4^{2-}$$

where underlining indicates a species in the organic phase (cf. ion exchange:

$$UO_2(SO_4)_2^{2-} + \underline{2(R_4N)_2SO_4} \rightleftharpoons \underline{(R_4N)_4UO_2(SO_4)_3} + SO_4^{2-})$$

Very few other elements are extracted, because few elements form anionic complexes in sulphate solution. Only those elements that are present as anions are significantly extracted, e.g. Mo as molybdate, Si as silicate, N as nitrate, and Co as an anionic complex like cobalticyanide.

Stripping of uranium from the solvent is analogous to elution from an ion exchange resin, and can be done in a variety of ways. When the Bufflex pilot plant was first operated, a mixture of ammonium nitrate and nitric acid mixture was used. The reaction can be represented as follows:

$$\underline{(R_3NH)_4UO_2(SO_4)_3} + 4NO_3^- \rightleftharpoons \underline{4R_3NHNO_3} + UO_2(SO_4)_2^{2-} + SO_4^{2-}$$

The plant ran very successfully on this strip for some months. However, there were slow side reactions, the mechanisms of which were never fully elucidated. All that need be of concern here is that there was an irreversible chemical change, or degradation, in the amine, leading to a loss of capacity, and emulsion problems on the plant. It was shown conclusively that this degradation did not take place to any significant extent in the absence of nitrate, and for this reason alone the nitrate strip was abandoned in favour of the so-called ammonium sulphate strip.

In the ammonium sulphate strip the amine-uranium complex is hydrolyzed with ammonia as follows:

$$\underline{(R_3NH)_4UO_2(SO_4)_3} + 4NH_4OH \rightleftharpoons \underline{4R_3N} + 4H_2O + UO_2(SO_4)_2^{2-} + SO_4^{2-} + 4NH_4^+$$

The pH value at which hydrolysis takes place is in the range 3.5 to 5. It varies from stage to stage, but is always kept low enough to ensure that uranium remains in solution. Ammonium sulphate is formed and is recycled after the precipitation of ammonium diuranate. In this way a high sulphate concentration is maintained in the aqueous phase, depressing the extraction coefficient of uranium and improving the stripping.

In the scrub section (which precedes the strip section), uranium in the organic phase is purified by selectively stripping the impurities, leaving most of the uranium in the organic phase. Obviously this process will work only for elements that are less readily extracted than uranium, such as iron, arsenic, etc. It is not suitable for removing molybdenum and cobalt, since these elements are extracted as well as, or better than, uranium.

In the regeneration section, the solvent is treated with sodium carbonate solution which removes the last traces of uranium and acid and converts the solvent entirely to free-base form. The main object of regeneration is to remove traces of anions like thiocyanate, which otherwise tend to build up and poison the solvent.

The aqueous phase leaving the strip section contains about 10 g/litre uranium as uranyl sulphate. Ammonium diuranate is precipitated from this solution by the addition of ammonia to a pH value of 7.0.

## 3. DESCRIPTION OF THE BUFFLEX PILOT PLANT

All the operations involving reactions between the solvent and aqueous phases described in the previous section, viz. of extraction, scrub, strip, and regeneration, are carried out in mixer-settler units.

There are many references in the literature to different designs of mixer-settler: the one for the Bufflex pilot plant is an 'internal' mixer-settler, and is based on a design developed by Oak Ridge National Laboratory [1]. A diagram of the mixer-settler is shown in Fig. 1.

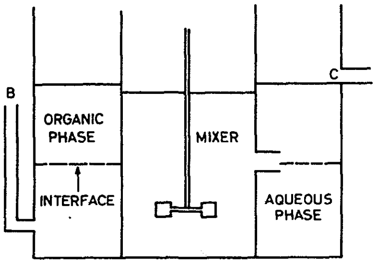

FIG. 1. Diagram of mixer-settler.

The aqueous and organic phases are introduced into the inner compartment, or mixer, and dispersed into a coarse emulsion by means of a turbine-type agitator. The mixed phases go from the mixer via outlet A into the settler, where the emulsion breaks into aqueous and organic phases. The aqueous phase leaves the mixer via B, and the organic phase via C. The height of the interface, i.e. the boundary between the aqueous and organic phases, depends on the difference in density between the two phases, and the difference in height between B and C. The former is constant for a particular process, and the height of the interface can be controlled by adjusting the latter.

The important parameters of mixer design are: (a) the residence time, which is the average time a phase remains in the mixer; and (b) the power for agitation, which is the power dissipated by the turbine in stirring the phases. It was shown experimentally [1] that, for geometrically similar mixers, the ORNL type of mixer can be scaled up over a wide range by keeping these two parameters constant.

The important parameter in settler design is the flow-rate of dispersed phase per unit area, and settlers have been scaled up by keeping this parameter constant.

The mixer-settlers for the Bufflex pilot plant were designed to have a residence time of 3 min, a power input of 20 hp/1000 gal, and a maximum flow-rate of the dispersed phase of 0.92 gal $ft^{-2}$ $min^{-1}$.

The layout of the plant is shown in Fig. 2. There are three banks of mixer-settler units — the extraction, scrub, and strip banks — and the regeneration unit. The solvent and aqueous phases are fed in at opposite ends of each bank, and they flow countercurrently to each other through the bank, this being the most efficient way of carrying out the solvent extraction process. There is a difference of one foot in height between adjacent mixer-settlers in a bank, permitting gravity flow of one phase. In the extraction bank it is the aqueous phase that flows by gravity, whereas in the other banks it is the solvent; the other phase is caused to flow in the reverse direction by pumping.

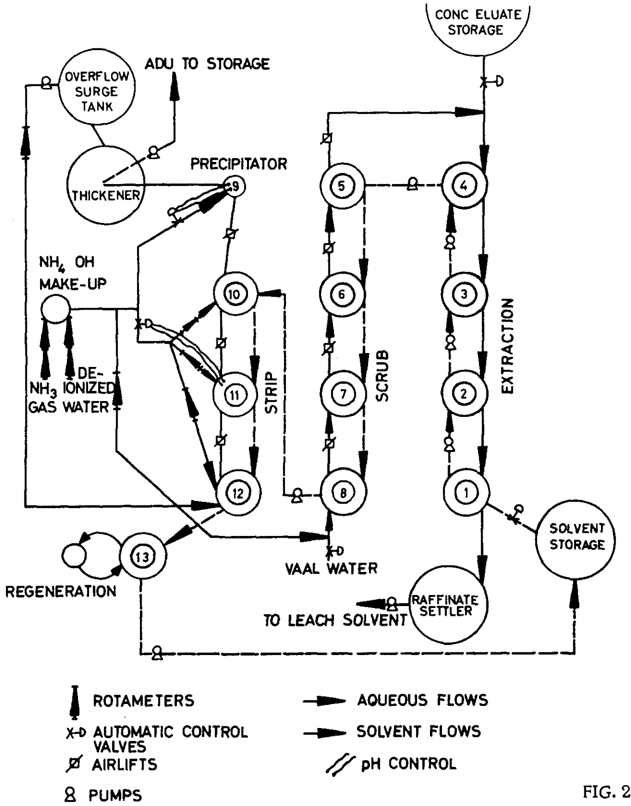

FIG. 2. Lay-out of Bufflex pilot plant.

## 3.1. Pumps

In the selection of an interstage pump for a solvent extraction plant it must be realized that a great deal of flexibility is required. The pump must be able to cope with a wide range of flow-rate. A normal centrifugal pump is not really suitable: if throttled back too much, it will not cope with the flow, whereas, if opened up too much, it will suck air and tend to lose its prime, when it will stop pumping completely.

Air lifts were used on the plant as far as possible. They are completely self-regulating, and maintenance is reduced to a minimum, as they have no moving parts. In spite of impressions to the contrary, they are quite efficient if properly designed. However, they are not suitable for lifting liquid to a great height, and their use was therefore restricted to the interstage pumps. Moreover, because it was feared that their use would lead to an excessive loss of paraffin by evaporation, they were not used for pumping solvent.

Centrifugal pumps made of rigid PVC were used for pumping solvent. Owing to a tendency of the solvent to foam, it was found by experience that a certain amount of air could be tolerated before they lost their prime. However, for general use a vertically mounted centrifugal pump, such as a Kestner, is to be preferred. This type is completely self-priming, since air entering the pump is free to escape and is not trapped by the centrifugal action of the impeller. There also is no need for a sealing gland and so the maintenance required is reduced.

### 3.2. Flow control

Flow control is more critical in a solvent-extraction plant than in an ion exchange plant. On the pilot plant, the normal system of flow control in uranium plants was used, viz. orifice plates with d-p cells controlling automatic controller-recorder units. In view of the need for accurate control of the flow-rate, vessels of known volume were built into the feed lines so that a flow-rate could be checked by merely closing the outlet and measuring the time taken to fill a vessel.

The use of more accurate flow controllers would seem to be desirable, though not essential. Magnetic flowmeters, or positive displacement meters of the oval gear type, would appear to be alternatives worth consideration.

### 3.3. Materials of construction

The mixer-settlers were made at the Government Metallurgical Laboratory of high-density Polythene by a centrifugal casting process. They were fairly satisfactory for the pilot plant, but are now showing signs of breaking at the welds. Polythene is not recommended as a constructional material for a full-scale plant. Some grades of Polythene are liable to stress-cracking in contact with amine solvent. Polythene cannot be welded satisfactorily after being in contact with solvent for some time, so that it would be difficult to repair Polythene tanks.

The most promising material of construction for mixer-settlers and tanks is mild steel with a suitable lining. Various lining materials are under investigation. Polypropylene backed with rubber was used to line the raffinate settler and has proved quite satisfactory, apart from a few blisters that developed soon after installation but did not spread. However, it is an expensive lining. The solvent storage tank is lined with Prodorfilm, and has been quite satisfactory, but this lining is not suitable for strongly acid conditions. It is probable that a suitable synthetic rubber lining, such as Neoprene, can be developed and some experimental formulations are being tested. Alternatively, tanks made of a laminate of cold-cured polyester resin and glass fibre may be satisfactory, and an experimental tank is under test.

Rigid PVC piping proved to be very satisfactory on the pilot plant and could safely be used on a full-scale plant. Alternatively, if a suitable synthetic rubber lining is developed, rubber-lined steel pipes will be quite satisfactory.

In general, genuine 316 stainless steel appeared to resist attack by the sulphuric acid eluate, but inferior grades of stainless steel corroded rapidly. In one instance, however, a 316 stainless-steel pump also corroded fairly rapidly, and for this reason this grade of stainless steel can only be recommended with some reservations. For equipment like turbine agitators, a more highly alloyed steel, such as 254 E, is quite satisfactory.

The windows in the mixer-settlers were made of Perspex, with a sealing gasket of Pliobond. They have shown no sign of deterioration after two years.

## 4. OPERATION OF THE BUFFLEX PILOT PLANT

### 4.1. Types of emulsion

The emulsion formed in a mixer can be either aqueous-continuous or organic-continuous. In the former case, small droplets of organic phase are suspended in the aqueous, whereas in the latter case the aqueous phase is dispersed in a continuous organic phase. With the ORNL design of mixer-settler, it is possible to produce either type of emulsion at will. If the turbine is immersed in aqueous phase on starting, an aqueous-continuous emulsion will be formed. An organic-continuous emulsion can be formed by immersing the turbine in organic phase before starting the stirrer.

The type of emulsion has an important bearing on the solvent loss. An aqueous-continuous emulsion usually breaks to give an aqueous phase that is rather cloudy, owing to fine droplets of organic phase that have not separated. An organic-continuous emulsion usually gives a clear aqueous phase, on breaking with very little entrained solvent. For this reason, to reduce the loss of solvent, it is necessary to maintain organic-continuous emulsions in M-S 1 and M-S 10 (i.e. the mixer-settlers from which aqueous streams leave the plant).

The type of emulsion formed can readily be checked by measuring its electrical conductivity: organic-continuous emulsions have almost zero conductivity, and aqueous-continuous emulsions have a conductivity about the same as that of the aqueous phase. A simple portable conductivity meter with probe electrodes was built for checking emulsions on the plant, and has proved to be invaluable.

### 4.2. Extraction

Extraction was carried out in four stages initially, but later this was reduced to three stages in order to increase the throughput of the plant. The solvent now enters the plant in M-S 2, and M-S 1 is used as an 'after-settler'.

Even with three stages, an extraction efficiency of 99.9% is readily attained. However, since the raffinate is returned to the leach circuit, nearly all the uranium in it is recovered and there is no great advantage in a very high extraction efficiency. The plant is therefore run to keep the solvent loading as high as possible, mainly to improve the efficiency of scrubbing and hence the purity of the product, but also to reduce reagent costs. The extraction efficiency under these conditions is 98 to 99%. The solvent loading is about 5 g U/litre.

## 4.3. Scrub

The scrub section was originally designed with four stages. The conditions were altered from time to time, as outlined in Table I.

TABLE I. CONDITIONS OF SCRUB SECTION

| Period from | Type of scrub |
|---|---|
| Start to 6/1/65 | 2 stages water, 2 stages 6% sulphuric acid |
| 6/1/65 - 2/2/65 | 4 stages water |
| 2/2/65 - 25/5/65 | 2 stages water |
| 25/5/65 - 1/6/65 | 3 stages 0.1M ammonia, using deionized water |
| 1/6/65 - 13/8/65 | 3 stages 0.1M ammonia, using drinking water |

A combined acid and water scrub was used originally because laboratory tests had shown that acid was more effective than water in removing arsenic, but that a water scrub was desirable to remove bisulphate, thus reducing the consumption of ammonia in ammonium diuranate precipitation. Although the acid used for scrubbing did not represent a cost to the solvent-extraction section (since it was returned to the leach circuit), once it was found that arsenic contamination was not a serious problem the circuit was simplified to a four-stage water scrub. When this proved effective, a two-stage water-scrub was tried, which also proved to be effective as regards most of the impurities.

Later on, when problems of crud formation and hafnium removal arose, a change was made to a dilute ammonia scrub, which is more effective than a water or dilute acid scrub. Initially, de-ionized water was used for this scrub, but later a change to plant water was made without any noticeable effect on the purity of the product.

## 4.4. Strip and regeneration

Discussion will be confined to the ammonium sulphate strip, since the nitrate strip was discontinued because of degradation of the solvent.

Loaded solvent from the scrub section enters the strip section via M-S 10 and leaves from M-S 12. The pH of the aqueous phases is maintained at the following values:

| | |
|---|---|
| M-S 10 | 3.7 to 3.9 |
| M-S 11 | 4.6 to 4.8 |
| M-S 12 | 5.0 to 5.5 |

The pH value of M-S 11 is controlled directly by means of electrodes immersed in the mixer, in which an aqueous-continuous emulsion is maintained. The pH values in M-S 10 and M-S 12 are controlled indirectly by the same recorder-controller unit as M-S 11, by splitting the controlled ammonia feed into three streams.

Solvent leaving M-S 12 normally contains less than 0.01 g/litre $U_3O_8$. However, the stripping efficiency is enhanced because the recycled ammonium sulphate contains 1.5 g/litre $NO_3$. This nitrate is brought into the system by the sulphuric acid eluate, which contains traces of nitrate. It is stripped from the loaded solvent and tends to build up in the ammonium sulphate, since it is not precipitated with the uranium. If the whole plant were converted to sulphuric acid elution, the nitrate concentration would fall to zero and the stripping efficiency would be slightly reduced. It would probably be necessary to include an extra stage to compensate for this loss of efficiency.

Regeneration is carried out with 10% sodium carbonate solution, which is recycled from the settler back to the mixer by means of an air lift. The carbonate solution is changed once a week. When the solution is fresh, its pH value is greater than 10. However, it falls quite rapidly with use and is maintained at a figure of 8.5 to 9.0 by bleeding in sodium hydroxide solution.

## 4.5. Crud formation

The formation of crud is common in solvent-extraction plants, and in fact the plant where it is not formed is the exception rather than the rule.

Crud consists largely of an emulsion of aqueous and organic phases, stabilized by a small amount of solid impurities, so that it is virtually permanent. It generally accumulates to a greater or lesser extent at the interfaces of the settlers. Under normal circumstances it does not affect the operation of the plant and is not of practical importance.

Crud formation was never a serious problem when the plant was running on the nitrate strip. However, as soon as a change was made to the ammonium sulphate strip, crud started building up very rapidly in the strip section. The result was that the aqueous phase going to precipitation carried crud over, resulting in a loss of solvent. Furthermore, because of the crud, it was impossible to maintain an organic-continuous emulsion in M-S 10 without increasing the rate of crud formation even further: consequently the aqueous phase carried over entrained solvent in addition to the solvent trapped in the crud. Nearly all the solvent was occluded by the ammonium diuranate on precipitation, and was not returned to the strip section with the ammonium sulphate recycled to M-S 12. Ammonium diuranate produced in this way contained up to 40% solvent.

Several causes of crud formation were traced. These were:

(1) Ammonium diuranate, which was formed as a result of running the strip section at too high a pH value. This was eliminated by reducing the pH of the strip section.

(2) Ammonia dissolving something from the rubber lining of the ammonia storage tank, causing crud. This was eliminated by making ammonium hydroxide continuously from de-ionized water and gaseous ammonia in a stainless-steel tank.

(3) Traces of silica in the solvent. It was not possible to eliminate the silica entirely, but it was somewhat reduced by using the more efficient dilute ammonia scrub.

It has not been possible to prevent crud formation in the strip section entirely, but the rate of formation has been reduced to a point where M-S 10 can be run with an organic-continuous emulsion.

The small amount of crud still formed is drained when necessary from the aqueous phase of M-S 10 by means of a siphon and is returned to M-S 7 in the scrub section. In this way it is possible to prevent crud from entering the precipitation section.

### 4.6. Precipitation and thickening

The pH value in the precipitation tank is maintained at 7.0 by control of the feed of ammonia by means of an automatic pH controller-recorder. Since ammonium diuranate tends to build up on the electrodes, causing erratic control, a spare set of electrodes is kept stored in HCl, and electrodes are changed over every hour.

The ammonium diuranate produced settles better than that produced by the normal process in uranium plants, and a 5-ft diam. thickener has proved quite satisfactory for this duty. The feed-rate to the thickener is normally 2 to 3 gal/min.

### 4.7. Ammonia make-up

Ammonium hydroxide is made up continuously in a stainless-steel tank by metering in de-ionized water and gaseous ammonia through Rotameters.

### 4.8. De-ionized water

De-ionized water was first made by passing plant water through a small commercial mixed-bed de-ionizer unit. As this has a fairly small capacity, it had to be regenerated frequently. For this reason, larger columns of anion and cation resin were installed in series with the mixed-bed unit, which now acts only as a final clean-up stage and is regenerated very infrequently.

## 5. SULPHATE ELUTION OF RESIN

Sulphate elution of resin, in addition to providing the feed for the solvent extraction plant, was considered very important in determining the long-term effect of elution with 10% sulphuric acid on polythionate build-up on the resin.

The tests were carried out in the Permutit resin columns of the uranium plant of Buffelsfontein Gold Mining Company Ltd. These columns each contain 330 ft$^3$ of resin, in a bed 9 ft in diameter by 5 ft deep. They are equipped for air-dome operation, and most of the elutions were carried out using an air dome.

Amberlite IRA 400 resin from two sets of columns was used for the tests. The resin in both sets was practically of the same age, and each set had treated approximately 240 million gallons of pregnant solution. In April 1964, the two sets of resin were thoroughly mixed, regenerated with caustic soda, and then distributed between two sets of columns. One set (No. 5) served as a control, and was eluted with nitrate solution. The other set (No. 6) was the test set, and was eluted only with 10% sulphuric acid.

The resin of sets 5 and 6 was sampled immediately after regeneration, and at intervals during the test period.

It was essential to feed pregnant solution of low nitrate content to set 6, to prevent nitrate contamination of the concentrated eluate, because this impurity interfered with the solvent-extraction process. The pregnant solution fed to set 6 was, except for its nitrate content, identical with that fed to set 5. A low nitrate content was obtained by the use of a separate pregnant solution tank for set 6, to which no nitrate-bearing solutions were recycled. The average nitrate content of the pregnant solution of set 6 was 0.038 g/litre, compared with 0.117 g/litre for the pregnant of set 6.

For most of the tests (from 22/4/64 to 6/3/65), an addition of $MnO_2$ of 3.1 to 3.9 lb/ton was used for leaching. From 20/3/65 onwards, the $MnO_2$ addition was increased to about 5.9 lb/ton, in order to increase the uranium recovery. The $U_3O_8$ content of the pregnant solution varied from 0.23 g/litre in the early stages to 0.29 g/litre for the increased $MnO_2$ leach.

## 5.1. Adsorptions and elutions

The performance of sets 5 and 6 was compared during the period April 1964 to June 1965. Set 5 was loaded and eluted according to normal plant practice. The flow-rate of pregnant solution during the adsorption cycle was between 120 and 140 gal/min. A breakthrough barren value of 0.006 g/litre was aimed at throughout. The air dome was formed after breakthrough. This was followed by a water flush of 1 bed volume, after which the air dome was readjusted to give 9 in. of liquid above the resin bed. The nitrate eluting solution used was the same as that used for the rest of the plant. The total nitrate concentration was 1M, and the acidity was equivalent to 0.4M nitric acid.

The elution cycle was as follows:

| | | Bed volumes | Flow-rate (gal/min) |
|---|---|---|---|
| Step 1 | Used eluate to pregnant-solution storage | 0.54 | 40 |
| Step 2 | Used eluate to concentrated-eluate storage | 3.78 | 30 |
| Step 3 | Used eluate to used-eluate storage | 4.03 | 40 |
| Step 4 | Fresh eluate to used-eluate storage | 3.66 | 30 |
| Step 5 | Water flush to used-eluate storage | 0.67 | 30 |
| Step 6 | Water flush to pregnant-solution storage | 0.76 | 30 |

This elution cycle was retained for the whole of the test period. After the elution, set 5 was backwashed with seven bed-volumes of water before going on standby.

### 5.1.1. Adsorption cycle of set 6

The adsorption cycle of set 6 was similar to that of set 5 except for the following:

(a) The backwash (7 bed volumes) was carried out before elution and after flush. This reversal of the normal procedure was done to allow the resin, during standby, to stand in 10% sulphuric acid, because it was believed at the time that this might tend to decompose the polythionates accumulating on the resin during the adsorption cycle.

The backwash effluent contained some uranium, and was therefore returned to the leach circuit.

(b) A royal barren step of 6 to 7 bed volumes was introduced, which was returned to the leach circuit. This was done partly to recover the sulphuric acid, and also because preliminary work had revealed the presence of uranium in the royal barren.

The adsorption flow-rate of set 6 was in the range 115 to 135 gal/min. This was somewhat lower than that of set 5, but these units were primarily production units apart from the tests being carried out so that it was not possible to match flow-rates exactly.

### 5.1.2. Elution cycle of set 6

The initial, conventional-water-displacement step was omitted, since this water served to dilute the concentrated eluate, and this was considered desirable for the solvent-extraction section.

After elution, the eluting solution was not displaced by water in the conventional manner, in order to allow the resin to stand in 10% sulphuric acid during the standby period. Moreover, it was felt that any dilution of the 10% sulphuric acid by water, which would result from an elutriant-displacement step, was undesirable because this would reduce the efficiency of elution.

A number of different elution cycles were tried. The flow-rate was kept constant at 30 gal/min throughout the tests. Some eluations were incomplete, as can be seen by the concentration of uranium in the eluate at the end of the elution (see Table IV). The elution cycles are summarized in Table II.

## 5.2. Regeneration

In March 1965 it was decided to regenerate sets 5 and 6 for the following reasons:

(1) The polythionate in set 6, and the silica in set 5, were increasing.

(2) It was nearly a year since the previous regeneration. On the plant it is customary to regenerate all sets at least once a year.

(3) Set 6 had a slightly lower capacity than set 5.

The regeneration was carried out by the standard procedure at Buffelsfontein, which had been developed especially for silica regeneration and the prevention of gel formation. The resin was transferred from the set of columns to a separate tank, where three bed volumes of 7% caustic soda was added. The mixture was agitated with air for 16 hours. The resin was then gravitated into two regeneration columns, flushed with water and then with 1% sulphuric acid until the pH value of the effluent was less than 2.

TABLE II. ELUTION OF SET 6 WITH 10% SULPHURIC ACID

| Elution cycle | Period | Used eluate to concentrated eluate (bed vol.) | Used eluate to used eluate (bed vol.) | Fresh eluate to concentrated eluate (bed vol.) | Fresh eluate to used eluate (bed vol.) | Fresh eluate to leach (bed vol.) |
|---|---|---|---|---|---|---|
| 1 | 22/4/64 - 22/7/64 | 4.8 | - | - | 4.8 | - |
| 2 | 23/7/64 - 28/10/64 | 3.8 | 2.0 | - | 3.8 | - |
| 3 | 29/10/64 - 10/11/64 | 3.8 | 4.2 | - | 3.8 | - |
| 4 | 11/11/64 - 17/12/64 | 5.0 | 2.0 | - | 5.0 | - |
| 5 | 18/12/64 - 6/2/65 | 6.0 | - | - | 6.0 | 2.0 |
| 6a | 7/2/65 - 6/3/65 | - | - | 6.0 | - | 6.0 |
| 6b | 20/3/65 - 20/6/65 | - | - | 6.0 | - | 6.0 |

Note: Both sets of columns were regenerated in March 1965. Set 6a was the elution cycle before regeneration, 6b the cycle after regeneration.

## 5.3. Results and discussion

### 5.3.1. Resin analyses

Resin samples were taken at intervals during the period of the test and analysed for silica, total sulphur polythionates, and cobalt. The results of these analyses are given in Table III.

It must be appreciated that the problems involved in obtaining truly representative samples and in conducting the analyses for relatively small quantities of impurities are such that no great accuracy can be expected. In fact, many inconsistent results were obtained, and the figures shown in Table III represent typical results obtained at the Buffelsfontein Analytical Laboratory and at the Government Metallurgical Laboratory.

It will be seen that the silica build-up in set 5 was more rapid than that in set 6, but the polythionate build-up was more rapid in set 6 than in set 5. This confirms that sulphuric acid is less efficient than nitrate in eliminating polythionates, even though set 6 was left to stand in sulphuric acid during the standby period. The regeneration was not very effective for the removal of polythionates.

The results for the analysis for cobalt are erratic, but there does not seem to be any reason why cobalt should build up more rapidly in set 6 than in set 5.

## TABLE III. RESULTS OF RESIN ANALYSES

Most of the analyses reported were done at the laboratory of Buffelsfontein Gold Mining Company

| Date resin sampled | $SiO_2$ | | Total S | | $S_4O_6$ | | Co | |
|---|---|---|---|---|---|---|---|---|
| | Set 5 (%) | Set 6 (%) | Set 5 (%) | Set 6 (%) | Set 5 (%) | Set 6 (%) | Set 5 (%) | Set 6 (%) |
| 29/4/64 (at start of investigation) | 1.8 | 1.8 | 0.2 | 0.2 | 0.02 | 0.02 | 2.0 | 2.0 |
| 2/11/64 | 4.1 | 2.5 | 0.9 | 4.7 | 0.03 | 1.1 | 1.7 | 1.9 |
| 28/11/64 | 3.4 | 2.2 | 0.7 | 2.3 | 0.06 | 1.0 | 2.2 | 2.1 |
| 13/2/65 | 4.2 | 2.2 | 0.7 | 2.4 | 0.04 | 0.7 | 2.1 | 2.3 |
| Before regeneration [a] | 4.3 | 1.8 | 2.6 | 3.9 | nil | 0.8 | 2.0 | 2.1 |
| After regeneration [b] | 0.8 | 0.8 | 2.6 | 4.0 | 0.03 | 0.7 | 2.0 | 2.0 |

[a] Set 5 sampled 22/3/65, set 6 sampled 8/3/65.

[b] Set 5 sampled 30/3/65, set 6 sampled 16/3/65.

### 5.3.2. Resin capacity

The uranium capacities of the resin from sets 5 and 6 were assessed in two ways: (a) by calculating the loading of the columns from plant records (these results are given in Table IV); and (b) by laboratory tests on resin samples (these results are given in Table V).

Considering Table IV, it can be seen that at first the capacity of set 6 was appreciably less than that of set 5. However, it is clear from the concentration of $U_3O_8$ in the eluate at the end of elution that elution was not complete, and therefore too much importance should not be attached to the results of elution cycles 1 to 4. For elution cycles 5, 6a and 6b, the capacity of set 6 was slightly, but significantly, lower that that of set 5.

A similar conclusion can be drawn from the results given in Table V.

## TABLE V. $U_3O_8$ CAPACITY OF RESIN FROM SETS 5 AND 6 FROM LABORATORY TESTS

| Date resin was sampled | $U_3O_8$ capacity (meq/g dry resin) | | Chloride capacity (meq/ g dry resin) | |
|---|---|---|---|---|
| | Set 5 | Set 6 | Set 5 | Set 6 |
| 2/11/64 | 2.27 | 1.98 | 2.25 | 2.08 |
| Before regeneration [a] | 2.30 | 2.25 | 2.10 | 2.07 |
| After regeneration [b] | 2.09, 2.6 | 1.97, 2.47 | 1.96 | 1.97 |

[a] Set 5 sampled 22/3/65, set 6 sampled 8/3/65.

[b] Set 5 sampled 30/3/65, set 6 sampled 16/3/65.

TABLE IV. $U_3O_8$ CAPACITY OF RESIN FROM SETS 5 AND 6

| Elution cycle of set 5 | $U_3O_8$ capacity (lb/ft³) | | $U_3O_8$ in eluate from set 6 at end of elution (g/litre) |
|---|---|---|---|
| | Set 5 | Set 6 | |
| 1 | 2.40 | 2.00 | 0.7 |
| 2 | 2.36 | 1.80 | 0.9 |
| 3 | 2.35 | 2.03 | 0.8 |
| 4 | 2.35 | 1.96 | 0.4 |
| 5 | 2.37 | 2.08 | <0.1 |
| 6a | 2.32 | 2.22 | <0.1 |
| 6b | 2.13 | 1.97 | <0.1 |

### 5.3.3. Adsorption and elution curves

Figure 3 shows the adsorption curve for set 6 when it was operating on elution cycle 5 (i.e. the elution was complete). The uranium leakage is low and compares well with that of set 5. The peak in the sulphate curve is caused by the displacement of the sulphuric acid used for elution. From these curves it appears that two bed volumes of royal barren returned to the leach circuit would be enough to prevent any loss of uranium or acid.

Figure 4 shows the elution curve of set 5, and Figs 5, 6 and 7 show the elution curves for set 6 on elution cycles 5, 6a and 6b, respectively. It is clear that elution with 10% sulphuric acid is efficient. There does not seem to be any great advantage in eluting with fresh acid for the whole cycle, and elution cycle 5 should be quite satisfactory for plant operation.

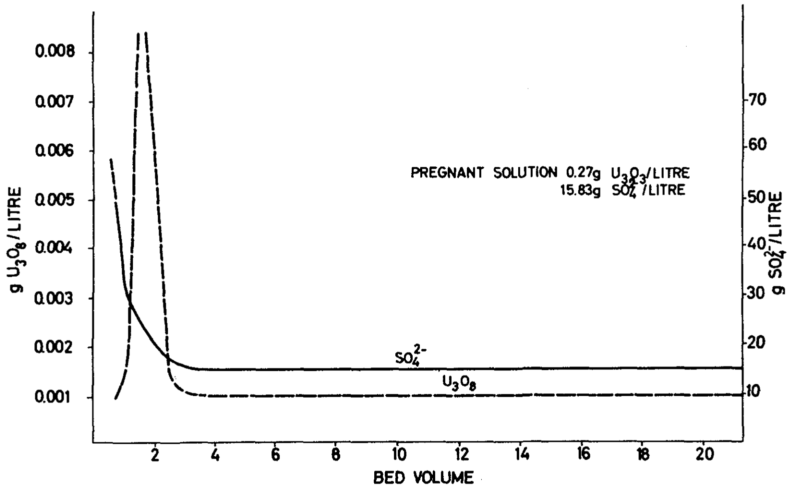

FIG. 3. Adsorption curve — set 6.

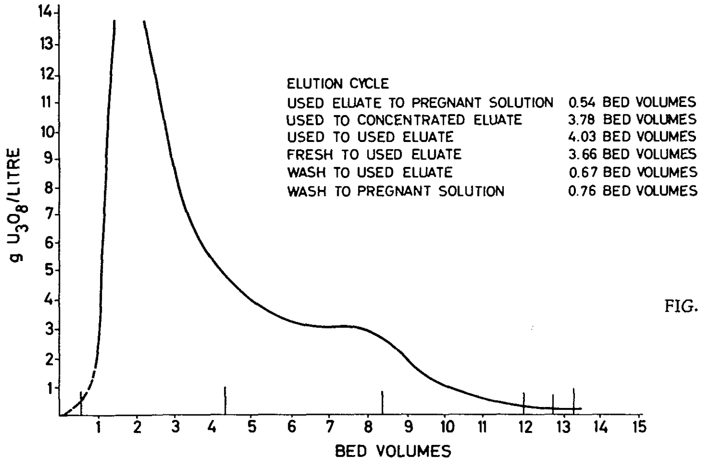

FIG. 4. Elution curve – set 5.

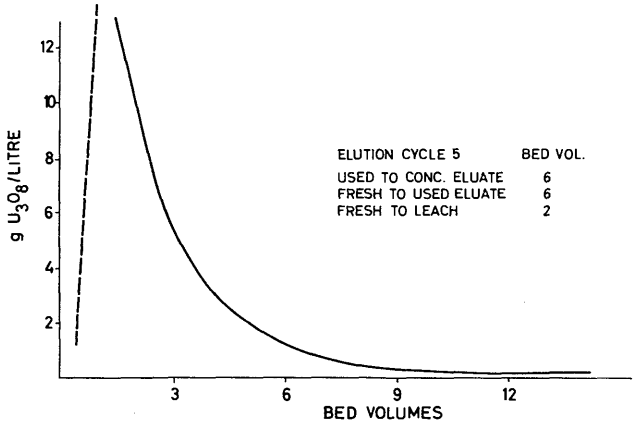

FIG. 5. Elution curve – set 6.

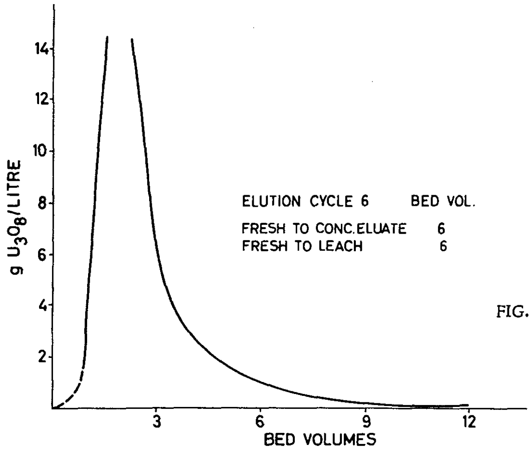

FIG. 6. Elution curve of set 6 before regeneration.

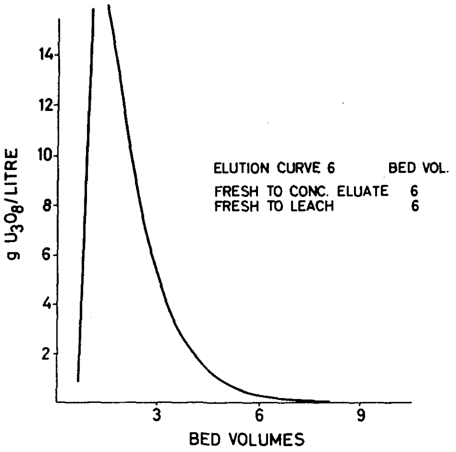

FIG. 7. Elution curve of set 6 after regeneration.

## 6. REAGENT CONSUMPTION AND COSTS

### 6.1. Solvent loss

Solvent loss can be a significant item in the operation of a solvent-extraction plant, and to cut down operating costs it is important to keep it to a minimum.

Any solvent present in the stream leaving the plant (in this case, the raffinate from the extraction section, and the ammonium diuranate slurry from the strip section) represents a loss. The solubility of the solvent in water is very low and most of the solvent in these streams is entrained as very small droplets. The amount of solvent loss in this way depends on the type of emulsion formed in the mixer. Before the formation of crud in the strip section was brought under control, an aqueous-continuous emulsion was maintained in M-S 10, and the loss of solvent in the ammonium diuranate was high. Since a change to an organic-continuous emulsion was made, the loss of solvent in this way has been considerably reduced.

The loss of paraffin by evaporation is significant on the Bufflex pilot plant, especially in summer. However, when a full-scale plant is built, the mixers, settlers and tanks can be closed with covers that fit tightly, and this loss will probably become insignificant. A certain amount of solvent is lost by leaks and spillage.

It has not been possible to assess accurately the loss of solvent by each of the various routes outlined above. However, the total cost of Alamine 336, isodecanol and paraffin used for solvent make-up when the plant is run on the dilute ammonia scrub is only 0.9 ¢/lb $U_3O_8$ produced. On a full-scale plant, the consumption of solvent should be appreciably less than this.

### 6.2. Sulphuric acid and ammonia

Provided that the sulphuric acid eluted in the royal barren is returned to leach, the consumption of acid in the elution cycle of the ion-exchange section is negligible. However, in the solvent-extraction plant, the solvent entering the extraction section is in a free-base form and picks up acid, which is eventually neutralized by ammonia in the strip and scrub sections and is therefore not recovered. The amount of acid consumed in this way is very nearly equal to the amount of ammonia used in the strip and scrub sections, and this fact can be used as a means of estimating acid consumption. Alternatively, the acid consumption can be estimated from a measurement of the amount of acid entering and leaving the extraction section. This necessitates the accurate measurement of the flow-rates of both the sulphuric acid and scrub, and this is not easy. By a combination of these methods, the acid consumption was found to be 1.0 lb/lb of $U_3O_8$ produced.

It follows from the previous paragraph that the consumption of acid and solvent is proportional to the flow-rate of the solvent. To minimize the consumption of these reagents, the solvent flow-rate should be kept as low as possible, i.e. the loading of uranium in the solvent should be kept as high as possible.

## 6.3. Costs

This discussion of the cost of ammonium diuranate produced by the Bufflex process will be confined to the cost of reagents. There seems to be little point in going into details of capital costs, since this will vary from mine to mine. The mixer-settlers themselves are not very expensive. Buildings, tanks and instruments will make up a large proportion of the capital cost, and considerable savings would result if buildings and tanks already in existence could be adapted to the process. However, as a very rough guide, the conversion of a uranium plant to the Bufflex process would probably cost somewhere between 100 000 and 200 000 rands.

TABLE VI. COST OF REAGENTS FOR THE PRODUCTION OF AMMONIUM DIURANATE BY THE CONVENTIONAL PROCESS AT BUFFELSFONTEIN

| Reagent | Uses of reagent | Reagent cost (¢/lb) | Reagent consumption (lb/lb $U_3O_8$) | Operating cost (¢/lb $U_3O_8$) |
|---|---|---|---|---|
| Nitric acid (100%) | Elution of resin | 3.77 | 2.86 | 12.33 |
| Sulphuric acid (100%) | Regeneration of resin | 0.50 | 0.07 | 0.03 |
| Caustic soda (100%) | Regeneration of resin | 6.00 | 0.03 | 0.18 |
| Lime | Iron precipitation | 0.77 | 0.97 | 0.75 |
| Ammonia | Ammonium diuranate precipitation | 6.00 | 0.512 | 3.07 |
| | | | | Total 16.36 |

The costs of reagents used in the production of ammonium diuranate by the conventional process at Buffelsfontein, and by the Bufflex process on the pilot plant using a dilute ammonia scrub, are summarized in Tables VI and VII.

