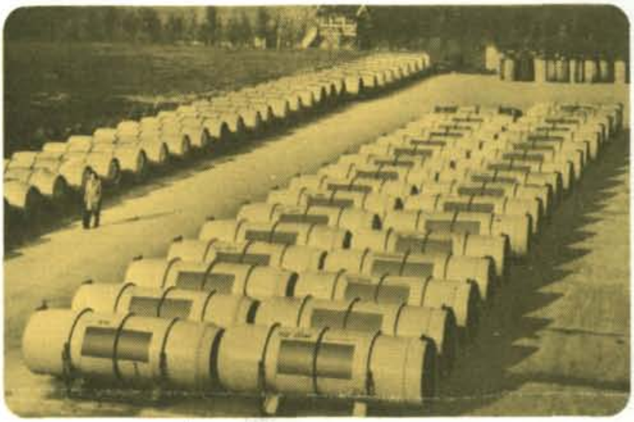

Proceedings
of an
Advisory
Group Meeting
Paris,
5 – 8 June 1979

PRODUCTION OF YELLOW CAKE AND URANIUM FLUORIDES

INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1980

PRODUCTION OF YELLOW CAKE AND URANIUM FLUORIDES

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PANEL PROCEEDINGS SERIES

PRODUCTION OF YELLOW CAKE AND URANIUM FLUORIDES

PROCEEDINGS OF AN ADVISORY GROUP MEETING
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
AND HELD IN PARIS, 5–8 JUNE 1979

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 1980

PRODUCTION OF YELLOW CAKE AND URANIUM FLUORIDES
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FOREWORD

Several tens of thousands of tonnes of uranium are currently produced per year in the form of 'yellow cake' from over 50 active ore processing plants. In addition there have been a number of plants which have been producers but have become inactive for various reasons over the past two decades, and also a number which are planned to come into operation in the not too distant future. It is therefore not surprising that scientists and engineers engaged in this industry and the research associated with its development have produced many publications describing the overall hydro-metallurgical technology involved and the operating flowsheets of many ore processing plants. However, it is surprising to discover within this literature how little has been devoted to the detailed description of the specific aspects of the processes associated with the actual 'yellow cake' end of the operation.

Consideration was therefore given to convening a meeting with the aim of bringing out some of this knowledge and experience and discussing the problems associated with this part of the operation.

The basic objective of the processes used for 'yellow cake' preparation is to prepare a uranium concentrate. However, the specifications of the product, which play a major role in determining the conditions used in those processes, are largely determined by the refining and conversion facility. It was therefore apparent that the subject of 'yellow cake' preparation could not be adequately covered in isolation. In addition, although descriptions of refining and conversion processes have appeared, there has been no previous IAEA meeting of experts to consider these subjects.

The IAEA thus considered it appropriate to convene an Advisory Group meeting to consider the total technology of that part of the fuel cycle concerned with 'yellow cake' preparation, its refining and conversion to uranium fluorides. At the invitation of the Commissariat à l'Energie Atomique the meeting was held in Paris from 5 to 8 June 1979.

A total of 46 participants from 18 countries and one international organization took part in the meeting, 20 papers and supplementary contributions being presented. Although a number of the papers cover a wide range of the subject matter, so far as possible the papers have been arranged in the Proceedings to follow the natural sequence of the operations and processes involved in taking the uranium from its original source through the various stages of concentration, purification, refining and, finally, conversion to fluorides. The technical sessions concluded with a Panel summary and discussion, the substance of which is also reproduced.

The Agency wishes to thank all the scientists and engineers who participated in the meeting. Thanks are especially due to the Panel Chairman, Dr. H. Page, and the Chairmen of the technical sessions: Dr. A.W. Ashworth, Mr. J. Craig, Mr. G. Lyaudet and Dr. S.A. Young. The success of the meeting owes much to Mr. G. Lyaudet who was responsible for the detailed arrangements in Paris. The Agency also wishes to record its appreciation to the French authorities for hosting the meeting and to COGEMA and COMURHEX for the cooperation and hospitality extended to the participants.

EDITORIAL NOTE

The papers and discussions have been edited by the editorial staff of the International Atomic Energy Agency to the extent considered necessary for the reader's assistance. The views expressed and the general style adopted remain, however, the responsibility of the named authors or participants. In addition, the views are not necessarily those of the governments of the nominating Member States or of the nominating organizations.

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CONTENTS

ORE PROCESSING AND REFINING OF URANIUM IN INDIA

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Abstract

ORE PROCESSING AND REFINING OF URANIUM IN INDIA.

Uranium ores of commercial importance in India are of comparatively low grade containing less than 0.1% of uranium. A mill for processing the ore has been operating for over 10 years. A plant for refining the yellow cake and producing uranium metal of nuclear purity was set up in 1959. A larger plant to produce reactor grade uranium oxide is also in operation. The paper brings out some of the salient features of ore processing. While the flowsheet adopted is of the conventional sulphuric acid leach – ion-exchange process, the leaching was optimized to achieve selective leaching of uranium with low acid consumption. Uranium is finally recovered by precipitation with magnesia. The refining of uranium is based on a tributylphosphate extraction process to obtain uranyl nitrate of nuclear purity. In addition to the yellow cake from the ore processing plant, the refinery also handles a small amount of a low grade uranium concentrate (essentially uranous fluoride) derived as a by-product of monazite processing. Before feeding this cake to the solvent extraction circuit a chemical pre-treatment is necessary. The process flowsheets for uranium metal and uranium dioxide are discussed in this paper. The present requirements of reactor grade natural uranium oxide and metal for power and research reactors in India are met by indigenous production. To meet future demands other deposits of uranium may have to be exploited and if there are any problems in their treatment, suitable modifications will be made in the processing methods.

INTRODUCTION

The disseminations in metamorphic rocks represent the most important uranium deposits in India. These are of comparatively low grade containing less than 0.1% of uranium. In general, physical beneficiation methods did not show promise of high grade at high recoveries for these ores. The economic recovery of uranium was a challenge for developing highly efficient chemical processes for the leaching, purification and concentration of uranium. A uranium mill processing 1000 tonnes of ore per day has been in operation at Jaduguda (Bihar) for over 10 years.

A plant for producing nuclear grade uranium metal, to meet the requirements of the research reactors based on natural uranium, was set up in Bombay in 1959. Another plant to produce uranium oxide (UO_2) suitable for compacting and sintering to high density has also been set up to meet the requirement of natural uranium oxide fuel for power reactors.

This paper describes the development of flowsheets for the chemical processing of uranium ores and the refining of uranium.

TABLE I. JADUGUDA ORE ANALYSIS

Mineralogical		Chemical	
Constituent	% by weight	Constituent	% by weight
Quartz	60.0	U_3O_8	0.07
Chlorite	20.0	SiO_2	67.20
Magnetite	9.0	FeO	6.37
Tourmaline	3.5	Fe_2O_3	7.87
Apatite	3.0	Al_2O_3	5.50
Sulphides	2.0	TiO_2	0.66
Ilmenite	1.0	MnO	0.13
Others	1.5	CaO	5.40
		MgO	2.20
		P_2O_5	1.04
		S	0.79
		Undetermined	Rest

TABLE II. COMPOSITION OF LEACH LIQUOR

Constituent	Concentration g/ltr
U_3O_8	0.6
Fe^{+++}	2.5
SiO_2	1.0
SO_4^{--}	25.0
P_2O_5	0.3–0.5
Mn^{++}	2.0–3.0
Rare earths (total)	0.2

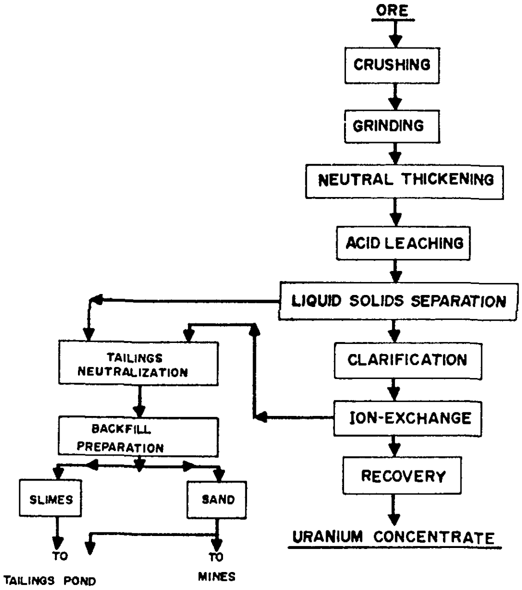

FIG.1. General flowsheet of Jaduguda uranium mill.

URANIUM FROM JADUGUDA ORE

Uraninite as disseminations is the chief uranium mineral in the ore. A portion of the uranium is chemically combined or physically locked in refractory oxides present in the ore. The associated gangue minerals vary to some extent from place to place in the deposit. A typical mineralogical and chemical analysis of the ore is presented in Table I.

The ore posed no special problems in processing except the tendency of phosphate to dissolve at high concentration of free acid. To prevent the precipitation of uranium and iron, as phosphates, the pH of the pulp has to be maintained at less than 1 and this caused problems in the subsequent ion-exchange process. A detailed study of the leaching behaviour of apatite, the phosphate-bearing mineral, led to a leaching procedure where the acid consumption as well as phosphate concentration of the leach liquor were considerably reduced. It was observed that the dissolution of apatite in sulphuric acid of moderate concentration is dependent not·only on the acid concentration but also on the concentration of Fe(III) and the temperature at which leaching is carried out. In the presence of 2 to 3 g/ltr of Fe(III) if the leaching is carried out at elevated temperature, maintaining the pH of the pulp at 1.5 to 2.0, the dissolution of phosphate is drastically reduced. On this basis the following leaching procedure was finally

TABLE III. TYPICAL ASSAY OF URANIUM CONCENTRATE ON DRY BASIS

Constituent	% by weight
U_3O_8	74.80
SiO_2	3.40
Cl^-	0.27
SO_4^{--}	0.52
P_2O_5	0.11
Fe (total)	0.38
Ca + Mg (as MgO)	6.31
Th	0.03
Rare earths	0.13

adopted. The ore, ground to 55% minus 200 mesh (BSS) is leached at 60% solids and 1.5 to 1.6 pH at 45 to 50°C. After 1 h ground pyrolusite is added (4 to 5 kg/t) and the leaching continued for 4 h. At the end of this period acid addition is stopped and the pH is allowed to rise to about 1.8 over a period of 8 h. During this stage some ferric phosphate is precipitated. Under these conditions, in plant practice, the average acid consumption has fallen to less than 20 kg of H_2SO_4 per tonne of ore, and the uranium solubilization is about 94%. A rough composition of a typical leach liquor, thus obtained, is shown in Table II.

The leach liquor is further processed by ion-exchange with chloride elution. The uranium recovery from the strong eluate is carried out by a two-stage neutralization with lime and magnesia. The choice of magnesia for final precipitation is made mainly on cost consideration. The yellow cake is collected wet and stored.

The flowsheet employed at the Jaduguda Uranium Mill is shown in Fig.1. A typical analysis of the yellow cake is given in Table III.

Sampling and analysis of the yellow cake

The sampling of the drummed wet-cake is carried out by drawing pipe samples from fixed positions, and a sample representing a lot is made by mixing individual drum samples. The wet-cake is further sampled to a convenient weight of about 250 g and then handled either as a dried sample or as a solution for further analysis and accounting. The uranium assay method is based on Davis and Gray's procedure (Australian AEC report AAEC/TM/552, Sydney, Australia).

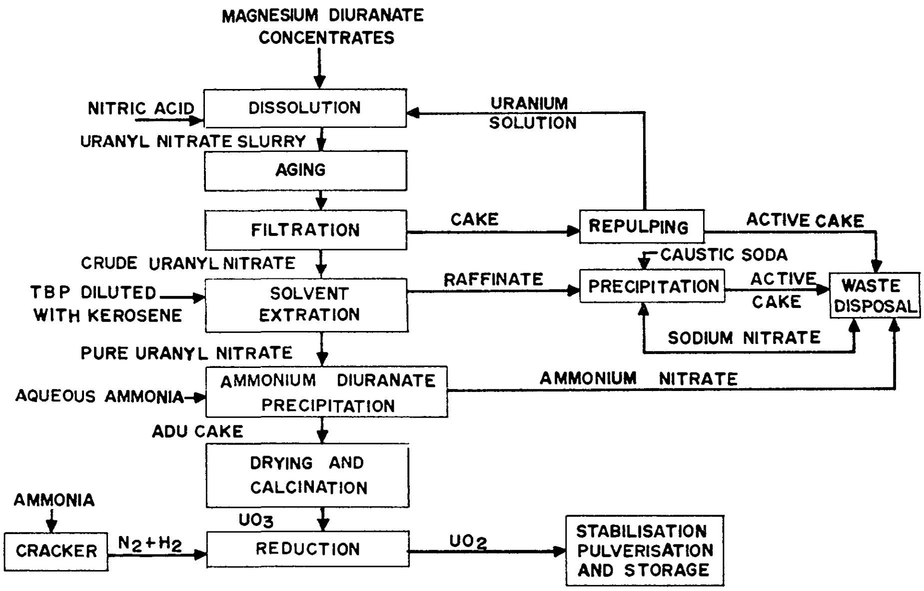

FIG.2. Production of nuclear grade uranium oxide.

URANIUM FROM MONAZITE

Facilities for the recovery of uranium from monazite sand already exist in the country. This by-product uranium is obtained from the thorium processing plant in the form of a crude uranium tetrafluoride cake containing 40 to 50% U_3O_8. It is essential to eliminate all the fluoride associated with uranium, remove most of the rare earths, iron and other impurities and upgrade the uranium content to about 70% U_3O_8 to make it acceptable as feed to the uranium refining plant. This is achieved by carbonate leaching of the crude cake in the presence of an oxidant, thus solubilizing the uranium as a tricarbonate complex followed by precipitation of uranium as sodium diuranate. Production from this source is not very large as it is dependent on the demand for thorium.

URANIUM METAL PRODUCTION

The refining of uranium concentrates to obtain products of nuclear purity consists of dissolution of the yellow cake in nitric acid, selective extraction of uranium using tri-n-butyl phosphate, scrubbing of the loaded solvent and re-extraction of the pure uranyl nitrate into the aqueous phase. Due to the type of

TABLE IV. TYPICAL ANALYSIS OF URANIUM OXIDE

Item	Analysis of UO_2
Physical	
Tap density	2.5 to 3.0 g/cm^3
Sieve analysis	100% through 100 mesh
Particle size	0.7 to 0.8 μm
Surface area	2.0 to 3.0 m^2/g
Chemical	
O/U Ratio	2.08 to 2.12
	Impurities (ppm on U basis)
Aluminium	Less than 10
Boron	0.1 to 0.3
Calcium	Less than 25
Cadmium	Less than 0.1
Copper	Less than 6
Chromium	Less than 10
Dysprosium	Less than 0.1
Iron	30.0
Fluorine	Less than 5
Gadolinium	Less than 0.04
Magnesium	Less than 3
Manganese	Less than 2
Molybdenum	Less than 5
Nickel	Less than 2
Silicon	25
Thorium	150

magnesia used for precipitation of yellow cake and its handling as a wet-cake, the dissolution step offers some problem in that the soluble silica gradually separates from the solution. Hence, an aging step is included to separate as much silica as possible.

The pure uranyl nitrate is converted into UO_3 and then by reduction to UO_2. Where the final product required is uranium metal, the UO_2 is converted to UF_4 by hydrofluorination and then reduced by calciothermy to obtain the metal ingots. A process for reduction of UF_4 by magnesium has also been standardized.

PRODUCTION OF URANIUM OXIDE

The development efforts were mainly directed towards the production of UO_2 powder which will give sintered pellets of high density. An ammonium diuranate (ADU) route, consisting of continuous precipitation of ADU from pure uranyl nitrate solution with aqueous ammonia solution followed by calcination and reduction, was selected for UO_2 production. Optimum conditions for UO_2 powder production were established and a sintered density of over 10.4 g/cm^3 was achieved. It was noticed that for each type of ADU produced, a particular calcination condition could be evolved so that the UO_2 powder can sinter to a high density. A stablization treatment of the powder was found to be necessary for handling it in the open. It was also established that a micronizing and blending step after stabilization helps in getting a homogeneous microstructure free from unsintered granules.

The process flowsheet employed at the Nuclear Fuel Complex plant is given in Fig.2. Analysis of a typical sample of UO_2 is given in Table IV.

CONCLUSION

The present requirement of reactor grade natural uranium metal and oxide for research and power reactors is met entirely by indigenous production employing the processes described above. To meet future demand other ore deposits of uranium will have to be exploited. In some cases it was noted, in preliminary studies, that the rare earth content of leach liquors will be significantly higher than in the case of the presently-processed Jaduguda ore. To take care of this and other similar problems, investigations have been carried out on the use of the Eluex process. Here the uranium, loaded on the ion-exchange resin, has been eluted with 1M sulphuric acid and then purified further by liquid/liquid extraction using a tertiary amine like Alamine-336. Using such a process, the rare earths content of the yellow cake is reduced from about 2000 ppm (as obtained by the ion-exchange method only) to less than 1 ppm.

Until now the development of flowsheets for ore processing and refining in India has been in line with general progress throughout the world. It is felt that a more specialized process, better adapted to the low grade ores occurring in India, should lead to the large-scale expansion of uranium production in the years to come.

DISCUSSION

A.W. ASHBROOK: What type and size are the columns in the solvent extraction circuit?

S. SEN: A batch counter-current liquid-liquid extraction apparatus consisting of five extraction tubes was used for solvent extraction studies on the Eluex process.

A. ABRAO: I would like to know whether some complexing agent is used during the solvent extraction, to avoid the co-extraction of thorium.

S.SEN: We have not used any complexing agent during solvent extraction (Eluex process) to avoid co-extracting of thorium.

A. HIMSLEY: 1. How were the lime and magnesia added? Were they dissolved in water or was the eluate solution used to convey them to the main body of eluate? 2. It is noted in Table III that the thorium concentration in the eluate is 0.03% by weight U_3O_8. Its concentration in the leach liquor is not given in Table II and I would like to know if the author can give us that figure?

S. SEN: 1. Lime and magnesia are added in slurry form, dissolved in water. 2. The figure for the concentration of thorium in the leach liquor is not readily available.

H.E. JAMES: Would Mr. Sen please elaborate on the optimized leach procedure used in the industrial plant for the processing of Jaduguda ore? To which pachuca is sulphuric acid added and what instrumentation is used to control the pH at the optimum level? Where is manganese dioxide added?

S. SEN: At Jaduguda ore is ground to 55% minus 200 mesh and the pulp density of feed to the first pachuca is maintained at 63%. The 98% sulphuric acid is added to the first three or four pachucas. It is less expensive to allow the iron-bearing minerals and metallic iron (from the grinding circuit) to be attacked initially by the acid and to add the oxidant afterwards to oxidize the ferrous iron. Manganese dioxide slurry is therefore pumped to the second operating pachuca. The pH of leaching in the first four pachucas is between 1.5 and 1.6, then it rises to about 1.8 in the last pachuca; pH meters with glass electrodes, specially protected against violent agitation with slurry, are used. In addition periodical manual checks on pH are carried out.

M. YUNUS: 1. Could you kindly elaborate on your statement "Stabilization of UO_2 powder", what is the condition of stabilization? 2. What was the quantity of material per batch of heap leach?

S. SEN: 1. The UO_2 powder is stabilized by air or air-CO_2 mixture in a rotary unit at room temperature. 2. The quantity of material treated per batch of heap leach varies between 6 and 10 t so far as the Chhinjra, Himachal Pradesh heap leaching field tests are concerned.

TECHNOLOGICAL STUDIES ON THE MANISA-KÖPRÜBAŞI URANIUM ORES OF TURKEY

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Abstract

TECHNOLOGICAL STUDIES ON THE MANISA-KÖPRÜBAŞI URANIUM ORES OF TURKEY.

At the end of the laboratory and pilot plant scale technological experiments on the uranium ores which are located in the Manisa-Köprübaşi basin, three main types of ore have been classified:

(i) Kasar type: The ores consist of secondary uranium mineralization (autunite, meta-autunite and torbenite) in loosely consolidated sands, gravels and clays of Neogene Age. Heap leaching has been carried out on 100 and 1000 t ore samples (0.05% U_3O_8) under economical conditions, such as 20 to 40 kg of H_2SO_4 per tonne of ore at ambient temperature; original size −20 cm, solid/liquid ratio of 10, 20 days, and 90% recovery of uranium has been reached. The uraniferous solutions (1 to 2 g of U_3O_8 per litre) obtained from the heap leaching operations were purified in a solvent extraction unit with a capacity of 100 ltr/h by using an Alamine 336-kerosene-decanol solution. The uranium in the purified and concentrated solutions (15 g of U_3O_8 per litre) was then precipitated as a yellow cake with 65 to 75% U_3O_8 content by means of magnesia milk.

(ii) Taşharman type: No specific uranium mineral has been detected in the mineralogical determination, although uranium is disseminated in phosphate minerals as dahllite and apatite. Uranium in the ore has been leached under rather uneconomical conditions; 100 kg of H_2SO_4 per tonne of ore, particle size −1 cm, 25°C, 30 days. In the SX-treatment of pregnant solutions phosphate ions, higher acidity than pH 1, and compounds formed as a chemical precipitation, hindered the SX-recoveries. In such cases, the addition of acid, dilution of pregnant solutions, membrane filtration, or 40°C temperature have been applied to decrease the uranium loss in the raffinate.

(iii) Carbonate type: Even if alkaline leaching at 65°C, or leaching with 400 kg of H_2SO_4 per tonne of ore, was carried out on −200 mesh ore samples, no acceptable uranium recoveries were obtained.

INTRODUCTION

Technological research has been carried out on the surface-formed uranium ores explored by the Mineral Research and Exploration Institute (MTA) at the Manisa-Köprübaşi area of Turkey. In these experiments the main aim was:

(1) To determine the chemical solubility behaviour of each type of ore. For this purpose, the ore was ground to minus 65 mesh and by applying agitating

TABLE I. TECHNOLOGICAL CLASSIFICATION OF KÖPRÜBAŞI URANIUM ORES

ORE	LABORATORY						PILOT										
	Agitating Leaching			Column Leaching			Heap Leaching (Screen size : As mined)										
	Sample: 250 gr (−65 mesh) S/L = 2/3, Time = 4 hours Temp.: 25°C			Sample: 10 kg (−2 cm) S/L = 1/2, Time = 10–15 days Temp.: 25°C			% U_3O_8	Amount of Ore (tonnes)	H_2SO_4 kg/t-ore	Leaching		Washing		Recovery % U_3O_8 based on Solution	Residue % U_3O_8	Recovery % U_3O_8 based on Residue	
	% U_3O_8	H_2SO_4 Kg/t-ore	Extraction % U_3O_8	% U_3O_8	H_2SO_4 kg/t-ore	Extraction % U_3O_8				Time (day)	Solution (tonne)	Time (day)	Solution (tonne)				
Kasar	0.05	20	96.3	0.100	20	98.1	0.049	100	20	20	15	24	30	86.4	0.006	87.4	Industrial Production Possible
Kasar	—	—	—	—	—	—	0.056	100	20	10	32	38	32	97.3	0.0052	90.7	
Kasar	—	—	—	—	—	—	0.024	1000	20	20	83	32	290	85.4	0.004	83.4	
Çetinbaş	0.150	40	89.1	0.150	40	89.7	0.030	50	30	4	6	35	22	96.6	0.0009	97.0	
Kayran	0.038	40	87.5	0.038	40	94.7	0.093	84	40	15	30	48	42	83.7	0.0014	84.9	
Topallı – Conglomerate	0.105	20	96.6	0.105	40	98.0	0.076	72	30	4	5	53	75	93.8	0.0062	91.3	
Topallı – Tuff	0.020	20	73.0	0.020	20	85.6	0.052	134	20	7	26	38	51	98.0	0.0053	89.8	
Tomasa	0.020	20	96.0	0.020	20	90.5	0.020	57	20	5	6	28	30	91.2	0.0024	88.0	
Taşharman – Conglomerate	0.040	75	89.0	0.030	100	49.1	—	—	—	—	—	—	—	—	—	—	
Taşharman – Tuff	0.041	75	92.7	0.120	100	32.0	—	—	—	—	—	—	—	—	—	—	
Kasar/Taş.Cong./Taş. Tuf.	—	—	—	0.038 W=62 kg R=2/1/1	80	93.3	0.060	100 R=2/1/1	85	8	18	16	110	70.3	0.023	61.6	
Yardere	0.038	25	94.1	0.038	80	88.7	0.036	50	80	30	40	18	30	40.0	0.018	50.0	
Yardere	—	—	—	—	—	—	0.090	57	185	60	56	27	23	26.0	0.060	33.3	
Tüllüce	0.027	80	92.6	0.027	80	64.2	X	X	X	X	X	X	X	X	X	X	
Kocadüz	0.022	392	93.5	X	X	X	X	X	X	X	X	X	X	X	X	X	
Gördes	0.030	320	26.7	X	X	X	X	X	X	X	X	X	X	X	X	X	

leaching to these ground samples, some parameters such as, (a) selection of the best reagent, (b) amount of reagent consumed, (c) leaching time and temperature, and (d) influence of the oxidant on the leaching process, have been investigated.

(2) To determine the optimal particle size range for which the static column technique could be used most effectively and economically.

(3) To verify the laboratory scale findings on a pilot plant scale, particularly the applicability of heap leaching.

EXPERIMENTS

Agitating leaching tests on the minus 65 mesh ores showed that there was no effect of oxidant ($KClO_3$) on the extraction of uranium. As far as the effect of temperature is concerned, with the temperatures of 65°C and ambient, no difference was achieved in the recoveries. Sulphuric acid, as a leaching reagent for uranium, was found to be superior to other reagents such as nitric acid, hydrochloric acid and sodium carbonate.

After these experiments, the possibility was studied of applying the Lixiviation Accélérée process to the ores from which uranium could be extracted with an economical amount of acid. The process has many advantages such as avoiding the necessity of grinding, agitation and filtration.

In the experiments, the ore was crushed to minus 2 cm using a jaw crusher and then 10 kg of sample was filled in a PVC column 10 cm in diameter and 1 m in height and an acid solution (1 ltr/d) was dropped on the ore by means of a dropper-pump. Each day, 1 ltr of pregnant solution filtered from the bottom of the column was then recycled in the same manner. This leaching operation went on until constant pH and EMF were reached. The washing was carried out first with a solution containing 10 to 20 g of H_2SO_4 per litre and then with water. After leaching, pregnant solutions and residues were analysed for uranium. In the recovery calculations, uranium in the residue was taken into consideration.

As a result of laboratory experiments on the ores which are separately located in the Köprübaşi basin, three main types of ores have been classified:

(1) Kasar type

These ore deposits (located in the Kasar, Çetinbaş, Kayran, Topalli and Tomaşa areas) consist of secondary uranium mineralization (autunite, meta-autunite and torbenite), in loosely consolidated sands, gravels, silts and clays of the Neogene Age.

The pilot plant tests of these ores [1] were started with Kasar ore. The ore samples taken by open-pit mining methods were loaded into six 24-t stalls without any size reduction, and wetted with uraniferous solution from the previous stall followed by a wash with an acid solution, adjusted so as to consume 20 kg of H_2SO_4 per tonne of ore, and thirdly by water. In these tests with the Kasar ores a uranium recovery above 90% was obtained, but optimum leaching time was rather long (8 weeks). It was noticed that an abundance of clays of the montmorillonite group had caused the formation of impervious layers that hindered the leaching.

To prevent the formation of such impervious layers, 100 t of ore (2.2 m high) was subjected to heap leaching under the same conditions as leaching in the stalls. Three weeks of leaching was enough to obtain the same uranium recovery as above, 90%.

In order to investigate the effects of the size on the heap permeability, 1000 t of ore (3 m high) was leached under the same conditions. It was found that no problems of percolation rate were likely to be encountered in heap leaching of Kasar ores in the open. The heap leaching results of Kasar-type ores have been summarized in the Table.

The uraniferous solutions (U_3O_8: 1 to 1.5 g/ltr, P_2O_5: 1.0 g/ltr, Fe : 3.8 g/ltr) obtained from the heap leaching operations were purified in a solvent extraction unit (four stages for extraction and two stages for stripping) with a capacity of 100 ltr/h by using 0.1M Alamine 336-kerosene-decanol solution. The uranium in the purified and concentrated solutions (15 to 20 g of U_3O_8) was then precipitated as a yellow cake with 65 to 75% U_3O_8 content by means of magnesia milk (20 g of MgO per litre). After drying at 105°C uranium concentrates are kept in 50 kg boxes for further studies.

In the SX-experiments optimal phase flow-rates (aiming at 1 to 5 ppm U_3O_8 in the raffinate) were determined as pregnant solutions: 75 to 80 ltr/h, organic phase: 15 to 20 ltr/h and stripping solution: 4 to 5 ltr/h with a 40 g amine loss per kilogram of U_3O_8.

The technical quality of the magnesia (due to sintered particles or uncalcined carbonate) caused the yellow cakes of almost all ores to have high CO_2 and MgO contents, being in the order of 4.0% and 8.0% respectively.

(2) Taşharman type

These ores are located in the Taşharman (conglomerate and tuffite) and Yardere areas. No specific uranium mineral has been detected in the mineralogical determination, although uranium is disseminated in phosphate minerals as dahllite and apatite.

Agitating and column leaching tests showed that extraction of uranium from Taşharman ores could be increased by decreasing the particle size or increasing the amount of acid per tonne of ore. Very poor recoveries (less than 50%) of uranium were obtained in column leaching tests of Taşharman ores (P_2O_5 : 3.7%, CO_2 : 1.0%) most probably due to the formation of gypsum and Fe-PO_4 complexes and causing serious short circuiting.

Therefore, –1 cm and –3 cm Taşharman ores were individually mixed with –5 cm Kasar ore for better percolation in the column leaching. With the –1 cm particle size 90% uranium recoveries were obtained.

Although almost perfect percolation was observed in the heap leaching of mixed ore (Kasar/Taş.Cong./Taş. Tuff = 2/1/1 weight ratio) recovery of uranium from the Taşharman ores stayed at the 35% level. The reason for this was considered to be the impossibility of the diffusion of the acid solutions into the original sized (–20 cm) Taşharman ore particles in the heap. Heap leaching of Yardere ore resulted in low recovery and the problem that whether a higher acid concentration or a lower heap height (e.g. 1 m) were applied, cementation and poor percolation were observed.

In the SX-treatment of Taşharman-type ore solutions produced by heap leaching, the following difficulties losing amine and uranium (up to 200 ppm) in the raffinate have arisen:

(i) The high acid consumption in the leaching resulted in solutions which contained higher amounts of other elements such as Fe: 14.8 g/ltr, P_2O_5: 13.3 g/ltr, Al: 12.7 g/ltr. This caused the formation of emulsion in the settling area and loss of uranium in the raffinate. The chemical analysis of the third phase, calcined at 800°C, explains the uranium loss; U_3O_8: 3.05%, SiO_2: 22.1%, Fe: 15.2%, Al_2O_3: 16.2%, P_2O_5: 16.1%, SO_4: 8.3%, Ca: trace.

(ii) Formation of $CaSO_4$ decreased the SO_4 ions in the aqueous phase and so more phosphate-uranyl complexes formed which were not selective for Alamine 336.

(iii) Acidity of pregnant solutions higher than pH 1 decreased the performance of the organic solvent.

(iv) Ambient temperatures below 10°C in winter increased the viscosity of the organic or third phase and thus separation of the phases in the SX-system became difficult.

To overcome these problems, some treatments have been applied evenly:

(i) Passing the pregnant solutions through a membrane filter before SX-operations.
(ii) Close pH control and bringing the pH to 1 by acid addition.
(iii) Pre-heating of solutions to 30 to 35°C.
(iv) Dilution of pregnant solutions with water.
(v) Decreasing the flow-rates of all phases in the mixer-settler unit.
(vi) Addition of more decanol in the organic phase.

As a result of this unsettled SX-treatment, lower grade yellow cake has been produced (e.g. U_3O_8 : 46.0%, CO_2 : 5.5%, P_2O_5 : 2.3%, MgO : 13.8%, Moisture : 21.8%, Na_2O : 4.5%) from Taşharman-type ores.

(3) Carbonate type

There are three main locations for these ores, Kocaddüz (CO_2 : 17.0%, CaO: 16.1%), Gördes and Tüllüce. This type is characterized by high calcite and dahllite with some apatite. Acid leaching and alkaline leaching (100 kg of Na_2CO_3 + 160 kg of $NaHCO_3$ per tonne of ore at 65°C) were carried out with −200 mesh Kocaddüz ore samples, but no acceptable uranium recoveries were obtained.

The Table gives the laboratory and pilot plant leaching test results of the Köprübaşi uranium ores.

CONCLUSION

The feasibility studies of the plant (aiming at 100 t of U_3O_8 per year as yellow cake) that will be installed in the area will start in the light of the information obtained from the pilot plant tests and from the exploration work still going on. Reasonably assured resources of uranium explored so far are estimated at 2500 t of U_3O_8 in the Köprübaşi area (Kasar type: 1200 t U_3O_8; Taşharman type: 900 t U_3O_8 ; Carbonate type : 400 t U_3O_8).

Recent drilling in the Ecinlitaş area near the original Kasar deposit has indicated ore at a depth of 60 to 120 m which is described as unoxidized. In the primary agitating and column leaching tests of drilled ore samples (− 14 mesh), 90% uranium recovery was obtained by consumption of 40 kg of H_2SO_4 per tonne of ore. Up to now, resources of this type of ore have been calculated as 300 t of U_3O_8 on the basis of 0.03% U_3O_8.

For Taşharman-type ores, experimental work will go on by carrying out DAL (Dilute Acid Leaching) and TLL (Thin Layer Leaching) to fix the optimal point between particle size and acid consumption for the higher uranium recoveries.

Consequently, in the near future, a definite decision for yellow cake production plant will be determined by the results of drilling of the Ecinlitaş ore and research work on the Taşharman ores.

REFERENCE

[1] SAĞDIK, U., BILGEN, N. ÇIRALI, B., GÖNEN, N., "Technological Pilot Plant Works on Manisa-Köprübaşi Uranium Ores", Report by M.T.A. Enstitüsü Teknoloji, Dairesi, Ankara, (Dec.1978).

DISCUSSION

R. BODU: I know from experience that it is difficult to determine accurately the yield from heap leaching. While it is possible to determine the volume of uraniferous liquor and its concentration, it is far more difficult to determine accurately the ore concentration in the bins, either before or after leaching. How did Mr. Sağdik sample the material in the bins?

U. SAĞDIK: Ore samples, about 24 t for each stall, were carried by trucks to the pilot plant. Nine shovels full of the ore were put into the stall and one shovel taken for the sample. So, for each stall, 2.4 t of ore sample were taken. By quartering of this amount, almost 800 kg of sample was crushed to 1 cm by means of a jaw crusher. Then 50 kg of sample was taken by quartering to be ground into – 65 mesh for chemical analyses. After leaching a similar procedure has been carried out during the discharging of the ore from the stall.

R. COLEMAN: What are the dimensions of the ore heaps (width, length and depth)?

U. SAĞDIK: The following are the dimensions of the 100 and 1000 t heaps.

Heap (t)	Width (m)	Length (m)	Depth (m)
100	8	7.5	2.2
1000	20	20	3.0

M. PERARNAU: The barren heap leaching liquor contains undissolved radioactive elements, particularly radium and its descendants. This liquor enters edible plants directly; are the latter used for human consumption? It must be remembered that plants can not only absorb radioactive products, but also concentrate them to a certain extent.

U. SAĞDIK: Acid soluble radioactive elements go into barren liquors by the heap leaching process. It is believed that after 5 years rain wash a 0.5 m thickness on the top soil could be available for plants to be grown. It should also be noted that much of the study of vegetation is simply to determine whether vegetative rehabilitation is possible at all.

S. SEN: Continuing on the question by Mr. Perarnau I would like to add that there is a difference when the ore is original and after it is attacked with an acid. The soluble radioactive elements in the latter case are likely to be picked up by the plants grown on the soil. I also wish to ask whether the grade of the uranium concentrate produced by heap leaching meets the specifications required by the refinery?

U. SAĞDIK: As seen in the paper, no problems have arisen from Kasar-type ores, but yellow cakes of Tasharman ores contain more MgO and CO_2 due to low U-content solutions (less than 10 g of U_3O_8 per litre) from SX-treatment.

RECUPERACION DE URANIO DESDE SOLUCIONES DE LIXIVIACION DE COBRE DE LA MINA CHUQUICAMATA SUR

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Abstract–Resumen

RECOVERY OF URANIUM FROM COPPER LEACHING SOLUTIONS FROM THE SOUTH CHUQUICAMATA MINE.

The paper deals with the recovery of uranium from copper leaching solutions containing between 10 and 18 ppm U_3O_8. The study, which covers a laboratory stage and a pilot plant stage, has shown the technical feasibility of producing yellow cake with U_3O_8 contents of between 13 and 20% by direct precipitation of eluates which, when purified in the laboratory, have contained up to some 85% U_3O_8.

RECUPERACION DE URANIO DESDE SOLUCIONES DE LIXIVIACION DE COBRE DE LA MINA CHUQUICAMATA SUR.

Se estudia la recuperación de uranio desde soluciones de lixiviación de cobre, que contienen entre 10 y 18 ppm de U_3O_8. El estudio comprende etapas de laboratorio y planta piloto y ha permitido demostrar la factibilidad técnica de producir torta amarilla, con contenidos de entre 13 y 20% de U_3O_8 por precipitación directa de eluídos, los que purificados en el laboratorio han alcanzado hasta un 85% de U_3O_8.

1. INTRODUCCION

La posibilidad de recuperar uranio en forma de concentrados a partir de los minerales oxidados de cobre de Chuquicamata fue demostrada en el año 1970.

A partir de esa fecha se realizaron estudios de laboratorio tanto por la Comisión Chilena de Energía Nuclear (C.CH.E.N.) como por universidades y otras instituciones de investigación chilenas. Dichos estudios indicaron que sería factible recuperar el uranio contenido en las soluciones de lixiviación de la Mina Chuquicamata Sur.

En base de estos antecedentes, en 1977 la C.CH.E.N. y la división Chuquicamata de Codelco-Chile firmaron un convenio mediante el cual se decidió la construcción de una planta piloto de intercambio iónico para estudiar la recuperación de uranio. El diseño, la construcción y la explotación de la planta corrieron a cargo del personal de ambas instituciones.

El yacimiento de cobre Chuquicamata-Sur está ubicado en la provincia de El Loa, 2 km al sur del mineral de Chuquicamata, situado éste a unos 1400 km al norte de Santiago de Chile. Tiene una extensión reconocida de 2,2 km de largo por 1,2 km de ancho y un espesor medio de 50 m. La cubicación estimada es de 155 millones de toneladas, con leyes medias de 1,35% en cobre y 10 ppm de uranio.

La mineralización por cobre corresponde a especies oxidadas, principalmente crisocola, y en menor proporción atacamita (copper pitch y copper wad). La mina se explota a tajo abierto y el mineral triturado con tamaño inferior a 6" se envía por una correa transportadora de 48" de ancha y 2 km de larga a la antigua planta de lixiviación de Chuquicamata.

En la planta de lixiviación, el mineral se tritura a 30% <3/8" y se deposita en bateas de 12 000–14 000 ton cortas, donde se lixivia por percolación con soluciones de ácido sulfúrico, en un sistema en contracorriente.

Las soluciones fuertes de lixiviación se purifican y envían a la planta de electro-obtención, donde se deposita el cobre electroquímicamente sobre una lámina inicial, obteniéndose como producto final los cátodos de cobre.

Conjuntamente con el cobre, parte del uranio contenido en el mineral se lixivia, alcanzando niveles de entre 10–18 ppm de U_3O_8 en la solución fuerte.

Dado que la producción de uranio sería en este caso marginal, se ha realizado el estudio sin introducir modificaciones en el circuito de obtención de cobre y mientras se efectuaba otro estudio en la planta de lixiviación destinado a mejorar las condiciones de recuperación de cobre.

Descripción de la planta piloto

La planta piloto de recuperación de uranio consta de una sección de intercambio iónico y otra de extracción por solventes.

La sección de intercambio iónico cuenta con cuatro columnas de acero revestidas de poliuretano de 1,8 m de diámetro y 12 m^3 de capacidad útil, además de los estanques para soluciones y las bombas de circulación.

La sección de extracción por solventes cuenta con una planta de siete mezcladores–decantadores de iguales dimensiones, con capacidad para 1 gal/min de solución acuosa, diseñada por Davy Powergas para la extracción de cobre, y utilizada sin modificaciones.

2. EXPLOTACION Y RESULTADOS DE LA PLANTA PILOTO

Para la explotación de la planta piloto de extracción de uranio se han utilizado soluciones de la planta industrial de lixiviación por percolación de los minerales de Chuquicamata Sur.

CUADRO I. ANALISIS TIPICO DE SOLUCIONES

	Cu (g/l)	F^{+2} (g/l)	Fe^{+3} (g/l)	SiO_2 (g/l)	P (g/l)	Al_2O_3 (g/l)	Mo (g/l)	Cl (g/l)	U_3O_8 (g/l)
Soluc. fuerte	36	1,5	3,5	2,5	1	15	0,006	0,7	0,010
Soluc. declorurada	36	5,0	0,5	2,0	2	17	0,002	0,1	0,014

La densidad de la solución en ambos casos es de 1,16.

CUADRO II. RECUPERACIONES PROMEDIO EN LA ETAPA DE CARGA DE INTERCAMBIO IONICO

	COLUMNA 1			**COLUMNA 2**			**COLUMNAS 1+2**		
Flujo por columna en gal/min	20	40	60	20	40	60	20	40	60
Flujo unitario en gal/min/pie^2	0,7	1,4	2,1	0,7	1,4	2,1	0,7	1,4	2,1
Tpo. residencia en min	40	20	13	40	20	13	40	20	13
Recuperación 1er día en%	51	63	60	74	57	64	87	84	86
Recuperación 2° día en %	38	46	48	75	72	66	84	85	82
Recuperación 3er día en%	29	28	38	68	69	56	77	78	72
Recuperación 4° día en%	22	24	28	60	65	51	69	73	64
Recuperación global en%	35	40	43	69	66	60	80	80	76

Esta operación debió llevarse a cabo sin perturbar la marcha normal de las operaciones para la obtención de cobre, motivo por el cual hubo que utilizar las soluciones sin ajuste previo de acidez, fluctuando el pH de éstas entre 1,7 y 2,1.

2.1. Caracterización de las soluciones de alimentación a intercambio iónico

Se han utilizado soluciones fuertes de lixiviación y soluciones decloruradas obtenidas en dos puntos distintos del circuito de obtención de cobre. Sus composiciones típicas se muestran en el Cuadro I.

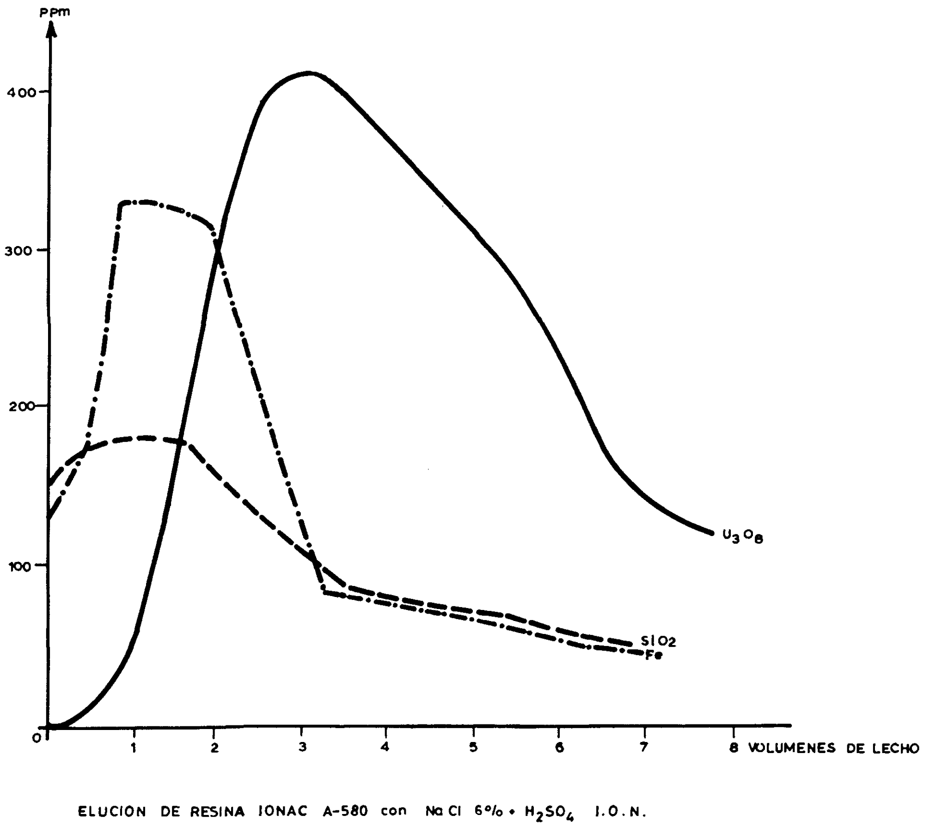

FIG.1. Curva típica de elución.

2.2. Intercambio iónico, ciclo de carga

Se han empleado en cada torre 3 m^3 de resina IONAC A 580, La carga de la resina se realiza haciendo circular la solución en flujo ascendente, de modo que el efluente de la primera torre se transforma en alimentación de la segunda y el efluente de ésta retorna al circuito de lixiviación de cobre.

Una vez completado el ciclo de carga, se detiene la alimentación, pasando la primera torre a las etapas siguientes de lavado y elución, mientras que la segunda torre pasa a ocupar el primer lugar en el ciclo de carga siguiente.

Se ha trabajado con flujos de 20, 40 y 60 gal/min, lo que corresponde a flujos unitarios de 0,7, 1,4 y 2,1 gal/min/pie^2. Debido a la alta densidad de las soluciones no ha sido posible trabajar con flujos mayores.

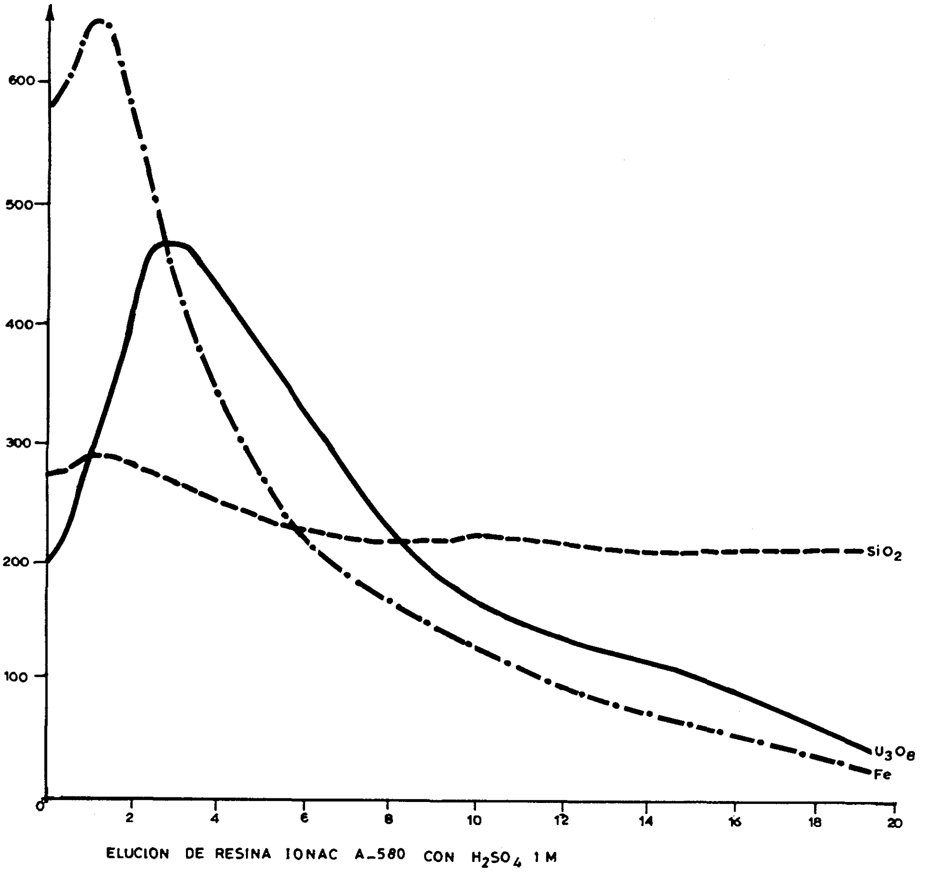

FIG.2. Curva típica de elución.

Al cabo de ocho meses de trabajo, las recuperaciones promedio en el ciclo de carga se situaron entre el 76 y el 80%, alcanzándose una capacidad de carga aproximada de 1,3, 2,3 y 3,1 g de U_3O_8/l de resina para flujos de 20, 40 y 60 gal/min respectivamente. En el Cuadro II se muestra un resumen de los resultados promedio obtenidos.

2.3. Intercambio iónico, ciclo de elución

La elución de la resina se efectúa en flujo descendente, con 8 volúmenes de lecho (24 m^3) de eluyente compuesto de NaCl al 6% y H_2SO_4 0.15N. Esos 8 volúmenes de lecho están formados por 4 volúmenes de reciclo y 4 volúmenes de eluyente fresco. El eluyente fresco se obtiene ajustando los niveles de NaCl y H_2SO_4 al sobrenadante de la precipitación anterior. El flujo de eluyente ha sido de 26 gpm lo que equivale aproximadamente a 2 volúmenes de lecho por hora.

Los 4 volúmenes de eluídos ricos obtenidos y enviados a precipitación directa contienen en promedio entre 220 y 360 ppm de U_3O_8.

Las impurezas eluídas junto con el uranio son principalmente sílice y fierro.

En la Fig.1 se muestra una curva típica de elución.

Al utilizarse la extracción por solventes, la elución se realiza con H_2SO_4 1M, pasando 20 volúmenes de lecho, de los cuales los 10 primeros son reciclo y los 10 últimos son, en parte, el refino de extracción por solventes (ajustado en H_2SO_4 a 1M) y, en parte, eluyente fresco. El flujo utilizado es de 26 gpm, equivalente a aproximadamente 2 volúmenes de lecho por hora.

Eluyendo en estas condiciones, la concentración obtenida en los primeros 10 volúmenes de eluído se sitúa entre 200y 350 ppm de U_3O_8.

Al igual que en el caso de la elución con NaCl, las principales impurezas eluídas junto con el uranio fueron el fierro y la sílice.

La Fig.2 representa una curva típica de elución.

2.4. Intercambio iónico – Regeneración y sulfatización de la resina

La regeneración de la resina se ha efectuado pasando a través del lecho de resina un flujo descendente de 26 gal/min (2 volúmenes de lecho por hora) de una solución de NaOH al 4% durante 3 horas.

En seguida la resina se lava con 6 m^3 de agua y se sulfatiza con 6 m^3 de solución de H_2SO_4 1M, en las mismas condiciones de flujo que el lavado alcalino de regeneración.

Las rpincipales impurezas extraidas durante la regeneración son: sílice, fósforo y molibdeno.

2.5. Extracción por solventes

Las pruebas de extracción por solventes se realizaron con la fracción concentrada de los eluídos sulfúricos. Cada experiencia tuvo una duración de 24 horas, empleándose en ellas 6 m^3 de eluído (2 B.V.).

Como extractante orgánico se empleó una solución de 3% de alamina y 2% de isodecanol en tridecano. Como reextractante se utilizó una solución de sulfato de amonio al 15%. A la solución acuosa de reextracción se inyectó amoníaco gaseoso para mantener un pH de 4,5 a 5,0.

Las soluciones de avance se envían a precipitación y la solución de refino se acondiciona y emplea en la etapa de elución.

CUADRO III. COMPOSICION DE LA TORTA AMARILLA OBTENIDA POR PRECIPITACION DIRECTA DE ELUIDOS

(en %)	CONCENTRADO 1	CONCENTRADO 2	CONCENTRADO 3
U_3O_8	12,1	17,9	21,5
SiO_2	6,7	16,6	14,4
Al_2O_3	5,2	4,2	6,2
Fe	25,7	13,0	8,2
P	9,7	7,1	2,8
Mo	0,5	1,8	1,4

He aquí un resumen de las condiciones de explotación y los resultados promedio obtenidos:

Alamine 336	3%
Isodecanol	2%
Relación O/A en E/S	2,0/13,3
Relación O/A operación E/S	1,0/1,14
Tiempo retención E/S (min)	1,23/1,31
Solución fuerte mg/l U_3O_8	372
Solución refino mg/l U_3O_8	88
Extracción %	76
Solución avance mg/l U_3O_8	1628
Solución gastada mg/l	14

2.6. Obtención de la torta amarilla

La torta amarilla se obtiene por precipitación de eluídos ricos o soluciones de avance de extracción por solventes.

En ambos casos, la precipitación se ha realizado a temperatura ambiente en un decantador de 15 m^3, en el que se ha depositado la solución; a ésta se ha agregado amoníaco gas hasta alcanzar un pH de 7 a 7,5 agitando simultáneamente mediante inyección de aire comprimido.

La concentración en U_3O_8 de la torta amarilla obtenida por precipitación directa de eluídos está comprendida entre el 12,8 y el 20,6%, mientras que la de los precipitados obtenidos a partir de las soluciones de avance de extracción por solventes ha fluctuado entre el 68 y el 78% de U_3O_8. El sobrenadante de la precipitación contiene de 40 a 68 ppm de U_3O_8.

En el Cuadro III se indica la composición de los precipitados obtenidos.

Las pruebas de purificación de la torta amarilla obtenida por precipitación directa de eluídos, realizadas en el laboratorio, han permitido obtener muestras de concentrado de un 84,74% de U_3O_8, con contenidos de fierro, cobre y molibdeno del 0,04, 1,0 y 0,78% respectivamente.

3. CONCLUSIONES

Se probó la factibilidad técnica de recuperar uranio, en forma de torta amarilla, a partir de las soluciones de lixiviación de cobre de la mina Chuquicamata Sur, sin producir interferencias en el proceso de producción de cobre.

Debido a la rápida declinación de la recuperación en la etapa de carga de intercambio iónico, resulta conveniente trabajar con ciclos de carga cortos. A este respecto, se está estudiando a nivel semipiloto el empleo de más de dos columnas en serie.

Dentro del rango de flujos de solución probados (0,7, 1,4 y 2,1 gal/min/pie^2) resulta conveniente trabajar con el flujo más alto, dado que, sin afectar sensiblemente la recuperación, se logra el más alto nivel de carga en la resina (3,1 g de U_3O_8/l de resina).

Si bien los concentrados obtenidos en la planta piloto no cumplen las especificaciones de pureza nuclear, pruebas de laboratorio indican que técnicamente es posible purificar la torta amarilla hasta alcanzar niveles comerciales.

DISCUSSION

S. SEN: Have you worked out any cost figures for the recovery of uranium from this dilute solution?

N. ANDALAFT: At present we have only been concerned with the technical details and problems of recovery of the uranium from the solution, so that we do not have figures relating to economics which can be said to have any relation to what might be the final process.

D.W. BOYDELL: First, how much uranium remains in the resin after the elution with NaCl and H_2SO_4? Second, what is the temperature of the sulphuric acid elution? Third, what is the concentration of uranium in the effluent?

N. ANDALAFT: First, although no figures from direct resin analysis are available, owing to the low reliability of such analyses, it can be estimated on the basis of solution balances that approximately 20% of the uranium loaded in the resin remains in it after elution with sodium chloride and between 30 and 50% remains after elution with sulphuric acid.

Second, the elution with sulphuric acid was always carried out at ambient temperature, i.e. between 10 and 20°C.

Third, the uranium concentration in the effluent increases between two successive alkaline washings of the resin. This variation can be seen in the table below, which shows the average uranium content in the effluent for four-day loading operations, between two successive regenerations of the resin.

	Effluent U_3O_8 (ppm)	Effluent 1st column U_3O_8 (ppm)	Effluent 2nd column U_3O_8 (ppm)
Load 1	10.7	5.5	2.0
Load 2	9.5	5.6	3.8
Load 3	12.0	7.3	3.4
Load 4	12.0	8.8	6.3

A. HIMSLEY: It is stated that the resin is loaded with between 1.3 and 3.1 g of U_3O_8/ltr. If this were completely eluted from the resin by using four bed volumes of the recycling eluant, the result would be an eluate of between 325 and 775 ppm U_3O_8.

The figures of 220 to 360 ppm given as the average concentration of the eluate would indicate a removal of only 0.88 to 1.44 g of U_3O_8/ltr of resin. If the difference remains in the resin, it could lead to a relatively high concentration of U_3O_8 in the final effluent. Could the author clarify this point?

N. ANDALAFT: As Mr. Himsley implies, it is effectively established in the operation of the pilot plant that the residual uranium content in the effluent is high and that, furthermore, this content increases with successive loadings between resin regenerations. The residual uranium content of the resin and also of the effluents has been indicated in the replies to Dr. Boydell's questions.

F.R. HARTLEY: You mentio that the copper solution contains between 10 and 18 ppm of U_3O_8. This would represent a relatively steady state concentration balanced through the whole inventory of the leaching and tank house circuits over a significant period of time. However, would you yet know how much copper is entering the circuit from the ore. That is how much will be available for extraction and what concentration the liquor will be once you start recovering the uranium from it?

N. ANDALAFT: It has actually been quite difficult to determine how much new uranium enters the solution from the ore. This is basically due to difficulties in sampling and analysis of the solids. Nevertheless laboratory leaching with recycling has indicated that these levels of uranium content in the solutions would be more or less the steady state level.

A. HIMSLEY: I would like to comment on this. In another similar operation the equilibrium level of uranium in the leach circuit went down to about one third of the previous equilibrium level.

IMPURITIES IN URANIUM PROCESS SOLUTIONS

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Abstract

IMPURITIES IN URANIUM PROCESS SOLUTIONS.

Several uranium purification circuits are presented in tabular form together with the average major impurity levels associated with each. The more common unit operations in these circuits, namely strong- and weak-base ion-exchange, solvent extraction and the precipitation of impurities are then discussed individually. Particular attention is paid to the effect and removal of impurities in each of these four unit operations.

1. INTRODUCTION

Uranium purification circuits are as varied as the ore types that are treated for uranium recovery. The major features of the more common circuits that have been employed are shown in Table I. Table II summarizes circuits that have been developed under special circumstances but which will be employed more frequently as these ore types are increasingly exploited in the future. Reference will be made to these circuits as each unit operation in uranium recovery is reviewed.

The nature of uranium mineralization in an ore will determine the severity of the conditions necessary to render the uranium content soluble. If all or part of the uranium is present in aggregations too small to be exposed directly to the leaching agent it may be necessary to dissolve barren material in order to liberate and dissolve the uranium. Uraninite occluded in pyrite, and uranium atoms contained within the crystal lattice of zircon are examples of occurrences that require severe leaching conditions for uranium dissolution. Similarly, the uranium-containing multiple oxides, brannerite, betafite and pyrochlore, are particularly refractory, and effective leaching conditions will render appreciable quantities of subsidiary minerals and gangue material soluble.

Figure 1 shows the unit operations in uranium ore processing. In general there will be a strong interaction between the process choices made for adjacent unit operations. There will, however, seldom be economic justification at the design stage for moderating the conditions of the leach (with consequent lower uranium extraction) to alleviate problems that may occur in the purification and

TABLE I. THE MORE COMMON URANIUM PURIFICATION CIRCUITS

No.	Leach	Example	No. of plants in this circuit	Purification			Yellow cake	
				primary	secondary	precipitate	major impurities	% U_3O_8
1	H_2SO_4	Dension, Ontario	5	SBIX	lime ppt.	NH_3/ADU	SO_4 2–5% SiO_2 1–2% Ca ~0.5%	80–92
2	H_2SO_4	Buffelsfontein, Transvaal	20	SX	nil	NH_3/ADU	SO_4 1–2% Na <0.5%	92–98
3	H_2SO_4	Blyvooruitzicht, Transvaal	14	SBIX	SX	NH_3/ADU	SO_4 3–5%	94–98
4	H_2SO_4	Uravan, Colorado	2	WBIX	nil	NH_3/ADU	PO_4 <0.5% V_2O_5 <0.5% SO_4 <2.0%	92–96
5	Na_2CO_3	Rio Algom, Utah	2	nil	nil	NaOH/SDU	SO_4 <1% CO_3 <2% SiO_2 <3%	75–80
6	$(NH_4)_2CO_3$	Atlantic Richfield, Texas	2	IX	H_2SO_4/ decarbonation	NH_3/ADU	Na <1% CO_3 <0.5%	85–90

NOTES: SBIX – strong-base ion-exchange
SX – tertiary amine solvent extraction
WBIX – weak-base ion-exchange
ADU – ammonium diuranate
SDU – sodium diuranate

TABLE II. SPECIAL PURPOSE PURIFICATION CIRCUITS

No.	Leach	Problem species in leach liquor	Example plant	Purification			Yellow cake	
				primary	secondary	precipitation	major impurities	% U_3O_8
7	HNO_3	Th	Palabora, Transvaal	TBP	nil	NH_3/ADU	Th $< 0.6\%$ SiO_2 < 300 ppm Fe < 60 ppm	98.5–99
8	Na_2CO_3	V,organics Mo	U.N.H. Partners, New Mexico	SDU	roast differential leach	acidification NH_3/ADU	Na $< 0.5\%$ V_2O_3 $< 0.5\%$ SO_4 1–5%	86–88
9	Na_2CO_3	Mo, organics	Cotter, Colorado	SDU	nil	acidification H_2O_2/UPO	Na $< 0.5\%$ CO_3 $< 0.5\%$ SO_4 $< 0.5\%$	90–95
10	H_2SO_4	V, Cu	Atlas, Utah	SBIX	SDU	acidification H_2O_2/UPO	Na $< 0.2\%$ V_2O_5 $< 0.8\%$ SO_4 $< 0.5\%$	92–96

NOTES: TBP – tributyl phosphate solvent extraction
UPO – uranium peroxide

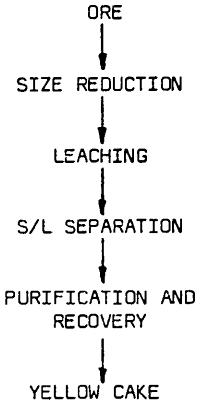

FIG.1. Unit operations in uranium ore processing.

recovery sections of a uranium plant. Existing technology may be adapted to treat any solution containing economic concentrations of uranium. In a number of recent uranium plants, however, uranium purification and recovery sections have proved to be a bottleneck to production, necessitating prolonged commissioning periods, loss of revenue and costly modifications.

2. STRONG-BASE ION-EXCHANGE

More uranium has been produced using strong-base ion-exchange as the primary method of purification than by any other process. The plants built during the first phase of expansion of the uranium industry in South Africa and Canada all used strong-base ion-exchange in fixed-bed downflow column contactors to treat semi-clarified sulphuric acid leach liquor. Both the equipment and the ion-exchange resins for these early plants were adopted with little change from the practices that had proved successful in the water treatment industry. More recent developments have aimed at the proving of both equipment and resins more suited to the special needs of the uranium industry. Considerable progress has been made in both these fields.

2.1. Ion-exchange equipment

The major disavantage of downflow contact of leach liquor with a fixed bed of resin is one of scale. The standard column for this duty has a diameter of 2.13 m, although columns of up to 3 m diameter have been used. Beyond this size range problems are encountered with the even distribution of solution flow through the resin bed. The height of a settled resin bed and specific flow rate that can be applied bear a direct relation to the pressure drop resulting from flow. High pressure drops are not only uneconomic but lead to external stresses on resin beads which result in bead distortion and breakdown and to channelling of solution flows within the bed.

The early ion-exchange plants had a capacity of several hundred tonnes of U_3O_8 per year. Productions an order of magnitude greater than this are now common. The multiplicity of columns required for these large productions would cancel many of the favourable economies that are available to large-scale operation.

Continuous upflow contactors (CIX), of which a number of designs have achieved commercial acceptance, have been developed to provide advantages not realized with downflow columns. These advantages have been described elsewhere [1, 2]. Perhaps it should be emphasized here that, with respect to the two performance criteria that are governed by the chemistry of the solutions treated – uranium recovery efficiency and product purity – CIX contactors are capable of exceeding the performance of downflow units for an identical duty, if correctly designed.

