ADVANCES IN URANIUM ORE PROCESSING AND RECOVERY FROM NON-CONVENTIONAL RESOURCES

PROCEEDINGS OF A TECHNICAL COMMITTEE MEETING
VIENNA, 26–29 SEPTEMBER 1983

INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1985

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FOREWORD

With the development of nuclear power, uranium has become established as an important source of energy which augments and diversifies the world's energy resources. Nuclear power has reached a stage of maturity and reliability and currently accounts for about 12% of the world's total electricity generation. Although the uranium industry is at the present time constrained by oversupply and depressed prices, this situation is not expected to continue indefinitely. Installed nuclear power generating capacity continues to increase and there need be no doubt about the long-term importance of uranium ore processing.

The technology of uranium extraction has also developed to an advanced state, compared with the early years of the industry in the 1940s and 1950s. Nonetheless, there continue to be further advances and refinements. These seek to improve uranium recovery, to reduce costs, to produce uranium concentrates of higher quality and to improve the nature of the tailings for their long-term disposal. At the same time, much effort is being directed to improving the economics of the recovery of uranium from phosphoric acid, which at the present time is only marginally competitive, and to develop processes for the recovery of uranium from non-conventional resources such as coal and natural waters, including seawater. These last processes, although technically feasible, will not be economically attractive for many years but are potentially important because they may allow access to vast uranium resources.

The Technical Committee Meeting on Advances in Uranium Ore Processing and Recovery From Non-conventional Resources was convened by the Agency within the framework of its continuing activities on nuclear raw materials. The meeting was held in Vienna from 26 to 29 September 1983. A total of 64 participants from 29 countries took part and 27 papers were presented. The present volume includes 18 of these papers.

The main topics covered by the technical sessions were: in situ and heap leaching, improvements in conventional acid and alkaline uranium ore processing, recovery of uranium from wet-process phosphoric acid and recovery of uranium from coal and from natural waters. The technical sessions concluded with three panel discussions dealing with pre-concentration and beneficiation, in situ and heap leaching, and recovery of uranium from wet-process phosphoric acid. The substance of these panels is also reproduced in this volume.

The Agency wishes to thank all the scientists and engineers who participated in the meeting, not only for the papers but also for the contributions to the discussions. Special thanks are due to the General Chairman, W.A. Gow (Canada) and to the Panel Chairmen, Z.M. Dogan (Turkey), W. Flöter (Federal Republic of Germany) and D. Naden (United Kingdom).

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REVIEW PAPER

RECENT ADVANCES IN URANIUM ORE PROCESSING

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Abstract

RECENT ADVANCES IN URANIUM ORE PROCESSING.

The paper reviews the major technological improvements in uranium ore processing in recent years. Semi-autogenous grinding, where applicable, has proven to be a significant innovation that has resulted in lower capital and operating costs. On the other hand, its successful application depends on careful and extensive predesign testing and on keeping mill feed variability to a minimum. Preconcentration of ores has been successful only in a few instances. Radiometric sorting is being used in the treatment of low-grade ores in South Africa and of ore from a vein-type deposit in the United States of America. Gravity concentration with Reichert Cones is being used in South Africa. There have been innovations in leaching techniques for very high-grade and very low-grade ores. Pressure leaching has been used in treating ores with a uranium content in the range of 0.5 to 2.5% and ores containing refractory uranium minerals. In situ, in place and heap leaching techniques have found favour in the treatment of very low-grade porous or fissured ores. Uranium plants have been turning to high-capacity thickeners and horizontal belt filters in an effort to improve the efficiency of solid-liquid separation and to reduce capital and operating costs. However, high-capacity thickeners require very close control and operate at lower underflow pulp density which results in increased losses of soluble uranium. There is still controversy over the relative advantages and disadvantages of belt filters. Ion exchange and solvent extraction processes have received much attention, probably more than any other unit operation in uranium ore processing. Continuous ion exchange (CIX), in its various forms, is the most recent innovation in ion exchange technology. The column systems that have been installed in recent years are the Himsley Column, the USBM-MCIX Column and the Cloete-Streat Column with its variants, the NIMCIX Column and the Davy Power Gas System. Two other systems that have been used are the Porter IX, with adsorption in a series of tanks, and the CHEM-SEPS in which loading, elution, scrubbing and backwashing are done in separate compartments connected through sequentially operated valves. New developments in the design of mixer-settlers for solvent extraction have been directed to reducing the shear in mixers and to reduce the area required for phase separation in order to reduce the size of the plant and the solvent inventory. Regarding precipitation, there has been a move from the use of ammonia and nitrates to strong sulphuric acid elution and stripping to reduce environmental problems. The technology for recovering uranium from wet-process phosphoric acid and from copper heap-leaching solutions continues to be improved. Research is also being done on the recovery of uranium from seawater and from coal, although suitable technology may not be available for several decades.

1. INTRODUCTION

Current practices for extracting uranium from ores are well documented, particularly in the OECD publication Uranium Extraction Technology [1]. To those of us in the mineral processing business it comes as no surprise to learn from this document that process selection and development for the treatment of uranium-bearing ores have been based on the uranium content, the mineralogical composition [2] and occurrence of the feed material, and the current state-of-the-art. These considerations are paramount for every step of the process and affect the chemistry involved, the specific technology applied, the equipment selection and the standards for economic evaluation. The choices between autogenous and conventional comminution, acid and alkaline leaching, solvent extraction and ion exchange are all dictated by the mineralogical and petrographic occurrence. Lower recoveries may be tolerated from low-grade ore than from high-grade ore and consequently attention will be directed to less efficient operations such as heap leaching. Where values other than uranium are present, the mineralogical composition and occurrence will be a factor in dictating the sequence in which the values are recovered.

The purpose of this paper is to serve as an introduction to the more detailed papers to follow on the general theme of advanced technologies in uranium ore processing, and recovery from non-conventional sources. In view of the above remarks, it is apparent that a problem arises as to the definition of an 'unconventional source'. Because of the variety of ways in which uranium occurs in nature, who is to draw the line between a 'conventional' and an 'unconventional'source? To that Canadian processor, the high-grade deposits recently discovered in Saskatchewan containing 2-3% uranium along with nickel sulphide and arsenide minerals are unconventional when compared with the low-grade conglomerates of Elliot Lake with which we Canadians have been familiar for 25 years. This is but one of many examples that could be cited.

Consequently, faced with this dilemma, it was decided to describe briefly the known sources to uranium, relate those sources to the processing strategies applied to them and then leave it to the reader to differentiate between the familiar and the mysterious.

2. URANIUM OCCURRENCE

Data published jointly in 1980 by the OECD and the IAEA [2] reported the world's reasonably assured resources of uranium, recoverable at US $ 130/kg U, to be 2 293 000 tonnes of U, with another two and three quarter million tonnes estimated. The proportion of these resources in the major types of deposits identified is given in Table I.

Detailed descriptions of these deposit types have been given in previous publications. In this paper only the characteristics that have major significance in today's processing state-of-the-art will be mentioned.

TABLE I. PROPORTION OF URANIUM RESOURCES IN THE MAJOR TYPES OF DEPOSIT

Deposit type	(%)
Sandstone	39
Quartz-pebble Conglomerate	17
Proterozoic Unconformity Related	15
Disseminated	14
Vein	7
Other	8

Sandstone deposits contain from 0.05 to 0.3% U_3O_8 as uraninite, pitchblende and coffinite in unoxidized deposits, and carnotite, tyuyamunite and uranophane in oxidized ores. The uranium occurs in the grain-binding material. These deposits can contain up to 5% calcite and minor amounts of sulphides.

Quartz-pebble conglomerates contain from 0.01 to 0.15% U_3O_8 as pitchblende, uraninite, brannerite and urarothorite. The presence of pyrite in concentrations of up to 5% is common, while gold is present in the South African deposits. Although mineralization occurs mainly in the cementing material, some values are present in the pebbles. Acid-consuming materials are not a serious problem occurring as sericite and chlorite.

The Proterozoic Unconformity-Related deposits are large and rich containing up to 2.5% U_3O_8, mainly as pitchblende and uraninite, in deposits containing up to 200 000 tonnes of uranium. The uranium minerals occur both in disseminated and massive form. These deposits may also contain arsenides and sulphides of nickel and other metals as well as gold. Although these deposits have been known to contain high percentages of carbonate, this is the exception rather than the rule.

Disseminated deposits are those associated with syenites, pegmatites, granites and the like. They contain from 0.05 to 0.15% U_3O_8 and exhibit a wide range of mineralogical characteristics. Some deposits such as the pegmatites of Canada and Namibia are easily treated by conventional acid leaching of the contained uraninite/uranothorite, while other deposits are highly refractory to economic processing methods.

Vein deposits are those in which the uranium minerals fill the cavities of host rocks. Pitchblende and uraninite are the most common minerals present, occurring as massive chunks as well as disseminations in the adjacent host rock. The uranium contents of these deposits vary from 0.1 to 2.5%, while in some deposits a range of sulphides and arsenides are present.

In addition to these five major types of uranium deposits, there are a number of low-grade sources that do not fit into this general scheme. These include uraniferous shales and lignites, phosphates, calcretes, porous limestone with the uranium occurring as thin carnotite coatings in the voids and limestone. These vary from less than 0.01% to as high as 0.1% U_3O_8.

3. URANIUM ORE PROCESSING

3.1. Crushing and grinding

Over the years since uranium was first mined the process used for comminution has moved from the classic approach of primary, secondary and possibly tertiary crushing in jaw, gyratory and cone crushers, followed by closed-circuit grinding in rod and ball mills, through a number of processing modifications aimed at reducing costs. In recent years the most interesting innovation has been the use of semi-autogenous grinding in a number of uranium processing operations [1]. The original installations were completely autogenous in that run-of-mine ore was charged directly to a wet grinding mill with a diameter to length ratio of about 3:1. The large pieces of ore would reduce smaller pieces to the desired grind and in turn be reduced through abrasion and impact. It was soon found that the addition of 15 cm diameter steel balls to comprise about 5% of the charge improved grinding efficiency, and the operation became known as semi-autogenous grinding or SAG.

Sandstone-type deposits are particularly suited to SAG because the uranium occurs only in the grain-binding material and reduction to grain size is all that is needed to liberate the uranium minerals. The conglomerate ores of Canada are also ground successfully by SAG units but because, in these ores, uranium occurs in the pebbles and breakage occurs across the matrix and pebbles, the whole ore must be ground to less than grain size. Consequently, the discharge from the SAG mill is ground further in conventional ball or pebble mill circuits. Similar SAG plus ball mill circuits are used on unconformity-related ores in Australia, and are planned for these occurrences in Canada.

The use of SAG mills can result in significant savings both in operating and capital costs [3]. The capital savings result from the elimination of one or more crushing stages while operating savings are due to less maintenance costs, and the near elimination of steel grinding media, which results in reduced oxidant and acid costs. On the other hand, the successful application of SAG depends on careful and extensive predesign testing.

The operation must be planned to keep mill feed variability to a minimum and this may require a blending strategy if there is a high degree of ore variability in the deposit such as can be met in vein and unconformity-related ores. If ore variability is excessive, it will be difficult to control the load in the mill and this in turn will allow excessive impact of the steel balls against the liners, which could result in liner failure. The testing must also determine the structural competence of the ore and thus its ability to form suitable grinding media.

The screens and other sizing equipment used in SAG circuits must be designed to handle wood pulp and like substances to avoid clogging and excessive circulating loads.

Generally speaking, where SAG is applicable it has proven to be a significant innovation in uranium ore processing circuits.

3.2. Preconcentration

The possibility of rejecting a portion of a uranium-bearing ore either at coarse sizes ahead of comminution, or at finer sizes ahead of leaching has challenged the ingenuity of uranium metallurgists since the 1950s. The advantages are obvious and include enhancing the feed grade, the elimination of reagent consumers ahead of leaching, and the production of a 'clean' tailing. To meet the challenge electronic ore sorting, gravity and high-intensity magnetic methods and flotation have been investigated. Only in a few instances have they met with success. The lack of acceptance has been due to excessive uranium loss combined with insufficient weight rejection to the tailings.

It should come as no surprise that the most successful preconcentration technology has been radiometric sorting, which of course is based on the ore characteristic specific to uranium. Modern sorters are capable of treating particles ranging from 20 to 160 mm by measuring the radiation and surface area of the particle, estimating its U_3O_8 grade and directing it to the retain or reject stream.

Radiometric sorting is currently used in the treatment of low-grade feeds where the uranium is a byproduct in South Africa, and in treating a vein-type deposit in the USA where the uranium occurs in isolated concentrations and preconcentration is attractive because the mine is 150 km from the leach plant. In South African experience the sorter rejects material ranging from 10–70 ppm U_3O_8 from feeds probably of 120–650 ppm. The American operation rejects material containing 0.015% U from feeds of 0.27% U.

The only other significant physical preconcentration currently in use is at the Palabora operation in South Africa where the tailings from the flotation plant are upgraded using Reichert Cones, shaking tables and magnetic separation to produce a 3.0% U_3O_8 concentrate from feed containing 35 ppm of U_3O_8 with a recovery of about 65%. The operation is feasible only because it is a byproduct to the copper operation.

3.3. Leaching

The mineralogy of the ore probably affects the leaching step more than any other operation in uranium ore processing. The type and concentration of the uranium minerals present, along with the characteristics of the gangue minerals, dictate the conditions to be used in leaching. Consequently, whether acid or alkaline leaching is used, the leaching conditions applied are as variable as the characteristics of the ores being treated. Until recently, however, the variability from one process to another has been in detail rather than in fundamentals.

Recently there has been a basic change in the thinking directed towards the processing of the very high-grade ores in the 0.5 to 2.5% range, and in the very low-grade ores of a few hundred parts per million where the major value is uranium. With high-grade ores it is necessary to think in terms of 99+% uranium extraction instead of 90–95% as is usual with ore containing 0.1–0.2% U_3O_8. Even with ores at the 0.5% U_3O_8 end of the scale, losses of over 5% are economically significant. To obtain these high leach extractions in short leach time, designers have turned to pressure leaching. The Key Lake operation in Canada is an example [4]. In addition to its use on high-grade ores, pressure leaching has been applied in treating ores containing refractory uranium minerals, and for reducing the size and the energy requirements of the leaching plant.

With very low-grade porous or fissured ores, in situ, in place and heap leaching techniques have found favour. In the USA at the start of 1981 some 11 in situ solution mining operations were producing over 2500 t U/a from porous low-grade sandstone deposits [1]. However, for a number of reasons, mostly economic, several of these operations have been discontinued. The technique involves pumping oxidized, alkaline leach liquor down to the sandstone beds no more than 150 metres below the surface. The uranium-bearing solution containing from 30–60 ppm of uranium is recovered by continuous ion exchange techniques.

In place and heap leaching are similar in principle. In both cases the leach solution is percolated down through beds of relatively coarse ore. On leaving the bottom of the beds, the solution is treated by ion exchange for uranium recovery. The main difference in the two processes is that the in place ore is often much coarser than the heap leached material.

The notable recent example of these two approaches is the Agnew Lake mine in Canada [5]. This mine was operated from 1978 to 1983 and was designed to treat two-thirds of the ore, a steeply dipping conglomerate containing about 0.05% U_3O_8, by in place leaching. The remaining third was treated by heap leaching after crushing to minus 20 mm and piled 6 m high on surface. The leaching solution was a sulphuric acid–iron solution oxidized by bacterial action. The in place leaching did not perform as expected, mainly because the individual pieces of ore were too large after blasting and the dip of the ore body was flatter than forecast so that percolation of the leachant was not effective. The surface heap leaching operation performed as predicted by the test programme and resulted in 80% recovery of the contained uranium in two to three years.

The current interest in the use of Caro's acid as an oxidant in the acid leaching of uranium ores is of note [6]. It is said that Caro's acid is effective and results in reduced acid consumption and lime consumption in tailings neutralization operations. It has been used successfully in Australia but the economics in a specific case will depend on the local cost of hydrogen peroxide. Calcine from the roasting or pyrite digested in sulphuric acid is also being used as an oxidant in several South African operations.

3.4. Liquid-solid separation

Traditionally, liquid-solid separation in uranium operations has been accomplished using vacuum drum and disc filters, and thickeners with, in some cases, assistance from cyclones ahead of the thickener. This practice has been no different to that used in hydrometallurgical operations in general. In the recent past uranium plants have been turning to high-capacity thickeners and horizontal belt filters in an effort to improve the efficiency of liquid-solid separation and reduce operating and capital costs.

The high-capacity thickeners result in a very significant reduction in capital cost for a given throughput. They also provide some operating savings in electrical and heat energy. On the other hand, the fast response time in these machines requires very close control, with automatic control being favoured [7]. These thickeners operate at lower underflow pulp density than conventional thickeners and this results in increased soluble losses.

There is still controversy as to the relative advantages and disadvantages of belt filters [8]. These units are more complex than one might expect and should not be contemplated without a thorough study of the available experience. However, there are several belt filter operations in uranium plants about which little has been published. Problems met with are being solved and presumably it will not be long before definitive accounts of their operation will be available.

Clarification of the leach liquor is necessary ahead of fixed-bed ion exchange and solvent extraction operations. Recent technology in Canada, Australia and the USA for this step generally has involved the use of downflow pressure sand filters. Gypsum precipitation has been a problem in these units but anthracite beds have been less prone to this problem than have sand beds. Usually a clarifying thickener of the high-capacity type has been installed ahead of the sand filters. This technology, although popular in recent plants, is still being evaluated [9].

3.5. Uranium recovery and purification

The operations concerned with the purification and upgrading of uranium-bearing leach liquor have always held a special fascination for uranium hydrometallurgists. Consequently, ion exchange and solvent extraction processes have been researched, developed and innovated probably more than any other steps in the uranium ore processing sequence. In a general survey it is possible to mention only the more significant newer developments that are attracting the greatest interest.

The more recent innovations in ion exchange technology are in the field of continuous ion exchange or CIX. The ability of these systems to treat low-grade uranium-bearing solutions without prior clarification has made them an attractive route for the treatment of turbide feedstocks from the leaching of low-grade ores and solution mining as well as in the treatment of mine waters.

Most of the CIX plants are designed around a form of fluidized-bed IX column in which the resin is fluidized by upflowing feed solution. Provision is also made for downflow of the resin and for discharge from the bottom of increments of the loaded resin and its transfer to elution. The detailed descriptions of these units are beyond the scope of this paper but can be found in a number of publications [10–14].

The column systems that have been installed in recent years are the Himsley Column, the USBM-MCIX Column and the Cloete-Streat Column, which has been modified and installed as the NIMCIX Column and the Davey Power Gas System. The NIMCIX or Davey Power Gas versions of the Cloete-Streat Column are used extensively in South Africa in the processing of run-of-mine ore and reclaimed tailings. In Canada the Himsley Column was used to treat low-grade solutions containing 0.1 g/L U_3O_8 from in place and heap leaching of conglomerate ore, and currently for the treatment of unclarified leach liquor containing about 0.5 g/L U in a conventional acid leach plant. In the USA both the USBM and Himsley Column have been used, the former in solution mining operations and the latter to treat mine water to reduce the uranium content from 2 ppm to 10 pp 10^9.

In addition to the column type CIX systems, two other developments have been used to recover uranium. These are the Porter IX system as used at the Rossing operation in Namibia and the CHEM-SEPS system used in the USA to recover uranium from copper dump leach liquors [15]. In the Porter system adsorption is effected in a series of tanks. Solution is introduced into the bottom of the tanks and flows up through a bed of resin. Air lifts transfer the resin from tank to tank counter-current to the solution flow and finally to a downflow, fixed-bed elution column. The CHEM-SEPS or Higgins Loop is a closed-loop system in which the loading, elution, scrubbing and backwashing are done in compartments separated by sequentially operated valves [16].

Although the solvent extraction process as applied to uranium ore treatment has received much attention from researchers in the past, current practice, whether for the direct treatment of leach liquor or for IX eluate, has not changed fundamentally in recent years. A tertiary amine in kerosene with isodecanol or tridecanol as modifiers has been, and still is, the preferred extractant with a wide variety of solutions being used to strip the solvent.

We have seen new developments in the design of mixer-settlers for SX operations. The object in the development is to reduce the shear in mixers, which results in crud formation, and to design a system that requires less area for phase separation to reduce plant size and solvent inventory. There have been a number of new designs, among which is the Krebs system used in France, Niger and Gabon and planned for new mills in Canada, South Africa and Australia.

Another interesting application of solvent extraction relative to uranium is its use to recover uranium from phosphoric acid [1]. Because it is not possible to selectively leach uranium from phosphate rock that contains about 0.01% U_3O_8, the uranium is recovered using pyrophosphoric acid (OPPA), di (2-ethyl-hexyl) phosphoric acid (DEPA) or octylphenyl phosphoric acid in kerosene diluent. The specific conditions vary depending on the characteristics of the acid but involve clarification, adjustment of the EMF to convert the uranium to the required oxidation state, two stages of SX and uranium precipitation. Indications are that phosphoric acid is a high-cost source of uranium but data are limited. The main difficulties, as reported by operators in the USA, Canada and Spain, are emulsion formation, corrosion and iron interference [1, 2].

Research into the recovery or uranium from seawater has centred on adsorption with hydrous titanium oxide (HTO) being the most favoured adsorbent at present [17]. Recently, however, it has been reported that some organic adsorbents show promise. The technology for extracting uranium from seawater is still in an early stage with many problems still to be solved. The very wide range in the reported estimated cost of producing uranium from this source is indicative of the extensive development work required.

3.6. Precipitation

Ammonia, magnesia and caustic soda have all been used to precipitate uranium from IX eluates and SX strip solutions depending on the type of uranium recovery process used. Until recently there has been little incentive to change precipitation procedures but, in Canada at least, pressures from environmental control agencies are forcing metallurgists to rethink the uranium recovery technology.

For example, at the Panel operation of the Rio Algom mill in the Elliot Lake area, nitrate elution/ammonia precipitation was rejected in favour of a strong sulphuric acid elution, followed by neutralization of the excess acid with lime and uranium precipitation with magnesia. Consideration has also been given at another site to hydrogen peroxide precipitation from a strong sulphuric acid strip solution using magnesia for pH control. Both these approaches would avoid releasing pollutants such as ammonia, chloride or sodium to the environment.

4. SUMMARY

To summarize this review, the major technological improvements in uranium ore processing in recent years are as follows:

(1) The use of semi-autogenous grinding circuits for sandstone ore in the USA and semi-autogenous grinding followed by a conventional ball mill/cyclone circuit on conglomerate and unconformity related ores in Canada and Australia;

(2) Radiometric sorting of conglomerates and vein deposits in South Africa and the USA, and gravity concentration with the Reichert Cone in South Africa;

(3) Pressure leaching of high-grade ores to achieve 99% recovery, and in situ, in place and heap leaching of low-grade porous and fissured ores with bacterial oxidation in some cases;

(4) The application of high-rate capacity thickeners, belt filters and pressure sand filter for liquid-solid separations;

(5) The increased use of continuous ion exchange systems on unclarified solutions followed in most cases by solvent extraction treatment of the IX eluate;

(6) Continued improvement in the design of mixer-settlers;

(7) A move from ammonia and nitrates to strong sulphuric acid elution and stripping to avoid downstream environmental problems;

(8) Continued development of technology for recovering uranium as a byproduct in phosphate and copper heap leaching operations and continued research related to recovery of uranium from seawater.

It is apparent from this overview that the current state-of-the-art is a result of applying a higher level of sophistication in equipment and plant design to the basic conventional processes introduced twenty or more years ago. There is little evidence that this trend will not continue for the next decade or so. As long as the demand and price structure remains on its present course, current technology with only marginal improvements is likely to be used, and then only on high-grade deposits or large low-grade deposits involving low mining costs.

The exploitation of unconventional sources such as seawater and coal should be pursued. It may well be decades before suitable technology is available but its development may be of great importance to countries with no domestic conventional sources.

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RECOVERY OF URANIUM FROM ORE

PERFORMANCE OF CARO'S ACID AS AN OXIDANT AT THE NABARLEK MILL

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Abstract

PERFORMANCE OF CARO'S ACID AS AN OXIDANT AT THE NABARLEK MILL.

Pyrolusite (manganese dioxide) was originally chosen as the oxidant at the Nabarlek Mill in northern Australia. Subsequent laboratory and plant trial investigations showed that if Caro's acid were to replace pyrolusite, acid consumption in the leaching circuit could be reduced by 15–20% for the same uranium extraction. Lime required to neutralize the tailings/raffinate slurry could also be similarly reduced. A Caro's acid generator was commissioned at Nabarlek in April 1983. Caro's acid is manufactured at the mill site by reaction of hydrogen peroxide with concentrated sulphuric acid. This installation is the first commercial utilization of Caro's acid in uranium processing. The system has operated successfully for three months and reagent savings have resulted in a reduction in operating costs of greater than $\$3 \cdot t^{-1}$ ore processed.

1. INTRODUCTION

An oxidant is generally required for the acid leaching of uranium ores. Historically, either pyrolusite (manganese dioxide) or sodium chlorate have been chosen, depending on cost and local availability. They act indirectly by maintaining iron, formed from the dissolution of gangue minerals or introduced during grinding, in the ferric state; this oxidises uranium by a surface electrochemical reaction:

$$UO_2 + 2Fe^{3+} \longrightarrow UO_2^{2+} + 2Fe^{2+} \qquad (1)$$

In Canada, the USA and France, sodium chlorate is generally used, but pyrolusite has been preferred in Australia, South Africa and India. When pyrolusite is used, the heavy metal manganese is a major contaminant in the acidic waste. Even after treatment with lime to pH 8.5, the residual manganese concentration in tailings water storage dams is 10-50 mg L^{-1}. If sodium chlorate is used, there is a buildup of sodium chloride in the tailings water which restricts its recycling to the mill.

In 1978, the Australian Atomic Energy Commission (AAEC) commenced collaborative research with Interox Chemicals Pty Ltd on the use of permonosulphuric acid (Caro's acid - H_2SO_5), a derivative of hydrogen peroxide, as an alternative to pyrolusite for the leaching of Australian uranium ores. Caro's acid is attractive on environmental grounds because the reduction products are sulphuric acid which is consumed in leaching, and water. Extensive laboratory testing by the AAEC was followed by plant trials carried out in 1981 by Interox Chemicals at the Nabarlek mill of Queensland Mines Limited (QML). The performance of the Caro's acid system during the trial period of 12 weeks led to a decision by QML to replace the existing pyrolusite system with Caro's acid.

Interox Chemicals have recently designed a new and simplified Caro's acid generator specific to QML requirements. All major equipment was delivered to Nabarlek in early 1983 and construction was completed by mid-April. The new plant was commissioned by Interox in April-May and, after a one week proving trial, was handed over to QML on 13 May.

This paper describes the Caro's acid plant and the metallurgical performance of the leaching and related mill circuits during the first three months of operation. Results of laboratory testwork are also briefly presented.

2. PROPERTIES OF CARO'S ACID

Caro's acid is produced by reacting hydrogen peroxide with sulphuric acid with cooling to remove the heat of dilution and reaction:

$$H_2SO_4 + H_2O_2 \longrightarrow H_2SO_5 + H_2O \qquad (2)$$

At Nabarlek, Caro's acid is made in a continuous plant located on the mill site with a flexible rate of production tied to rate of consumption, so storage is unnecessary. A high yield of Caro's acid is favoured by excess sulphuric acid and the use of high strength reagents. At Nabarlek, Caro's acid is made using 98 wt% H_2SO_4 and 70 wt% H_2O_2 at a mole ratio, H_2SO_4:H_2O_2, of about 3:1. A typical product composition (wt%) is 27% H_2SO_5, 0.4% H_2O_2, 61% H_2SO_4 and the balance water. After manufacture, Caro's acid should be kept at 10-20°C to avoid excessive decomposition (half-life 10 days at 40°C [1]).

Hydrogen peroxide is also an effective oxidant in acid media but it tends to decompose catalytically in the presence of metal ions such as copper and iron:

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (3)$$

Caro's acid has a greater stability to catalytic decomposition, especially at high temperatures, and is preferred in leaching applications.

From the viewpoint of handling and safety, Caro's acid may be considered as a solution of hydrogen peroxide in sulphuric acid, exhibiting the properties of both reagents. In common with all peroxides, Caro's acid slowly decomposes to oxygen but the rate can be accelerated by some metallic contaminants. Consequently, Caro's acid must always be stored in vented containers. Caro's acid can also oxidise organic materials, and if a volatile compound such as acetone is contacted with concentrated reagent, the compound may ignite.

Suitable materials of construction for Caro's acid plants are limited to stainless steels (304 L and 316 L) and glass-filled PTFE for gaskets. Proper weld and surface preparation (pickling) is essential and care must be taken to provide adequate venting for vessels and pipework. However, if these precautions are taken, Caro's acid is readily handled and is no more hazardous than hydrogen peroxide which is widely used in the chemical industry.

3. THEORETICAL COMPARISON OF OXIDANTS

Equations (4) to (7) show that Caro's acid is a stronger oxidising agent than other oxidants commonly used in uranium ore leaching:

$$H_2SO_5 + 2H^+ + 2e^- \longrightarrow H_2SO_4 + H_2O \qquad E_0 = 1810 \text{ mV} \quad (4)$$

$$1/3\ ClO_3^- + 2H^+ + 2e^- \longrightarrow 1/3\ Cl^- + H_2O \qquad E_0 = 1450 \text{ mV} \quad (5)$$

$$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O \qquad E_0 = 1210 \text{ mV} \quad (6)$$

$$2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+} \text{ (sulphate)} \qquad E_0 = 640 \text{ mV} \quad (7)$$

Equations (4) and (6) predict that acid consumed in oxidation by manganese dioxide is twice that for Caro's acid. On the basis of equivalent weights, reagent requirements per gram of Fe^{2+} oxidised are as shown in Table I. In theory, for every kilogram of pyrolusite consumed, the alternative use of Caro's acid should

TABLE I

COMPARISON OF REAGENT CONSUMPTIONS FOR OXIDATION

(per g Fe^{2+} oxidised)

Oxidant	Oxidant Consumption (g)	Acid Consumption (g)
Manganese dioxide	0.777	1.75
Pyrolusite (79% MnO_2)	0.983	1.75*
Sodium chlorate	0.317	0.875
Caro's acid	0.304 (as H_2O_2)	0.875

* Assumes that other minerals in pyrolusite do not dissolve under acid conditions

decrease acid consumption by at least 0.89 kg. For convenience, Caro's acid consumption will be expressed as the quantity of hydrogen peroxide required for its formation (see equation (2)). On this basis, 3.2 times as much pyrolusite should be required as Caro's acid (as H_2O_2).

The reduction of Caro's acid (equation (4)) produces an amount of sulphuric acid equivalent to that required for its formation, and water. Pyrolusite is reduced to manganous ion. As manganous ions are almost completely (95%) precipitated at a tailings neutralisation pH of 8.5, lime required for removal of manganese can be determined from the equation

$$MnSO_4 + Ca(OH)_2 \longrightarrow Mn(OH)_2 + CaSO_4 \qquad (8)$$

From the stoichiometry of equation (8), the elimination of manganese gained by the use of Caro's acid should decrease lime requirements by 0.67 kg for every kilogram of pyrolusite consumed in leaching. In simpler terms, the expected lime saving (kg t^{-1} ore) is equal to 0.76 times the acid saving (kg t^{-1} ore) in leaching.

4. LABORATORY AND PLANT TRIAL EVALUATIONS OF CARO'S ACID

Detailed descriptions of laboratory testwork and plant trial results have been presented previously [2,3]. This work is summarised briefly.

4.1 Laboratory testwork

Four ores (Nabarlek, Ranger, Koongarra and Jabiluka) from the Alligator Rivers region, Northern Territory, Australia, were examined. As pyrolusite was originally chosen as oxidant for these ores, it was adopted as a standard for the assessment of Caro's acid. The experimental program consisted of pairs of leaching and neutralisation experiments conducted under strictly controlled conditions to compare uranium extractions and reagent consumptions. Reagent savings and the ratio of oxidant consumptions were used as a measure of performance. Later in the program, a brief comparison with sodium chlorate was also undertaken.

4.1.1 Laboratory results

The major findings of the study to compare Caro's acid and pyrolusite were as follows:

(i) Uranium extraction. For all ores, uranium extraction in batch and continuous tests was unaffected whether pyrolusite or Caro's acid was used as oxidant.

(ii) Oxidant consumption. The ratio of oxidant consumptions was very close to the stoichiometric value of 3.2.

(iii) Acid consumption. For all ores, Caro's acid reduced the acid consumption in leaching by 12-25 per cent. The average acid saving (kg t^{-1} ore) was significantly greater than predicted from the reaction of manganese dioxide alone. A useful rule-of-thumb is that acid saving is four times the Caro's acid consumption. This increase can be attributed to the dissolution of impurities in pyrolusite (mainly iron, aluminium and magnesium).

(iv) Lime consumption. Caro's acid reduced the lime required to neutralise tailings liquor by 18-29 per cent. The average lime saving (kg t^{-1} ore) for neutralisation of tailings was 0.71 times the acid saving.

(v) Compositions of neutralised liquors. For Caro's acid as oxidant, manganese concentrations in tailings liquors at pH 8 ranged from 0.3-6.0 mg L^{-1} compared with 120-360 mg L^{-1} for pyrolusite. If Caro's acid were used, neutralising to pH 8 may not be necessary as manganese concentrations at pH 7 were only 2-35 mg L^{-1}. In the range pH 7-8, the concentrations of other environmentally significant heavy metals are less than 1 mg L^{-1} [4].

From an environmental standpoint, Caro's acid is also preferable to sodium chlorate. However, the theoretical data given in Table I indicate that there should be no acid saving from the alternative use of Caro's acid. Batch and continuous leaching tests confirmed similar acid consumptions for Caro's acid and sodium chlorate, but consumptions of sodium chlorate were much higher than predicted from Table I.

In batch leaching tests, close control of redox potential could not be achieved with sodium chlorate. If the desired potential was achieved at the start of leaching, it continued to rise throughout leaching and oxidant consumption was excessive. Compared to Caro's acid, the consumption of sodium chlorate was 42 per cent greater than stoichiometric requirements. In continuous tests, potential was readily controlled using sodium chlorate; yet, oxidant usage was double that predicted from theory. The high consumptions of sodium chlorate are caused by its slow rate of reaction under mild leaching conditions (pH 1.8, 40°C).

4.2 Plant trials

Two trials, each lasting about six weeks, were carried out in June and August 1981 at the Nabarlek mill. Reagent consumptions were compared with those in the four-week periods before and after each trial. During the five-month evaluation period, a wide range of ore grades (1.2-3% U_3O_8) and types were encountered.

Results of the trial confirmed laboratory predictions concerning uranium extraction and reagent savings and demonstrated that the use of Caro's acid would reduce average ore treatment costs by at least $2/tonne ore. These savings, coupled with the operational and environmental advantages of the Caro's acid system, led to the decision by QML to change to Caro's acid.

5. NABARLEK MILL

The Nabarlek mill is located in the tropical Alligator Rivers region. The high grade orebody, now averaging 1.7% U_3O_8, was completely mined by opencut methods and stockpiled before the commencement of milling in June 1980. The major host rocks are quartz, chlorite, feldspar and muscovite schists, with hematite frequently present. The primary mineral is uraninite, with sklodowskite, curite and rutherfordite the most common secondary minerals. In both primary and secondary ores, there are small amounts of unnamed refractory uranium-titanium and uranium-silicate minerals.

Ore is treated by conventional acid leaching and solvent extraction (SX) processes. The leached solids are separated from the uranium-bearing solution by counter current decantation (CCD) washing with recycled raffinate. Uranium is recovered from clarified pregnant liquor in mixer-settlers using a tertiary amine solvent. After stripping with ammonium sulphate, uranium is precipitated with ammonia followed by calcination to produce a high grade yellowcake. The tailings/raffinate slurry from the CCD circuit is neutralised with lime to pH 8.25-8.75 before discharge to the mined-out pit. Decant water from the pit is recycled to the plant via a storage pond. A more detailed description is given in a recent OECD/NEA publication [5].

5.1 Leaching circuit

The leaching circuit consists of six mechanically-agitated tanks in series. Ore is ground to 50% less than 75 μm and leached as a 45 wt% slurry at 38-45°C without heating. At the average ore throughput of 8.3 t h^{-1}, residence time is 24 h. Sulphuric acid (98%) is added automatically to the first two tanks to control pH at 1.5-1.7 and to tank No. 5 for a pH of about 1.6-1.7. Conductivity probes measure the free acid concentrations in all tanks.

5.1.1 Pyrolusite system

Originally a pyrolusite slurry was added to the first leaching tank via a ring-main system to control redox potential at 500-550 mV*. The pyrolusite handling circuit incorporated an open stockpile from which a hopper was filled periodically, using a front end loader. From the hopper the pyrolusite was fed to a ball mill in closed circuit with a spiral classifier (grind size 80% less than 75 μm) and then pumped via a dewatering cyclone to a slurry holding tank.

Soon after operations commenced, a number of problems were apparent. The low intermittent flow of pyrolusite slurry caused frequent blockages of lines and pumps. Line blockages were partially overcome by a splitter box arrangement which allowed a larger volume of flow. Operation and maintenance of the system were labour-intensive and control of redox potential was poor. In addition, performance of the system was often severely affected by mechanical problems in the pyrolusite grinding circuit and excess addition from recycled pyrolusite spillages.

After seven months of operation, the circuit was modified and 75% of the estimated pyrolusite requirement was added to the ball mill in the ore grinding circuit. Final control of oxidation potential was achieved by the addition of oxidant to leach tank

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*All redox potentials quoted for leaching conditions are relative to a saturated silver chloride electrode at the leaching temperature. The most highly oxidised solution is assumed to have the most positive potential.

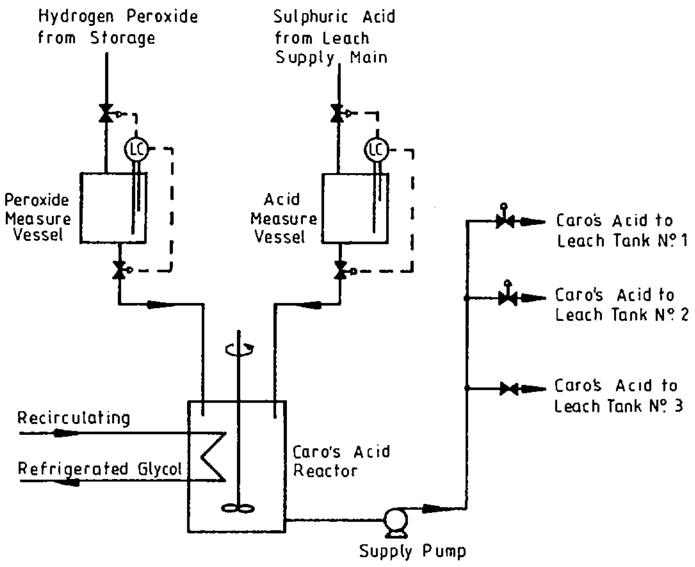

FIG. 1. The Caro's acid generator.

No. 1 using the original pyrolusite grinding circuit. Although this arrangement greatly reduced labour and maintenance requirements, effective control of oxidation potential was not achieved.

5.2 Neutralisation circuit

The neutralisation circuit consists of three pachuca tanks in series. Total residence time is about 3 h. A lime slurry is pumped into the first tank to allow pH in the second tank to be controlled automatically at the set point.

6. CARO'S ACID SYSTEM

The Caro's acid supply system at Nabarlek is shown in Figure 1. It consists of three main elements - the reaction vessel with its cooling system, the reagent metering system and the control system for oxidant supply to the leaching tanks. Sulphuric acid and 70 wt% hydrogen peroxide are fed to the reaction vessel so that the rate of production of Caro's acid is matched to the demand of the leaching circuit. The storage capacity of the reaction vessel is equivalent to about eight hours' supply.

All wetted parts of the vertical reaction vessel are constructed of 316 L or 304 L stainless steel. Internal coils and conventional agitator stirring are provided to remove the heat of reaction. Refrigerated ethylene glycol is pumped through the coils to maintain an average reactor temperature of 10°C. A standard water cooler package system, which includes a compressor, an air-to-Freon condenser, an expansion valve and a glycol-to-Freon heat exchanger, provides refrigeration.

Sulphuric acid (98 wt%) and hydrogen peroxide are fed into the reactor via measure vessels at a mole ratio of 3:1. Acid is supplied from the mill storage tanks. Hydrogen peroxide is stored on site in two 65 m^3 stainless steel tanks which feed the measure vessel via a head tank. As Caro's acid is pumped from the reactor to the leaching circuit, the level in the reactor drops until a level sensing probe is exposed. A signal from the probe then automatically opens the outlet valves on the measure vessels. Both reagents flow by gravity into the reactor until the measure vessels are empty; the outlet valves then close and the reagent inlet valves re-open to allow the measure vessels to refill. When this step is complete, the operating cycle waits until the Caro's acid in the reactor drops below the operating level before charging another batch to the reactor.

Caro's acid is pumped from the reaction vessel to leach tanks Nos. 1, 2 and 3. Automatic valves control the flows to tanks 1 and 2 in response to the difference in set points and redox potentials measured by probes in each tank. Oxidant demand for tank No. 3 is reasonably constant and oxidant flow is periodically adjusted by a simple manual control valve and rotameter to maintain the desired potential. Redox potential is also measured in tank No. 6.

In addition to the operating systems described above, a number of interlocks and sensing instruments are provided to allow safe and completely automatic operation of the generator. Apart from start-up and routine monitoring, the Caro's acid system makes no demand on operating staff.

7. PERFORMANCE OF THE CARO'S ACID SYSTEM

The performance of the Caro's acid supply system is considered in three sections: the metallurgical performance of the leaching and neutralisation circuits; the operational features of the system; and the environmental considerations.

7.1 Metallurgical performance

Metallurgical performance was assessed by comparing reagent consumptions and leaching efficiencies for Caro's acid and pyrolusite. The variability of ore grade makes it difficult to obtain direct comparisons for equivalent ores. Consequently, average

TABLE II

LEACHING CONDITIONS FOR CARO'S ACID

Tank No.	Expected Temperature(1) (°C)	pH	Redox Potential (mV)
1	35.5 - 37.5	1.50 - 1.60(2)	490(2)
2	37.5 - 39	1.50 - 1.65(2)	500(2)
3	38 - 40	1.65 - 1.75	485(2)
4	38.5 - 41	1.75 - 1.95	470 - 480
5	39 - 42	1.65(2)	460 - 470
6	39 - 41	1.80 - 1.85	455 - 465

(1) In warmer weather, temperatures would be 3-4°C higher and pH set points probably greater by 0.05 to 0.15 units.

(2) Set points. Depending on ore type, acid set points in tanks 1 and 2 may be varied within the indicated range.

results were compared over the four-week periods used for general metallurgical accounting in the mill. During previous trials [3], it was established that acid and oxidant consumptions are related to ore grade; thus, despite the averaging procedure adopted, direct comparisons are only meaningful if the average and variation in head grade are reasonably similar. In general, Caro's acid data for 12 weeks (3 periods) to the end of July 1983 are compared with pyrolusite results for the accounting year up to the date of changeover to Caro's acid.

7.1.1 *Leaching circuit operating conditions*

The operating conditions selected for the leaching circuit using Caro's acid are summarised in Table II. Although some changes were made, the pH levels are essentially those derived from many months of operation on pyrolusite and can therefore be assumed to minimise acid consumption and result in effective uranium extraction.

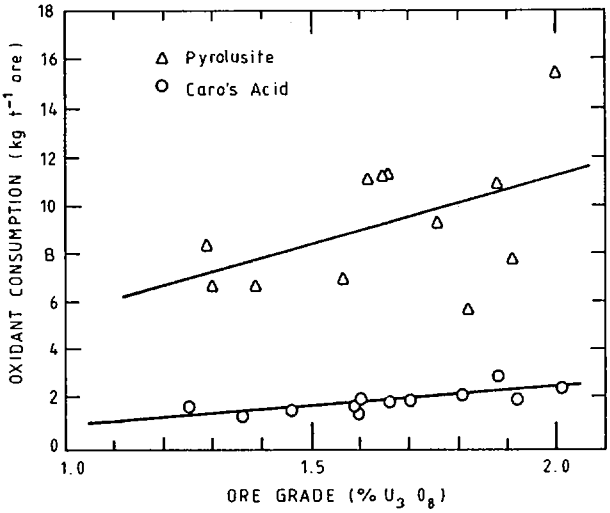

FIG.2. Weekly average consumptions of oxidants as a function of ore grade.

The most significant change to the leaching circuit was transferring acid addition from tank 6 to tank 5. This resulted in a lower pH in tank 5 and a more uniform pH profile throughout the circuit. With the previous arrangement, the pH in tank 5 often approached a level (above pH 2.1) at which Fe^{3+} could precipitate, which meant that oxidant would be wasted in maintaining a satisfactory potential. The modification also provided greater contact time for acid added during the later stages of leaching. A further change was also necessary. At the time of commissioning the Caro's acid system, there was a seasonal decrease of 3-4°C in ambient (and leaching) temperature. To compensate for this change, the operating pH levels were set marginally lower than those in the preceding months when pyrolusite was used.

Redox potentials were selected on the basis of laboratory and plant trial results with Caro's acid. Potentials previously maintained in the mill were erratic and tended to be higher than necessary.

As operating experience with Caro's acid is limited, the set points selected for initial operation may not be optimum and some minor improvements in overall performance can be expected as more data are generated.

7.1.2 Oxidant consumption

The weekly consumptions of Caro's acid, as 100% H_2O_2, are shown in Figure 2 as a function of average ore grade. For the

TABLE III

COMPARISON OF OXIDANT CONSUMPTIONS

Period	Oxidant	Ore Grade (% U_3O_8)	Oxidant Consumption (kg t^{-1} ore)
12 weeks to 25/7/83	Caro's acid	1.65	1.87
12 weeks to 24/4/83	Pyrolusite	1.65	9.2
42 weeks to 24/4/83	Pyrolusite	1.63	9.2

TABLE IV

COMPARISON OF ACID CONSUMPTIONS

Period	Oxidant	Ore Grade (% U_3O_8)	Acid Consumption (kg t^{-1} ore)		
			Leaching	SX	Total
12 weeks to 25/7/83	Caro's acid	1.65	38.5	14.6	53.1
12 weeks to 24/4/83	Pyrolusite	1.65	46.3	15.9	62.2
42 weeks to 24/4/83	Pyrolusite	1.63	43.0	17.9	60.9
		1.65*	43.2*	17.9	61.1

* Adjusted to ore grade of 1.65% U_3O_8 to allow direct comparison with other data

twelve weeks of operation with Caro's acid, average consumption was 1.87 kg t^{-1} ore for a grade of 1.65% U_3O_8. The pyrolusite usage for the twelve weeks before changeover is shown in Figure 2 to have a much greater scatter of results. Caro's acid and pyrolusite consumptions are compared in Table III. Average pyrolusite usage was 9.2 kg t^{-1} ore.

The ratio of pyrolusite to Caro's acid consumption is 4.9. This is significantly greater than the theoretical value of 3.2 because of the wastage of pyrolusite caused by poor control of redox potential and carryover of unreacted pyrolusite.

7.1.3 Acid consumption

Acid consumption data for the mill are summarised in Table IV.

The acid saving in leaching gained from the use of Caro's acid is considerably different whether a short or longer term comparison is made with pyrolusite. However, acid is not only consumed in leaching, but also in SX where pH of pregnant liquor must be adjusted for optimum recovery of uranium. Longer-term results also show that Caro's acid produced a significant reduction in acid requirements for solvent extraction. This apparent saving suggests that the pH profile selected for Caro's acid, particularly in the final two tanks, has resulted in a slightly greater dissolution of gangue which would otherwise have occurred in the CCD circuit. As a result, acid required for pH adjustment in SX is correspondingly lower.

The data in Table IV show that the overall acid saving ranged from 8.0 to 9.1 kg t^{-1} ore or 18.5 to 19.7 per cent. Laboratory work (section 4.1.2) has demonstrated that the acid saving due to the use of Caro's acid, for equivalent redox potentials, is equal to four times the consumption of Caro's acid. On this basis, a saving of 7.5 kg t^{-1} ore is predicted for the average Caro's acid consumption of 1.87 kg t^{-1} ore. In practice, a slightly greater saving (10-20%) may be realised at Nabarlek when account is taken of the higher than necessary potentials that generally resulted from the use of pyrolusite.

7.1.4 Uranium extraction

The head grade at Nabarlek varies significantly on a daily, and even weekly, timescale. Although tailings grades also fluctuate over a wide range (0.032-0.06% U_3O_8), they tend to be fairly independent of ore grade and are best used to compare efficiency of uranium extraction.

Average tailings grades for the last 18 four-week periods are shown in Figure 3. There is a tendency for slightly lower grades during the hotter months of the year and, conversely, higher values during the cooler periods. Tailings grades for Caro's acid fall within the normal operating band. The average of 0.047% U_3O_8 is higher than the year-to-date pyrolusite result of 0.042%, but lower than the 0.049% obtained for the same period last year.

The effect of gradual seasonal changes on leaching temperature does not account for the relatively high monthly fluctuations

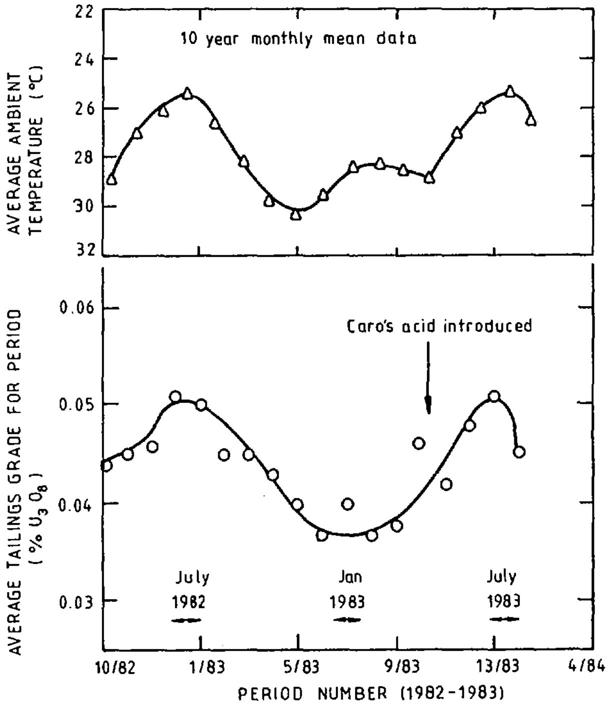

FIG.3. Variation in tailings grade at Nabarlek Mill.

in tailings grades. These fluctuations could be caused by changes in ore mineralogy (proportion of refractory uranium) or failure to maintain satisfactory leaching conditions. The dominant role of mineralogy has been verified in laboratory testwork. Table V compares laboratory leaching results for numerous Nabarlek composites. Tailings grades range from 0.037 to 0.076% U_3O_8 for similar conditions. (Mill data are also available for samples 3-5 and are in good agreement with laboratory results.)

For all samples, optimum pH was about 1.7. Under these conditions, an increase in acid consumption of 10 kg t^{-1} ore decreased tailings by only 0.002-0.003% U_3O_8, whereas a decrease of the same magnitude caused tailings grades to rise by as little as 0.004-0.005%. Thus, changes in mineralogy have a much greater impact on tailings grades than relatively substantial deviations from optimum acid requirements.

When encountered for extended periods, more refractory lower grade ore such as sample 5 has a marked effect on the monthly tailings grade. Since operation with Caro's acid commenced, this ore type was processed for about 8 days.

TABLE V

LABORATORY LEACHING OF NABARLEK ORES

Duration of Leaching : 24 h
Temperature : 40-45°C
Redox potential : 475-500 mV for 8-12 h

Sample No.	Ore Grade (% U_3O_8)	pH	Acid Consumption (kg t^{-1} ore)		Tailings Grade (% U_3O_8)	
			Caro's Acid	Pyrolusite	Caro's Acid	Pyrolusite
1	1.61	1.7	40	48	0.058	0.062
2	1.88	1.7	48	57	0.043	0.041
3	1.65	1.8	45	54	0.040	0.040
		1.6	60	70	0.037	0.037
4	1.75	1.8	39	45	0.048	0.047
		1.2	98	-	0.040	-
5	1.48	1.8	25	-	0.076	-
		1.6	41	47	0.066	0.067
		1.2	88	-	0.061	-

7.1.5 Lime consumption

The neutralisation circuit treats the tailings slurry from the CCD washing circuit and a raffinate bleed stream from solvent extraction. Lime (95% available $Ca(OH)_2$) consumption cannot be related readily to variations in leaching because of the time lag before any changes reach neutralisation and the dampening effects of other mill circuits. For example, following the elimination of the pyrolusite from the leaching circuit, about 20-30 days were required for the Mn concentration in raffinate to decrease from the usual level of 1400-1800 mg L^{-1} to a new equilibrium value of 30 mg L^{-1}.

Before Caro's acid was used, the neutralisation set point was pH 8.75 in tank 2. This figure was chosen so that the manganese

TABLE VI

COMPARISON OF LIME REQUIREMENTS

Period	Oxidant	Neutralisation pH	Lime Consumption (kg t^{-1} ore)	Lime* Saving (kg t^{-1} ore)	Lime* Saving (%)
42 weeks to 24/4/83	Pyrolusite	8.75	40.7	-	-
12 weeks to 24/4/83	Pyrolusite	8.75	41.2	-	-
12 weeks to 25/7/83	Caro's acid	8.75-8.00	26.0	14.7	36.0
2 weeks	Caro's acid	8.75	31.6	9.1	22.4
2 weeks	Caro's acid	8.5	29.3	11.4	28.0
4 weeks	Caro's acid	8.25	27.8	12.9	31.7
4 weeks	Caro's acid	8.0	20.1	20.6	50.6

* Compared to 42-week data for pyrolusite

concentration in the tailings storage pit could be kept below 10 mg L^{-1}. With the virtual elimination of manganese from mill circuits, the set point has been gradually decreased to pH 8.0. Comparison of lime requirements for both oxidants at the same pH is therefore limited. Available data are summarised in Table VI.

Lime savings range from 9.1 kg t^{-1} ore (22%) for the same neutralisation pH of 8.75, to 20.6 kg t^{-1} ore when the additional saving gained by decreasing pH to 8.0 is included. Depending on the manganese concentration in the tailings storage pit, the neutralisation set point may be further reduced to pH 7.5-7.0; this will result in a further decrease in lime consumption.

Batch laboratory tests predict (section 4.1.2) that, for the same pH, the lime saving resulting from the use of Caro's acid should be 0.71 times the acid saving in leaching. If the lower reactivity of industrial lime and the less efficient reaction of lime in a continuous circuit are taken into account, a factor of about 0.9 could be expected in the mill. For the average acid

TABLE VII

CONTROL OF OXIDATION POTENTIAL WITH PYROLUSITE

Day	Tank 1		Tank 2		Tank 6	
	Mean(1)	Std Dev(2)	Mean(1)	Std Dev(2)	Mean(1)	Std Dev(2)
1	572	11	534	1	595	5
2	538	13	528	5	587	4
3	509	4	494	15	541	26
4	521	10	485	11	493	3
5	518	20	557	22	519	16

(1) Daily averages
(2) Standard deviation of hourly means

saving of 8.6 kg t^{-1} ore, the predicted lime saving at pH 8.75 is 7.7 kg t^{-1} ore, compared with the actual saving of 9.1. One reason for this discrepancy is the almost impossible task in the mill of maintaining perfect measurement and control of pH in the range 8-9.

7.2 Operating performance

The major operating advantage of Caro's acid is that it enables much better control of redox potential in the mill circuit. As pyrolusite is a solid, it reacts relatively slowly and, therefore, makes it difficult to maintain a constant redox potential, particularly for ores of varying oxidant requirements. This leads to either a redox potential above set point, with excessive reagent usage, or a low redox potential and a slight loss in uranium extraction. In practice, average potentials at Nabarlek tended to be maintained well above desired set points.

The control of potential can be analysed in two ways:- by observing the variation in mean hourly and daily values and the fluctuation in instantaneous readings. The typical day-to-day variation in potential with pyrolusite is shown in Table VII. Although the standard deviations of the hourly means are not great, there is considerable daily variation.

TABLE VIII

CONTROL OF OXIDATION POTENTIAL WITH CARO'S ACID

Day	Tank 1 (3)		Tank 2 (4)		Tank 6	
	Mean (1)	Std Dev (2)	Mean (1)	Std Dev (2)	Mean (1)	Std Dev (2)
1	490	3.9	500	3.9	457	2.6
2	491	1.6	500	1.3	460	1.1
3	490	3.7	500	1.4	460	1.8
4	489	4.4	500	0.7	458	2.0
5	490	1.5	500	0.9	455	0.7
6	490	0.8	500	0.3	455	1.6
7	490	0.4	500	0.3	456	3.2
8	490	0.7	500	1.0	470	1.8
9	490	0.3	500	0.7	468	0.8
10	490	0.7	500	1.7	465	1.2
11	490	0.7	500	1.6	465	2.3

(1), (2) See Table VII
(3) Set point 490 mV
(4) Set point 500 mV

The degree of control achieved with Caro's acid is shown in Table VIII. There is almost no day-to-day variation and good control is achieved at the set point. Compared with pyrolusite, the standard deviation of the hourly mean in tank 1 is reduced from about 11 mV to less than 2 mV.

Other operating advantages of Caro's acid are that it is much easier to handle than pyrolusite and that the system is completely automated. The system is also designed to ensure a continual supply of oxidant; this was achieved during the start-up and commissioning periods and has been maintained.

TABLE IX

CONCENTRATION OF MANGANESE IN MILL CIRCUITS (mg L^{-1})

Sample Location	Pyrolusite (1)		Pyrolusite (1)		Caro's Acid	
	pH	Mn	pH	Mn	pH	Mn
Recycled Process Water	7.29	1.6	6.95	2.8	7.10	< 1
Leach Discharge	1.85	1800	1.90	2950	1.45	59
Raffinate	1.98	1110	2.09	1780	2.20	38
CCD Tailings	-	-	2.16	1090	2.23	31
Neutralisation						
Tank No. 1	4.33	830	8.13	38	8.35	0.22
2	8.74	0.4	8.54	9	8.00	0.46
3	9.31	< 0.1	8.50	1	8.03	0.46

(1) Surveys carried out at 2-week interval

Minor problems encountered during commissioning were overcome while maintaining control of oxidation potential. When the Caro's acid supply pump had to be replaced to allow repair of a leaking case gasket, oxidant demand was met by direct addition of hydrogen peroxide to the leaching tanks. A further problem was caused by the sticking of an automatic valve on the sulphuric acid measure vessel. This fault was rectified by fitting a larger actuator and changing the stem packing. Both modifications were made with no effect on the leach circuit as the buffer capacity of the reactor was adequate to maintain a supply of Caro's acid.

7.3 Environmental considerations

Virtual elimination of the heavy metal manganese from mill circuits and effluents is an important environmental consideration in favour of the use of Caro's acid. The concentrations of Mn in various mill circuits for pyrolusite and Caro's acid as oxidants are compared in Table IX.

The use of Caro's acid does not completely remove manganese as Nabarlek ore contains about 0.03% Mn as naturally occurring minerals, about 25% of which is dissolved during leaching.

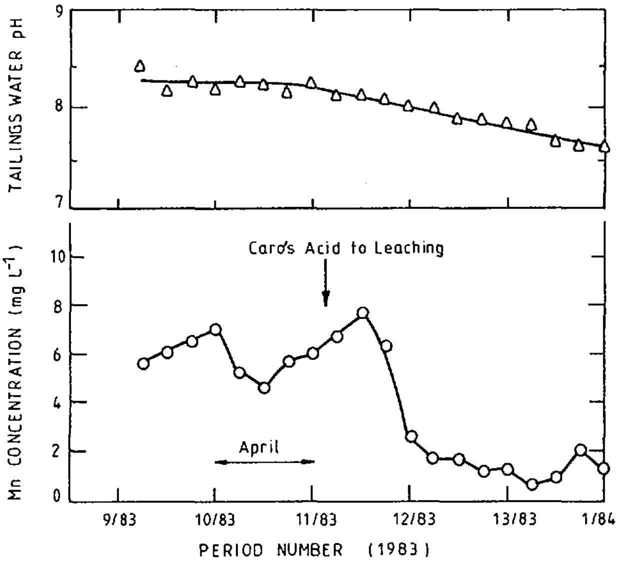

FIG.4. Variation in manganese concentration in tailings storage pit since changeover to Caro's acid.

The most important impact of Caro's acid is the reduction in the concentration of manganese in the tailings storage pit. Average weekly results (from daily samples) shown in Figure 4 indicate that within three months Mn levels decreased by a factor of at least three, to less than 1.5 mg L^{-1}. At the same time, it has been possible to decrease the pH in the storage pit from about 8.3 to 7.7.

In addition to reducing the dissolved manganese concentration, Caro's acid will also decrease the amount of precipitated Mn held with the tailings in the storage pit. Assuming average concentrations after leaching of 2400 and 60 mg L^{-1} for pyrolusite and Caro's acid respectively, the use of pyrolusite deposits about an extra 220 t Mn/year which could be partly mobilised by possible long-term changes in pH.

8. ECONOMIC COMPARISON OF CARO'S ACID AND PYROLUSITE

8.1 Reagent and operating costs

Compared to pyrolusite, the use of Caro's acid reduces reagent costs in leaching and neutralisation, and operating costs associated with the oxidant supply system. Reagent costs are compared in Table X. Savings vary between Aus. $3 and $3.3 t^{-1}

TABLE X

COMPARISON OF REAGENT COSTS

Period	Oxidant	Ore Grade (% U_3O_8)	Cost Saving for Caro's Acid ($ t^{-1} ore)
12 weeks to 25/7/83	Caro's acid	1.65	-
12 weeks to 24/4/83	Pyrolusite	1.65	3.25
42 weeks to 24/4/83	Pyrolusite	1.63	3.00

ore processed, depending on the period of comparison. Long-term lime savings at (pH 8.0 or below) are expected to be greater than the average figure achieved during the first 12 weeks of operation (pH 8.75-8.00). This could increase reagent savings by an additional $0.75 t^{-1} ore.

Power and maintenance costs for the Caro's acid system are estimated to be $0.2 t^{-1} ore less than for the pyrolusite grinding and handling circuit, reduction in power requirements being the major factor.

Labour requirements for the Caro's acid system are minimal. The generator and supply piping need only routine inspection. However, no cost saving has been credited for the Nabarlek system since labour demands for the pyrolusite circuit were not sufficient for a full-time operator. For a larger mill, there may be a saving in labour costs.

8.2 Capital costs

The plant and equipment required for Caro's acid and pyrolusite systems are very different. Caro's acid plants are relatively expensive for small throughputs. The factors which inflate the cost of small generators include:

(1) a high proportion of instrumentation and control circuits, with costs that are almost independent of scale; and

(2) sizes of stainless steel piping are dictated by mechanical factors rather than flow velocity, much larger throughputs could be achieved for similar piping costs.

In Australia, capital costs are estimated to be equivalent for a hydrogen peroxide usage of 200-250 t/year (about 1000 t/year pyrolusite). This estimate is based on the Nabarlek generator which incorporates a high degree of automation, self-monitoring and excess capacity. The peak continuous output from the generator is double the maximum capacity that the mill could sustain. A lower cost unit could be designed to less stringent specifications.

9. CONCLUSIONS

The leaching circuit at the Nabarlek mill has operated very successfully for three months with Caro's acid as oxidant. A comparison of the metallurgical performance of the circuit for pyrolusite and Caro's acid has shown that a sulphuric acid saving of around 19 per cent has been achieved. In addition, consumption of Caro's acid was slightly lower than predicted. The virtual elimination of manganese from mill process streams has allowed a reduction in the neutralisation pH of tailings/raffinate slurry. As a result, the saving in lime consumption has increased from an expected 20 to about 40 per cent.

The Caro's acid generator has performed to design specifications and ensured a continual supply of oxidant to the leaching circuit. Compared to pyrolusite, the major operational advantage of the Caro's acid system has been the much better control of redox potential. Variations in hourly mean potentials have been reduced from 11 to less than 2 mV.

The use of Caro's acid has reduced operating costs by greater than \$3.0 t^{-1} ore processed; this compares more than favourably with predicted savings which were the basis for the decision to change from pyrolusite to Caro's acid.

ACKNOWLEDGEMENTS

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DISCUSSION

J. BITTE: Did you study other methods of leaching without using Caro's acid?

R.J. RING: All the tests were with atmospheric pressure leaching using either pyrolusite or Caro's acid. We did not try pressure leaching or other methods. The gangue minerals in the Alligator Rivers region are very reactive. So the leaching conditions must be kept fairly mild to get the best selectivity for uranium as opposed to the gangue minerals. In addition, acid consumption is much higher at high temperatures or at higher acid concentrations.

Z. DOGAN: Just for curiosity what is the meaning of the name of Caro's acid?

R.J. RING: It is named after the German chemist who first discovered it, Heinrich Caro, in 1898, I believe.

I. LINDHOLM: Is there any change in the radium content in solution when you use Caro's acid instead of manganese dioxide?

R.J. RING: We have analysed the radium content both in the leaching circuits and in the neutralization circuits and there is no change in the concentration of radium. We were slightly worried about the radium being precipitated with the manganese ions but that is not the case.

J.P. HEBERT: To have a more complete view of the economics, may we know the price of the installation of the generator of Caro's acid including its environmental equipment?

R.J. RING: Some information is proprietary. Capital costs in Australia are estimated in the paper. If one compares a pyrolusite installation with an installation using Caro's acid, the breakeven cost is of about 1000 tons of pyrolusite per year. Smaller Caro's acid generators tend to be slightly more expensive because the cost of piping, instrumentation and accessories is not proportional to the size. In very small sizes one has to put large parts for strengthening and the same instrumentation. This cost is a high proportion of the total cost.

K. CHITUMBO: Does the use of Caro's acid have any effect on the solvent extraction process?

R.J. RING: There has been no noticeable change in the operation of the solvent extraction circuit since the changeover to Caro's acid.

A.M. ANTUNES FIUZA: When you speak of a reduction in acid consumption of about 19%, are you taking into account the sulphuric acid needed to produce the Caro's acid?

R.J. RING: Yes. The acid required for the preparation of Caro's acid is taken into account. In fact, sulphuric acid consumption in the mill is measured by an integrator on the main acid line. The acid required from the generator is taken from the main line after the integrator.

URANIUM EXTRACTION BY CONTINUOUS CARBONATE LEACHING IN A PIPE AUTOCLAVE

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Abstract

URANIUM EXTRACTION BY CONTINUOUS CARBONATE LEACHING IN A PIPE AUTOCLAVE.

The paper describes uranium extraction tests carried out on lujavrite in a pipe autoclave. Lujavrite is an igneous rock from the Ilimaussaq massif in South West Greenland. It is strongly alkaline, which precludes the use of acid leaching. Besides, it contains approx. 1% of villiaumite, NaF. The ore is low grade with 400 ppm of uranium contained mainly in the rare mineral steenstrupine, which is a complex phosphosilicate of the rare earths. Carbonate leaching is effective only at temperatures above 240°C in a concentrated solution of $NaHCO_3$. In return it is accomplished in 20 min, provided that the ore fineness corresponds to 80% minus 200 mesh. The ore is wet ground with the bicarbonate solution in a ball mill. The slurry with a solid-liquid ratio of 1:1 is pumped into the pipe autoclave at a rate of 3 m^3/h and at a pressure of 120 atm. Leaching takes place in the presence of oxygen at max. 280°C. For the separation of leach liquor from solid residue, a belt filter is used to provide effective washing. The solution is recycled because of the low-grade ore. Uranium separation is done by either NaOH precipitation or reduction to UO_2.

INTRODUCTION

Peculiarities of the ore

The low-grade uranium deposit at Kvanefjeld is part of the alkaline Ilimaussaq intrusion in South Greenland. The uranium mineralized rock members are nepheline syenites, named lujavrites. The principal uranium-bearing mineral steenstrupine is a complex sodium-REE phosphosilicate in which Fe, Mn, Th and U are minor constituents.

A special feature of this ore body is the content of water-soluble minerals: sodium fluoride, sodium silicate, typically 1% of each, and an organic substance that displays all the characteristics of humus.

Sulphides are sparse, the most important one being sphalerite (ZnS) of which the content is generally less than 0.5%.

Grade and tonnage

The ratio waste rock/ore is very favourable, even though blocks from the original roof of the intrusion form large xenoliths within the ore material. In the lujavrites under consideration the steenstrupine is in the main finely disseminated throughout the rock, yielding a uranium content of 300–400 ppm and a thorium content of 800–1000 ppm.

The latest drill core investigation in 1977 suggested that a reserve of 30 000 tonnes of U_3O_8 is reasonably assured, so in spite of the low grade considerable effort has been invested in order to make this reserve commercially exploitable.

Extraction procedures studied

Acid leaching

The lujavrite belonging to the peralkaline nepheline syenites has a high content of sodium-rich silicates, which dissolve in acid more rapidly than the uranium-bearing steenstrupine. This causes excessive consumption of acid (400 kg H_2SO_4 per tonne of ore) not to mention the silicic acid produced, which makes further processing nearly impossible.

Sulphating roasting

A practicable alternative is heating the ore to 700°C in an atmosphere containing SO_3, whereby the uranium is mainly converted into sulphate, which is subsequently extracted with water. This method has been tried with some success on a sample from the upper, less alkaline and more weathered part of the deposit [1].

Carbonate pressure leaching (CPL)

A general procedure for this type of ore should be based on carbonate leaching, but recovery is very low at moderate temperatures. Only above 200°C will a strong carbonate solution cause decomposition of steenstrupine. Under suitable oxidizing conditions, the uranium will be extractable as a carbonate complex.

The present paper reviews the results on a laboratory and a pilot-plant scale with the so-called CPL process, which seems to have the best possibilities of commercial application.

LABORATORY INVESTIGATIONS

Grinding

The ore is wet ground with the carbonate leach liquor, as this makes for better uranium recovery than dry grinding. Other advantages are: elimination of dust problems, lower energy consumption and simpler classifiers.

The recovery is clearly favoured by a very find grind. On the other hand, this hampers solid-liquid separation; as a compromise we have therefore opted for 80% minus 200 mesh.

Leaching

Test work on a variety of samples yielded the result that the optimal leaching temperature is 260°C and liquor composition 120 g/L $NaHCO_3$, 20 g/L Na_2CO_3. Oxygen consumption is low, but for some of the samples oxidation requires a certain pressure. In the laboratory autoclaves 6 atm of O_2 has proved sufficient.

The steenstrupine, which contains less than 1% of uranium, is not really dissolved during the leaching process but gradually decomposes and the detritus is removed by attrition in the agitated suspension. Factors like pulp density, method of agitation and reaction time, are therefore interdependent and must be evaluated in connection with the equipment used. From the laboratory results it is estimated that 1 kg of ore suspended in 1 L of liquor can be extracted within 20–40 minutes.

It must be mentioned that recovery is in general far from 100%. Depending on differences in the ore, it may fluctuate between 65 and 80%.

Filtration

In the laboratory separation of pregnant liquor from residue by vacuum filtration presents no problem. With regard to a continuous process it is, however, necessary to know the conditions of obtaining the requisite capacity. Tests with this purpose were carried out, and the results served to select the pilot-plant filters.

Upgrading the pregnant liquor

Before precipitating the uranium, it would be desirable to have the liquor more concentrated than it is after just one extraction (250–300 mg U/L). This may be achieved by reusing the same liquor for treating fresh ore several times before precipitating uranium.

A series of experiments was performed to ascertain that this procedure would not reduce leaching efficiency. In fact, 25 ore samples were extracted successively with the same carbonate solution without decline in uranium yield.

Uranium precipitation

As yellow cake

The uranium carbonate extract obtained has a good relative purity in the sense that other metals dissolve only slightly under the chosen conditions. Precipitation should then take place simply by base addition. However, the above-mentioned organic matter in the ore has been decomposed to a multiplicity of compounds, some of which are powerful complexing agents rendering the yellow cake precipitation incomplete. Moreover, the high concentration of $NaHCO_3$ consumes a large amount of base before precipitation takes place.

As UO_2

An alternative is precipitation of UO_2 by reduction. Certainly, the organic compounds also form complexes with U(IV), but if the reduction is done with iron powder at 265°C the complexing agents are destroyed and the UO_2 is precipitated along with Fe_3O_4, from which it can be separated magnetically.

OUTLINE OF A CONTINUOUS PROCESS

On the basis of data obtained we have suggested a process in which the ore is ground with carbonate leach liquor to a suitable suspension, which is continuously fed to an autoclave with sufficient residence time. The residue is then filtered off and the liquor reused for grinding and extraction. A fraction of the pregnant liquor is removed from the circuit for precipitation of the uranium, after which the liquor is conditioned to its original carbonate content and returned to the circuit.

This simple scheme is complicated by the occurrence of water-soluble sodium fluoride and sodium silicate in the ore. When the circulating liquor has been used for some time, it will be saturated with NaF, and this mineral is henceforth left undissolved in the residue from which it must be extracted by a subsequent washing with water. The presence of sodium silicate means a contribution of alkali to the leach liquor, which must be neutralized by addition of CO_2.

Sulphur in the ore is generally between 0.1 and 0.2%. It is partially oxidized to sulphate in the process, thereby consuming some of the reagent sodium carbonate.