It can be seen that the operating cost of the Bufflex process is 12.34 cents per pound of $U_3O_8$, less than the conventional process. The difference in cost is largely that of the nitric acid used for elution in the conventional process. In the Bufflex process, the sulphuric acid used for elution is recycled to leach and does not represent a charge to the ion-exchange section.

It should be noted, however, that this is the saving obtained with old IRA 400 resin. If IRA 405 resin in good condition were used instead, the consumption of nitric acid in the conventional process would decrease and the saving would be less. Allowing for this factor, it is estimated that the saving would still be not less than 5 cents per pound of $U_3O_8$.

TABLE VII. COST OF REAGENTS FOR THE PRODUCTION OF AMMONIUM DIURANATE BY THE BUFFLEX PROCESS ON A PILOT-PLANT SCALE

| Reagent | Uses of reagent | Reagent cost (¢/lb) | Reagent consumption (lb/lb $U_3O_8$) | Operating cost (¢/lb $U_3O_8$) |
|---|---|---|---|---|
| Alamine 336 | Solvent make-up | 64.38 | 0.006 | 0.386 |
| Isodecanol | Solvent make-up | 16.68 | 0.009 | 0.150 |
| Paraffin | Solvent make-up | 3.47 | 0.108 | 0.375 |
| Sulphuric acid | (1) Regeneration of resin<br>(2) (see section 6.2) | 0.50 | 1.00 | 0.501 |
| Ammonia | (1) Ammonium diuranate precipitation<br>(2) Solvent scrub | 6.00 | 0.352 | 2.11 |
| Caustic soda | (1) Regeneration of resin<br>(2) Regeneration of solvent<br>(3) Regeneration of water de-ionizer | 6.00 | 0.058 | 0.348 |
| Sodium carbonate | Regeneration of solvent | 3.94 | 0.019 | 0.075 |
| Hydrochloric acid | Regeneration of water de-ionizer | 6.06 | 0.005 | 0.030 |
| Vaal water | Scrub | | | 0.042 |
| | | | | Total 4.017 |

## 7. PURITY OF THE PRODUCT

Is the uranium produced by the Bufflex process of nuclear grade or not? Unfortunately, this is by no means a simple question to answer. There are many specifications for nuclear-grade uranium, drawn up by different countries for different uses of uranium. In general, they follow the same pattern, but differ greatly in detail. One of the most stringent of these is the Canadian specification, and this has therefore been used as the criterion for the Bufflex product. The specification of the South African Atomic Energy Board is more lenient and is also given in Table VIII for comparison.

Composite samples of the ammonium diuranate slurry produced at the pilot plant were taken daily on a routine basis. They were analysed spectrographically for a number of elements, and also chemically for molybdenum. The results obtained are summarized in Table VIII.

There did not appear to be a significant difference in the purity of the products obtained when the different scrubs were used and the results for these are therefore not listed separately.

### 7.1. Arsenic

In general, the arsenic content was below 10 ppm, but occasionally it has been higher. The maximum value recorded was 50 ppm. The fact that it was normally low shows that the scrub section is able to remove arsenic efficiently. The occasional high results are thought to be due to variations in the arsenic content of the sulphuric acid scrub, but there are no analytical figures to prove this.

Arsenic is not specified in the Canadian specifications for nuclear-grade uranium. It absorbs thermal neutrons to roughly the same extent as iron, and accordingly a specification of 35 ppm for arsenic is suggested. There should be no difficulty in meeting this specification.

### 7.2. Boron

On the whole, the boron results are quite satisfactory, since the boron content was normally below 0.3 ppm (the limit of detection). Any results above this value are thought to be due to contamination by dust in the strip and precipitation sections of the pilot plant.

### 7.3. Cobalt

A small amount of cobalt (5 - 15 ppm) was invariably present. This was probably due to the extraction of traces of cobalt cyanide complexes from the sulphuric acid eluate.

Cobalt is not mentioned in the Canadian specification but is definitely an undesirable impurity, since it captures neutrons to about the same extent as hafnium. For this reason, a specification of 5 ppm is suggested for cobalt. It would be difficult to meet this specification consistently with the Bufflex process, but further decontamination may be achieved in subsequent processing.

TABLE VIII. RESULTS OF SLURRY ANALYSIS COMPARED WITH CANADIAN AND S.A. ATOMIC ENERGY BOARD SPECIFICATIONS

| Element | Results on basis of uranium | | Canadian Specification (ppm based on uranium) | S.A. Atomic Energy Board Specification (ppm based on uranium) |
|---|---|---|---|---|
| | Range of reported results (ppm) | General reported results (ppm) | | |
| Aluminium | | < 10 | 30 | 50 |
| Arsenic[a] | 50 - < 10 | < 10 | | |
| Gold | | < 1 | | |
| Barium | | < 3 | | |
| Boron[a] | 1 - < 0.3 | < 0.3 | 0.2 | 1.8 |
| Beryllium | | < 0.3 | | |
| Bismuth | | < 1 | | |
| Cadmium | | < 0.3 | 0.2 | 1.0 |
| Cobalt[a] | 17 - < 3 | 7 ± 3 | | |
| Chromium | < 10 - < 3 | < 10 | 10 | 65 |
| Calcium | | 1 | | |
| Copper | < 10 - < 3 | < 10 | 10 | |
| Iron | 140 - < 3 | 13 ± 5 | 35 | 150 |
| Gallium | <3 - < 1 | < 3 | | |
| Germanium | <3 - < 1 | < 3 | | |
| Indium | | < 1 | | |
| Magnesium[a] | 12 - < 3 | < 3 | 40 | 25 |

TABLE VIII. (cont.)

| | | | | |
|---|---|---|---|---|
| Manganese | < 3 - < 1 | < 1 | 5 | 25 |
| Nickel[b] | < 3 - < 1 | < 3 | 15 | 100 |
| Niobium | | < 10 | | |
| Sodium | | < 10 | | |
| Lead | < 10 - < 3 | < 10 | | 50 |
| Antimony | | < 3 | | |
| Silicon[a] | 10 - 80 | 25 ± 10 | 20 | 85 |
| Tin | | < 3 | | |
| Thallium | | < 1 | | |
| Vanadium | < 10 - < 3 | < 10 | 30 | |
| Zinc | | < 10 | | |
| Zirconium[a] | 100 - 170 | 150 | | |
| Molybdenum[a] | 40 - 15 | 25 ± 5 | 1 | |

[a] Discussed in the paper.

[b] On a few occasions higher results were obtained, but these were almost certainly due to contamination during sample preparation, and are not typical.

### 7.4. Iron

In general, the iron content is low (10 - 60 ppm), even though it is present in large amounts in the sulphuric acid eluate. High results for iron are almost certainly due to contamination from some source. With proper precautions to prevent contamination, there should be no difficulty in keeping the iron content below 36 ppm (i.e. the Canadian specification).

### 7.5. Magnesium

In general the magnesium content is low (less than 3 ppm), but occasionally a series of higher results was recorded. This was probably due to a quantity of badly de-ionized water entering with the de-ionized water used for the making of ammonium hydroxide used for the stripping and precipitation of uranium. Even under these conditions, there should be no difficulty in meeting the Canadian or S.A. Atomic Energy Board's specifications of 40 and 25 ppm respectively.

### 7.6. Silicon

Samples of the product were analysed for silicon. The results obtained indicated that the silicon content varies from 10 to 80 ppm. These results are not very accurate, being at the limit of detection of the method used. They do, however, show that the silicon content is not much greater than 30 ppm.

### 7.7. Zirconium and hafnium

The zirconium content of the few samples analysed for zirconium was in the range 100 to 170 ppm.

Zirconium is not mentioned in the Canadian specification, but in itself is not an undesirable impurity.

It was not possible to analyse for hafnium directly, since it was below the limit of detection. However, natural zirconium invariably contains about 2% hafnium, so that by calculation the hafnium content of the uranium is about 3 to 4 ppm.

Hafnium is not mentioned in the Canadian specification but, from its absorption cross-section for thermal neutrons, a specification of 5 ppm appears to be reasonable.

### 7.8. Molybdenum

The molybdenum content of the product was in the range 15 to 40 ppm, which is much higher than the very stringent Canadian specification of 1 ppm.

It should be noted that molybdenum is not in itself an undesirable element in nuclear-grade uranium; indeed, in some instances, fuel elements have been made of uranium-molybdenum alloys [2]. However, in the gaseous-diffusion process for isotope enrichment it accumulates at the product end, so that the feed to this plant must have a low molybdenum content.

It would be difficult to meet the specification of 1 ppm with the Bufflex process, but further decontamination may be achieved in subsequent processings.

## 8. CONCLUSIONS

The Bufflex experiment has demonstrated that a solvent-extraction process treating the sulphuric acid eluate from the ion-exchange columns is feasible.

Ion-exchange resin can be eluted successfully with 10% sulphuric acid, but will have a uranium capacity slightly lower than resin eluted with nitrate. The difference is small, and is probably due to a polythionate build-up. The slightly shorter adsorption cycles appear to be of no real significance, provided the production of uranium is maintained. The reagent costs for elution will not be increased as a result of the shorter adsorption cycles.

Except for polythionate, the poison build-up and general performance of resin eluted with 10% sulphuric acid are no worse than those of resin eluted with nitrate.

Since polythionate poisoning is not as serious a problem at Buffelsfontein as it is at some other mines, it is possible that a larger build-up of this poison would occur at those mines. However, it seems unlikely that it will build up to such an extent that it will affect the operation of the columns.

The operating cost of the Bufflex process is cheaper than that of the conventional process by at least 5 cents per pound of $U_3O_8$ produced. Although detailed figures for the capital cost of the full-scale plants required have not yet been calculated, these costs should not be large enough to affect the economic feasibility of the process.

The uranium produced is pure enough to pass even the most stringent nuclear-grade specification, except as regards cobalt, molybdenum, silica, and hafnium. Laboratory tests have shown that 80 to 90% of the hafnium is readily removed by a dilute ammonia scrub, reducing the hafnium content to less than 1 ppm. To confirm this by plant tests, a more sensitive method for the analysis of hafnium will have to be developed.

Laboratory tests on the removal of cobalt and molybdenum are still in progress. It should be noted that, if necessary, cobalt could be eliminated by changing to a reverse leach-procedure. If the ammonium diuranate is processed further to $UF_4$, most of the molybdenum would be removed by the 'French process' for making $UF_4$.

In general, the silica content is only slightly above specification, and is frequently below it.

## ACKNOWLEDGEMENTS

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## REFERENCES

[1] RYON, A.D., LOWRIE, R.S., Experimental basis for the design of mixer-settlers for the Amex solvent extraction process, Oak Ridge National Laboratory, Rep. ORNL 3381.

[2] HARRINGTON, C.D., RUEHLE, A.E., Uranium Production Technology, Van Nostrand, New York (1959) 438-40.

# ESTUDIOS DE CARACTERIZACION Y CONCENTRACION FISICA DE CUARCITAS URANIFERAS ESPAÑOLAS

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**Abstract — Resumen**

INVESTIGATIONS ON THE NATURE AND PHYSICAL CONCENTRATION OF SPANISH URANIFEROUS QUARTZITES. A study was made of a sample of radioactive material from Santa Elena (Jaén) containing 130 ppm $U_3O_8$, 600 ppm $ThO_2$, 4.96% $ZrO_2$ and 14.29% $TiO_2$. Over 150 million tons of material were examined. In the light of the studies carried out the material can be defined as a rutilo-zirconiferous quartzite with a double radioactivity source due to the uranium enclosed in the zircon lattice structure and to the presence of monazite. The possibility of brannerite or davidite being present can be discarded. There is likewise no conclusive evidence of the presence of sphene, rutile being the most abundant titanium mineral. The author determined the features of the ore with a view to its physical concentration and applied magnetic and gravimetric separation and the flotation process. The use of oleic acid as collector has permitted good zircon recovery.

ESTUDIOS DE CARACTERIZACION Y CONCENTRACION FISICA DE CUARCITAS URANIFERAS ESPAÑOLAS. Se ha estudiado una muestra de material radiactivo procedente de Santa Elena (Jaén) con 130 ppm de $U_3O_8$, 600 ppm de $ThO_2$, 4,96% de $ZrO_2$ y 14,29% de $TiO_2$. El material examinado es considerable: más de 150 millones de toneladas. De acuerdo con los estudios realizados se puede definir como una cuarcita rutilo-circonífera con dos fuentes de radiactividad debidas al uranio englobado en la red del circón y a la presencia de monacita. Se descarta la posibilidad de existencia de brannerita o davidita. Tampoco existen pruebas concluyentes de que contenga esfena, siendo el rutilo el mineral de titanio más abundante. Se han determinado las características de la mena con vistas a su concentración física. Se ha ensayado la separación magnética, gravimétrica y flotación. El empleo de ácido oleico, como colector, ha dado buenas recuperaciones de circón.

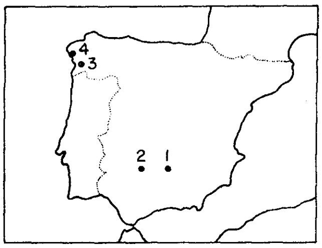
## 1. INTRODUCCION

Desde hace años [1] se conoce la presencia de radiactividad en numerosos puntos de la Zona de Despeñaperros comprendida entre Aldeaquemada y Santa Elena (Jaén), y Almuradiel y Almagro (Ciudad Real) (figura 1). El estrato radiactivo está constituido por una cuarcita rutilo-circonífera, procedente de areniscas metamorfizadas.

Según una cubicación citada en [2] las reservas alcanzan a 155 520 000 t equivalentes a 102 000 t $U_3O_8$, 39 000 t $ThO_2$, 9 000 000 t $ZrO_2$ y 28 000 000 t $TiO_2$. Las leyes eran bajas y variables, entre 130 ppm $U_3O_8$ y 0,34% $U_3O_8$, 250 y 630 ppm $ThO_2$, 6,6 y 22,6% $TiO_2$ y 2,1 y 7,9% $ZrO_2$. A pesar de las dificultades técnicas que encierra, la explotación de estos yacimientos se ha estudiado repetidamente debido a la gran cantidad de mineral que contienen.

La mayoría de los trabajos fueron realizados desde el punto de vista mineralógico [1, 2, 3, 4], aunque también en el año 1956 el Battelle Memorial Institute [4] realizó algunos tanteos sobre el tratamiento metalúrgico del mineral. El interés fundamental se centró en la recuperación de uranio y torio, aunque posteriormente se pensó también en realizar una valorización total de la mena recuperando circonio y titanio.

Los distintos autores están de acuerdo en que la radiactividad del mineral procede de dos fuentes: los circones y el cemento o minerales intergranulares. Sin embargo hay gran discrepancia, pues Alia [1] atribuye fundamentalmente la radiactividad a los circones, y el resto a la existencia de brannerita; Mingarro y Arribas [2] creen que el uranio se encuentra, en su mayoría, en el cemento intergranular, y además Arribas [3] supone otra fuente de actividad en la esfena. Por último,



1 SANTA ELENA (Jaén)
2 FUENTEOBEJUNA (Córdoba)
3 PORRIÑO (Pontevedra)
4 PLAYAS GALLEGAS

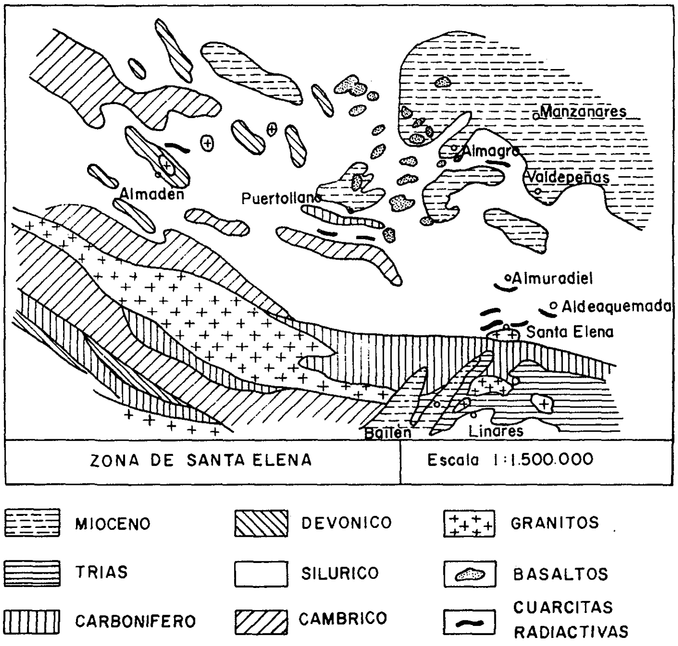


FIG. 1. Mineralizaciones de circón más importantes en España y detalle de los afloramientos de las cuarcitas de la zona de Santa Elena.

Smith [4] coincide con Alia en la importancia de los circones y localiza el resto de actividad en los concentrados de titanio, atribuyéndola a la guadarramita (mezcla de davidita e ilmenita).

Ante esta situación se inició una investigación que permitiese fijar los componentes del mineral y tamaños de liberación, especialmente con miras a su concentración física y tratamiento hidrometalúrgico para recuperar uranio, titanio, circonio y torio. Se realizaron ensayos de concentración física y actualmente se está dedicando atención a la lixiviación.

## 2. MINERAL

Se trabajó con material tomado de una muestra de 100 t (lote 9.03) de mineral bastante homogéneo con tamaños de hasta 40 cm, de color rojo obscuro en la superficie y gris en la fractura, compacto y de grano fino. Por desmuestre mecánico se separó la muestra necesaria para los estudios a un tamaño de 2 mm.

El análisis cuantitativo (%) de los elementos más importantes fue: $Al_2O_3$ (4,04); CaO (0,25); $Fe_2O_3$(8,63); $P_2O_5$ (0,22); $SiO_2$ (65,34); $ThO_2$(0,06); $TiO_2$ (14,29); $U_3O_8$ (0,013) y $ZrO_2$ (4,96).

Según los estudios mineralógicos precedentes [3 y 4] cabía esperar como:

a) Minerales esenciales: cuarzo (30-80%), circón (10-20%), rutilo, ilmenita, esfena y leucoxeno (30%).

b) Minerales accesorios: Turmalina, sericita-moscovita, clorita-biotita, magnetita, óxidos de hierro, sustancias carbonosas, inclusiones de pizarra.

La identificación de todos los minerales constituyentes por observación petrográfica de secciones transparentes de la roca resultó bastante difícil pues las preparaciones aparecían muy teñidas de óxidos de hierro, y la edad del yacimiento ha dado lugar a granos microscópicos muy rodados en los que no se pueden distinguir las formas cristalinas ni medir las propiedades ópticas.

De los minerales citados por Arribas y Smith únicamente se pudieron identificar en la muestra el cuarzo, la turmalina, el circón y el rutilo. La distinción entre los minerales opacos fue prácticamente imposible. Había unos cristales amarillos redondeados de difícil definición que podrían corresponder a la variedad amarilla del rutilo [5]; también podrían corresponder a la esfena ya que algunos cristales mostraban las líneas típicas de exfoliación. Heinrich [6] indica además que los granos detríticos de esfena se parecen mucho a los de rutilo amarillo.

También se confirmó la existencia de la materia carbonosa citada por Arribas, que aparece en la pulpa de mineral molido.

Los tamaños medios de los cristales eran de unas 100 $\mu$m para el cuarzo y de 50 $\mu$m para el circón y el rutilo. Los minerales opacos se presentaban en un tamaño intermedio entre el del cuarzo y el rutilo.

## 3. ESTUDIOS DE CARACTERIZACION MINERALOGICA

Partiendo de la información anterior y teniendo en cuenta las dificultades indicadas, se realizaron una serie de ensayos por separación física a escala de laboratorio, en cuyo control se utilizó el análisis mineralógico, fotomicrografías, análisis de rayos X y análisis químico y radiométrico.

## 3. 1. Ensayos

La marcha general es la indicada en la figura 2 y comprendió la molienda al tamaño de liberación, la separación de lamas y arenas seguida de una clasificación por tamizado y de separación de cuarzo por bromoformo ($\rho = 2{,}80$), acabando por la separación magnética en un aparato Frantz-Isodinamic con inclinación de 10° y recogiendo fracciones cada 0,2 A entre 0 y 1,6.

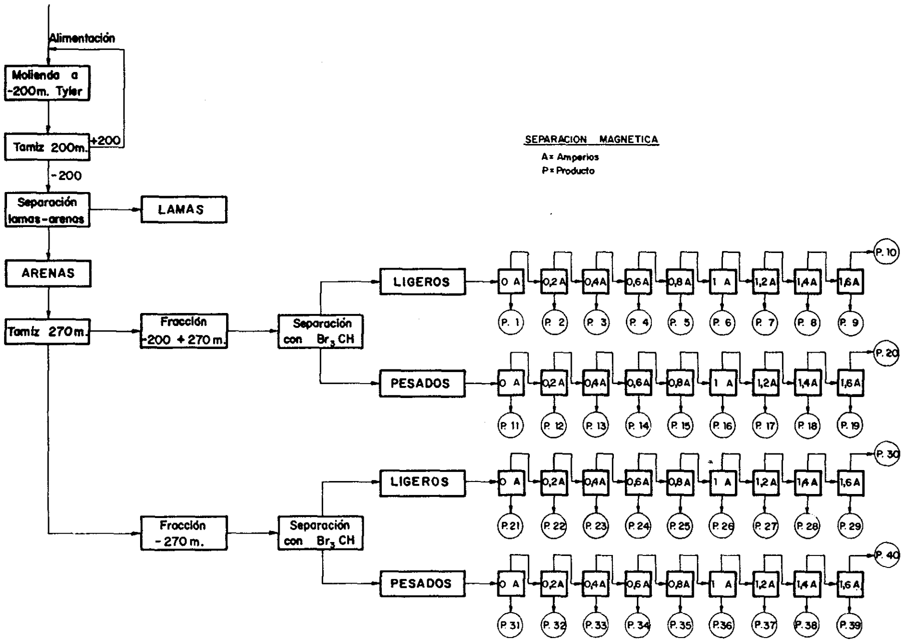


FIG. 2. Diagrama de flujo de los ensayos de separación en laboratorio de mineralogía.

## 3. 2. Análisis

El análisis microscópico se realizó por recuento de puntos según la técnica descrita por Barringer [7], contando: cuarzo, circón, minerales transparentes de titanio (rutilo y su variedad amarilla) y opacos. Para pasar a porcentajes en peso se tomaron las densidades de: 2,6, 4,7 y 4,2 para cuarzo, circón y minerales de titanio, respectivamente. La técnica, aunque laboriosa, fue más rápida que el análisis químico.

El análisis radiométrico se realizó sobre las muestras de las que no se tenía peso suficiente para análisis químico, o cuando interesaba una información aproximada. Se realizó por recuento de partículas $\alpha$ en un contador de centelleo.

En el análisis por rayos X, los debyegramas se realizaron con la radiación CoK$\alpha$, empleando filtro de hierro, en cámaras de 114,59 mm de diámetro a 30 kV, 10 mA y tiempos de exposición de 3 h.

### 3.3. Resultados

De los ensayos de molienda a 48 mallas y análisis mineralógico se obtuvieron los resultados que se indican en la tabla I, en los que se observa que a -65 mallas se libera el 30% del cuarzo, mientras que el circón y el cuarzo sólo se liberan para tamaños inferiores a -200 mallas. En la figura 3 se incluyen algunas fotomicrografías de las fracciones de tamizado.

TABLA I. TAMAÑOS DE LIBERACION

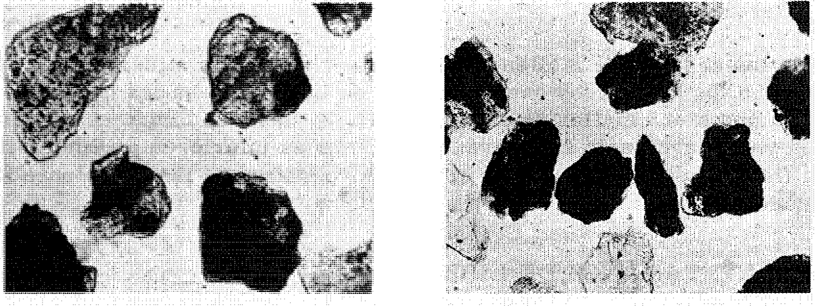
| Tamiz, mallas Tyler | Rechazos (%) | Volumen (%) | | | | |
|---|---|---|---|---|---|---|
| | | Circón liberado | MT de Ti liberado | Cuarzo liberado | Opacos liberado | Granos mixtos |
| + 65 | 0,91 | 0,2 | 0,2 | 31,3 | - | 68,3 |
| +100 | 4,45 | 0,5 | 0,4 | 25,0 | - | 73,9 |
| +150 | 9,69 | 0,2 | 0,8 | 28,3 | - | 70,5 |
| +200 | 7,88 | 2,5 | 3,6 | 33,6 | - | 60,1 |
| +270 | 11,47 | 21,3 | 17,8 | 55,9 | 4,8 | - |
| -270[a] | 65,59 | 32,4 | 20,2 | 38,1 | 9,1 | - |

[a] El análisis microscópico se ha efectuado sobre el producto deslamado.

Por otra parte, la fracción de -270 mallas se separó por elutriación en siete productos y se analizó uranio y, semicuantitativamente, circonio. La ley original era de 70 ppm $U_3O_8$ y 1,3% $ZrO_2$; en los productos recogidos hubo uno (-53 + 46,5 $\mu$m) con fuerte concentración en uranio y circonio, pues tuvo 170 ppm $U_3O_8$ y $>10\%$ $ZrO_2$, y otro (-5,8 $\mu$m), con ligero enriquecimiento, 100 ppm $U_3O_8$ y $\sim 1,4$ $ZrO_2$; el resto tuvieron de 40 a 60 ppm $U_3O_8$.

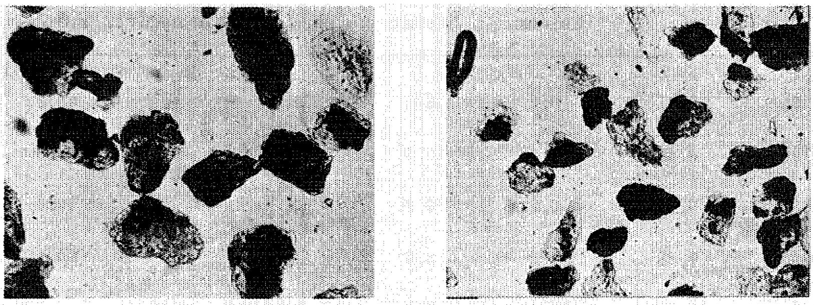
En la tabla II se dan los resultados de un ensayo típico de separación, incluyendo el análisis microscópico y la actividad $\alpha$; por otra parte, en la figura 4 se dan seis fotomicrografías de algunos productos obtenidos, pudiéndose observar en la de concentrados de circón la redondez de los bordes de los cristales y las inclusiones, aspecto típico de los granos detríticos.

Podría sorprender la forma en que se han separado los minerales, esto es, el rutilo entre las fracciones magnéticas y el circón en las fracciones no magnéticas (P. 20 y P. 40), ya que aunque ambos, el circón y el rutilo, son minerales no magnéticos, casi todos los autores consideraron al circón algo más magnético que al rutilo. Por ejemplo, Davis [8] da para la fuerza de atracción magnética del circón un valor de



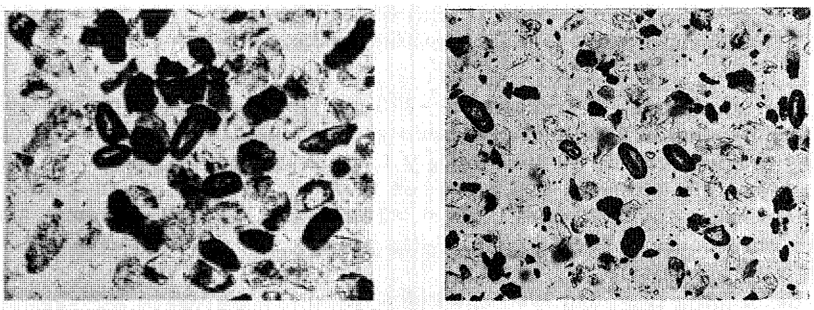
a) Fracción -48+65.-m.
Cuarzo liberado y cristales mixtos con circón.

b) Fracción -65+100.-m.
Cuarzo liberado y mixtos con circón ocluido



c) Fracción -100+150.-m.
Cuarzo liberado, mixtos y circón liberado

d) Fracción -150+200.-m.
Abundancia de circón liberado junto a mixtos



e) Fracción -200+270.-m.
liberación de todos constituyentes

f) Fracción -270.-m
Aparición de cristales partidos

FIG. 3. Fracciones de tamizado de mineral original (luz natural X 90).

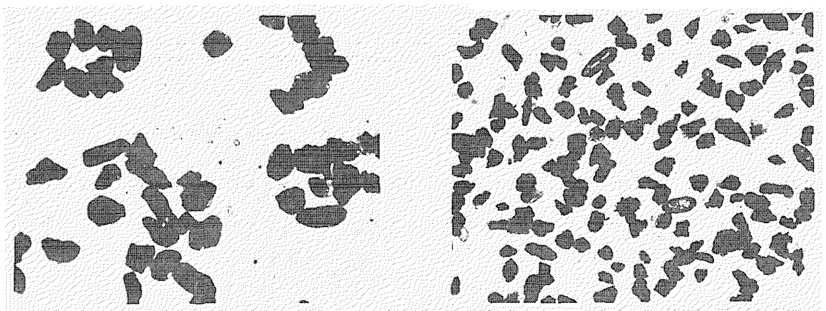
1,01 y para el rutilo 0,37, siendo 100 la del hierro y 40,18 la de la magnetita. Sin embargo, el contenido en hierro de los minerales puede hacer variar completamente este cuadro. Incluso, se ha recogido algo de circón en la fracción más magnética, lo cual está de acuerdo con Pullar [9] que indica la existencia, en muchos yacimientos, de circón con inclusiones ferruginosas, que lo hacen magnético, variando su

## TABLA II. SEPARACION MAGNETICA EN SEPARADOR ISODINAMICO FRANTZ

| | Producto | Peso (%) | Análisis microscópico (% peso) | | | Actividad |
|---|---|---|---|---|---|---|
| | | | Circón | MT titanio | Cuarzo | |
| | Alimentación | 100, 00 | 8, 6 | 19, 0 | 57, 1 | 100 |
| | -200 + 270 mallas | 26, 96 | - | - | - | 26 |
| | -270 mallas | 37, 80 | - | - | - | 50 |
| | Lamas | 35, 24 | - | - | - | 24 |
| | Fracción ligera total | 44, 27 | 0, 5 | 4, 6 | 91, 5 | 8 |
| Fracción pesada -200 270 mallas | P.11 (0 A) | 0, 05 | 7, 3 | 35, 2 | 1, 5) | |
| | P.12 (0, 2 A) | 0, 10 | 3, 9 | 36, 5 | 7, 3) | |
| | P.13 (0, 4 A) | 0, 11 | 3, 9 | 94, 6 | 1, 4) | 1 |
| | P.14 (0, 6 A) | 2, 05 | 0, 4 | 94, 6 | 4, 9) | |
| | P.15 (0, 8 A) | 1, 85 | 2, 3 | 90, 8 | 6, 8) | 4 |
| | P.16 (1, 0 A) | 0, 92 | 2, 0 | 93, 1 | 4, 8) | |
| | P.17 (1, 2 A) | 0, 41 | 3, 0 | 88, 4 | 8, 4) | |
| | P.18 (1, 4 A) | 0, 31 | 2, 2 | 88, 1 | 9, 5) | 2 |
| | P.19 (1, 6 A) | 0, 15 | 11, 4 | 76, 9 | 11, 9) | |
| | P.20 (No magn.) | 3, 19 | 75, 6 | 19, 4 | 4, 8 | 14 |
| Fracción pesada -270 mallas | P.31 (0 A) | 0, 05 | 7, 5 | 88, 5 | 2, 5) | |
| | P.32 (0, 2 A) | 0, 05 | 8, 7 | 80, 6 | 2, 3) | |
| | P.33 (0, 4 A) | 0, 05 | 7, 9 | 80, 8 | 2, 5) | |
| | P.34 (0, 6 A) | 1, 39 | 1, 3 | 88, 0 | 1, 6) | |
| | P.35 (0, 8 A) | 1, 59 | 0, 5 | 83, 9 | 6, 0 | 12 |
| | P.36 (1, 0 A) | 0, 51 | 2, 3 | 91, 8 | 5, 8) | |
| | P.37 (1, 2 A) | 0, 41 | 2, 2 | 93, 2 | 4, 5) | 4 |
| | P.38 (1, 4 A) | 0, 26 | 5, 8 | 90, 4 | 4, 0) | |
| | P.39 (1, 6 A) | 0, 21 | 4, 9 | 87, 5 | 7, 5) | |
| | P.40 (No magn.) | 6, 83 | 74, 3 | 18, 3 | 7, 3 | 30 |

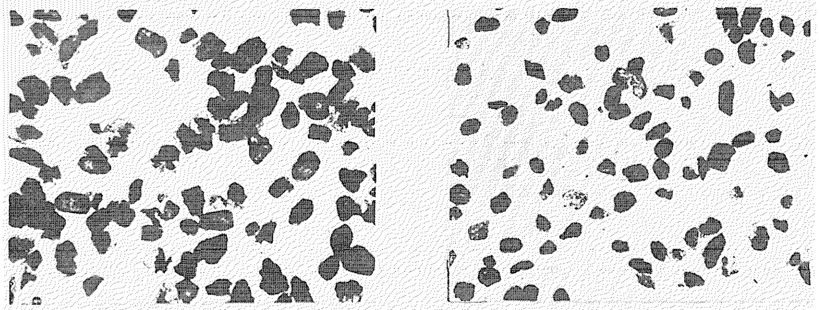
susceptibilidad con la cantidad de hierro presente, que puede ser bastante como para que aparezca entre los miembros de menor susceptibilidad del grupo de la ilmenita.

Según los resultados que se presentan en la tabla II, el 44% de la actividad se localiza en los concentrados de circón, el 24% en los de



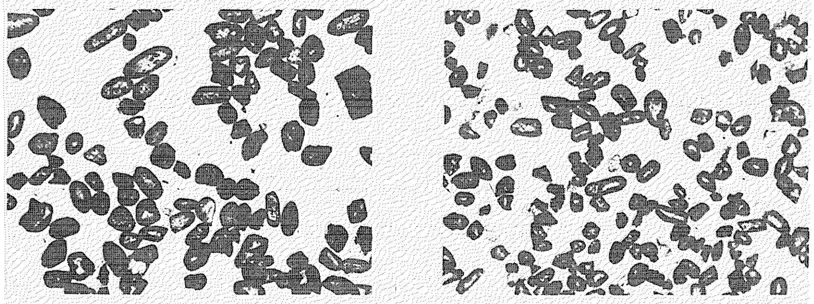
a ) Ilmenita - rutilo rojo.
P-13 , 0,4 A , -200+270.-m

b ) Ilmenita- rutilo rojo
P-33, 0,4 A , -270.-m



c ) Rutilos amarillos.
P-18 , 1,4 A , -200+270 -m

d ) Rutilo amarillo y cuarzo
P-38 , 1,4 A, -270,-m.



e ) Circón.
P-20, No magnético,-200+270-m.

f ) Circón, cuarzo y rutilo amarillo.
P-40, No magnético,-270 -m.

FIG. 4. Fotomicrografías de productos de concentración (luz natural X 90).

titanio, *el 8% en la fracción ligera total* y el 24% en las lamas. Esto último está de acuerdo con lo indicado para la fracción menor de 270 mallas.

Del 24% de actividad que corresponde a los concentrados de titanio (teniendo en cuenta los resultados del análisis microscópico, hay que considerar como concentrados de titanio toda la fracción magnetita pesada), sólo el producto magnético recogido a 0,8 A, al tamaño de -270 mallas, supone el 50%, o sea el 12% de la actividad total. Esta concentración también ocurre en el tamaño de -200 + 270 mallas, pero no de manera tan acusada.

Para intentar dilucidar esta cuestión se efectuaron análisis espectrográficos semicuantitativos de los productos de la fracción pesada correspondiente a -270 mallas (P. 31 a P. 40, ambos inclusive, de la tabla II). En la tabla III aparecen los resultados.

Hay dos hechos significativos. Por una parte, el aumento en el contenido de $P_2O_5$ y $La_2O_3$, con máximos de 1,5 y 0,2%. respectivamente, en el producto recogido a 0,8 A. Por otra, la concentración de hierro que se distribuye en dos zonas, alta para los productos recogidos desde 0 a 0,8 A y baja para los restantes. El contenido más bajo, 0,4%, corresponde al concentrado de circón.

Paralelamente a estos análisis, se determinó el contenido de $U_3O_8$ y $ThO_2$, en todos los productos del ensayo, uniendo las dos fracciones de tamizado, y el de $ZrO_2$, $TiO_2$ y CaO en los más significativos. Se dan los resultados en la tabla IV.

Por último, se realizaron debyegramas de los productos P. 15, P. 20, P. 34, P. 35, P. 39 y P. 40 y se compararon las lecturas de los correspondientes a los productos P. 34 (0,6 A, -270 mallas), P. 35 (0,8 A, -270 mallas), P. 39 (1,6 A, -270 mallas) y P. 40 (no magnético, -270 mallas), respectivamente, con los valores de espaciados e intensidades de los minerales más probables, tomados de las fichas de Hanawalt.

De las leyes de $ThO_2$, $P_2O_5$ y $La_2O_3$ y de los debyegramas correspondientes, se deduce que la actividad alta de la fracción magnética recogida a 0,8 A, puede ser debida a la existencia de monacita, que se libera a 270 mallas.

La distribución de los concentrados de hierro y de titanio en las fracciones magnéticas (tabla III), pueden depender de la presencia de las dos variedades de rutilo, rojo y amarillo. El color rojo y su intensidad dependen del contenido de hierro [10]. El rutilo amarillo, con menor proporción de hierro se ha recogido, efectivamente, en las fracciones menos magnéticas.

El pequeño contenido en calcio de la muestra (tablas III y IV), descarta la posibilidad de la existencia de esfena.

Resumiendo se puede decir que la muestra estudiada tuvo la composición mineralógica siguiente:

| Minerales principales | |
|---|---|
| Cuarzo | 55% |
| Circón | 8% |
| Rutilo | 16% |
| Arcillas | 15% |
| Micas | 5% |

| Minerales accesorios (<1%) |
|---|
| Ilmenita |
| Magnetita |
| Monacita |
| Materia carbonosa |

El rutilo se presentó en sus dos variedades roja y amarilla en una proporción de 2,3:1.

Los responsables de la radiactividad de la muestra fueron el circón, fundamentalmente, y la pequeña cantidad de monacita. El circón es una variedad uranífera, semejante al existente en Poços de Caldas (Brasil) aunque con menor contenido en uranio [11].