Upflow resin contactors are capable of treating unclarified solutions containing appreciable quantities of suspended solids. The limits to the solids content of the slime thus treated are set by the difference in relative density between the resin beds and the fluid medium, and by the effective viscosity of the slime. Operation with conventional strong-base resins is limited to around 8% solids for pulps which have favourable viscosity characteristics. A recently announced heavy resin [3] having a relative density in the sulphate form of 1.26 (compared to the more usual 1.10 to 1.15) will extend the operating range of upflow columns to around 15% solids. However, the full advantages of operating a resin system in the presence of loaded solids are realized when the major solid/liquid separation steps between leach and purification are eliminated. In this way, resin contactors are operated at a solids content similar to that under which leaching is conducted. Russian technology in this field has been described in an earlier IAEA publication [4].

The kinetics of uranium absorption from a relatively thick leach pulp are slower than for a clear solution, owing to increased resistances to uranium transport external to the resin beads in the fluid phase. Resin-in-pulp (RIP) systems usually require a large-size resin bead to facilitate resin/pulp separation which introduces additional diffusional resistances within the resin beads. The purification available from RIP systems is essentially the same as that offered by conventional means.

2.2. Absorption

The selectivity with which strong-base anion exchange resins absorb uranyl sulphate complexes from solution is well documented [5, 6]. The predominant

TABLE III. SUMMARY OF THE ION-EXCHANGE REACTIONS AND EQUILIBRIUM CONSTANTS AT 25°C IN THE SIX-COMPONENT SYSTEM AMBERLITE IRA 400, Na_2SO_4, NaCl, $NaNO_3$, H_2SO_4 AND UO_2SO_4

Ion exchange reaction		Equilibrium constant
$R_2SO_4 + 2HSO_4^-$	$\rightleftharpoons 2RHSO_4 + SO_4^{2-}$	$K^{HSO_4}_{SO_4} = 5.10$
$2R_2SO_4 + UO_2SO_4$	$\rightleftharpoons R_4UO_2(SO_4)_3$	$K^{UO_2(SO_4)_3}_{SO_4} = 7381.80$
$R_2SO_4 + UO_2(SO_4)_2^{2-}$	$\rightleftharpoons R_2UO_2(SO_4)_2 + SO_4^{2-}$	$K^{UO_2(SO_4)_2}_{SO_4} = 41.41$
$R_2SO_4 + 2NO_3^-$	$\rightleftharpoons 2RNO_3 + SO_3^{2-}$	$K^{NO_3}_{SO_4} = 72.93$
$R_2SO_4 + 2Cl^-$	$\rightleftharpoons 2RCl + SO_4^{2-}$	$K^{Cl}_{SO_4} = 5.10$

reactions may be represented as

$$2R_2SO_4 + UO_2SO_4 \rightleftharpoons R_4UO_2(SO_4)_3$$

and

$$UO_2(SO_4)_2{}^{2-} + R_2SO_4 \rightleftharpoons R_2UO_2(SO_4)_2 + SO_4{}^{2-}$$

Substantial competition to uranium absorption is afforded by a number of reactions of the form

$$R_2SO_4 + 2X \rightleftharpoons 2RX + SO_4{}^{2-}$$

where X may be bisulphate, nitrate, chloride or other monovalent ions. The effect of these ions in equilibrium absorption is shown in Table III.

Bisulphate ion is alway present in acid leach liquors. The quantity is governed by both the total sulphate concentration in solution and the pH, as indicated by the equation

$$HSO_4{}^- \rightleftharpoons H^+ + SO_4{}^{2-}$$

The equilibrium ratio for this reaction is often quoted as being of the order of 0.01. In fact this value is valid only for very dilute solutions; a more correct value

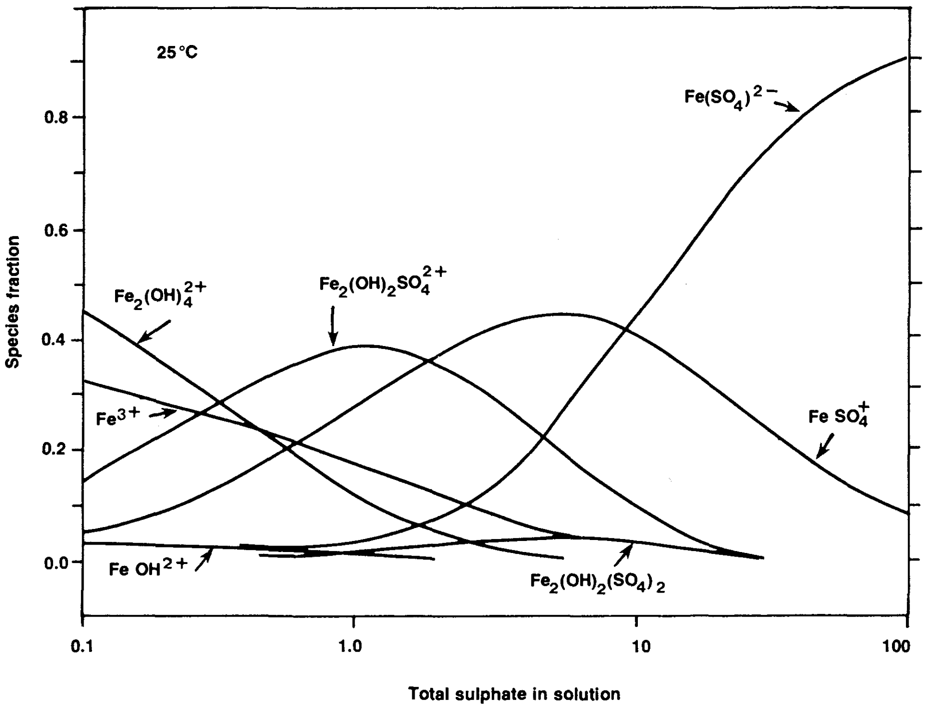

FIG.2. Distribution diagram: system Fe(III) — OH^- — SO_4^{2-} Fe(III) = 0.05M, 1 = 3.0, pH = 2.0.

for leach solutions having an ionic strength of 1.0 to 1.5 at 25°C is closer to 0.1. A recent investigation [6] into equilibria between strong-base ion-exchange resin and uranyl sulphate solutions containing nitrate and chloride ions has shown that an appreciable fraction of the uranium in the resin phase is present as the $UO_2(SO_4)_2^{2-}$ complex, and the greater part as $UO_2(SO_4)_3^{4-}$. The activities of ionic species in solution were calculated using the extended Debye-Huckel equation, whereas resin-phase activities were correlated by the use of the Wilson equation. Table III contains a summary of a number of these reactions and their equilibrium constants (calculated by using the activity of each species). Ferric ion species were not included in this study.

Groenewald [8] has calculated equilibrium distributions in the system Fe(III) — SO_4^{2-} — OH^- using a number of published stability constants. These curves (Fig. 2) indicate that the only anionic ferric species present in sulphate leach liquors is $Fe(SO_4)_2^-$. The existence of the complex $(Fe(OH)(SO_4)_2^{2-}$ has often been canvassed to explain the decrease in ferric absorption at pH's

TABLE IV. THE CONCENTRATION OF COMPETING IONS REQUIRED TO REDUCE EQUILIBRIUM URANIUM EXTRACTION BY 50% FROM ACID LIQUORS

Ionic species	Reference solution (g/ltr)	Strong-base IX resin (g/ltr)	Weak-base IX resin (g/ltr)	Tertiary amine (g/ltr)
Cl	nil	3–3.5	3–3.5	2.6
NO_3	nil	2.5–3.0	2.5–3.0	1–2
SO_4	25.0	>100	>100	50–70
pH	1.7	0.8–1.2	0.7–1.0	0.3–0.5
Fe^{3+}	2.2	7–10	>10	no effect
U_3O_8	50 ppm	20–25	15–22	5–7 ($5^{v}/v\%$)

below 2.0. This decrease is probably owing to increased competition from bisulphate ions.

Table IV shows the effect of competing ions on the absorption of uranium. The concentration necessary to reduce the absorption of uranium into a number of organic media is shown with reference to the behaviour of a standard pregnant solution. For example, between 3 and 3.5 g/ltr of chloride ion will reduce the loading of a strong-base resin from between 20 and 25 g/ltr U_3O_8 when in equilibrium with a solution containing 50 ppm U_3O_8 to a loading of 10 to 12.5 g/ltr U_3O_8.

The equilibrium loading attainable in a resin-purification system has a bearing on elution costs, equipment size and product purity. Because all the ion-exchange sites in a resin are converted during elution to the ionic form represented by the eluting solution, the consumption of eluant per kilogram of uranium eluted is directly proportional to the uranium loading on the resin entering the elution circuit. This loading is in turn limited by the equilibrium value achievable. The size of continuous ion-exchange contactors is directly related to the rate of uranium transport into and out of the resin beads. The rate of uranium absorption from a solution is governed in part by the equilibrium absorption because the difference in uranium content between the initial state of the resin and the equilibrium state represents a driving force for mass transfer. Finally, the lower

TABLE V. THE CONCENTRATION OF COMPETING IONS REQUIRED TO REDUCE EQUILIBRIUM URANIUM EXTRACTION BY 50% FROM ALKALINE CARBONATE LIQUORS

Ionic species	Reference solution (g/ltr)	Strong-base IX resin (g/ltr)
Cl	nil	2–4
SO_4	nil	2–6
CO_3	2–8	30–80
pH	10.5	<8
U_3O_8	150 ppm	120–130
U_2O_5	nil	<1.0

the equilibrium loading of uranium the greater will be the amount of extraneous ions that are carried forward into the elution circuit.

The absorption of uranium from alkaline leach solutions is marked by very favourable equilibrium loadings. The reaction is usually represented by

$$4RX + UO_2(CO_3)_3^{4-} \rightleftharpoons R_4UO_2(CO_3) + 4X^-$$

Equilibrium loadings of over 100 g/ltr U_3O_8 in the absence of competing ions suggest that an ionic species of lower valence may be involved. Chloride and sulphate exert a strong depressing effect on equilibrium loadings, which are more sensitive to pH and to the carbonate concentration than are the analogous values in the acid-sulphate system. The behaviour of vanadium ions, which are often encountered in alkaline leach liquors, is strongly pH dependent. Pentavalent vanadium is absorbed in preference to uranium in the pH range 8 to 10.5 whereas uranium absorption is favoured at pH's of 10.8 to 11.3 [11]. Molybdenum is absorbed from alkaline leach solutions but is held less strongly than the uranium carbonate complex and will be displaced from the resin as the uranium concentration in the resin phase increases. The effect of competing ions on the absorption of uranium from carbonate leach solutions is shown in Table V.

2.3. Resin poisons

Strong-base ion-exchange resins are liable to poisoning or fouling in some applications. A resin poison may be defined as a substance that enters the resin during absorption but is not removed during elution. This leads to a progressive increase in the quantity of the poison in the resin. Most poisons or fouling agents can be removed by special regeneration procedures that are applied when the presence of the poison begins to exert a deleterious influence on plant performance.

Silica is the most universal of the resin-fouling agents. Electron microprobe studies on sections of resin beads which exhibit silica poisoning have shown that the silica deposits in a layer (often no more than 10% of the bead radius in thickness) immediately inside the surface of the bead. This silica is present in polymerized form and does not occupy exchange sites within the resin. As the silica deposit ages, the phenomenon of synerisis occurs, water is released from the silica gel and the silica becomes progressively more difficult to remove. However, if treatment with caustic soda solution is practised at regular intervals the silica may be removed by a relatively mild treatment [9]. The effect of silica fouling is to slow the rate of diffusion within the resin bead and thus the rate of uranium absorption and elution. The behaviour of molybdenum appears to closely resemble that of silica and may be removed in the same way.

Cobalticyanide poisoning was a problem for a number of the first generation uranium plants on South African mines. With the renewed interest in ion-exchange processes for the recovery of uranium from gold tailing slimes dams, the subject of cobalticyanide poisoning has been re-investigated. It has been proved [10] that the ionic species responsible for the permanent poisoning of resin is $(Co(CN)_5OH_2)^{2-}$. This complex is formed as part of a complex reaction sequence following contact of cyanide ion with cobalt or cobalt minerals in the leach pulp during gold recovery. Polymerization occurs inside the resin bead to form an insoluble compound resistant to all but the most severe chemical treatment. As with silica, cobalt poison does not occupy exchange sites but exerts a very strong retarding effect on the kinetics of ion exchange. The most stable species in the chain of cobalt cyanide complexes is $(CO(CN)_6)^{3-}$. If sufficient time is allowed all the anionic cobalt present will convert to the hexacyanide form. This has in fact occurred in the case of slimes dam material in South Africa. The $(CO(CO)_6)^{3-}$ complex, although having a strong affinity for anion resins, does not polymerize within the resin bead and may be displaced by an excess of strong eluting reagent when necessary.

Leach solutions occasionally contain organic compounds that will result in fouling of an ion-exchange resin. Fulvic and humic acid and related substances are often responsible. The procedures developed to combat this problem in water treatment practice are often effective: for example a rinse with warm 10% brine solution to which a trace of sodium hypochlorite may be added. In severe cases a nitrate/nitric acid eluant has been found effective. If the rate of organic pick-up is very high, then a nitrate elution will remove both uranium and the organic species to the concentrated eluate which may be subjected to a further stage of purification, by, for example, the selective precipitation of uranium by hydrogen peroxide. However, organic fouling is best avoided if possible by absorption of these compounds on activated charcoal before ion exchange.

2.4. Elution

Table VI summarizes a number of conditions of elution that have been found to be satisfactory in large-scale operation. Elution is a slow process governed by the diffusion of uranium species through the resin beads. The rate of elution varies with the square of the bead diameter, so the size distribution of the resin is an important consideration when evaluating elution curves. Temperature is a prime variable in elution. The holding time necessary for efficient elution is strongly affected by temperature changes. An increase in the temperature of 10.5% sulphuric acid from 20°C to 45°C will allow the contact time of resin in a fixed-bed elution system to be cut by 65% for the passage of 14 bed volumes of acid to achieve eluted resin values of less than 1 g/ltr U_3O_8.

Elution may be effected in either continuous or fixed-bed contactors. CIX elution will usually be chosen for the situation in which frequent transfers of resin to elution occur from a CIX absorption contactor. Fixed-bed elution is usually conducted by the split elution technique whereby contact of the resin with fresh eluate is preceded by contact with return eluate recycled from the previous elution cycle. The recycle eluate after passage through the loaded resin is termed concentrated eluate and this is reserved for precipitation. In this manner the concentration of uranium in the concentrated eluate is increased over that which would be obtained on a once-through basis. Additional rinse displacement and backwash steps are required for fixed-bed elution. Reference [14] contains full details of a typical fixed-bed elution cycle.

The efficiency of elution should be evaluated with reference not to the percentage of uranium removed from the resin but to the actual concentration of uranium remaining on the resin after elution. This latter value determines the limit of the concentration of uranium that is achievable in the barren solution when the eluted resin is returned to absorption service. An increase in the uranium content of resin entering elution has little effect on the time required for elution, which is determined chiefly by the required residual uranium content.

Elution of uranium absorbed as a carbonate complex appears a somewhat easier duty than the elution of uranium absorbed as sulphate complexes. Few investigations of a fundamental character have been carried out in the carbonate system, although plenty of ad hoc loading and elution testwork has been reported [12, 13].

TABLE VI. ELUTION REAGENTS USED WITH STRONG-BASE ION-EXCHANGE RESINS

Reagent	Concentration (g/ltr)	Temperature (°C)	Contact time (h*)	Flowrates (m/h)	Absorbed species
HNO_3	25	20–25	1–13	0.7–0.9	$UO_2(SO_4)_3^{4-}$
$(NH_4)NO_3$	50–75				
SO_4					
H_2SO_4	105–120	20–25	8–12	1.5–2.0	$UO_2(SO_4)_3^{4-}$
		45–50	3	6–8	
NaCl	50–55	20–25	6	2–5	$UO_2(SO_4)_3^{4-}$
H_2SO_4	10				
NaCl	60	25	6	1–3	$UO_2(SO_4)_3^{4-}$
NaCl	90–110	10–20	3–4	1.5	$UO_2(CO_3)_3^{4-}$
$NaHCO_3$	4				
$NaHCO_3$	50–80	20–25	4–5	215	$UO_2(CO_3)_3^{4-}$
$(NH_4)_3CO_2$	70–120				

* Contact time for the given conditions sufficient to give a residual uranium value on the eluted resin of < 1 g/ltr.

Neutral or alkaline eluting reagents are used to avoid the evolution of CO_2 and the consumption of carbonate that would accompany treatment of carbonate-form resin with an acid solution. Sodium chloride dosed with a small amount of sodium bicarbonate is the most generally used elutant. As with sulphate systems there are good reasons for employing an elutant that does not introduce extraneous ions into the plant. This is of particular importance in alkaline leach circuits where it is customary to recycle barren solutions after ion-exchange to the leach to conserve alkaline carbonate reagents. If the resin has been converted completely to the chloride form by elution with sodium chloride, then this absorbed chloride will be displaced into the barren solution when the resin is returned to absorption service. A large proportion of this chloride will return in the pregnant solution after leach and exert a depressing effect on resin loading to which alkaline systems are so sensitive.

As shown in Table V a strong alkaline carbonate solution may be used to elute uranyl tricarbonate and this system should be considered for use whenever possible.

3. SOLVENT EXTRACTION

Solvent extraction has been the most popular choice for uranium purification circuits in recent years. Tertiary amines of the general formula R_3N, where R may be an alkyl group containing eight or ten carbon atoms, are universally used in acid leach circuits. These amines begin to convert to the uncharged free-base form at pH's above 3.0 and thus cannot be used for the extraction of uranium from alkaline solutions. Quaternary liquid amines are commercially available but show poor selectivity for uranium at the relatively high pH's and salt concentrations present in most alkaline leach liquors.

3.1. Equipment

Solvent extraction in uranium ore processing plants is invariably carried out in mixer settlers, although other types of equipment have been investigated. A good review of the various types of mixer settler units commercially available is contained in Ref. [15].

The size of ion-exchange equipment is determined by the relatively slow kinetics of the transport of uranium in and out of resin beads. The separation of the process fluid from the resin is not a design limitation. By contrast, the kinetics of uranium transport in solvent extraction are rapid. Mixers are designed on a residence time for the aqueous phase of between 20 and 60 s for extraction and around 120 s for stripping. The rate limiting step in solvent extraction, which has a bearing on the size and cost of installed equipment, is that of phase disengagement. Relatively large settling areas must be provided after each mixing stage. Values of between 4 and 15 m^3/h of mixed phases per square metre of settler area are used for the design of extraction settlers. A number of patented devices are in use for the enhancement of phase disengagement rates. These include baffles, trays inclined in the plane of the settler, and various types of packing. A disadvantage of many of these systems is that they are liable to fouling by crud, which forms at the liquid/liquid interface in all solvent extraction operations to varying degrees. The more successful devices provide for convenient visual inspection into the settler and for cleaning that can be carried out while the settler is in operation.

Although a McCabe-Thiele construction on an extraction or stripping isotherm will often indicate that the required duty can be accomplished in two or three stages, it is customary to provide at least four stages for both extraction and stripping to provide some flexibility in plant operation.

3.2. Extraction, scrubbing and stripping

The formulas describing the extraction of uranium by tertiary amines are:

$$2(R_3NH)_2SO_4 + UO_2(SO_4)_3^{4-} \rightleftharpoons (R_3NH)_4\,UO_2(SO_4)_3 + 2SO_4^{2-}$$

$$(R_3NH_2)SO_4 + UO_2SO_4 \rightleftharpoons (R_3NH)_2\,UO_2(SO_4)_2$$

Tertiary amine solvents differ from strong-base ion-exchange resins in their ability to extract uranium from solutions containing appreciable quantities of acid. The extraction equilibrium isotherms presented in Fig.3 illustrate the behaviour of uranium in a Bufflex or Eluex circuit (number 3 in Table I) in which uranium absorbed by a strong-base ion-exchange resin is eluted by sulphuric acid and then subjected to a second stage of purification in which uranium is selectively extracted from the concentrated eluate. Although the elution of the resin is favoured by strong acid the extraction of uranium by tertiary amines is depressed as acid strength increases. In practice, a compromise is made at around 10 to 12% sulphuric acid.

A major difference in practice between the United States of America and South Africa is in the attention given to the scrubbing of loaded solvent. From three to five stages are usual in South Africa whereas plants in the United States of America often dispense with this step. Scrubbing in the Purlex circuit (number 2 in Table I) improves the purity of the final product by removing a number of species from the organic phase that are less strongly extracted than uranium. These may include thorium, zirconium, arsenic, iron and silica. Moreover, phase disengagement and pH control in the stripping stages are improved if the solvent has been scrubbed. Scrubbing also serves to economize on alkali usage in either the strip or precipitation stages, especially following extraction of uranium from acid solutions when an appreciable fraction of the amine may be present in the bisulphate form.

The reaction

$$2(R_3NH)HSO_4 \rightleftharpoons (R_3NH)_2SO_4 + H_2SO_4$$

is displaced to the right by water scrubbing. Ammonia may be added to the scrub solution to enhance this effect.

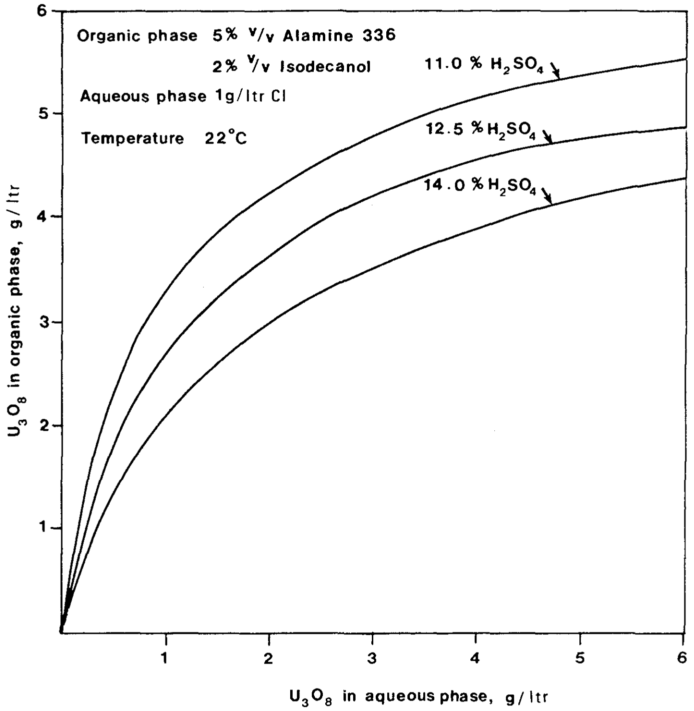

FIG. 3. Equilibrium isotherm for the extraction of uranium from acid solutions by Alamine 336.

One reason for the popularity of solvent extraction is the ease with which uranium may be stripped from tertiary amine solvents. Almost any salt, acid or base is effective (see Table VII). Stripping with sodium and ammonium chloride or sulphate is often used to achieve a partial separation between uranium and molybdenum. Molybdenum is strongly extracted by tertiary amines and only a minor amount accompanies uranium into the strip liquor, the balance of the molybdenum being removed, if present, in the regeneration stage.

Sodium carbonate stripping removes all the molybdenum with the uranium into the loaded strip solution. A final U_3O_8 product of good purity can be obtained in the presence of variable amounts of molybdenum by precipitating the uranium as a peroxide with hydrogen peroxide from a solution acidified to below pH 4.

After stripping it is usually necessary to regenerate the solvent, that is, remove those anionic species which, although present in trace quantities in the aqueous feed to solvent extraction, are strongly held in the solvent phase. These species include, in additiön to molybdenum, gold and base metal cyanide

TABLE VII. STRIP REAGENTS USED WITH TERTIARY AMINE SOLVENTS

Reagent	Concentration (g/ltr)	Number of stages
NH_3 $(NH_4)_2SO_4$	pH 3.2–4.8 120–200	3–4
NaCl	pH 2–3 90–100	4
Na_2CO_3	50–100	2–4
NH_4Cl	50–90	4

complexes, thiocyanate, and zirconium. Regeneration may be operated continuously, on a batch basis as required, or on a slip stream that is re-blended into the solvent returning to the extraction stages. Regeneration is effected by 10% sodium carbonate solution adjusted to pH 10 to 11.5 with caustic soda. Any uranium that is not removed in the stripping stages will appear in the regeneration aqueous liquor. However, a well-operated strip circuit should recover 99.8% of the uranium contained in the entering solvent. Spent regeneration solution is discarded in batches and may, in South Africa, be treated for gold recovery.

3.3. The organic phase

The organic phase in solvent extraction has three components; the amine, a modifier, and a diluent. The choice of amine is limited to those commercially available in quantity at a competitive price, although a number of amines synthesized in the laboratory have been shown to contain properties superior to those in common use. The concentration of amine on a volume/volume basis is chosen to suit the concentration of uranium in the feed solution. Amine concentrations of from 2 to 17.5% have been used for uranium concentrations varying from 40 ppm to 8 g/ltr. Molybdenum complexes have a limited solubility in the organic phase and the amount of amine may be increased to accommodate molybdenum and avoid troublesome precipitates beyond that required for uranium extraction.

A modifier is added to increase the solubility of the extracted species in the organic phase. These additives prevent the appearance of a third phase and inhibit the formation of stable emulsions. Tributyl phosphate and a number of long-chain alcohols are in common use. Isodecanol is the most frequently employed and has the advantage of minimizing the primary phase disengagement time and entrained solvent loss. However, high concentrations of modifier will increase the overall solubitily of the organic phase in aqueous solutions. Concentrations of modifier of from 30 to 100% of the amine concentration are usual.

Both paraffinic and aromatic diluents or a mixture of both are employed. Aromatic diluents have the advantage that they require the addition of either none or a low concentration of modifier. However, they are often more expensive than paraffin. A flashpoint of at least 40°C is recommended for the diluent. Olefin content should be less than 2% because unsaturated compounds are prone to oxidation and may give rise to chemical problems in operation. Reference [15] contains details of test procedures for the determination of the parameters necessary to define a solvent extraction system. Continuous bench-scale or pilot-plant investigations are recommended for ores and solutions for which no closely-related operating experience is available.

3.4. Operational problems experienced with solvent extraction

It has been suggested that silica forms an anionic complex with sulphate in solution, which is responsible for the observed presence of silica in the solvent phase. Silica may give rise to operational problems owing to the formation of a fleecy white crud in the scrubbing and stripping stages. Thorough scrubbing of the loaded solvent appears to be the best remedy.

The time for primary-phase disengagement to occur is usually shorter for aqueous-continuous mixed phases compared to organic-continuous suspensions. The phase continuity for mixing may be chosen as required. Organic-continuous operation at a local organic to aqueous ratio of 1.05 to 1.50 is often employed to minimize emulsion formation when silica and suspended solids are present in the aqueous feed. Local aqueous to organic phase ratios are controlled by the recycle of solvent to the mixer from the settler.

Organic contamination of solvents can arise from a variety of causes; traces of flotation reagents, emulsifying agents, lubricating oil and other contaminants are best excluded at their source. Regular cleaning plus the exclusion of direct sunlight will assist in the control of fungus growths in the solvent. Traces of organic compounds with carboxylic acid functional groups occur occasionally and will give rise to poor stripping efficiency. It is difficult to trace the origin of these organic acids and they may arise either from oxidation of components of the solvent phase or they may be present in the aqueous feed to the plant.

TABLE VIII. ELUTION REAGENTS USED WITH WEAK-BASE ION-EXCHANGE RESINS

Reagent	Concentration (g/ltr)	Temperature (°C)	Contact time (h)	Flow (m/h)
HNO_3 $(NH_4)NO_3$	< 5 60	25	6–8	1–2
H_2SO_4 $(NH_4)_2SO_4$	45 480	25	3.5	10–15
NaCl pH 1.9	60–70	20–25	3–4	6–8

4. WEAK-BASE ION-EXCHANGE

The weak-base ion-exchange resins employed in uranium purification have the same chemical functionality as tertiary amine solvents. However, the solid matrix of ion-exchange resins results in somewhat different chemical properties for the resins. In comparison with strong-base resins weak-base resins have slower uranium absorption kinetics and often lower equilibrium capacities. Moreover, they are not as tolerant to free acidity in the uranium bearing solutions as are amine solvents and are more difficult to strip, requiring solutions having a relatively high concentration of neutral salt or acid salt mixtures (see Table VIII).

Weak-base resins have a higher selectivity for uranium over ferric ion and vanadium than do strong-base resins, and uranium purity may be further improved by scrubbing [16]. The tertiary amine structure of these resins is not ionized at high pH's and this property may be used to ensure the complete removal of any strongly absorbed ionic poisons from the resin.

The advent of resins with improved properties tailored to the particular requirements of uranium purification is likely to result in the more widespread use of weak-base resins in the future.

5. PRECIPITATION OF IMPURITIES

The low selectivity of strong-base resins for uranium from acid leach solutions requires that an additional purification step precede ammonium diuranate (ADU) precipitation. In circuit number 1 of Table I, lime is added to the strong eluate

TABLE IX. ANALYSIS OF ELUATE BEFORE AND AFTER IMPURITY PRECIPITATION AT DENISON MINES

Substance	Strong eluate (g/ltr)	Pure eluate (g/ltr)
U_3O_8	21	20
Fe	0.8	0.08
ThO_2	1.0	0.02
Ti	0.3	0.10
Re_2O_3	1.0	0.02
SO_4	50	35

from ion-exchange to produce a precipitate containing iron, calcium, sulphate, thorium, rare earths, titanium and some occluded uranium. If arsenic is present it will be co-precipitated as ferric arsenate. Current practice at Denison Mines Ltd. [17] is described to illustrate this technique.

Precipitation is carried out in three rubber-lined pachuca tanks in series. The pH of the first tank is controlled with lime slurry to regulate the sulphate concentration at 35 g/ltr. This level is chosen to reduce gypsum precipitation in subsequent process lines and equipment, to ensure a low residual value of calcium in solution, and to result in a final ADU that is readily washed free of sulphates. Phosphoric acid is added to the second tank to complex thorium, rare earths and titanium. Ammonia addition is controlled at pH 3.5 in the third tank to precipitate the complexed impurities and ferric iron. The resulting slurry is filtered. The washed filter cake may be recycled to the leach to recover the contained uranium and in the case when phosphoric acid is omitted, to make use of the oxidizing power of the ferric ion.

Typical analyses for the Denison Mines plant are given in Table IX.

Circuit numbers 8, 9 and 10 in Table II make use of a preliminary precipitation of sodium diuranate from alkaline solutions followed by redissolution and final precipitation either as uranium peroxide or ADU. The procedure at United Nuclear Homestake Partners (number 8) is unique. The sodium diuranate (SDU) precipitate is roasted in the presence of carbonate at 870°C. The resulting intermediate calcine is given a water leach to remove sodium vanadate before redissolution in sulphuric acid and final precipitation as ADU.

The purity that is required for the final product from a uranium ore processing plant represents an assessment of the price and marketability of the uranium concentrate and the cost of achieving a higher purity. The results of this assessment will vary with the amenability of the ore and the location of the mill.

REFERENCES

[1] HAINES, A.K., The development of continuous fluidized-bed ion-exchange in South Africa, and its use in the recovery of uranium, J.S. Afr. Inst. Min. Metall. 78 12 (July 1978) 305–15.

[2] HIMSLEY, A., Uranium extraction from turbid liquids by continuous ion-exchange process, CIM (Can. Min.Metall.) Bull. (Sept.1977) 148–54.

[3] GIDDEY, T., The benefits of the use of high density resins in fluidized bed contactors, Klipfontein Organic Products, Chloorkop, Transvaal (to be published).

[4] SKOROVAROV, D.I., et al., "Processing of low-grade ores in the USSR". Uranium Ore Processing (Proc. Symp. Washington, 1975), IAEA, Vienna (1976) 141–53.

[5] STRELOW, F.W.E., BOTHMA, C.J.C., Anion exchange and a selectivity scale for elements in sulphuric acid media with strongly basic resin, Anal. Chem. 1139 (1967) 595.

[6] KORKISCH, J., Ion-exchange separation of uranium and thorium from ore pulps and clear solutions, At. Energy Rev. 8 3 (1970) 535.

[7] SMITH, R.P., "The prediction of multi-component ion-exchange equilibria with particular reference to the system involved in the recovery of uranium", unpublished PhD thesis, University of Natal, Durban (1976).

[8] GROENEWALD, T., The Ferric-hydroxide-sulphate System in Hydrometallurgical Practice, Chamber of Mines Research Organisation, Transvaal, South Africa (1971), Research Report 15/71.

[9] BOYDELL, D.W., et al., The new uranium recovery circuit at Blyvooruitzicht, CIM (Can. Min. Metall.) Bull. 72 804 (May 1979).

[10] FLEMING, C.A., HANCOCK, R.D., The mechanism of the poisoning of anion-exchange resins by complexes of cobalticyanide, J.S. Afr. Inst. Min. Metall. 79 11 (June 1979).

[11] HENRICKSON, Process for separating uranium and vanadium values, US Patent 3157462 (Nov. 1964).

[12] MERRIT, R.C., The Extractive Metallurgy of Uranium, Colorado School of Mines Research Institute, Golden, USA (1971) Ch. 6.

[13] THE DOW CHEMICAL COMPANY, The Recovery of Uranium from Carbonate Leach Solutions with Dowex 21K Resin, Dow Chemical USA, Golden, Co.

[14] AYRES, D.E.R., WESTWOOD, R.J., The use of the ion-exchange process in the extraction of uranium from Rand ores with particular reference to practice at the Randfontein uranium plant, J.S. Afr. Inst. Min. Metall. 57 7 (Feb. 1957).

[15] RITCEY, G.M., ASHBROOK, A.W., Solvent extraction, principles and applications to process metallurgy, Part 2, Elsevier, Amsterdam, Netherlands (1979).

[16] HAINES, A.K., et al., "The use of weak-base resins in the recovery of uranium from unclarified leach liquors", Mineral Processing (Proc. 11th Int. Cong. Cagliari, April 1975), Istituto di Arte Mineralia, Cagliari, Italy (1975).

[17] La ROCQUE, E., PAKKALA, E., Current leaching and product recovery practice at Denison Mines Limited, CIM (Can. Min. Metall.) Bull. 72 803 (1979) 172–76.

DISCUSSION

A. ABRAO: Do you have any practice in using macroporous resins to avoid fouling? What about the fouling by organic matter?

D. BOYDELL: We have found that macroporous resins load silica at a greater rate than do gel-type resins. With respect to organic fouling our experience is limited because this condition does not occur in ion-exchange feed solutions originating from the treatment of Witwatersrand ores, nor are macroporous resins in use in large-scale plants. However, indications from pilot plant work using these resins in a solution containing humates and/or fulvates are as follows:

(i) A strong-base macroporous resin loads organic matter in the uranium absorption contactor;
(ii) Substantially all this organic matter is removed during uranium elution with sodium chloride solution;
(iii) In the same service, a strong-base gel-type resin showed fouling which proved more difficult to remove, however, an ammonium nitrate/nitric acid eluant proved effective in preventing organic build-up in the resin.

PRODUCTION OF PURE YELLOW CAKE BY ION-EXCHANGE PROCESSES EMPLOYING SULPHATE ELUTION

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Abstract

PRODUCTION OF PURE YELLOW CAKE BY ION-EXCHANGE PROCESSES EMPLOYING SULPHATE ELUTION.

Recovery of uranium by ion-exchange processes from impure acid leach liquors is described, which produce a concentrated and pure eluate employing 10% sulphuric acid elution. In situations where resin is loaded to 45 g/ltr or more the acid consumption at ambient temperature is less than 4 kg of H_2SO_4 per kilogram of U_3O_8. Precipitation with an alkali such as ammonia or magnesia produces a yellow cake of high purity.

Introduction

Ion exchange resins have been used extensively for the extraction of uranium from leach liquors. As the loaded resin can be stripped most easily with nitrate ions it has been the practice to employ an acidified nitrate solution for this purpose.

In recent years there has been some concern expressed by environmental authorities about the use of nitrate as an eluting agent. This is because the nitrate ion left on the resin after elution is displaced by sulphate and goes out in the tailings.

Because of this there is a trend towards the use of sulphuric acid as an eluting agent. It is recognized that the bisulphate ion is not as efficient and elutes somewhat more slowly than nitrate. It is usual to employ an acid strength of around 100 - 125 g/l H_2SO_4 at which concentration the bisulphate ion is almost completely dissociated.

The eluate obtained from such a system contains a large amount of sulphuric acid which must be neutralized to precipitate the yellow cake. It is obviously uneconomical to consume alkali to neutralize this large amount of acid and consequently a recovery process for the acid is indicated.

This has been achieved in the past by employing a solvent extraction plant to separate the uranium from the acid and returning the acid for further use. This process is known as the Eluex or Bufflex process and aside from recovering the acid it effects some degree of purification since the solvent is more selective for uranium than other contaminating ions such as ferric ions.

We have been able to show how a considerable reduction in the amount of eluant required to elute a loaded resin (1) by employing a multi-stage counter-current elution column.

Whilst this reduces the acid consumption and subsequently the amount of alkali for precipitation it nevertheless does little to make a purification step other than increase the ratio of uranium to the unwanted impurities although an acid scrub may be applied to obtain some degree of purification.

However, in some cases, the percentage of such impurities may be greater than those obtained from an Eluex operation and indeed may fall outside the specifications laid down by the uranium refineries.

To produce an eluate which is pure enough to form a yellow cake within such specifications, a purification process has been developed which is achieved within the ion-exchange system and which results in a purer and concentrated eluate of small volume. This process is referred to by the HIMIX (pronounced HI-MIX) sulphate elution in multi-stage elution column.

Elution of Resin Using Sulphate

In normal usage, the elution column employed in the Himsley Continuous Ion Exchange system produces a strong eluate with less free acid to neutralize than required in a fixed bed system. This is because the elution of resin is done in one tall column containing several batches of resin (2). Each batch of loaded resin is slurried into the bottom of the elution column from the measuring chamber using eluate from the eluate storage tank.

When the resin is delivered into the bottom of the elution column it lifts the resin within the column as a solid undisturbed plug as there are no protrusions within the column that can cause any resistance to the rising plug of resin. There is virtually no mixing of the previous batches of resin and no noticeable slip of liquid through the bed.

When all of the resin has entered the bottom of the elution column, the plug of resin is pushed down to form one compact bed of resin thus ejecting from the bottom the volume of eluate which was used to transport the resin into the elution column and this is returned to eluate storage. The uppermost batch of resin is subsequently rinsed free of eluant and transferred as a slurry to the absorption column for further loading.

The resin is eluted by the downflow of eluant through a packed bed of resin. The elution column contains several batches of resin, the number of which is dependent upon the rate laws governing the elution process. High strengths of eluate are obtained because of the downflow counter-current series-elution technique.

The major governing factors for obtaining good elution are the concentration of exchanging ions and time of contact. Less eluant is required if a longer period of contact is provided. The total time of contact in the elution column depends upon the number of batches in the column and the time between elution cycles. For example, if there are six batches in the elution column and 2 hours between elutions, then the total time that the resin is in contact with the eluant is 12 hours. This provides ample time for complete elution to occur using minimal volumes of eluant.

The volume of eluant required per elution cycle is determined by the number of batches in the column and the total amount of eluant required to strip the resin. The latter can be determined from a test (or existing data) with the resin to be used in the main plant and eluant at a flow rate of 1.5 BV^s/h . For example, if it is found that 14 bed volumes of eluant are required to elute the resin to less than 1 g/l U_3O_8 then by having seven batches of resin in the elution column, the number of bed volumes of eluant required per elution cycle is 14/7 = 2.

The amount of acid neutralized per unit weight of U_3O_8 produced will depend upon the loading of the resin when it leaves the absorption column. If, due to low feed concentration or strong competition from other anions, the loading is low, then the acid consumption will be high.

The consumption of acid per unit weight of U_3O_8 produced may be determined from the following formula:

$$\mathrm{kg}\ .\ H_2SO_4/\mathrm{kg}\ .\ U_3O_8 = \frac{L \times V_e}{\bar{C}_o} \qquad \ldots\ldots \ (1)$$

See Appendix 1 for nomenclature

Fig. 1 shows graphically this equation on the assumption that the eluant is 120 g/l H_2SO_4. The parameters are bed volumes of eluant (V_e) used per elution cycle.

It will be appreciated that after elution the resin is in the bisulphate form and when it is placed in the absorption or loading column the bisulphate ion will be displaced by sulphate resulting in the formation of sulphuric acid. Alternatively, the eluted resin may be rinsed with water to form sulphuric acid for use in the process. The amount of sulphuric acid so produced is equivalent to the capacity of the resin and can come off at a strength around 15 g/l or so for use in the leaching circuit or for washing of filters.

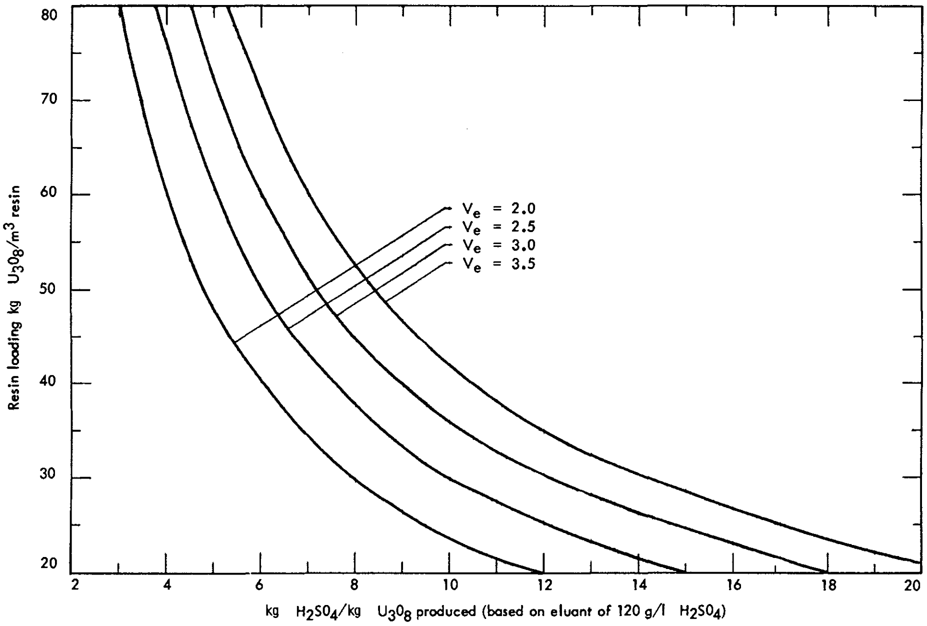

FIG.1. Consumption of H_2SO_4 by multi-stage elution.

In such cases the sulphuric acid thus recovered would reduce the consumption of the acid figure given by the above equation.

The concentration of uranium in the eluate would be equal to the resin loading divided by the number of bed volumes of eluant used per elution cycle. Thus, if the resin loading were 60 g/l U_3O_8 and the number of bed volumes of eluant required per elution cycle is 2 then the eluate concentration would be 30 g/l U_3O_8.

However, the impurities on the resin would remain in the eluate which could show up in the yellow cake and may place it outside the specification limits by the refinery.

It may be possible to obtain a sufficient degree of purification by carrying out an acid scrub process on the batch of resin before it enters the elution column. This could be done in the measuring and backwash chamber ahead of the elution column by passing a dilute acid solution through the bed which would remove iron, chlorides and nitrates from the resin.

When sulphuric acid is used as an eluant it is necessary to remove some of the sulphate from the eluate by precipitation with lime thus reducing the high sulphate contamination of the yellow cake that would otherwise occur. This first stage precipitation process may also be used to reduce any heavy metals by raising the pH to around 3.5 at which level they will precipitate. This practice, of course, is also carried out when using an acidified nitrate eluant and is a known procedure.

However, in those cases where excessive contamination occurs it is possible to obtain a more pure eluate by using the HIMIX process.

HIMIX Process

This process (3) was developed for use when 100 to 125 g/l H_2SO_4 is employed as an eluant in conjunction with the Himsley continuous ion exchange system (4). At modest cost it results in better purification of the eluate than is obtained by the acid scrub and iron and sulphate precipitation referred to earlier. Acid consumption in the region of 3 to 5 kg H_2SO_4/kg U_3O_8 produced can be achieved by the HIMIX process when using 120 g/l H_2SO_4 as an eluant.

The process is applied to the measured batch of resin in the measuring chamber. The first step comprises draining the chamber of its liquid contents to the feed tank. The measuring chamber is filled with high-grade eluate which enables the resin to take up uranium to a very high level because the solution is at a pH around 3.5 and there is very little competition from other ions. A small pump may be used to recycle solution from the top to the bottom of the measuring chamber at a flow just sufficient to fluidize the resin bed and this provides sufficient mixing over a certain period of time for the resin to reach equilibrium with the high-grade eluate.

The liquid contents of the measuring chamber are then displaced with eluate and the resin transferred to the elution column employing eluate in the usual manner.

The displaced spent high-grade eluate contains some uranium which is recovered by returning it to the pregnant feed tank. This amount of recycled uranium causes an increase in the feed concentration which will enhance the resin loading although it is unlikely that this will affect the equipment size or performance to any significant degree. The volume is small and there is no noticeable increase in flow.

The eluate from the elution column is dosed with lime or powdered limestone to precipitate sulphate as gypsum along with some additional alkali to raise the pH to the point where any iron and other contaminants would precipitate. The supernatant solution produces a pure yellow cake when neutralized with ammonia or magnesia to pH 7.

This supernatant liquor is referred to herein as high-grade eluate, part of which is used to fill the measuring chamber. The high concentration of uranium in

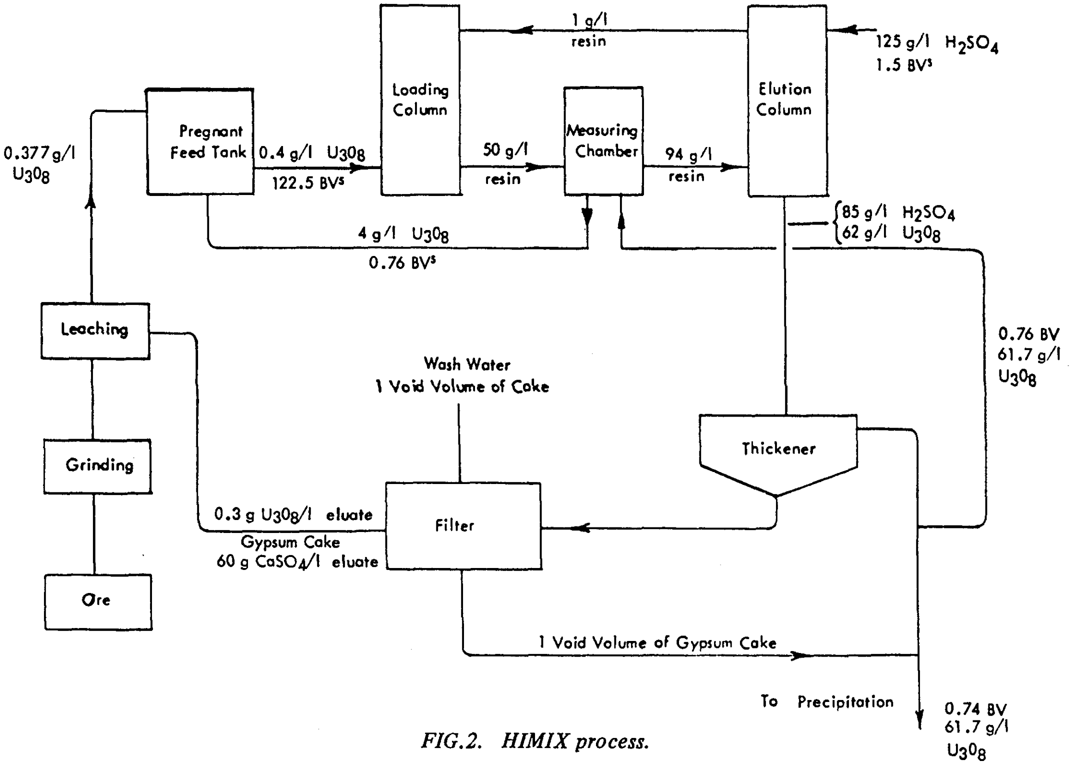

FIG.2. HIMIX process.

TABLE I

	EXAMPLES	
	1	2
Resin loading before conditioning (g/l U_3O_8)	50	60
Resin loading after conditioning (g/l U_3O_8)	94	121
Concentration in conditioning liquor (g/l U_3O_8)	61.7	80
Sulphate in free acid of conditioning liquor (g/l SO_4)	3	3
U_3O_8 recycled per elution cycle (grams U_3O_8)	3.0	31.7
Feed concentration before U_3O_8 recycle (g/l U_3O_8)	0.375	0.375
Feed concentration after U_3O_8 recycle (g/l U_3O_8)	0.4	0.7
Bed volumes of feed liquor to load resin	123	84
Eluant concentration (g/l H_2SO_4)	125	125
Resin capacity (eq./l)	1.25	1.25
Consumption of 95% $CaCO_3$ (g/g U_3O_8 produced)	2.87	4.9
Consumption of 100% MgO (g/g U_3O_8 produced)	0.05	0.085
Consumption of 100% H_2SO_4 (g/g U_3O_8 produced)	4.15	7.1
Bed volumes of conditioning liquor to precipitation	0.74	0.34
Consumption of 100% H_2SO_4 if bisulphate is recovered from resin for use elsewhere (g/l U_3O_8 produced)	2.86	4.78

This table has been prepared using the following values:

V_e = 1.5 Bed Volumes $\quad$ R = 2 g/l $CaSO_4$

P = 0.5% $\quad$ r = 1 g/l U_3O_8

Cr is obtained from equilibrium data and the value for Example 1 is 4 g/l and for Example 2 is 27 g/l U_3O_8.

this pure eluate effectively displaces impurities on the resin and as there is no competition from the bisulphate ion at this pH and the molar ratio of uranium to sulphate is high, it induces the formation of uranium ions such as $UO_2(SO_4)_2^{2-}$ and $U_2O_5(SO_4)_3^{4-}$. Both of these forms enable the resin to take up more uranium than usually is the case when treating the average pregnant feed liquor where uranium is present in the tetravalent form $UO_2(SO_4)_3^{4-}$. Resin loadings of over 120 g/l U_3O_8 have been produced after high-grade eluate conditioning.

The HIMIX circuit is shown in Fig. 2 with some estimated operational data and Appendix 1 gives the equations which enable the results to be determined.

A summary of advantages of the HIMIX process is:

1. High quality yellow cake produced
2. Low chemical consumption
3. Smaller precipitation circuit
4. Low operating cost
5. Low capital cost as it eliminates the need for a separate solvent extraction plant (Eluex)

Two examples of results are shown in Table I which have been calculated using the formulae.

Test work has been carried out both in our own laboratories and those of a uranium producer to confirm certain aspects of the process. This work now has advanced to a point where a small pilot plant is to be installed so as to obtain data from a continuous operation.

A multi-stage counter-current elution column installed at a mine has shown that it is possible to strip the resin down to less than 1 g/l using only 2 bed volumes per elution cycle and a total of 10 bed volumes of eluant for the resin, i.e., the elution column contains 5 batches of resin. This is done at ambient temperature and we anticipate that by increasing the number of batches and thereby the total residence time it will be possible to achieve even better results. A further reduction in acid could be obtained at more elevated temperatures and work in this direction is planned.

APPENDIX 1

U_3O_8 in eluate

$$\frac{\bar{C}_e - r}{V_e} \quad \text{g/l } U_3O_8 \text{ eluate}$$

SO_4 in free acid of eluate (B)

$$\frac{96\,L}{98} - \frac{48\,E}{V_e} \quad \text{g/l eluate}$$

SO_4 to be precipitated (F)

$$= B - D \text{ grams/l}$$

$$= \frac{96\,L}{98} - \frac{48\,E}{V_e} - D \text{ grams } SO_4\text{/l eluate}$$

$CaSO_4$ precipitated (S) $= \frac{136}{96} F$ grams $CaSO_4$/l eluate

95% $CaCO_3$ (G) required to precipitate sulphate $= \frac{100}{0.95 \times 136} (S + R)$ g/l eluate

U_3O_8 entrained with gypsum cake (K) $= \frac{PS}{100}$ grams U_3O_8/l eluate

U_3O_8 concentration (C_p) in supernatant liquor after first stage precipitation -

$$C_p = \frac{\bar{C}_e - r}{V_e} - K \text{ g/l eluate}$$

Conditioning liquor volume (V_c) applied to resin

$$V_c = \frac{\bar{C}_e - \bar{C}_o}{C_p - C_r} \text{ Bed Volumes}$$

Conditioning liquor volume (V_p) passed to precipitation of yellow cake

$$V_p = \frac{\bar{C}_o - r - C_rV_c - KV_e}{C_p} \text{ Bed Volumes}$$

CHEMICAL CONSUMPTION

95% $CaCO_3$/g U_3O_8 $= \frac{V_e\ G}{\bar{C}_o - r - C_rV_c - KV_e}$

100% MgO/g U_3O_8
(for neutralization only) $= \frac{V_e\ (D - 0.7R)}{2.4\ (\bar{C}_o - r - C_rV_c - KV_e)}$

100% H_2SO_4/g U_3O_8 $= \frac{V_e\ L}{\bar{C}_o - r - C_rV_c - KV_e}$

NOMENCLATURE

Resin loading after conditioning	$\bar{C}_e$	g/l
Resin loading before conditioning	$\bar{C}_o$	g/l
Eluant volume per elution cycle	V_e	bed volumes
U_3O_8 in conditioning fluid recycled to feed tank	C_r	g/l
U_3O_8 entrained in gypsum cake	P	%
Eluant strength	L	g/l H_2SO_4
Capacity of resin	E	eq./litre
$CaSO_4$ remaining dissolved in solution	R	g/l
U_3O_8 on resin after elution	r	g/l
Conditioning liquor passed to MC	V_c	bed volumes
Conditioning liquor passed to precipitation	V_p	bed volumes
U_3O_8 concentration in conditioning liquor	C_p	g/l U_3O_8
SO_4 residual in conditioning liquor (not associated with uranium)	D	g/l

REFERENCES

1. Himsley, A., and Farkas, E.J., "The Theory and Practice of Ion Exchange", Soc. Chem. Ind. Conf., Cambridge, England, July 1976.
2. U.S. Patent 4,018,677.
3. Patent applied for
4. U.S. Patent 4,035,292

DISCUSSION

D. BOYDELL: I should like to draw attention to the work reported by Haines (1975) in which a purer eluate was obtained by recycle of strong uranium-containing eluate. At the top of a Nimcix elution contactor, reloading of uranium onto the resin was observed accompanied by reduction in the iron content on the resin and in the eluate passing out of the system.

A. HIMSLEY: The effect reported by Haines* was, as far as I can recall, that the iron content in the eluate from the top of the Nimcix elution column (which operates as a fluidized bed by upflow of eluant) is greater than the iron content in the eluate at some point below the top. There is nothing unusual about this because the resin at the lower levels has had most of the iron content stripped from the resin and therefore a sample of eluate from that lower point contains very little iron.

However, the effluent from the top of that type of elution column contains, along with the eluted iron, some uranium which can be recovered by returning it to the leach circuit and which presumably is the 'recycle' referred to in the comment of Dr. Boydell. This small amount of uranium thus recycled has no significant effect upon the equilibrium loading of the resin.

Many years prior to the Haines' paper referred to by Dr. Boydell, it was a practice at some uranium mills to return this uranium and iron-containing first fraction of the eluate from fixed-bed ion-exchange plants to the leach circuit in order to lessen the iron content in the eluate.

The observed increase in loading (not 'reloading') on the resin is undoubtedly due to the fact that the equilibrium loading for uranium is lower in the dilute pregnant liquor than in the concentrated and relatively iron-free eluate (at this lower level) even in the presence of the bisulphate ion concentration.

The purification described in my presentation is done by a uranium-rich solution at pH 3.5 and from which most impurities have been precipitated. At this pH and concentration, impurities in the loaded resin are displaced by uranium which goes onto the resin in the forms described in the paper, thus enabling much more uranium to be taken up by the resin. Therefore, any impurities that may still be left on the resin become a much smaller percentage in the precipitated yellow cake.

The multi-stage counter-current downflow elution column reduces the acid consumption to a level where the cost of neutralization of this high grade eluate is low in terms of chemicals consumed per unit weight of yellow cake produced..

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* International Mineral Processing Congress, Cagliari, Italy, April 1975.

CARACTERISTICAS DE SUSPENSIONES DE URANATO AMONICO

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Abstract–Resumen

CHARACTERISTICS OF AMMONIUM URANATE SUSPENSIONS.

It is very important to know the properties of suspensions of industrial ammonium diuranate (ADU) for the thickening, filtering, stirring, pumping and drying operations performed in uranium ore processing plants. Continuous operation is a very attractive feature in these processes since it requires little manpower, reduces risks of radiation contamination and ensures more homogeneous products. This paper studies the behaviour and quality of different products resulting from ammonia neutralization of aqueous extracts from the extraction with amines of fertile uraniferous solutions. The influence of the following factors is investigated: neutralization agent (aqueous ammonia or gas); operating mode (continuous or non-continuous); and precipitation temperature (between 5 and 60°C). The effects taken into account are the quality and nature of the resulting product and the rheological characteristics and behaviour of the suspensions obtained as regards thickening, filtering, stirring and pumping.

CARACTERISTICAS DE SUSPENSIONES DE URANATO AMONICO.

El conocimiento de las propiedades de las suspensiones del diuranato amónico técnico (ADU) es muy importante en relación con las operaciones de espesamiento, filtración, agitación, bombeo y secado que se presentan en las plantas de tratamiento de minerales de uranio. La marcha continua en estas operaciones es muy atractiva porque necesita poca mano de obra, reduce los riesgos de contaminación radiactiva y da productos más homogéneos. Esta comunicación estudia el comportamiento y calidad de diversos materiales resultantes de la neutralización amoniacal de extractos acuosos procedentes de la extracción con aminas de soluciones fértiles uraníferas. Se ha investigado la influencia de los factores: agente de neutralización (amoníaco acuoso o gas), forma de trabajo (discontinua y continua), y temperatura de precipitación (entre 5 y 60°C). Como respuestas se han tenido en cuenta: la calidad y naturaleza del producto resultante, las características reológicas y comportamiento de las suspensiones obtenidas respecto a espesamiento, filtración, agitación y bombeo.

1. INTRODUCCION

Las especificaciones para los concentrados de uranio (yellow cake) se han ido haciendo cada vez más estrictas y muchas plantas han tenido que modificar sus procedimientos de precipitación. La mayoría de estos cambios se refieren a la sustitución de las operaciones discontinuas o en una sóla etapa por circuitos de precipitación continua en varias etapas. La técnica continua, entre otras, presenta las siguientes ventajas:

- Menos mano de obra;
- Producto más homogéneo;
- Menor contaminación;
- Más facilidad de automatización.

El principal objetivo de una operación de precipitación es lograr un concentrado de buenas características físicas y al mismo tiempo que cumpla las especificaciones en cuanto a contenido de uranio e impurezas. Frecuentemente estos dos requerimientos son incompatibles, así un producto con ley elevada en uranio puede espesar, filtrar, repulpar y ser bombeado con dificultad por su carácter viscoso.

El empleo de NH_3 como agente neutralizante o precipitante va siendo cada vez más extendido, ya que se logran concentrados con bajo nivel en sodio y además la eliminación de sales amónicas se puede lograr a temperaturas inferiores a 400°C [1], con lo que se obtiene un concentrado más puro. El "diuranato amónico" técnico (ADU) obtenido por precipitación con amoníaco es una mezcla de productos de diferentes características y composiciones, entre otros: diuranato amónico, sulfatos básicos de uranilo, óxidos de uranilo hidratados, etc. La proporción de cada uno de estos productos depende, principalmente, de las condiciones de precipitación (temperatura, pH, etc.). Por tanto, al variar estas condiciones varían también las características y composición del producto técnico (ADU).

Cada planta tiene sus propias condiciones de precipitación y no hay mucha información al respecto. Para el programa nuclear español era importante lograr concentrados con buenas características físicas y leyes altas. Por ello se inició el estudio correspondiente partiendo de los extractos acuosos de la planta de Saelices el Chico (Salamanca) y utilizando amoníaco como agente precipitante.

2. TECNICAS EXPERIMENTALES

2.1. Extracto acuoso

El extracto acuoso utilizado procedía de la batería de extracción con disolventes de la planta de Saelices el Chico [2] de ENUSA. Dicha batería consta de una fase de extracción con cuatro etapas de mezcladores-sedimentadores y otra fase de reextracción, también con cuatro etapas en contracorriente. La solución orgánica de extracción es Alamine 336 (2,5% vol.), isodecanol (1,5% vol.) y

CUADRO I. COMPOSICION EXTRACTO ACUOSO DE LA BATERIA DE EXTRACCION

Componente	U_3O_8	Fe	Na	Cl^-	$SO_4^{=}$	$PO_4^{\equiv}$
Concentración (g/l)	28,0	0,04	27,0	20,4	43,6	< 0,005

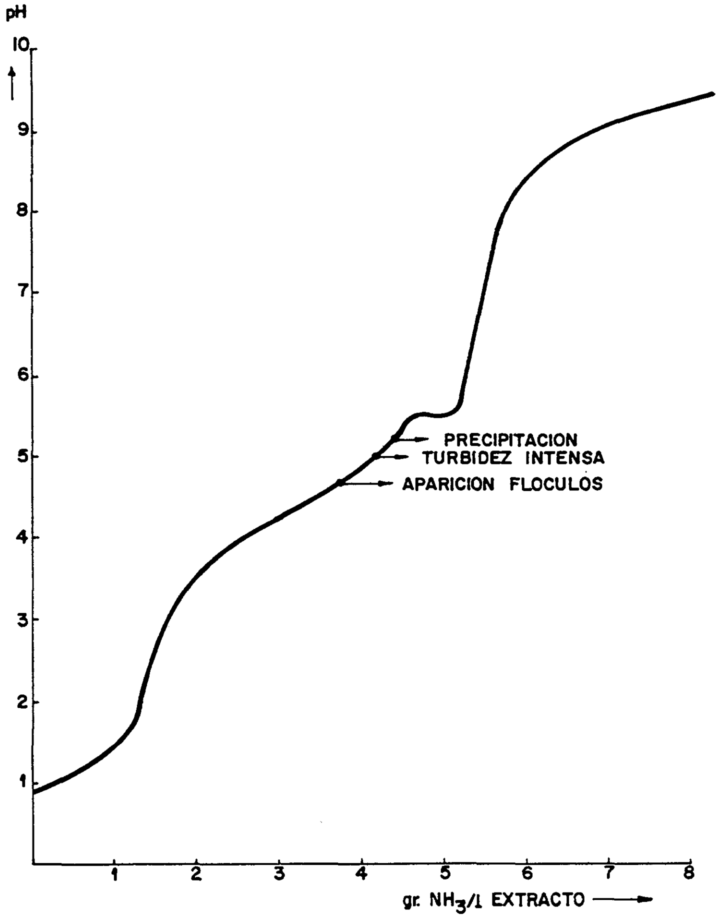

FIG.1. Neutralización del extracto acuoso con solución amoniacal 5,2M.

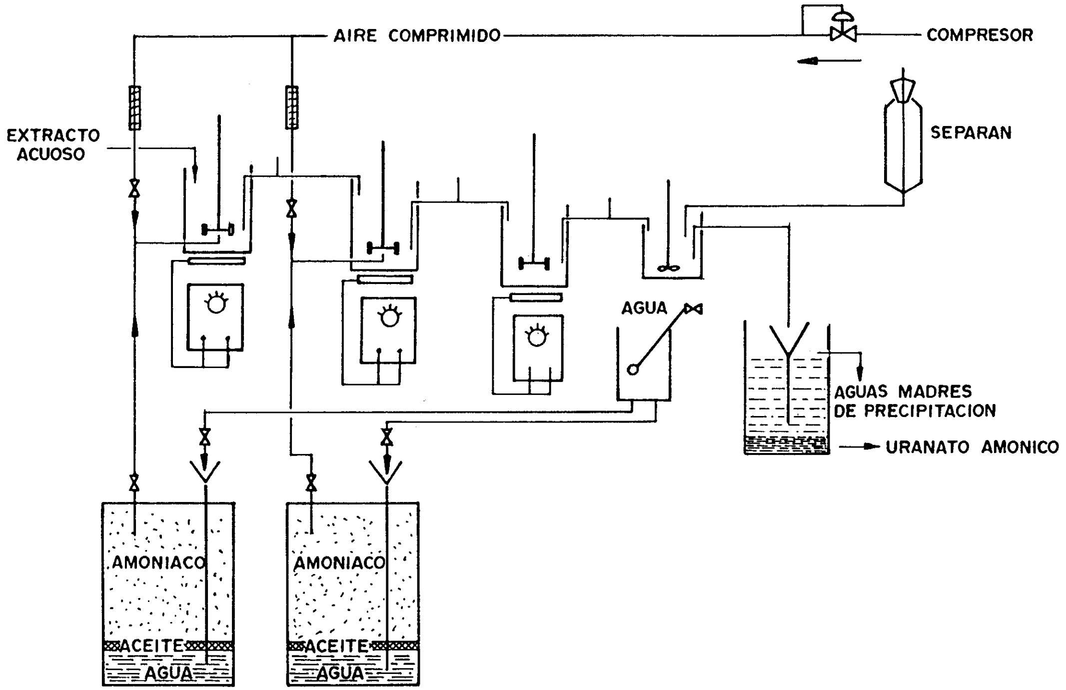

FIG.2. Instalación de laboratorio para precipitación continua de concentrados con amoníaco gas.

queroseno (96%). El agente de reextracción es solución NaCl 1M débilmente ácida (5 g H_2SO_4/l). La composición del extracto de la citada batería (Cuadro I) está comprendida dentro del intervalo normal de composiciones en dicha planta.