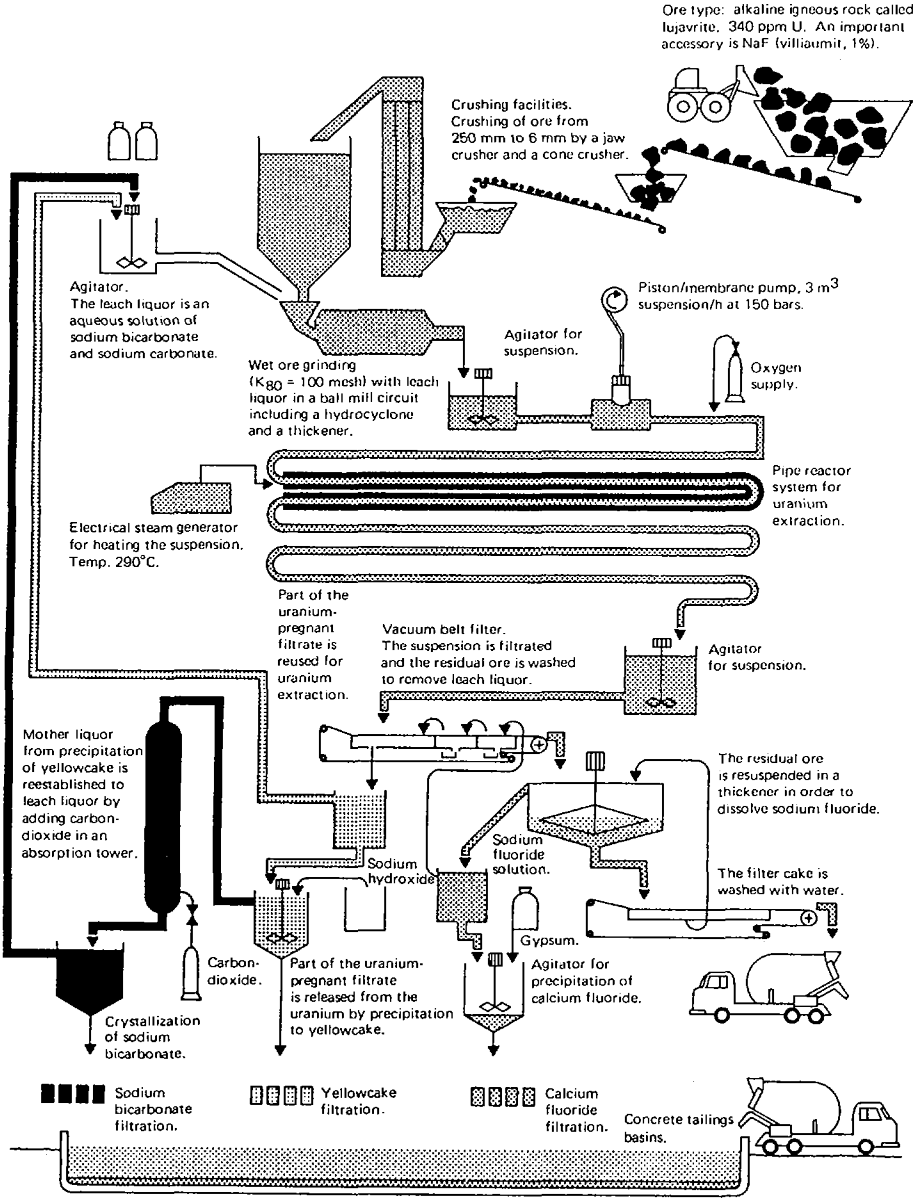

FIG.1. Risø carbonate pressure leaching process pilot plant. Flowsheet for uranium extraction.

PREPARATION AND PROCESSES OF THE PILOT PLANT (Fig.1)

Ore sampling

To a depth of about 60 m only minor amounts of water-soluble minerals are found. So to get a fully representative sample, we cut an adit some 150 m below the surface. 4700 t was chosen from the mined material and shipped to Risø National Laboratory, Denmark.

Crushing and grinding

The crushing station, which for reasons of space is placed 500 m from the rest of the plant, is equipped with a jaw crusher followed by a cone crusher. The product passes a 6 mm screen and is conveyed to a storage silo.

Wet grinding, which is integrated in the extraction circuit, must have a corresponding capacity of 2.2 t/h. To this end a 1200 mm ball mill was chosen charged with 4000 kg of steel balls which should be able to reduce 2.2 t/h from max. 6 mm to 80% minus 74 μm (200 mesh). The ground material leaves the mill with a solid/liquid ratio of 65/35. It is diluted to 25/75 and pumped to a hydrocyclone. The coarse fraction returns to the mill, while the fine fraction is thickened to the density desired in the leaching. The thickener overflow is used for the above dilution.

Pressure leaching

The demand for a reaction temperature near 300°C, a pressure up to 120 atm and a continuous operation favours a tubular flow autoclave with so narrow a bore that the turbulence provides the mechanical agitation of the suspension. At the same time an appropriate flow rate involves a pressure that can be so adapted that it is well above the steam pressure at any point throughout the autoclave. The main advantages are: short retention time, high thermal efficiency and relatively low capital investment and operation costs.

The principle has been employed in the Federal Republic of Germany since 1967 for the Bayer dissolution of bauxite and is dependent on the development of a reliable slurry feed pump.

Our autoclave is composed of a heat exchanger, a supplementary heating zone, a main reaction zone and a pressure let-down pipe.

The heat exchanger consists of a 184 m double-walled pipe. The diameter of the inner pipe is 20 mm and the annular space is 5 mm across. The supplementary heating is done by three 45 m steam mantles, which can be fed with up to 300°C saturated steam. An electrically heated steam generator provides 400 kg/h.

The reaction zone is composed of several sections which can be engaged or bypassed according to the reaction time needed. The total length is 1890 m and the diameter 28 mm.

After the reaction is completed, the suspension is cooled in the heat exchanger and finally gives off its pressure by passing a pressure let-down pipe with a reduced bore (length 50 m, diameter 10 mm). Because of the projected use for alkaline solutions, the construction material is all low-alloy steel. The long pipe is coiled in bundles, but the dimensions still necessitate placing it in the open air. The pipe bundles are thoroughly insulated and protected by an aluminium casing.

The feed pump is a piston-membrane pump in which the piston work is transferred to the slurry via a hydraulic fluid and a rubber membrane. The sturdy valves are made of hardened steel and rubber. Three units with a phase displacement of 120° yield a total of 3 m^3/h at 150 atm. A necessary prepressure of 3 atm is provided by a circulation pump.

Oxygen is supplied by a battery of cylinders through a reduction valve and a flowmeter. The addition may take place at different positions along the flow path.

Filtration

Considering that the amount of circulating liquor should be kept at a minimum and also removed as completely as possible from the residue, we have decided on a belt filter. The filtercloth runs on a track supported by a row of vacuum-connected steel trays, which move at the same speed as the cloth. Periodically the vacuum is disconnected for a few seconds and the trays are quickly pushed back to their initial position, after which the cycle is repeated.

The filter cake is washed with just sufficient liquid to displace the residual uranium pregnant liquor.

Repulping and thickening

Besides some uranium and carbonate, the filter cake still contains most of the solid NaF, which is slightly soluble in a strong sodium bicarbonate solution. The residue is therefore repulped and washed by decantation in a series of thickeners. The clarified overflow is passed through a strongly basic anion exchanger to remove the uranium, after which the fluoride is precipitated with $CaSO_4$ (waste gypsum from fertilizer manufacture).

The underflow is sent to the tailings pond.

RESULTS

The ball mill cycle (Fig.2)

With a power consumption of 73 kW/t and a ball wear of < 1 kg/t, the ball mill has steadily produced a grind of 80% minus 200 mesh.

The classification has benefited by a simple level control applied to the vessel from where the suspension is pumped to the hydrocyclone.

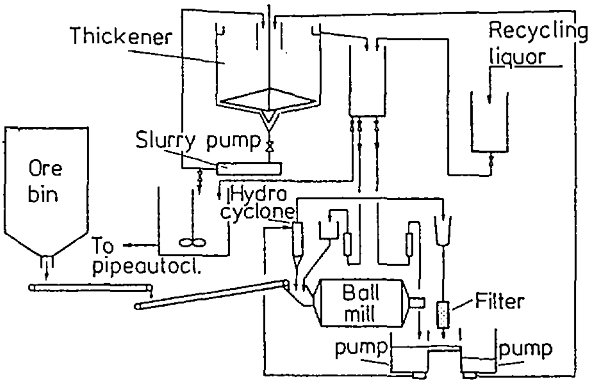

FIG.2. Ball mill circuit.

The piston membrane pump

Given the volumetric capacity of the pump, the effective capacity depends on the slurry composition. Test runs have shown that 1 t of ore per m^3 of fluid is about the heaviest suspension that can be safely pumped. This corresponds to 2.2 t/h of ore.

The pipe autoclave

The processing of 2.2 t/h at 255°C requires 153 kW of supplementary heat, the recovery in the heat exchanger being 85%.

Initial startup takes 4 hours when no latent heat is present in the system. It is done with water, and as the desired temperature is attained a switchover to ore suspension is performed.

Plug flow conditions prevail in the narrow pipe, and mixing between consecutive plugs is small.

Pressure and temperature are distributed approximately as shown in Table I.

Some ore types give off the obtainable uranium in 20 minutes, others take more time. Probably the oxidation is the rate determining step since a delay in oxygen addition leads to lower uranium recovery.

Scale formation in the pipe is first noticed by increasing pressure, next by slower heat transfer. Scale formation seems to be an inherent problem in pipe autoclaves. In the bauxite dissolution process it consists mainly of sodium aluminium silicate. In our case it is much the same, but mixed with compounds of Mn, Fe, Zn, Pb, REE, Th and Ra, which are characteristic of the ore. The scale must be removed by flushing with 1% H_2SO_4 containing an inhibitor to prevent corrosion of the iron pipe.

TABLE I. PRESSURE AND TEMPERATURE DISTRIBUTION IN THE PIPE AUTOCLAVE

	Pressure (atm)	Temperature (°C)
Heat exchanger (in)	100–89	20–220
Heating zone	89–79	220–255
Total reaction zone	79–59	255–245
Heat exchanger (out)	59–50	245–40
Pressure let-down pipe	50–1	40

Erosion is negligible in the main parts of the autoclave since not even the scale is eroded. In the pressure let-down pipe where the linear velocity is 14 m/s wear is perceptible.

Filtration

The filter area is 5.6 m × 1 m of which 1.4 m^2 is used for the primary filtration while the three counter-current washings occupy 1.4 m^2 each. 600 L/h is used in the first washing step in order to obtain constant volume of circulating liquor. 300–350 L/h is left in the sucked-out cake, the remainder being evaporated.

Repulping and thickening

In the pilot plant we only have one thickener from which the underflow is filtered on another belt filter. This arrangement gives an efficient final washing and the best possible concentration of the overflow. For reasons of economy, however, a series of decantation thickeners is recommended for a commercial plant.

Precipitation of uranium

Eighty per cent of the extracted uranium now exists in a strong $NaHCO_3$ solution containing 1500 mg U/L and 20% in the thickener overflow in a NaF solution containing 150 mg U/L. The latter is passed through an ion exchanger, which retains the uranium and leaves an almost pure NaF solution.

TABLE II. CAPITAL COST OF THE KVANEFJELD URANIUM PROJECT
Annual production 4.2 million tonnes of ore.

	US $ X 10^3
Mine	28 111
Premining	10 000
Crushing plant	13 444
Ore handling and storage	7 667
Milling	145 000
Tailings disposal	31 555
Industrial infrastructure	54 000
Social infrastructure	38 555
Administration, startup, etc.	19 111
Total	347 443

Excluding interest accrued during the construction phase. US $1.0 = D.Kr. 9.0.

TABLE III. OPERATING COSTS OF THE KVANEFJELD URANIUM PROJECT
Annual production 4.2 million tonnes of ore.

	Total (US $ X 10^3)	Per tonne of ore (US $)
Mining	11 917	2.83
Milling	29 004	6.91
Replacement	3 993	0.95
Maintenance, buildings	2 321	0.55
Social infrastructure	1 667	0.40
Administration	7 660	1.82
Main office and marketing	671	0.16
Total	57 233	13.62

US $1.0 = D.Kr. 9.0.

By addition of NaOH the strong pregnant liquor yields a yellow cake that is not very pure. The most conspicuous impurities are Na and SiO_2. The supernatant, which retains about 150 mg U/L due to organic complexing agents, is carbonized with CO_2 and reintroduced in the mill cycle.

Precipitation of fluoride

Addition of a calculated amount of gypsum to the NaF solution precipitates the fluoride almost completely as a CaF_2 sludge.

Tailings disposal

So far little experience has been obtained regarding the behaviour of tailings except that residual solubility is low. A few elements exceed the limit for drinking water. The most important ones are Na^+ 1700 ppm, SO_4^{--} 600 ppm and F^- 20 ppm.

PREFEASIBILITY STUDY

A prefeasibility study has been carried out for the deposit in Greenland. In this study it is assumed that the mine will supply 4.2 million tonnes of ore annually to the mill, corresponding to a production of 3 million pounds of yellow cake. The capital cost for the total plant installed in Greenland is calculated at US $347 million (Table II). Operation costs for the total plant are US $13.6 per tonne of ore, of which mining costs amount to US $2.8 per tonne and milling costs US $6.9 per tonne (Table III).

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DISCUSSION

W. GOW: Do you have problems with scale formation in the autoclave? How often do you have to flush the scale out?

E. SØRENSEN: We flush the scale out every 24 hours in the plant, but it may be more or less often according to the operating parameters. We have not made special studies of the rate at which the scale develops under different conditions.

W. FLÖTER: What is the availability of the pipe reactor? How much time is needed for maintenance?

J. JENSEN: We have no maintenance in the pilot plant. We have made some changes in the autoclave during the test period, but we have had no maintenance as such in the pilot plant.

D. NADEN: What is the velocity of the slurry in the pipe reactor?

E. SØRENSEN: It is about 1.5 m/s. It should be sufficient to create enough turbulence to keep the particles suspended.

DEVELOPMENT AND APPLICATION OF SOLVENT EXTRACTION, RESIN ION EXCHANGE (RIP) AND LIQUID MEMBRANE PROCESSES FOR URANIUM RECOVERY

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Abstract

DEVELOPMENT AND APPLICATION OF SOLVENT EXTRACTION, RESIN ION EXCHANGE (RIP) AND LIQUID MEMBRANE PROCESSES FOR URANIUM RECOVERY.

Approximately 50% of uranium produced is recovered by solvent extraction (SX), while resin ion exchange (IX) accounts for approximately 25% and combined IX/SX accounts for most of the remainder. The selection of SX or IX is normally based on detailed considerations of technical feasibility, economic and environmental factors and on the availability of suitable process equipment. The development of improved SX and IX equipment and processes with reduced costs therefore allows greater freedom in selecting the most appropriate process routes and can fundamentally change the economics of uranium recovery, particularly from low-grade and byproduct sources. The development of the Davy McKee Combined Mixer Settler (CMS) for solvent extraction has overcome the disadvantages of high organic recycle, overmixing of aqueous and organic phase and the need for a low suspended solids content of the feed, all inherent in the design of conventional mixer settlers with pump mixers. The effect on equipment size and organic inventory is significant, especially when treating high flows of low uranium tenor solution. The equipment has been convincingly demonstrated at the laboratory, pilot and commercial plant scale in the recovery of uranium as a co-product in gold/uranium plants. Resin ion exchange to recovery of uranium directly from leach pulps (RIP) reduces the need for solid liquid separation and results in large savings in uranium mill capital costs. RIP has, however, not found a wide use largely owing to the operating problems of equipment.
Davy McKee have now developed and piloted an RIP contactor that is more compact and has lower capital costs than conventional equipment. In addition, operating costs are lower and it is easier to operate and maintain. Detailed process and engineering studies have been carried out for uranium recovery from a cyanide leach raffinate stream in a gold/uranium plant. In addition, a new liquid membrane process in the recovery of uranium from phosphoric acid has been developed and is discussed.

1. INTRODUCTION

The recovery of uranium from leach solutions can be accomplished commercially by a variety of techniques including direct precipitation, solid ion exchange and solvent extraction, either alone or in combination. Currently the most widely used unit operation is direct solvent extraction with approximately 50% of commercial plants exploying this technique. Of the remaining commercial plants approximately 25% employ combined ion exchange/solvent extraction process routes and 25% use ion exchange only. The number of plants that directly precipitate uranium from leach liquor is small.

The choice between ion exchange, solvent extraction or combined processes is normally based on a detailed consideration of technical, economic and environmental factors. The decision can be affected by equipment and process developments. Four recently developed uranium recovery systems with which Davy McKee has been associated or has pioneered are as follows:

i) The Combined Mixer-Settler (CMS)

ii) The Continuous Counter-Current Ion Exchange Contactor (CCIX)

iii) A Resin-in-Pulp (RIP) system

iv) The Liquid Membrane (LM) process for recovery of uranium from phosphoric acid.

The selection and advantages of solvent extraction, ion exchange (CCIX and RIP) and membrane processes for uranium recovery from solutions, however produced, are discussed below, special attention being given to the more recently developed unit operations.

2. DISCUSSION OF PROCESS APPLICATIONS

For the purposes of designing extraction equipment solutions containing uranium may be classified as clear solutions eg following filtration or clarification of liquors from a wide range of sources, cloudy solutions (before clarification) and liquors with high solids content eg leach slurries (or pulps). These solutions may be acid sulphate or phosphoric acid or alkaline (usually sodium carbonate).

Solvent extraction has always been the preferred extraction technique for recovery from clear solutions, while until recently fluid bed continuous ion exchange has been used for solutions containing up to 1% solids and resin in pulp (RIP) technology has found a unique use for recovery directly from leach slurries

Solvent extraction has chemical advantages over ion exchange for recovery from acid solutions and solutions with high salts content while ion exchange is the only extraction technique suitable for recovery from carbonate solutions.

Ion exchange has two inherent process advantages over the solvent extraction route. It can treat solutions with a high suspended solids content and it does not introduce potential process and environmental contaminants into the discharge solutions. Further, it can have a cost advantage in the treatment of high flowrates of low uranium tenor solution.

Liquid membrane extraction operates by direct transfer of uranium through the membrane phase to the internal phase and the membrane phase does not load. Liquid membrane technology is especially useful when the extraction coefficients of both solvent extration reagents and ion exchange resins are low eg uranium recovery from phosphoric acid. Liquid membranes therefore offer a new opportunity for difficult process situations.

3. COMBINED MIXER SETTLER

3.1. Introduction

The operation of the various sections of the solvent extraction process for the recovery of uranium from dilute acid leach solutions are usually characterised by feed flow ratios in the range 1:20 to 20:1 organic to aqueous phase. Under such conditions the overall operation of the widely used mixer settler becomes inefficient and recycle of the minority aqueous or oganic phase is practised to enable the mixer settler to operate in the preferrred organic/aqueous ratio range of 1:2 to 2:1 [1].

The adverse consequences of this requirement for all plants employing impeller induced recycle are threefold:

i) the contacting equipment has to accommodate an internal minority phase flow greatly in excess of the minority phase flow requirement based on overall process considerations.

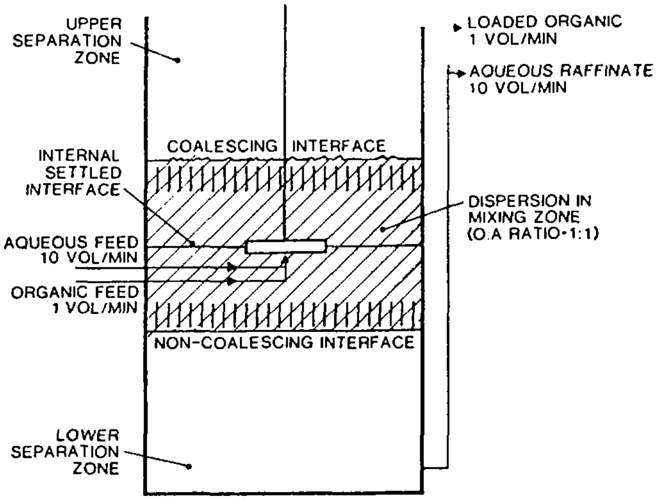

FIG.1. Davy McKee CMS unit.

ii) the provision of large diameter recycle lines with their accompanying valves increases plant capital cost and operational complexity.

iii) the increased pumping duty imposed by the recycle requirement increases the potential for overmixing with a consequent increase in settler size and entrainment loss.

Davy McKee's CMS design concept, shown schematically in Fig 1, overcomes the problems related to minority phase recycle.

3.2. Description of the Davy McKee Combined Mixer Settler (CMS)

The Davy McKee CMS contactor consists of a single vessel in which three zones co-exist under operating conditions; an upper separation zone containing separated organic phase, a lower separation zone containing separated aqueous phase and a central, impeller agitated, zone containing dispersion. Mass rotation/turbulence damping baffles are positioned at the boundaries between the central mixing and upper and lower separation zones.

The major feature of the CMS concept is that the organic:aqueous ratio in the dispersion is independent of the

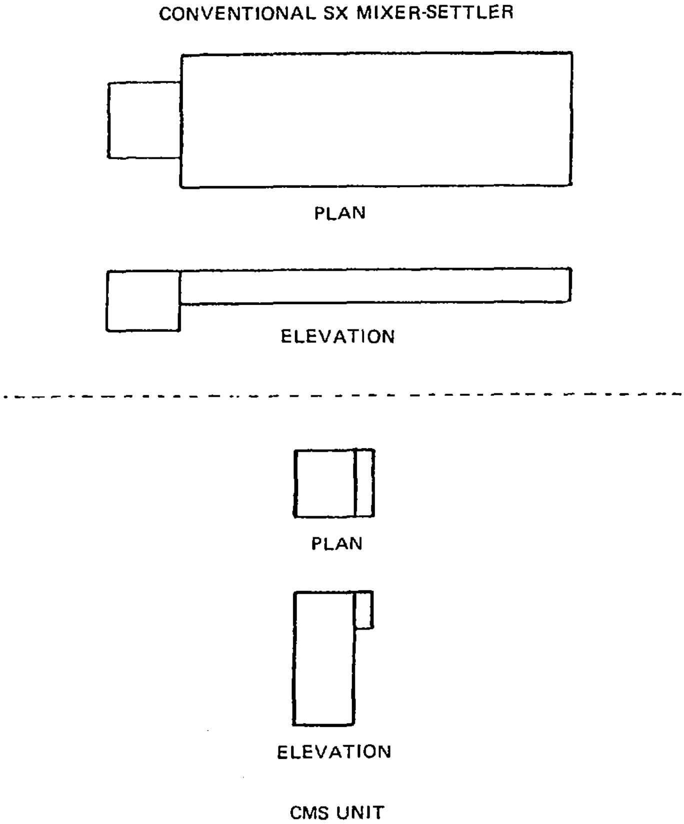

FIG. 2. Comparison of space requirements.

feed flow ratio but is a function of the position of the impeller relative to the settled interface between the organic and aqueous phases within the vessel. As this settled interface position is directly related to the positions of the organic and aqueous weirs, control of the organic:aqueous ratio in the mixing zone at any preferred value can be readily achieved.

The elimination of the need to recycle the minority phase also means that its flow through the CMS unit is significantly less than that through a comparable conventional mixer-settler. Therefore, by selecting to have the minority feed phase dispersed, the minority phase coalescence rate can be replaced by the majority phase separation rate as the determinant of separation area requirements. As majority phase separation rates of up to 50 m^3/m^2h have been shown to be achievable during CMS operation a marked reduction in equipment plot area results. A comparison of plot area requirements for conventional and CMS equipment when treating an aqueous flow of 350 m^3/h is given in Fig. 2, the comparable separation rates being 4.4 and 30 m^3/m^2h aqueous flow.

At feed flow O/A ratios at, or close to, 1:1, the minority phase coalescence rate again becomes the determinant of separation area and it might be expected, therefore, that the separation area requirements of the CMS and conventional mixer settlers would become comparable. However, this is not the case, as the coalescence rates of dispersion produced by the CMS have been shown to be markedly faster than those produced by more conventional equipment, values of 20 to 30 m^3/m^2h single phase being obtained when treating unclarified aqueous feed. Thus, economically attractive application of the CMS to high grade leach solution treatment is indicated.

Another important feature of CMS operation is the tolerance to suspended solids. Pilot and commercial plant operation in South Africa, and laboratory studies in Davy McKee's Research and Development facility in the UK using South African and Australian derived solids, have all clearly demonstrated that the CMS can continuously handle feed streams containing significant amounts of suspended solid without any of the problems that such conditions would bring to the operation of conventional mixer settlers. Thus, the CMS offers the possibility of reducing the major capital and operating costs of the up-stream solid liquid separation section.

The ability of the CMS to treat 'dirty' feed solution without problem is seen as a significant advantage over conventional equipment. However, operation with feeds containing low or nil suspended solids has also been demonstrated at laboratory and pilot plant scale. Significant decreases in separation area requirements compared to conventional mixer settlers were again demonstrated, although smaller flow/unit area loadings were indicated compared to CMS operation with solid containing systems.

3.3. Commercial/Development Status

The Combined Mixer Settler is an in-house, patented, Davy McKee concept which has been successfully developed to commercial scale as a low capital cost alternative to conventional mixer settlers in the uranium solvent extraction process [2].

Three commercial scale plants have been built in South Africa, a three stage 100 m^3/h aqueous flow unit for the Millsite operation of the Randfontein Estates Gold Mining Company, a 4 stage 250 m^3/h aqueous flow unit for the Western Areas Gold Mining Company, and a two stream, four stage per stream, 700 m^3/h total aqueous flow unit for the Randfontein Estates Gold Mining Company's Cooke site operation. The latter two plants were commissioned in 1982 and have been in continuous operation since that date.

All three commercial plants incorporate integral organic recovery systems, as at the high aqueous phase loading rates used, organic entrainment values from the CMS units are higher than those resulting from the operation of more conventional equipment. Each plant has a different system, the REGM Cooke plant using dispersed air flotation, the WAGM plant using sand bed coalescers and the REGM Millsite plant using a gravity after settler.

The principal cost advantages resulting from the adoption of Davy McKee's CMS as the preferred equipment design are those related to capital. Detailed analysis of this capital cost advantage, based on the use of the CMS in extraction only on a typical South African uranium plant of 250 m^3/h aqueous capacity, has shown that a 25 to 30% differential between a CMS and a conventionally based plant exist [3]. Application of the CMS in other areas of the solvent extraction flow sheet, as discussed later, has been estimated to increase this capital cost saving to 40-50%.

3.4. Future Potential

3.4.1. Extraction Section

Successful CMS operation is not confined to systems described above. Laboratory based work has shown that operation with feed flow ratios of 1:1 also yields a commercially attractive performance. Successful application of the CMS to high grade leach solutions typically produced in Canada, Australia and Central Africa is therefore indicated. Similarly, demonstration of successful operation with clarified aqueous solutions has occurred at both laboratory and on-site pilot plant scale. However, recent confirmation that Australian derived leach residue solids act similarly to South African leach residue solids in respect of CMS operation, suggests that the unique solid tolerance of the CMS will be of significance in many of the major uranium producing areas of the world. Consequently capital cost benefits in the solvent extraction and upstream solid-liquid separation areas of the flowsheet similar to those demonstrated by the commercial CMS operation in South Africa are to be expected.

3.4.2. Scrub, Strip and Regeneration Sections

Current commercial CMS based solvent extraction plant operations in South Africa utilise conventional mixer settlers in the above sections. The reasons for this are primarily economic and not technical, resulting from the limited capital cost contributions of these sections in a typical South African uranium solvent extraction plant flowsheet. This is not, however, the case when treating high grade U_3O_8 feeds, and studies have indicated that application of CMS technology in these areas could yield plant capital cost savings of 40 to 50% compared to conventional designs.

Present knowledge, based in part on previous pilot plant operation in South Africa, and current developments by Davy McKee, has indicated that the present CMS design can be successfully applied to the scrub, chloride strip and regeneration sections of conventional uranium circuits with considerable capital cost benefits. Application in the ammonium sulphate 'hydrolysis' strip process is not currently considered viable due to the requirement for vigorous agitation to avoid localised high pH and ADU precipitation.

4. RESIN ION EXCHANGE

4.1. Design of Equipment for Uranium Extraction by Resins

The slow kinetics of ion exchange processes require that the residence times of the resin in the system should be long while low capital and operating costs are achieved by short solution residence times, efficient resin utilisation and counter-current flow of resin and solution. These objectives are achieved by difference methods in the fluid bed ion exchange and the stirred contactor resin-in-pulp systems described below.

4.2. Fluid Bed Ion Exchange

The treatment of solutions containing low concentrations of suspended solids is possible using fluidised bed technology. Although a number of different designs are available they can be classified into either column (eg Cloete-Streat, NIMCIX and Himsley) or horizontal vessel (eg Porter) types.

The Davy McKee design is based on the Cloete-Streat fluidised bed column concept which operates in a continuous, counter-current mode (CCIX). It consists of a vertical loading column separated into discrete stages by perforated plates which prevent the free mixing of resin and solution with the column. In operation the resin is fluidised in each stage by the upward flow of the feed solution which is controlled so that resin is not flushed from the contacting stages. Counter-current resin flow is achieved by allowing the feed solution to back flow. The adverse density relationship prevents this system being used for solutions with high solids content. Resin elution may be carried out in a multistage, fluid bed column contactor similar to the loading column or in a single packed bed contactor. The latter flowsheet is shown in Fig. 3. [4].

The Cloete-Streat CCIX design results in a compact plant which is amenable to automatic operations and is capable of extractions from solutions containing suspended solids. However the ability of the CMS to process acid sulphate solutions containing significant quantities of suspended solids has extended the operating range of the solvent extraction process into this type of solution. Fluid bed CCIX will, however, continue to find an application in recoveries from carbonate solution and when zero contamination by organics is important.

Many fluid bed CCIX columns are currently in commercial operation worldwide and equipment of this design may therefore be considered to be well-proven. Davy McKee has constructed plants in South Africa at the Rand Estate Gold Mining Company Plants of Mill and Cooke Site.

4.3. Resin-in-Pulp (RIP)

4.3.1. Introduction

The resin in pulp (RIP) process eliminates the need for ore washing and solid-liquid separation in the uranium recovery flowsheet and therefore significantly reduces plant capital costs. A study carried out by Davy McKee has shown that a capital cost saving of 35% can be made in the post leach section of the flowsheet which translates to a 15% saving in the overall uranium mill cost ie ore crushing to ammonium diuranate (ADU) precipitation [4] [5].

The wide scale use of RIP depends on the operation of a reliable method of separating resin and pulp. In RIP plants currently operating in the USA resin and pulp are air-lifted to vibrating external screens, this method has limitations in terms of pulp density, resin concentration and throughput however.

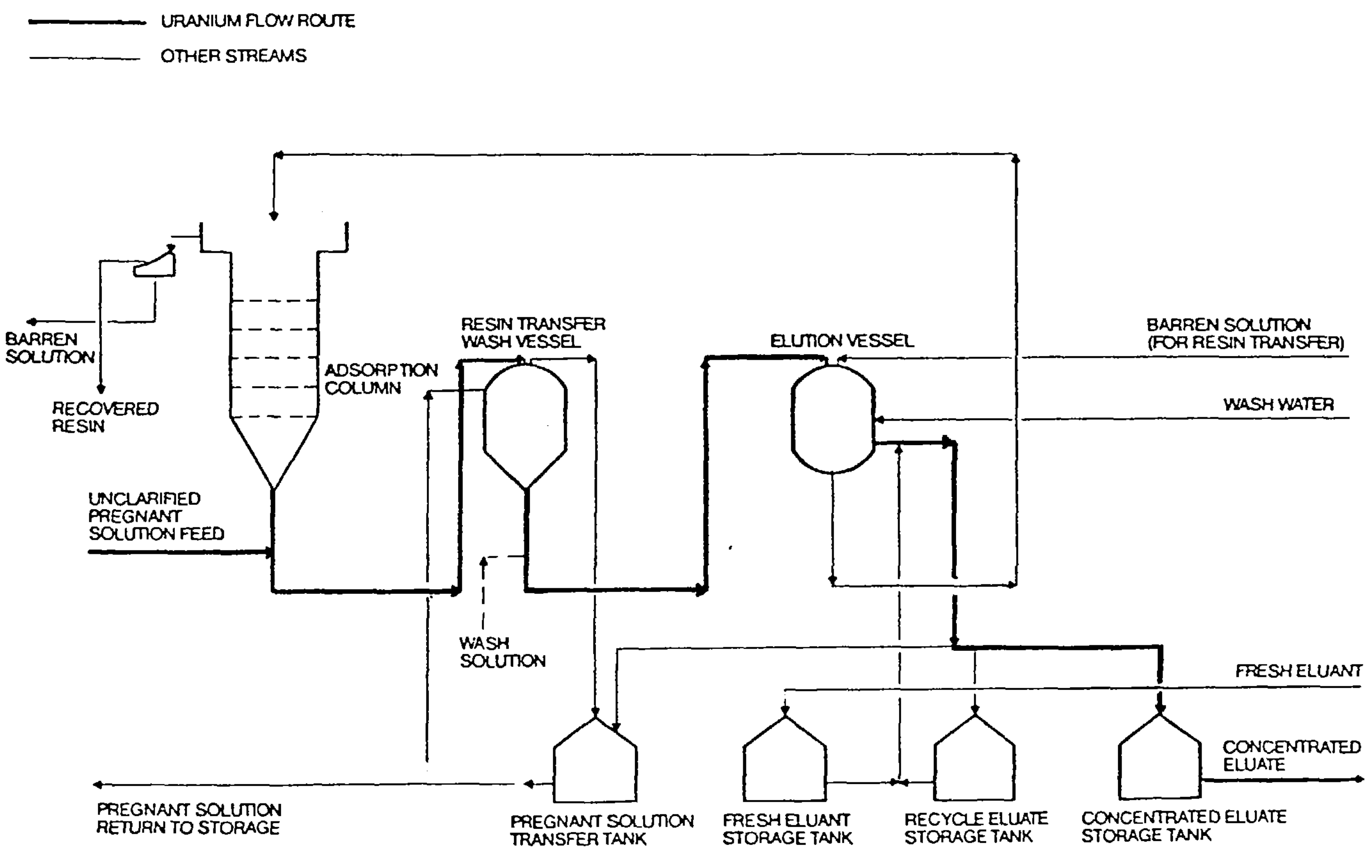

FIG.3. CCIX flowsheet.

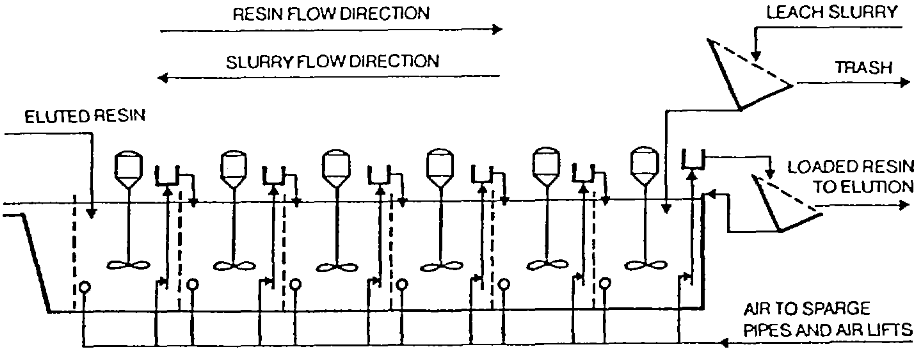

FIG.4. Davy McKee RIP contactor.

An improved system of retaining carbon in the contacting stages in carbon-in-pulp (CIP) recovery of gold has recently been developed and demonstrated by Mintek in South Africa. These operating CIP plants use air swept interstage screens and it is this system which has been adopted and improved by Davy McKee in the new high resin concentration (HRC) RIP process.

4.3.2. Description of the High Resin Concentration (HRC) Contactor

The Davy McKee HRC contactor is shown diagrammatically in Fig. 4. The contactor typically consists of a series of connecting stages with a box-type configuration in horizontal arrangement, each stage having a common side wall with the next. At least part of the common wall can consist of an air-swept screen and feed slurry, introduced into the first contactor passes from stage to stage through the screens. The screen wire spacing is selected to be intermediate between the resin bead size and the ore particle size so that the resin is retained in the stage while the slurry passes through. The curtain of air bubbles in front of the screen causes the resin to float rapidly upwards in order to prevent screen blocking. Resin is moved either periodically or continuously in countercurrent flow using air lifts and loaded resin is passed from the last stage to washing screens then to elution. Resin elution can be carried out in similar HRC equipment or, alternatively, in packed bed or multistage fluid bed contactors.

The advantages of the HRC contactors for uranium recovery from pulps over conventional RIP contactor currently in use in the USA are as follows:

a) Deep submerged air-swept screens enable a high slurry flowrate to be achieved in the presence of high resin concentrations.

b) The high resin concentration allows a significant reduction in slurry contact time and hence a reduction in stage volume and equipment capital cost.

c) The compact continuous countercurrent equipment with no external screening leads to a significant reduction in operating costs and increased ease and reliability of operation.

The contactor design is the subject of patent applications [6].

4.3.3. HRC Contactor Development Programme

The HRC contactor resin screening system was developed in a two stage pilot plant with a capacity of approximately 115 litres/minute of slurry flow in the Davy McKee pilot facility in Stockton-on-Tees, England. The initial development work was carried out using both synthetic and real slurries obtained from a uranium production site. Both wedge wire and woven wire screens with a range of screen wire spacing were used in the test programme and the interaction of the following variables were observed.

a) Screen variables - screen type and wire spacing, screen exposed area and depth.

b) Slurry variables - density, viscosity and flowrate.

c) Resin variables - bead size and concentration in the slurry.
d) Air cleaning of screens - air flowrate, location of air curtain.

e) Method of slurry agitation in the stage to assist retention of the air curtain at the screen surface.

At the same time a programme of kientic studies was carried out on resins obtained from various sources, including resins aged in operating uranium extraction plants, in order to select preferred resin types and to develop a process design technique for countercurrent operation in stirred contactors.

The programme was completed by a case study of uranium recovery from a gold plant tailings stream from an operating gold/uranium plant. The settling rate and filtration characteristics of the material are such that it was difficult to treat it in any other way than by RIP and hence it is physically typical of many other applications in which the ore has a high clay content or in carbonate leach slurries.

The ore was leached in the laboratory in order to determine leach rates and tests were carried out to determine resin loading characteristics. A pilot plant programme in the Davy McKee HRC pilot plant was also carried out on leached ore to determine screen design parameters, air usage, etc.

The results of the development programme are as follows:

a) Sufficient information is now available on the effect of slurry characteristics, resin concentration on screen throughput to enable the deep submerged air-swept screens to be designed on a case by case basis.

b) The number of countercurrent contacting stages, resin inventory, residence time per stage, flow etc can be calculated following the determination of resin kinetics and loading in bench scale tests.

c) Combining the information from (a) and (b) above on resin kinetics and screen throughput the size of each RIP contactor can be determined.

4.3.4. RIP Plant and Operating Costs

Using the information generated in the experimental programme case study the capital and operating cost have been estimated for leaching and RIP uranium recovery (including resin elution and regeneration) of 10,000 tonnes per month of ore following a cyanide leach for gold recovery. Ore milling costs were not included as this has already been carried out for gold recovery. Solvent extraction (SX) purification of the solution and ammonium diuranate precipitation capital and operating costs have however been included.

Both the gold leach and the uranium leach and RIP were carried out using a 40% w/w solids slurry and it was assumed that following RIP the barren plant tailings would be pumped to the tailings dam at the same concentration. A problem associated with acid uranium leaching following gold leach by cyanide is the need to either destroy cyanide or to treat the HCN produced and this entailed additional capital and process costs.

Table 1. Costs of Uranium Recovery from Slimes
10,000 tpm ore, uranium recovered
a) 8,000 Kg/month
b) 5,000 Kg/month

Capital costs			US$
Leach Plant (including HCN recovery)			1,300,000
RIP Plant (including resin)			1,620,000
SX and ADU precipitation (including SX reagent)			1,200,000
Total Capital Cost			4,120,000
Operating costs			**c/tonne ore**
Leach plant			527
RIP and SX			149
Downstream costs (including lime for neutralisation)			84
Total Operating Costs			760
Cash Flow	**$44/ Kg U O**	**$55/ Kg U O**	**$66/ Kg U O**
Monthly revenue $ (a)	352,000	440,000	528,000
(b)	220,000	275,000	330,000
Monthly operating cost $	76,000	76,000	76,000
Net monthly revenue $ (a)	276,000	364,000	452,000
(b)	144,000	199,000	254,000
Capital payback time - months (a)	15	11	9
(b)	29	21	18

The results of the cost study, modified for wider applicability, have been converted to capital and operating costs and these are summarised in Table 1. Two rates of uranium production have been assumed, 8,000 kg/month and 5,000 kg/month. A simplified cash flow taking into account operating costs (including labour and maintenance) of the leach and RIP, SX and ADU precipitation sections has also been carried out and the revenue and payback time of the plant has been calculated. Details of taxation etc will vary from location to location and are not given. In order to take into account variations in uranium price three selling prices $44, $55 and $66/kg U_3O_8 have been assumed.

The Table shows that even at a uranium price as low as \$44/kg the proposed RIP uranium plant is economically attractive. Such byproduct streams should therefore be reconsidered as a source of uranium in view of the development of a reliable RIP contactor.

5. URANIUM EXTRACTION BY LIQUID MEMBRANES FROM WET PROCESS PHOSPHORIC ACID

5.1. Introduction

Approximately 2000 t/a of U_3O_8 are now produced as a byproduct from wet process phosphoric acid making this a minor but still significant source of uranium. All commercial processes currently in operation use solvent extraction (SX) technology.

i) Di-Ethyl Hexyl Phosphoric Acid (DEHPA) and Trioctyl Phosphine Oxide (TOPO). The extraction co-efficient of DEHPA-TOPO decreases markedly as the concentration of acid increases and the process cannot be considered for use on acid produced in the high strength (34% P_2O_5) hemihydrate process.

ii) Octyl Phenyl Phosphoric Acid (OPPA). This reagent is employed to extract tetravalent uranium and it has a high extraction co-efficient. The reagent is cheaper than the DEHPA-TOPO mixture and can potentially be used to extract uranium from higher strength acids.

Both of the above solvent extraction systems can suffer from phase disengagement problems and it is normally necessary to utilise extensive pretreatment facilities ie for removal of solids and organics from the feed.

5.2. Liquid Membrane (LM) Technology

Liquid Membrane (LM) technology offers a new approach to the recovery of uranium from phosphoric acid [8] [9]. The production of a liquid membrane system initially involves the generation of a water-in-oil emulsion. The dispersed phase droplets also known as internal phase droplets are about 1 to 10 microns in diameter [7]. The internal phase is directly analagous to the stripping medium employed in the SX process. The internal phase droplets are surrounded by an organic membrane phase which contains a complexing agent. In the case

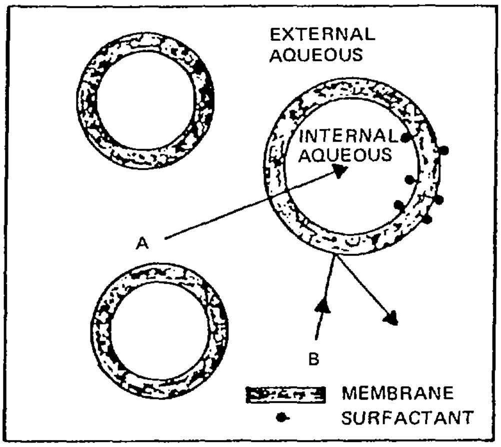

FIG.5. The liquid membrane system.

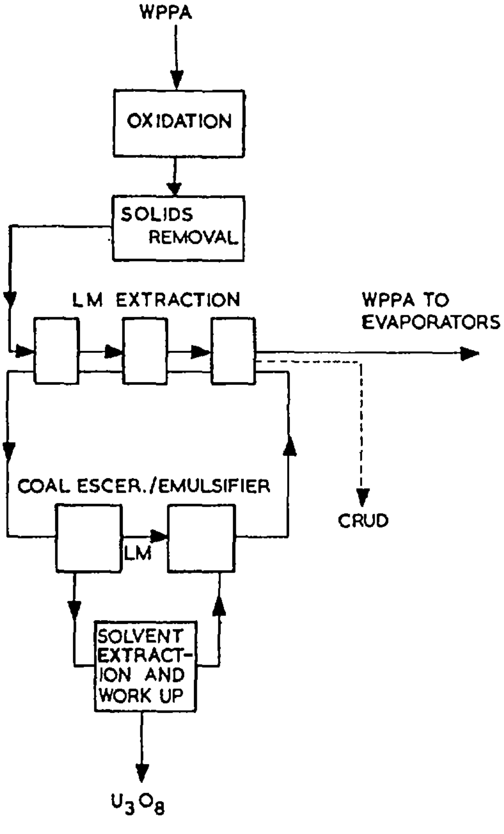

FIG.6. Liquid membrane block diagram: U from WPPA.

of uranium recovery from phosphoric acid this agent would be either DEHPA-TOPO or OPPA. Emulsion stability is achieved by the addition of a surfactant to the organic phase.

The emulsion is then dispersed in phosphoric acid feed liquor in the form of globules having diameters in the range of 0.1 to 1.0 mm. Each globule contains many thousands of the internal phase droplets. For simplicity in illustrating the principle of selective LM separation of species A and B a globule may be depicted as a single sphere (see Fig. 5). Uranium is extracted from the feed solution into the membrane phase and is then re-extracted into the aqueous internal phase. The capacity of the emulsion is high as the organic phase never achieves saturation loading.

5.3. Liquid Membrane Flowsheet

Fig. 6 illustrates conceptually the LM extraction flowsheet as it would be applied to uranium recovery from phosphoric acid. The process consists of three steps ie:

i) Emulsion Making in which the organic phase (containing for example DEHPA-TOPO) is contacted with depleted strip liquor (internal phase) in an emulsifier to generate a stable water-in-oil emulsion.

ii) Extraction in which the emulsion is contacted with uranium-bearing acid. This operation is performed in mixer-settlers.

iii) Emulsion Breaking in which the emulsion is separated into its component parts ie: membrane for recycling and uranium-rich internal phase for further processing to recover uranium.

The liquid membrane process has been developed from fundamental studies in which the basic steps of the process were defined in detail on a laboratory scale, through a bench scale programme in which most of the process was tested on a continuous basis at a feed acid flowrate of 0.1 l/min. The development was demonstrated in field trials in which all steps in the process were run continuously at an acid flowrate of 1.0 l/min. A five month on-site test programme was carried out and numerous 48 to 100 hour runs were made.

5.4. Advantages of LM Technology

The LM process has been studied using DEHPA-TOPO extractant as this is the most commonly employed extractant.

The advantages of LM over solvent extraction include lower operating costs than conventional processes, the ability to treat black acids directly without prior cooling and the ability to treat high strength acids (up to 45% P_2O_5). Hence the process would be applicable to the recovery of U_3O_8 from hemihydrate acid.

5.5. Current Status of LM Technology

Exxon (USA) invented and developed the technology used in the LM process and hold numerous patents. Davy McKee have conducted work under contract to Exxon for copper recovery and uranium recovery for phosphoric acid. Davy McKee have also been involved in the development of the technology, hold a patent in the field of emulsion breaking and have a licence agreement with Exxon to develop and commercialise the process.

The point has been reached where the participation of a phosphoric acid producer would be beneficial to the further development of the technology. There is scope for further improving LM technology [9] and definitive scale-up data in critical areas must be outlined in order to establish the design basis for a full scale plant.

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DISCUSSION

E. SØRENSEN: Is there a concentration difference between the two sides of the liquid membrane?

D. NADEN: There will be a concentration of uranium into the internal phase, depending on the concentration of the extractant within the emulsion. And of course, in the case of this extraction process, there is a reduction from U-VI to U-IV within the globule, within the internal phase droplet, and this can lead in fact to a very high concentration of uranium in the internal phase. It is in all respects very similar to solvent extraction. What you can do in solvent extraction you can also do in liquid membranes. The advantage is that it is now a transfer process rather than a loading process and so loading in the globule can be far higher than loading in a droplet of organic phase in a conventional solvent extraction process.

W.T. RUHMER: We have experienced problems with work in resin-in-pulp because of the difficulty in screening out all the extraneous material (like wood fibre and plastic from explosives) that you find in underground ore. A very effective and efficient means of removal has to be designed. In addition, the resins themselves tend to degrade at an unacceptable rate due to the abrasiveness of the pulp in which the resin is being agitated. Have you developed any resins recently that could withstand these abrasive conditions?

D. NADEN: I think the problem of extraneous materials is being overcome now in South Africa in the CIP plants, by the design of a suitable screening. Having identified the problem, equipment is being installed to solve it. On the question of the resins, Davy McKee do not develop resins but we are in contact with the resin manufacturers. The abrasive nature of the pulp will change from one location to another. RIP has been used in the USA, in Wyoming, for some twenty years now, and they claim losses from the slime stream of about 30% per annum. Actual losses are probably closer to 60% per annum. One should not use RIP with an extremely abrasive material. Also, one should try to settle out the larger material, maybe that larger than 200 mesh, and to have a splitting system of some sort: cyclone washing combined with cyclone washing of the oversize and combined with RIP of the mixed wash solution and the undersize.

Z. DOGAN: I had the impression that liquid membranes will one day just about replace solvent extraction. Do you think there is such a possibility?

D. NADEN: I do not believe anything is going to replace solvent extraction. Liquid membranes have a place in extractive metallurgy: their place will be in extraction from difficult solutions, like the ones we described here today, where the equilibrium coefficient is low. They are going to be used for the specialized, the difficult things, like recovery of metals from very dilute solutions.

Z. DOGAN: What surfactants are you using in the liquid membrane systems?

D. NADEN: There is nothing mystical about the surfactants. They are chain amine compounds.

I. EZAHR: You said that the liquid membrane process can be used with concentrated phosphoric acid. What is the highest concentration of acid that the process can tolerate?

D. NADEN: The liquid membrane process can be used with all commercial grades of phosphoric acid up to 40–45% P_2O_5. This includes acid recovered from the hemi-hydrate process ore from evaporation of the so-called green or black acids. We are limited to 45% P_2O_5 because we are using DEPA/TOPO but one could use the process on more concentrated acids using other reagents such as OPPA.

K. CHITUMBO: You indicated that the operating costs of the liquid membrane process are lower than those of conventional solvent extraction by about 15 dollars per kg of recovered uranium. Is this correct?

D. NADEN: You have to be careful with these comparisons. The figure I gave applies to the extraction of uranium from black acids, but the difference could be much less if you are dealing with a white acid or a pale green acid.

K. CHITUMBO: What are the specific areas where you cut down the cost?

D. NADEN: Costs are lower for several reasons: there is no need to cool the acid before the liquid membrane extraction, the kinetics are improved by the higher temperatures and the organic inventory is reduced. Two years ago we presented a paper at the Manchester University Meeting in which these things are explained in great detail.

UTILISATION DES COLONNES PULSEES DANS LE TRAITEMENT INDUSTRIEL DES MINERAIS D'URANIUM

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Abstract–Résumé

USE OF PULSED COLUMNS IN THE INDUSTRIAL PROCESSING OF URANIUM ORES.

In France considerable progress has been made with pulsed columns in reprocessing in the last 20 years. Research on applications outside the reprocessing field was initiated as a result of this success. A major extension programme was undertaken by the Marcoule Institution of the Commissariat à l'énergie atomique (CEA) which focused on increasing the scale and simplifying components. A commercial enterprise was set up at the same time to market solvent extraction equipment based mainly on studies and experiments carried out by the CEA. A large-scale industrial application for extracting uranium from leach liquors has thus been developed.

UTILISATION DES COLONNES PULSEES DANS LE TRAITEMENT INDUSTRIEL DES MINERAIS D'URANIUM.

En France, les colonnes pulsées ont connu depuis vingt ans un développement important dans le retraitement. Leur succès a conduit à rechercher des applications en dehors du retraitement. Un programme important d'extrapolation a été entrepris dans l'Etablissement de Marcoule du Commissariat à l'énergie atomique, portant sur l'augmentation des dimensions et sur la simplification des composants. Parallèlement, un groupement d'intérêt économique a été constitué pour commercialiser les équipements d'extraction par solvant, à partir surtout des études et des expériences réalisées par le CEA. C'est ainsi qu'une application industrielle à grande échelle a pu être effectuée pour l'extraction de l'uranium à partir des liqueurs d'attaque des minerais.

1. RAPPEL DES CARACTERISTIQUES DES COLONNES PULSEES

Une colonne pulsée est un extracteur continu (fig.1) qui comprend:

– un cylindre vertical contenant un garnissage constitué de plateaux fixes perforés ou en chicane (fig.2);

– deux parties plus larges aux extrémités: l'une de ces parties sert de décanteur unique, l'autre permet l'introduction d'une phase;

– un système de pulsation qui agite périodiquement les phases: le système de pulsation peut être constitué par un tube parallèle à la colonne (appelé jambe de pulsation) de diamètre environ 3 fois plus faible et dans lequel on injecte périodiquement de l'air comprimé.

Dans l'extraction liquide-liquide, une phase est continue et l'autre dispersée. Les débits traités dans une colonne varient avec:

– la nature et les propriétés physico-chimiques des phases telles que la viscosité, la masse volumique et la tension interfaciale;

– les caractéristiques de pulsation, c'est-à-dire l'amplitude et la fréquence;

– le rapport des débits des phases.

Une phase continue est choisie a priori, généralement la phase réceptrice. Une caractéristique très intéressante des colonnes pulsées est qu'elles acceptent sans recyclage un débit de phase dispersée pouvant atteindre 10 à 15 fois celui de la phase continue.

En fonctionnement normal, la phase lourde est alimentée en haut et soutirée au fond; pour la phase légère c'est l'inverse.

La dispersion, caractérisée par le taux de rétention (fraction du volume de colonne occupé par la phase dispersée), est obtenue par la pulsation. La figure 3 donne un faisceau de courbes de variation du taux de rétention en fonction du produit amplitude-fréquence.

Il existe une valeur critique du taux de rétention pour laquelle la colonne s'engorge, c'est-à-dire que les phases ne sortent plus par l'extrémité normale. Cette valeur varie aussi avec les caractéristiques de pulsation et le rapport des débits des phases. A cette valeur du taux de rétention correspond, toutes choses égales d'ailleurs, un débit maximal (somme des débits des deux phases) pouvant transiter dans la colonne. On l'appelle débit d'engorgement (fig.4). Pour une utilisation industrielle on choisit un débit total qui n'excède pas 90% de ce débit.

Le fonctionnement est régulé en maintenant stable le niveau d'interphase. On détecte sa position et on agit sur le soutirage de la phase lourde pour le maintenir. Ce soutirage peut être réalisé par un pot sous pression modulée, par un air-lift ou par écoulement gravitaire régulé par une vanne. La détection du niveau d'interphase peut être réalisée par bullage d'air, par sondes de conductivité et par absorption de rayonnement. Ce dernier système, extérieur à la colonne, est peu sensible à la variabilité des phases et à la présence des crasses que l'on rencontre toujours à l'interphase.

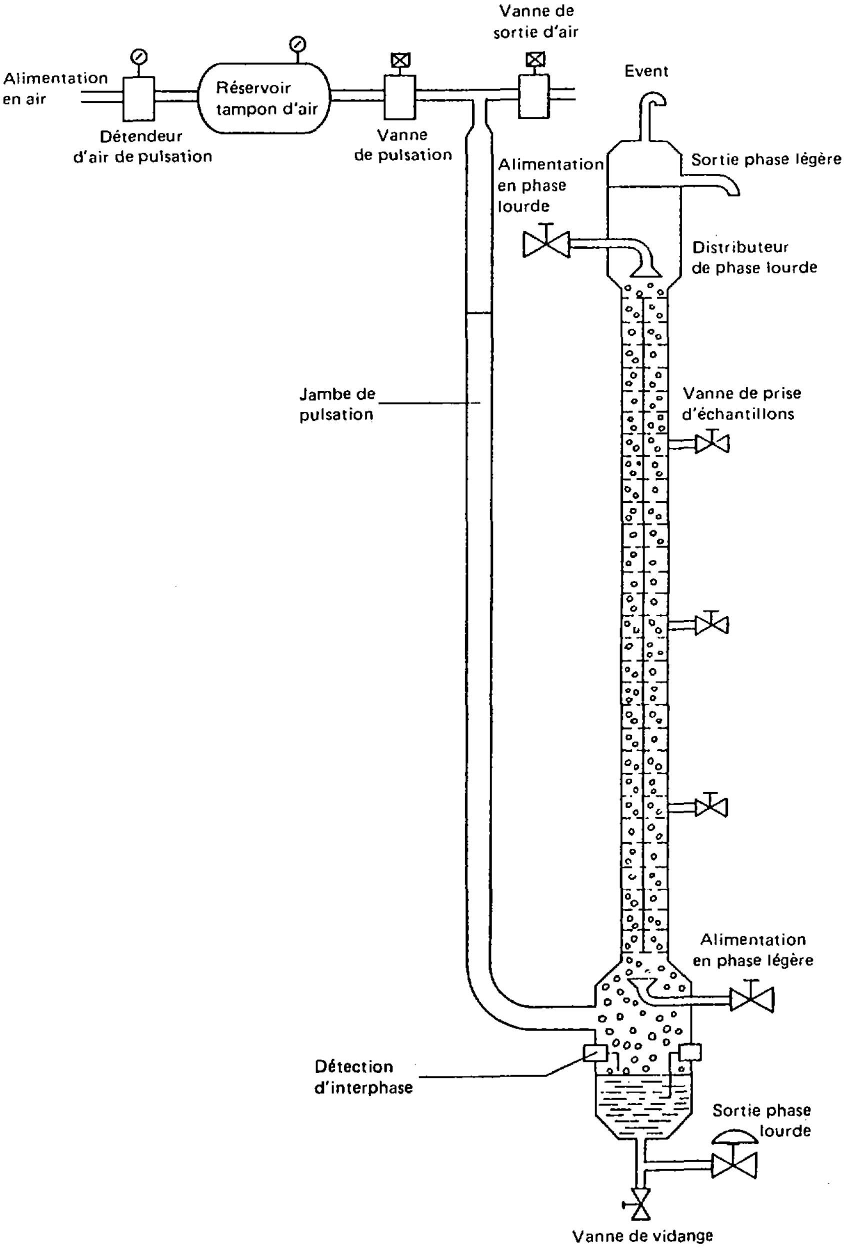

FIG.1. Schéma de principe d'une colonne pulsée pour extraction liquide-liquide.

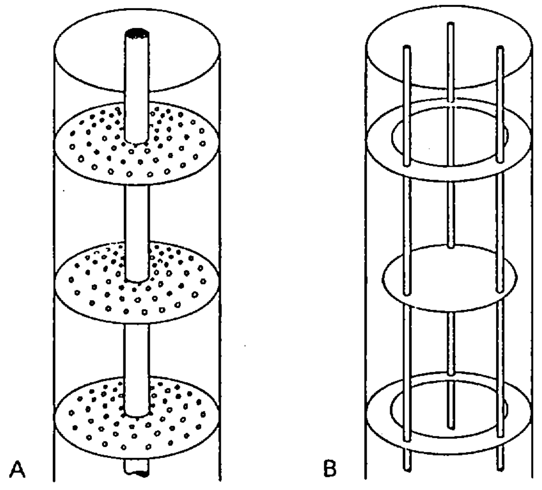

FIG.2. Les deux principaux types de plateaux. A: empilement à plateaux perforés; B: empilement à disques et couronnes («chicanes»).

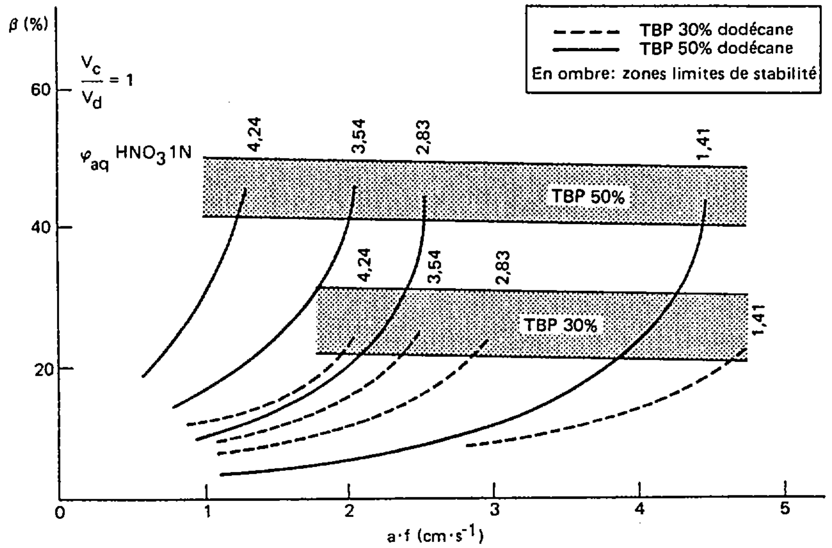

FIG.3. Rétention en fonction du produit amplitude X fréquence (a·f) à différents débits spécifiques pour une colonne de 300 mm de diamètre.

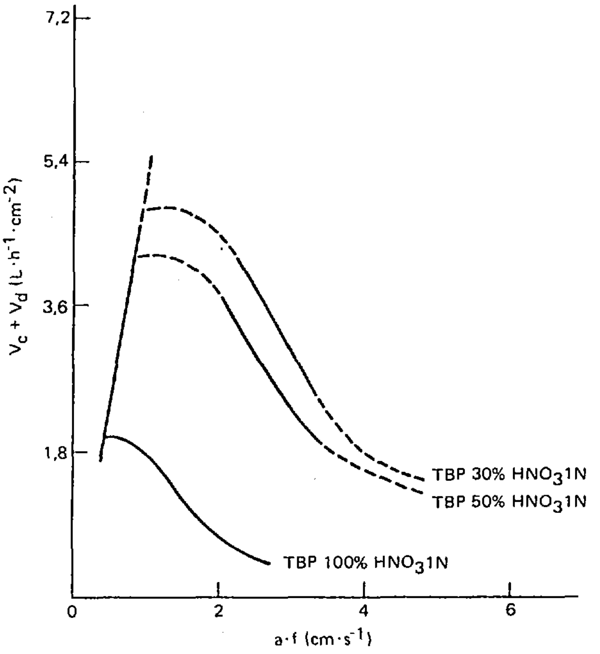

FIG.4. Capacité d'une colonne pulsée en fonction du produit amplitude X fréquence (a · f).

TABLEAU I. COLONNES PULSEES A PLATEAUX PERFORES. INFLUENCE DU DIAMETRE SUR LA HEET[a]

Diamètre de colonne (m)	0,3	0,6	1
HEET (m)	0,7 – 0,8	1 – 1,2	2

[a] HEET: hauteur équivalente à un étage théorique.

2. DEVELOPPEMENT DES COLONNES PULSEES

Les colonnes pulsées construites jusqu'alors présentaient les deux caractéristiques principales suivantes:

- faible diamètre (inférieur ou égal à 400 mm);
- un garnissage constitué de plateaux perforés.

L'extrapolation des colonnes à des diamètres plus importants (2 m par exemple) conduisait à une diminution d'efficacité comme on peut le voir sur le tableau I.

En outre le coût de fabrication des plateaux perforés de grande dimension était très élevé.

Les études conduites au CEA pour l'application des colonnes pulsées aux extractions solide-liquide ont abouti à la conception de plateaux de type «chicane» comme on peut le voir sur la figure 2. L'emploi de ces plateaux pour les extractions liquide-solide a conduit à des résultats très intéressants: l'efficacité varie peu quand le diamètre augmente (HEET = 75 à 100 cm pour tous les diamètres entre 0,1 et 1 m).

Les débits spécifiques varient avec les systèmes solvant-solution utilisés. Pour le mélange TBP à 30% dans le dodécane et les solutions nitriques d'uranium, on peut atteindre 4 $L\cdot h^{-1}\cdot cm^{-2}$ en extraction. Le système Alamine 336 –kérosène– solution de sulfate d'uranyle permet d'atteindre 1,5 à 3 $L\cdot h^{-1}\cdot cm^{-2}$ en extraction. Cela signifie que l'on peut traiter 50 à 70 $m^3\cdot h^{-1}$ dans une colonne d'un diamètre de 1,8 m.

Tous les essais ont été effectués par le Groupe de génie chimique du Service des ateliers pilotes du Centre de Marcoule (France).

3. APPLICATION INDUSTRIELLE: EXTRACTION DE L'URANIUM A PARTIR DES SOLUTIONS OBTENUES DANS LE TRAITEMENT DES MINERAIS

3.1. Société des mines de Dong Trieu (Groupe Total), Usine de Jouac

L'équipement d'extraction de cette usine est uniquement constitué de colonnes pulsées fournies par Eries. Actuellement, l'installation comprend trois colonnes dont les caractéristiques figurent sur le tableau II. Les colonnes pulsées ont fonctionné normalement dans les conditions figurant sur le tableau III, la réextraction étant réalisée au moyen d'une saumure de chlorure de sodium.

On voit que l'efficacité de l'extraction, compte tenu de la teneur élevée en uranium et en chlorure du solvant retour de réextraction, est très bonne.

3.2. Société industrielle des minerais de l'ouest (Groupe Cogéma), Usine de Bessines

Une colonne a été mise en service à Bessines (figure 5) pour compléter la capacité des ateliers d'extraction par solvant qui comprennent deux lignes de quatre mélangeurs-décanteurs d'extraction et une ligne de trois mélangeurs-décanteurs de réextraction. La réextraction est réalisée au moyen d'une solution d'ammoniaque et de sulfate d'ammonium.

Les caractéristiques de la colonne sont indiquées dans le tableau II et son fonctionnement est résumé dans le tableau III. L'efficacité est tout-à-fait comparable à celle de quatre mélangeurs-décanteurs.

TABLEAU II. CARACTERISTIQUES TECHNIQUES DES COLONNES PULSEES

		Dong-Trieu		Simo
	D-310	D-311	D-320	
Hauteur utile (m)	8	8	12	6
Hauteur totale (m)	12,4	14,2	16,4	12,2
Diamètre (m)	1,3	1,8	1,3	1,8
Pulsation	Périodique	par air	comprimé	
Garnissage				
– disques	28	16	26	14
– couronnes	24	14	26	14
Transparence (%)	25	25	25	25

TABLEAU III. RESULTATS DE MARCHE DES COLONNES

	Dong-Trieu			Simo
	D-310	D-311	D-320	
Opération	Extraction	Extraction	Réextraction	Extraction
Phase dispersée	Aqueuse	Aqueuse	Organique	Aqueuse
Taux de rétention (%)	14,1 – 17,7	27,7 – 34,2	16,2 – 20,5	25 – 45
Alimentation U ($g \cdot L^{-1}$)	2 – 2,9	1,4 – 2,9	–	0,5 – 0,8
Solvant U ($g \cdot L^{-1}$)	0,25 – 0,6	0,25 – 0,5	–	<0,03
Solvant chargé U($g \cdot L^{-1}$)	5,7 – 7	5,6 – 7,4	–	3 – 4
Raffinat U ($mg \cdot L^{-1}$)	5,5 – 8,8	2,9 – 7,1	–	⩽2
Rendement extraction (%)	99,6 – 99,9	99,8 – 99,9	–	99,6 – 99,9
Solution de réextraction U ($g \cdot L^{-1}$)	–	–	19 – 32	–
Débit spécifique ($L \cdot h^{-1} \cdot cm^{-2}$)	2,6 – 3	1,4 – 2,1	0,65 – 1,3	2,2 – 2,8

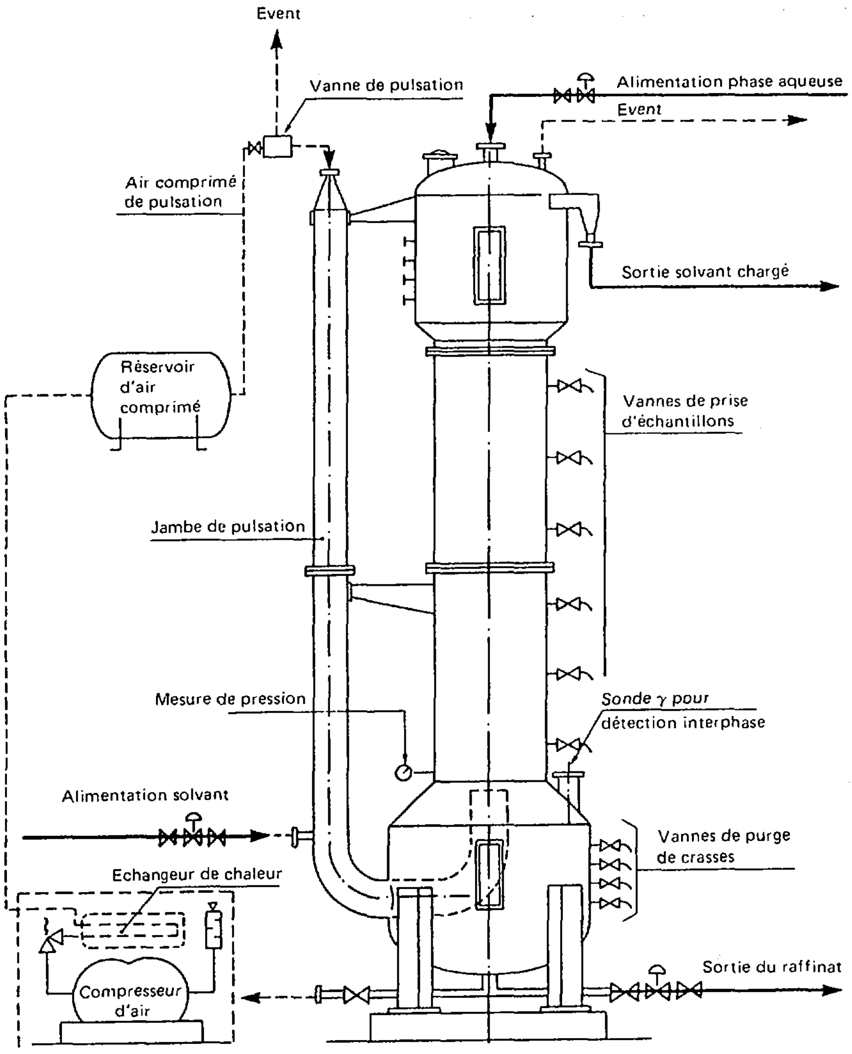

FIG.5. Schéma de la colonne pulsée de l'usine de Bessines.

3.3. Observations communes

Le fonctionnement de la colonne est stabilisé par régulation du débit de soutirage de la phase aqueuse (raffinat). Le niveau d'interphase est repéré au moyen d'un gamma densimètre.

Les crasses sont soutirées périodiquement au moyen de vannes placées sur le décanteur inférieur. En procédant de cette façon, elles ne perturbent pas la marche de la colonne. Les pertes en solvant par entraînement sont plutôt inférieures à celles obtenues avec les mélangeurs-décanteurs et elles n'excèdent pas 0,3 $L \cdot m^{-3}$ (300 pp10^6).

4. CONCLUSION

Les colonnes pulsées avec ce type de plateaux ne posent pas de problème particulier pour leur utilisation dans les usines de traitement de minerais d'uranium. Les résultats obtenus sont comparables à ceux des mélangeurs-décanteurs.

Les colonnes pulsées présentent des avantages économiques: investissements, immobilisation de solvant et espace au sol plus faibles.

On peut recommander leur emploi dans l'état actuel de cette technique:

- pour les usines traitant des débits de solutions uranifères qui ne dépassent pas 170 $m^3 \cdot h^{-1}$;
- pour les accroissements modulaires de capacité (jusqu'à 85 $m^3 \cdot h^{-1}$).

Pour les débits élevés, en supposant qu'on ne puisse construire de colonne de plus de 2 m de diamètre, il faut une colonne pour 85 $m^3 \cdot h^{-1}$. Les études en cours permettent d'envisager la construction de colonnes de plus grande taille, plutôt avec des pulseurs mécaniques. Ainsi une colonne de 2,5 m de diamètre permettrait de traiter 135 $m^3 \cdot h^{-1}$ et, avec 3 m, près de 200 $m^3 \cdot h^{-1}$.

ANNEXE

Société des mines de Dong Trieu

Cette société, acquise récemment par le groupe Total, possède et exploite un gisement d'uranium dans le Limousin, à une trentaine de kilomètres au nord de Bellac. Elle possède aussi à Jouac une usine pour traiter ses minerais d'une capacité de l'ordre de 35 $t \cdot h^{-1}$ en minerai et de 550 t d'uranium par an.

Elle utilise un procédé acide classique qui passe par une purification uniquement par extraction par solvant (Hostarex 327 – kérosène – tridécanol), la réextraction étant réalisée au moyen d'une saumure de chlorure de sodium.

Société industrielle des minerais de l'ouest

Cette société, aujourd'hui filiale à 100% de la Cogéma, exploite trois usines en France (l'Ecarpière, Bessines et Lodève) qui traitent les minerais que lui fournit la Cogéma.

L'usine de Bessines (Limousin, à 30 km au nord de Limoges) a une capacité nominale annuelle de 1 100 000 t de minerai et 1500 t d'uranium. Elle traite actuellement environ 600 000 t de minerais et produit environ 950 t d'uranium par an.

Elle utilise un procédé acide classique dans lequel la seule purification est réalisée par extraction par solvant (alamine 336 – kérosène – tridécanol), la réextraction étant ammoniacale pour produire un diuranate d'ammonium.

DISCUSSION

D. NADEN: I am particularly interested in the design and prediction of operation of these columns. I know how mixer-settlers are designed: McCabe-Thiele diagrams are drawn and stepped off and certain assumptions are made about efficiencies and this determines the number of stages, and so forth. What are the design criteria for columns of this type? How do you decide how many crowns and discs are needed and how tall the column should be?

J.P. JOUIN: For the distance between the crowns and the discs we have defined, after the pilot tests, that a transparency of 25% is needed. This transparency defines the height of the discs and of the crowns that must be placed in a vertical cylinder. That is the first point. As for the second point: we have compared, on our experimental columns, the equivalent height of a theoretical stage according to the McCabe-Thiele diagram and we have thus defined the vertical height for a theoretical stage. I have given the figures: in our case, for a column with a diagmeter between 10 cm and 1 m, we consider that the height of a theoretical stage is between 70 cm and 1 m. This defines the height of the column. So we have arrived to a height of 6 m for Bessines, and this 6 m includes also a safety factor.