TABLA III. RESULTADOS DE LOS ANALISIS ESPECTROGRAFICOS SEMICUANTITATIVOS DE LOS PRODUCTOS RECOGIDOS EN EL SEPARADOR MAGNETICO DE LA FRACCION PESADA A -270 MALLAS

| % de | 0 A<br>P.31 | 0,2 A<br>P.32 | 0,4 A<br>P.33 | 0,6 A<br>P.34 | 0,8 A<br>P.35 | 1,0 A<br>P.36 | 1,2 A<br>P.37 | 1,4 A<br>P.38 | 1,6 A<br>P.39 | No magn.<br>P.40 |
|---|---|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | 2 | 2 | 2 | 2 | 2 | 2 | 1 | 1 | 0,8 | 0,3 |
| $B_2O_3$ | <0,3 | <0,3 | <0,3 | <0,3 | <0,3 | <0,3 | <0,3 | <0,3 | <0,3 | <0,3 |
| BaO | <0,003 | <0,003 | <0,003 | <0,003 | <0,003 | <0,003 | <0,003 | - | - | 0,003 |
| CaO | <0,04 | <0,04 | <0,04 | <0,04 | 0,05 | <0,04 | 0,04 | <0,04 | <0,04 | 0,1 |
| CoO | <0,02 | <0,02 | <0,02 | <0,02 | <0,02 | - | <0,02 | - | - | - |
| $Cr_2O_3$ | 0,2 | 0,05 | 0,1 | 0,08 | 0,1 | 0,2 | 0,08 | 0,06 | 0,2 | 0,02 |
| CuO | 0,1 | 0,06 | 0,02 | 0,01 | 0,01 | 0,03 | 0,02 | 0,01 | 0,05 | 0,01 |
| $Fe_2O_3$ | 14 | 14 | 14 | 11 | 12 | 7 | 5 | 4 | 4 | 0,4 |
| $La_2O_3$ | 0,02 | 0,03 | 0,01 | 0,04 | 0,2 | 0,1 | 0,08 | 0,03 | - | - |
| $Li_2O$ | <0,002 | <0,002 | 0,002 | 0,002 | <0,002 | 0,002 | 0,002 | 0,002 | <0,002 | 0,002 |
| MgO | 0,04 | 0,06 | 0,3 | 0,05 | 0,08 | 0,04 | 0,04 | 0,03 | 0,02 | <0,02 |
| MnO | 0,09 | 0,2 | 0,3 | 0,06 | 0,09 | 0,02 | 0,02 | 0,01 | 0,01 | 0,01 |
| NiO | 0,2 | 0,02 | 0,01 | 0,004 | 0,01 | 0,004 | 0,004 | 0,004 | 0,004 | - |
| $P_2O_5$ | <0,7 | 0,8 | 0,7 | 0,7 | 1,5 | 1 | 0,8 | 0,8 | 0,7 | 0,7 |
| PbO | 0,004 | 0,007 | <0,004 | 0,003 | 0,008 | 0,004 | 0,004 | 0,004 | 0,004 | 0,008 |
| $SiO_2$ | 10 | 20 | 6 | 6 | 9 | 18 | 18 | 18 | 17 | 20 |
| SnO | 0,004 | 0,007 | 0,004 | <0,004 | 0,008 | 0,01 | 0,01 | 0,01 | 0,01 | <0,004 |
| $TiO_2$ | 10 | 10 | >12 | >12 | >12 | >12 | >12 | >12 | >12 | >12 |
| $V_2O_5$ | 0,1 | 0,2 | 0,15 | 0,1 | 0,4 | 0,6 | 0,4 | 0,4 | 0,5 | 0,1 |
| $Y_2O_3$ | <0,2 | <0,2 | <0,2 | <0,2 | <0,2 | <0,2 | <0,2 | <0,2 | - | <0,2 |
| $ZrO_2$[a] | 2 | 3 | 0,4 | 0,1 | 0,2 | 0,8 | 2 | 2 | 1 | >3 |

[a] El patrón utilizado contenía solamente el 3% de $ZrO_2$.

No parece probable la existencia de davidita, o de su variedad guadarramita, ni de brannerita. Tampoco hay pruebas concluyentes de la presencia de esfena.

## 4. ENSAYOS DE TRATAMIENTO

Del estudio mineralógico se desprende que, a pesar del tonelaje del yacimiento, su interés en el momento actual es escaso. No obstante, se hicieron algunos tanteos de concentración y aunque los estudios se interrumpieron durante cuatro años, se ha empezado de nuevo a trabajar en ellos.

### 4. 1. Molienda

Se ha determinado la curva típica que corresponde a la de un mineral de una dureza de tipo medio en las primeras etapas de la molienda y de tipo entre blanda y semiblanda en las etapas finales (para un cernido superior al 55% por el tamiz de 200 mallas).

### 4. 2. Lixiviación directa

Unicamente se hicieron unos ensayos previos de ataque ácido y alcalino a 80°C, 24 h con pulpa del 50% en sólidos. Por via ácida se empleó ácido sulfúrico de 100 g $H_2SO_4/l$, 1 kg $Fe^{3+}$ /t y 1 kg $MnO_2/t$. En la lixiviación alcalina se usó una disolución con 50 g $Na_2CO_3/l$ y 50 g $NaHCO_3/l$. La extracción de uranio en los dos casos fué inferior al 0,1%. Por consiguiente, hay que recurrir a métodos más drásticos y preferiblemente sobre productos procedentes de concentración física.

### 4. 3. Concentración física

Los primeros ensayos de concentración gravimétrica realizados (criba y mesa), así como los de concentración magnética y electrostática, resultaron negativos, por lo que dados los tamaños de liberación se pensó en la flotación como el método más prometedor para la obtención de un concentrado de circón.

Después de unos ensayos de tanteo con colectores aniónicos y catiónicos, se decidió realizar un planteo a base de ácido oleico como colector y aceite de pino como espumante. Se empleó mineral molido (93%) a menos 270 mallas y sin deslamar, en forma de pulpa al 20% en sólidos y con 20 min de acondicionamiento. El diseño comprendió las variables y niveles siguientes:

| | | | |
|---|---|---|---|
| A. Dosis de colector g/t | 300 | 600 | 1200 |
| B. pH de la pulpa | 3, 5 | 5 | |
| C. Tiempo de flotación, min | 3 | 6 | |
| D. Presencia de depresor $Na_2SiO_3$ g/t | 0 | 400 | |

En la tabla V se dan los resultados obtenidos, recuperaciones de circón y rutilo. Las mejores recuperaciones, para ambos, se tuvieron a pH 7 y con dosis de colector de 600 y 1200 g/t, sin que fuese

TABLA IV. RESULTADOS DE LOS ANALISIS QUIMICOS DE LOS PRODUCTOS RECOGIDOS EN LA SEPARACION MAGNETICA

| Producto | Análisis (%) | | | | | Distribución | Distribución |
|---|---|---|---|---|---|---|---|
| | $U_3O_8$ | $ThO_2$ | $ZrO_2$ | $TiO_2$ | CaO | $U_3O_8$ (%) | $ThO_2$ (%) |
| Alimentación | 0,0101 | 0,060 | 5,16 | 16,00 | 0,30 | 99,9 | 99,9 |
| Lamas | 0,0070 | 0,055 | - | 12,50 | - | 25,8 | 33,0 |
| Fracción ligera | 0,0050 | 0,050 | - | 1,75 | - | 23,0 | 37,6 |
| Magn. a 0,4 A | 0,0114 | 0,064 | - | - | - | 0,4 | 0,3 |
| Magn. a 0,6 A | 0,0103 | 0,063 | 0,59 | 48,50 | 0,40 | 3,6 | 3,7 |
| Magn. a 0,8 A | 0,0129 | 0,123 | 4,36 | 50,00 | 0,20 | 4,6 | 7,2 |
| Magn. a 1,0 A | 0,0105 | 0,123 | 3,08 | 53,25 | 0,25 | 1,6 | 3,1 |
| Magn. a 1,6 A | 0,0075 | 0,075 | - | 48,40 | - | 1,3 | 2,2 |
| No magnético | 0,0379 | 0,075 | 42,82 | 11,75 | 0,20 | 39,6 | 12,8 |

## TABLA V. FLOTACION CON ACIDO OLEICO – RECUPERACION DE CIRCON

| Dosis de $SiO_3Na_2$ (g/t) | Tiempo de flotación (min) | pH de la pulpa | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 3,5 | | | 5 | | | 7 | | |
| | | Dosis de ácido oleico (g/t) | | | | | | | | |
| | | 300 | 600 | 1200 | 300 | 600 | 1200 | 300 | 600 | 1200 |
| | | Recuperación de circón | | | | | | | | |
| 0 | 3 | 72,3 | 47,9 | 48,0 | 43,3 | 45,4 | 79,8 | 25,9 | 93,1 | 93,3 |
| | 6 | 74,5 | 51,7 | 62,4 | 52,6 | 56,3 | 91,8 | 33,9 | 96,5 | 96,4 |
| 400 | 3 | 56,1 | 52,1 | 49,7 | 60,2 | 25,1 | 59,9 | 85,8 | 88,3 | 90,6 |
| | 6 | 62,4 | 61,7 | 73,5 | 68,2 | 46,6 | 80,3 | 90,7 | 96,0 | 96,4 |
| | | Recuperación de rutilo | | | | | | | | |
| 0 | 3 | 22,1 | 34,9 | 29,4 | 27,1 | 20,1 | 57,7 | 48,2 | 85,6 | 82,9 |
| | 6 | 27,7 | 42,7 | 39,3 | 39,1 | 32,3 | 77,1 | 60,9 | 94,1 | 94,3 |
| 400 | 3 | 28,8 | 21,3 | 19,2 | 31,5 | 26,9 | 58,3 | 72,8 | 83,4 | 87,0 |
| | 6 | 39,4 | 29,6 | 35,9 | 36,0 | 37,8 | 76,8 | 79,5 | 91,5 | 95,6 |

significativa la presencia de depresor. La relación de concentración fue muy pobre, 1,5 aproximadamente. El mejor concentrado de circón, aunque sólo con el 20% de $ZrO_2$, se obtuvo en las condiciones siguientes: 3,5 de pH, 300 g/t de ácido oleico, 6 min de agitación y sin la adición de depresor. La recuperación en estas condiciones fué pequeña: 74,5%.

El trabajo se continúa en la actualidad; se está tratando de eliminar en primer lugar cuarzo a tamaño grueso, realizar una remolienda y en el producto fino intentar el enriquecimiento en uranio, circonio y titanio, para lixiviarlos luego y proceder a su separación.

## REFERENCIAS

[1] ALIA, M., «Radioactive deposits and possibilities in Spain», Actas Conf. int.util.EAFP, VI, Nac.Unidas (1956) 196-97.

[2] MINGARRO MARTIN, E., ARRIBAS MORENO, A., La radiactividad en la zona de Despeñaperros, estudio de un posible yacimiento de uranio, Informe nº 27, Lab.Petrografía, JEN, Madrid (1956).

[3] ARRIBAS MORENO, A., Estudio petrográfico, mineralógico y metalogénico de los yacimientos españoles de minerales radiactivos, Tesis doctoral, Facultad de Ciencias, Madrid (1961).

[4] SMITH, W.L., The distribution of the uranium in a quarzite from the Despeñaperros zone, Spain, and an evaluation of the possible concentration of its various ore minerals, Battelle Memorial Institute, Columbus, Ohio (1957).

[5] MILNER, H.B., Sedimentary Petrography, Thomas Murby & Co, London (1952).

[6] HEINRICH, E.W., Mineralogy and Geology of radioactive raw materials, McGraw-Hill, New York (1958).

[7] BARRINGER, A.R., The preparation of polished sections of ores and mill products using diamond abrasives, and their quantitative study by point counting methods, Bull.Inst.Mining Met. (London, 1954).

[8] DAVIS, Bulletin, 7, Minnesota School of Mines.

[9] PULLAR, S.S., Proc.of the Australas.Inst. Mining Met.205 (1963) 85.

[10] DANA, The System of Mineralogy, John Wiley & Son, New York (1952) 557.

[11] MAFFEI, F.J., PUCCI, J.R., FERREIRA, W., «Aspectos químicos de la mena de zirconio uranífera de Poços de Caldas (Brasil)», Actas Conf.int.util. EAFP, VIII, Nac.Unidas (1956) 138-41.

# LIGNITOS RADIACTIVOS ESPAÑOLES, NATURALEZA Y SOLUBILIZACION DEL URANIO

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**Abstract — Resumen**

SPANISH RADIOACTIVE LIGNITES; NATURE AND SOLUBILITY OF THE URANIUM. The authors describe the features of some 70 samples of radioactive lignites from various places in Spain (Huesca, Lerida, Teruel, Galicia and Murcia) with uranium contents varying between 20 and 1200 ppm. They carried out experiments on extraction of the uranium from these ores both by direct treatment and after roasting to eliminate organic matter and bring about concentration. The acid method was considered for leaching of the uranium from the substances in question using agitation and static bed techniques. Investigations were also carried out on the effect of the variables represented by grain size, amount of acid, temperature time and oxidants, in addition to those involved in the roasting process.

LIGNITOS RADIACTIVOS ESPAÑOLES, NATURALEZA Y SOLUBILIZACION DEL URANIO. Los autores presentan las caracteristicas de unas 70 muestras de lignitos radiactivos procedentes de distintos puntos de España (Huesca, Lérida, Teruel, Galicia y Murcia) con leyes de uranio comprendidas entre 20 y 1200 ppm. El beneficio del uranio de estos minerales se ha abordado por tratamiento directo y después de someterlos a tostación, lo que eliminó la materia orgánica y produjo enriquecimiento. La lixiviación del uranio de los productos indicados se consideró por vía ácida, utilizando técnicas de agitación y de lecho estático. Se investigó la influencia de las variables tamaño de grano, dosis de ácido, temperatura, tiempo y oxidante, además de las implicadas en los procesos de tostación.

## 1. INTRODUCCION

La presencia de uranio en materias carbonosas ha sido señalada con frecuencia y se han realizado intentos para recuperar el uranio de las mismas. En Estados Unidos se efectuaron intensas investigaciones en este campo [1, 2, 3] y se elaboraron diversos proyectos [4], pasándose recientemente a la etapa de explotación industrial. En Europa también se realizaron investigaciones, siendo de destacar los trabajos realizados en Yugoslavia [5].

El descubrimiento de los lignitos radiactivos en España es relativamente reciente: finales de 1963 y principios de 1964. No obstante, los índices descubiertos han sido numerosos y se tiene gran esperanza en ellos como futuras fuentes de uranio.

De acuerdo con los afloramientos y la continuidad de las capas el tonelaje es considerable. En muchos puntos los trabajos de exploración se han podido seguir fácilmente porque existen minas de lignito en explotación, o abandonadas pero accesibles. De los índices considerados hasta ahora los más prometedores son las cuencas de Calaf y una pequeña adyacente a la misma, con una superficie de unos 60 km$^2$, y la de Fraga-Mequinenza-Almatret, con una extensión aproximada de 150 km$^2$.

En la tabla I se dan los análisis de algunas de las muestras recogidas. Hay una gran diversidad de leyes, con algunos valores realmente intere-

TABLA I. RELACION DE ALGUNAS DE LAS MUESTRAS DE LIGNITOS PROCEDENTES DE DISTINTOS YACIMIENTOS

| Origen | Ref. | $H_2O$ (%) | Cenizas (%) | Muestra original (%) | | | | | Cenizas $U_3O_8$ (ppm) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $SO_4$ | $P_2O_5$ | $CO_3$ | Mo | $U_3O_8{}^a$ | |
| Calaf | L-2 | 4,1 | 93,0 | 8,2 | 0,19 | 3,25 | - | 50 | 54 |
| Calaf | L-3 | 2,7 | 80,8 | 10,5 | 0,62 | 1,10 | - | 900 | 1114 |
| Calaf | L-6 | 7,5 | 50,7 | 2,9 | 0,32 | 2,84 | - | 347 | 685 |
| Calaf | L-8 | 4,5 | 75,1 | 8,6 | 0,57 | 0,70 | - | 655 | 872 |
| Calaf | L-18 | 2,1 | 43,2 | 16,0 | 0,22 | 0,30 | - | 1150 | 2662 |
| Calaf | L-19 | 4,2 | 73,0 | 14,8 | 0,32 | 0,80 | - | 1130 | 1548 |
| Calaf | L-21 | 6,0 | 38,2 | 5,4 | 0,03 | 0,04 | 0,018 | 299 | 783 |
| Calaf | L-22 | 4,5 | 43,0 | 5,7 | 0,05 | 0,04 | - | 140 | 323 |
| Calaf | L-24 | 8,7 | 39,7 | 6,0 | 0,07 | 0,03 | 0,012 | 186 | 469 |
| Calaf | L-25 | 16,6 | 55,8 | 13,6 | 0,11 | 0,08 | 0,019 | 294 | 527 |
| Calaf | L-66 | 3,3 | 38,5 | 4,0 | 0,12 | 1,15 | 0,006 | 395 | 1025 |
| Calaf | L-67 | 7,1 | 58,1 | 6,2 | 0,23 | 0,07 | 0,021 | 1225 | 2110 |
| Calaf | L-68 | 5,6 | 31,6 | 5,22 | 0,23 | 2,63 | 0,006 | 152 | 480 |
| Calaf | L-69 | 4,1 | 32,1 | 3,3 | 0,11 | 1,20 | 0,010 | 304 | 948 |
| Fraga | L-40 | 7,7 | 67,8 | - | - | - | - | 102 | 150 |
| Fraga | L-42 | 22,5 | 66,8 | - | - | - | - | 84 | 126 |
| Fraga | L-43 | 23,4 | 32,6 | - | - | - | - | 117 | 359 |

TABLA I (cont.)

| Origen | Ref. | $H_2O$ (%) | Cenizas (%) | Muestra original (%) | | | | | Cenizas $U_3O_8$ (ppm) |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $SO_4$ | $P_2O_5$ | $CO_3$ | Mo | $U_3O_8$[a] | |
| Fraga | L-45 | 8, 6 | 83, 6 | - | - | - | - | 118 | 141 |
| Fraga | L-46 | 11, 2 | 78, 4 | - | - | - | - | 40 | 51 |
| Fraga | L-49 | 28, 8 | 33, 9 | - | - | - | - | 182 | 537 |
| Fraga | L-51 | 22, 0 | 26, 8 | - | - | - | - | 47 | 175 |
| Fraga | L-52 | 25, 0 | 10, 8 | - | - | - | - | 25 | 231 |
| Teruel | L-53 | 6, 7 | 91, 3 | - | - | - | - | 175 | 192 |
| Teruel | L-54 | 5, 9 | 92, 4 | - | - | - | - | 597 | 644 |
| Teruel | L-55 | 4, 1 | 93, 5 | - | - | - | - | 228 | 244 |
| Teruel | L-57 | 4, 7 | 95, 6 | - | - | - | - | 63 | 66 |
| Pobla de Segur | L-60 | 15, 7 | 44, 4 | - | - | - | - | 77 | 173 |
| Pobla de Segur | L-62 | 9, 6 | 14, 5 | - | - | - | - | 131 | 903 |
| Pobla de Segur | L-63 | 10, 2 | 20, 6 | - | - | - | - | 198 | 961 |
| P. García Rodríguez | L-34 | 0, 2 | 88, 7 | 0, 42 | 0, 2 | 0, 16 | < 0, 01 | 30 | 33 |
| Berga | L-35 | 7, 1 | 13, 2 | 1, 7 | 0, 08 | 1, 27 | < 0, 001 | 10 | 102 |
| C. de Berges | L-36 | 2, 0 | 85, 6 | 6, 0 | 0, 26 | 1, 52 | < 0, 01 | 43 | 50 |
| Murcia | L-37 | - | - | - | - | - | - | - | 56 |

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[a] ppm $U_3O_8$.

santes y que justifican su investigación. Sin embargo, dada la limitación de recursos de nuestro país, se consideró conveniente realizar una investigación escalonada ligando los trabajos de prospección e investigación geológico-minera con los de metalurgia extractiva. En este sentido la investigación metalúrgica se dedicó fundamentalmente a la etapa de lixiviación como fase clave desde el punto de vista de rendimiento y de costes.

La solubilización del uranio se ha abordado, por una parte, sobre la base del lignito original triturado a tamaño grueso y cuyos estériles de lixiviación se podrían aprovechar como combustible y, por otra, en la recuperación del uranio de las cenizas procedentes ya de una tostación o combustión adecuada para la disolución del uranio, ya de las cenizas de una posible central térmica cuyo subproducto sería el uranio. Los resultados obtenidos son prometedores y la investigación geológica prosigue con la realización de sondeos complementarios, con la ayuda de testigos.

En cuanto al análisis químico de los lignitos o de sus cenizas, cabe comentar ligeramente el contenido en impurezas:

El contenido en sulfatos estuvo comprendido entre el 6 y el 37% y gran parte del mismo proviene de las inclusiones de yeso. Si se considera su repercusión sobre el proceso de tratamiento la incidencia mayor correspondería al método alcalino de ataque, para el que habría que prever consumos altos, 66 - 410 kg/t, de carbonato sódico. Esto hizo que se dejara para más adelante el estudio de la lixiviación alcalina.

La ley en carbonatos fue muy variable: menos de 0,1 a 6,2% $CO_3$. El consumo de ácido a que equivaldría su existencia estaría comprendido entre menos de 16 kg/t y 100 kg/t de cenizas.

Los contenidos en fosfatos fueron variables, entre 0,1 y 1% $P_2O_5$, y sería de prever la necesidad de una precipitación del concentrado en dos etapas para los eluidos de cambio de ión, aunque bastaría la operación en una fase para la extracción con disolventes.

La concentración de cal, procedente del yeso y caliza, fue alta: 66-23% CaO. También se tuvieron leyes altas en hierro, 9-18%, que en su mayoría se solubilizó en la lixiviación. Los contenidos en molibdeno fueron inferiores a los previstos de los análisis espectrográficos semicuantitativos.

Desde el punto de vista geológico no parece que haya gran diferencia con otros yacimientos de lignitos radiactivos, en que el uranio está retenido y concentrado en el carbón de baja calidad. En la actualidad se están realizando determinaciones petrográficas sobre los testigos de sondeos y también ensayos de concentración física.

## 2. TOSTACION

Los lignitos radiactivos españoles tienen poderes caloríficos bajos, inferiores a 4000 kcal/kg. Su contenido en cenizas es de 30 a 40%. Esto, unido a la baja ley del mineral original, indujo a pensar en su combustión como un método para elevar la ley de alimentación al mismo tiempo que se podía incrementar la capacidad de una planta de tratamiento.

Por otra parte, se lograría un menor consumo de reactivos por kilogramo de uranio solubilizado, mayor recuperación de uranio, mejores características de sedimentación y filtración de las pulpas y soluciones más puras de materia orgánica. Todos estos extremos han sido comprobados en los ensayos realizados, descritos más adelante.

Las tostaciones se hicieron en un horno de mufla con regulación automática de temperatura. Se observó que la temperatura de 450°C era suficiente para conseguir una buena eliminación de materia orgánica. Temperaturas más altas (hasta los 900°C) dieron pérdidas por calcinación similares. Hay que tener en cuenta, además, que no se deben sobrepasar los 600°C, pues ello produciría una sinterización del material que se reflejaría en una menor recuperación de uranio.

## 3. LIXIVIACION

Según se ha indicado antes se consideró el ataque de los productos tostados y del mineral original. Además, se estudió tanto la lixiviación con agitación como en lecho estático, ambas con ácido sulfúrico. De esta forma se tuvo una comparación entre los dos tipos de ataque y, por otra parte, la lixiviación estática permitió obtener una visión más detallada del fenómeno de disolución tanto del uranio como de las impurezas.

### 3.1. Lixiviación estática

Estos ensayos se realizaron en columnas de vidrio de 72 mm de diámetro, con una altura de lecho aproximada de 25 cm, estando el peso de muestra comprendido entre 750 y 1000 g. La granulometría de la alimentación fue -5 mm. Las dosis de ácido estuvieron comprendidas entre 125 y 360 kg $H_2SO_4$/t distribuidas en 9-18 ciclos de solución ácida, cada uno de los cuales constaba de 12 h en fase de riego y otras 12 h en período de maduración. Todos los ataques se realizaron a temperatura ambiente (18°C).

### 3.1.1. Lignitos originales

En la tabla II se presentan los resultados obtenidos en la lixiviación estática de lignitos. Para muestras sin tostar las recuperaciones de uranio variaron considerablemente de unas a otras y estaban en el intervalo del 27 al 92%, con valores medios del 60%. Fueron, pues, valores generalmente bajos aunque no podía atribuirse a un defecto de ácido, pues en todas las muestras la acidez libre presentaba valores suficientemente elevados (> 25 g $H_2SO_4$/l). El potencial de oxidación también tuvo valores adecuados.

Las concentraciones en impurezas no fueron excesivamente altas, especialmente en lo que se refiere a fosfatos. El hierro se hallaba en su mayor parte en el estado férrico. Se observó que la disolución de uranio e impurezas fue simultánea en las primeras etapas del proceso, y la obtención de soluciones relativamente libres de impurezas será probablemente difícil.

Los líquidos procedentes de estos ataques presentaron intensas coloraciones pardo-negruzcas producidas por la presencia de materia orgánica, lo cual afectará a las etapas de purificación, tanto si se hace por extracción con disolventes para formar emulsiones como si se efectúa por cambio de ión, en cuyo caso se produciría un envenenamiento de la resina. La eliminación previa de materia orgánica de estos líquidos de lixiviación sería difícil y costosa.

TABLA II. LIXIVIACION ESTATICA DE LIGNITOS – RESULTADOS GLOBALES DE ALGUNAS DE LAS MUESTRAS

| Muestra | Acido sulfúrico | | Volumen recogido (l/t) | Efluentes | | | | | Recuperación (%) |
|---|---|---|---|---|---|---|---|---|---|
| | U (g/t) | Conc. (g/l) | | Potencial intervalo (mV) | Acidez máxima g $H_2SO_4$/l | Conc. media final (g/l) | | g $U_3O_8$/l (intervalo) | |
| | | | | | | Fe (t) | $P_2O_5$ | | |
| Productos sin tostar | | | | | | | | | |
| L-8 | 125 | 40 | 3400 | 450 - 540 | 26,6 | 4,2 | 0,44 | 0,22 - 0,41 | 89,7 |
| L-8 | 125 | 80 | 1900 | 450 - 530 | 31,3 | 6,4 | 0,66 | 0,15 - 0,63 | 90,1 |
| L-18 | 125 | 40 | 3400 | 370 - 500 | 21,9 | 2,8 | 0,16 | 0,12 - 0,24 | 47,2 |
| L-18 | 125 | 80 | 1800 | 350 - 510 | 27,5 | 4,4 | 0,18 | 0,12 - 0,39 | 43,1 |
| L-67 | 200 | 100 | 2190 | 500 - 525 | 73,5 | 9,8 | 0,83 | 0,25 - 0,80 | 92,3 |
| L-68 | 200 | 100 | 1950 | 400 - 415 | 72,5 | 3,3 | 1,04 | 0,019 - 0,125 | 55,1 |
| L-69 | 200 | 100 | 1950 | 375 - 410 | 91,2 | 3,1 | 0,57 | 0,010 - 0,079 | 26,9 |
| Productos tostados | | | | | | | | | |
| L-8 | 125 | 40 | 2800 | 340 - 540 | < 3 | 9,6 | 1,93 | 0,13 - 2,61 | 94,6 |
| L-8 | 125 | 80 | 1200 | 330 - 450 | < 3 | 15,3 | 4,05 | 0,30 - 6,85 | 90,6 |
| L-18 | 125 | 40 | 2800 | 270 - 500 | < 3 | 6,6 | 0,69 | 0,08 - 2,40 | 87,6 |
| L-18 | 125 | 80 | 1200 | 270 - 420 | < 3 | 8,5 | 1,16 | 0,40 - 3,64 | 84,9 |
| L-67 | 300 | 100 | 2800 | 420 - 650 | 66,0 | 25,2 | 1,48 | 0,10 - 3,62 | 98,8 |
| L-68 | 360 | 100 | 3100 | 200 - 460 | 71,0 | 6,3 | 2,32 | 0,014 - 0,56 | 88,8 |
| L-69 | 300 | 100 | 2500 | 200 - 480 | 70,0 | 4,7 | 1,39 | 0,022 - 0,83 | 91,2 |

### 3.1.2. Lignitos tostados

Se utilizaron como alimentación las cenizas de tostación a 450°C. Los resultados fueron, en todos los casos, mayores que los obtenidos de los correspondientes productos sin tostar.

Se utilizaron dosis de ácido (kg/t de ceniza) iguales o mayores que en el caso de muestras sin tostar. La acidez libre resultó inferior a la obtenida para muestras sin tostar. En algunos casos aquélla fue muy baja, afectando las recuperaciones que hubiesen sido probablemente más altas con el empleo de dosis mayores de ácido.

Los valores del potencial fueron en la mayoría de los casos suficientemente elevados para una buena marcha de la lixiviación. En algunas muestras comenzó con valores bajos en los primeros riegos, tal vez originados por la presencia de materia orgánica debida a una tostación incompleta, como parece indicar la coloración de los líquidos obtenidos en estos primeros riegos; sin embargo, pronto alcanzó valores aceptables.

Los líquidos parecían exentos de materia orgánica (salvo lo indicado en el punto anterior). Las concentraciones de hierro y fosfatos fueron mayores que las obtenidas con productos sin tostar, repitiéndose el hecho (quizá más acentuado en este caso) de que su solubilización tuvo lugar en los primeros riegos. Aunque la finalidad de estos estudios no fue determinar la influencia de los diversos factores que podían afectar a la lixiviación sino más bien obtener una idea del comportamiento y variabilidad de las muestras se observó que, para una misma dosis de ácido, el empleo de soluciones más diluidas conducía a mejores y más rápidas extracciones de uranio pero se obtenían soluciones fértiles más diluidas.

Resumiendo, se advirtió que el consumo de ácido fue relativamente elevado tanto para muestras tostadas como sin tostar. Sin embargo, puesto que en la mayoría de los casos la acidez residual de los últimos riegos era elevada (figuras 1 y 2), cabía la posibilidad de la recirculación de estos líquidos para un mejor aprovechamiento del ácido. Un circuito en contracorriente de este tipo presentaría además las ventajas de obtener soluciones fértiles de composición más homogénea.

En la tabla III se hace un estudio comparativo de los resultados obtenidos en la lixiviación estática de tres muestras de lignitos. Su comportamiento general varió de unas a otras como corresponde a sus distintas características. Así, la L-67 respondió bien al ataque ácido tanto si estaba tostada como si no lo estaba, mientras que las otras dos apenas si se atacaban sin tostar. Las diferencias se mantuvieron en los datos de consumo de ácido: la muestra L-67 consumió más ácido por peso de muestra atacada cuando se tostó previamente, mientras que para la L-68 y L-69 el consumo se redujo en un 25%. Esto se reflejó en el coste del ácido consumido en lixiviación que fue algo mayor para la muestra L-67; en cambio, en las otras dos se redujo, con la tostación, a menos de la mitad.

## 3.2. Lixiviación con agitación

Los ensayos se realizaron a escala de laboratorio utilizando pesos de muestra que oscilaban de 100 a 500 g. El producto se molió a -35 mallas. Para la obtención de las cenizas se tostaron los lignitos a un tamaño máximo de 5 mm y posteriormente se realizó la reducción a la granulo-

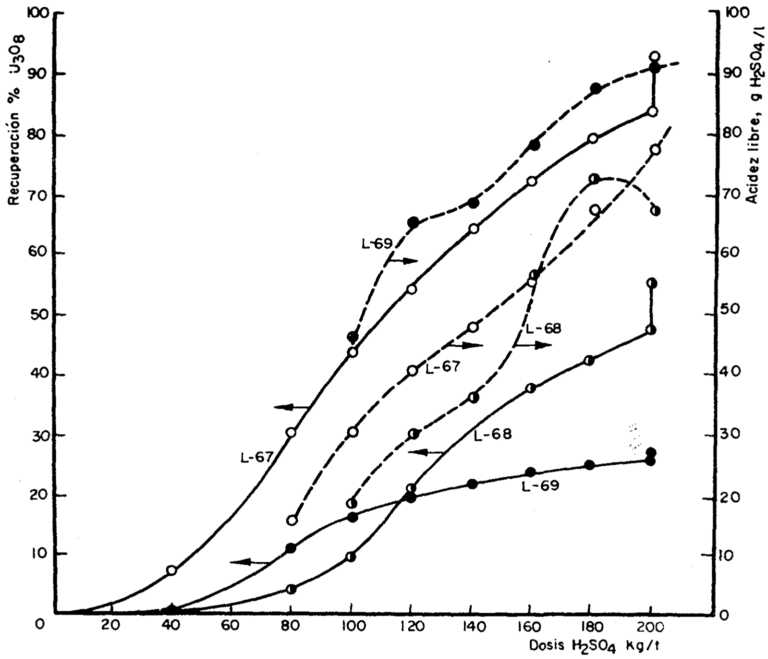

FIG. 1. Recuperación de uranio por lixiviación estática de lignitos sin tostar.

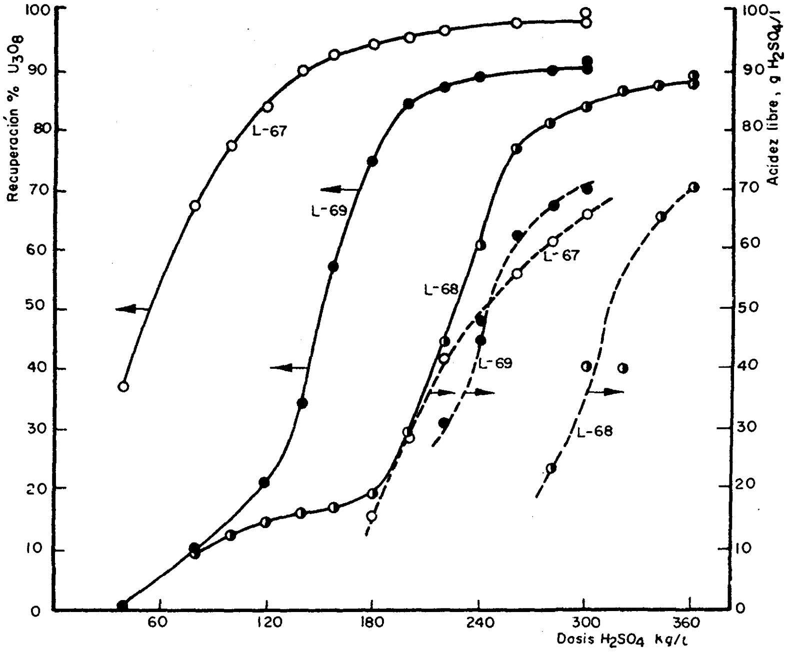

FIG. 2. Recuperación de uranio por lixiviación estática de lignitos tostados.

TABLA III. LIXIVIACION ESTATICA - COMPARACION DE LIGNITOS SIN TOSTAR Y TOSTADOS

| Muestras | L-67 | L-68 | L-69 |
|---|---|---|---|
| Lignitos originales | | | |
| Ley, g $U_3O_8$/t | 1221 | 208 | 291 |
| Recuperación, % $U_3O_8$ | 92,3 | 55,1 | 26,9 |
| Pérdida peso, % | 27,9 | 0 | 1,1 |
| Ley residuos, g $U_3O_8$/t | 131 | 93 | 215 |
| Pérdida uranio, g $U_3O_8$/t | 94 | 93 | 213 |
| Consumo $H_2SO_4$, kg/t | 88 | 109 | 73 |
| Consumo $H_2SO_4$, kg/kg $U_3O_8$ solubilizado | 78 | 947 | 942 |
| Coste $H_2SO_4$, pts/kg $U_3O_8$ solubilizado | 117 | 1420 | 1413 |
| Lignitos tostados | | | |
| Ley, g $U_3O_8$/t | 1920 | 528 | 928 |
| Recuperación, % $U_3O_8$ | 98,8 | 88,8 | 91,3 |
| Pérdida peso, % | 20,5 | 5,5 | 8,7 |
| Ley residuos, g $U_3O_8$/t | 28 | 62 | 89 |
| Pérdida uranio, g $U_3O_8$/t | 22 | 59 | 81 |
| Consumo $H_2SO_4$, kg/t | 190 | 243 | 178 |
| Consumo $H_2SO_4$, kg/t original | 110 | 77 | 57 |
| Consumo $H_2SO_4$ kg/kg $U_3O_8$ solubilizado | 100 | 517 | 210 |
| Coste $H_2SO_4$, pts/kg $U_3O_8$ solubilizado | 150 | 776 | 315 |

metría citada. La relación líquido/sólido empleada en el ataque fue de 2/1 para los dos tipos de productos. El resto de las variables dependió de cada ensayo particular.

### 3.2.1. Lignitos originales

Se hizo un número reducido de ensayos, puesto que no se tenían muchas esperanzas en ellos. Los resultados conseguidos (tabla IV) pusieron de manifiesto el escaso interés de un tratamiento según esta línea. Las recuperaciones fueron bajas en todos los casos, pese a que los potenciales de oxidación estaban todos por encima de los valores mínimos necesarios y las dosis de ácido utilizadas dieron unos valores finales del pH muy bajos. Las demás condiciones, especialmente la temperatura, estaban a unos niveles suficientemente altos para esperar incrementos sensibles en la recuperación al aumentar los niveles de dichas variables. La calidad de los líquidos fue deficiente con elevado contenido en materia orgánica.

TABLA IV. LIXIVIACION CON AGITACION DE LIGNITOS - RESULTADOS GLOBALES DE ALGUNAS DE LAS MUESTRAS ESTUDIADAS

| Muestra | Condiciones | | | | | Conc. en líquidos (g/l) | | | Extracción |
|---|---|---|---|---|---|---|---|---|---|
| | $H_2SO_4$ (kg/t) | Temperatura (°C) | Tiempo (h) | (pH) | (mV) | $U_3O_8$ | Fe(t) | $P_2O_5$ | $U_3O_8$ (%) |
| Productos sin tostar | | | | | | | | | |
| L-3 | 200 | 60 | 12 | 0,7 | 490 | 0,285 | 14,6 | 2,22 | 63,6 |
| L-8[a] | 125 | 60 | 12 | 0,5 | 490 | 0,230 | 7,5 | 0,61 | 70,4 |
| L-18 | 150 | 60 | 12 | 0,6 | 480 | 0,795 | 7,1 | 0,34 | 63,5 |
| L-19 | 125 | 60 | 12 | 0,7 | 590 | 0,435 | 5,6 | 0,45 | 71,6 |
| Productos tostados | | | | | | | | | |
| L-3 | 150 | 60 | 12 | 1,1 | 410 | 0,540 | 2,9 | 2,70 | 82,1 |
| L-8 | 90 | 60 | 12 | 1,2 | 500 | 0,425 | 5,6 | 2,30 | 93,3 |
| L-18 | 95 | 60 | 12 | 1,2 | 495 | 1,040 | 4,9 | 1,00 | 82,6 |
| L-19 | 95 | 60 | 12 | 1,3 | 500 | 0,730 | 3,2 | 1,60 | 88,7 |
| L-67 | 150 | 20 | 12 | 0,9 | 480 | 0,985 | 20,2 | 1,86 | 94,0 |
| L-67 | 300 | 20 | 12 | 0,7 | 470 | 1,005 | 24,3 | 2,10 | 95,6 |
| L-67 | 150 | 20 | 24 | 1,2 | 475 | 1,015 | 22,2 | 1,96 | 94,9 |
| L-67 | 300 | 20 | 24 | 0,8 | 460 | 1,015 | 26,0 | 2,12 | 96,2 |
| L-67 | 150 | 60 | 12 | 1,8 | 500 | 1,015 | 13,8 | 1,50 | 95,7 |
| L-67 | 300 | 60 | 12 | 1,4 | 520 | 1,035 | 31,7 | 2,22 | 97,5 |

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[a] Se añadió 30 kg $MnO_2$/t.