2.2. Precipitación

Las experiencias previas de precipitación se hicieron en discontinuo, la mayoría en recipiente de 35 l de capacidad. Se estudiaron principalmente: el tipo de reactivo, solución 5,2M NH_4OH y NH_3 gas (1 vol. NH_3, y 2 vol. aire); la temperatura, intervalo 15 – 60°C. La adición del reactivo se hizo de acuerdo con la curva de neutralización del extracto, Fig.1; consistió en una dosificación inicial rápida del amoníaco hasta pH 5,0 (antes de comenzar la precipitación), adición lenta del reactivo durante la precipitación (30 min) y período de maduración final incluyendo ajuste de pH hasta 7 – 7,5 (90 min).

Para las experiencias de precipitación continua en varias etapas se montó el dispositivo indicado en la Fig.2, que se componía de:

a) Tres vasos de 2 l (capacidad útil 1,7 l), cada uno con su equipo de agitación, calefacción eléctrica regulable y distribuidor de gas;
b) Un frasco Mariotte con Separán NP-10 al 0,025% y vaso conagitador;
c) Recipiente decantador de 20 l;
d) Distribución amoníaco – Botella gas comprimido, depósito nivel constante, válvulas control de flujo, gasómetros y eyector para mezclar con aire;
e) Distribución aire – Compresor, válvula reguladora de presión, medidor de caudal.

De acuerdo con los resultados previos de la precipitación discontinua, las experiencias de precipitación continua se realizaron en el intervalo de 35°– 45°. Por lo que respecta a la forma de adición del amoníaco (siempre en forma de gas) los ensayos se agruparon en dos tipos:

- Precipitación rápida en 1ª etapa (pH 7,1 a 7,3),
- Ajuste a pH 5 en 1ª etapa y precipitación lenta en 2ª etapa (pH 7,1 – 7,3).

En ambos casos la 3ª etapa fue para maduración del precipitado y ajuste final del pH. El tiempo total de residencia fue de 2 h.

La floculación de las pulpas de precipitación se hacía con 5 g/m^3 de Separán NP-10. El lavado se hacía repulpando el precipitado con 11 vol.agua/vol. pulpa sedimentada o 27 l agua/kg concentrado seco, añadiendo otros 2 g/m^3 de floculante.

CUADRO II. PULPAS ADU DE LA PLANTA DE SAELICES EL CHICO (SALAMANCA)

Pulpa	P-1	P-2	P-3
Procedencia	T.F.[a]	T-3[b]	T-3[b]
Temperatura precipitación, °C	34°	40°	35°
pH 1er tanque	4,5	5,0	5,0
pH 2^{o} tanque	5,5	6,0	6,0
pH 3er tanque	7,0	7,0	7,0

[a] Torta filtro tambor.
[b] Rebose 3er tanque.

También se experimentó con pulpas ADU de la planta de Saelices, cuya instalación de precipitación [2] está compuesta básicamente de tres tanques de precipitación en serie, espesador, tanque repulpador y espesador de lavado. Las pulpas lavadas y decantadas se llevan a un filtro de tambor rotativo y las tortas se repulpan en un segundo tanque repulpador para ser bombeadas a una estufa de secado de bandejas. Se tomaron los tres tipos de pulpa indicados en el Cuadro II, la muestra P-1 se tomó de la torta del filtro de tambor, las P-2 y P-3 se tomaron del rebose del 3er tanque de precipitación.

2.3. Agitación de pulpas concentradas y medida de potencias

Las pulpas ADU obtenidas por precipitación, una vez espesadas y/o filtradas hasta la concentración en sólidos deseada, se vertían a un vaso para comprobar su fluidez o agitabilidad.

Para las determinaciones previas se contaba con dos dispositivos convencionales de agitación, con velocidades de 300 – 900 rev/min y 1000 – 2200 rev/min. Aquellas pulpas cuyas características físicas parecían adecuadas se las estudiaba con más detalle en un agitador experimental modelo ELB de Chemineer. Este último equipo permitía una regulación continua de la velocidad de giro, el empleo de diferentes tipos y tamaños de turbinas, así como la medición de la potencia en eje necesaria para la agitación de las pulpas o suspensiones concentradas.

2.4. Medidas reológicas

Las determinaciones reológicas de las pulpas ADU se hicieron con un viscosímetro de tipo rotacional y cilindros concéntricos, el Rhéomat 15-T de Contraves.

3. RESULTADOS

3.1. Curva de neutralización del extracto acuoso

La neutralización del extracto acuoso con solución 5,2M NH_4OH a 40°C y 1,5 h, Fig.1, indicaba que hasta pH $\sim$ 2,0 el amoníaco se utilizaba prácticamente en neutralizar la acidez libre del extracto. Desde pH 2,0 hasta 5,2 en que empieza la formación del precipitado, se formaban sales básicas solubles. La presencia de éstas se detectaba por la forma de la curva de neutralización y los cambios de coloración, con intensificación gradual del color amarillo. La zona de máxima formación de ese tipo de sales se sitúa entre los pH 3,5 y 4,5 y prácticamente acaba donde empezaba la aparición de flóculos. La precipitación más abundante se manifestó a un pH de 5,5; por encima de pH 5,7 y hasta un valor de 8,0 la subida fue rápida y casi lineal, es decir, la precipitación era escasa.

3.2. Precipitaciones previas discontinuas

La temperatura fue el factor predominante en las precipitaciones discontinuas con respecto a las características físicas de las pulpas. Por debajo de 30°C aquellas sedimentaban, espesaban, filtraban y se agitaban con dificultad. Entre 35° y 60°C las características cambiaban y las pulpas ofrecían un mayor índice de manejabilidad. En el primer caso, las pulpas resultaban viscosas, mientras que en el segundo resultaban fluidas. La fluidez, que iba relacionada con las características de sedimentación, espesamiento, filtración y agitabilidad, aumentaba con la temperatura.

De las experiencias de precipitación discontinua se dedujo que, en relación con las características físicas de las pulpas ADU, es indiferente utilizar amoníaco en solución acuosa o amoníaco gas.

Los resultados que se expondrán en las secciones siguientes corresponden a los de precipitación continua en etapas. El intervalo de temperaturas en este tipo de precipitación, 35 – 45°C, se consideró el más idóneo de acuerdo con los ensayos discontinuos.

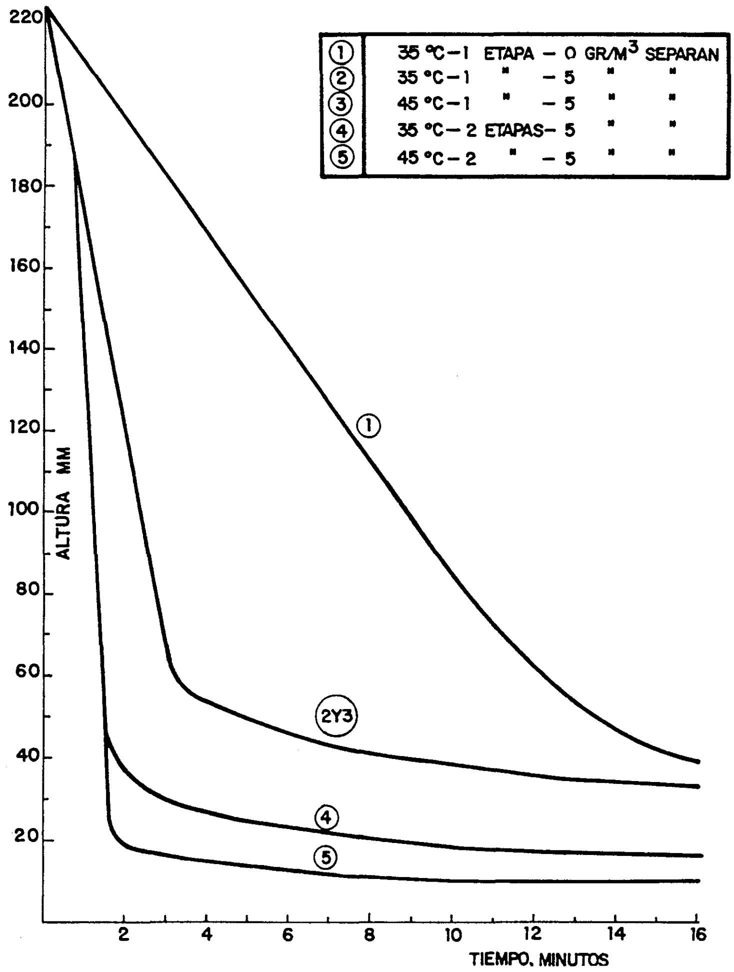

FIG.3. Sedimentación de pulpas de uranato amónico de precipitación continua con NH_3 *gas.*

3.3. Sedimentación, espesamiento y filtración

En la zona de temperaturas antes indicada fue de mayor importancia la distribución de pH en las etapas, es decir, la forma y velocidad con que se llevó a cabo la precipitación en cada etapa, que la temperatura. Cuando la precipitación se hacía en forma rápida los productos eran diferentes a cuando se hacía de forma más lenta.

La velocidad de sedimentación de las pulpas dependía de las condiciones de precipitación (Fig.3). Las gráficas 1 (sin floculante), 2 y 3 corresponden a los ensayos de precipitación rápida en la 1ª etapa, y las gráficas 4 y 5 a los ensayos de precipitación lenta o en la 2ª etapa. Las pulpas primeras sedimentaban y espesaban a menos velocidad que las segundas. El efecto de la temperatura es poco acusado, en cambio el del floculante es muy fuerte.

Las condiciones de precipitación se reflejaron también en el grado de espesamiento que alcanzaban las pulpas por decantación durante 19 h o en el grado de escurrido de las tortas de filtración (Cuadro III). En las columnas de la izquierda donde se recogen, con fines comparativos, unos valores de pulpas de precipitación discontinua, se ve claramente el efecto de la temperatura sobre el porcentaje en sólidos de las pulpas espesadas. Este efecto de la temperatura no es tan claro en las experiencias continuas, pero en cambio, sí lo es el de la forma o velocidad de precipitación.

Cuando la precipitación se hizo en forma rápida en la 1ª etapa, el producto obtenido por sedimentación y espesamiento sólo llegaba al 30 – 33% en sólidos, en cambio, si la precipitación se hacía de forma más lenta y gradual, el contenido en sólidos rebasaba claramente el 40%. Algo parecido ocurría con las tortas de filtración a vacío en laboratorio, las de precipitación rápida quedaban con un 40% de humedad, mientras que en las tortas de precipitación lenta la humedad disminuía al 29 y 33%.

Las tortas ADU del filtro de tambor de la planta de Saelices procedentes de la precipitación rápida según las condiciones de P-1, Cuadro II, tenían un espesor medio de 3 – 4 mm, eran de carácter viscoso y se lavaban con mucha dificultad ya que la mayor parte del agua de lavado resbalaba sin penetrar. Por otra parte, tenían un alto contenido en humedad y, por consiguiente, un bajo porcentaje de sólidos, 38%. Al cambiar a las condiciones de P-2 (precipitación lenta y 40°C), la pulpa que salía del 3^{er} tanque alcanzaba, por simple decantación durante 19 h, un 58% en sólidos; con la misma distribución de pH y 35°C (P-3) el porcentaje en sólidos por decantación fue del 56% y, al mismo tiempo, la torta del filtro aumentó su espesor a 8 – 9 mm siendo mucho más porosa y fácil de lavar que la P-1.

3.4. Agitación y bombeo

En una operación continua de obtención de concentrados, las características físicas de la pulpa ejercen su mayor influencia en el repulpado de las tortas de filtración y en el siguiente paso de bombeo hasta el horno de secado. Si las pulpas ADU tienen carácter viscoso su manejo se hace difícil, y para su repulpado y bombeo hay que diluirlas excesivamente con agua; por ello con dichas pulpas la operación continua de obtención de concentrados (yellow cake) queda gravemente dificultada en sus fases finales, es decir, desde la descarga de las tortas del filtro hasta el secado.

CUADRO III. CONTENIDO DE SOLIDOS EN PULPAS ADU DECANTADAS O FILTRADAS

CONCEPTOS	PRECIPITACION DISCONTINUA (D) CONTINUA (C) °C						
	(D) Sol. acuosa 5,2M NH_3			(C) NH_3 gas[a]			
	25°	33°	40°	35° – 1R	35° – 2R	45° – 1R	45° – 2R
pH 1^{er} reactor	–	–	–	7,1	5,1	7,3	5,1
pH 2° y 3^{er} reactores	–	–	–	7,1	7,2	7,3	7,1
pH final	7,2	7,2	7,2	7,1	7,2	7,3	7,1
% p/p decantación	19,1	31,7	46,1	33,2	41,2	29,7	46,1
% p/p filtración	–	–	–	59,4	66,9	60,1	70,6

[a] 1R: Precipitación 1^{er} reactor. 2R: Neutralización a pH 5,1 en 1^{er} reactor, precipitación en 2° reactor.

CUADRO IV. AGITACION MINIMA NECESARIA EN DISTINTAS PULPAS ADU

Escala	Condiciones precipitación				% sólidos pulpa	Velocidad periférica	
	D o C[a]	Amoníaco	°C	R o L[b]		m/min	pie/min
	D	Acuoso 5,2M	25	–	25,0	≥ 236	≥ 774
			33	–	52,7	149	489
			40	–	55,6	98	321
		Gas	39	–	55,1	101	331
	C	Gas	35	R	55,0	241	791
			35	R	51,0	114	374
			45	R	52,7	162	531
			45	R	50,0	131	430
			35	L	55,0	122	400
			35	L	50,0	96	315
			45	L	60,9	122	400
			45	L	55,0	82	369
Planta (Saelices)	C	Gas	34	R′	38,0 (P-1)	No agita	
			34	R′	28,0 (P-1)	187	613
			40	L	58,0 (P-2)	115	377
			35	L	56,0 (P-3)	187	613

[a] "D", precipitación discontinua; "C", precipitación continua.

[b] "R", precipitación rápida 1ª etapa (R′ – rápida en 3ª etapa); "L", precipitación lenta.

El comportamiento frente a la agitación de las pulpas ADU o, lo que es equivalente, su grado de fluidez, se determinaba siguiendo el criterio de "la mínima velocidad periférica del rodete que permita tener toda la pulpa agitada de forma homogénea". Siguiendo este criterio se han recogido en el Cuadro IV los resultados más importantes. Con fines comparativos se incluyeron también algunos valores de precipitaciones discontinuas.

En las precipitaciones discontinuas la influencia de la temperatura fue muy acusada; al aumentar ésta, las pulpas se hacían cada vez más fluidas y, por ello, se podía agitar con mayor contenido en sólidos y menor intensidad de agitación. El empleo de amoníaco gas en lugar de solución amoniacal no cambió prácticamente los resultados.

Los uranatos de precipitación continua de laboratorio mostraron un comportamiento entre aceptable y bueno frente a la agitación, para un contenido en sólidos de las pulpas comprendido entre el 50 y el 61%. Los efectos de las variables sobre la velocidad periférica fueron:

– Aumento temperatura precipitación de 35° a 45°C	– 19 m/min
– Cambio precipitación rápida (1R) a lenta (2R)	– 56 m/min
– Dilución media pulpa de 56 a 51,5% sólidos	– 56 m/min

La influencia de la temperatura en el intervalo 35 – 45°C fue pequeña. Más acusada fue la de la velocidad de precipitación que fue del mismo orden que la de la dilución.

Por lo que se refiere a la agitabilidad de las pulpas de la planta de Saelices, la P-1, o sea la de precipitación rápida en el 3er tanque, resultaba tan viscosa que para poderla agitar había que bajar el nivel de sólidos hasta el 28%. Por el contrario, las pulpas P-2 y P-3 (de precipitación lenta) resultaban fluidas y se agitaban con unas concentraciones en sólidos y velocidades periféricas similares a las de laboratorio (35-2R y 45-2R). Las pulpas de 35°C no resultaban tan fluidas como las de 40°C, pero sí lo suficiente como para poder ser repulpadas y bombeadas.

Hay que resaltar que entre las pulpas de precipitación rápida de laboratorio en la 1ª etapa y las de precipitación rápida en la 3ª etapa (P-1) de la planta de Saelices había una notable diferencia en su comportamiento. Estas últimas resultaban mucho más viscosas que las primeras, seguramente porque en las de laboratorio el precipitado tuvo más tiempo para madurar y transformarse en productos más cristalinos durante la estancia en las etapas 2ª y 3ª.

Medidas experimentales de la potencia de agitación con pulpas de características físicas diferentes mostraron que para el cálculo de agitadores y suponiendo una pulpa de fluidez normal se podía tomar como valor conservativo un número de potencia igual a 3. Este valor fué el utilizado para el cálculo de los equipos repulpados de la planta de Saelices el Chico y la planta experimental de Don Benito (Badajoz).

También se realizaron unas experiencias de bombeo con el fin de determinar si era posible bombear pulpas hasta un horno de solera múltiple. Se empleó una pulpa al 50% en sólidos cuyas características de fluencia eran del tipo de las de precipitación lenta a 35°C. Se utilizaron bombas peristálticas con cuerpo de neopreno, mostrándose que podían alcanzarse con facilidad alturas superiores a 7 m, es decir, que se podría utilizar este tipo de bombas para alimentar pulpas ADU suficientemente fluidas a un horno de secado.

3.5. Reología

En realidad todas las propiedades o características físicas de las pulpas ADU estan relacionadas con la reología, no obstante, aquí sólo nos referimos a medidas específicamente reológicas.

Las pulpas ADU analizadas con el Rheomat 15-T se comportaron como fluidos plásticos, es decir, necesitaban una agitación determinada, o lo que es lo mismo, una tensión mínima de cizallamiento para licuarse. La ecuación de Bingham para este tipo de fluidos es

$$T = f_B + \eta_B S$$

siendo: "T", tensión de cizallamiento o esfuerzo cortante; "f_B", umbral de fluencia; "η_B", viscosidad plástica y "S" velocidad de cizallamiento o de corte.

El umbral de fluencia depende de las condiciones de precipitación. Las pulpas viscosas P-1 de la planta de Saelices tenían un f_B = 1094 dinas/cm^2 con un 23% en sólidos. Por el contrario, una pulpa fluida como la P-3 (también de dicha planta) daba un f_B = 109 dinas/cm^2 con un 57% en sólidos.

3.6. Composición y pureza de los concentrados

Hasta aquí se ha expuesto el comportamiento físico de las pulpas ADU frente a una serie de operaciones tales como sedimentación, espesamiento, filtración, agitación y bombeo, y se ha apuntado el aspecto reológico de dichas pulpas. Es preciso hablar también de la calidad química de los concentrados sólidos.

En el Cuadro V se recoge la composición de los concentrados obtenidos por precipitación continua en laboratorio. Los precipitados decantados durante 19 h y lavados siguiendo la técnica descrita anteriormente se filtraron y secaron a 110°C, o se calcinaron a 375°C, en ambos casos hasta peso constante. Esta última temperatura se eligió de las curvas de descomposición térmica [1] y de los termogramas realizados en la J.E.N.

El contenido en uranio está referido a base seca y el de impurezas a base uranio. En la parte inferior del Cuadro se recogen los límites mínimos y máximos de penalización de las especificaciones internacionales más usuales para concen-

CUADRO V. COMPOSICION CONCENTRADOS DE PRECIPITACION CONTINUA

Precipitación		Secado °C	Análisis cuantitativo %						
			U(B/seca)	Impurezas (B/U)					
Temp. °C	Etapa			Cl^-	$SO_4^=$	$PO_4^{\equiv}$	Fe	Na	NH_4
35	1ª	110	73,9	0,08	1,06	0,01	0,17	1,72	2,26
45	1ª	110	74,1	0,03	0,53	0,12	0,18	1,73	2,15
35	2ª	110	70,1	0,09	77,97	0,33	0,17	1,50	3,55
45	2ª	110	69,1	0,01	11,2	0,08	0,18	1,61	4,18
35	1ª	375	78,1	0,05	1,19	0,09	0,18	1,82	0
45	1ª	375	78,1	0,04	0,60	0,12	0,19	1,83	0
35	2ª	375	74,4	0,04	7,91	0,36	0,18	1,62	0
45	2ª	375	74,2	0,04	11,0	0,08	0,19	1,73	0
		Mínimo	50	0,12	10,0	1,07	1,54	–	–
Límites penalización								0,78 (Allied)	
		Máximo	65	0,36	12,3	7,1	3,10	–	–

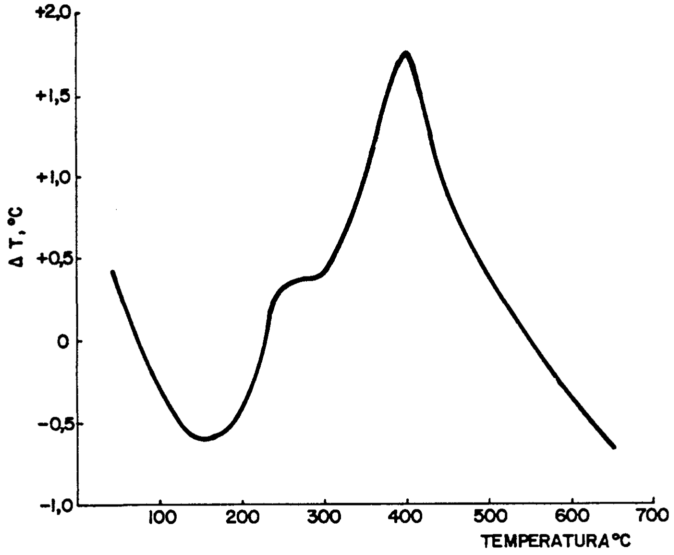

FIG.4. Análisis térmico diferencial (ATD) uranatos de precipitación continua. Precipitación en el 1º reactor.

trados uraníferos: Allied Chemical Corporation, Kerr-McGee Corporation, USAEC, UKAEA e Hifrensa (para reactores de U natural).

Los cuatro productos de precipitación secos a 110°C cumplen perfectamente las especificaciones internacionales en lo que respecta al uranio, cloruros, fosfatos y hierro. El contenido en sulfatos de los concentrados de precipitación rápida (1ª etapa) era muy bajo porque predominaban los óxidos hidratados de uranio. En los de precipitación lenta (etapa 2ª), el contenido en sulfatos aumentó debido a la precipitación de sulfatos básicos de uranilo, 8% a 35°C y 11% a 45°C. Este último valor estando comprendido entre los niveles máximo y mínimo de penalización. A temperaturas más altas (60°C), el contenido en sulfatos fue aún más alto [3]. El contenido en sodio rebasa los límites fijados por la Allied Chemical Corporation.

La eliminación de sulfatos y sodio por lavado intensivo es poco práctica, puesto que la mayoría de aquellos forman parte de compuestos de uranio insolubles en agua [4]. Si se desea rebajar el contenido en sulfatos por debajo de las especificaciones hay que procurar que la temperatura de precipitación sea inferior a 45°C, o bien, calcinar a una temperatura de 700–800°C [3]. Por lo que se refiere al sodio, como su concentración es relativamente baja, si se desea disminuir su contenido podría ser suficiente un lavado de la torta con sulfato amónico, para provocar un desplazamiento del Na^+.

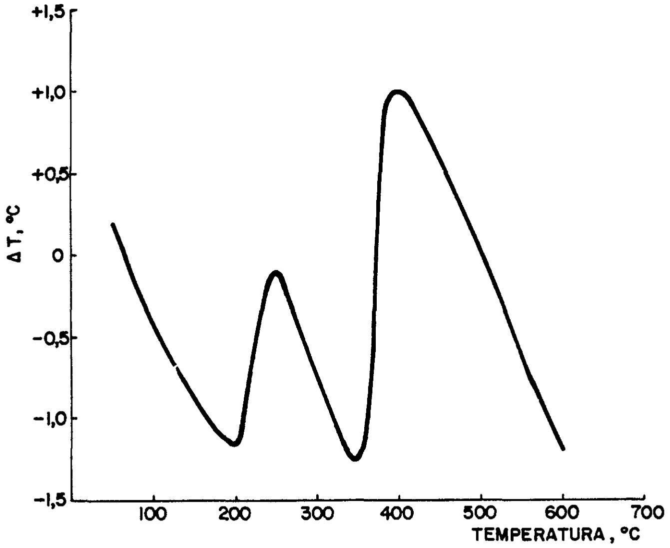

FIG.5. Análisis térmico diferencial (ATD) uranatos de precipitación continua. Precipitación en el 2º reactor.

Con la tostación a 375°C se logra una eliminación total del ión amonio y del agua, con lo que se consigue aumentar la ley en uranio.

Se estudió el comportamiento térmico de los cuatro concentrados de precipitación continua de laboratorio en un termoanalizador Mettler. Las curvas de análisis termogravimétrico diferencial (TGD) fueron bastante parecidas entre sí, no observándose máximos o mínimos específicos. Las gráficas de análisis térmico diferencial (Figs 4 y 5) muestran como principal diferencia entre los concentrados de precipitación rápida (Fig.4) y los de precipitación lenta (Fig.5) un pico endotérmico a 350°C, debido a una transformación de los sulfatos básicos de uranilo a trióxido de uranio.

Unos difractogramas realizados en un aparato de difracción de rayos X marca JEOL, con polvo de los concentrados de precipitación continua en laboratorio, mostraron que las 8 líneas principales de los de precipitación rápida (etapa 1ª) coincidían con las de un óxido hidratado amoniacal de carácter amorfo [5],

$$UO_3\ 1-3/4\ H_2O-NH_3,$$

mientras las 8 líneas principales de los de precipitación lenta correspondían a las de un sulfato básico de uranilo de carácter cristalino,

$$(UO_2)_3\ (SO_4)_2\ (OH)_2 \cdot 8H_2O.$$

No habrá diferencias apreciables entre los concentrados obtenidos a 35° y 45°C.

Las líneas de emisión de todos los productos tostados a 375°C coincidían con las del γ-UO_3, variedad tetragonal del trióxido de uranio, que parece ser la estable a dicha temperatura, independientemente de la composición de partida del concentrado sin tostar.

El presente trabajo confirma que el diuranato amónico técnico (ADU) no es un producto de composición química definido, no sólo por otros iones coprecipitados o adsorbidos, sino porque al variar las condiciones de precipitación hay predominio de uno u otro compuesto uranífero, con lo cual cambian también la composición media y las características físicas del concentrado.

4. DISCUSION Y CONCLUSIONES

El principal objetivo en una instalación de concentrados de uranio es lograr un producto (yellow cake) con unas características físicas satisfactorias y que cumpla con las especificaciones internacionales en lo que respecta a contenido de uranio e impurezas. Estos dos requerimientos son frecuentemente incompatibles, por lo que hay que llegar a una solución de compromiso.

Por características físicas se entiende principalmente el grado de manejabilidad de las pulpas y comprende las fases de sedimentación, espesamiento, filtración, repulpado, bombeo y secado. Como se ha visto en esta comunicación, cuando en el concentrado hay predominio de los sulfatos básicos cristalinos, todas esas fases se llevan a cabo sin problema alguno, las pulpas son fluidas y su reología es adecuada para un proceso continuo. Por el contrario, si predominan los óxidos o hidróxidos hidratados las pulpas resultan viscosas y se presentan problemas en todas las fases anteriores, hasta el punto de que un proceso totalmente continuo puede hacerse inviable, al menos en la parte final de repulpado y bombeo.

Del análisis de los datos experimentales se dedujo que hay una relación entre la capacidad de espesamiento de una pulpa ADU y su facilidad de manejo. Así se estableció como criterio simple el de que "aquellas pulpas que en 19 h espesan $\geqslant$ 40% en sólidos tienen buenas características físicas" y son aptas para un proceso totalmente continuo.

La formación de sulfatos básicos de uranilo es mayor en una precipitación lenta que en una precipitación rápida, lo que origina que las características físicas mejoren pero la calidad química disminuya. Como la formación de esos sulfatos básicos es función de la temperatura, hay que buscar una solución de compromiso que satisfaga a los requerimientos físicos y químicos. La solución de compromiso recomendada para una operación de precipitación continua de concentrados ADU es la siguiente:

- 1ª etapa: pH ≅ 5 (hasta aparición de flóculos).
- 2ª etapa: pH 6 – 6,5 (precipitación prácticamente completa).
- 3ª etapa: pH 7 – 7,5 (ajuste final de pH y maduración).

En las tres etapas la temperatura sería de unos 35°C.

Las suspensiones o pulpas de precipitación serían decantadas, lavadas y filtradas hasta una concentración en sólidos superior al 40%, repulpadas y bombeadas hasta un horno. Parece preferible calcinar a una temperatura de 375 ± 25°C, puesto que el producto es más puro y más denso que si el secado se hiciese a temperaturas inferiores a los 300°C, con lo que tendría ventajas a efectos de envase y transporte. Si se desea eliminar sulfatos por calcinación, la temperatura del horno ha de ser 700–800°C [3], pero puede insolubilizarse parcialmente el uranio [4].

REFERENCIAS

[1] ATMORE, M.G., "The chemistry of uranium oxide production in South Africa, 1946–1956", A Joint Symposium, Hortors Ltd, Sudáfrica 2 (1957) 192–198.

[2] JAEN, P.G., JOSA, J.M., MEMBRILLERA, J.R., OTERO, J., SERRANO, J.R., "Mining and processing of uranium deposits in Salamanca, Spain", Geology, Mining and Extractive Processing of Uranium, Inst. of Mining and Metall., Comisión de las Comunidades Europeas, Londres (1977).

[3] RODRIGUEZ, B., "Obtención de concentrados de uranio-Purlex– de baja ley en sulfatos" (Figura entre las Actas presentes).

[4] MERRIT, R.R., The Extractive Metallurgy of Uranium, Colorado School of Mines Research Institute, USAEC (1971).

[5] Inorganic Index to the Power Diffraction File, Am. Soc. Test. Mater., Spec. Tech. Publ. (US).

DISCUSSION

A. ABRAO: Do you have any experience in the precipitation of ADU with urea (homogeneous precipitation) from uranyl sulphate?

J.L. MERINO: We have not used this reaction because we do not feel that it is of practical interest.

H.E. JAMES: Could Mr. Merino give more information on the type of flocculant added to the ADU precipitates to improve their settling characteristics? (see Fig.3). Secondly, has Mr. Merino done any work on the removal of the flocculant from the yellow cake by washing and/or calcination, i.e. will the use of flocculants not result in contamination of uranium oxide concentrates with resultant penalties from the UF_6 conversion refineries?

J.L. MERINO: The flocculant used was a synthetic polyacrylamide-based one (Separán MP-10). This flocculant has been used successfully in laboratory and pilot plant operations.

In reply to Mr. James' second question, I should say that no experimental work has been done, for the following reason: with the doses added the amount of flocculant retained in the precipitate will remain far below the international specifications for organic matter in yellow cake. We believe that even if all the flocculant added remained in the solid phase its removal by washing or calcination would be unnecessary.

S. SEN: Were any studies made on the effect of NH_3: air ratio (during continuous precipitation) on the settling and filtration characteristics of the ADU slurry produced?

J.L. MERINO: No studies were made of the effect of the NH_3: air ratio on the physical characteristics of the slurries. No influence of the type of reagent, whether aqueous or gaseous (NH_3: air ratio 1 : 2), on these characteristics was observed during batch precipitation. We believe that this ratio will have no practical effect, since the batch precipitation slurries behave similarly to those of the slow-neutralization continuous-precipitation type.

OBTENCION DE CONCENTRADOS DE URANIO-PURLEX DE BAJA LEY EN SULFATOS

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Abstract–Resumen

OBTAINING PURLEX URANIUM CONCENTRATES WITH LOW SULPHATE CONTENT.

The paper studies precipitation of uranium concentrates from aqueous extracts originating with the Purlex process. It analyses the influence of precipitation temperature on the sulphate content of the products and on the physical and washing characteristics of the precipitates. The thermal elimination of sulphates in relation to precipitation, washing and roasting conditions is discussed. A thermogravimetric analysis of concentrates and products in relation to their thermolysis is also made. It is concluded that products complying with specifications for sulphates can be obtained by precipitation at medium temperature (30–45°C), filtration and calcining at approximately 700°C.

OBTENCION DE CONCENTRADOS DE URANIO-PURLEX DE BAJA LEY EN SULFATOS.

Se estudia la precipitación de concentrados de uranio a partir de extractos acuosos del proceso "Purlex". Se analiza la influencia de la temperatura de precipitación en el contenido de sulfatos de los productos y en las características físicas y de lavado de los precipitados. Se considera la eliminación térmica de sulfatos frente a las condiciones de precipitación, lavado y tostación. Se incluye análisis termogravimétrico de concentrados y productos relacionados con su termolisis. Se concluye que se pueden obtener productos que cumplen especificaciones de sulfatos por precipitación a temperatura media (30–45°C), filtración y calcinación a unos 700°C.

1. INTRODUCCION

Al considerar al proceso de extracción con aminas, existe una tendencia general a realizar la reextracción del uranio con sulfato amónico a pH controlado, precipitando finalmente el uranio en el extracto acuoso con amoníaco. Este proceso se utilizará en el proyecto Quercus, para el beneficio de minerales de uranio de la zona de Salamanca.

Puesto que la precipitación del uranio tiene lugar en soluciones concentradas de sulfatos, es de interés conocer las condiciones de precipitación y tostación, para que el contenido de sulfatos en los concentrados se mantenga inferior a los límites de las especificaciones.

Es bien conocido que la denominación técnica "diuranato amónico" (ADU) no corresponde a un compuesto estequiométrico. Para el ADU que se obtiene a partir de soluciones de nitrato de uranilo, varía ampliamente la relación NH_3/U, en función de las condiciones de precipitación con amoníaco. Según Cordfunke [1], el sistema ADU comprende cuatro compuestos:

$I = UO_3 \cdot 2\,H_2O$; $II = 3\,UO_3 \cdot NH_3 \cdot 5\,H_2O$;
$III = 2\,UO_3 \cdot NH_3 \cdot 3\,H_2O$; $IV = 3\,UO_3 \cdot 2\,NH_3 \cdot 4\,H_2O$.

Las composiciones intermedias representan mezclas de dos fases. Por neutralización con amoníaco, la formación de compuestos depende del pH de equilibrio: a un pH de precipitación inicial se obtiene el compuesto I, a un pH intermedio se forma fase II y a un pH algo superior a 7 predomina el compuesto III. Con un exceso de amoníaco se forma también el compuesto IV.

Stuart y Whateley [2] describen el ADU como un sistema continuo de fórmula $UO_2\,(OH)_{2-x}\,(ONH_4)_x \cdot m\,H_2O$, tomando x los valores del intervalo (0; 0,7). La turbidez inicial, que se observa al añadir lentamente hidróxido amónico a la solución de nitrato de uranilo, se debe a la formación de trióxido de uranio hidratado, $UO_2\,(OH)_2 \cdot H_2O$. El precipitado de ADU se forma por un mecanismo de intercambio catiónico:

$$UO_2\,(OH)_2 + xNH_4^+ \longrightarrow UO_2\,(OH)_{2-x}\,(ONH_4) + xH^+$$

Woolfrey [3] estudia el efecto del pH de precipitación en la composición del ADU, apoyándose en el mismo mecanismo de reacción.

En la neutralización del extracto acuoso de iones uranilo, amonio y sulfato con hidróxido amónico, se puede considerar de forma simplificada que el producto de precipitación está formado por uranatos de amonio, sulfato amónico retenido, y dos constituyentes, que tienen un efecto decisivo sobre las características físicas del precipitado y su contenido en sulfato. Se trata de los óxidos hidratados de uranio y sulfatos básicos de uranilo, o uranilo y amonio. Los óxidos hidratados son gelatinosos, causando dificultades en la separación sólido-líquido, mientras que el sulfato básico de uranilo es un sólido cristalino que sedimenta y filtra fácilmente.

La temperatura y la velocidad de neutralización influyen notablemente en la formación de sulfato básico de uranilo. Por neutralización a temperatura superior a 30°C y a velocidad lenta, se obtienen precipitados fácilmente filtrables [4], porque se forma una gran proporción de sulfato básico de uranilo. En concordancia, los resultados de Nugent y Reid [5] indican un intenso efecto creciente de la temperatura en el contenido de sulfatos.

A un pH intermedio próximo a 5,5 se favorece la formación de sulfato básico de uranilo, siempre que la neutralización se realice a velocidad relativamente lenta y que el pH final no sea muy elevado. En efecto, un exceso de hidróxido amónico puede tranformar el sulfato básico de uranilo en ADU. Los valores de pH final entre 7 y 7,5 son los más usuales, de acuerdo con la descripción [6] de varias fábricas de concentrados de uranatos amónicos, estando comprendida la temperatura de precipitación en el intervalo 30–50°C.

El repulpado con agua puede tener escaso efecto en la eliminación de sulfatos, si el precipitado contiene proporciones elevadas de sulfato básico de uranilo. Por otra parte, una dilución excesiva con agua puede producir peptización del precipitado, causando problemas de separación sólido-líquido, debido a la formación de óxidos hidratados de uranio.

Varios investigadores [7–9] han estudiado la descomposición térmica del ADU y los compuestos que se forman en la termolisis. La conversión final del ADU a U_3O_8 es casi completa a 650°C, según indican las termogravimetrías realizadas en este laboratorio. De una manera simplificada puede considerarse que la descomposición térmica del ADU, con eliminación de agua, amoníaco y nitrógeno, tiene lugar en tres etapas:

$$\mathrm{ADU} \longrightarrow UO_3 \cdot 2\,H_2O \longrightarrow UO_3 \longrightarrow U_3O_8$$

El agua y el amoníaco se eliminan en su mayor parte a temperaturas inferiores a 400°C. El trióxido de uranio hidratado se forma principalmente en el intervalo 250–300°C, deshidratándose en gran medida entre 320 y 370°C. A unos 400°C el trióxido de uranio empieza a descomponerse lentamente. En una zona del intervalo 550–650°C, la conversión a U_3O_8 suele ser muy rápida y casi total, completándose entre 650 y 800°C.

La descomposición térmica de los concentrados de uranio es más compleja que la descrita para el ADU, debido a la presencia de sulfato. Notz y Haffe [10] indican que el sulfato de uranilo en atmósfera de aire se convierte en U_3O_8 por encima de 700°C, eliminándose óxidos de azufre con velocidad máxima a unos 850°C.

Exceptuando el ión sulfato, las demás impurezas del concentrado de uranio del proceso Purlex satisfacen sin dificultad las especificaciones. En este trabajo se ha tratado de establecer las combinaciones más adecuadas de tratamiento, tanto en las condiciones de precipitación y lavado como de tostación, de modo que los concentrados uraníferos cumplan especificaciones de sulfatos, manteniendo buenas características físicas de los precipitados en cuanto a la separación sólido-líquido.

2. PARTE EXPERIMENTAL

2.1. Técnica experimental

2.1.1. Preparación de soluciones para precipitación

Para realizar ensayos de precipitación se utilizó una solución sintética de composición similar al extracto acuoso: U_3O_8, 20 g/l; $SO_4^=$, 200 g/l; pH 4,5;

se preparó por disolución de trióxido de uranio con ácido sulfúrico, adición de sulfato amónico y ajuste de pH con hidróxido amónico. Se utilizó como reactivo de precipitación hidróxido amónico 4N y como floculante solución de Separán al 0,025%.

2.1.2. *Precipitación de concentrados*

La solución de iones uranilo, amonio y sulfato se precipitó con hidróxido amónico 4N, empleando agitación magnética y manteniendo la temperatura del ensayo (± 1°C). La velocidad de adición del reactivo se reguló para alcanzar un pH final de 7,4 en 80–90 min, continuando la agitación hasta completar a dos horas el tiempo total de precipitación, reajustando el pH final. Se adicionó floculante en la proporción de 5 mg/l de extracto acuoso, dejando sedimentar hasta una hora antes de efectuar la filtración.

2.1.3. *Filtración y repulpado*

La torta amarilla se separó por filtración a vacío. Para efectuar el repulpado, la torta se dispersó en agua, en la proporción en peso agua/U_3O_8 = 20, manteniendo la dispersión durante 15 min por agitación magnética. Previa adición de floculante, se filtró a vacío.

2.1.4. *Secado y tostación*

La torta se secó a 70°C durante 16–20 h, se molió y se secó durante 3 h a 100°C, controlando eventualmente pérdidas de peso. Las muestras se calcinaron 2 h en horno de mufla de regulación automática, a cada temperatura indicada en el programa de ensayos.

2.1.5. *Análisis químicos*

- Uranio. Precipitación con hidroxiquinoleina y gravimetría como U_3O_8; pequeñas cantidades se determinaron por espectrofotometría con arsenazo III.
- Sulfato. Gravimetría como sulfato bárico.
- Amonio. Destilación como NH_3 y volumetría.

2.1.6. *Termogravimetría*

Los ensayos de TG se realizaron en una termobalanza Mettler, con registro de peso, termogravimetría diferencial y análisis térmico diferencial. Condiciones generales: 0,2 g de muestra; velocidad de calefacción, 6°C/min; caudal de aire, 5 l/h.

Se aplicó TG a los concentrados y a los siguientes productos relacionados con su termolisis:

- Sulfato de uranilo. Se preparó a partir de trióxido de uranio, por disolución con ácido sulfúrico, cristalización y secado a 85°C.
- Sulfato amónico p.a.
- Sulfatos de uranilo y amonio. Se calcinó una mezcla de ADU y sulfato amónico (relación molar $SO_4^=/U = 2$) entre 200°C y 400°C durante dos horas, se lixivió con agua (uranio soluble, 94%) y se separó por evaporación un sólido cristalino.
- Mezcla de diuranato amónico y sulfato amónico p.a., siendo la relación molar $SO_4^=/U = 1$.

2.2. Planteamiento de experiencias

2.2.1. Precipitación y tostación

Se establecen varios niveles de ensayo para las variables que tienen mayor incidencia en el contenido de sulfatos del precipitado: temperatura de precipitación, condiciones de lavado y temperatura de tostación.

Para la temperatura de precipitación se eligen niveles de 30°C, 45°C y 60°C, teniendo en cuenta que por debajo de 30°C el precipitado no tiene las características físicas requeridas. Condiciones de lavado: nulo y tres repulpados.

A fin de establecer la temperatura mínima de secado y tostación, para hacer disminuir los sulfatos hasta límites dentro de especificaciones, se ensayan por vía isotérmica niveles de temperatura múltiplos de 100°C, hasta 800°C. Para elegir la temperatura superior, se ha considerado la termolisis del sulfato de uranilo, que es muy estable.

2.2.2. Termogravimetría

Para interpretar la descomposición térmica de los sulfatos, se realizan análisis termogravimétricos de muestras de las tortas de precipitación y muestras de otros compuestos (2.1), relacionados con la termolisis del concentrado: sulfato de uranilo, sulfato amónico, ADU, ADU + sulfato amónico y sulfatos de uranilo y amonio.

2.3. Resultados

2.3.1. Oclusión de sulfato amónico

El sulfato amónico retenido por oclusión en el concentrado se evalúa a partir de los datos de análisis de las aguas madres de precipitación (Cuadro I). En los cálculos se desprecia la pérdida de uranio en las aguas madres, por ser inferior a 0,1%.

CUADRO I. OCLUSION DE SULFATO AMONICO EN EL CONCENTRADO NO LAVADO

Concepto	Determinación	Temperatura de precipitación 30°C	45°C	60°C
Aguas madres	Densidad	1,131	1,136	1,128
	$SO_4^=$, g/l	197	199	192
	Residuo de evaporación,[a] g/l	273	278	267
Precipitado	Pérdida de peso[a]/U	1,63	1,09	0,35
	% $SO_4^=$ ocluido (base U)	37%	25%	8%

[a] Secado a 100°C.

CUADRO II. ELIMINACION DE SULFATO POR LAVADO

Determinación	Temperatura de precipitación 30°C	45°C	60°C
Disminución de % $SO_4^=$ (base U) en la torta			
Un repulpado	32,6%	20,2%	5,9%
Dos repulpados	36,2%	23,2%	6,5%
Tres repulpados	36,7%	23,9%	6,7%
Composición del concentrado			
a) Con un repulpado			
% $SO_4^=$ (base U)	5,1%	8,6%	20,7%
% U	71,6%	70,4%	65,2%
b) Con tres repulpados			
% $SO_4^=$ (base U)	1,2%	5,4%	20,0%
% U	74,5%	72,7%	65,7%

2.3.2. Eliminación de sulfato por lavado

Los datos de análisis de sulfatos en aguas de repulpado permiten calcular el % $SO_4^=$ eliminado por repulpado (Cuadro II). En el mismo Cuadro se incluyen los resultados de uranio y sulfatos en las tortas lavadas con uno y tres repulpados.

CUADRO III. TOSTACION DE CONCENTRADOS URANIFEROS. EFECTO DE LA TEMPERATURA DE TOSTACION EN LA ELIMINACION DE SULFATOS

Temperatura de precipitación en °C	Temperatura de tostación en °C	Muestras no lavadas		Muestras lavadas	
		% U	% $SO_4^=$ (base U)	% U	% $SO_4^=$ (base U)
30	–	57,00	38,51	74,51	1,24
30	200	59,46	38,40	78,79	1,26
30	300	61,87	38,42	80,07	1,22
30	400	64,55	38,02	81,33	1,18
30	500	67,24	33,82	82,91	1,07
30	600	67,98	33,47	83,73	0,87
30	700	76,60	15,31	84,56	0,12
30	800	84,62	<0,1	84,65	<0,1
45	–	60,84	29,73	72,69	5,44
45	200	64,09	29,70	76,63	5,45
45	300	65,56	29,50	77,68	5,39
45	400	68,69	29,35	78,59	5,29
45	500	70,66	26,79	80,63	5,07
45	600	70,77	26,32	81,33	4,96
45	700	78,45	9,76	84,60	0,17
45	800	84,67	<0,1	84,69	<0,1
60	–	60,73	26,91	65,67	20,04
60	200	64,02	26,85	68,78	20,07
60	300	66,64	26,79	69,08	19,98
60	400	69,21	26,85	69,77	19,91
60	500	70,96	24,52	73,60	18,78
60	600	71,16	24,27	73,79	18,43
60	700	81,03	5,92	84,37	0,20
60	800	84,46	<0,1	84,55	<0,1

2.3.3. Eliminación de sulfatos por tostación

Se comparan en el Cuadro III los resultados de U y $SO_4^=$ para las muestras de concentrados, secadas y calcinadas a varias temperaturas, por vía isotérmica (2.1). Los resultados de % $SO_4^=$ se refieren a base U para comparar con las especificaciones (Cuadro IV).

CUADRO IV. ESPECIFICACIONES DE CONCENTRADOS URANIFEROS

Constituyente	Allied Chemical Corporation	Kerr-McGee Corporation	USAEC	UKAEA	CEA[a]
% U[b]	65,00	60,00	(63,60)	50,00	63,00
% U_3O_8	76,65	70,75	75,00	58,96	74,29
% Humedad	5,00	–	10,00	10,00	5,00
% (base U)[c]					
$SO_4^=$	12,31	10,50	10,00	11,80	11,75
PO_4^{-3}	1,08	1,07	4,00	7,10	2,00
Cl^-	0,15	0,25	0,30	0,12	0,36
F^-	0,15	0,15	0,10	–	0,24
Fe	1,54	–	–	–	3,10
Na	0,78	–	–	–	–
K	4,60	–	–	–	–
Ca	1,15	1,00	1,50	1,78	1,75
As	1,06	1,00	2,00	0,58	2,35
B	0,15	0,15	0,20	0,05	0,23
$CO_3^=$	2,00	2,00	4,00	1,18	4,70
Mo	0,15	0,15	0,60	0,71	0,70
V_2O_5	0,23	0,18	2,00	2,40	2,35

[a] Reactores de uranio natural (Francia).

[b] Límite mínimo de U (muestra seca), suponiendo que se cumple la distribución de isótopos del uranio natural: % (U-235) = 0,711 ± 0,001%.

[c] Impurezas expresadas como % constituyente (base U). Estos valores representan límites máximos sin penalización.

2.3.4. Análisis termogravimétrico

Se han interpretado los registros termogravimétricos de las muestras de concentrados y productos relacionados con su termolisis: sulfato de uranilo, sulfato amónico, ADU, ADU + sulfato amónico (relación molar $SO_4^=/U = 1$) y sulfatos de uranilo y amonio (análisis químico: $\% U = 51{,}7$; $\% SO_4^= = 31{,}7$; $\% NH_3 = 3.85$).

CUADRO V. ANALISIS TERMOGRAVIMETRICO DE SULFATO DE URANILO[a]

Intervalo de temperatura en °C	Pérdida de peso		Transformaciones
	% pérdida	Velocidad máxima % pérdida/min (temp en °C)	
85–160	Peso constante	–	–
160–340	11,0 (–2,5 H_2O : 10,9)	1,5 (200)	– Pérdida de agua de cristalización. – Desv. endotérmica, máx. a 200°C.
340–730	Peso casi constante (pérdida : 0,2)	–	–
730–860	21,0 (estequiom. : 20,95)	2,6 (840)	– Conversión a U_3O_8 y eliminación de sulfatos. – Desv. endotérmica, máx. a 830°C.

[a] Sulfato de uranilo, $UO_2SO_4 \cdot 2{,}5\ H_2O$: 191,7 mg. Registro gráfico : TG-811. Velocidad de calefacción : 6°C/min. Caudal de aire : 5 l/h.

Nota: Residuo de U_3O_8 a 880°C, referido a UO_2SO_4 : 76,6% (estequiométrico : 76,7%).

Se incluyen los datos obtenidos para sulfato de uranilo (Cuadro V), sulfatos de uranilo y amonio (Cuadro VI) y tres muestras de concentrados (Cuadro VII).

En el Cuadro VIII se comparan los datos termogravimétricos de las muestras de concentrados y productos relacionados con su termolisis, considerando únicamente los intervalos de temperatura que tienen interés práctico en la eliminación de sulfatos del concentrado. Para cada intervalo de temperatura se indica la velocidad máxima de pérdida de peso (temperatura) y velocidad media de pérdida, expresando ambas en % pérdida/min (mg/min para 100 mg de muestra), así como la evaluación de sulfatos que se eliminan por encima de 680°C.

CUADRO VI. ANALISIS TERMOGRAVIMETRICO DE SULFATOS DE URANILO Y AMONIO[a]

Intervalo de temperatura en °C	Pérdida de peso		Transformaciones
	% pérdida	Velocidad máxima %/min (temp. en °C)	
120–220	9,9	2,9 (160)	– Pérdida de agua de cristalización : $H_2)/U = 1,5$. – Desv. endotérmica, máx. a 160°C.
220–430	1,0	–	–
430–530	10,1	2,2 (510)	– Eliminación total de amoníaco y parcial de sulfato.
530–730	Peso casi constante (pérdida : 0,1)	–	–
730–870	17,9	2,6 (860)	– Eliminación de sulfato y conversión a U_3O_8.

[a] Sulfatos de uranilo y amonio (relación molar por análisis químico: $2UO_2^{++}/2{,}98\ SO_4^=/2{,}08\ NH_4^+$): 200 mg. Registro gráfico: TG-816. Velocidad de calefacción: 6°C/min. Caudal de aire: 5 l/h.

Nota: Residuo de U_3O_8 a 880°C : 61,0%.

3. DISCUSION DE RESULTADOS

3.1. Eliminación de sulfatos por lavado

La oclusión de sulfato amónico en las tortas de precipitación disminuye mucho con la temperatura (Cuadro I); 37% de $SO_4^=$ a 30°C; 25% a 45°C y 8% a 60°C (% $SO_4^=$ se refiere a base U, salvo otra indicación).

Un repulpado con agua (agua/U_3O_8 = 20) permite eliminar la mayor parte del sulfato amónico de oclusión (Cuadro II), disminuyendo el porcentaje de sulfatos de

CUADRO VII. ANALISIS TERMOGRAVIMETRICO DE CONCENTRADOS[a]

Temperatura de precipitación en °C	Intervalo de temper. (TG) en °C	Pérdida de peso		Transformaciones
		% pérdida	Velocidad máx. % pérd./min (temp. en °C)	
30	20–430	11,8	0,6 (340)	– Pérdida de agua y amoníaco.
45	20–430	11,7	0,5 (340)	– Formación de trióxido de uranio.
60	20–430	12,9	0,6 (340)	– Reducción lenta de UO_3, desde 400°C.
30	430–520	4,8	0,8 (490)	– Pérdida de agua y amoníaco. – Eliminación parcial de sulfato.
45	430–520	1,8	0,4 (490)	
60	430–520	2,1	0,4 (490)	
30	520–690	apr. 0,2	–	
45	520–690	apr. 0,2	–	–
60	520–690	apr. 0,2	–	
30	690–870	16,0	2,0 (830)	– Eliminación de sulfato.
45	690–870	13,9	1,8 (830)	– Desviación endotérmica con máx. a 830°C.
60	690–870	13,0	1,8 (830)	

[a] Concentrados no lavados : 200 mg. Registros gráficos : TG-805 (30°C), TG-806 (45°C) y TG-807 (60°C). Velocidad de calefaccción : 6°C/min. Caudal de aire : 5 l/h.

Nota: Resíduos de calcinación a 870°C (U_3O_8) : Precipitación a 30°C : 67, 2%; a 45°C : 71,7%; a 60°C : 71,6%.

las tortas en 33% (30°C), 20% (45°C) y 6% (60°C), de modo que las tortas lavadas contienen 5,1% (30°C0, 8,6% (45°C) y 20,7% (60°C). En consecuencia, el concentrado lavado de precipitación a 30–45°C cumple especificaciones de sulfatos (Cuadro IV), siendo el porcentaje de uranio superior a los límites admitidos: 71,6% (30°C) y 70,4% (45°C).

Después de un triple repulpado, las tortas de uranio contienen 1,2% (30°C), 5,4% (45°C) y 20,0% (60°C) de $SO_4^=$. El concentrado de precipitación a 60°C

CUADRO VIII. DATOS TERMOGRAVIMETRICOS DE CONCENTRADOS DE URANIO Y COMPUESTOS RELACIONADOS. ELIMINACION DE SULFATOS POR TERMOLISIS

Muestras	Intervalo de temperatura[a] en °C	Velocidad de pérdida de peso. % pérdida/min (temp. en °C)		% pérdida de peso	% $SO_4^=$ eliminado a temperatura >680°C[b]	% $SO_4^=$ total[c]
		máxima	media			
Sulfato amónico	260–430	16,4 (400)	2,35	100	nulo	72,6
Sulfato de uranilo $UO_2SO_4 \cdot 2,5\ H_2O$	730–860	2,4 (840)	0,81	21,0	23,6	23,6
Sulfatos de uranilo y amonio	430–530	2,2 (510)	0,61	10,1	–	31,1
	730–870	2,6 (860)	0,72	17,9	20,1	–
ADU	430–530	–	–	0,5	–	–
	690–870	–	–	nula	–	nulo
ADU + $(NH_4)_2SO_4$ $SO_4^=/U = 1$	430–530	1,2 (490)	0,44	7,4	–	21,0
	690–870	1,6 (840)	0,43	13,0	14,6	
Concentrados no lavados, Precipit. 30°C	430–520	0,8 (490)	0,32	4,8	–	21,9
	690–870	2,0 (830)	0,53	16,0	18,0	
45°C	430–520	0,4 (490)	0,12	1,8	–	18,1
	690–870	1,8 (830)	0,46	13,9	15,6	
60°C	430–520	0,4 (490)	0,14	2,1	–	16,3
	690–870	1,8 (830)	0,43	13,0	14,6	

Cuadro VIII (continuación)

Muestras	Intervalo de temperatura[a] en °C	Velocidad de pérdida de peso. % pérdida/min (temp. en °C)		% pérdida de peso	% $SO_4^=$ eliminado a temperatura >680°C[b]	% $SO_4^=$ total[c]
		máxima	media			
Concentrado lavado. Precip. a 60°C	720–860	1,3 (840)	0,44	11,0	12,4	13,2

[a] Velocidad de calefacción, 6°C/min; aire, 5 l/h.

[b] Evaluación: (% $SO_4^=$) = (% pérdida) X 1,125. El factor 1.125 se deduce de la conversión de UO_2SO_4 a U_3O_8 : $\frac{3\ SO_4^=}{3\ SO_2 + 2\ O_2} = 1.125$

[c] Análisis de % $SO_4^=$, referido a muestra seca original.

no cumple especificaciones por lavado intenso, porque el sulfato básico de uranilo es la forma predominante de sulfato.

3.2. Eliminación de sulfatos por tostación

Para conseguir la eliminación necesaria de sulfatos de las tortas que no cumplen especificaciones, es preciso calcinar a una temperatura entre 700°C (Cuadro III), con independencia del tratamiento previo de la torta amarilla. Por tostación a temperatura inferior a 700°C, la proporción de sulfatos eliminados de las tortas es escasa, e insuficiente en cuanto a especificaciones del producto calcinado. En cambio el producto de calcinación a 800°C no contiene prácticamente sulfatos.

En resumen, considerando el efecto del lavado (3.1) y de la tostación en la eliminación de sulfatos, se pueden seguir dos alternativas para la obtención de concentrados que cumplan especificaciones de sulfatos:

a) Precipitar a cualquier temperatura entre 30°C y 60°C y calcinar directamente la torta de filtración a una temperatura del intervalo 700–800°C, suprimiendo la etapa de lavado. El contenido de uranio alcanza valores del orden del 80%.
b) Precipitar a temperatura entre 30°C y 45°C y efectuar un lavado y secado.

La torta amarilla secada (100°C) no requiere ninguna tostación, puesto que satisface especificaciones de uranio y sulfatos: 73–75% de U; 1–5% de $SO_4^=$. Sin embargo, calcinando a una temperatura de unos 300–400°C, si bién el sulfato no se elimina, aumenta notablemente el porcentaje de U, hasta un valor en torno al 80%. La ley elevada de los productos finales puede tener importancia desde el punto de vista del almacenamiento y transporte.

3.3. Análisis termogravimétrico

Los resultados de la termogravimetría dinámica (Cuadro VIII) confirman que a temperatura inferior a 700°C no se produce una eliminación práctica de sulfatos por tostación del concentrado.

La TG de los concentrados no lavados indica (Cuadro VII) que casi todo el sulfato se elimina en dos intervalos de temperatura: 430–520°C y principalmente 690–870°C. En realidad a 690–870°C se descompone más del 80% del sulfato total.

Aunque las tortas no lavadas contienen cantidades grandes de sulfato amónico de oclusión, a temperatura inferior a 430°C no se produce eliminación de sulfato, lo cual está en aparente contradicción con los resultados de la TG del reactivo sulfato amónico, que indica un desprendimiento total por debajo de 430°C.

Para explicar el comportamiento termogravimétrico del sulfato amónico de oclusión, debe admitirse que en el intervalo de descomposición del sulfato amónico, que se inicia a unos 260°C, tiene lugar una reacción entre los productos de la termolisis de sulfato amónico y compuestos de uranio del concentrado, para formar probablemente sulfatos de uranilo y amonio. Con este supuesto guardan buena concordancia los siguientes resultados:

a) La TG de una mezcla de ADU y sulfato amónico presenta dos intervalos de eliminación de sulfatos (Cuadro VIII), coincidiendo con la termolisis de sulfatos de las tortas no lavadas.

b) El producto de calcinación de una mezcla de ADU y sulfato amónico hasta 400°C se disuelve en gran parte en agua y cristaliza como sulfatos de uranilo y amonio, determinándose por análisis una relación molar: $2\ UO_2^{++}/2{,}98\ SO_4^{=}/2{,}08\ NH_4^{+}$.

c) La TG del producto sulfatos de uranilo y amonio indica también la eliminación de sulfatos (Cuadro VI) dentro de los intervalos de temperatura citados anteriormente: a 430–530°C se produce eliminación parcial de sulfato y total de nitrógeno; a 730–860°C se completa la descomposición del sulfato, coincidiendo con la conversión de sulfato de uranilo en U_3O_8 (Cuadro V).

4. CONCLUSIONES

A partir del extracto acuoso "Purlex" se consiguen precipitados que tienen buenas características para la separación sólido-líquido, efectuando la precipitación con amoníaco a pH 7,4 a una temperatura desde 30°C (30–45–60°C), manteniendo una evolución lenta del pH, con un tiempo de retención de dos horas.

Sin embargo, los precipitados contienen cantidades elevadas de sulfatos. En cuanto a su eliminación, pueden seguirse dos alternativas, para que el concentrado cumpla especificaciones de sulfatos:

- Precipitación en el intervalo 30–45°C, lavado del precipitado con agua y secado. Por precipitación a 45°C, en las condiciones de neutralización indicadas, lavando el precipitado por repulpado con agua, se obtiene un concentrado que, secado a 100°C, contiene 5,4% de $SO_4^{=}$ (base U) y 72,7% de U. Calcinado a 300–400°C contiene 5,3% de $SO_4^{=}$ y 78% de U.
- Calcinación a temperatura elevada entre 700 y 800°C, con lo que se pueden eliminar prácticamente los sulfatos, con independencia de la temperatura de precipitación y sin que el precipitado exija un lavado previo.

La termogravimetría dinámica confirma los resultados de la tostación por vía isotérmica. A temperatura inferior a 690°C no es posible efectuar la eliminación necesaria de sulfatos, puesto que se desprende menos del 20% del sulfato total, en gran medida en el intervalo 430–520°C.

El sulfato amónico de oclusión no tiene un comportamiento termolítico como tal compuesto, que se desprendería a temperatura inferior a 430°C, porque al progresar la TG se convierte en sulfato de uranilo y amonio, que presenta la eliminación de sulfatos en los intervalos 430–530°C y 730–870°C.

REFERENCIAS

[1] CORDFUNKE, E.H.P., J. Inorg. Nucl. Chem. **24** (1962) 303.
[2] STUART, W.I., WHATELEY, T.L., J. Inorg. Nucl. Chem. **31** (1969) 1639.
[3] WOOLFREY, J.L., The Effect of pH on the Properties of Ammonium Uranate precipitated with Gaseous Ammonia, Informe AAEC/E 397, Comisión de Energía Atômica de Australia (1976).
[4] MERINO, J.L., Características de suspensiones de uranato amónico, Informe JEN/ S.T.M./ R-21-76 (Nov. 1976).
[5] NUGENT, REID, Uranium in South Africa 1946–56, Hortors Ltd, South Africa 2 (1957) 170–173.
[6] MERRIT, R.C., The Extractive Metallurgy of Uranium Colorado School of Mines Research Institute, USAEC (1971) 379–491.
[7] PRICE, G.H., STUART, W.I., Thermal Decomposition of Ammonium Uranates, Informe AAEC/E 276, Comisión de Energía Atômica de Australia (1973).
[8] BALL, M.C., BIRKETT, C.R., BROWN, D.S., JAYCOCK, M.J., J. Inorg. Nucl. Chem. **36** (1974) 1527–29.
[9] WOOLFREY, J.L., The Preparation and Calcination of Ammonium Uranates – A Literature Survey, Informe AAEC/TM 476, Comisión de Energía Atômica de Australia (1968).
[10] NOTZ, K.J., HAFFE, H.H., J. Inorg. Nucl. Chem. **25** (1963) 851–57.

DISCUSSION

S. SEN: In a recent publication from South Africa it has been mentioned that roasting above 500°C results in a concentrate with slower reaction kinetics for subsequent nitric acid dissolution in the refinery. Has any work been carried out in Spain on this aspect?

B. RODRIGUEZ: JEN have conducted dissolution experiments involving various calcined products (U_3O_8) with nitric acid, but these experiments are unrelated to the calcined concentrates discussed in this paper, which are not, in principle, intended for SX (TBP) purification processes. The paper discusses elsewhere an alternate means of obtaining uncalcined concentrates which meet specifications.

R.B. COLEMAN: Do you have any information regarding filtration rates for precipitates produced at the various precipitation temperatures?

B. RODRIGUEZ: The filtration rates have not been determined, but it has been observed that filtration times are cut considerably with higher precipitation temperatures.

A. ABRAO: We have operated one pilot plant for uranium purification. The final product was ADU. The precipitation was done by introducing NH_3 to the uranyl sulphate solution. The co-precipitation of $(NH_4)SO_4$ reached up to 40%. This problem was overcome by doing the reverse precipitation, that is, the uranium solution was added to an ammonia solution, keeping the mixture at $pH>7$ during the entire precipitation. The precipitate has then less than 0.5 SO_4.