D. NADEN: How do you define transparency?

J.P. JOUIN: We define transparency by the percentage of cross-section occupied by a disc, a crown, in relation to the total cross-section of the column. We take the surface of a disc, or the surface of a crown, and this surface corresponds to 25%, in our case, of the total surface of the section of the column.

F. BANHA DELMAS: Could you repeat your explanation of the determination of the height equivalent of a theoretical plate?

J.P. JOUIN: As in the case of mixer-settlers, the equilibrium curve between the organic solvent and the aqueous phase is constructed. The number of stages is obtained from this curve. Then, the height of a theoretical stage is determined experimentally and the total height of the column is obtained by multiplying the number of stages by the theoretical height given by the experimentally determined height. For our solvents, and for a cross-section of 1 m^2, the height equivalent of a theoretical plate is 1 m.

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APPAREIL AUTOMATIQUE DE DOSAGE EN LIGNE DE L'URANIUM DANS LES USINES DE CONCENTRATION

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Abstract–Résumé

AUTOMATIC SYSTEM FOR IN-LINE DETERMINATION OF URANIUM IN CONCENTRATION PLANTS.

The paper outlines the possibilities for the automatic in-line measurement of uranium in uranium concentrate plants using the "delayed neutron" nuclear method. After explaining the principle behind the method, the paper describes the system, a full-scale model of which has been built at the Central Laboratory for Analyses and Control, Grenoble Nuclear Research Centre. As the ultimate aim is to introduce into plants continuous monitoring of the uranium concentration at different points in the production line, specifications for the construction of an industrial prototype are currently being drawn up.

APPAREIL AUTOMATIQUE DE DOSAGE EN LIGNE DE L'URANIUM DANS LES USINES DE CONCENTRATION.

Ce mémoire expose les possibilités de dosage en ligne automatique de l'uranium dans les usines de concentrés uranifères par la méthode nucléaire dite «des neutrons retardés». Le principe de la méthode étant exposé, on décrit l'appareil dont une maquette à l'échelle 1 a été réalisée au Laboratoire central d'analyses et de contrôle du Centre d'études nucléaires de Grenoble. Le but final étant d'introduire en usine un contrôle continu de la concentration en uranium en différents points de la chaîne de production, le dossier de fabrication d'un prototype industriel est en cours de réalisation.

1. CHOIX DE LA METHODE ANALYTIQUE

Nous avons choisi une méthode nucléaire dite «des neutrons retardés». L'analyse par cette méthode est non destructive et rapide (une mesure toutes les 10 minutes). En outre, la solution qui passe au travers de l'analyseur peut être ensuite recyclée dans l'usine.

2. PRINCIPE DE LA METHODE

Lorsque l'on irradie une solution contenant de l'uranium avec une petite source neutronique (californium 252), on provoque un taux de fission de ^{235}U

TABLEAU I. LES DIFFERENTS GROUPES DE NEUTRONS RETARDES ET LEUR PERIODE MOYENNE

Groupes	Fission ^{235}U (n. thermiques)	
	Période (s)	Abondance relative (%)
1	55,72	0,033 ± 0,003
2	22,72	0,219 ± 0,009
3	6,22	0,196 ± 0,022
4	2,30	0,395 ± 0,011
5	0,610	0,115 ± 0,009
6	0,230	0,042 ± 0,008
Abondance totale (neutrons/10^4 fissions)		165,4 ± 4,2

TABLEAU II. PRECURSEURS LES PLUS REPRESENTATIFS DES DIFFERENTS GROUPES

Groupes	Précurseurs	Périodes (s)
1	^{87}Br	55,7
2	^{88}Br	15,9
	^{137}I	24,6
3	^{89}Br	4,5
	^{138}I	6,5
4	^{90}Br	1,6
	^{139}I	2,4
	^{144}Cs	1,0
5	^{140}I	0,86
6	^{93}Br	0,20

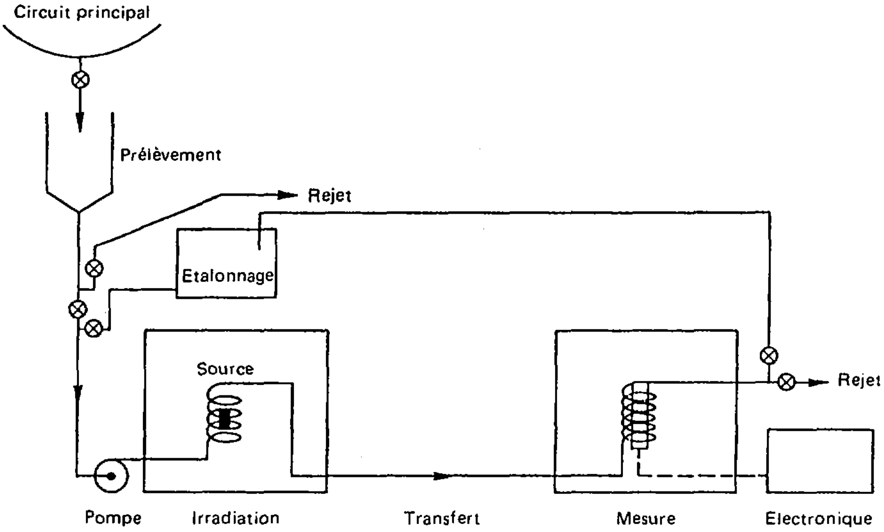

FIG.1. Schéma de principe de la maquette.

proportionnel à la concentration en cet élément. Parmi les produits de fission formés, certains décroissent par perte de neutrons. Ces neutrons sont appelés «neutrons retardés».

Ces produits de fission émetteurs de neutrons peuvent être classés en 6 groupes comme indiqué dans le tableau I où on constate que les périodes correspondantes varient entre 55 et 0,2 secondes et que les groupes 4, 3 et 2 sont prépondérants.

Malgré le faible nombre de neutrons émis (environ 165 n pour 10^4 fissions), cette méthode est intéressante car elle permet de s'affranchir de l'activité gamma de la solution d'uranium. Le signal recueilli provient uniquement des neutrons émis par ces éléments.

Les principaux émetteurs de neutrons sont: ^{87}Br, ^{88}Br, ^{89}Br, ^{137}I et ^{138}I (voir tableau II).

3. MAQUETTE A L'ECHELLE 1 REALISEE AU LABORATOIRE CENTRAL D'ANALYSES ET DE CONTROLE DE GRENOBLE

3.1. Schéma de principe (fig.1)

L'ensemble est constitué de trois blocs principaux:

- un bloc d'irradiation, avec la cellule d'irradiation et la source de neutrons (^{252}Cf); une protection biologique est réalisée autour de ce bloc;

– un block de comptage, avec la cellule de mesure et les emplacements des détecteurs de neutrons; une protection neutronique est nécessaire pour éliminer l'interférence due aux neutrons de la source;

– un bloc électronique comprenant un ensemble d'acquisition de données, et un bloc de calcul.

Après optimisation des différents paramètres, les caractéristiques de la maquette sont les suitantes:

– volume de la cellule d'irradiation: $V_i = 1$ L;
– volume de la cellule de mesure: $V_m = 1$ L;
– volume des tubes de transfert: $V_t = 0{,}2$ L;
– détecteurs neutrons: 3 détecteurs ^{3}He 65NH45;
– la circulation de la solution au travers de l'appareil se fait à l'aide d'une pompe volumétrique industrielle, à débit variable (débit maximum ≈ 770 L/h).

3.2. Mesure

Le schéma de la chaîne de mesure inclut:

– les détecteurs avec THT,
– le préamplificateur,
– l'amplificateur,
– le discriminateur,
– l'échelle de mesure,
– le calculateur.

3.3. Traitement des résultats

Actuellement, un petit programme d'étude sur minicalculateur nous permet d'obtenir la teneur de la solution. L'acquisition des données se fait directement dans le minicalculateur au travers d'une interface adaptée à l'électronique de mesure.

4. DETERMINATION DES CONDITIONS DE FONCTIONNEMENT DE L'APPAREIL ET VERIFICATION DES RESULTATS OBTENUS

4.1. Détermination du débit optimum (D_0)

La courbe représentée à la figure 2 nous montre la variation du taux de comptage, pour une solution de concentration d'environ 3 g/L d'uranium, en fonction du débit de cette solution au travers de l'appareil.

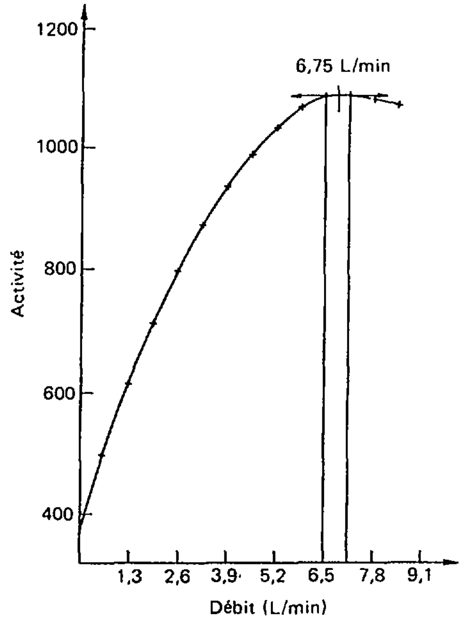

FIG.2. Détermination expérimentale du débit optimum.

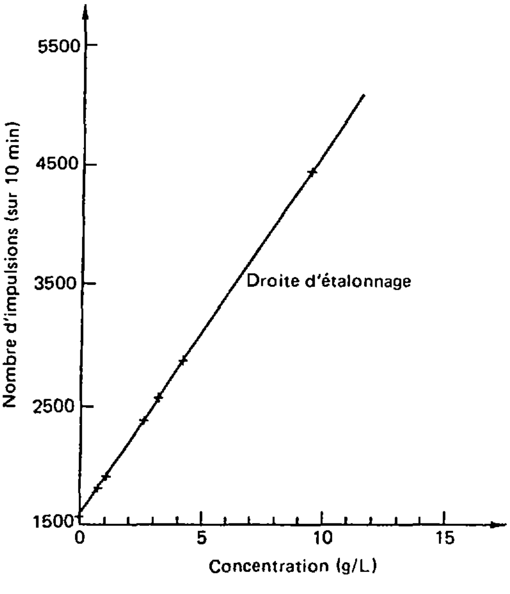

FIG.3. Détermination d'une courbe d'étalonnage.

TABLEAU III. RESULTATS DE TROIS METHODES DIFFERENTES[a]

	Etalonnage			Mesure	
Réf.	Chimie (g/L)	Activation (g/L)	Moyenne (g/L)	Neutrons retardés (coups/10 min)	Calcul teneurs (g/L)
F	9,40	9,4	9,40	4452	9,38
E	4,20	4,2	4,20	2859	4,16
D	3,10	3,0	3,05	2562	3,19
I	2,70	2,4	2,55	2373	2,57
C	1,08	1,1	1,09	1920	1,08
G	0,80	0,8	0,80	1818	0,75
H	$< 0,002$	0,00075	0	1581	0
K	$< 0,002$	0,00045			
	$Y = ax + b$ $a = 1,001$ $b = -0,056$ $r^2 = 0,99$		$Y' = a_1 x + b_1$ $a_1 = 305,1$ $b_1 = 1590$ $r^2 = 0,99$		

---

[a] Ces essais ont été effectués en milieu nitrique pour faciliter la mise en solution de l'uranium. Il a été vérifié, par ailleurs, que les résultats sont identiques en milieu sulfurique.

Le débit optimum ainsi défini est compris entre 6,5 et 7 L/min. Ce résultat confirme l'optimisation théorique (7 L/min). Les conditions de fonctionnement sont telles que:

- $V_i = V_m = 1$ L,
- $V_t \approx 0,2$ L;
- $D_0 \approx 6,5$ L/min.

4.2. Etude du signal en fonction de la concentration.

V_i, V_t, V_m, D_0 étant fixés, la seule variable est alors la concentration en uranium de la solution.

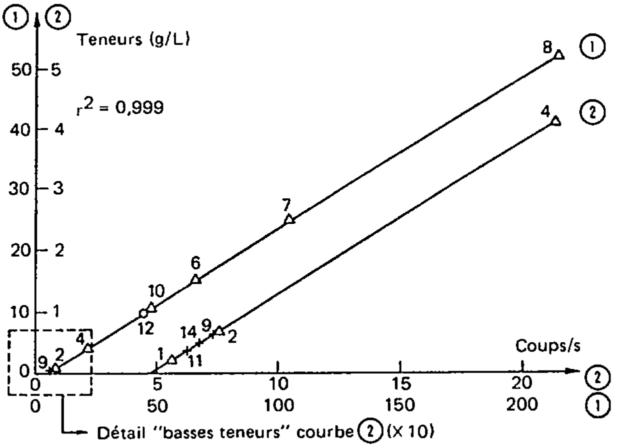

FIG.4. Courbe de régression linéaire de la réponse de l'analyseur pour des solutions dont les concentrations en uranium varient de 0,2 à 50 g/L.

Détermination d'une courbe d'étalonnage

Pour établir cette courbe, nous avions à notre disposition 8 solutions nitriques d'uranium de concentrations connues. La figure 3 nous montre qu'entre zéro et 10 g/L en uranium la courbe d'étallonnage est bien une droite.

Vérification de cette méthode par rapport à d'autres méthodes d'analyse

Le tableau III nous montre les correspondances entre les trois méthodes. Comme valeurs d'étalonnage, nous avons pris les valeurs moyennes entre le dosage chimique et l'activation neutronique (mesure de ^{239}Np).

L'étude en laboratoire pour déterminer les caractéristiques principales du dispositif et mesurer les performance du système étant terminée, ainsi que la mise au point technologique des différents constituants de la maquette, cet appareillage a été transporté à Bessines, au laboratoire de la Cogéma situé à proximité de l'usine de concentration.

5. VERIFICATION DE LA LINEARITE DE LA REPONSE DE L'ANALYSEUR EN FONCTION DES CONCENTRATIONS EN U (tableau IV et figure 4)

Pour couvrir une gamme de concentrations en uranium entre 0,2 g/L et 50 g/L, on utilise:

– des solutions d'usine: solution d'attaque (SO_4H_2) et de réextraction ($SO_4(NH_4)_2$);

– des solutions synthétiques (NO_3H) ou (SO_4H_2).

TABLEAU IV. VERIFICATION DE LA LINEARITE DE LA REPONSE DE L'ANALYSEUR POUR DES SOLUTIONS DONT LA CONCENTRATION EN URANIUM VARIE DE 0,2 A 50 g/L[a]

Echantillon	N° 1	N° 2	N° 4	N° 6	N° 7	N° 8	N° 9	N° 10	N° 11 (SIMO)	N° 12 (SIMO)	N° 14 (SIMO)
Milieu	NO_3H	NO_3H	NO_3H	NO_3H	NO_3H	NO_3H	SO_4H_2	SO_4H_2	SO_4H_2	$SO_4(NH_4)_2$	SO_4H_2
Teneurs (g/L)	0,237	0,653	4,048	15,17	24,90	51,90	0,643	10,68	0,351	10,22	0,490
Réponse[b] (coups/s)	5,68	7,53	21,43	65,80	104,37	210,53	7,34	47,90	6,29	44,80	6,79

[a] Voir aussi la figure 4.

[b] Par la méthode des neutrons retardés.

TABLEAU V. DOSAGE DE SOLUTIONS DANS TROIS GAMMES DE TENEURS

Etalonnage «basses teneurs» (0 à 1 g/L)

Etalons (U en g/L)	0	0,237	0,653	0,837	0,643	0,351	0,490
Milieu	–	HNO_3	HNO_3	HNO_3	SO_4H_2	SO_4H_2	SO_4H_2
Réponses[a] (coups/s)	4,77	5,68	7,53	8,21	7,43	6,29	6,79
Teneurs[a] (g/L)	0	0,221	0,669	0,835	0,624	0,369	0,490

Etalonnage «teneurs moyennes» (1 g à 10 g/L)

Etalons (U en g/L)	4,05	7,61	10,22	10,68
Milieu	HNO_3	HNO_3	$SO_4(NH_4)_2$	SO_4H_2
Réponses[a] (coups/s)	21,43	36,54	44,80	47,90
Teneurs[a] (g/L)	3,98	7,85	10,0	10,76

Etalonnage «fortes teneurs» (10 à 50 g/L)

Etalons (U en g/L)	10,22	10,68	15,17	24,20	51,90
Milieu	$SO_4(NH_4)_2$	SO_4H_2	HNO_3	HNO_3	HNO_3
Reponses[a] (coups/s)	44,80	47,90	65,80	104,37	210,53
Teneurs[a] (g/L)	10,12	10,89	15,41	25,10	51,85

[a] Méthode des neutrons retardés.

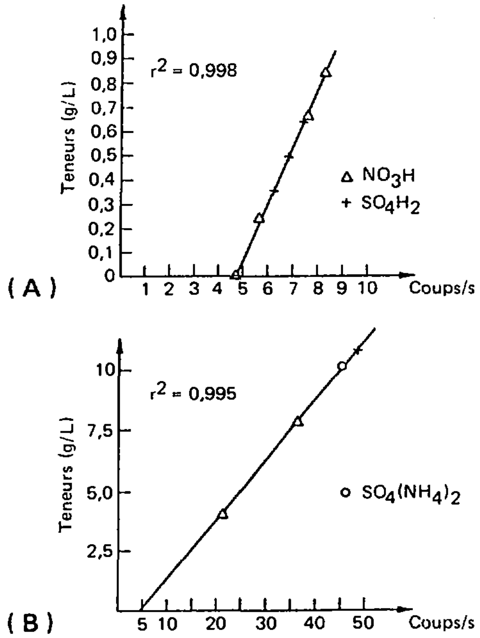

FIG.5. Courbes de régression pour l'étalonnage «basses teneurs» (A) et «teneurs moyennes» (B).

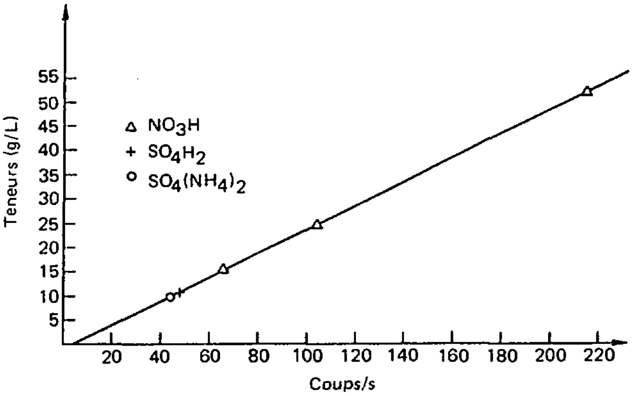

FIG.6. Courbe de régression pour l'étalonnage «fortes teneurs».

6. DOSAGE DE SOLUTIONS DANS TROIS GAMMES DE TENEURS (tableau V et figures 5 et 6)

a) Etalonnage «basses teneurs»: 0 g/L à 1 g/L.
b) Etalonnage «teneurs moyennes»: 1 g/L à 10 g/L.
c) Etalonnage «fortes teneurs»: 10 g/L à 50 g/L.

TABLEAU VI. SECTIONS EFFICACES DE FISSION

Noyau	Nombre de masse	Nombre de neutrons produits par fission	Section efficace de fission (barns)	Nombre de neutrons produits par fission	Section efficace de fission (barns)
^{232}Th	232			2,36	0,03
^{233}U	233	2,49	531,1	2,51	2,37
^{235}U	235	2,42	582,2	2,50	1,59
^{238}U	238			2,66	0,125
^{239}Pu	239	2,87	742,5	2,88	1,83
	Neutrons thermiques			Neutrons rapides	

TABLEAU VII. ESSAIS CONCERNANT L'INTERFERENCE EVENTUELLE DE THORIUM

Teneurs Th (mg/L)	0	200	400
Teneurs U (Chimie, g/L)	9,11	9,11	9,11
Teneurs U[a] (neutrons retardés, g/L)	9,04	9,20	9,07

[a] Teneur moyenne: 9,10 g/L.

7. ETUDE DES INTERFERENCES EVENTUELLES

7.1. Interférences dues à la méthode

7.1.1. Les solutions peuvent contenir du thorium (tableaux VI et VII)

Le tableau VI indiquant les sections efficaces de tous les noyaux qui peuvent subir la fission nous permet d'expliquer le choix des neutrons thermiques pour doser ^{235}U. En effet, ^{233}U et ^{239}Pu sont absents des solutions d'uranium naturel; de plus, le ^{232}Th ne peut subir la fission qu'avec des neutrons rapides. Le seul signal mesuré provient de ^{235}U.

Des essais sur des solutions contenant du thorium ont été effectués pour vérifier la thermalisation des neutrons au moment de l'irradiation.

On constate donc qu'il n'y a pas d'interférence due au thorium.

7.1.2. Les solutions peuvent aussi contenir des traces de bore

Le bore, du fait de sa grande section efficace de capture pour les neutrons thermiques, peut créer, à partir d'une certaine teneur, une atténuation du flux de neutrons, et donc du signal, et donner un dosage par défaut pour l'uranium (section efficace de capture: 795 barns pour le bore naturel et 4017 barns pour le bore 10). Pour une solution d'origine d'environ 10 g/L d'uranium, et jusqu'à 5 mg/L de bore, il n'y a pas d'interférence. A partir de 10 mg/L de bore dans la solution, l'atténuation due au bore sera de 2% jusqu'à 13% pour une teneur en bore de 100 mg/L, l'atténuation étant proportionnelle, dans cette gamme, à la teneur en bore.

7.1.3. Les solutions peuvent contenir des terres rares

Certaines terres rares ont des sections efficaces de capture pour les neutrons thermiques très importantes:

– samarium:	5600 barns
– europium:	4300 barns
– gadolinium:	46000 barns
– dysprosium:	950 barns

Nous avons choisi le gadolinium pour étudier l'interférence des terres rares. La solution de départ étant de 10 g/L en U, les résultats des essais sont donnés dans le tableau VIII.

TABLEAU VIII. RESULTATS DES ESSAIS POUR LE GADOLINIUM

Teneur Gd_2O_3	1 mg/L	10 mg/L	100 mg/L
Teneur mesurée en U (g/L)	9,77	9,41	7,33
Atténuation relative de la teneur U (%)	2,3	5,9	26,7

TABLEAU IX. RESULTATS DES ESSAIS SUR UNE SOLUTION DE NITRATE D'URANYL DOPEE[a]

Molybdène (g/L)	Sodium (g/L)	«Chimie»[b] Uranium (g/L)	«Neutrons retardés»[c] Uranium (g/L)
0	0	10,07	9,96
0,5	0,24	10,08	10,21
1,0	0,48	10,08	10,15
2,5	1,2	10,01	10,14
5,0	2,4	10,02	10,05
10	4,8	10,06	10,05

[a] Dopant: Na_2MoO_4.
[b] Moyenne: 10,05 g/L; coefficient de variation: 0,3%.
[c] Moyenne: 10,09 g/L; coefficient de variation: 0,9%.

Cependant, la concentration en gadolinium dans les solutions réelles d'usine devant se situer au niveau de 0,1 à 0,01 mg/L, nous n'avons jamais remarqué d'atténuation dans toutes les solutions d'usines étudiées.

7.1.4. Sections efficaces des neutrons pour certains éléments présents dans les solutions

Fe: 0,2 barns
Al: 0,27 barns
Cl: 33,8 barns
Mo: 2,7 barns
Na: 0,53 barns
S: 0,5 barns

Avec une section efficace de capture de 2450 barns, le cadmium pourrait atténuer le dosage de l'uranium. Cependant, cet élément ne se trouve pas en concentration suffisante dans les solutions.

TABLEAU X. DOSAGE D'URANIUM EN PHASE ORGANIQUE

Références	1/5	2/5	3/5	4/5	5/5	n° 6	Réextraction
Milieu	Solvant						$SO_4(NH_4)_2$
«Chimie» Teneurs (g/L)	1,21	2,44	3,55	4,71	5,93	5,845	9,94
Réponse Neutrons retardés (coups/s)	10,74	15,26	19,50	24,04	28,58	28,21	43,72
Teneurs Neutrons retardés (g/L)	1,23	2,42	3,54	4,74	5,94	5,84	9,935

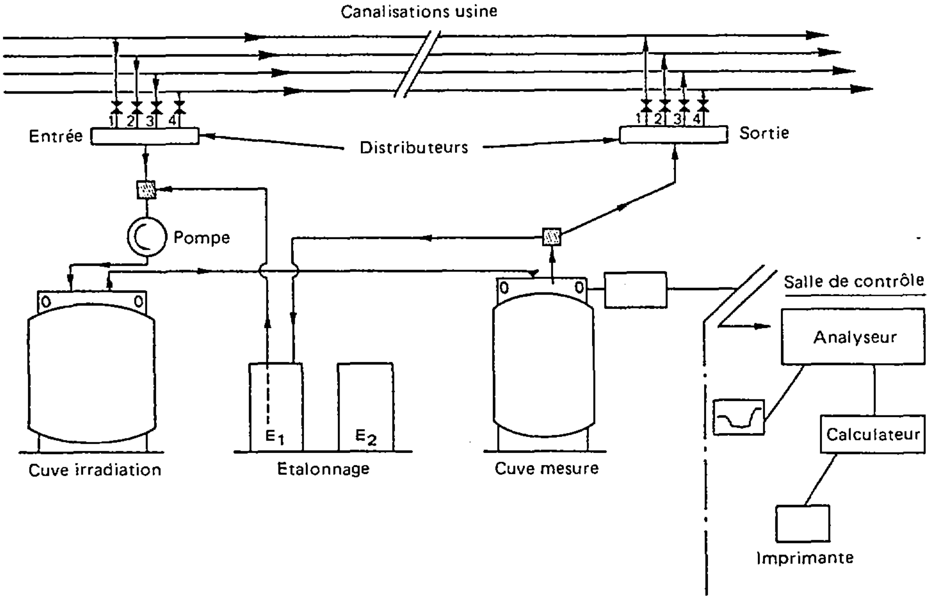

FIG. 7. Schéma du projet d'installation du prototype en usine.

7.2. Essais sur solutions dopées

Suivant l'origine des minerais, certaines solutions sont fortement chargées en molybdène, et les méthodes classiques de dosage de l'uranium sont perturbées.

Le tableau IX nous permet de conclure que la méthode de dosage de l'uranium par les neutrons retardés est insensible à la présence de Mo dans la solution (jusqu'à 10 g/L de Mo) et de Na (jusqu'à 5 g/L environ). Le sel de molybdène utilisé étant du $NaMo_2O_4$, nous avons étudié en même temps l'influence du sodium sur le dosage de l'uranium.

7.3. Essais en milieu organique

Comme on peut le voir d'après les chiffres indiqués au tableau X, les essais sont concluants.

8. CONCLUSIONS

Cette méthode d'analyse s'applique aux solutions dont la concentration en uranium varie de 0,2 g/L à plus de 100 g/L.

La précision de la mesure, au niveau de 0,2 g/L, est voisine de 10%, et, au niveau de 100 g/L, est de 1%.

Avec cet appareil, il est possible d'analyser par exemple:

- les solutions d'attaque (sulfurique);
- les solutions de réextraction ($SO_4(NH_4)_2$);
- la phase solvant (possibilité de contrôler en permanence la charge du solvant).

Enfin, en étalonnant avec des solutions de même nature, il est possible de doser l'uranium dans des saumures de 130 g/L.

Actuellement le dossier de fabrication d'un prototype industriel est en cours de réalisation. La figure 7 montre le projet d'installation en usine.

DISCUSSION

NAEEM-UL-ZAMAN: What is the size of the californium source you use?

P. GUAZZONI: This is a californium source of 150 micrograms or about 0.82 millicuries.

K. CHITUMBO: Are the results affected if the sample is not in radiometric equilibrium?

P. GUAZZONI: This method quantifies all ^{235}U nuclei without regard to their physical or chemical form. One can even determine the uranium content in an enriched uranium solution, up to a certain limit, provided that the degree of enrichment is known.

S. AJURIA: The radiometric disequilibrium has no effect on this method because you are measuring directly the fission of ^{235}U nuclei. The presence of daughters in whichever proportion does not matter.

H.J. STEINER: How long does it take to have the results after the sample has been introduced in the apparatus?

P. GUAZZONI: About ten minutes. You can modify the elapsed time according to the concentration of uranium in the sample and according to the relative precision you wish to have. If you wish to work systematically at a level of 0.2 g/L, it may be useful to count for a longer time to improve the statistics. At the limit, you can count for one hour if you need to do this for a particular sample.

H.J. STEINER: What is the precision at low concentrations?

P. GUAZZONI: At a concentration of 0.2 g/L the relative precision is about 10%. This equipment is not designed for working with traces; it is designed to work with a lower limit of about 0.1 g/L with a relative precision of about 15% at that level. Our next equipment will be able to work at the trace level.

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MODULAR PLANTS FOR SMALL DEPOSITS

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Abstract

MODULAR PLANTS FOR SMALL DEPOSITS.

The large investment required to recover uranium from small deposits is the greatest obstacle to their economic development. Various concepts (caravan mill, pure mill or semimobile mill) have been elaborated in different countries. Studies have also been made in Spain to develop a simple and economic flowsheet suitable for the beneficiation of small uranium deposits. An acid heap-leaching and solvent extraction process was chosen because there is already a great deal of experience of it in Spain. Modifications were necessary to make the equipment easy to transport and also to have a low and reusable investment when this flowsheet is used for small deposits. The aim was to develop a modular plant with all the elements fitted in compact units that needs little site preparation and little time and effort to connect the units. A standard small portable crushing plant can be borrowed and the mining operation and heap construction can be put to contract. There is a solvent extraction unit (150 m^3/d) in continuous operation (24 h/d) and concentrate precipitation and handling facilities. The whole of the equipment is standard and as light as possible. Little civil engineering is required and the erection of the plant only needs a few months. The uranium capacity of these modular plants is between 35 and 50 t U_3O_8/a. Special consideration has been paid to regulations and the environmental aspects.

1. SMALL DEPOSITS

Most uranium is produced from large or medium-sized deposits. However, there are many small ore bodies with a considerable potential of uranium that are not exploited because in isolation they do not justify the high plant investment.

The economic viability of an ore body depends on its size and reserves, on its metallurgical behaviour, the mining conditions, and on its location and available infrastructure. We can retain the basic aspects of the reserves without entering into an analysis of all of them. Deposits with mineralization between 25 and 500 t U_3O_8 will be discussed here. Their exploitation is problematic because the proven value (US $80/kg U) will be between 2 and 40 million dollars.

It is possible to consider their exploitation in a conventional plant placed close to several small or medium-sized deposits, or it is possible to transport the ore from one small ore body to where there is a large one if the distance is short.

The mining, haulage to the plant and the milling expenses would be basically the charges on the product. When the ore body is isolated or very far from a treatment plant, however, it cannot support a conventional plant whose amortization costs would be prohibitive. Consequently, it is necessary to minimize the components of the costs.

The costs are composed of

$$C = PE + MO + H + PT + CT + GF$$

where C = total cost
PE = previous expenses, exploration and others
MO = mining expenses
H = haulage
PT = previous concentration
CT = chemical treatment cost
GF = general expenses of the facility.

The mining and milling costs have two components, the amortization cost of the investment, and the operating costs. The latter are composed of fixed costs, which are relatively independent of the quantity of ore treated, and others that are proportional to the treated ore. Consequently, it will be necessary to carry out a study of the different components in order to eliminate some of them and to minimize the rest. In other words, it is necessary to look for a solution that is cheap and easy to operate.

2. APPROXIMATION TO THE SMALL DEPOSITS BENEFIT

The cost of uranium production depends basically on the mineral treated and its behaviour. A low grade of uranium ore increases the expense, whereas the quantity of uranium has little effect on the total expense. On the other hand, referring to the product cost, the amount of uranium (grade and recovery) has a decisive influence because it is the factor that divides the costs generated by the ore. The treatment rate also affects the costs [1]. These are reduced by 22% at a capacity of 1000 t/d from those for a capacity of 200 t/d of ore.

Unfortunately, when we consider small ore bodies we cannot gain any profit from economy of scale because the short life of the ore body entails very high amortization charges. Work capacities will be lower than 200 t/d of ore for small deposits. The cost distribution for a conventional plant of this capacity is:

Mining	45.2%
Haulage	7.5%
Plant operation	36.8%
Plant amortization	10.5%

If we apply this conventional technique to small deposits, we can see that:

(a) Mining has a great share, almost half the costs. These could be reduced by in situ leaching if the ore body is suitable. If not, the cheapest possible mining should be tried. For instance opencast mining is 20% cheaper than underground mining.

(b) Haulage up to some 50 km also presents a considerable contribution. Consequently, it is necessary to place the mill as near as possible to the mine. Approximately \$0.05/t per km could be saved in this way.

(c) The operating costs of the plant are second in magnitude after the mining ones. This value depends basically on the ore, but they are also a function of the flow diagram and the treatment rate. To exploit small ore bodies it would be necessary to choose the best operating method in order to reduce the fixed operating expenses to a minimum.

(d) The amortization of a plant with 15 years of operating time is also considerable. For a conventional plant of 200 t ore/d the investment would presumably be US \$5 million at the beginning of 1983. For this plant and with an ore body of 1 Mt of ore, the amortization cost would be \$5/t. The problem is that the deposits considered here would have a capacity between 25-500 t U_3O_8 and with 212 t U on average. For this plant and only one ore body the amortization cost would represent \$23/kg U, which is prohibitive. The solution would be to reduce the investment and to set up the plant in such a way that most of the equipment could be recovered. Various studies on this have already appeared [2–4].

Considering the distribution of the investment for a conventional plant some steps [5] that are functions of the flow diagram and the plant capacity are obtained. As an approximation and for a conventional layout composed of acid leaching and solvent extraction the following per cent distribution can be assumed [6].

Pretreatment	10
Grinding	20
Leaching	15
Solid-liquid separation	25
Concentration and purification	12
Precipitation, calcining and packing	6
Tailings disposal	7

It may be seen that the solid-liquid separation, grinding and leaching make the greatest contributions. Heap leaching avoids grinding and solid-liquid separation, and reduces the leaching contribution to less than half. With this new flowsheet the investment would be reduced to about 45% of that of a conventional plant. For the exploitation of small deposits a simple flowsheet is essential [7]; this could be acid heap-leaching and solvent extraction. Moreover, the investment

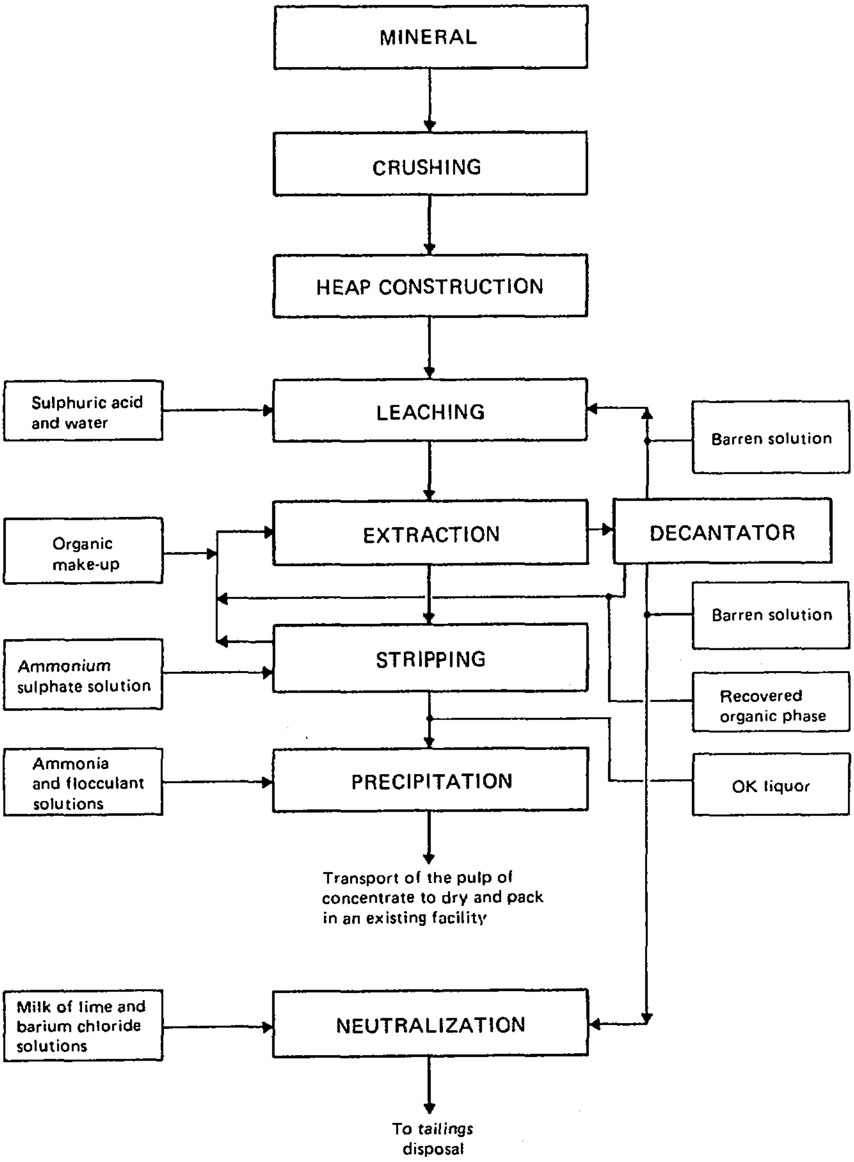

FIG.1. Block diagram of basic flowsheet.

would be reduced by putting the mining, crushing, haulage and heap building out to contract.

The life of the deposit requires the amortization of the equipment to be spread over several successive applications, that is to say, for several small ore bodies. This implies recovery of the equipment and its transport to the new location. The time used between two applications will be a function of:

Disassembly time
Plant transport
Assembly in the new location.

To reduce these periods of time to a minimum the best solution would be a modular system that requires the shortest assembly time in situ. This way the necessary amortization would concern only the infrastructure elements and the transport and plant assembly. Wheel-based modules would offer the lowest assembly problems, but this solution is rather expensive because of the truck costs. Another slower possibility would be to consider the plant as a compromise between its capacity and its ability to be transported by truck. It could be quickly assembled in the new location by crane. This is the solution studied and recommended in Spain. The use of modular plants requires:

Good plant design
Standardization of elements using light materials, e.g. glass-fibre reinforced polyester (FRP)
Detailed and co-ordinated procedure for assembly and disassembly
Good co-ordination of areas with previous preparation of the ground before the arrival of the equipment and its final assembly.

3. APPLICATION TO A MODULAR PLANT

3.1. Flowsheet

In exploiting small deposits it is best to choose the simplest flowsheet possible. Figure 1 shows a block diagram comprising open-pit mining, crushing, heap-leaching, solvent extraction, precipitation, thickening and transport of the uranium concentrate, neutralization and elimination of the effluents. Grinding, conventional leaching, solid-liquid separation, clarification and drying of the uranium concentrate have been eliminated from this diagram. This last operation may be carried out in a bigger plant, somewhat farther from the location. Besides, operations such as mining, crushing and PAD construction for leaching may be contracted to a local firm to be made for 6 months each year, for instance. After leaching the operation would be continuous, 24 hours per day and 7 days per week. A flowsheet of this type may recover 80% or more of the uranium.

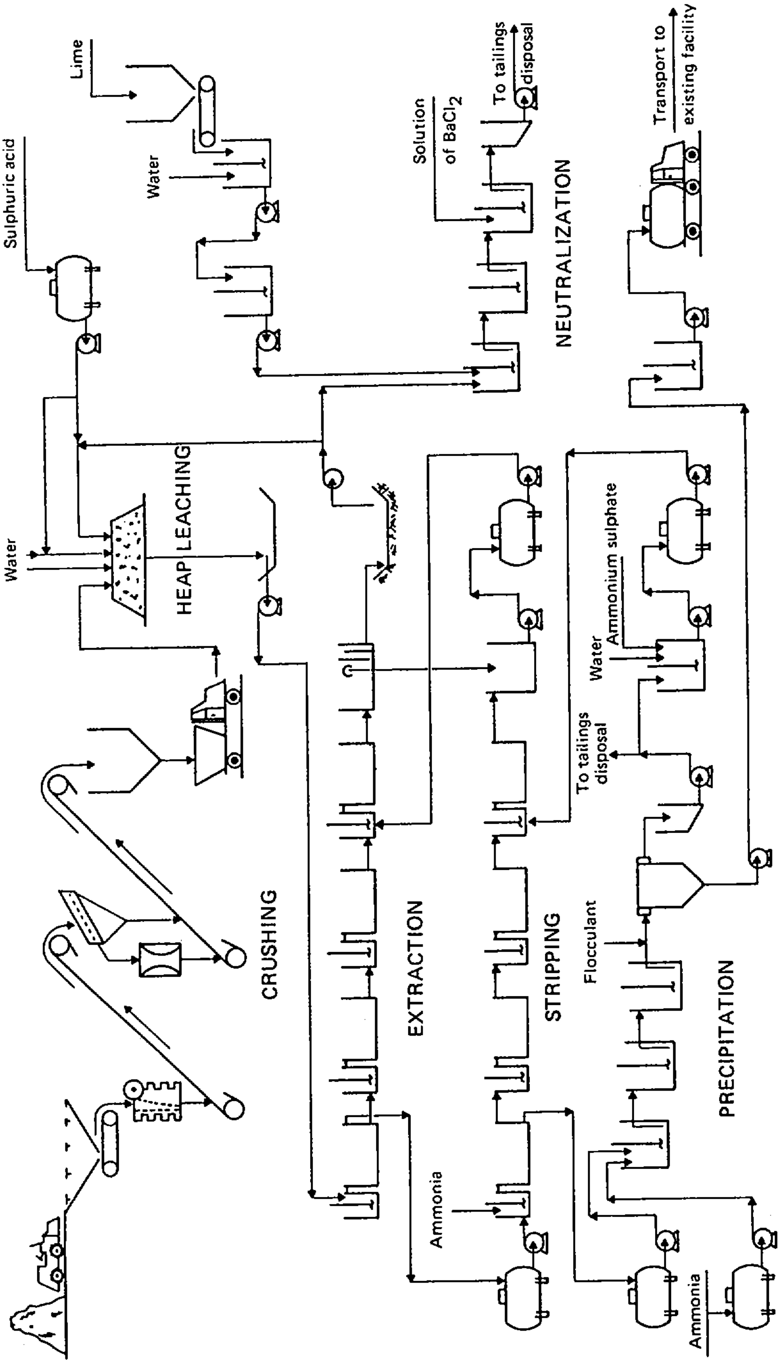

FIG.2. Diagram of simplified flowsheet.

TABLE I. EQUIPMENT LIST (UNITS)

1. Crushing and PAD building

Contract

2. Leaching

Pregnant solution and raffinate ponds (2)
Tank of sulphuric acid (1)
Pumps of: shower (1), sulphuric acid (1), raffinate (1), and pregnant solution (2)

3. Extraction

Extraction battery: mixers (4) and settlers (4)
Tanks of organic phases (2)
Deposit of recovered organic phase
Decantation of entrained organic phase
Pumps of organic phases (3), and recovered organic phase (1)

4. Stripping

Stripping battery: mixers (4) and settlers (4)
Deposit for preparing the strip solution (1)
Tanks of strip solution (1) and uranium-laden aqueous solution (1)
Pumps of strip solution and uranium-laden solution (3), and strip solution preparation (1)

5. Precipitation

Precipitation reactors (3)
Lamella thickener (1)
Tank of ammonia solution (1)
Deposit of ammonium diuranate pulp (1)
Container truck for liquids (1)
Pumps of ammonia solution (1), liquor of precipitation (1), concentrate pulp (2) and flocculant solution (1)

6. Neutralization

Bin of lime (1)
Lime feeder (1)
Deposit for preparing the milk of lime (1)
Deposit of milk of lime (1)
Neutralization reactors (3)
Pumps of milk of lime (2), neutralized pulp (1), and barium chloride solution (1)

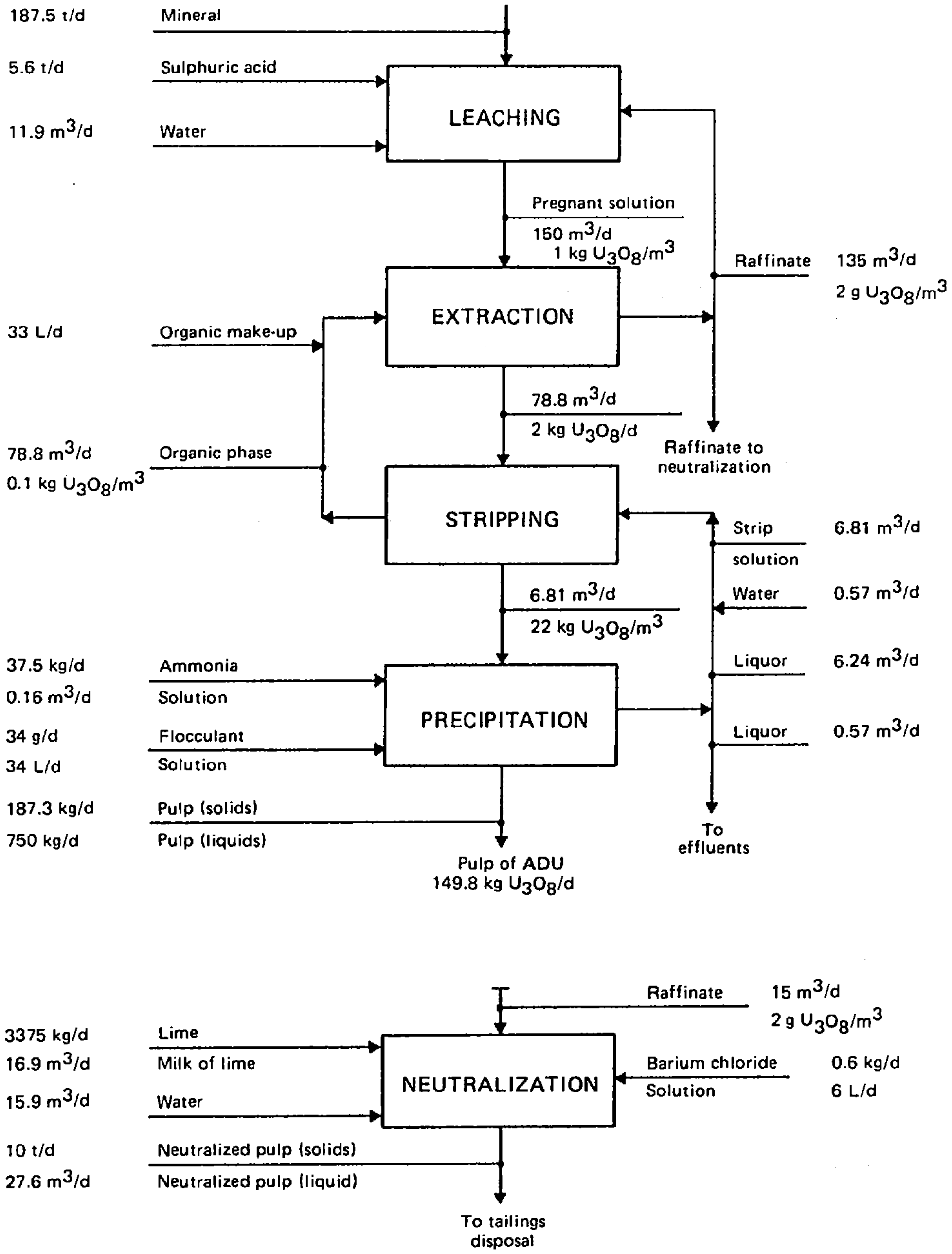

FIG. 3. Quantitative block diagram of a plant treating 150 m^3/d of pregnant solution.

A simplified flowsheet is shown in Fig.2. Table I gives a list of the equipment. The procedure is the same as that used in other heap-leaching operations [8, 9], but with the following considerations:

(a) Mining, crushing and heap building can be carried out on a contractual basis for periods shorter than the operating time. This way the costs could be lower, because the work could be done at a higher rate. A disadvantage would be the financial cost of ore storage in the heap.
(b) The maximum quantity of extraction raffinates is recycled to the leaching. This way the water supply is reduced and consequently the equipment for neutralization is smaller and wastes are less. Heap-leaching permits a low liquid-solid ratio.
(c) Recovery can be made with a conventional AMEX process. Stripping is made with ammonium sulphate-ammonia in order to obtain the maximum raffinate recycling.
(d) The uranium concentrate is precipitated and thickened in the same plant. For drying and packing it is sent to a main factory for inclusion in the latter's production.

The large solid wastes remain on the leaching ground where they must be covered with soil and stabilized. Liquid effluents are neutralized and the pulp is stored in a dam which retains the radioactivity because the radium has been fixed by the barium sulphate.

Figure 3 shows the quantitative diagram for a plant that treats 150 m^3/d of pregnant solution in an extraction battery. This is equivalent to 187.5 t ore/d. If the ore grade is 0.1% U_3O_8, the production will be 149.8 kg U_3O_8/d, with a yield of 80%.

3.2. Modular design

In designing this modular plant, the largest settler capable of being transported on a normal truck has been considered, together with the least infrastructure needed and quick assembly on site. A module composed of two extraction settlers is 2.7 × 2.2 × 1.3 m [10]. This allows the treatment of 150 m^3 pregnant solution per day, which is equivalent to some 50 t U_3O_8/a. From the modular point of view:

(a) Crushing may be put on contract. The contractor can carry it out with one of the several plants available for civil works.
(b) Leaching pumps and flowmeters are assembled in a structure and interconnected. They are connected to the shower pipelines and to those that come from the ponds. Flexible pipelines are used together with rapid fittings. The heaps and ponds are abandoned after each operation.

(c) The extraction equipment is composed of the following modules: two modules of two extraction mixers each, two of two extraction settlers each, one module of four stripping mixers, and another with four settlers. There is an additional module with all pumps and flowmeters. The tanks for organic phases, strip solution and uranium-laden aqueous solution are independent modules.
(d) The precipitation equipment is assembled in two modules, one for the reactors, pumps and flowmeters, and another with the lamellae thickener, its pump and the deposit for the pulp of thickened uranium concentrate.
(e) For the neutralization system there are two modules, one for preparing the milk of lime and another for the neutralization reactors and the effluent pump.

The lightest materials have been selected. FRP has been widely used.

Rigid pipelines are reserved for internal elements to the modules and for the main leaching pipelines. The remainder are flexible pipes connected by rapid fittings.

The low-tension electrical distribution is made from hermetic boards connected with simple fittings. Energy is taken from the public grid or a diesel generator.

Most of the equipment is placed in the open air. Prefabricated houses are foreseen for extraction-precipitation, analysis labs, offices and dressing rooms. The necessary site preparation is very modest, requiring only conditioning of the ground for heaps, ponds and roads. Concrete is needed for minor footways, foundations and slabs for buildings. The process area is protected against spills. These are abandoned when the plant is transferred to another location.

Ten normal (16 t) trucks are needed to transfer this plant. The area required for the chemical plant is 0.35 ha. The total area will depend on the size of the ore body and may be estimated as 0.23 m^2/t for solid wastes and 0.006 m^2/t for liquid wastes.

3.3. Operating procedure

When exploiting small deposits with modular plants it is necessary to prepare the transfer from one ore body to another very carefully in order to reduce the time loss. When the modular plant is already available the main stages of the exploitation are:

(a) Preparation of the mine, mining, crushing and heap building
(b) Preparation of the process area
(c) Transport and assembly of the chemical units
(d) Uranium concentrate production
(e) Disassembly and transport of the modules to a new deposit
(f) Land restoration in the exhausted deposit.

TABLE II. PRODUCTION COSTS FOR A SMALL ORE BODY

Basic data			
Number of ore bodies	1	Total production (t U_3O_8)	500
Size (t U_3O_8)	625	Mineral (t)	625 000
Operation time (a)	10	Investment (I) (US $)	817 000
Places	1	Working capital (WC) (US $)	82 000

M.1	Raw materials and auxiliary			
	Concept	Consumption/t	US $/unit	Total cost
	Mineral	1 t	15	9 375 000
	Reagents			
	Sulphuric acid	30 kg	0.06	1 062 500
	Lime	17 kg	0.05	510 000
	Ammonia	0.3 kg	0.36	68 100
	Barium chloride	0.003 kg	0.50	1.000
	Tertiary amine	0.004 kg	1.67	4 200
	Decilic alcohol	0.003 kg	0.83	1 600
	Kerosene	0.13 kg	0.36	29 300
	Others			2 300
			TOTAL	1 679 000
M.2	Supplies and services			
	Water	0.17 m^3	0.06	6 400
	Electrical power	10 kW·h	0.08	500 000
	PAD	0.23 m^2	6.67	958 000
			TOTAL	1 464 400
M.3	Direct manpower (0.63 man·h/t X 3.8 $/man·h X t)			1 500 000
M.4	Indirect manpower[a] (M.3 X 0.1)			150 000
M.5	Manager and technicians (M.3 X 0.2)			300 000
M.6	Supplies (I X 0.005 X 10 a)			40 900
M.7	Maintenance (I X 0.05 X 10 a)			409 000
M.8	(a) Amortization of the modules			629 000
	(b) Amortization of the rest of the plant			188 000
M.9	Taxes (I X 0.01 X 10 a)			81 700
M.10	Insurance (I X 0.01 X 10 a)			81 700
		TOTAL PRODUCTION COST (TPC)		15 898 700
G.1	Commercial and technical expenses (TPC X 0.01)			159 000
G.2	Administration (TPC X 0.02)			318 000
G.3	Interest on the capital			867 400
		TOTAL GENERAL EXPENSES		1 344 400
			TOTAL COST	17 243 100

---

[a] Personnel not directly engaged in the process but excluding staff in G.2.

The time loss in the use of the facility is caused by stages (c) and (e). This is estimated as four months for each new application. The other stages are independent and may be carried out while the plant is operating elsewhere.

The number of ore bodies that can be treated and the operation time are functions of the ore body size, as can be seen below.

Ore body size (t U_3O_8)	500	250	125	62.5	31.2	15.6
Number of ore bodies	1	2	4	8	16	32
Operation time (a)	10.4	10.8	11.4	12.8	15.4	20.8

for an operation time of 330 d/a.

3.4. Requirements

As an example of the use of a modular plant a deposit producing 500 t U_3O_8 has been chosen. In addition, the cost analysis of five other ore bodies (3.3) has been considered. Consumption and supply values for the basic case are stated in Table II. It is worth considering that:

(a) Mineral mining wastes are not taken into account; the mineral alone has to bear all the mining expenses.

(b) Reagents: the highest cost is for sulphuric acid, 30 kg/t, followed by lime, 17 kg/t, and then ammonia, 0.3 kg/t.

(c) Services: water consumption is small, 0.17 m^3/t, as a consequence of the recycling of the extraction effluents. The electrical power is also low, 10 kW·h/t, because no grinding and conventional leaching are used. The power supply is less than 125 kW. Among the services are included the requirements for the heaps, which are proportional to the treated ore and in the order of 0.23 m^2/t for a heap height of about 4–4.5 m.

(d) Manpower: direct manpower is estimated at 15 men, working continuously in three shifts with three operators each. Others remain in the lab and at other tasks. Thirty per cent has also been included for indirect manpower, but maintenance is not included here.

3.5. Investments

Investments will fix the amortization costs and the capital interest. A modular plant has a fixed investment which will be amortized over its whole life. Besides, every exploitation will generate some costs to be amortized by this same ore body because they cannot be transferred to another one.

Table III indicates the investment for a plant with a unique location, which amounts to US $817 000. To simplify the study of its application to several ore bodies the total investment has been divided in two blocks. One represents 77%

TABLE III. INVESTMENT FOR THE URANIUM PRODUCTION WITH A MODULAR PLANT

Concept		US $	%
A.	Modular plant in factory		
	Equipment	425 000	52.0
	Transport	16 000	2.0
	Assembly	41 000	5.0
	Piping	25 000	3.1
	Instrumentation and control	33 000	4.0
	Electricity	49 000	6.0
	Engineering and others	40 000	4.9
		629 000	77.0
B.	Application to an ore body		
	Transport (400 km)	3 000	0.4
	Land	16 000	2.0
	Foundations and civil work	25 000	3.1
	Site erection and startup	46 000	5.5
	Services	33 000	4.0
	Environmental impact	49 000	6.0
	Engineering, insurance, licences etc.	16 000	2.1
		188 000	23.0
	TOTAL	817 000	100.0

and corresponds to the modular plant and is recovered. The other represents 23% and is equivalent to the corresponding part of an exploitation or application; this investment is not recovered and must be amortized by each deposit.

In the first block the main amount (52%) corresponds to the process equipment. Within the non-recoverable part the main concepts are the licences and the environmental aspects (6%) and the assembly and startup with 5.5%. This block does not include the necessary land for the heaps because this depends on the treated ore, and so this item has been transferred to the operation expenses.

For each location the total investment will be increased by US $188 000, say, as the investment necessary to build a new plant and decondition the exhausted one.

3.6. Costs

A cost exercise for a unique ore body and plant to produce 500 t U_3O_8 has been made to illustrate the politics of the modular plant use. The operation time would be 10.4 years. The treated ore would be 625 000 t of ore with a grade equal to 1 kg U_3O_8/t.

Table II shows the production costs. The different concepts have been separated [11]. Data correspond to the total production (500 t U_3O_8). The main aspects of the production cost are:

Mining	54.4%
Reagents	9.7%
Services	8.5%
Manpower	11.3%
Amortization	4.7%
Interest on the capital	5.0%

The details of the different costs can be seen in Table II. The interest on the capital is calculated using the following expression:

$$I = C \times t \times i - \left(\sum_{n=1}^{n=t-1} (t-n) \right) \times (C/t) \times i$$

where I = total interest
C = investment
i = annual rate, 0.15 (15%)
t = operation time in years

The total cost of uranium production is US \$15.7/lb U_3O_8. The sales price could be obtained by the addition of the drying and packing costs, and the profit and taxes.

The cost is low but it should be taken into account that the basic case is the most favourable. It is interesting to calculate other less favourable conditions. This has been done for deposits with various amounts of uranium production (t U_3O_8/deposit) up to 500 t U_3O_8. The results are the following:

Ore body (t U_3O_8)	500	250	125	62.5	31.2	15.6
Number of ore bodies	1	2	4	8	16	32
Operation time (a)	10.4	10.8	11.4	12.8	15.4	20.8
Cost (US \$/lb U_3O_8)	15.7	16.2	17.3	19.6	24.5	36.1

The production costs are plotted against the number and capacity of the treated deposits in Fig.4. A grade of 1‰ U_3O_8 and a uranium recovery of 80% are assumed.

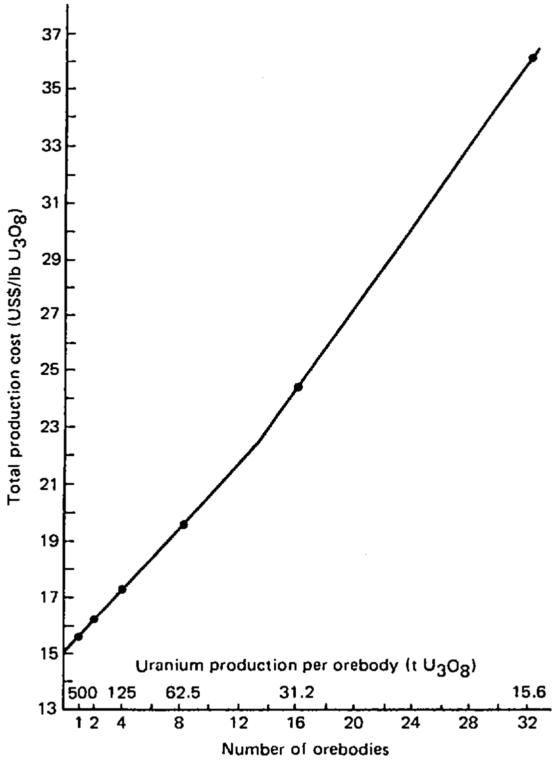

FIG.4. Effect of the number of ore bodies on the total cost of uranium production.

Analysis of the results suggests that the cost increases linearly when the number of deposits treated increases, i.e. when the ore body size decreases.

Amortization is most important for small deposits, because of the higher number of new locations. Another item that has considerable influence is the interest on the capital, because this is higher as a consequence of the longer life of the modular plant. Amortization and interest represent 23.0, 33.8 and 49.0% of the production costs for the last three cases indicated above. It seems that deposits or a group of small deposits close together with 36 t U_3O_8 of total reserves could be exploited using modular plants that could be used at other locations.

4. PERSPECTIVES

In accordance with the concepts discussed above, it can be seen that modular plants could be a solution to exploiting small deposits. Their use in several deposits is necessary to charge each a proportion of plant amortization and the expenses caused by the plant location. The example considered refers to a plant with few compact elements. In Spain we have designed more compact plants [12], especially for pilot-plant study of uranium recovery from phosphoric acid. The equipment is assembled in six standard containers whose sides may be lowered to facilitate equipment operation and the equipment is interconnected by the minimum number of pipes.

A fundamental aspect must be taken into account in radioactive facilities such as uranium exploitation plants. This concerns authorizations, regulations and so on. Because of the difficulty of obtaining permission miners may well refrain from exploiting small ore bodies and reject them.

The use of modular plants may in any case make it easier to obtain the requisite permission. These authorizations may be divided into two types: those concerning the modular plant itself, available for all the applications, and those referring to the plant location and ore body exploitation, which would be separate for each case and could be attended to at the same time as it is decided to exploit the deposit and the preliminary work starts. Finally, it would only be necessary to unite both permissions to cover all the legal requirements.

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DISCUSSION

K. CHITUMBO: The ore grade in your example was 0.1% U_3O_8. Could a modular plant be used for an ore with 600 ppm U_3O_8?

A. MORAL: What we have shown is, of course, only an example. Each ore is different and for each ore you must apply the corresponding data. Generally speaking if your ore can be processed efficiently you can use a modular plant.

THE ACID PRESSURE LEACHING PROCESS FOR THE KEY LAKE PROJECT, CANADA

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Abstract

THE ACID PRESSURE LEACHING PROCESS FOR THE KEY LAKE PROJECT, CANADA.

Key Lake ore contains 2.5% U_3O_8, 2.5% Ni and 1.5% As. A new leaching process will be applied to yield a saleable product and to establish environmentally acceptable mining and milling operations. The process involves pressurized acid leaching, CCD, solvent extraction, bulk precipitation of nickel and arsenic, yellowcake precipitation, radium removal, ammonium sulphate crystallization and subaerial tailings deposition secured against seepage by an underdrainage system. The first process idea was developed in the laboratories of the Uranerz GmbH at Bonn, in 1976. The Key Lake process was optimized at the pilot plant of Sherritt-Gordon, Canada, between 1977 and the end of 1979. Engineering was carried out in 1981 by Wright Engineers. Construction of the facilities started in late 1981 and will be completed in 1983. The core of the Key Lake mill is the two-stage leaching section comprising four storage pachucas followed by four primary leach pachucas, 10 secondary vertical autoclaves and a neutralization section for the bulk precipitation of arsenic and nickel with subsequent radium removal. The solvent extraction plant with four mixer-settlers for extraction, four for scrubbing, four for stripping and two for regeneration is of Krebs design. The Key Lake operation will produce 12×10^6 lb/a U_3O_8.

1. PRESSURIZED LEACHING IN URANIUM PRODUCTION

Pressurized leaching is applied to ores from which it is difficult to extract the uranium and which only can be economically leached when the leaching temperature and the partial pressure of oxygen are elevated. At present about 10–15% of the uranium concentrate of the western world is produced by pressurized leaching. Of this about 4–5% are leached in alkaline solutions and 5–10% in acidic solutions. The leaching temperature in the autoclaves is in the range of 40 to 90°C and the oxygen partial pressure is about 500 kPa. The latter is much higher than in common pachuca leaching where only oxygen-enriched air is applied. About 20% of the uranium product is acid leached in pachucas, while the major part, i.e. 65–70%, of the yellowcake is produced by atmospheric leaching, 5–10% heap leaching and in situ leaching included.

The principles of pressure leaching are described in Refs [1–7].

TABLE I. CHEMICAL COMPOSITION OF THE FEED ORE

Component	Per cent Ave.	Min.	Max.
Uranium (U_3O_8)	2.5	2.0	3.0
Nickel	2.5	1.5	3.5
Arsenic	1.4	0.9	3.0
Iron	3.5	2.5	5.0
Aluminium	9.3	6.0	11.0
Magnesium	3.0	1.0	4.0
Sulphur	1.0	0.5	3.0
Silica	50	40	70

TABLE II. PRODUCT SIZE DISTRIBUTION OF THE GROUND ORE

Micron	Mesh	% passing
500	32	100
250	60	80
125	115	60
88	170	50
44	325	40

2. THE KEY LAKE ORE

Uranium, nickel, arsenic and sulphur are the most important ore-forming elements of the mineralization. The uranium is present in the form of oxides (uraninite and sooty pitchblende) and as silicate (coffinite), nickel is mineralized as sulphoarsenide (gersdorffite), sulphide (millerite) and arsenide (niccolite). Other ore minerals are of minor importance.

The uranium and the nickel minerals vary in their grain sizes between several mm and minus 10 μm. They are intergrown to each other and with the silicates of the matrix.

The chemical composition of the ore is described in Table I. The different grades of the run of mine ores are blended to the average mill feed grade of 2.5% U_3O_8.

The host rock of the ore minerals has two different formations, the older mylonized basement and the younger Athabasca sandstone covering the basement. Several tectonic movements created the breccia type of the basement ore and the impregnation of uranium and nickel minerals in the pores and fissures in the covering sandstone [8, 9].

Crushing and grinding of ore to 100% minus 0.5 mm (80% minus 0.3 mm) is necessary to liberate the ore particles from the matrix and to permit efficient acid leaching [10].

The distribution size of the ground ore is given in Table II.

3. DEVELOPMENT OF THE KEY LAKE PROCESS

A firm that possesses experience in the leaching of uranium from the complex silver, copper, cobalt, bismuth, arsenic ore from the Black Forest, Germany, Uranerz-Bonn (UEB) started leaching tests with boulders from Key Lake in the summer of 1975. Preliminary tests showed that fine grinding was necessary and that pressurized acid leaching was preferable rather than alkaline leaching because of the arsenic. Tests using cationic ion exchange resulted in a patent application by UEB on 6 May 1976. The application of the Bonn-Process has been registered in Canada since 13 July 1977 under No.280.432 (a description of the process is given in Ref.[11]).

Extended bench-scale tests and piloting of a process based on pressurized acid leaching and solvent extraction were carried out in 1977 to 1979 by Uranerz Exploration and Mining Limited, Canada, together with Sherritt Gordon Mines Ltd, Canada, in Fort Saskatchewan. The result was the establishment of a new process route for the Key Lake uranium/nickel ore. The process involves crushing and grinding of the blended ore to <0.5 mm, storage of the ore pulp for grade control, two-stage acid leaching with pachuca leaching first, followed by pressurized leaching in autoclaves under oxygen atmosphere (Fig.1). The leached pulp enters the countercurrent decantation (CCD) circuit for solid/liquid separation. The solids are neutralized with lime and disposed in the tailings pond. Uranium is extracted from the clarified leach solution by solvent extraction and precipitated as ammonium diuranate. Ammonia is not recovered but sold as a crystallized ammonium sulphate fertilizer. The barren strip solution is neutralized with lime in two stages to precipitate nickel, iron and arsenic first and subsequently the radium with the addition of barium chloride. The alkaline precipitate of the heavy metals is combined with the leach residues after neutralization and disposed of together in the tailings pond.

The Key Lake process is described in detail in Refs [4, 12–16].

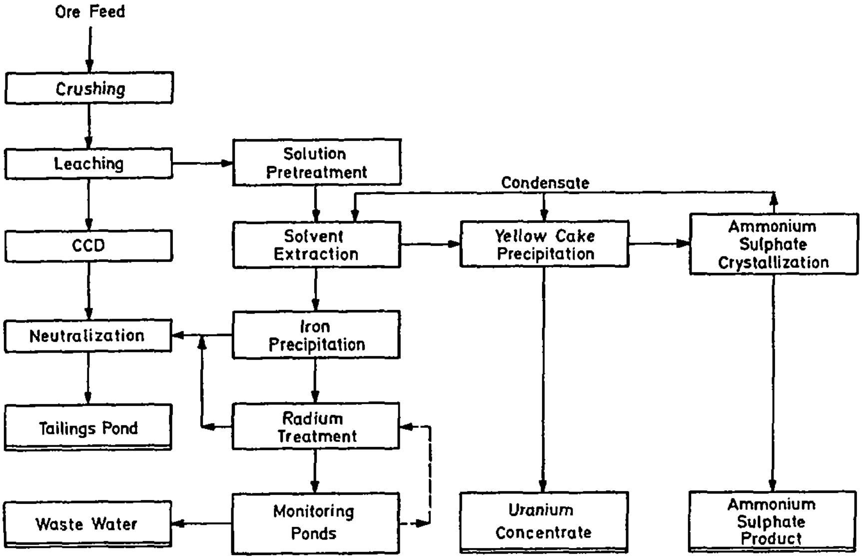

FIG.1. Key Lake flowsheet.

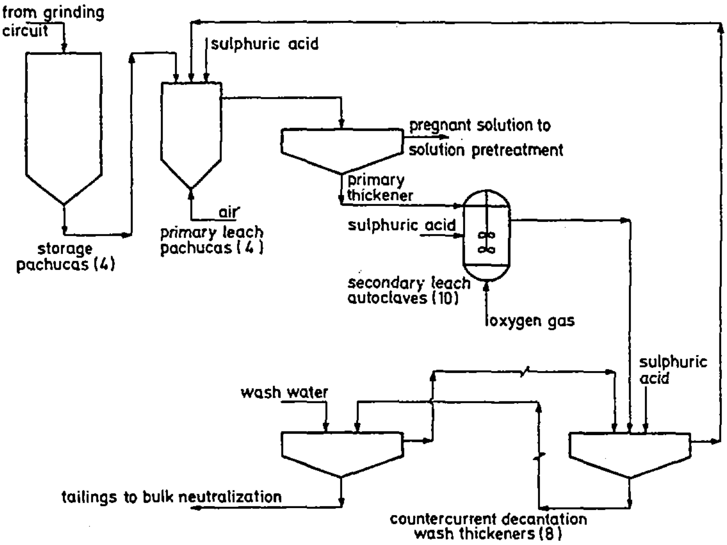

FIG.2. Schematic diagram of the Key Lake leach CCD circuit.

4. DESIGN OF THE LEACH CIRCUIT

The design is based on pilot tests with a wide range of ore types and blends from both orebodies, i.e. Gaertner and Deilmann orebodies, and in particular on

Gaertner sandstone ore
Gaertner basement ore (high, medium and low in uranium, nickel, arsenic)
Deilmann sandstone ore
Deilmann basement ore (high and medium in uranium, nickel, arsenic).

Various composites of these ore types were leached in a pilot plant comprising atmospheric pachuca leaching, pressure leaching and wash thickening. The schematic diagram is given in Fig.2, see also Refs [10, 17, 18].

The ore pulp is stored and conditioned at 40–50% solids in 4 pachuca tanks (6.5 m dia) and primary leached in 4 pachucas in series (3.0 m dia) for 2 hours. The primary leach pulp of 15% solids is thickened to 40% solids and secondary leached in a series of up to 10 autoclaves (3.34 m dia, 33.4 m^3 volume each) for 3–4 hours.

The optimum criteria for the pressurized stage were established as follows:

Ore grind	80% < 0.3 mm
Specific gravity of pulp	1.3–1.6 kg/L
solids	40–50%
pH of leach pulp	<1.0
Number of autoclaves	10
Leaching time	3.5 h in 8 autoclaves (2 for standby)
Temperature	70°C
Oxygen pressure	600 kPa
U_3O_8 recovery	99%

The Key Lake process is based on pressure leaching because of the very good results of the pilot tests. The great effect of an increased partial pressure and temperature on the residence time and consequently on decreasing the reagent consumption and cost is shown in Fig.3.

Figure 4 shows that 8 autoclaves in series are sufficient to yield 99.0% recovery even for feed ore with 50% of difficult-to-leach ore types. The residence time is 3.5 h in total, which is considerably lower than for atmospheric agitation leaching [10, 17].

5. SELECTION OF TYPE OF AUTOCLAVE

Prior to final installation of the autoclaves a comprehensive study was made on comparing the capability of vertical and horizontal autoclaves [19, 20]. The major criteria for this comparison were that the Key Lake Project in a remote

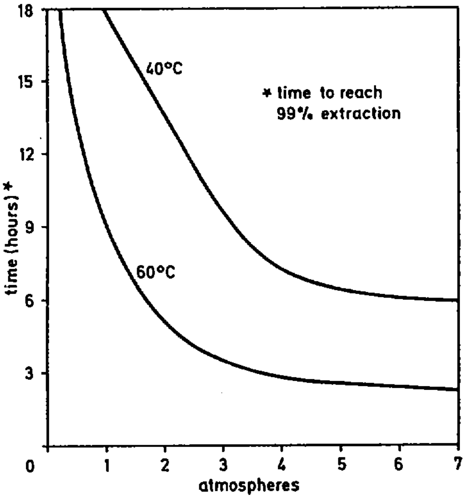

FIG.3. Effect of oxygen partial pressure.