TABLA IV (cont.)

| Muestra | Condiciones | | | | | Conc. en líquidos (g/l) | | | Extracción $U_3O_8$ (%) |
|---|---|---|---|---|---|---|---|---|---|
| | $H_2SO_4$ (kg/t) | Temperatura (°C) | Tiempo (h) | (pH) | (mV) | $U_3O_8$ | Fe(t) | $P_2O_5$ | |
| Productos tostados | | | | | | | | | |
| L-67 | 150 | 60 | 24 | 1,4 | 490 | 1,030 | 13,3 | 1,86 | 96,4 |
| L-67 | 300 | 60 | 24 | 1,0 | 510 | 0,995 | 33,0 | 2,26 | 98,1 |
| L-68 | 150 | 20 | 12 | 3,6 | 120 | 0,005 | 9,0 | 0,72 | 2,0 |
| L-68 | 300 | 20 | 12 | 1,4 | 220 | 0,175 | 11,1 | 2,70 | 67,4 |
| L-68 | 150 | 20 | 24 | 4,0 | - | 0,035 | 5,1 | 0,82 | 15,4 |
| L-68 | 300 | 20 | 24 | 1,4 | 150 | 0,145 | 14,5 | 2,53 | 56,4 |
| L-68 | 150 | 60 | 12 | 4,3 | - | 0,010 | 7,6 | 0,05 | 4,0 |
| L-68 | 300 | 60 | 12 | 2,3 | - | 0,215 | 23,4 | 0,93 | 77,3 |
| L-68 | 150 | 60 | 24 | 5,6 | - | 0,005 | 5,6 | - | < 2 |
| L-68 | 300 | 60 | 24 | 2,2 | - | 0,185 | 21,6 | 0,96 | 73,6 |
| L-69 | 150 | 20 | 12 | 1,3 | - | 0,135 | 7,1 | 1,12 | 32,3 |
| L-69 | 300 | 20 | 12 | 1,2 | - | 0,310 | 12,4 | 1,39 | 69,2 |
| L-69 | 150 | 20 | 24 | 1,2 | 360 | 0,380 | 5,2 | 1,15 | 78,6 |
| L-69 | 300 | 20 | 24 | 1,1 | 360 | 0,405 | 5,6 | 1,56 | 89,9 |
| L-69 | 150 | 60 | 12 | 0,9 | 415 | 0,435 | 3,6 | 1,15 | 84,5 |
| L-69 | 300 | 60 | 12 | 1,8 | - | 0,370 | 32,9 | 0,81 | 82,3 |
| L-69 | 150 | 60 | 24 | 2,7 | - | 0,390 | 3,6 | 0,86 | 85,1 |
| L-69 | 300 | 60 | 24 | 1,3 | 390 | 0,425 | 7,9 | 1,70 | 93,2 |

TABLA V. COMPARACION DE LA LIXIVIACION CON AGITACION DE LIGNITOS SIN TOSTAR Y TOSTADOS

| Muestras | L-3 | L-8 | L-18 | L-19 |
|---|---|---|---|---|
| Cenizas, % | 80,8 | 75,1 | 43,2 | 75,0 |
| Ley original, g $U_3O_8$/t | 900 | 655 | 1150 | 1130 |
| Ley cenizas, g $U_3O_8$/t | 1114 | 872 | 2662 | 1548 |
| *Lixiviación lignitos originales* | | | | |
| Acido sulfúrico, kg/t | 204 | 123 | 150 | 125 |
| $MnO_2$, kg/t | 30 | 0 | 0 | 0 |
| Pérdida peso, % | 2 | 12 | 24 | 18 |
| Rendimiento, % $U_3O_8$ | 63,6 | 70,4 | 63,5 | 71,6 |
| Residuos, g $U_3O_8$/t | 333 | 219 | 523 | 421 |
| Pérdida, g $U_3O_8$/t | 326 | 193 | 398 | 345 |
| Consumo y costes: | | | | |
| Acido sulfúrico, kg/kg $U_3O_8$ | 357 | 267 | 205 | 154 |
| Manganesa, kg/kg $U_3O_8$ | 52 | 0 | 0 | 0 |
| Coste reactivos, Pts/kg $U_3O_8$ | 795 | 400 | 307 | 231 |
| Lixiviación cenizas | | | | |
| Acido sulfúrico, kg/t | 150 | 90 | 96 | 96 |
| $MnO_2$, kg/t | 0 | 0 | 0 | 0 |
| Pérdida peso, % | 2 | 4,8 | 5,7 | 4,1 |
| Rendimiento, % $U_3O_8$ | 82,1 | 93,3 | 82,6 | 88,7 |
| Residuos, g $U_3O_8$/t | 241 | 64 | 468 | 194 |
| Pérdida, g $U_3O_8$/t | 236 | 61 | 440 | 186 |
| Consumo y costes: | | | | |
| Acido sulfúrico, kg/kg $U_3O_8$ | 164 | 111 | 43 | 70 |
| Manganesa, kg/kg $U_3O_8$ | 0 | 0 | 0 | 0 |
| Coste reactivos, Pts/kg $U_3O_8$ | 246 | 166 | 64 | 105 |
| Conversión a base lignitos originales | | | | |
| Acido sulfúrico, kg/t | 121 | 68 | 41 | 70 |
| $MnO_2$, kg/t | 0 | 0 | 0 | 0 |
| Pérdida, g $U_3O_8$/t | 190 | 46 | 190 | 136 |
| Rendimiento, % $U_3O_8$ | 78,9 | 93,0 | 83,5 | 88 |
| Coste reactivos, Pts/t | 182,5 | 102 | 61,5 | 105 |

### 3.2.2. Lignitos tostados

Paralelamente a lo ocurrido en el caso de lixiviación estática, los resultados fueron mejores que para los lignitos originales (tabla IV). En la tabla V se han resumido los datos más interesantes para la comparación del comportamiento frente a la lixiviación con agitación de productos tostados y sin tostar. En ella se ve la ventaja que supone el tratamiento del lignito previamente tostado, tanto para las recuperaciones globales de uranio, como para el consumo y coste de ácido. Además, los líquidos obtenidos estaban libres de materia orgánica.

Las variables que más afectaron a la solubilización del uranio (tabla IV) fueron la dosis de ácido y la temperatura; la influencia del tiempo, en el intervalo considerado, fue nula o muy pequeña. Para las diferentes muestras la magnitud de los efectos fue distinta. Para conseguir buenas solubilizaciones las dosis de ácido deben ser elevadas, con valores comprendidos entre 150 y 300 kg/t, utilizando también temperaturas próximas a 60°C. Estos valores señalan un orden de magnitud alrededor del cual debe centrarse una investigación más detallada. Otro punto a considerar es el empleo de agentes oxidantes en algunas de las muestras que presentan potenciales redox excesivamente bajos.

## 3.3. Influencia de la temperatura de tostación en la solubilización de uranio

Se estudió la posible influencia de la temperatura de tostación sobre la solubilización del uranio. Se consideraron temperaturas de 400, 600, 800 y 900°C. Las cenizas se molieron a -35 mallas y se atacaron durante 24 h utilizando dos dosis de ácido (200 y 300 kg $H_2SO_4$/t) y dos temperaturas (20 y 60°C). Las extracciones de uranio, en porciento, fueron:

| Condiciones de ataque | | Temperatura de tostación (°C) | | | |
|---|---|---|---|---|---|
| kg $H_2SO_4$/t | Temperatura (°C) | 400 | 600 | 800 | 900 |
| 200 | 20 | 91,4 | 88,7 | 44,4 | 50,3 |
| 200 | 60 | 94,2 | 87,2 | 56,9 | 57,4 |
| 300 | 20 | 92,7 | 88,7 | 44,4 | 50,3 |
| 300 | 60 | 94,2 | 85,7 | 52,7 | 57,4 |

Al margen de las pequeñas influencias debidas a las condiciones de ataque, los resultados pusieron de manifiesto que las temperaturas altas de tostación originaban pérdidas altas de uranio, especialmente por encima de los 600°C. El intervalo de tostación más adecuado es el de 400 a 450°C. Actualmente se están realizando estudios más detallados sobre esta variable.

## 3.4. Comparación de lixiviación estática y con agitación

Los resultados obtenidos con muestras sometidas a ambos tipos de lixiviación indican que pueden conseguirse recuperaciones del mismo orden, quizá ligeramente superiores en lixiviación estática. A continuación se indican los resultados para una serie de cenizas, tratadas con la misma dosis de ácido en ambos tipos de lixiviación, y aquellos cuyos intervalos de solubilización corresponden a ataques realizados en distintas condiciones de temperatura y concentración de ácido.

| Muestra | Uranio solubilizado (%) en lixiviación | |
|---|---|---|
| | Estática | Con agitación |
| L-8 | 90,6 - 94,6 | 93,3 |
| L-18 | 84,9 - 87,6 | 82,6 |
| L-67 | 98,8 | 95,6 - 97,7 |
| L-68 | 88,8 | 67,4 - 77,3 |
| L-69 | 91,3 | 82,3 - 93,2 |

Estas ligeras diferencias en favor de la lixiviación estática pueden atribuirse a la distinta forma de adición del ácido, que en el caso de la lixiviación con agitación tuvo lugar al comienzo del ensayo y con una sola adición, mientras que en la lixiviación estática se hizo una distribución gradual a lo largo de los distintos riegos. Esto puede dar lugar a un mayor consumo de ácido por parte de la ganga y consecuentemente a una disminución en la solubilización del uranio en la lixiviación con agitación.

### 3.5. Costes de reactivos

Las tablas III y V dan los resultados metalúrgicos y los consumos y costes de reactivos para distintas muestras de lignitos tostados y sin tostar, para lixiviación estática y lixiviación con agitación respectivamente.

Los resultados metalúrgicos y consumos de reactivos se han comentado anteriormente. Por lo que se refiere a los costes de reactivos, éstos resultaron mucho más pequeños cuando se atacaban las cenizas de tostación que cuando se trataba de lignitos originales. Esto se debe, por una parte, a una mayor extension del ataque y, por otra parte, a un menor consumo de reactivos cuando se refieren a lignitos sin tostar.

Se observa una gran diferencia en los costes de reactivos entre las distintas muestras consideradas. A ello contribuyen fundamentalmente la ley en uranio, el contenido en cenizas y el consumo de ácido. Este último podría reducirse mediante un circuito en contracorriente para lixiviación estática o utilizando un ataque en dos etapas en lixiviación con agitación.

## 4. CALIDAD DE LOS LIQUIDOS Y RECUPERACION

Los líquidos procedentes de productos sin tostar presentan, por su elevado contenido en materia orgánica, características desfavorables para posteriores tratamientos, lo que unido al bajo rendimiento de lixiviación y al elevado consumo de reactivos hace que no sean muy prometedores los circuitos basados en ellos.

Por lo que se refiere a la lixiviación de productos tostados, los líquidos no contienen materia orgánica y se consideran adecuados para su recuperación, bien por cambio de ión o por extracción con aminas, debiendo basarse la elección, de una u otra técnica, en un estudio experimental.

Las concentraciones de uranio, mediante un circuito apropiado en contracorriente, puede considerarse que oscilarían, en las muestras estudiadas, entre 0,2 y 1 g $U_3O_8/l$. El contenido en hierro de los líquidos sería en general elevado, estando la mayor parte en forma férrica, y en cuanto a los fosfatos, su concentración sería más bien baja.

Un circuito aconsejable para este tipo de productos consistiría en una etapa de reducción de tamaño, tostación a 450°C, molienda posterior a -35 mallas, lixiviación en dos etapas, recuperación del uranio por extracción y obtención de un concentrado por precipitación. Como alternativa se podría introducir la lixiviación estática sobre cenizas trituradas.

## REFERENCIAS

[1] WOODY, R.J., GEORGE, D.R., PETROW, H., BREYMANN, J.B., PORTER, E.S., Laboratory investigation of Dakota lignites, USAEC, Report WIN-54 (1957).

[2] PITMON, G.R., PETER, M.A., GARDNER, H.E., WINSLOW, G., SHIMMIN, R.L., Pilot plant testing of Dakota lignites, USAEC, Report WIN-81 (1957).

[3] PORTER, E.S., PETROW, H.G., Recovery of uranium from lignites, Mining Engng, 1004-1006 (1957).

[4] MITCHELL, R.J., Uranium bearing lignite - North Dakota newest industry, Met. Min. Process. 2 3 (1965) 16-23.

[5] JOVANOVIĆ, M., PACOVIĆ, N., «El ataque alcalino del uranio de las cenizas de carbón», 2a Conf. int. util. EAFP, 2, Nac. Unidas (1958) 549.

# LIXIVIACION ESTATICA DE MINERALES ESPAÑOLES DE URANIO

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**Abstract — Resumen**

STATIC LEACHING OF SPANISH URANIUM ORES. The paper summarizes the experience acquired in Spain during seven years of investigation on the static leaching of uranium ores. The operations covered minerals showing wide variations with regard to both uranium content (250 and 2000 ppm) and the type of rock and gangue (granites, shales, sandstones, sulphides, carbonates, limonites etc.). The studies were carried out on quantities of material varying from a few kilograms to several tons. Leaching agents included water, solid reagents (pyrites), alkaline carbonates and sulphuric acid. The systems used consisted of both simple layouts and other, more elaborate schemes including recycling of the liquors. The uranium was recovered from the liquors first by direct precipitation and later by ion-exchange and extraction with amines.

LIXIVIACION ESTATICA DE MINERALES ESPAÑOLES DE URANIO. La memoria resume la experiencia española de siete años de estudio sobre lixiviación estática de minerales de uranio. Se ha estudiado una gran variedad de minerales tanto en lo que respecta a ley de uranio (250 y 2000 ppm), como a la naturaleza de las rocas y gangas (granitos, pizarras, areniscas, sulfuros, carbonatos, limonitas, etc.). Los estudios se han realizado en diferentes escalas, desde kilogramos a varias toneladas. Los agentes de lixiviación han sido variables: agua, reactivos sólidos (piritas), carbonatos alcalinos y ácido sulfúrico. Los circuitos empleados se refieren tanto a esquemas sencillos, como a otros más elaborados con recirculaciones de líquido. La recuperación del uranio de los líquidos se resolvió inicialmente por precipitación directa, pero luego se efectuó mediante cambio de ion y extracción con aminas.

## 1. INTRODUCCION

La solubilización del uranio a partir de minerales dispuestos en lecho estático se observó en las pérdidas de uranio ocurridas en Portugal y en el aprovechamiento de este fenómeno para el beneficio de minerales de baja ley [1]; los investigadores ingleses también estudiaron [2, 3] la solubilización del uranio por riego con agua combinado con la adición de pirita, azufre y la acción de las bacterias.

En Francia se trabajó mucho en este campo siguiendo, en principio [4], técnicas de lixiviación a largo plazo con soluciones diluidas. En esta misma línea se pasó a realizar ensayos en escala piloto, mostrando las grandes posibilidades de tales métodos [5].

En Argentina [6] se aplicó la lixiviación por percolación a minerales de uranio y cobre. Suecia también empleó esta técnica con gran intensidad [7, 8].

Portugal presentó en la Tercera Conferencia Internacional sobre la Utilización de la Energía Atómica con Fines Pacíficos, en Ginebra [9], un interesante ejemplo de lixiviación con soluciones ácidas concentradas y recuperación del uranio en una instalación compacta de cambio de ion. En Estados Unidos se aplica no sólo la lixiviación por capilaridad o por inmersión [10] sobre pilas de mineral, sino también en el interior de las minas. También del Canadá aparecen recientemente referencias en la bibliografía. Por último, cabe recordar el gran incremento en la lixiviación bacteriana de minerales de cobre.

En España se observó, en los años 1958 - 59, que algunos de los minerales perdían fácilmente el uranio con agua [11]. En el año 1960 se empezaron una serie de investigaciones sobre diferentes minerales con el fin de:

a) Evitar la pérdida del uranio existente en los minerales depositados a la intemperie por la acción de los agentes atmosféricos.

b) Beneficiar por lixiviación natural [12, 13], primero, y finalmente por ataque ácido, alcalino o lixiviación bacteriana a boca mina, aquellos minerales de uranio que por su baja ley, situación geográfica u otras causas no resulten rentables en plantas convencionales.

c) Seleccionar los métodos más adecuados de tratamiento de líquidos para recuperar el uranio en ellos contenidos.

El trabajo experimental realizado ha sido importante tanto en lo que se refiere a la fase de lixiviación, como a la de tratamiento de los líquidos resultantes de la misma.

Para la lixiviación se utilizaron diversas técnicas que, sobre una base del peso de mineral, se pueden clasificar en:

a) Ensayos con 1,5 kg de mineral triturado a -5 mm, promediando los errores de desmuestre. Se utiliza una columna de 70 mm de diámetro con una altura de lecho de 250 mm.

b) Experiencias con 10-15 kg de mineral triturado a 5 mm. Se realizan en tubos con un diámetro de 10 cm y una altura de lecho aproximada de 125 cm.

c) Ensayos de laboratorio con muestras de 100-500 kg, en lechos de mineral de 20 y 40 cm de diámetro y alturas de 1,90 m en el primer caso y de 0,90 m y 2,70 m, en el segundo.

d) Ensayos a escala piloto, en una instalación de doce cubículos, de sección rectangular de 1,50 × 1,25 m y una altura total de 2,5 m, lo que da una capacidad de 6-7 t/cubículo.

e) Ensayos semiindustriales en eras con solera impermeabilizada con capacidades de 500 a 3000 t de mineral.

De los factores que gobiernan la lixiviación estática de minerales de uranio, los que se han considerado con más detalle han sido:

El tipo de mineral y ganga con distintas especies mineralógicas de uranio, roca encajante (pizarras, granitos, areniscas, etc.) y minerales accesorios (pirita, carbonatos, fosfatos, etc).

El tamaño de trituración entre 5 y 30 mm.

Los reactivos: con pirita y sulfato ferroso, en lixiviación natural; ácido sulfúrico, clorato sódico y sulfato férrico, en lixiviación ácida, y por último carbonato-bicarbonato sódico y permanganato potásico en lixiviación alcalina. Además del tipo de reactivo se ha considerado las dosis y la concentración en los que se añaden disueltos.

La forma de riego continua y discontinua y dentro de esta última modalidad, en la que alternan períodos de riego y maduración, el líquido se ha distribuido bien uniformemente o bien de forma intermitente.

El tiempo de tratamiento es más o menos prolongado, dependiendo del tipo de reactivo utilizado; así, por ejemplo, con soluciones de ácido sulfúrico ha oscilado entre 10 y 30 días mientras que con el empleo de

TABLA I. COMPOSICION MINERALOGICA Y QUIMICA DE ALGUNAS MUESTRAS

| | Los Ratones 1) | Peñascal 1) | Yacimiento A 2) | Yacimiento B 2) | Eureka 3) |
|---|---|---|---|---|---|
| Especies mineralógicas de uranio | Pechblenda<br>Autunita | Autunita<br>Oxidos negros | Pechblenda<br>Coffinita<br>Coracita<br>Gummitas<br>Uranotilo | Coffinita<br>Pechblenda<br>Uranotilo<br>Autunita<br>Fosfuranilita | Pechblenda<br>Tucholitas<br>Gummitas<br>Carnotita |
| Especies de la ganga | Pirita | Pirita<br>Marcasita | Calcita<br>Sulfuros de hierro<br>Limonita | Pirita | Calcita<br>Siderita<br>Pirita<br>Calcosina<br>Malaquita<br>Azurita |
| Composición química (%) | | | | | |
| $U_3O_8$ | 0,18 | 0,23 | 0,062 | 0,043 | 0,172 |
| S. Oxidado | 0,58 | 0,12 | 0,21 | 0,15 | 0,08 |
| S. Total | 0,95 | 1,19 | 1,64 | 0,42 | 0,70 |
| Fe total | 1,43 | 1,42 | 4,45 | 3,90 | 1,40 |
| $P_2O_5$ | 0,31 | 0,14 | 0,04 | 0,08 | 0,03 |
| $CO_3$ | 0,07 | 0,60 | 0,20 | 0,06 | 4,85 |
| Ca | 0,81 | 0,76 | - | - | 0,60 |
| Mg | 0,25 | 0,57 | - | - | 0,48 |
| Cu | - | - | - | - | 0,73 |

Roca encajante: 1) Granitos; 2) Pizarras; 3) Areniscas.

reactivos sólidos los tiempos estuvieron comprendidos entre 6 meses y 2 años.

Se puede decir que se cuenta con una gran información sobre el comportamiento de los minerales españoles frente a la lixiviación estática, y se está en condiciones de pasar a una etapa de explotación industrial. A continuación se resume esta experiencia según los minerales, las modalidades del proceso de lixiviación y la técnica de recuperación del uranio de las soluciones fértiles.

## 2. MINERALES ESTUDIADOS

Se han realizado estudios de lixiviación estática con una gran variedad de muestras que, atendiendo a la roca encajante, pueden clasificarse en graníticas, pizarras, areniscas y lignitos. La tabla I da la composición química y mineralógica de algunas de las muestras estudiadas. Las muestras procedían de los distintos yacimientos españoles, en explotación o en período de investigación. Las leyes en uranio de las muestras abarcan un intervalo muy amplio, estando comprendidas la mayor parte de ellas entre 250 y 2000 ppm de $U_3O_8$.

Esta variedad se manifiesta también en lo que se refiere a las especies mineralógicas de uranio, ganga y roca encajante. Unas muestras contenían minerales primarios de uranio (coffinita, pechblenda) mientras que en otras predominaban los minerales secundarios (autunita, torbernita, uranotilo, saleita, etc). Entre los componentes de la ganga, con influencia en el proceso de la lixiviación, cabe citar los sulfuros, carbonatos, fosfatos, limonitas, etc. Finalmente, por lo que respecta a la roca encajante, ya se han indicado antes los distintos tipos.

## 3. EXPERIENCIAS EN LIXIVIACION NATURAL

Las muestras estudiadas han mostrado una gran variabilidad en su comportamiento frente a la lixiviación natural, tanto en lo que se refiere al uranio solubilizado como a la velocidad de lixiviación.

La tabla II resume los resultados obtenidos en la lixiviación de una serie de muestras de distintos tipos y refleja el porcentaje máximo de uranio solubilizado por riego con agua. Desde el punto de vista de la recuperación del uranio por este sistema pocas muestras dan resultados satisfactorios, pero atendiendo a la posibilidad de pérdidas durante el almacenamiento se observa que la mayoría de ellas dan lugar a solubilizaciones de importancia.

Entre los resultados obtenidos interesa resaltar:

a) La extrapolación de los resultados a tiempos más largos. Los ensayos de este tipo son, en general, de larga duración. El examen de las curvas porcentaje de uranio solubilizado versus tiempo indica que son de tipo hiperbólico, respondiendo a una ecuación general del tipo $y = x/(A + Bx)$, y haciendo $z = (x/y)$ resulta la ecuación de una recta, $z = A + Bx$, que puede ajustarse fácilmente.

La comprobación con minerales de distinta procedencia mostró la posibilidad de predecir con buena aproximación, partiendo de los resultados obtenidos en los seis primeros meses, las solubilizaciones que pueden obtenerse en períodos superiores a un año.

TABLA II. RESULTADOS FINALES DE LIXIVIACION NATURAL

| Mineral | Ley alimentación $U_3O_8$(%) | Intervalo de pH | Tiempo semanas | Solubilización de $U_3O_8$(%) |
|---|---|---|---|---|
| 1. Técnica A) | | | | |
| A1, Pozo 16 | 0,219 | 2,9 - 2,0 | 23 | 57,0 |
| A1, Pozo 15 | 0,201 | 3,5 - 1,8 | 23 | 81,2 |
| A1, Pozo 22 | 0,080 | 7,8 - 6,5 | 14 | 4,4 |
| A1, Pozo 19 | 0,202 | 4,7 - 2,7 | 23 | 11,7 |
| A1, Pozo 20 | 0,188 | 3,0 - 1,5 | 23 | 84,8 |
| A1, Pozo 10 | 0,061 | 2,9 - 1,8 | 23 | 89,3 |
| A1, Pozo 12 | 0,043 | 2,9 - 1,7 | 23 | 69,5 |
| A2, Zona D, pozo 6 | 0,294 | 7,7 - 6,3 | 14 | 0,4 |
| A5, Esperanza | 0,097 | 4,1 - 2,7 | 23 | 24,3 |
| A3, Zona 17, pozo 2 | 0,233 | 3,4 - 1,7 | 23 | 91,8 |
| Zona | 0,173 | 5,9 - 3,6 | 11 | 0,2 |
| A2, Zona D, pozo 7 | 0,058 | 7,3 - 5,8 | 23 | 0 |
| B1, Zona 7, pozo 4 | 0,161 | 4,5 - 3,6 | 23 | 23,1 |
| B3, Zona Caridad, pozo 2 | 0,073 | 3,3 - 1,9 | 23 | 57,5 |
| B1, Zona 7, pozo 1 | 0,146 | 3,7 - 1,8 | 23 | 28,5 |
| B3, Zona 19, pozo 1 | 0,043 | 5,9 - 3,6 | 23 | 0 |
| B1, Zona 7, pozo 3 | 0,089 | 4,2 - 2,2 | 23 | 23,5 |
| B3, Zona 19, pozo 3 | 0,328 | 6,1 - 4,6 | 23 | 0 |
| B4, Zona 8 y 9, pozo 1 | - | 6,2 - 4,3 | 23 | 0 |
| 2. Técnica B) | | | | |
| Casa del Gallo | 0,368 | 6,5 - 5,9 | 73 | 4,4 |
| Villares de Yeltes | 0,729 | 6,7 - 5,6 | 82 | 0,5 |
| Ratones 204 | 1,1 | 2,7 - 1,7 | 75 | 68,3 |
| Fe 806 | 0,436 | 5,0 - 3,5 | 88 | 10,5 |
| Fe LN - 03 | 0,090 | 4,5 - 4,0 | 28 | 12,8 |
| Esperanza 805 | 0,270 | 3,5 - 2,3 | 47 | 84,6 |
| Caridad | 0,042 | 2,5 - 2,0 | 42 | 98,8 |
| Caridad ELN - 2 | 0,047 | 2,5 - 1,8 | 50 | 65,7 |
| Caridad ELN - 2 | 0,047 | 2,2 - 1,5 | 50 | 61,3[a] |
| 3. Técnica C) | | | | |
| Valderrascón 701 | 0,179 | 2,5 - 1,9 | 68 | 75,5[b] |
| Valderrascón 701 | 0,179 | 2,5 - 1,9 | 68 | 69,5[b] |
| Caridad ELN - 2 | 0,047 | 2,6 - 2,0 | 60 | 30,9 |

Técnica: A) 1,5 kg; B) 15 kg; C) 150 kg de muestra.

[a] Riego pobre; [b] con distinta granulometría (-5 y -12 mm).

La figura 1 muestra, para cuatro minerales, los puntos experimentales y las curvas de regresión obtenidas con los resultados de las 25-30 primeras semanas y también con todos los datos experimentales. En la gráfica se han representado los valores de y en función de x; las ecuaciones de las rectas de regresión de (x/y) en función de x son las siguientes:

| Mineral | Recta con 25-30 semanas | Recta con todos los resultados |
|---|---|---|
| Valderrascón | $(x/y) = (1,31\ x + 3,16) \cdot 10^{-2}$ | $(x/y) = (1,27\ x + 3,65) \cdot 10^{-2}$ |
| Caridad | $(x/y) = (3,19\ x + 7,60) \cdot 10^{-2}$ | $(x/y) = (3,09\ x + 9,20) \cdot 10^{-2}$ |
| Carretona | $(x/y) = (1,70\ x + 23,1) \cdot 10^{-2}$ | $(x/y) = (2,10\ x + 18,1) \cdot 10^{-2}$ |
| Ratones | $(x/y) = (1,09\ x + 14,2) \cdot 10^{-2}$ | $(x/y) = (1,20\ x + 96,0) \cdot 10^{-2}$ |

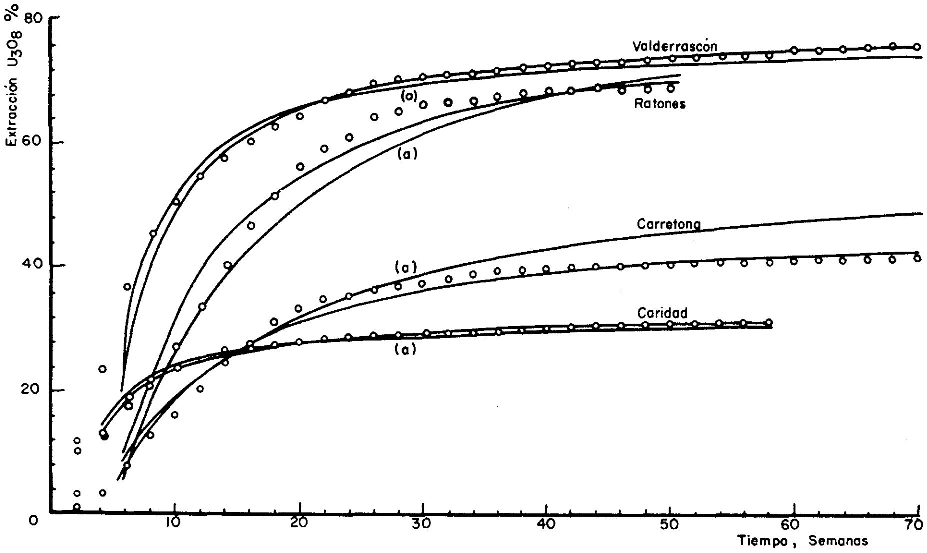

FIG. 1. Extracción de uranio en función del tiempo. Puntos experimentales y curvas de regresión con datos de 30 (a) y 60-70 semanas.

b) Extrapolación de resultados de laboratorio a escala de campo. A pesar de que existen una serie de circunstancias en la lixiviación natural en el campo (tales como condiciones climatológicas, acción de bacterias, etc) que son difíciles, sino imposibles, de reproducir en ensayos a escala de laboratorio, se ha encontrado, no obstante, una correlación estrecha entre los ensayos realizados con 150 kg de mineral y los resultados obtenidos en era según puede verse en la figura 2 para el mineral de Carretona (granítico).

## 4. LIXIVIACION CON ADICION DE PIRITA

La aplicabilidad de este tipo de lixiviación depende fundamentalmente del mineral. La tabla III da un resumen de los resultados obtenidos con

TABLA III. RESULTADOS DE LIXIVIACION CON ADICION DE REACTIVOS SOLIDOS

| Mineral | Ley alimentación $U_3O_8$(%) | Condiciones | | | Intervalo de pH | Resultados finales | |
|---|---|---|---|---|---|---|---|
| | | Granulometría (mm) | Pirita (kg/t) | $FeSO_4 \cdot 7H_2O$ (kg/t) | | Tiempo (semanas) | Uranio solubilizado (%) |
| Fe | 0,090 | -25 | 10 | 5 | 2,9 - 2,0 | 31 | 62,5 |
| Fe | 0,090 | -12 | 10 | 10 | 2,9 - 1,9 | 29 | 50,5 |
| La Virgen | 0,115 | -12 | 5 | 5 | 3,5 - 3,6 | 25 | 0,3 |
| La Virgen | 0,115 | -12 | 5 | 10 | 3,4 - 3,7 | 25 | 0,2 |
| La Virgen | 0,115 | -12 | 10 | 5 | 3,6 - 3,7 | 25 | 0,2 |
| Valdemascaños | 0,076 | -25 | 2,5 | 6,6 | 3,6 - 3,6 | 73 | 6,8 |
| Valdemascaños | 0,076 | -15 | 2,5 | 6,6 | 4,2 - 3,6 | 73 | 7,8 |
| Valdemascaños | 0,076 | -15 | 9 | 7,5 | 4,2 - 3,3 | 103 | 65,5 |
| Valdemascaños | 0,113 | -25 | 3,5 | 9,8 | 3,5 - 3,9 | 109 | 10,7 |
| Valdemascaños | 0,113 | -15 | 3,5 | 8,8 | 3,8 - 3,9 | 109 | 6,2 |
| Valdemascaños | 0,113 | -15 | 9,0 | 8,8 | 3,8 - 3,4 | 114 | 18,0 |
| Carretona | 0,121 | -17 | 4,0 | 7,1 | 2,5 - 1,9 | 72 | 41,2 |
| Carretona | 0,121 | -17 | 4,5 | 3,0 | 2,9 - 1,9 | 72 | 47,3 |
| Carretona | 0,132 | - 5 | 4,0 | 7,1 | 2,9 - 1,9 | 72 | 59,1 |
| Caridad | 0,047 | -25 | 10 | 7,0 | 2,5 - 2,2 | 25 | 59,0[a] |
| Caridad | 0,047 | -25 | 10 | 7,0 | 2,2 - 1,9 | 25 | 85,0[a] |
| Caridad | 0,047 | - 5 | 10 | 7,0 | 2,5 - 2,2 | 25 | 44,5 |

TABLA III. (cont.)

| Mineral | Ley alimentación $U_3O_8$(%) | Condiciones | | | Intervalo de pH | Resultados finales | |
|---|---|---|---|---|---|---|---|
| | | Granulometría (mm) | Pirita (kg/t) | $FeSO_4 \cdot 7H_2O$ (kg/t) | | Tiempo (semanas) | Uranio solubilizado (%) |
| Ratones | 0,063 | - 6 | - | 5,0 | 2,6 - 2,1 | 6 | 80,3 |
| Ratones | 0,063 | - 6 | - | 10,0 | 2,6 - 2,2 | 6 | 80,4 |
| Ratones | 0,265 | - 12 | - | 5,0 | 2,7 - 1,2 | 22 | 92,3 |
| Ratones | 0,265 | - 12 | - | 10,0 | 2,7 - 1,2 | 22 | 90,1 |
| Ratones | 0,265 | - 30 | - | 5,0 | 2,7 - 1,3 | 22 | 84,8 |
| Ratones | 0,265 | - 30 | - | 10,0 | 2,6 - 1,3 | 22 | 85,9 |
| Ratones | 0,265 | - 30 | - | 10,0 | 2,8 - 1,7 | 30 | 86[b] |
| Peñascal | 0,251 | - 12 | 10 | 8,0 | 3,0 - 1,2 | 30 | 97,1 |

---

[a] Obtenidos con distinta dimensión del lecho.

[b] En escala piloto.

distintos tipos de minerales; puede observarse en ella que hay algunos con respuesta nula (por ejemplo, las muestras de la Virgen debido indudablemente a la presencia de carbonatos) y en otros la solubilización alcanzada no es suficiente desde el punto de vista práctico. Finalmente hay

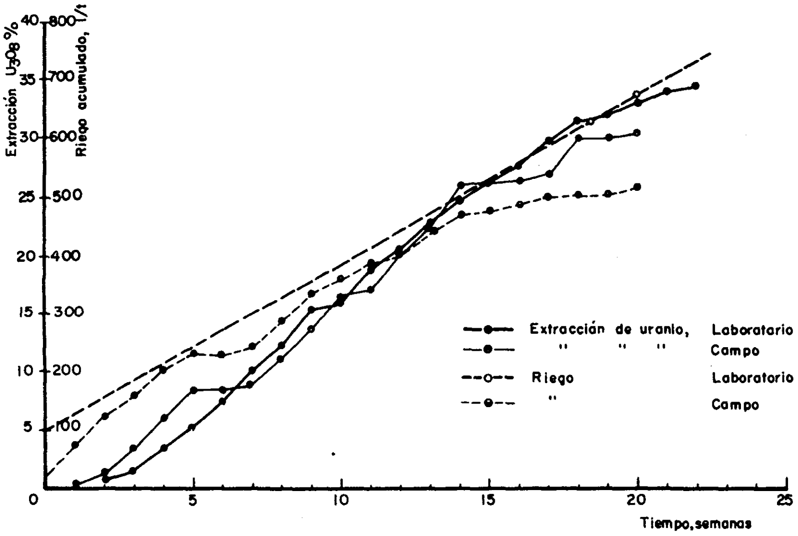

FIG. 2. Comparación de los resultados de laboratorio y campo. Mineral de Carretona.

otros que se prestan bien a un tratamiento de este tipo, ofreciendo incluso ciertas ventajas sobre la lixiviación con soluciones ácidas como, por ejemplo, los minerales de Ratones y Peñascal que, por su alto contenido en fosfatos solubles, producen soluciones fértiles más fáciles de manejar cuando se utilizan reactivos sólidos.

Interesa destacar algunos resultados obtenidos en experiencias encaminadas al estudio de la influencia de ciertas variables. Con una muestra de mineral de pizarras (Caridad) se ensayó la dimensión del lecho, tamaño de partícula y distribución del líquido de riego. Los resultados obtenidos al cabo de 25 semanas fueron:

| Dimensión del lecho | Tamaño de partícula (mm) | Forma de riego[a] | Solubilización del uranio (%) |
|---|---|---|---|
| 100 x 1250 | -25 | Intenso | 59,0 |
| 100 x 1250 | -25 | Pobre | 55,7 |
| 100 x 1250 | -5 | Intenso | 44,5 |
| 100 x 1250 | -5 | Pobre | 42,7 |
| 100 x 900 | -25 | Pobre | 85,0 |

[a] Riego intenso 50(l/t x d) distribuidos uniformemente;
riego pobre 5(l/t x d) añadidos diariamente de una sola vez.

Por otra parte, una muestra (lote 210) de mineral granítico con pirita, procedente de la mina los Ratones se ensayó con dos granulometrías y dos dosis de sulfato ferroso en un lecho de 400 X 900 mm y con una distribución de riego de 30 (l/t X d) obteniéndose los resultados:

| Tamaño de partícula (mm) | Dosis de sulfato ferroso (kg/t) | Solubilización del uranio (%) |
|---|---|---|
| -30 | 5 | 84,8 |
| -30 | 10 | 85,9 |
| -12 | 5 | 92,3 |
| -12 | 10 | 90,1 |

La distribución del riego parece que tuvo poca influencia en el mineral de pizarras. La granulometría tuvo influencia variable y de forma contraria en pizarras y granitos. En las primeras debe atribuirse este fenómeno a la mejor aireación del lecho con granulometría más gruesa, lo que viene confirmado a su vez por los rendimientos obtenidos con una geometría del lecho que favorece la aireación (mayor diámetro y menor altura). Por el contrario, en las muestras de granitos, el rendimiento fue mayor con granulometrías más finas, pues en este caso la permeabilidad de lecho se vio poco afectada en el intervalo considerado y la solubilización estuvo controlada por los tamaños más gruesos en los què las pérdidas fueron mayores.