B. RODRIGUEZ: We have not conducted reverse precipitation experiments, because the addition of uraniferous solution to ammonia solution causes very rapid precipitation, resulting in the formation of precipitates with poor physical properties.

A REVIEW OF UNITED STATES YELLOW CAKE PRECIPITATION PRACTICE

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Abstract

A REVIEW OF UNITED STATES YELLOW CAKE PRECIPITATION PRACTICE.

The various process flowsheets used to produce concentrated uranium solutions are reviewed. The choices of flowsheets are affected by ore alkalinity, uranium mineralization, and the impurities solubilized during leaching. The techniques used to precipitate yellow cake from concentrated uranium solutions are reviewed. Consideration is given to precipitation chemistry, reagent requirements, and process equipment and costs for precipitation, dewatering, drying and calcining.

At present there are about 30 operating plants in the United States of America which produce yellow cake as a saleable uranium product. This number is approximate because of the large number of in-situ operations. Some of these in-situ operations are of a commercial size, but most are pilot plant size. This review primarily considers conventional milling operations. The yellow cake precipitation techniques used by the various in-situ operations essentially parallel the conventional processes.

A large number of flowsheet variations are used to treat ores in the USA. The selection of the flowsheet is affected by a number of factors:

Ore alkalinity

Nature of the uranium mineralization

Impurities solubilized during leaching such as molybdenum, vanadium, silicon, zirconium, arsenic, and phosphorus.

Acid leaching is not used by any mills where feed ore averages more than 6% calcium carbonate. Mild acid leaching is the most common where mineralization is uraninite and coffinite. However, some coffinite-bearing ores contain considerable uranium-bearing asphalts which require rather severe leaching conditions to achieve adequate uranium solubilization.

The most common flowsheet used in the USA is shown in Fig. 1. With this flowsheet the ground ore is leached with sulphuric acid, the solids are separated

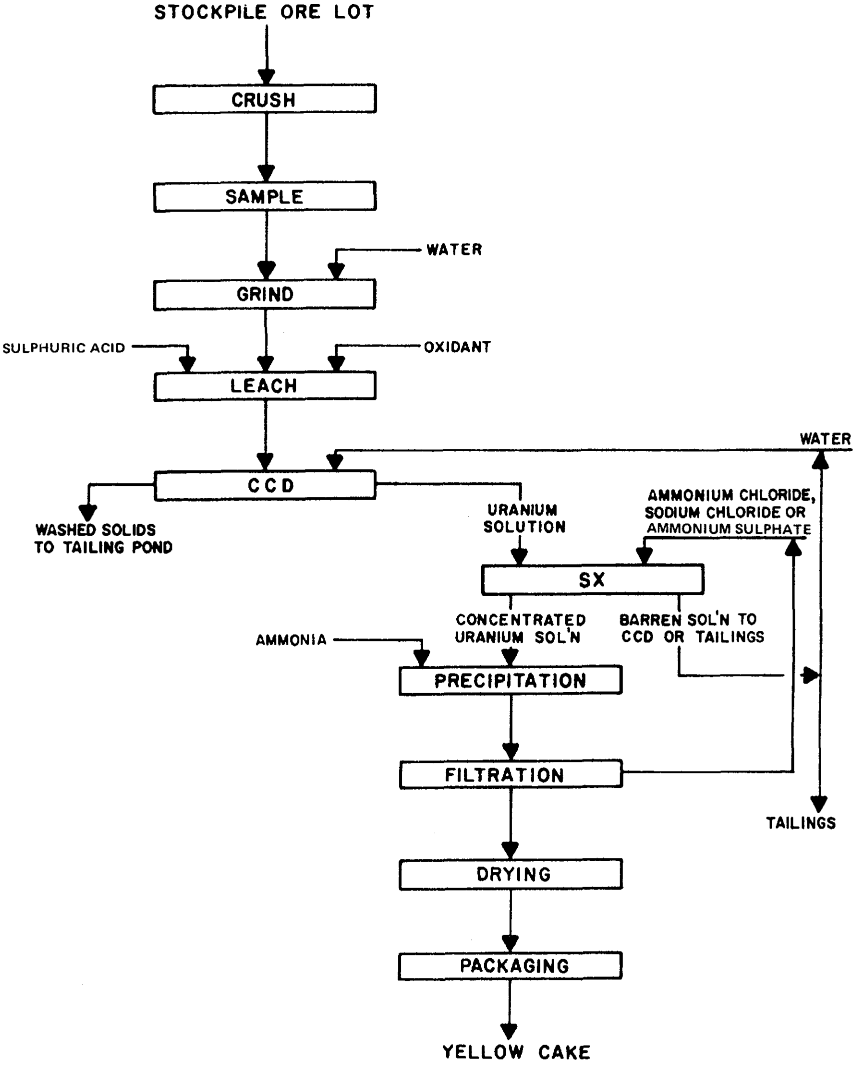

FIG.1. Concurrent atmospheric acid leach, solvent extraction, and ADU precipitation.

and washed using counter-current decantation thickeners, and the uranium is concentrated using solvent extraction (liquid ion-exchange) into sodium chloride, ammonium chloride, or ammonium sulphate stripping solutions. Yellow cake (ammonium diuranate) is precipitated from these strip solutions by the addition of ammonia. The choice of the strip solution used is dependent on the impurities co-extracted by the solvent. For example, silicon and zirconium will hydrolyze during stripping with ammonium sulphate. A heteropoly amine molybdophosphate complex can form during stripping with sodium and ammonium chlorides.

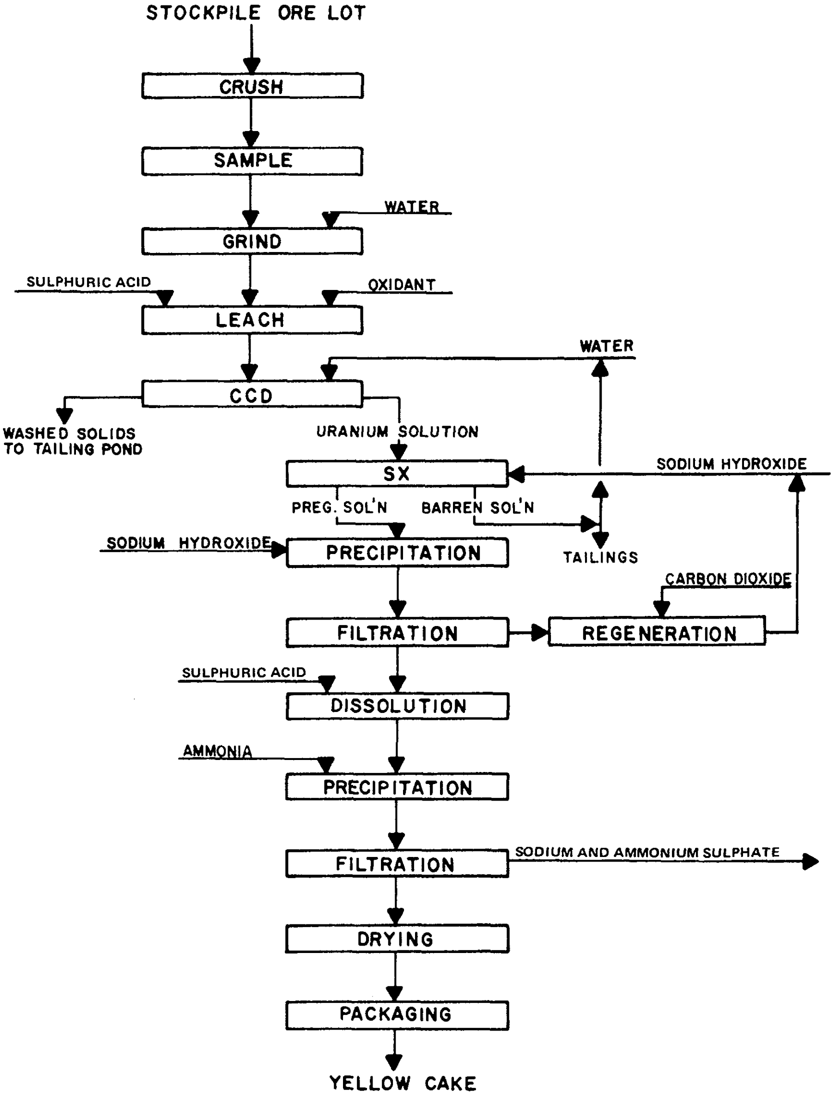

FIG.2. Concurrent atmospheric acid leach, solvent extraction, and SDU precipitation.

The flowsheet illustrated in Fig.2 was used by a number of mills which operated during the 1950s and 1960s. This flowsheet utilizes leaching, countercurrent decantation, and solvent extraction to concentrate the uranium. The solvent is stripped by a sodium carbonate solution. Sodium diuranate is precipitated from the sodium carbonate strip solution by the addition of sodium hydroxide. The sodium diuranate is then converted to ammonium diuranate.

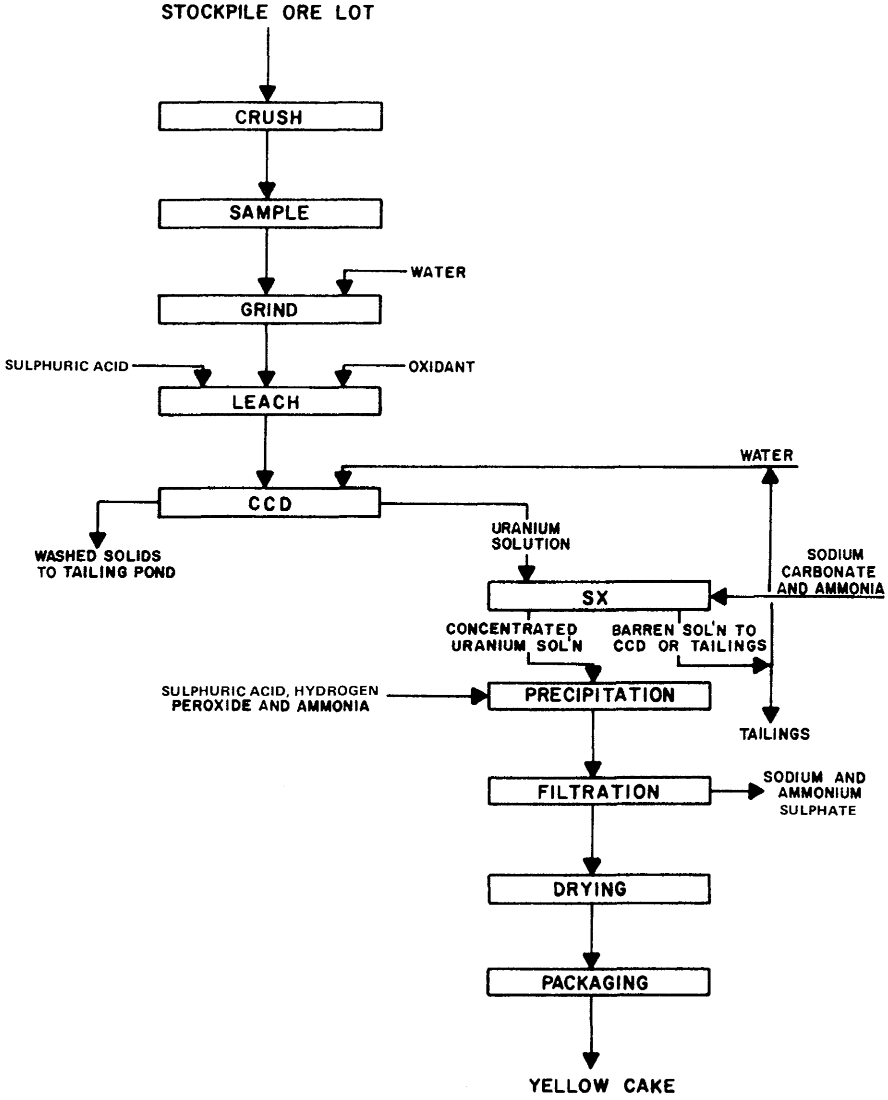

FIG.3. Concurrent atmospheric acid leach, solvent extraction, and uranium peroxide precipitation.

This flow-sheet will be used by a mill presently in the design stage. It will allow for handling of uranium ores containing considerable molybdenum, up to one-half of the uranium content, without experiencing any penalty problems with the final product. The molybdenum will concentrate in the sodium diuranate filtrate and will be recovered as a high quality ammonium molybdate product.

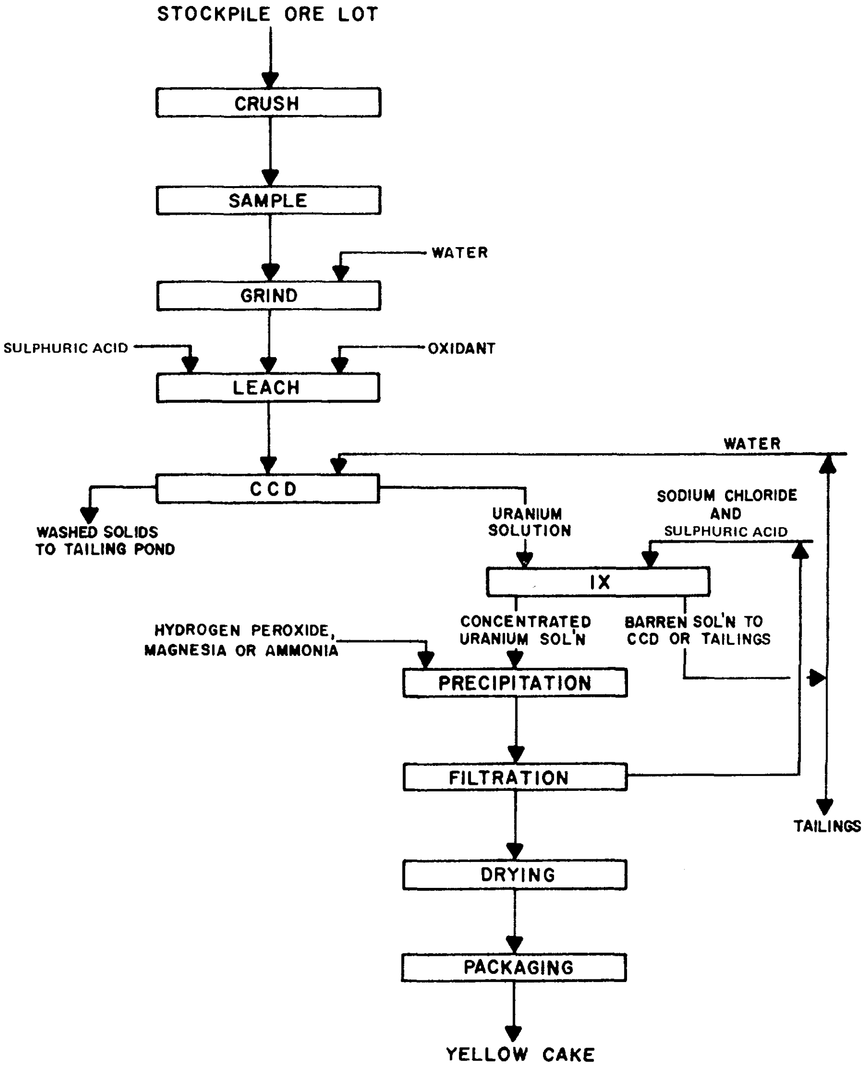

FIG.4. Concurrent atmospheric acid leach, ion-exchange, and ADU precipitation.

The flowsheet shown in Fig.3 is a modification of flowsheet 2 which allows for producing specification product with a single stage of precipitation. After stripping with sodium carbonate, the carbonate is destroyed by acidulation with sulphuric or nitric acid. The addition of hydrogen peroxide effects precipitation of uranium peroxide. The uranium peroxide precipitation allows for good separation from molybdenum, vanadium, and phosphorus impurities.

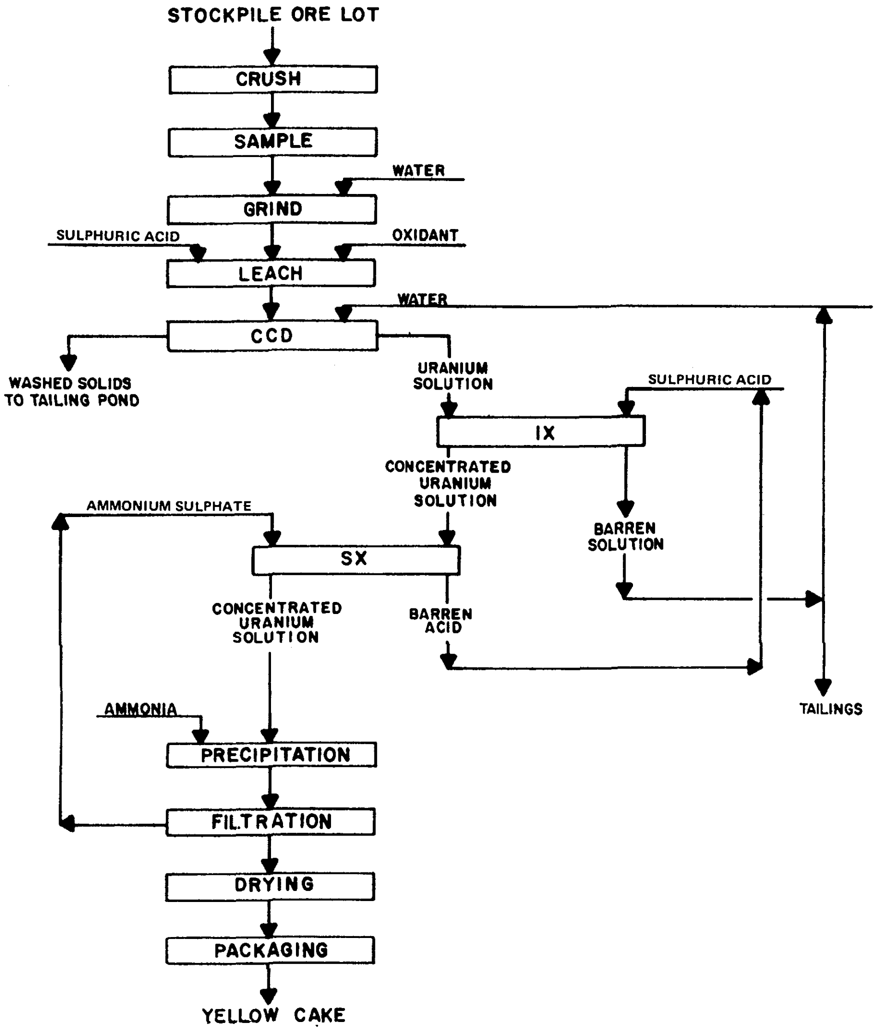

FIG.5. Concurrent atmospheric acid leach, ion-exchange, Eluex, and ADU precipitation.

The flowsheet illustrated in Fig.4 is very similar to that shown in Fig.1 except that resin ion-exchange is used to concentrate the uranium. Depending on the level of impurities in the strip solutions, the uranium is precipitated as either ammonium diuranate or uranium peroxide.

Figure 5 shows a flowsheet which has the potential for lower operating costs than that shown in Fig.4. In this flowsheet the uranium is first concentrated by resin ion-exchange, transferred to 3N sulphuric acid, re-extracted by a solvent

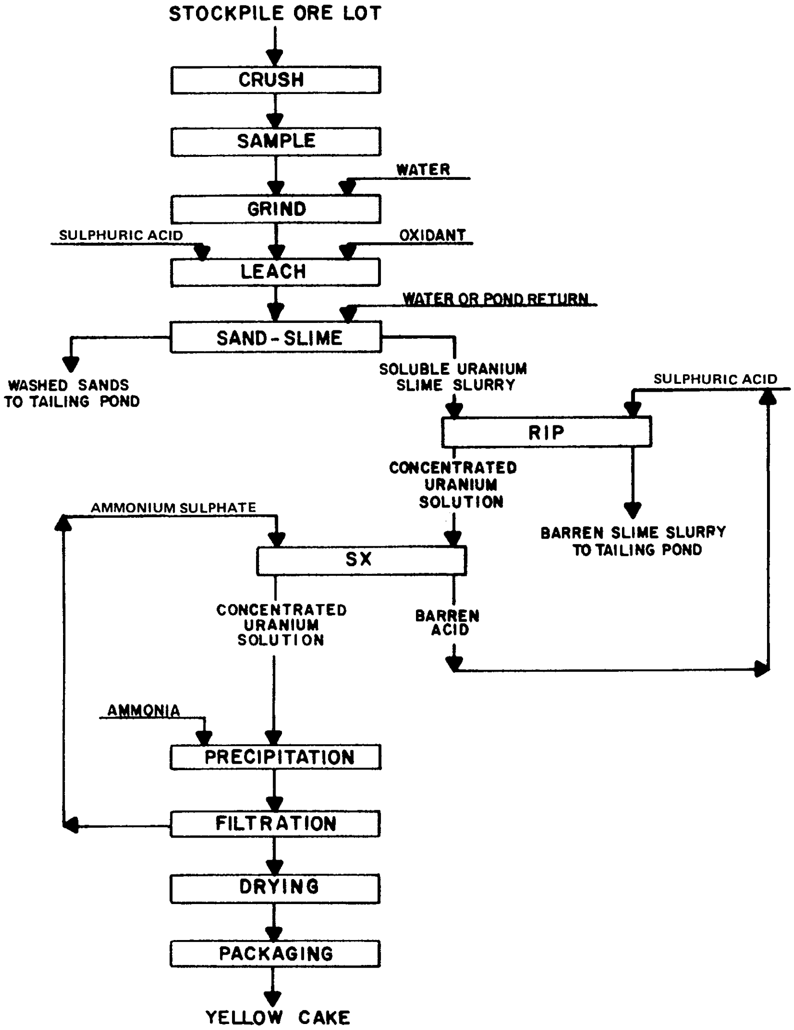

FIG.6. Concurrent atmospheric acid leach, resin-in-pulp, Eluex, and ADU precipitation.

extraction (liquid ion-exchange) step, and stripped into an ammonium sulphate solution. This flowsheet allows for maximum recycle of the stripping solutions.

The flowsheet depicted in Fig.6 is a lower cost version of that shown in Fig.5. The ground ore is leached with sulphuric acid, the sands and slimes are separated by cyclones with the sands being washed in classifiers or cyclones, and the uranium is transferred from the slime pulp onto ion-exchange resin. This flowsheet eliminates the high capital cost of the countercurrent decantation

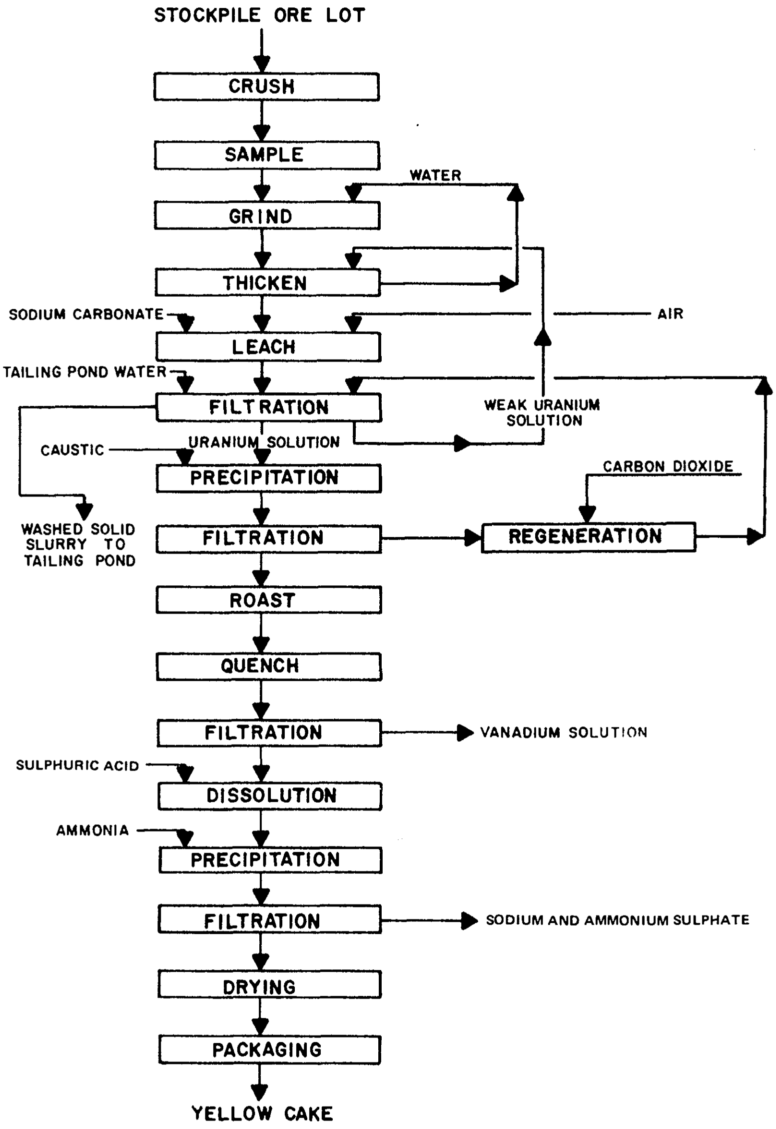

FIG. 7. Alkaline leach, SDU precipitation, and ADU precipitation.

thickeners. All the United States mills using resin-in-pulp use 'Eluex' to further concentrate the uranium into an ammonium sulphate solution.

Figure 7 shows the most complicated flowsheet presently used for the alkaline leaching of uranium ores in the USA. The three alkaline mills all use vacuum filters for the liquid/solid separation, and precipitate sodium diuranate as an intermediate product. The sodium diuranate cannot meet the specifications of the refineries and therefore must be further purified. Purification of the precipitated sodium diuranate is performed differently at each of the mills. The various methods of purification are considered later in this paper.

The seven flowsheets discussed to this point indicate that the recovery of uranium from ores as practised in the United States is a complex process. This complexity relates only to the leaching, liquid/solid separation, and exchange, and not to the precipitation of the yellow cake product. The yellow cake precipitation is one of the more simple portions of the various processes.

The solutions produced by acid leaching or by alkaline leaching and concentrating the uranium by an exchange step contain the uranium as either sulphate or carbonate anions. The most common species of these anions are: uranyl trisulphate [$UO_2(SO_4)_3^{4-}$] and uranyl tricarbonate [$UO_2(CO_3)_3^{4-}$].

Uranium from uranyl sulphate solutions is generally precipitated as either ammonium diuranate or uranium peroxide:

Ammonium diuranate

$$2UO_2(SO_4)_3^{4-} + 2NH_3 + 6H_2O \longrightarrow (UO_2)_2SO_4(OH)_2{\cdot}4H_2O$$

$$2UO_2(SO_4)_3^{4-} + 6NH_3 \longrightarrow (NH_4)_2U_2O_7 + 4SO_4^{2-}$$

Uranium peroxide

$$UO_2(SO_4)_3^{4-} + H_2O_2 + 2H_2O \longrightarrow UO_4{\cdot}2H_2O + 3SO_4^{2-} + 2H^+$$

The precipitation of ammonium diuranate is the most common. Care must be taken during the precipitation of ammonium diuranate to avoid the formation of basic uranium sulphate. It is seen that the formation of basic uranium sulphate requires one-third the ammonia necessary to form ammonium diuranate.

As is shown, uranium peroxide is formed by the addition of hydrogen peroxide to uranyl sulphate solutions. The formation of hydrogen ion during the precipitation may require the addition of a base to maximize the precipitation efficiency. The precipitation of uranium peroxide is used by a number of mills to avoid the payment of penalties for impurities such as vanadium, molybdenum, or phosphorus.

The recovery of uranium from uranyl tricarbonate solutions is done by the addition of sodium hydroxide to effect the precipitation of sodium diuranate:

$$2UO_2(CO_3)_3^{4-} + 14NaOH \longrightarrow Na_2U_2O_7 + 6Na_2CO_3 + 8OH^- + 3H_2O$$

At present in the USA, direct precipitation of sodium diuranate is the only method of uranium recovery practised by the alkaline leach mills. Concentration of alkaline leach liquors by ion-exchange was practised in the 1950s and 1960s in conventional mills and is presently practised by some in-situ leaching operations.

The sodium diuranate does not have sufficient purity to allow the sale of the product without substantial penalties. Therefore, all present producers of sodium diuranate use one of the following purification steps:

Vanadium removal by roasting

$$Na_2U_2O_7 + NaVO_3 + Na_2CO_3 \longrightarrow Na_2U_2O_7 + VO_3^- + CO_3^{2-} + 3Na^+$$

Sodium removal by metathesis

$$Na_2U_2O_7 + (NH_4)_2SO_4 \longrightarrow (NH_4)_2U_2O_7 + 2Na^+ + SO_4^{2-}$$

Conversion to ammonium diuranate or uranium peroxide

$$Na_2U_2O_7 + 6H_2SO_4 \longrightarrow 2UO_2(SO_4)_3^{4-} + 2Na^+ + 6H^+ + 3H_2O$$

Vanadium can be removed by roasting the sodium diuranate with sodium carbonate. This procedure converts the vanadium to sodium metavanadate. The sodium metavanadate is removed from the yellow cake by water leaching.

Metathesis with concentrated ammonium sulphate solutions is used occasionally to lower the sodium content. The metathesis allows for partial conversion of the sodium diuranate into ammonium diuranate.

A third method of purification is to dissolve the sodium diuranate in sulphuric acid. This causes the conversion to the uranyl sulphate ion which allows for re-precipitation of the uranium as uranium peroxide or ammonium diuranate.

The following section deals with the present precipitation practices within the United States. Because many of the mills are now more than 20 years old, much of the equipment being used was not intended for the present use. Therefore, wide ranges are observed in the data. The numerical values which indicate the best efficiency, in all probability, could be used for design purposes.

In the precipitation of ammonium diuranate, Table I, the temperature is always elevated (50 to 85°C). The precipitation retention times range from 2 h for some continuous circuits to 6 h for some batch precipitation circuits. The

TABLE I. OPERATING PRACTICE: AMMONIUM DIURANATE PRECIPITATION

Temperature	Digestion time	Ammonia addition
50 – 85°C	2 – 6 h	0.22 kg NH_3/kg U_3O_8

TABLE II. OPERATING PRACTICE: URANIUM PEROXIDE PRECIPITATION

Temperature	Digestion time	Hydrogen peroxide addition
20 – 25°C	2 – 8 h	0.18 – 0.25 kg H_2O_2/kg U_3O_8

TABLE III. OPERATING PRACTICE: SODIUM DIURANATE PRECIPITATION

	Direct precipitation from leach solution	Precipitation from carbonate strip solution
Temperature	50 – 80°C	20 – 30°C
Digestion time	6 – 12 h	2 – 4 h
Free NaOH	4 – 6 g/ltr	4 – 6 g/ltr
Sodium hydroxide addition	5 – 6 kg NaOH/kg U_3O_8	3 – 4 kg NaOH/kg U_3O_8

ammonia addition will vary with the amount of free acid in the concentrated uranium solution, but generally is fairly close to the 0.22 kg/kg U_3O_8 listed in Table I.

Precipitation of uranium peroxide, Table II, generally is performed at ambient temperature to minimize the decomposition of the excess hydrogen peroxide. Digestion times range from 2 to 8 h, depending on the sulphate level in the solution. The hydrogen peroxide additions are 0.18 to 0.25 kg H_2O_2/kg U_3O_8, depending mainly on the amount of impurities which must be complexed by the peroxide.

TABLE IV. OPERATING PRACTICE: THICKENING

	Ammonium diuranate	Uranium peroxide	Sodium diuranate
Rise rate (m/h)	0.1 – 0.5	0.5 – 2.0	0.6 – 1.1
Underflow density (% solids)	15 – 30	30 – 50	35 – 40

The practices for precipitating sodium diuranate from alkaline leach solutions and sodium carbonate strip solutions differ greatly, as shown in Table III. Precipitation from leach solutions is performed at elevated temperatures (50 to 80° C) for fairly extended periods (6 to 12 h). Much of the precipitate is recycled to maximize the surface area for precipitate growth. Precipitation from strip solutions is done at ambient temperature for fairly short retention times (2 to 4 h). The terminating precipitation conditions are similar for both procedures. The primary control is the sodium hydroxide excess (4 to 6 g/ltr NaOH). Because of the more dilute solutions, precipitation from leach solutions requires more sodium hydroxide (5 to 6 kg NaOH/kg U_3O_8) versus precipitation from carbonate strip solutions (3 to 4 kg NaOH/kg U_3O_8).

Table IV lists the conditions used for the thickening of yellow cake precipitates. The highest rise rates (0.5 to 2.0 m/h) and highest underflow densities (30 to 50% solids) are achieved when precipitating uranium peroxide. The high thickener rise rates achieved with sodium diuranate (0.6 to 1.1 m/h) are due to direct recycling up to 100% of the overflow solution. The low rise rates used with ammonium diuranate precipitates (0.1 to 0.5 m/h) are because much of the overflow solution is discarded to tailings after polishing filtration.

Underflow densities are low with ammonium diuranate (15 to 30% solids) as compared to sodium diuranate (35 to 40% solids). The higher densities with the sodium diuranate are due primarily to improved precipitate crystal growth effected by recycling a major portion of the solids as seed to the precipitation.

Most mill operators in the USA employ single-stage thickening as the means of initially dewatering the yellow cake precipitation slurry prior to the final dewatering step. Some mills, however, use two-stage counter-current thickening for product washing and/or metathesis in conjunction with dewatering. The practice of counter-current washing and thickening generally is limited to the older mills, especially those mills using sodium chloride stripping.

Table V lists the dewatering rates and discharge percent solids for the three yellow cake precipitates from three types of dewatering devices. Again, uranium peroxide dewatering shows the fastest rates and generates the highest per cent

TABLE V. OPERATING PRACTICE: DEWATERING

	Ammonium diuranate	Uranium peroxide	Sodium diuranate
Vacuum filtration			
Rate (kg/h per m^2 of filter area)	25 – 125	45 – 1000	15 – 40
Filter cake (% solids)	30 – 50	40 – 70	30 – 50
Pressure filtration			
Rate (kg/h per m^2 of filter area)	0.4 – 10	ND	0.4 – 15
Filter cake (% solids)	30 – 65	ND	40 – 60
Centrifuging			
Rate (kg/h per m^2 of bowl area)	55 – 180	ND	95 – 120
Discharge (% solids)	50 – 75	65 – 75	60 – 70

ND = no data available

solids discharge from both vacuum and centrifuge operations. Pressure filtration of uranium peroxide has been performed at one mill where ammonium diuranate is the normal product, but no quantitative data are available.

The dewatering operation parameters vary widely for sodium and ammonium diuranate. This wide variance primarily occurs in the older mill operations. Originally, much of the filtration equipment was sized to handle precipitation slurry directly without the benefit of intermediate dewatering with a thickener. Also, much of the early sizing was done before the techniques to optimize crystal growth were known, such as recycling of the precipitate. Thus, as improved operating methods were introduced into these original mill operations, much of the original dewatering equipment became oversized with respect to the yellow cake production rate.

Dewatering with solid bowl and basket centrifuges is now the preferred practice in the newer mills and the older operations that have been remodelled. Centrifuge operations, when properly designed for the precipitate, provide high capacity dewatering, and can produce a high per cent solids discharge of efficiently washed yellow cake. A properly sized single-stage dewatering thickener, combined with a well-engineered centrifuge provides a high capacity operation with a product washed free of soluble impurities.

TABLE VI. OPERATING PRACTICE: DRYING AND CALCINING

	Ammonium diuranate	Uranium peroxide
Drying		
Temperature (°C)	120 – 400	150 – 200
Rate (kg/h per m^2 of dryer area)	17 – 25	20 – 30
Calcining		
Temperature (°C)	400 – 850	700 – 800
Rate (kg/h per m^2 of hearth area)	6 – 15	12 – 15
Retention time (h)	1.5 – 2.0	1.0 – 1.5

The conditions used for drying and calcining ammonium diuranate and uranium peroxide are listed in Table VI. At present no sodium diuranate is produced as the final product. The drying data range from steam-heated processors to direct-fired hearth driers and calciners.

Most of the mill operations in the USA that precipitate ammonium diuranate from sodium chloride strip solutions operate calciners at high temperatures to eliminate chloride contamination and to produce a dense product. Several mill operations that precipitate ammonium diuranate from ammonium sulphate strip solutions are able to calcine at lower temperatures and produce products within all specifications. However, in some cases, after the start of the mill operation, higher calcining temperatures were required to meet the contract specifications. Unfortunately, this has resulted in a few serious equipment failures when calciners were operated well above the design temperatures.

Uranium peroxide precipitates are low in impurities and do not require calcining to meet chemical specifications. However, high temperature calcining is practised to produce a greater than 95% U_3O_8 product having high density. The calcination rate for the uranium peroxide is fairly fast because there is no high temperature endothermic decomposition such as occurs when calcining ammonium diuranate.

The last portion of this paper covers a cost comparison of the various precipitation methods. Hazen Research, Inc., recently has been involved in a number of preliminary and feasibility cost estimates which have included most flowsheets for uranium concentration and precipitation. In addition, our plant consulting activities have made available a considerable amount of cost data from operating mills. The information listed in Table VII is an averaged summary of the available cost data.

TABLE VII. COST COMPARISON OF PRECIPITATION ROUTES (US Dollars)

Strip reagent	Sodium chloride	Ammonium sulphate	Sodium carbonate	Sodium carbonate
Precipitation reagent	NH_3	NH_3	H_2O_2	NaOH
Product	Ammonium diuranate	Ammonium diuranate	Uranium peroxide	Sodium diuranate
Costs (US Dollars/kg)				
Reagent	$0.37	$0.18	$0.44	$0.40
Labour and expense	$0.14	$0.14	$0.14	$0.16
Capital	$0.15	$0.24	$0.20	$0.27
Total	$0.66	$0.56	$0.78	$0.83

Precipitation of ammonium diuranate from ammonium sulphate strip solutions has the lowest reagent cost since ammonia is the only chemical required. The capital is somewhat higher since four stripping stages and one scrub stage are assumed for the solvent extraction circuit.

The sodium chloride stripping and ammonium diuranate precipitation using ammonia has the lowest capital cost. The relatively high cost of hydrogen peroxide (about $1.00 per kilogram of 100% H_2O_2) gives the uranium peroxide the highest reagent cost. The complexity of the sodium diuranate precipitation and subsequent conversion to ammonium diuranate gives this system the highest overall cost.

In summary, considering the available technology, operating dependability, product purity, and costs of uranium precipitation, we believe that two recovery and precipitation methods are preferable. The first is acid leaching, solvent extraction, ammonium sulphate stripping, and ammonia precipitation, provided that the ore feed is amenable to acid leaching and has a low content of soluble impurities, i.e. molybdenum, arsenic, phosphorus, zirconium, etc. Ion-exchange may be used for intermediate concentration. If the ore contains relatively large amounts of soluble impurities, the preferred process would include acid leaching, solvent extraction, sodium carbonate stripping, and uranium peroxide precipitation.

DISCUSSION

R. COLBORN: For operating practice of drying and calcining, what retention times are used for the drying step for ammonium diuranate?

J. LITZ: The wide variety of devices used – thermal processors through direct-fired hearth furnaces – do not have similar retention times nor drying temperatures. Therefore, there is not a single answer with regard to drying rate.

F.E. McGINLEY: Would the author (Mr. Litz) care to comment on the safety hazards of using peroxide for uranium precipitation?

J. LITZ: Incidents which have occurred with peroxide have all involved storage. These have been due to non-ideal storage vessels or dilution of the delivered 70% H_2O_2 with too low a quality water.

P.G. ALFREDSON: Your paper's description of precipitation techniques makes no reference to pH or to the number of tanks used. Would you comment on this please?

J. LITZ: Plants using continuous precipitation normally have three stages: first stage – 4 to 5 pH; second stage – 6.5 to 7.5 pH; third stage – digestion. Batch precipitation usually is done with rapid neutralization to 6.5 to 7.5 pH.

S. SEN: In Table V, the filtration rate for uranium peroxide has been indicated to be in the range of 45 to 1000 kg/h per square metre of filter area. Could Mr. Litz indicate the reasons for such a wide variation in the filtration rate?

J. LITZ: Depending on the precipitation techniques used, uranium peroxide will contain different amounts of hydration. Single, batch precipitation will produce a low hydration product with poorer filtration characteristics than the high hydration crystals that can be formed if the majority of the precipitate is recycled as seed.

F.R. HARTLEY: 1. In Table VII does the reagent cost in the comparison between chloride and ammonium sulphate strips include ammonia for stripping in the $(NH_4)SO_4$ process?

2. In the early Australian plants we deliberately controlled to form some basic sulphate which was subsequently decomposed by boiling before filtration. Your comment please?

J. LITZ: 1. The costs do include the ammonia required for stripping. Ammonia is still the lowest cost soluble base in the USA.

2. Because of the high temperatures normally used for calcination, sulphate is not a major concern. The typical precipitation product consists of both ADU and basic uranyl sulphate. Precipitations are controlled to give the best physical product at most operations.

D. BOYDELL: It is South African practice to include up to five scrubbing stages between extraction and stripping in solvent extraction circuits employing ammonium sulphate stripping. This procedure allows a number of impurities that would otherwise cause basic hydroxide precipitates in the strip stages to be removed and avoids the necessity for additional or alternative and more expensive purification stages. Would Mr. Litz comment?

J. LITZ; Engineering practice in the USA has not included scrubbing stages in most extraction circuits. We at Hazen Research recognize the benefits of scrubbing and attempt to include recommendations for scrubbing whenever we develop process criteria for solvent extraction steps.

PURIFICATION ET CONCENTRATION DES SOLUTIONS URANIFERES DANS LES USINES DE LA SOCIETE INDUSTRIELLE DES MINERAIS DE L'OUEST

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Abstract–Résumé

PURIFICATION AND CONCENTRATION OF URANIUM-BEARING SOLUTIONS AT THE PLANTS OF THE SOCIETE INDUSTRIELLE DES MINERAIS DE L'OUEST.

The author describes the various processes for purification of uranium-bearing solutions used at the plants of the Société industrielle des minerais de l'Ouest (SIMO) from their commissioning up to the present time, together with the purification circuit adopted at the two plants at present operating in Niger.

PURIFICATION ET CONCENTRATION DES SOLUTIONS URANIFERES DANS LES USINES DE LA SOCIETE INDUSTRIELLE DES MINERAIS DE L'OUEST.

L'auteur indique les différents procédés de purification des solutions uranifères utilisés dans les usines de la Société industrielle des minerais de l'Ouest (SIMO) depuis leur mise en service jusqu'au stade actuel ainsi que le schéma de purification retenu pour les deux usines existant actuellement au Niger.

INTRODUCTION

Les solutions uranifères obtenues habituellement lors de la solubilisation de l'uranium contenu dans les minerais et après la séparation solide-liquide contiennent l'uranium sous sa forme oxydée U VI, et cette forme se retrouve dans les solutions aqueuses à l'état de cation UO_2^{2+}

Cette forme a la possibilité de s'associer aux ions SO_4^{2-} et CO_3^{2-} pour former des complexes du type $[UO_2\,(SO_4)\,n]^{2-2n}$ ou $[UO_2(CO_3)_3]^{4-}$.

Comme la solubilisation de l'uranium contenu dans les minerais n'est pas spécifique, on trouve dans les solutions aqueuses la plupart des cations qui sont présents dans les minerais et qui seront passés en solution sous forme de produits solubles, sulfates ou carbonates, en fonction de l'agent retenu pour la solubilisation.

Comme les traitements habituellement réalisés dans l'hydrométallurgie de l'uranium conduisent généralement à la fabrication d'un sel facilement transportable vers une usine de raffinage, les solutions uranifères sont traitées par des réactifs alcalins dans la plupart des cas.

Mais, dans ces conditions, le produit obtenu contient, à quelques variantes près, toutes les substances qui ont suivi l'uranium. C'est la raison pour laquelle on a recherché, dès le début, la possibilité de purifier d'abord puis de concentrer ensuite les solutions uranifères de façon à obtenir un sel d'uranium contenant le minimum d'impuretés gênantes pour le traitement ultérieur du raffinage.

1. STATUT ET ACTIVITES DE LA SIMO EN FRANCE

La Société industrielle des minerais de l'Ouest (SIMO) traite la plus grande partie des minerais français d'uranium. En effet, sur une production française de l'ordre de 2300 tonnes d'uranium, environ 2000 tonnes sortent d'usines appartenant à la SIMO ou exploitées par elle.

Actuellement, cette société est une filiale à 51% de la Compagnie générale des matières nucléaires (COGEMA), à 40% de la Caisse des dépôts et consignations et à 9% du groupe Péchiney Ugine Kuhlmann (PUK). Le groupe PUK est opérateur dans les trois usines françaises de la société.

Ces usines sont implantées à proximité des sites miniers et traitent des solutions uranifères obtenues par attaque sulfurique, oxydante et par chaux des minerais. Le concentré final obtenu est livré ensuite à l'usine de raffinage située en France à Malvesi près de Narbonne.

Sur les trois usines exploitées, deux fournissent comme produit final un concentré se présentant sous forme solide, la troisième délivrant une solution de nitrate d'uranyle.

2. USINES PRODUISANT UN CONCENTRE SOLIDE

Ce sont les deux usines appartenant à la SIMO et situées l'une à Gétigné près de Nantes (usine de l'Ecarpière), l'autre à Bessines près de Limoges (usine de Bessines). Ces usines, qui ont été construites dans les années 1957 et 1958, ont été conçues pour fabriquer de l'uranate de magnésie. Cette fabrication a été modifiée ces dernières années pour obtenir de l'uranate d'ammonium.

2.1. Usine de l'Ecarpière

Elle a été mise en service en 1957 et a la possibilité de traiter environ 300 000 tonnes de minerai par an. La production d'uranium est de l'ordre de 550 tonnes par an.

Les principales caractéristiques des minerais sont les suivantes:

Uranium	0,5 – 3,5‰
Silice	60 – 85%
Fe_2O_3	1,2 – 3,0%
Al_2O_3	7 – 18,0%
CaO	0,2 – 1,0%
MgO	0,2 – 2,0%
P_2O_5	0 – 0,3%

On trouve aussi dans ces minerais, mais en quantités négligeables, du molybdène et du vanadium qui n'interfèrent pas au cours du traitement.

La solution sulfurique après élimination de la partie solide est traitée sur quatre lignes de résines. La composition de cette solution (pH: 1,4 – 1,8) est environ la suivante, en grammes par litre:

U	0,3 – 1,0
Fe^{2+}	0,5 – 2,5
Fe^{3+}	0,5 – 3,5
Al	0,5 – 3,0
P_2O_5	0,5 – 1,5
SO_4^{2-}	8,0 – 15,0
Cl	0,3 – 0,7

L'élution des résines était faite, depuis l'origine jusque vers 1976, par une solution de chlorure de sodium d'environ 1 $\underline{M}$ et acidifiée sulfurique (0,1 – 0,2 $\underline{N}$) suivant les schémas classiques que l'on retrouve dans la littérature. La composition de cette solution uranifère est environ la suivante, en grammes par litre:

U	6,0 – 8,0
Fe^{2+}	0,02 – 0,06
Fe^{3+}	0,2 – 1,0
P_2O_5	0,3 – 1,0
SO_4^{2-}	20,0 – 40,0
Cl	35,0 – 60,0

Cette solution uranifère, ayant donc déjà subi une purification et une concentration au niveau du passage sur les résines, était traitée par des agents alcalins de façon à obtenir le concentré solide.

Ce traitement comportait deux stades de précipitation. Le premier stade comprenait l'emploi de la chaux de façon à obtenir, en fin de réaction, un pH de l'ordre de 3,0 à 3,5. Cette chaux entraîne la formation d'un précipité de sulfate de calcium contenant des hydroxydes et des phosphates. Un apport de sel ferrique était réalisé pour assurer complètement la complexion des phosphates et éliminer ce composé sous forme de phosphate.

Après une décantation et une filtration, la solution uranifère était précipitée à la magnésie et le pH obtenu en fin de réaction était de l'ordre de 7. La composition du produit obtenu, appelé uranate de magnésie, était la suivante:

U	66,0 – 73,0%
Fe^{3+}	1,0 – 3,0%
P_2O_5	0,1 – 0,4%
SO_4^{2-}	0,3 – 1,5%
Cl	0,02 – 0,2%
F	0,01 – 0,1%
SiO_2	0,5 – 1,5%
Mg	0,2 – 0,6%
H_2O	1,5 – 10,0%

A partir de 1976, les circuits de concentration et de purification de cette usine ont été modifiés de façon à pouvoir obtenir comme produit final le diuranate d'ammonium. La transformation a consisté à remplacer l'élution chlorosulfurique par une élution sulfurique au niveau des résines échangeuses d'ions.

L'élution est faite par une solution à 120 grammes par litre environ en acide sulfurique et les éluats obtenus ont la composition suivante, en grammes par litre:

U	5,0 – 7,5
Fe^{2+}	0,02 – 0,06
Fe^{3+}	0,5 – 1,7
P_2O_5	0,5 – 1,5
H_2SO_4	110 – 140
Cl	0,3 – 0,6

Ces éluats sont ensuite purifiés par une extraction liquide-liquide dans laquelle l'agent d'extraction est une amine tertiaire (tri-iso-octylamine) en solution dans un solvant aliphatique (kérosène R). Cette solution organique renferme aussi un alcool lourd (tridécanol) destiné à éviter la formation de la troisième phase dans les différents étages d'extraction.

Le solvant chargé en uranium est lavé par une solution sulfurique puis est envoyé dans le circuit de réextraction. Cette réextraction est faite par une solution ammoniacale de sulfate d'ammonium à environ 100 grammes par litre en sulfate d'ammonium.

La composition de la solution uranifère après réextraction (pH : 3,5 à 4,0) est la suivante, en grammes par litre :

U	16 – 25
SO_4^{--}	80 – 110
NH_3	30 – 43

Cette solution est ensuite précipitée par de l'ammoniaque à chaud et, après séchage, la composition de l'uranate obtenu est la suivante :

U	70,0 – 76,0%
Fe^{3+}	50 – 400 ppm
Ca	50 – 250 ppm
Na	50 – 350 ppm
K	20 – 150 ppm
H_2O	1,0 – 6,0%

2.2. Usine de Bessines

Cette usine, mise en service en 1958, peut traiter environ 600 000 tonnes de minerai par an. La production actuelle d'uranium est de l'ordre de 1000 tonnes ar an.

Les principales caractéristiques des minerais sont les suivantes :

Uranium	0,8 – 5,0‰
Silice	57,0 – 75,0%
Fe_2O_3	1,4 – 5,2%
Al_2O_3	2,5 – 11,0%
CaO	0,6 – 1,4%
MgO	0,2 – 1,5%

De même que pour la précédente usine, on trouve aussi, mais en très faibles quantités, du chrome, du molybdène et du vanadium qui ne perturbent pas les circuits d'exploitation de l'usine.

La solution sulfurique obtenue après solubilisation de l'uranium (pH : 1,5 à 1,7) a la composition suivante, en grammes par litre :

U	0,5 – 0,7
Fe	0,4 – 0,7
P_2O_5	0,3 – 0,5
SO_4^{--}	6,0 – 10,0
Cl	0,4 – 0,7

A partir de cette solution, le traitement était légèrement différent de celui retenu pour la précédente usine. Il y avait deux circuits fonctionnant en parallèle. Une partie de la solution uranifère était traitée dans un atelier d'extraction liquide-liquide qui utilisait une amine secondaire, remplacée ultérieurement par une amine tertiaire (tri-iso-octylamine), en solution dans un solvant aliphatique. Le solvant chargé était ensuite élué par une solution de chlorure de sodium, légèrement acidifiée sulfurique. La composition de la solution uranifère obtenue était la suivante, en grammes par litre:

U	35 – 40
Cl^-	16 – 22
SO_4^{--}	80

L'autre partie de la solution uranifère était traitée sur des résines échangeuses d'ions et ces résines étaient éluées par une solution de chlorure de sodium, acidifiée sulfurique. La composition de la solution uranifère obtenue était alors la suivante, en grammes par litre:

U	4 – 6
Cl^-	25 – 30
SO_4^{--}	50

Ces éluats uranifères, venant donc de l'élution des résines et de la réextraction du solvant, étaient mélangés, ce qui donnait une solution de composition suivante, en grammes par litre:

U	8 – 11
P_2O_5	0,2 – 0,4
Fe^{3+}	0,2 – 0,5

Cette solution était alors traitée d'une manière identique à celle de l'usine de l'Ecarpière, ce qui aboutissait à un concentré d'uranate de magnésie de caractéristiques similaires.

La transformation d'une partie des circuits de l'usine s'est effectuée pour obtenir un diuranate d'ammonium comme produit final. Actuellement, les circuits de concentration et de purification sont comme il suit. Il y a toujours en parallèle un étage de concentration et de purification constitué par une fixation sur les résines ou sur le solvant qui est toujours à base d'amine tertiaire. L'uranium fixé sur les résines est récupéré par une élution sulfurique des résines dans des conditions analogues à celles de l'usine de l'Ecarpière et cet éluat est traité dans un nouvel atelier d'extraction liquide-liquide.

L'extraction de l'uranium est faite par l'amine tertiaire habituelle: la tri-iso-octylamine. On obtient alors un solvant chargé qui est mélangé à celui provenant du premier atelier d'extraction liquide-liquide. Tout l'uranium se retrouve ainsi dans cette phase organique, et la récupération est faite dans l'atelier général de réextraction par une solution de sulfate d'ammonium et d'ammoniaque dans les conditions habituelles. Cette solution uranifère, qui titre environ 15 à 20 g d'uranium par litre, est ensuite précipitée à chaud par de l'ammoniaque dans des conditions semblables à celles de l'usine de l'Ecarpière.

3. QUALITES DES URANATES

Les impuretés étant ordinairement données en teneur par rapport à l'uranium, nous indiquons quelques valeurs de ces impuretés contenues dans les concentrés de diuranate d'ammonium (en pourcentages par rapport à U):

Ca	0,01 – 0,06
K	$\leqslant 0{,}001$
Na	0,01 – 0,03
Mg	$\leqslant 0{,}010$
Fe	0,02 – 0,10
PO_4	0,02 – 0,16
V	$< 0{,}003$

4. USINE PRODUISANT UN CONCENTRE LIQUIDE

La troisième usine exploitée par la SIMO, située à St. Priest-la-Prugne, entre Roanne et Vichy, a été mise en service en 1960 et peut traiter environ 190 000 tonnes de minerais par an. La production d'uranium est de l'ordre de 450 tonnes par an.

Les principales caractéristiques des minerais sont les suivantes:

Uranium	1,8 – 3,5‰
Silice	75 – 90%
$Fe_2O_3 - Al_2O_3$	5%
CaO	0,1 – 0,3%
MgO	0,01 – 0,10%

Le schéma de traitement est très différent de celui des deux précédentes usines: c'est le procédé de la double précipitation calcique. La solution uranifère obtenue après la séparation liquide-solide a une composition moyenne, en grammes par litre, de l'ordre de:

U	1,5 – 2,0
Fe	2,5 – 6,5
P_2O_5	0,4 – 0,6
SO_4^{--}	15,0 – 20,0
Cl	0,4 – 0,6

Cette solution est traitée par un lait de chaux jusqu'à obtenir un pH de l'ordre de 3,0 à 3,3, ce qui permet d'éliminer le Fe III contenu dans cette solution. Après la séparation liquide-solide, la solution est encore traitée à la chaux jusqu'à obtenir un pH de l'ordre de 7 en fin de précipitation. Tout l'uranium contenu dans la solution uranifère est alors précipité sous la forme d'un produit appelé uranate de chaux dont la concentration est faible puisqu'il contient le sulfate de calcium:

U	35 – 43 %
Fe	1,0 – 2,0%
CaO	8,0 – 15,0%
Al_2O_3	5,0 – 8,0%
SiO_2	5,0 – 8,0%

Suivant la qualité des minerais, on trouve aussi du fluor.

Après filtration, le produit solide est repris par une solution sulfonitrique et l'uranium contenu dans le produit solide est ressolubilisé sous la forme nitrate avec une composition, en grammes par litre, de:

U	55,0 – 65,0
Fe	3,0 – 4,0
Al	7,0 – 10,0
CaO	15,0 – 20,0
P_2O_5	0,10 – 0,15

Cette solution est ensuite purifiée dans un atelier d'extraction liquide-liquide. La phase organique utilisée est cette fois le tributylphosphate en solution dans un solvant organique (dodécane). Après extraction de l'uranium, le solvant chargé est traité par de l'eau, ce qui permet d'obtenir une solution de nitrate d'uranyle très pure. Cette solution est ensuite concentrée par évaporation et son titre est de l'ordre de 400 à 440 g d'uranium par litre, avec les impuretés suivantes données par rapport à l'uranium:

Ca	0,01 – 0,08%
Na	$\leqslant$ 0,010%
Fe	$<$ 0,001%
Al	$<$ 0,005%
PO_4	$<$ 0,002%

CONCLUSION

Il est bien évident que les procédés décrits ci-dessus et qui aboutissent à un concentré solide répondant aux normes précisées par le raffineur sont lourds. Mais ceci tient peut-être à des considérations historiques liées à la manière dont l'industrie de l'hydrométallurgie de l'uranium s'est développée en France.

Au cours des dernières années, et en liaison avec la COGEMA, le groupe PUK a été amené à participer à la réalisation d'autres usines où des techniques plus simples permettent d'aboutir à la préparation d'un concentré conventionnel, avec un schéma ne comportant qu'un seul étage de purification. Ce sont ces techniques qui ont été mises en œuvre dans les deux usines actuellement en service au Niger dans lesquelles la purification et la concentration des solutions uranifères est faite simplement dans un atelier d'extraction liquide-liquide utilisant un solvant aminé. La première usine, appartenant à la Société des mines de l'Aïr (SOMAÏR), utilise comme agent de réextraction une solution de carbonate de sodium. La solution de réextraction est traitée par de la soude, ce qui conduit à l'obtention d'un uranate de soude dont la teneur en sodium est cependant supérieure à la limite indiquée dans le cahier des charges.

La seconde usine, appartenant à la Compagnie des Mines d'Akouta (COMINAK), utilise, après une extraction par un solvant aminé, une réextraction au chlorure de sodium et une précipitation à la magnésie conduisant à l'uranate de magnésie. Cependant, les minerais traités dans cette usine contenant du molybdène qui se retrouve fixé sur le solvant, la phase organique, après son traitement par la solution de chlorure de sodium, est mise en contact avec une solution de carbonate de sodium qui permet de retirer le molybdène. La solution ainsi obtenue est traitée par de la chaux pour récupérer le molybdène sous forme de molybdate de chaux.

Bien que ces concentrés ne répondent pas exactement aux spécifications, ils ont été retenus à cause de la simplicité avec laquelle ils peuvent être mis en œuvre dans des régions où les problèmes géographiques et humains ont leur importance.

La pratique actuelle paraît néanmoins tendre vers la fabrication d'un concentré d'uranium plus élaboré, ou tout au moins contenant des impuretés à des teneurs de plus en plus faibles. C'est la raison pour laquelle il semble que la fabrication de l'uranate d'ammonium réponde le mieux aux normes qui se dessinent actuellement, mais on peut se demander s'il faut s'arrêter à ce sel ou continuer le cycle de traitement pour obtenir comme produit final l'oxyde UO_3, ce qui est relativement aisé à partir d'un diuranate d'ammonium.

De même, il est possible d'obtenir un concentré d'uranium, le tétrafluorure UF_4, directement dans l'usine de concentration sans passage par le «yellow cake» habituel, et on peut très bien imaginer que les dernières étapes de purification soient faites à partir de ce composé.

On voit donc qu'il est possible techniquement de dépasser le stade de purification obtenu par la fabrication d'un «yellow cake» conventionnel. Le problème est surtout économique puisqu'il s'agit d'investissements à réaliser dans une usine de concentration dont la durée de vie est généralement associée à celle du gisement.

PRODUCTION OF URANIUM OXIDE CONCENTRATES BY THE NUCLEAR FUELS CORPORATION OF SOUTH AFRICA

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Abstract

PRODUCTION OF URANIUM OXIDE CONCENTRATES BY THE NUCLEAR FUELS CORPORATION OF SOUTH AFRICA.

South Africa has a relatively long history of large-scale production of uranium from many of its gold mines. The final processing is undertaken in a single plant, operated by Nufcor for the producing mines, which has been in continuous commercial use for over 25 years. The plant is adapted to the handling of incoming material of varying chemical and physical qualities, and the equipment can be readily adjusted for optimum performance at widely different levels of production. This paper describes the plant equipment and its operation, emphasising the special conditions which led to its design and the features which have contributed to its success.

All aspects of the operation are described, from collecting aqueous uranium slurry at the mines through drying and calcining to the sampling, analyses, packing and final transport of oxide concentrates for export.

INTRODUCTION

Ammonium diuranate slurry produced by the South African gold mining industry is converted to uranium oxide concentrates in a plant operated by the Nuclear Fuels Corporation of South Africa (Nufcor). The total quantity of uranium which has passed through this single plant since its commissioning in 1953 is relatively large – almost 100 000 t of U_3O_8, or probably about one-sixth of the total non-communist world production of uranium to date. The operation has continued without interruption for over 25 years, and in that period of time there have been very few major changes to the equipment or its method of operation. These achievements – one hundred million kilograms of oxide and a quarter of a century of production – present a suitable occasion for publishing a general description of Nufcor's plant and process.

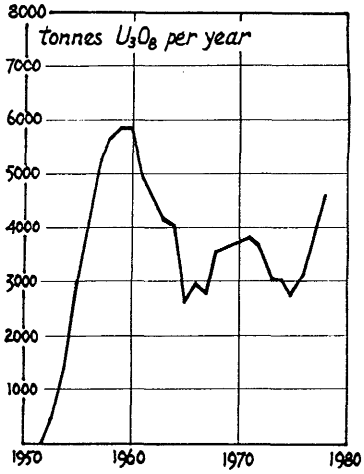

FIG.1. Annual production in the Nufcor plant.

HISTORY OF THE NUFCOR PLANT

South African uranium production started in late 1952. In that year, after pilot trials at two of our gold mines, a quantity of 40 t of U_3O_8 was separated from gold plant residues in our first commercial-scale uranium plant at the West Rand Consolidated Mines. The production of uranium concentrates in the form of oxide followed in 1953, when the present Nufcor plant, at that time known by the name of Calcined Products, was commissioned by the Combined Development Agency of the USAEC and the UKAEA. The pattern of our annual uranium production since that time, rising rapidly to a peak of nearly 6000 t of U_3O_8 within 6 years, is shown in Fig.1.

From the outset, the production of high quality oxide has been a co-operative enterprise by our mining industry. Since 1960, when the Agency ceded the plant to the South African Atomic Energy Board, production has been conducted under the aegis of our Chamber of Mines in a manner very similar to that which had been adopted long before for the refining of South African gold.

In the early 1950s it was forecast that it would be feasible to extract uranium, as a by-product of gold, from many of the mines in the Transvaal and Orange Free State. The location of the main gold mining areas, and the position of the gold mines which were producing uranium at the peak of activity in 1959, are shown in Fig.2. On both geographical and technical grounds there was a clear case for co-operation. Accordingly uranium extraction plants were built on only 17 of these 26 mines,

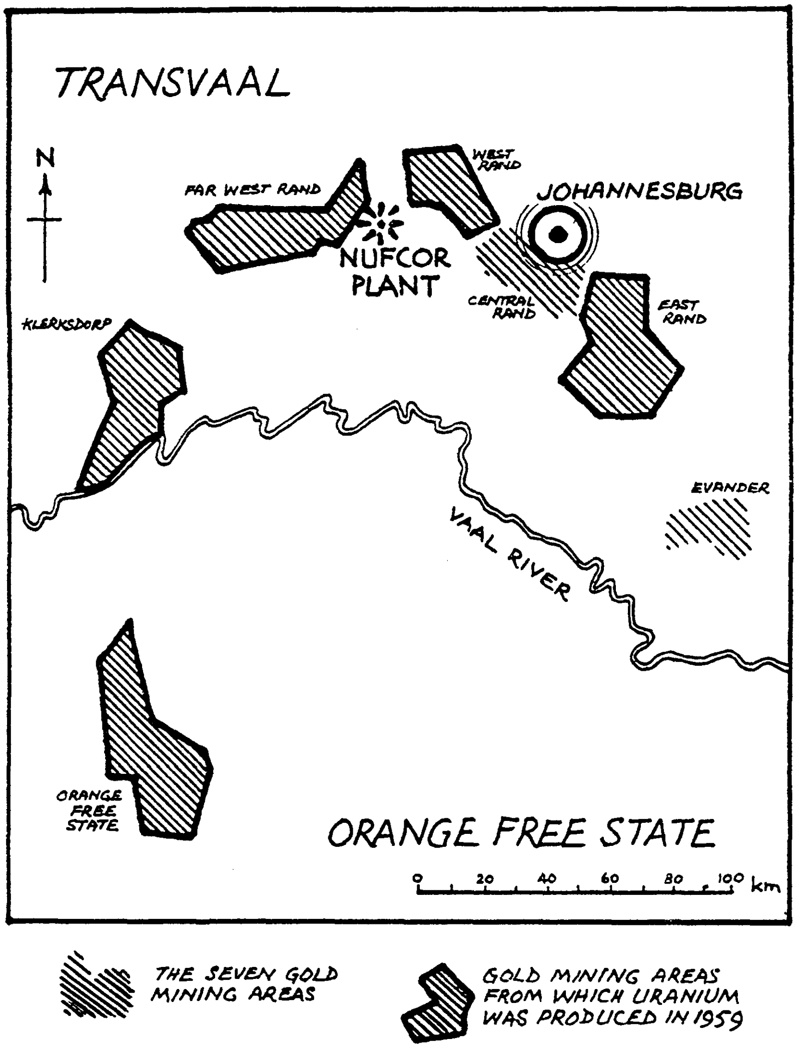

FIG.2. Location of the Nufcor plant in relation to the uranium-producing gold mines.

to treat the similar ore from one or more neighbours. At these plants the uranium was recovered as a precipitate of relatively pure ammonium diuranate (ADU), concentrated from the original ore some 1000 times. It was possible therefore, and also economically and technically advantageous, to transport the product to a central plant for further treatment and concentration. The position chosen for Nufcor's factory is also shown in Fig.2.