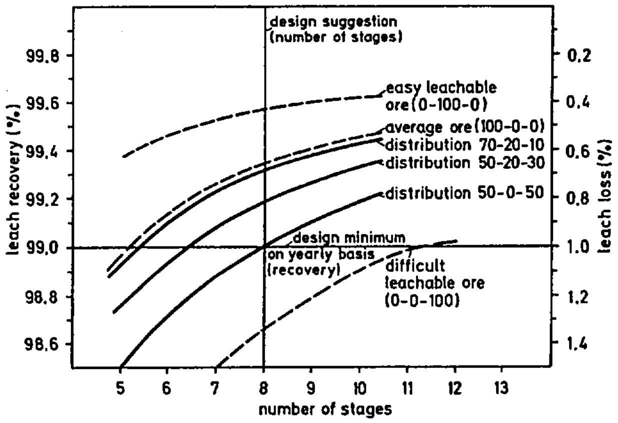

FIG.4. Summary of results of uranium extraction calculations.

location in Northern Saskatchewan, with a variable mill feed grade (i.e. 2.0–3.0% U_3O_8) and a possible variable production rate, i.e. between 10 and 12 × 10^6 lb U_3O_8 (plus), necessitates a leach system with very high flexibility and availability.

It is, however, realized that horizontal autoclaves would have a simpler layout, requiring less piping and structural steel than a plant with a series of vertical autoclaves. Apart from the capital cost difference between the two

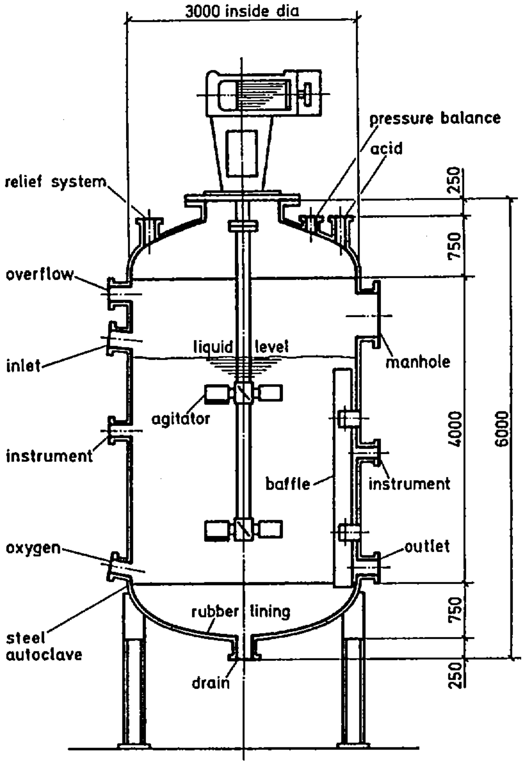

FIG.5. Schematic cross-section of vertical autoclave.

types of autoclaves, it was found that availability and flexibility would be the deciding items in minimizing the cost over the total lifespan of the project.

A system of eight vertical autoclaves was compared with one of three horizontal autoclaves (four compartments each) on the basis of test work and calculations on:

(1) Temperature and process control (heat balance)
(2) Capital and operating cost
(3) Flexibility

Despite the slightly higher total capital cost for the vertical autoclaves, the vertical type was favoured because of its very good temperature control at about 70°C and maximum of flexibility and availability for the variable Key Lake ore.

A schematic cross-section of the vertical autoclaves selected is shown in Fig.5. The actual volume is 33.4 m^3. They are of carbon steel and lined internally with 12 mm thick rubber. They contain ore slurry to not more than 70% of the autoclave volume.

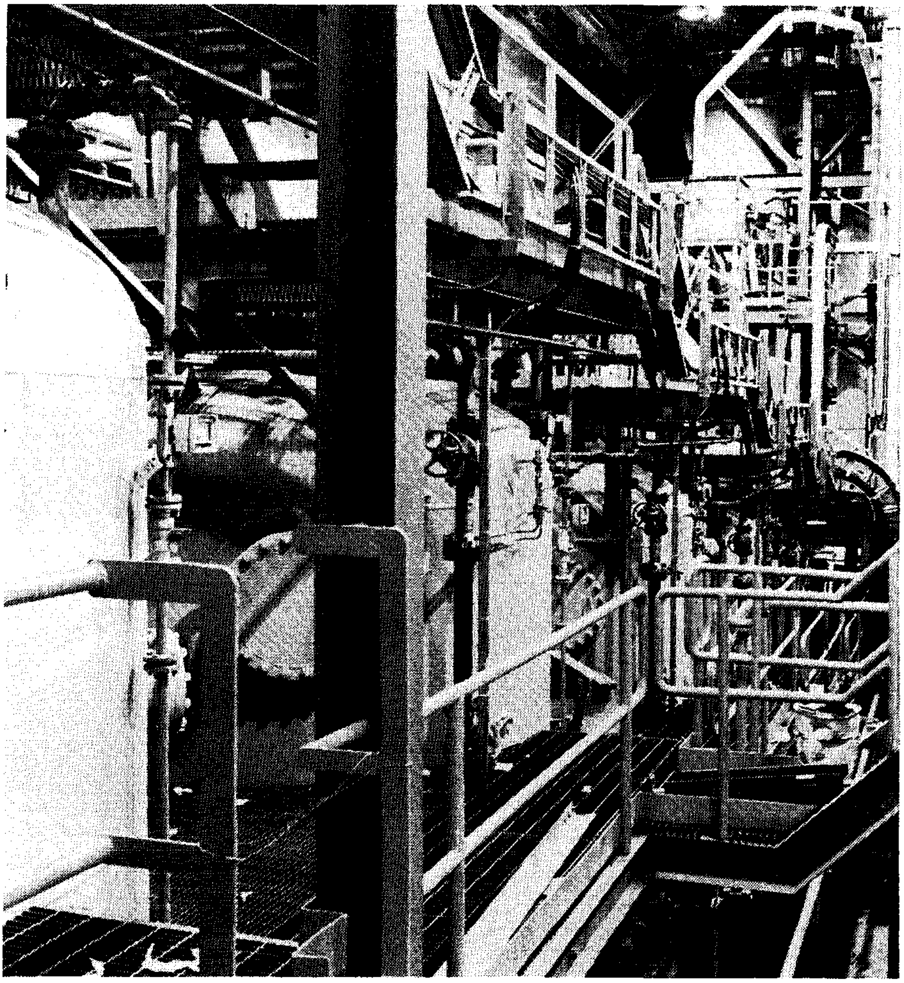

FIG.6. Installed vertical autoclave.

The autoclaves are designed for continuous operation, 24 hours per day, 7 days per week. They are arranged in series, with slurry flowing by gravity through any eight autoclaves in series at rates varying from 17 to 66 m^3/h (Fig.6). Oxygen is introduced into the autoclaves by spargers at a pressure of about 700 kPa and dispersed into the slurry by the agitator.

The agitators are of the double-impeller type. Shaft and impeller are butyl rubber covered 316 stainless steel. The impeller is 37 kW (50 hp) at 70 to 110 rev/min.

The autoclaves are manufactured by Johnson Boiler & Tank Ltd, Vancouver, and the mixer by Greey Mixing, Canada.

6. SOLID/LIQUID SEPARATION

Solid/liquid separation after leaching is performed in a series of eight CCD tanks, 60 ft diameter each. The construction of the tanks is conventional. The thickener underflow is neutralized and discharged to the tailings pond.

The overflow from the CCD thickeners contains approx. 15 g U_3O_8/L. More than 65 g H_2SO_4/t ore are added to the CCD pulp to maintain the pH value below 1.0. Under this condition no uranium is precipitated as uranium arsenate and the washing loss on uranium is $<0.15\%$. The strong acidic solution from the CCD is combined with the lower grade and clarified solution from the pachuca leach for further polishing filtration (<5 ppm solids). Filtration is supported by polyox flocculents (30 g/t solution). The uranium content of the clean solution ranges between 5–6 g U_3O_8/L and is directly treated by solvent extraction. The pH of the pregnant solution is maintained to pH < 1.0. For Refs see [6, 21–23].

7. SOLVENT EXTRACTION OF URANIUM

The solvent extraction plant is built according to the Krebs System and comprises 13 units installed in the following sections:

Units	Sections
4	Uranium extraction
3	Arsenic scrub
4	Uranium stripping (re-extraction)
1	Regeneration of organic
1	Ammonium sulphate scrub

The solvent consists of 6% tertiary amine, 3% isodecanol, 91% kerosine [6].

The principles of the Krebs unit are shown in Fig.7. The most characteristic items are (a) the conical pump for an adjusted flowrate, (b) the small mixer with a low tip speed; (c) the launder, (d) the cover, and (e) the settling compartment for final phase separation. The material of construction for the Krebs plant is fibre-reinforced plastic.

8. NEUTRALIZATION AND RADIUM REMOVAL

The barren strip solution from the solvent extraction plant is treated as shown in Fig.8. The leach residues from CCD are neutralized with burnt lime and mixed with the sludges from neutralizing the nickel, iron and arsenic-bearing raffinate. The bulk precipitates are discharged to tailings with recycling of the supernatant to neutralization of the heavy metals [10].

ⓐ conical pump to provide liquid transfer and enhance phase coalescence
ⓑ agitator selected on the basis of mixing requirements
ⓒ superimposed launder providing further phase separation
ⓓ removable covers
ⓔ settler for final separation.

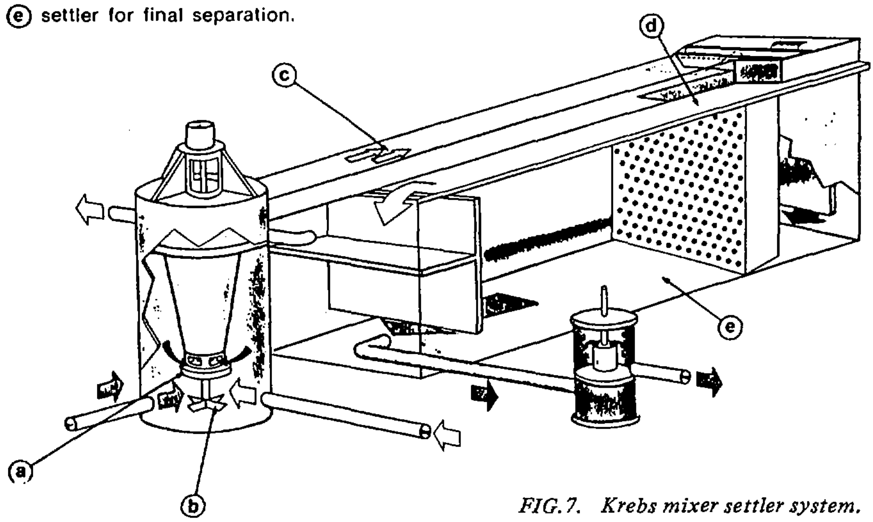

FIG.7. Krebs mixer settler system.

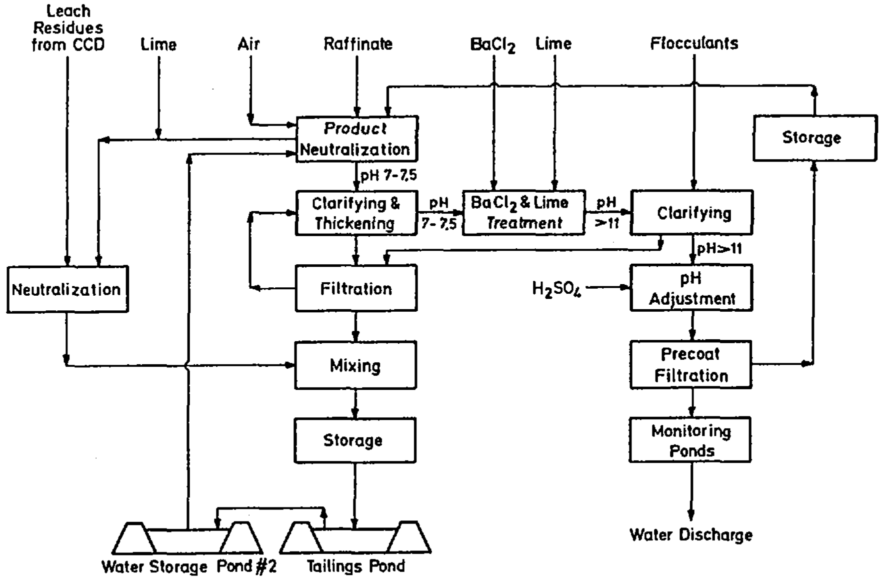

FIG.8. Key Lake neutralization and radium treatment.

TABLE III. KEY LAKE CONCENTRATE (UNCALCINED) (%)

Uranium	75
Arsenic	0.015
Boron	<0.0001
Calcium	0.019
Carbonate	0.330
Fluorine	0.004
Iron	0.006
Magnesium	0.002
Molybdenum	0.057
Nickel	0.002
Sulphate	1.440
Thorium	<0.015
Titanium	0.002
Vanadium	0.0002

The filtrate from the heavy metal precipitation is treated with barium chloride for co-precipitation of radium. After clarifying and precoat filtration of the solution excess water is monitored and discharged into running water.

9. THE YELLOWCAKE PRODUCT

The uranium is precipitated from the pregnant strip solution (25 g U_3O_8/L) by gaseous ammonia at pH 7–8. The precipitate is dewatered by a centrifuge to <60% solids and dryed to yellowcake in a multiple hearth dryer. The product is according to specifications [18]. The analysis is shown in Table III.

All discharged slurries and solutions are contained in the tailings pond. The dimensions are 650 m width, 684 m length and 10 m depth. The pond was completely constructed and built prior to startup of the mill. The solids of the leach wastes and radium sludge settle together quickly in layers of only 5–7 cm thickness, thus incorporating the radioactive material and diminishing radiation. The supernatant is recycled to the mill. A cross-section of the tailings dam is given in Fig.9.

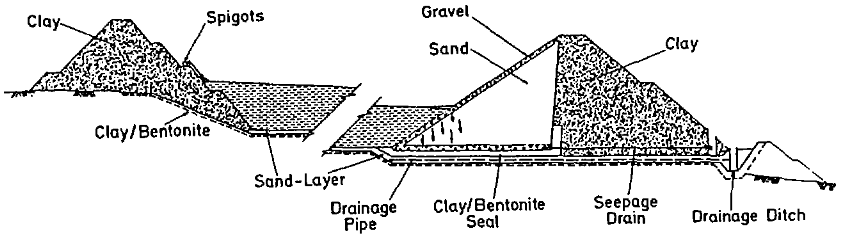

FIG.9. Key Lake Tailings Pond.

TABLE IV. CAPITAL COST ESTIMATE OF THE LEACHING PLANT 1981

		$\$ \times 10^6$
Building	60 m X 20 m, 19 m height, plumbing, fire protection, lighting, power outlets	4 965
Equipment	4 storage pachucas (6.5 m dia) 4 rubber-lined leach pachucas (3 m dia) 1 primary thickener 10 vertical autoclaves (3 m dia) piping instrumentation electrical motors and cables, lighting	10 137
Leaching plant	direct cost total	15 102
	indirect costs	3 013
Grand Total		18 115

10. ENGINEERING AND CONSTRUCTION SCHEDULE

The deposits were discovered in July 1975 and geologically developed during 1975 to 1977. Metallurgical testing started in parallel and piloting was finalized in mid-1979. The Environmental Impact Statement was presented to the Department of the Environment in October 1979 and approval was issued after extensive public hearings in August 1981. Detailed engineering, lake dewatering, mine development and mill construction started in 1981 and were completed in September 1983 [10].

The engineering and construction schedule was controlled by applying the Critical Path Method (CPM) and the PERT Method. The schedules were revised twice a year.

11. CAPITAL COST

The total capital cost of the Key Lake project are Can$ 459 million. Of this the capital costs for the pressurized leaching plant directly and indirectly are about Can$ 18 million. Some details of the capital costs are given in Table IV.

The total capital cost expended was below that budgetted.

12. STARTUP OF PRODUCTION

Commencement of the startup of the project was scheduled first for the middle of 1983, but this date was affected by a long strike in the spring of 1982. The new schedule was the end of September 1983 in order to reach full production of 1×10^6 lb U_3O_8 per month at the begin of 1984.

Hiring and training of employees started mid-1983. The full staff in operation, administration and management will be 472 people, with about half on site at any one time.

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DISCUSSION

W.T. RUHMER: I must congratulate Dr. Flöter on an excellent paper. We have been doing pressure leaching test work for some years now, also in collaboration with Sherritt-Gordon. I must say that I am amazed at the 99% extraction that you are able to achieve. On the western front wall we have a rather refractory ore: with normal atmospheric pressure leaching at 60°C we only achieve a 78% extraction in 24 hours. Our pressure leach test work indicated that we could get up to 93% extraction so we installed a pilot plant. We started using a horizontal full compartment Sherritt-Gordon-type autoclave at 150°C and a pressure of 11 to 12 atmospheres with oxygen injection. The partial pressure of oxygen, was about 900 kPa. The relative density of the pulp was 1.55 and we were able to get a 93% extraction in 2 hours, which looked very favourable. The cost of the plant was, however, three times that of an atmospheric pressure leach plant. The biggest problem was the materials of construction. Our autoclave was lined with 6 mm of chemical lead and 230 mm of acid-proof brick. This stood up very well but the big problem was the impellers. We tried many types of materials of construction including ceramics, which were too brittle and just broke, and we eventually had to opt for titanium.

L'USINE DE LODEVE: UN PROCEDE ALCALIN COMPLEXE POUR UN MINERAI D'URANIUM COMPLEXE

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Abstract–Résumé

THE LODEVE PLANT: A COMPLEX ALKALINE PROCESS FOR A COMPLEX URANIUM ORE.

The Lodève plant (Massif Central, France) has to process ores with complex and difficult characteristics and employs an equally complex and difficult process to do so. Although it has been necessary to call upon various technological innovations, plant operation is now (as a result of the combined efforts of groups from the General Nuclear Materials Company (Cogéma and the Western Ore Industrial Company (Simo) and with the help of the Krebs Engineering Company and a number of suppliers) close to reaching its rated value and can only improve with the modifications which are now being effected.

L'USINE DE LODEVE: UN PROCEDE ALCALIN COMPLEXE POUR UN MINERAI D'URANIUM COMPLEXE.

L'usine de Lodève (Massif Central, France), qui doit traiter des minerais de caractéristiques complexes et difficiles, applique un procédé également complexe et difficile. Bien qu'on ait fait appel à plusieurs innovations technologiques, elle a atteint aujourd'hui, grâce aux efforts conjugués des équipes de la Compagnie générale des matières nucléaires (Cogéma) et de la Société industrielle des minerais de l'ouest (Simo), et avec l'aide de la Société d'ingénierie Krebs et de certains fournisseurs, un régime de marche proche du nominal que des modifications en cours de réalisation ne pourront qu'améliorer.

1. MISE AU POINT DU PROCEDE

1.1. Contexte géologique du gisement. Particularités minéralogiques et chimiques des minerais de Lodève

Les minéralisations uranifères de Lodève sont situées dans une formation permienne en bordure sud du Massif Central.

La découverte des premiers indices remonte à 1957. Les reconnaissances par sondage se sont poursuivies jusqu'en 1974, date à laquelle a été prise la décision d'exploitation.

Les premiers travaux miniers remontent à 1975, l'extraction à ciel ouvert à 1978 et en mine à 1979. L'usine a démarré au deuxième semestre 1981. La Compagnie générale des matières nucléaires (Cogéma) à laquelle appartient ce gisement dispose de 20 000 tonnes de réserves, à une teneur moyenne supérieure à 0,2% U. La production annuelle est de 1000 tonnes.

1.1.1. Données géologiques

Le permien de Lodève est constitué d'autunien gris, surmonté de saxonien rouge, le passage de l'un à l'autre se faisant par alternance de faciès gris et rouges. Cette formation, non plissée mais faillée, a un pendage de 15° vers le sud et repose en discordance sur l'antécambrien et du cambrien dolomitique et schisteux. Le bassin est limité à l'est et à l'ouest par deux failles nord-sud et vers le sud par du trias venant en transgression.

L'uranium est essentiellement réduit et localisé dans l'autunien gris dont la puissance est de l'ordre de 500 mètres.

On peut ramener les minéralisations uranifères à deux types:

a) Aspect stratiforme

L'autunien gris est constitué par une pélite fondamentale dans laquelle viennent s'individualiser des couches plus ou moins enrichies en matières organiques diffuses a priori favorables à l'uranium. On en compte plus d'une soixantaine. Elles peuvent, suivant les localisations, être minéralisées ou non et sont d'autant plus fréquentes et puissantes que l'on s'approche de la base de la série.

L'uranium est:

– soit diffus dans les parties les plus noires des couches: il n'est pas visible au microscope;

– soit filonien et exprimé sous forme de pechblende en association avec des matières organiques plus évoluées (type bitume); ces filons recoupent les couches, mais ne débordent pas, en général, dans la pélite fondamentale.

b) Aspect réseaux filoniens

Au voisinage des grandes failles est-ouest (Riviéral, Saint-Julien), il existe des réseaux filoniens riches en matières asphaltiques dans lesquelles la pechblende est présente sous forme d'inclusions fines (taille de l'ordre de 1 à 10 μm). Ces réseaux très denses et très développés forment des amas englobant les couches et la pélite fondamentale. Ainsi, les réserves de Mas Lavayre, qui est le principal gisement de Lodève, sont constituées, pour une part, par des amas riches.

1.1.2. Particularités minéralogiques et conséquences pour le traitement

Le traitement des minerais de Lodève a présenté de nombreuses difficultés. Une bonne partie d'entre elles est due aux matières organiques gênantes par leurs propriétés et, également, par leur association avec l'uranium; les autres proviennent des différents constituants du minerai.

1.1.2.1. Carbonates naturels

Le teneur en carbonates est élevée (6 à 10% de CO_2). Il s'agit essentiellement d'ankérite (dolomie ferrifère) et très localement de sidérite. Leur existence a orienté le traitement vers la voie alcaline.

1.1.2.2. Matériaux phylliteux

Le minerai est très riche en matériaux phylliteux, principalement illite et interstratifiés, illite-montmorillonite. Ces minéraux sont inertes chimiquement en milieu alcalin, mais leur fragilité, surtout avec un broyage fin, a posé des problèmes au niveau de la séparation liquide-solide par filtration: recherche du floculant le plus efficace et mise au point du mode de préparation et de condionnement le plus approprié.

1.1.2.3. Sulfures

La teneur en soufre est en moyenne comprise entre 0,6 et 0,8%. La pyrite est sans doute le constituant majeur, mais il existe d'autres sulfures (blende en particulier), des sulfates et il n'est pas exclu qu'une partie du soufre soit liée aux matières organiques.

Les diverses tentatives de flottation des sulfures n'ont pas donné de bons résultats. En pratique, les rendements en soufre n'ont guère dépassé 50% et le concentré, du fait de la flottabilité des matières bitumineuses, contenait une fraction notable de l'uranium. De plus, les essais de reprise acide sur ces produits n'ont abouti qu'à des rendements médiocres en uranium.

Au total, on a dû renoncer à une séparation physique préalable des porteurs de soufre. Ceci a eu deux types de conséquences:

- production inévitable de sulfate de soude: ce produit n'étant pas rejetable dans l'environnement, il a fallu le cristalliser et, pour en faire un produit de qualité, le débarrasser auparavant des autres polluants;
- la mise en solution de l'uranium relativement réfractaire exigeant une concentration élevée en carbonate de soude ($100\ g \cdot L^{-1}$), il a été nécessaire d'adopter un schéma assez particulier de préattaque-attaque pour obtenir une liqueur de production avec le minimum de carbonate et la totalité des sulfates et de l'uranium.

1.1.2.4. Molybdène

Il n'est que partiellement lié à la minéralisation uranifère. Il semble surtout exister dans les niveaux supérieurs (entre 0 et 150 m). En dessous, les teneurs sont inférieures à 100 pp10^6 (cas de l'essentiel des réserves du Mas Lavayre). Il est peu probable qu'il dépasse 10% en moyenne par rapport à l'uranium. Lorsqu'il est concentré, il apparaît sous forme de taches bleues d'ilsémanite dès que le minerai est exposé à l'air humide.

Dans le procédé, le molybdène se retrouve dans l'effluent aqueux et il est éliminé sous forme de MoS_3 avant épuration sur charbon actif et cristallisation du sulfate de soude.

1.1.2.5. Zirconium

Le minerai de Lodève contient du zirconium soluble en milieu alcalin. Sa teneur est faible (une à quelques parties pour cent par rapport à l'uranium), mais cet élément se retrouve intégralement dans le concentré final et rend le raffinage plus difficile, ce qui entraîne des pénalités. Il est vraisemblablement lié à des silicates complexes riches en uranium et assez mal définis.

1.1.2.6. Matières organiques

Ces matières organiques sont gênantes de plusieurs façons. On a rencontré principalement trois types de difficultés.

a) Association de matières bitumineuses et d'uranium

Les premières études effectuées sur des minerais provenant de couches à uranium diffus dominant donnaient des rendements du même ordre dans toutes les tranches granulométriques jusqu'à 300 μm: les grains restaient pénétrables par les solutions carbonatées. Par contre, les minerais filoniens du Mas Lavayre se sont montrés très sensibles à la maille de broyage. Rapidement, il est apparu qu'il fallait broyer à moins de 200 μm (d'où la maille adoptée: 95% des produits inférieurs à 160 μm). Ceci est sans aucun doute dû aux fines disséminations de pechblende dans les bitumes qui exigent, sinon une libération totale, au moins un broyage suffisant pour que la pénétration des réactifs soit convenablement assurée.

b) Pouvoir réducteur

Il ne fait aucun doute que la mise en solution difficile de l'uranium est essentiellement due au pouvoir réducteur des matières organiques. Pour obtenir un rendement satisfaisant, il a fallu adopter des conditions d'attaque sévères:

TABLEAU I. CONSTITUANTS CHIMIQUES ESSENTIELS D'UN MINERAI TYPE (EN %)

Constituant chimique	%	Constituant chimique	%
SiO_2	51	V_2O_5	0,04
H_2O^-	1,8	MoO_3	0,01
H_2O^+	0,8	Na_2O	3,3
S total	0,6	K_2O	2,7
SO_3	0,05	MnO	0,06
P_2O_5	2,3	MgO	2,5
CO_2	6,9	CuO	0,01
Fe_2O_3	1,9	CaO	3,3
FeO	3,3	UO_3	0,4
Al_2O_3	14	ZrO_2	0,03
		TiO_2	0,6

température de 140° C, concentration en Na_2CO_3 élevée, oxydation par l'oxygène, utilisation d'hydroxyde ferrique.

c) Dégradation des matières organiques en milieu alcalin oxydant

Au cours de l'attaque, on obtient des liqueurs noires, riches en produits assimilables à des humates alcalins et provenant des matières organiques diffuses des couches et, éventuellement, de bitumes ayant subi une dégradation bactérienne.

Ces matières organiques sont gênantes dès l'attaque, car certaines d'entre elles ont des propriétés tensio-actives (cas des minerais relativement superficiels). L'utilisation de l'oxygène, nécessaire par ailleurs, au lieu d'air à gros débit, a permis de limiter les risques d'émulsion et de moussage. Mais la formation parallèle d'hydrogène et d'oxyde de carbone a conduit à une surveillance et à un renouvellement permanent de l'atmosphère des autoclaves.

Quoique la pré-attaque se soit révélée bénéfique à ce point de vue (une partie des matières organiques dissoutes pendant l'attaque se refixe sur les solides au cours de cette opération), certaines difficultés subsistent lors du traitement des liqueurs. L'existence probable de complexes uranium-matières organiques rend plus délicate la précipitation d'un préconcentré uranifère. Les effluents doivent être purifiés sur charbon actif avant cristallisation du sulfate de soude.

1.1.3. Analyse chimique d'un minerai type

Les constituants chimiques essentiels du minerai sont indiqués au tableau I.

1.2. Etudes de traitement en laboratoire et en pilote

Les premières études remontent à 1963 et se sont poursuivies jusqu'en 1975. Elles ont porté sur le rôle des paramètres fondamentaux et la comparaison autoclaves-pachucas. Si ce dernier type d'appareil apparaissait à peu près plausible pour les premiers minerais connus (Mas d'Alary), il s'est révélé insuffisant lorsque les premiers échantillons du Mas Lavayre sont arrivés.

1.2.1. Méthodes d'étude: essais de laboratoire et pilotage

Les études se sont particulièrement développées à partir de 1975, date à laquelle on a pu disposer de carottes de sondage à peu près représentatives. Elles ont été effectuées essentiellement en autoclaves de laboratoire, de 1000 g de minerai de capacité utile, et ont permis de préciser les grandes lignes du procédé. Le caractère très réfractaire de l'essentiel des réserves de Lodève et la présence de sulfures difficilement flottables ont conduit à un schéma d'attaque en deux temps:

– les solutions riches d'attaque tournent sur elles-mêmes afin d'augmenter la concentration en carbonate dans cette boucle;

– les solutions de lavage sont renvoyées vers la pré-attaque afin d'aboutir à une liqueur de production aussi pauvre que possible en carbonate.

Le pilotage s'est déroulé, pour l'essentiel, de mars à septembre 1977 avec les premiers échantillons du Mas Lavayre provenant de travaux miniers. Des campagnes complémentaires se sont déroulées fin 1978 et au cours du premier semestre 1979. Le point de départ réside dans les opérations de préattaque et attaque. En accord avec la société L'Air liquide, expérimentée dans le domaine de l'utilisation chimique de l'oxygène, on a choisi un autoclave d'assez grandes dimensions de manière à traiter le problème de la meilleure utilisation de l'oxygène. Cet appareil ne pouvant fonctionner que par charge, on a été conduit logiquement au pilotage en séquentiel.

Les figures 1 et 2 donnent le découpage dans l'espace sur un cycle et le découpage dans le temps sur trois cycles, soit une semaine. On voit qu'il a suffi de trois équipes spécialisées: l'une dans le broyage, l'autre dans la pré-attaque et la troisième effectuant les filtrations. Bien entendu, le broyage et les filtrations ont été, à l'intérieur de chaque poste, réalisés en continu.

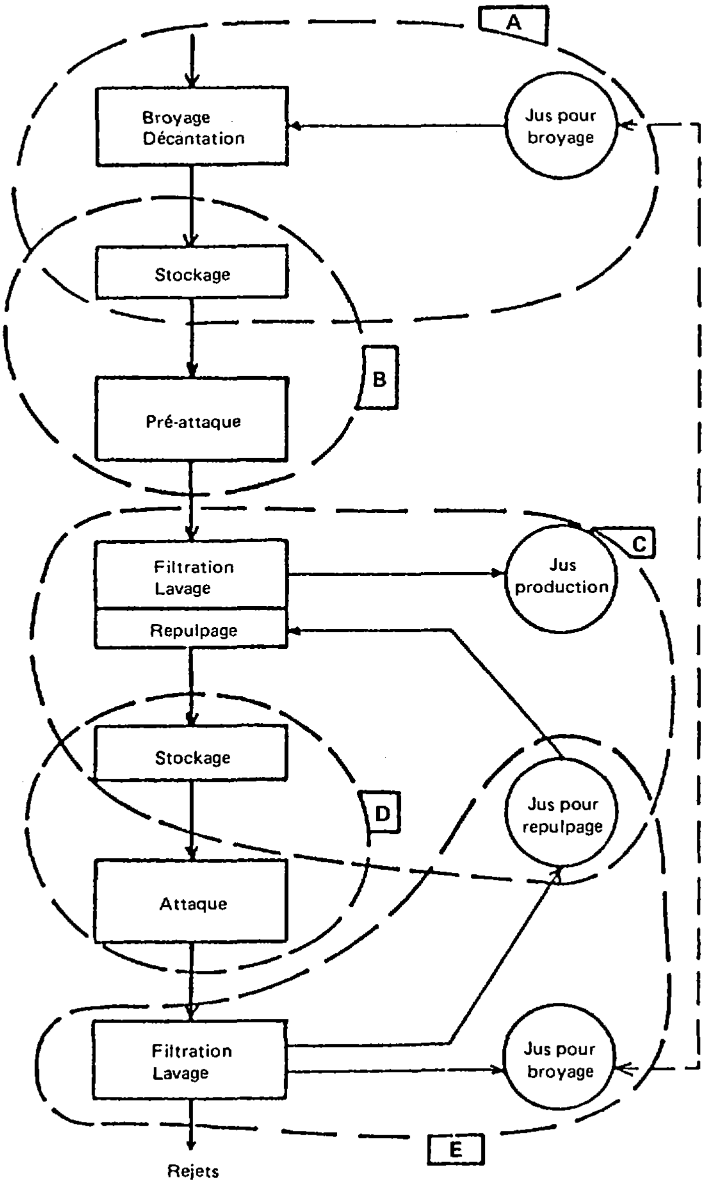

FIG. 1. Pilotage alcalin des minerais de l'Hérault (France): découpage du séquentiel dans l'espace sur un cycle.

Jours de la semaine	Diman.	Lundi		Mardi		Mercredi		Jeudi		Vendredi		Samedi	
Opérations	Poste 2	Poste 1	Poste 2	Poste 1	Poste 2	Poste 1	Poste 2	Poste 1	Poste 2	Poste 1	Poste 2	Poste 1	Poste 2
A • Broyage • Décantation	—				━				- - -				
B • Préattaque en autoclave		—				━				- - -			
C • Filtration • Lavage • Repulpage			—				═				- - -		
D • Attaque en autoclave				—				━				- - -	
E • Filtration • Lavage					—				═				- - -

FIG.2. Pilotage alcalin des minerais de l'Hérault (France): découpage du séquentiel dans le temps sur une semaine.

1.2.1.1. Broyage

a) Equipement

L'ensemble broyage-décantation a fonctionné à un débit de 80 $kg \cdot h^{-1}$, comportant:

- une trémie, de capacité 100 L environ,
- un broyeur à barres,
- un classificateur à vis,
- un broyeur à boulets,
- un épaississeur,
- un ensemble de pompes pour liquides et pulpes,
- des cuves pour la préparation du floculant, le stockage des liquides et de la pulpe.

b) Fonctionnement

Chaque broyage a duré la totalité d'un poste. La maille de broyage a été fixée à 5% de plus de 160 μm, le pourcentage de moins de 50 μm étant de l'ordre de 60%.

C'est à partir de ces données et d'essais faits par les constructeurs sur d'autres lots de minerai que l'appareillage a été dimensionné.

Le décanteur a permis d'obtenir une sous-verse épaissie jusqu'à 50% de solides.

1.2.1.2. Pré-attaque et attaque

a) Equipement

La pré-attaque et l'attaque ont été effectuées successivement dans un autoclave de 750 L de capacité utile, équipé d'un agitateur à deux hélices.

Cet appareil a été utilisé à 6 bars pour l'ensemble des essais et le plus souvent à 140° C.

De l'oxygène était introduit sous l'hélice inférieure de l'agitateur, pratiquement en bord de pales.

Le chauffage, le maintien en température et le refroidissement de la pulpe étaient obtenus au moyen de deux serpentins. A l'intérieur de ces serpentins circulait un fluide thermique, chauffé par une chaudière (puissance: 140 thermies/heure), ou refroidi par un échangeur à circulation d'eau. La mise en température et le refroidissement jusqu'à 70°C duraient au total deux heures.

b) Fonctionnement

Au cours du fonctionnement en palier, on a suivi l'évolution des rendements de dissolution et des consommations en oxygène.

Cette dernière donnée a permis de déterminer les quantités d'oxygène à injecter dans chaque autoclave industriel. Ces appareils sont en effet placés en série et fonctionnent en continu. Au total, la consommation est de l'ordre de 12 $kg \cdot t^{-1}$ et la quantité perdue dans les gaz sortants de 4 kg.

Après les premières campagnes, la durée de pré-attaque a été fixée à 3 heures et celle d'attaque à 6 heures, les conditions de température et de pression restant les mêmes dans les deux cas.

On a également suivi par chromatographie en phase gazeuse l'évolution des teneurs en oxyde de carbone, hydrogène et hydrocarbures des gaz sortants, la formation de ces composés provenant de l'attaque et de l'oxydation partielle des matières organiques.

Les rendements de dissolution de l'uranium ont régulièrement dépassé 95%, les trois quarts étant mis en solution lors de la pré-attaque. De même, l'essentiel des sulfures était transformé en sulfates au cours de cette opération.

1.2.1.3. Filtrations, pré-attaque, attaque

a) Equipement

Deux filtres à bande Philippe identiques, de surface utile 0,5 m^2, ont été installés, l'un pour extraire les jus de production après la pré-attaque et l'autre pour filtrer et laver les résidus d'attaque.

A sa sortie de l'autoclave, la pulpe passait dans un tambour floculateur. Le filtre était alimenté par une goulotte appropriée.

De l'eau à environ 60°C, dont le débit était contrôlé par un rotamètre, était utilisée pour les lavages.

A la sortie du filtre de pré-attaque, le gâteau était repulpé par un malaxeur avec des jus provenant de la filtration de l'attaque précédente.

Un ensemble de pompes péristaltiques assurait le transfert des pulpes, l'alimentation des jus recyclés, la distribution en floculant et le soutirage des liqueurs des bouteilles à vide.

Quatre cuves jaugées permettaient de stocker les liqueurs de production (1 cuve), les liqueurs riches (1 cuve) et les liqueurs pauvres (2 cuves).

b) Fonctionnement

Chacun des deux filtres a été spécialisé pour l'une des deux opérations pour observer si l'une d'elle conduisait à un colmatage plus rapide que l'autre.

Les débits d'alimentation ont été de l'ordre de 300 $kg \cdot h^{-1}$ de solides après pré-attaque et de 200 après attaque. Les filtrabilités respectives ont dépassé 1200 et 500 $kg \cdot m^{-2} \cdot h^{-1}$. Avec 280 $L \cdot t^{-1}$ d'eau à la pré-attaque, le rendement de séparation a été voisin de 93% et a été supérieur à 99,3% à l'attaque avec 850 L d'eau.

En définitive, le pilotage des filtres à bande a fourni beaucoup de renseignements utiles que n'auraient pas apportés des essais sur Buchner et a permis de dimensionner convenablement les équipements nécessaires.

Le pilotage de la suite du schéma de procédé, traitement des liqueurs uranifères, obtention d'un préconcentré calcique, fabrication d'un uranate de magnésie et récupération du molybdène, traitement des effluents, a été effectué à petite échelle avec des débits variant de 5 à 10 $L \cdot h^{-1}$, et n'a pas fait l'objet d'un enchaînement continu. Les informations recueillies ont été cependant suffisantes pour définir les équipements industriels principaux.

1.2.2. Choix des étapes du procédé de traitement chimique

Ce choix a été guidé par quatre principes:

- la mise en solution de l'uranium aussi complète que possible;
- l'obtention d'un concentré uranifère répondant aux normes internationales;
- la récupération du molybdène sous forme de sulfure;
- le traitement des résidus solides et des effluents liquides afin de respecter les normes en vigueur en France: salinité, matières en suspension, uranium et radium.

1.2.3. Caractéristiques du procédé retenu

1.2.3.1. Préparation mécanique

La maille de broyage a été fixée à 160 μm (D 95), ceci pour tenir compte à la fois de la mise en solution de l'uranium et des difficultés de la séparation liquide/solide.

L'installation est dotée d'un broyeur à barres, d'un broyeur à boulets en circuit fermé sur une classification par cyclonage et d'un épaississeur fournissant à l'entrée de la pré-attaque une pulpe à 50% de solides.

Le broyage en milieu alcalin pose des problèmes de corrosion lorsque le milieu est trop bicarbonaté. L'addition de la quantité de chaux nécessaire à la pré-attaque directement dans des liqueurs de broyage a permis d'éviter ce type de difficulté.

1.2.3.2. Mise en solution de l'uranium et du molybdène (figure 3)

a) Chimie de la mise en solution

La mise en solution s'est avérée particulièrement difficile.

La voie acide n'ayant pas pu être retenue, surtout à cause de la consommation excessive d'acide, on a choisi la voie alcaline qui aboutit à la formation de l'ion uranyl tricarbonate suivant la réaction:

$$UO_3 + Na_2CO_3 + 2\ NaHCO_3 \rightarrow UO_2Na_4(CO_3)_4 + H_2O$$

ou

$$UO_3 + CO_3^{2-} + 2\ HCO_3^- \rightarrow UO_2(CO_3)_3^{4-} + H_2O$$

Les paramètres de l'attaque sur lesquels on a joué en premier lieu sont:

- la granulométrie,
- la température et la pression,
- la durée d'attaque,
- le choix et les concentrations en réactifs,
- la teneur finale en carbonate-bicarbonate,
- l'utilisation de l'oxygène à la place de l'air.

Les essais expérimentaux ont conduit aux paramètres suivants:

- une granulométrie de 160 μm,
- une température de 140°C,
- une pression en oxygène à 6 bars,
- une durée d'attaque de 6 heures,
- une concentration en réactifs élevée: alcalinité en fin d'attaque de 90 à 100 $g \cdot L^{-1}$ exprimée en Na_2CO_3.

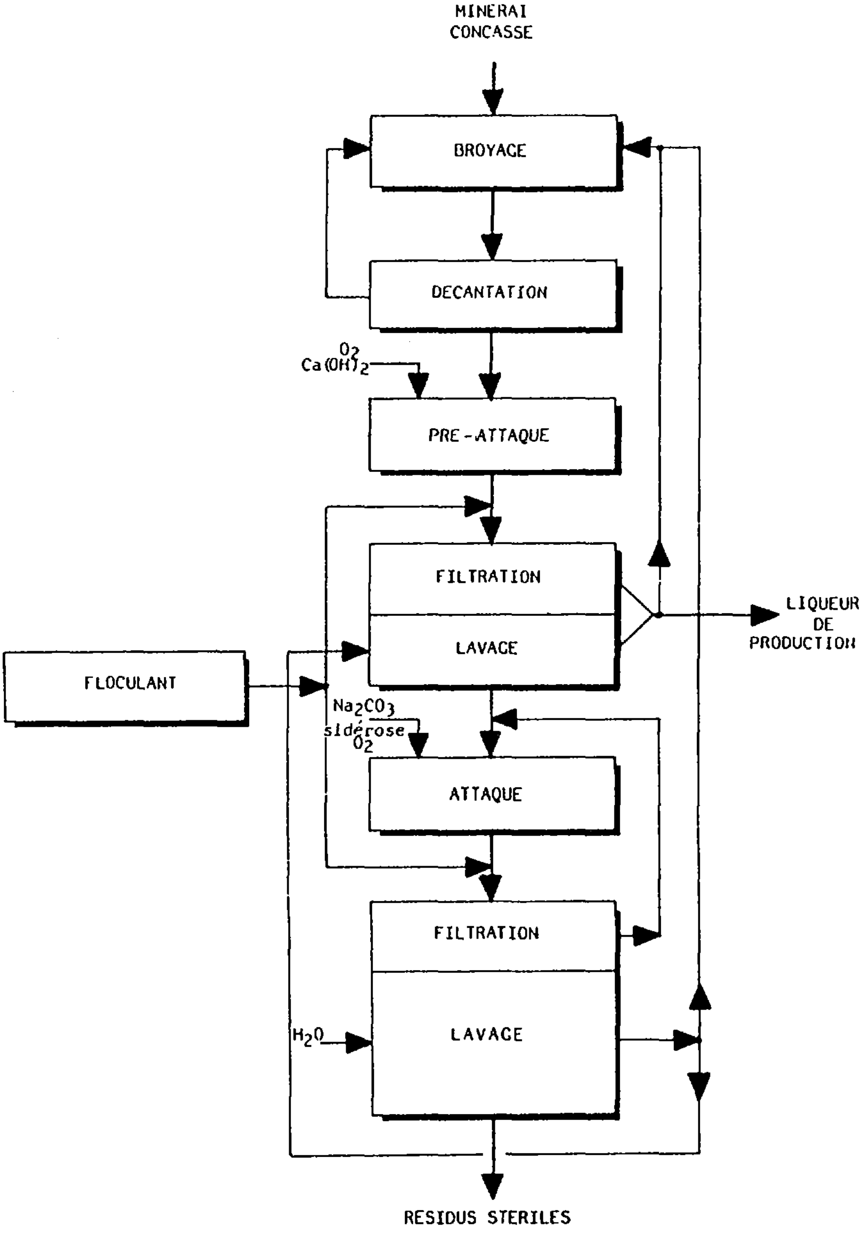

FIG. 3. Mise en solution de l'uranium.

Dans ces conditions, l'uranium est mis en solution avec des rendements élevés (95%) à condition d'ajouter à l'attaque 10 kg·t^{-1} d'hydroxyde ferrique sous forme de sidérite.

b) Nécessité d'une attaque en deux temps

Pour mettre en solution l'uranium, on pouvait concevoir une attaque alcaline simple dans les conditions indiquées ci-dessus. En réalité, le problème se complique en raison de deux difficultés majeures:

– la mise en solution de sulfates et de matières organiques qui colorent les liqueurs en noir (humates alcalins);

– la teneur finale en carbonate de sodium nécessaire pour dissoudre l'uranium qui est beaucoup trop élevée pour le reprécipiter sous forme d'uranate.

Ces deux problèmes, à savoir la quantité prohibitive de carbonates et la mise en solution de matières organiques et de sulfates, excluaient un schéma simple de ce type.

On a donc conçu un schéma d'attaque qui permette la mise en solution de l'uranium à un niveau élevé, qui limite la dissolution des matières organiques, et qui conduise à une liqueur de production compatible avec la suite du traitement, c'est-à-dire sans excès important de réactifs en fin de réaction et avec de petites quantités de matières organiques dissoutes.

C'est pour ces raisons qu'a été choisi un schéma d'attaque en deux temps, qui dissocie les liqueurs de production et d'attaque et leur confère une certaine indépendance.

Les principales réactions sont les suivantes:

Pré-attaque

$$UO_2 + \tfrac{1}{2} O_2 + Na_2CO_3 + 2\ NaHCO_3 \rightarrow Na_4UO_2(CO_3)_3 + H_2O \qquad (1)$$

$$CaSO_4 + Na_2CO_3 \rightarrow \underset{\swarrow}{\underline{CaCO_3}} + Na_2SO_4 \qquad (2)$$

$$2\ FeS_2 + \tfrac{15}{2} O_2 + 8\ Na_2CO_3 + 7\ H_2O \rightarrow 2\ Fe(OH)_3 + 4\ Na_2SO_4 + 8\ NaHCO_3 \qquad (3)$$

$$2\ NaHCO_3 + Ca(OH)_2 \rightarrow Na_2CO_3 + \underset{\swarrow}{\underline{CaCO_3}} + 2\ H_2O \qquad (4)$$

La réaction (3) est très importante et s'arrête par manque de Na_2CO_3. Le rôle de la chaux (réaction (4)) est donc de transformer le bicarbonate en carbonate de sodium afin que la réaction (3) se poursuive.

On voit donc que la grande consommation de réactifs est essentiellement due à la présence de sulfures.

TABLEAU II. COMPOSITION MOYENNE DES LIQUEURS DE PRODUCTION

U (sous forme de $UO_2Na_4(CO_3)_3$)	3 $g \cdot L^{-1}$
Na_2CO_3	3 $g \cdot L^{-1}$
$NaHCO_3$	15 à 25 $g \cdot L^{-1}$
Na_2SO_4	25 à 30 $g \cdot L^{-1}$
Mo	50 à 500 $mg \cdot L^{-1}$
Zr	40 à 100 $mg \cdot L^{-1}$
Matières organiques (DCO)	800 à 1200 $mg \cdot L^{-1}$

Attaque

A cette étape sont introduits de l'oxygène, de la sidérite ($FeCO_3$) et du carbonate de sodium.

$$2\ FeCO_3 + 2\ Na_2CO_3 + \tfrac{1}{2}\ O_2 + 5\ H_2O \rightarrow 2\ Fe(OH)_3 + 4\ NaHCO_3$$

La sidérite permet de libérer l'hydroxyde ferrique et le bicarbonate de sodium.

1.2.3.3. Les problèmes de séparation solide-liquide

a) Filtration pré-attaque

Elle sépare les liqueurs de production du solide allant à l'attaque.

La filtration est précédée d'une floculation avec un produit particulier pouvant être utilisé sur des pulpes à forte concentration en solide et donnant dans le milieu considéré une filtrabilité acceptable. Par contre, le temps de contact pulpe-floculant doit être assez long.

L'installation est équipée de deux filtres à bande de 40 m^2 chacun pour un débit de solide de 750 $kg \cdot m^{-2} \cdot h^{-1}$. La température doit être maintenue au minimum à 60°C et la dépression à 650 mbars.

Le lavage est limité à un déplacement, soit 280 $L \cdot t^{-1}$, ce qui permet d'avoir un rendement de lavage supérieur à 90%.

Les liqueurs de production doivent cependant être clarifiées avant la suite du procédé.

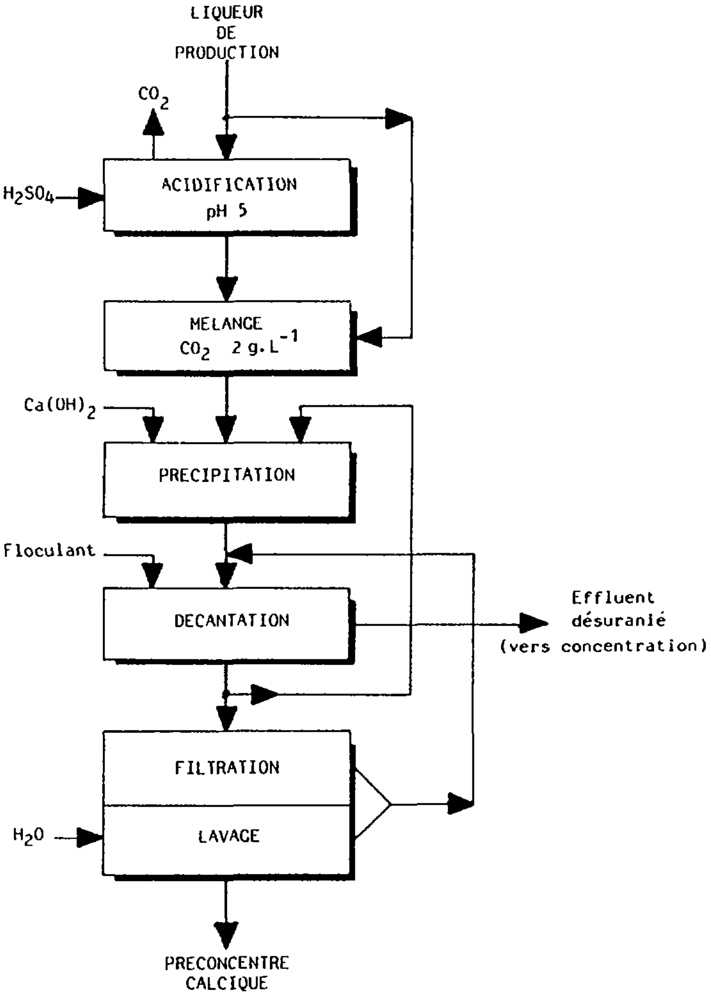

FIG. 4. Obtention du préconcentré calcique.

b) Filtration attaque

La floculation est identique à celle indiquée pour la préattaque. L'usine dispose de 4 filtres à bande de 40 m^2 chacun, soit 160 m^2 de surface utile pour un débit de 375 kg·m^{-2}·h^{-1}.

Le lavage se fait avec un débit de 750 à 850 L·t^{-1} et conduit à un rendement de lavage supérieur à 99%.

1.2.3.4. Traitement des liqueurs uranifères contenant du molybdène

L'objectif est maintenant d'obtenir un concentré uranifère répondant aux normes internationales. La composition moyenne des liqueurs de production est indiquée au tableau II.

a) Obtention d'un préconcentré uranifère (figure 4)

Le milieu alcalin conduit en général à des liqueurs uranifères qui se prêtent à une précipitation directe. C'est la cas de la plupart des usines utilisant un traitement alcalin.

Dans le cas du minerai de Lodève, la présence de molybdène en solution et de matières organiques dissoutes interdit une précipitation directe. Comme d'autre part, le milieu alcalin ne permet pas de purification-concentration par solvants ou résines échangeuses d'ions, celle-ci ne pouvait passer que par la fabrication d'un concentré intermédiaire.

On a choisi la précipitation à la chaux après avoir réalisé une préneutralisation à l'acide sulfurique pour transformer la plus grande partie du carbonate de sodium en sulfate et aboutir ensuite par addition de chaux à une précipitation totale de l'uranium.

Les principales réactions sont indiquées ci-après.

Pré-neutralisation (acidification partielle)

$$UO_2Na_4(CO_3)_3 + 3\,H_2SO_4 \rightarrow UO_2SO_4 + 2\,Na_2SO_4 + 3\,CO_2\nearrow + 3\,H_2O$$

$$2\,Na_2CO_3 + H_2SO_4 \rightarrow 2\,NaHCO_3 + Na_2SO_4$$

$$2\,NaHCO_3 + H_2SO_4 \rightarrow 2\,CO_2\nearrow + 2\,H_2O + Na_2SO_4$$

L'acidification n'est faite que partiellement afin de laisser suffisamment de CO_2 pour que l'uranium soit sous forme d'uranyl tricarbonate.

Précipitation à la chaux

$$2\,NaHCO_3 + Ca(OH)_2 \rightarrow \underset{\swarrow}{\underline{CaCO_3}} + Na_2CO_3 + 2\,H_2O$$

$$Na_2CO_3 + Ca(OH)_2 \rightarrow \underset{\swarrow}{\underline{CaCO_3}} + 2\,NaOH$$

$$2\,UO_2Na_4(CO_3)_3 + 6\,NaOH \rightarrow Na_2U_2O_7 + 6\,Na_2CO_3 + 3\,H_2O$$

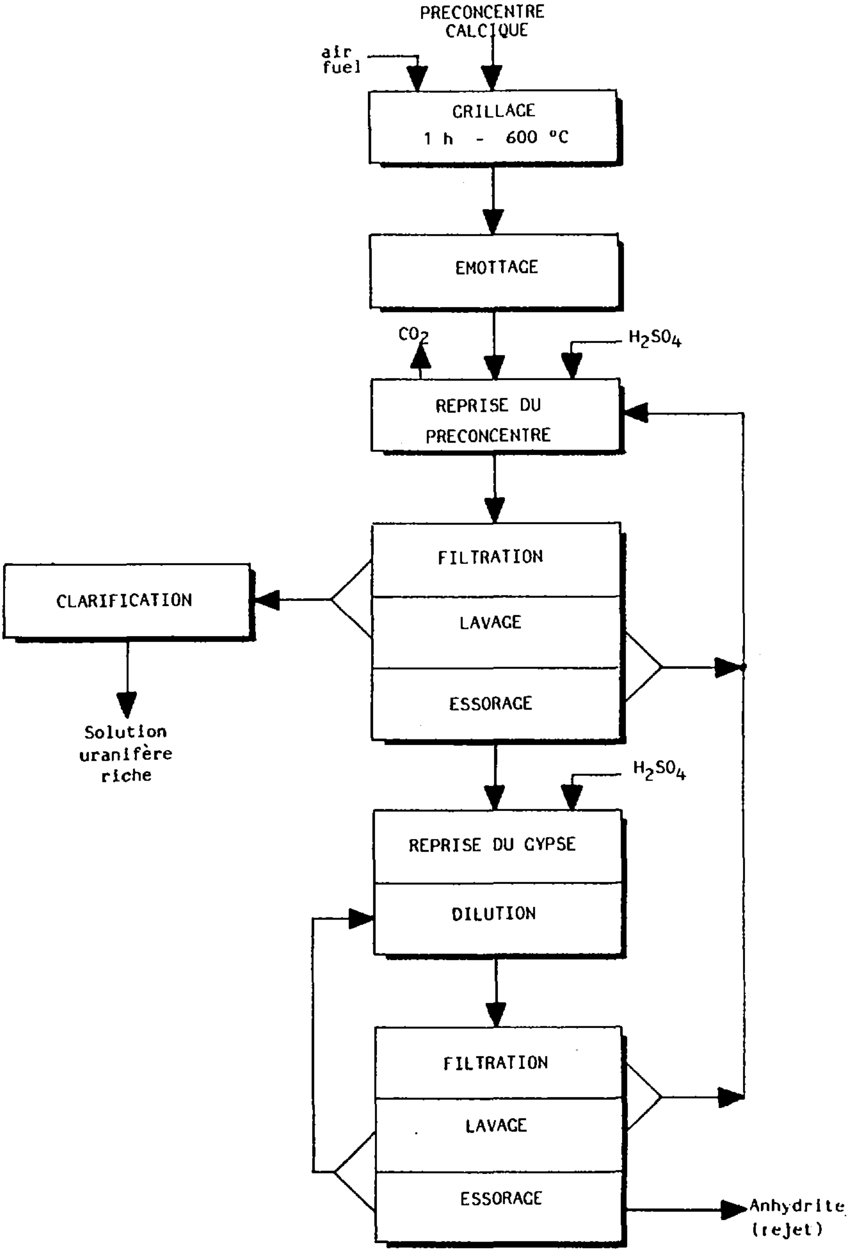

FIG.5. Retraitement du préconcentré calcique.

Dans un milieu contenant un minimum de soude libre, le molybdène reste soluble; les matières organiques sont, par contre, fixées en partie par la chaux. Le préconcentré contient 25 à 30% d'U, le reste étant essentiellement constitué par du carbonate de calcium.

b) Traitement du préconcentré calcique (figure 5)

Le traitement se réalise en trois temps énumérés ci-après.
Grillage du préconcentré à 600°C pour décomposer les matières organiques.
Reprise acide du préconcentré grillé pour remettre en solution l'uranium. Les réactions sont les suivantes:

$$Na_2U_2O_7 + 3\ H_2SO_4 \rightarrow 2\ UO_2SO_4 + Na_2SO_4 + 3\ H_2O$$

$$\left.\begin{array}{l} CaCO_3 + H_2SO_4 + H_2O \rightarrow CaSO_4, 2\ H_2O + CO_2\uparrow \\ Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4, 2\ H_2O \end{array}\right\} \text{formation de gypse}$$

On obtient donc un mélange de gypse et de solution de sulfate d'uranyle (environ 30 $g \cdot L^{-1}$ en U) et de sulfate de sodium. Cette solution servira ensuite à fabriquer le concentré marchand.
Traitement du gypse pour récupérer l'uranium qui s'y trouve (0,3 à 0,6%). Pour cela, on attaque le gypse par de l'acide sulfurique concentré et on forme de l'anhydrite:

$$CaSO_4, 2\ H_2O \xrightarrow{H_2SO_4 \text{ concentré}} CaSO_4 + 2\ H_2O$$

La solution contenant l'acidité libre et l'uranium libéré par le gypse est recyclée à la reprise du préconcentré.

c) Précipitation du concentré uranifère final: uranate de magnésie (fig.6)

La solution uranifère riche, précédemment obtenue est traitée par un lait de magnésie pour obtenir le concentré marchand selon les réactions:

$$H_2SO_4 + MgO \rightarrow MgSO_4 + H_2O$$

$$UO_2SO_4 + MgO + x\ H_2O \rightarrow \underline{UO_3, x\ H_2O}\downarrow + MgSO_4 \quad \text{avec} \quad 1 \leqslant x \leqslant 2$$

L'effluent magnésien ne contient que quelques $mg \cdot L^{-1}$ d'uranium.

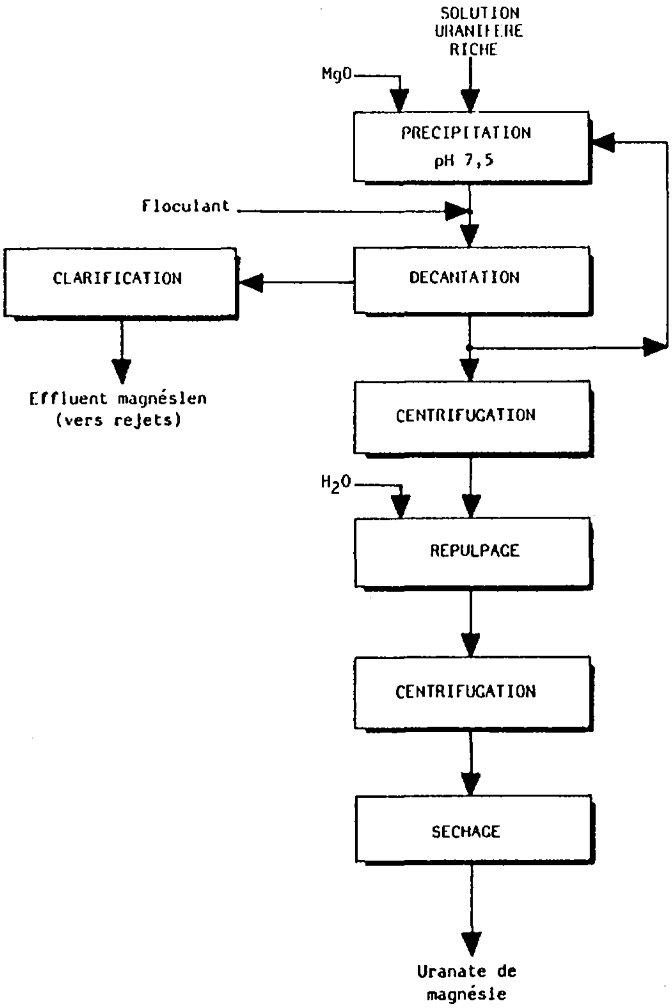

FIG. 6. Précipitation de l'uranate de magnésie.

1.2.3.5. Traitement des effluents (figure 7)

L'effluent désuranié provenant de la précipitation calcique contient:

- un élément valorisable: le molybdène,
- des matières organiques en solution,
- des traces d'uranium,
- du sulfate de sodium, résultant de l'oxydation des sulfures et de l'acidification du carbonate de sodium.

Cet effluent correspond à un volume de 1,5 m^3 par tonne de minerai (fig.7).

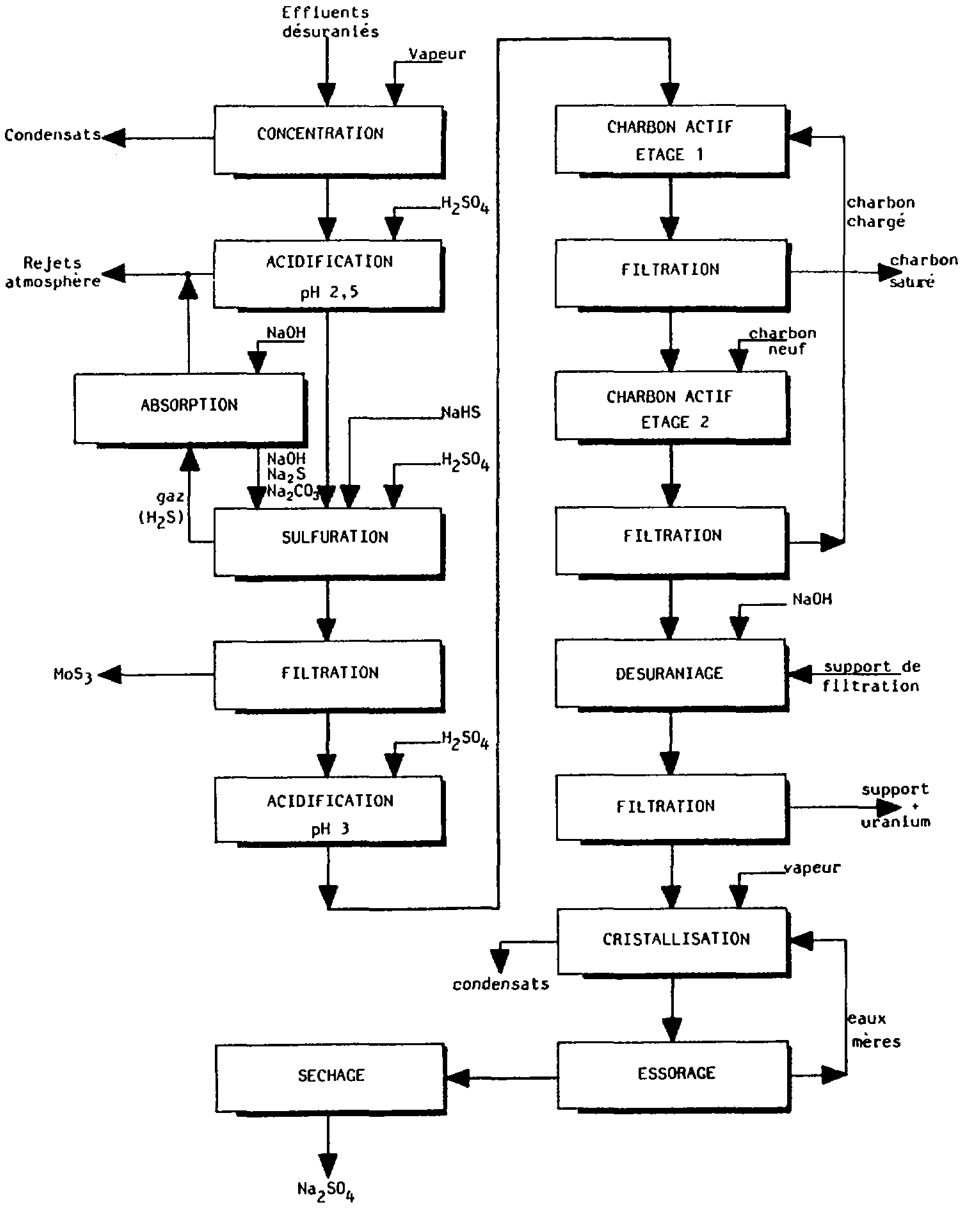

FIG. 7. Traitement des effluents.

a) Concentration par évaporation

Cette opération a pour but de réduire le volume des effluents d'un facteur d'environ 8 correspondant à une teneur en Na_2SO_4 voisine de 27%. Dans les opérations de purification ultérieures, la température doit être maintenue à un niveau qui évite la cristallisation du sulfate de soude.

b) Récupération du molybdène sous forme sulfure

Après concentration des liqueurs, on procède à l'extraction du molybdène sous la forme d'un concentré sulfuré impur titrant 10 à 12% en poids de molybdène.

Ceci se passe en milieu acide selon le principe suivant:

Neutralisation de NaOH et Na_2CO_3

$$2\ NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2\ H_2O$$

$$Na_2CO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO_2\nearrow$$

Précipitation du sulfure de molybdène:

$$H_2MoO_4 + 2\ H_2SO_4 + 4\ NaHS \rightarrow 2\ Na_2SO_4 + H_2S\nearrow + MoS_3 + 4\ H_2O$$

Les meilleurs rendements sont obtenus à un pH voisin de 3; on a alors une quantité minimale de CO_2 dans la solution.

Pour compenser le dégagement de gaz sulfhydrique, il faut un excès de sulfhydrate de sodium de l'ordre de 30% par rapport à la stoechiométrie.

Les gaz libérés (H_2S et CO_2) sont absorbés par une solution de soude dans une colonne à garnissage. Le sulfure de sodium formé est recyclé à la précipitation du molybdène.

Le précipité de MoS_3 que l'on recueille contient du sulfate de sodium en imprégnation, ainsi que des matières organiques entraînées lors de l'acidification.

Sa commercialisation nécessitera donc un traitement complémentaire.

Les effluents de précipitation qui contiennent encore un peu de molybdène et des matières organiques sont ensuite traités par charbon actif.

c) Purification du sulfate de sodium

Elimination des matières organiques et du molybdène résiduel par le charbon actif:

Le charbon actif n'est efficace qu'en milieu acide (pH compris entre 2 et 3).

L'épuration est en fait une adsorption des matières organiques et du molybdène par la très grande surface active du charbon.

L'opération est réalisée par un contre-courant charbon-solution, afin de minimiser la quantité de charbon mis en œuvre (15 $kg \cdot m^{-3}$).

Les paramètres opératoires de cette opération sont les suivants:

- pH de la solution: 2 à 3
- temps de contact: 30 min
- débit de charbon: 15 $kg \cdot m^{-3}$ de solution
- nombre d'étages: 2
- température: 55°C.

Le charbon saturé est ensuite rejeté avec les résidus de la lixiviation. Il n'est pas, pour l'instant, régénéré.

La solution épurée doit avoir des teneurs très basses en molybdène et en matières organiques car l'absence de coloration est une qualité majeure du sulfate de sodium. Cette solution est alors presque prête pour la cristallisation. Il ne reste plus qu'à éliminer l'uranium qui s'y trouve.

Elimination des traces d'uranium. Désuraniage.

Le teneur en uranium est alors de 20 à 50 $mg \cdot L^{-1}$. Le désuraniage est effectué en remontant le pH à 8,5 par la soude et en ajoutant un support de filtration qui sert d'amorce à la précipitation de l'uranium.

On arrive ainsi à des teneurs de l'ordre de 1 à 2 $mg \cdot L^{-1}$ d'uranium dans le sulfate de sodium avant cristallisation.

d) Obtention du sulfate de sodium

La solution concentrée et épurée est ensuite cristallisée selon le principe suivant:

- chauffage de la solution par l'intermédiaire d'un échangeur;
- évaporation par détente. Ceci permet l'évacuation des calories et la croissance des cristaux;
- centrifugation des cristaux formés et recyclage des eaux mères vers l'échangeur.

Le sulfate de sodium ainsi purifié est enfin séché, enfûté et vendu.

2. LES PROBLEMES POSES PAR LA CONCEPTION ET LA REALISATION DE L'USINE DE LODEVE

2.1. Généralités

Pour mettre en œuvre le procédé alcalin non classique décrit dans la première partie, il a fallu résoudre un ensemble de problèmes relatifs principalement à la mise en solution de l'uranium, à la limitation des dilutions des liqueurs uranifères et au traitement des effluents.

Par ailleurs, l'augmentation considérable des coûts énergétiques pendant la phase des études initiales a imposé une réflexion globale sur les économies d'énergie, qui a conduit au choix de technologies particulières dans ce domaine.

Enfin, l'installation d'une usine hydrométallurgique dans un site naturel, comme celui de Saint-Martin-du-Bosc, et les courts délais imposés ont représenté des contraintes supplémentaires pour le développement du projet.

2.2. Contraintes technologiques liées au procédé

2.2.1. Mise en solution de l'uranium. Limitation des dilutions dues aux entrées d'eau

Les caractéristiques du minerai de Lodève ont imposé un broyage fin et une attaque alcaline sévère.

2.2.1.1. Préparation mécanique des minerais

Le pilotage avait démontré que la séparation solide-liquide après attaque sur filtres à bande sous vide était particulièrement sensible au taux de fines obtenu au broyage. Le taux maximum souhaitable est de 60% de particules de taille inférieure à 60 μm, dont 30% maximum inférieures à 10 μm.

L'installation devait donc fournir une pulpe broyée contenant à la fois peu d'égarés supérieurs à 160 μm pour obtenir un rendement d'attaque acceptable et le moins possible de particules très fines pour assurer à la fois le débit de filtration et le rendement de lavage désirés sans consommation excessive de floculants.

Pour arriver à ce résultat, on a choisi de mettre en place une chaîne de préparation mécanique du minerai constituée par un concassage primaire à mâchoires, en fond mine (0–300 mm), un atelier de concassage à l'usine de 300 $t \cdot h^{-1}$ et un atelier de broyage humide de 60 $t \cdot h^{-1}$ conçu pour ne pas dépasser le taux de fines précité.

Le concassage s'effectue en deux étages (étages secondaire et tertiaire) équipés d'appareils giratoires en circuit fermé fournissant un produit réduit à moins de 20 mm (D 80 < 16 mm).

L'unité de broyage comprend un broyeur à barres de Φ 2,75 m × 3,96 m du type à débordement en circuit ouvert et un broyeur à boulets de Φ 3,66 m × 3,96 m du type à grille de décharge.

Ce dernier fonctionne en circuit fermé sur une classification par hydrocyclone, dont la surverse alimente un épaississeur de Φ 25 m ayant pour rôle d'assurer une densité constante ($d = 1,5$) de la pulpe envoyée à la pré-attaque.

Après les mises au point industrielles au démarrage, une plus grande souplesse d'exploitation a été recherchée, notamment par la possibilité de réglage de la dilution dans les broyeurs, et l'utilisation de pompes à vitesse variable pour l'alimentation des cyclones.