En la actualidad se están realizando unos ensayos, en tubos de 40 cm de diámetro, con un mineral granítico en los que se varía la altura de lecho (1 y 3 m), la granulometría (-12 mm y -25 mm), la dosis de pirita (3 y 9 kg/t) y se utilizan dos formas de riego.

Para el trabajo a diferentes escalas, 150 kg (tubos) y 6 t (cubículos), se tuvo una buena correlación. A continuación se dan los resultados obtenidos con un mineral granítico triturado a 30 mm y con adición de 10 kg/t de sulfato ferroso:

| Riego Nº | Solubilización de uranio (%) | |
|---|---|---|
| | Escala (150 kg) | Escala (6t) |
| 10 | 30,1 | 27,6 |
| 15 | 40,3 | 39,8 |
| 20 | 49,7 | 50,0 |
| 50 | 76,5 | 77,6 |
| 80 | 85,9 | 86,4 |

En ambos casos, se pudo comprobar que al consumirse la pirita del mineral hubo un aumento del pH, un fuerte descenso en las concentraciones de hierro y sulfato y se paró la solubilización del uranio.

## 5. RESULTADOS CON REACTIVOS QUIMICOS

### 5.1. Resumen de resultados

La tabla IV resume los resultados obtenidos con diferentes muestras de minerales a escalas y condiciones diferentes. En términos generales puede decirse que estos resultados son del mismo orden que los conseguidos en condiciones equiparables de reactivos en la lixiviación con agitación.

Se han encontrado algunas dificultades relacionadas fundamentalmente con el flujo de la solución lixiviante a través del lecho. Los minerales de pizarras presentan, en general, mayores dificultades de este tipo acentuándose a medida que la granulometría es más fina. Los minerales graníticos se prestan muy bien a este tipo de lixiviación. Las principales dificultades observadas se presentaron en minerales que contenían carbonatos (> 4% $CO_3$) o fosfatos fácilmente lixiviables. Los primeros daban lugar al desprendimiento de carbónico así como a la precipitación de sulfato cálcico en el lecho dificultando la buena distribución de la solución de lixiviación y la creación de zonas de precipitación del uranio. Para solventar estos inconvenientes se ha ensayado, entre otros sistemas, la aglomeración previa, el curado ácido y la distribución lenta del ácido en los primeros riegos, habiéndose conseguido resultados satisfactorios.

La presencia de fosfatos, fácilmente solubles, puede dar lugar a su precipitación en las partes inferiores del lecho llegando incluso a su bloqueo. Se consiguió reducir este efecto mediante una lixiviación a pH controlado de forma que fuera gradual la disolución de los fosfatos.

Los resultados obtenidos en la lixiviación con carbonato-bicarbonato han sido probres debido, probablemente, a que este reactivo exige temperaturas más altas y granulometrías más finas.

### 5.2. Influencia de algunos factores

Aparte de los factores propios del mineral (especies de uranio, ganga, roca encajante) sobre los que no se puede actuar, es interesante destacar la influencia de algunos factores externos que se ha observado en los estudios experimentales.

No se puede medir independientemente el efecto de las variables, ya que están ligadas todas entre sí; no obstante, puede conseguirse información sobre el grado de influencia de las más interesantes.

A continuación se resumen los resultados obtenidos a distintas granulometrías con muestras de minerales graníticos (Carretona), de areniscas y pizarras.

| Mineral | Roca | Granulometría | Uranio solubilizado (%) |
|---|---|---|---|
| Carretona | granito | -5 mm | 93,4 |
| Carretona | | -12 mm | 95,3 |
| Eureka | arenisca | -5 mm | 98,3 |
| Eureka | | -12 mm | 91,8 |
| Salamanca | pizarra | -12 mm | 83,2 |
| Salamanca | | -25 mm | 85,3 |

Puede verse que la granulometría del producto influye de forma distinta según sean las características del mineral. Se ha observado que en aquellos minerales en los que la distribución del uranio está desplazada hacia los tamaños finos, las granulometrías más gruesas dan solubilizaciones iguales o superiores, mientras que en aquellos otros que tienen una fracción importante del uranio en los tamaños gruesos, una reducción del tamaño de partícula se traduce en un mayor rendimiento de la lixiviación. Este fenómeno puede utilizarse para obtener una información previa sobre la influencia de la granulometría.

En lo que se refiere a la dosis y concentración de ácido se ha observado que si se mantiene la misma dosis el empleo de soluciones diluidas conduce inicialmente a extracciones de uranio mayores que en el caso de la utilización de líquidos más concentrados; por otra parte, estos últimos dan lugar a la solubilización de impurezas en mayor cantidad. Las figuras 3, 4 y 5 muestran estos puntos para minerales distintos; por lo que se refiere a la extracción final del uranio no se puede observar una influencia clara de la concentración de la solución lixiviante, si bien parece que tiende a aumentar ligeramente con la concentración. Así, en el tratamiento de areniscas se obtuvieron, en porcentaje, las extracciones de uranio siguientes:

| Muestra | Concentración del ácido (g/l)[a] | |
|---|---|---|
| | 50 | 75 |
| 1002 | 80,7 | 87,1 |
| 1003 | 71,5 | 74,6 |
| 1005 | 68,2 | 74,9 |
| 1006 | 67,4 | 73,5 |
| 1007 | 64,2 | 74,9 |
| 1008 | 68,1 | 73,7 |
| 1009 | 70,5 | 77,9 |
| 1010 | 82,3 | 85,7 |

[a] Dosis de ácido, 150 kg/t.

TABLA IV. RESUMEN DE RESULTADOS DE LIXIVIACION ESTATICA CON SOLUCIONES CONVENCIONALES DE ATAQUE

| Mineral | Lote | Ley $U_3O_8$ (%) | Granulometría (mm) | Reactivo | | Tiempo (d) | Solubilización $U_3O_8$ (%) |
|---|---|---|---|---|---|---|---|
| | | | | Tipo | Dosis (kg/t) | | |
| Areniscas | | | | | | | |
| Eureka | 1001 | 0,396 | -5 | $H_2SO_4$ | 200 | 10 | 98,3 |
| Eureka | 1001 | 0,396 | -5 | $H_2SO_4$ | 110 | 9 | 95,0$^a$ |
| Eureka | 1001 | 0,396 | -12 | $H_2SO_4$ | 95 | 8 | 91,7$^a$ |
| Eureka | 1001 | 0,396 | -5 | $Na_2CO_3$ | 50 | 54 | 37,0 |
| Eureka | 1001 | 0,396 | -5 | $Na_2CO_3$ | 90 | 49 | 36,6 |
| Eureka | 1002 | 0,158 | -5 | $H_2SO_4$ | 150 | 10 | 80,7$^b$ |
| Eureka | 1003 | 0,088 | -5 | $H_2SO_4$ | 150 | 10 | 72,8$^b$ |
| Eureka | 1009 | 0,146 | -5 | $H_2SO_4$ | 150 | 10 | 74,2$^b$ |
| Eureka | 1010 | 0,104 | -5 | $H_2SO_4$ | 150 | 10 | 84,0$^b$ |
| Granitos | | | | | | | |
| Ratones | 208 | 0,180 | -5 | $H_2SO_4$ | 50 | 10 | 97,8 |
| Ratones | 208 | 0,180 | -5 | $H_2SO_4$ | 20 | 10 | 94,9 |
| Ratones | 208 | 0,180 | -12 | $H_2SO_4$ | 25 | 7 | 96,2$^a$ |
| La Virgen | 405 | 0,056 | -5 | $H_2SO_4$ | 75 | 10 | 70,5 |
| La Virgen | 405 | 0,056 | -5 | $H_2SO_4$ | 150 | 10 | 89,6 |
| Carretona | ELN - 1 | 0,089 | -5 | $H_2SO_4$ | 38 | 10 | 86,0 |
| Carretona | ELN - 1 | 0,089 | -5 | $H_2SO_4$ | 62 | 10 | 88,8 |
| Carretona | ELN - 1 | 0,089 | -5 | $H_2SO_4$ | 36 | 9 | 87,5$^a$ |
| Carretona | 202 | 0,135 | -12 | $H_2SO_4$ | 43 | 20 | 95,3$^a$ |
| Valdemascaños | 809 | 0,331 | -5 | $H_2SO_4$ | 75 | 10 | 92,6 |
| V. Peralonso | 810 | 0,349 | -5 | $H_2SO_4$ | 75 | 10 | 92,5 |
| Gallo | 205 | 0,390 | -5 | $H_2SO_4$ | 48 | 12 | 98,1 |
| Valderrascón | 701 | 0,206 | -5 | $H_2SO_4$ | 50 | 10 | 97,3 |
| Escalona | | 0,255 | -5 | $H_2SO_4$ | 30 | 10 | 98,5 |
| Ratones | 210 | 0,260 | -5 | $H_2SO_4$ | 75 | 10 | 98,8 |
| Ratones | 210 | 0,260 | -12 | $H_2SO_4$ | 60 | 26 | 97,0 |
| Ratones | 210 | 0,260 | -12 | $H_2SO_4$ | 30 | 16 | 56,8 |
| Peñascal | 209 | 0,232 | -5 | $H_2SO_4$ | 75 | 10 | 97,1 |
| Peñascal | 209 | 0,232 | -12 | $H_2SO_4$ | 46 | 21 | 93,7 |

TABLA IV. (cont.)

| Mineral | Lote | Ley $U_3O_8$ (%) | Granulometría (mm) | Reactivo | | Tiempo (d) | Solubilización $U_3O_8$ (%) |
|---|---|---|---|---|---|---|---|
| | | | | Tipo | Dosis (kg/t) | | |
| Pizarras | | | | | | | |
| Esperanza | 805 | 0,202 | -5 | $H_2SO_4$ | 75 | 10 | 95,6 |
| Caridad | 811 | 0,306 | -5 | $H_2SO_4$ | 50 | 10 | 97,3 |
| Fe | 806 | 0,430 | -5 | $H_2SO_4$ | 50 | 10 | 85,1 |
| Fe | 806 | 0,430 | -5 | $H_2SO_4$ | 75 | 10 | 86,9 |
| Fe | 806 | 0,430 | -5 | $H_2SO_4$ | 100 | 10 | 88,1 |
| 34 sondeos marginales (resultados medios) | | 0,052 | -5 | $H_2SO_4$ | 60 | 10 | 82,3 |
| 22 muestras superficiales (resultados medios) | | 0,396 | -5 | $H_2SO_4$ | 60 | 10 | 79,4 |
| Lote M | | 0,113 | -25 | $H_2SO_4$ | 69 | 30 | 85,7 |
| Lote M | | 0,113 | -25 | $H_2SO_4$ | 35 | 30 | 84,8[a] |
| Lote M | | 0,113 | -12 | $H_2SO_4$ | 33 | 30 | 83,2[a] |

[a] Ensayos efectuados en contracorriente.

[b] Las diferencias en las respuestas podrían atribuirse al distinto contenido en carbonatos de las diferentes muestras.

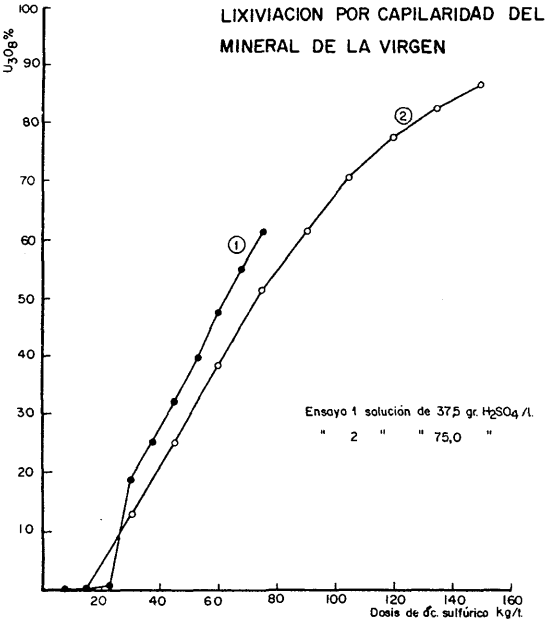

FIG. 3. Solubilización de uranio.

Juntamente con la dosis de ácido se ha comprobado que el tiempo de retención (incluyendo los períodos de riego y maduración intermedia) ejerce gran influencia. Los datos de la figura 6 muestran una relación lineal entre la ley del residuo y el inverso del tiempo para distintas dosis de ácido. Este hecho puede utilizarse para extrapolar los resultados obtenidos a tiempos más largos. En algunos minerales resistentes el hecho de doblar el tiempo de tratamiento de 10 a 20 d ha supuesto aumentos de 4 a 10 unidades en el porcentaje de extracción.

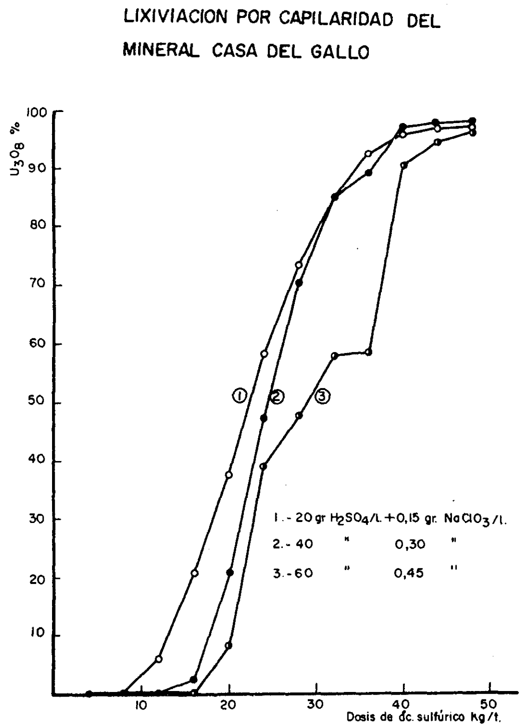

FIG. 4. Solubilización de uranio.

Se han realizado ensayos para comparar la lixiviación por capilaridad y por inmersión (lecho inundado), utilizando minerales de areniscas, con caliza, y graníticos. Las condiciones se mantuvieron iguales excepto la relación líquido/sólido que fué en la técnica de inmersión la mitad de la empleada en la de capilaridad. Los resultados muestran una mayor velocidad inicial de solubilización en la técnica por inmersión, pero la solubilización final fué ligeramente inferior, según puede verse en los siguientes valores:

| Tiempo | Areniscas | | Granitos | |
|---|---|---|---|---|
| | Inmersión | Capilaridad | Inmersión | Capilaridad |
| 2 d | 88,3 | 28,1 | 79,5 | 36,8 |
| final | 94,1 | 98,3 | 83,2 | 86,0 |

## 5.3. Circuitos

En los estudios realizados se han utilizado fundamentalmente, dos tipos de circuitos, uno simple en el que todos los riegos se hacían con solución «fresca», y otro en el que los líquidos circulaban en contracorriente con el mineral.

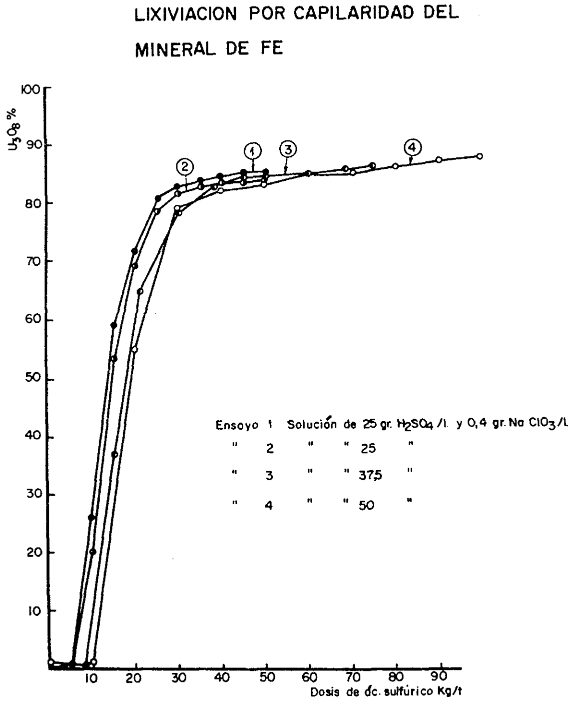

FIG. 5. Solubilización de uranio.

El circuito simple se ha ensayado con todos los minerales estudiados mientras que el de contracorriente se consideró solamente en aquellos minerales que por su naturaleza se prestaban más a este tipo de circuitos, fundamentalmente por exigir una acidez residual y consumo de ácido elevado. Las ventajas que presenta un circuito de este tipo se traducen en un menor consumo de ácido, menor volumen de solución fértil, más rica en uranio y de composición más homogénea. Por otra parte, las desventajas de este circuito frente al simple son relativamente pequeñas.

En la tabla IV puede observarse que con la contracorriente se consiguen reducciones importantes en el consumo de ácido con rendimientos similares (Eureka, Carretona, Lote M). En el mineral de Ratones no hay apenas diferencias en el consumo debido a que necesita una acidez residual baja.

Por lo que se refiere a las soluciones fértiles, los resultados obtenidos fueron:

| Circuito | Volumen recogido | Intervalo de concentración | | Acidez máxima |
|---|---|---|---|---|
| | ($m^3/t$) | (g $U_3O_8$) | (pH) | (g $H_2SO_4$/l) |
| Mineral de pizarras | | | | |
| Simple | 2, 73 | 0, 05-0, 76 | 0, 7-2, 3 | 28 |
| Contracorriente (4 etapas) | 0, 72 | 0, 80-1, 60 | 0, 9-2, 3 | 12 |
| Areniscas | | | | |
| Simple | 3, 50 | 0, 05-3, 10 | 0, 4-3, 0 | 62 |
| Contracorriente (4 etapas) | 1, 0 | 3, 60-4, 30 | 1, 1-1, 4 | 10 |

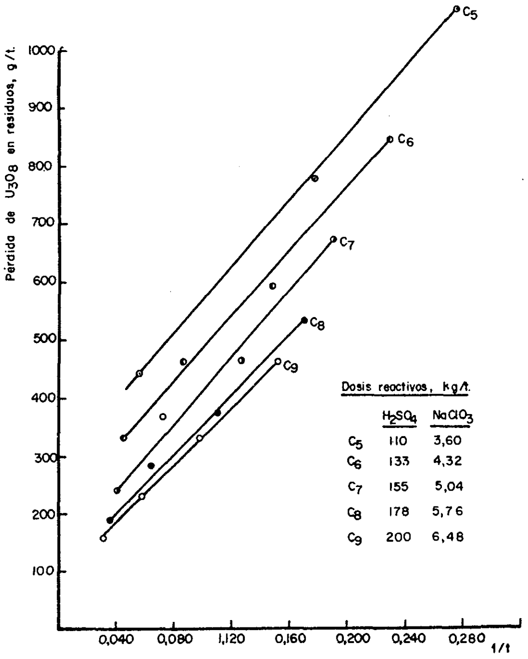

FIG. 6. Pérdida de uranio en los residuos del mineral Eureka en función de la inversa del tiempo de retención expresado en días.

## 5.4. Comparación frente a la lixiviación con agitación

En una serie de minerales se ha observado un paralelismo entre los resultados obtenidos en la lixiviación estática y con agitación, para dosis

TABLA V. ALGUNOS RESULTADOS COMPARATIVOS DE LA LIXIVIACION CON SOLUCIONES CONVENCIONALES: EN LECHO ESTATICO Y CON AGITACION

| Mineral | Tipo de lixiviación | | | |
|---|---|---|---|---|
| | Estática | | Con agitación | |
| | Dosis $H_2SO_4$ | Solubilización $U_3O_8$ (%) | Dosis $H_2SO_4$ | Solubilización $U_3O_8$ (%) |
| Fe | 50 | 85,5 | 50 | 86,4 - 92,0 |
| Fe | 75 | 86,9 | 75 | 83,3 - 92,0 |
| Eureka | 200 | 96,6 | 200 | 96,9 |
| Virgen | 150 | 89,6 | 125 | 80,5 |
| Esperanza | 75 | 95,6 | 50 | 95,5 |
| Villares de Yeltes | 75 | 94,0 | 100 | 95,0 |
| Carretona | 43[a] | 95,3 | 50 | 94,9 |
| Valdemascaños | 75 | 92,6 | 75 | 94,8 |
| Alameda | 75 | 90,1 | 100 | 94,1 |
| Resultados medios de 15 sondeos de Fe | 60 | 83,5 | 60 | 85,5 |
| Resultados medios de 11 muestras superficiales de pizarras | 60 | 80,4 | 60 | 86,6 |

| | |
|---|---|
| Condiciones de lixiviación estática | -5 mm, 15 - 20°C y 10 d |
| Condiciones de lixiviación con agitación | -35 mallas, 30 - 60°C y 12 - 24 d |

[a] En contracorriente.

de ácido similares, según puede observarse en los datos resumidos en la tabla V.

Si bien existen factores como, por ejemplo, la temperatura, que pueden dar lugar a variaciones importantes en la solubilización del uranio, los resultados de ataque con agitación pueden servir para determinar de forma aproximada los que pueden esperarse en la lixiviación estática.

## 6. RECUPERACION DEL URANIO DE LOS LIQUIDOS

La recuperación del uranio solubilizado se ha considerado fundamentalmente por tres procedimientos: precipitación química directa, resinas de cambio de ion y extracción con aminas. Además, se realizan ensayos de fijación en turbas y productos diversos. Atendiendo a la naturaleza de los líquidos habría que distinguir según su origen: de condiciones suaves de ataque (lixiviación natural, o con reactivos sólidos) que tienen pH relativamente altos, o ataque con soluciones ácidas que dan pH finales bajos. Además, hay que tener en cuenta la naturaleza de los circuitos de ataque en una etapa, frente a los diagramas con recirculación de líquidos o contracorriente.

La precipitación química directa se ha utilizado con líquidos procedentes de lixiviación natural o de ataque con reactivos sólidos. En el laboratorio se han ensayado el empleo de sosa cáustica, magnesia y cal, trabajando en una etapa, y la combinación de cal-sosa y de cal-cal para dos etapas. Partiendo de líquidos con 1,8 g $U_3O_8$/l y pH 2,2 se obtuvieron concentrados con leyes de 10,2; 7,2; 3,7; 22,3 y 4,7% $U_3O_8$, respectivamente, con costes de reactivos de 71,5; 8,6; 21,4 y 8,1 Pts/kg $U_3O_8$ para el empleo de sosa, cal, cal-sosa y cal-cal, respectivamente [13].

En las instalaciones semiindustriales de campo se utilizó cal, pero aparte de tener leyes bajas (2-3% $U_3O_8$), resultaban productos con gran proporción (12%) de cal libre. Estos concentrados había que volverlos a tratar y presentaban los inconvenientes de consumos altos de reactivos (600-700 kg/t de ácido) y malas características físicas de manipulación.

La precipitación directa de las soluciones procedentes del ataque ácido dió productos todavía peores a causa del gran número de impurezas que junto al uranio se solubilizan.

Como alternativa se ensayó el empleo de resinas de cambio de ion, en columnas, seguida de la elución y precipitación directa de los eluidos. Se ha investigado la influencia del pH desde los valores altos [2, 3] de lixiviación natural, a los normales de cambio de ion 1,6 - 1,8 e incluso otros muy bajos 1,1; junto a ello la composición, variable, de la solución fértil a lo largo del ciclo de tratamiento y el tipo de agente eluyente, cloruros y nitratos a concentraciones variables.

Las recuperaciones fueron superiores al 99,5% con capacidades de resina de 50 a 85 g $U_3O_8$/l lecho, con 4 a 5 volúmenes de lecho a precipitación. La operación a los valores extremos de pH hubo que descartarla por la mala calidad de los concentrados o por los costes altos de reactivos. Con los líquidos relativamente puros de lixiviación natural se tuvieron buenos concentrados: $U_3O_8$(80%), $SO_4$(1), $P_2O_5$(0,2) y Fe (7,5). Esto se mantuvo para los líquidos de ataque ácido en sus primeras etapas de ataque, con concentración alta en uranio, aunque luego disminuía la calidad a menos que se recurriese a la precipitación en dos etapas.

Se tuvieron costes de reactivos de 19 a 21 Pts/kg $U_3O_8$ para soluciones de lixiviación natural [13, 14] y de 40 a 80 Pts/kg $U_3O_8$ para los líquidos procedentes del ataque sulfúrico. La mayor contribución al coste de estos últimos fue debida a la etapa de ajuste de pH en soluciones con gran acidez libre procedente del ataque en una fase sin contracorriente.

Por último se consideró [13, 15] la extracción con aminas para líquidos con 2 a 0,2 g $U_3O_8$/l, cuyo pH se ajustó a valores comprendidos entre 1,2 y 1,8. Se lograron recuperaciones superiores al 99,5%, con extractos acuosos de 16-18 g $U_3O_8$/l, en el peor de los casos, y de 36 a 40 g/l para las alimentaciones altas en uranio. Desde un punto de vista económico el mejor agente de reextracción fue el cloruro sódico 1 M.

Se tuvieron en general concentrados buenos: $U_3O_8$(78-89%), $SO_4$(0,3-12), Cl(0,05-0,1), Fe(0,1-1,3) y $P_2O_5$(< 0,1). Unicamente con soluciones de concentración muy baja en uranio y alta en impurezas la calidad de los concentrados disminuyó a leyes del orden del 70% $U_3O_8$. Los costes de reactivos, comprendida fase orgánica, para alimentaciones con más de 0,5 g $U_3O_8$ fueron de unas 20 Pts/kg $U_3O_8$, mientras que para los líquidos diluidos, 0,2 g $U_3O_8$/l, se duplicaron.

Al igual que en cambio de ion hay que cuidar el circuito de solubilización del uranio con el fin de mantener la calidad más uniforme posible y tener líquidos con valores de pH de salida dentro del intervalo de trabajo de extracción; en el tratamiento de líquidos de ataque en una etapa con gran acidez final una gran proporción del coste de reactivo era debida a la fase de ajuste de pH.

Comparando las tres técnicas indicadas, se ve que tanto el cambio de ion como la extracción conducen a buenos concentrados con costes de reactivos razonables, posiblemente favorables a la extracción tanto desde el punto de vista de calidad como de coste de reactivos. Por otra parte tanto una como otra se pueden llevar a cabo en unidades prácticas que permitan su realización en una amplitud de sitios. No obstante, en la decisión se tienen que considerar otros factores como el aspecto de composición en los líquidos a tratar y la movilidad de la instalación.

Para circuitos en contracorriente o con reciclado de colas, que se vayan a explotar durante más de dos años es posible que la extracción con disolventes sea la solución más adecuada. Por el contrario para circuitos de de ataque en una sola etapa con ciclo corto y gran variación en la concentración del principio al final de la operación parece aconsejable el cambio de ion.

En España hay un proyecto de instalación de cambio de ion para tratar 1,6 $m^3/h$ de líquido fértil, que tiene cuatro columnas de 270 litros de resina y que está destinada a servir varias instalaciones de lixiviación próximas. Para ello el equipo se ha dispuesto de forma que el conjunto de columnas, bombas y depósitos de eluyentes esté montado sobre un camión, mientras que los depósitos de recepción de líquidos y de precipitación están situados al pie de cada mina. Una instalación de este tipo para servicio de dos eras de lixiviación costaría un millón de pesetas.

Por otra parte, se diseñó y construyó [16] una instalación de extracción con aminas para 2 $m^3/h$, a base de mezcladores sedimentadores compactos, con elementos de construcción y estructuras normalizados, atornillados y desmontables que ha funcionado normalmente y trata incluso líquidos de 0,2 g $U_3O_8$/l. El coste de esta unidad resultó ligeramente inferior al millón de pesetas.

## REFERENCIAS

[1] SOUSA BYRNE, J., Natural leaching of low grade ores in Portugal, Simposio de la Sociedad Europa de Energía Atómica, Lisboa-Guarda (1957).

[2] WELLS, R. A., Observations on natural leaching, Simposio de la Sociedad Europea de Energía Atómica, Lisboa-Guarda (1957).

[3] MILLER, R. P., NAPIER, Elizabeth, WELLS, R. A., AUDSLEY, A., DABORN, G. R., Natural leaching of uranium ores. Part 1, Preliminary test on Portuguese ores; Part 2, A study of the experimental variables, y Part 3, Application to specific ores, Trans. Inst. Mining Met. (London) 72 4, 217-254 y 72 7 (1962-63) 507-517, discusiones.

[4] MOURET, P., POTTIER, P., Lixiviation par capillarité des minerais d'uranium, Energie Nucléaire, 3 4 (1961) 251-260.

[5] LECOQ, J., MOURET, P., POTTIER, P., SUGIER, P., Application de la lixiviation par capillarité à l'extraction de l'uranium dans les minerais, VI$^{e}$ Congrès International de la Préparation des Minerais, Cannes 1963, Compte Rendu Scientifique, 274-289. Revue Ind. minér., avril 1964 (Saint-Etienne, 1964).

[6] BUHLER, M.F., FERNANDEZ, O., RODRIGUEZ, J.R., POZZI, G., Aplicación del método del fosfato uranoso a la recuperación de uranio del mineral argentino de Malargüe, Mendoza, Actas 2a Conf. int. util. EAFP 2, Nac. Unidas (1958) 486-491.

[7] SVENKE, E., Recuperación del uranio a partir de esquistos aluminosos uraníferos, Actas Conf. int. util. EAFP VIII, Nac. Unidas (1956) 105-109.

[8] HORMANDER, O., GELIN, R., How Sweden is developing its low grade $U_3O_8$, World Mining 16 3 (1963) 28-31.

[9] ANDRADE, J.F., PICH, H.C., VIDEIRA, F.M., Chemical treatment of uranium ores at the mines in a semi-mobile plant, 3a Conf. int. util. EAFP 12, Nac. Unidas (1965) 187.

[10] MASHBIR, D.S., Head leaching of low grade uranium ore, Mining Congress J., 50 12 (1964) 50-54.

[11] JOSA, J.M., ESCUDERO, E., CORDERO, G., Recuperación del uranio de los minerales españoles, Energía Nuclear (Madrid) 5 18 (1961) 64.

[12] BATUECAS RODRIGUEZ, T., GARCIA CORRAL, M.A., Métodos de beneficio de minerales de uranio por lixiviación natural. Estudios, realizaciones y programa de desarrollo en este campo de la JEN. Su aplicación al aprovechamiento integral de yacimientos de uranio, Ponencia II, 4.4, Forum Atómico Español, Primeras Jornadas Nucleares (Madrid, mayo 1963).

[13] CORDERO, G., JOSA, J.M., Lixiviación natural de minerales de uranio, Energía Nuclear (Madrid) 9 33 (1965) 22.

[14] ESTRADA, J., URIARTE, A., Tratamiento por cambio de ion de disoluciones de lixiviación natural de minerales de uranio, Energía Nuclear (Madrid) 6 22 (1962) 43-54.

[15] RAMOS, L., REGIFE, J.M., Tratamiento por extracción con aminas de soluciones de lixiviación natural de minerales españoles, Energía Nuclear (Madrid) 5 19 (1961) 48-55.

[16] REGIFE, J.M., CORDERO, G., Instalación transportable para extracción con aminas, Energía Nuclear (Madrid) 9 38 (1965) 410-418.

# RANSTAD - A NEW URANIUM-PROCESSING PLANT

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## Abstract

RANSTAD – A NEW URANIUM PROCESSING PLANT. A short outline is given of the decisions concerning the erection and operation of the Ranstad mill which was recently taken into operation. It is followed by a brief description of the geological conditions and the planning of the mining system, plant location, and the factory. The main part of the paper describes processes and equipment of the plant which has a capacity to treat approx. 850 000 tons of low-grade ore (alum shale) per year. The operational experience so far is also reviewed. The economy of uranium production at Ranstad is discussed and some development possibilities are indicated.

## 1. INTRODUCTION

The decision to erect a uranium mill at Billingen Mountain in central Sweden was made in 1958. The mill, named Ranstad, would produce 120 tons of uranium per year and start operation in 1963. The capacity was considered sufficient to cover the Swedish demand up to 1970. In 1959 the project work on the plant was discontinued for about one year while a study was made of the possibilities and conditions for import of uranium. After a governmental decision the erection was then continued. In 1962 the completion of the plant was intentionally delayed for one more year.

The Ranstad mill went into operation in the middle of 1965. Depending on present world uranium supply and price situation the production during the first year of operation has been limited to between 25 and 40% of the nominal capacity of the plant.

## 2. GEOLOGICAL CONDITIONS

The general geological conditions are given in Figs 1 and 2. As seen the rock series of the Billingen Mountain mainly consists of sandstone, alum shale, limestone, and claystone. The various layers are virtually horizontal as seen in Fig. 3.

The uranium is confined to a relatively thin bed of the alum shales in the Cambrian series. The alum shales contain several layers of bituminous limestone lenses (stinkstone). The uranium-rich shale lies between two of these stinkstone layers and has a thickness of about 4.5 m. The uranium content varies with the depth. For a bed of 3.5 m the mean value is 300 g/t or somewhat more. In the shale there are 'kolm'-lenses, a kind of coal, rich in ashy material, having a uranium content as high as 3000 - 4000 g/t. The total content of uranium in the uranium-rich shale of Billingen Mountain area is considerable - about 1 million tons of uranium.

Normally the zone of high-uranium shale is located deep below the surface, where it can be removed only by underground mining, but in the vicinity of the Ranstad plant there is a relatively large area of shale with shallow overburden, suitable for open-cast mining.

## 3. CHOICE OF MINING SYSTEM AND PLANT LOCATION

The location of the plant was influenced by several factors. The main reason for the chosen location, however, was the possibility of open-cast mining which was considered somewhat cheaper to start with than underground mining. The exact localization of the plant was mainly determined by the transportation cost of ore and solid waste.

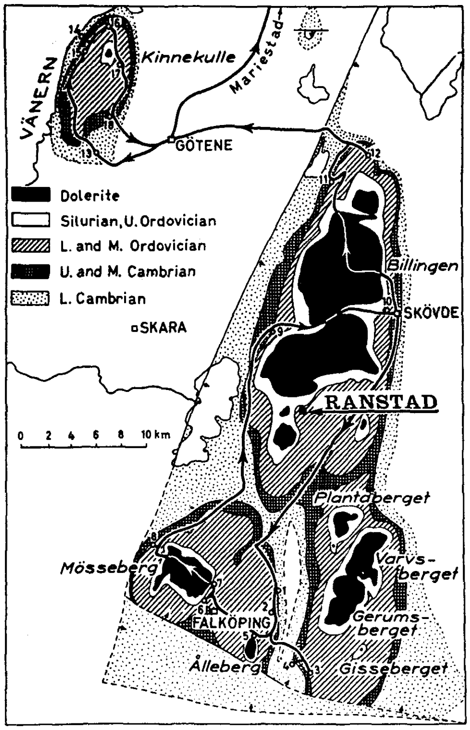

FIG. 1. Map of Mt. Kinnekulle and the Billingen-Falbygen district.

## 4. PLANNING OF THE FACTORY

In planning consideration was given to the economy, organization, and landscape conservation, and in addition to comfort and aesthetics. Also the demands on possibilities for increasing the production fourfold within a given plan were taken into account.

The dominating economic factor was the cost of transportation of that material which is transported to and through the various parts of the plant and from these to the waste disposal area.

The factory is organized in several processing units. These are: (a) the mine, primary crusher and silos, (b) dressing plant, (c) weathering pile and leaching plant, and (d) neutralization plant and waste area. In

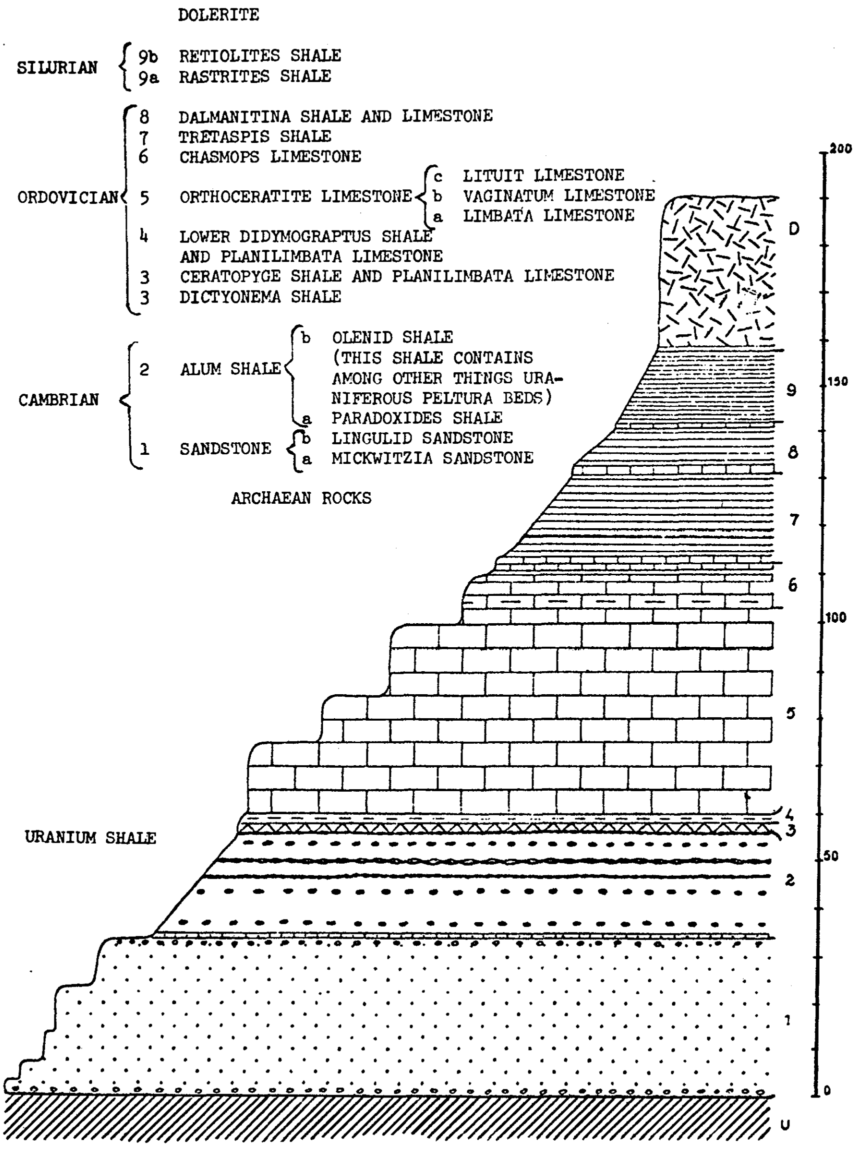

FIG. 2. The stratigraphy of the Billingen-Falbygen district.

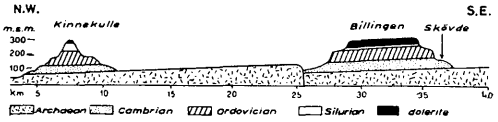

FIG. 3. Diagrammatic section from Västergötland.

addition to these units there are buildings for supply of water, steam and power, workshop and stores, garage, office and laboratory etc. The plant layout is given in Fig. 4. As can be seen, an attempt had been made to split up the factory into blocks with straight roads. Within each block the activities are as related as possible. The demands for landscape conservation have had great influence on the planning of the open-cast mining and waste disposal areas.