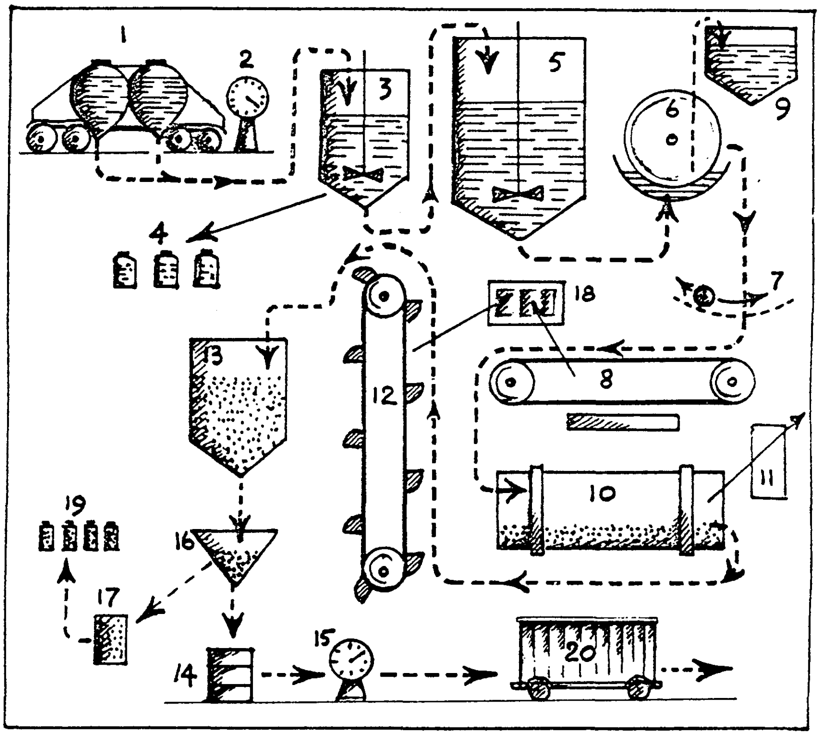

FIG.3. The Nufcor plant process: 1 road tanker; 2 weighbridge; 3 ADU sampling tank; 4 ADU samples; 5 ADU storage tank; 6 ADU filter; 7 ADU extruder; 8 ADU dryer; 9 filtrate settling tank; 10 calcining furnace; 11 wet scrubber; 12 bucket elevator; 13 dry storage hopper; 14 steel drum; 15 platform scale; 16 falling stream sampler; 17 primary sample; 18 dust filters; 19 secondary samples; 20 shipping container.

DESCRIPTION OF THE PLANT OPERATIONS

The process itself is in principle a very simple one. It consists first of blending the ADU products received from the various mines to ensure a constant grade of product, then removing the water to reduce the weight for shipment, and finally transforming it to a stable and high grade oxide. In the following paragraphs the main features of Nufcor's plant operations are described in sequence, as they are shown in Fig.3.

(a) Transport of ADU slurry

At the present time (May 1979), ADU is collected by Nufcor from 14 different uranium recovery plants on the mines. The material from these plants varies to some degree in its physical and chemical quality, depending not only on the nature of the ore from which it is recovered, but also on the recovery method used by the mine. For this reason, and particularly for accountability to the producing mines, each load of ADU collected from a mine is moved separately in a sealed container until it can be weighed and sampled by Nufcor.

The road tankers in Nufcor's fleet have two separate stainless steel compartments of the Spitzer sphero-conical design. Each compartment has capacity for about 13 t of ADU as an aqueous slurry, containing the equivalent of about 3.5 t of U_3O_8. The tankers can without difficulty make the longest return journey, that is to say 700 km for collection from mines in the Orange Free State, within 1 day.

(b) Weighing, sampling and storage of ADU slurry

The quantity of ADU slurry in each compartment is determined by weighing the tanker at Nufcor's plant before and after pumping the load into one of two rubber-lined sampling tanks. The slurry is mixed in the tank with agitator paddles on a vertical shaft, and primary samples are then drawn by suction into flasks through stainless steel tubes passed down through the depth of the liquid during agitation. After sampling, the slurry is pumped to one of a bank of larger interconnected storage tanks, also rubber-lined and fitted with agitator paddles, where if required it can be mixed with ADU from other mines before further treatment. This very flexible storage system has been of great importance for the smooth operation and uniform output of the continuous Nufcor process, despite somewhat differing batches of feedstock.

(c) Filtration and extrusion

The continuous and automatic part of the plant process starts with filtration to remove most of the water from the slurry, followed by extrusion, drying and calcining. This sequence is followed in three similar production lines which can be operated simultaneously in parallel, each consisting of a pair of rotary drum filters, an extruder, a belt dryer, and a rotary calcining kiln. Each of these lines was originally designed to have a capacity of almost 2000 t of U_3O_8 per year, giving a total installed capacity, which was fully used in 1959 and 1960, of just under 6000 t per year. Changes to the physical characteristics of the ADU slurry and recent modifications to the equipment have however substantially increased the capacity of these continuous production lines.

The six rotary drum vacuum filters are cloth-covered, each with an area of about 10 m^2, turning at about 7 revolutions in an hour. The filter cake is either blown off with air at 4 lbf/in^2 and removed with a scraper[1] or is removed indirectly via a transfer roller. For certain types of slurry, optimum filter performance is maintained by using external sprays of diluted slurry to dampen the cake and seal any cracks during the protracted drying cycle.

The filters are totally enclosed, with sealed hoods, and are kept under slight negative pressure. The energy consumed in this part of the process, mostly in the filtration vacuum pumps, is about 200 kW·h per tonne of U_3O_8.

In each of the three production lines the pair of filters is mounted on a platform above a perforated steel plate, on which the filter cake falls. The cake is then pressed by a pair of rollers through 6 mm-diameter holes in the plate to form spaghetti-like extrusions on the dryer belt below.

(d) Drying

While they are being dried, these extrusions of ADU filter-cake crack into 6 mm pellets which, although abraded and shrunk during subsequent parts of the process, determine the characteristic granular texture of concentrates from this plant.

The ADU is dried in a heated air stream. For this purpose the extrusions are carried on a steel belt which has a width of about 2.5 m and an effective drying length of about 10 m. The dryer is totally enclosed, under slight negative pressure, and air is drawn into it by fans. The air is heated, by steam and electricity, to 130°C before circulating over the belt, and the moist air is then exhausted outside the building. After passing through the dryer the chips of ADU are removed by screw conveyor into a calcining furnace.

(e) Calcining

The three calcining furnaces are horizontal cylinders of stainless steel, 1 m diameter and 6 m long. They are supported and turned, on electrically-driven rollers, and are heated externally by a large number of Calrod elements, surrounded by heavy thermal insulation. The calcining temperature, measured within the bed of material, reaches just under 500°C while the material is tumbled and slowly moved along the length of the furnace by means of helical vanes. The chips are transformed successively from yellow ADU at the inlet, through orange UO_3, to grey-green concentrates consisting of a mixture of UO_2 and UO_3 in the approximate proportion U_3O_8. The total energy for this calcining operation (heating and drive) is about 300 kW·h per tonne of U_3O_8.

(f) Bulk storage of dry concentrates

The concentrates emerging from the calcining furnace are first lifted to an upper floor by bucket elevator, and then moved by a screw conveyor system into any one of a bank of storage hoppers. These hoppers have at present a total capacity of about 60 t, and serve only to retain the concentrates until they can be sampled and packed. This stage completes the continuous part of the operation.

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[1] 1 $\text{lbf/in}^2 = 6.895 \times 10^3$ Pa.

(g) Sampling and packing of lots

There are two sampling/packing/weighing stations. The stream of concentrates falling from the storage hoppers into the drums passes first through a Vezin-type rotating sampler which removes a 10% cut from the stream. This material is then moved by a vibrating feeder to a second Vezin sampler, which removes a 10% cut of the first and thus deposits a 1% sample into the sample container. The weight of a primary sample representing the customary 10 t lot of concentrates is therefore 100 kg. As a precaution against contamination or interference, the sample is collected in a closed stainless steel vessel standing in a locked compartment until packing of the lot is complete.

The main stream, plus material rejected by the second Vezin sampler, is at the same time packed into tared 210 litre 16-gauge steel drums, which are filled on a vibrating platform to contain approximately 350 kg of concentrates, and then weighed. The drums are closed, and are later sealed by welding a lock-nut on the clamping ring. The two print-out platform scales at the weighing stations are assized every 3 months, checked daily, and are compared frequently in use by cross-weighing empty and full drums.

(h) Despatch of concentrates

Full drums of concentrates are stacked upright in a covered store until they are required for despatch. Then they are assembled in standard 6-m ribbed steel shipping containers fitted with a wooden floor on which chocks can be fastened. The maximum weight which may be loaded into such a container is normally taken up by about 45 drums, and these are placed in a two-tier interlocking array which can be securely wedged with a minimum of timber. The containers are sent by road and rail to the port of Durban for shipment.

(i) Sample preparation and analysis

The preceding paragraphs describe the route taken by the main stream of uranium through the plant, including weighing of the incoming ADU and outgoing concentrates. To complete the description it is necessary to say how the uranium content of this material, and its quality, are measured by Nufcor.

The primary samples of ADU slurry, referred to in (b), are divided into several portions, of which three are sent to the Nufcor laboratory for uranium assay by X-ray analysis.

The primary sample which is representative of the packed concentrates, referred to in (g), is split by mechanical rifflers into several secondary samples. A pair of these is used first to determine in duplicate the weight lost by the material when it is calcined again to 800°C for at least 9 h; and then, after sample

TABLE I. COMPOSITION OF SOME URANIUM CONCENTRATES PREPARED BY NUFCOR IN 1978

Constituents expressed as a percentage of dried concentrates

U_3O_8	95.89
SiO_2	0.34
SO_4	2.66
PO_4	0.03
Th	0.013
Cl, Br, I (as Cl)	0.002
Ca	0.09
CO_3	0.023
F	0.008
NH_4	< 0.01

Constituents expressed as parts per million of uranium

Al	400	Mo	29
As	55	Na	267
B	2.6	Nb	1.2
Ca	946	Nd	1.0
Cd	<1.0	Ni	1.3
Ce	0.9	Pb	2.7
Co	18	Pr	0.4
Cr	13	Rb	<3
Cu	7	Sb	<3
Dy	1.3	Sm	0.9
Er	0.9	Sn	1.3
Eu	0.2	Ta	<0.2
Fe	705	Tb	0.5
Gd	1.0	Ti	2.7
Hf	2.0	Tm	0.3
Ho	0.2	V	1.6
K	98	W	1.4
La	0.5	Y	3.3
Li	<1.0	Yb	0.3
Lu	0.1	Zn	<10
Mg	43	Zr	155
Mn	48	r.e. oxides	14

preparation and further splitting into smaller samples, for uranium assay. Another secondary sample is used for the determination of impurities.

Nufcor's concentrates are appreciably hygroscopic, and the purpose of prolonged re-calcination of sample material at 800°C is to stabilize the product before it is sealed in sample bottles. Measurement of the weight lost during this re-calcination is certified by Nufcor as a 'weight loss factor' to be applied to all uranium assays of these samples, in order to reduce those measurements to the values applicable to the concentrates at the time when they were packed and weighed. Nevertheless, whether a sample has been prepared by Nufcor or has been received from a customer's sampling station, the sample is again dried, to a constant weight in an oven at 110°C, before assaying.

Uranium content, whether of ADU or concentrates, is determined by Nufcor with an X-ray fluorescent spectrometer which is calibrated daily using standard solutions prepared from pure U_3O_8, and with frequent checks against chemical assay by the ether-separation gravimetric method. Impurities are measured on the relevant samples, again after drying to constant weight at 110°C, using wet chemical means or an optical emission spectrograph as appropriate. The composition of Nufcor concentrates prepared recently, and which may be taken as typical of much of the production derived from our present sources of uranium, is shown in Table I.

WASTE PRODUCTS

The main effluents from the plant are in the form of water containing dissolved salts, and air containing dust and vapours. Both of these streams remove uranium from the process, but virtually all of this is recovered and returned to the plant.

The liquid waste arises largely from the filtrate removed from the ADU slurry delivered by the mines. To this is added all wash water used in the plant. This water is pumped into one or more of a series of large rubber-lined tanks for settling out any uranium-bearing solids. Any dissolved uranium in the decanted supernatant liquors can be re-precipitated, then separated – also by decantation, and returned to the storage tanks for blending with incoming ADU. After this treatment the purified liquid effluent contains less than 10 parts per million by weight of uranium and is disposed of on the tailings dam of a neighbouring gold mine.

Uranium dust is efficiently recovered from all process air which passes through the plant equipment. Air drawn through the calcining furnaces passes through the water curtain of a wet scrubber, and air from all other parts of the process, such as conveyors, samplers, and packing units, passes into reverse-jet bag filters. The cleaned air from these scrubbers or filters is vented to atmosphere through a stack.

HEALTH PRECAUTIONS

Several parts of the process give rise to substantial quantities of uranium-bearing dust. An important precaution at the plant is therefore the detection and elimination of uranium dust from the outside of equipment and the atmosphere.

The first precaution is to keep an exceptionally high standard of cleanliness throughout the process areas, to give immediate attention to spillage, and to enforce a strict adherence to the customary change-room procedures.

The primary dust control measure is to maintain negative pressure inside equipment. In order to check that the general level of contamination is low, the air is sampled monthly by drawing it through clean filters located at 33 marked points in the plant. Uranium dust on these filters is measured by X-ray fluorescence in the plant laboratory, and normally shows that the sampled air contains no more than about 10 micrograms per cubic metre, whereas the accepted limit for continuous (8 h) exposure is 150 $\mu g/m^3$. Moreover in the vicinity of any plant operation such as drum filling, where accidental emission of dust is possible, all operators are obliged to wear dust masks continuously. As a further check on the efficacy of these control measures, urine samples are routinely analysed, and confirm that the quantity of uranium dust which could be inhaled or ingested by workers in the Nufcor plant is exceedingly low.

Radiation levels throughout the plant are measured annually, and the conclusions, supported by the evidence of film-badge monitors carried routinely by all staff, are that workers carrying out their normal duties in areas where the radiation levels are highest may, at most, accumulate a radiation dose no more than one-tenth of the currently adopted permissible levels for continuous exposure.

CONCLUSION

The Nufcor plant is physically small, and is kept in efficient operation by a relatively small number of skilled staff. One or more of the processing units have been continuously in operation since the start of uranium production in South Africa. If this central plant had not been available to the industry then its operations would no doubt have been undertaken separately, and on a small scale, by each producing mine or group of neighbouring mines, as they are by many uranium producers elsewhere. They would however then forego the economy of size and the flexibility arising from the centralized operation of the Nufcor plant, and moreover would lose the advantage of having, under the management of one central company for the entire industry, both the preparation of the final uranium product for the market and the negotiation of its sale.

DISCUSSION

R.B. COLEMAN: 1. Do your environmental regulations allow only the use of dry baghouse filters for emission control? 2. What is the allowable U_3O_8 in air emission from the scrubbers?

S.A. YOUNG: 1. No. We also use wet scrubbing to remove dust. 2. We use highly efficient scrubbers which reduce the uranium emission to a very low level.

F.E. McGINLEY: I understood the sampling but it was not clear to me at what points the materials are weighed. Please clarify.

S.A. YOUNG: Each load of ADU is weighed, by gross and tare weighing the tanker, immediately on arrival. Oxide concentrates are weighed in each drum immediately after it has been filled.

B.C. SMART: How often is the tank trailer, used for ADU slurry transport, cleaned out? What size heel is left in the tanker?

S.A. YOUNG: Each compartment of each tanker is cleaned out, by washing and draining, after the load of ADU has been pumped into the sampling tank. There is no heel left in the tanker.

C.P. FERREIRA: Could you tell us something about what is done with the radioactive effluents with regard to human and environmental protection?

S.A. YOUNG: In liquid plant effluent the uranium is reduced by precipitation and decantation to well below 10 ppm. The purified liquid is then disposed of on a tailings dam. Gases and vapours are passed through bag filters and wet scrubbers to remove contamination before exhaust to atmosphere.

ПРАКТИКА ПОЛУЧЕНИЯ ЖЕЛТОГО КЕКА

Б.БОШИНА
Комиссия по атомной энергии ЧССР,
Прага,
Чехословацкая Социалистическая Республика

Abstract–Аннотация

YELLOW CAKE PRODUCT PRACTICE.

The flow sheets of uranium ore processing plants at present operating throughout the world terminate with the production of yellow cake. The demands of the refineries on the quality of this commodity have become more stringent with time. The impurity content of yellow cake depends to a considerable extent on the nature of the technical operations preceding precipitation. As a rule the purity of the final product is greater when the uranium is precipitated from re-extractants or regenerators consisting of weakly basic resins. An analysis of 80 uranium precipitation flow sheets demonstrates the advantages of using ammonia, while to some extent use is made of caustic soda, magnesium oxide, hydrogen peroxide or calcium oxide; precipitation is carried out in one or two stages at high temperature. Use of a particular chemical is governed by its availability, price, effect on the environment, degree of filtrate utilization, etc. It may be anticipated that the perfecting of precipitation flow sheets will be directed towards achieving maximum concentration of uranium in the solutions before precipitation, reduction in the volume of liquid flows through the equipment, an improvement in the filtration qualities of the precipitate, etc. The paper gives the flow sheet for precipitation of uranium by means of gaseous ammonia from sulphate-carbonate solutions. For drying yellow cake use has been made of spray driers. The dry product is easily sampled and transported.

ПРАКТИКА ПОЛУЧЕНИЯ ЖЕЛТОГО КЕКА.

Технологические схемы заводов по переработке урансодержащих руд заканчиваются получением желтого кека. Требования аффинажных заводов, предъявляемые к качеству этого продукта со временем повышались. Содержание примесей в желтом кеке в значительной мере зависит от типа технологических операций, предшествующих осаждению. Как правило, чистота конечного продукта выше при осаждении урана из реэкстрагенов или регенератов слабоосновных смол. Анализ около 80 технологических схем осаждения урана показывает, что чаще всего для осаждения урана используется аммиак, реже – едкий натр, окись магния, перекись водорода или окись кальция; осаждение проводится в одну или две стадии при повышенной температуре. Применение конкретного химического вещества определяется его доступностью, ценой, требованиями минимального загрязнения окружающей среды, степенью использования фильтрата и т.д. Можно ожидать, что усовершенствование технологических схем осаждения пойдет по направлению максимального концентрирования урана в растворах перед осаждением, сокращения объемов жидких потоков через оборудование, улучшения фильтрационных свойств осадков и т.п. В статье обсуждается технологическая схема осаждения урана газообразным аммиаком из сульфатно-карбонатных растворов. При сушке желтого кека применяются распылительные сушилки. Сухой продукт удобен для отбора проб и хорошо транспортируется.

ВВЕДЕНИЕ

Конечный продукт заводов по переработке урансодержащих руд может иметь разное содержание урана и примесей, различный химический состав. Эти факторы определяются требованиями аффинажных заводов, доступностью и ценой химикатов и т.д. Анализ около восьмидесяти технологических схем показывает, что для осаждения урана чаще всего применяется аммиак, реже используется окись магния, едкий натр, перекись водорода, окись кальция. Конкретный реагент или условия прохождения процесса осаждения должны отвечать возможностям и требованиям первой стадии очистки на аффинажных заводах и приводить к возможно меньшему загрязнению окружающей среды. В литературе имеются данные о возможности исключения операции осаждения из типичной схемы переработки руд [1, 2]. При этом могут получаться кристаллические продукты, тетрафторид урана или другие соединения, как правило, ядерной чистоты. Можно ожидать, что в большинстве стран будут и дальше применяться несложные процессы, ведущие к получению желтого кека. Это – несложная задача, если предыдущие технологические процессы хорошо отделяют примеси и хорошо концентрируют уран. Поэтому при разработке технологической схемы переработки конкретного исходного сырья необходимо уделять одинаковое внимание всем технологическим операциям, учитывая их взаимозависимость. Общее усовершенствование технологических схем переработки бедных или упорных руд, например, применение более селективных ионитов, жидких или твердых экстрагентов, применение сорбционного оборудования усовершенствованной конструкции, создает условия для получения более концентрированных и менее загрязненных растворов, подаваемых на операцию осаждения урана [3]. Тем самым, как правило, создаются благоприятные условия для применения одностадийного осаждения с минимальными объемами жидких потоков на конечных операциях. В этой статье обсуждаются некоторые вопросы, связанные с получением желтого кека в Чехословакии.

ОСАЖДЕНИЕ УРАНА ИЗ КАРБОНАТНОЙ СРЕДЫ

При использовании в технологической схеме процессов сорбции из пульпы, когда смолу регенерируют сульфатными растворами в карбонатной среде, можно создать хорошие условия для осаждения урана, фильтрации и сушки желтого кека. Практика показывает, что иногда даже незаметные изменения технологического параметра приводят не только к повышению производительности аппаратов, но одновременно и к понижению эксплуатационных расходов. Осаждение урана аммиаком из карбонатно-сульфатного раствора можно представить следующим образом:

$$Na_4[UO_2(CO_3)_3] + 3H_2SO_4 \rightarrow UO_2SO_4 + 2Na_2SO_4 + 3CO_2 + 3H_2O$$

$$2UO_2SO_4 + 6NH_3 + 3H_2O \rightarrow (NH_4)_2U_2O_7 + 2(NH_4)_2SO_4$$

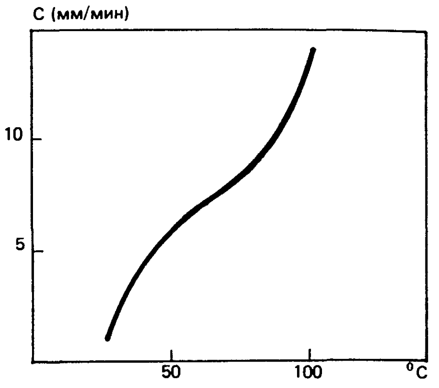

Рис. 1. Влияние температуры на скорость седиментации.

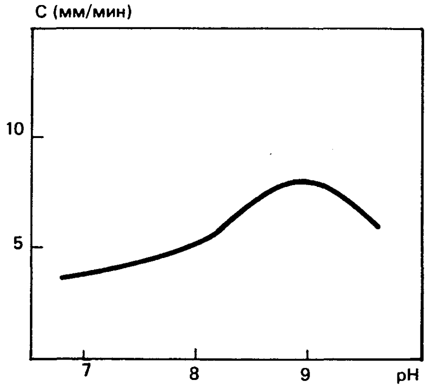

Рис. 2. Влияние pH-осаждения на скорость седиментации.

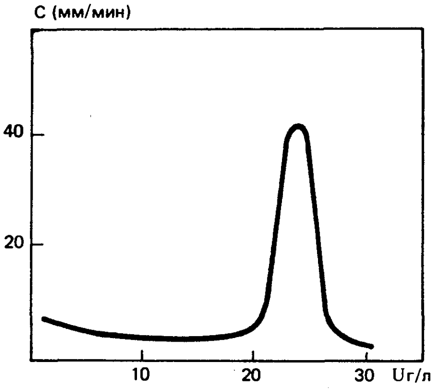

Рис. 3. Влияние содержания урана в растворе на скорость седиментации.

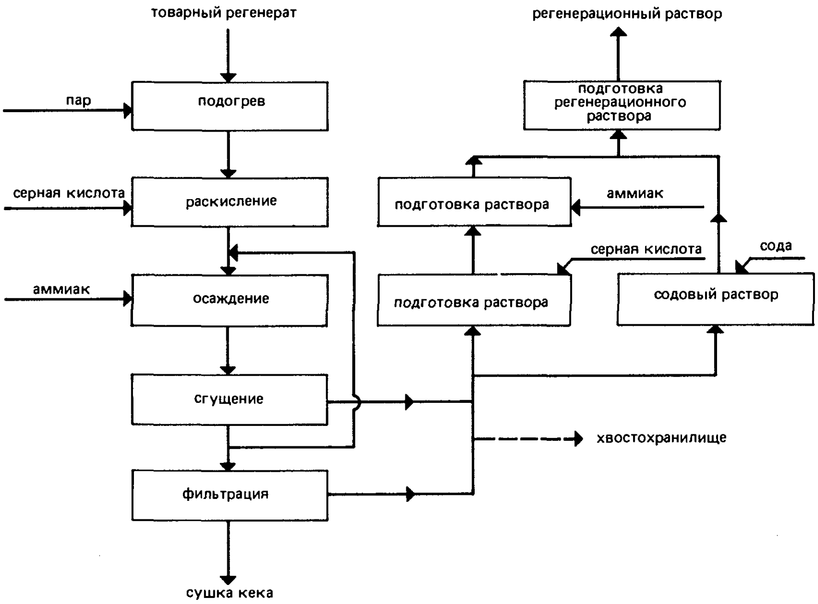

Рис. 4. Схема осаждения урана из сульфатно-карбонатного раствора.

Если полученная пульпа химического концентрата хорошо сгущается, то она, как правило, и хорошо фильтруется с получением кеков с низким содержанием влаги. Например, в зависимости от плотности снимаемого при фильтрации кека производительность сушки меняется следующим образом: для содержаний твердой фазы в кеке, равных 40%, 48% и 59%, теоретическая производительность сушки составляет 100%, 182% и 285%, соответственно.

Формирование осадка полидиураната аммония определяется следующими факторами: температурой осаждения, концентрацией урана в растворе, pH-осаждения, перемешиванием, прозрачностью раствора и др. Нами были получены следующие зависимости влияния этих факторов на скорость осаждения:

а) температура осаждения: повышение скорости осаждения с ростом температуры вызвано изменением вязкости раствора и укрупнением частиц осадка, которое заметно даже визуально. Для конкретных условий найдено, что в диапазоне температуры осаждения 30 - 50°C получается наибольший прирост скорости осаждения (рис. 1);

б) pH-осаждения (при $t = 60^0C$): при значениях pH, меньших 9, скорость растет, при pH > 9 – падает (рис. 2);

в) содержание урана в растворе (при $t = 60^0C$, $pH_{ос.} = 7,5$): наблюдается резкое повышение скорости осаждения при содержании урана 20 - 27 г/л в исходном растворе (рис. 3);

г) зародыши кристаллизации: прибавление осадка полиураната аммония (при $pH=6$, $t=60^0C$) значительно повышает скорость осаждения уже при повышении количества исходного урана на 4%. Положительное влияние зародышей при $t < 50^0C$ не обнаружено;

д) солевой состав: вышеуказанные данные получены для исходных растворов с содержанием урана 5-6 г/л и SO_4^{2-} — 120 г/л. Повышение концентрации SO_4^{2-} до 160 г/л влияния на скорость осаждения не оказывает.

На основе этих данных предложена общая схема получения желтого кека, показанная на рис.4. Схема позволяет перерабатывать фильтрат с высокой степенью использования солей(> 98%), из фильтрата готовится содовый раствор, фильтрат далее доукрепляется серной кислотой до получения необходимой концентрации SO_4^{2-} в регенерационном растворе, далее нейтрализуется аммиаком и создается карбонатная среда. Разница в концентрациях SO_4^{2-} на входе и выходе технологической схемы вызвана потребностью в осуществлении регенерации смолы. На операции получения желтого кека практически расходуется аммиак и сода. Расход аммиака находится в стехиометрически необходимом отношении к расходу серной кислоты для регенерации смолы. Серную кислоту можно в определенном отношении заменить другими сульфатными соединениями, например сульфатом натрия, тем самым можно понизить расход аммиака. Схема аналогична осаждению урана из нитратных, хлоридных растворов.

ОБОРУДОВАНИЕ

Схема не требует разработки нестандартного оборудования; полностью пригодны стандартные аппараты, используемые в химической промышленности. Могут использоваться аппараты с классическим сгустителем и барабанным вакуумным фильтром с прижимным валом. Получаемый желтый кек хорошо фильтруется с производительностью несколько десятков килограммов кека с 1 м^2 в час. Аппараты изготовляются из углеродистой стали, футерованной резиной, или из нержавеющей стали. Схема поддается автоматической регулировке, применяются pH-метры обыкновенной конструкции, связанные с регулирующими вентилями на линиях подачи химикатов. Используются жидкий аммиак, концентрированная серная кислота (94%) и порошкообразная сода. Перемешивание в аппаратах раскисления и осаждения осуществляется воздухом, который одновременно удаляет из системы углекислый газ.

СУШКА ЖЕЛТОГО КЕКА

Практически используются сушильные аппараты различных типов, которые дают продукты с разной влажностью и с различной величиной зерна. Как правило, первой операцией аффинажных заводов является растворение желтого кека, этот процесс определяет требования к параметрам продукции сушилок. Желательно, чтобы свойства желтого кека в то же время отвечали требованиям, предъявляемым к транспортировке, складированию и отбору проб. Этим требованиям хорошо отве-

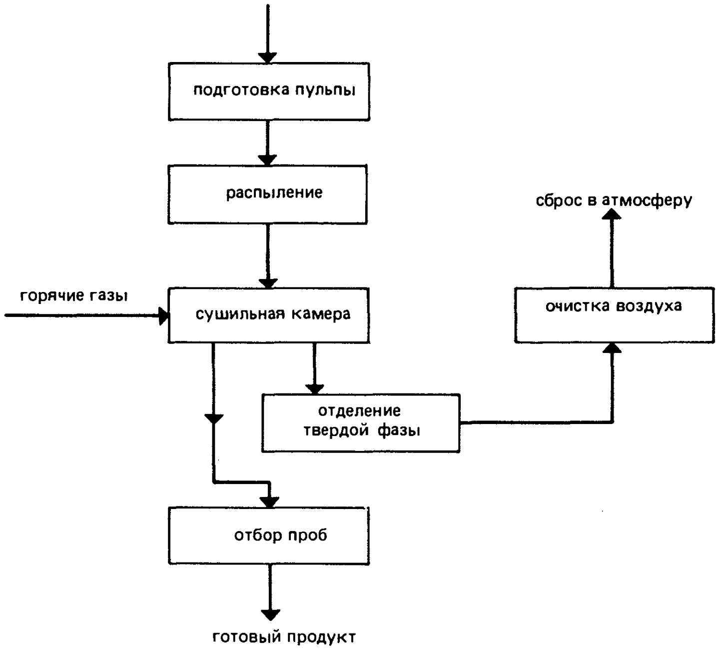

Рис.5. Схема сушки желтого кека.

чает порошкообразный продукт, полученный при температуре газов, выходящих из сушильной камеры, не выше 120°С. Распылительные сушилки, используемые в пищевой промышленности, при сушке красок и т.д., можно использовать и для сушки желтого кека. Принцип сушки заключается в испарении воды с большой поверхности капель продукта, получаемых распылением в сушильной камере, куда подводится поток горячих газов. Содержание влаги в продукте после сушки меньше 1%, продукт отсасывается и отделяется от потока носителя системой циклонов, рукавных фильтров и скрубберов. Такой продукт удобен для отбора проб и легко загружается в различного вида транспортные контейнеры. Желательно, чтобы сухой продукт имел малое количество мелких частиц, которые хуже отделяются под действием центробежной силы. Крупность распыляемых капель (а значит и крупность зерна сухого продукта) зависит от применяемого распылительного устройства. Конструкция с быстро вращающимися распылительными кольцами имеет ряд преимуществ по сравнению с использованием обычных воздушных форсунок. Скорость их вращения достигает 10 000 - 11 000 об/мин , размер капель получается за счет этого более однородным. Сушка может быть рассчитана на производительность от 1 т/сут до 20 т/сут и более (в пересчете на сухой продукт). Для уменьшения абразивного действия на стенки отверстий вращающегося кольца, в них вставляются сменные вкладыши из твердого материала [4]. Схема сушильной установки показана на рис. 5. Конечный продукт содержит около 12% SO_4^{2-}, 3-5% NH_3, содержание влаги – около 1% (этот солевой состав получается без промывки кека на фильтре). Продукт имеет текучие свойства, почти 95% порошкообразного продукта имеет размер $< 0{,}04$ мм.

ТЕХНИКА БЕЗОПАСНОСТИ

При работе с желтым кеком учитывается то, что работа ведется с водным раствором, мокрым или сухим продуктом с содержанием урана, равным нескольким десятков процентов. Опасность внешнего действия излучения продуктов через стенки аппаратов почти отсутствует. Аппараты должны быть снабжены вытяжкой, в помещениях должен поддерживаться небольшой перепад давления. Периодически замеряется уровень излучения обслуживающих площадок, государственный надзор следит за сбросными газами сушильной установки и за выходом газов из вытяжной вентиляционной системы. Государственные нормы выдерживаются без особых усилий. Государственная норма по загрязненности площади составляет 3300 расп./мин со 150 $см^2$; по запыленности помещения – 2 $мг/м^3$ и 1,85 $Бк/м^3$.

При подготовке аппаратов раскисления регенерата к ремонтному осмотру имел место случай регистрации повышенного γ-излучения по сравнению с остальными аппаратами (40-300 мР/ч). Выяснилось, что причиной излучения являются твердые отложения на стенке аппарата, которые являются химическими соединениями, содержащими радий, и продуктами его распада. Твердые частицы выделяются из товарного регенерата, этот процесс ускоряется под действием серной кислоты и нагревания раствора. Это, по всей вероятности, малорастворимые фосфаты и арсенаты, содержащие радий. В аппаратах осаждения эти отложения не обнаружены. Дезактивация поверхности может проводиться раствором щелочи (через 24 часа активность понижается на 50%).

ЗАКЛЮЧЕНИЕ

Осаждение урана из сульфатно-карбонатной среды имеет определенные преимущества, например по сравнению с осаждением из нитратной или нитратно-сульфатной среды. При применении сульфатно-карбонатной среды для регенерации смолы после сорбции с последующим осаждением урана газообразным аммиаком обеспечивается:

- эффективная регенерация смолы, особенно при применении нового типа оборудования – колонн с транспортной пульсацией смолы [5] и смол нового типа (слабоосновных пористого типа);
- коррозионная стойкость оборудования;
- меньшее загрязнение окружающей среды (сульфат-ион менее вреден по сравнению с нитрат- и хлор-ионом);
- возможность осуществления замкнутого цикла фильтрата и полного оборота воды хвостохранилища в процесс;

– получение осадка с хорошей фильтруемостью;
– возможность повторного использования компонентов; ион аммония легче устраняется из раствора и желтого кека, чем ион натрия;
– полной автоматизации процесса;
– требованиям по содержанию примесей в желтом кеке и т.д.

Распылительные сушилки могут найти свое применение при сушке желтого кека, учитывая их производительность, надежность, обеспечение безопасности труда и меньшего загрязнения окружающей среды.

ЛИТЕРАТУРА

[1] TAKENAKA, S., KAWATE, H., "Some recent improvements in a uranium processing pilot-plant at the Ningyo-Toge mine", Uranium ore processing (Proc. Panel, Washington, 1975) IAEA, Vienna (1976) 55.

[2] LEGER, J.E., BOUTONNET, G., Energ. Nucl. (Paris) **15** 1 (1973) 13.

[3] SEIDL, D.S., "Stored technology for possible use in uranium ore processing", Uranium ore processing (Proc. Panel, Washington, 1975) IAEA, Vienna (1976) 79.

[4] DAMGAARD-IVERSEN, J., "Spray drying in mineral processing" (Proc. IXth Int. Congr., Praha, 1970) Praha (1970).

[5] КАРПАЧЕВА, С.М., Пульсационная аппаратура, Хим.Промышл. №2 (1978) 128.

AUSTRALIAN EXPERIENCE IN THE PRODUCTION OF YELLOW CAKE AND URANIUM FLUORIDES

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Abstract

AUSTRALIAN EXPERIENCE IN THE PRODUCTION OF YELLOW CAKE AND URANIUM FLUORIDES.

Five uranium mills operated in Australia in the period 1954–1963, and the Rum Jungle plant continued in operation till 1971, producing a total of ~10 000 t of yellow cake. Both ion-exchange and solvent extraction were used for uranium concentration and purification; yellow cake was precipitated with magnesia or caustic soda and generally dewatered on vacuum filters and dried at <300°C. The product grade was <80% U_3O_8 for the ion-exchange mills but >85% U_3O_8 for the solvent extraction mills. Significant impurities in the highest grade of yellow cake produced at Rum Jungle in the late 1960s were sodium (~2%), sulphate (0.9%), silica (0.2%) and iron (0.2%). Both the recommissioned Mary Kathleen mill and the proposed mills (except Yeelirrie which will use an alkaline leaching flowsheet) incorporate solvent extraction, ammonia precipitation of yellow cake, centrifuges for solid/liquid separation and high temperature (>500°C) dryer-calciners, which are regarded as the best available proven technology. They will produce a high-grade product (>95% U_3O_8) which should readily meet the most stringent current specifications for yellow cake. During the 1970s, the AAEC carried out research and development on the processes for the production of nuclear grade uranium dioxide and uranium hexafluoride from Australian yellow cake. These processes include dissolution of yellow cake in nitric acid, purification by solvent extraction using tributyl phosphate in kerosene, precipitation, dewatering and drying of ADU, evaporation and denitration of uranyl nitrate to UO_3, calcination (of ADU) and reduction to UO_2, fluorination to UF_4 with hydrogen fluoride, a novel process for the conversion to UF_6 via catalyzed oxidation of UF_4, and the production of fluorine. Such studies have produced an understanding of the necessary technology on the pilot plant scale and enabled some improvements in the processes and technology.

INTRODUCTION

The search for uranium in Australia began in earnest in 1944 after approaches from the United Kingdom and United States governments. Promising discoveries were made and the first mines began operation in 1954. During the period 1954-1971, five mills (Table 1) produced about 10 000 t of yellow

TABLE 1

YELLOW CAKE PRODUCTION IN EARLY URANIUM MILLS

Mill	Port Pirie	Rum Jungle A	Rum Jungle B	Rum Jungle C	Moline	South Alligator	Mary Kathleen A
Operating Company or Major Shareholder	Government of South Australia	Territory Enterprises Pty Ltd.			United Uranium NL	South Alligator Uranium NL	Mary Kathleen Uranium Ltd
Period of Operation	1955 - 1962	1954 - 1962	1962 - 1966	1966 - 1971	1959 - 1964	1959 - 1962	1958 - 1963
Ore Grade, % U	0.7 - 0.9	∿0.3	∿0.3	0.4	0.3 - 0.7	1.1	0.15
Production Rate, t U_3O_8 per year	155	180	180	180	125	50	900
Purification							
- Process	Ion Exchange	Ion Exchange	Solvent Extraction	Solvent Extraction	Solvent Extraction	Solvent Extraction	Ion Exchange
- Strip/Eluent	1M NaCl+0.05M H_2SO_4	0.9M NaCl+0.09M H_2SO_4	1M NaCl	1M NaCl	1M NaCl	1M NaCl	1M NaCl+0.05M H_2SO_4
Precipitation							
- No. of Stages	Two	Batch	Batch	Batch	Batch	Batch	Two eluates - two stage
- Reagents	Lime/magnesia	Magnesia	Magnesia	Caustic Soda	Magnesia	Magnesia	Magnesia
- pH	3.0-3.5/6.5-7.0	7.0		6.0	7.0-7.5		3.5/7.0
- Temperature, °C	55	Ambient	up to 85	60			
Solid Liquid Separation							
- Thickening/Settling	Thickened	Settled/Thickened	Settled/Thickened	Settled/Thickened	Settled	Settled	Thickened
- Equipment	Rotary drum vacuum filter	Rotary drum vacuum filter	Rotary drum vacuum filter	Rotary drum vacuum filter	Disc filter	Plate & frame press	Rotary drum vacuum filter
- No. of Stages	2	2	2	2			3
- Wet Product Moisture Content, wt %		55-60					∿40
Drying-Calcination							
- Equipment	Belt dryer	Belt dryer	Belt dryer	Oil-fired multi-hearth calciner	Belt dryer	Batch tray dryer	Conveyor dryer
- Temperature, °C	∿320	∿320	∿320	800			120-180
- Product Grade, % U_3O_8	~80	50-70	80-90	90-93	85-88	84	~80
- Product Moisture, % H_2O		∿5	2-3	0.5			3-5
References	Almond (1958) South Australian Dept. of Mines (1962)	Anon (1959) Baker (1958) Barlow (1962)	Allman et al.(1968)	Allman et al.(1968)	Bellingham (1961) Murray & Fisher (1968)	Murray & Fisher (1968)	Couche & Hartley (1958) Harris et al. (1961) Hartley (1968) MKU (1962)

cake. Four of them were shut down in 1962-63 because of the completion of contracts with the Combined Development Agency and the United Kingdom Atomic Energy Authority and because of the slump in uranium demand, but the Rum Jungle mill continued in operation until 1971. The Mary Kathleen mill was placed on a "care-and-maintenance" basis and recommissioned in 1975.

As commercial nuclear power stations were installed in many countries, interest in uranium exploration intensified in the late 1960s and early 1970s, leading to significant new discoveries in the Alligator Rivers region of the Northern Territory, the Frome embayment in South Australia and at Yeelirrie in Western Australia. In August 1977, the Australian Government announced its decision to proceed with new uranium developments. Five companies have prepared draft environmental impact statements for proposed mills (Table 2) and three have already received Government approval to proceed.

In the early mills (based on acid leach flowsheets), both ion exchange and solvent extraction were used for uranium concentration and purification and yellow cake was precipitated with magnesia or caustic soda. Both the recommissioned Mary Kathleen and proposed mills incorporate solvent extraction and ammonia precipitation except the Yeelirrie project which will use an alkaline leaching flowsheet.

This paper reviews the history and development of these practices which have been described principally in AAEC(1962, 1972), AAES(1958), and AIMM (1968) and by Stewart(1967a, 1967b). The paper outlines the effect of the purification and precipitation steps on the quality of the yellow cake product and describes the pilot plant studies carried out at the AAEC Research Establishment on the purification of yellow cake for conversion to nuclear grade uranium dioxide powder and uranium hexafluoride.

EARLY URANIUM MILLS

Table 1 summarises the major characteristics of the flowsheets used in the early mills for concentration and purification of uranium, precipitation, solid-liquid separation and drying-calcination of the yellow cake product. The operations of the Rum Jungle mill are of particular interest. It was commissioned in 1954 using ion exchange and magnesia precipitation (called Rum Jungle A flowsheet in this paper). In 1962, the ion exchange units were replaced with a solvent extraction circuit and magnesia precipitation continued (Rum Jungle B), while in 1966 caustic precipitation was introduced and the belt dryer for yellow cake drying was replaced with a multiple hearth calciner (Rum Jungle C). Similarly, the early Mary Kathleen

TABLE 2

YELLOW CAKE PRODUCTION IN PROPOSED AUSTRALIAN URANIUM MILLS

Mill	Mary Kathleen B	Ranger	Nabarlek	Jabiluka	Koongarra	Yeelirrie
Operating Company or Major Shareholder	Mary Kathleen Uranium Ltd	Ranger Uranium Mines Pty Ltd	Queensland Mines Ltd	Pancontinental Mining Ltd	Noranda Australia Ltd	Western Mining Corp.
Ore Grade, % U	0.1	0.33	1.60	0.33	0.26	0.12
Initial Production Rate, t U per year	500	2500	900	2500	900	3000
Solvent Extraction						
Organic Extractant	5 vol % Alamine 336 3 vol % alcohol 92 vol % diluent		4 vol % Alamine 336 2.4 vol % isodecanol 93.6 % kerosene		3 vol % amine 2 vol % modifier 95 vol % diluent	Alkaline leaching flowsheet incorporating vanadium separation, direct precipitation of uranium with NaOH. Crude yellow cake dissolved in sulphuric acid.
Stripping:						
- Strip solution	Aq. $(NH_4)_2SO_4$	Aq. $(NH_4)_2SO_4$	Aq. $(NH_4)_2SO_4$	Aq. $(NH_4)_2SO_4$	Aq. $(NH_4)_2SO_4$	
- No. of stages	4		4	4	4	
Precipitation						
- Reagent	NH_3	NH_3	NH_3/Air	NH_3	NH_3/Air	NH_3
- pH	7.0–7.5	7-8	7.2 - 7.5	7.5		
Solid-Liquid Separation						
- No. of Thickener stages	2	2	2	2	2	
- Dewatering	Centrifuge	Centrifuge	Centrifuge		Centrifuge	Filter
- Wet Product Moisture Content, % H_2O	30-40	40		40		
Drying-Calcination						
- Equipment	Oil-fired multi-hearth calciner	Oil-fired multi-hearth calciner	Oil-fired multi-hearth calciner	Oil-fired multi-hearth calciner	Oil-fired multi-hearth calciner	Oil-fired multi-hearth calciner
- Temperature, °C	700	600-800	500			260-650
- Product Grade, % U_3O_8	96–99	up to 95	>90			95
- Product Moisture, % H_2O	∼0.1			2 (max.)		
References	Baillie & Thomas (1972) MKU (1978)	RUM (1974)	QM (1979)	PM (1977)	NA (1978)	WMC (1978)

operations incorporated ion exchange and magnesia precipitation (Mary Kathleen A) whereas the recommissioned mill (Mary Kathleen B in Table 2) uses solvent extraction and ammonia precipitation.

Ion Exchange

The Port Pirie, Rum Jungle A and Mary Kathleen mills used strong base anion exchange with Deacidite FF resin which was eluted with approximately 1 M NaCl+0.05 M H_2SO_4. Sets of four ion exchange columns were used with two (in initial operations) or three columns on absorption and one (or two) being eluted or on standby. When breakthrough of the second column occurred, the first was loaded to saturation and was then taken off-line for elution. At Port Pirie, because of the high ferric/uranium ratio in the pregnant liquor which adversely affected uranium absorption on the resin, the amount of absorbed iron was reduced by continuing the absorption cycle for 5 hours after the resin in the first column was saturated so that uranium slowly replaced the iron complex on the resin. Three-column absorption was therefore essential (Almond 1958).

Table 3 summarises typical elution cycles for these mills. At Port Pirie and Rum Jungle A, a three-split elution technique was developed (two-split elution was used initially) such that the first third of the eluate passed to precipitation, the second third was recycled to become the first third for the elution of the next column, and the last third became the second third for the next column (Baker 1958). At Mary Kathleen, an initial flush of 1.25 bed volumes of dilute sulphuric acid (pH 1) was used to remove most of the adsorbed rare earths (lanthanons), the contaminants of primary concern. Some of the absorbed ferric iron was also removed in this stage. During subsequent elution cycles, two streams were produced, a high sulphate bleed and the normal eluate. Control of ion exchange systems was automatic with flowrates set so that elution time was less than the absorption time.

Care was taken to minimise poisoning of the resin by such substances as silica, alumina, titanium dioxide and by the adverse effect of ferric ion as mentioned above. Resin poisoning at Rum Jungle by silica and alumina was probably due to dirty pregnant liquor. Serious silica fouling was a problem at Mary Kathleen A, and the silica and rare earth contents of the yellow cake product exceeded the specification limits in the early months of operation. This was overcome by incorporating an initial flush with dilute acid to remove rare earths in the elution cycle as mentioned previously and construction of a regeneration plant using 5% NaOH for removal of silica (Harris et al. 1961). Alternatively, the fouling could have

TABLE 3

ELUTION CYCLES FOR ION EXCHANGE PLANTS

Port Pirie[#] (South Australian Dept. of Mines 1962)			Rum Jungle A (Baker 1958)			Mary Kathleen A (Harris et al. 1961)		
Stage	Composition	Bed Vol.	Stage	Composition	Bed Vol.	Stage	Composition	Bed Vol.
Flush	Dilute acid	1.0	Flush to IX columns	Dilute acid pH 1.6	0.94	Backwash	Dilute acid pH 1	2.5
Backwash	Dilute acid	2.0	Backwash to leaching circuit	Dilute acid pH 1.6		Flush to pregnant liquor storage	Dilute acid pH 1	1.25
First eluent	1M NaCl+0.05M H_2SO_4	0.5	First eluent to pregnant liquor	0.9M NaCl+0.09M H_2SO_4	0.55	Flush to pregnant liquor storage	Return eluent	0.7
First eluent to precipitation		6.0	First eluent to precipitation		6.74	First eluent to high sulphate bleed	1M NaCl+0.05M H_2SO_4	1.7
Second eluent to precipitation		0.5	Second eluent to precipitation		0.55	Main eluent to precipitation		8.5
Second eluent to first eluent		5.5	Second eluent to first eluent		7.29	Fresh eluent to return eluent tank		10.0
			Third eluent to second eluent		6.90	Flush to return eluent tank	$\sim$1M H_2SO_4	0.8
Flush to second eluent	Dilute acid	1.5	Flush to second eluent	Dilute acid pH 1.6	0.94	Flush to return acid tank	Dilute acid pH 1	0.9

[#] Early two-split elution

been alleviated by aging the pregnant liquor, reducing the volume of barren liquor which passed through the resin (by using moving bed rather than fixed bed ion exchange equipment) or by incorporating an acid ammonium fluoride wash in the elution cycle (Couche & Hartley 1958), but none of these approaches was more desirable or economic than continued operation of the existing mill (Hartley 1968).

Solvent Extraction

In the early to mid-1950s, the development of organic extractants with high distribution coefficients and selectivity for uranium from sulphate solutions led to the rapid application of solvent extraction in uranium recovery. The first such mills in Australia were the Moline and South Alligator mills which commenced operation in 1959 (Bellingham 1961, Murray & Fisher 1968). The Rum Jungle mill was converted to solvent extraction in 1962 (Allman et al. 1968, Goldney 1963, Stewart 1967c).

At the Moline mill,the solvent initially comprised 5 vol % tri-isooctyl amine (TIOA) in kerosene with 4 vol % nonanol (Bellingham 1961). However because of difficulties in the supply of TIOA, Alamine 336 (tricaprylamine) was substituted (Murray & Fisher 1968); this has been adopted for all subsequent mills. The early mills used stripping with 1 M sodium chloride in preference to sodium carbonate, nitrate or sulphate (and in conjunction with the use of magnesia or caustic soda for yellow cake precipitation) on the grounds of its effectiveness and economics (Bellingham 1961).

The changeover from ion exchange to solvent extraction purification at Rum Jungle in 1962 led to a substantial improvement in the grade of the product from 60-70% U_3O_8 previously to 87-90% U_3O_8, corresponding to a large reduction in the impurity content of the yellow cake. Table 4 compares analytical data for leach liquor and strip solution from the Rum Jungle C mill and illustrates the efficiency of the solvent extraction purification process.

At Moline, buildup of molybdenum (present in leach liquor at $\sim 1\ \mathrm{mg\cdot \ell^{-1}}$) in the stripped solvent was prevented by treating a tenth of the recycled solvent with 10% sodium carbonate solution (Bellingham 1961). This proportion was increased to a fifth when a brown precipitate, thought to be a molybdenum-uranium-amine complex, was found in solvent tanks (Murray & Fisher 1968). By contrast, provision for scrubbing the recycled solvent with sodium carbonate was included in the Rum Jungle B plant but was found to be unnecessary (Goldney 1963).

TABLE 4

IMPURITY CONCENTRATIONS IN TYPICAL URANIUM MILL PRODUCTS

($\mu g\ g^{-1}$ U basis)

Impurity Element	Leach Liquor	Strip Solution	Strip Solution (+ Scrubbing)	UF_4 via Modified PNC Process	Typical Yellow Cake	Canadian Spec. for UO_2 Powder	ERDA Spec. for natural UF_6
Aluminium, Al	2 400 000		20	20	270	25	(a)
Boron, B			0.5	0.5	< 5	0.3	
Cadmium, Cd	1 200		1.5	< 0.5	< 5	0.2	(a)
Calcium, Ca	29 000			< 10	550	50	(a)
Chromium, Cr			25	< 5		15	(a)
Copper, Cu	190 000	180	10	5	150	10	(a)
Iron, Fe	1 900 000	1 000	350	30	2 200	50	(a)
Magnesium, Mg	1 900 000	31 000	4	< 5	400	10	(a)
Manganese, Mn	690 000	260	< 1	4	80	5	(a)
Molybdenum, Mo	1 500	200	2	< 1	< 13	2	2 800
Nickel, Ni	26 000	150	< 3	4	25	20	(a)
Silicon, Si	290 000	3 500	110	35	1 000	50	100
Silver, Ag			0.2	< 1		1	(a)
Sodium, Na	150 000		< 20		28 000	100	(a)
Vanadium, V	22 000	100	3		< 13	100	28 000
Zinc, Zn	22 000		< 15	< 10		100	(a)
References	Allman et al. 1968 Ryan 1973	Allman et al. 1968	Ryan 1973	Fardy & Buchanan 1976	Allman et al. 1968	Chalder 1961	Alfredson 1972a

(a) Al + Ba + Bi + Cd + Ca + Cr + Cu + Fe + Pb + Li + Mg + Mn + Ni + K + Ag + Na + Sr + Th + Sn + Zn + Zr < 300

Precipitation and Solid-Liquid Separation

All the early Australian mills used magnesia precipitation of yellow cake except for Rum Jungle C. The Port Pirie and Mary Kathleen A mills used continuous two-stage precipitation whereas the other mills used only a single batch precipitation process. Except for the small Moline and South Alligator River mills, all early mills used two or three stages of rotary drum vacuum filters for solid-liquid separation which was preceded by various thickening or settling and washing steps.

Two-Stage Precipitation

At Port Pirie, the eluate from ion exchange was heated to 55°C and pumped to a continuous iron precipitation unit which consisted of three conical base tanks in series. A 5% lime slurry was fed to the first tank to maintain the pH in the exit slurry from the third tank at 3.0-3.5. Ferric hydroxide and calcium sulphate were precipitated, and the pulp was thickened and filtered. The filter cake was slurried with weak sulphuric acid and returned to the leaching circuit. The filtrate, washings and overflow from the thickener were pumped to the first stage of the uranium precipitation unit which was identical with the iron precipitation unit. A 3% magnesia slurry was fed to the first tank to raise the pH in the product slurry from the third tank to 6.5-7.0. This slurry was thickened and filtered on a rotary drum vacuum filter, repulped with water and filtered again to reduce the sulphate and chloride concentrations. It was then transported to the dryer (Almond 1958, South Australian Dept. of Mines 1962).

At Mary Kathleen A, the iron and uranium in the high sulphate eluate were bulk precipitated with low grade magnesia (2-3% SiO_2) slurry at pH 7.0-7.5, and the precipitate, after thickening, was fed to the first of the two stages of precipitation for the normal eluate. The overflow was discarded to the tailings dam. In the first stage unit for the normal eluate, comprising three precipitation tanks in series, low grade magnesia was added automatically to the first tank to maintain pH 3.5 in the last tank. The precipitate, mainly ferric hydroxide, was thickened, filtered and returned to the leaching circuit. The thickener overflow and filtrate were then fed to the uranium precipitation unit and precipitated with high grade magnesia (0.6% SiO_2) to give pH 7.0 in the third tank. The yellow cake precipitate was thickened then filtered in three stages (with intermediate repulping). The overflow from the yellow cake thickener was recycled to the ion exchange elution circuit while the filtrates and washings were discarded through the high sulphate circuit (Harris et al. 1961, MKU 1962).

Single-Stage Precipitation

In the Moline and South Alligator mills, precipitation was carried out daily on a batch basis in stirred tanks to which magnesia slurry was added over a period of hours until the final pH was in the range 7.0-7.5. Repeated decant washings were made in the precipitation tanks. After allowing the precipitate to settle, the supernatant was pumped to a plate and frame press, and the filtrate recycled for makeup as strip solution, with some being rejected as a sulphate bleed. The precipitate was then decant washed with fresh water until the chloride concentration in the washings was less than 1 $g \cdot \ell^{-1}$. The washings were filtered with the plate and frame press and discarded. The precipitate was finally filtered using a disc filter (Murray & Fisher 1968).

At Rum Jungle A, uranium in eluate was precipitated in two mechanically agitated, conical bottom tanks with 25-30% slurry of magnesia (90% MgO) by neutralising to pH 7.2-7.5 over about 6 hours. The precipitate was allowed to settle and the clear liquor siphoned off. Water was added to the precipitation tanks, agitated, and the slurry was pumped to a thickener. During early operations with only one stage of filtration, it was difficult to maintain the chloride content of the product within specification limits. This problem was overcome when a two-stage filtration system was introduced (Baker 1958).

Allman et al. (1968) described developments in yellow cake precipitation with magnesia in the Rum Jungle B mill. Improved settling and filtering characteristics were achieved and the grade of the product increased from 81.1 to 87.7% U_3O_8 by operating at 85°C rather than at ambient temperature and by adopting a "hot wash" of the precipitate to decompose complex uranium sulphate compounds thereby reducing its sulphate content. Hot washing involved pumping the settled concentrate into another conical bottom tank containing water heated to 85°C and allowing it to settle.

In its simplest form, precipitation of yellow cake from strip solution with caustic soda, for example, may be described as

$$2UO_2SO_4 + 6NaOH \rightarrow Na_2U_2O_7 + 2Na_2SO_4 + 3H_2O$$

The diuranate can probably never be obtained in aqueous solution even in the presence of a large excess of alkali. The precipitate is more accurately described as a uranate or hydroxyuranate,which are cation-exchanged modifications (Stuart & Whateley 1969) of the parent $UO_2(OH)_2.H_2O$ as follows:

$$UO_2(OH)_2 + xNa^+ \rightarrow UO_2(OH)_{2-x}(O\text{-}Na^+)_x + xH^+$$

The absorption of Na^+ is favoured at higher pH and a continuous range of composition, i.e. Na : U ratio, is possible. Typical yellow cake precipitates contain Na : U ≑ 0.3. In practice the precipitate also contains sulphate, chloride and other impurities as absorbed or occluded ions.

Allman et al. (1968) postulated that the sulphate contaminant in the precipitate was a mixture of sodium sulphate and a complex, with the empirical formula $Na(UO_2)_2(OH)_3SO_4$, which behaved as though it was $3UO_2(OH)_2.UO_2SO_4.Na_2SO_4$. This compound decomposed in boiling water as follows:

$$3UO_2(OH)_2.UO_2SO_4.Na_2SO_4 \rightarrow 3UO_2(OH)_2 + UO_2SO_4 + Na_2SO_4$$

and could also result in the release of hydrogen ions

$$3UO_2(OH)_3.UO_2SO_4.Na_2SO_4 + 2H_2O \rightarrow 4UO_2(OH)_2 + H_2SO_4 + Na_2SO_4$$

When significant quantities of basic sulphate were present, further addition of precipitant was essential.

$$3UO_2(OH)_2.UO_2SO_4.Na_2SO_4 + 2NaOH \rightarrow 4UO_2(OH)_2 + 2Na_2SO_4$$

These reactions were instrumental in the adoption of hot washing of the precipitate at Rum Jungle.

Formation of the basic sulphate was fairly slow and occurred mainly at pH 4.8-5.1. By raising the pH to 5.1 as rapidly as possible, the formation of all but small amounts of sulphate impurity was avoided.

The Rum Jungle C mill switched to caustic soda as precipitant because it was cheaper than magnesia which also had the disadvantages that it was a solid reactant which took about 2 hours to fully react, its reactivity varied from shipment to shipment, and it contained undesirable impurities such as silica and carbonate. Sodium hydroxide gave a slightly higher grade product than magnesia but with poorer settling, filtering and drying characteristics (Allman et al. 1968).

TABLE 5

COMPARISON OF RUM JUNGLE YELLOW CAKE PRODUCTS

		MgO Precipitated Yellow Cake (Rum Jungle B)	NaOH Precipitated Yellow Cake (Rum Jungle C)	Allied Chemical Corp. Specifications#	
				Standard Concentrates	Maximum Limit Concentrates
Uranium,	U	75.7	78.6	75.0	65.0 min
Moisture,	H_2O	0.4	0.4	2.00	5.00
Carbonate,	CO_3			0.20	0.50+
Fluorine,	F			0.01	0.10
Halogens,	Cl+I+Br	0.007	0.004	0.05	0.10
Phosphate,	PO_4	0.039	0.027	0.10	1.00
Sulphate,	SO_4	0.84	0.89	3.00	12.00
Vanadium,	V_2O_5	0.001	0.001	0.10*	0.75
Arsenic,	As	0.0003	0.0001	0.05	0.10
Boron,	B	0.0005	0.0005	0.005	0.10
Calcium,	Ca	0.05	0.04	0.05	1.00
Iron,	Fe	0.18	0.18	0.15	1.00
Magnesium,	Mg	0.37	0.03	0.02	0.50
Molybdenum,	Mo	<0.001	<0.001	0.10*	0.30
Potassium,	K	0.09	0.12	0.20*	3.00
Silica,	SiO_2	0.54	0.18	0.50*	2.50
Sodium,	Na	1.7	2.3	0.50*	7.50
Titanium,	Ti	0.003	0.0015	0.01	0.05

\# Specifications apply on a dry weight basis (except for moisture on as received basis)

* Surcharges apply above these values

\+ Applies only if >0.5% Na

Yellow cake grade and handling characteristics deteriorated steadily after caustic precipitation was introduced corresponding to increases in the concentration of sodium in the product and depletion of calcium and magnesium in plant circuits. Filtration rate was improved by reducing the concentration of caustic soda solution from 14 to 9 wt % and by filtering at 90°C. Addition of flocculent before precipitation improved product handling but not product grade. Pilot plant tests showed that these parameters depended on the rate of addition of precipitant, even at the stage when no precipitate was visible. Slowing down the rate of precipitation (added over several hours) substantially increased the rate of filtration but resulted in significant quantities of sulphate in the product; however this was easily removed by hot washing at 90°C for 5 hours and adding caustic to the hot wash. Further dilution of the precipitant to 5% caustic soda and introducing it via a spray nozzle manifold instead of an open pipe improved filtration rates by a factor of 10 and considerably reduced dryer operating time and costs. These changes directly affected the composition, nucleation and growth of the seed crystals of the precipitate and reduced local inhomogeneities in solution. Precipitation temperature was subsequently reduced to 60°C and pH to 6.0 (Allman et al. 1968).

Table 5 compares analytical data for magnesia and caustic soda precipitated yellow cake products from Rum Jungle A and B operations. After the change to caustic precipitation, the concentrations of uranium and sodium increased (the latter was consistently greater than the Standard Concentrates limit of the Allied Chemical Corp., the most stringent of the yellow cake specifications) while the concentration of magnesium was, of course, reduced.

Drying - Calcination

The early uranium mills used relatively low temperature drying in the range 150-300°C; no calcination occurred under these conditions. The filter cake was typically extruded through a drilled stainless steel plate and conveyed into the dryer which was heated with hot air from an oil-fired furnace. The small South Alligator mill used batch-tray drying in an oil-fired furnace. In all cases, the yellow cake product contained several per cent of residual moisture.

The drying operation at Rum Jungle was substantially improved in 1966 by the installation of an oil-fired, multiple-hearth calciner which operated at a nominal temperature of 800°C and a residence time of 30 minutes. The resultant product typically contained <0.5% moisture with a corresponding increase of a few per cent in the U_3O_8 content.

Packaging and Sampling

The dried product was crushed to -6 mm, cooled and packaged in polythene-lined 44-gallon drums. At some mills, each drum of yellow cake was sampled on a random basis with a motorised auger before final weighing and sealing.