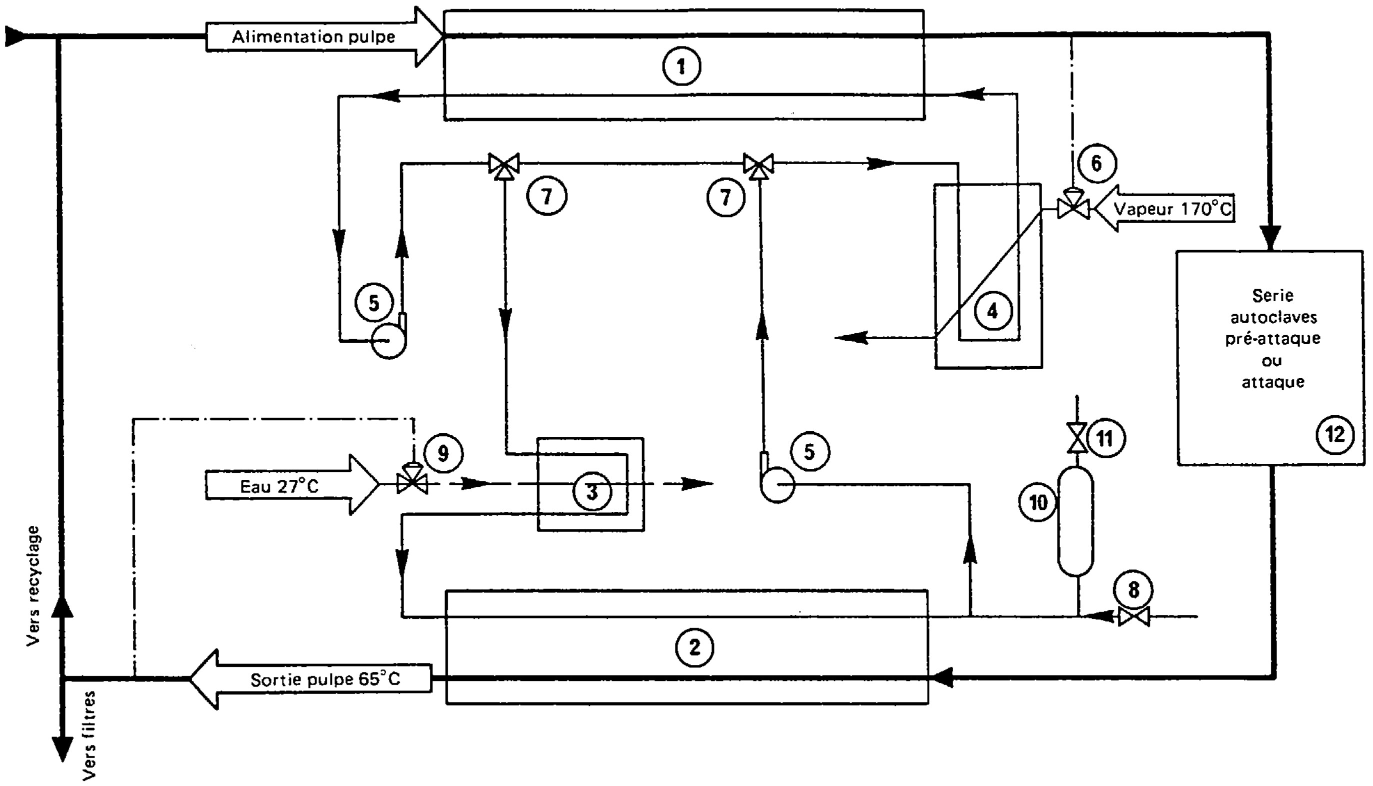

FIG.8. Schéma de principe du chauffage et du refroidissement des pulpes à la pré-attaque et à l'attaque dans l'usine de Lodève. 1:Echangeur eau/pulpe uranifère; fonction:chauffage de la pulpe. 2:Echangeur eau de boucle/pulpe uranifère; fonction:refroidissement de la pulpe. 3:Echangeur eau de refroidissement/eau de boucle; fonction:refroidissement eau de boucle. 4:Echangeur vapeur 8 bars/eau de boucle; fonction:élévation de la température de l'eau de boucle. 5:Pompes de circulation eau de boucle. 6:Vanne régulée par la température de consigne (140° C) de la pulpe. 7:Deux vannes, trois voies pour by-passage des échangeurs 1 et 4 lors du recyclage de la pulpe (vannes synchronisées). 8:Vanne de remplissage eau de boucle. 9:Vanne régulée par la température de consigne (65°C) de la pulpe. 10:Réservoir de dilatation. 11:Soupape de sécurité. 12:Ensemble autoclaves pré-attaque ou attaque.

2.2.1.2. Stockage du minerai concassé avant broyage et ajustement de la consommation de carbonate de soude

L'atelier de concassage fonctionnant à un poste et cinq jours par semaine, contre trois postes et sept jours par semaine à l'atelier de broyage, un stockage entre concassage et broyage a été créé. Il est constitué par quatre silos métalliques de 2100 t, précédés d'une chaîne d'échantillonnage dont le but est de connaître en particulier la teneur en soufre du minerai, de régler en fonction de cette donnée la consommation de carbonate et, éventuellement, d'effectuer des mélanges de différentes qualités de minerais pour pondérer leurs teneurs en soufre et en uranium.

En fait, la reprise du minerai par extracteur à soc, avant concassage, permet une préhomogénéisation des minerais.

2.2.1.3. Attaque des minerais

L'attaque est réalisée dans deux séries d'autoclaves disposés en cascade (6 à la pré-attaque et 12 à l'attaque) assurant un temps total de séjour de 9 heures, dans des conditions assez sévères (température 140°C, pression 6 bars) avec injection d'oxygène.

Dans la mesure où la sédimentation de la pulpe à la densité d = 1,5 est très lente, il n'a pas été utile de prévoir de vannes pour court-circuiter les autoclaves, ce qui élimine une cause importante d'entretien. Néanmoins, il a été prévu de pouvoir changer en marche, sous la pression de 6 bars, les paliers d'agitateurs.

a) Gaz combustibles dans les autoclaves: dispositifs de sécurité

Le pilotage avait démontré que, moyennant une purge convenable, les teneurs de l'atmosphère des autoclaves en monoxyde de carbone (CO), méthane (CH_4) et hydrogène (H_2) étaient inférieures aux limites d'inflammabilité. Néanmoins, pour tenir compte d'un accroissement accidentel (plus grande richesse en matières organiques, par exemple) une surveillance permanente des gaz combustibles a été mise en place.

Le contrôle des teneurs se fait au moyen d'un prélèvement automatique séquentiel suivi d'une mesure séparée pour chaque gaz et du calcul de la composition de l'atmosphère des autoclaves par micro-ordinateur qui la compare aux valeurs de consigne.

L'ensemble fournit sur un écran de télévision les différentes courbes de teneurs en CO, H_2, O_2 et l'histogramme du poste précédent.

Des soupapes de sécurité, disposées sur les tubes d'évent des autoclaves, permettent de limiter les surpressions accidentelles en marche.

b) Chauffage et refroidissement de la pulpe (figure 8)

Pour tenir compte des quantités élevées de chaleur à mettre en œuvre et des problèmes d'entretien, le principe du chauffage de la pulpe au moyen d'échangeurs extérieurs aux autoclaves, de préférence au système de serpentins intérieurs, a été retenu.

La température d'alimentation en pulpe des filtres à bande ne peut dépasser 65° C; il est donc nécessaire de refroidir la pulpe à la sortie de chaque ligne d'autoclaves.

L'ensemble des opérations de chauffage et de refroidissement est réalisé au moyen d'échangeurs spéciaux, en acier austénoferritique, pulpe-liquide intermédiaire caloporteur et permet de récupérer une grande partie de la chaleur de réchauffage de la pulpe avant autoclaves. Cette conception a permis d'économiser de l'ordre de 6500 $t \cdot a^{-1}$ de fuel, de réduire les surfaces d'encombrement grâce aux très bons coefficients de transfert de chaleur et de faciliter les opérations d'entretien.

Une attention particulière a été portée aux problèmes de démarrage et d'arrêt de cet ensemble qui contient plus de 1000 m^3 de pulpe chauffé à 140°C. En particulier, des capacités supplémentaires de transfert de chaleur ont été mises en place pour réchauffer ou refroidir rapidement la pulpe pour des remises en route ou des arrêts de l'installation.

Des précautions particulières ont été prises pour prévenir les risques de bouchage et d'abrasion par la pulpe: tamisage de la pulpe pour éliminer les corps étrangers (particules de bois et de plastique), vitesse de circulation, facilité de démontage des échangeurs.

Le choix de l'acier des échangeurs a été fait après essai d'un module en vraie grandeur avec des pulpes très abrasives.

La pression nécessaire à la circulation de la pulpe dans les autoclaves et dans les tuyauteries en amont, de l'ordre de 10 bars, est fournie par des pompes volumétriques à manchon, délivrant en un seul étage la pression désirée et offrant l'intérêt de ne pas introduire d'eau dans le procédé.

c) Dilution

La dilution par de l'eau introduite dans le procédé, notamment par les paliers de pompes centrifuges, les filtres à bande et les recyclages accidentels, a pour conséquence l'accroissement de la consommation de réactifs et des volumes d'effluent à évaporer (consommation d'énergie). C'est pourquoi on a porté une grande attention à ce problème et fait certains choix technologiques pour réduire autant que possible les dilutions.

Des paliers à bague flottante limitant les entrées d'eau au presse-étoupe ont été utilisés, d'une façon systématique pour les pompes centrifuges sur les liquides chargés.

d) Filtrations après préattaque et attaque

Pour tenir compte de la sensibilité de la filtration aux taux de fines, des surfaces de 80 m^2 à la préattaque et 160 m^2 à l'attaque, soit une surcapacité de 25%, ont été mises en place.

La technologie adoptée pour le glissement de la bande vers les glissières des boîtes à vide permet un fonctionnement sans pratiquement aucune eau de lubrification, ce qui limite des entrées d'eau dans le procédé.

e) Clarification des liqueurs uranifères

Les liqueurs produites à la filtration après préattaque sont assez chargées en solides et doivent, de ce fait, être clarifiées pour éviter la pollution du concentré uranifère en silice notamment.

Dans un premier temps, un clarificateur lamellaire a été mis en place. Ses performances s'étant avérées insuffisantes, il a été décidé de compléter la clarification au moyen d'une batterie de filtres à sable devant produire des liqueurs dont la teneur en matières en suspension est de l'ordre de 10 $mg \cdot L^{-1}$.

L'ensemble d'alimentation, de chauffage et de refroidissement de la pulpe, l'attaque en autoclaves en deux étapes, ainsi que les précautions vis-à-vis des dilutions constituent une réalisation originale à partir d'équipements mis au point spécifiquement pour le minerai de Lodève.

2.2.2. Traitement des liqueurs uranifères

Cet atelier a été surdimensionné pour tenir compte des variations de teneurs en uranium dans les minerais (la fourchette variant de 2 à 4‰ environ).

Les équipement liés à l'obtention et au traitement du préconcentré sont calculés pour une capacité d'environ 230 $kg \cdot h^{-1}$. Ceux liés au concentré marchand d'uranate de magnésie sont calculés pour environ 350 $kg \cdot h^{-1}$ ce qui permettrait d'assurer sans modification le passage à une deuxième phase d'exploitation après extension éventuelle. L'ensemble des équipements ne présente pas de grandes particularités, sauf en ce qui concerne le grillage du préconcentré pour lequel un four à soles multiples a été adopté et le séchage du concentré réalisé par atomisation. Certaines précautions ont cependant été prises dans la réalisation des réacteurs de reprise sulfurique après grillage, dont les risques d'entartrage par le gypse sont apparus importants.

C'est ainsi que la mise en place d'échangeurs extérieurs a été prévue au cas où l'entartrage aurait été confirmé à l'exploitation.

Compte tenu des sources d'approvisionnement faciles en gaz propane dans la région de Lodève, il a été décidé de doter le four grillage et le sécheur du concentré de brûleurs mixtes fuel domestique/propane. Depuis son démarrage, l'atelier fonctionne au propane.

2.2.3. Traitement des effluents

En complément des normes habituellement exigées pour les installations classées en France, un certain nombre de contraintes concernant la pollution du milieu environnant ont été imposées à la Cogéma par l'administration, notamment en ce qui concerne la quantité et la qualité des rejets liquides.

2.2.3.1. Eaux résiduaires de l'usine

Elles ont été limitées en réalisant chaque fois que cela a été possible des recyclages dans le procédé. Ceci a impliqué la création de circuits particuliers, par exemple pour la récupération des liqueurs uranifères résultant des égouttures ou fuites des équipements et des eaux de lavage des planchers, en gardant à l'esprit la nécessité de limiter les dilutions.

En ce qui concerne les effluents sulfatés issus de la précipitation calcique, l'évaporation totale appliquée annule tout rejet liquide, mais comporte un résidu salin qu'il faut éliminer. On reparlera de ce traitement dans le paragraphe suivant.

L'usine produit en définitive un rejet limité à environ 80 $m^3 \cdot h^{-1}$ pour lequel une station de traitement et de contrôle a dû être créée en vue de respecter les différentes normes de température et de pH, les demandes biologique et chimique en oxygène, les quantités limites de sels dissous totaux, d'uranium et de radium.

2.2.3.2. Cas particulier de l'effluent sulfaté: préparation d'un sulfate de sodium de qualité marchande

Dans la mesure où cet effluent est polluant par les quantités de sels et de matières organiques contenues, un traitement spécifique par évaporation totale a été retenu, en s'efforçant toutefois de valoriser le sulfate de soude et le molybdène contenus.

En effet, l'étude des différents rejets ou utilisations possibles de l'effluent sulfaté (incorporation aux eaux des bétons de remblayage de la mine, stockage dans des mines désaffectées ou sur des aires étanches, etc.) a montré que la seule possibilité intéressante était la commercialisation du sulfate de soude, à condition de produire les qualités adaptées au marché (les meilleures qualités doivent contenir moins de 20 pp10^6 en molybdène et environ 50 pp10^6 en carbone organique) et de conditionner les produits pour la vente en vrac selon la pratique habituelle. Une étape de concentration par évaporation ramène le débit de 85 à 90 $m^3 \cdot h^{-1}$ à une quantité de solution concentrée, voisine de 10 $m^3 \cdot h^{-1}$.

La purification est réalisée ensuite par un ensemble d'ateliers disposés en amont de l'étape de cristallisation et traitant les solutions concentrées à environ 25% en sulfate de soude et comprenant:

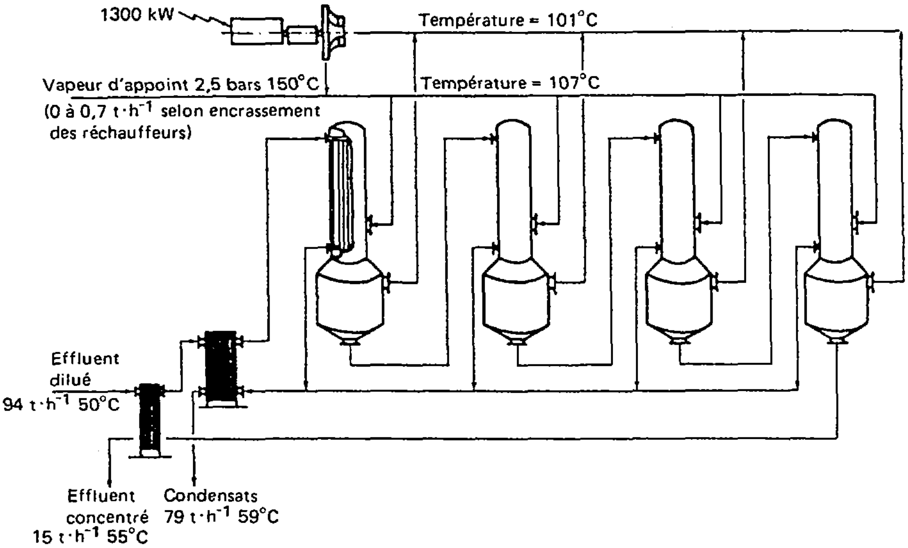

FIG. 9. Ensemble des évaporateurs de la concentration.

- un atelier de récupération du molybdène qui opère une première purification et récupère environ 75% du molybdène contenu sous forme d'un concentré impur;
- un atelier de purification par charbon actif qui assure la qualité finale en molybdène et en matières organiques;
- un atelier de désuraniage qui élimine pratiquement toute trace d'uranium.

Ces ateliers ont posé principalement deux séries de problèmes:

- d'une part, les risques de cristallisation des solutions concentrées en sulfate de soude ont conduit à généraliser certaines précautions (traçage électrique de l'ensemble des tuyauteries, réacteurs à double enveloppe, calorifugeage, etc.);
- d'autre part, la génération de gaz sulfhydrique a impliqué la mise en œuvre de mesures sévères de sécurité; en particulier, l'installation de lavage à la soude a été doublée et calculée pour assurer des teneurs en H_2S dans les gaz effluents inférieures à 1 $pp10^6$ (seuil olfactif); enfin, l'ensemble des installations a été érigé à l'extérieur, de façon à éviter toute accumulation de gaz toxique.

2.2.3.3. Economie d'énergie (figure 9)

L'importance des volumes à évaporer (environ 94 $t \cdot h^{-1}$) a posé le problème du choix de la technologie la plus économe en énergie.

L'étude a consisté à comparer les techniques d'évaporation classique par multiples effets chauffés à la vapeur et la recompression mécanique des buées dont pratiquement toute l'énergie d'évaporation est fournie par un compresseur entraîné électriquement.

Dans une première phase, cette dernière solution a été retenue pour l'étape de concentration qui correspond à une évaporation d'environ 84 $t\cdot h^{-1}$, ce qui permet une économie d'environ 5700 $t\cdot a^{-1}$ de fuel par rapport à la solution classique.

Des dispositions ont été prises dans la conception de l'usine pour l'adaptation future d'une seconde installation de recompression mécanique pour l'étape de cristallisation, qui devrait représenter une économie supplémentaire d'environ 3000 $t\cdot a^{-1}$ en fuel.

L'investissement correspondant est en cours de réalisation, et devrait être en service à la rentrée 1983.

2.3. Contraintes liées à l'installation d'une nouvelle usine

2.3.1. Implantation

L'usine a été installée à l'intérieur de l'enceinte de la Division minière sur des terrains très pentés, qui ont conduit à créer une série de plateformes sur lesquelles les différents ateliers ont été implantés, entraînant ainsi un volume de terrassement important.

Le plan masse retenu est du type «éclaté» dans la mesure où il a été nécessaire de réserver assez de place pour les extensions éventuelles, et d'assurer des accès aux différents ateliers et aux stockages de réactifs.

L'usine est constituée par une série d'ateliers indépendants: concassage, broyage, attaque filtration, traitement des liqueurs uranifères, un ensemble de traitement des effluents, un atelier d'entretien et les services généraux nécessaires, comprenant en particulier une chaufferie au fuel de 9200 thermies par heure.

Des bassins tampons pour les liqueurs de production et les effluents sulfatés et totalisant environ 15 000 m^3 ont été implantés pour assurer une plus grande souplesse de marche lors de la phase de démarrage.

L'alimentation en eau de l'usine (environ 170 $m^3\cdot h^{-1}$) est faite à partir des eaux d'exhaure de la mine, qui ont nécessité un traitement particulier pour éliminer les matières en suspension et le radium contenus.

Bien que les quantités de réactifs à transporter soient importantes (de l'ordre de 70 000 $t\cdot a^{-1}$), il n'a malheureusement pas été possible de doter l'usine d'un embranchement ferroviaire, à cause du coût trop élevé des ouvrages à créer dans une zone relativement accidentée. Cependant, une solution intermédiaire de transport par remorque porte-wagon a pu être mise au point avec la SNCF.

2.3.2. Protection de l'environnement

En accord avec l'administration, et dans le cadre des lois des 10 et 19 juillet 1976, une attention particulière a été portée aux problèmes d'environnement.

Les résidus solides de lixiviation sont en particulier renvoyés dans les carrières d'extraction de minerai exploitées avant le démarrage de l'usine. Le transport depuis l'usine jusqu'à ces carrières a nécessité la mise en place d'un convoyeur de 800 m de long avec une pente de 10%, qui s'est avérée être la limite admissible pour le produit transporté.

Par ailleurs, les eaux de ruissellement de la zone de stockage de minerai en amount de l'usine ainsi que celles de la zone de l'usine elle-même sont stockées dans des bassins étanches et indépendants, en vue de leur contrôle avant rejet dans l'environnement. Un recyclage vers la station de traitement de la mine est possible en cas de dépassement des normes.

Le schéma général des eaux fait l'objet de la figure 10.

L'ensemble de l'atelier de concassage ainsi que les silos de réactifs et le stockage de sulfate sont conçus pour assurer une teneur maximale de poussières de 30 $mg \cdot m^{-3}$ dans l'air traité.

Une mention particulière est à faire pour le local de conditionnement du concentré d'uranium, pour lequel la Cogéma a adopté une conception garantissant un niveau particulièrement bas de pollution par les poussières à l'intérieur de l'atelier (0,25 $mg \cdot m^{-3}$), le rejet de l'air filtré à l'atmosphère étant au maximum de 5 $mg \cdot m^{-3}$.

D'une façon générale, pour l'ensemble des ateliers, la configuration «vestiaires ville, vestiaires usine» a été adoptée pour éliminer les risques de pollution extérieure.

Enfin, en ce qui concerne la protection contre le bruit, certains ateliers ont été munis de bardages acoustiques (broyage, recompression mécanique de l'effluent sulfaté) et des dispositions particulières ont été adoptées (silencieux sur le refoulement des pompes à vide).

2.4. Contraintes liées aux délais de réalisation

Comme pour tout projet de cette importance, une organisation spécifique a été créée pour faire les choix fondamentaux et maîtriser les aspects budget et délais.

L'équipe mise en place était constituée par les ingénieurs du laboratoire de recherche et de l'atelier pilote de Bessines, actuellement regroupés au sein du Service d'études de procédés et d'analyses, la Société d'ingéniérie Krebs, chargée des études de détail et du chantier de construction et une cellule de projet, assurant la direction du projet et représentant le maître d'ouvrage, la Cogéma.

Les principaux membres de la future équipe exploitante de la Société industrielle des minerais de l'ouest (Simo) ont été intégrés dès que possible à cette organisation.

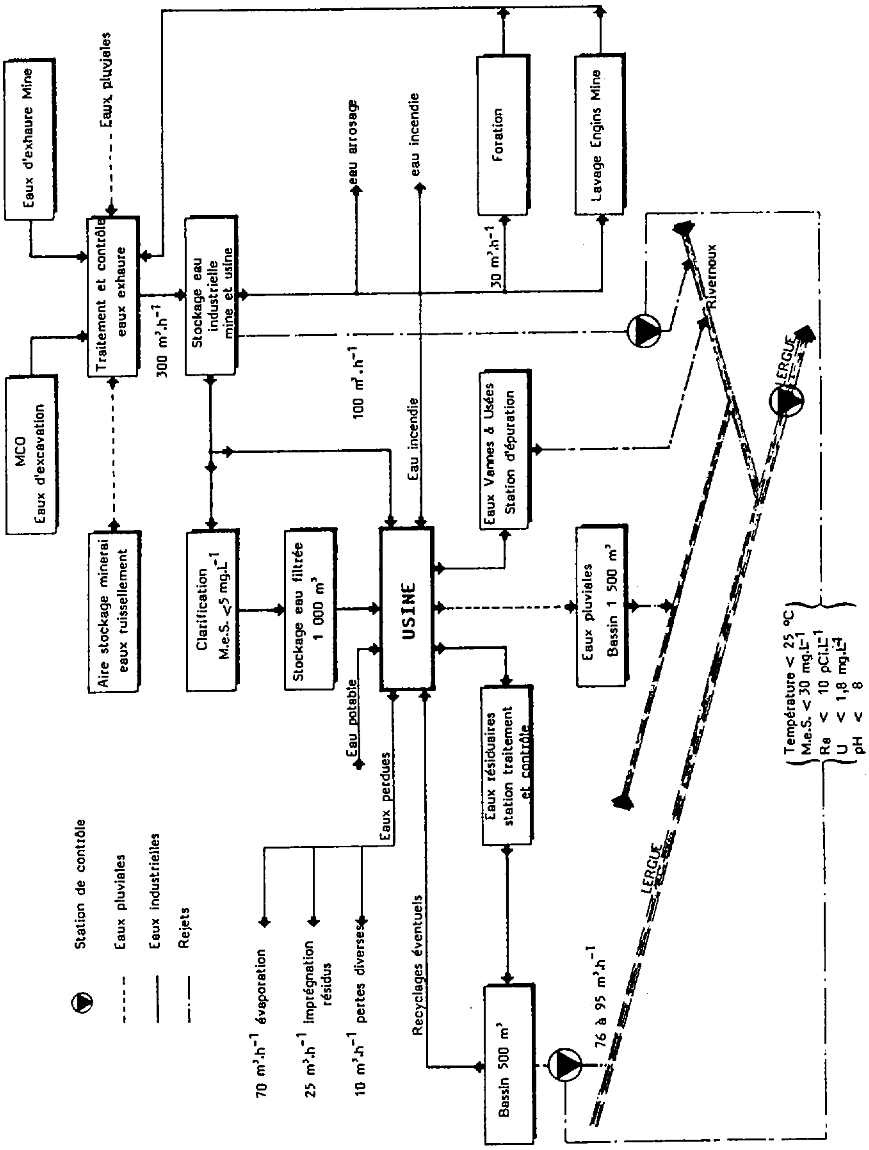

FIG.10. Usine de Lodève: schéma général des eaux.

Les difficultés rencontrées sont pratiquement toutes liées à l'extrapolation à l'échelle industrielle d'un procédé original, débouchant par conséquent sur la construction d'une usine prototype. Ceci a eu pour résultat notamment de multiplier les vérifications par pilotage, voire, comme on l'a déjà dit, de «tester» les technologies avant les décisions de choix. Par exemple, des essais ont été menés avec les fournisseurs pour définir les pompes volumétriques, les échangeurs et les cribles sur les circuits de la pulpe, pour délimiter les risques de corrosion des aciers en milieu carbonaté. Elles ont aussi entraîné certains retards dont les incidences sur les plannings ont pu être limitées, au moins en grande partie, par la mise en place de moyens exceptionnels lors de la phase de chantier.

Les risques de dérapage ont en particulier été importants pour les ateliers de purification et de conditionnement du sulfate de soude dans la mesure où les spécifications de qualité ont été longues à mettre au point avec les clients potentiels et ont donné lieu à des pilotages tardifs.

Les autres difficultés ont concerné, dans une moindre mesure, l'établissement des dossiers administratifs pour l'obtention des permis de construire et d'exploiter, qui ont conduit à un certain nombre d'échanges avec l'administration et à des modifications en cours de projet.

Néanmoins, l'ensemble de la réalisation, depuis les études de détail juqu'aux mises en service, a pu être mené en une trentaine de mois, sauf pour l'atelier de molybdène, dont la mise au point a été décalée d'environ un an.

Le premier uranate de qualité marchande a été produit le 16 avril 1981 alors que les études de réalisation avaient démarré en octobre 1978.

3. EXPLOITATION INDUSTRIELLE: PREMIERE EXPERIENCE

La mise en service d'une usine demande toujours un certain temps d'adaptation au cours duquel sont corrigés les défauts ou insuffisances du matériel et des circuits. Dans le cas d'un procédé classique éprouvé, et pour peu que le personnel d'exploitation soit expérimenté, ce temps ne dépasse pas généralement un an.

A Lodève, aux problèmes habituels, se sont ajoutés ceux dus à la nouveauté du procédé (figure 11) et de certains matériels, et à l'inexpérience d'opérateurs en général jeunes et assez qualifiés mais occupant souvent leur premier emploi.

La période de mise au point, qui n'est pas complètement aujourd'hui achevée, s'est donc étendue sur près de deux ans, mais il faut noter néanmoins que le programme de 1982 a été réalisé, au moins en ce qui concerne la production d'uranium.

La mise en service de l'usine de Lodève a commencé dès la fin de l'année 1980, mais ce n'est qu'au début 1981 que les silos ont été remplis de minerai.

L'enchaînement des différents ateliers a été très progressif et des précautions particulières ont été prises lors de la mise en service des secteurs présentant a priori le plus de risques par leur nouveauté.

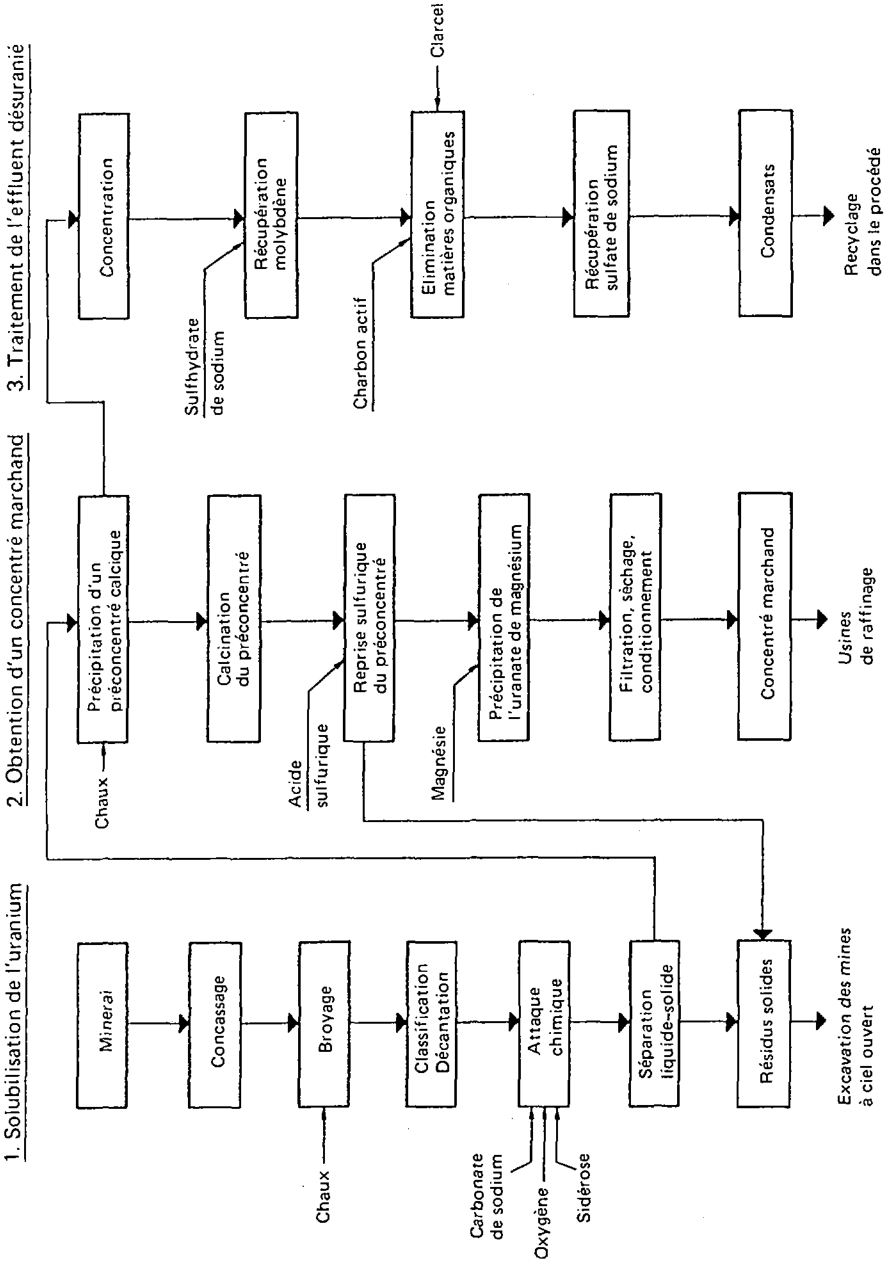

FIG.11. Schéma simplifié du traitement des minerais de Lodève.

C'est ainsi que les autoclaves ont été d'abord remplis d'eau afin de tester la dispersion de l'oxygène. Puis ils ont été alimentés en pulpe stérile pour vérifier l'agitation. Enfin, après fermeture, la montée en température a été progressive et les étanchéités ont été sévèrement contrôlées. Après toutes ces vérifications, les autoclaves ont enfin été alimentés en minerai.

3.1. Concassage

Au démarrage, le débit nominal de cet atelier n'a pu être atteint en raison de bourrages (crible-trémie-transporteurs) entraînant des arrêts fréquents. Le minerai s'est avéré beaucoup plus collant que prévu dès que l'humidité atteignait 6 à 7%.

Outre l'aménagement des jetées des transporteurs et autres interventions classiques lors de la mise au point d'un atelier de concassage, diverses améliorations ont permis d'atteindre le nominal, au moins avec des minerais pas trop humides.

3.2. Broyage

La double limite recherchée pour la granulométrie des pulpes broyées (moins de 5% supérieur à 160 μm et moins de 60% inférieur à 50 μm) n'a pas encore été complètement atteinte.

Les améliorations apportées à la boucle de classification (actuellement deux cyclones en parallèle) ont permis d'obtenir une meilleure fiabilité et surtout une plus grande reproductibilité de la granulométrie. Actuellement, pour avoir un taux de fines pas trop élevé, il faut accepter jusqu'à 8 ou 10% de particules supérieures à 160 μm. Les modifications prévues doivent améliorer ces résultats. Une granulométrie voisine de celle recherchée devrait être obtenue cette année.

3.3. Lixiviation

Ce secteur est l'un de ceux qui a fait l'objet, lors du projet, des études les plus approfondies. C'est là, en effet, que l'on trouve le plus d'innovations technologiques:

— pompes à pulpes haute pression: là les débits nominaux n'ont pas été tout-à-fait atteints, mais les caractéristiques de la pulpe à pomper étaient parfois différentes de celles prévues;

— les autoclaves: tels qu'ils sont conçus, ils n'ont pas posé beaucoup de problèmes; les problèmes de détail, tels que des fuites, sur les passages d'arbre d'agitateur et les manchons inter-autoclave, et les usures des pales d'agitateur ont trouvé des solutions originales et efficaces;

— les échangeurs de chaleur: il en a été beaucoup question dans la seconde partie et il n'y a eu qu'assez peu d'arrêts de leur fait (quelques fuites sur des soudures).

3.4. Séparation solide-liquide

De nombreuses difficultés sont apparues dans ce secteur. Outre des conditions de travail rendues pénibles par un dégagement de vapeur intense à partir de pulpes de 65°C et d'eaux de lavage très chaudes auxquelles il a été remédié ensuite par un système de captage au-dessus des filtres, on a rencontré deux types de problèmes:

– problèmes de matériel: le matériel a présenté certaines faiblesses de construction qui ont été progressivement corrigées; ces problèmes ont été parfois accentués par des conditions de marches anormales, quoique momentanées, lors des premiers mois de mise en service;

– problèmes de procédé: l'envoi d'une pulpe trop riche en fines conduit à des débits spécifiques aux limites des possibilités des filtres et à des consommations excessives de floculant; les améliorations progressives de la granulométrie et la plus grande régularité de fonctionnement ont permis de ramener la consommation de floculant à un niveau acceptable; le lavage sera également plus efficace quand on pourra laver le gâteau avec des eaux totalement dépourvues d'uranium.

3.5. Traitement des liqueurs uranifères

Dans ce secteur, les difficultés sont venues principalement du grillage du préconcentré. Le four lui-même, une fois le revêtement des soles supérieures modifié pour résister au sulfate de sodium présent dans la liqueur imprégnant le préconcentré humide, n'a pas apporté de difficulté particulière. En revanche, les dispositifs annexes (sas de sortie, broyeur) restent assez fragiles et entraînent un moins bon fonctionnement de la reprise acide du préconcentré.

En fait, le problème majeur est un problème de procédé. Ce traitement, en dehors du grillage destiné à détruire les matières organiques, ne permet pas de purification vis-à-vis de certaines impuretés qui, telles le zirconium ou le molybdène, sont précipitées par la magnésie si elles sont présentes avec l'uranium à ce stade. C'est pourquoi des études récentes menées par le Service d'études de procédés et d'analyses (SEPA) ont montré qu'il est possible d'améliorer le procédé existant et même de le remanier profondément pour le rendre à la fois plus efficace et plus simple.

3.6. Traitement de l'effluent liquide

Certains ateliers, tels que la précipitation du molybdène et le désuraniage, ont été mis en service bien après les autres et n'ont donc pas atteint la même maturité.

Le fonctionnement de chaque unité est influencé par celui de la précédente. Des améliorations sont attendues des modifications, parfois de faible ampleur, qui sont en cours d'étude ou de réalisation. Par exemple, une meilleure qualité du charbon actif peut permettre un meilleur fonctionnement du désuraniage;

une précipitation plus complète du molybdène entraîne une plus faible consommation de charbon actif et aussi une meilleure filtration.

Beaucoup de difficultés viennent de ce qu'un arrêt dans une unité entraîne rapidement des cristallisations de sulfate de sodium (solution à t $< 50°C$). Une plus grande régularité de marche doit éviter la répétition de ces inconvénients.

3.7. Résultats globaux

La plupart des performances prévues ont été atteintes. Certaines d'entre elles restent encore difficiles à maintenir longtemps. Toutes les difficultés font l'objet d'efforts qui portent progressivement leurs fruits.

Les débits nominaux sont presque partout atteints: 300 $t \cdot h^{-1}$ au concassage, 1 500 $t \cdot d^{-1}$ du broyage à la filtration, 80 $m^3 \cdot h^{-1}$ au traitement des liqueurs et des effluents.

Les rendements d'attaque sont fluctuants. Ceci est dû:

– à des passes de minerais parfois très réfractaires; on l'avait vu lors des pilotages;

– à des teneurs en soufre élevées, connues trop tard (car la station d'échantillonnage avant silos n'a pas encore bien fonctionné); il y a alors insuffisance de carbonate et de chaux qu'on ne rattrape qu'avec retard;

– à un taux un peu trop élevé de particules supérieures à 160 μm.

Les rendements de lavage sont également insuffisants pour les causes suivantes:

– un taux de fines trop élevé qui conduit à une surfloculation défavorable au lavage;

– un lavage effectué au moins en partie avec des liqueurs recyclées d'une teneur non négligeable en uranium.

Les consommations des réactifs principaux sont encore un peu fortes, surtout à cause d'un volume spécifique de liqueurs supérieur à la valeur nominale (1,1 $m^3 \cdot t^{-1}$).

Les concentrés produits sont insuffisamment purs, notamment quant à leur teneur en zirconium, calcium et sodium, occasionnellement en molybdène.

Dans tous les cas, les causes sont connues et les solutions sont en cours d'application.

DISCUSSION

K.K. BERI: How many hydrocyclones are there in the classification stage?

J.P. HÉBERT: Based on the pilot-plant results, we installed initially one hydrocyclone. We have, however, added a second one and the results are good, so we will install it definitively.

K.K. BERI: Could you describe the high-pressure membrane pumps in more detail?

J.-P. HÉBERT: These are sleeve-type volumetric pumps. The sleeve is elastic and is compressed by an exterior liquid upon which a mechanical action is exerted. There are no bearings in pumps like these and there is, therefore, no water introduced to the process. This is in accordance with the objective of limiting as much as possible the introduction of water to the process to avoid having to evaporate this water afterwards. Another important aspect is that we must maintain within the autoclave a pressure of more than 10 bars, which is required for the process. If we had used centrifugal pumps, we would have needed two or three pumping stages. This is complicated and costly in energy and in maintenance. In short, we are quite pleased with the pumps.

D. NADEN: What is the concentration of uranium in the solution leaving the belt filters?

J.-P. HÉBERT: I believe this concentration is of the order of 2 g/L.

D. NADEN: Did you consider using a resin-in-pulp process which would recover the uranium directly from the pulp?

G. LYAUDET: We have done an alkaline leach under very severe conditions. We have dissolved, not only uranium, but also molybdenum and organic matter. Under these circumstances we did not think we could use resins if we wanted to avoid going to a pre-concentrate.

D. NADEN: May I make a contribution on this case by telling you of some work we did. We separated molybdenum and uranium using solid ion-exchange resins and eluting with a hot ammonium carbonate solution. Uranium can then be precipitated by steam stripping from solution.

G. LYAUDET: This is true. Molybdenum can, of course, be separated from uranium, but it is not too easy and it can be very complicated in the presence of organic matter.

K.K. BERI: Did you try to recover the molybdenum by flotation before leaching?

J.-P. HÉBERT: Initially we tried to eliminate the sulphides using flotation as a pre-treatment. But we did not succeed and we abandoned this approach.

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A TECHNO-ECONOMIC EVALUATION OF EIGHT PROCESS ROUTES FOR THE RECOVERY OF URANIUM FROM WITWATERSRAND LEACH PULPS

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Abstract

A TECHNO-ECONOMIC EVALUATION OF EIGHT PROCESS ROUTES FOR THE RECOVERY OF URANIUM FROM WITWATERSRAND LEACH PULPS.

The sections of the recovery process dealt with in the paper involve liquid-solid separation, and concentration-purification. A flowsheet incorporating rotary-drum filtration, followed by clarification of pregnant filtrate and solvent extraction, is used as the standard against which seven other flowsheets are compared. These flowsheets employ either countercurrent decantation, belt, or tilting-pan filtration for liquid-solid separation, followed by clarification-solvent extraction, or continuous ion exchange-solvent extraction for concentration-purification. Where possible, actual performance data are compared with estimated data for the selected route. A subsequent independent study of the four most favoured routes confirmed the findings concerning operating costs, and details are included in the paper.

1. INTRODUCTION

As uranium-recovery operations increased in magnitude (up to about 450 000 tons per month), the high capital and operating cost of the time-honoured method involving rotary-drum filtration, clarification, and solvent extraction was subjected to close scrutiny.

In the case of countercurrent decantation economies of size are possible because of the linear relationship between cost and thickener diameter, whereas capacity is proportional to surface area.

The considerable success of the Council for Mineral Technology's continuous ion-exchange system makes it a strong contender for incorporation in the ideal circuit.

2. POSSIBLE FLOWSHEETS

In this paper rotary-drum filtration, followed by clarification and solvent extraction, is used as the standard against which the alternative routes are compared. The possible routes after leaching are outlined in Fig.1. These process routes are shown diagrammatically in Figs 2 to 9.

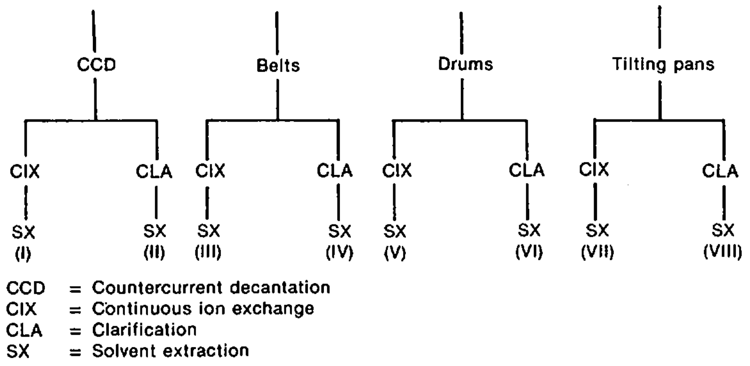

FIG.1. Possible routes after leaching.

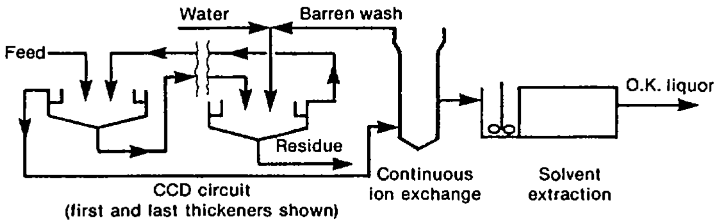

FIG.2. Flowsheet I: countercurrent decantation, continuous ion exchange, and solvent extraction.

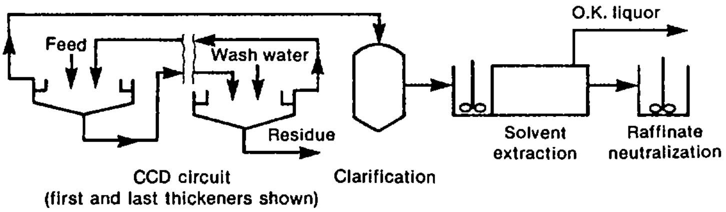

FIG.3. Flowsheet II: countercurrent decantation and solvent extraction.

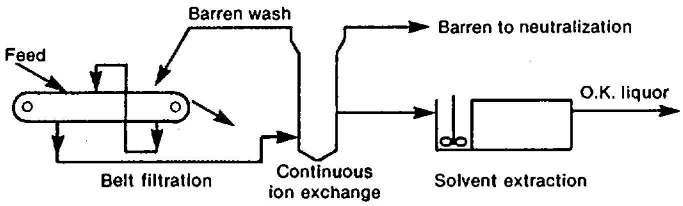

FIG.4. Flowsheet III: belt filtration, continuous ion exchange, and solvent extraction.

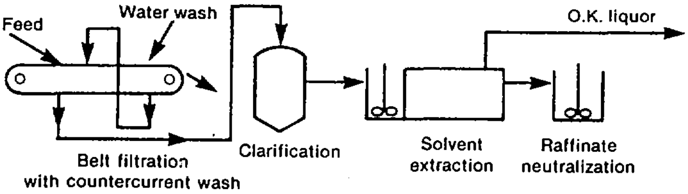

FIG.5. Flowsheet IV: belt filtration and solvent extraction.

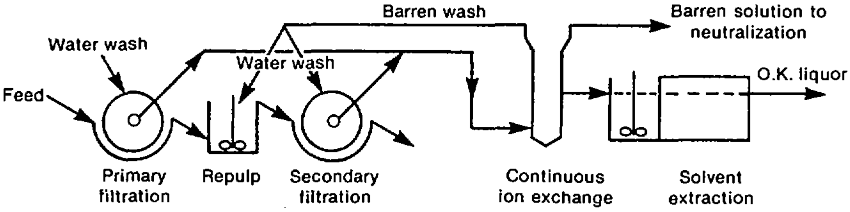

FIG.6. Flowsheet V: rotary-drum filtration, continuous ion exchange, and solvent extraction.

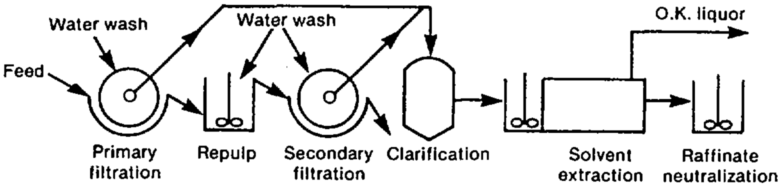

FIG.7. Flowsheet VI: rotary-drum filtration and solvent extraction.

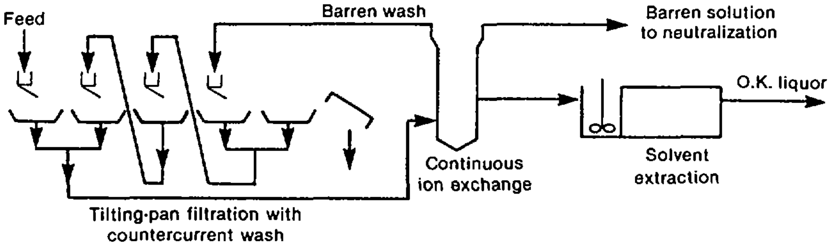

FIG.8. Flowsheet VII: tilting-pan filtration, continuous ion exchange, and solvent extraction.

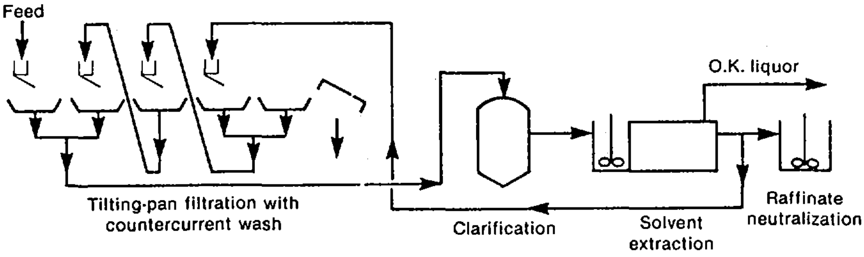

FIG.9. Flowsheet VIII: tilting-pan filtration and solvent extraction.

3. FINANCIAL RANKING

The purpose of this study is to evaluate the various possible process routes, financially and technically, and to recommend a final process flowsheet in view of the findings.

The following financial ranking is based on the eight examples considered.

Flowsheet	Order of financial evaluation	Process route	Comparative incremental net present value[a]
II	1	CCD–CLA–SX	100.0
I	2	CCD–CIX–SX	72.7
IV	3	BELT–CLA–SX	71.9
VIII	4	PAN–CLA–SX	57.4
III	5	BELT–CIX–SX	37.6
VII	6	PAN–CIX–SX	23.1
VI	7	DRUM–CLA–SX	00.0[b]
V	8	DRUM–CIX–SX	34.3

[a] Discounting at 15%. For reasons of confidentiality no monetary units are indicated, neither is the date of calculation revealed.

[b] Base example.

Combining this ranking with technical considerations, the following preliminary choices were made as far as route is concerned.

Flowsheet	Order of technical-financial evaluation	Process route	Comparative capital cost	Comparative operating cost	U_3O_8 losses (%)
II	1	CCD–CLA–SX	100.0	75.2	0.56
I	2	CCD–CIX–SX	90.1	100.0	1.22

4. RESIN COBALTICYANIDE POISONING VERSUS LOSS OF SOLVENT

Doubts about cobalticyanide resin poisoning in flowsheet I prompted the following sensitivity analysis, i.e. the two examples were examined in more detail.

Flowsheet	Order of financial evaluation	Process route	Comparative incremental net present value
II	1	CCD–CLA–SX	100.0
I	2	CCD–CIX–SX	72.7

The difference in total net present value (NPV) between the two examples is 27.3.

It was shown that the resin-replacement interval would need to increase from 12 to 21 months for the incremental NPV for flowsheet I to equal that for flowsheet II. Conversely the solvent loss incurred by flowsheet II would need to rise from an estimated 200 to 400 ppm for the incremental NPV to be reduced to the same level as that for flowsheet I.

In view of the high level of doubt, as far as resin poisoning is concerned, it was decided to adopt flowsheet II.

5. TECHNICAL CONSIDERATIONS

There are certain basic technical advantages and disadvantages inherent in the various process routes. These are as follows.

(1) Liquid-solid separation

(a) Countercurrent decantation (CCD)

Advantages

(i) Low capital cost
(ii) Low operating-labour requirement
(iii) Minimum number of moving parts (pumps and rake mechanisms) leading to low maintenance cost
(iv) Small number of large units
(v) Full throughput can be maintained with one or more units off line, although a reduction in recovery would result
(vi) Possible extra U_3O_8 dissolution due to longer contact time
(vii) Low water consumption as it is possible to recycle raffinate.

Disadvantages

(i) A large volume of low-grade solution produced, necessitating large clarification-solvent extraction or continuous ion-exchange plants
(ii) Relatively high consumption of flocculant.

(b) Belt filters

Advantages

(i) Relatively high filter duty and low cake moisture
(ii) Countercurrent washing facility
(iii) Flood-wash at all times leads to better recovery
(iv) Throughput can be varied, although changes in recovery would result
(v) Small surface area of plant.

Disadvantages

(i) Mechanically complicated
(ii) A large number of smaller capacity units required
(iii) Large surface-wear area
(iv) Wet and corrosive atmosphere attacks framework
(v) Need for elaborate spillage containment and recycle systems
(vi) Leakage between wash dams.

(c) Tilting-pan filters

Advantages

(i) Countercurrent washing facility
(ii) Vacuum shut off during cell filling which minimizes cloth blinding
(iii) No cloth training, creeping, or folding problems (as with belt filters)
(iv) Better vacuum-seal arrangement
(v) Each cell cloth can be replaced separately
(vi) Very large units available, up to 245 m^2
(vii) Good control over spillage
(viii) Batch-type wash approaches laboratory conditions
(ix) Reported low maintenance cost and high on-line time.

Disadvantages

(i) Unproved for the application under consideration
(ii) Complete unit must be shut down to change a single cloth
(iii) Limited speed (2½ min cycle time) limits capacity
(iv) Large surface area required for building
(v) High capital cost.

(d) Drum filters

Advantages

(i) Known operating and maintenance procedures
(ii) No cloth training, creeping, or folding problems (as with belt filters)
(iii) The possibility of an immediate large increase in throughput (with lower recovery) by conversion from double- to single-stage filtration.

Disadvantages

(i) High capital and maintenance costs
(ii) High operating-labour requirements
(iii) Size limitation requires a large number of units
(iv) Power failure can cause considerable inconvenience, compared with belts and tilting pans
(v) Cloth changing causes high filter downtime and requires trained personnel
(vi) Low filter duty ($t/m^2 \cdot 24$ h), compared with tilting pans or belts
(vii) High power consumption.

(2) Concentration/purification

(a) Continuous ion exchange (CIX)

Advantages

(i) Clarification of pregnant solution unnecessary
(ii) Lower resin inventory than for a fixed-bed plant
(iii) Low capital cost as compared with a large solvent-extraction plant
(iv) Easy access to resin portions for regeneration
(v) Re-use of CIX barrens possible (no solvent contamination) in the leach section, thus savings in consumption of leach acid and water.

Disadvantages

(i) Unless a reverse leach is practised (i.e. uranium recovery prior to gold recovery), there is a potential cobalticyanide poisoning problem
(ii) Silica poisoning of resin would necessitate a continuous bleed-off for treatment
(iii) U_3O_8 concentration in barren solution higher than that for solvent extraction.

(b) Solvent extraction

Advantages

(i) Process well understood; there are many plants operating successfully in the industry
(ii) Extremely efficient as far as uranium recovery is concerned
(iii) Instrumentation and control leading to automation well developed.

Disadvantages

(i) Requires a feed low in undissolved solids, hence the need for clarification
(ii) Capital cost high when compared with a CIX plant
(iii) Potential fire hazard
(iv) The raffinate is contaminated with organics which are harmful to rubber.

6. DETERMINATION OF OPERATING COSTS

6.1. Cost centres

(1) Power

Data for power consumption were abstracted from equipment specifications.

(2) Water

Water consumption for the process alternatives was determined from material balances as indicated on the relevant flowsheets.

(3) Reagents

The major reagent costs for acidic liquid-solid separation, ion exchange, clarification, and solvent extraction were determined on the basis of laboratory tests and typical plant performance.

These reagents include flocculant, sulphuric acid, solvent components, ion-exchange resin, filter aid, etc.

(4) Maintenance

The annual cost was based upon expected spares consumption, maintenance labour, filter-cloth replacements, etc.

(5) Labour

Estimates were made of the operating-labour requirement for each process alternative. Supervisory senior staff and day-gang costs were not included as they were considered to be the same for each alternative. Care was taken to exclude labour costs for the sections not under study (i.e. feed dewatering, leach, reagent handling, precipitation).

The data are summarized in Tables I and II.

7. RECOVERIES OF U_3O_8

A series of material balances was calculated to determine the recovery for a 6-stage countercurrent-decantation plant under conditions of recycle of continuous ion exchange (CIX) barren solution and solvent extraction (SX) raffinate, assuming that imperfect interstage mixing would lead to an overflow concentration equal to 90% of the underflow solution concentration for each stage.

The calculations were repeated for a 5-stage plant to quantify the effects of having one unit off line and to assess the justification of installation of a sixth stage.

TABLE I. DESIGN PARAMETERS FOR DETERMINATION OF OPERATING COSTS

Process	CCD	Belts	Drums	Pans	Clarification		CIX		Solvent extraction		
	1	2	3	4	5	6	7	8	9	10	11
Feed rate (t or m^3/h)	700	700	700	700	700 Soln ex. stages 2, 3, 4	1617 Soln ex. stage 1	700 Soln ex. stages 2, 3, 4	1617 Soln ex. stage 1	50 Eluate ex. stages 7, 8	700 Soln ex. stage 5	1617 Soln ex. stage 6
Number of units	6	12	39	8							
Power (kW)	1500	6600	9500	4800	250	600	230	600	50	280	685
Water (m^3/h)	582	1008	1397	1008							
Reagent consumption											
Liquid-solid separation											
Flocculant (g/t)	90	70	100	120							
Clarification											
Flocculant (g/t)					5	5					
CIX											
Resin (m^3/a)							600	900			
Solvent extraction											
Solvent (ppm)									200	200	200

Exclusions: Caustic soda for filter-cloth treatment.
Loaded solvent scrubber water considered the same for 9, 10, and 11.

TABLE II. COMPARATIVE ANNUAL OPERATING COSTS: REAGENTS AND MAINTENANCE

Process	CCD	Belts	Drums	Pans	Clarification		CIX		Solvent extraction		
Reagents											
Liquid-solid separation											
Flocculant	25.9	20.1	28.7	34.5							
Clarification											
Flocculant					1.5	3.7					
Media replacement					2.9	7.0					
Caustic treatment					3.7	9.1					
Total					8.1	19.8					
CIX											
Resin							57.5	86.2			
Sulphuric acid							7.6	11.5			
Total							65.1	97.7			
Solvent extraction											
Solvent									1.2	17.1	39.6
Maintenance	9.2	27.4	37.7	17.5	0.2	0.3	1.3	2.3	0.4	1.7	2.8
Total	35.1	47.5	66.4	52.0	8.3	20.1	66.4	100.0	1.6	18.8	42.4

Note: For reasons of confidentiality no monetary units or dates when calculated are indicated.

CCD	*Recovery* (%)
6-stage water wash	99.84
6-stage SX raffinate wash	99.73
6-stage CIX barren wash	98.78
5-stage water wash	99.56
5-stage SX raffinate wash	99.46
5-stage CIX barren wash	98.51
Belt filters	
1-stage water wash	98.27
1-stage CIX barren wash	97.98
Drum filters	
2-stage water wash 2nd stage	97.69
2-stage CIX barren wash 2nd stage	97.19

Tilting-pan filters

As for belt filters

CIX

Irrespective of volume throughput, the U_3O_8 concentration of the CIX barren solution was set at 0.002 g/L (the portion of the barren solution recycled to the liquid-solid-separation step as wash fluid is given).

	Percentage recycled
Countercurrent decantation	100
Belt filter	54
Drum filter	70
Tilting-pan filter	54

SX

The procedure used was as that described for CIX except that the raffinate level was set at 0.0002 g/L.
For the CIX-SX combination SX losses are considered to be nil since raffinate is completely recycled.

7.1. Overall recoveries

Process	Liquid-solid separation (%)	CIX or clarification (%)	SX (%)	Overall (%)
CCD-CIX-SX	98.78	100.00	100.00	98.78
CCD-CLA-SX	99.73	100.00	99.70	99.44
BELT-CIX-SX	97.98	99.26	100.00	97.25
BELT-CLA-SX	98.27	100.00	99.89	98.16
DRUM-CIX-SX	97.19	99.34	100.00	96.55
DRUM-CLA-SX	97.69	100.00	99.89	97.58
PAN-CIX-SX	97.98	99.26	100.00	97.25
PAN-CLA-SX	98.27	100.00	99.89	98.16

8. COMPARISON BETWEEN EXPECTED AND ACTUAL PERFORMANCE

Countercurrent decantation	*Expected*	*Actual*
Tons treated per month	455 000	451 258
No. of thickener stages in series	6	5[a]
Ratio of pregnant solution to solids treated (m^3/t)	2.69	2.55
Flocculant addition (kg/t)	0.040	0.036
Soluble loss of U_3O_8 as a percentage of head value	0.26	1.50[b]
Solvent extraction		
Average raffinate value, U_3O_8 (g/L)	0.0002	0.0002
Extraction efficiency (%)	99.70	99.85
Total solvent loss (ppm)	200	176

[a] Due to problems with the 1st stage clarification system one CCD thickener was taken off line and used as a pre-settler.

[b] This had an adverse effect on soluble loss.

TABLE III. MORE DESIGN PARAMETERS FOR DETERMINATION OF OPERATING COSTS

Process route		CCD–CIX–SX	CCD–CLA–SX	BF–CIX–SX	BF–CLA–SX
Capacity	t/solids, h	231	231	231	231
Clarification					
Pregnant soln flow	m^3/h		472.5		277.2
Flocculant bed clarifier: cross-section area	m^2		87.5		39.6
CIX absorption					
Pregnant soln flow	m^3/h	472.5		277.2	
Number of streams		2		2	
Flow per stream	m^3/h	236.3		138.6	
Pregnant soln value, U_3O_8	g/L	0.035		0.060	
70% equilibrium load, U_3O_8	g/L	13		18	
Number of stages		9		9	
Diameter of column	m	4.08		3.13	
Total cycle time	min	382		328	
Elution					
Number of streams		2		2	
Flow per stream	m^3/h	4.2		2.77	
Eluate value, U_3O_8	g/L	2.0		3.0	
Diameter of column	m	1.725		1.4	
Cycle time	min	115		97	
Average resin flow	m^3/h	0.667		0.472	
Fraction of stage vol. moved	%	68		62	
Number of stages for 18 h retention time		8		8	
Total resin inventory	m^3	172		100	

SX – extraction					
Aqueous pregnant flow	m^3/h	8.4	472.5	5.54	277.2
Pregnant soln value, U_3O_8	g/L	2.0	0.035	3.0	0.060
Organic aqueous ratio		1.1:1	1.2:1	1.1:1	1.2:1
Solvent loading, U_3O_8	g/L	2.7	1.7	4.0	2.7
Solvent advanced flow	m^3/h	6.2	9.5	4.1	6.0
Recirculation	m^3/h	3.1	557.5	2.0	326.0
Total solvent flow	m^3/h	9.3	567.0	6.1	332.0
Mixed phase flow	m^3/h	17.7	1039.5	11.64	609.2
Number of stages		4	4	4	4
Settler area	m^2	6	180	6	105
Total organic inventory	m^3		800		475
Scrubbing, stripping, regeneration					
Organic flow	m^3/h	6.2	9.5	4.1	6.0
Aqueous flow	m^3/h	2.0–2.5	3.2–4.8	1.6–2.75	2.4–3.0
Organic aqueous ratio		2.5–3.0:1	2–3:1	1.5–2.5:1	2.5–3:1
Mixed phase flow	m^3/h	8.2–8.7	12.7–14.8	5.7–6.85	8.4–9.0
O.K. liquor flow	m^3/h	2.5	4.8	2.75	3.0
O.K. liquor tenor, U_3O_8	g/L	6.7	3.5	6.0	5.4
Number of stages		6	6	6	6
Settler area	m^2	4	6	4	4

9. DETERMINATION OF OPERATING COST FOR A SECOND APPLICATION

In a subsequent project, the four most favoured process routes as determined in the first study were re-evaluated independently as far as operating cost is concerned. These were as follows.

Flowsheet	*Process route*
I	CCD–CIX–SX
II	CCD–CLA–SX
III	BF (belt filtration)– CIX–SX
IV	BF–CLA–SX

shown diagrammatically in Figs 2 to 5.

Material balances and basic equipment sizing for the solution-treatment sections are shown in Table III. For reasons given in Section 10 the wash ratio was fixed at 2.5.

10. RECOVERIES OF U_3O_8 IN A SECOND APPLICATION

10.1. Countercurrent decantation

	Recovery (%)
7-stage SX raffinate wash	99.32
7-stage CIX barren wash	97.61
6-stage SX raffinate wash	98.98
6-stage CIX barren wash	97.27

Although the improvement resulting from an increase from 6 to 7 stages is not spectacular, 7 stages were accepted, thus allowing for one stage to be taken out of commission if this were necessary.

A further reduction in wash ratio is not advisable as soluble losses would increase to over 3% with SX and over 7% with CIX, if the wash ratio were reduced to 2.

With a wash ratio of 2.5 the pregnant solution value at 0.035 g/L is extremely low, and therefore a further increase in wash ratio is to be avoided.

10.2. Belt filters

	Recovery (%)
SX raffinate wash	98.21
CIX barren wash	97.54

10.3. Losses occurring through bleeding

Additional losses occur through bleeding. In the case of CCD this is assumed to be 10% and in the case of belt filters 60% with CIX barren at 0.002 g/L, and SX raffinate at 0.0005 g/L.

10.4. Overall recoveries

Process	%	
CCD–CIX–SX	97.27	(6-stage CIX barren wash)
CCD–CLA–SX	98.98	(6-stage SX raffinate wash)
BELT–CIX–SX	97.54	(CIX barren wash)
BELT–CLA–SX	98.21	(SX raffinate wash)

11. DETERMINATION OF OPERATING COSTS

The design parameters for the determination of operating costs and an operating cost summary are given in Tables III and IV, respectively.

11.1. Expected consumption of reagents

Flocculant

CCD (g/t)	120
Belt filters (g/t)	50
Clarification (g/t)	20

Other reagents

CIX resin (% inventory/a)	10
SX organic (ppm)	200
Ammonia (kg/m^3)	1.85
Resin regeneration (% moved/d)	10

11.2. Operating parameters, liquid-solid separation

CCD

Wash ratio, liquid in overflow to liquid in underflow	2.5
Ratio of pregnant solution to solids (m^3/t)	2.05
Number of stages	6
Wash efficiency per stage (%)	90
Thickener underflow moisture (%)	45

Belt filters

Ratio of pregnant solution to solids (m^3/t)	1.2
Number of wash stages	2
Wash displacement (%)	85
Residue cake moisture (%)	25

12. OPERATING COST COMPARISON

From the comparison indicated in Table IV it was concluded that the two treatment routes involving belt filters showed higher totals both with respect to operating costs and to soluble losses. The clarification SX treatment route showed slightly higher operating costs but significantly lower losses.

13. COMPARISON BETWEEN ANTICIPATED AND ACTUAL PERFORMANCE

CCD	*Anticipated*	*Actual*
Tons treated per month	150 000	199 059
Number of thickener stages in series	6	6
Tons of pregnant solution to solids treated (m^3/t)	2.04	1.83
Flocculant addition (kg/t)	1.20	19
Soluble loss, U_3O_8 (%)	1.02	1.50[a]
Solvent extraction		
Average raffinate value, U_3O_8 (g/L)	0.0005	0.0017
Extraction efficiency (%)	98.98	95.75
Total solvent loss (ppm)	200	106

[a] Increased soluble loss due to excessive solids feed rate.

TABLE IV. OPERATING COST SUMMARY

Process route	CCD–CIX–SX	CCD–CLA–SX	BF–CIX–SX	BF–CLA–SX
Total labour	11.3	7.7	15.9	13.0
Operating	10.3	6.8	13.3	10.6
Maintenance	1.0	0.9	2.6	2.4
Specified stores	29.6	40.5	19.7	27.2
CCD	17.1	17.1		
BF			10.5	10.5
Clarification		2.7		1.7
CIX	9.2		5.9	
SX	3.3	20.7	3.3	15.0
Maintenance	13.6	13.6	17.6	17.2
CCD	7.6	7.6		
BF			12.9	12.9
Clarification		0.9		0.4
CIX	5.2		3.9	
SX	0.8	5.1	0.8	3.9
Power	7.7	8.1	21.6	21.6
CCD	4.6	4.6		
BF			19.4	19.4
Clarification		1.8		1.1
CIX	2.7		1.8	
SX	0.4	1.7	0.4	1.1
Water	2.9	2.9	2.2	2.2
Total	65.1	72.8	77.0	81.2
Solution losses	15.6	5.0	23.0	12.8
Total (for comparison)	80.7	77.8	100.0	94.0

Note: No monetary units or date of compilation indicated for reasons of confidentiality.

14. ACTUAL PLANT OPERATING STATISTICS FOR THE TWO FEASIBILITY STUDIES

CCD	*Study I*	*Study II*
Tons treated per month	451 258	199 059
Number of thickener stages in series	5	6

Screen analysis of pulp	*Study I*	*Study II*
> 300 μm		
< 300 > 150 μm	2.7	3.7
< 150 > 75 μm	24.2	22.4
< 75	73.1	73.9

Relative density of pulp		
Feed pulp	1.483	1.474
First thickener underflow	1.524	1.549
Final thickener underflow	1.504	1.553

Wash data		
Ratio of pregnant solution to solution in underflow (m^3/t)	2.9	2.6
Wash-solution value (g/L U_3O_8)	0.0002	0.002
Ratio of pregnant solution to solids treated (m^3/t)	2.55	1.83

Operation	*Study I*	*Study II*
Thickening rate ($t/m^2 \cdot 24$ h)	3.50	2.92
Flocculant, Magnafloc 351		
Addition rate per stage (kg/t)		
1	0.015	0.004
2	0.006	0.003
3	0.006	0.003
4	0.005	0.003
5	0.004	0.003
6	–	0.003
	0.036	0.019
Soluble loss, U_3O_8 as % of head value	1.5	1.5
Suspended solid in overflow (ppm)	146	643

Analysis U_3O_8	*Study I*	*Study II*
Final thickener, unwashed underflow (kg/t)	0.024	0.033
Final thickener, washed underflow (kg/t)	0.021	0.032

Pregnant solution

Clarification

First stage	Gravity settling tank CCD 1 thickener	Hopper flocculant bed
Flocculant, Magnafloc 351		
Consumption (kg/t)		0.001
Solution flowrate m^3/m^2 clarifier area/24 h	8.28	119.96
Suspended solids after first-stage clarification (ppm)	49	21

Second stage

Type of clarifier	Sand pressure filter
Flocculant, Magnafloc 351	
Consumption (kg/t)	
Solution flowrate, m^3/m^2 clarifier area/24 h	283.44
Suspended solids after second-stage clarification (ppm)	24

Analysis	g/L	
U_3O_8	0.080	0.040
Fe^{++}	0.66	2.20
Fe^{3+}	1.50	0.70
H_2SO_4	4.88	2.90
Mn^{++}	1.51	2.40
NO_3^-	0.01	0.02
SiO_2	0.73	1.72
S_4O_6 (ppm)	4.00	28.5

	Study I	*Study II*
Anionic Co (ppm)	1.00	5.474
Cl^- (ppm)	750.00	223.30
CNS^- (ppm)	3.00	23.00
pH value	1.43	1.87
Solvent extraction		
Extraction, number of stages	4	3
Average value of feed solution ($g/L\ U_3O_8$)	0.080	0.040
Suspended solids in feed solution (ppm)	24	21
Average flowrate, m^3/m^2 of settler area/24 h		
Feed solution	40.9	59.6
Organic phase	52.8	71.5
Organic/aqueous ratio in mixers	1.29	
Average raffinate value ($g/L\ U_3O_8$)	0.0002	0.0017
Extraction efficiency (%)	99.85	95.75
Organic make-up (%)		
Amine	6	4
Third-phase inhibitor	2	1
Diluent	92	95
Amino loss, assayed ppm	3.9	11
inventory ppm	9.9	5
Total organic loss, inventory ppm	176	106
Average solvent loading ($U_3O_8\ kg/m^3$)	3.10	1.03

Scrubbing	*Study I*	*Study II*
Number of stages	2	3
Scrubbing solution, reagent, % not determined		
No. 1 scrubber, soft water, and ammonium hydroxide		
No. 2 scrubber, soft water, and ammonium hydroxide		
Flowrates m^3/m^2 of settler area/24 h	8.5	28.2

Stripping		
Stripping pH value		
No. 1 stripper	3.7	3.5
No. 2 stripper	4.2	4.2
No. 3 stripper	4.5	5.6
No. 4 stripper	4.6	
No. 5 stripper	5.1	
Stripping efficiency (%)	99.91	99.33
O.K. liquid, av. value (g/L U_3O_8)	5.19	2.33
Regeneration		
pH value	12.3	10.9
Reagent consumption (kg/t solids treated)		
Amine (Alamine 336)	0.020	0.008
Diluent (Mobil 3745)	0.440	0.178
Third-phase inhibitor (Isodecanol)	0.031	0.008
Ammonia	0.145	0.038
Caustic soda	0.018	0.064
Sodium carbonate	0.021	0.024
Hydrochloric acid	0.031	
Precipitation	*Study I*	*Study II*
Average flowrate of O.K. liquor (L/min)	422	82
pH value of precipitation	7.5	7.3
Temperature (°C)	29	Amb
Precipitation residence time (min)	59	57
ADU thickener		
Feedflow, m^3/m^2 of thickener area/24 h	6.81	2.66
Underflow density	1.154	1.080

15. CONCLUSIONS

It is believed that the choice involving CCD-clarification-solvent extraction for the two applications considered was the correct one. Apart from initial ‘teething problems’, actual operating performance compared favourably with that predicted.

In a third application, not considered here, the decision was made to adopt the CCD–CIX–SX route. Being a reverse-leach operation, i.e. uranium recovery prior to gold, there was little danger of cobalticyanide poisoning of the resin. It was calculated that the expected increase in resin life would more than compensate for the lower uranium recovery.

ACKNOWLEDGEMENT

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DISCUSSION

D. NADEN: What intrigues me, Mr. Ruhmer, is the information that you did not give us about the performance of the CCD-CIX-SX option. Is this information available?

W.T. RUHMER: It is available. There is only one problem: as a result of the deterioration in the uranium market, the plant is not operating as designed or anticipated. In fact, it might be closed down and, therefore, it is not very easy to compare the CCD-CIX with the other two options. That particular plant had serious problems with its CIX section. It took them approximately three years to rectify the problems both with the CCD thickeners and the CIX plant which had to be rebuilt. It was originally constructed from fibreglass and it was a disaster. It was rebuilt using stainless steel. The plant has now been operating very well indeed. The latest figures have been affected by the change in circumstances: dropping tonnage and a reduction in the demand for uranium. But it is possible to abstract some figures that could give you some idea of how it compares with the CCD/SX option.

Z. DOGAN: What is the type of floculant used in your circuit?

W.T. RUHMER: We use Magnafloc 351, which is a polyacrylamide.

K.K. BERI: You said you are using 100% raffinate recycle. Does that not cause an accumulation of impurities in the system?

W.T. RUHMER: You always have a bleed in your last-stage thickener underflow which goes to the tailings dam. When I say there is no bleed, I am not quite direct in that statement. What is actually happening is that you are feeding 100% of the raffinate or the CIX barren into the tail end of the thickener plant and that progresses countercurrently. But there is actually a bleed which is the solution with the thickener underflow being neutralized and discharged to the tailings dam.

RECOVERY OF URANIUM FROM PHOSPHORIC ACID

EXTRACTION OF URANIUM(IV) FROM WET PHOSPHORIC ACID WITH A KEROSENE SOLUTION OF NONYLPHENYL PHOSPHORIC ACIDS

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Abstract

EXTRACTION OF URANIUM(IV) FROM WET PHOSPHORIC ACID WITH A KEROSENE SOLUTION OF NONYLPHENYL PHOSPHORIC ACIDS.

A uranium(IV) recovery process from wet phosphoric acid produced by the dihydrate method was elaborated. Decomposition of phosphate rock containing more than 0.01% U is carried out with sulphuric acid, partially applying 10–20% waste sulphuric acid derived from a titanium oxide plant. A solution of this acid containing $FeSO_4$ is introduced into the reactors through the phosphogypsum filter cake, in the washings to the last but one filter zone, applying the countercurrent system. This enables a partial recovery of uranium from phosphogypsum. Crude wet process phosphoric acid is filtered off and then clarified with mineral-carbon adsorbents, in order to reduce the content of organic compounds included in the phosphate rocks and those introduced into the decomposition process to lower the foam stability. After separating the clarified precipitate, the clear phosphoric acid is introduced to extraction cycle I, where U(IV) is effectively extracted using a kerosene solution of equimolar mixture of mono- and di-nonylphenyl phosphoric acids (NPPA). The NPPA process is characterized by a very high distribution coefficient (K_e = 3–50) and a high stability and resistance to deterioration. A three-stage NPPA countercurrent extraction system is followed by five-stage oxidative stripping using 8M H_3PO_4 containing 0.2% $NaClO_3$. This U-laden acid is not reduced back, but is diluted to 5–6M H_3PO_4 and U(IV) is directly extracted by a kerosene solution of a mixture of D2EHPA and TOPO. Ammonium uranyltricarbonate is precipitated from this solution by the action of NH_3 and CO_2. Over 90% uranium recovery is obtained.