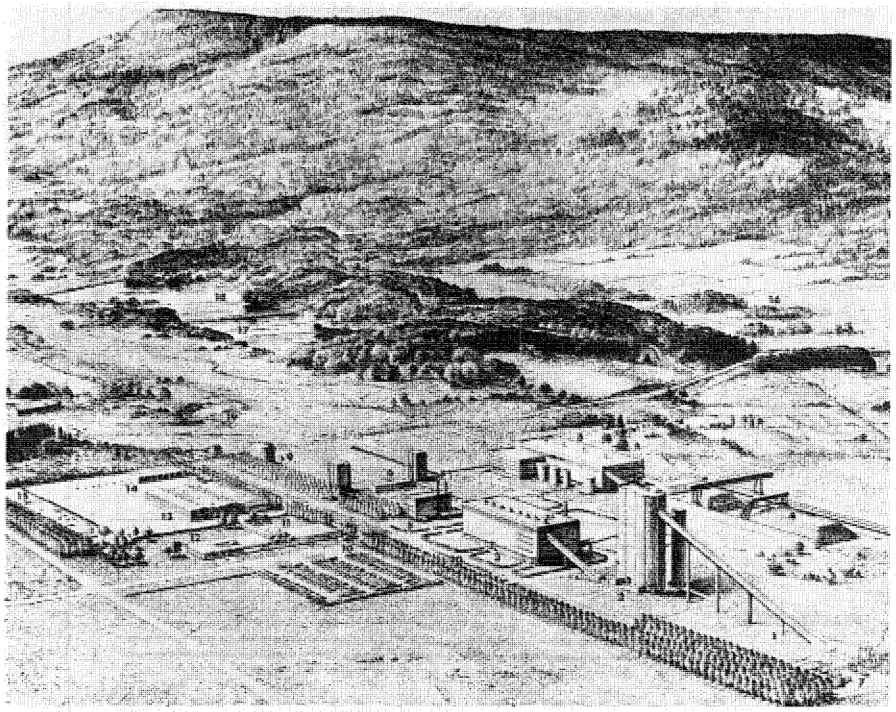

FIG. 4. The Ranstad plant layout. 1. Conveyor, 2. bunkers and screens, 3. dressing plant, 4. weathering pile, 5. leaching plant, 6. neutralization plant, 7. transformer station, 8. steam boiler and water supply, 9. oil storage, 10. main entrance and parking place, 11. dining rooms, dressing rooms, etc., 12. office and laboratory, 13. workshop and storage, 14. garage, 15. storage area for materials, 16. waste area, 17. water reservoir, 18. retain basin, 19. sanitary effluent treatment plant, 20. tunnel to underground crushing station.

## 5. PROCESSES AND EQUIPMENT

The following description [1, 2] of processes and equipment is given with reference to the full capacity of the plant. However, the capacity of the plant during its first year of operation has deliberately been limited to between 25 and 40% of its nominal value.

### 5.1. Mining

The high-uranium shale at the selected open-cast mining area is covered by a low-uranium shale of 2.5 m and an average of 3 m of limestone above which there is an average of 7.5 m of alluvium. The high-uranium shale is about 3.5 m thick. Thus, the ratio by volume between overburden and ore is 4:1. The open pit mine will have a life of 15 years if 800 000 metric tons of high-uranium shale are removed annually. Figure 5 gives a section through the mining area.

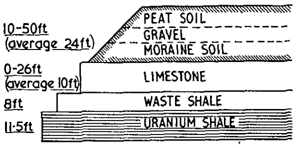

FIG. 5. Geological section in the first opencast mine area; overburden ratio approximately 3. 5 : 1.

High-uranium shale is mined by ordinary benching methods including drilling, blasting and loading into 35 ton trucks with a 4 m³ shovel. The trucks transport the shale to the underground crushing plant through a two-way tunnel 1.4 km long.

An electric walking dragline with a 59-m boom and a 12-m³ bucket strips the overburden in advance of the benching. The limestone and shale overburden must be drilled and blasted before being removed by the dragline. Fully mechanized one-man operated electro-hydraulic rotary drills are used.

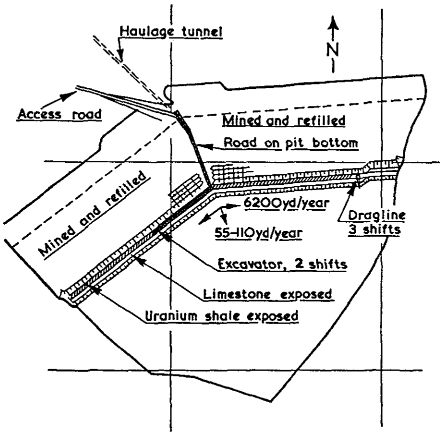

FIG. 6. Plan showing mining method.

Figure 6 shows the layout of the mining operations. The dragline strips overburden in a 20 m wide cut at one side of the central road while high-uranium shale is mined from a previously stripped cut at the other side. When mining and stripping operations reach the border of the site, the machines return to the central road and then start to work in the opposite direction. For each cut, 20 m wide and 1000 m long, the depth and thickness of the high-uranium shale is determined in advance through a sample-drilling programme. In Fig. 7 the results of such a drilling programme is given.

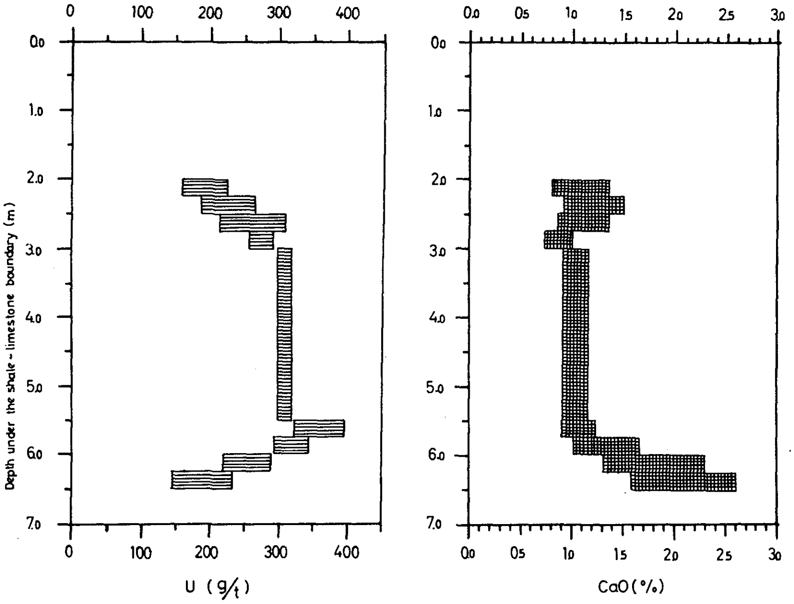

FIG. 7. Average content of uranium and lime in the shale (95% confidence limits based on a set of 20 drill cores).

## 5.2. Crushing and classifying

The ore leaving the truck hopper passes over a travelling-bar grizzly to the gyratory crusher for primary crushing (see flow sheet given in Fig. 8). The ore is reduced to 350 mm maximum size. The bottom of the primary crusher plant is 63 m below ground. Material is taken from the crusher bottom via a conveyor belt to the top of the storage silos where it is screened. Particles below 6 mm in size are removed as waste while particles plus 6 mm minus 40 mm and plus 40 mm minus 350 mm in size, are stored for further processing.

Spontaneous ignition occurs readily in crushed shale if stored in silos for long periods. Therefore it is necessary to withdraw the material uniformly from all parts of the silos. This requirement has been taken care of in the design of the silo bottoms. The storage capacity of the silos is 8500 tons. The ore is fed into the silos during 11 shifts per week at a rate of 1800 tons per shift. Withdrawal takes place during the feed shifts.

The ore from the silos is conveyed to the heavy-media separation units (HMS) where a sink-and-float process removes the limestone disseminated throughout the shale. The density of the shale particles varies mostly between 2100 and 2300 kg/m$^3$ while the density of the limestone is about 2600 kg/m$^3$. A magnetite slurry with a density of about 2300 kg/m$^3$ is used for separation. The high purity of Swedish magnetite easily permits the use of such a high slurry density. The HMS units are equipped with revolving drums that lift the sink product (mostly limestone) which is discharged as waste. Magnetite is recovered by passing the float product across a washing screen, then passing the washings through a magnetic separator.

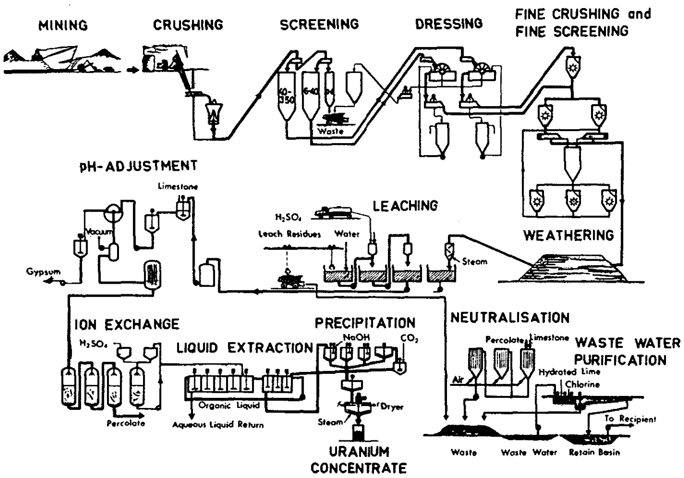

FIG. 8. Flow sheet for the Ranstad Uranium Mill.

The effect of the HMS step is shown in Table I, where experimental results from separation in a heavy liquid (mixture of tetrabromoethane and kerosene) are given. It should be observed that the 'effective' density of the magnetite slurry is greater than its measured value because of the flow conditions in the HMS units.

Untreated shale had the following composition: uranium 0.0292%; iron 5.73%; sulphur 6.66%; CaO 6.72%.

TABLE I. CALCULATED PERCENTAGE AND YIELD OF SHALE AT VARIOUS LIQUID MEDIUM DENSITIES

| Density ($g/cm^3$) | Yield of shale (%) | Uranium content (%) | Yield of uranium (%) | Pyrite content (%) | CaO content (%) |
|---|---|---|---|---|---|
| 2.20 | 8.3 | 0.0506 | 14.3 | 11.21 | 0.84 |
| 2.30 | 48.6 | 0.0332 | 54.9 | 12.26 | 1.20 |
| 2.33 | 67.7 | 0.0321 | 74.0 | 12.80 | 1.29 |
| 2.35 | 73.5 | 0.0319 | 79.8 | 12.94 | 1.30 |
| 2.38 | 80.2 | 0.0318 | 86.8 | 13.11 | 1.33 |
| 2.40 | 82.5 | 0.0317 | 89.1 | 13.19 | 1.34 |
| 2.43 | 84.5 | 0.0317 | 91.2 | 13.27 | 1.37 |

The plus 40 mm minus 350 mm float product is crushed in an impact crusher and joined with the plus 6 mm minus 40 mm float product. Both are then crushed in an intermediate impact crusher stage. The ore is screened on 3-mm square-mesh wire screens. The oversize particles are collected in crusher feed hoppers and fed to the last impact crusher stage. The undersize material is then joined with the ore from the intermediate impact crusher stage to be fed onto the screens.

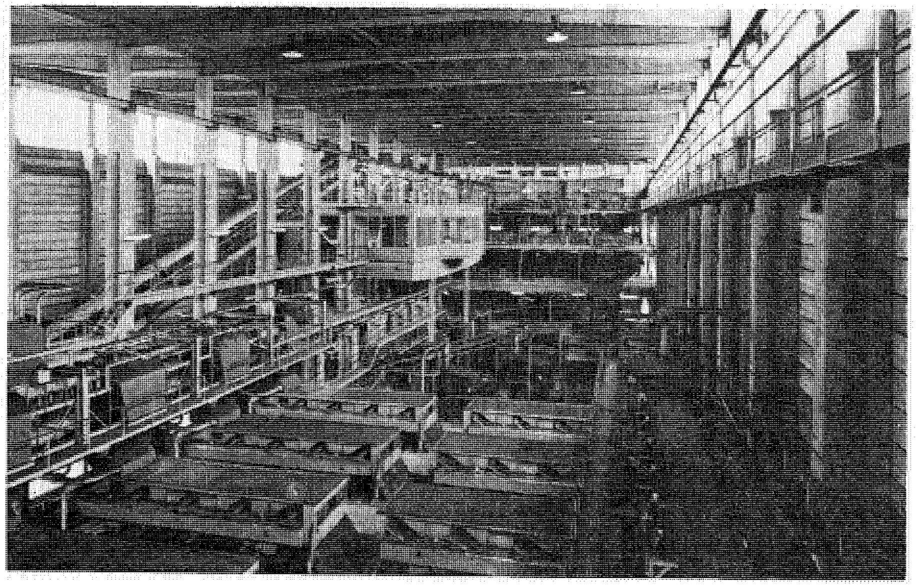

FIG. 9. Interior from the dressing plant.

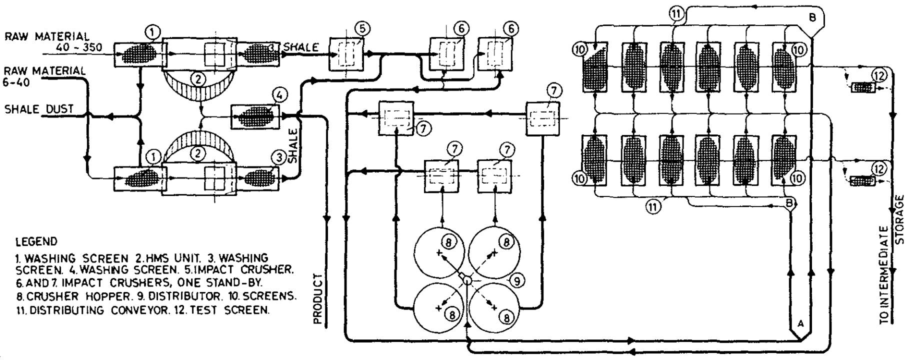

FIG. 10. HMS flow sheet and plan of classifying plant.

The HMS plant and secondary crushing plant are housed in the same building. An interior view from the dressing plant is shown in Fig. 9. Figure 10 is a flow sheet and plan showing the relative position of various parts of the equipment. The calculated feed to the HMS plant is 400 tons per hour. Of these, 325 are float product, and 75 are separated as sink product (tailing).

The screens, which accept both ore from the intermediate impact crusher stage and ore circulating back from the final stage are dimensioned to handle a total of 1000 tons per hour. There are 12 resonance screens. Test screening is conducted on a bleed line to make certain that the entire surface of all screens is functioning. When a tear occurs in a regular screen it will pass oversize to the test screen. Oversize will pass over the test screen and at a certain amount of accumulated oversize material an electric warning signal is triggered.

The removal of dust (particles minus 0.1 mm) is essential for the leaching process. Dust is removed in the crushers and other places by high volume of air flow (1000 $m^3$ per ton ore). Dust content and the particle size of ore leaving the dressing plant is optimized for the leaching process.

## 5.3. Weathering storage and leaching

Ore from the dressing plant is given an intermediate storage outdoors. During the storage volatile hydrocarbons (methane, ethane etc.) are given off, and the uranium is oxidized from the tetravalent to the hexavalent stage. Due to these changes a higher yield is achieved in the leaching step. The profitable effect of the weathering is favoured by oxygen, water and increased temperature. During the storage the pyrite in the shale also reacts to a certain degree. Based on laboratory experiments the optimal storage time was calculated to between two and three weeks. The difference in yield between unstored shale and shale stored for three weeks was calculated to be more than 10%.

Ore is piled by an automatic stacker in such a manner that no segregation occurs during stacking. In building up a pile a series of transverse layers are made on the rectangular shaped area. A pyramid of ore is first made at one end of the storage area. Next the entire bottom layer is placed to a depth of about three feet. The pile is then built up by successive layers 10 m long, but each layer is shifted in relation to the preceeding one, by a distance that corresponds to the natural angle of repose of the stacked ore. The weathering pile is shown in Fig. 11.

The leaching process has been optimized on the basis of the following variables: leaching time, leaching temperature, average acidity, particle size, and dust content.

Leaching is carried out in four 25 by 25 by 5 m concrete basins. The basins contain 2000 tons of shale each and one basin is loaded every day. The basin walls are lined with a sheet of neoprene rubber covered by acid-resisting brickwork. The basins have filter bottoms comprising granite stone rows between which are layers of gravel. The combined leaching and filtration makes use of sulphuric acid. The shale from the weathering pile is heated and moistened direct with steam to a temperature of approx. 70°C and passed into a leaching basin. A total of four leaching solutions and two wash waters are used. Leaching solutions are added so that shale meets fresher solutions as the process advances. Newly charged shale is percolated with a used leaching solution while the last leaching stage receives a freshly prepared solution consisting of sulphuric acid added to the wash water from an earlier basin. Two thirds of the leaching liquid is added from below; the remaining third enters from the top. The quantity added is sufficient to permeate all cavities in the shale bed; 0.35 $m^3$ of liquid are used for 1.0 ton of shale. This solution is then displaced with the next leaching solution.

TABLE II. ANALYSIS OF SHALE, LEACHING RESIDUE AND LEACHING LIQUID

| | Shale (%) | Leaching residue (%) | Leaching liquid (g/litre) |
|---|---|---|---|
| $SiO_2$ | 44.9 | 45.5 | 0.8 |
| $Al_2O_3$ | 12.3 | 12.0 | 18.0 |
| $Fe_2O_3$ | 8.7 | 7.1 | 14.0 |
| CaO | 1.5 | 1.2 | 1.1 |
| MgO | 0.8 | 0.7 | 4.8 |
| $Na_2O$ | 0.3 | 0.3 | 0.8 |
| $K_2O$ | 4.8 | 4.7 | 5.2 |
| S | 6.9 | 6.4 | |
| P | 0.08 | 0.01 | 1.7 |
| As | 0.008 | 0.007 | 0.12 |
| U | 0.03 | 0.008 | 0.567 |
| $C_{org}$ | 15.5 | 15.5 | |

After the leaching cycle the leaching solution contains about 0.6 g/litre uranium plus iron, aluminium, magnesium, potassium, phosphate and sulphate. The leaching residue remaining after leaching is similar in appearance and equal in volume to the shale fed into the leaching system. Table II gives representative analyses of shale, shale residue and leaching solution. An interior view from the leaching plant is shown in Fig. 12.

### 5.4. Ion exchange, extraction and precipitation

For the Ranstad project the following possibilities were studied for the concentration step:

(a) Ion exchange – elution with ammonium nitrate acidified with nitric acid – precipitation with sodium hydroxide or magnesium oxide

(b) Ion exchange – elution with sulphuric acid – precipitation with sodium hydroxide or magnesium oxide

(c) Ion exchange – elution with sodium chloride acidified with sulphuric acid – precipitation with sodium hydroxide or magnesium oxide

(d) Amine extraction — re-extraction with sodium carbonate or other agents – precipitation with sodium hydroxide

(e) Extraction with dialkyl-phosphoric acid – re-extraction with sodium carbonate – precipitation with sodium hydroxide

(f) Ion exchange – elution with sulphuric acid – extraction with dialkyl-phosphoric acid (D2EHPA) – re-extraction with sodium carbonate – precipitation with sodium hydroxide.

Although alternative (d) (amine extraction) seemed to have the best economy, it was not chosen because of suspected problems concerning difficulties with molybdenum and the poisoning effect of traces of extractant in the effluents to the recipient.

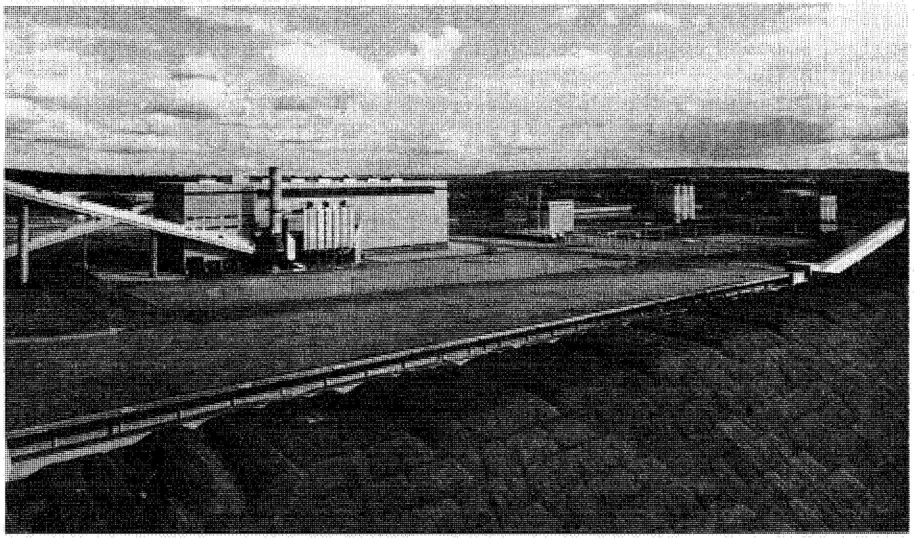

FIG. 11. Plant area with weathering pile in front, dressing plant, steam boiler and neutralization plant in the background.

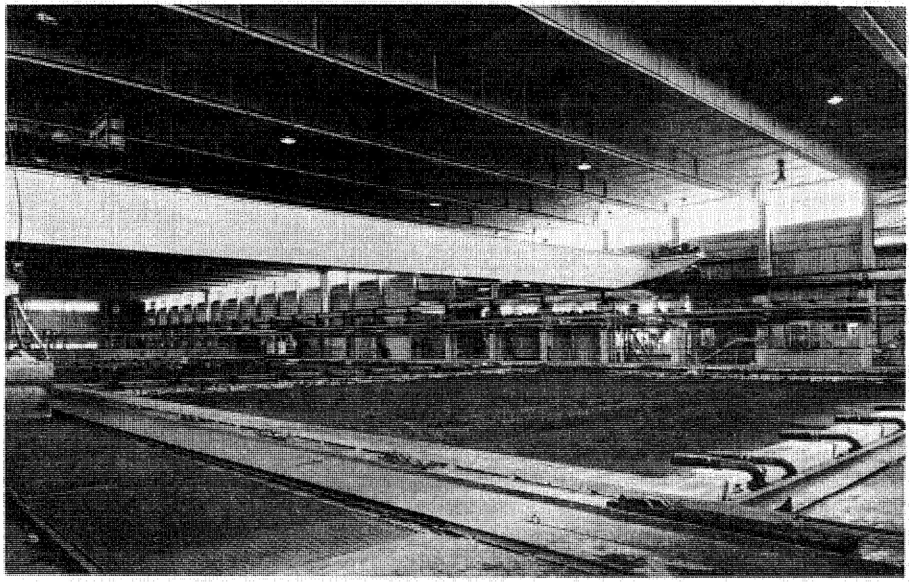

FIG. 12. Interior from the leaching plant.

The final choice was alternative (f) (the Eluex process). Besides the rather good economy of this alternative, the Eluex process was found to have the possibility of future development into a process which without further purification steps would give uranium oxide of nuclear grade.

The ion exchange step is rather conventional. To increase the uranium capacity of the ion exchanger the pH of the leach solution is raised to about 1.8 by adding ground limestone. After filtration on a drum filter and a precoat filter the solution is passed through two or three columns in series. Loaded columns are eluted (split elution) with 1.5 M sulphuric acid at 60°C.

The uranium in the eluate is extracted with D2EHPA in kerosene at 40°C (10% D2EHPA, 5% TPB, 85% kerosene) and is re-extracted from the organic phase at 40°C with sodium carbonate solution (80 g/litre $N_2CO_3$). The uranium is precipitated from this solution at 80°C with diluted sodium hydroxide. After washing the precipitate is thickened and dried in an electric dryer. The dry precipitate is in the form of a free-flowing powder. As the barren solution from the precipitation step is treated with carbon dioxide and used as re-extraction agent and the uranium-free eluate is used in the leaching step, there are no losses of uranium in the Eluex process.

The extraction-, precipitation- and drying equipment described below was developed within the AE Company.

The extraction tank is divided into five mixing and five settling sections. Both the organic phase and the water phase flow through the tank without being influenced by any pumping action of the mixers, which means that the interface between the two phases will not be altered if one or several of the mixers stop. These conditions are achieved by placing in- and outlets in the various sections in suitable positions. The construction of the re-extraction tank is based on the same principle.

The precipitation equipment is designed for continuous operation. Careful control of pH and agitation gives easily settling precipitate. The precipitate is removed discontinually and washed in a thickener.

The dryer was designed with special regard to hygienic conditions and mild treatment of the precipitate particles.

Table III gives analyses of eluate, uranium carbonate solution and uranium precipitate.

### 5.5. Waste treatment

Two types of waste are obtained from the chemical processes; the leaching residue and the barren solution from the ion-exchange step.

The leaching residue is unloaded by a grab crane and transported on trucks to the waste disposal area, a low level area surrounded by hills. The waste area has a capacity for solid residue of about 100 million tons.

The barren leach solution is treated in pachuca tanks with ground limestone in the neutralization plant and air is blown into the tanks to oxidize the divalent iron to trivalent. Gypsum, aluminium- and iron phosphates and hydroxides are precipitated in this step. The sludge is pumped onto the leaching residue in the waste area. The water from the waste area is collected in a special reservoir, from which it is pumped back to the neutralization plant, where it is treated with lime and chlorine. The water is decanted in the water treatment plant and then it is pumped to the retain basin. From there the water will - in suitable portions depending on the season of the year and water supply in lakes and creeks - be pumped across Billingen to recipients on the western slopes of the mountain.

TABLE III. ANALYSIS OF ELUATE, URANYL CARBONATE SOLUTION AND URANIUM CONCENTRATE

| | Eluate (g/litre) | Uranyl carbonate solution (g/litre) | Uranium concentrate (%) |
|---|---|---|---|
| U | 19.2 | 44.2 | 70.9 |
| Mo | 0.143 | 0.29 | 0.0077 |
| Fe (tot) | 0.277 | 0.0094 | 0.0148 |
| Al | 0.036 | 0.005 | 0.0048 |
| Mg | 0.010 | 0.001 | 0.0012 |
| Ca | 0.24 | 0.003 | 0.0047 |
| Na | 0.076 | 23.4 | 7.4 |
| K | 0.008 | 0.007 | 0.0060 |
| As | 0.077 | 0.0018 | 0.0005 |
| V | 0.015 | 0.00003 | 0.00005 |
| $SiO_2$ | 0.048 | 0.007 | 0.018 |
| $PO_4$ | 3.07 | 0.020 | 0.0170 |

## 6. OPERATIONAL EXPERIENCE

Apart from the mining which has gone on for some years the mill was taken into operation in the middle of 1965. The dressing plant started in May, the leaching plant in September and the first batch of dried uranium concentrate was produced in October.

During the testing period the plant was operated at reduced capacity. Until the end of December 1965 the capacity was limited to 25% and from that date to 40% of the nominal capacity of the plant. The 40% capacity means that most of the units run at the nominal capacity but for a shorter period of time per day.

In Figs 13 and 14 material flow sheets are given for shale and uranium. The Sankey diagrams are based on the preliminary operational experience but figures given are for the full production capacity of the mill.

### 6.1. Mining, crushing and classifying

The most serious problem in the mine and crushing plant has been freezing of the goods in the silos during this year's (1965/6) extraordinarily cold winter. Apart from this no special problems are expected when the mill runs at full capacity.

The operation of the HMS units has been very successful. The amount of sink (tailing) has been lower and the quality ($CaCO_3$-content) of the float has been better than planned. On the other hand, depending on operating conditions, the crushing of the shale has produced somewhat more dust than planned and the capacity of the screens has been a bit too low. However, there will apparently be no difficulties to run the classifying plant at full capacity.

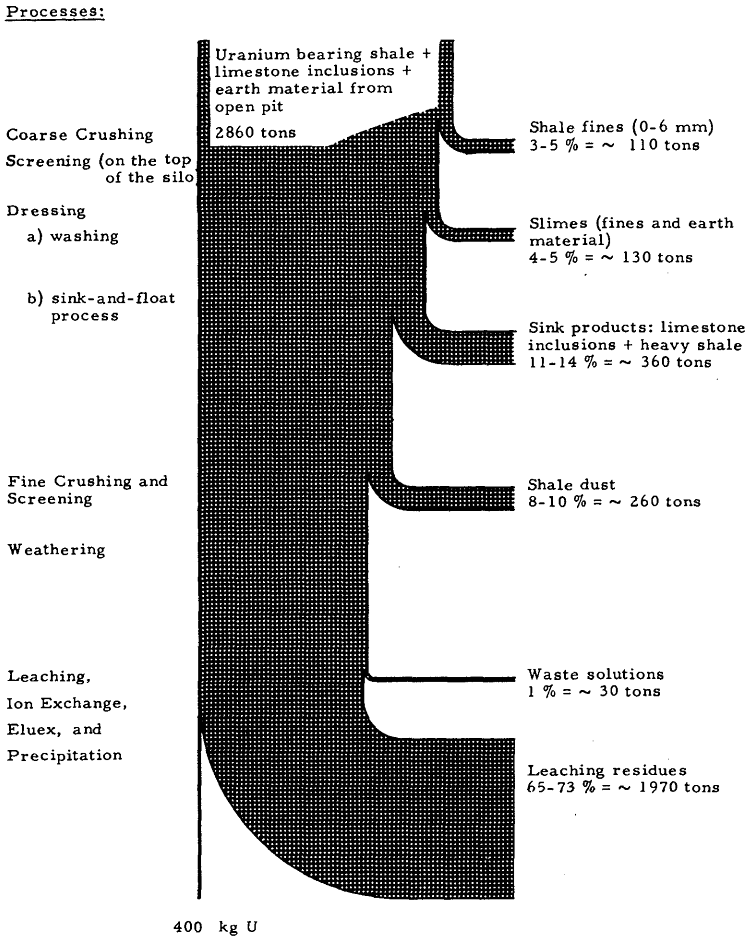

FIG. 13. Materials flow sheet for 1-d shale handling at full plant capacity.

### 6.2. Weathering storage and leaching

Although the equipment in the weathering storage has functioned well it has been found that the necessary storage time is longer than planned and probably as long as five weeks on the average. At full capacity of the mill the storage time will be only about two weeks and so the storage must be enlarged or made more effective by other means (e.g. by means of moistening and airblowing).

The equipment in the leaching plant has operated according to expectations and will most probably not give rise to any serious problems during full capacity runs. Only some minor troubles with the equipment for loading of the shale into the leaching basins will have to be taken care of. The leaching process has worked as planned and given the expected yield (after the prolonged storing found necessary).

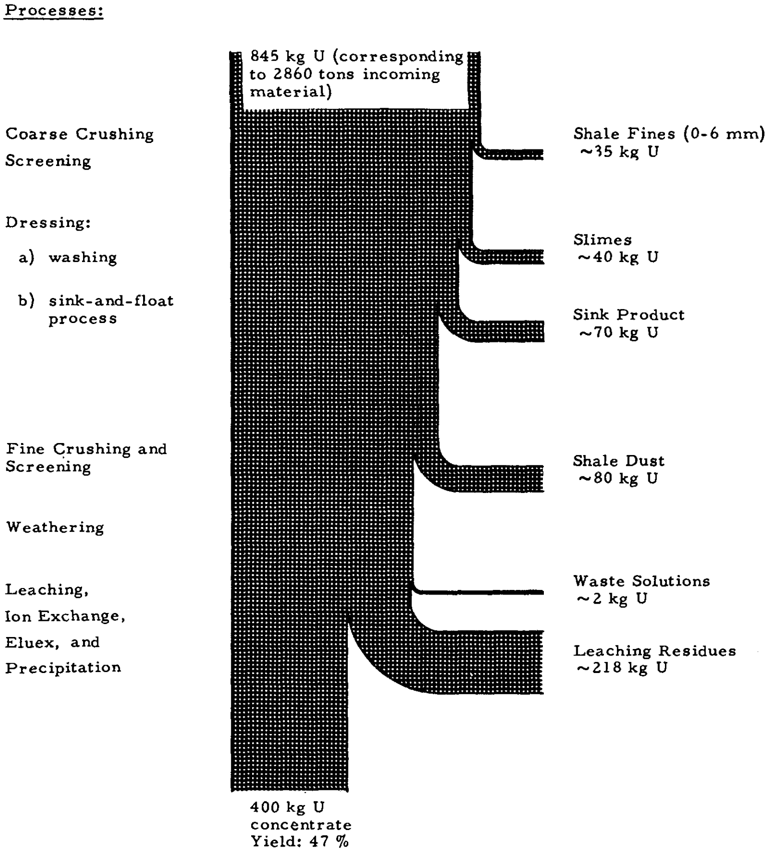

FIG. 14. Materials flow sheet for 1-d production of uranium concentrate at full plant capacity.

## 6.3. Ion exchange, extraction and precipitation

The equipment in the ion exchange plant has functioned well except for some serious trouble with the drum filter in the beginning. The ion exchange process has suffered from a several times more rapid poisoning of the ion exchanger than was expected. However, the poisoning has been of a temporary type and the resin has been regenerated to full capacity.

In the extraction plant there has been a severe corrosion of the equipment made in Mo-containing austenitic stainless steel (AISI-316). Probably the extraction tank must be replaced as well as some other equipment in connection with it. Apart from the corrosion problem the extraction equipment and the extraction process have worked as planned.

The precipitation and drying equipment and processes have functioned well after initial troubles. The uranium concentrate has the expected free-flowing character.

The rapid poisoning of the ion exchanger and the severe corrosion of the stainless steel equipment may have a common cause and depend upon the presence of polythionates formed during unfavourable conditions in the weathering storage.

### 6.4. Waste treatment

The solid waste treatment has worked as planned except for the handling of the dust from the dressing plant. The neutralization plant has suffered from some problems with the pumps for handling heavy limestone slurry. Otherwise, the waste treatment has functioned well and probably there will be no serious problems when the mill runs at full capacity.

## 7. ECONOMY OF URANIUM PRODUCTION

### 7.1. Investment

The investment per daily ton is about 50 000 kr ($10 000). In 1957 the projected investment was 116.5 Mkr. Recalculated to 1965 year's prices this corresponds to 143-145 Mkr (see Table IV).

### 7.2. Plant-operating cost

On the basis of the first year of operation the yearly cost for operation of the Ranstad mill at full capacity has been estimated to between 16.3 and 17.8 Mkr. The salary cost (186 employers in total) is 4.7 Mkr.

Yearly around 850 000 tons of ore have to be treated to give a uranium production of 120 tons. The cost per ton treated ore then will be 19 - 21 kr ($3.7-4). The cost per kg uranium produced will be 136-148 kr ($10-11

TABLE IV. INVESTMENT COSTS

| | Buildings (Mkr)[a] | Equipment (Mkr) | Total (Mkr) |
|---|---|---|---|
| Mine, crushing and classifying plants | 29.3 | 26.7 | 56.0 |
| Storage, leaching, ion exchange, extraction, precipitation and neutralization plants | 18.4 | 25.3 | 43.7 |
| General | 28.1 | 15.9 | 44.0 |
| Total | 75.8 | 67.9 | 143.7 |
| | | | ($28 M) |

[a] Mkr = million Swedish kronen.

per lb $U_3O_8$). In 1957 the same cost was calculated to be 21 kr ($ 8.9 per lb $U_3O_8$) and the difference in cost is related to the rise in salaries between 1957 and 1965.

The costs given above do not include amortization charges.

Combining the present plant with a by-product plant based on roasting of the leaching residue (see section 8) would lower the production cost per kilogram of uranium considerably but still give a cost above the present world market price.

## 8. DEVELOPMENT POSSIBILITIES

It was foreseen from the beginning that the uranium from the Ranstad mill would not be produced at costs competitive with the (present) world market prices. Attempts were made to improve the economy of the Ranstad factory through by-product winning. As early as 1957 a study was made of a plant based on roasting of leaching residue. The plant would produce steam, power, sulphuric acid and raw material for porous concrete production. However, both technique and economy of such a plant were considered too uncertain to warrant a project.

Technical developments in the last years have made it possible to revive this study of a plant for by-product winning at Ranstad. The new study is also based on roasting of the leaching residue and the products are mainly the same as given above. However, the use of the roasted leaching residue has been extended to include several other building materials, e.g. light-weight aggregate, tiles and pozzolana.

An alternative would be to roast the shale before leaching, whereby a higher uranium recovery would be possible. However, this process calls for slurry leaching, requires rather low roasting temperatures (600-650°C) and furthermore seems to make a higher investment necessary. At present this alternative is not as favourable as the preceding one. At higher prices on the uranium market it might, however, be preferred if an increase in uranium production becomes necessary.

## REFERENCES

[1] HÖRMANDER, O., GELIN, R., How Sweden is developing its low grade $U_3O_8$, World Min. 16 (March 1963) 28-31.

[2] OLSSON, G., Ranstad - a new Swedish opencast mine, Symp. on opencast mining, quarrying and alluvial mining, London, 16-19 November 1964, paper 33.

# ПОДЗЕМНОЕ ВЫЩЕЛАЧИВАНИЕ – СПОСОБ ЭКОНОМИЧЕСКОГО ИЗВЛЕЧЕНИЯ УРАНА ИЗ БЕДНЫХ РУД

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СССР

**Abstract — Аннотация**

UNDERGROUND LEACHING – A METHOD FOR THE ECONOMIC EXTRACTION OF URANIUM FROM LOW-GRADE ORES. The method of underground leaching of uranium ores has a number of advantages over extraction followed by processing of the ores in factories. It has been studied in two types of deposit, occurring in rock masses and sandy shales. Research techniques were worked out accordingly for the leaching of uranium from large-grained ore (-200 mm) and from layers in natural stratification. Special models were constructed permitting the simulation of underground leaching conditions. The results obtained were checked in field conditions on experimental plots and experimental underground blocks. The investigations demonstrated the practicability of the process of underground leaching of uranium from certain ores and made it possible to work out flow-sheets and routines for an industrial process, information about which is given in the paper.

ПОДЗЕМНОЕ ВЫЩЕЛАЧИВАНИЕ – СПОСОБ ЭКОНОМИЧНОГО ИЗВЛЕЧЕНИЯ УРАНА ИЗ БЕДНЫХ РУД. Метод подземного выщелачивания урановых руд имеет ряд преимуществ перед добычей и переработкой руд на заводах. Он изучался на двух типах месторождений, залегающих в скальных породах и песчано-глинистых пластах. Соответственно была разработана методика исследования для выщелачивания урана из крупнокусковой руды (минус 200 мм) и из пластов в естественном залегании. Были созданы специальные модели, позволяющие имитировать условия подземного выщелачивания. Полученные данные проверялись в полевых условиях на опытных участках и опытных подземных блоках. Исследования позволили показать практическую реальность процесса подземного выщелачивания урана из некоторых руд и отработать схемы и режимы промышленного процесса, сведения о которых приводятся в докладе.

Существующие технологические схемы извлечения урана из руд на сегодня достаточно совершенны, особенно в части переработки добытого сырья. Однако извлекать уран по этим схемам из бедных руд практически невозможно по экономическим соображениям.

Среди изучаемых в СССР различных направлений по утилизации бедных урановых руд подземное их выщелачивание также пользуется достаточным вниманием.