CURRENT AND PROPOSED MILLS

Table 2 summarises the main features of the flowsheets used in the recommissioned Mary Kathleen plant and in the proposed future mills in the Northern Territory and Western Australia. Except for the Yeelirrie mill which will use an alkaline leaching circuit, all these mills have adopted, as the best available proven technology (Alfredson et al. 1978), solvent extraction for concentration and purification of uranium, stripping with 1.5 M $(NH_4)_2SO_4$ (at controlled pH), ammonia precipitation of yellow cake, solid-bowl centrifuges instead of rotary drum vacuum filters for solid-liquid separation, and oil-fired multiple-hearth dryer-calciners operating at 500-800°C.

For the future mills, solvent extraction is preferred over ion exchange for uranium recovery from clarified leach solutions because capital and operating costs are lower, and operating efficiency and selectivity are higher (PM 177, RUM 1974). Continuous ion exchange from unclarified solutions is regarded as not adequately proven (NA 1978).

When the Mary Kathleen plant was recommissioned, solvent extraction was preferred to the existing ion exchange process because, in spite of its higher capital expenditure, it has substantially lower operating costs. A standard Amex flowsheet was adopted with the addition, after the extraction stages, of one scrubbing stage (with water) to reduce the level of such impurities as the rare earths. Stripping uses ammonium sulphate in four stages, with pH control on stages 2 and 3 using 5% ammonium hydroxide solution. Continuous precipitation is carried out in two stages with the pH adjusted to 7.5 in the second stage. Ammonia was chosen for stripping and precipitation because it was cheaper than other alkaline reagents, does not introduce any impurity ions such as sodium, and enables a very high grade product to be produced by calcination. The precipitate is washed in two thickeners to 30% solids, and the underflow from the second is pumped to a solid-bowl centrifuge which gives a product containing 30-40% moisture. The centrifuge was preferred to the previous three-stage rotary drum vacuum filtration system because of its enclosed operation (thereby eliminating possible contamination of the work area), ability to handle a slimy precipitate and slight economic advantages (Baillie & Thomas 1972, MKU 1978).

R & D RELATED TO YELLOW CAKE PRODUCTION

Solvent Extraction

Both Rum Jungle (Allman et al. 1968) and AAEC workers (Alfredson 1970, Ryan 1973) have considered the feasibility of producing a nuclear purity product at a uranium mill by adding scrubbing stages for the loaded organic in the amine solvent extraction flowsheet, a technique similar to that used in the South African Bufflex and Purlex processes. Since extraction of impurities is generally reduced as the uranium loading of the solvent is increased, it is essential to operate as near uranium saturation of the solvent as possible. Scrubbing the loaded solvent with sulphuric acid can then reduce the co-extraction of iron and arsenic (Faure and Tunley 1969). Ryan (1973) attempted a statistical optimisation of a standard amine solvent extraction flowsheet which incorporated scrubbing with 1.5 M ammonium sulphate (with acid addition in the scrubbing stages to maintain the pH in the range 2 to 4) and stripping with 1.5 M ammonium sulphate in the pH range 4 to 7, in an effort to obtain a nuclear purity product. However, none of the operating variables had a statistically significant effect on the purity of the product over the range of variables investigated. A high- but not nuclear-purity product solution was obtained (Table 4). Iron, cadmium, silicon and molybdenum were consistently above that allowable in the nuclear grade uranium dioxide powder product (Chalder 1961) to which this work was oriented.

Precipitation

Further studies of precipitation techniques at Rum Jungle (Connolly 1968) were not developed sufficiently to be implemented before the mill closed down in 1971. The use of urea as a precipitant was investigated in both pilot plant and production trials. It was attractive because it was cheaper than caustic soda and easier to handle. Satisfactory precipitation was obtained in production tests at ~100°C and the precipitate settled and filtered more rapidly than did the caustic precipitated material. However, the sulphate concentration in the product increased and was attributed to the formation of sodium-ammonium-uranyl sulphates during very slow or homogeneous precipitation. These sulphates were not decomposed by hot washing.

Because of the importance attributed to the early stages of yellow cake precipitation involving the possibility of forming a basic sodium-uranium sulphate complex below pH 5, a closed loop precipitation system was investigated in which feed solution, neutralising agentand recirculating precipitate slurry were mixed under highly turbulent conditions to give an immediate pH of ~7 (Connolly 1968). Rapid uniform mixing of the reactants would also reduce zones of higher or lower (in particular) pH. The temperature was in the range 40-50°C with residence times up to about one hour. A second stage stirred tank was also incorporated in which no further precipitant was added but a greater residence time was allowed for conditioning the product. However, in pilot plant tests, the sodium and sulphate concentrations in the yellow cake were slightly lower, but it settled much more slowly than the standard mill product.

R & D ON PRODUCTION OF URANIUM FLUORIDES

During the past ten years, the AAEC Chemical Engineering Section has carried out pilot plant studies of the processes for the production of nuclear grade uranium dioxide (Alfredson 1970, 1972b) and uranium hexafluoride (UF_6) from Australian yellow cake to establish the necessary technology and improve the processes and equipment where possible. Of the three major processes available for UF_6 production, namely wetway processes involving solvent extraction purification followed by either ADU precipitation or denitration to UO_3 and the dryway process (Alfredson 1972b), the first two were chosen for investigation, particularly the ADU route, because the original emphasis of the work was on the production of nuclear grade uranium dioxide of natural enrichment. In addition, Fardy & Buchanan (1976) studied, on the laboratory scale, a modified PNC process (Takada et al. 1971) for the production of high purity uranium tetrafluoride (UF_4) from Rum Jungle leach liquor.

In this section, major emphasis is placed on those processes which are affected by the quality of the yellow cake feed material, namely dissolution and solvent extraction, and the remainder are only briefly outlined. These studies were based on a high grade yellow cake from Rum Jungle C operations.

Dissolution

The dissolution step was designed to process yellow cake as well as recycled materials, e.g. ADU and uranium dioxide powder and pellets, and to permit dilution and adjustment of acidity of the solutions. In general, a dissolver product solution containing 300 $g \cdot \ell^{-1}$ of uranium and 0.5 to 4 M nitric acid was required as the feed for solvent extraction. An existing 0.1 m^3 dissolver, constructed from AISI 321 stainless steel, heated via steam coils and agitated by sparging with air, was used. A reflux condenser was mounted on top of the dissolver and served to minimise loss of nitric acid fumes from the dissolver, recover some of the nitrogen oxide off-gases, and allow removal of the exothermic heat of dissolution. The off-gases were then scrubbed with 10 wt % sodium carbonate or hydroxide solution in a packed column before being discharged through de-entrainment separators to the building ventilation system.

Yellow cake in batches containing up to 25 kg of uranium dissolved readily within an hour at 100°C. The Rum Jungle yellow cake contained only 0.25 wt % silica and no difficulties were encountered in the subsequent solvent extraction operations. Nevertheless, aging the solution for 4 hours at 100°C was included to precipitate the insoluble silica in a more filterable form. Tests with a solid bowl centrifuge indicated that the silica could be readily removed if necessary (Alfredson et al. 1975).

Solvent Extraction

Uranium purification was accomplished by solvent extraction using 20 vol % tributyl phosphate (TBP) in odourless kerosene as the solvent and mixer-settler contactors (Alfredson et al. 1975), following UKAEA practice (Page et al. 1960). Two identical 16-stage mixer-settler units were used, one for extraction and scrubbing and one for stripping. Initially a high acid flowsheet was used which required a feed solution containing 300 $g \cdot \ell^{-1}$ of uranium and 4 M free acid, 6 extraction stages, 10 scrubbing stages (with 1 M nitric acid) and 16 stripping stages (with 0.05 M nitric acid). Two aspects of the system were optimised while maintaining a high purity product; the acid consumption and the throughput of the mixer-settler units.

Essentially all the free acid in the feed solution and that added in the scrubbing stages is discharged in the raffinate waste stream and must be recovered for an economic large-scale operation. Littlechild (1967) briefly reported a modified UKAEA flowsheet in which the acid scrub was replaced by recycling of part of the purified product and reducing the scrub volume. This increased the uranium concentration in the scrubbing stages and in the loaded organic, the throughput of the mixer-settlers, and enabled a more concentrated product containing less free acid to be produced. As mentioned earlier, increasing the uranium saturation of the solvent is advantageous in reducing the co-extraction of impurities.

The effect of free acid concentration in the feed was also examined. Some free acid is essential if low uranium values (<50 mg·ℓ$^{-1}$) in the raffinate are to be achieved when the uranium in the recycled organic is up to 100 mg·ℓ$^{-1}$. McCabe-Thiele calculations indicated that five extraction stages were adequate for free acid concentrations in the feed of 1.0 or 3.0 M. With only 0.5 M free acid, a uranium concentration in the raffinate of 50 mg·ℓ$^{-1}$ cannot be obtained because of a pinch in the extraction stages.

With a uranium concentration in the loaded organic of 70 g·ℓ$^{-1}$, approximately 12 ideal stages are required to give a 100 g·ℓ$^{-1}$ product and reduce the uranium concentration in the stripped organic to <50 mg·ℓ$^{-1}$. Difficulties were encountered in reducing the uranium concentration in the stripped organic below 1 g·ℓ$^{-1}$ in the 16-stage stripping unit. This problem was overcome by heating the strip solution to 60°C: the temperatures in the stripping stages varied from 60 to 30°C. Under these conditions, the uranium concentration in the product increased to 120 g·ℓ$^{-1}$, while the concentration in the stripped organic was <5 mg·ℓ$^{-1}$. Note that heating the loaded organic rather than the strip solution would have been more effective in improving the efficiency of stripping. Figure 1 summarises the recommended flowsheet arising from this work (Alfredson et al. 1975).

The mixer-settler units were designed for a uranium throughput of 1.5 kg·h^{-1}, corresponding to a total phase flowrate of 47 ℓ·h^{-1} in the stripping stages. The above modifications in the flowsheet reduced the total phase flowrate required and increased the throughput to 2.1 kg·h^{-1}. This was further increased to 2.5 kg·h^{-1} by increasing flowrates, with acceptable losses of uranium in the raffinate (40 mg·ℓ$^{-1}$ corresponding to ∿0.01% of the uranium feed).

The purity of the uranyl nitrate product solution was generally within the limits of the Canadian specification for nuclear grade uranium dioxide powder (Table 6) and was not adversely affected by the above changes which reduced the acid consumption by 87 per cent and increased the uranium throughput by 66 per cent, compared to the original design basis (Alfredson et al. 1975).

Conversion to Uranium Dioxide and Uranium Tetrafluoride

The preparation of ceramic grade UO_2 powder from purified uranyl nitrate solution via precipitation of ADU, filtration, drying, calcination and reduction was investigated in bench and pilot plant scale

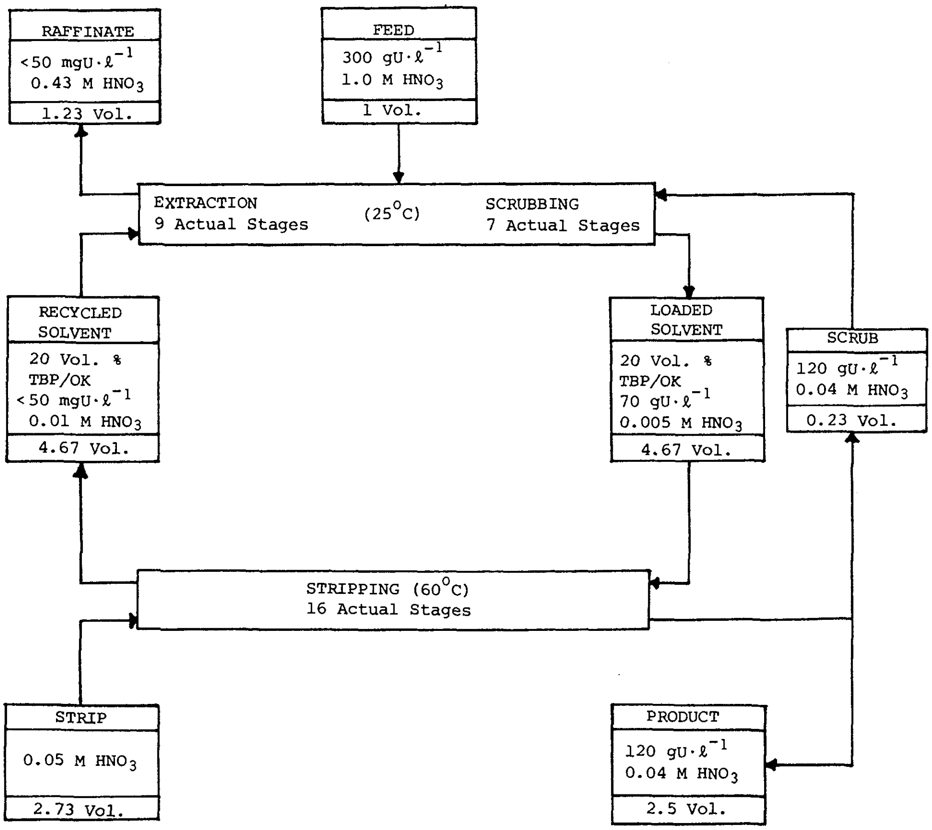

FIG.1. Recommended low acid solvent extraction flowsheet. (After Alfredson et al. 1975.)

equipment. The influence of precipitation conditions in single and two-stage systems on the rates of settling and filtration and on the fabrication of the subsequent UO_2 powder was investigated by Janov et al. (1971, 1975). They showed that the most important variable affecting the properties of the precipitate, such as crystallite and agglomerate sizes, settling and filtration rates and nitrate content, was the pH at which precipitation occurred. In two-stage precipitation using ∿2 ℓ stirred tank reactors, in which ADU was partially precipitated at pH 3-4 and the remainder in the pH 7-8 range, the properties of the precipitate were determined by the proportion of uranium precipitated in the first stage. When 90 per cent of the uranium was precipitated at pH 3.5, it contained large agglomerates and it settled and filtered

TABLE 6

IMPURITY CONCENTRATIONS IN PURIFIED URANYL NITRATE SOLUTIONS (after Alfredson et al. 1975)

($\mu g\ g^{-1}$ U basis)

Impurity Element		Feed Solution - Rum Jungle Yellow Cake	Product from High Acid Flowsheet	Product from Low Acid Flowsheet	Canadian Spec. for UO_2 Powder
Aluminium,	Al	25	<10	10	25
Boron,	B	< 1	< 0.1	0.2	0.3
Cadmium,	Cd	<10	0.3	0.1	0.2
Calcium,	Ca	1 000	<10	2	50
Chromium,	Cr	5	10	<10	15
Copper,	Cu	50	10		10
Iron,	Fe	3 000	15	20	50
Magnesium,	Mg	500	4	20	10
Manganese,	Mn	5	<1	2	5
Molybdenum,	Mo	<10	<0.5	1	2
Nickel,	Ni	100	7	3	20
Silicon,	Si		15	15	30
Silver,	Ag		0.1	0.2	1
Sodium,	Na	35 000	20	<20	100
Vanadium,	V	<5	<3	< 1	100
Zinc,	Zn	200	15	20	100

5-10 times more rapidly than ADU precipitated at pH 7.2. Approximately 75 per cent of the nitrate (2 wt %) in such precipitate could be removed by washing once with demineralised water; more extensive washing caused only a slight further reduction in nitrate content and significantly reduced the filterability of the precipitate. This was attributed to partial peptisation of the precipitate as nitrate and ammonia was removed from it. When less than ∿83 per cent of the uranium was precipitated in the first stage, the slurry properties were similar to those of ADU precipitated in only one stage operating at the second stage pH (Janov et al. 1971).

These workers also carried out pilot plant studies using a single-stage (25 ℓ) precipitator, and compared solid bowl centrifuge and rotary drum vacuum filter units for dewatering of ADU slurries. As the pH of precipitation increased in the range 7.2 to 8.0, the slurry settled more slowly to give a lower pulp density, filtered more slowly and gave an increased moisture content in the filter cake. Precipitation at 80°C and pH 7.5 offered no advantages over operation at 50°C (at the same pH with ammonium hydroxide solution as precipitant) and no significant differences were found using ammonia gas diluted with three times its volume of air. The solid bowl centrifuge was more efficient than the rotary drum vacuum filter in that it produced a clearer discharge at a higher rate. The residual moisture content in the ADU cake was approximately the same for both units (Janov et al. 1975).

Batch-tray drying (Janov et al. 1975) and continuous spray drying (Levins et al. 1972) were investigated and both batch-tray (Alfredson & Janov 1971) and continuous pulsed fluidised bed reactor systems (Fane & LePage 1975) were developed for calcination-reduction to UO_2 powder, generally in the range 600 to 700°C.

Concentration of uranium solutions up to 1000 $g \cdot \ell^{-1}$ was demonstrated in a 0.74 m^2 thermosiphon evaporator (Levins & Alfredson 1974) and thermal denitration to UO_3 in a 0.1 m diameter fluidised bed reactor was investigated (Fane et al. 1974).

Conversion of ceramic grade UO_2 powder to UF_4 was readily achieved on a batch basis in a 0.15 m diameter fluidised bed reactor by reaction with ∿30 vol % hydrogen fluoride (HF) at 300°C. Greater than 99 per cent conversion was achieved in less than 3½ hours. Reaction at higher temperatures and/or higher HF concentrations led to significant temperature excursions and sintering of the UF_4 product which prevented complete conversion to UF_4 (Janov et al. 1979).

Production of Uranium Tetrafluoride via an Aqueous Route

Various aqueous processes have been investigated overseas for the production of a high purity UF_4 product directly at the mine site and are claimed to offer overall cost savings in the production of UF_6 (Hardy 1972). The PNC process (Takada et al. 1971) is one such process and involves recovery of uranium from sulphate leach liquor by extraction with the tertiary amine, tri-n-octylamine(TNOA). While still in the organic phase, the uranium is converted from a sulphate to a chloride species by washing with 8 M HCl. The chloride species is then stripped from the organic phase with 0.05 M HCl, electrolytically reduced to the tetravalent form, and precipitated as hydrated uranium tetrafluoride ($UF_4 \cdot \frac{3}{4} H_2O$) at 95°C by adding hydrofluoric acid. The $UF_4 \cdot \frac{3}{4} H_2O$ is dehydrated at 350°C, and the amine solvent and chloride are recycled.

A modified version of the PNC process was investigated on the laboratory scale starting with Rum Jungle leach liquor. Alamine-336 was substituted for TNOA in the solvent extraction flowsheet, and the use of chemical reductants such as zinc, iron and hydrogen was considered in lieu of electrolytic reduction. Washing of the precipitate was important to reduce zinc and iron in precipitated solids to acceptable levels. Table 4 compares analytical data for feed and strip solutions from the amine extraction process with UF_4 product produced via electrolytic reduction. A high purity product was obtained which was slightly inferior to the reported PNC product (Fardy & Buchanan 1976).

The process appears technically feasible but would suffer from higher costs at remote mines for labour, supplies and infrastructure. Obviously a satisfactory additional margin for selling UF_4 rather than yellow cake must also be obtained.

Conversion of Uranium Tetrafluoride to Uranium Hexafluoride

An improved Fluorox process (Scott et al. 1960) for the production of UF_6 has been investigated in laboratory equipment as well as bench and pilot plant scale fluidised bed reactors. In this improved process, patented by the AAEC (e.g. Ekstrom & McLaren 1976) on the basis of laboratory (Batley & Ekstrom 1974, Ekstrom et al. 1974) and bench scale experiments (Batley et al. 1974), the reaction of UF_4 powder with oxygen to form gaseous UF_6 and solid uranyl fluoride at about 650°C is catalysed by platinum (5 wt %) supported on gamma alumina or calcium fluoride.

$$2UF_2 + O_2 \rightarrow UF_6 + UO_2F_2$$

The UO_2F_2 is reconverted to UF_4 in a second fluidised bed reactor by successive gas-solid reactions using hydrogen (which is also catalysed) and hydrogen fluoride below 500°C. The process is very unusual in that gas-solid reactions are catalysed by a second solid.

Pilot plant tests were based on UF_4 purchased from both British Nuclear Fuels Ltd (BNFL) and Commissariat a l'Energie Atomique (CEA). In typical batch experiments with 20 kg beds containing 15-30 wt % BNFL UF_4 (diluted with inert alumina or uranyl fluoride), the addition of 1.2 wt % catalyst (% of total feed) increased the reaction rate at 650°C by a factor of ∿10 to a value essentially the same as that measured in thermobalance tests. With CEA UF_4, 5 wt % catalyst in the bed was required to increase the reaction rate by only a factor of 4. When fresh batches of UF_4 were added to the UO_2F_2/catalyst mixture from previous experiments, the rate of UF_4 conversion decreased. The catalyst was apparently poisoned with prolonged use in the pilot plant (which was not observed in smaller scale tests) but was regenerated by the recycle reactions involving reduction and hydrofluorination. A further difficulty related to the formation of intermediate uranium fluorides which tended to reduce the yield of UF_6 and block off-gas filters. Both these problems could be overcome but with economic penalties which made further development unattractive (Janov et al. 1979).

Slight modifications are being made to the pilot plant so that UF_6 can be produced by the fluorination of UF_4 with fluorine.

Fluorine is produced by the electrolysis of hydrofluoric acid dissolved in a potassium-hydrogen fluoride electrolyte (Ring & Royston 1972). During 1973, a 1500A fluorine cell experimental facility was used to investigate the operation of medium temperature fluorine cells (using $KF.2HF$ electrolyte) and to give an insight into the many facets of fluorine production (Royston et al. 1975). The plant contained all the elements of a full scale commercial plant and was operated continuously for three months to produce over 2000 kg of fluorine.

DISCUSSION

Yellow cake from the ion exchange mills which used magnesia precipitation contained 50–80% U_3O_8. Direct precipitation of yellow cake from Rum Jungle eluate gave a product containing 50–70% U_3O_8 whereas two-stage precipitation at Port Pirie and Mary Kathleen gave ~80% U_3O_8. By comparison, the products from the solvent extraction mills were generally in the range 85–90% U_3O_8 for precipitation with magnesia and 90–93% U_3O_8 for precipitation with caustic soda. At Rum Jungle, Allman et al. (1968) obtained a substantial improvement in the grade (81 →88% U_3O_8) of magnesia precipitated yellow cake by giving attention to the precipitation and washing stages, including the use of hot washing to decompose basic uranium-sodium sulphate complexes and thereby reduce the sodium and sulphate contents of the product. Most of the difference in grade between the magnesia and sodium precipitated yellow cakes was attributable to the coincidental improvement in drying and calcination which resulted from the replacement of the belt dryer by an oil-fired multi-hearth calciner.

Early yellow cake products exceeded current yellow cake specifications for many impurities including moisture, chloride, phosphate, sulphate, magnesium, silica, sodium and rare earths. Many of these impurities were eliminated by changes in elution of ion exchange columns, the use of solvent extraction and improvements in the precipitation, washing and drying-calcination steps. Significant impurities in the highest grade of yellow cake produced at Rum Jungle (93% U_3O_8) in the late 1960s were sodium (2%), sulphate (0.9%), silica (0.2%) and iron (0.2%). This product exceeds the Allied Chemical Corp. specification for 'Standard Concentrates' but not that for 'Maximum Limits Concentrates' and would attract surcharges, in particular, for sodium (Table 5). However, the specifications required by other converters are less demanding and would be met.

The recommissioned Mary Kathleen and proposed new mills have adopted what they regard as the best available proven technology to produce a high grade product generally containing >95% U_3O_8 which should readily meet the most stringent specifications for yellow cake.

AAEC research and development studies have investigated the wetway processes for the purification of uranium by solvent extraction using tributyl phosphate as the extractant, and subsequent processing to nuclear grade uranium dioxide and uranium hexafluoride. No difficulties were encountered in reaching the required purity standards, particularly with high grade yellow cake from Rum Jungle as starting material.

REFERENCES

AAEC (1962) - Uranium in Australia, A Collection of Articles on the History and Development of the Uranium Mining Industry in Australia, AAEC.

AAEC (1972) - Papers presented to the AAEC Symposium on Uranium Processing, Lucas Heights, 20-21 July, 1972. AAEC/E238.

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

AIMM (1968) - Symposium on Uranium in Australia, Papers delivered at the Symposium on Uranium in Australia, Rum Jungle, 16-21 June, 1968, (Eds. - Berkman, D.A., Cuthbert, R.H. and Harris, J.A.), Rum Jungle Branch, The Australasian Institute of Mining and Metallurgy.

Alfredson, P.G. (1970) - The production of nuclear grade uranium dioxide powders from Australian ores. Aus. I.M.M. Proceedings, No. 233, 61-68. Also AAEC/TM514.

Alfredson, P.G. (1972a) - Review of methods and technology for the production of uranium hexafluoride. Paper VIII in AAEC (1972).

Alfredson, P.G. (1972b) - Pilot plant development of processes for production of nuclear grade uranium dioxide. Development and Innovation for Australian Process Industries, Proceedings of 1972 Australian Chemical Engineering Conference, Newcastle, pp. 71-80. Also AAEC/E245.

Alfredson, P.G., Charlton, B.G., Ryan, R.K., & Vilkaitis, V.K. (1975) - Pilot plant development of processes for the production of purified uranyl nitrate solutions. AAEC/E344.

Alfredson, P.G. & Janov, J. (1971) - Investigation of batch-tray calcination-reduction of ammonium diuranate to uranium dioxide. AAEC/TM599.

Alfredson, P.G., Crawford, R.E. & Ring, R.J. (1978) - Review of recent developments in uranium extraction technology, AAEC/E466.

Allman, M.B., Harris, J.A., & Bayly, M.G. (1968) - Treatment of Rum Jungle uranium ore, in AIMM (1968), pp. 90-124. Also Atomic Energy in Australia, 13 (3), 22-38 (1970).

Almond, J.N. (1958) - Treatment of Radium Hill concentrates for the recovery of uranium, in AAES (1958), pp. 67-74.

Anon (1959) - Uranium recovery at Rum Jungle. Mine & Quarry Eng., 25 (12), 522-531.

Baillie, M.G. & Thomas, J.A. (1972) - Planned changes in the Mary Kathleen treatment plant for future operations, Paper VI in AAEC (1972).

Baker, F.H. (1958) - The production of uranium ore concentrates at Rum Jungle, in AAES (1958), pp. 59-66.

Barlow, T. (1962) - Rum Jungle, in AAEC (1962), pp. 29-35.

Batley, G.E., Ekstrom, A., Fane, A.G., Janov, J. & Johnson, D.A. (1974) - AAEC Unpublished work.

Batley, G.E. & Ekstrom, A. (1974) - Studies of topochemical heterogeneous catalysis. 2. Catalysts for the reaction of UF_4 with oxygen. J. Catal., 34, 360-367.

Bellingham, A.I. (1961) - The application of solvent extraction to the recovery of uranium from El Sherana ore. Aus. I.M.M. Proceedings, No. 198, 85-109.

Chalder, G.H. (1961) - Uranium dioxide powder for the manufacture of high density sintered pellets, Specification No. MET-61, Issue I, AECL-1327.

Connolly, D.L. (1968) - Territory Enterprises Pty Ltd Unpublished work.

Couche, R.A. & Hartley, F.R. (1958) - Features of the development of chemical processing for Mary Kathleen ores, in AAES (1958), pp. 75-85.

Ekstrom, A., Batley, G.E. & Johnson, D.A. (1974) - Studies of topochemical heterogeneous catalysis. 1. The catalytic effect of platinum on the reaction of UF_4 with O_2, and of UO_2F_2 and UO_3 with H_2. J. Catal., 34, 106-116.

Ekstrom, A. & McLaren, A.B. (1973) - Australian Patent 464,235.

Fane, A.G., Charlton, B.G. & Alfredson, P.G. (1974) - The thermal denitration of uranyl nitrate in a fluidised bed reactor. AAEC/E284.

Fane, A.G. & LePage, A.H. (1975) - The production of sinterable uranium dioxide from ammonium diuranate. Part III. Continuous production in a pulsed fluidised bed reactor. AAEC/E347.

Fardy, J.J. & Buchanan, J.M. (1976) - AAEC Unpublished work.

Faure, A., & Tunley, T.H. (1969) - The Purlex process, Nuclear Active, July 1969, 19-23.

Goldney, L.H. (1963) - Solvent extraction at Rum Jungle. Hydrometallurgy - Paper No. 19 presented at 1963 Annual Conference of Australasian Institute of Mining and Metallurgy, Adelaide.

Hardy, C.J. (1972) - Possible trends and methods for the production of high purity products. Paper VII in AAEC (1972).

Harris, J.W., Boag, J. & Hemingway, P. (1961) - Some technical aspects of treatment operations at Mary Kathleen Uranium Ltd, Aus. I.M.M. Proceedings, No. 198, 207-226.

Hartley, F.R. (1968) - Treatment of Mary Kathleen uranium ore - a review, in AIMM (1968), pp. 138-160. Also Atomic Energy in Australia, 13 (2), 18-30 (1970).

Hartley, F.R. (1972) - Conventional processes to produce yellow cake, Paper II in AAEC (1972).

Janov, J., Alfredson, P.G. & Vilkaitis, V.K. (1971) - The influence of precipitation conditions on the properties of ammonium diuranate and uranium dioxide powders. J. Nucl. Mat., 44, 161-174. Also AAEC/E220.

Janov, J., Alfredson, P.G. & Vilkaitis, V.K. (1975) - Pilot plant development of processes for the production of ammonium diuranate. AAEC/E333.

Janov, J., Charlton, B.G. & LePage, A.H. (1979) - AAEC Unpublished work.

Levins, D.M. & Alfredson, P.G. (1973) - Performance of a thermosiphon evaporator for concentration of uranyl nitrate solutions. AAEC/E278.

Levins, D.M., Alfredson, P.G., Hurst, R.C. & MacBride, P.R. (1972) - Spray drying of ammonium diuranate slurries. AAEC/E226.

Littlechild, J.E. (1967) - Operational development of a uranium ore solution and extraction plant. I.Chem.E. Symposium Ser. No.26, 107-110.

MKU (1962) - Mary Kathleen, in AAEC (1962), pp. 37-50.

MKU (1978) - Mary Kathleen Uranium Ltd. Description of operations. Brochure.

Murray, R.J. & Fisher, W.J. (1968) - The treatment of South Alligator Valley uranium ores, in AIMM (1968), pp. 125-137. Also Atomic Energy in Australia, 13 (1), 2-8 (1970).

NA (1978) - Noranda Australia Ltd Koongarra Project: Draft Environmental Impact Statement, December 1978.

Page, H., Shortis, L.P. & Dukes, J.A. (1960) - The processing of uranium ore concentrates and recycle residues to purified uranyl nitrate solution at Springfields, Trans. Instn. Chem. Engrs, 38, 184-196.

PM (1977) - Pancontinental Mining Ltd The Jabiluka Project: Draft Environmental Impact Statement, December 1977.

QM (1979) - Queensland Mines Ltd Final Environmental Impact Statement Nabarlek Uranium Project, January 1979.

Ring, R.J. & Royston, D. (1973) - A review of fluorine cells and fluorine production facilities. AAEC/E281.

Royston, D., Ring, R.J., Burwell, A., LePage, A.H., Janov, J. & Vilkaitis, V.K. (1975) - AAEC Unpublished work.

RUM (1974) - Ranger Uranium Mines Pty Ltd Environmental Impact Statement, February 1974.

Ryan, R.K. (1973) - Optimisation study of the amine extraction of uranium ore, M.Sc. Thesis, University of New South Wales.

Scott, D.C., Adams, J.B. & Bresee, J.C. (1960) - Fluorox process: production of UF_6 in a fluidised bed reactor. ORNL-2797.

South Australian Department of Mines (1962) - Radium Hill, in AAEC (1962), pp. 21-28. Also Atomic Energy in Australia, 5 (1), 21-25 (1962).

Stewart, J.R. (1967a) - Status report from Australia, Processing of Low Grade Uranium Ores, Proceedings of a Panel, IAEA, Vienna, June 1965, pp. 3-8. Also Atomic Energy in Australia, 10 (1), 12-15 (1967).

Stewart, J.R. (1967b) - Uranium ore processing research in Australia, Processing of Low Grade Uranium Ores, Proceedings of a Panel, IAEA, Vienna, June 1965, pp. 67-78. Also Atomic Energy in Australia, 10 (2), 8-17 (1967).

Stewart, J.R. (1967c) - Rum Jungle uranium project. Atomic Energy in Australia, 10 (3), 2-9.

Stuart, W.I. & Whateley, T.L. (1969) - Composition and structure of ammonium uranates. J. Inorg. Nucl. Chem., 31, 1639-1647.

Takada, S., Amanuna, T. & Fukuda, G. (1971) - Uranium processing pilot mill at the Ningyo-Toge mine, Recovery of Uranium from its Ores and Other Sources, Proceedings of IAEA Symposium, Sao Paulo, Brazil, August, 1970, pp. 97-109.

WMC (1978) - Western Mining Corp. Yeelirrie Uranium Project W.A. Draft Environmental Impact Statement and Environmental Review and Management Program, June 1978.

DISCUSSION

A. ABRÃO: 1. Why do you use only 20% TBP kerosene instead of 30 to 35% for example?

2. When using 16 stages for stripping the uranium, how does this affect the economy of the process?

P.G. ALFREDSON: Our solvent extraction flowsheet was based on published UKAEA practice, as indicated in the paper, which uses 20 vol.% TBP in kerosene. Dr. Page may wish to comment on the reasons for this choice. We used multipurpose 16-stage mixer-settler units for our work and it was convenient therefore to devote one unit to the stripping operation. In a production facility, 12 stages at 60°C would be adequate.

S. SEN: 1. It appears that modifications are being made in the fluorex pilot plant, so that UF_6 can be produced by fluorination of UF_4 with fluorine. It is stated that 2000 kg of fluorine was produced. For the fluorex process, no fluorine is required. In that case what was the end use of the fluorine produced and how was it disposed of in the environment?

2. Can the author indicate the range of particle size of the UF_4, the bed height, the fluidization velocity and the pressure of the F_2 gas used for fluorination of UF_4 with fluorine?

P.G. ALFREDSON: The fluorine was destroyed by reaction with caustic potash solution which was regenerated with lime. The resultant calcium fluoride sludge was disposed of by hand burial. This took place in 1973.

We will be using both BNFL and CEA UF_4 for the production of UF_6 via fluorination with fluorine later this year. The powders we have are mostly −200 mesh BSS. Bed heights (of UF_4 in inert alumina) will be approximately 0.6 to 0.9 m. Fluidizing velocities will be $\sim 5 \times V_0$ (5 times minimum fluidizing velocity). The fluorine will be obtained from 6 lb cylinders at ~3.5 MPa when full.

M. PERARNAU: The flow diagrams proposed for the new Australian plants all include calcination of the concentrates produced. Is this calcination carried out to meet specifications, or also to obtain a better price per kilogram of U_3O_8 produced, so as to offset the additional cost of the operation?

P.G. ALFREDSON: It is intended that the proposed new mills will produce high-grade yellow cake products, consistent with conventional processing technology, which will readily meet the present specifications for yellow cake. Inclusion of drier-calciners, instead of only driers, does also give some flexibility for ironing out problems which may arise from earlier process steps and permits rather more to be packed in a drum for shipment.

H.E. JAMES: I have a comment to make regarding the reference, in the section "Current and proposed mills", of Dr. Alfredson's written text to continuous ion exchange (CIX). According to his reference NA 1978 "Noranda Australia Ltd. Koongarra Project: Draft Environmental Impact Statement, December 1978", CIX was not considered by the planners of their new uranium mill in the Northern Territory, because "recovery of uranium by CIX from unclarified solutions is regarded as not adequately proven". I wish to draw Dr. Alfredson's attention to a paper recently published in the journal of the Canadian Institute of Mining and Metallurgy (CIM Bulletin May 1979, p.127–134) by Boydell et al. entitled: "The new uranium recovery circuit at Blyvooruitzicht". In this paper details are given of the first year's operation of the NIMCIX plant for uranium recovery from unclarified acid leach liquors. This plant has now been in operation on a full industrial scale for 2 years and has demonstrated beyond doubt that CIX must be regarded as fully proven.

P.G. ALFREDSON: Thank you, Dr. James, for this information. Obviously, what constitutes best available proven technology will change as the years go by.

H. PAGE: As a comment and an answer to the first question of Mr. Abrão the reason for the choice of 20% volume/volume TBP in kerosene was that we did not want to encounter third-phase formation as is possible when higher concentrations of TBP in kerosene are used. Our plant, using 20% TBP can be loaded to 8% weight/volume uranium at forward extraction which is reduced to approximately 7% weight/volume uranium in the loaded solvent. A second point concerned economics of backwashing. We at Springfields use a 12-stage backwash and use heated backwash at 60°C (both solvent and water) and that takes out all the uranium from the solvent and gives a product concentration of uranium in the aqueous of between 11 and 12% weight/volume which is further concentrated by evaporation. I am not quite sure why you went to a 16-stage backwash, Dr. Alfredson.

P.G. ALFREDSON: The answer is simply that 16-stage units were convenient for pilot plant, affording plenty of stages for almost anything we might want to do in SX flowsheet development.

H. PAGE: I would agree with you in the sense that once you start building the box the difference in cost between 8, 10 or 12 stages for example is not all that much and it can be quite important in the economics of ensuring you get all the uranium into the right phase.

S. SEN: What about the decomposition of TBP when you strip at 60°C?

P.G. ALFREDSON: That has not been a problem that we have encountered in our pilot plant work. I am uncertain as to how many hundred hours we may have operated but we have not observed any problems in that regard. I should mention that we were washing our organic solutions with sodium carbonate and dilute acid as a routine procedure before they were recycled for extraction.

INFORME SOBRE EVOLUCION Y PERSPECTIVAS EN ESPAÑA

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Abstract–Resumen

PROGRESS REPORT AND FUTURE PLANS IN SPAIN.

Past and present uranium processing operations in Spain are described. Yellow cake concentrates have been produced in several plants; the total current output is approximately 220 t/a of U_3O_8. At present the major production is derived from the El Elefante installation, which uses a combination of heap leaching and amine solvent extraction. A new acid leach-amine SX plant (the Quercus installation) is under construction; this unit will have an output of 550 t/a of U_3O_8. Future plans for the recovery of uranium from phosphoric acid at Huelva and the planning for production of refined uranium products are also discussed.

INFORME SOBRE EVOLUCION Y PERSPECTIVAS EN ESPAÑA.

Se describen los procesos pasados y actuales de fabricación de concentrados de uranio en España. Los concentrados ("Yellow Cake") se producen en varias plantas; la producción total actual es aproximadamente de 220 t/a de U_3O_8. Actualmente, la mayor producción proviene de la instalación "El Elefante", donde se utiliza un proceso de lixiviación estática en pila y extracción con aminas. Se encuentra en contrucción una nueva planta de lixiviación-extracción con aminas (la instalación Quercus); esta unidad tendrá una capacidad productiva de 550 t/a de U_3O_8. Se exponen también planes futuros para la recuperación del uranio del ácido fosfórico en Huelva y trabajos para la fabricación de productos refinados de uranio.

1. INTRODUCCION

En España existen tres centrales nucleares en funcionamiento, una de ellas emplea como combustible uranio natural y las otras dos utilizan uranio enriquecido. Las centrales actualmente en construcción o en proyecto, pendientes de la aprobación del plan energético nacional, emplearán todas ellas uranio enriquecido.

Este planteamiento ha determinado la política seguida en España para establecer el producto final en el concentrado "Yellow Cake". En efecto, España no dispone de instalaciones para el enriquecimiento del uranio y, por consiguiente, esta operación se realiza en el extranjero (EE.UU., URSS y en un futuro en Francia a través de su participación en Eurodif), partiendo estas instalaciones del concentrado "Yellow Cake". El consumo de uranio natural, del orden de 125 t/a, no justifica económicamente el proceso de refino y las siguientes etapas para la obtención de los elementos combustibles.

Sin embargo, se ha dedicado también a esta parte un gran esfuerzo de investigación y desarrollo que ha cristalizado en unas instalaciones piloto que van desde el concentrado hasta la obtención de tetrafluoruro de uranio, y se dispone de la información necesaria para pasar a nivel productivo, caso de que las circunstancias así lo aconsejen.

2. OBTENCION DE CONCENTRADOS

2.1. Fábricas en funcionamiento

2.1.1. Fábrica de uranio General Hernández Vidal

2.1.1.1. Proceso inicial

Esta fábrica, con una capacidad de producción entre 60 y 80 t U_3O_8/a, empezó a funcionar a finales del año 1959, realizando la concentración mediante un sistema de cambio de ión en lecho fijo con elución nítrica. El producto final se basaba en la obtención de un concentrado sódico de uranio, en un proceso discontinuo.

Puesto que la fábrica trataba menas de distintas características, se obtenían eluidos de composición variable y, en función de esta composición, se utilizaban tres procedimientos alternativos de precipitación. El circuito era el mismo [1] y estaba formado por cuatro tanques agitados de 30 m^3 para precipitación discontinua y lavado del precipitado; dos filtros prensa de placas y marcos con una superfície filtrante de 15 m^2, provistos de sendas bombas de alimentación; un secadero de bandejas con una capacidad de 240 kg de concentrado por carga, que trabajaba a 110°C con circulación forzada de aire, calentado con vapor mediante un intercambiador de calor; dos tolvas de almacenamiento de concentrados desde las que se envasaba en bidones mediante un tornillo que reducía el tamaño al exigido en las especificaciones.

Los tres procedimientos empleados, en función de la calidad del eluido, fueron los siguientes:

- *Precipitación directa en una etapa.* Se aplicaba a menas que daban eluidos bajos en fosfato y hierro total. Se precipitaba a 40–60°C con NaOH al 30–33% hasta pH 7. La suspensión se dejaba decantar y el uranato espesado se lavaba con agua y, trás nueva decantación, se filtraba, secaba y envasaba.

- *Precipitación en dos etapas con cal y sosa.* El eluido se calentaba con vapor directo a 40–60°C y se añadía lechada de cal al 10% hasta pH 2,8, que evolucionaba hasta pH 3,0–3,2. Se dejaba decantar el precipitado, y se trasvasaba el líquido claro a otro tanque, filtrando el precipitado en uno de los filtros prensas. La torta se reciclaba a lixiviación para recuperar el uranio y el líquido, junto con el procedente de la decantación, se llevaba a otro de los tanques de precipitación, se calentaba a 40–60°C y se precipitaba con NaOH al 30–33%, siguiendo el mismo tratamiento que en la precipitación directa. Sin embargo, esta técnica presentaba varios inconvenientes. De una parte, la cantidad de uranio en la torta de la primera precipitación era alta y la calidad del producto final no siempre se ajustaba a especificaciones, por su elevado contenido en calcio y en sílice, aportada por la lechada de cal.
- *Precipitación fraccionada con sosa.* Para evitar los inconvenientes del proceso anterior se utilizó el siguiente procedimiento [2]: Se llenaba el tanque a precipitar y se analizaba la concentración de hierro y fosfatos. Se calentaba a 35–40°C y seguidamente se añadía sulfato ferroso hasta ajustar a una relación molar Fe/P igual a 2. La sal ferrosa se oxida en el medio nítrico del eluído a hierro férrico. A continuación se añadía NaOH al 30–33% hasta pH 3,0–3,2, precipitando fosfato férrico que se decantaba, previa adición de floculante y se filtraba. Los líquidos de filtración y decantación se trataban como en la precipitación en una etapa. De esta forma la cantidad de uranio reciclado en el precipitado es muy baja y el concentrado se ajusta a las especificaciones.

2.1.1.2. Proceso actual

En al año 1970 se sustituyó la etapa de cambio de ión por extracción con aminas, realizándose la reextracción con una solución de NaCl 1M acidulada con 5 g H_2SO_4/l. El equipo de precipitación se ha mantenido pero la precipitación se realiza con solución acuosa de amoníaco, a una temperaturade 45°C hasta llevar el pH del líquido a 7,0–7,5.

El concentrado precipitado (ADU) se decanta, se lava en el mismo tanque y, tras nueva decantación se filtra, seca y envasa como se hacía en el proceso inicial. Mediante control de la evolución del pH y manteniendo la temperatura en el valor indicado, se consiguen concentrados de características físicas aceptables para la sedimentación y filtración y dentro de especificaciones. Un análisis típico de los concentrados obtenidos es el siguiente (en tanto por ciento): U (72); SO_4 (6,2); Cl^- (0,12); Fe (0,35); Na (1,3); As (<0,1); Mo (<0,05), V_2O_5 (<0,2) $U_{insol.}$ ($<1{,}10^{-3}$). Las impurezas referidas al uranio.

2.1.2. Instalación "El Elefante"

Esta instalación, con una capacidad de producción de 125 t U_3O_8/a, utiliza un proceso de lixiviación estática en pila, recuperando el uranio de los líquidos fértiles mediante extracción con aminas y reextracción con una solución de NaCl 1M y 5 g H_2SO_4/l [3]. El extracto acuoso, con un contenido de 20–30 g U_3O_8/l, se precipita con amoníaco gas diluido con aire en proporción 1:5, en un sistema continuo formado par tres tanques agitados en serie, de igual capacidad.

Se controla el pH en cada tanque, 5,5 en el primero, 6,5 en el segundo y 7,5 en el tercero y, así mismo, la temperatura, ya que ambos parámetros son fundamentales para obtener concentrados de composición química y características físicas adecuadas [4].

El tiempo total de retención es de 1 h y el rebose del tercer tanque se envía a un decantador, al que se añade floculante y del que se extrae la pulpa espesa, que se repulpa con sulfato amónico y se decanta de nuevo en otro espesador cuya descarga se envía a un filtro rotativo a vacío en el que se lava con agua. Los reboses de los espesadores y filtro se pasan por filtros de arena para retener las partículas de uranato. Cuando la pérdida de carga en estos filtros aumenta, los sólidos retenidos se lixivian con ácido sulfúrico y esta solución se junta con el extracto acuoso que entra en precipitación.

La torta de filtración, con 50–60% p/p de sólidos, se envía a un tanque agitado y de él se bombea a unas bandejas que se introducen por cargas en una estufa, donde se calientan a 300°C. La calefacción se realiza con propano, calentando el aire que circula por la estufa en un cambiador de calor con los gases de combustión.

Tras el secado, las bandejas se descargan en una tolva a través de un triturador, que reduce el concentrado a un tamaño máximo de 6 mm. Desde la tolva se carga en bidones mediante un alimentador de tornillo. Un análisis típico de los concentrados obtenidos es el siguiente (en tanto por ciento): U_3O_8 (90); SO_4 (6,1); Fe (0,8); Cl^- (0,06); Na (0,8); $U_{insol.}$ (0,001); As (0,1); Mo (0,05); V_2O_5 (0,2).

Todo el conjunto se encuentra en un edificio separado del resto de la instalación, existiendo unos extractores de aire, que pasando a través de unos filtros de mangas, retienen los posibles polvos que puedan producirse. Hay un control de polvos y de la radiactividad ambiental.

2.1.3. Instalación Lobo-G

Se trata de una instalación experimental [5] con una capacidad de producción de 30 t U_3O_8/a y que, básicamente, está formada por dos líneas, una de lixiviación estática en pila y otra de lixiviación con agitación, lavado con ciclones en contracorriente, seguido de una etapa de resina en pulpa con elución sulfúrica en columna y extracción con aminas de la solución fértil de lixiviación juntamente con el eluído de cambio de ión. La reextracción se realiza con solución de NaCl 1M acidulada con 5 g H_2SO_4/l.

Los extractos acuosos, conteniendo 20–25 g U_3O_8/l, se precipitan con amoníaco gas diluido con aire en proporción 1:5, en un proceso continuo que se lleva a cabo en tres tanques agitados en serie, con un tiempo de retención total de 1 h. El pH se ajusta a 5,5, 6,5 y 7,5 en los tanques 1°, 2° y 3° respectivamente, manteniéndose la temperatura a 35–40°C. El precipitado se decanta en un espesador y la pulpa espesa se lava en un segundo decantador, enviándose la descarga de éste a un tanque agitado desde el que se alimenta al horno. Los reboses de los espesadores se pasan por sendos clarificadores para retener las partículas de uranato antes de reciclarlos a la preparación de agente de reextracción o de eliminarlos.

El concentrado del segundo espesador se bombea a un horno de solera múltiple, calentado con gas propano a 450°C, que trabaja en depresión mediante un extractor que envía los gases, junto con el polvo arrastrado, a una columna de platos, regada con el extracto acuoso que entra en precipitación, y que retiene las partículas de concentrado, el amoníaco y, al mismo tiempo, eleva la temperatura del extracto al valor necesario para la precipitación.

La descarga del horno se recoge en unos recipientes cerrados que se descargan en una tolva, a través de un triturador, y desde la que se llenan los bidones mediante un alimentador de tornillo. Todo este conjunto es estanco para evitar la salida de polvos de uranato. Los concentrados obtenidos dan una composición muy semejante a la citada en 2.1.2.

Toda la zona de tostación y manipulación del concentrado seco se ha ubicado en una nave independiente para reducir al máximo los problemas de polución. Dentro de la nave se lleva un control de partículas en suspensión y de la actividad de estas partículas.

2.2. Fábrica en proyecto

Actualmente se está construyendo una fábrica que trata una mena convencional de uranio y hay en proyecto dos instalaciones para la recuperación del uranio del ácido fosfórico.

2.2.1. Proyecto Quercus

Esta instalación [3], que actualmente está en construcción, tiene una capacidad de proyecto de 555 t U_3O_8/a y se basa en un proceso convencional en el que el uranio se recupera de la solución fértil mediante extracción con aminas y reextracción con sulfato amónico a pH controlado.

El extracto acuoso, que llega a pH 4,5–4,7 con 20 g U_3O_8/l y 200 g SO_4/l, se precipitará con amoníaco gas diluido con aire en relación 1:3, a una temperature de 35°C, de forma continua en tres tanques agitados en serie, controlando la distribución del pH en valores 5,5, 6,5 y 7,5 en los tanques primero, segundo y tercero respectivamente. El tiempo total de retención en el sistema es de 1 hora. En estas condiciones se obtienen concentrados de fácil manipulación y con un contenido en sulfatos suficientemente bajo [6].

El rebose del último tanque pasa a un decantador cuya descarga se centrifuga, lavándose en la misma centrífuga con agua. El rebose del espesador junto con los líquidos de centrifugación se pasan por unos filtros de arena carbón y se recirculan para la preparación del agente de reextracción.

La pulpa descargada de la centrífuga se recoge en un depósito agitado y se bombea a un horno de solera múltiple en el que se calcina a 350–400°C. El producto del horno, con un contenido mínimo previsto del 90% en U_3O_8, se recoge en una tolva desde la que se almacena en bidones.

2.2.2. Recuperación del uranio del ácido fosfórico

En la actualidad existen dos proyectos para la recuperación del uranio del ácido fosfórico, mediante un proceso de extracción en dos ciclos con D2EHPA-TOPO, realizándose la reextracción en el segundo ciclo con una solución acuosa 0,5M en $(NH_4)_2\ CO_3$ y adición de amoníaco gas para mantener el pH entre 9–10, valor al que precipita el tricarbonato de uranilo y amonia (AUTC).

Trás la separación por centrifugación del AUTC y lavado sobre la centrífuga, se calcina a 550°C obteniéndose un concentrado con 96–98% en U_3O_8.

Se están preparando dos proyectos para dos fábricas de ácido fosfórico, ambas situadas en Huelva, una que producirá 120 t U_3O_8/a partiendo de una capacidad de tratamiento de 3700 m^3/d de ácido fosfórico y otra más pequeña que producirá 30 t U_3O_8/a.

El diagrama de flujo se ha comprobado en una planta piloto, con una capacidad de 7 m^3/d de ácido fosfórico [7] montada en la fábrica propiedad de Fosfórico Español, S.A. en Huelva.

3. PROCESOS DE REFINO Y HEXAFLUORURO

En este campo la J.E.N. ha realizado un amplio esfuerzo investigador tanto para la purificación de concentrados de uranio, como para la obtención de óxidos, tetrafluoruro y hexafluoruro de uranio, materiales de partida para la fabricación de elementos combustibles.

3.1. Purificación de concentrados

Los primeros intentos de purificación se orientaron a utilizar el sistema nitrato de uranilo – eter etílico – agua [8–10] en columnas de pulverización y relleno.

Sin embargo, este proceso fué desplazado por otro que empleaba fosfato de tributilo. En la J.E.N. se montó una planta piloto para 10 t/a utilizando columnas pulsadas [11, 12].

En 1962 se empezó el estudio para la transformación del equipo, sustituyendo las columnas pulsadas por mezcladores sedimentadores [13]. Posteriormente se hicieron algunas modificaciones [14, 15] quedando: una zona de disolución y filtración, una nave de extracción con siete etapas de extracción, cinco de lavado, nueve de reextracción y dos de acondicionamiento de la fase orgánica y finalmente una zona de precipitación de ADU. La capacidad de esta instalación es de 1 t U_3O_8/d trabajando con una alimentación de 345 g U_3O_8/l con HNO_3 1M. Como agente de reextracción se emplea agua desmineralizada o de condensación, obteniéndose un extracto acuoso con 105 g U_3O_8/l. La temperatura de trabajo en reextracción es de 55°C.

Las mayores dificultades de este proceso se encontraron en la filtración de la suspensión de ataque con nítrico de los concentrados, que fue objeto de especial atención para conseguir la insolubilización de la sílice [16] que causaba los mayores problemas en extracción.

La instalación ha funcionado en diferentes campañas habiéndose obtenido más de 120 t de uranio de pureza nuclear así como la información necesaria, tanto en lo referente a proceso como a materiales y equipo, para la extrapolación a capacidades del orden de 3000 t U_3O_8/a, que se consideran necesarias para la rentabilidad de este proceso y que, caso de que las necesidades del programa nuclear español lo exijan, se utilizaría para su construcción.

3.2. Obtención de tetrafluoruro de uranio

3.2.1. Electrolisis

Los primeros trabajos para la obtención de tetrafluoruro de uranio se encaminaron a la reducción electrolítica de soluciones sulfúricas y precipitación con ácido fluorhídrico [17, 18]. Trás abandonar esta línea de investigación se volvió a considerar y se montó una planta piloto [19] formada por diez celdas con una capacidad total de 450 l y un caudal de electrolito de 50 l/h conteniendo 70 g U/l en forma hexavalente y 137 g $SO_4^=$/l. Trás un funcionamiento de varios meses, tiempo en el que se recopiló la información necesaria, se cerró esta actividad ya que la línea de trabajo en lecho fluido se presentaba más adecuada para la obtención de tetrafluoruro nuclearmente puro.

3.2.2. Fluoruración en lecho móvil

Los primeros estudios para la obtención de tetrafluoruro por vía seca se encaminaron a la fluoruración directa con bifluoruro amónico, realizándose un amplio trabajo de investigación a escala de laboratorio [20], en el que se abordó tanto el estudio del proceso como de materiales de construcción y que llevó a la construcción de un horno vertical continuo, de lecho móvil [21] alimentado con pellets de bifluoruro amónico y de diuranato amónico, procedente de la instalación de purificación con TBP.

Este horno piloto sirvió para comprobar el proceso así como los materiales de construcción necesarios en cada una de sus partes.

Sin embargo, dado que la utilización de la técnica de lechos fluidizados se presentaba más prometedora, se dirigió en este sentido el enfoque para la obtención industrial de tetrafluoruro y óxido de uranio.

3.2.3. Lechos fluidizados

En esta dirección se ha centrado el proceso de obtención de los compuestos, óxido de uranio UO_2 y tetrafluoruro que sirven de base para la preparación de elementos combustibles. Trás una serie de estudios [22–27], se eligió un proceso que, partiendo del extracto acuoso de la etapa de purificación, conteniendo 105 g U_3O_8/l, seguían cuatro etapas: evaporación hasta obtener una concentración de 1,180 g U/l correspondiente al hexahidrato $UO_2(NO_3)$. 6 H_2O; calcinación a UO_3; reducción con hidrógeno, de amoníaco craquizado, a UO_2 y, finalmente fluoruración con HF para obtener el tetrafluoruro de uranio.

Sobre la base de este diagrama se construyó una planta piloto [28] que incluía las cuatro etapas citadas y cuya capacidad era de 13 kg U/h en la etapa de fluoruración. Esta planta, además de varias campañas cortas para su puesta a punto, realizó una campaña de trabajo de diez meses funcionando 24 h/d y siete días por semana con un coeficiente de utilización del 82%.

Terminada esta campaña y con la información necesaria para poder diseñar una instalación de producción industrial, en el caso de que las necesidades del programa nuclear español así lo aconsejaran, se ha cerrado esta actividad.

3.3. Obtención de hexafluoruro y conversión

En esta línea se han hecho algunos trabajos que, realmente, no han pasado del nivel de laboratorio ya que, dado que no se ha planteado en España el problema del enriquecimiento del uranio 235, no se consideró necesario realizar una investigación más profunda [29].

Siguiendo la línea de la planta piloto de producción de tetrafluoruro de uranio comenzó el estudio de la obtención del hexafluoruro utilizando fluor en lecho fluidizado y posterior purificación por rectificación [30]. Sin embargo, los trabajos se pararon por las razones antes citadas.

REFERENCIAS

[1] JOSA, J.M., ESCUDERO, E., "La etapa final de obtención del concentrado de uranio", Fábrica de Uranio General Hernández Vidal, Junta de Energía Nuclear, Madrid (1966) 142–155.

[2] ESCUDERO, E., Precipitación de Eluidos de Cambio de Ión, Informe interno, JEN (1962).

[3] JOSA, J.M., El complejo fabril uranífero de Saelices el Chico (Salamanca), Energ. Nucl. 22 116 (1978) 381–391.

[4] MERINO, J.L., "Características de suspensiones de uranato amónico", Figura entre las Actas presentes.

[5] GASOS, P., GONZALEZ, E., OTERO, J., NADAL, P., "Instalación experimental para menas de uranio alteradas", Primer Congreso Mediterráneo de Ingeniería Química, Barcelona, 21–24 Noviembre 1978.

[6] RODRIGUEZ, B., "Obtención de concentrados de uranio – Purlex - de baja ley en sulfatos", Figura entre las Actas presentes.

[7] CORDERO, G., GUTIERREZ JODRA, L., OTERO, J.L., JOSA, J.M., "Recuperación del uranio del ácido fosfórico", Nuclear Power and its Fuel Cycle (Actas Conf. Int. Salzburgo, 1977) 2, OIEA, Viena (1977) 377.

[8] GUTIERREZ JODRA, L., PEREZ, A., OROZ, A., "The system uranyl nitrate-diethil ether-water, extraction by water in spray and packed columns from uranyl nitrate other solutions", Nuclear Engineering CEP, Symposium series **12** 50 (1954).

[9] OLTRA, F., PEREZ, A., GUTIERREZ JODRA, L., Extracción de nitrato de uranilo con éter, a partir de soluciones acuosas en columnas de pulverización, An. R. Soc. Esp. Fís. Quím., Ser. B **51** (1955) 501;

[10] PEREZ, A., El sistema nitrato de uranilo – éter etílico – agua, Tesis doctoral, Universidad de Madrid (1955).

[11] RAMOS, L., BERBERANA, M., PEREZ, A., GUTIERREZ JODRA, L., "Estudio en planta piloto de la purificación de concentrados de uranio mediante extracción con fosfato de tributilo", Peaceful Uses of Atomic Energy (Actas 2ª Conf. Int. Ginebra, 1958) **4**, NU, Ginebra (1958) 58.

[12] BERBERANA, M., "Purificación de uranio con TBP en una columna de laboratorio pulsada", Sté européenne d'énergie atomique (SEEA), Actas Simp. Extraction par solvant (1959).

[13] REGIFE, J.M., RAMOS, L., Purificación de concentrados de uranio en España, Primeras Jornadas del Forum Atómico Español, Madrid, mayo 1963, Ponencia II-d-7 (1963).

[14] REGIFE, J.M., RAMOS, L., BERBERANA, M., Planta de purificación de concentrados de uranio del Centro Nacional de Energía Nuclear Juan Vigón, Rev. Metal. (Madrid) **3** 1 (1967);

[15] BERBERANA, M., SAN SEGUNDO, T., Purificación de concentrados, Energ. Nucl. **77** (1972) 321–332.

[16] SAN SEGUNDO, T., Filtración de disoluciones nítricas de concentrados de uranio, Tesis doctoral, Universidad Central de Madrid (1970).

[17] BATUECAS, T., ACEÑA, M., DE LA CRUZ, F., FERNANDEZ CELLINI, R., "Obtención de fluoruro de uranio (IV) por electrolisis con cátodo de mercurio", Peaceful Uses of Atomic Energy (Actas 2ª Conf. Int. Ginebra, 1958) **4**, NU, Ginebra (1958) 73.

[18] ACEÑA, M.L., et al., Estudio de la preparación de fluoruro de uranio y amonio par electrolisis con cátodo de mercurio, An. R. Soc. Esp. Fís. Quím., Ser. B **59** (1963) 85.

[19] ESTEBAN, A., et al., Obtención de UF_4 por reducción electrolítica, Informe interno JEN 278, Madrid (1974).

[20] PEDREGAL, J., AGUILAR, F., "Obtención de UF_4 por el método de fluoruración directa", Peaceful Uses of Atomic Energy (Actas 2ª Conf. Int. Ginebra, 1958) **4**, NU, Ginebra (1958) 88.

[21] PEDREGAL, J., AGUILAR, F., Un nuevo método de obtención de tetrafluoruro de uranio, Energ. Nucl. **3** (1959).

[22] GONZALEZ, V., RODRIGO, A., International Powder Technology and Bulk Solids Conference, Harrogate, Reino Unido, mayo 1971.

[23] BRIGGS, G.C., y colab., USAEC Report NLCO-685 (Junio 1957) 52.

[24] HARRINGTON, C.D., RUEHLE, A.E., Uranium Production Technology, D. Van Nostrand Company Inc. Princeton, New Jersey (1959) 80.

[25] RODRIGO OTERO, A., CORELLA TUDANCA, J., An. R. Soc. Esp. Fis. Quím., Serie B. Química **67** 12 (1971) 1207.

[26] FERNANDEZ RODRIGUEZ, L., Trabajo presentado a la XIII Reunión Bienal de la Real Sociedad Española de Física y Química, 1967, Pendiente de publicación en los An. R. Soc. Fís. Quím.

[27] RODRIGO OTERO, A., RODRIGUEZ HERNANDEZ, B., FERNANDEZ RODRIGUEZ, L., JEN 166-DMa/I 20, Madrid (1966).

[28] RODRIGO OTERO, A., GONZALEZ, V., Obtención de UO_3, UO_2 y UF_4, Energ. Nucl. **77** (1972) 333–353.

[29] GUILLEN, J.M., DARNAUDE, N., Obtención de hexafluoruro de uranio a partir de tetrafluoruro utilizando fluor como agente de fluoración, Energ. Nucl. **5** (1961).

[30] ESTEBAN, A., ROJAS, J.L., Aspectos generales de la purificación por rectificación del hexafluoruro de uranio, Energ. Nucl. **78** (1972).

THE QUALITY ASPECTS OF URANIUM MILL AND CONVERSION PLANT TECHNOLOGY

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Abstract

THE QUALITY ASPECTS OF URANIUM MILL AND CONVERSION PLANT TECHNOLOGY.

The feed to the conversion plant is solid uranium concentrates, with individual ore and mill characteristics, from approximately 40 sources, ammonium diuranate slurry, and uranium fluoride slurry. Process problems in solvent extraction, process condition adjustments and blending to effect solvent extraction separation of impurities are discussed. The plant methods used to control and remove subsequent impurities from uranyl nitrate are described as it is converted to enrichment grade uranium hexafluoride.

1. SOURCES OF FEED TO CONVERSION

All feed to the Kerr-McGee Nuclear Corporation Sequoyah Conversion Facility was dried ore concentrates through 1977. In the last 12 months over 98% of the feed was dry concentrates. The balance was a slurry of ammonium diuranate. There are several sources of secondary uranium becoming available. An additional uranium fluoride concentrate will be used for a conversion feed material in equipment now in the start-up phases of operation at Kerr-McGee's Sequoyah Conversion Facility.

There is increasing interest in slurries. There are two primary reasons to ship slurry. Environmental considerations in the case of an accident favour a heavy-wall tank. There is an economic incentive by saving drying energy. The drying capital cost is substantial because of the required dust control. In an economic evaluation, the drying energy costs must be compared with transportation and disposal costs at the conversion facility. Some additional needs for slurry processing arise where a mill or drying equipment are not near the uranium sources as in the case of smaller in-situ operations.