1. INTRODUCTION

Currently about 2100 tons of U_3O_8 are recovered annually from wet phosphoric acid [1, 2] and many new plants are planned for Western Europe, Japan, Israel and Canada. The solutions used vary according to the kind of stock being processed, the characteristics of the fertilizer plant and the accessibility of liquid ion exchangers [1–4].

Work is less advanced in this area in the countries of the Council for Mutual Economic Assistance, mainly because in all these countries, except Poland, Kola apatite containing minimum amounts of uranium has been the basic stock for the production of fertilizers.

Investigations into uranium circulation in the Police Chemical Works and into the clarification of phosphoric acid [5] and the extraction of uranium using a kerosene solution of alkylphosphoric acids [6] have made it possible to work out a technological concept for a method of uranium recovery from phosphoric acid [7] for our wet phosphoric acid plant located in Police.

2. TECHNOLOGICAL ASSUMPTIONS OF THE URANIUM RECOVERY METHOD

The technological concept does not assume any significant changes in the production of acid or fertilizer. The uranium recovery system will be added to the centre of the phosphoric acid clarification and extraction in the liquid-liquid system. The concept assumes decomposition in a cascade reaction system with forced pulp circulation and adiabatic reception of reaction heat. Decomposition of phosphate rocks containing more than 0.01% U is carried out partially with sulphuric acid and partially with 10–20% H_2SO_4, using waste sulphuric acid derived from a titanium oxide works. The phosphogypsum produced in the decomposition process is washed countercurrently on the filter. In the next to last washing zone this waste sulphuric acid is introduced into the washing liquid [8]. The introduction of the waste sulphuric acid, containing ferrous sulphate, into the phosphogypsum filter cake and into the washing liquids not only makes the P_2O_5 content lower in phosphogypsum waste but also permits the partial recovery of uranium compounds adsorbed and occluded on the calcium sulphate crystals [9].

The ferrous sulphate dissolved in post-hydrolytic sulphuric acid or in the form of suspension makes uranium recovery, in principle, impossible in the 6^+ oxidation state. This technological variant should be excluded since an oxidizing agent would have to be used. The application of $NaClO_3$ as a standard reagent would cause unfavourable corrosive conditions (chlorides being present), which are particularly disadvantageous to the circulatory system. The ClO_3^- and Cl^- ions would be displaced to the centre of filtration, the evaporation and adsorption stage of fluor containing gases. The introduction of an oxidizing agent into the reactors would cause, moreover, increased emission of noxious vapours of Cl_2 and ClO_2, making conditions difficult and dangerous for the staff.

Although, according to Hurst [10, 11], under oxidizing conditions the optimum uranium distribution occurs for lower uranium shifts to phosphogypsum, this variant of the process would require a specific reactor system and materials with greater corrosion resistance. Therefore it is proposed that the decomposition process be carried out in a standard system used in Polish phosphoric acid plants. The correction process of uranium oxidation should be carried out outside the decomposition centre, best of all in the wet phosphoric acid clarification process.

The aim of the clarification process of raw phosphoric acid is to reduce the content of organic compounds originally included in the phosphoric stock as well as those introduced into decomposition reactors in order to lower the foam stability, such as olein alcohol, oleoacetyl alcohol, or other organic defoamers. The content of calcium sulphate suspension and inorganic salts diminishes in the process as well. The clarification and decolourization of the acid makes it easier to carry out the extraction since the phase is easier to distribute, the wastes from the ion exchanger and kerosene are less, and the extraction capacity of the liquid exchanger remains at least the same.

This can be achieved by introducing the filtered-off crude phosphoric acid into a tank provided with a stirrer or a circulating pump and adding simultaneously 0.1–2 wt% of mineral-carbon adsorbent. This substance is produced by thermal treatment of bleached earth impregnated with oil compounds. This waste product from the oil industry is carbonized in a Herreshoff multishelf furnace.

In the filtrate tank, where the clarification takes place, correlation of the uranium oxidation number is also carried out by the ox-redox reaction using ferrous sulphate as reducing reagent. The process takes place at about 60–70°C with a retention time of 0.5 h and aims to produce a Fe^{2+} concentration of 0.15–0.20 wt%.

The suspension obtained in this way is filtered off on the filter press and the sediment, after washing with a small amount of water, is either drawn off together with phosphogypsum or used in granulation of the NPK fertilizer.

The introduction of the clarification process, which is indispensable to the technology of uranium recovery, is favourable for the production process of wet phosphoric acid and its application can facilitate the phosphogypsum crystallization process, concentration and storing of the phosphoric acid, as also prolonging the period of effective work of the installation during intervals for cleaning. In our plants the sludges from the storage tanks are periodically returned to the decomposition stage, causing a disturbance of several hours in the correct course of the phosphogypsum crystallization process. The lowering of the concentration of organic compounds in the raw phosphoric acid will facilitate the course of the concentration process, since acid purified in this way is less susceptible to foaming and post-crystallization.

The clear phosphoric acid is then introduced to extraction cycle I where uranium (U^{4+}) is subjected to effective countercurrent extraction.

3. EQUILIBRIUM DATA FOR URANIUM EXTRACTION IN A PHOSPHORIC ACID KEROSENE SOLUTION OF NONYLPHENYL PHOSPHORIC ACIDS

It is becoming a common practice in production installations (Western Co. Fertilizers Ltd, Earth Science, ORNL, TVA) to extract uranium in the 4+ oxidation state by means of octylphenyl phosphoric acid (OPPA) [1–4, 12–14]. It is also possible under these conditions to use a mixture of octylpyrophosphoric and mono- and dioctyl phosphoric acids (OPAP) [4–6]. The kerosene solution of these acids, although it has great extraction ability (distribution coefficient $K_u = 80-90$) and selectivity, has several properties that limit its industrial-scale application. During storage and circulation this substance undergoes chemical degradation and loses its extracting ability [6].

A more advantageous effect can be obtained by using as a liquid exchanger a kerosene solution of nonylphenyl phosphoric acids (NPPA) [7]. Although there are structural affinities between this acid and octylphenyl phosphoric acid (OPPA), to treat them as analogous in the extraction context would be too great a simplification.

3.1. Preparation of the liquid exchanger (NPPA)

The preparation was produced by phosphorylizing nonylphenol according to the reaction

$$6ROH + P_4O_{10} \longrightarrow 2(RO)_2PO_2H + 2ROPO_3H_2$$

using the reagents:

Phosphorus pentoxide – P_4O_{10}, molecular mass 141.94 produced by Ferak (FRG)
Nonylphenol – $C_9H_{19}C_6H_4OH$, molecular mass 220.3 technological raw material produced by the Blachownia Chemical Plant
Extraction kerosene – PN 68 (C-96040)

Three moles of nonylphenol were placed in a four-neck flask and during stirring 1.1 mole of phosphorus pentoxide was added in small portions at such a rate that the temperature in the flask did not exceed 70°C. Then the mixture was heated for five hours in nitrogen atmosphere at 95–105°C by an infra-red radiator. After cooling, a dark liquid product, brownish-orange in colour, was obtained. This was an equimolar mixture of mono- and dialkyl phosphates containing approximately 2% of free H_3PO_4 and minute quantities of trialkyl phosphates. The preparation contained 8.0% of P and its 1% solution had pH = 2.2. The acid value determined in an alcohol-ether mixture was 239.0 mg KOH/g. The kerosene solution of NPPA is resistant to orthophosphoric acid and acidic hydrolysis. At 90°C it is characterized by poor water solubility. It does not form any kerosene-insoluble salts or complex compounds.

3.2. The effect of process parameters on the extraction of uranium from phosphoric acid by means of NPPA kerosene solution

The water-phase samples for the experiments were prepared from 85% reagent phosphoric acid (analytically pure) to which uranyl sulphate produced by Chemapol – Neratowice (Czechoslovakia) and $FeSO_4 \cdot H_2O$, which is necessary to reduce U^{6+} to U^{4+}, were introduced. The extraction was conducted in a Unipan 357 thermostat shaker and the separation of phases was carried out in glass separator funnels.

The equilibrium distribution coefficient K_u represents the ratio of uranium equilibrium concentration in the organic phase (g/dm^3) to that in the raffinate phase (g/dm^3). Maintaining the same process parameter for the back-extraction, the uranium recovery ratio η_u (%), which gives the total extraction and back-extraction yield, was determined as the ratio of the quantity of uranium contained in the re-extract to the quantity contained in the phosphoric acid introduced into the extraction process. The extraction yield η_E (%) is defined as the ratio of the quantity of uranium contained in the NPPA kerosene solution to the initial quantity of uranium in the phosphoric acid. The stripping yield η_e is derived from the relationship:

$$\eta_R = \eta_u \cdot \eta_E^{-1} \times 100$$

The coefficients η_u, η_R, and η_E and the equilibrium distribution coefficient K_u are calculated on the basis of the determination of uranium content in the raffinate and in the re-extract.

The uranium content is determined with a modified spectrophotometric analysis [15] and the Korkisch method [16], using the colour reaction of U(IV) with Arsenazo III. Extinction was measured by a Specol 20 at wavelength $\lambda = 665$ nm.

3.2.1. The effect of NPPA concentration

Figure 1 shows the equilibrium curve K_u as a function of NPPA concentration in the organic phase. This relationship was determined for a phosphoric acid solution of 28% P_2O_5 concentration containing 0.3% Fe^{2+} at 20°C.

Figure 2 presents the relationship between the uranium recovery yield η_u and uranium concentration in the organic phase when phosphoric acid produced from Florida Central phosphate rocks with 28.2% P_2O_5 content is used as the water phase. No equilibrium relationship is given because of the insufficient equilibrium concentration of uranium in the raffinate phase which, together with the interfering effect of considerable quantities of impurities, makes analytical determination of uranium in this phase impossible. For comparison, the relationship η_u is presented for pure phosphoric acid containing 28% P_2O_5 and 0.3% Fe^{2+}. The extraction was deliberately conducted at the water-to-organic

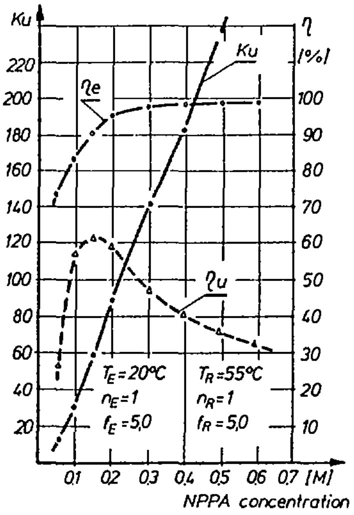

FIG.1. The effect of NPPA concentration in the kerosene phase on the equilibrium distribution coefficient K_u for phosphoric acid of 28% P_2O_5 concentration.

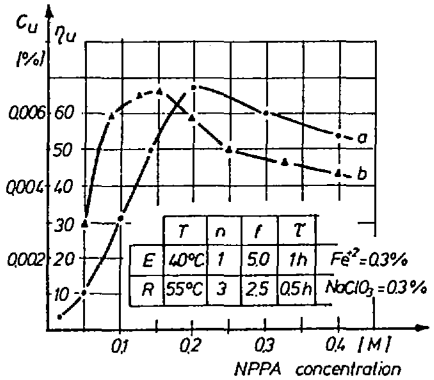

FIG.2. Relation between the degree of uranium recovery η_u and uranium concentration in the stripping solution and NPPA concentration for: (a) crude wet phosphoric acid (Florida Central) of 28% P_2O_5; (b) pure phosphoric acid of 28% P_2O_5 concentration.

phase ratio f_E = 5.0 since this value ensures a considerable uranium concentration. In the experiment back-extraction was carried out in three stages at 55°C and a volume ratio of organic to water phase f_R = 2.5. The relationship determined shows that the optimum NPPA concentration is obtained in the range 0.1–0.2M NPPA. Above an NPPA concentration of 0.2M the total efficiency of the process decreases and the separation of phase deteriorates.

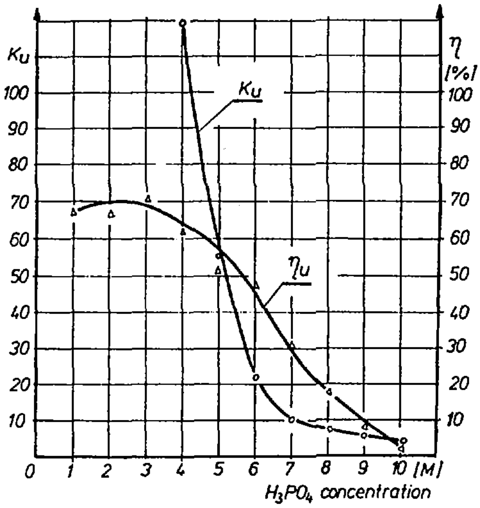

FIG.3. The effect of phosphoric acid concentration in the water phase on the equilibrium distribution coefficient K_u at the NPPA concentration of 0.16M.

The results obtained point to the exceptionally advantageous properties of this ion exchanger. For example, in one-step extraction at the acid-to-organic phase volume ratio f = 5.0, using a solution of 0.16M NPPA concentration, 92% of uranium is extracted from wet phosphoric acid.

3.2.2. The effect of phosphoric acid concentration

The extraction of uranium from phosphoric acid of varied concentration (1–10M H_3PO_4) containing 0.015% Cl was studied. The variation in the distribution coefficient K_u is shown in Fig.3. The extraction was carried out in a single step at 40°C, $f_E = 5.0$ and with 0.2% Fe^{2+} concentration in the aqueous phase. Stripping was carried out for 0.5 hour in a single back-extraction at $f_R = 5.0$ and T = 55°C using 10M H_3PO_4. From the relationship obtained conclusions can be drawn as to the conditions of the antagonistic process, i.e. the process of back-extraction. This process should be conducted using phosphoric acid of at least 7M H_3PO_4 concentration. Particularly important and advantageous is the small difference between the values of K_u for acid of 8–10M H_3PO_4 concentration. It permits the use of a kerosene solution of di-2-ethylhexil phosphoric acid (D2EHPA) and trioctylphosphine oxide (TOPO) in the second cycle of extraction without changing the oxidation state of uranium (U^{6+}) and after only correction of the phosphoric acid concentration.

TABLE I. PROCESS CONDITIONS FOR VARIOUS TYPES OF WET PHOSPHORIC ACIDS

Type of acid	P_2O_5 concentration (%)	K_u
Raw acid	26–32	24–95
Concentrated acid	40–42	7– 8
Concentrated acid (shipping grade)	50–54	3– 4

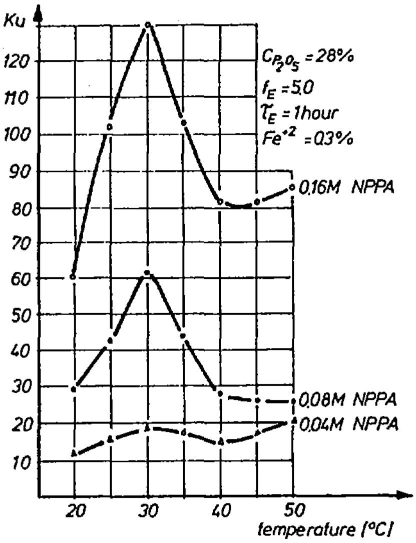

FIG.4. Dependence of equilibrium distribution coefficient K_u on extraction temperature.

Table I gives the estimated values of distribution coefficient K_u for three types of acids used in fertilizer technology. The given intervals are the result of the variability of acid composition (impurities and excessive sulphuric acid). It follows from the data that the process of extraction should be conducted using raw wet phosphoric acid of 26–32% P_2O_5 concentration produced by the dihydrate method, i.e. the solution produced in the Polish plants.

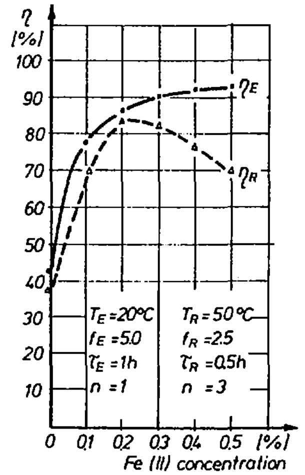

FIG.5. Relationship between the extraction yield η_E and stripping yield η_R and the concentration of Fe^{2+} introduced in the form of ferrous sulphate.

3.2.3. The effect of extraction temperature

The decomposition of the phosphoric raw materials by the dihydrate method is conducted in the temperature range from 70 to 80°C. Due to filtration and storing, the temperature of the acid drops to about 40–50°C.

Figure 4 shows the dependence of distribution K_u on temperature for pure phosphoric acid of 28% P_2O_5 concentration and 0.3% Fe^{2+} content. This relationship has been determined for three different NPPA concentrations. Although the maximum occurs at the temperature of 30°C, it is still possible to recover uranium with great efficiency with an NPPA concentration of 0.16M at 50°C and the cost of wet phosphoric acid can be eliminated from the technological system.

3.2.4. The effect of Fe^{2+} concentration

Figure 5 shows the relationship between the efficiency of the extraction η_E and stripping process yield η_R and ferrous ion concentration in a phosphoric acid solution of 28% P_2O_5 concentration containing, before extraction, 0.01% U. The stripping process was carried out as a triple back-extraction with $f_R = 2.5$ using 8M H_3PO_4 containing 0.2% $NaClO_3$. The relationship indicates that a minimum of 0.15% must be introduced into the acid; however, quantities of the ferrous ion change the stripping process for the worse and can result in an accumulation of this cation, which in turn can reduce its extraction ability. Under the technological conditions of the Police Chemical Plant, the addition of Fe^{2+} required is very

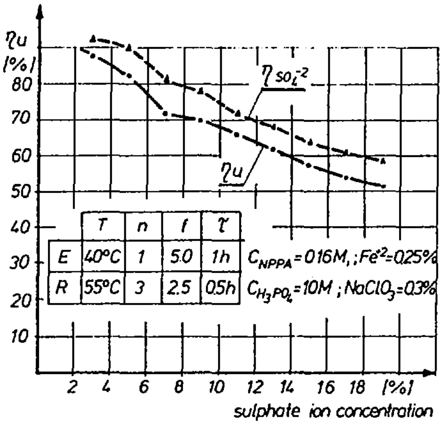

FIG. 6. The effect of sulphuric acid concentration in the wet phosphoric acid on the recovery of uranium η_u *(%) and relationship for displacement of* SO_4^{2-} *ion to the stripping solution* $\eta_{SO_4^{2-}}$ *(%).*

small, since the phosphate rock is decomposed by a mixture of sulphuric acid and waste post-hydrolytic sulphuric acid from titanium oxide which contains 0.8 to 1.2% of $FeSO_4$.

3.2.5. The effect of impurities contained in wet phosphoric acid

Several test determinations of the effect of the various constituents present in the wet phosphoric acid in the course of the extraction process were carried out. Two-level measurements of the effect of SO_4^{2-}, F^-, SiF_6^{2-}, Na^+, Ca^{2+}, Fe^{3+}, Mg^{2+} and NH_4^+ ions showed that the concentrations of sulphuric acid and fluorosiliceous acid have a vital influence on the extraction process.

Figure 6 shows the effect of sulphate ion, contained in the wet phosphoric acid produced from Florida Central phosphate raw material, on the uranium recovery field η_u. This relationship points out the necessity of conducting the decomposition of phosphorate raw material using low levels of sulphate ion concentration, which is a logical conclusion but not always realizable in industrial practice.

A decrease in the sulphate ion can be obtained by prolonging the storage retention time or desulphurizing the wet phosphoric acid by adding chalk or phosphate rock to the raw acid.

Studies on model solutions of phosphoric acid show that an addition of 0.1% of H_2SiF_6 to the wet phosphoric acid results in about 5% decrease of uranium recovery η_u. Moreover, further additions of up to 2% do not have any significant effect on the process of uranium recovery.

3.3. The stripping process

Studies of the process of NPPA extraction indicated that a change in the reaction produces an increase in the efficiency of the stripping process. Studies of the effect of adding $NaClO_3$ showed that an addition of 0.1–0.2% $NaClO_3$ ensures the proper efficiency of the stripping process using circulating phosphoric acid solutions. However, the addition of excessive quantities of $NaClO_3$ reduces the uranium recovery. At higher temperatures the stripping process proceeds with greater efficiency and then it is possible to reduce the quantity of $NaClO_3$ introduced.

When choosing a technological variant, taking into account energy and corrosion aspects, a temperature in the range of 45–55°C should be used for this process.

An analysis of the extraction process from the point of view of the phosphoric acid concentration shows that this factor has a decisive effect on the ratio of uranium recovery. One can therefore conclude that if extraction from a solution with a low P_2O_5 concentration is efficient, then stripping uranium at high P_2O_5 concentrations in the water phase should also be highly efficient.

Experiments showed that the maximum stripping process yield η_R occurs in the range 8–10M H_3PO_4. This fact proves that this liquid exchanger (NPPA) has more advantageous properties than the OPPA system, which required phosphoric acid above 10M H_3PO_4 for back-extraction.

After the uranium has been extracted, the wet phosphoric acid is concentrated up to 40–42% P_2O_5 and then used in the production of complex fertilizers or phosphate fodder. The kerosene solution containing 0.03–0.06% uranium is subjected to the stripping process carried out in at least five stages at 55–60°C.

The uranium back-extraction process is very efficient when phosphoric acid solutions concentrated above 8M H_3PO_4 and containing 0.15–0.2 wt% of $NaClO_3$ are used. With a phase ratio of $f_R = 1.0$ and $n = 5$ it is possible to obtain a stripping degree of $\eta_e = 85–95\%$.

3.4. Technological evaluation of the extraction scheme

The basic assumption of the investigations was the elaboration of an extraction scheme effectively extracting uranium from wet process phosphoric acid, taking into consideration all the technological conditions of the Polish fertilizer industry. While considering the extraction of uranium from phosphate raw materials in the reducing conditions present in these plants, preference was given to a scheme capable of extracting U(IV) directly. Results of the equilibrium investigations, together with initial quarter-technical investigations, point to several advantageous properties of the scheme in comparison with liquid ion exchangers used for the recovery of uranium from wet phosphoric acid.

The very high extraction power of NPPA is worth emphasizing, being more than three times greater for crude industrial wet phosphoric acid than that of OPAP [10, 14] commonly used in industry. Uranium can be effectively extracted with a solution of NPPA, even at temperatures of 50–60°C, with the acid used directly from storage tanks and thus without needing to cool it.

According to Arnold et al. [14], OPAP does not change composition in the circulation scheme, but uranium extraction was more strongly affected by the composition of wet phosphoric acid. The most important impurities in wet phosphoric acid with regard to uranium extraction are Fe^{3+} concentration, F^- and SiF_6^{2-}, and to a lesser degree SO_4^{2-}. In the case of the NPPA process, these are fluorine compounds, Fe^{3+} in particular. The influence of sulphate concentration (Fig. 1) is, however, markedly unfavourable and this can be minimized by conducting the phosphate raw material decomposition at a low level of sulphate concentration.

Because of these properties, NPPA can be applied for uranium extraction in kerosene solutions of half the concentration of OPAP and that will undoubtedly diminish the extractant cost considerably.

In comparison with OPAP (a mixture of mono- and di-octylphenyl phosphoric acid, whose synthesis and purification are remarkably troublesome) the application of NPPA has a variety of advantages, although it also has crucial limitations.

Nonphenyl phosphoric acids, in view of the significant decrease in their extraction power with increasing wet phosphoric acid concentration, are not suitable for uranium recovery from phosphoric acid (40–42% P_2O_5) produced by hemihydrate methods.

The purification of crude acid with mineral and mineral-carbon adsorbents as a pre-extraction process does not diminish the extraction power of NPPA. Deterioration of these properties is observed in the use as extractants of octylpyrophosphoric acid esters, constituting the product of P_4O_{10} and n-octanol addition. This scheme, despite an extraction power identical with that of NPPA, is unstable as it even loses its extraction power during storage.

The characteristic of being readily soluble in aliphatic solvents is one of the important advantages of the scheme applied, but its greatest advantage is its very good and quick phase separation, more profitable than in the case of OPAP and OPPA. This property permits the application of centrifugal extractors.

4. SECOND CYCLE OF THE URANIUM EXTRACTION USING A MIXTURE OF D2EHPA AND TOPO

In order to concentrate uranium and extract it from the stripping solution the application of the II cycle of uranium extraction is beneficial without changing the oxidative conditions. A change in the ion-exchanger system effectively extracts

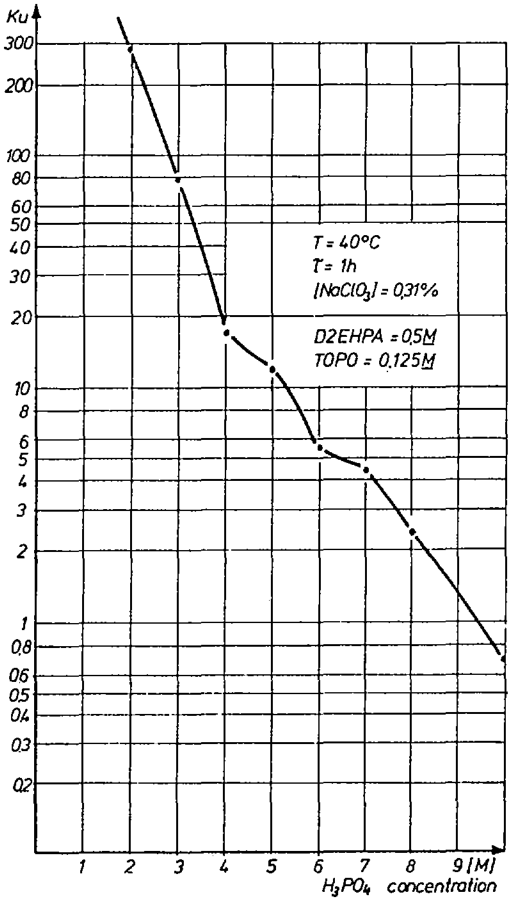

FIG.7. The effect of phosphoric acid concentration on the distribution coefficient K_u at 0.5M D2EHPA and 0.125M TOPO kerosene solutions.

uranium from the stripping solution of phosphoric acid containing $NaClO_3$. The application of a D2EHPA and TOPO kerosene solution satisfies the condition completely. This system is characterized, however, by the unfavourable dependence of the degree of extraction on the phosphoric acid concentration. This relationship is presented in Fig.7.

The immediate uranium extraction from stripping solution of 8M H_3PO_4 concentration proceeds with a low efficiency ($K_u = 1 - 2$) and thus it is necessary to dilute the phosphoric acid to a concentration of about 5–6M H_3PO_4. This operation allows us to carry out the extraction process with a distribution coefficient $K_u = 5-6$, with the ratio of acidic phase to the organic $f_E = 5.0$, at 35°C and with a five-stage extraction. The uranium concentration in the organic phase will be about 0.25–0.75 wt% of U with a 90% degree of extraction.

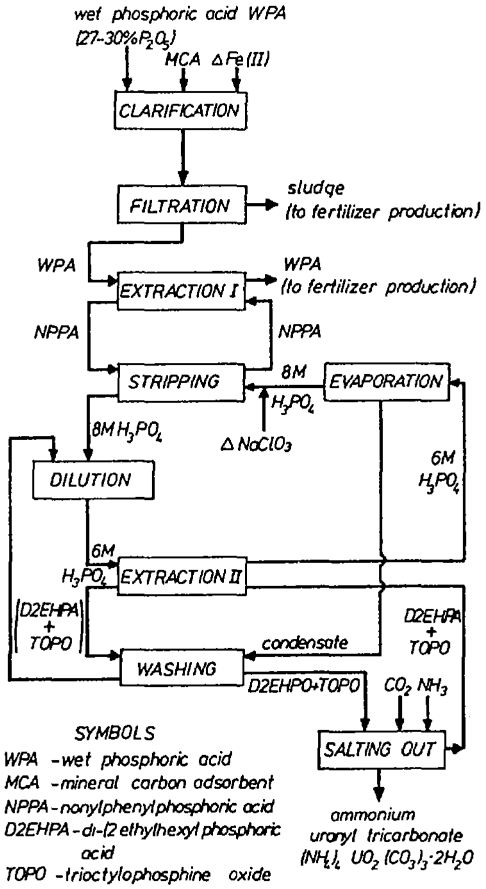

FIG.8. Simplified technological system for uranium recovery from wet phosphoric acid.

The liquid phase from the extraction II cycle of the concentration of 5-6M H_3PO_4 is then concentrated to 8M H_3PO_4. The condensate is used for the washing of the organic phase, i.e. kerosene solution of D2EHPA and TOPO from the extraction II process.

It is possible to separate uranium compounds from the deacidified organic phase containing 0.25-0.75% uranium by salting out with ammonium-uranyl carbonate and introducing ammonia and carbon dioxide. After the uranyl salt, which afterwards can be subjected to calcination, has been extracted and filtered off, the organic phase is returned to the extraction II process. The full technological system is presented in Fig.8.

The only energy-consuming process in the proposed solution is the concentration of the stripping solution II (5-6M H_3PO_4) to that required for back-extraction

($8M\ H_3PO_4$). Here it should be stressed that the mass of this stream is many times lower than that of the stream of the wet phosphoric acid from which uranium is recovered.

In recovering uranium from wet phosphoric acid produced in a plant with an annual capacity of 110 000 t P_2O_5, one should evaporate 4-5 m^3 of water per hour in the process of acidic phase evaporation after the extraction II process. For comparison, the amount of evaporated water with the raw acid concentration to the acid of 42% of P_2O_5 amounts in this installation to 17–20 $m^3\ H_2O/h$.

5. CONCLUSION

On the basis of our investigations, it can be stated that the proposed process can guarantee uranium recovery with an efficiency of about 85–95%.

According to the equilibrium data presented, initial semi-technical investigations of uranium extraction from wet phosphoric acid, gained from Moroccan II phosphate rock, were conducted. The phosphoric acid used for extraction was previously clarified under industrial conditions (Police Works) applying mineral-carbon adsorbent.

The investigations of uranium extraction with a kerosene solution of NPPA (produced in Rokita Works, Poland) were conducted applying multistage batteries of centrifugal extractors, type EWW-80 designed at the Nuclear Investigation Institute in Warsaw.

Although the volume of the mixing device was scarcely 80–100 cm^3, an installation composed of four extractors connected in series and one clarification extractor could extract uranium from wet phosphoric acid at 20–100 dm^3/h. The investigations were conducted at temperatures from 20–60°C, NPPA concentrations of 0.1–0.25M, and concentrations of 24–29% P_2O_5 and 0.1–0.5% Fe (II) in wet phosphoric acid. Using four- and two-spatular stirrers at 1500–2200 stirrer turns/min and an acid phase to organic ratio of 3–12, emulsion creation can be avoided and exact phase separation obtained.

The content of the organic phase in the raffinate at the output of the extraction battery was stated to be lower than 0.1%, and the uranium content in the organic phase resulted in 0.5–1.0 g U/dm^3 while in the raffinate $5\text{–}20 \times 10^{-3}\ g/dm^3$.

At present the later stage of the method is being investigated. In the programme of uranium recovery from wet phosphoric acid, the uranium recovery is planned at the Police Chemical Works (360 000 t P_2O_5/a) and GZPN Gdańsk Works (110 000 t P_2O_5/a), assuming the application of only chemical reagents produced by Polish industry.

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DISCUSSION

NAEEM-UL-ZAMAN: In Pakistan we are producing nitrophosphate by attacking the phosphoric rock with nitric acid. In that case we have a nitric aqueous phase. Could you apply the NPPA process in this case?

H. GÓRECKI: We have only applied this process to wet-process phosphoric acid produced by attacking the rock with sulphuric acid. I don't know how the process would work in a nitrate medium.

I. EZAHR: Have you tested your process with industrial acids? If so, what were the impurities present?

H. GÓRECKI: We tested this process on three sorts of acids: Morocco 2 contained about 31% and Florida 68 and 72% P_2O_5. Morocco 2 acid is better for extraction, because the content of organic phase after extraction is about 100–50 ppm. Florida is worse and it is very important that the amount of mineral carbon adsorbents is lower when we used Morocco acid, about three times; about 0.5% is the content of adsorbents introduced to Morocco, but to Florida it is about three times higher. As for other impurities in these systems, nonylphenyl phosphoric acid is better than OPPA because the influence of impurities is lower. It is very important that the fluoride and fluorosilic acid are not so important, only sulphuric acid. The decomposition process must be carried out if concentration of sulphuric acid is about 1–2%.

M.M. BOUKHRIS: What is the efficiency of the centrifugal extractors you were using?

H. GÓRECKI: These extractors have a very great efficiency. The mixing vessel has a volume of 50 to 100 cm^3 and their capacity is about 100 to 200 L/h. Mixing is very good and the apparatus is very compact. But I cannot say more about this, because the Institute of Nuclear Science in Warsaw, which developed this equipment, is applying for a patent.

J.P. HEBERT: How much residual organic solvent is left in the uranium-free acid returned to the phosphoric acid process?

H. GÓRECKI: We tried to adsorb the organic phase to about 200 ppm using this same mineral adsorbent. This operation was in the preliminary clarification of phosphoric acid using about 0.5–2% of mineral carbonate solvent and we use storing vessels in this operation and, after clarification, we return the sludge from this operation to the phosphoric acid in which uranium was extracted. This clarification was repeated and then the mineral carbonate solvent sludge was washed and introduced into phosphogypsum or to a granulation of NPK fertilizer. We can reduce the contents of the organic phase to about 25–30 ppm with this method.

F. BANHA DELMAS: In your report you indicated that the raffinate contains less than 1% residual organic phase. This seems rather high because in the case of traditional processes the raffinate contains 100–500 ppm of the residual solvent. Can you clarify this?

H. GÓRECKI: I said that this was the result of a semi-technical examination and we had great problems. It was important with centrifugal extractors to find a good phase separation and after four months of investigation we found conditions and apparatus which gave very good separation.

I. EZAHR: Do you use iron to reduce U(IV)? If so, does an excess of iron interfere with the solvent extraction process?

H. GÓRECKI: We have two ways of correcting the oxidation state. First, we introduce ferrous sulphate mixed with waste sulphuric acid; the second way is that we add ferrous sulphate during clarification. This is only a small amount and we don't observe any accumulation of fluoride. The only problem is an increase in the concentration of ferric iron when the phosphoric acid is recirculated. The concentration of ferrous iron increases after the extraction but this can easily be removed with DEPA using periodically an additional extractor. This process is complicated but it is very, very useful.

RESEARCH ON URANIUM RECOVERY FROM PHOSPHORIC ACID IN ISRAEL: PROGRESS AND PROSPECTS

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Abstract

RESEARCH ON URANIUM RECOVERY FROM PHOSPHORIC ACID IN ISRAEL: PROGRESS AND PROSPECTS.

The economic conditions of uranium recovery from 'wet process' phosphoric acid (WPA) are very unfavourable at present because of the high production costs and the low price of uranium. Cost estimates of the solvent extraction processes currently in use for uranium recovery from WPA show that a major part of the cost is due to the need to clean the WPA both pre and post uranium extraction. Research and development aimed at improving the economics of the existing recovery processes by using solid extractants or adsorbents for uranium is reviewed. Three processes are discussed and compared: co-precipitation of uranium with phosphogypsum, extraction with solvent containing resins, and adsorption on selective ion exchangers.

1. INTRODUCTION

Phosphate rock is the only source of uranium in Israel. Research on the possibilities of uranium recovery as a byproduct of the Israeli phosphate industry, currently going on in the Negev Nuclear Research Center (NRCN), has been reviewed in a previous publication [1]. Various phosphatic uranium sources have been investigated, including calcined phosphate rock and the HCl based IMI phosphoric acid process. However, it has been realized that under the prevailing uranium market only conventional 'wet process' phosphoric acid (WPA) is a feasible source for uranium recovery.

The relatively small scale of WPA production in Israel (at present about 120 000 t P_2O_5/a) imposed a start with inferior economic conditions for uranium recovery by the known solvent extraction (SX) processes. Our main research efforts are therefore directed to develop novel ideas for improved uranium recovery processes.

2. SCOPE OF RESEARCH

Current processes for the recovery of uranium from WPA use liquid-liquid extraction with selective solvents (e.g. OPPA, OPAP, DEHPA-TOPO) to separate the uranium from the bulk of crude phosphoric acid. Impurities in the WPA, mainly organic matter and finely dispersed solids, cause operational difficulties which are characteristic of liquid-liquid systems, such as interphase crud formation, hindered phase separation, solvent losses and WPA contamination.

Appropriate acid cleaning, both pre and post uranium extraction, is essential to these SX processes. The cleaning operations required complicate the recovery process. Moreover, the efficiency depends on the nature of the impurities and they usually impose a considerable burden on the economics of uranium recovery.

Another limitation of the SX processes arises from their decreased affinity for uranium at high P_2O_5 concentrations, which confines their practical applicability to dihydrate WPA (28–30% P_2O_5).

The above-mentioned operational difficulties of the SX processes are typical of liquid-liquid systems, being caused by interfacial surface effects. The guideline of the research being performed by the NRCN is, therefore, to use solid carriers or extractants for separating the uranium, rather than liquid solvents.

Two different routes are being investigated. The first one is based on co-precipitation of uranium with the phosphogypsum formed in the course of phosphate rock acidulation to produce WPA. The second is based on adsorption of uranium from filtered WPA on solid extractants.

3. THE PHOSPHOGYPSUM PROCESS [2]

The basic concept of this process is the ability of tetravalent uranium ions to co-precipitate with the phosphogypsum formed during the acidulation of phosphate rock with sulphuric acid. The present development, which is related to H_2SO_4 based 'wet' processes, is an extension of previous research on the recovery of uranium from the IMI process which utilizes HCl to decompose the phosphate rock [3].

When phosphate rock is digested under reductive conditions, the uranium, which is reduced to its tetravalent oxidation state, co-precipitates with the phosphogypsum and thus separates from the WPA. Reductive conditions are created by the addition of a reducing agent (e.g. metallic iron) to the digesters. After filtration of the resulting phosphoric acid, the uranium-bearing phosphogypsum cake is subject to leaching with a mineral acid, preferably H_2SO_4. The uranium is recovered from the leach liquor by common methods of solvent extraction or ion exchange. Similar processes have been developed simultaneously and independently also by ORNL [4], Nissan [5] and Alluswiss [6].

TABLE I. EFFICIENCY OF CO-PRECIPITATION OF URANIUM WITH PHOSPHOGYPSUM: DEMONSTRATIVE DATA

Iron concentrations (g/L)		Added impurities		Uranium precipitated
Fe^{2+}	Fe^{3+}	Type	wt%	(%)
–	17	–		17
1–2	1–2	–		92
1–2	10	–		72
1–2	1–2	Al_2O_3	0.68	48
1–2	1–2	Al_2O_3	1.36	34
1–2	1–2	SiO_2	0.5	63
1–2	1–2	SiO_2	1.0	54

Experimental conditions: (1) continuous dihydrate phosphogypsum experiment with Israeli phosphate rock; (2) controlled amounts of impurities were added for studying their effect.

The main object of the research and development programme was to study the effects of various parameters of the WPA production process on the efficiency of uranium precipitation and on its leaching. Mainly domestic phosphate rock was used for the experimental work. Some of the experiments were carried out in a continuous bench-scale facility producing WPA (28% P_2O_5) at a rate of 0.5–1 kg/h. Recently a larger pilot-plant, which handles about 10 kg/h phosphate rock, has been operated. Some demonstrative results of the experimental work are shown in Table I.

It has been clearly shown that only reduced uranium (U^{4+}) is co-precipitated with the phosphogypsum. It is assumed that U^{4+} ions can replace Ca^{2+} ions in the various compounds that form the phosphogypsum because their ionic radii are very close to each other (0.97 Å for U^{4+}, 0.99 Å for Ca^{2+}). It is further reasonable to assume that U^{4+} enters the crystalline structure of its carrier compounds as fluoride or phosphate complexes that are very stable.

The dominating factor in the co-precipitation process is probably the concentration of fluoride ions. The higher the fluoride content of the WPA, the more efficient is the precipitation. On the other hand, excess of Al_2O_3 or SiO_2, which are strong fluoride binders, decreases the precipitation yield of uranium. This effect can be explained by the role that fluoride ions have in catalysing the reduction of uranium ions [7] and by the ability of certain fluoride compounds (e.g. CaF_2) to be effective carriers of U^{4+} [8]. It is therefore concluded that uranium precipitation is very sensitive to the composition of the phosphate rock.

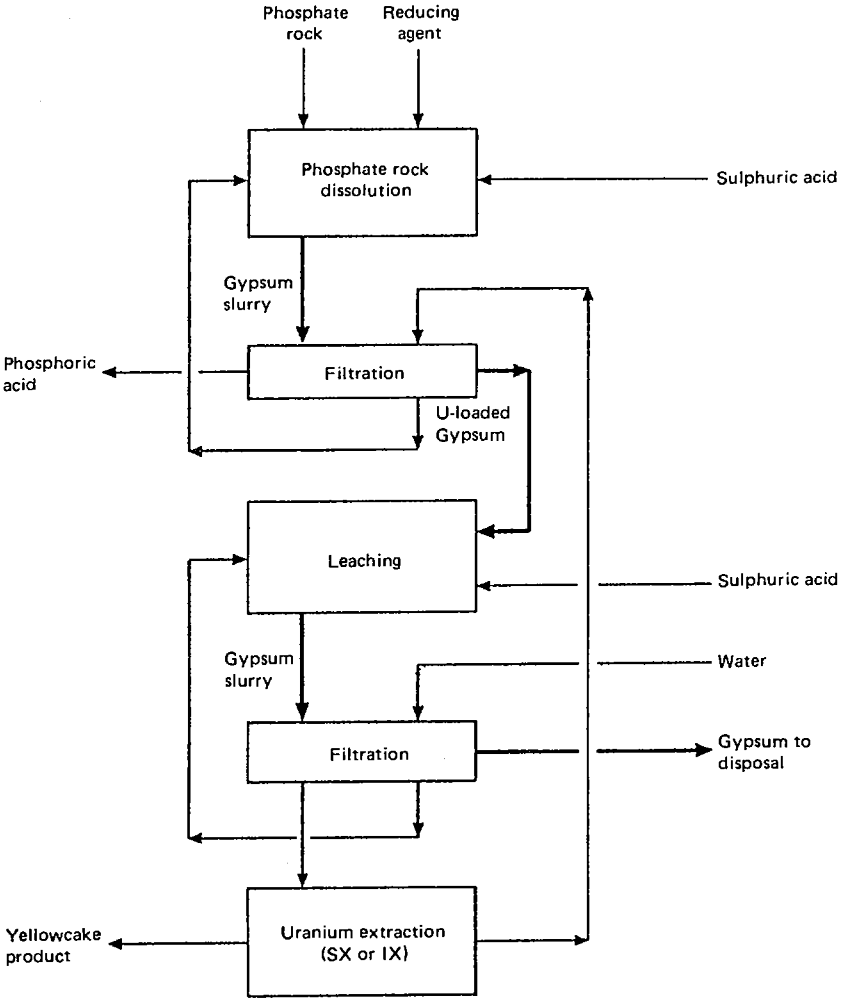

FIG.1. A generalized flowscheme of the phosphogypsum process for recovery of uranium from WPA.

It has also been shown that uranium is precipitated more easily and more efficiently with 'hemihydrate' gypsum ($CaSO_4 \cdot \frac{1}{2}H_2O$) rather than with 'dihydrate' gypsum ($CaSO_4 \cdot 2H_2$).

The leaching of uranium from the phosphogypsum seems to pose no special problems. However, it was observed that more efficient precipitation required more severe conditions of leaching (acid concentration, temperature, oxidation, contact time). The best results were obtained with conversion of the crystallization form of the gypsum (hemihydrate to dihydrate and vice versa), indicating the incorporation of U^{4+} ions within the structure of the calcium sulphate crystals.

TABLE II. COST ESTIMATES FOR THE PHOSPHOGYPSUM URANIUM RECOVERY PROCESS
Basis: 120 000 t P_2O_5/a, 50 t U/a; mid-1982 dollars.

	Single filtration	Dual filtration[a]
1. Investment ($1000)[b]		
Reduction	400	400
Leaching	4900	–
Uranium recovery	4600	4600
Total ($1000)	9900	5000
2. Operating costs ($/kg U)		
Chemicals and utilities	32.00	19.00
Labour[c]	10.00	10.00
Maintenance[d]	9.40	4.50
Indirect expenses[e]	59.40	30.00
Total ($/kg U)	110.80	63.50
Total ($/lb U_3O_8)	42.80	24.50

[a] These plants include phosphogypsum processing units after WPA filtration that can be used for uranium leaching.
[b] Installed equipment, battery limit only, including extractants.
[c] 25 man-year staff, average 20 000 $/man-year.
[d] 5% of investment (excluding extractant).
[e] 30% of investment annually, accounting for interest, depreciation, taxes etc.

A general flowscheme of a uranium recovery process based on phosphogypsum precipitation is shown in Fig. 1.

Implementation of this process in a WPA plant requires the addition of three process units:

(a) Reduction of the digesters content
(b) Leaching of uranium from the loaded phosphogypsum, filtration of the phosphogypsum cake and its disposal
(c) Recovery of uranium from the leach liquor and precipitation of yellowcake.

The costs of constructing and operating such a facility have been estimated for typical Israeli conditions (Table II).

The leaching system, comprising agitated vessels and an additional phosphogypsum filter, accounts for nearly half of the total investment. Therefore, WPA production processes based on phase conversion of the gypsum and applying dual-filtration systems offer significant economic advantages for uranium recovery via the phosphogypsum route. Examples of such processes are the Central-Prayon DH process and the Nissan C and Fisons' HD process [9]. Phosphogypsum purification processes, such as ICI or Giulini [10], offer the same advantages.

Based on the preceding discussions, it can be seen that the phosphogypsum uranium recovery route has certain advantages over common SX processes:

(a) It is viable for both hemihydrate WPA (40–45% P_2O_5) and dihydrate WPA (28–30% P_2O_5)
(b) There is no direct contact between organic solvents and crude WPA, hence no cleaning operations are required
(c) The methods for recovery of uranium from the leach liquor of the phosphogypsum are well known and relatively cheap.

The main disadvantage of this process arises from its sensitivity to the exact composition of the phosphate rock, which limits its applicability.

Other drawbacks are caused by the need to reduce the contents of the phosphate rock digesters. First, the iron concentration in the WPA is increased, possibly affecting its quality. Secondly, metallic parts of the acidulation system (e.g. agitators and slurry pumps) may be subject to enhanced corrosion due to the reductive environment, unless suitable metals are used (Hastalloy C).

The economic analysis confines the applicability of the phosphogypsum uranium recovery process to but a few WPA plants.

In spite of the above-stated drawbacks and limitations, it is expected that when appropriate conditions prevail this process is superior to SX uranium recovery processes.

4. SOLID EXTRACTANTS

The expected significant advantages of solid extractants over liquid solvents encouraged research in this direction despite unsuccessful previous attempts [11]. The research done at the NRCN covers two alternatives:

(a) Solvent containing or impregnated resins
(b) Ion-exchange resins.

4.1. Solvent containing resins (SCR)

The Applied Research Institute of the Ben Gurion University of the Negev in Israel is developing, in collaboration with the NRCN, a selective solid extractant for uranium. It comprises a resin matrix containing copolymerized DEHPA-TOPO, which is the active (or functional) substance of the extractant [12]. Experimental similar SCR samples have been produced also by Bayer in the Federal Republic of Germany under the trade name Levextrel DEHPA-TOPO.

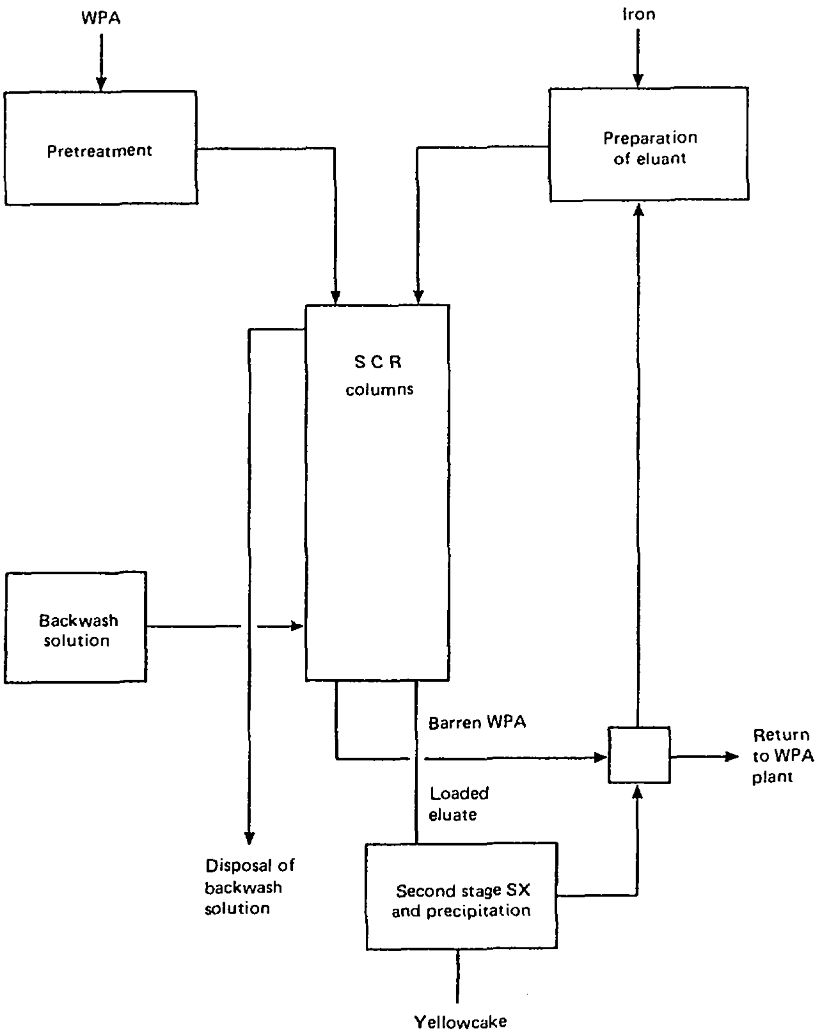

FIG.2. Process flowscheme for the recovering of uranium from WPA with solvent containing resins (SCR).

Various samples of SCR have been tested for their performance in adsorbing uranium from WPA. The capacity was very moderate (about 1–3 g U/kg resin) and the rate of uranium uptake was very slow. Equilibrium was not reached even after five hour's contact time. In practice, that implies the need for high resin volumes for efficient uranium recovery.

Expected operational problems, such as resin stability and active substance (DEHPA-TOPO) leakage, have not yet been thoroughly examined.

TABLE III. COMPARISON OF COST ESTIMATES FOR THE RECOVERY OF URANIUM FROM WPA WITH LIQUID AND SOLID EXTRACTANTS
Basis: 120 000 t P_2O_5/a, 50 t U/a; mid-1982 dollars.

	SX (OPAP)	SCR	IX
1. Investment ($1000)[a]			
Pretreatment	4100	3000	2300
First stage separation	2300	2100	1900
Purification and precipitation	1200	1200	500
Post-treatment	1400	–	–
Total ($1000)	9000	6300	4700
2. Operating costs ($/kg U)			
Chemicals and utilities	35.00	22.00	12.00
Labour[b]	12.00	10.00	8.00
Maintenance[a]	8.50	5.50	4.00
Indirect expenses[a]	54.00	37.80	28.20
Total ($/kg U)	109.50	75.3	52.20
Total ($/lb U_3O_8)	42.20	29.00	20.10

[a] See Table II.

[b] 30 man-year for SX, 25 for SCR and 20 for IX; average 20 000 $/man-year.

Fouling of the extractant with organic matter from the WPA seems to be negligible.

A uranium recovery process using DEHPA-TOPO containing resins resembles in principle the well-known SX processes which use the same extractant as a liquid solvent [13, 14]. The first SX cycle that separates the uranium from the bulk of the WPA is replaced by SCR columns. Uranium is loaded on the resin from 28–30% P_2O_5 WPA in its oxidized (UO_2^{2+}) state. Reductive stripping (elution) is achieved with 40% P_2O_5 WPA that contains about 20 g/L of Fe^{2+} [15]. The uranium concentration in the 'core' of the eluate is about 3–5 g/L.

Elution of the loaded uranium with sodium or ammonium carbonate is impossible because this basic medium converts the acidic DEHPA to its respective salt which is not held by the resin matrix [16]. A second cycle is therefore required, in analogy to the common DEHPA-TOPO processes. At this stage the usual second SX cycle is believed to be the most suitable choice for this purpose. Relevant information is published in the literature [13, 14].

Auxiliary operations of this process include pretreatment of the WPA feed (cooling, oxidation and partial clarification), replenishment of solvent lost by leakage from the resin and preparation of eluting solutions. Post-treatment of the barren WPA is unnecessary.

Preliminary design and cost estimates of a conceptual industrial plant have been prepared, based on operational data of an experimental bench-scale facility [17]. The basic process flow scheme is shown in Fig.2, and the economic evaluation is summarized in Table III and compared with a similar SX process. The operational simplification and the economic advantages offered by the SCR in comparison with SX are clearly seen. However, further improvements in uranium recovery from WPA can be achieved by overcoming the above-mentioned limitations of the SCR, namely: active substance leakage, the impossibility of using basic carbonate solutions as eluates, and the slow kinetics of uranium uptake.

4.2. Ion exchangers (IX)

The logical extension of the concept of solid extractants which offers solutions to the above-stated limitations is to use ion-exchange resins having functional groups with appropriate affinity for uranium. Although ion-exchangers are widely used to recover uranium from sulphate leach liquors [18], attempts to use this technique for WPA failed to show economic and technological feasibility. The main reason was the low selectivity and capacity of the available resins for uranium [11] in P_2O_5 solutions.

Recently it has been found that some new chelating ion-exchange resins are able to adsorb uranium efficiently from phosphoric acid solutions. These resins contain hydroxy-phosphonic [19] or amino-phosphonic [20] functional groups.

According to available information [19, 21] uranium is loaded on these resins from 28% WPA in its reduced oxidation state (U^{4+}) in the presence of ferrous ions (Fe^{2+}). Adsorption of hexavalent uranium was also observed [22]. Elution is accomplished with ammonium carbonate solutions. Yellowcake is easily precipitated directly from the eluate by partial evaporation which drives off ammonia and carbon dioxide [23, 24].

Based on this information, research commenced at the NRCN aimed at developing an industrial process for the recovery of uranium from WPA with ion exchangers.

The specific resin studied at present is manufactured by Duolite International under the trade name of ES-467. This is the only commercially available amino-phosphonic ion exchanger [20].

The experimental programme of this research was divided into two parts. The chemistry of uranium uptake by the resin was studied using pure phosphoric acid solutions spiked with uranium and other accompanying impurities. Simultaneously, bench-scale IX columns were operated with crude WPA in order to identify problems that might be encountered in an industrial plant and to evaluate the parameters of a complete recovery process. A pilot-plant is expected to be put on stream in Autumn 1983 adjacent to the WPA plant of Rotem Fertilizers Ltd.

It was confirmed that the resin Duolite ES-467 has a high affinity for uranous ions (U^{4+}) and a high selectivity relative to other ions, including hexavalent uranium (UO_2^{2+}). Only Fe^{3+} is co-adsorbed to some extent on the resin.

Increased P_2O_5 concentration of the aqueous phase adversely affected the affinity of the resin for uranium. However, even with 45% WPA the distribution coefficient was satisfactory for practical purposes. The rate of adsorption is slow, and there are indications that both external mass transfer and internal rate processes (pore diffusion or chemical reaction) are significant in controlling the kinetics of adsorption. Higher temperatures, in the range of 60–70°C, enhance adsorption rate and improve selectivity of U^{4+} over Fe^{3+}.

Elution was accomplished with solutions of ammonium carbonate, whose yellow colour indicated that the uranium was eluted as the carbonate complex of uranyl. Partial oxidation probably took place within the resin by air dissolved in the eluant. The rate of elution was therefore slow, causing a very long and unpractical tail of uranium in the eluate. A special oxidation procedure, which is based on the redox couple $Fe^{2+}/Fe^{3+}-U^{4+}/UO_2^{2+}$, was developed in order to improve the efficiency of elution. This procedure is selective for uranium and does not damage the resin, which is otherwise very sensitive towards oxidizers.

The main problem observed when the IX process was operated with crude WPA is the carryover of organic matter to the eluate solution along with the uranium. The resin is fouled to some extent with organic impurities of the WPA, which are stripped off the resin with the basic eluant. The presence of organic matter in the eluate interferes with the efficient precipitation of the yellowcake. A way to overcome this difficulty was developed and was integrated into the adsorption elution cycle.

Both the selective oxidation procedure and the organic wash are proprietary to the NRCN [25].

A general block diagram of a uranium recovery process based on Duolite ES-467 resin is shown in Fig.3.

Pretreatment of the WPA feed consists essentially of oxidation-state control (reduction). Clarification is desirable when fixed-bed columns are used. There is no need to cool the acid nor to remove organic matter. These steps are a must in SX processes.

The slow rate of adsorption causes a long 'exchange-zone' in the IX system which requires large resin volumes for an industrial facility. Properly designed 'merry-go-round' systems or continuous IX equipment can save appreciable amounts of resin, but the required bed volume remains relatively high. Preliminary cost estimates, which are based on data obtained from the bench-scale columns operation, show that the expected uranium recovery costs are competitive with current market prices. Details are summarized in Table III.

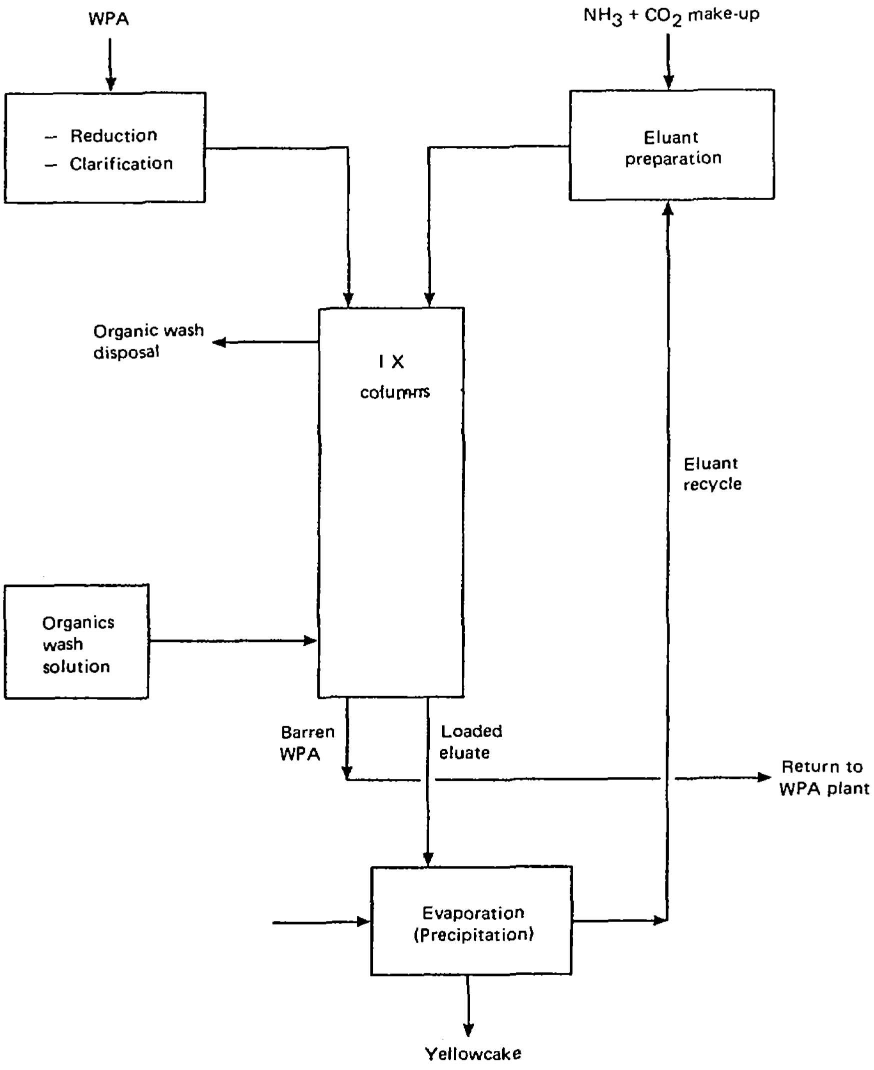

FIG.3. Process flowscheme for the recovering of uranium from WPA with ion exchangers (IX).

TABLE IV. COMPARISON OF PROCESSES FOR RECOVERY OF URANIUM FROM WPA

	SX[a]	SCR	IX	PG
1. Pretreatment				
Cooling	++[b]	++	–	–
Valency control	++	++	++	++
Clarification	++	+	+	++
Organic matter removal	++	+	–	–
2. Second-cycle purification	++	++	–	++
3. Post-treatment	++	–	–	–

Remarks:

[a] SX – solvent extraction; SCR – solvent containing resins; IX – ion exchange, PG – phosphogypsum co-precipitation.

[b] ++ essential and necessary; + desired but not essential; – unnecessary.

The main drawback of this IX process is the requirement for reduction, which results in an increase of iron concentration in the WPA. The advantages of this process are therefore most significant when low-iron WPA is used.

5. SUMMARY

The most promising alternative can be seen from the comparison of the different methods of uranium recovery from WPA. Four methods have been considered in this paper:

(a) Solvent extraction (as a basis for comparison)
(b) Phosphogypsum co-precipitation
(c) Solvent containing resins
(d) Ion-exchange resins

The auxiliary operations which are required for each method are listed in Table IV, according to the general discussions in the preceding paragraphs. It is easily seen that the most simple conceptual process is based on ion exchange and the most complicated one applies solvent extraction to separate uranium from the crude phosphoric acid.

This conclusion is even more emphasized by the cost estimations which show the significant economic advantages of solid extractants, especially of ion exchangers. The economic attractiveness of the phosphogypsum route with dual-filtration WPA plants is offset by its limited applicability.

In spite of these conclusions, it must be borne in mind that each process has pros and cons which are affected by the exact composition of the WPA. Therefore, a proper choice and design of a suitable uranium recovery process must be based on specific phosphate rock and local conditions of the WPA plant.

ACKNOWLEDGEMENT

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DISCUSSION

D. NADEN: Does gypsum precipitate in the ion-exchange bed?

Y. VOLKMAN: We have used acid that was aged for about 24 hours and we haven't any problems with gypsum precipitation.

D. NADEN: Is the iron in solution adsorbed into the resin and if so, can it be eluted?

Z. KETZINEL: The iron content in our solutions is very low, it is about 2 to 3 g/L. It is adsorbed into the resin and it is not eluted because it precipitates. We have procedures to remove it, but these are not described in the text.

A. MORAL: You said that your process doesn't require prior removal of the organic material. I think that when precipitating phosphogypsum most of the organic materials are also precipitated. Then, when you leach this phosphogypsum to solubilize the uranium, the organic materials go into solution as well.

Y. VOLKMAN: We have tested this process mainly with the Israeli phosphate and a very small portion of the organic material precipitates with the phosphogypsum. It does not interfere. I don't know, however, what is the situation with other phosphates.

E. SØRENSEN: I am afraid that I didn't understand the graph you showed with Florida, Morocco and Israeli phosphate; it showed that 40% at most was precipitate, but at the same time you said 90%.

Y. VOLKMAN: Yes. When this graph was taken we had only small quantities of different phosphate rocks. The main work was done with Israeli phosphate rock, which we have, of course, in large quantities, so we can operate a continuous facility. We had only small quantities of Morocco, Florida and other phosphate rocks, so we could perform only batch tests. When we compared the batch tests with the continuous tests, we saw that the precipitation is proportional to the amount of solids. In the batch tests the concentration was never above 10%, but in the continuous process we have 30%, that is as required by the phosphoric acid manufacturer and then we had about three times higher.

F. BANHA DELMAS: It seems to me that it is very difficult to do an ion-exchange operation in a fixed bed with such a high-density acid and with a high content of insoluble solids. There is also a continuous precipitation that can block the bed. Have you found any of these problems?

Y. VOLKMAN: We find blocking of the column when we use fixed bed columns and when we do not clarify the acid. If we use fluidized bed columns we don't need to clarify the acid and there are no blocking problems. The clarification must only ensure that the loading time is shorter than the blocking time, because blocking occurs anyhow. It is not necessary to clarify the acid until it is crystal clear.

F. BANHA DELMAS: What is the density of the resins you use in this operation?

Y. VOLKMAN: The density of the resins we use is very close to the density of the phosphoric acid.

P. GASÓS: I don't think that all the uranium will precipitate with the phosphogypsum. Which is then the distribution of uranium between the phosphogypsum and the phosphoric acid?

Y. VOLKMAN: The precipitation is not total. It depends, as I have shown, on the fluorite content. It depends on the phosphoric rock itself. Sometimes it is 90%, sometimes it is 40% or 20%; it depends on the phosphate rock itself.

THE NEW URAPHOS PROCESS AND THE MOBILE PILOT PLANT

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Abstract

THE NEW URAPHOS PROCESS AND THE MOBILE PILOT PLANT.

Uranium is currently separated from phosphoric acid by solvent extraction processes. By far the most frequently used reagent is a synergetic mixture of TOPO and D2EHPA. Urangesellschaft mbH and Chemische Fabrik Budenheim have jointly developed a solvent extraction process, called the Uraphos process, to extract uranium from phosphoric acids of up to 40% P_2O_5 using a tertiary amine as extraction reagent. In 1982 Urangesellschaft mbH constructed a pilot plant to be continuously operated on 200 L/h of phosphoric acid to demonstrate the feasibility of the Uraphos process. This pilot plant is completely enclosed in standard 20 ft containers so that it could be easily transported to anywhere in the world either by car, train or ship. From June to December 1982 the Uraphos pilot plant was operated at the phosphoric acid plant of Chemie Linz AG, Austria. Despite the relatively low uranium content of 65 ppm U in the phosphoric acid produced there, the test campaign was a full success, e.g. an overall uranium recovery could be maintained at a level of over 90%. The final uranium product, a uranium-diuranate with approx. 82% U_3O_8, produced during the demonstration campaign in Linz immediately met the standards for uranium concentrates set forth by Allied Chemical.

1. THE URAPHOS PROCESS

1.1. Historical review

The firm of Chemische Fabrik Budenheim R.A. Oetker (CFB), among other activities, runs a plant designed to extract pure phosphoric acid from technical phosphoric acids. In the 1970s they found that uranium builds up with a byproduct. To examine ways of uranium extraction on that basis, Uraphos Entwicklungsgesellschaft b.R. was formed in 1977. Its shareholders were CFB and Urangesellschaft mbH (UG), each with 50%, and its research programme included the uranium extraction from both the byproduct of the CFB acid purification process and the usual filter acids according to the H_2SO_4 wet process. The laboratory research work started in 1978 and was finished in 1981 with a preliminary process design.

The research results were so encouraging that in 1980 both firms founded Uraphos Chemie GmbH, which was to assume the task of exploiting and marketing the new Uraphos process and the three patents that had been applied for in the meantime.

In 1981 the planning of a mobile pilot plant was started. The pilot plant took up operation in mid-1982. CFB ceased to be a partner of the project in 1982 and Uraphos Entwicklungsgesellschaft b.R. was dissolved. Uraphos Chemie GmbH was taken over completely by UG and its place of business was changed to Berlin (West). Since then any work concerning the uranium extraction from phosphoric acid has been performed by Uraphos Chemie GmbH alone.

1.2. Laboratory research work

The basic idea of laboratory research work was to use tertiary amines known in conventional uranium extraction from ores also for uranium extraction from phosphoric acid. In the following the term 'phosphoric acid' always means acid produced by the wet process with H_2SO_4 which mostly contains 25 to 30% of P_2O_5.

The first tests with synthetic pure phosphoric acids having a uranium content of 160 ppm showed that only triodecyl amine (TDDA or trilauryl amine) among the amines may be used successfully. The extraction rates, however, declined substantially when the total acidity and the content of foreign ions such as Fe^{3+} or F^-rose. Because of the use of complexing agents it was possible to solve such problems. In this connection a long-chain $(NaPO_3)_n$ added to the phosphoric acid turned out to be very efficient.

According to extensive tests the stripping of the loaded amine showed the best results when about 5 to 10% aqueous solutions of Na_2CO_3 were used.

When searching for the optimum solvent of the amine, it was found that pure aliphatic hydrocarbons showed the best extraction results.

A solvent, which during further work proved to be advantageous in any respect, is Exsol D 200/240 (Esso) with an aromatic compound content of only 0.8%.

The TDDA dissolved in the solvent finally is an ion exchanger of limited loading capacity. The most favourable concentration turned out to be 2% of TDDA in the solvent. Given that content, in the light phase a maximum concentration of about 700 ppm U can be achieved. In this connection approximately 1 mol $(NaPO_3)_n$/mol TDDA is added to the phosphoric acid, i.e. approx. 6.2 g $(NaPO_3)_n$/L light phase.

It is characteristic for uranium extraction by TDDA that only 4-valent uranium is received from the phosphoric acid but no 6-valent uranium.

1.3. Process design

When the individual tests had been finished, a small countercurrent extraction plant made of glass was used for further examinations. The first extraction stage comprised five conventional mixer-settlers and had a phosphoric acid throughput of about 10 L/h. In the beginning the plant used phosphoric acids of approx. 30% P_2O_5 which were diluted from acids containing 54% P_2O_5. Later technical filter acids were used which had been treated according to the CFB purification process before.

In the course of this one-year operation of the laboratory-scale plant a Uraphos process design developed. Its main characteristics are described below:

In principle, it is a single-stage process, winning uranium directly from the stripping solution by adding NaOH by which uranium precipitates in the shape of $Na_2U_2O_7$ containing approx. 60% uranium (referred to dry substance). To purify that precipitate, it is dissolved in H_2SO_4, the solution is diluted and then extracted by means of the same extractant without the addition of $(NaPO_3)_n$. From the aqueous phase of the subsequent stripping the uranium can directly be precipitated, filtered, and calcined, if applicable, to U_3O_8 by conventional methods.

In both parts of the process the same extractant (Exsol D 200/240 + 2% TDDA) and the same stripping solution (5% Na_2CO_3 solution) is used, which simplifies the process considerably.

The Uraphos process may be divided into three parts:

(a) Pretreatment of filter acid
(b) Extraction plant
(c) Refining the uranium precipitate.

Parts (a) and (b) are tied to the location of a phosphoric acid plant. As the transportation of the uranium precipitate does not cause any problems, part (c) of the plant might either be built at a logistically more favourable place, or several extraction plants might deliver their uranium precipitate to one larger refinery. Operation together with several phosphoric acid plants, for instance, would result in a considerable reduction in the investment cost.

In detail, the Uraphos process is structured as follows:

Phosphoric acid conditioning (a)

The filter acid is purified of organic matter, if any, by means of activated carbon. If necessary, the total acidity and the content of foreign ions are reduced by the addition of NaOH, SiO_2 and CaO. Solids are separated. Subsequently, the acid, for instance with iron or phosphorus, is adjusted to a redox potential of below 250 mV. The relation of redox potential and uranium output is shown in Fig.1.

Extraction circuit I (b)

The pretreated acid is mixed with a 10% $(NaPO_3)_n$ solution and extracted in countercurrent by means of the light phase containing 2% TDDA. The phosphoric

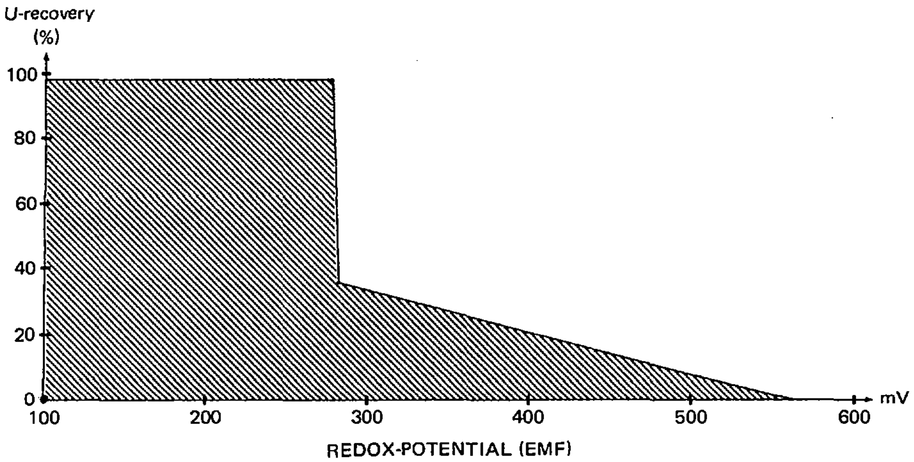

FIG. 1. Uraphos process: uranium recovery as a function of EMF. Basis: phosphoric acid (27% P-205) from Moroccan rock phosphate.

acid, without any further post-treatment, will be recycled to the phosphoric acid plant.

Solvent scrubbing (b)

The loaded light phase is scrubbed with about 1.5% H_2SO_4, so that the acid components are removed.

Stripping circuit I (b)

The light phase is now stripped with 5% Na_2CO_3 solution to which some NaOH is added. As a result, any acid components are buffered and the CO_3^{2-} groups of importance for the uranium complexing are preserved. The amine contained in the light phase is at the same time regenerated due to the basic stripping and will be recycled directly into the storage tank.

Precipitation I (b)

By further additions of NaOH to the pregnant strip solution, some iron hydroxide precipitates which may be filtered out without any problem. Rare earths contained in the phosphoric acid may be found in this precipitate in a possibly rather concentrated form, as the quantity of iron precipitate represents 1% of the iron content of the filter acid only. By further additions of NaOH at pH 13.3 $Na_2U_2O_7$, which still contains P_2O_5 impurities, precipitates. It is then washed and filtered. The filtrate flows back to the acid conditioning.