Идея подземного выщелачивания не нова, ее разработали и изучают в настоящее время в разных отраслях промышленности. В ряде случаев эти работы нашли промышленное применение, например добыча рассолов поваренной соли для содовых заводов (Польша, ФРГ, Румыния, СССР), получение серы по методу Фраша (США), выщелачивание меди из старых отвалов (США, СССР, Испания и др.), выщелачивание карнолитов и сильвинитов (США, Канада). В других же областях эта проблема еще не вышла из стадии опытных установок. Как показал научно-технический анализ, метод подземного выщелачивания полезных ископаемых в своей основе имеет ряд потенциальных преимуществ перед добычей руд и переработкой их на заводах. Он позволяет расширить ресурсы урана за счет вовлечения в эксплуатацию бедных руд.

При подземном выщелачивании исключаются дорогостоящие операции выдачи сырья на поверхность и, таким образом, открываются дополнительные перспективы по снижению стоимости получаемого урана.

Этим методом можно извлекать уран из старых рудных закладок локальных залежей, а также из таких месторождений, которые не эксплуатируются из-за сложных горно-геологических условий.

Социальные аспекты в урановой промышленности СССР имеют решающее значение, поэтому научные направления, позволяющие исключить ряд вредных для организма человека операций и облегчить условия труда, встречают особую поддержку. Немаловажную роль играет исключение в этом процессе проблемы накапливания радиоактивных отходов на поверхности.

Указанные соображения дали возможность вести исследования по подземному выщелачиванию урановых руд высокими темпами, позволившими к концу 1965 года осуществить на некоторых предприятиях постоянную добычу урана указанным способом.

Исследования проводились по комплексному плану с привлечением специалистов геологов, гидрогеологов, физико-химиков, технологов. Общее руководство и координация работ осуществлялись специальным научно-техническим советом.

Метод подземного выщелачивания изучался на двух типах месторождений, залегающих в скальных породах и в песчано-глинистых пластах. Отсюда и методика исследования в одном случае была разработана для выщелачивания урана из крупнокусковой руды (минус 200 мм), в другом – из пластов в их естественном залегании. Исследования проводились на специальных моделях, позволяющих в определенной степени имитировать условия подземного выщелачивания. Полученные данные проверяли в опытных подземных блоках с количеством руды от 1700 до 11 000 т.

В проведенных исследованиях было уделено внимание выбору подходящего реагента, изучению кинетики процесса, возможностей его интенсификации, проверки миграции радиоактивных и химических элементов во внешнюю среду и пр.

Исследования позволили показать практическую реальность процесса подземного выщелачивания урана из некоторых руд и отработать схемы и режимы промышленного процесса.

Извлечение урана в подземных условиях из скальных пород требует определенного комплекса предварительных горных работ. Для этого руда отбивается с помощью буровзрывных работ и магазинируется в подземных блоках. Разрушение рудного массива производится с помощью высокопроизводительных систем ведения горных работ. Для устранения потерь раствора под блоком и блоковыми восстающими на почве штрека укладывается надежная гидроизоляция. Система орошения замагазинированной руды состоит из двух насосных установок и набора форсунок. Форсунки расположены таким образом, чтобы при орошении смачивалась полностью вся поверхность руды (рис. 1). В качестве реагента применяются общеизвестные растворители, кроме того, исследуется возможность применения процесса бактериального выщелачивания.

Разработанные режимы предусматривают периодичность орошения по типу капиллярного выщелачивания. Продукционные растворы, пройдя всю толщу руды, собираются на днище, затем направляются в специальную емкость, смонтированную на нижнем горизонте, откуда поступают на поверхность для дальнейшей переработки (рис. 2).

В результате буровзрывных работ отбивается руда, ситовая характеристика, а также физические свойства которой видны из табл. 1 и 2.

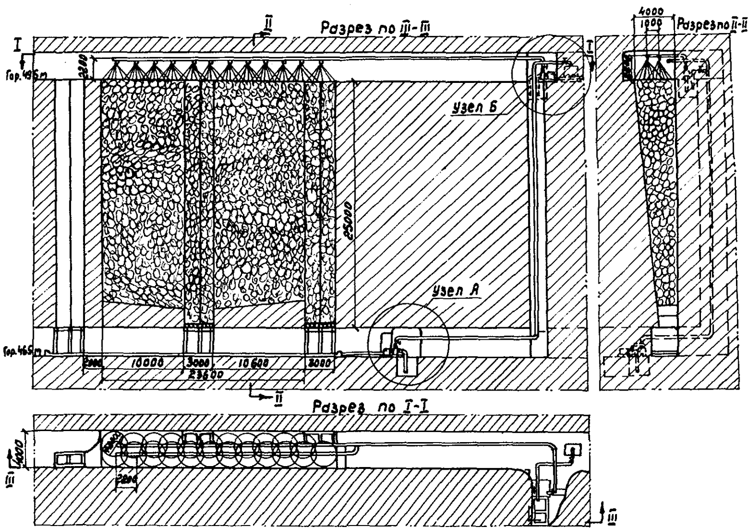

Рис. 1. Орошение руды в блоке.

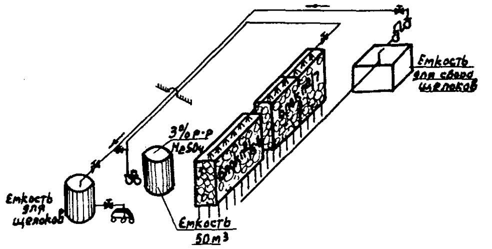

Рис. 2. Схема цепи аппаратов.

Система горных работ основывается на новейших достижениях в этой области и позволяет разрушать и магазинировать отбитую руду в подземные блоки с выдачей на поверхность не более 10% от общего количества отбитой руды. Подземные блоки сооружаются высотой 30 и 60 м с количеством руды до 100 тыс. т и более в каждом.

Извлечение урана из продукционных растворов осуществляется с помощью экстракционно-сорбционного процесса, после чего растворы вновь используются для выщелачивания.

Применение процесса подземного выщелачивания позволило исключить из процесса добычи урана ряд производственных операций, что видно из следующих данных (табл. 3).

Сокращение числа трудоемких и дорогостоящих операций значительно снизило стоимость добываемого металла. Стоимость всех операций по переводу урана в раствор при подземном выщелачивании крупнокусковой руды с учетом достигаемого извлечения составляет около 20% от общей стоимости добытого урана.

По описанному методу подземного выщелачивания в настоящее время в СССР на одном руднике успешно производится промышленная

## ТАБЛИЦА 1. СИТОВАЯ ХАРАКТЕРИСТИКА РУДЫ

| Класс, мм | Выход класса, % |
|---|---|
| − 200 + 100 | − 22,3 |
| − 100 + 50 | − 19,2 |
| − 50 + 25 | − 27,7 |
| − 25 | − 30,8 |

## ТАБЛИЦА 2. ФИЗИЧЕСКИЕ СВОЙСТВА РУДЫ И ПОРОДЫ

| | |
|---|---|
| 1. Объемный вес руды (сухой) | 2,2 т/м$^3$ |
| 2. Удельный вес руды | 2,6 т/м$^3$ |
| 3. Влажность | 8,5 % |
| 4. Коэффициент крепости по шкале Протодьяконова: | |
| гранит-порфириты массивные | 12 − 15 |
| гранит-порфиры зон дробления | 8 − 10 |
| маргели, аргиллиты и песчаники | 2 − 6 |
| 5. Коэффициент рудоносности | 0,25 − 1,0 |
| 6. Мощность рудного тела забалансовых руд | 20 м |
| 7. Распределение полезного компонента | Крайне неравномерное |

обработка бедных урановых руд. После отработки промышленных руд этот рудник должны были закрыть, несмотря на то, что в недрах оставалось еще большое количество урана в бедных рудах (добыча которых и извлечение из них урана обычными способами экономически нецелесообразна). На рис.3 виден характер оруденения и соотношение массивов промышленной и бедной руд.

Кроме того, в СССР проводятся работы по извлечению урана на месторождениях пластового типа. Подземное выщелачивание из пластовых месторождений в принципе не отличается от тех схем, которые неоднократно описывались в патентах, например Левингстона, Менке (США) и др.

Сущность этого метода довольно проста и заключается в том, что в рудный пласт через серию нагнетательных скважин подается реагент, переводящий уран из минералов в раствор, а из другой серии скважин, расположенных на определенном расстоянии от нагнетательных скважин, тем или иным средством откачиваются урансодержащие растворы.

По ряду признаков некоторые урановые руды несомненно пригодны для осуществления такого процесса выщелачивания в подземных условиях.

К этим признакам мы относим низкое содержание урана в рудах, не позволяющее рентабельно их отрабатывать механическим способом, окисленную форму урановой минерализации, обуславливающую относительно легкий переход урана в раствор, проницаемость рудного пласта, совмещение в ряде случаев рудоносного и водоносного пластов, наличие

### ТАБЛИЦА 3. ОСНОВНЫЕ ОПЕРАЦИИ ПРИ ОБЫЧНОМ СПОСОБЕ ДОБЫЧИ УРАНА И ПРИ ДОБЫЧЕ МЕТОДОМ ПОДЗЕМНОГО ВЫЩЕЛАЧИВАНИЯ

| Обычный способ добычи урана | Добыча урана по методу подземного выщелачивания |
|---|---|
| 1. Вскрытие месторождения | 1. Вскрытие месторождения |
| 2. Подготовка горизонтов и блоков | 2. Подготовка горизонтов и блоков |
| 3. Отбойка руды в блоках | 3. Разрушение руды буровзрывными работами |
| 4. Выдача руды из блока | |
| 5. Закладка образованных пустот в результате добычи полезного ископаемого | |
| 6. Горизонтальная и вертикальная транспортировка руды под землей | |
| 7. Перевалка руды в бункера и погрузка из бункера | |
| 8. Транспортировка руды на завод | |
| 9. Обогащение руды | |
| 10. Выщелачивание урановых руд на гидрометаллургическом заводе | 4. Извлечение урана в раствор из замагнизированной руды |
| 11. Выщелачивание урановых руд на гидрометаллургическом заводе | |
| 12. Сорбция урана из пульпы на гидрометаллургическом заводе | 5. Сорбция урана из раствора |
| 13. Создание хвостохранилища | |
| 14. Транспортировка и складирование хвостов | |
| 15. Очистка дебалансовых сбросных растворов | |
| 16. Создание отвалов попутно добытых забалансовых руд на руднике | |
| 17. Организация карьерного хозяйства по добыче закладочных материалов и транспортировка их к месту закладки выработанного пространства | |

практически непроницаемых глин в подстилающих породах (под урановым пластом) и т.д.

С учетом указанных положений, после проведения ряда исследовательских и опытных работ на двух месторождениях СССР, организована опытно-промышленная отработка локальных урановых залежей.

В результате применения этого способа себестоимость урана значительно снижена по сравнению с его стоимостью в основном производстве. Это месторождение служит примером использования локальных залежей, отработка которых механическим способом нерентабельна.

Успешное осуществление описанных работ стало возможным благодаря определенной организации научных исследований, сочетающих лабораторные исследования с параллельной проверкой полученных данных в полевых условиях на опытных участках и опытных подземных блоках.

Исследования показали, что процесс подземного выщелачивания в том виде, в каком он существует сегодня, относится к классу экстенсивных процессов. По механизму и кинетике он подразделяется нами на два типа.

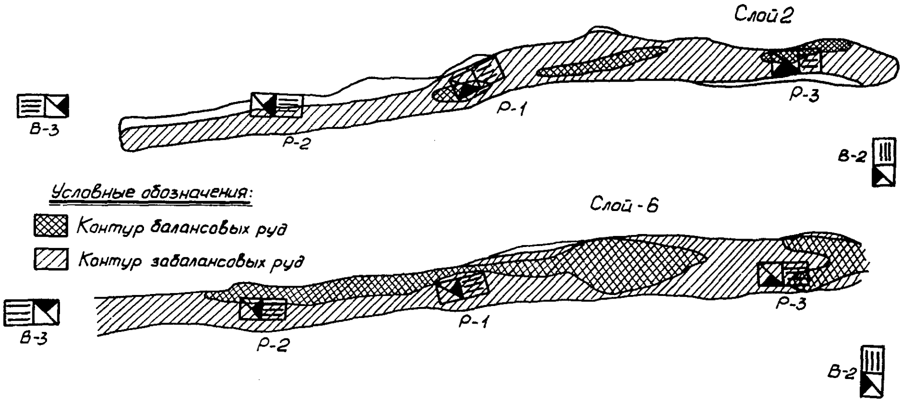

Рис. 3. Контур залегания балансовых и забалансовых руд.

При выщелачивании крупно кусковой руды в блоках он подобен процессу капиллярного выщелачивания, а извлечение урана из проницаемой руды в пластовых условиях протекает по законам фильтрационного выщелачивания и имеет много общего с перколяционным процессом.

Дальнейшие исследования направлены на интенсификацию процесса подземного выщелачивания как путем физико-химических исследований, так и путем рационального построения технологического процесса отработки тех или иных урансодержащих залежей и рудных тел.

# RECOVERY OF URANIUM FROM LOW-GRADE SANDSTONE ORES AND PHOSPHATE ROCK

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## Abstract

RECOVERY OF URANIUM FROM LOW-GRADE SANDSTONE ORES AND PHOSPHATE ROCK. This paper is concerned principally with commercial-scale experience in the United States in the recovery of uranium from low-grade sources. Most of these operations have been conducted by the operators of uranium mills as an alternative to processing normal-grade ores. The operations have been generally limited, therefore, to the treatment of low-grade materials generated in the course of mining normal-grade ores. In some circumstances such materials can be treated by simplified procedures as an attractive source of additional production. The experience gained in uranium recovery from phosphate rock will be treated in some detail. The land pebble phosphate rock of central Florida generally contains about 0. 01 to 0. 02% $U_3O_8$. While no uranium is being recovered from this source at the present time, it does represent a significant potential source of by-product uranium production because of the large tonnages being mined.

## INTRODUCTION

The uranium mills in the western United States process sandstone ores with average uranium content generally in the range of 0. 1 to 0. 4% $U_3O_8$. In both open-pit mining operations and underground mines some waste rock is generated which contains sufficient uranium to warrant its segregation for subsequent treatment. The uranium content of some of this material which has been processed is generally in the range of 0. 02 to 0. 10% $U_3O_8$. In addition some simplified flowsheets have been employed to produce either an intermediate product for further treatment in a conventional plant, or a refined product needing little or no additional processing.

The land pebble phosphate rock of central Florida generally contains about 0. 01 to 0. 02% $U_3O_8$. The production of marketable phosphate rock in Florida reached 16. 4 million long tons in 1964 and about 20 million tons in 1965. However production of high analysis fertilizers in 1966 is 25 to 30% higher than for a comparable period in 1965. This represents a large resource of uranium, most of which should be recoverable at costs of less than $10 per pound of $U_3O_8$.

### Characteristics of the sandstone ores

The principal uranium reserves in the western United States are in sandstone-type deposits. From the metallurgist's viewpoint the most important characteristics of the ores are the constituents which consume reagents, interfere with processing operations, or represent potential by-products.

In most of the sandstone ores the sand itself is barren. Uranium and other values occur as interstitial material and coatings on the sand particles. Calcium carbonate is commonly present in significant amounts ranging from 1 or 2% to perhaps 20 to 30%. The ores commonly contain from several per cent to 20% bentonitic clays, and a small amount of soluble organic matter. Despite the clay content, the rock is typically fairly porous and poorly consolidated. Molybdenum is frequently present in sufficient concentrations to be troublesome, but seldom sufficient to be attractive to recover as a by-product. Vanadium is the principal by-product, obtained largely from the carnotite-type ores of the Uravan Mineral Belt. With the notable exception of the carnotite-type ores, the uranium is usually found in a reduced valence state as coffinite and uraninite. The pyrite content is variable, but generally low in comparison with the highly siliceous conglomerate ores, such as those of Canada and South Africa. In those deposits containing uranium in a reduced condition, the pyrite content may be on the order of 0.1 to 1.0%.

### Waste rock treatment methods

The treatment of low-grade sandstone rock containing 0.02 to 0.1% $U_3O_8$ has been accomplished by either:

(a) Heap leaching of the mined rock either at the mine site or at the mill if ore transportation costs are not burdensome; or

(b) A scuffing operation, followed by a sand-slime separation and concentration of the slime into an upgraded product.

### Heap leaching

The procedure is by no means new, having been practised successfully at the Urgeirica mill in Portugal in the early 1950's. It was as a result of the observation of natural or spontaneous leaching of these ores that the contribution of bacterial activity to the solubilization of the uranium was first recognized. Most of the domestic ores contain too little pyrite and too much calcium carbonate to make bacterial leaching effective without supplementary addition of a source of sulphur. As a low cost source of acid, the barren solution from nearby uranium mills containing both ferric iron and some remaining sulphuric acid is frequently available for a leach reagent for the heap leach operations.

The chief concerns in constructing heap leach piles are to lay them out in such a manner that the permeability is reasonably consistent throughout the pile area, that drainage is good from the bottom of the pile, and that solution losses are held to a minimum.

Because of the natural porosity of the sandstone ores, fine crushing is necessary. Rock can generally be used for heap leaching without further size reduction. The area in which the pile is to be built, which may be as much as 400 ft on a side, is carefully graded into a series of gently sloping shallow troughs, about 6 m wide and 15 to 30 cm deep. The surface of this area is covered with an impervious plastic or thin rubber sheeting. Small diameter perforated asbestos or other non-metallic pipes are laid the length of the troughs to form solution collecting lines. In some cases a bed of gravel or fine stone is then laid on top of the pipes. An alternate method is to cover the pipe with a screen sleeve to prevent blinding of the perforations.

The ore is first moved on top of the prepared site with a front-end loader. Once a sufficient bed of ore is laid down, however, the bottom dumping ore trucks may discharge directly onto the top of the pile. The proper depth of ore in a pile depends upon the permeability of the pile and the practical considerations of the ore-handling operations. The compaction resulting from running heavy equipment over the pile during its construction has proved acceptable. Once sufficient ore has been accumulated on the leach site, a bulldozer is used to level off the surface and divide it into a series of shallow rectangular depressions into which the leach solution can be directed.

One recently constructed heap leach pile is about 10 m deep. The time required for the solution to percolate through this pile – solution retention time – is estimated to be about two weeks.

At one location, a barren raffinate from the normal uranium milling circuit is used for the heap leaching. It contains about 2-2.5 g/litre total iron, about half of which is ferric. The free acid content, after spiking with some additional acid, is about 10 g/litre sulphuric acid. This solution is pumped into the shallow ponds on the heap and allowed to percolate through the bed. Another practice is to apply the calculated acid requirement as a concentrated solution containing about 35% sulphuric acid initially, followed by recycled dilute solutions or by water [1].

Methods of handling the pregnant liquor draining from the heap leach vary with the circumstances. Where the heap leach operation is conducted near an ore processing plant, the liquor can be introduced into the mill circuit at a point where the mill solution has about the same uranium content. Since the uranium concentration in the solutions from heap leaching characteristically decline gradually over an extended period of time, a thickening circuit, or some other multiple stage ore washing circuit offers a series of washing stages at which solutions of various contents can be introduced.

Recovery of values from heap leach operations is somewhat difficult to measure with any degree of confidence, since the ore is generally only roughly sampled at the time the pile is constructed. The extraction period may vary from one or two months to more than a year. However, indications to date are that recoveries on the order of 50 to 80% are being achieved. Once the leaching is completed the pile of leached rock is left on its site, and the next leach pile must be constructed on a new piece of ground.

The cost of conducting a heap leach operation must be compared carefully with conventional milling costs before any conclusion can be reached that the heap leaching approach is preferable. By way of illustration, if one considers a value of $8.00 per pound of $U_3O_8$ in a finished product, the difference of 25% in recovery on an ore containing 0.10% $U_3O_8$ would be $4.00 per ton.

In some US mills there is substantial milling capacity available in excess of the current rate of ore processing, and incremental costs of processing limited quantities of additional ore do not exceed $4.00 per ton. For ores containing 0.10% $U_3O_8$ or more haulage to a mill for processing by conventional means is usually more profitable than heap leaching at the mine.

## Upgrading plants

Six milling plants have been built in the United States which may be considered to be primarily upgrading plants, or plants in which the larger part of the ore feed is processed in an upgrading circuit. These upgrading units have all been constructed near ore deposits for which the transportation costs to existing mills was high or even prohibitive, due either to the long distances involved, or the low tenor of the ores.

It is difficult to find any definition of an upgrading plant which will reasonably fit most of these plants. In general, one or more of the normal ore processing steps have been omitted or shortened at some sacrifice in recovery, product grade, or both. A minimum installation generally includes equipment for crushing and grinding or scuffing the ore, followed by separation of the sand and slimes. The sand is discarded, and the slime fraction is shipped to a conventional mill. Such operations achieve a rejection of one half to three fourths of the weight of the ore, at a sacrifice in recovery of the order of 20 to 30% of the values. The losses are principally due to the strong adherence of part of the slimes as a coating on the sand particles, rather than values locked in the coarse sand grains. It has proved worthwhile in most instances to acid wash the sands before discarding them to improve uranium recovery. Fifty per cent or more of the uranium in the sands may be recovered in this manner. The acid solution is neutralized, and the resultant precipitate is thickened, filtered and dried. Alternatively, where the attrition grinding is performed wet, the acid leach liquor is sometimes returned to the grinding step. The acidity is neutralized by the acid consuming constituents in the ore, and the precipitated uranium reports with the slimes.

The product from these operations is a fine slime with a content usually in the range of 0.2 to 0.8% $U_3O_8$. In the case of carnotite-type ores, vanadium values are about three to five times as high as the uranium content. The physical characteristics of these products would make them difficult to handle at the conventional mill if it were not for the fact that they can be blended with larger volumes of other ores being fed to process. The upgraded product usually can be fed into the leach circuit at the main mill, by-passing the crushing and grinding steps. At one plant the upgraded product is pelletized with salt and fed to a salt roasting kiln to convert the vanadium to a water soluble sodium vanadate. The roast also greatly improves the handling properties of the ore thereafter.

Two of the upgrading plants which operated in the USA were nearly complete ore processing plants, each producing a yellow cake. One of the plants, however, lacked final product drying equipment, because the company had adequate facilities for this operation at another plant.

The Maybell, Colorado, plant of Union Carbide Corp. [2] was unusual in two unit operations, the ore grinding operation, and the ion exchange step. Following the crushing operation the ore was stored in either of two bins depending on whether it was high or low grade. The low grade ore was ground in a rod mill. The slime fraction was thickened, and the sand fraction acid washed and discarded. The thickened slime pulp was fed to a leach circuit along with the higher grade ore. After the leach, the sands and slimes were separated, the slimes again being thickened. The slime underflow at about 20 to 25% solids was fed to the resin-in-pulp circuit.

The resin-in-pulp operation was the first commercial-scale application of the Infilco-Techmanix unit which permitted a mixing of resin and pulp in open tanks without confining the resin in baskets as was the previous practice [3, 4]. The resin was advanced from stage to stage counter-current to the flow of pulp by means of air lifts and vibrating screens. This system has a number of advantages over the basket equipment in that it is more compact, less expensive to construct, requires less maintenance, and requires a lower resin inventory.

Western Nuclear, Inc., at its 'Spook Upgrader' located in Converse County, Wyoming, has employed a simplified leach circuit to treat a large orebody at an isolated location [1]. The average grade of the ore is 0.13% $U_3O_8$, with no other constituents in economically recoverable concentrations. The crushed ore, 85% minus $\frac{1}{4}$-in. size, is fed to an agglomerator in which it is mixed with sufficient sulphuric acid to leach the uranium and sufficient water to bring the moisture content to 12%. The agglomerator is a rubber lined tube 20 m long by $2\frac{1}{2}$ m in diameter. The agglomerated ore is bedded in tanks about 3 m deep. After a curing period of about 14 h the thick bed of ore could be percolation leached. Excellent recoveries, about 90%, were achieved in a total leach cycle time of 72 h. The pregnant solutions were further processed in conventional ion exchange columns, the eluate precipitated with ammonia, and the product shipped as a wet slurry. The plant did not require either thickening or filtration equipment, thus reducing its construction cost compared with a conventional plant. The plant was built in the open, with a roof over some equipment. Therefore it was not operated during cold weather. The agglomeration step, which permitted rapid percolation of leach solutions through a thick bed of ore is a useful technique which may receive further attention in the future.

## Uranium recovery from Florida phosphates

During the early 1950's the US Atomic Energy Commission entered into several research contracts to develop methods for recovery of uranium from phosphate rock. Although considerable effort was directed toward methods of leaching the uranium, no process could be found which would selectively extract uranium from phosphate rock. Alkaline leach methods were completely ineffective. Acid leaching resulted in the dissolution of uranium in about the same proportion as the dissolution of the phosphate rock. For this reason, the procedures for uranium recovery were all based on by-product recovery from phosphoric acid, which is produced by digestion of the rock with sulphuric acid at an intermediate stage in the manufacture of high analysis fertilizers and other phosphate chemicals.

Much of the phosphate rock which is used for fertilizers is not converted to acid; it is either directly applied to the soil or simply wet with sulphuric acid and cured to produce superphosphate. The uranium in these products is not presently recoverable. However, the technology of production of phosphate fertilizers is undergoing a substantial change, and is rapidly shifting toward the production of higher grade products. Additionally, world fertilizer production, which from 1954 through 1962 grew at a rate of 5.5% annually, has in the last several years expanded at a rate of over 10% [5]. It appears that a major upswing in the growth trend has occurred. The consumption of phosphate rock in the US in 1956 was about 11 500 000 metric tons, of which about 2 000 000 tons was used in manufacture of wet process phosphoric acid [6]. During 1965, about 8 million tons of phosphate rock containing an estimated 1200 tons of $U_3O_8$ was converted into wet process phosphoric acid. The production of normal and enriched superphosphate now accounts for less than 40% of output and is declining yearly. Ammonium phosphates are rapidly increasing in production; output so far in fiscal year 1966 has increased 30% over 1965 and has almost reached the production level of triple superphosphates and other concentrated fertilizers [7].

The rapid expansion which has already taken place in the manufacture of wet process phosphoric acid, together with projected further expansions, indicate that there will be about 2000 tons of $U_3O_8$ per year recoverable from this source by 1970. Unless it is recovered during the manufacturing operations, however, this uranium is lost. Thus our resources of uranium in phosphate rock are being wasted at a steadily increasing rate.

Three companies have operated by-product uranium recovery units for extended periods in the US. The first commercial unit, that of Blockson Chemical Company, Division of Olin Mathieson Chemical Corporation, in Joliet, Illinois, commenced production in 1952 using a chemical precipitation method [6]. The second by-product unit, that of International Minerals and Chemical Corporation near Bartow, Florida, commenced production early in 1955, and was the first to employ solvent extraction [8]. The third unit, US Phosphoric Products Division, Tennessee Corporation, in East Tampa, Florida, started up in 1957, also employing a solvent extraction flowsheet [9]. Each of these plants has been the subject of at least one published paper which gives a far more detailed analysis of its process than is possible to do here. However, some of the considerations that led to a particular choice of plant design, or that limited the effectiveness of a unit operation, are not evident in these papers, and it is in these areas that I will place my emphasis.

The Blockson plant was the only large-scale producer of technical grade phosphate chemicals from wet process phosphoric acid. The plant treated Florida pebble phosphate rock, delivered by barge up the Mississippi River to Joliet, Illinois. Briefly, the method employed for uranium recovery began with the partial neutralization of wet process phosphoric acid to form mono-sodium phosphate at a pH of 4 to 5. The bulk of the impurities were precipitated at this stage, and were filtered off. They consisted largely of calcium, iron, and aluminium phosphates and silicates. The addition of a strong oxidizing agent such as chlorine to the acid prior to the neutralization step resulted in retention of about 80 to 90% of the uranium in solution. After filtration, the addition of sodium hydrosulphite to the filtrate precipitated 90 to 95% of the uranium as a gelatinous uranous phosphate. This product could be filtered off after addition of a diatomaceous earth filter aid and was not difficult to upgrade to a product containing 40 to 60% $U_3O_8$. Overall recovery was 60 to 70%.

All of Blockson's phosphate rock was calcined as a pre-treatment to eliminate organic constituents which could not be tolerated in many of the end products. The calcination step was found to be detrimental to the subsequent dissolution of the uranium in the acid treatment of the rock and reduced the dissolution of uranium as much as 10 to 20%.

There is no specific information on which to judge whether the organic materials present in the rock would have interfered with subsequent uranium recovery operations if the rock had not been calcined. The question is of interest because of the large quantities of ammonium phosphate fertilizers now being produced. In manufacture of these products the wet process acid is neutralized to the mono or diammonium phosphate. The Blockson method might be applicable to this process. This method, although generally producing a lower uranium recovery than solvent extraction, has considerable merit in such areas as simplicity of control, cost of installation, and reagent requirements and consumption.

The International Minerals and Chemical Corporation built its by-product unit for uranium recovery in connection with the construction of the Bonnie Plant, a new plant for production of high grade phosphates, near Bartow, Florida [8]. The uranium recovery unit was designed to extract uranium from in-process phosphoric acid without neutralizing the acid in order to minimize interference with the production of triple superphosphate. The phosphate ion is in itself a strong complexing ion for uranium. The phosphoric acid produced in the plant generally contained 24 to 30% $P_2O_5$ and 0.1 to 0.2 g $U_3O_8$/litre. The acid was, of course, saturated with calcium sulphate. Fluorine, iron, and aluminium were the other principal contaminants, present in concentrations of 2 to 15 g/litre.

Ion exchange resins, anionic or cationic, were not effective extractants of uranium from such solutions. Saturation resin loadings were generally in the range of 0.1 to 0.2 g $U_3O_8$/litre of resin.

Of the many solvents which were tested, the alkyl pyrophosphate esters proved to have the most favourable extraction coefficients. The active solvent had to be made on the site from an aliphatic alcohol, generally of 8 to 10 carbon atoms, and phosphorous pentoxide. These 'pyro' esters unfortunately are more or less chemically unstable, and tend to hydrolyze to the 'ortho' esters fairly readily. The hydrolysis is accelerated in the presence of strong acids, and by increased temperatures. The uranium extraction coefficient of the active solvent also varies to a substantial extent with change in temperature in the range of 80 to 130°F, being substantially inferior at the higher temperatures. These solvent properties were very important to the design and operating efficiency of the plants.

In spite of prior pilot-plant experience, considerable difficulty was encountered before commercial-scale uranium recovery units could be made to operate consistently.

The basic steps of the process were essentially the following:

(1) Phosphoric acid cooling and clarification
(2) Reduction with scrap iron
(3) Solvent extraction
(4) Uranium re-extraction and precipitation
(5) Reagent preparation
(6) Product drying and packaging.

At the International Minerals plant, the crude phosphoric acid delivered to the uranium units was at a temperature of 130 to 150°F. The acid was cooled by air in cooling towers. After settling out the precipitated gypsum resulting from evaporation in the cooling step, the acid was percolated through reduction pits containing scrap iron to reduce the uranium to the tetravalent state. These pits did not perform well. The stationary bed of scrap iron became passivated fairly rapidly by formation of an adherent coating of an iron phosphate and gypsum. As noted in the flowsheet given on page 376 of Ref. [10], the reduction pits were eventually replaced by a rotary No. 316 stainless steel drum operated in the same manner as a ball mill. The agitation provided in the mill kept the iron surfaces clean and effectively reduced the emf of the acid. The desired emf after reduction was 0.0 mV.

Of the several different types of equipment which were tried for solvent extraction, only centrifuges proved satisfactory for separating organic from aqueous phases. Due to the slowness of phase disengagement, and the strong tendency of organic tars and/or waxes from the phosphate rock, together with fine solid particles, to stabilize emulsions, pulse columns proved to be totally ineffective for this solvent extraction application. The mixer-settlers, which have been used with great success in uranium recovery from conventional ores, also were found to be unsuited to the task due to the severe emulsion problem. The centrifuges which were successfully employed were the Sharples Nozljector centrifuge, Models DH-256 and DH-3. The emulsion problem was never completely solved, and even under the best of conditions the kerosine loss was about one per cent of the volume of acid treated. The serious nature of the emulsion problem was not fully appreciated in pilot operations, in part because the emulsifying properties of the acid change fairly rapidly with time. The emulsions tended to be stabilized by the continuing formation of very fine solid particles in the acid, much of it gypsum, which collected at the organic-aqueous interface. This problem is substantially lessened if the phosphoric acid is allowed to stand for a few days before solvent extraction. However, such a procedure is impracticable in a commercial operation.

### Nature of the solvent

The solvent employed at the International Minerals plant was produced from 'decyl alcohol', a mixture of isomers of trimethyl heptanol. The alcohol, mixed with about an equal volume of kerosine, was reacted with $P_2O_5$ in water-cooled jacketed tanks in which the temperature of the exothermic reaction was kept below 155°F. The solvent inventory in the plant was generally at a level which resulted in recycling the entire inventory about every 24 hours. Under these conditions the loss of the pyro ester through degradation and other causes was about one third of the inventory per cycle. The rate of solvent degradation appeared to be affected by time, temperature, and the type and concentration of the acids with which it was contacted. There was no evident correlation of the rate of solvent degradation and the amount of uranium extracted. It follows, therefore, that in any plant design, an important consideration is to keep the total solvent inventory to a minimum. After a period of recycling in which sufficient fresh pyro ester was added each cycle to maintain its concentration at about 5% by volume, the concentration of the alkyl ortho phosphoric acid reached 10% by volume, and the total phosphate content of the organic phase was about three times the level in fresh solvent. After 3 to 4 weeks standing, a sample of a newly prepared ester, which had not been used in the plant, was found to contain about 80% pyro and

20% ortho ester. Thus it is evident that the rate of decomposition is greatly accelerated during contact with acid solutions.

A procedure was tried in which $P_2O_5$ was added directly to barren recycled solvent in order to react with the ortho ester and produce further pyro ester from it. However, this procedure did not appear to be nearly as effective or economical as the use of freshly made solvent.

In evaluating the performance of solvents it was the practice to measure the extraction coefficient of each solvent as a basis for comparing its uranium complexing power with that of other solvents. The extraction coefficient is generally determined for a single stage as the ratio of uranium concentration in the organic phase to the concentration in the aqueous phase at equilibrium. In this system, however, substantial differences in the extraction coefficient were found for a given solvent, depending on the concentration of active solvent in the organic phase, even though the concentration of the uranium in the organic phase was well under its saturation capacity.

Better correlations were obtained when uranium concentrations in the organic phase were first corrected to theoretical concentration in 100% active solvent. Thus a concentration of 1 g/litre $U_3O_8$ in an organic phase containing 5% by volume of pyro ester would be converted to 20 g/litre concentration in the 100% pyro ester. On this basis, the solvents which proved workable on a commercial scale exhibited extraction coefficients on the order of 400 to 800 or higher when freshly prepared. With repeated cycling the extraction coefficient of a solvent will drop substantially from its original value. In spite of their chemical instability the pyro esters were preferred. The extraction coefficient of octyl pyro phosphoric acid was 10 to 100 times higher than octyl ortho phosphoric acid. In practice it was possible to obtain uranium concentrations of about 1 g/litre $U_3O_8$ in loaded solvent from a concentration of 0.15 to 0.22 g/litre in the feed phosphoric acid using a solvent flow of approximately one-tenth of the acid flow rate.

## Solvent stripping

Removal of uranium from the loaded solvent was accomplished by a single stage of stripping employing a 12% solution of HF or a mixed acid containing 25% sulphuric acid and 12% HF. In the event, the pregnant organic phase still carried some emulsion from the extraction step, a carry-over of phosphoric acid into the strip solution could easily occur. Since the efficiency of the single-stage stripping operation was dependent upon the simultaneous re-extraction of the uranium and its precipitation as uranium tetrafluoride, the maintenance of an adequate fluoride ion concentration was essential. The rapid and accurate analysis for fluoride ion in a mixture of hydrofluoric, sulphuric and phosphoric acids was essential to the control of the precipitation step.

The separation of the precipitated uranium from the mixed solvent and strip solution was performed in a single operation in a solid bowl Tolhurst centrifuge which was adapted to permit the continuous separation of the two liquid phases while the solid phase was accumulated. Periodic shut-down was necessary for removal of the uranium.

The final product after drying was a crude uranium tetrafluoride generally containing 40 to 60% $U_3O_8$ equivalent. This product was delivered to an AEC refinery for further processing. Although the product could not be fed directly to the refinery circuit due to its fluoride content, it could be fed along with recycled scrap materials into a multiple hearth roaster where it was converted to an oxide.

The crude fluoride product would not meet the specifications in general use at the present time, and an additional purification step will undoubtedly be required for any future commercial installation. Further work would be needed to establish a satisfactory procedure, but it should not be difficult to do.

The solvent extraction process for recovery of uranium from wet-process phosphoric acid has proven to be quite difficult to control. One aspect that was not fully appreciated prior to commercial operations was the wide fluctuation in the uranium concentration in the phosphoric acid feed to the plant. One would think that the concentrations of the uranium and other minor constituents in the feed acid would remain at a fairly consistent level; the phosphate rock from which it was produced had come from several mining operations and had undergone desliming, spiral separation and flotation upgrading operations followed by blending in stockpiles. Nevertheless, variations of as much as 50% in the uranium concentration of the daily composite samples of the feed acid, e.g. 0.15 to 0.23 g $U_3O_8$/litre, were quite common. Variations in feed grades during a day may have been still greater. Since the concentration of the uranium in the feed acid was not subject to the control of the uranium plant operator he was faced with two choices:

(1) Operate for maximum solvent loading and achieve thereby minimum reagent consumption at the risk of losing some recovery if the uranium concentration in the feed rose rapidly and exceeded the uranium absorption capacity of the solvent.

(2) Operate for maximum uranium recovery by purposely circulating sufficient solvent to prevent saturation capacity from being reached.

The latter mode of operation proved the more economical because the higher recovery achieved actually lowered the average reagent consumption per pound recovered and greatly simplified the work of keeping the various flows in balance. Each of the principal unit operations in the process — acid cooling, clarification, reduction, solvent extraction, stripping, and precipitation — is dependent on the efficiency of each of the operations preceding it. The system is in a dynamic balance, the organic solvent and aqueous stripping solutions recycling continuously. Although it is a complex system to control, it has been done with a reasonable degree of success.

## REFERENCES

[1] MASHBIR, D. S., Heap leaching of low grade uranium ores, Min. Congr. J. 50 (Dec. 1964) 50-54.
[2] New contractor unravels difficult ore, Chem. Engng 66 (May 1959) 52-54.
[3] Resin rides an air-lift, Chem. Wkly 89 (Mar. 1957) 73-79.
[4] HOLLIS, R. F., McARTHUR, C. K., The resin in pulp method for recovery of uranium, Min. Engng 9 5 (1957) 443-49.
[5] DAVAN, C. F., HOUSEMAN, C. T., Plant food minerals: A forecast to 1980, Min. Engng 17 12 (1965) 85-88.
[6] STOLTZ, E. M., Jr., Recovery of uranium from phosphate ores, Proc. 2nd UN Int. Conf. PUAE 3 (1958) 234.

[7] UNITED STATES DEPARTMENT OF COMMERCE, Bureau of the Census, Current Industrial Reports, Series M28D(66)-3.