TABLE I. SEQUOYAH CONCENTRATE SUMMARY – JANUARY 1978 TO DECEMBER 1978[1]

				SOURCES												
ITEM	SPECIF.^{2} %	REJECT LIMIT %	1978 AVG. OF ALL LOTS	1	2	3	4	5	6	7	8	9	10	11	12	13
Number of Lots			>600	<50	<50	<20	<20	<20	>200	<20	<50	<50	<20	<20	<20	<20
Uranium^{4}	60.0 or 62.5 Min	62.5^{7}	75.70	71.24	76.94	78.72	68.71	70.00	74.55	77.47	71.34	75.92	76.15	80.88	80.59	79.38
1. Extractable Organic^{5}	0.10	0.10	0.03	0.05	0.02	0.03	0.18	0.02	0.02	0.01	0.04	0.04	0.02	0.02	0.02	0.02
2. Nitric Acid Insoluble U^{6}	0.10	0.10^{8}	0.03	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.11	0.28	0.04	<0.01	0.01	0.01
3. Molybdenum(Mo)^{6}	0.15	0.75	0.07	<0.01	<0.01	<0.01	0.11	<0.01	0.08	0.12	<0.01	0.16	0.02	0.21	0.38	0.79
4. Vanadium (V)^{6}	0.10	0.85	0.05	0.04	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.07	0.25	0.18	<0.01	0.07	<0.01
5. Calcium (Ca)^{6}	1.00	1.50	0.26	1.53	0.64	<0.05	<0.05	0.59	0.10	0.10	0.34	0.51	0.32	<0.05	0.19	0.16
6. Thorium (Th)^{6}	2.00	2.50	0.07	<0.05	<0.05	<0.05	<0.05	1.00	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
7. Zirconium (Zr)^{6}	2.00 or 0.50	0.50	<0.30	<0.30	<0.30	<0.30	1.38	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30	<0.30
8. Boron (B)^{6}	0.15	0.15	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	<0.010	0.01	<0.010
9. Phosphorous(P)^{6}	0.35	0.70	0.08	<0.05	<0.05	<0.05	0.06	0.06	<0.05	<0.05	0.42	0.11	0.05	<0.05	<0.05	0.05
10. Halogens (Cl,Br, I as Cl)^{6}	0.25	0.50	0.14	0.08	<0.05	<0.05	<0.05	<0.05	0.19	<0.05	0.39	<0.05	<0.05	<0.05	0.33	0.51
11. Fluoride (F)^{6}	0.15	0.15	<0.01	0.01	0.01	<0.01	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	0.02	0.01
12. Carbonate(CO_3)^{6}	2.00	3.00	0.18	0.61	0.17	0.06	2.88	0.26	0.09	0.37	0.11	0.02	0.07	0.02	0.14	0.15
13. Sulfur (S)^{6}	3.50	4.50	0.92	1.54	0.83	2.08	0.39	1.64	0.77	0.90	0.70	0.34	1.02	1.35	0.59	1.11
14. Arsenic (As)^{6}	1.00	2.00	<0.05	<0.05	<0.05	<0.05	<0.05	0.06	<0.05	<0.05	<0.05	0.15	<0.05	<0.05	<0.05	<0.05
15. Amenability Drop Test^{5}	5.0	5.0	4.4	4.4	4.4	4.3	4.4	4.7	4.3	4.5	4.4	4.6	4.2	4.4	4.4	4.4
16. Sodium (Na)^{6}	---	---	1.49	0.82	2.98	0.01	15.75	0.71	1.59	0.10	3.00	2.28	2.34	0.03	0.13	0.15
17. Magnesium (Mg)$^{6-7}$	1.00	1.50	0.08	0.80	0.18	<0.01	0.05	0.01	0.02	<0.01	0.06	0.02	0.02	0.01	0.06	0.03
18. Iron (Fe)$^{6-7}$	1.50	2.00	0.66	0.62	0.41	0.21	0.17	0.49	0.26	0.17	3.79	2.26	0.50	0.21	0.21	0.13
19. Silicon (Si)$^{6-7}$	1.00	1.50	0.56	0.90	0.41	0.22	0.21	0.70	0.23	0.15	2.55	0.59	1.26	0.29	0.59	0.31
Loss on Heating at 110°C^{5}	7.50^{7}	7.50	2.40	6.35	0.92	0.39	2.13	0.67	4.33	0.64	2.73	0.03	0.40	0.05	0.58	0.90

[1] *Average of the results for each of the tests are shown for the number of lots received in the laboratory during the period.*

[2] *Specifications shown are for limits without penalty.*

[4] *Net sample weight basis.*

[5] *Concentrate as-received basis.*

[6] *Uranium basis.*

[7] *Not a specification for all contracts.*

[8] *A uranium yield penalty is applied.*

2. EXAMINATION OF FEED ANALYSES AND CONTAMINANTS

While the probability of an increase in slurry is likely, the major conversion feed has been dry ore concentrates. Solid ore concentrates have been received from approximately 40 mills in 9 years of operation. The contaminants in the ore concentrate have been found to be very important. The two major concerns are that the final UF_6 product meets enrichment specifications and that the solvent extraction feed does not cause process upsets or reduce uranium recovery.

A summary of the 1978 analytical results of several hundred lots of concentrate is included in Table I. Both United States of America and other sources of concentrate are included. A lot is a quantity of material as defined by the shipper. The number of drums in a lot ranged from 27 to 71. To eliminate sources with start-up impurities and to have a sufficient number of lots for comparison, those sources with six or less lots have been eliminated from Table I. The average analysis applies to all lots received in 1978.

The 13 remaining sources will be examined by each contaminant or analysis. An arbitrary value of twice the overall average for 1978 was chosen for this presentation. For investigation of the cause of the anomalies, two sources of processing information were used. One was *The Extractive Metallurgy of Uranium* by Robert C. Merritt, 1971. The other was the Appended Table A of Uranium Extraction Flow Sheets from *Uranium Ore Processing,* IAEA, 1975.

The objective is to determine where contaminants can be related to the mill process. In some instances the flow sheets were not available. The analysis will be reviewed by item in the left column. The source or mill is identified only by number due to possible proprietary concerns. Most values are on a percent-of-uranium basis. In Table I it should be noted that some contaminants can be above the specification and be processed with a surcharge. The column adjacent to the specification column is the present reject level.

2.1. Discussion of mill impurities

(1) Extractable organic – The 0.18 was from source 4, for which the flow sheet was not available. From occasional past investigations this is sometimes due to a mill equipment problem.

The ore concentrate in source 4, which exceeded the extractable organic, was accepted, due to unusual circumstances, with a mutually agreed surcharge.

(2) Nitric acid insoluble – Sources 8 and 9 have very similar flow sheets. The 0.11 and 0.28 are several times the average of 0.03. It should be noted that these two sources have a total of 12 analyses that are twice the average. Sodium and iron are particularly high. These sources, due to a lack of secondary purification, do not produce as pure an ore concentrate as the others.

(3) Molybdenum and Vanadium – Many of the mills utilize
& (4) separate molybdenum and vanadium recovery circuits. Accordingly no review was made of these contaminants.

(5) Calcium – Both source 1 and 5 use lime in the precipitation. The source 2 flow sheet was not available.

(6) Thorium – The source of this material suggests that the thorium is related to the ore body rather than to the process.

(7) Zirconium – As mentioned previously this flow sheet for source 4 was not available. It is of interest that sodium and carbonate are also high and the uranium is the lowest of these 13 sources.

(8) Boron – All sources were below 0.01.

(9) Phosphorous – This single occurrence is from source 8 which does not have any secondary purification.

(10) Halogens – Reported as chloride – In source 6 a chloride is used in the stripping operation. Also a chloride is used just prior to the precipitation in source 8. The flow sheets are not similar. The flow sheets for sources 12 and 13 were not available. Source 6 is not twice the average, but does illustrate a process relation.

(11) Fluoride – Any fluoride present in the ore, or that enters the mill process, may be partially combined as an acid-insoluble compound. Source 5 would precipitate any soluble fluorides. The flow sheet for source 12 was not available.

(12) Carbonate – In source 1, a precipitation from a carbonate solution is used. In source 7 a secondary stream of uranium is precipitated and is a carbonate-bearing material. This material is fed to the mainstream of the mill just prior to final precipitation. As stated previously, the flow sheet from source 4 was not available.

(13) Sulphur – The flow sheet for source 3 was not available.

(14) Arsenic – In source 9 this is probably due to the process, since there is no secondary purification. This source has six contaminants that are twice the average.

(15) Amenability drop test – This test is designed to avoid a class of surfactants. These surfactants reduce efficiency in the re-extraction of the uranium. Surfactants have been known to cause emulsions in primary extraction.

(16) Sodium – The flow sheets for sources 2 and 4 were not available. Again, source 8 has no secondary purification.

(17) Magnesium – In the source 1 processing, magnesium is used in the final precipitation. The source 2 flow sheet was not available.

(18) Iron – Both occurrences of iron are from sources 8 and 9 which, again, do not have secondary purification.

(19) Silicon – The quantity present in source 8 is absent from source 9 which has a very similar flow sheet.

Possibly the occurrence in source 8 is due to silicon entrapped or attached material in IX that is removed in elution. In source 10 a sodium carbonate type leach is used. This is known to allow silicon in the product unless there is a subsequent decontamination step in the process which causes silicon separation.

3. THE CAUSES OF ORE CONCENTRATE CONTAMINANTS

From this review of ore concentrate contaminants there is sufficient information to conclude that the mill process flow sheet is of primary significance. In one case, thorium, the primary contaminant cause is thought to be due to the ore, as previously stated.

4. PROCESS DESCRIPTION OF SOLVENT EXTRACTION AND CONVERSION

4.1. General

The ore concentrate is weighed and sampled, digested and then purified through solvent extraction. The uranyl nitrate is denitrated to UO_3, reduced with hydrogen to UO_2, hydrofluorinated with anhydrous HF to UF_4 and finally fluorinated to UF_6 using elemental fluorine.

4.2. Sampling plant

The sampling plant is a two-stage falling stream type, similar in function to one that was used by the USAEC at Grand Junction, Colorado. The weight of the sample collected is approximately 1.0% of the lot weight.

4.3. Digestion and solvent extraction

The ore concentrate is digested in nitric acid. This feed to solvent extraction is about 500 g of uranium per litre and is 1.5 N in free nitric acid.

Solvent extraction is performed with a solvent of 30 volume % tributyl phosphate (TBP) in hexane.

The aqueous feed solution is mixed with solvent in centrifugal pumps and discharged into decanters for phase separation. There are six primary pumper-decanters and two scrub decanters, (to remove some contaminants, e.g. part of the molybdenum). Re-extraction is performed in a pulse column with < 0.01 N HNO_3 in water.

This pure solution of uranyl nitrate is concentrated by evaporation first from about 80 g/ltr to 450 g of uranium per litre of solution. A second evaporation concentrates the solution to 1000 to 1200 g of uranium per litre, as molten uranyl nitrate hexahydrate.

4.4. Conversion of pure $UO_2(NO_3)_2$ to UF_6

The uranyl nitrate is denitrated in four horizontal continuous calciners to UO_3. The UO_3 is reduced to UO_2 in a two-stage fluid bed reactor with dissociated ammonia as the hydrogen source.

The UO_2 is hydrofluorinated in two mechanically stirred fluid beds to produce UF_4. The UF_4 is reacted with elemental fluorine in a tower-type reactor to UF_6. The nominal capacity is 9000 t of uranium per year.

The fluorine is supplied from a 60 cell, 6000 A fluorine plant.

5. PROBLEMS AND CONTROL OF CONTAMINANTS IN SOLVENT EXTRACTION

5.1. Problems in solvent extraction

The contaminant problems in the operation of solvent extraction (SX) can be grouped generally into physical blockages, emulsions and occasional carry over of contaminants into the re-extraction pulse column.

The most frequent physical blockage occurs from the collection of sand and other particles in the decanter bottom control valve. This results in failure of the aqueous stream to discharge and raises the aqueous-solvent interface. The higher aqueous level decreases phase disengagement volume and can cause aqueous entrainment with the solvent into the scrub section. This type of problem is occasional and can be managed, but it is anticipated that sand-particulate removal equipment will be added.

There has been much discussed and written about the cause of emulsions. The writer's opinion is that when normally identifiable causes are absent, the cause is probably for multiple reasons. It also appears that the causes are not arithmetically additive but possibly an exponential function.

Some of the known contributors to emulsions will be discussed. The element silicon, not as sand but as a hydrated compound,is frequently present. Iron is another element that is noted. A third element that is found is zirconium. The silicon and iron based materials appear to have higher volume to weight ratios than other materials.

Another category of causes of problems is the degradation of solvent into mono- and di-butyl phosphates. The degradation products are usually accompanied with high uranium in the raffinate. Monobutyl phosphate is soluble in the aqueous phase. Others have established that zirconium will combine with the di-butyl phosphate and cause emulsion-type problems.

A separate type of problem is the phosphate. It usually orginates with the feed. The phosphate and the silicic acid can, with molybdenum (or possibly vanadium), form a heteropoly acid. This can cause contamination by carry over of molybdenum into the SX product.

5.2. Corrective measures for SX problems

When silicon compounds are observed from SX or digestion samples, the digestion time period is increased to 1.5 to 2.0 h at 220°F.

Carry over of contaminants, particularly Mo, by attachment to incompletely saturated TBP can occur. This is averted by keeping the TBP near 95% uranium saturation as it enters the re-extraction pulse column.

The rework of solvent to keep it free of degraded TBP and uranium is done in two steps. Ammonium sulphate is used to remove free uranium from the stripped solvent. The second step is a treatment with sodium hydroxide. The NaOH removes mono- and di-butyl phosphates. Additionally, it strips any attached uranium from the TBP. This clean solvent is the liquid that contacts the raffinate or waste stream (aqueous) before the raffinate exits.

Thorium is controlled by processing with certain materials which render the thorium insoluble. The thorium then continues in the aqueous phase to the waste stream. The zirconium compounds appear to exhibit the same lack of solubility.

As a general practice when a source of concentrate is known to cause emulsions these materials are blended with 'good' feed. This is a practical approach to the emulsion problem but there must be available sufficient quantities of good concentrate.

At times, the solvent extraction system develops emulsions in normal operation without a definable cause. A laboratory check is made for silica. According to the literature, when hydrated silica is present an acidity increase will sometimes correct the problem. During emulsion problems the solvent recycle rate around the decanters may be reduced to increase the phase separation. A third action is verification that the solvent is 95% uranium saturated.

As with many processes, one element has been selected as a process control. This element is Mo and is run twice each shift when there are no indications of problems.

In reviewing the contaminants and these process controls to produce pure $UO_2(NO_3)_2$, it should be noted that these observations are from a production viewpoint. When this facility was placed in operation, nearly 20 years of previous similar operations had occurred. When there is no adverse affect upon production rate, the quality of the product or the environment, there is little additional effort to determine precisely how a contaminant acts or reacts with the process.

5.3. Raffinate disposal

The solvent extraction aqueous waste or raffinate is a source of ammonium nitrate. In some undeveloped areas this may be of particular economic value.

Most of the concentrates are ammonium diuranate which produces an acid solution containing NH_4NO_3. This solution is neutralized with anhydrous ammonia.

6. CONTROL OF CONTAMINANTS IN CONVERTING PURE $UO_2(NO_3)_2$ to UF_6

6.1. Purity of uranyl nitrate and re-contamination

The uranyl nitrate from SX is sufficiently pure and has met specifications for blending into reactor UO_2 pellets. There is some re-contamination of the product with chromium from stainless steel equipment. The fluorination process actually reduces the molybdenum concentration slightly. There has been at least one known occasion where boron entered with anhydrous HF. The product UF_6 can contain HF which must be controlled to be less than 75 lbf/in^2 abs. at 200°F.[1]

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[1] 1 lbf/in^2 = 6.895×10^3 Pa.

6.2. Chromium control

The boildown (second evaporation) equipment, denitrators and reduction equipment are of stainless steel construction. Chromium is introduced, primarily from boildown. As the uranium proceeds through the process to fluorination, chromium fluorides are formed. This chromium fluoride chemistry is complex and will not be discussed. These contaminants are solidified in the heat exchangers that separate the UF_6 by solidification from other gases. The chromium fluoride compounds are particulates that are filtered from liquid UF_6 by using sintered monel filter tubes.

6.3. HF control

Control of HF is achieved by limiting the HF entering fluorination with the fluorine. This is accomplished by refrigerating the fluorine gas to -100 to -120°F which partially condenses the HF. In a period of malfunction of this refrigeration equipment, excessive HF is condensed with the UF_6. In this case a gas rich in HF with some UF_6 is withdrawn from the full UF_6 cylinder into cold UF_6 solidification heat exchangers.

7. INCENTIVES FOR HIGH PURITY ORE CONCENTRATE OR URANIUM COMPOUNDS

7.1. Mill designs, ore bodies and purity

The uranium mills are designed for a primary ore-body source. Mills accept ore from several sources. Due to shipping costs, in most cases, the ores will be of similar geological materials. Several mines can be served by one mill.

From a purification and conversion viewpoint, the economic penalty for processing materials of low quality may not be high enough. The value of contained uranium has increased to the point that concentrate reprocessing costs or capital costs for higher purity are greater than the penalty paid for conversion of ‘out of specification’ material. This is the writer’s view which is primarily from a purification and conversion viewpoint.

7.2. Production and capital costs for uranium compounds

The materials of construction for solvent extraction and conversion are exotic as compared to most parts of the ore processing mill. Stainless steel is used from digestion through reduction, monel and inconel are used in hydrofluorination, monel is used in fluorination and part of the fluorine system.

Purification and conversion will always be necessary for some concentrates. Production costs are lower at higher rates. A conversion plant can receive materials from about 40 concentrators so there may not be an economic optimum matching with a mill to produce UO_3, UO_2 or UF_4.

Environmental disposal of nitrates and/or fluorides would be a difficult problem. The severity would depend upon the mill processes.

It is thought that a unique process, e.g. the Excer or Japanese PNC, may present a break-through. Hydrated UF_4 would not be acceptable fluorinational feed.

8. CONCLUSION

The solvent extraction purification of uranium concentrates and conversion to UF_6 is a versatile process. This statement is supported by the receipt of about 40 dry concentrates, ammonium di-uranate slurry and uranium fluoride slurry. The process produces enrichment grade UF_6 consistently.

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DISCUSSION

P. MICHEL: I should like to ask Mr. Craig what type of difficulty can be expected from the presence of extractible organics in the ore concentrate. Is this a question of emulsions in the solvent extraction, or something else?

J.W. CRAIG: The extractible organics test is to detect one class of surfactants that cause problems as emulsions in the re-extraction of pure uranium into water (with 0.01 N nitric acid).

S.A. YOUNG: Mr. Craig referred to the probable increase in shipment of slurry to save the cost of drying. This presumably depends on costs of transport and drying, but in his experience what transport distances seem to make this advantageous?

J.W. CRAIG: One slurry source has been shipping 400 to 500 miles. A second source is about the same distance but slightly (perhaps 100 miles) greater.

Kerr-McGee is also considering shipping from their own mill which is over 800 miles.

H. PAGE: 1. Have there been any problems of crystalization between digestion and solvent extraction?

2. In view of the range of concentration being processed at Kerr-McGee has he considered filtration between digestion and solvent extraction?

J.W. CRAIG: 1. There has been one problem, in the last 2 to 3 years, with crystalization but this was at about 700 g/ltr which is well above the 500 g/ltr normally used.

2. Yes, filtration has been considered and would be helpful, it would reduce some general S-X problems.

S. SEN: 1. When you are referring to boron specification, is it elemental boron or boron equivalent of the elements with high neutron capture cross-section?

2. In paragraph 4 of sub-section 5.2, there is a mention of "certain materials which render the thorium insoluble". Can you please give some details of these materials?

J.W. CRAIG: 1. In the case of boron the concentration was as elemental boron. All sources were at a low level which was $<0.05\%$ on a U basis.

2. The mention of "certain materials" with thorium is somewhat proprietary. It is suggested that a handbook on thorium compounds will show some insoluble thorium compounds which may be helpful on specific processes.

B.C. SMART: What has been the experience processing uranium fluoride slurries, and what level of fluoride will be accepted without penalty?

J.W. CRAIG: The fluoride slurry equipment has been 'shaken down' with ADU slurry. The supplier has not delivered material, so there is no operating experience.

The additional costs were covered by contract price for the fluoride slurries. Thus, there is not a penalty since these costs were negotiated into the price for conversion.

DU CONCENTRE D'URANIUM A L'HEXAFLUORURE

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Abstract–Résumé

FROM URANIUM CONCENTRATE TO HEXAFLUORIDE.

The paper describes the type of uranium concentrates received at the Malvesi plant, the refining process and the preparation of UF_4 and uranium metal of that plant. The processes operated at Pierrelatte for converting UF_4 to UF_6 are described. The paper concludes with tabulations of data on specifications and properties of the various materials and a description of analytical procedures.

DU CONCENTRE D'URANIUM A L'HEXAFLUORURE.

Le mémoire ci-après décrit le type de concentrés d'uranium que reçoit l'usine de Malvesi, les opérations de raffinage et la production d'UF_4 et d'U métal dans cette usine. L'auteur décrit aussi les procédés utilisés à Pierrelatte pour transformer l'UF_4 en UF_6. On trouvera à la fin du mémoire des tableaux qui renseignent sur les spécifications et les propriétés des différentes matières, et un exposé des méthodes d'analyse.

1. GENERALITES

Dans le cycle du combustible, la *conversion* désigne l'ensemble des opérations physico-chimiques qui vont contribuer à la transformation de l'uranium contenu dans les concentrés, soit en métal, soit en hexafluorure, de pureté nucléaire.

Le marché mondial de la conversion, lié au développement des réacteurs à uranium enrichi, si l'on fait exception de la Chine et de l'URSS, intéresse cinq producteurs du monde occidental:

Sociétés productrices	Productions (t) 1977	Productions (t) 1980
Kerr Mac Gee (Etats-Unis)	4 500	9 000
Allied Chemical (Etats-Unis)	12 000	12 000
Eldorado (Canada)	4 500	4 500
BNFL (Grande-Bretagne)	5 000	9 000
COMURHEX (France)	8 000	12 500
	34 000	43 500

Créée en décembre 1970, la société COMURHEX (Société pour la conversion de l'uranium en métal et hexafluorure) regroupe les moyens de l'industrie privée et du Commissariat à l'énergie atomique dans le domaine de la conversion chimique de l'uranium. C'est une filiale à 51% de la Société du cycle de l'uranium Péchiney Ugine Kuhlmann (SCUP), à 39% de la Compagnie générale des matières nucléaires (COGEMA) et à 10% de la Compagnie de Mokta.

Deux usines participent à la transformation des concentrés. L'usine de Malvesi, située près de Narbonne (Aude), effectue l'extraction et la purification de l'uranium ainsi que la transformation en tétrafluorure (UF_4) et en lingots de métal. La capacité de traitement est actuellement de 8000 t, dont 7000 t pour l'UF_4 et 1000 t pour le métal. Les concentrés venant de France ou de l'étranger, ainsi que les réactifs, sont livrés par route et par fer. Le tétrafluorure est expédié à l'usine de Pierrelatte en camions citernes spécialement aménagés.

L'usine de Pierrelatte (Drôme) produit de l'hexafluorure (UF_6) depuis 1962. La capacité de l'usine, du niveau de 8000 t en 1977, pourrait atteindre 12 500 t en 1980. A l'occasion de cette extension, Pierrelatte utilisera un nouveau procédé dans lequel le concentré, sous forme d'oxyde ou de diuranate d'ammonium (DUA), est transformé directement en tétrafluorure, puis en hexafluorure dont les impuretés sont éliminées par distillation fractionnée.

L'hexafluorure fabriqué à Pierrelatte est destiné:

- aux usines d'enrichissement par diffusion gazeuse:
  - l'usine de Pierrelatte CEA
  - les trois usines américaines
  - les usines soviétiques;
- à l'usine d'enrichissement par ultra-centrifugation d'Almelo (Pays-Bas) du Groupe URENCO, auquel participent l'Allemagne fédérale, les Pays-Bas et la Grande-Bretagne;
- ultérieurement, à l'usine d'Eurodif.

L'hexafluorure est expédié par route, fer et mer, en conteneurs spéciaux d'un poids unitaire de 8,5 t d'uranium.

2. LES CONCENTRES

L'usine de Malvesi reçoit des concentrés solides et liquides. Les concentrés solides, livrés en fûts de 200 litres et en conteneurs de 1 m^3, sont essentiellement des uranates de magnésium, de sodium, parfois d'ammonium et, quelquefois, des oxydes. Les concentrés liquides sont uniquement des nitrates d'uranyle.

Exception faite de quelques lots d'uranium appauvris ou légèrement enrichis en provenance des usines de retraitement, les concentrés d'uranium naturel sont d'origines très diverses: ils viennent soit de France (Bessines, Ecarpière, Forez, Gueugnon), soit de l'étranger (Niger, Gabon, Afrique du Sud . . .). A leur entrée dans l'usine, les concentrés seront très soigneusement échantillonnés et analysés.

3. LA PURETE NUCLEAIRE

Deux voies peuvent être et sont effectivement utilisées pour obtenir la pureté nucléaire indispensable pour que l'uranium puisse être utilisé ultérieurement dans les réacteurs de puissance: la voie humide, qui consiste à éliminer les impuretés dès le début de la conversion (fig. 1), et la voie sèche, qui permet d'éliminer les impuretés au dernier stade de la conversion (fig. 2).

Les opérations physico-chimiques mises en œuvre dans la **voie humide** sont les suivantes:

- la dissolution des concentrés, à l'aide d'acide nitrique;
- la purification du nitrate d'uranyle par solvant en colonnes pulsées;
- la précipitation du diuranate d'ammonium ou DUA;
- la calcination du DUA en UO_3;
- la réduction de l'UO_3 en UO_2;
- l'hydrofluoration de l'UO_2 en UF_4;
- fluoration de l'UF_4 en UF_6.

Les opérations physico-chimiques de la **voie sèche** sont les suivantes:

- calcination du DUA en UO_3;
- réduction de l'UO_3 en UO_2;
- hydrofluoration de l'UO_2 en UF_4;
- fluoration de l'UF_4 en UF_6;
- purification de l'UF_6 par distillation.

Actuellement, la voie humide est la seule méthode économique susceptible de conduire simultanément, via l'UF_4, au métal utilisé dans les réacteurs graphite-gaz et à l'oxyde fritté UO_2 enrichi dans les réacteurs à eau légère.

La voie sèche, théoriquement aussi valable que la précédente, permet par contre, en assurant la pureté nucléaire au dernier stade de la conversion, de corriger à moindre frais toute pollution accidentelle dans le cycle de fabrication. Il est fort possible que, dans un avenir assez proche, les mineurs s'orientent de plus en plus vers la production de concentrés susceptibles d'être traités directement par la voie sèche, en particulier d'oxydes, de DUA et même de tétrafluorure de voie aqueuse. Les dernières traces d'impuretés de ces concentrés, préalablement purifiés sur le site minier, seraient en effet susceptibles d'être éliminées par distillation.

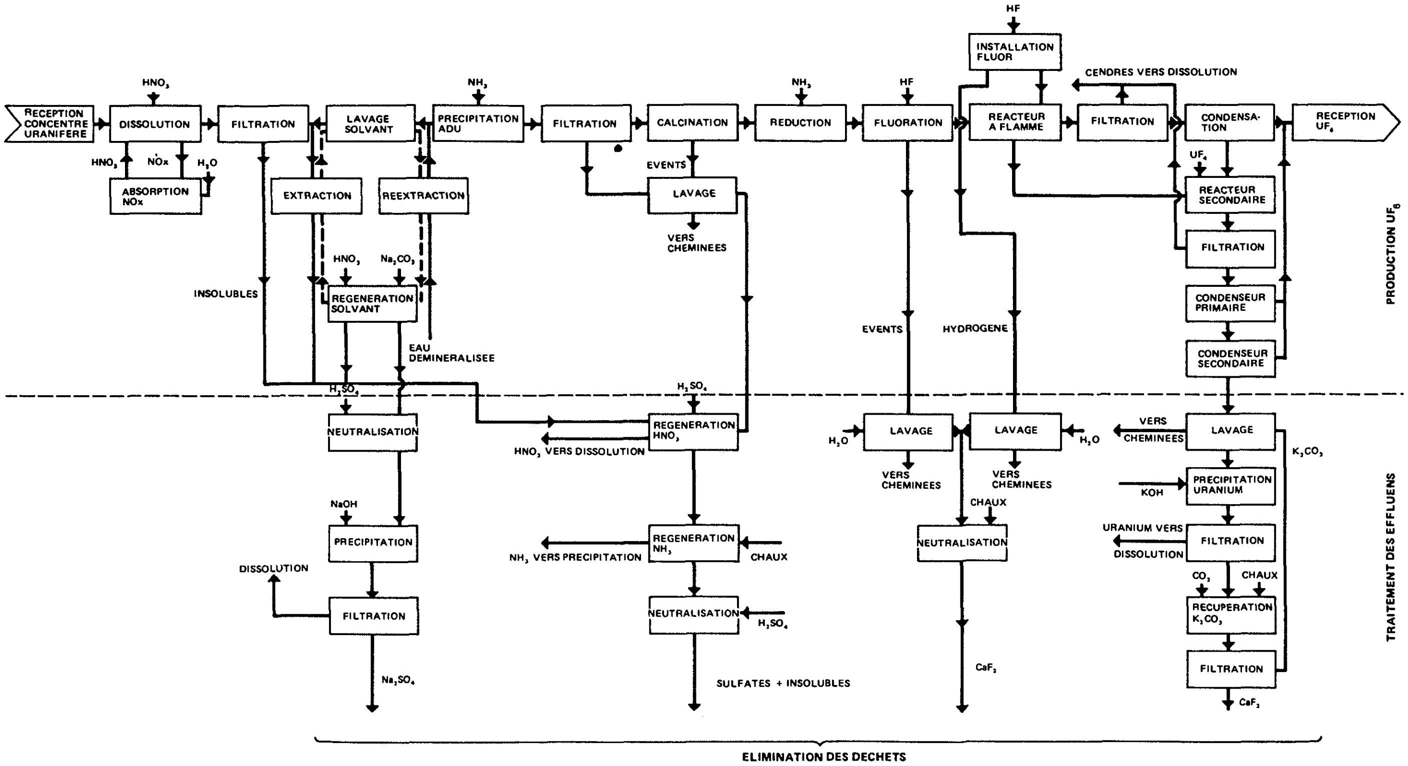


FIG.1. Conversion de l'hexafluorure d'uranium (voie humide).

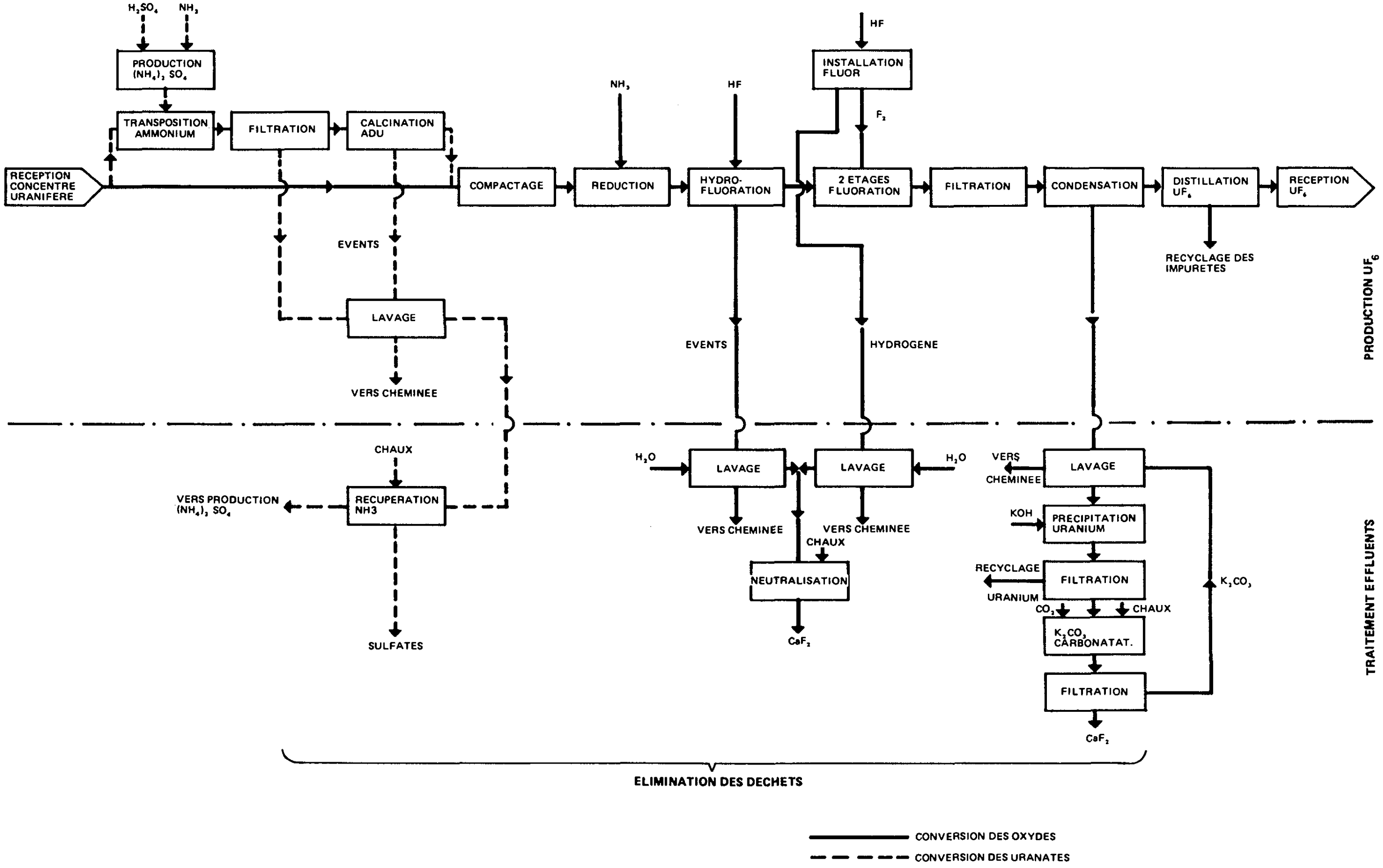


FIG.2. Conversion de l'hexafluorure d'uranium (voie sèche).

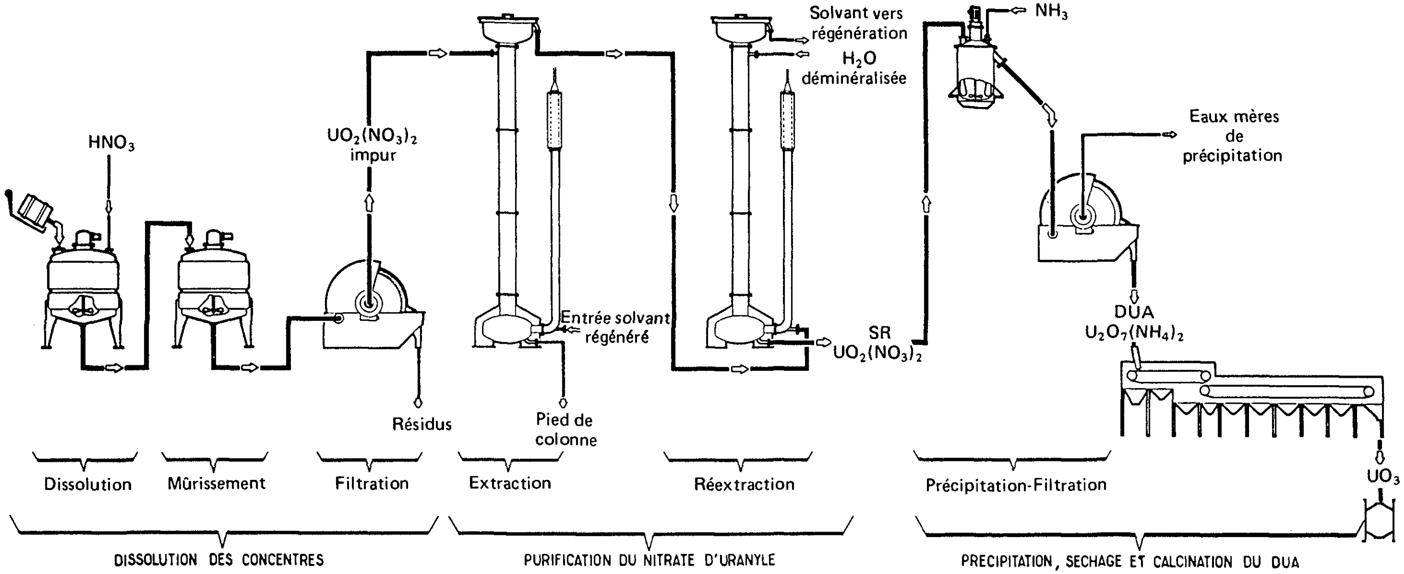


FIG.3. Schéma général d'une unité de conversion de concentrés uranifères en hexafluorure d'uranium.

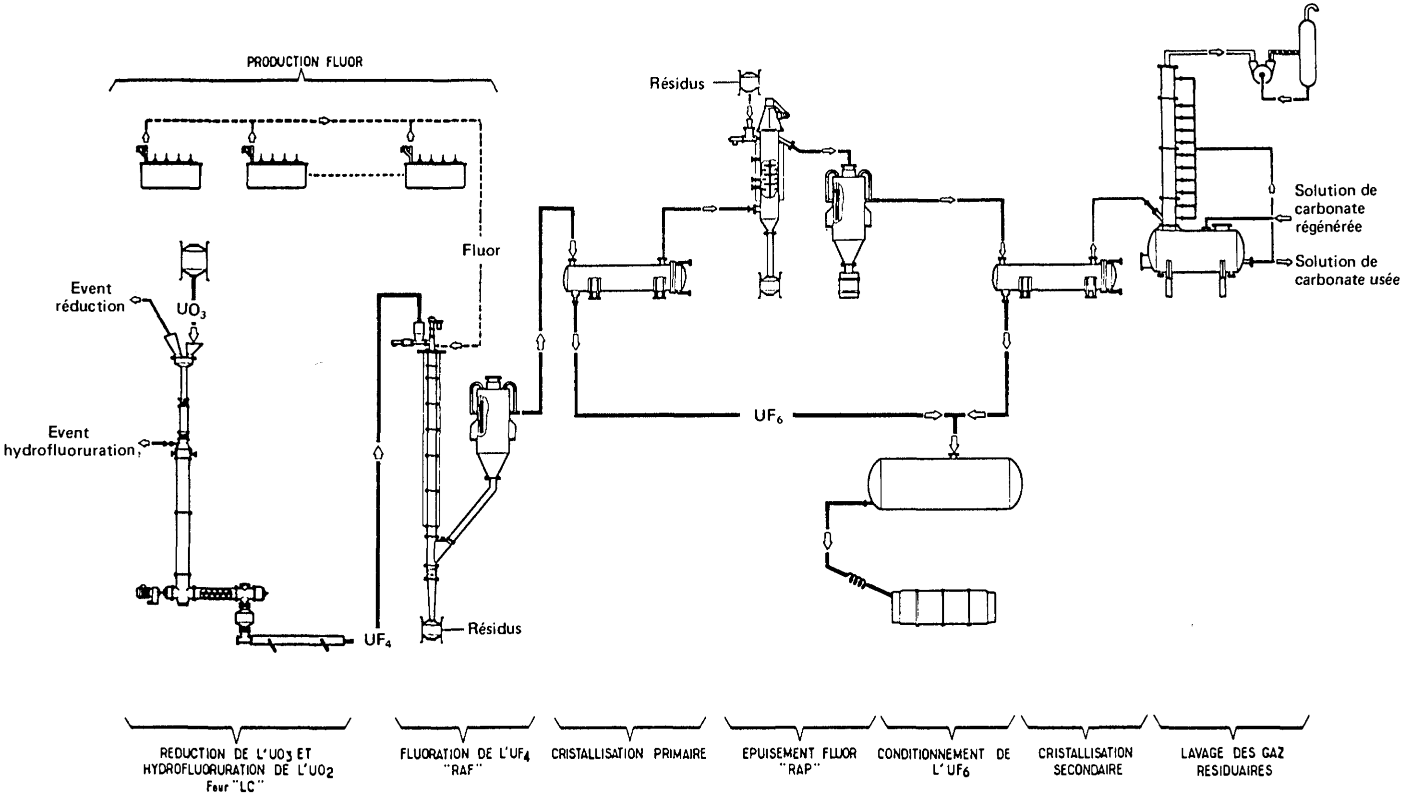


FIG. 3. Schéma général d'une unité de conversion de concentrés uranifères en hexafluorure d'uranium (suite).

4. CONVERSION DU CONCENTRE EN TETRAFLUORURE A L'USINE DE MALVESI (fig.3)

4.1. Dissolution du concentré

Après attaque du concentré par l'acide nitrique, à une température de 90°C, et élimination des insolubles par filtration, on obtient un «jus d'attaque» titrant de 600 à 800 g/l d'uranium.

4.2. Purification

Elle consiste à extraire l'uranium de la phase aqueuse titrant 400 g/l d'uranium à l'aide d'un solvant organique, mélange de tributylphosphate (40%) et de dodécane (60%).

Le TBP forme un complexe stable avec le nitrate d'uranyle, ce qui en permet la séparation d'avec les autres impuretés qui restent dans la phase aqueuse. Le complexe (TBP, uranyle) se forme conformément à l'équation:

$$UO_2^{2+}\,(aq.) + 2NO_3^-\,(aq.) + 2TBP \rightleftarrows UO_2(NO_3)_2,\ 2TBP$$

La constante d'équilibre s'écrit:

$$K = \frac{UO_2(NO_3)_2,\ 2TBP}{(UO_2^{2+}\ aq.)\ (NO_3^-\ aq.)^2\ (TBP\ org.)^2}$$

$$\text{soit: } UO_2(NO_3)_2,\ 2TBP = K\ (UO_2^{2+}\ aq.)\ (NO_3^-\ aq.)^2\ (TBP\ org.)^2$$

Cette relation exprime que la quantité d'uranium transférée dans la phase organique, à l'équilibre, est directement proportionnelle:

- à la concentration de U dans la phase aqueuse;
- au carré de la concentration de l'ion nitrate de la phase aqueuse;
- au carré de la concentration du TBP non complexé de la phase organique.

L'atelier d'extraction liquide-liquide comporte trois colonnes pulsées à plateaux perforés:

- une colonne d'extraction;
- une colonne de lavage du solvant;
- une colonne de réextraction.

La régénération du solvant nécessite en outre une colonne de lavage alcalin suivie d'une colonne de réacidification. La solution de nitrate d'uranyle purifiée est stockée et analysée avant d'être utilisée dans la suite des opérations.

4.3. Précipitation et calcination

Le diuranate d'ammonium est obtenu par addition d'ammoniac dans la solution préchauffée de nitrate d'uranyle. Il se forme selon la réaction:

$$2UO_2(NO_3)_2 + 6NH_3 + 3H_2O \rightarrow (NH_4)_2\, U_2O_7 + 4NH_4NO_3$$

Le mode opératoire utilisé conduit à un produit de très grande surface spécifique particulièrement réactif. Après filtration sur filtre rotatif, séchage et calcination dans un four tunnel à sole mobile, le DUA est tranformé en plaquettes orangées de trioxyde UO_3.

4.4. Réduction–hydrofluoration

L'originalité et la supériorité du procédé utilisé à Malvesi et mis au point par le CEA à l'usine du Bouchet (au sud de Paris) résident en ce qu'il consiste à réaliser les deux opérations dans la même four dit «four LC» mettant en œuvre la technique du «lit coulant».

La réduction exothermique:

$$3UO_3 + H_2 \rightarrow 3UO_2 + 3H_2O \quad \text{avec} \quad \Delta H = -26 \text{ kcal/mole}$$

est tempérée par le craking de l'ammoniac, réaction endothermique:

$$2NH_3 \rightarrow 3H_2 + N_2 \quad \text{avec} \quad \Delta H = +11 \text{ kcal/mole}$$

L'hydrofluoration est également exothermique:

$$UO_2 + 4HF \rightarrow UF_4 + 2H_2O \quad \text{avec} \quad \Delta H = -42 \text{ kcal/mole}$$

et doit être, comme la réduction, soigneusement contrôlée pour éviter le frittage des grains d'UO_2 et d'UF_4, frittage qui en atténuerait quelque peu la réactivité.

Il se forme aussi de l'oxyfluorure d'uranium aux dépens de l'UO_3 non réduit par l'hydrogène:

$$UO_3 + 2HF \rightarrow UO_2F_2 + H_2O$$

Le tétrafluorure contient en moyenne 1,5% d'UO_2 et 1,5% d'UO_2F_2, composés qui seront sans incidence, bien entendu, sur la pureté nucléaire du métal ou de l'hexafluorure, mais feront augmenter sensiblement les consommations ultérieures de magnésium et de fluor, réactifs onéreux.

5. CONVERSION DU TETRAFLUORURE EN METAL A L'USINE DE MALVESI

Jusqu'en 1957, le tétrafluorure était réduit par le calcium. Le prix du calcium «nucléaire» devenant trop élevé, il a été, depuis lors, remplacé sans difficulté par le magnésium.

La magnésiothermie mise en œuvre à Malvesi comporte les étapes décrites ci-dessous.

Un mélange intime d'UF_4 et de grenaille de magnésium est placé dans un creuset en acier. Le creuset est introduit dans un four électrique. La montée en température, très lente jusqu'à 600°C, atteint en quelques minutes 1500°C lorsque la réaction s'amorce.

L'uranium (point de fusion: 1130°C) s'accumule au fond du creuset tandis que le fluorure de magnésium (point de fusion 1260°C) surnage.

On sort le creuset qui est placé sur une rampe de refroidissement.

On ouvre le creuset, on extrait le lingot d'uranium qui est débarrassé de ses scories et décapé par l'acide nitrique qui élimine en particulier le magnésium qui, parfois, le recouvre partiellement. Après sablage, le lingot est prêt pour expédition.

Le fluorure de magnésium récupéré est utilisé pour fabriquer une brasque réfractaire destinée à protéger les parois du creuset.

La réduction se fait selon:

$$UF_4 + 2Mg \rightarrow U + 2Mg\,F_2 \quad \text{avec} \quad \Delta H = -79 \text{ kcal/mole,}$$

les réactions secondaires étant:

$$UO_2 + 2Mg \rightarrow U + 2MgO \quad \text{avec} \quad \Delta H = -19 \text{ kcal/mole, et}$$

$$UO_2F_2 + 3Mg \rightarrow U + 2MgO + MgF_2 \quad \text{avec} \quad \Delta H = -143 \text{ kcal/mole.}$$

Nous donnons ci-après les caractéristiques d'un creuset permettant d'obtenir des lingots de 450 kg:

- diamètre: 720 à 500 mm
- hauteur: 1885 mm
- volume: 560 l
- poids à vide: 816 kg
- poids du mélange: 696 kg
- poids de brasque: 540 kg
- épaisseur: 50 à 100 mm.

6. CONVERSION DU TETRAFLUORURE EN HEXAFLUORURE A L'USINE DE PIERRELATTE (fig.3)

Rappelons que l'hexafluorure d'uranium a été préparé pour la première fois par Moissan en faisant réagir le fluor sur l'uranium métal. Plus tard, Ruff l'a obtenu par action du fluor sur UF_4. Actuellement, la synthèse de l'UF_6 se fait presque exclusivement par addition de fluor à l'UF_4.

6.1. Production de fluor

Industriellement, le fluor est obtenu par électrolyse d'un bain fondu de KF, 2HF (80 à 100°C).

La cellule est en monel (alliage de nickel et de cuivre), les anodes sont en carbone amorphe et les cathodes en acier.

Le fluor se dégage à l'anode et l'hydrogène à la cathode selon les relations électrochimiques ci-après:

- réaction cathodique: $2HF \rightarrow H_2^{\nearrow} + 2F^- - 2e$
- réaction anodique: $\underline{2F^- \rightarrow F_2 + 2e}$

$$2HF \rightarrow H_2^{\nearrow} + F_2^{\nearrow}$$

- tension d'électrolyse: 9 à 10 volts
- intensité nominale: 6000 ampères
- production horaire: environ 3,5 kg/cellule.

6.2. Synthèse de l'hexafluorure

Elle se fait selon la réaction principale:

$$UF_4 + F_2 \rightarrow UF_6$$

à laquelle il convient d'associer les réactions secondaires:

$UO_2 + 3F_2 \rightarrow UF_6 + O_2$, et

$UO_2F_2 + 2F_2 \rightarrow UF_6 + O_2$

oxyde et oxyfluorure accompagnant toujours, en faible quantité, le tétrafluorure.

On observe également la formation de fluorures intermédiaires, non volatils, qui constituent les résidus de fabrication.

L'unité de production comprend:

- un réacteur à flamme (RAF) en monel;
- un dépoussiéreur en acier;
- un réacteur secondaire en monel;
- en ensemble de condensation;
- une colonne de lavage.

Le fluor en excès réagit avec l'UF_4 en produisant une flamme dont la température atteint probablement 1500°C. Les poussières entraînées par les gaz de réaction sont arrêtées par un filtre. L'hexafluorure est piégé dans des cristallisoirs refroidis à −15°C. Le fluor en excès est consommé dans un réacteur à plateaux. Les résidus de fabrication évoqués précédemment sont recyclés, soit en mélange avec l'UF_4 dans le RAF, soit dans le réacteur secondaire.

Les gaz résiduaires contenant HF ainsi que des traces de fluor et d'UF_6 sont neutralisés par une solution de carbonate de potassium CO_3K_2.

L'ensemble de l'installation est en dépression, ce qui non seulement évite de comprimer le fluor en provenance des cellules, mais assure en outre une très grande sécurité de fonctionnement en éliminant pratiquement toute fuite d'hexafluorure dans l'atelier.

L'atelier principal de Pierrelatte assure la production d'UF_6 avec deux RAF en parallèle. L'UF_4 est stocké dans un silo d'une capacité de 500 t en uranium. L'UF_6 liquide est stocké dans des jaugeurs avant d'être coulé dans des conteneurs de transport.

Un atelier de production d'hexafluorure, mettant en œuvre les techniques de voie sèche exposées très brièvement ci-dessus, fonctionne régulièrement depuis le début de 1979.

7. CONTROLE ANALYTIQUE

Le contrôle analytique est évidemment d'une importance vitale. La pureté nucléaire requise aux divers stades de la chaîne de fabrication, qui conduisent du concentré à l'hexafluorure, implique la mise en œuvre de techniques analytiques sophistiquées: spectrographie à l'infra-rouge, spectrographie à l'ultra-violet, chromatographie en phase gazeuse, spectrophotométrie, etc.

Les spécifications très contraignantes exigées pour l'UF$_6$ destiné à l'enrichissement ne tolèrent aucune dérive, ce qui a même conduit la COMURHEX à mettre au point un appareillage spécial apte à résoudre certains problèmes particuliers tels que le dosage en continu, par chromatographie, d'un mélange d'HF, de fluor et d'UF$_6$.

La pureté acquise en amont doit être conservée jusqu'au produit fini. De ce fait, il importe de contrôler de façon quasi continue les matières premières et les cycles de fabrication afin de pouvoir déceler en temps opportun toute perturbation susceptible d'altérer la qualité du produit fini.

8. SECURITE

La toxicité des produits manipulés dans les installations de la COMURHEX a été prise en considération dans la conception même des procédés.

La mise en dépression de la chaîne de fabrication, des cellules d'électrolyse aux colonnes de lavage, interdit pratiquement toute émanation intempestive de fluor, d'acide fluorhydrique et d'hexafluorure dans les ateliers.

Toute fuite sur l'appareillage se traduit par une entrée d'air immédiatement décelée par contrôle des gaz. D'autre part, un certain nombre de compteurs sensibles à la présence d'uranium dans l'air analysent en permanence l'atmosphère des ateliers.

Les interventions du personnel sur l'installation se fait obligatoirement avec le port de vêtements de sécurité tels que le scaphandre autonome si nécessaire.

Les gaz résiduaires de procédé après traitement, l'air aspiré dans les ateliers, sont rejetés dans une cheminée de 50 mètres. Un enregistreur d'aérosol contrôle d'ailleurs en permanence les teneurs en uranium et fluor.

Le remplissage des conteneurs en UF$_6$, opération dans laquelle l'UF$_6$ est sous pression, est fait dans un local de conditionnement spécialement équipé. Des manœuvres préliminaires d'étanchéité, tant sur l'installation que sur les conteneurs de stockage et de transport, sont effectuées à chaque coulée.

9. RECUPERATION DES DECHETS

9.1. Usine de Malvesi

Cet atelier reçoit tous les sous-produits uranifères des autres fabrications afin de récupérer l'uranium pour recyclage. On distingue:

- les pieds de colonne, contenant de 10 à 20 mg/l d'U;
- les eaux mères de précipitation, contenant de 1 à 2 mg/l d'U;
- le fluorure de magnésium contenant de 1 à 2% d'U;
- de l'UO_3 et de l'UF_4 impropres à la fabrication du métal et de l'hexafluorure.

Les solides sont dissous par l'acide nitrique. L'uranium en solution sera soit précipité sous forme d'uranate de calcium ou de sodium, soit complexé par l'ion CO_3.

Les effluents proprement dits sont:

- des jus épurés alcalins;
- des jus forts contenant de 30 à 60 g/l d'U;
- du fluorure de Mg sans U qui sera séché et vendu.

9.2. Usine de Pierrelatte

La récupération de l'uranium des effluents fluorés et des poussières désactivées se fait par dissolution de l'uranium à l'aide de carbonate de potassium (complexe carbonaté très soluble) et précipitation, par la potasse ou la soude, de l'uranate correspondant qui sera expédié à Malvesi (fig.3). Les résidus sont recyclés immédiatement pour la fabrication d'UF_6. Les effluents fluorés en provenance de la salle d'électrolyse sont neutralisés par la chaux.

10. TRAITEMENT DES EFFLUENTS

10.1. Usine de Malvesi

Les effluents liquides et solides en provenance des différents ateliers contiennent du nitrate d'ammonium, divers nitrates, de l'acide nitrique, du fluorure d'ammonium, de l'acide fluorhydrique, de l'acide sulfurique, du carbonate de sodium, du solvant, de l'uranium, etc.

Après séparation de l'uranium, les effluents neutralisés par la chaux sont expédiés sur un terrain d'épandage où des micro-organismes détruiront le nitrate d'ammonium.

Les effluents gazeux, fluorés en l'occurrence, subissent un traitement analogue à celui évoqué ci-après pour l'usine de Pierrelatte.

10.2. Usine de Pierrelatte

Les gaz résiduaires de la fabrication de l'UF$_6$ sont traités par du CO_3K_2 (dissolution de l'uranium) et par la potasse pour la précipitation de l'uranate de potassium envoyé à Malvesi.

Les effluents de la salle d'électrolyse sont neutralisés à la chaux (précipitation de fluorine F_2Ca). Les effluents rejetés contiennent moins de 2 mg/l d'uranium.

Annexe 1

MATIERES PREMIERES, PRODUITS INTERMEDIAIRES, PRODUITS FINIS

1. Uranate de magnésium: U_2O_7Mg

Masse moléculaire: 612 (U: 77,78%).
Teneur en U des uranates livrés à Malvesi:
- de Bessines: 66% (61 à 70)
- d'Ecarpière: 65% (61 à 66).

2. Nitrate d'uranyle: $UO_2(NO_3)_2$

Masse moléculaire: 394 (sel cristallisé: $UO_2(NO_3)_2 . 6H_2O$).
Décomposition dès 180°C: $UO_2(NO_3)_2 \rightarrow UO_3 + N_2O_4 + \frac{1}{2} O_2$

3. Diuranate d'ammonium: $U_2O_7(NH_4)_2$

Sel jaune; masse moléculaire: 624 (U: 76,28%).

4. Oxydes d'uranium

UO_2: sel noir; masse moléculaire: 270 (U: 88,15%).
UO_3: sel orange; masse moléculaire 286 (U: 83,22%).

5. Tétrafluorure d'uranium: UF_4

Sel vert; masse moléculaire: 314 (U: 75,6%).
Densité tassée: 2,5; densité réelle: 6,5.

6. Hexafluorure d'uranium: UF_6

Sel incolore; masse moléculaire: 352 (U: 67,6%).

Densité du liquide: 3,67 à 64°C.
Densité du solide: 4,92 à 64°C.
Se sublime sans fondre.

Température (°C)	Tension de vapeur (mmHg)
57	760
21	82,5
−26	0,10

Point triple: 64°C sous 1134 mmHg.

Spécifications

- tension de vapeur du conteneur;
- pourcentage minimum en poids d'UF_6: 99,5;
- maximum en ppm par rapport à l'U naturel:

antimoine	1
brome	5
chlore	100
niobium	1
phosphore	50
silicium	100
tantale	1
titane	1

- maximum en ppm par rapport à ^{235}U:

chrome	1500
molybdène	200
tungstène	200
vanadium	200

- maximum en ppm par rapport à l'U naturel:

$$Al + Ba + Bi + Cd + Ca + Cr + Cu + Fe + Pb + Li + Mg + Mn + Ni + K + Ag + Na + Sn + Cr + Th + Zn + Zr = 300$$

7. Solvant

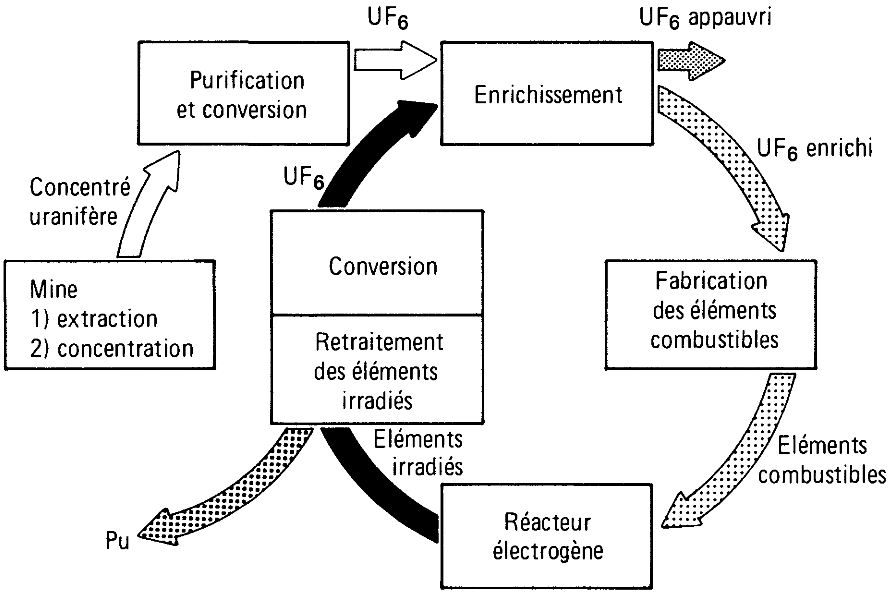
	TBP	Dodécane	Solvant
Formule	(n, $C_4H_9O)_3PO$	$C_{12}H_{26}$	TBP(40%), Dod(60%)
Densité à 20°C	0,980	0,760	0,848
Point ébullition à 760 (°C)	289	187–212	187–289
Point éclair (°C)	146	63	90
Masse moléculaire	266	170	–

Solubilités: TBP: 0,6% dans l'eau
Eau: 6,7% dans le TBP.

Annexe 2

CYCLE DE L'URANIUM

Réacteurs électrogènes à eau légère



□ U naturel: environ 0,7% ^{235}U et 99,3% ^{238}U

▨ U enrichi: environ 3% ^{235}U et 97% ^{238}U (environ 1/5 de l'U naturel)

■ U dégradé: environ 0,9% ^{235}U et 99,1% ^{238}U (environ 1/5 de l'U naturel)

▒ U appauvri: environ 0,2% ^{235}U et 99,8% ^{238}U (environ 4/5 de l'U naturel)

Annexe 3

SPECIFICATIONS DES CONCENTRES URANIFERES

1. Spécifications générales

1.1. Les concentrés uranifères ne doivent contenir aucun corps étranger ne découlant pas directement du traitement des minerais dont ils proviennent.

1.2. Les concentrés uranifères doivent présenter une coulabilité suffisante pour permettre leur échantillonnage normal dans une station d'échantillonnage par prélèvement d'une quote-part dans un flot de produit.

1.3. La granulométrie des concentrés uranifères doit permettre leur passage dans un tamis à maille carrée de 6 mm.

1.4. La teneur isotopique du produit doit être «normale» selon les spécifications de l'Energy Research and Development Administration (ERDA).

1.5. Les concentrés uranifères doivent répondre aux conditions du test de compatibilité réf. MOOPR 75.04, dont le texte peut être communiqué sur demande.

1.6. Les spécifications chimiques définies ci-après ont été établies en fonction de l'expérience acquise par COMURHEX. Au cas où l'analyse des concentrés uranifères mettrait en évidence d'autres impuretés préjudiciables à la conversion, COMURHEX se réserverait la possibilité de proposer le rejet du produit ou l'application de pénalisation. Par ailleurs, au cas où les teneurs en impuretés constatées dépasseraient certaines des teneurs limites ci-après, COMURHEX pourrait proposer, cas par cas, une pénalisation au lieu du rejet.

2. Spécifications chimiques

Les concentrés ne contiendront pas moins de 60% d'uranium.

Sauf précisions contraires, les concentrations en impuretés données ci-dessous sont exprimées en pourcentage de l'uranium total:

Eléments	*Teneurs limites sans pénalités*	*Teneurs limites de rejet*
Humidité (H_2O), en pourcentage du poids de concentrés	–	10
Matières organiques extractibles	–	0,1
Uranium insoluble dans HNO_3	–	0,1
Vanadium	–	0,3
Molybdène	0,2	0,6
Zirconium	0,2	2
Bore	–	0,2
Phosphates (exprimés en PO_4)	–	1
Halogènes (exprimés en Cl)	–	0,25
Fluor	0,15	0,30
Carbonates (exprimés en CO_3)	2	3
Arsenic	1	2,5
Sulfates (exprimés en SO_4)	–	10
Calcium	1	5
Sodium	1	15
Silicium (exprimé en SiO_2)	–	5

Annexe 4

INFLUENCE DES IMPURETES SUR LE RAFFINAGE DES CONCENTRES URANIFERES PAR EXTRACTION LIQUIDE-LIQUIDE

L'action gênante de ces impuretés se manifeste essentiellement sous quatre aspects:

1. Elles perturbent plus ou moins les différentes étapes du procédé (matières organiques, carbonates, fluorures, phosphates, silice, sulfates, zirconium), et il en résulte une diminution des capacités de production.

2. On retrouve ces impuretés plus ou moins partiellement dans le nitrate d'uranyle purifié (matières organiques, chlorures, fluorures, molybdène).
3. Elles contribuent à la corrosion des installations (chlorures, fluorures).
4. Elles sont indésirables dans les effluents (uranium insoluble, arsenic, sodium).

Uranium insoluble

L'uranium insoluble dans l'acide nitrique diminue le rendement de mise en solution et se retrouve finalement dans les rejets.

Arsenic

COMURHEX n'a pas beaucoup d'expérience sur le comportement des quantités importantes d'arsenic dans les concentrés. Il est probable que cet élément se retrouve également dans les rejets et plus particulièrement dans les «pieds de colonne».

Bore

Cet élément est probablement éliminé en grande partie sous forme de fluorure volatil, lors de la fabrication des tétrafluorures.

Calcium

Le calcium ainsi que le magnésium, le fer et d'autres impuretés contribuent à augmenter la consommation d'acide nitrique lors de la mise en solution des concentrés.

Chlorures

On sait que les chlorures en présence d'acide nitrique sont très agressifs vis-à-vis de l'acier inoxydable.

Carbonates

Lors de l'attaque du concentré par l'acide nitrique, les carbonates se décomposent avec effervescence en provoquant des mousses abondantes, ce qui entraîne une diminution de la vitesse de dissolution et, par conséquent, une diminution de la capacité de production de l'atelier.

Fluorures

Les ions fluorures forment des complexes et peuvent ainsi perturber la purification de l'uranium par le TBP. C'est ainsi qu'on le retrouvera plus ou moins partiellement dans la solution de réextraction. On peut atténuer ces effets inhibiteurs en ajoutant du fer ou de l'aluminium, éléments qui formeront des complexes stables avec les ions fluorures.

Molybdène

Le comportement du molybdène dans la purification avec des solvants contenant du TBP est assez voisin de celui de l'aluminium; c'est pourquoi on le retrouvera en quantité non négligeable dans la solution de réextraction. De plus, la solubilité du molybdène est fonction de l'acidité, ce qui entraîne parfois la formation de dépôts sur le garnissage des colonnes et, par suite, une diminution dans la capacité de production. On utilise d'ailleurs cette tendance à l'insolubilité du molybdène pour en éliminer le maximum lors de la dissolution nitrique des concentrés.

Filtration: Le précipité contenant le molybdène sera traité par une solution alcaline qui dissoudra le molybdène en laissant l'uranium sous forme insoluble.

Sodium

Le sodium qui reste dans les pieds de colonne est considéré comme un élément indésirable dans les rejets.