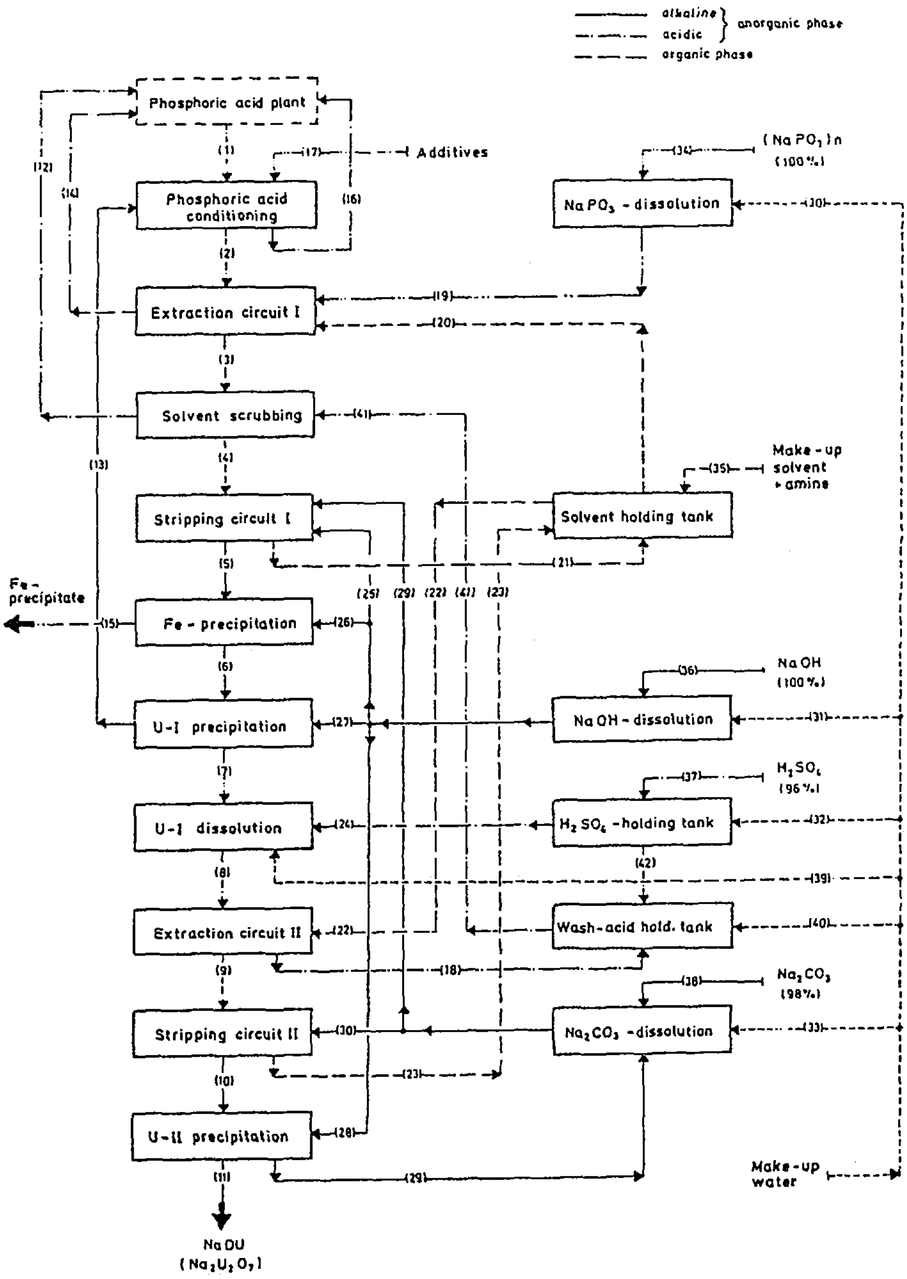

FIG. 2. Uraphos pilot plant: simplified process flow diagram.

U I dissolution (c)

The yellow uranium precipitate, which in a wet state contains approx. 30% uranium, is dissolved in 30% H_2SO_4 and the solution is diluted to about 1.5% H_2SO_4 by addition of water.

Extraction circuit II (c)

The weak uranium-containing sulphuric acid is extracted in countercurrent with the same light phase of extraction circuit I. The acid, which no longer contains uranium, is recycled to solvent scrubbing.

Stripping circuit II (c)

The loaded light phase is stripped by means of 5% Na_2CO_3 solution, thus regenerated and then recycled to the storage tank.

U II precipitation (c)

By the addition of NaOH to the loaded Na_2CO_3 solution, uranium in the shape of pure $Na_2U_2O_7$ precipitates. It is filtered out at 80°C and contains about 42% of uranium in a wet state, and approx. 70% in a dry state (= 83% U_3O_8).

The whole process is shown in Fig.2.

1.4. Phosphoric acid conditioning

In current processes to extract uranium from filter acids the conditioning of the acids usually influences the plants' profitability to a large extent. The conditioning has the object of reducing to an acceptable level those substances in the phosphoric acid that interfere with uranium extraction. In general, filter acids, if they are not produced from calcined rock phosphates, contain organic humic acid components which produce unpleasant reactions when they come into contact with the organic solvent. Among these is the formation of stable emulsions or third phases, which usually require cost-intensive special chemical treatments.

In addition, at a temperature of about 70°C the filter acids contain a certain quantity of solids and substances dissolved up to the saturation limit, such as $CaSO_4$ and Na_2SiF_6. When cooled down, those solids precipitate at different intervals, to the detriment of the company. In the extraction process these solids cause third phases, called 'gunk' or 'crud'. On the one hand, they require special treatment and, on the other, they often cause considerable losses of expensive extractants. Thus, conditioning generally involves separation of the organic impurities by means of activated carbon adsorption and liquid-solid separation after the filter acid has cooled down and has been stored for half a day or one day.

In the case of uranium extraction processes extracting 6-valent uranium only (D2EHPA-TOPO processes), a more or less intensive oxidation of the phosphoric acid, according to the redox potential, follows in order to transform the uranium into U^{6+}.

As in the OPPA and OPAP processes, the Uraphos process extracts the uranium in the shape of U^{4+}. This is why the filter acid usually has to be reduced. The easiest way to achieve this is by means of iron scrab, without, however, increasing the acid's iron content by more than 0.1% Fe, according to the redox potential.

Acid conditioning is of vital importance for the efficiency of the subsequent uranium extraction. Thus, a well cleaned acid is very desirable. At the same time any conditioning refers to the total acid throughput and is therefore rather cost-intensive in relation to the uranium content. The target is to determine reliably which conditioning is optimum for a certain phosphoric acid in terms of profitability and so a pilot plant is required. This must involve all process stages of importance for an industrial uranium extraction plant, including all conditioning measures on a sufficient scale. In addition, the results obtained by the pilot plant must be representative for the raw material to be used in the future. This means that the phosphoric acid used in a pilot plant for uranium extraction must be identical with that to be used later by the commercial plant. As this will always be fresh filter acid, the pilot plant must be built and run directly at the phosphoric acid plant. This would mean, however, constructing a special pilot plant at any phosphoric acid plant considered for uranium extraction. To avoid the cost of this a reusable pilot plant would be highly desirable.

2. THE MOBILE URAPHOS PILOT PLANT

In view of these considerations, Urangesellschaft decided in 1981 to build a transportable and thus reusable pilot plant for the Uraphos process in a two-stage programme. The first part of the programme referred to a pilot plant for the Uraphos extraction process itself. In the case of the successful pilot testing of the Uraphos process, a pilot plant for acid conditioning meeting all imaginable requirements was to be integrated.

2.1. Development and construction of the pilot plant for the uraphos process

The pilot plant's design had to consider criteria that in part influenced each other mutually. Some of them were:

Easy transportability
Continuous operation up to the final product precipitation
Scale serving as a basis for the scale-up to a commercial plant
Complete plant requiring connections for water, phosphoric acid, and electric power only

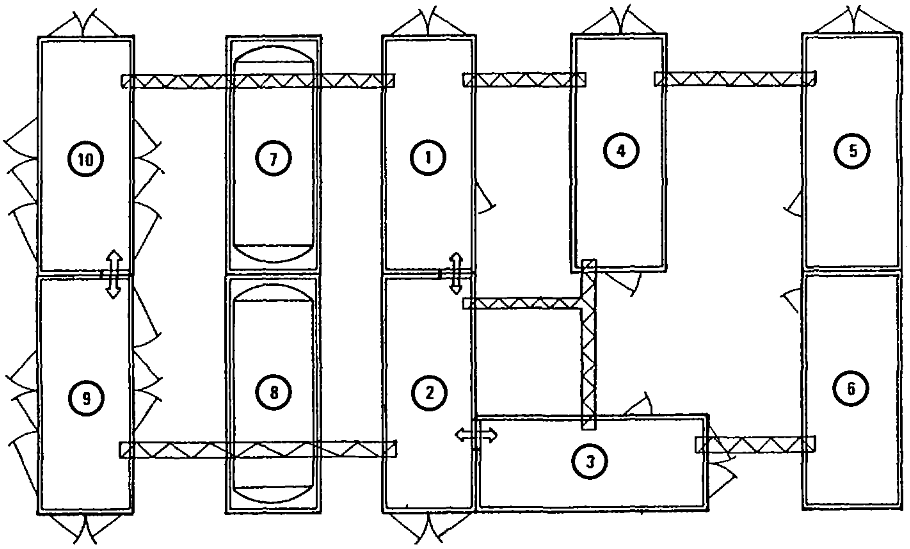

FIG. 3. Space requirements for the mobile pilot plant: 26.6 m × 16.2 m = 431 m^2.
Container 1 = Extraction I
Container 2 = Solvent scrubbing
Container 3 = Stripping I; extraction II; stripping II
Container 4 = Iron precipitation; uranium precipitation
Container 5 = Electric power
Container 6 = X-ray fluorescent analysis; measuring and control room
Containers 7, 8 = Phosphoric acid tanks
Containers 9, 10 = Phosphoric acid conditioning

Integrated analytical laboratory
Piping easy to modify.

On the basis of those requirements, the following results were finally achieved.

The pilot plant was built in 20 ft standard containers permitting road, rail or sea transport. The plant's capacity is 200 L/h of phosphoric acid. The electrical distribution is installed in a separate 20 ft container and another 20 ft container holds the control board and the analytical laboratory.

Using this concept and the process design resulting from laboratory examinations, the plant was designed and in July 1981 Lurgi Chemie was given the order to construct the plant. In the course of the engineering work the pilot plant expanded to a total of six 20 ft containers and two 20 ft tank containers. Containers 1 to 4 containing the extraction plant itself are insulated containers whose interior is lined with stainless steel. Container 5 comprises the entire power input and distribution and container 6 a control board and an X-ray fluorescence spectrometer. Tank containers 7 and 8 are of stainless steel and hold approx. 19 m^3 of phosphoric acid. Figure 3 shows containers 1 to 8 forming the pilot extraction plant.

The pilot plant was completed late in April 1982 and took up operation in Frankfurt in May/June 1982. For this purpose, after termination of the water tests, 19 m^3 of phosphoric acid conditioned by CFB were transported to Frankfurt, extracted and delivered back to CFB.

The essential data of the pilot extraction plant are as follows:

Throughput of approx. 200 L/h of phosphoric acid
Extraction circuit I: 6 glass-fibre reinforced polyester mixer-settlers
  Solvent scrubbing: 1 glass-fibre reinforced polyester mixer-settler
  Stripping circuit: 3 glass-fibre reinforced polyester mixer-settlers
Extraction circuit II: 2 glass-fibre reinforced polyester mixer-settlers
  Stripping circuit II: 2 glass-fibre reinforced polyester mixer-settlers.

The extractors of extraction circuit I have a mixer volume of 7.6 L and a settler volume of 77 L, the other mixer-settlers a volume of 7.6 L and 24 L, respectively. Devices to recycle the light or heavy phases are built in.

All containers are provided with air conditioning and the total plant is approved by the Federal German Technical Control Board (TÜV).

The plant is operating continuously, except the filtration which is carried out in centrifuges to be run in batch quantities.

2.2. First test campaign at Chemie Linz AG, Austria

Chemie Linz AG operates a phosphoric acid plant with approx. 45 000 t P_2O_5/a. The phosphoric acid produced is manufactured into fertilizer. Chemie Linz AG's blackish-brown filter acid showed the following analysis:

24.00% P_2O_5
3.50% H_2SO_4
2.50% HF
0.45% Fe
1300 ppm C
65 ppm U
1.50% solids.

Chemie Linz AG and Uraphos Chemie GmbH agreed to test the pilot plant under operating conditions with the above filter acid from July to December 1982.

As up to then no pilot plant for acid conditioning was available, in June 1982 a 3 m^3 stainless-steel tank and a disc pressure filter were installed at Chemie Linz AG. Thus, the filter acid could be conditioned and filtered to such an extent that a representative pilot operation was ensured. Chemie Linz AG's filter acid was characterized by a high content of organic substances, high total acidity and

TABLE I. OPERATION DATA OF URAPHOS PILOT-PLANT TEST CAMPAIGN

Data averaged over the complete test campaign	
Operating time	150 h
Phos acid input	43.41 t
Phos acid throughput	273 kg/h
Quantity of U in phos acid input (≙ 68 ppm U)	2 951 g U
Quantity of U in phos acid output (≙ approx. 11 ppm U)	462 g U
U recovery	84.3%
Data averaged over the second part of the test campaign	
Operating time	82.5 h
Phos acid input	22.79 t
Phos acid throughput	273 kg/h
Quantity of U in phos acid input (≙ 68 ppm U)	1 550 g U
Quantity of U in phos acid output (≙ approx. 5 ppm U)	121 g U
U recovery	92.2%
Operating personnel, incl. analyst	9 men

a high iron content. At the same time the uranium content was comparatively small.

Mid-July 1982 the pilot plant was transported by rail to Linz. The installations within the containers were reinforced by inflatable sacks so that no shipping damage occurred. In this respect the container design proved successful, as the whole plant was operative within three days only.

From August to October 1982 the pilot plant was operated with continuously changing adjustments in order to examine the influence of various operating conditions on the uranium recovery. By doing so, the process design derived from laboratory tests had to be modified several times. In this context it proved advantageous that the entire pilot plant had only flexible tube connections. All modifications could be performed by the operating staff. For the operation of the entire plant five persons were required on day shifts, one analyst being included.

After all modifications had been finished in October and the optimum operating conditions had been determined, a two-week campaign took place in November, the pilot plant being run in without any interruption in three shifts 24 hours a day (Table I).

After termination of the test campaign all substances containing uranium were analysed. In the final product produced 2252 g U were found and in the plant's solution supplies 207 g U. Table I shows that in the extraction process

2951 – 462 = 2489 g U were extracted, of which 2252 + 207 = 2459 g U were identified. Thus the deficit corresponds to about 1% only. The results show that the pilot plant enables reliable statements on the uranium output with the Uraphos process to be made at any time.

The average uranium recovery of about 92% obtained in the second half of the test campaign must be regarded as very high in view of Chemie Linz AG's filter acid which is comparatively difficult to extract.

The phosphoric acid running off the extraction was clear and green, and the contents of solvents were in the range of solubility of Exsol D 200/240 (below 10 ppm). The reason for this is the purely aliphatic character of Exsol D 200/240 and the composite coalescer installed from Knit Mesh Ltd, Great Britain, which provided for excellent coalescence of dispersed drops.

The $Na_2U_2O_7$ produced showed the following analysis:

U_3O_8	81.60%
Fe_2O_3	0.20%
P_2O_5	0.30%
CaO	0.30%
Na_2O	9.13%
SiO_2	0.05%
TiO_2	0.08%
V_2O_5	0.05%
K_2O	0.05%
Total	91.70%

Thus the final product at the first run came up to the purity standards required for subsequent conversion. Without any difficulty the Uraphos process could also allow the precipitation of $(NH_4)_2U_2O_7$, which would reduce the Na_2O content considerably.

The Uraphos process does not produce uranium-containing solutions that might lead to losses. Therefore it is characteristic for this process that the uranium recovery of the first extraction phase corresponds to the total uranium recovery.

2.3. Planning and construction of the pilot acid conditioning plant

On the basis of the data obtained during the test campaign at Chemie Linz AG, a process for step-by-step acid conditioning was designed and planned concretely early in 1983. The resultant pilot plant was built in two further 20 ft containers and involves the possibility of carrying out the following conditioning measures partly or as a whole on the scale of 250 L/h of phosphroic acid:

Reduction of acidity
Removal of interfering ions by precipitation
Separation of solids by means of thickener and filter press

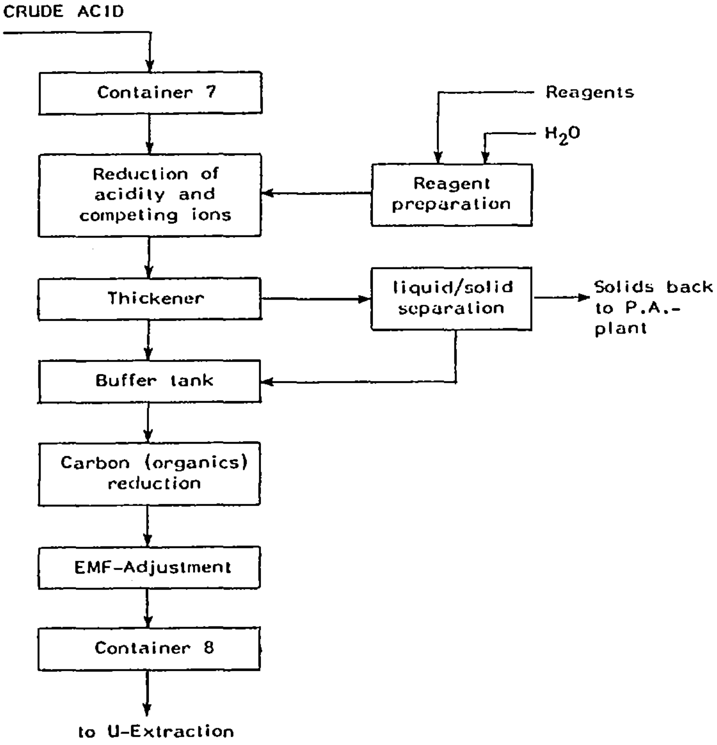

FIG.4. Uraphos pilot plant: simplified process flowsheet of acid conditioning.

Separation of organic components by activated carbon columns
Reduction of phosphoric acid by means of red phosphorus or iron scrap in one column.

The process design is shown in Fig.4.

The test run in Linz demonstrated that the X-ray fluorescence spectrometer originally installed was not able to cope with the quantities of samples. Therefore it was replaced with a more powerful Philips PW 1400 spectrometer, which allows quick and reliable analysis of all elements with an atomic number of 11 (sodium) upwards in solutions, rock phosphate, gypsum, iron residues, and yellowcake. Thus, the pilot plant's analytical equipment and capacity now meets all requirements.

The complete pilot plant came into operation in Frankfurt in 1983. As shown in Fig.4 the space required for the installation of the complete pilot plant amounts to about 430 m^2. After a successful termination of the startup period, the pilot plant was given its first complete test run using a phosphoric acid from a Dutch fertilizer producer from October 1983 to January 1984. Both the pretreatment plant and the extraction plant operated to complete satisfaction.

TABLE II. COST OF CHEMICALS USED IN THE LINZ PILOT CAMPAIGN

Chemicals	Cost of chemicals in DM/t of filter acid treated
$(NaPO_3)_n$	0.18
Na_2CO_3	0.69
H_2SO_4	0.06
NaOH	0.72
Total	1.64

3. PROFITABILITY

The first test campaign at Chemie Linz AG showed that the pilot plant provides all data required for the design of a commercial plant. In addition, it is possible to determine all data specific to a particular phosphoric acid as regards

Consumption of chemicals
Consumption of solvents
Consumption of extracting reagents
Uranium recovery
Quantity and quality of final product.

The conditioning cost cannot be determined until the time of completion of the pilot acid conditioning plant.

The Uraphos process requires only easily obtainable mass-produced chemicals. The chemical costs listed in Table II should be regarded as specific for the acid in Linz and have not yet been optimized.

The costs of the extractant and the solvent are more important in economic terms. The price of the extractant (Exsol D 200/240 plus 2% TDDA) at present amounts to 1.06 DM/L and 1.32 DM/kg, respectively. Thus the cost of the Uraphos extractant is about 20% of that of the D2EHPA-TOPO extractant. In consideration of the extremely small solvent losses during the Linz test campaign, the maximum cost of extractant losses should be less than 0.04 DM/t of filter acid. Thus the cost of chemical for the extraction of Chemie Linz AG's phosphoric acid amounted to approx. 1.68 DM/t of filter acid or (at an exchange rate of 2.50 DM/US \$) 4.20 US \$/lb U_3O_8 recovered. In consideration of the low uranium content of 68 ppm U in the acid, this seems to be fairly low.

4. OUTLOOK

Uraphos Chemie GmbH is seeking co-operation with phosphoric acid producers in order to invest jointly in a commercial uranium extraction project. For this purpose the Uraphos pilot plant is available for test campaigns at phosphoric acid plants abroad, thus enabling a reliable basis for a feasibility study of uranium production with the Uraphos process to be elaborated.

DISCUSSION

I. EZAHR: You said that the phosphate rock you used contains 1300 ppm of organic matter. Can you confirm this?

U.M.J. BOIN: That figure is correct. The carbon content was determined by oxidizing all the organic material to CO_2 and measuring the amount of CO_2 by infra-red spectrometry.

K. CHITUMBO: What are the amine losses in this system?

U.M.J. BOIN: Solvent losses are not greater than the natural solubility of the aliphatic solvent in phosphoric acid, which is below 50 ppm carbon.

G. LYAUDET: Have you made an economic evaluation of this process? How does it compare with the classical D2EHPA/TOPO process?

U.M.J. BOIN: So far we have determined that one pound of U_3O_8 recovered by the Uraphos process will cost us US $4.20, at an exchange rate of 2.50 DM per US $. Consumption of the amine extractant will add up to US $4.20 per pound of U_3O_8.

H.J. STEINER: This is not the full cost because you have not considered the cost of pretreatment. Do you have a figure for the total cost of the recovery of uranium?

U.M.J.BOIN: This is only the cost of extraction. At this stage of development we still do not have a figure for the overall cost. We are just building our pretreatment plant so we cannot make precise statements about pretreatment costs.

H.J. STEINER: What is the effect of acid concentration on the process? You have used a 22–24% P_2O_5 acid as feed. What happens if you use an acid with 28 or 30% P_2O_5?

U.M.J. BOIN: This would not have an important effect. We can work with acids containing up to 40% P_2O_5.

H.J. STEINER: What is the effect of acid concentration on the distribution coefficient?

U.M.J. BOIN: As I pointed out before, we only have ion exchange and there is a certain loading of the light phase, to a maximum, and we cannot talk about distribution coefficients.

I. EZAHR: Your pilot plant can treat 200 L/h acid. Why did you choose this size and not a smaller one? Assuming that the acid has been pretreated in a proper way and that one has a stable acid and can perform the extraction with high efficiency, then the results obtained from a small pilot plant can be extrapolated very easily.

U.M.J. BOIN: We believe that the maximum scaling factor that should be used is 1000. One cannot go from laboratory tests to a plant of 200 000 tonnes of P_2O_5 per year.

THE D2T PROCESS OF URANIUM RECOVERY FROM PHOSPHORIC ACID: A PROCESS MODEL

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Abstract

THE D2T PROCESS OF URANIUM RECOVERY FROM PHOSPHORIC ACID: A PROCESS MODEL.

A computer program is discussed which gives the mass and energy balances and concentrations for the D2T process of uranium recovery from phosphoric acid. The program permits a quick calculation and/or simulation and sensitivity studies for any phosphoric acid or problem related to that process. The structure of the program is divided into three blocks: acid preconditioning; first and second cycles of concentration; and drying of the final product. The calculation program, made in Fortran language, takes 152 inputs, and gives basic information for 123 process flows with a total of 1265 outputs. Finally, and as an example, a study is shown of the varying composition of the strip solution versus the iron content in the initial phosphoric acid.

1. INTRODUCTION

The association of uranium and phosphates has been known since the beginning of the century, the radioactivity having been used as a way of exploring for phosphates. The concentration of uranium in phosphate rocks changes from one deposit to another but, in general, it is within the range of 30 to 200 g U_3O_8/t and, related to the phosphoric base, it is from 0.3 to 0.5 kg U_3O_8/t P_2O_5.

Initial experiments to extract uranium selectively from phosphate rock were not successful. Other attempts were made to recover the uranium values along all steps of the processing of phosphate rock to produce fertilizers and other products, although in the process in which the uranium is retained by the solids the recovery is very low, between 50 and 60%, together with high solvent entrainment. Present technology indicates that significant quantities of uranium can only be recovered at a reasonable cost as a byproduct of the manufacture of wet-process phosphoric acid.

The available industrial processes for uranium recovery from wet phosphoric acid were basically developed in the 60s and 70s. They used the solvent extraction process with an active reagent for the uranium and dissolved in kerosene.

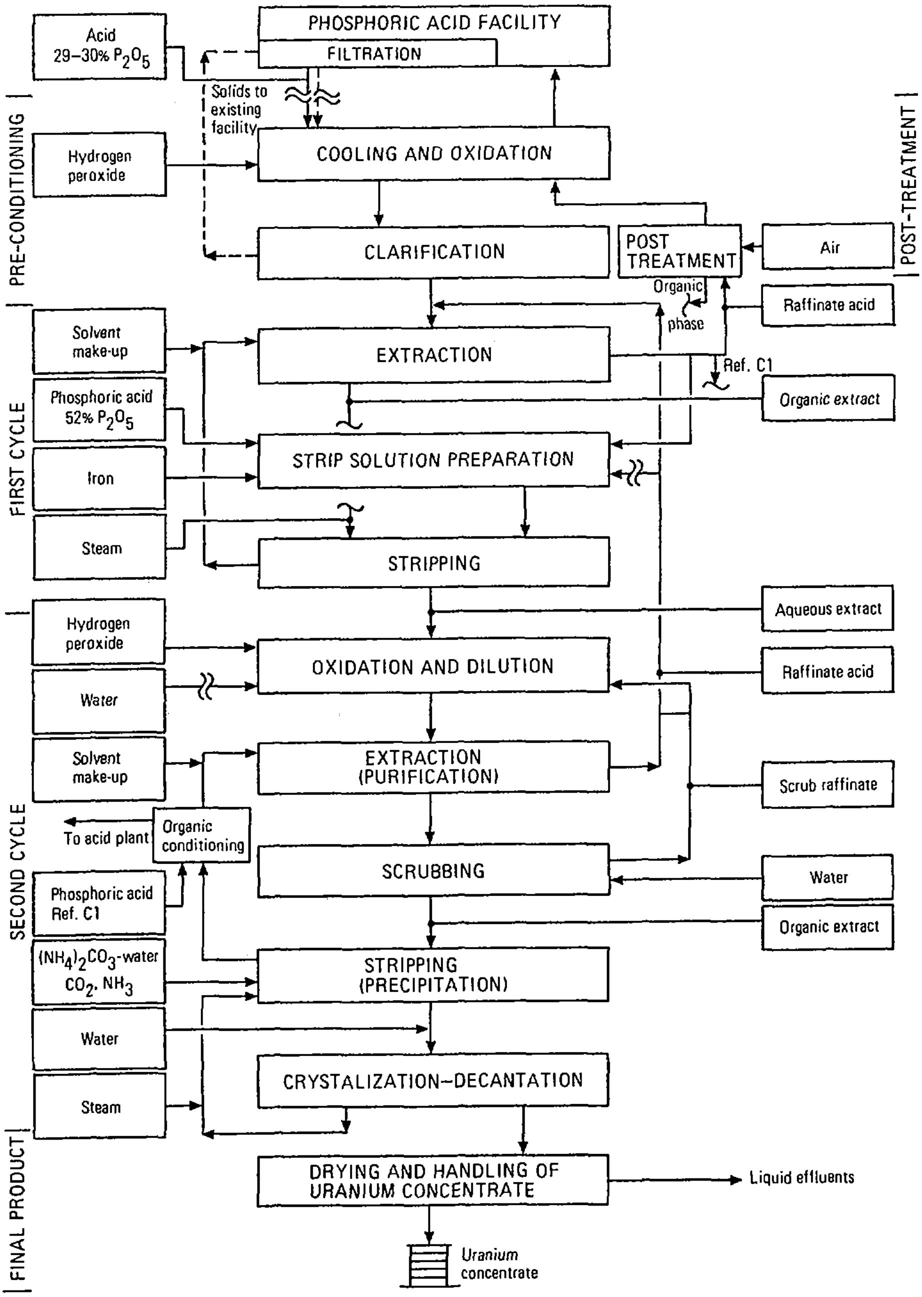

FIG.1. Block diagram of uranium recovery from phosphoric acid.

Depending on the active reagent, a distinction is made between the methods of:

(a) Alkylpyrophosphoric acids (octylpyrophosphoric acid OPPA)
(b) The synergistic combination of Di-2 (etil-hexil) phosphoric acid (D2EHPA) and trioctylphosphine oxide (TOPO), or D2T
(c) The acid or ester of phenyl phosphoric acid (OPAP or MOPPA and DOPPA, since it is the equimolecular mixture of the monomer and the dimer).

The difference between the several solvents or methods from a chemical point of view is of a lower conceptual order for the D2T and OPAP processes and more essential with regard to the OPPA process. Nevertheless, in their practical realization from the phosphoric acid to a commercial uranium concentrate acceptable in the free market all the processes have several common stages. Sometimes the practical realization is more important than the chemistry of the process.

In all cases the uranium recovery process has to work with dilute acid (28–30% P_2O_5). So the uranium balance between the aqueous phase (phosphoric acid) and the organic phase (solvent) shifts toward the latter and the acid leaves free of uranium.

A block diagram of the uranium recovery process is shown in Fig.1. The specific steps are:

Pretreatment (cooling, clarification, uranium oxidation, carbon treatment);
Uranium recovery from acid by solvent extraction;
Concentration of uranium in an intermediate product (low-quality solid or liquid); together with the previous step this constitutes the first cycle;
Purification of the intermediate product, separating uranium from the impurities;
Obtaining a uranium concentrate; together with the previous step this constitutes the second concentration cycle;
Handling of uranium concentrate;
Post-treatment of the uranium-exhausted acid to separate the entrained solvent; this solvent can affect the anti-corrosive linings of the phosphoric acid plant equipment and, moreover, it can present some problems with the use of the acid (tripolyphosphates).

This is the process for uranium recovery from phosphoric acid which, with its variations in reagents, final product, equipment, technological solutions and even operating preferences, constitutes the range of technologies available in the first half of the 1980s.

In Spain the Junta de Energía Nuclear developed its own process which uses a synergistic combination of D2EHPA and TOPO as active reagent. Several details of this process are presented.

The phosphoric acid from an existing facility is received as a filtrate acid. In the pre-conditioning section the following steps take place: first, the acid is cooled, using a flash-type evaporator before acid oxidation to convert all the uranium to the U^{6+} valence state, then the acid is aged and solids are settled out and finally it is clarified with sand filters, and passed through activated carbon columns. In this way the solids and humic materials are removed from the acid, resulting in clean phosphoric acid.

In the first concentration cycle the pretreated phosphoric acid is brought into contact with a solvent mixture consisting of 0.5M D2EHPA and 0.125M TOPO dissolved in kerosene, the operation temperature being 40–45°C. A four-stage countercurrent extraction system is used, although more or less stages can be used depending on specific process requirements. Mixer-settlers are used in the two cycles of this process.

Then the uranium-laden extract goes through three stages of reduction stripping at 50°C. The strip solution is a phosphoric acid (8M) with 15–30 g Fe^{2+}/L obtained by a mixture of three phosphoric acids: the raffinate from the first concentration cycle, the raffinate from the second cycle and concentrated phosphoric acid. Contact of this solution with the organic extract reduces the uranium to the tetravalent state, whereupon the uranium is transferred quantitatively to the aqueous phase. When the organic to aqueous flow ratios and the ferrous iron concentration are controlled uranium can be concentrated, in three stages, 70 to 80 times compared with its grade in the crude phosphoric acid. From this step the organic phase is recycled to the solvent extraction circuit.

The uranium (U^{4+}) in the aqueous extract (10–15 g U_3O_8/L) is oxidized with hydrogen peroxide or sodium chlorate. Moreover, the extract is diluted to 32% P_2O_5 and then sent through the second D2EHPA/TOPO solvent extraction circuit at 30°C. The process uses 0.3M D2EHPA and 0.075M TOPO in kerosene. The stripped acid is returned to the first cycle, while the organic extract is scrubbed to remove any entrained P_2O_5, and in this way P_2O_5 is minimized in the final product and reagent consumption is reduced during the stripping step. This scrubbing step uses three stages with water at 20–25°C.

A part of the washing raffinate is used to dilute the first-cycle aqueous extract and the rest is sent to the first cycle, mixed with the raffinate from the second solvent extraction circuit.

Uranium is removed from the organic phase at 50°C by two stages of stripping with ammonium carbonate. A relatively pure ammonium uranyl tricarbonate (AUTC) precipitates. It is filtered out of solution, and is calcined to yield high-grade U_3O_8.

After the AUTC concentrate has been filtered out the mother liquor is recycled to the stripping circuit.

Barren organic phase, with the D2EHPA in ammonium form, is regenerated using the raffinate acid from the first cycle, before sending it back to the solvent extraction circuit.

The overall uranium recovery from phosphoric acid is between 89 and 91%.

2. STRUCTURE OF THE COMPUTER PROGRAM

The program for balance calculation is prepared in Fortran IV language for a UNIVAC 1100/81 computer.

The program is divided into three independent blocks: pretreatment, first and second uranium concentration cycles, and final product. The flow diagram of the program is shown in Fig.2. It can be seen that there is a considerable number of recycled flows. This is the reason for the choice of three blocks. Each block has all data and information necessary to calculate the mass and energy balances.

A technician has only to supply the computer with the characteristics of the phosphoric acid from an existing facility and some other data corresponding to the controls of result output. The characteristic data of the process are incorporated in the program for each block.

As a consequence of those recycled flows the calculation of the balances is not easy, and it is necessary to establish some hypotheses which are analysed during the calculation. A conventional method of convergence is used. A determinated value is given to the interest parameter. Afterwards, the parameters of implicated flows are calculated and a new value of that parameter is obtained. Both values are compared and if the difference is larger than a previously established figure, a new value is given to that parameter and the calculation is repeated until its difference is lower than the established value.

This program can also be used with phosphoric acid facilities that produce two kinds of acid obtained with phosphate rock of different origins. In this case the output gives two lists of results, one for each acid, for the pretreatment section and for the solvent extraction step of the first uranium concentration cycle. The two uranium-laden organic phases obtained are mixed together and treated in only one stripping section. Besides, it is possible to choose the raffinate acid to prepare the strip solution. To simplify, only one phosphoric acid is considered in this paper.

First, the program reads the characteristics of the phosphoric acid from an existing facility. The calculation of the oxidant flow is done when the uranium is in the reduced state; in this case hydrogen peroxide is used. Afterwards, the flows of flocculant solutions are calculated. These are directly computed when the uranium exists in the hexavalent state.

At first the value of the clarified acid flow, which is introduced into the solvent extraction circuit, is not known. Therefore a hypothesis with a value equal to A_1 is established. Another hypothesis with a value equal to B_1 is defined for the flow of phosphoric acid that returns to the uranium recovery plant after filtering the solids pulp generated in the pretreatment section.

Next, some parameters of the pretreatment section are calculated. A new value B_2 is obtained and this value is compared with the previous B_1 and the calculation repeated until the difference B_1-B_2 is lower than the previously allowed value.

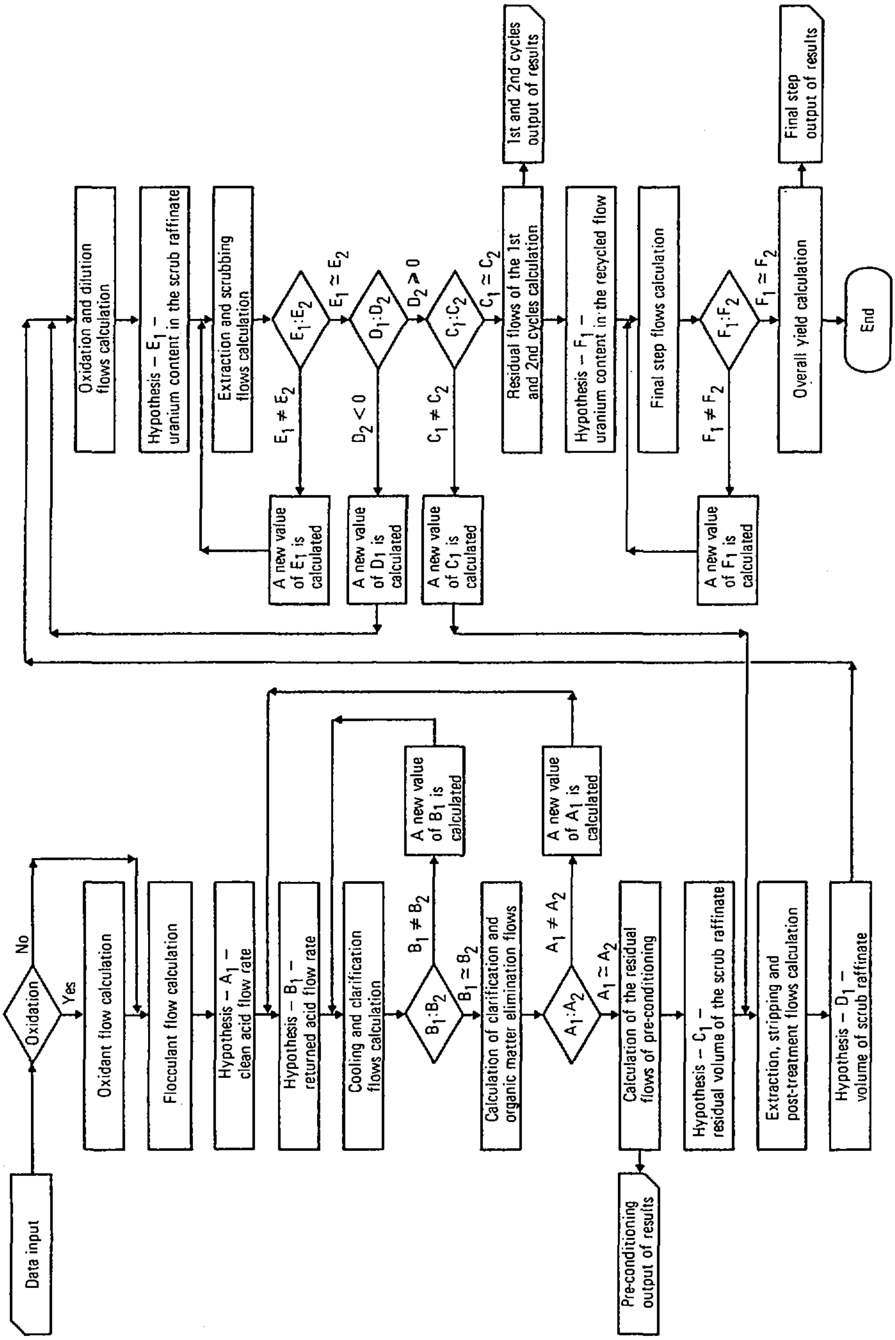

FIG.2. Flow diagram for the calculation of mass and energy balances.

When the correct value of B is known, the following step is to calculate the flows of the clarification and organic material elimination stages. In this way a new value of A_2 is obtained and the calculation is repeated until the difference A_1-A_2 is lower than the allowed value. Previously to the output of the pretreatment stage results, the program computes the parameters of the flows that have not been calculated before.

The second block is the most complicated, as a consequence of the number of recycled flows, and of the strip solution preparation, which is made up from a mixture of three different acids: raffinate from the first cycle, raffinate from the second cycle and concentrate acid with 50–54% P_2O_5.

The calculation is started with the hypothesis of $C_1 = 0$, which corresponds to the residual flow of scrubbing water from the uranium-laden organic phase of the second cycle. This flow is joined by the raffinate of the second cycle and recycled to the first cycle.

Using that value, several parameters corresponding to flows of extraction, stripping, post-treatment of the raffinate acid and strip solution are calculated.

The program includes the corresponding equations of the extraction and stripping systems.

In this way, the flow of the first-cycle extract is computed, and then hypothesis D_1 is set up, which refers to the total flow of scrubbing water of the uranium-laden organic phase in the second cycle. Afterwards the flows of hydrogen peroxide and dilution water of the first-cycle extract are calculated. At this point a new hypothesis E_1 is defined. It refers to the flows of the solvent extraction and scrubbing steps of the second cycle. The values E_1, D_1 and C_1 are determinated and calculations are repeated until the differences are lower than the allowed values. At the end of the second-cycle calculations the output for the first and second cycles is given independently.

The last block corresponds to the final product, i.e. the filtration of the AUTC pulp, drying and handling of the concentrate, and treatment of the gas effluents. One hypothesis F_1 is defined which corresponds to the uranium content of the filtrate. When the calculations of this third block are finished, a new value F_2 is computed. This value is compared with F_1 and the calculations are repeated until the difference F_1-F_2 is lower than the allowed value. Finally, the overall yield is calculated, and the results of this final step are produced.

3. INPUT AND OUTPUT STRUCTURE

The program is divided into four sections and each one of them is subdivided into flows. The sections and the corresponding flows are: pretreatment (27), first cycle of concentration (32), second cycle (32) and final product (32).

TABLE I. OUTPUT OF RESULTS: RELATION OF PARAMETERS OBTAINED FOR DIFFERENT FLOWS

Parameters	Phosphoric acid	Organic phase	Pulp of uranium concentrate	Reagents and utilities
Flowrate (t/d)	x	x	x	x
Flowrate (m^3/d)	x			
Mean density (kg/m^3)	x			
Flow of P_2O_5 (t/d)	x			
Flow of U_3O_8 (kg/d)	x	x	x	
P_2O_5 concentration (%)[a]	x			
P_2O_5 concentration (kg/m^3)[b]	x			
U_3O_8 concentration (kg/m^3)[b]	x	x		
Fe_t concentration (kg/m^3)[b]	x			
Fe^{2+} concentration (kg/m^3)[b]	x			
Solids concentration (kg/m^3)[c]	x			
Organic material concentration (kg C/m^3)[c]	x			
Temperature (°C)	x	x	x	x
Thermal head (kcal/d)	x	x	x	x
Flow of solids (t/d)	x			
Flow of liquid (m^3/d)	x	x	x	x
Flow of Fe_t (kg/d)	x			
Flow of Fe^{2+} (kg/d)	x			
Flow of organic material (kg/d)	x			
Flow of pulp (m^3/d)			x	
Pulp density (kg/m^3)			x	
Percentage of solids (%)			x	
Flow of solids (t/d)			x	

[a] Referred to total weight.
[b] Referred to clean liquid.
[c] Referred to total flow.

These sections include all information and data to calculate the balances and, in consequence, the characteristics of the phosphoric acid from the existing facility are the only data supplied to the computer. These are:

Capacity of phosphoric acid (t P_2O_5/d)
Percentage of P_2O_5 (%)
Acid density (L + S) (kg/m^3)
Total iron concentration (kg/m^3)[1]
Ferrous iron concentration (kg/m^3)[1]
Uranium concentration (kg U_3O_8/m^3)[1]
Organic matter concentration (kg C/m^3)[2]
Solids concentration (kg/m^3)[3]
Solids density (kg/m^3)
Acid temperature (°C)
Room temperature (°C)
Percentage of fluorides (%)

For each section, the output is:

A flow diagram together with a list for flow identification;
A list of operation conditions; the output corresponding to the pretreatment section includes a list of the characteristics of the phosphoric acid;
Output of the results.

The parameters for each flow are shown in Table I. In addition to the parameters of flowrate, P_2O_5 and U_3O_8 and their concentrations, other factors that affect the process, like solids and organic material concentration and the total iron and ferrous iron, are considered.

At the end of each section its overall uranium yield is obtained, as well as other data about the process and the program running.

The total output has 41 pages DIN A-4 size, in which there are four flow diagrams, four lists of flow identification, four lists of operation conditions and one list of characteristics of the phosphoric acid: in short, 152 inputs and 1265 results corresponding to 123 flows.

4. APPLICATIONS

As an example, several interesting cases are analysed. This program is a very effective tool to calculate the balances, and moreover, it permits sensitivity studies to find out the very best conditions for the process. Also, it may be used

---

[1] Referred to cleaned liquid.

[2] Referred to total volume.

TABLE II. PRETREATMENT SECTION: EFFECTS OF THE QUALITY OF THE PHOSPHORIC ACID FROM THE EXISTING FACILITY

Phosphoric acid			Pretreatment section			
Grade ($g\ U_3O_8/L$)	Solids (kg/m^3)	Organic matter (kg/m^3)	Clarified acid (m^3/d)	Losses U_3O_8 (kg/d)	P_2O_5 (t/d)	Flocculant consumption (kg/d)
0.120	20	1.5	2760	1.9	5.7	104.4
0.150	10	1.5	2772	1.17	2.8	52.2
0.150	20	0.5	2722	2.35	5.7	104.4
0.150	20	1.5	2760	2.35	5.7	104.4
0.150	20	2.5	2798	2.35	5.7	104.4
0.150	30	1.5	2748	3.54	8.7	156.6
0.180	20	1.5	2760	2.82	5.7	104.4

as a correcting instrument to anticipate the consequences of possible modifications of the process conditions. Besides, the variations in the uranium, solids, organic material and iron contents can be analysed.

Table II summarizes the variation of the clarified acid flowrate, the U_3O_8 and P_2O_5 losses, together with the flocculant consumption as a function of the uranium grade and of solids and organic material content of the phosphoric acid for the pretreatment section. The results are plotted in Fig.3, where it can be seen that the clarified acid volume decreases proportionally to the increase in solids content. Moreover, the flowrate also increases with the organic material content on account of the water volume used to wash the active carbon bed previously to its regeneration. Furthermore, U_3O_8 and P_2O_5 losses become proportionally larger as the solids content increases.

From Fig.4 it can be seen how the solids concentration affects the overall yield. This effect is small when the solids concentration is between 10 and 20 g/L, whereas between 20 and 30 g/L it is larger.

An important aspect in the uranium recovery process is the strip solution preparation. The strip solution is phosphoric acid (8M) with 15–30 g Fe^{3+}/L.

This stripping operation is a critical step and it is necessary to keep reducing conditions with a minimum Fe^{2+}/Fe^{3+} ratio equal to 2. The strip solution is prepared by mixture of three phosphoric acids:

(a) Raffinate of the first concentration cycle, which has 28–30% P_2O_5 and an iron concentration that depends on the phosphate rock;

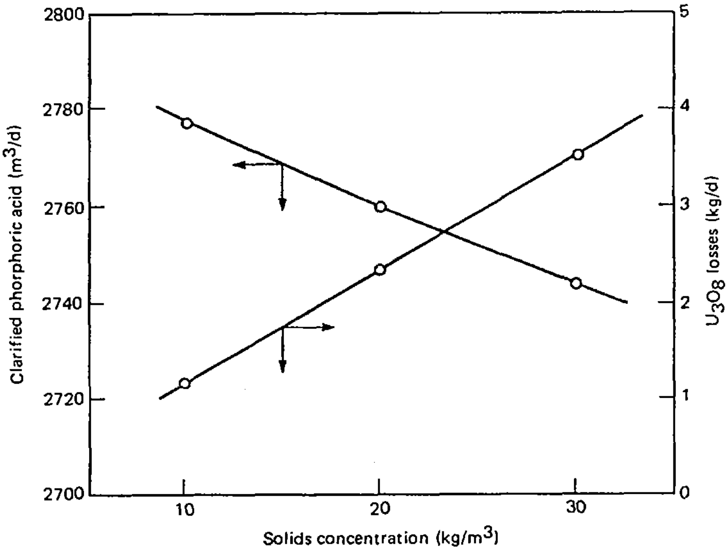

FIG.3. Effect of solids concentration in the phosphoric acid plotted against volume of clarified phosphoric acid and U_3O_8 losses.

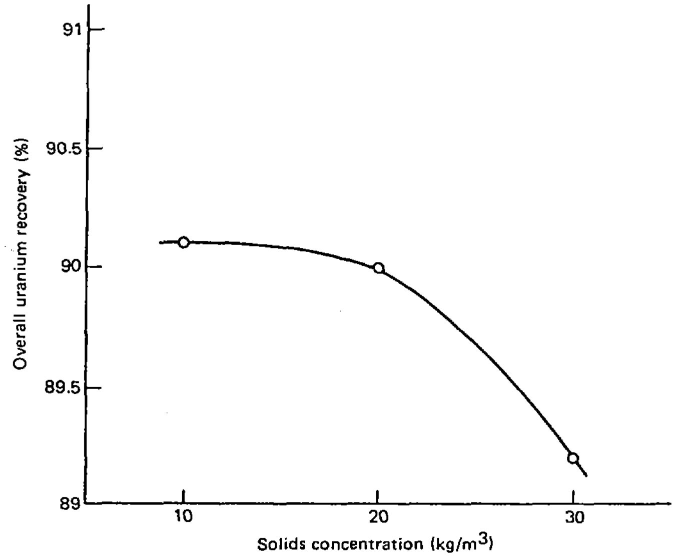

FIG.4. Effect of solids concentration in the phosphoric acid plotted against overall uranium recovery.

TABLE III. EFFECT OF IRON CONCENTRATION IN THE INITIAL PHOSPHORIC ACID ON COMPOSITION OF THE STRIP SOLUTION, AND ON IRON METAL AND OXIDANT CONSUMPTION

Phosphoric acid[a]		Strip solution composition[b]				Consumption	
			Acid (m^3/d)				
Fe_t (g/L)	Fe^{2+} (g/L)	Fe_t (g/L)	Raffinate 1st cycle	Raffinate 2nd cycle	Concentrated	Iron metal (t/d)	Oxidant H_2O_2 (kg/d)
3	1	15	3.5	26.0	9.9	0.18	239
4	1.33	15	6.1	23.1	10.2	0.18	239
5	1.7	15	9.4	19.5	10.5	0.17	239
6	2	15	14.0	14.4	11.0	0.17	239
7	2.33	15	20.2	7.7	11.5	0.16	239
8	2.7	15.7				0.16	250
9	3	17.5				0.18	279
10	3.33	19.5				0.20	311
11	3.7	21.5				0.22	343
12	4	23.5	27.1	0.1	12.2	0.23	375
13	4.33	25.0	26.7	0.5	12.2	0.25	399
14	4.7	27.0	26.7	0.5	12.2	0.27	431
15	5	29.0	26.5	0.7	12.2	0.29	462

[a] Initial phosphoric acid: 0.150 g U_3O_8/L; 28% P_2O_5; solids 20 kg/m^3; organic matter 1.5 kg C/m^3.

[b] Strip solution: 37% P_2O_5.

(b) Raffinate of the second concentration cycle, which has about 31% P_2O_5 and an iron concentration that depends on the initial strip solution;

(c) Concentrate phosphoric acid with about 52% P_2O_5, which is obtained from raffinate phosphoric acid of the first cycle.

The ferric iron in the mixture is reduced to the ferrous state with iron metal.

The minimum total iron concentration for the strip solution with 37% P_2O_5 in shown in Table III for different ferric and ferrous iron concentrations of the initial phosphoric acid. It can be seen that for initial concentrations less than

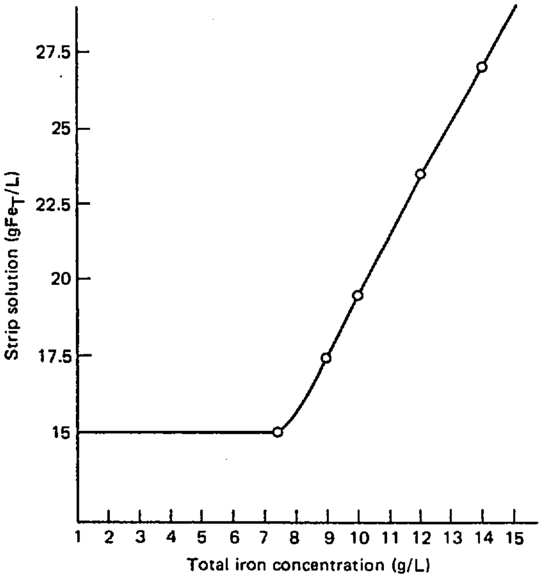

FIG.5. Effect of iron concentration in crude phosphoric acid plotted against minimum iron concentration in the strip solution.

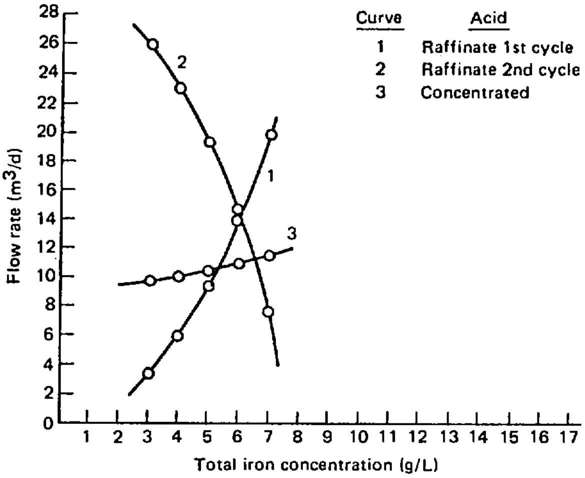

FIG.6. Effect of iron concentration in crude phosphoric acid plotted against composition of the strip solution (15 g Fe$_t$/L).

8 g Fe_t/L the strip solution may have the lowest iron concentration of the process, i.e. 15 g/L. This concentration increases, quasi-proportionally, up to 29 g/L for an initial concentration of 15 g Fe_t/L. The results are shown in Fig.5.

Likewise, Table III shows the amount of iron metal necessary to reduce the ferric iron to the ferrous state. It also shows the oxidant consumption that is necessary to oxidize the tetravalent uranium of the aqueous extract to the hexavalent state before being introduced into the second solvent extraction cycle. As a consequence, the iron metal and the oxidant consumption increase when the iron concentration of the phosphoric acid increases.

Finally, Fig.6 plots the effect of the iron assay of the initial phosphoric acid on the different contributions of the three afore-mentioned flows to make up the strip solution with 15 g Fe_t/L. It can be seen that the increase in the iron content raises the contribution of the first-cycle raffinate, whereas it reduces the corresponding contribution of the raffinate from the second cycle, while the concentrate acid volume increases slightly.

DISCUSSION

W.A. GOW *(Chairman)*: How much does your model depend on the equipment parameters? Can it be easily adapted to different conditions?

P. GASÓS: This model was developed for our process and our equipment but it can be applied to other processes with some modifications. For instance, the solvent extraction section is described by several subroutines and these could be changed.

W.A. GOW: Does this require much effort? In some of the modelling work that we have done on grinding circuits the actual sampling and determination of the parameters is sometimes a very difficult job.

P. GASÓS: This has been applied for the equipment we have for this process.

ALI KEBIR: How does your model take into account the different equilibrium conditions that correspond to different acids?

A. MORAL: The equilibrium conditions are different for different acids, of course. In our model we have a subroutine to calculate the distribution and operating conditions. For each set of conditions we change the subroutine.

RECOVERY OF URANIUM FROM COAL AND NATURAL WATERS

RECOVERY OF URANIUM FROM COAL ASH

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Abstract

RECOVERY OF URANIUM FROM COAL ASH.

Laboratory and pilot-scale investigations of uranium recovery from coal ash are described with special attention to the use of stack gases as a source of leaching reagents. The liquid-solid separation properties of slurry are determined and the selective separation of uranium by ion exchange and other methods are evaluated. A rough cost estimate is made.

1. INTRODUCTION

The basic energy production in Yugoslavia is provided by coal and water power, the rest being produced by oil and nuclear power. In terms of reserves, uranium represents roughly one tenth of all energy resources. The distribution of energy resources is uneven throughout the country. There is only one economically attractive uranium ore deposit, Žirovski vrh, located in the extreme north-west of Yugoslavia. The deposit is considered of medium size as ore reserves and low grade in uranium concentration. The mill feed will have a grade of approximately 0.1% of uranium. Ore mining and processing are both considered relatively difficult. The basic reasons for this are as follows:

Underground mine
Non-uniform shape of ore bodies
Heavily populated area with much tourism
Very pure surface and underground waters
High rainfall and low evaporation rate (1.5 m net rainfall per year)
Sharp relief and inconvenient geological structure of the soil.

The plant was designed to treat about 200 000 tons of the ore per year and to produce 120–180 tons of ammonium diuranate (ADU) per annum in order to supply uranium concentrate for refuelling the nuclear power plant already in operation. The concept of the uranium ore treating plant was elaborated by domestic research institutes, especially Jožef Stefan Institute in Ljubljana, and by foreign and domestic engineering companies. The flowsheet features [1] a totally closed water balance in the acid ore treatment process and dry tailings disposal. This is believed to be the most acceptable flowsheet for the given site conditions, the rest being standard equipment: rod mill, two-stage acid leach with high-rate thickener inbetween, horizontal belt filters, amine solvent extraction, ADU precipitation and raffinate neutralization and finally purification followed by the reuse of the total quantity of the purified raffinate. The deposit at Žirovski vrh could possibly provide more uranium concentrate for the subsequent nuclear power plants but probably not satisfy all planned requirements. It is therefore not surprising that significant interest exists in exploration for new deposits and for the recovery of uranium from non-conventional resources. The most developed programmes are concerned with the recovery of uranium from phosphoric acid. Here the biggest phosphate fertilizer producers are involved, e.g. in Prahovo and Kutina. Typical for uranium recovery from phosphoric acid and for the Žirovski vrh uranium mine project is that domestic institutes have been or are intensively involved in the process development. It is also intended to provide as much equipment as possible from domestic suppliers. Very little has been published regarding progress in developing a uranium-phosphoric acid process but it is felt that the projects are now in the pilot-plant stage, which should give design figures for full-scale operation. The realization of these projects could possibly double the uranium production in Yugoslavia. Environmental concerns have had a big influence on the projects mentioned above; in the case of the Žirovski vrh mine a new modified acid process has been developed, and uranium extraction from intermediates in fertilizer production also reflects more and more stringent environmental concern and regulations.

The environment impact was one of the considerations that activated the work in respect to uranium recovery from coal.

2. URANIUM-BEARING COAL

The activities described in this paper are related to the process development for uranium recovery from black coal mined in the Istrian Peninsula. At present one thermal plant is fired with this coal but the reserves suggest that the deposit could supply several times greater power production. Estimates show that, roughly, power plants producing 500 MW can consume the quantity of coal that contains the uranium required to supply a 500 MW nuclear power plant [2]. One particular property of the coal should be emphasized, namely the sulphur content, which is approximately 10%. Two questions are raised by this: (1) whether it is possible to use this sulphur for sulphuric acid production, and (2) whether more installed

TABLE I. TYPICAL ASH SAMPLE COMPOSITION

Component	Concentration (wt%)
SiO_2	4.5
Na	1.0
Ca	18.1
K	0.26
Mg	4.6
Fe	2.6
Al	2.3
V	0.26
Total sulphur as	
SO_4	27.5
U	0.015

capacities could be accepted from the standpoint of existing and future tourism in this part of the Adriatic coast. Consequently, our work on uranium recovery from the coal should contribute to deciding what measures have to be accepted in a possible future increase in the power generating capacity or, more simply, in the increased tonnage of coal burned.

Burning coal produces approximately 15% of fly has (in relation to the feed) which contains one to more hundred ppm of uranium, some vanadium, aluminium, silica, magnesium and some other minor metallic components. Fly ash represents about 80% by weight of all residues after burning but contains significantly more than 80% of the total uranium present in the residues. Consequently, coal and fly ash were exclusively used as raw materials in the tests. The typical composition of the ash sample is given in Table I.

3. PRELIMINARY HYDROMETALLURGICAL TESTING

Preliminary testing was done in 1 kg batches. Ash and ground coal were tested using the acid and alkaline leaching method. Fly ash samples were all very

TABLE II. RESULTS OF PRELIMINARY HYDROMETALLURGICAL TESTING

	T (°C)	pH	Time (h)	U recov. (%)	Leach reagent cons. (kg/t)
Acid leach					
Ash	70–95	0.7–1.7	6–22	86–92	750–950
Coal	75–90	0.5–1.2	6–22	10–20	160–180
Alkaline leach (atm. press.)					
Ash	80–100	15–200 g/L Na_2CO_3 8–144 g/L $NaHCO_3$	6–22	15–55	300 Na_2CO_3
Coal	75–95	250–300 g/L Na_2CO_3 70–200 g/L $NaHCO_3$	6–23	20–50	20–100 Na_2CO_3

fine, 98% passing 300 μm, and did not require any pretreatment. The following parameters were studied in the preliminary laboratory bench testing:

Uranium recovery
Acid and oxidant consumption
pH and free acid concentration
Temperature
Leaching time
Solids content in the slurry
Redox potential
Liquid-solid separation by filtration
Liquor composition and ion exchange.

The results of the preliminary hydrometallurgical testing are given in the Table II.

Acid leaching tests were performed at 30% solids in the slurry and alkaline leach tests at 25% solids, both figures being considered as maxima for adequate agitation. In alkaline leaching CO_2 was introduced to maintain the proper bicarbonate and carbonate ratios, otherwise free sodium hydroxide was formed. The temperatures required were achieved by heat release during the reaction of the ash with the sulphuric

TABLE III. RESULTS OF LEACHING TESTS, 0.5 t BATCHES

Leaching temperature (°C)	60–80
Leaching time (h)	4–6
Solids in slurry (%)	25–30
Final pH	1.05–1.85
Final redox potential (mV)	420–485
Uranium recovery (%)	88–92
Acid consumption (kg H_2SO_4)	707–788
Oxidant consumption (kg/t)	none

acid, cooling being required at the beginning. Acid coal leaching and alkaline leaching required external heating.

The results show in all cases high or extremely high reagent consumption. Only acid leaching of the ash gave high uranium recoveries. Filtration of leached slurries shows relatively good filtration rates when filtering acid ash slurry (600–2500 $kg \cdot m^{-2} \cdot d^{-1}$) and alkaline coal slurry (350–970 $kg \cdot m^{-2} \cdot d^{-1}$), and very poor results using acid coal and alkaline ash leached slurries. On the basis of these results we decided to continue testing the fly ash – sulphuric acid system in more detail.

Relatively good results obtained by acid leaching of the ash in respect to uranium recovery (86–92%) in six hours at 30% solids in the slurry and encouraging filtration rates without flocculant were widely jeopardized by an enormous acid consumption. For this reason soon we tested the possibility of the use of an SO_2/air mixture to acidify the ash. In a simple leaching apparatus provided with an SO_2/air mixture inlet we obtained encouraging results, i.e. 90% uranium recovery, with no use of sulphuric acid. The efficiency of SO_2 absorption was low, about 30–40% [3].

4. PILOT-SCALE FLY ASH ACID LEACHING

The preliminary 1 kg batch tests already described were repeated using 3 and 20 kg batches. The preliminary results were reproduced. Finally, 500 kg batches were leached in pachuca-type agitators, slurry was vacuum filtered on a batch horizontal filter and uranium was separated from the leach liquor by means of ion-exchange resins in static bed columns. Waste materials were treated. The results are given in Table III.

It should be noted that no external heating was applied, but that, on the contrary, cooling during acid addition was required. Four to six hours leaching was sufficient and prolonging the time up to 12 hours did not increase the recovery at all. Acid addition over 700 kg per ton of ash was required to obtain a recovery of almost 90%. It should be noted that over 90% recovery was achieved using the ash produced at 1200–1300°C in the boiler. No refractory behaviour was observed as reported by many investigations [4, 5]. In contradiction to the laboratory results, in pilot-scale leaching no oxidant was required to obtain satisfactory oxidizing conditions. We explain this by oxidation by the air used for the agitation. The tests described showed similar results to previous laboratory testing with some differences already discussed. Once again high acid consumption was observed. Finally, it should be noted that during leaching tests rather severe corrosion of ordinary stainless steel [316] was observed and for this reason rubber-lined pachuca was used.

5. URANIUM RECOVERY FROM LEACH SLURRY

This section discusses further processing steps. Table IV shows the result of the filtration. The soluble losses were determined and were about 1% when 2 tons of wash water were used per ton of solids and 8% when 1.2 tons of water were used. In spite of a relatively good cake formation rate, the overall filterability is very poor. This is due to the high cake moisture content and consequently high wash water requirements in order to obtain adequate moisture displacement. Settling tests showed that only very dilute underflows could be obtained (15–25% solids) and settling rates were poor (500 $\mathrm{kg \cdot m^{-2} \cdot d^{-1}}$). In conclusion, the liquid-solid separation properties of the acid slurries were poor.

The leach liquor obtained by filtration and washing the filter cake had the composition shown in Table V.

The leach liquor is very dilute in respect to its uranium content and shows a rather high sulphate concentration. A high vanadium content as compared with the uranium concentration is observed. The low uranium concentration requires the use of solid ion-exchange resins. The pH value of the leach liquor was adjusted to 1.9–2.0 and the redox potential was decreased to 300 mV in order to reduce the vanadium. Three columns with resin were used for the extraction. We used anionic resin Amberlite IRA 410. The elution was done by chloride or nitrate solutions. The results are given in Tables VI and VII.

The final solutions were impure and were further purified by neutralization of the eluate by means of sodium hydroxide and then by decantation of water and redissolving of uranium with a sodium carbonate solution. Impurities were filtered off, the uranyl carbonate solution was acidified and ADU or uranium peroxide was precipitated. The yellowcake obtained met all specifications for technical concentrates.

The waste raffinate has been neutralized by means of ash (150 kg/m^3 of raffinate). The solution at pH 8 was effectively purified from Fe, AL and V (all less than 0.3 ppm) but soluble sulphates as Na, Mg, K were present in significant concentrations.

TABLE IV. RESULTS OF THE FILTRATION TESTING OF ACID SLURRY

1. Flocculated slurries (Separan NP10)	Flocculant addition (ppm)	480 ± 50	
	Cake depth (mm)	15 ± 5	
	Filterability[a] (kg·m^{-2}·h^{-1})	46	
	Moisture content (%)	52	
2. Non-flocculated slurries	Cake depth (mm)	15 ± 5	50 ± 10
	Filterability[a] (kg·m^{-2}·h^{-1})	43	70
	Moisture content (%)	52	52

[a] Filterability for the whole cycle including 2 t of wash water per ton of dry solids.

TABLE V. THE COMPOSITION OF THE LEACH LIQUOR

Component	Concentration (ppm)
U	30
Mg	6 300
Al	1 500
Fe	3 400
V	360
Mo	15
Na	1 050
Ca	175
SO_4^{2-}	60 000

TABLE VI. THE RESULTS OF EXTRACTION AND RE-EXTRACTION

Uranium recovery	98%
Resin loading	15 g U/L
Elution solution	0.6–1.2M Cl or NO_3 and 0.2M acid
Elution temperature	20–50°C

TABLE VII. ELUATE COMPOSITION

Component	*Concentration* (ppm)
U	2 000
SO_4	18 000
Cl	35 000
V	10
Mo	15
Fe	180
Mg	40
Al	35

6. USE OF SULPHUR DIOXIDE FOR LEACHING

As mentioned before, preliminary testing showed that SO_2 may be used for H_2SO_4 generation and in this way high acid additions can be avoided.

The generation of dilute sulphuric acid and ferric sulphate solutions for the leaching of different ores is well known in the literature [6]. An indirect way of using SO_2 from stack gases with the intermediate production of sulphuric acid has also been proposed [7] and recently the direct absorption and simultaneous oxidation by air were proposed [8].

In our case we concluded that only the successful use of SO_2 from stack gases can render uranium extraction from the ash attractive.

Small-scale tests were carried out with the scrubber column with a capacity of 1 kg/h fly ash using the stack gases from a real thermal power plant. The tests were planned to give enough information for pilot-scale design. The scrubber was 2 m high and had a diameter of 200 mm. Four sprays were installed and recirculating pumps supplied the slurry to the sprays. The basic parameters that influence the SO_2 absorption rate and efficiency were:

pH
Redox potential
SO_2/O_2 ratio
Residence time (velocity)
Ionic strength of the solution
Temperature
Gas/liquid ratio
Iron content and valence state.

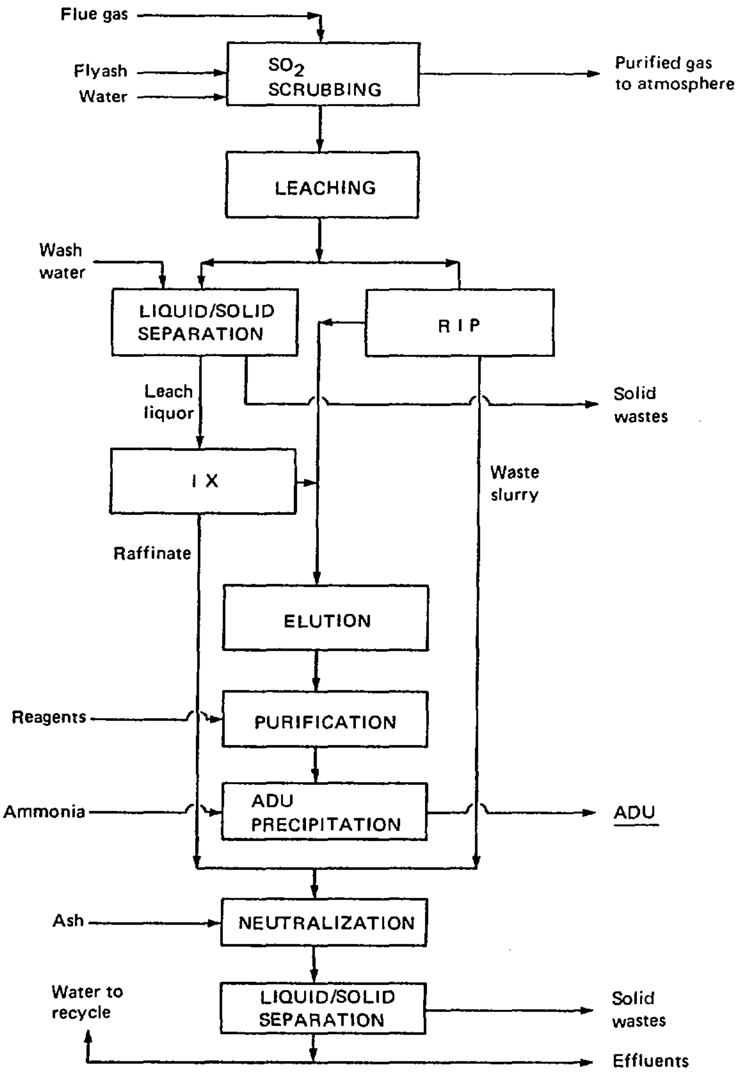

FIG.1. Flowsheet for uranium recovery from fly ash.

With the proper choice of these parameters it was possible to obtain the following conditions and results in respect to uranium recovery and SO_2 removal:

pH	1.5–2.5
E	300–500 mV
T	20–40°C
SO_2 absorption	40–95%
Uranium recovery	90–95%
Reseidence time	2–5 seconds
U concentration in solution	30 g/m^3

These data are comparable with the data published on SO_2 removal from stack gases using similar techniques [9, 10].

7. CONCLUSIONS

The results show that the ash produced in a conventional thermal power plant at more than 1200°C may be treated for uranium recovery. Flue gas containing SO_2 is used as a leaching reagent source, thus replacing sulphuric acid and oxidant. About 90% uranium recovery is achieved and 40 to 95% SO_2 is removed from the gas. Liquid-solid separation is considered as the difficult part of the process; large equipment would be required and dilute solutions produced. The resin-in-pulp process may overcome some difficulties. Resin loadings at the ion-exchange step are low due to very dilute solutions but recovery is acceptable. Elution may be done with a 0.6N NaCl solution (sea water) acidified with H_2SO_4. Eluates are impure; however, simple dissolving and selective precipitation with good recovery yields technically pure concentrates. Waste liquids may be neutralized by means of ash additions.

Direct operating costs would thus include above all the energy for gas pumping to overcome the pressure drop in the scrubbers and for slurry pumping, and then probably for filtration. The chemicals required involve ion-exchange resins and minor quantities of sulphuric acid, sodium hydroxide and ammonia for concentrate precipitation. The cost of the equipment would be significant but can be drastically reduced if scrubbers replace the electrostatic fly ash filters, as already shown in full-scale operation [9].

The results obtained justify continuing the investigations and the pilot plant is being designed at present with the flowsheet shown in Fig. 1.

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DISCUSSION

P. GASÓS: What kind of burner are you using for the combustion of the coal? The combustion temperature is usually about 1200°C. At this temperature insolubilization of the uranium is high and acid consumption during leaching will also be higher. Have you considered the possibility of using fluidized bed combustion? This requires lower temperatures and there is less insolubilization of uranium.

A.STERGARŠEK: We use ash produced in a commercial thermal power plant. We have no intention of investigating other combustion processes because we think it is very unlikely that they will be adopted by power plants. I am sure that in the future we will have more power plants of the existing conventional type, although they may be of different capacity. The temperature of combustion in these plants is high, but this is the product we have to treat.

W. FLÖTER: Your uranium recovery is very good. We have done similar tests and we did not get 90% recovery. On the other hand, the uranium content of the ash is very low so that you can only spend about 8 to 10 dollars to process one ton of ash. This is going to be difficult.

A. STERGARŠEK: Yes. Uranium by itself will not pay for the process. However, it we are to increase substantially the number and capacity of coal-fired power plants we will have enormous emissions of SO_2 that will be unacceptable. Environmental considerations are basic to our project. This is a means of reducing SO_2 emissions and of recovering uranium as a byproduct.

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URANIUM RECOVERY AS A BYPRODUCT FROM RADIOACTIVE COAL

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Abstract

URANIUM RECOVERY AS A BYPRODUCT FROM RADIOACTIVE COAL.