[8] GREEK, B. F., ALLEN, O. W., TYNAN, D. E., Uranium recovery from wet process phosphoric acid, Ind. Engng Chem. 49 (1957) 628.

[9] CRONAN, C. S., Capryl pyrophosphate ester extracts uranium from wet process phosphoric acid, Ind. Engng Chem. 49 (1957) 628.

[10] MANNING, P. D. V., LeBARON, I. M., CRAMPTON, F., "Recovery from phosphate rock", Uranium Ore Processing (CLEGG, J. W., FOLEY, D. D., Eds), Addison-Wesley Publishing Co., Reading (1958) 376.

# RECOVERY OF URANIUM FROM URANIUM MINE WATERS AND COPPER ORE LEACHING SOLUTIONS

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## Abstract

RECOVERY OF URANIUM FROM URANIUM MINE WATERS AND COPPER ORE LEACHING SOLUTIONS. Waters pumped from uranium mines in New Mexico are processed by ion exchange to recover uranium. Production is approximately 200 lb $U_3O_8$/d from waters containing 5 to 15 ppm $U_3O_8$. Recoveries range from 80 to 90%. Processing plants are described.

Uranium has been found in the solutions resulting from the leaching of copper-bearing waste rock at most of the major copper mines in western United States. These solutions, which are processed on a very large scale for recovery of copper, contain 2 to 12 ppm $U_3O_8$. Currently, uranium is not being recovered, but a potential production of up to 6000 lb $U_3O_8$/d is indicated. Ion exchange and solvent extraction research studies are described.

## INTRODUCTION

In the United States, about 200 lb/d of low cost $U_3O_8$ is being recovered commercially by ion exchange processing of the natural drainage waters from uranium mines. A much greater potential source of uranium that remains to be exploited is the acid solutions that are recycled through the mine dumps at open pit copper mines for the purpose of recovering copper. A recent survey by the Bureau of Mines revealed that 14 major mines are processing about 40 000 US gal/min of dump leaching solutions for recovery of copper and that these solutions contain 1 to 12 ppm $U_3O_8$. It is probable that similar solutions produced at copper mines in other parts of the world also contain uranium, and these solutions, therefore, represent a significant source of low cost uranium. The purpose of this paper is to review for this Panel commerical practice in recovering uranium from uranium mine waters and present the results of research by the Bureau of Mines in recovering uranium from copper waste dump leaching solutions.

## RECOVERY OF URANIUM FROM MINE WATERS

Since 1963, uranium has been recovered from the drainage waters pumped from the uranium mines in the Ambrosia Lake District of New Mexico. Production is about 200 lb $U_3O_8$/d from a total flow of approximately 3000 gal/min. The uranium content of waters pumped from the mines ranges from 2 to 20 ppm $U_3O_8$ but averages less than 10 ppm, and on the basis of the flow rate and production data, it appears that the average recovery of $U_3O_8$ is approximately 6 ppm.

The two principal operations recovering uranium from mine waters are Kerr-McGee Oil Industries and Homestake-Sapin Partners. Both employ ion exchange systems in which ion exchange resins are contained in two columns connected in series; the solution flow is up rather than down as in conventional ion exchange columns. The reason for this type of operation is that the solutions contain appreciable amounts of suspended solids. With downflow operation, the compacted resin bed acts as a filter and a high degree of clarification would be necessary to avoid blockage of the resin bed during the long loading cycles. With upflow operation, the resin bed is expanded and the suspended solids pass through.

At both installations the columns are 8 ft in diameter by 14 ft high. At Homestake, a single set of two columns is in operation, whereas four sets of two columns are used at the Kerr-McGee plant. The top of each column is fitted with a peripheral overflow launder to collect the overflowing solutions, and the bottoms of the columns are fitted with perforated plates to support the resin and to provide for uniform distribution of the feed water. At the Homestake installation, mine water is pumped from a small collecting sump through the first column and then by another pump through the second column, the overflow from which is discarded. At the Kerr-McGee installation, feed to the columns is by gravity from an elevated storage tank and the pairs of columns are set at different elevations so that the overflow from the first column passes by gravity flow through the second column. At the Homestake mill, the solution flow is approximately 5 gal/min per square foot of resin bed area. The resin inventory is 400 $ft^3$ of minus 16- plus 20-mesh strong base anion exchange resin per column and bed expansion is approximately 25%. This gives a working bed depth of about 10 ft. At the Kerr-McGee plant, the same resin type is used. The resin inventory, however, is only 150 $ft^3$ per column, but the solution flow is 10 gal/min per square foot of resin bed area. Bed expansion is estimated at 100%, which gives a working depth of 6 ft.

At both installations, loaded resin containing 2 to 4 lb $U_3O_8/ft^3$ (32 to 64 g/litre) is periodically removed from the lead column by hydraulic transfer, and the partly loaded resin in the second column is transferred to the lead column. The second column then is filled with regenerated resin. The loaded resin is eluted in a conventional column by downflow of a solution of sodium chloride and sodium bicarbonate. At the Kerr-McGee installation, the entire mine water recovery plant is located at the mill site, and the pregnant eluate is pumped to the main processing mill. Initially the eluate was combined with a chloride solution resulting from the stripping (backwashing) of the uranium-bearing amine extractant in the regular mill circuit, and the combined solutions were neutralized with ammonia to recover the uranium. More recently, the uranium-bearing eluate has been introduced into the feed liquor to the solvent extraction circuit to achieve further purification and to simplify precipitation.

The Homestake uranium mill is located 16 miles from the mine water treatment plant and loaded resin is transported via tank truck to the mill for elution or regeneration. The uranium-bearing eluate is acidified with HCl and heated to destroy carbonate and is neutralized with sodium hydroxide to precipitate the uranium. This product then is combined with normal uranium precipitate from the mill circuit and dried.

# RECOVERY OF URANIUM FROM COPPER WASTE DUMP LEACHING SOLUTIONS

In the United States, copper is obtained primarily from deposits mined by open-pit mining techniques, and in the process of mining very large tonnages of waste material mineralized with small amounts of copper must be moved. This waste rock is piled near the mines and in the the past 15 years copper recovered from these wastes by leaching and cementation has become extremely important. For example, in 1964, 125 000 tons of copper were recovered in this manner from solutions containing an average of perhaps 1.5 g Cu/litre. From this it can be calculated that leaching operations were conducted on a scale involving the recovery of copper from 60 million gal/d, or 40 000 gal/min. The production of copper in this manner is even larger today, and within a few years probably will exceed 200 000 t/yr.

In 1965, the US Bureau of Mines made a survey of the copper leach solutions at 14 large copper mines in the western United States. The survey disclosed that these solutions contain 1 to 12 ppm of $U_3O_8$, with an average of about 4 ppm, but six of the mines, whose solution flow represented half of that sampled in the survey, had an average grade of 10 ppm $U_3O_8$. This is equivalent to 1600 lb $U_3O_8$/d, and with the completion of expanded leaching operations in the next few years, perhaps as much as 6000 lb $U_3O_8$/d may be available from this source.

Laboratory investigations of uranium recovery have involved both solvent extraction and ion exchange resin techniques on solutions obtained from one of the major copper mining companies. The composition of the solutions used was essentially as shown in Table I.

TABLE I. COPPER LEACH SOLUTION ANALYSIS (g/litre)

| $U_3O_8$ | Cu | $Fe^{++}$ | $Fe^{+++}$ | Al | Mg | $SO_4$ |
|---|---|---|---|---|---|---|
| 0.01 | 0.01 | 7 | 0.3 | 6.5 | 8 | 70 |

## Solvent extraction investigations

Laboratory studies were made to investigate the recovery of uranium from copper leach solutions by solvent extraction. Two classes of extractants were evaluated: (1) A straight chain tertiary amine (tricaprylyl amine); and (2) a quaternary ammonium compound (tricaprylyl methyl ammonium chloride). Both of these extractants are produced commercially in the United States and are used for recovery of uranium and vanadium from sulphuric acid solutions. It is common practice to employ these extractants as 3 to 5% solutions with 3 to 5% of a long chain alcohol in kerosine, but to minimize entrainment losses the mixed solvents were made up with 2% amine, 1% isodecanol, and 97% kerosine. The capacity of this solvent would be about 2 g $U_3O_8$/litre when processing uranium-bearing solutions produced by acid leaching typical domestic uranium ores.

The only variable in solution composition over which control could be exercised is the pH. Typically, this varies from about 3.5 after copper cementation to 2.0 after acidification before recycling of the copper barren solution to the leaching dumps. However, on the assumption that only a portion of the total solution flow would be processed for uranium recovery, acidification to an even lower pH would be possible if this solution after uranium removal were combined with unacidified solution. The effect of pH, therefore, was studied over the range 1.5 to 3.5. This was done by equilibrating a volume of the solvent with 20 volumes of aqueous solution. The results are presented graphically in Fig.1 and show that the quaternary amine works better in the pH range 2.3 to 3.5, whereas the tertiary amine is more effective at lower pH values.

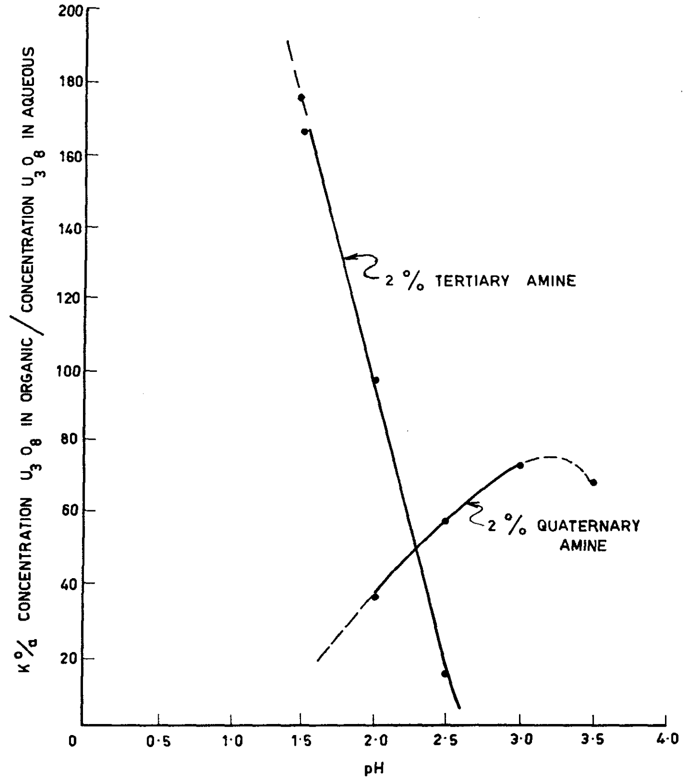

FIG. 1. Effect of pH on extraction of uranium with tertiary and quaternary amines.

On the basis of these preliminary tests, extraction isotherms were determined for the quaternary amine at pH 3.5 and for the tertiary amine at pH 1.5, and these data together with McCabe-Thiele plots are presented in Figs 2 and 3. Figure 2 shows that when loading the quaternary amine to only 0.3 g $U_3O_8$/litre, five extraction stages are required to achieve 95% extraction. Figure 3 shows that the tertiary amine can be loaded to 0.5 g $U_3O_8$/litre while achieving 95% extraction in three stages.

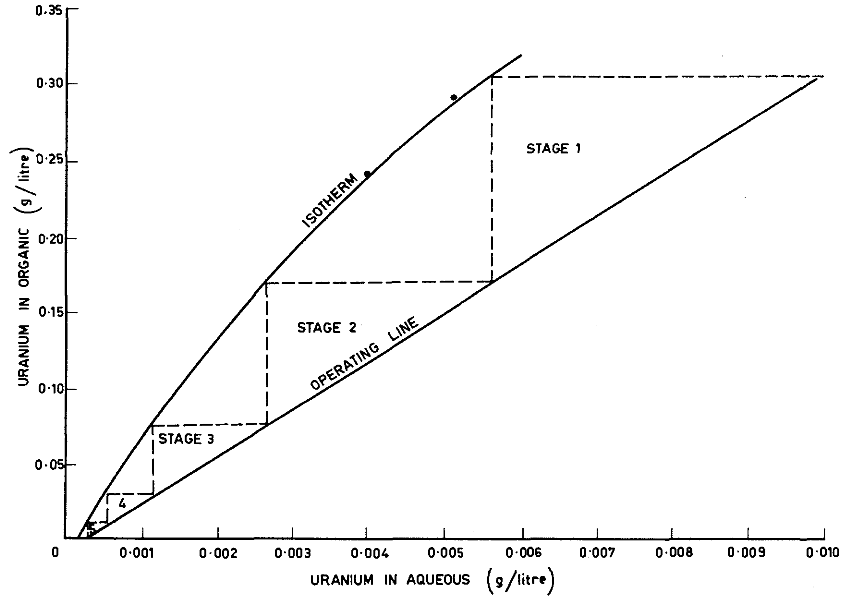

FIG. 2. Distribution isotherm showing extraction of uranium from copper leach solution with 2% quaternary amine and application of the McCabe-Thiele diagram.

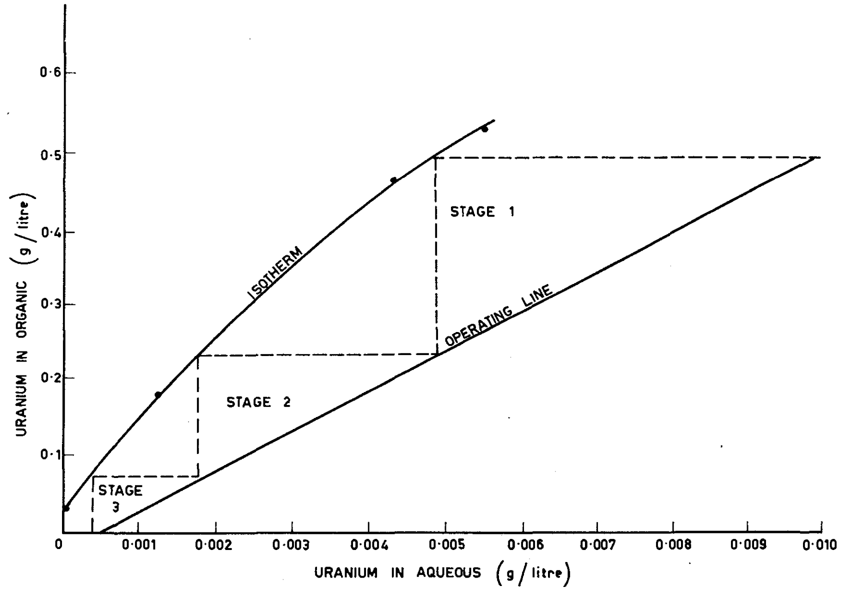

FIG. 3. Distribution isotherm showing extraction of uranium from copper leach solution with 2% tertiary amine and application of the McCabe-Thiele diagram.

On the basis of these preliminary tests, a small solvent extraction circuit, composed of three interconnected mixers and settlers, was assembled for continuous testing with the tertiary amine. The test conditions were pH 1.5; aqueous flow, 110 ml/min; organic flow, 2.45 ml/min; total equivalent flow, 1 gal $ft^{-2} min^{-1}$. The operating profile is shown in Fig. 4 and is in excellent agreement with the results predicted from Fig. 3.

Stripping of the loaded solvent from the continuous extraction was studied in batch stripping tests using sulphate, chloride, and nitrate solutions. Although nitrate and chloride solutions are more effective, sulphate solutions are preferred because these do not introduce extraneous ions into the copper leaching system. The tertiary amine could not be stripped with strong sulphuric acid but was readily stripped with a 1-molar sodium or ammonium sulphate solution at pH 4.5, from which a specification-grade concentrate was obtained by simple neutralization.

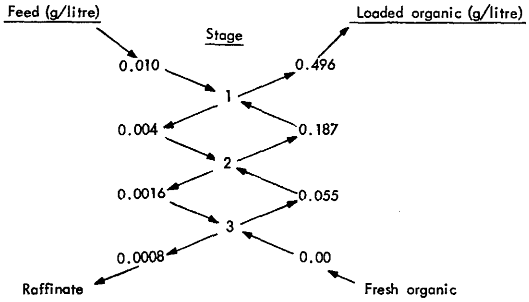

FIG. 4. Summary of continuous solvent extraction tests showing extraction of uranium from copper leach solution with 2% tertiary amine.

Although the solvent extraction investigations demonstrated that it is technically feasible to recover uranium from these low-grade solutions, economic evaluations indicate that the use of ion exchange resin techniques would be more economic. This is primarily because solvent losses alone probably would amount to \$1.08-1.26/lb $U_3O_8$.

## Ion exchange investigations

In recovering uranium by ion exchange resin techniques from copper-waste dump leach solutions containing very small concentrations of uranium, the cost of equipment and resin would account for a major portion of the operating costs. Therefore, the ion exchange investigations were directed primarily at the development of an ion exchange system that will minimize these costs.

It was initially assumed that columns patterned after those employed to recover uranium from mine waters in the Grants, New Mexico, area could be used, but preliminary laboratory tests showed that sorption of uranium from these solutions was very unfavourable and that flow rates in excess of 5 gal/min per square foot of resin bed area in this type of column were not practical. Consequently, an improved method of contacting resins and solutions at high flow rates was sought.

In an ion exchange column operating with solution upflow, the resin bed is expanded, and the volume of resin contained in a column varies inversely with the solution flow rate. In addition, because of the expansion of the resin, vertical mixing of resin occurs within the column. This mixing which becomes more pronounced as the solution flow rate rises, combines with the decreased resin inventory to impair the capacity and efficiency at high flow rates. However, testing established that if a column is baffled or otherwise constructed to limit vertical mixing of the resin, the efficiency and capacity are considerably improved. Further improvements in operation were obtained by periodically withdrawing loaded or partly loaded resin from the bottom of the column and adding fresh resin at the top, thereby achieving a countercurrent movement of solution and resin. Accordingly, laboratory columns 0.5 in. in diameter by 8 ft high and 2 in. in diameter by 18 ft high, and operating on these principles, were constructed and tested. Details of the design of the arrangement to limit axial mixing of the resin cannot be disclosed at this time because patents on the design are being sought. The Government's purpose in obtaining patent protection is to ensure that all who are interested in utilizing a column of this type can do so without paying royalties.

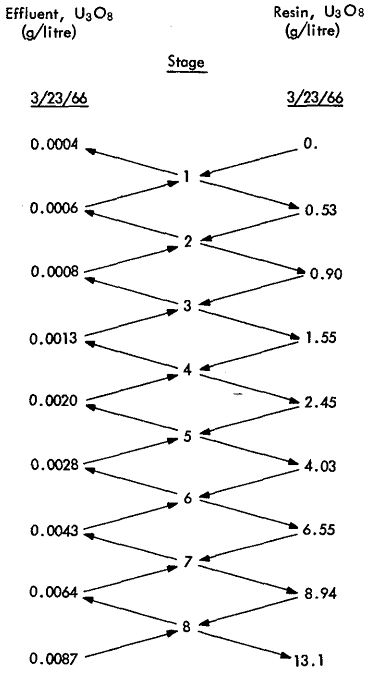

FIG. 5. Uranium profiles from 2-in. countercurrent ion exchange column tests.

Figure 5 shows an operating profile for an eight-stage, 2-in. diameter by 18-ft high column. These data were obtained when operating at a flow rate of 10 gal/min, per square foot of resin bed area at resin loadings of 13.1 g $U_3O_8$/litre. This is 82% of the maximum loading obtainable with this solution. The resin inventory in the column was 5 litres, and during operation 133 ml of fresh resin were added at the top of the column and 133 ml of loaded resin withdrawn at the bottom at 4-h intervals. Under these conditions at least 97% of the uranium was recovered. This compares with a resin loading of only 9.6 g $U_3O_8$/litre of resin, or 60% of the maximum possible loading, and a recovery of 95% when operating an unbaffled column at only 5 gal/min per square foot of resin bed area.

Because of the success experienced with the 2-in-diameter column, a 14-in. diameter by 32-ft high, eight-section column is being constructed and will be tested at a copper mine during this summer. Prototype sections of this larger column have been tested and shown to be more efficient than the smaller diameter column. This is attributed to a reduction in wall effect, which decreases the bed expansion and allows use of more resin in proportion to the solution flow rate.

These new ion exchange resin contactors have also proven to be exceptionally efficient when used to recover uranium from solutions or slurries derived by acid leaching uranium ores. When in the future uranium must be produced from low-grade ores, these significantly more efficient ion exchange contactors may bring about important savings in plant construction and operating costs.

# SUMMARIES OF DISCUSSIONS AND RECOMMENDATIONS

# REPORT OF THE CHAIRMAN

A.P. ZEFIROV

The first panel to be convened on the processing of low-grade uranium ores was very timely, as is proved by the great interest shown by many States Members of the IAEA. The discussions were conducted on a high scientific and technical level and leading experts in this field were represented. Twenty-two representatives from fifteen countries took part in the work of the Panel.

All participants in the Panel reported on the state of affairs in their own country in the field of scientific research, experimental work and industrial practice in the processing of low-grade uranium ores. At the same time, the speakers suggested further promising lines of research and also noted the most pressing problems connected with the introduction of low-grade and marginal uranium ores into industrial practice by using more economic methods of processing.

Apart from the general reports, twelve technical reports were heard and discussed, in which attention was mainly concentrated on questions relating to the most effective processing techniques for various types of refractory and complex uranium ores. The exchange of information showed that in most countries engaged in research a high scientific level has been attained and modern engineering and technical facilities are employed.

On the basis of its general analysis the Panel considered it possible not only to give an account of the work being carried out, but also to make recommendations and select the most pressing problems for the immediate future.

In the course of the discussions the participants discussed from all angles the results that had been obtained in industrial practice and scientific research in regard to the various technological processes. The Panel also emphasized that a study of the nature of the raw material is of special importance since the technological methods to be employed may depend on its mineralogical composition.

Uranium ores are divided into various types, depending on their composition. In this connection the panel considers it desirable to evaluate them from the technical and economic points of view, depending on the nature of the mineralization and consequently the type of ore being dealt with.

The Panel drew attention to the necessity of further developing the most economic methods of preconcentration, in particular of crushing and grinding. Such technical improvements as the running together of all the stages of crushing into one stage, grinding other than in ball-mills, etc. have made possible considerable economies in many countries.

Preconcentration is of very great and sometimes even crucial importance in the processing of low-grade and marginal ores, especially when they contain various different useful minerals. In most countries a great deal of very interesting scientific research has recently been carried out on this problem. Many different concentration techniques are already employed in industrial practice and have a considerable effect on the economics of uranium production.

In the processing of low-grade and marginal uranium ores the processes of radiometric sorting play an exceptionally important part since they permit the separation of a considerable quantity of gangue and yield a richer product for subsequent concentration and hydrometallurgical processes.

Radiometric sorting is a new process worked out by the scientists of various countries in connection with research into problems of uranium ore processing. It has become widespread at present and is successfully employed in four countries. Radiometric sorting is a very effective and important method of beneficiating low-grade uranium ores. Being a new process, it offers considerable possibilities of further improvement and development, both as to the process itself and as to the design of the radiometric apparatus. Depending on the composition of the ore and other factors, radiometric concentration is used either as the only concentration process, or in combination with other such processes.

In the Panel's view, scientists and engineers alike should devote special attention to further study of this very promising process.

Gravity concentration has been employed in the processing of low-grade uranium ores mainly to separate the ore into various fractions of different mineral composition, which are then separately processed by hydrometallurgical methods. New types of equipment for gravity separation are now in widespread use: they include hydrocyclones, centrifuges, jigging machines and other apparatus.

Unfortunately, of the basic preconcentration processes flotation has not yet proved effective as a means of concentrating uranium minerals as such. The work done in this respect has not yet borne fruit and this process is at present used only as an auxiliary technique. However, many practical examples point to the usefulness of flotation for other purposes, such as the separation of ores or radiometric and gravitational concentrates into different mineralogical fractions – sulphide, carbonate and silicate. The resulting economy in the use of chemicals and other materials in this case more than repays the expenditure in arranging for separate hydrometallurgical treatment of the flotation products.

The Panel considered it important to carry out further fundamental research on the flotation of uranium minerals and to study the possibility of employing this technique with a view to the more economic processing of low-grade uranium ores.

Thus from its discussion of the processing of low-grade uranium ores the Panel concluded that work on the study and introduction of concentration processes should be continued, and recommends that every effort should be made to develop research in the following fields: study of the mineralogical composition of low-grade ores and their industrial classification; further improvement of the preconcentration processes, in particular crushing, grinding and the disintegration of clay materials; and further study and development of the techniques of radiometric sorting and gravity and flotation concentration.

The Panel considers it would be extremely useful to organize, as soon as possible, a meeting of scientists and specialists in radiometric sorting to discuss progress in the various countries and future plans in this field.

The Panel notes that leaching is the basic operation in the processing of uranium ores and has a considerable influence on the technological and economic aspects of the whole process of uranium extraction.

The choice of a leaching method is determined by the composition of the ore. Acid leaching is the commonest at present since it is the most economic and gives a high extraction of uranium. Alkaline leaching is employed only for high-carbonate ores since it is usually dearer and gives a slightly lower extraction of uranium. The process of alkaline leaching has become commoner recently due to refinements in the process.

A basic improvement in acid leaching was the working out of the process of selective leaching of uranium from low-grade ores at controlled values of pH and oxidation-reduction potential without heating of the pulp or with only slight heating. This gives a sufficiently high extraction of uranium and low consumption of reagents, and solutions free from impurities are obtained, improving the performance of the subsequent processes of sorption and extraction. The effectiveness of leaching at the high acidity and temperature levels used for refractory ores is being increased thanks to more economic use of reagents and wide use of automatic control for maintaining the optimum parameters for the process.

The cost of acid is often a decisive economic factor in acid leaching. It can be reduced by the production of acid in situ and also by producing it directly in the leaching process (autoclave leaching, heap leaching, bacterial leaching).

A series of methods of reducing the cost of carbonate leaching processes has been suggested: the use of oxygen in pachuca and autoclave leaching, flotation of reagent-consuming minerals and the introduction of additional heat utilization equipment. For further improvement of the processes, fundamental research must be carried out on the solubility of uranium and gangue minerals in alkaline and acid solutions.

The reports read testify to the increased interest in the processing of low-grade ores and products from preconcentration of ore by the employment of special methods. Ores can be processed by the heap and percolation leaching methods, using solutions of sulphuric acid or sodium carbonate. In heap leaching favourable conditions for bacterial leaching may be established.

The leaching of broken ore, below cut-off grade, in underground stopes, and also the leaching of permeable deposits, presents great interest. Such deposits are leached in situ by the introduction of the solution to the bed under pressure, and the uranium-bearing solution is pumped out through specially drilled holes. Distribution of information regarding these methods and further development of research work will allow more economic processing of low-grade ores.

Many low-grade ores at present being considered as possible sources of uranium (shales, phosphates, lignites etc.) contain constituents of possible commercial value. Some of these ores can only be treated on the basis of the recovery of two or more products; by-product operations are therefore of considerable importance and should receive attention in the development of further research programmes.

Development and introduction of sorption and extraction methods for recovery of uranium from solutions and pulps has made possible basic improvements in uranium ore processing technology.

The ion-exchange method for the recovery of uranium from clear solutions and dilute ore pulps has been developed to a high degree of efficiency. Further research should be carried out on ion-exchange recovery of uranium from dense pulps and special attention should be devoted to the development of resins with high physical and sorption properties and also of resins which can selectively extract the valuable constituents accompanying the uranium.

The methods of uranium recovery by a solvent from clear solutions have been brought to a fairly high level of development, and these methods have been used commercially for several years. Although in certain countries equipment for solvent-in-pulp extraction has been developed, further work is necessary before this method can be applied commercially.

For the extraction of the valuable constituents accompanying the uranium, solvents with heightened selectivity properties for various elements must be developed.

It is also important to develop more physically stable solvents, in particular to improve the economics of recovery of uranium from phosphates – a large potential source of uranium production.

The Panel made a number of recommendations in addition to those outlined above. Full details of these are given in the following summary of discussions.

# SUMMARY OF DISCUSSIONS AND RECOMMENDATIONS

## PRECONCENTRATION

In summarizing the information presented to the Panel on preconcentration of low-grade ores, it is necessary to point out that preconcentration techniques depend to a large extent on the nature of the mineralization concerned. The Panel therefore expressed the view that it would be worthwhile for the Agency to collect and disseminate information on the relative importance of the different ore types for which various preconcentration techniques have proved successful. Appropriate subdivisions would include lignite and other organic-rich ores, sandstone ores, hydrothermal ores, placer ores, refractory ores, pegmatitic ores, etc.

Having regard, then, to the need for more data on the types of resources available throughout the world, the Panel made the following comments and recommendations regarding various possible methods of preconcentration.

Crushing and grinding should always be given careful attention, particularly where it is proposed to either discard, or leach without further treatment, the whole of one or more of the size fractions produced. Crushing and grinding are most important where radiometric sorting or gravity separation are used because of the limitations on the particle sizes which may be treated by these methods. Initial comminution is also critical where it is proposed to carry out heap leaching. Further, certain low-grade sandstone ores in which the uranium occurs only in the inter-granular material may be upgraded successfully by a 'scuffing' type grinding operation followed by sand-slime separation, the sand fraction being discarded.

Although gravity separation has not been found widely applicable to date in the treatment of uranium ores, heavy medium separation has been used in several countries for particular ores. Gravity methods show promise in certain applications, amongst which might be mentioned particularly, treatment of pegmatite-type minerals.

Recent developments in the use of hydrocyclones and centrifuges for ore dressing are promising and should be pursued, with particular emphasis on their use for concentrating low-grade uranium ores.

Magnetic separation has not to date proved of use in the treatment of uranium ores, but the possibility of using it for selected ores in the future should not be overlooked.

Flotation has been used successfully in a number of countries to separate the ore into carbonate-rich and silica-rich fractions for separate treatment by alkaline and acid leaching. Flotation has also been successfully employed to remove the sulphides so as to reduce reagent consumption, particularly during alkaline leaching, and to recover by-product metals. Flotation is thus recommended as a possible treatment method in all cases where the characteristics of the gangue minerals create difficulties in subsequent dissolution operations. The Agency should collect and disseminate information on advances in flotation practices as applied to uranium-bearing ores.

Radiometric sorting is a very useful and important method for preconcentration of uranium ores. It has been used successfully in four countries, but further development of the method would appear possible. The Agency is seen as having an important role to play in this further development, perhaps by the organization of a study-group type meeting of specialists in the field. It is considered important that the radiometric method be given close attention in relation to processing of ores in the lower grade ranges.

Roasting is a preconcentration method which is well-known, but not usually applicable to uranium ores except those containing a significant proportion of volatile constituents or clay materials.

### Recommendation

The Agency should

(a) Collect and disseminate information on preconcentration of low-grade uranium ores, particularly in respect to

(i) relative importance of different ore types for which various processing techniques have proved successful;
(ii) gravity separation methods;
(iii) flotation methods;
(iv) radiometric sorting; and
(v) methods applicable for separation of organic and clay materials from ores.

(b) Consider the organization of a study-group type meeting to discuss developments in radiometric sorting if this is recommended by the Standing Committee which is proposed in the general recommendations of the Panel.

## SOLUBILIZATION OF URANIUM FROM ORES

Leaching of low-grade ores, waste dumps and products from preconcentration of ore by spraying and percolation is being widely used in many countries; fresh or recirculated water with or without special attention to conditions favourable for bacterial leaching is being employed. In other cases, the ore piles are sprayed with weak sulphuric acid or solutions of sodium carbonate. Bacterial leaching in the presence of sulphide minerals appears to be very promising. Underground leaching of uranium minerals is expected to be economically advantageous because of the elimination of many steps that occur in conventional treatment processes.

Leaching of broken ore, below cut-off grade, in specially prepared underground stopes and leaching of permeable deposits in situ by introduction of the leach solutions under pressure and collection of the pregnant solutions through suitably placed drill holes are being rapidly developed.

Distribution of information regarding these methods and further development work should be encouraged, as lower grade ores can be treated and marginal methods of preconcentration can become economical.

Conventional sulphuric acid leaching at controlled pH, or more intense leaching in stronger acid for dissolution of Brannerite and similar minerals, has become more efficient through more economical use of reagents and heat and better equipment; also by increased use of automatic control to maintain optimum process conditions.

The cost of acid — a major constituent of processing costs — can be reduced by production in situ; for instance, by autoclave leaching of sulphide ores, by formation of acid sulphides by heap leaching, or bacterial action. Acid can also be produced efficiently by auto-oxidation of $SO_2$.

Alkaline leaching has been advanced by means of such cost-saving features as: the use of oxygen in pachuca leaching; steam stripping; flotation of reagent consuming minerals; and additional heat-saving equipment. Likewise, pressure leaching techniques have been developed to improve the efficiency, especially for more refractory ores.

Nevertheless, more fundamental research work is required on the mechanism of uranium solubilization and on the solution of gangue minerals in sodium carbonate and acid systems. Acid cure leaching has been shown to be, in some cases, the best method for treatment of very slimey ores, particularly those containing clay minerals which strongly absorb uranium.

The research and development work on new economical processes for recovery of uranium from shales, clays, lignites and phosphates should be augmented because of the extensive reserves of these materials in many countries.

Uranium recovery by ion exchange resin during the actual leaching stage is an interesting development, which warrants further work. Acid leaching during autogenous milling has shown promise in large-scale tests and is of interest for refractory ore treatment.

The attack of uranium ores by chlorination procedures has been mentioned briefly during the discussion. The ability of halogens to attack uranium minerals and the properties of uranium halides suggest that the halogen processes should receive more attention in the future, particularly as regards regeneration of reagents.

Uranium is sometimes present in solutions obtained by processing for extraction of other elements. The possibility that leaching conditions for recovery of other elements may be modified to increase extraction of uranium should not be overlooked.

The necessity of controlling radiological as well as chemical contaminants in the effluent from uranium leaching plants was also mentioned during the discussions.

### Recommendation

The Panel recommends that the Agency

(a) Keep the extraction metallurgy of uranium under constant review to take into account theoretical and technological developments;

(b) Promote the exchange and spread of information, particularly on bacterial, underground and other promising methods of leaching; and

(c) Support fundamental research in solubilization of uranium from ores and award research contracts to appropriate laboratories.

## RECOVERY OF URANIUM FROM SOLUTIONS AND SLURRIES

Ion exchange methods for recovering uranium from clear solutions, and from dilute ore pulps, have been developed to a high degree of efficiency. While some further improvements may be possible, the scope for such improvements is limited. However, the Panel considered that further work on ion exchange recovery at high pulp density should be undertaken, with particular emphasis on the development of resins with better physical and sorption properties.

While solvent extraction from clear solutions has been highly developed and has been in commercial use for a number of years, one troublesome feature of the process is the high toxicity of the effluents from such plants. The presence of amine type solvents in these effluents, even in trace quantities, is undesirable and efforts should be made to develop methods for removal of these materials from the waste solutions, or for treating them to eliminate their objectionable characteristics.

Although equipment for solvent-in-pulp extraction has been under development in several countries, further work is needed before the process can be applied on a commercial scale. Panel members felt that the Agency should encourage exchange of information on the most promising solvent-in-pulp methods.

The development of improved solvents with more selectivity for various elements is important. In particular, to improve the economics of recovery of uranium from phosphates — a large potential source of production — a more physically stable solvent should be developed.

Production of nuclear-pure products in uranium-ore processing plants is becoming increasingly important, mainly because of the resultant saving in production costs. The Panel members felt that the Agency should encourage the exchange of information and experience in this area and that it should consider establishing chemical and physical standards for various refined uranium products.

Promising sources of significant uranium production are mine waters and leached waste-dump solutions with very low concentration of uranium. Suitable extraction methods for recovery of uranium from such sources are currently being investigated. The Panel considered this area worthy of further effort.

The precipitation of uranium from carbonate solutions is receiving attention and some fundamental work in this field would seem well worthwhile. Precipitation of uranium from mine waters with lime, as practised in one country, would appear a useful method where a suitable ion exchange plant does not exist. However, it was felt that the method could well benefit from further work on several technical aspects, including work on the problem of flocculents.

Many low-grade ores at present being examined as possible sources of uranium contain other constituents of possible commercial value. In fact, some of these sources may be practical to treat only on the basis of the recovery of two or more products. By-product operations are, therefore, of considerable importance and should receive careful attention in the development of further research programmes.

## Recommendations

The Agency should closely follow progress in various aspects of uranium ore processing and stimulate efforts in this field by: setting up a system for accumulation and dissemination of information; awarding research contracts; holding special meetings; etc.

Special emphasis should be given to ion exchange recovery at high pulp density; solvent-in-pulp extraction; recovery of uranium from phosphates, shales, clays and lignites; recovery of uranium and other valuable constituents from polymetallic ores; and the instrumentation and automation of uranium extraction metallurgy processes.

The Agency should consider the question of specification standards for nuclear-grade uranium products.

## GENERAL RECOMMENDATIONS OF THE PANEL

The Panel recommends that the Agency encourage a continuing exchange of information among its Member States on the subject of the extraction metallurgy of uranium in general and on methods of treating low-grade ores in particular; and that the Agency should encourage research in the extraction metallurgy of uranium as a means of ensuring that supplies of uranium at reasonable cost will always be available to support expanding nuclear power programmes.

As a means of achieving the objectives stated above, the Panel recommends that a Standing Committee composed of experts from Member States and Agency staff be appointed to advise and assist the Agency with respect to:

1. A review of world uranium resources concerning type, grade and amount which might be carried out in co-operation with other international organizations active in this field such as ENEA. To collect and disseminate information on the relative importance of the different ore types for which appropriate methods of treatment have proved successful.
2. Collecting and disseminating information on specification standards for uranium products with a view to the particular application or process in which the product is to be used, or the limitations of the manufacturing process employed.
3. A periodical review of progress in uranium ore processing technology to be followed by a suggestion for possible international collaboration in research and development.
4. The setting up of a system to accumulate and disseminate through the Agency available information concerning processing of uranium ores.
5. The promotion of fundamental research relating to specific aspects of the extraction metallurgy of uranium.
6. The arrangement of exchange visits among Member States of scientists and engineers.
7. The arranging at appropriate times of conferences, symposia, panel meetings and study groups to consider and discuss various aspects of the extraction metallurgy of uranium.

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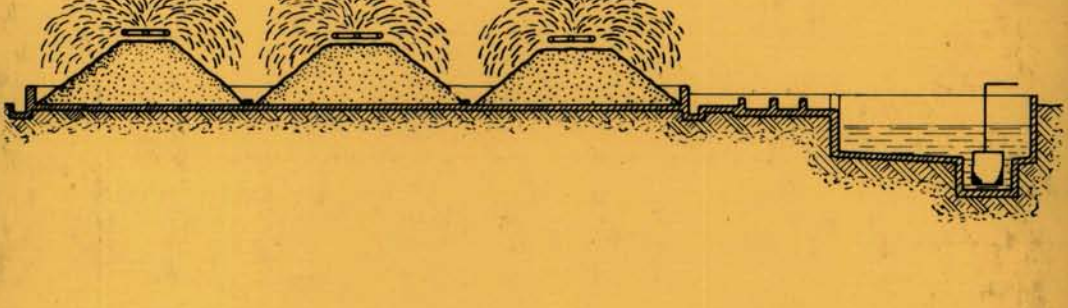

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