The coal in the Calaf area, Barcelona, deposit is characterized by its uranium content and high sulphur and ash grade. Reasonably assured resources are about 200 Mt of coal containing 40 000 t U_3O_8. Some studies have been carried out at a pilot plant aimed at both thermal exploitation and uranium recovery. Prior coal washing is necessary. Design and operation parameters for a heavy media separation plant have been determined. The fluid-bed combustion technology was selected, followed by uranium recovery from the ash. This combustion technology involves close temperature control and a very short residence time. In this way an acceptable uranium solubilization has been obtained. At the same time, limestone additions have been considered to keep most of the sulphur in the combustion bed and, in this way, reduce the environmental damage otherwise produced by SO_2 emissions. The uranium distribution in the fly ash and bed overflow has been studied to find out the necessary conditions for concentrating the uranium in a single product. Leaching conditions for uranium solubilization with sulphuric acid have been established. A flowsheet with the global benefit of this coal is included.

1. INTRODUCTION

Spain possesses some lignite deposits, and the presence of uranium in significant quantities has been detected in the Calaf basin, Barcelona. The resources of that area have been established by the Junta de Energía Nuclear (JEN) and other companies [1] as:

182 Mt of lignite with 40 000 t U_3O_8 (reasonably assured resources).
65 Mt of lignite with 12 000 t U_3O_8 (speculative resorces).

The approximate median composition of these lignites is as follows: ash 40%; organic coal 40%; volatile matter 30%; sulphur 8% – one half pyritic and the other half organic – with a heating value of 4000 kcal/kg.

According to the ASTM coal classification this lignite could be considered as a subbituminous A or B type. The median grade of uranium is 210 ppm U_3O_8, but its distribution is not uniform, there are some areas with 300–400 ppm U_3O_8 and others with very low uranium assays, therefore lignite and uranium mining will be directed to the uranium-rich bed.

In the sixties some laboratory studies were performed on uranium recovery, but both the low price of uranium at that time and the low quality of lignite showed that mining was not profitable and the programme was cancelled.

As a result of the petroleum crisis the situation has again changed and a new research programme has been initiated with a triple objective: uranium recovery, use of coal for energy and the environmental impact.

2. ESTABLISHING THE SITUATION

Direct leaching of lignite was left out of the laboratory studies carried out in the sixties [2] because of the very low efficiencies of uranium solubilization and the very bad quality of the pregnant solutions. In these lignites most of the uranium is associated with the humines [3], therefore it is necessary to destroy the coal structure to obtain uranium solubilization, which involves the simultaneous study of uranium production and the use of coal for power generation. In recent years coal technology has developed considerably in three main directions: fluidized-bed combustion (FBC); gasification to get a substitute natural gas; and liquefaction for obtaining synthetic fuels.

The FBC process is the most suitable for uranium and heat production for several reasons. It is possible to work at low temperature (800–850°C); very close temperature control is possible; and the residence time in the furnace is very short, all of which is of capital importance to uranium solubilization from ash. On the other hand, the FBC process allows an important part of sulphur to settle in the bed, by using limestone, thus reducing the environmental impact from SO_2 emission.

The general study scheme has been as follows: coal washing has been considered since in the Calaf basin the structure of lignite beds is formed by three or four levels of lignite stratified with marls and limestones. The lignite levels are no thicker than 1 m and in many cases are about 10–20 cm, so industrial mining would require extraction of the whole bed. It is obvious that a material extracted in this way demands a separation process to remove the lignite from the marls and limestones. After gangue (marls and limestone) separation, the lignite has about 40% of ash assay.

The FBC process has been selected in order to utilize the coal profit for power generation for the afore-mentioned reasons. The use of limestone in the combustion process has been considered and its incidence in relation to SO_2 emission and uranium recovery from ash has been evaluated.

The uranium is kept in the combustion products, overflow and fly ash, and its distribution and possible magnetic concentration have been studied, bearing in mind the association of uranium and iron oxides from pyrite.

Finally, uranium recovery from combustion and concentration products has been considered. Leaching with sulphuric acid and sodium carbonate has been studied both at atmospheric pressure and overpressure.

TABLE I. AVERAGE COMPOSITION OF LIGNITIFEROUS BED

Component	Weight (%)	Ash (%)	U_3O_8 (ppm)	Sulphur (%)	Heating value (kcal/kg)
Lignite	47.5	40	400	8.5	3900
Limestone	24.7		70	1.0	
Marl	27.8		45	5.0	

3. LIGNITIFEROUS BED WASHING

The concentration studies were carried out in the S.T.M. Laboratory focusing them in two ways [4]:

(a) Conventional washability tests to establish the best conditions to separate lignite from marls and limestones;

(b) Tests with various concentration processes in order to find a possible lignite enrichment process after marls and limestones have been removed.

Finally, the conditions established under (a) were checked at the pilot-plant level.

For these studies a sample was used whose average composition – considering all the levels that make the bed – was that given in Table I.

3.1. Washability studies

Some laboratory studies were made with the classic method to determine the coal washability curves [5, 6]; they were also made in relation to uranium.

The criterion for establishing the best separation density was to obtain the maximum uranium recovery while avoiding that the ash assay in the float surpassed that of lignite free of marls and limestones. The density selected was 2.0 kg/m^3.

The pilot-plant tests were carried out with $-\frac{1}{2}$ in crushed material and three different methods were used according to size:

(a) Cone separator (250 kg/h); dense-medium: magnetite suspension 2.0 kg/m^3 for (-12.5×1.7) mm

(b) Cyclone (4 m^3/h); dense-medium: magnetite suspension 1.72 kg/m^3 (equivalent to 1.93 kg/m^3 in a static method [7]) for (-1.7×0.84) mm

(c) Water-cyclone (5 m^3/h) for (-840×75) μm.

The laboratory tests were confirmed by the results from the pilot plant. However, these were really a little lower, due to the deterioration of the dense-medium by marls. Results are given in Table II.

TABLE II. COAL WASHABILITY STUDIES. PILOT-PLANT RESULTS

Product	Weight (%)	Ash (%)	U_3O_8 (ppm)	Sulphur (%)	Heating value (kcal/kg)	U_3O_8 recovery[a] (%)
Float	44	46	340	7.5	3600	69.1
Sink[b]	56	80	120	4.1		30.9

[a] The recovery values include the uranium content of marl and limestone (~15% total U_3O_8) that is not recoverable with the float.

[b] Fraction −75 μm included (86% ash, 12 ppm U_3O_8, 13.3% weight).

TABLE III. SCALE-UP OF THE PILOT-PLANT RESULTS

Product	Weight (%)	Ash (%)	U_3O_8 (ppm)	U_3O_8 recovery (%)	Coal recovery[a] (%)
Float	50	47	340	89.5	88.5
Sink	50	83	100	10.5	11.5

[a] Referred to the uranium in the lignite.

3.2. Enrichment studies

Mineralogical studies [8] showed that lignite free of marls and limestones is very difficult to enrich, because its principal impurities are very fine: pyrite <15 μm and sericitic argillaceous <30 μm. However, some concentration tests with lignite ground to −53 μm have already been performed. Both microcyclons and a wet high-intensity magnetic separator (WHIMS) were ineffective.

3.3. Scale-up to the industrial level

The washing pilot-plant results will improve in an industrial plant because the fine particle ratio will be lower than in the pilot plant and, therefore, the influence of those size categories that produced low results will be less.

According to these results, with run of the mine material crushed to −120 mm and processed by:

'Drew-boy' separator for the −6 mm category (75% by weight)

Dense-medium cyclone for the (−6 X 0.6) mm category (19% by weight)

Water cyclone for −0.6 mm category (6% by weight)

the figures given in Table III would be obtained.

4. COMBUSTION

4.1. Description of the pilot-plant scale AFBC facilities

The experimental facility is an atmospheric fluidized-bed unit made up of:

(a) Coal and limestone feed system. The feeding is independently made by means of two screw feeders with variable speed. The feeds fall down into the bed near to the distribution plate.

(b) Bed solids drain system. The drain line is provided through the bottom of the combustor. Drainage is continuous.

(c) Cooling system. The cooling is carried out with water or air by means of several tubes inside the bed or the cooling jacket.

(d) Combustor. The combustor shell consists of a 100 mm refractory stainless steel pipe, which could be changed for another ceramic. The air distribution plate is assembled in the lower part with about 20 machined bubble caps. Several measurement and control elements are also included.

(e) Gas exhaust cleaning system. Fly ash removal is carried out by cyclones and a sinterized stainless steel bag filter. The filter efficiency is higher than 99% for particles of less than 1 μm.

(f) Instrumentation and controls. The pressure and temperature measurements are made by manometers and K-type thermocouples and they are continuously monitored and printed on paper recorders. The thermocouples, 23 in all, are assembled so that it is possible to know the lengthwise temperature profile of the installation. There are temperature measurement points in front of and behind the distribution plate, and at 8, 20 and 40 cm over the plate, etc. The basic absolute pressures and pressure drops are measured in the combustor, filter box and rotameter and orifice plates for air. The screw feeder revolutions are also recorded. O_2 and SO_2 are continuously analysed in the flue gas. The oxygen concentration is detected in a paramagnetic analyser and the SO_2 by a fluorescent analyser.

The combustion air flow rate, the cooling air flow rate and the coal and limestone feed rates are manually controlled.

4.2. Process and variables

4.2.1. Limestone use

The lignite combustion can be performed with limestone in order to keep the SO_2 in situ, and so avoid the environmental impact.

The fundamental equations are:

$$\text{Coal} + O_2 \rightarrow CO_2 + SO_2 + Q_1$$

$$CaCO_3 \rightarrow CO_2 + CaO - Q_2$$

$$CaO + \frac{1}{2} O_2 + CO_2 \rightarrow CaSO_4 + Q_3$$

The process temperature becomes determined by its physico-chemistry at about 850°C.

In this way, an important part of sulphur is kept in the bed, but the ash has a very high CaO content, because the sulphur grade in the lignite is high too, and it is necessary to use very high Ca/S ratios. The uranium grade in the ash and the process thermic efficiency decrease because of the limestone descomposition reaction and the very low use efficiency of limestone.

4.2.2. Direct combustion of lignite

An inert product is not necessary (except in startup) to maintain the process fluidodynamic conditions in the combustor because of the high ash grade of the lignite.

In this case the problems due to the use of limestone do not exist; however, auxiliary equipment to capture the SO_2 is necessary. For this purpose a commercial installation could be used and the possibility of producing sulphuric acid from the SO_2 could also be considered.

TABLE IV. COMBUSTION RESULTS

	With limestones		With limestone	
	Overflow	Fly ash	Overflow	Fly ash
Combustion temperature (°C)	850		850	
Fluidization velocity (°C)	150		150	
Lignite feed (kg/h)	4.8		5.6	
Ca/S ratio (molar)	3.9		–	
Feed/products ratio (weight)	1.27		2.13	
Sulphur capture (%)	~90		–	
Limestone efficiency	29		–	
O_2 in flue gas (%)	3.2		3.1	
SO_2 in flue gas (ppm)	400		>8000	
Weight distribution (%)	71.5	28.5	65.5	34.5
Uranium content (g U_3O_8/t)	120	560	300	1540
Uranium distribution (%)	35.0	65.0	27.0	73.0
Sulphur content (%)	4.7	3.7	5.7	3.3

4.3. Combustion studies

The tests were intended to provide information on the sulphur retention, combustion temperature, products distribution, etc. Table IV shows some data that can be considered typical for some tests made with and without limestone.

4.3.1. Tests with limestone

For 90% sulphur capture Ca/S molar ratios near 4 are necessary, but above this value the limestone efficiency decreases quickly, requiring an important increase in the Ca/S ratio to obtain only small increments in the sulphur capture, so for 95% sulphur capture the Ca/S molar ratio must be about 10.

The limestone efficiency is very low, about 30% for the best limestones and for a 90% sulphur capture.

The uranium grade of the ash is low, 500–600 ppm, because of the CaO and $CaSO_4$ content.

4.3.2. Tests without limestone

In this case the flue gas SO_2 concentration is very high, more than 8000 ppm, and this involves an auxiliary facility to capture the SO_2.

The uranium assay of the ash is about 1540 ppm U_3O_8 and, sometimes, 3000 ppm has been obtained from the finest ash.

5. PHYSICAL CONCENTRATION OF COMBUSTION PRODUCTS

Although concentration studies were carried out on the products from combustion with and without limestone, the latter will be mainly considered, because the great alkaline materials content of the former and their high acid consumption make it more interesting to burn without limestone addition and to recover the potential sulphuric acid from the flue gases. In such a way, one of the advantages of FBC is discarded, i.e. the possibility of keeping the sulphur in the bed. However, the use of this type of combustor is essential for the recovery of the uranium as it allows a tight control of the combustion temperature and a short residence time of the particles, both aspects being extremely important to avoid the insolubilization of the uranium.

Combustion products are divided in two types, bed overflow and fly ash, the characteristics of which are showed in Table IV. The uranium assay of most of these products is rather low, and their concentration was tried in order to obtain a better product to feed to the leaching stage. An attempt was made to take advantage of the greater uranium assay of finer sizes and of the iron-uranium

TABLE V. PHYSICAL CONCENTRATION OF THE OVERFLOW:
Combustion without limestone.

Product	Weight (%)	U_3O_8 (ppm)	U_3O_8 recovery (%)
Concentrate	23	660	46
Waste	77	225	54

association in the ash, by means of its magnetic properties derived from the high pyrite content of the original lignite, which transforms to iron oxides.

In spite of the low uranium assay (300 ppm) in the overflow of combustion with limestone, it amounts to 27% of the uranium fed to the combustor, so that several combined treatments of sizing and WHIMS were tried using the above-mentioned properties of the combustion products with unsuccessful results. Since the overflow contains a substantial proportion of coarse particles, the size reduction of this fraction was considered in order to improve the separation, but this was also unseccessful as there was no differential enrichment but rather a homogenization of the uranium in the various fractions.

Studies with the overflow show that simple sizing was more interesting than its combination with WHIMS operation. For the overflow from the combustion without limestone the best technical results were obtained with a sizing through 200 μm. The products obtained are shown in Table V.

Such a low U_3O_8 recovery and uranium assay in the concentrate (46% and 660 ppm, 78% and 405 ppm in the extreme cases) made the incorporation of the overflow into the rest of combustion products uneconomic, at least at present uranium prices.

Applying the afore-mentioned properties of combustion products to the fly ash from combustion without limestone, the fraction -20 μm was considered as a concentrate, while the $+20$ μm (51.2% by weight of the fly ash) was treated by a WHIMS installation at 1 tesla, the magnetic product being considered as a concentrate and the non-magnetic one as a waste.

In such a way a concentrate with 61% by weight of the fly ash and a uranium assay of 2100 g U_3O_8/t was obtained, with a recovery of 83% of the total uranium in the fly ash.

These separation and concentration processes are expensive, especially at these small particle sizes. Besides, they involve 17% uranium losses and the uranium assay increase in the concentrate is rather small; therefore, these separation and concentration steps were disregarded.

Consequently, only the fly ash from combustion without limestone will be leached for uranium recovery. It represents about 34.5% by weight of all combustion products, with a grade of 1540 g U_3O_8/t, and the uranium recovery is 73% of the total uranium fed to the combustor.

6. URANIUM RECOVERY FROM ASH

Uranium leaching from the combustion products was studied and also from several fractions obtained through various physical concentration processes but, in this case, the tests were abandoned early because sensitive increases in uranium solubilization did not result. These studies showed that uranium solubilization by carbonate-bicarbonate solutions was almost nil in ash from combustion processes without limestone, even at high pressure and temperature.

In ash from the combustion process with limestone the leaching was not considered because of the high anhydrite and lime content.

A very high sulphuric acid dose is necessary for an acceptable uranium solubilization efficiency; this variable and temperature are the most important variables in leaching. Also, the combustion temperature has a great influence on uranium solubilization. In the FBC process the influence of the combustion temperature on leaching efficiency is not very great until 850°C but over 900°C some vitrification processes begin and uranium solubilization quickly decreases.

The sulphuric acid consumption is, in all cases, very high, and the minimum dose necessary is in the range of 300–400 kg/t. At this dose the residual acidity in leaching liquors is about 10–15 g H_2SO_4/L, and the uranium solubilization is nearly 80–85%. Under these conditions, uranium recovery from the spent bed – in processes with or without limestone – is left out, because the acid cost is higher than the value of the uranium, uranium grades being in the range 120–300 g U_3O_8/t. A similar situation occurs with limestone combustion fly ash, whose uranium grade is 560 g U_3O_8/t and the minimum acid dose is 350 kg H_2SO_4/t.

The only product that can be profitably treated is the fly ash from combustion without limestone. Its uranium grade is rather high ($>$1500 g U_3O_8/t) and it is possible to get uranium solubilizations over 80%, with the afore-mentioned acid dose. Besides, the uranium content in these fly ashes amounts to over 70% of total uranium fed to the combustor.

The most important mineralogical components in the fly ash are quartz, sericite, argil, anhydrite, haematite-goethite and micas. Uranium is dispersed and no microscopic discrete mineral can be detected. There is an iron-uranium association, which was considered in order to concentrate the uranium via magnetic separation, but the results were not positive because the iron minerals from roasted pyrite are very fine, less than 15 μm.

The principal metallic components are as follows: Al (6–8%); Fe (8–9%); Mo (0.015–0.020%); V (0.010–0.015%); Ti (0.4–0.5%) and U_3O_8 ($\cong$0.15%).

TABLE VI. LEACHING RESULTS

Component	Concentration (g/L)	Solubilization (%)
U_3O_8	0.635	82.5
V	0.060	>90
Al	3.5	~10
Mo	0.008	<10
Fe_t	9.7	
Fe^{2+}	1.2	
SiO_2	1.2	
SO_4^{2-}	110	
H_2SO_4	7.5	
Redox potential (mV)	560	
Residue weight (%)	84.2	
Residue assay (U_3O_8 ppm)	320	

The possibility of aluminium recovery was disregarded because the aluminium grade was too low and the iron assay too high. Only vanadium could be considered as a byproduct.

The best conditions for fly ash leaching from combustion processes without limestone addition are as follows:

Acid dose (kg/t)	350
Temperature (°C)	80
Leaching time (h)	12
Liquid/solid ratio	2

No oxidant addition is necessary because the redox potential of the leaching liquors is high enough (>550 mV) and most of the iron is in the ferric state.

For the above-mentioned conditions, the leaching results are shown in Table VI.

Uranium solubilization is not very high but the increments from more drastic leaching conditions do not balance the additional reagent costs. Furthermore, the iron, aluminium, molybdenum and sulphates contents of the solution are raised. Vanadium solubilization is high, over 90%, and its concentration in the pregnant liquor is a tenth of that of uranium. This point should be considered in the extraction diagram.

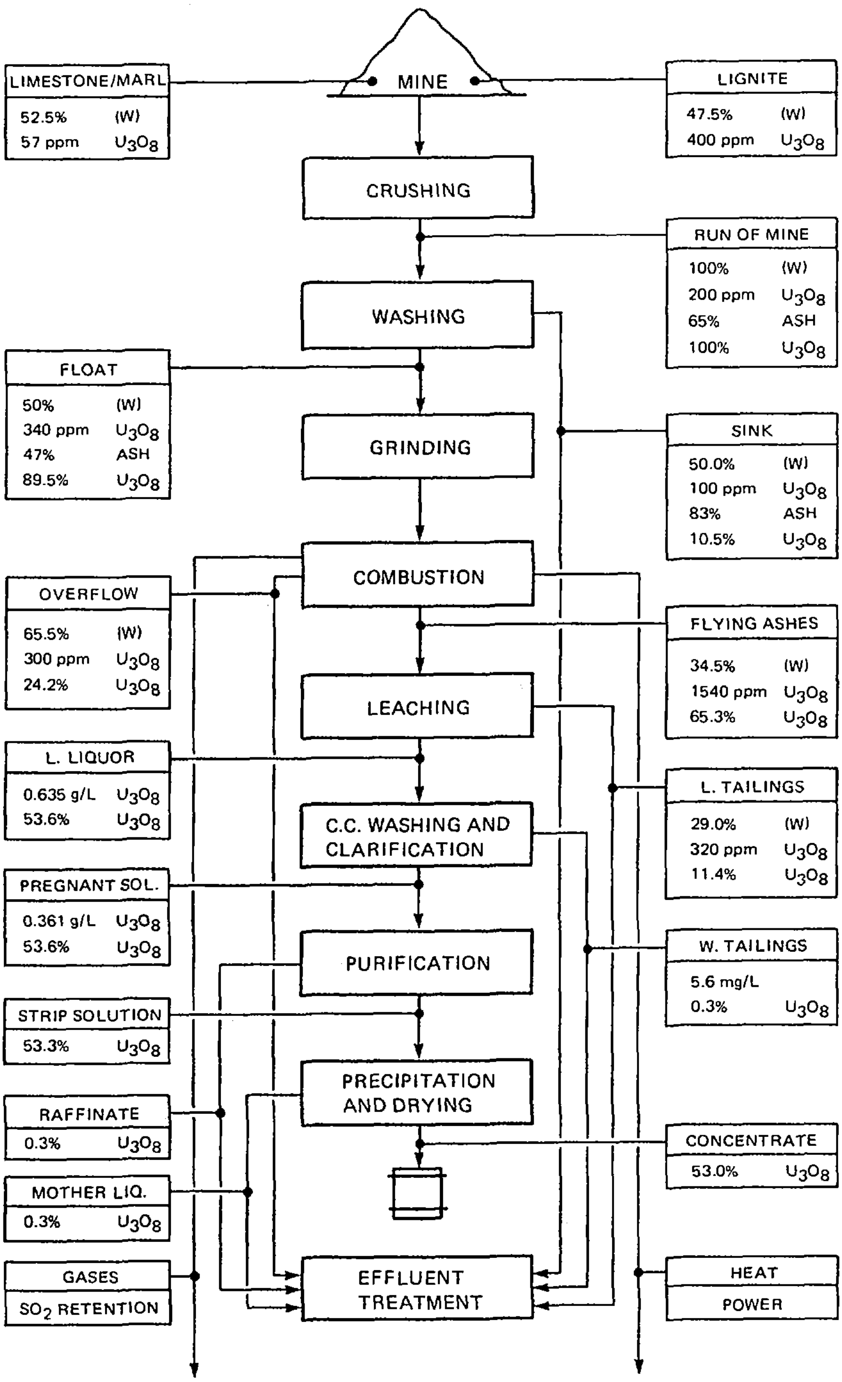

FIG. 1. General scheme of uranium recovery.

TABLE VII. PREGNANT LIQUOR COMPOSITION

Component	Concentration (g/L)
U_3O_8	0.361
Fe_t	5.5
V	0.039
Mo	0.005
Al	2.0
SiO_2	0.68
SO_4^{2-}	62.6
H_2O_4	4.3

The settling and thickening characteristics are poorer than those of conventional uranium ores. A 1 $m^2 \cdot t^{-1} \cdot d^{-1}$ unit area is necessary and a 50 wt% solid concentration is got in the underflow for a dose of 120 g/t synthetic flocculant.

A five-stage countercurrent thickener arrangement and using 2.5 m^3/h washing ratio results in an efficiency of over 99.5%. The composition of the pregnant solution is given in Table VII.

From these results the development of a demonstration plant with a feed of 1000 kg/h lignite has been envisaged. Its general scheme is shown in Fig.1.

The aim of this plant will be fundamentally to check the results attained and also to study several parameters such as fluidization velocity and feed size that could not be studied in our current pilot plant. At the same time the extraction-reextraction stage will be studied in a cyclic manner, in order to determine the possible accumulative effects of the presence of silica and molybdenum. The need for a soda washing stage for this element will also be studied.

The influence on uranium recovery on lignite feed coming from different beds in the basin will be determined.

An evaluation of production costs has been made [9] with the following basis: (a) capacity 1000 t/d of fly ash; (b) the ash has no value, as it is considered a tailing from the combustion process; (c) the mining costs are put down to the power production plant; (d) crushing and grinding are not necessary because the fly ash size is very fine; (e) the heating for the leaching process is got from sulphuric and dilution heat and from the ash. Under these premises the transformation cost has been evaluated as US $56/kg U.

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DISCUSSION

Z. DOGAN: The lignites you are treating contain 8% sulphur, half of which is pyritic. Did you try to eliminate this pyritic sulphur by physical methods?

P. GASÓS: We tried wet high-intensity magnetic separation, flotation and microcycloning. None of these methods were successful so we abandoned this approach and decided to use fluidized bed combustion. At first we tried to settle the sulphur in the bed but the consumption of limestone was very high and now we are burning the coal directly in the fluidized bed.

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MISE AU POINT ET QUALIFICATION D'UN ECHANGEUR MINERAL A BASE DE TITANE POUR L'EXTRACTION DE L'URANIUM DES EAUX NATURELLES

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Abstract–Résumé

DEVELOPMENT AND TESTING OF A TITANIUM-BASED INORGANIC ION EXCHANGER FOR EXTRACTING URANIUM FROM NATURAL WATERS.

Since uranium concentrations present in various kinds of natural water – especially sea water – constitute considerable potential reserves, it seemed that it would be of interest to study it and how they could be extracted. An inorganic ion exchanger based on hydrated titanium oxide was developed in this connection. The circumstances of its fabrication and its main properties are described. As a first step, the product was tested in sea water: an experimental system operating at a rate of 100 L/h was run continuously for three months in the Mediterranean Sea near Marseilles. The most important results are described. Fixation efficiencies are estimated at 30%. The saturation capacity is above 200 pp10^6. Elution is performed using an ammonium carbonate solution. In the second stage, the product was used to purify mine drainage water, which has a uranium content of 2–7 mg/L, and to recover uranium from river water with a uranium content of about 15 pp10^9. The results obtained in both cases are given. The paper concludes with a brief economic evaluation of the above processes.

MISE AU POINT ET QUALIFICATION D'UN ECHANGEUR MINERAL A BASE DE TITANE POUR L'EXTRACTION DE L'URANIUM DES EAUX NATURELLES.

Compte tenu de l'importance des réserves potentielles représentées par les concentrations d'uranium dans un certain nombre d'eaux naturelles, en particulier dans l'eau de mer, il est apparu intéressant d'examiner les conditions de leur extraction. Dans ce contexte, un échangeur minéral à base d'oxyde de titane hydraté a été mis au point. Les conditions de sa préparation et de ses principales propriétés sont exposées. Ce produit a été dans un premier temps testé sur l'eau de mer: une installation expérimentale fonctionnant au débit de 100 L/h a été exploitée pendant trois mois en continu sur l'eau de la Méditerranée près de Marseille. Les principaux résultats sont exposés. Les rendements de fixation sont estimés à 30%. La capacité de saturation est supérieure à 200 pp10^6. L'élution est effectuée par une solution de carbonate d'ammonium. Dans un second temps, le même produit a été appliqué à la purification d'eaux d'exhaure de mines, dont la teneur en uranium est de 2 à 7 mg/L, et à la récupération d'uranium d'eaux de rivière dont la teneur est d'environ 15 pp10^9. Dans les deux cas les résultats obtenus sont exposés. Une évaluation économique sommaire de ces procédés termine ce mémoire.

Compte tenu des énormes réserves potentielles en uranium dans l'eau de mer, il a paru intéressant au Commissariat à l'énergie atomique de définir les conditions technico-économiques de son extraction.

Après avoir effectué une revue bibliographique, il est apparu que les adsorbants minéraux les plus efficaces étaient ceux à base de titane. Les produits commercialisés essayés ne s'étant pas révélés performants, nous avons été conduits à préparer un oxyde de titane hydraté (OTH) adapté à nos besoins.

Après définition des conditions de fabrication, nous avons construit une petite unité pilote de fabrication et essayé le produit obtenu. Les résultats ont montré qu'il est techniquement possible d'extraire l'uranium de l'eau de mer et d'autres eaux plus simples grâce à ce type de produit.

1. PREPARATION DE L'OTH; SES CARACTERISTIQUES

L'oxyde de titane hydraté (OTH) est préparé à partir de tétrachlorure de titane technique que l'on précipite par de l'ammoniaque dilué. Le produit le plus performant a été obtenu dans les conditions suivantes : pH de fin de précipitation : 5,5; température : 45°C; mûrissement : 3 heures à 45°C; filtration puis lavage à l'eau permutée. Le séchage du gel est effectué à température ambiante sous courant d'air.

On obtient alors une masse translucide apparemment vitreuse qui est en fait constituée de microcristaux d'anatase (TiO_2). Lorsque ce produit est plongé dans l'eau, il éclate en petits grains dont la granulométrie dépend essentiellement des conditions de sèchage. Ce sont ces grains qui sont utilisés en colonne.

L'OTH est fabriqué à l'aide d'un petit pilote dont le schéma de procédé est représenté sur la figure 1.

Les granules d'OTH ainsi obtenus ont les caractéristiques suivantes (fractions granulométriques):

- 3% < 0,25 mm,
- 21% de 0,25 à 0,5 mm,
- 70% de 0,5 à 1 mm,
- 6% supérieurs à 1 mm.

La fraction inférieure à 0,25 mm sera écartée pour la constitution des colonnes d'extraction.

La surface spécifique du produit, mesurée par la méthode BET à l'azote, dépend des conditions de précipitation et de mûrissement. Le maximum est de 300 m^2/g pour 4 heures de mûrissement, le minimum de 55 m^2/g sans mûrissement. Le produit que nous avons utilisé a une surface de 190 m^2/g. En fait la surface spécifique ne semble pas être un paramètre prépondérant pour la fixation de l'uranium.

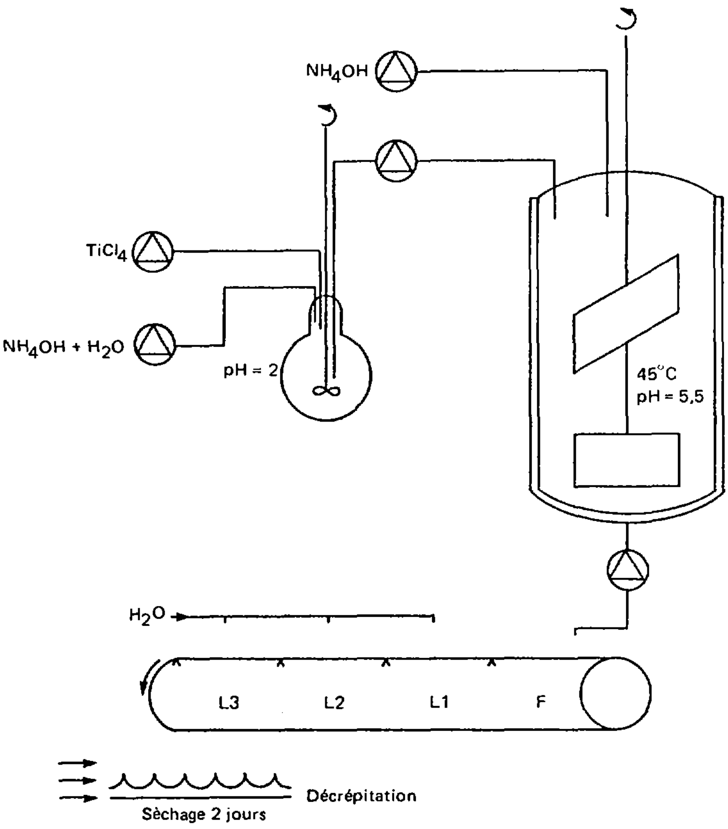


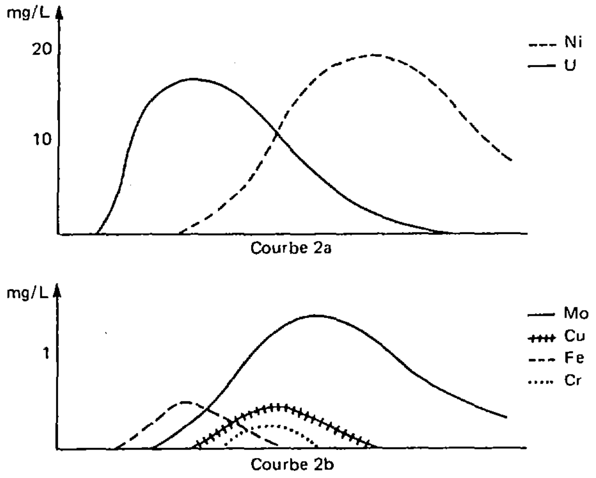
FIG.1. Schéma du procédé de fabrication de l'OTH.

La densité apparente du produit est très proche de 1, la densité réelle est de 2,4.

On peut considérer que l'OTH est insoluble dans l'eau de mer. En effet, après passage de plus de 200 000 volumes de lit en laboratoire, la perte en titane est inférieure à 0,1%. Par contre, l'OTH n'est pas stable en dessous de pH 1,5, ce qui proscrit toute élution par un acide fort. La solubilité en milieu fortement basique est en revanche très faible.

La capacité maximale d'adsorption pour l'uranium à l'équilibre dans l'eau de mer est de l'ordre de 350 μg/g. En colonne, la capacité maximale atteinte a été de 270 μg/g.

L'OTH n'étant pas stable en dessous de pH 1,5, il est préférable d'éluer par le carbonate d'ammonium 1M. Ce type d'élution a cependant un inconvénient majeur: la précipitation des carbonates alcalino-terreux, principalement du



Courbe 2a

Courbe 2b

FIG.2. Elution des différents éléments.

magnésium dans le cas de l'eau de mer, autour des grains. Ceci conduit, après un certain nombre de cycles, à un colmatage des colonnes par cimentation. Il est toutefois possible de régénérer le produit par un acide faible concentré (acétique, formique ou oxalique). On élimine ainsi totalement les alcalino-terreux et le fer mais ce mode d'élution ne peut convenir pour l'uranium qui n'est pratiquement pas élué.

2. ESSAIS EN EAU DE MER

Les essais ont été conduits sur un petit pilote en mer Méditerranée près de Marseille. Plusieurs colonnes de différentes hauteurs de lit étaient en place. Nous donnerons ci-dessous les résultats obtenus dans le cas le plus favorable (hauteur de lit minimale).

La température moyenne de l'eau pendant les essais a été de 21°C, le débit spécifique étant de 3 $m^3/m^2/h$. Avant passage sur les colonnes, l'eau de mer était filtrée à 10 μm pour éviter les colmatages.

2.1. Résultats

Il est apparu que l'uranium se fixe principalement sur les deux premiers centimètres du lit : seule zone où l'on peut atteindre la saturation. Lors de nos essais, la hauteur minimale étant de 3 cm, nous avons fixé dans ce cas 69 μg U/g d'adsorbant soit environ 177 μg/g Ti avec un rendement moyen de 27%.

Le rendement de fixation instantané de 100% au départ chute très rapidement aux environs de 30%.

Après lavage de la colonne à contre-courant pour éliminer l'excès d'eau de mer, on fait passer une solution de carbonate d'ammonium 1M au débit de 10 V/V·h. La figure 2 montre en 2a la courbe d'élution de l'oxyde de titane hydraté. On peut voir que la teneur maximale de l'éluat est de 17 mg/L, la valeur moyenne, hors tête et queue d'élution, étant de 9 mg/L. On a donc un facteur de concentration de l'ordre de 3000.

Les courbes 2a et 2b de la figure 2 montrent également l'élution des autres métaux.

On voit que seul le fer s'élue en même temps que l'uranium, les autres éléments ont une élution retardée. Les valeurs moyennes des concentrations dans les éluats sont les suivantes (en mg/L):

- Cr : 0,017
- Fe : 0,07
- Co : 0,11
- Zn : 0,20
- Cu : 0,23
- Mo : 0,80
- Ni : 11,0

L'eau de mer utilisée pour les essais a une teneur en nickel de 2,1 μg/L. On a donc pour le nickel un rendement de fixation-élution de 52%.

2.2. Reconcentration

La solution d'élution ayant une teneur en uranium de 9 mg/L, un enrichissement en uranium est indispensable pour disposer d'une solution permettant d'obtenir un oxyde d'uranium. Pour cela nous avons choisi les résines échangeuses d'ions. Après essai de différentes résines anioniques et chélatantes (amidoxime, aminophosphorique, iminodiacétique), ce sont les résines anioniques qui ont été retenues. Cependant, pour obtenir un rendement de fixation correct, il est nécessaire d'éliminer de la solution une partie du carbonate d'ammonium. Le procédé le plus simple est la distillation qui permet de récupérer le carbonate d'ammonium pour un recyclage.

Le rendement de fixation sur la résine est de 100% pour une solution à 0,15M.

L'élution de la résine est effectuée par un mélange de nitrate de sodium 1M et d'hydrogénocarbonate de sodium 0,05M. La teneur moyenne de l'éluat obtenu est de 3,5 g U/L ce qui représente un facteur de concentration de 10^6 par rapport à l'eau de mer.

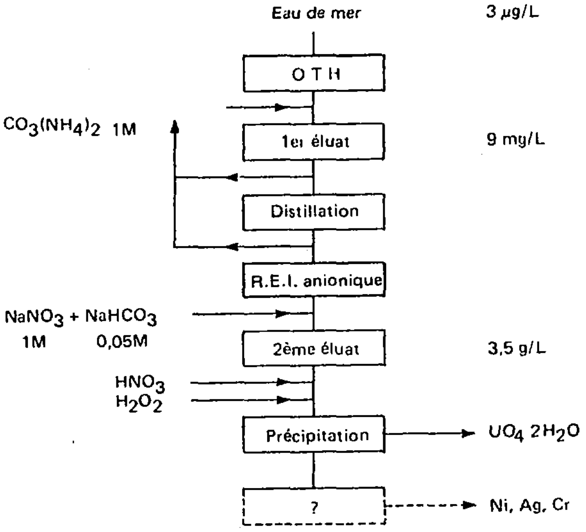


FIG.3. Schéma général du procédé eau de mer.

Dans l'éluat, on retrouve également les autres éléments. Le nickel n'est pas reconcentré et reste à une teneur d'environ 10 mg/L. Le molybdène est présent à 4 mg/L, le chrome et le cuivre à 1 mg/L. Nous avons noté la présence d'argent qui n'avait pas été détecté dans la solution d'entrée; la teneur reste tout de même très faible (<0,1 mg/L).

2.3. Obtention d'un oxyde d'uranium

Nous avons employé la méthode de précipitation par H_2O_2 qui présente l'avantage d'être très sélective. Pour cela, il faut ramener le pH entre 1,5 et 2. La réaction suivante est complète à 50°C:

$$UO_2^{2+} + H_2O_2 + 2\ H_2O \qquad UO_4,\ 2\ H_2O + H_3O^+$$

Par ce procédé schématisé sur la figure 3, nous avons pu obtenir 250 mg d'uranium sous forme de peroxyde.

2.4. Evaluation économique

Si le prix de revient de l'OHT est relativement raisonnable (de l'ordre de 35 FF/kg) il n'en est pas de même du prix de revient de l'uranium ainsi produit.

Une rapide estimation, considérant tous les paramètres optimaux réunis (pas de pompage, pas de perte de produit, pas de régénération), nous a conduits à un prix de revient supérieur à 18 500 FF/kg U pour 100 tonnes U/an (1800 $/lb U_3O_8).

Or nous sommes placés dans des conditions idéales. Ceci montre que, même au cas où les prix de l'uranium croîtraient de façon importante, ce type de procédé a très peu de chances de voir le jour.

3. EXTRACTION DE L'URANIUM DES EAUX D'EXHAURE DE MINES

Les eaux d'exhaure ont une charge saline faible comparativement à l'eau de mer, et une teneur en uranium environ 1000 fois plus forte. D'autre part, en France, les normes de rejet actuelles étant de 1,8 mg U/L, la plupart des eaux d'exhaure ont besoin d'être traitées.

Dans la majorité des cas, l'épuration peut se faire avec des résines échangeuses d'ions qui donnent d'excellents résultats. Dans le cas que nous avons étudié, l'eau d'exhaure est fortement chargée en chlorures (plus de 1 g/L), et les essais avec des résines échangeuses d'ions ont donné des résultats décevants.

Après une étude poussée en laboratoire, nous avons installé une unité pilote de 1 m³/h comprenant trois colonnes de 70 kg chacune. La figure 4 représente schématiquement l'installation. L'eau d'exhaure passe à un débit spécifique de 15 V/V·h.

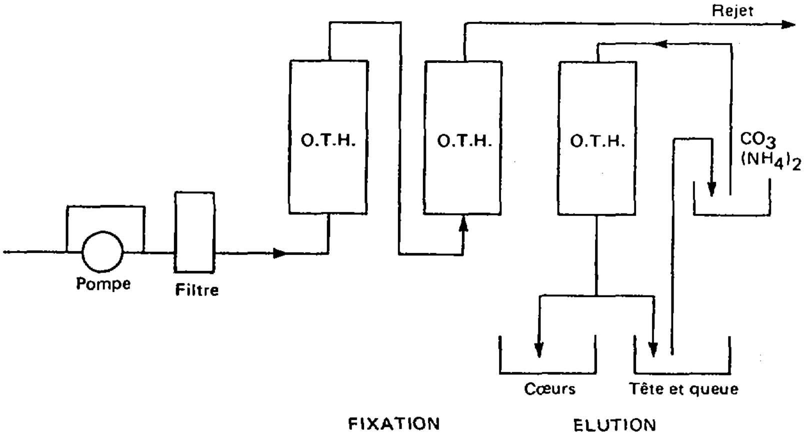


FIG. 4. Schéma de l'installation pilote de récupération de l'uranium dans les eaux d'exhaure.

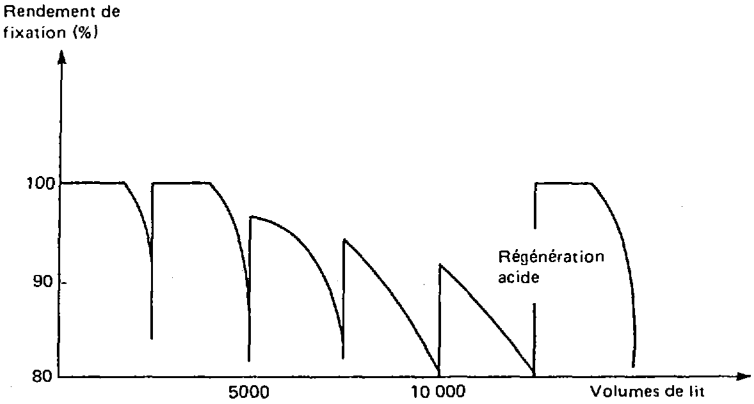


FIG.5. Eaux d'exhaure: évolution du rendement de fixation pour des cycles successifs.

3.1. Résultats

L'évolution du rendement de fixation pour une série de cycles successifs est représentée sur la figure 5.

Le facteur moyen d'épuration est de 94%, la teneur moyenne d'entrée ayant varié de 2 à 7,6 mg/L avec une moyenne de 3,72 mg/L. Le facteur d'épuration diminue avec le nombre de cycles (environ 2% par cycle). Ceci est dû principalement à la précipitation de carbonate de calcium lors de l'élution.

3.2. Elution

L'élution se fait dans les mêmes conditions que pour l'eau de mer, mais les rendements ne sont pas excellents puisqu'ils sont en moyenne de 86%. Il semble là encore que ce soit la précipitation de carbonates alcalino-terreux qui en est la cause.

La teneur moyenne des éluats est de 750 mg U/L. Cette teneur assez faible est due à une cinétique d'élution très lente. A une vitesse d'élution de 0,25 V/V·h, on peut obtenir des éluats à 1 g/L. A 50°C, les éluats ont une teneur de 3 g/L.

Malgré certaines difficultés d'élution, les résultats obtenus sur cette eau d'exhaure sont meilleurs que ceux des résines classiques. Même si le prix de revient de l'uranium ainsi produit est très supérieur à celui des traitements de minerais classiques, ce procédé est viable car l'épuration est nécessaire.

Nous ajouterons que l'OTH a été également testé en laboratoire sur des eaux d'exhaure ne contenant pas de chlorures et très peu de calcium. Nous avons obtenu un rendement global fixation-élution de 93%. Cependant, dans ce cas, l'OHT ne peut concurrencer les résines échangeuses d'ions classiques à cause de son prix de revient et d'un procédé plus délicat.

Il reste que dans certains cas particuliers et difficiles, ce produit peut être tout à fait compétitif.

4. EXTRACTION DE L'URANIUM DES EAUX DE RIVIERES

Si les grands fleuves contiennent environ 1 μg U/L, certaines rivières peuvent en contenir naturellement 10 μg/L. D'autre part, les teneurs peuvent être plus importantes dans les régions minières (en aval des mines à cause des eaux d'exhaure).

Pour des raisons de politique écologique, nous avons recherché et découvert une rivière éloignée de tout site minier ou nucléaire contenant environ 15 μg U/L. Nous avons installé récemment sur cette rivière une unité pilote comprenant trois colonnes de 5 kg d'OTH, placées en parallèle, et dans lesquelles percole l'eau à des débits variant de 10 à 100 V/V·h.

Il est naturellement prématuré de donner les résultats de cette expérimentation mais des études de laboratoire effectuées sur une eau similaire, bien que légèrement plus chargée en uranium, laissent espérer un rendement global de l'ordre de 50 à 60%.

5. CONCLUSION

Les études faites sur la récupération de l'uranium des eaux naturelles ont permis de dégager les points énumérés ci-après.

L'extraction de l'uranium de l'eau de mer est techniquement possible, mais semble difficile a envisager car le prix de revient est prohibitif. Il est probable que ce procédé sera abandonné par tout le monde, du moins avec les procédés à base d'adsorbants minéraux.

L'extraction de l'uranium des eaux de rivières ne peut fournir des quantités aussi importantes que l'eau de mer, mais le prix de revient de l'uranium produit devrait être 5 à 6 fois plus faible, et de ce fait ce procédé peut être envisagé dans l'avenir.

Le problème de l'uranium dans les eaux d'exhaure est quelque peu différent car les normes légales de rejet des installations industrielles nécessitent une extraction de l'uranium. Dans la plupart des cas, les résines échangeuses d'ions ne peuvent être concurrencées par les adsorbants minéraux. Mais, dans quelques cas difficiles, et notamment dans les eaux chargées en chlorures, le procédé OTH, bien que d'un maniement plus délicat, est parfaitement compétitif.

URANIUM EXTRACTION FROM SEAWATER

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Abstract

URANIUM EXTRACTION FROM SEAWATER.

A short review of the international activities and the state-of-the-art in the area of uranium extraction from seawater is presented. A description of the major extraction concepts is given along with the results of an economic analysis of uranium production costs for recovery from seawater. The calculations show that uranium production costs from \$250–300/lb U_3O_8 seem realistic based on present-day sorber performance; however, production costs around \$150/lb U_3O_8 and possibly lower seem conceivable in the future, depending on progress in the development of suitable sorber systems.

1. URANIUM RESERVES IN SEAWATER

Many publications from both Western [1–3] and Eastern countries [4] point out the large uranium reserves in the world's oceans of about 4.5×10^9 t U, with the uranium occurring in a remarkably uniform concentration of about 3.3 μg/L. In addition some further 5×10^3 t U enter yearly through rivers and submarine eruptions. It is pointed out here that only a one per cent reduction of this enormous reservoir would yield an amount of uranium ten times as large as today's known and estimated reserves. However, the concentration of 3 μg/L or pp 10^9 is several orders of magnitude lower than the leanest ore-body being mined today (see Table I).

Despite the low concentration, the recovery of uranium from seawater seems easier than from complex ores and probably the major problem lies in the handling of the large water masses rather than in the extraction itself.

2. CHEMICAL BONDING OF URANIUM IN SEAWATER

According to Refs [3, 4], the occurrence of uranium in seawater is nearly exclusively in a state of solution. The presence of suspension matter in surface-near zones is estimated to be less than 0.5–1.5 mg/L; the adsorption on these suspensions is assumed to be less than 0.1–3.7 ppm uranium.

TABLE I. URANIUM CONCENTRATIONS IN VARIOUS SUBSTANCES AND CORRESPONDING RESERVES

Uranium-bearing substance	Average concentration (ppm)	Reserves (10^6 t U)
Conventional uranium ores	350–5000 and more	4–5
Phosphates	100–200	5–10
Red mud (bauxite)	8–12	0.09–0.1
Lignite	0.1–1	0.15–1.5
Granite	4	4×10^3
Manganese modules	4–7	10–14
Shelf sediments	1–4	$3–4 \times 10^5$
Seawater	0.003	4.5×10^3

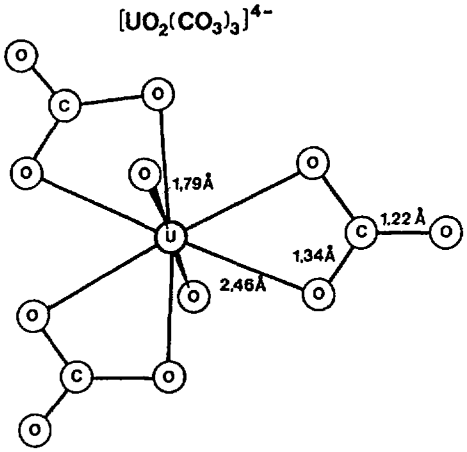

FIG. 1. Uranyl tricarbonate complex.

Experiments indicate that the dissolved state of uranium in seawater is predominately influenced by the CO_2 concentration and pH value. Thus the bicarbonate-carbonate buffers present in the seawater enhance the formation of uranyl carbonates, especially the uranyl tricarbonate complex shown in Fig.1. The tricarbonate complex is stable at pH = 8.2, however, decomposes rapidly in the presence of H_3O^+ ions [3]. The seawater present in carbonate complexes show the stability regions given in Table II.

TABLE II. STABILITY REGIONS OF URANYL CARBONATES

Complex	pH stability region from	pH maximum stability
$[UO_2(CO_3)_3]^{4-}$	7.25 to 11	8.35
$[UO_2(CO_3)_2]^{2-}$	6 to 8.25	7
$[UO_2CO_3]$	5 to 7	6

TABLE III. MAIN COMPONENTS OF ELEMENTS DISSOLVED IN SEAWATER

Element	Concentration (mg/L)
Chlorine	19 000
Sodium	10 721
Magnesium	1 350
Sulphur	901
Calcium	410
Potassium	398
Bromine	67
Carbon	28
Strontium	7.7
Boron	4.6
Fluorine	1.3

Based on an average seawater salt content of about 3.5%, the salt concentration is $10^6 - 10^7$ times larger than the uranium concentration. The component distribution of the various elements present is described in Refs [2–4]. The major components of the dissolved salts are Cl, Na, Mg, S, Ca, Br, C, Sr and B. They represent together more than 99.9% (see Table III). The remaining trace elements are shown in Table IV. V, Fe, Ni, Cu and Zn are dissolved in concentrations comparable to U. The presence of Au is 1000 times, and of Th and Pb 100 times lower. Au occurs as chloride, whereas the other heavy metals are carbonates or hydroxides.

TABLE IV. SELECTED TRACE ELEMENTS AND THEIR CONCENTRATION IN SEAWATER

Element	Concentration ($\mu g/L$)
Lithium	170
Rubidium	120
Aluminium	10
Molybdenum	10
Iron	10
Zinc	10
Copper	3
Uranium	3
Vanadium	2
Nickel	2
Titanium	1
Tin	0.8
Cobalt	0.5
Chromium	0.5
Silver	0.04
Gold	0.003

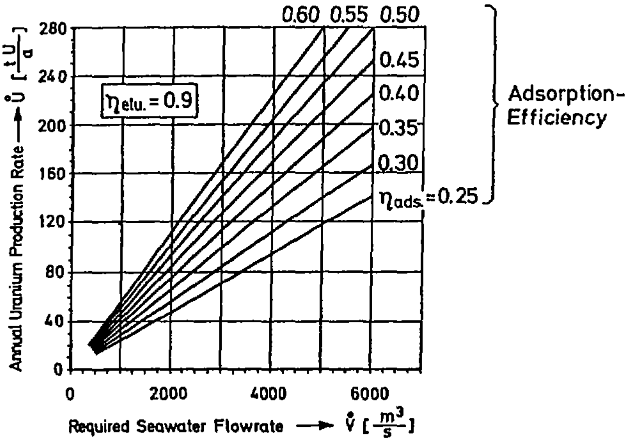

FIG.2. Annual uranium production rate as a function of the required seawater flowrate.

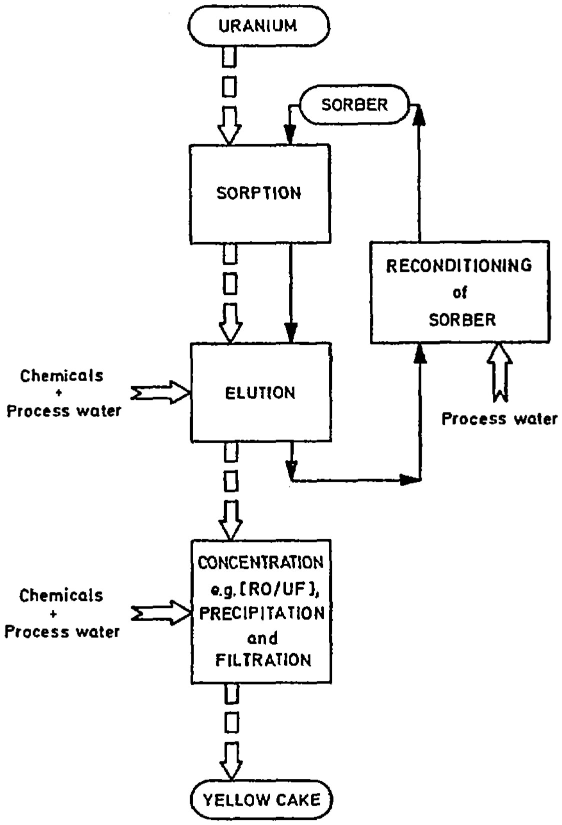

FIG.3. Flow diagram of process cycle.

3. BASIC METHODS OF THE EXTRACTION OF URANIUM

As mentioned earlier and can be easily seen from Fig.2, the recovery of uranium from seawater requires the processing of large amounts of water, depending on the efficiency of the adsorption and elution process. Therefore R&D activities should centre around two problem areas:

(1) Development of the optimal, i.e. the most effective and most selective, extraction system and the associated chemical engineering

(2) Development of an economic method of contacting large amounts of water with such an extraction system.

As to the first point, Fig.3 shows the flow diagram of the process cycle chosen. Of the different extraction methods, e.g. ion flotation, co-precipitation, solvent extraction and adsorption, the latter is generally believed to be the most advantageous and therefore pursued world wide. There exist, however, two adsorption methods: fluidized-bed or fixed-bed adsorption, and the choice of which mainly depends on the performance and the mechanical strength of the adsorber in use. Intensive research activities for suitable adsorbers concentrated in the past on hydrous titanium oxide (HTO) in the inorganic area and more recently on ion-exchange resins in the organic area. While HTO is a moderate system with problems arising from its insufficient mechanical stability, some ion-exchange resins seem very promising and give rise to great expectations. However, the entire adsorption-desorption performance has to be considered in each case, since most sorber systems with high adsorption rates have poor elution efficiencies or vice versa. The adsorption-elution cycle may then be followed by conventional processing and refinement techniques as applied in terrestrial ore processing.

With respect to the second point, there exists a variety of extraction concepts with different philosophies depending on given natural boundary conditions. Since large water volumes have to be processed, it may seem desirable for energy considerations to utilize natural ocean currents, tidal currents or even wave energy to drive the water through the adsorption units. These systems are generally referred to as current-driven or wave-energy concepts. However, there are concepts where the water is actively transported through the system by pumps. These pumping concepts are based on idealized calculations that estimate the required pumping energy to be only 2–3% of the nuclear energy content of the water.

Furthermore, depending on the geographical and physical conditions of the environment, prospective uranium production plants (current-driven or pumping concepts) may be designed either as floating units that are moored or move through the water, or as land-based units. Countries, for example, that do not have warm ocean currents in the vicinity of their costal line will have to develop concepts operating in the open sea, whereas others may design land-based production plants.

4. STATUS OF TECHNOLOGY

The activities of 14 research groups have been presented and discussed at an international "Topical Meeting on the Recovery of Uranium from Seawater" at the Massachusetts Institute of Technology in Boston, December 1980. The proceedings of this conference [5] together with the 1982 follow-up Progress Report [6] still give the most complete and up to date state-of-the-art review of the research activities going on in the world today. A second international meeting was held in Tokyo, Japan, in October 1983. In addition there are several other older papers of general interest, but still with many interesting references, e.g. Bals [2], Schwochau et al. [3], Exxon Nuclear Co. [7–10], Best and Driscoll [11], Koske et al. [12] and Kanno [13].

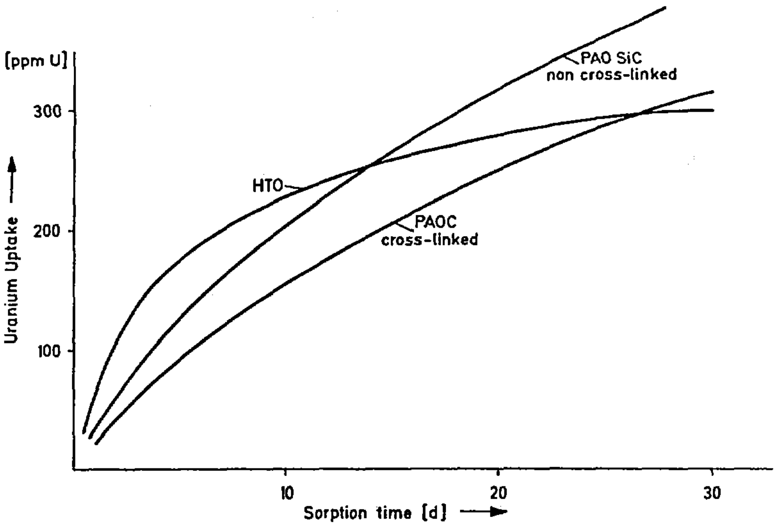

FIG.4. Comparison of typical sorption performance for HTO and PAO.

4.1. Development of sorber systems, elution and final concentration

In the Federal Republic of Germany and Japan HTO, a product of the readily available mineral ilmenite, has long been preferably applied as the main sorber system, both in its pure state as well as admixed with other oxihydrates. However, because of its lack of sufficient mechanical stability, more attention has recently been given to the organic polyacrylamidoxine (PAO), a direct derivative of polyacrylnitrile (PAN) which is a major product of the synthetic fibre industry.

So far it seems proven that PAO is the better system, because of its higher sorption capacity even under absolutely equal geometric conditions (see Fig.4). Furthermore, since stability against attrition is of major importance for the sorber evaluation, especially for fluidized-bed systems, PAO shows considerable advantage over HTO owing to its outstanding mechanical stability. PAO may also be exposed to adsorption in the form of fibres with very small diameters offering very large geometric surfaces within a given volume. Another striking advantage of PAO over HTO is its lack of affinity with earth alkali ions present in seawater. Contrary to this, HTO adsorbs Ca and Mg ions at 100-fold higher rates than U, which again burdens the elution step substantially.

The work on sorber evaluation in the Federal Republic of Germany has come to a preliminary termination with regard to the HTO system. At the same time R&D effort has been increased on the more promising PAO system including the work on the elution optimization, where the stability of the active adsorption centres towards the elution conditions has to be improved. Both systems – HTO

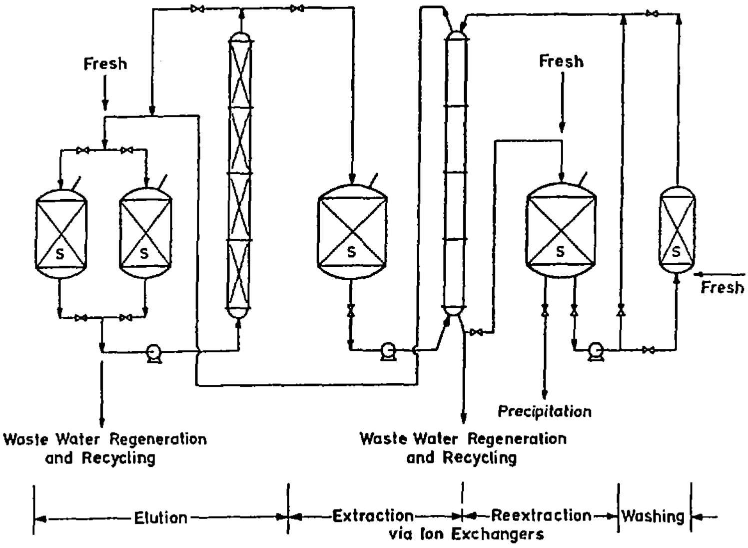

FIG.5. Eluate work-up.

and PAO – are preferably eluted with aqueous solutions of sodium bicarbonate and sodium carbonate, which are recycled, providing particularly favourable environmental conditions.

The further processing of the eluates (10–200 ppm U content) to obtain concentrates up to 2% U for yellowcake precipitation may be performed by different methods. The original concept of evaporative concentration must be abandoned owing to its high energy demand. In Japan and the Federal Republic of Germany the eluate concentration is preferably achieved by ion exchange using solid- and liquid-liquid extraction processes and regenerating the elution medium by electrodialysis. Concentration by RO/UF technology may also be applied with special membranes. A three-stage, 20-bar process is expected to require a low unit effort and energy requirement.

4.2. Plant concept development

For several years detailed investigations with corresponding experiments have been carried out in Japan, the Federal Republic of Germany, Sweden and the USA to develop specific plant concepts.

Because of the warm Kuroshio current which passes the south-eastern coast of Japan a stationary land-based concept is under development in that country [14]. Mechanical pumps transport the seawater through the adsorption plant (pumping concept) from where the depleted water is discharged into the sea and carried away by the ocean current. Past research has been conducted on a laboratory scale and was mainly concerned with the development of suitable adsorbers [15, 16], contacting methods, i.e. primarily fixed-bed, elution techniques and overall economic analyses of various plant concepts [17]. In 1984 the Metal Mining Agency of Japan planned to start operation of a M$10.3 pilot plant at Nio, Seto Island, that aims to win 10 kg/a of uranium [18]. If the concept proves feasible in the tests from 1984 to 1987 a semi-commercial plant with a minimum capacity of several tons per year is planned by 1990.

Since there are no warm ocean currents in the vicinity of the German coast, R&D activities in the country concentrate on floating production plants operating in the open sea [19–23]. Under the sponsorship of the Federal German Ministry for Research and Technology (BMFT) investigations are carried out to determine the conditions under which the kinetic energy of natural ocean currents may be utilized for internal water transport through a floating or semi-submersed adsorption plant [19]. Detailed hydrodynamic tests in water tunnels and towing tanks with and without wave influence have been conducted and have been supplemented with structural analyses under realistic load conditions of the marine environment. First results from subsequent economic analyses of the overall process indicate that a considerable increase in the present sorber performance is necessary for this concept to realize plant dimensions that are technically and economically feasible.

Parallel investigations include floating systems on barges, single or multi-hull ships or semi-submersibles with active water transport. This can be done either indirectly by moving the adsorption unit through the water and using the resulting dynamic pressure analogue to the current-driven concept [19, 20] or directly by mechanical pumps [21, 22]. Hydrodynamic model tests to minimize the external and internal flow losses and to allow more realistic estimates of the required pumping energy are being conducted. Field tests in the open sea with a 2 m × 3 m float were also carried out [21]. Further field tests on a lab-scale and a semi-technical scale are currently under way to demonstrate the fundamental feasibility of uranium extraction from seawater from a chemical and process engineering point of view and to get preliminary results on the effectivity and marine technological feasibility of the two German concepts currently under development.

In Sweden the feasibility of a floating unit using wave energy is being studied [24] under the sponsorship of the National Swedish Board for Technical Development. The system is based on the principle that waves will rush up a sloping plane, which is partly submerged in the sea, and fill a reservoir with water to a level higher than the still-water level of the sea. This difference will create a pressure head which can be utilized to force seawater through the adsorption beds.

In the USA the extensive Exxon-Oregon State feasibility study [7–10] was prepared in 1978. According to this study, a land-based uranium-from-seawater plant is not economically feasible in the USA. Other system design studies conducted by MIT resulted in a catamaran-like ship as a floating carrier for the adsorption beds [25, 26]. The catamaran hull was chosen for its stability

TABLE V. COMPARISON OF URANIUM PRODUCTION COSTS BY VARIOUS AUTHORS

Costs in DM/kg U_3O_8 and \$/kg U_3O_8		UEB (HTO) [28]	UEB (PAOC) [28]	MIT [25]	Kanno A [17]	Kanno C [17]	Dornier system [22]	Sweden [27]
Depreciation	DM	719	632	269	1300	813	319	570
	\$	299	264	112	541	339	133	237
Sorber	DM	676	260	158	19	19	DM 181 \$75	DM 233 \$97
	\$	282	109	66	8	8		
Elution and refinement	DM	373	25	348	369	213		
	\$	155	10	145	154	89		
General operation	DM	579	434	32	370	261	571	
	\$	241	181	13	154	109	238	
Energy	DM	120	54	180	152	161	181	
	\$	50	22	75	63	67	75	
Miscellaneous	DM	–	–	–	20	20	–	–
	\$	–	–	–	9	8	–	–
Total	DM	2467	1405	987	2230	1487	1252	803
	\$	1027	586	411	929	620	521	334

as well as its natural ability to separate inlet from outlet flows. In operation, the seawater loading cycle would take place at sea, after which the ship would return to port, trans-ship its resin load and return to the sea for another cycle. Elution would be carried out on shore where a single plant serves several ships.

5. ECONOMIC ANALYSES

Ever since the idea of extracting uranium from the sea was conceived a variety of analyses have been carried out to estimate the economy of the extraction process. A summary of such analyses, as given earlier in Ref.[19], indicates that over the years there has existed quite a difference in opinion about possible uranium production costs. This underlines the difficulty and the uncertainty of such analyses and points out how cautiously their results have to be interpreted. It is very difficult to compare different production methods because of varying assumptions, different simplifications and boundary conditions underlying each individual case. Nevertheless, research activities in the past have brought forth new insights such that predictions of recent analyses [17, 22, 25, 27, 28] (Table V) lie remarkably close and in most cases range between \$250–300/lb U_3O_8, in some cases even lower. These predictions can be regarded as realistic estimates based on today's technology. Essential improvements may be expected through augmentation of the sorber performance. An increase in the uranium uptake rate would decrease the required amount of sorber material and hence lower sorption and elution costs. The same effect could be achieved by bringing down sorber costs and increasing its durability, i.e. its chemical stability. Improvements in sorber kinetics, e.g. for PAO, would, however, require a density increase in order to admit a higher uranium supply by increasing the bed operating velocity without exceeding the admissible bed extensions. At the same time higher bed operating velocities would allow smaller sorber bed areas, reducing the size of the sorption unit and thus cutting capital investment costs, which are the major contributor to uranium production costs (40–50%). Production costs around \$150/lb U_3O_8 and possibly lower seem conceivable in the future, depending on the progress in the improvement of the sorber system.

Another interesting economic aspect arises from the fact that uranium costs have only little influence on electricity costs, e.g. an increase of the uranium price by \$250/lb U_3O_8 would cause an electricity price increase of no more than \$0.01/kW·h, which is about the increase estimated for the desulphurization of coal-operated power plants. Hence, electricity produced from nuclear energy with uranium extracted from the sea, even with today's technology, would in many countries still be cheaper than coal- or oil-produced electricity.

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DISCUSSION

NAEEM-UL-ZAMAN: What is the granulometry of the HTO used in your tests?

J. BITTE: Our HTO is in the form of cylindrical pellets 1.5 mm high and 1.5 mm in diameter. This is, of course, a compromise. The chemical performance would be better with smaller particle sizes, but we need larger sizes from the point of view of process engineering. With the smaller sizes we would need a very fine mesh under the fluidized bed and that would cause high energy losses. The size of 1.5 mm is the optimum we obtained from our hydrodynamic and chemical tests. We use the same size for PAO.

NAEEM-UL-ZAMAN: What are the losses of HTO per cubic metre of water treated?

J. BITTE: It is difficult to give a quantitative figure. HTO losses are about 100% in one year. In addition, most of the uranium is adsorbed on the outer surface of the HTO and most of this uranium is lost by attrition.

PANEL REPORTS

PANEL I

PHYSICAL BENEFICIATION

REVIEW AND RECOMMENDATIONS

Physical beneficiation of uranium ores is undertaken with one or all of the following objectives in mind

(1) To improve the grade of the ore in order to achieve increased production from an existing or projected mill
(2) To discard deleterious minerals that are undesirable during leaching or during extraction
(3) To produce cleaner tailings that can be rejected without creating any environmental problems.

Beneficiation processes utilize differences in the properties of various ore fractions such as differences in colour, size, shape, density and surface properties or radioactivity to effect a separation by a number of techniques including radiometric sorting, electro-optical sorting, screening, gravity separation, floating, magnetic separation, and attrition scrubbing.

With a few notable exceptions physical beneficiation has not been applied successfully for concentrating uranium and when it has beeen used, it has improved economic performance but its application has not been mandatory for achieving economic viability. Beneficiation processes have the potential for substantial savings and, therefore, no metallurgical investigation should proceed without some consideration of the various methods available.

The members of the Panel believe that standardized, systematic procedures for the further testing of a specific ore for its response to physical beneficiation (and other) ore processing methods would be of value to many of the IAEA's Member States. It would be very useful to define a sequence of standardized testing steps for the characterization of uranium ores with respect to their amenability to each one of the various preconcentration processes available. These test procedures should be designed so that the results would be a measure of the best results possible by various physical concentration methods and they should be independent (as much as possible) of machinery characteristics and human error in machinery operation, the effects of which are difficult to evaluate in some test methods. For example, heavy-liquid testing of sized fractions provides results that can only be approached by gravity separation equipment.

PANEL II

IN SITU AND HEAP LEACHING

REVIEW AND RECOMMENDATIONS

The current depression in the uranium market has forced the industry to reduce the number and extent of in situ and heap leaching operations and has adversely influenced further research efforts. However, the members of the Panel agree that these leaching techniques can be successfully applied in many instances and that they deserve much more attention.

1. IN SITU LEACHING

In situ leaching has been extensively developed, especially in the last ten years. and sufficient data are available for engineers to plan an operation with confidence. Many computer programs have been developed to aid analysis and design. These programs are easily obtainable at low cost from several sources. Although in situ leaching is reasonably well understood, there is still a need for further research work in the following areas:

(a) The relationship between bore-hole spacing, rock permeability and solution recovery rates
(b) The use of leach solutions containing naturally occurring ions to reduce the potential environmental impact
(c) Detailed studies of the environmental effects of in situ leaching and of means for reducing them.

2. HEAP LEACHING

Heap leaching is a comparatively inexpensive processing method with the potential for wide application. It can be successfully used for exploiting deposits that would otherwise be left untouched because of their small size or low grade or both. It can also be used by developing countries when there is a need to limit capital expenditures. The members of the Panel believe that research and testing to further improve this technology should be encouraged. The following topics requiring additional investigation were identified:

(a) The use of physical beneficiation to upgrade the ore prior to leaching
(b) Types and strengths of leaching solutions
(c) Efficient distribution of leaching solutions on the top of the heap and studies on the flow of such solutions through the heap

(d) The effect of grain size and size distribution on percolation rates and on uranium recovery
(e) The use of agglomerated pellets in heap leaching and techniques for their production
(f) Bacterial action within the heap and means of promoting it
(g) The effect of climatic conditions on heap leaching
(h) Environmental effects of heap leaching and means for reducing them.

The members of the Panel also believe that it would be very useful to:

(i) Develop computer programs to aid in the design, analysis and economic evaluation of heap leaching systems
(j) To develop standardized procedures for reporting cost data on heap leaching operations. The Panel notes that although the literature contains many reports that include cost data, these data are often incomplete and difficult to compare with one another and with cost data from other competitive processes.

Finally, the members of the Panel noted that heap leaching is much more complex than it appears at first glance and that its use must be approached with caution. Serious difficulties may be found if the entire operation is not properly planned.

PANEL III

RECOVERY OF URANIUM FROM WET-PROCESS PHOSPHORIC ACID

REVIEW AND RECOMMENDATIONS

Uranium recovered from wet-process phosphoric acid accounts for about 5% of current world production. The cost of recovery, about US$/kg, is higher than the average cost of extraction from conventional ores. It is therefore unlikely that this byproduct uranium will gain a greater share of the market unless the economics of recovery can be improved. Nevertheless, uranium from phosphoric acid is a potentially important resource and for many countries it may be the only significant uranium resource.

Several processes have been developed for the recovery of uranium from phosphoric acid. These processes generally involve:

(a) Complete digestion of the phosphoric rock with sulphuric acid at 75–80°C
(b) Pretreatment of the resultant phosphoric acid to cool it to 40–50°C, to remove organic matter, gypsum and other suspended solids and to adjust the oxidation potential
(c) Extraction of the uranium by one or two stages of solvent extraction
(d) Post-treatment of the barren (uranium-free) phosphoric acid to remove organic solvent residues and to heat it to 65°C before returning it to the phosphoric acid plant
(e) Stripping of the uranium-loaded organic solvent
(f) Production of a uranium concentrate by precipitation, filtration and drying.

The members of the Panel identified the following research topics as having the potential for significant cost reductions in the recovery of uranium from wet-process phosphoric acid:

(a) Development of an extractant that can remove uranium efficiently from freshly made phosphoric acid without pretreatment or with minimal pretreatment. Such an extractant should tolerate high acid concentrations and the presence of organic material and should be efficient at high temperatures, i.e. temperatures equal to or near to that of the freshly made acid;
(b) Improved methods for the removal of traces of organic solvent after uranium extraction;
(c) Development of solid extractants that would meet the criteria set forth in paragraph (a) and that would at the same time eliminate the problem of organic traces in the barren (uranium-free) acid;

(d) Improvements in equipment design and in materials of construction to reduce or eliminate corrosion problems;

(e) Improvements in equipment design to reduce air entrainment which makes it difficult to control the oxidation potential and promotes excessive emulsion formation and 'crud' buildup.

The Panel also noted that there was a need for a comprehensive review of uranium recovery from wet-process phosphoric acid.

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