Phosphates

Les phosphates sont considérés comme des inhibiteurs d'extraction. Ils contribuent à la formation de composés insolubles qui se déposent sur le garnissage des colonnes au cours de la purification par solvants.

Silice

La silice colloïdale a tendance à se déposer sur les plateaux perforés de colonnes de purification. Ce comportement est facilité par la forte acidité de la phase aqueuse. L'élimination de la silice peut être menée à bien en laissant «mûrir» les jus d'attaque.

Sulfates

Les sulfates insolubles perturbent la mise en solution des concentrés; ils inhibent également l'extraction par solvants. Ils diminuent donc la capacité de mise en solution et d'extraction.

Vanadium

COMURHEX n'a pas d'expérience particulière sur le comportement de ces éléments au cours de la purification par solvants.

Zirconium

En milieu peu acide le zirconium peut former des précipités assez mal définis par hydrolyse. Même en milieu acide ces précipités sont pratiquement impossibles à redissoudre. On pense également que le zirconium accélère la dégradation du TBP en phosphate de dibutyle, monobutyle et peut-être même en butanol. L'élimination du zirconium se fait au moment de l'attaque des concentrés par addition d'acide phosphorique. La difficulté de traitement réside dans l'hétérogénéité des teneurs en zirconium, hétérogénéité qui ne permet pas de doser convenablement les ajouts d'acide phosphorique. Ce précipité est en outre particulièrement volumineux, ce qui entraîne de sérieuses difficultés de filtration et, par voie de conséquence, une diminution notable de la capacité de production.

Matières organiques

On sait que la présence de quantités trop importantes de matières organiques se traduit par de sérieuses difficultés lors de la purification par solvants: difficultés qui vont jusqu'à la formation d'émulsions stables. Sous certaines conditions, il est possible de les détruire par addition d'oxydants tels que permanganate de potassium ou des chlorures qui peuvent devenir oxydants en milieu nitrique concentré. Les matières organiques semblent parfois inhiber les étapes ultérieures du cycle de conversion: précipitation du diuranate d'ammonium puis réduction de l'UO_3 en FO_2 et fluoration de l'UO_2 en UF_4.

COMURHEX a mis au point un test susceptible de juger l'aptitude des concentrés à être purifés par solvants (voir Annexe 5); ce test est surtout sensible à la présence des matières organiques et de silice colloïdale.

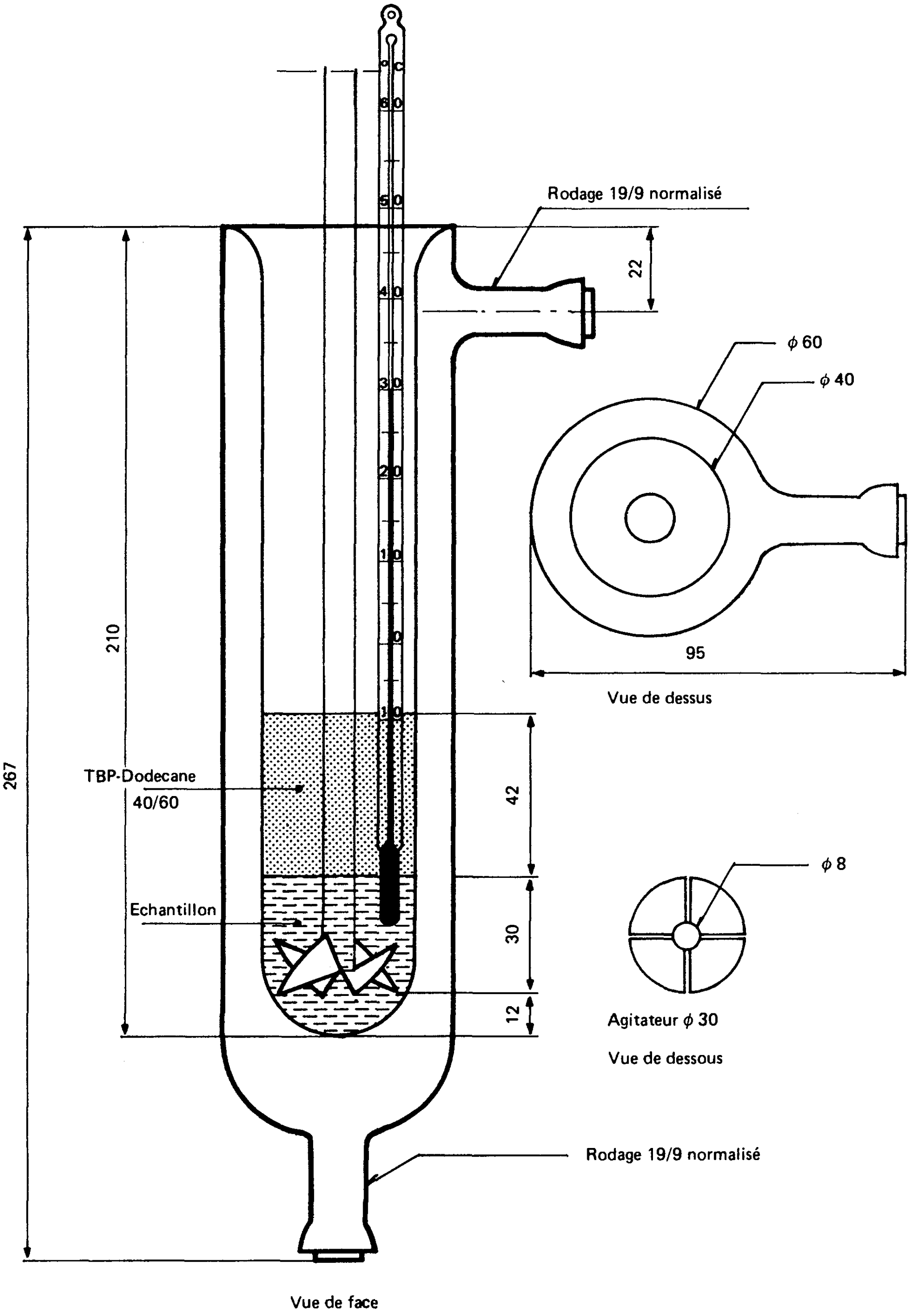


FIG.4. Mélangeur-décanteur (dimensions en mm).

Annexe 5

ESSAI D'APTITUDE D'UN CONCENTRE URANIFERE A L'EXTRACTION PAR SOLVANT

1. Objet

Le présent document a pour objet la description d'une méthode d'essai permettant de caractériser l'aptitude d'un concentré uranifère à être purifié par extraction par un mélange de phosphate de tributyle et de dodécane après mise en solution dans l'acide nitrique.

2. Principe

Le concentré est mis en solution dans l'acide nitrique. La solution obtenue est filtrée après mûrissement pour séparer la silice, puis agitée dans des conditions opératoires bien définies avec un mélange de phosphate de tributyle et de dodécane. Après arrêt de l'agitation, on mesure la durée de séparation des phases.

3. Appareillage

Matériel courant de laboratoire et appareil mélangeur conforme au schéma de la figure 4.

4. Réactifs

- Eau distillée (1).
- Acide nitrique concentré (environ 14 N) (2).
- Mélange TBP-dodécane: à 600 ml de dodécane, ajouter 400 ml de phosphate de tributyle et homogénéiser (3).
- Origine des réactifs:
  - Acide nitrique R.P., d = 1,38, pour analyses, PROLABO 20.422.
  - Dodécane technique, PROLABO 23.583.
  - Phosphate de tributyle, PROTEX.

5. Mode opératoire

5.1. Préparation de la solution à essayer

Dans un vase à saturations de 500 ml, introduire 65 ml d'acide nitrique concentré (2) et chauffer à environ 50°C. Verser par petites fractions dans le vase à saturations une quantité de concentré contenant approximativement 65 g d'uranium.

Recouvrir le vase avec un verre de montre et laisser mûrir le mélange pendant quatre heures dans une étuve à 90°C.

Filtrer la solution sur clarcel dans un entonnoir Büchner de 7 cm de diamètre. L'épaisseur de la précouche, préparée en versant une suspension de clarcel dans de l'eau (1) sur deux filtres en papier (filtration rapide), est de l'ordre d'un centimètre et demi.

Laver le gâteau formé sur le filtre par environ 40 ml d'eau (1) chaude.

Dans le filtrat, après homogénéisation et refroidissement, doser l'uranium et l'acidité libre.

Diluer le filtrat avec les quantités calculées d'eau (1) et d'acide nitrique concentré (2) pour obtenir une solution titrant 350 g/l d'uranium et d'acidité libre 2 N.

5.2. Essai de décantation

Introduire 50 ml de solution ainsi obtenue dans le réacteur thermostaté à 30°C. Quand la solution est à la température du thermostat, agiter pendant deux minutes (900 tours par minute), puis verser lentement dans le réacteur 50 ml de mélange TBP-dodécane (3), en maintenant l'agitation et en faisant couler le mélange le long des parois du vase.

Maintenir l'agitation pendant dix minutes puis, après l'avoir arrêtée, mesurer au chronomètre la durée de séparation des phases, jusqu'à ce que l'interface soit nette ou jusqu'à ce que l'épaisseur de l'émulsion qui sépare les phases paraisse constante.

6. Interprétation de l'essai

Un concentré est considéré comme apte à la purification par extraction par solvant lorsque le temps de décantation est de l'ordre d'une minute. Néanmoins, même pour des temps plus faibles, l'apparition de volutes en quantités importantes à l'interface peut entraîner des difficultés lors de l'extraction à l'échelle industrielle.

Dans cet essai, on ne met pas en évidence la capacité d'extraction du solvant pour le concentré considéré.

Remarques

Pour que le test soit significatif, il est nécessaire que la géométrie de l'appareillage soit exactement conforme au schéma et que la vitesse de rotation de l'agitateur soit de 900 tours par minute.

La concentration en uranium doit être de 350±5 g/l. L'acidité libre a moins d'importance; toutefois, elle doit être comprise entre 1,5 et 2 N.

Limites de l'essai

Un essai positif ne signifie pas nécessairement que la purification industrielle par solvant ne posera aucun problème, car celle-ci peut être perturbée par d'autres facteurs. Par contre, si le test est négatif, l'expérience a montré que des difficultés apparaissent lors des opérations de purification.

DISCUSSION

F.R. HARTLEY: I wonder whether Mr. Perez would enlarge on the problem of sodium in the effluent. I am not clear what is the intrinsic nature of the problem. Is sodium used as an indirect measure of total dissolved solids or of a toxic anion?

A. PEREZ: Sodium releases into the environment are severely regulated in France. The maximum allowable level is about 300 mg/l expressed as sodium sulphate. At Lodève, in Southern France, we are currently building an ore treatment plant designed to use alkaline attack by sodium carbonate. The liquid wastes from this process consist essentially of sodium sulphate solutions which we cannot discharge into the river. We are therefore forced to concentrate and crystallize the sodium sulphate. The crystals obtained are stored in a monitored area, and amount to about 20 000 t per year. The investments corresponding to this special sodium sulphate treatment will account for 5 to 10% of the total cost of the plant. I should also like to state that plants in most countries which produce yellow cake use ammonia to precipitate ADU. In Niger and Gabon, where French industry has built many ore treatment plants, this process is not feasible because of the prohibitive cost of transporting imported ammonia. Hence, the three plants currently operating in Niger and Gabon (total annual capacity about 5000 t of uranium) produce either sodium uranate or magnesium uranate. The corresponding concentrates contain about 12–15% Na in relation to U (sodium uranate) or about 2–4% Na in relation to U (magnesium uranate). This is the sodium found by Comurhex in the Malvesi refining operation.

S. SEN: Do you have any experience of the effect of thorium or rare earths on your refinery operation?

A. PEREZ: In reply to Mr. Sen's question, I should like to state that, in France, until the end of the 1960s, we processed U and Th concentrates from Madagascar. These concentrates were obtained from uranothorianite ores, concentrated on the spot by gravimetric treatment (shaking tables, jigs and spirals). The concentrates assayed about 20% U and 50% Th. Purification was carried out at the Bouchet plant, which is now shut down. Nitric acid dissolution and TBP treatment were used to separate uranyl nitrate containing only some tens of ppm Th, and very pure thorium nitrate.

P. ALFREDSON: Your paper, Mr. Perez, describes the use of 40% TBP in dodecane as the solvent for purification. Would you like to comment on the high concentration of TBP that is used in your process compared with the much lower concentrations used by other converters?

A. PEREZ: The 40% concentration is high. We use a system in which the aqueous phase is continuous, not the organic phase. Using this condition the solvent ratio 40/60 enables us to produce relatively high concentrations of uranium at purification. We work with a concentration of approximately 160 g/l. Attack of the concentrate gives us 600 to 700 g uranium per litre. After filtration we dilute to give 160 g/l at the purification stage. This 40/60 is the outcome of experience at Malvesi and a compromise between high concentration in the aqueous phase and the elimination of impurities.

URANIUM REFINING IN SOUTH AFRICA
The production of uranium trioxide, considering raw material properties and nuclear purity requirements

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Abstract

URANIUM REFINING IN SOUTH AFRICA: THE PRODUCTION OF URANIUM TRIOXIDE, CONSIDERING RAW MATERIAL PROPERTIES AND NUCLEAR PURITY REQUIREMENTS.

Conventional practice results in raw materials being delivered to the uranium refineries in a form more suitable for transportation than for processing, and therefore the refineries are required to treat these raw materials to produce an acceptable intermediate feed stock. During this treatment, it is advantageous to include a purification step to ensure that the feed stock is of the required purity for nuclear grade uranium hexafluoride production, and this usually results in ammonium diuranate slurries of the required quality being produced as the intermediate feed stock. All subsequent processing steps can therefore be standardized and are effectively independent of the origin of the raw materials. It is established practice in South Africa to transport uranium as an ammonium diuranate slurry from the various mines to the Nufcor central processing plant for UOC production, and therefore the process for the production of uranium hexafluoride in South Africa was designed to take cognizance of existing transport techniques and to accept ammonium diuranate slurries as the raw material. The South African refinery will be able to accept ammonium diuranate slurries which differ considerably, depending on the producing mine, and to process these slurries directly to uranium trioxide of sufficiently consistent quality to be considered as a suitable intermediate feed stock, and to ensure that subsequent processing steps are virtually independent of mine of origin. This approach, however, has the disadvantage that the uranium hexafluoride produced does not immediately comply with nuclear grade requirements and has to be purified by distillation. The impurities are such that a relatively simple distillation system is required. This paper discusses the conditions under which the various ammonium diuranate raw materials, exhibiting a wide range of properties, can be effectively processed to produce a uranium trioxide of acceptably consistent properties. Mention is also made of the uranium hexafluoride distillation process adopted.

1. INTRODUCTION

1.1. Local considerations

South Africa has traditionally exported uranium as uranium oxide concentrates. Overseas refiners accepting these concentrates together with other solid uranium concentrates have been obliged to dissolve these raw materials before any further processing can take place. In view of this requirement it has become normal practice to include a purification step before the precipitation of the ammonium diuranate feed stock for the uranium trioxide production unit. The purification is normally performed by solvent extraction in nitrate medium and hence the concentrates received by the plants are dissolved in nitric acid.

The ammonium diuranate feed stock precipitated from the purified solution is of nuclear grade, and the final uranium hexafluoride produced by the conventional refinery is therefore also nuclear grade material. A further result of the enforced dissolution, and subsequent purification, of the various uraniferous raw materials is that the ammonium diuranate precipitated exhibits consistent physical and chemical properties.

In developing a process for the refining of uranium ores in South Africa, it was necessary to take into account the following factors:

(1) The wealth of experience already accumulated by the Nuclear Fuel Corporation, Nufcor, in its transportation and handling of ammonium diuranate slurries and the conversion of such slurries into uranium oxide concentrates,

(2) That while South Africa is essentially a country with considerable mineral resources, its water resources are somewhat limited, and

(3) The refining of uranium is not a new art and extensive information is available in the literature describing various processes and the applications thereof.

Bearing these three basic premises in mind, it was decided that the South African refining process should be a combination of already established dry-way processing steps but designed to accept the uranium diuranate slurries, as supplied by the mining industry, as the feed material. It was expected that considerable development work would have to be done before uranium from the wide range of South African ore types could be successfully converted from crude ammonium diuranate slurry to nuclear grade uranium hexafluoride in a single integrated refinery, employing the most direct processing route. Consequently provision was made for the piloting of each step. With one or two minor exceptions, the pilot work has been completed and work has now commenced on the construction of the large-scale refinery.

2. AMMONIUM DIURANATE PRODUCTION

2.1. Processing technique

A brief discussion of the major techniques employed by South African mines for the production of ammonium diuranate is given in this sub-section.

On most South African mines, uranium is produced as a by-product of the gold recovery process. Certain producers use a flotation process to produce a pyrite concentrate from the crushed ore, and this pyrite concentrate containing high uranium and gold values is also used for the production of sulphuric acid.

Uranium is recovered from the crushed ore by dissolution in sulphuric acid and the gold by dissolution in cyanide solution. The ore slurry must be alkaline for cyanidation in order not to lose the cyanide as volatile hydrocyanic acid, and therefore the ore slurry requires treatment in both acid and alkaline media. The majority of the mines follow the so-called 'reverse leach' process in which the uranium is leached first, using an oxidant and sulphuric acid, and, after removal of the uranium solution by filtration, the filter residue is repulped and cyanided for gold extraction. The advantages of the 'reverse leach' are higher gold recoveries and no formation of polythionates which act as resin poisons. Certain mines do, however, still use the forward leach where the gold is leached first and the uranium leached from the cyanidation residue. Both leach methods result in the recovery of the uranium values as a uranyl sulphate solution.

The uranyl sulphate solution is processed by two separate routes depending on the producing mine, certain mines using a solvent extraction process while others use an ion-exchange process.

In the solvent extraction process the sulphate leach solution is contacted with an organic phase in a mixer and the resultant mixed phase channelled into a settler where the organic and aqueous phases separate. The organic phase, or extractant, consists of an amine dissolved in kerosene, and problems of 'third phase' formation have resulted in the modification of the extractant by the addition of isodecanol by some producers and by the addition of a high aromatic solvent by others.

After loading, the solvent passes into a scrubbing section where impurities in the organic phase are removed by contact with a suitable aqueous phase. This scrubbing operation results in the removal of some uranium and hence the aqueous phase from the scrubbing section is returned to the loading section to avoid any uranium loss.

The scrubbed solvent flows to the strip section where the uranium is removed from the organic phase by contact with an ammonium sulphate solution. The pH of the aqueous phase in the strip section is controlled, by ammonia addition, at a value just below that which would cause the precipitation of ammonium diuranate. The aqueous phase from the strip stage passes to the uranium

TABLE I. CHARACTERISTICS OF MATERIAL OBTAINED

Mine	Production ($kgU \cdot h^{-1} \cdot (area)^{-1}$)	Type	pH	Slurry specific gravity	Sulphate content in ADU (%)	Mean particle size (μm)
9	30.0	S-C	7.6	1.44	0.34	14.5
10	30.0	S-C	7.5	1.40	0.37	12.3
4	27.7	S-C	7.5	1.42	0.43	1.9
3	20.5	S-F	7.3	1.33	0.57	7.6
7	18.7	S-F	7.4	1.31	5.77	18.3
6	17.2	S-F	7.2	1.31	3.64	7.8
11	16.8	S-F	7.0	1.26	4.00	13.5
5	7.4	I-F	6.0	1.18	2.57	0.6
8	7.0	I-F	6.2	1.21	2.49	4.9

S-C = solvent-centrifuge
S-F = solvent-filter
I-F = ion-exchange-filter

precipitation unit, while the organic phase is recycled to the loading section. The uranium is precipitated from the sulphate solution as ammonium diuranate by the addition of ammonia. Ammonia addition is usually as gaseous ammonia, but one producer uses an aqueous ammonia addition. The ammonium diuranate produced is recovered either by filtration or by centrifuge, depending on the producer's preference. In both cases however the ammonium diuranate is re-slurried for transportation to the refinery by road tanker.

The ion-exchange plant consists of three or four columns packed with a strong-base anion-exchange resin. The operation of the plant is to feed the sulphate leach solution through the first and second columns operating in series, and the system is so designed that when uranium is detected in the solution leaving the second column the first column is fully loaded. The fully-loaded column is then taken off line and the leach solution passed through the second and third columns. The cyclic loading of the columns is continued in this way.

After a fully-loaded column is taken out of the loading cycle the resin is eluted using a solution of nitric acid and ammonium nitrate. Since the uranium loads onto the resin as a uranium sulphate complex ($UO_2(SO_4)_2^{2-}$) the eluate also contains sulphate. The pH of the eluate is adjusted to a value of 3 by the addition of calcium oxide, and this adjustment results in the precipitation of iron and other impurities which are filtered off. Ammonia is then added to adjust the pH to a value of 7 in order to precipitate the uranium as ammonium diuranate which is then recovered by filtration. All producers using the ion-exchange process add ammonia as a gas. As with the solvent extraction process the ammonium diuranate filter cake is re-slurried and transported to the refinery by road tanker.

Depending on the technique used the ammonium diuranate produced can therefore be divided into three types:

(i) Purification by solvent extraction and separation of the precipitated ammonium diuranate by centrifuge – Type S-C;
(ii) Purification by solvent extraction and separation of the precipitated ammonium diuranate by filtration – Type S-F;
(iii) Purification by ion-exchange and separation of the precipitated ammonium diuranate by filtration – Type I-F.

2.2. Characteristics of material obtained

The ammonium diuranate slurries produced by the three different production techniques have varying physical properties. From a refinery production point of view, however, the most important property is clearly the rate at which the material can be processed and this rate serves as a basis for comparing the characteristics of the varying ammonium diuranates produced. The processing rate is simply the rate at which the ammonium diuranate can be fed into the

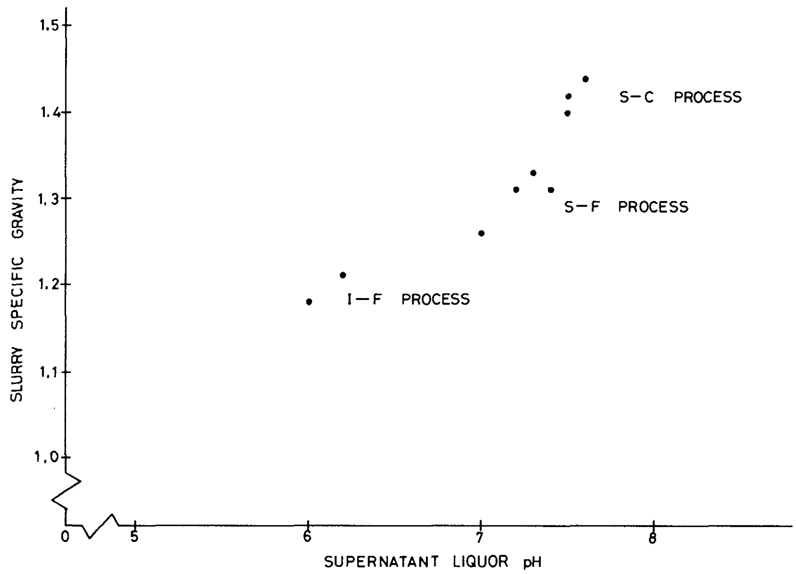

FIG.1. Variation of specific gravity with pH of ammonium diuranate slurry.

uranium trioxide production plant, and is measured as a function of the ammonium diuranate filter loading. The actual process used for uranium trioxide production is discussed in sub-section 3.1. Table I lists the pH, slurry specific gravity, sulphate content and mean particle size in micrometres of the various ammonium diuranate slurries as a function of the processing rate achieved. Reference to Table I indicates that the three mines employing the solvent-centrifuge technique produce an ammonium diuranate which can be processed at a rate far higher than that achieved with ammonium diuranate from the two mines using the ion-exchange-filter technique, while the processing rate for the mines using the solvent-filter technique falls between these two. The average processing rates for the three different ammonium diuranate types are as follows:

(i) Solvent-centrifuge type	29.2 $\mathrm{kgU \cdot h^{-1} \cdot (area)^{-1}}$
(ii) Solvent-filter type	18.3 $\mathrm{kgU \cdot h^{-1} \cdot (area)^{-1}}$
(iii) Ion-exchange-filter type	7.2 $\mathrm{kgU \cdot h^{-1} \cdot (area)^{-1}}$

It is interesting to note, from Table I, that the processing rate for each mine in a given type varies very little from the appropriate mean value.

It can be seen from Table I that the slurry specific gravity achieved for each type is also fairly constant and Fig.1 shows the variation of slurry specific

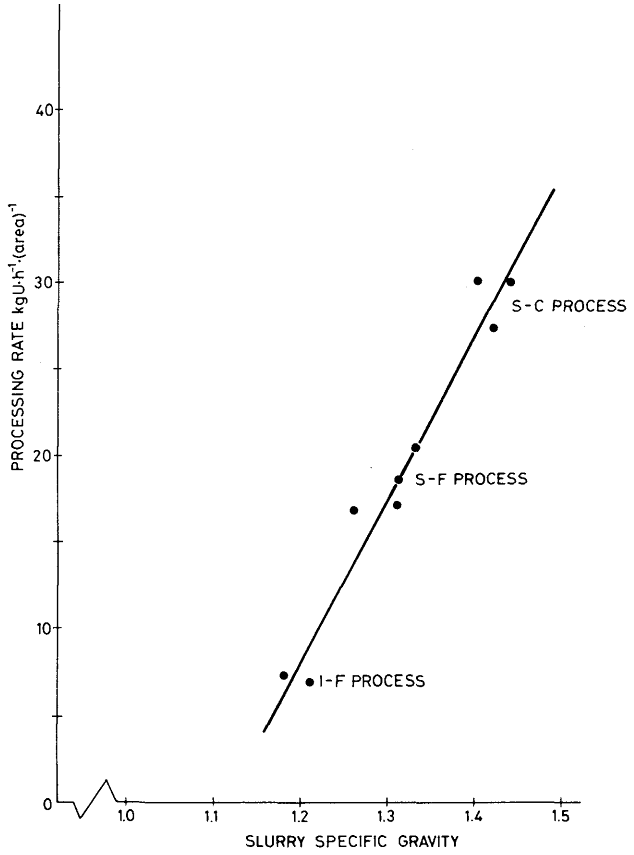

FIG. 2. Processing rate as a function of specific gravity of ammonium diuranate slurry.

gravity with the pH of the supernatant liquor of the ammonium diuranate slurry. This figure shows quite clearly that there is a dependency between the ammonium diuranate slurry specific gravity and the supernatant liquor pH and clearly the ammonium diuranate production technique determines the settling characteristics of the ammonium diuranate slurry. Intuitively one would expect the processing rate to be a function of the slurry specific gravity and this is borne out by the results tabulated in Table I. This effect is also shown graphically in Fig. 2 where the processing rate is plotted against the slurry specific gravity. Preliminary experiments have been undertaken to determine whether or not a simple adjustment of the ammonium diuranate slurry pH will have the effect of increasing the slurry specific gravity and thereby allow a greater processing rate to be achieved. These experiments have, however, thus far proved to be unsuccessful.

Consideration of the percentage sulphate in the ammonium diuranate shows that for the solvent-centrifuge technique a fairly consistent value of approximately 0.38% is obtained while for the ion-exchange-filter technique the value is 2.53%. For the solvent-filter technique however, the range of sulphate percentage in the ammonium diuranate varies from as little as 0.57% up to a maximum of 5.77% with the mean value being of the order of 3.5 to 4.5% depending on whether the low value of 0.57% is included or not. The quantity of sulphate can only be ascribed to the techniques employed by the various mines for the precipitation and washing of the ammonium diuranate slurry.

In respect of the particle size distribution of the ammonium diuranate slurry a wide range of values is obtained and again this variation can only be ascribed to precipitation techniques and conditions. From the results obtained thus far it is impossible to say precisely what effect the particle size has on the processing properties of the ammonium diuranate, although experience obtained in subsequent processing to uranium tetrafluoride would seem to imply that the lower the mean particle size, the greater the care required to maintain the correct conditions in the reduction and hydrofluorination stages.

3. URANIUM TRIOXIDE PRODUCTION

3.1. Laboratory investigations

Laboratory scale investigations on the production of uranium trioxide were performed using a thermobalance.

The thermobalance consisted of two weighed crucibles placed within a furnace. The sample to be analysed was placed in one crucible and, following normal practice, a reference material, aluminium oxide, was placed in the second crucible. A thermocouple was placed at the base of each crucible. The furnace acted as a gas seal around the crucibles so that the gaseous reactants and products could be contained and exhausted under controlled conditions. When the balance was in operation the mass of the crucibles, the temperature of the reference crucible and the differential temperature between the two crucibles was recorded on a time basis. The control of the electrical input to the furnace was such that the temperature rise of the furnace could be set at 1° intervals between rates of 1 and 25°C/min or at a fixed rate of 100°C/min.

The course of the reaction could be determined from the recorded curves and information as to the rate of mass change, the temperature over which the reaction occurred and the endo- or exothermicity of the reaction obtained.

The experimental programme on the thermobalance investigated the dependency of the physical properties of the resultant uranium trioxide on

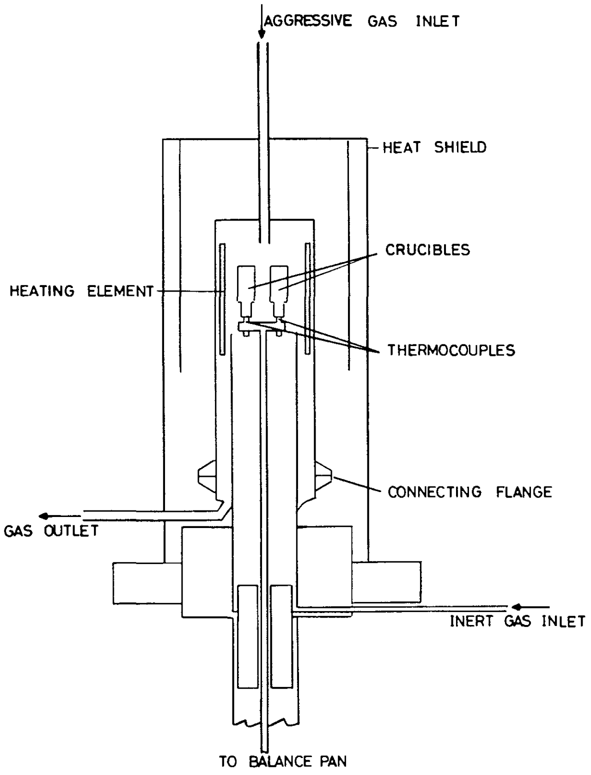

FIG.3. Schematic drawing of thermobalance.

varying drying and calcining times and temperatures for the ammonium diuranate feed material. A schematic drawing of the thermobalance is shown in Fig.3.

The laboratory investigations have so far, due to practical considerations, only been conducted on ammonium diuranate produced by one mine, and this mine used the solvent-filter technique for ammonium diuranate production. An experimental programme is at present planned to extend this investigation to the ammonium diuranate produced by all mines.

3.1.1. Drying

The results of the experimental programme for the drying of ammonium diuranate revealed that the optimum drying temperature was in the range

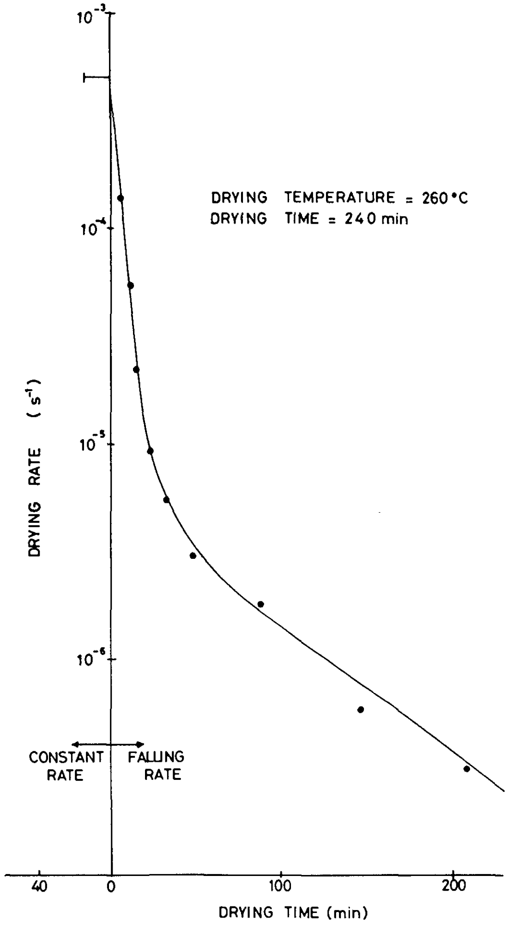

FIG. 4. Drying rate as a function of time at 260° C.

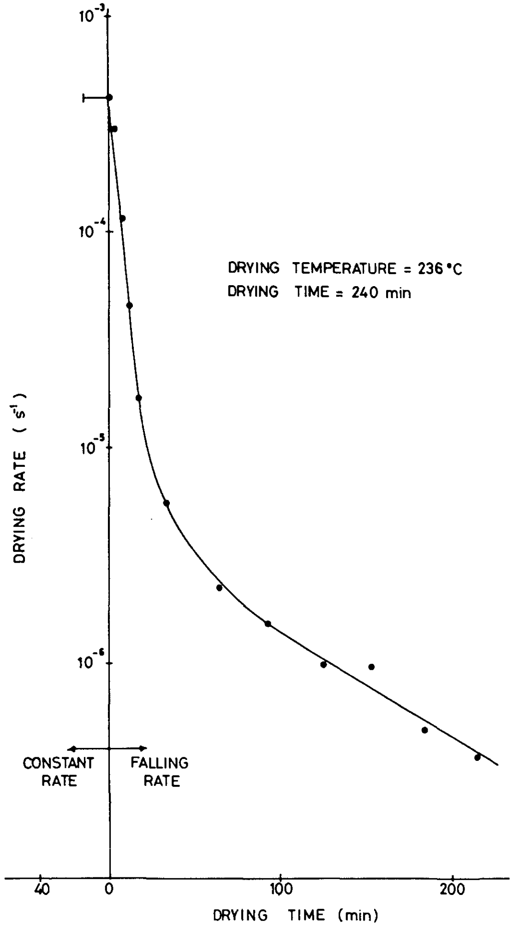

FIG. 5. Drying rate as a function of time at 236° C.

TABLE II. THERMOBALANCE RESULTS, DRYING

Maximum drying temperature (°C)	Duration Of experiment (min)	Constant drying rate (s^{-1})
95	240	1.01×10^{-4}
175	240	2.69×10^{-4}
236	240	4.14×10^{-4}
315	240	6.87×10^{-4}
422	120	1.16×10^{-3}
190	240	2.83×10^{-4}
260	240	5.09×10^{-4}
270	240	5.25×10^{-4}
340	240	6.99×10^{-4}
220	240	3.64×10^{-4}
285	240	5.63×10^{-4}
222	240	3.15×10^{-4}
258	240	5.06×10^{-4}
261	240	4.78×10^{-4}
222	240	3.91×10^{-4}
261	240	4.45×10^{-4}
220	240	4.05×10^{-4}
266	240	5.16×10^{-4}
222	240	3.09×10^{-4}

220 to 285°C. Drying outside this temperature range resulted in the uranium trioxide produced during the subsequent calcination step containing increased quantities of U_3O_8.

The curves depicting drying rate as a function of time were all similar in shape and showed both constant rate and falling rate regions. Examples are given in Figs 4 and 5. The maximum drying rate, which corresponds to the constant rate region, increases with increasing drying temperature, and the values obtained are given in Table II. Figure 6 presents a standard Arrhenius

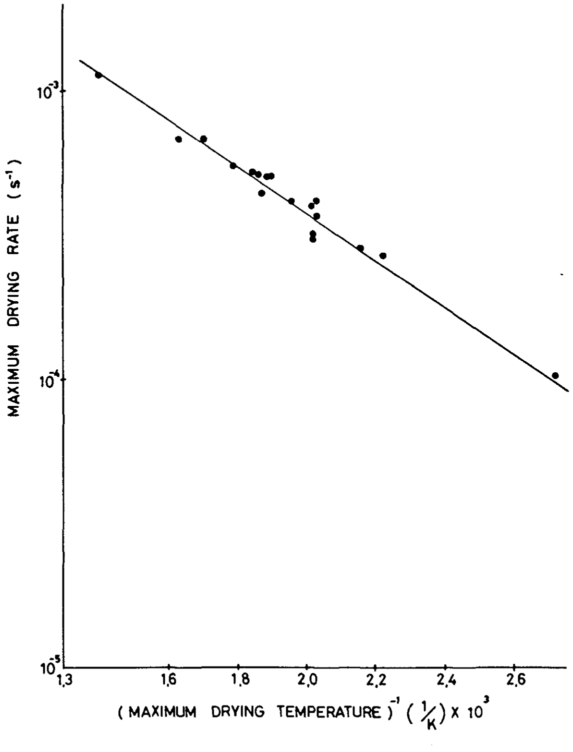

FIG. 6. Drying rate as a function of drying temperature.

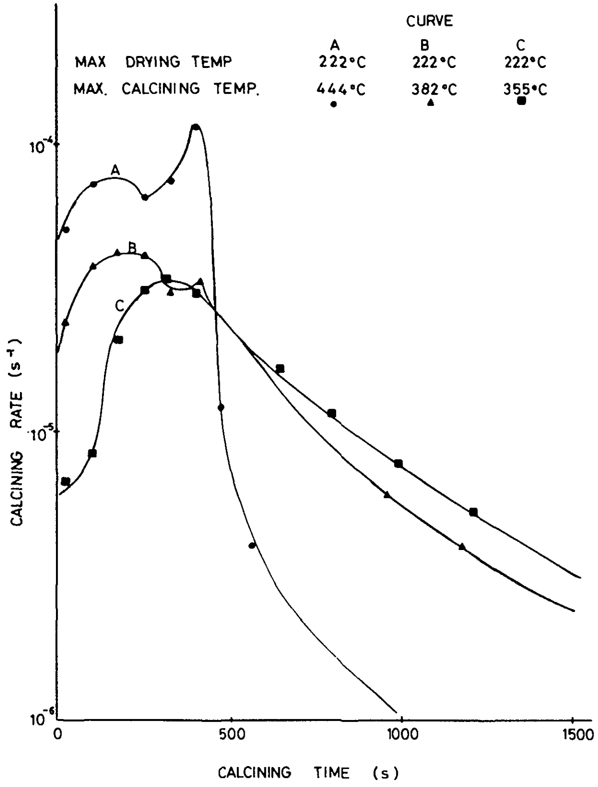

FIG. 7. Calcining rate as a function of time.

plot of drying rate versus drying temperature, and the values of the activation energy E and the factor A for the rate equation

$$r = A \exp\left(-\frac{E}{RT}\right)$$

where r is the maximum drying rate (s^{-1})
T is the drying temperature (K)
R is the universal gas constant $8.314\ j \cdot K^{-1} \cdot mol^{-1}$

are $E = 1.5706 \times 10^4\ J \cdot mol^{-1}$
$A = 1.6356 \times 10^{-2}\ s^{-1}$

The variation of sample mass with time, as recorded on the thermobalance, did not reach a completely asymptotic value even after 4 hours. This very slight continuing mass decrease may possibly have been caused by the slow decomposition of impurities, such as ammonium sulphate, present in the ammonium diuranate, or the onset of calcination at an extremely low rate and not necessarily by the removal of water. Both Figs 4 and 5 indicate that after approximately 130 min the rate of mass change had decreased to a value of approximately $1 \times 10^{-6}\ s^{-1}$.

The maximum drying temperature has a relatively small effect on the specific surface area of the uranium trioxide produced, provided that calcination occurs below about 390°C. (This effect is shown graphically in Fig.11.) The maximum drying temperature has a considerable effect on calcining and this is discussed in sub-section 3.1.2.

3.1.2. Calcining

The results of the experimental programme for the calcining of dry ammonium diuranate to uranium trioxide revealed that the optimum maximum calcining temperature was in the range 350 to 400°C. If the maximum calcining temperature was increased beyond 413°C, U_3O_8 was formed as well as the required uranium trioxide, and this effect was accompanied by the product colour changing from orange to dark green.

The curves depicting calcining rate as a function of time were all similar in shape and such curves for different calcining temperature and the same drying temperature are shown in Fig.7. The tendency for the production of U_3O_8 at calcining temperatures in excess of 413°C is clearly shown in curve A in Fig.7. The production of the U_3O_8 was typified by the occurrence of a second reaction, after the rate of the initial calcining reaction had started to decrease. The presence of this reaction is also indicated in curve B of Fig.7.

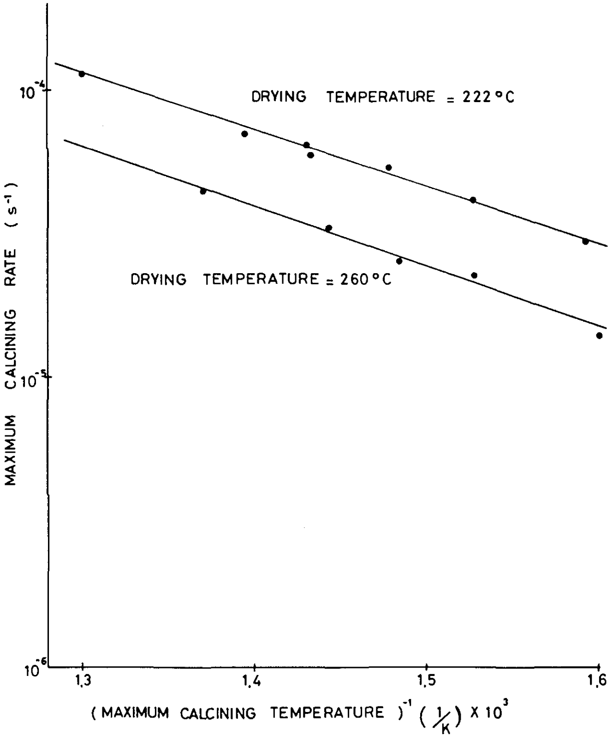

FIG. 8. Calcining rate versus calcining temperature as a function of drying temperature.

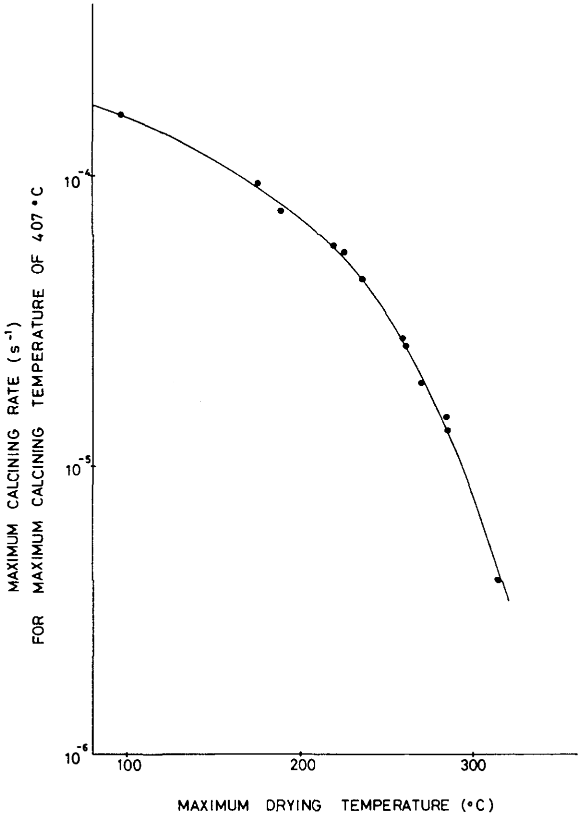

FIG. 9. Maximum calcining rate as a function of maximum drying temperature.

TABLE III. THERMOBALANCE RESULTS, CALCINING

Maximum calcining temperature (°C)	Start calcining temperature (°C)	End calcining temperature (°C)	Calcining time (min)	Maximum calcining rate (s^{-1})	Fractional mass decrease during calcining
382	300	380	26.1	4.30×10^{-5}	2.9×10^{-2}
382	312	379	24.9	2.27×10^{-5}	1.6×10^{-2}
404	235	400	20.1	5.40×10^{-5}	3.3×10^{-2}
426	272	415	16.6	6.47×10^{-5}	3.3×10^{-2}
420	318	409	11.6	3.34×10^{-5}	1.6×10^{-2}
425	282	413	12.5	5.98×10^{-5}	3.2×10^{-2}
444	263	416	8.8	7.00×10^{-5}	3.7×10^{-2}
457	330	430	15.8	4.52×10^{-5}	1.8×10^{-2}
496	290	430	4.4	1.16×10^{-5}	4.4×10^{-2}
352	308	352	43.2	1.40×10^{-5}	1.5×10^{-2}
355	266	355	26.3	3.00×10^{-5}	1.4×10^{-2}
401	310	401	20.4	2.57×10^{-5}	1.5×10^{-2}
405	150	403	20.5	1.62×10^{-4}	8.3×10^{-2}
406	242	400	17.7	9.42×10^{-5}	4.7×10^{-2}
410	240	409	21.1	4.37×10^{-5}	2.1×10^{-2}
404	360	402	17.1	0.40×10^{-5}	0.3×10^{-2}
407	236	407	27.5	7.59×10^{-5}	4.1×10^{-2}
405	298	403	20.0	2.72×10^{-5}	1.5×10^{-2}
407	330	407	30.0	1.92×10^{-5}	1.1×10^{-2}
407	274	407	25.3	5.76×10^{-5}	3.2×10^{-2}
407	340	399	7.8	1.45×10^{-5}	0.8×10^{-2}
404	344	392	8.6	1.30×10^{-5}	0.8×10^{-2}

In this experiment, calcination was performed at 382°C, but the presence of U_3O_8 could not be visually detected.

Due to a continual extremely slow rate of mass loss, at the end of the drying stage, the exact temperature at which calcination began could not be determined but appeared to fall within the range 270 to 320°C.

All the curves on Fig.7 indicate that within 30 min the calcining rate had decreased to a value of approximately 2×10^{-6} s^{-1}.

The maximum calcining rate increased with increasing calcining temperature and this effect is clearly shown in Figs 7 and 8. The maximum calcining rate decreased with increased drying temperature and this effect is shown in Figs 8 and 9. The appropriate experimental results are listed in Table III.

Figure 8 presents a standard Arrhenius plot of calcining rate versus calcining temperature, as a function of drying temperature, and the values of the activation energy E and the factor A for the rate equation

$$r = A \exp\left(-\frac{E}{RT}\right)$$

where r is the maximum calcining rate (s^{-1})
T is the calcining temperature (K)
R is the universal gas constant 8.314 $J \cdot K^{-1} \cdot mol^{-1}$

are $E = 3.7385 \times 10^4\ J \cdot mol^{-1}$ for a drying temperature of 222°C
$E = 4.1862 \times 10^4\ J \cdot mol^{-1}$ for a drying temperature of 260°C
$A = 3.8223 \times 10^{-2}\ s^{-1}$ for a drying temperature of 222°C
$A = 4.6049 \times 10^{-2}\ s^{-1}$ for a drying temperature of 260°C

The values of A and E obtained were dependent on the drying temperature, but insufficient results are currently available to determine the exact dependence.

Figure 9 is a curve depicting the maximum calcining rate as a function of the maximum drying temperature for a maximum calcining temperature of 407°C, and shows that the maximum calcining rate decreasing considerably with increasing drying temperature.

Figure 10 is a curve depicting the fractional mass change during calcining as a function of the maximum drying temperature, and shows that the fractional mass change during calcining decreases with increasing drying temperature.

Increasing the maximum temperature during the drying stage results in a decrease of both the maximum calcining rate and the fractional mass change during calcination, and this effect could be caused by either premature calcining, and/or additional decomposition of impurities such as ammonium sulphate during drying at the higher temperatures.

The molecular structure of ammonium diuranate is assumed to be represented by either $(NH_4)_2U_2O_7$ or $(NH_4)_2U_4O_{13}$ or a combination of these two formulae. The molecular masses of these compounds per atom of contained uranium are 312 and 299 respectively. The molecular mass of uranium trioxide is 286, and therefore the theoretical fractional mass changes during calcining from ammonium diuranate to uranium trioxide are 0.091 and 0.045 respectively. The maximum drying temperatures corresponding to calcining fractional mass changes of 0.091 and 0.045 can be seen from Fig. 10 to be 75°C and 185°C

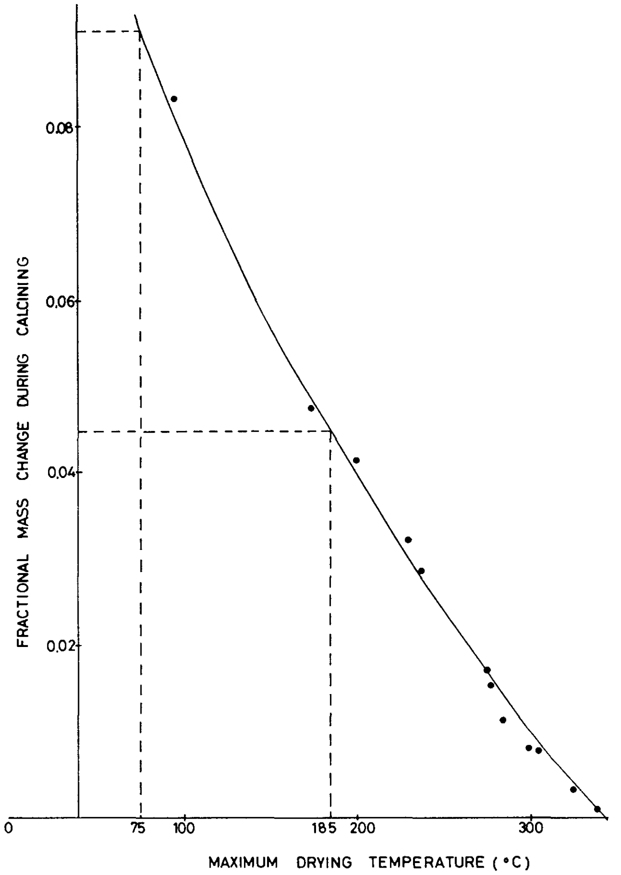

FIG.10. Fractional mass change as a function of maximum drying temperature.

respectively. These temperatures do not fall in the maximum drying temperature range of 220 to 285°C as recommended in sub-section 3.1.1, and imply that calcining has possibly started at a temperature lower than the range of 270 to 320°C as stated previously.

The specific surface area of the uranium trioxide produced was found to increase with maximum calcining temperature up to 420°C, with the most drastic increase occurring between 380 and 400°C. The surface area decreased if the maximum calcining temperature was increased from 420 to 450°C but this was accompanied by the production of U_3O_8 instead of uranium trioxide. This trend is shown in Fig.11.

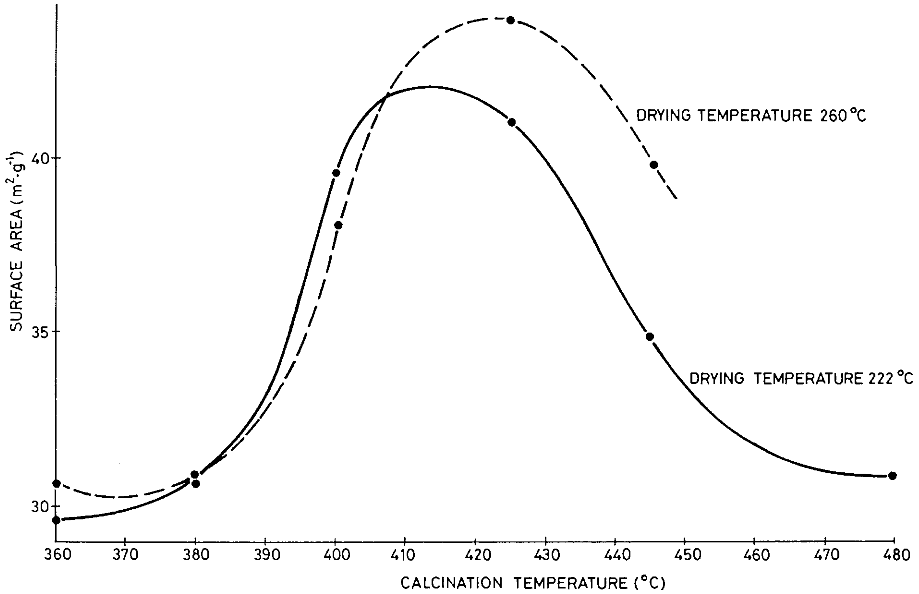

FIG. 11. Surface area as a function of calcination temperature.

3.2. Processing technique

The plant required to convert ammonium diuranate into uranium trioxide consists of the following seven components:

(i) A receiving, treatment and bulk storage system
(ii) A rotary drum filter with feed and vacuum systems
(iii) An extruder
(iv) A drier
(v) A calciner
(vi) Supply air heating systems
(vii) An exhaust gas scrubbing system.

The system was designed to allow variations in the following operating parameters:

(i) Drier residence time
(ii) Calciner residence time
(iii) Maximum drier temperature

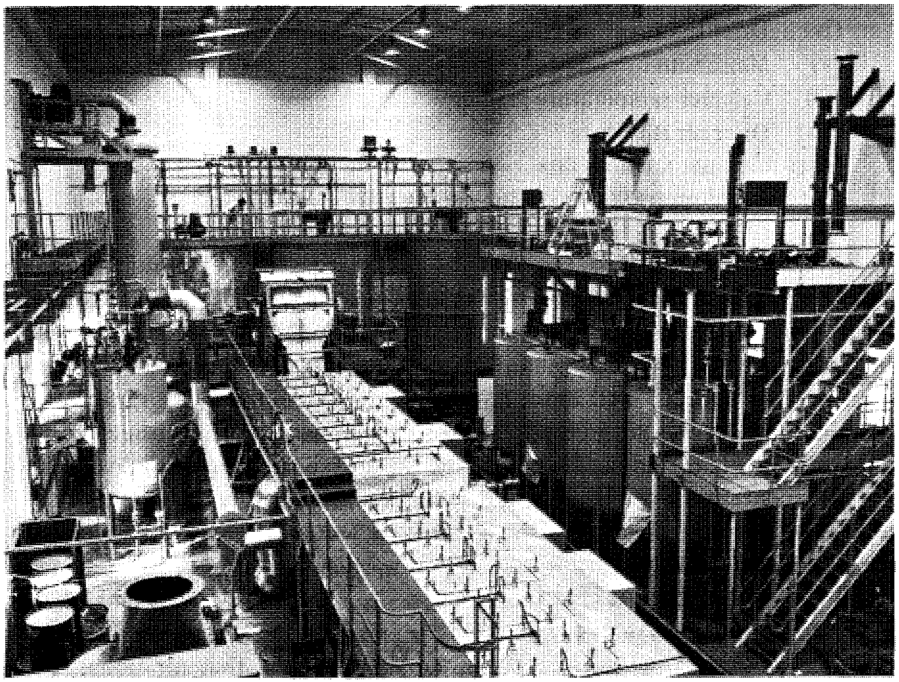

FIG.12. Overall view of pilot plant for converting ammonium diuranate into ammonium trioxide.

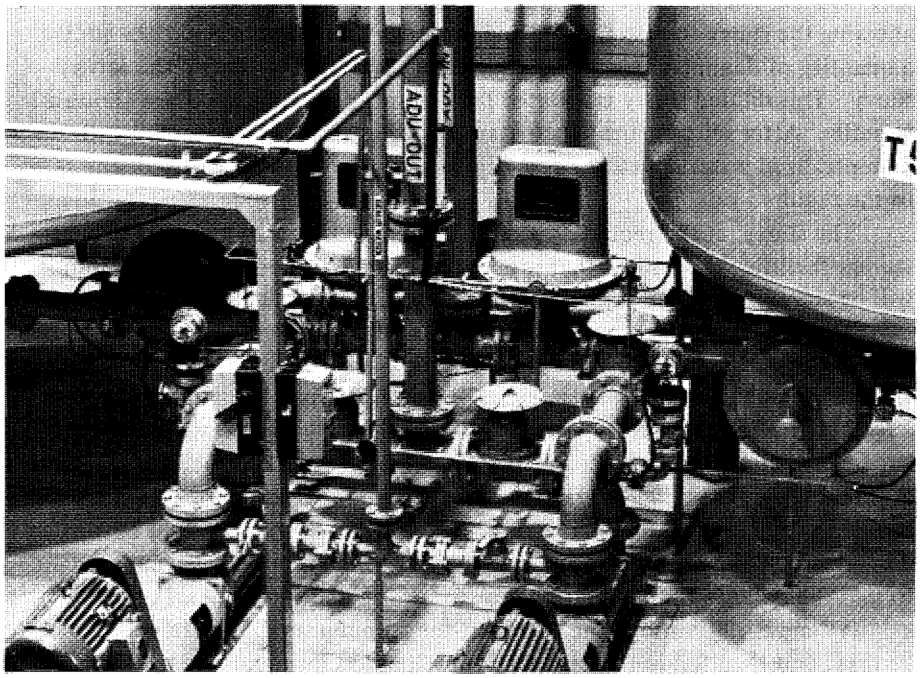

FIG.13. Ammonium diuranate pumping system.

(iv) Drier temperature gradient
(v) Maximum calciner temperature
(vi) Calciner temperature gradient
(vii) Drier air flow rate
(viii) Calciner air flow rate
(ix) Uranium trioxide production rate.

In designing the system for receiving and treating the ammonium diuranate feed material to the plant, the wealth of experience gained by Nufcor was drawn upon. Using precisely the same techniques developed by them, the ammonium diuranate slurry will be delivered in Nufcor tankers in batches of up to 25 t containing as much as 7800 kg of uranium as crude ammonium diuranate. Sampling and analysis according to Nufcor's requirements will be undertaken and the results obtained used to verify the quantities intended for delivery.

The contents of the tanker will be emptied into a receiving tank and, after satisfactory verification of the quantity of uranium delivered, pumped into a batch processing tank for settling and washing as required.

Pilot work to date has indicated the possible desirability of reducing the concentration of ammonium sulphate in the ammonium diuranate and this is achieved by washing the slurry. It is anticipated however, that additional experimental work at pilot scale will lead to techniques of plant operation which eliminate the need to wash the slurry. Washing is presently achieved by allowing the slurry to settle, decanting the supernatant liquor and then adding a quantity of demineralized water equivalent in volume to that of the settled slurry. This diluted slurry is agitated for a number of hours and then allowed to settle. After settling, the supernatant liquor is once again decanted and demineralized water added as necessary to bring the specific gravity of the slurry to the required value.

The slurry, at the required specific gravity, will then be pumped to bulk storage facilities to await further processing. The decanted supernatant liquor will be stored separately prior to further processing and final disposal.

The production of uranium trioxide from the ammonium diuranate will be achieved in a somewhat conventional two-stage drier-calciner process. The washed ammonium diuranate slurry will be pumped from the storage tanks to a feed tank supplying a rotary drum vacuum filter. This filter will be relatively large when compared with the quantity of material to be filtered, but the range in filterability expected gives processing rates varying by a factor of 5 from the fastest to the slowest values. The filter cake formed in the filter will be discharged into an extruder while the filtrate will be led via the vacuum circuit to join the decanted supernatant liquor for processing and disposal.

After passing through the extruder, the ammonium diuranate pellets will be dried and then fed to the calciner for calcination into uranium trioxide.

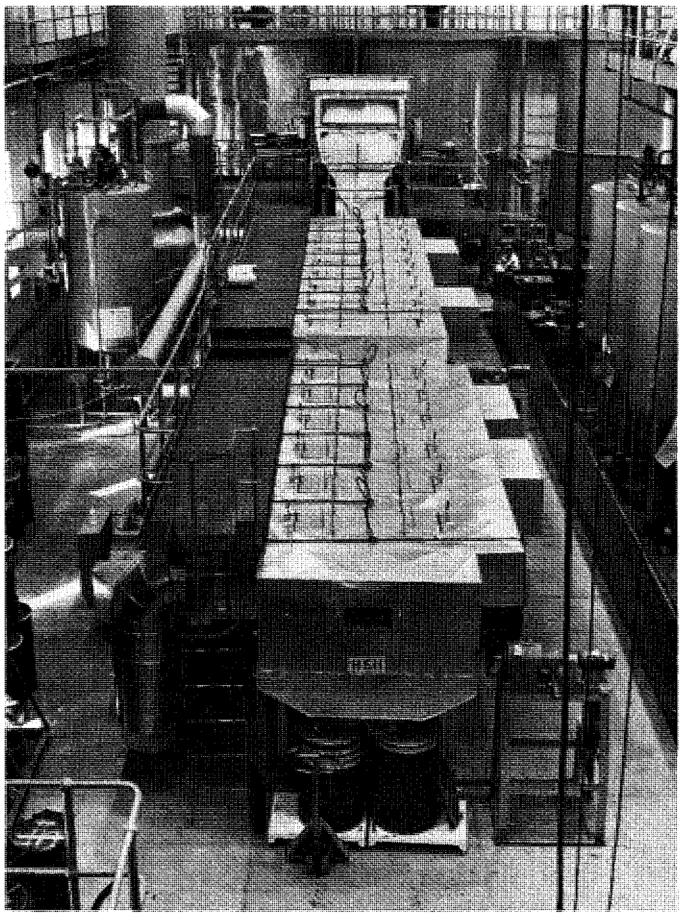

FIG.14. Overall view of dryer-calciner.

Both the drier and calciner will be constructed in a similar fashion, based on the experience already gained at pilot plant scale. Each will consist of a totally-enclosed moving stainless steel belt on which the pellets will lie. Heat will be supplied by a counter-current cross-flow of hot air over the belt. The speed of the belt may be set to give a residence time varying from 0.4 to 4.0 h while the temperature and flow rate of the air may be adjusted as required.

The uranium trioxide produced will be transferred to storage bins to await further processing.

Theoretically the production rate of uranium trioxide may be varied by adjusting the rotational speed of the vacuum drum filter and the level of the

TABLE IV. DRYING/CALCINING RESULTS

Mine	Run No.	Drying temperature (°C)	Calcining temperature (°C)	Specific surface area ($m^2 \cdot g^{-1}$)	U^{4+} in UO_3 (%)	ADU particle size (μm)	Sulphate in UO_3 (%)
3	01	276	410	46.7	1.39	7.6	1.11
	02	280	405	50.1	0.48		
	03	285	395	50.1	0.28		
	04	285	382	48.1	0.71		
	05	272	356	40.0	0.36		
	06	274	419	45.0	1.71		
4	01	288	357	23.5	0.37	1.9	0.79
	02	272	379	26.7	0.36		
	03	282	402	28.3	0.70		
	04	282	403	28.0	0.49		
	05	274	415	27.7	2.06		
5	01	278	360	12.7	0.73	0.6	2.61
	04	277	388	14.6	0.88		
	05	280	399	16.0	0.90		
	06	279	407	15.5	0.89		
	07	279	372	13.5	0.80		
	08	277	398	14.2	0.94		

ammonium diuranate slurry in the filter pan. Practical experience to date has shown that for a given set of filter operating conditions the properties of the ammonium diuranate slurry control the rate of processing and that these properties are a function of the production technique.

The process, as described, is being piloted and has been found to operate completely satisfactorily. Currently, the pilot plant has a capacity of up to 1200 kg of uranium per day as ammonium diuranate and the uranium trioxide produced is consistently suitable for further processing. General views of the pilot plant are shown in Figs 12, 13 and 14.

The ammonium diuranate slurries produced by eleven mines have been processed at pilot plant scale, and the results obtained have indicated that the proposed process for the direct conversion of ammonium diuranate, as produced at the mine, into uranium trioxide for further processing, is feasible. Certain of the properties of the ammonium diuranate and uranium trioxide produced from the mines, identified by the numbers 3 to 11 inclusive, are discussed in sub-section 3.3.

3.3. Characteristics of material produced

From the laboratory investigation it became apparent that the ammonium diuranate pellets produced in the extruder of the drier-calciner unit should be subject to a drying temperature with a maximum value in the range 220 to 285°C and a calcining temperature with a maximum value in the range 350 to 400°C.

Table IV gives examples of the conditions used in the drying and calcining tests for mines 3, 4 and 5 only. Tests were performed on all the other mines, but the range of temperatures investigated was considerably less in these other cases. In Table IV the specific surface area of the uranium trioxide produced is given, and these results are also shown graphically in Fig.15. Figure 15 shows the uranium trioxide specific surface area as a function of calciner maximum temperature and the results obtained are similar to those obtained during the laboratory investigation. An interesting feature is that the specific surface area of the uranium trioxide changes quite dramatically dependent on the type of ammonium diuranate production technique employed, with the specific surface area of uranium trioxide produced at a calcination temperature of 400°C for the ion-exchange-filter technique being some 30% of that for the material obtained from the solvent-filter technique. The corresponding value for uranium trioxide produced from ammonium diuranate obtained by the solvent-centrifuge technique is 56%. Table V, however, lists the specific surface area at 400°C maximum calcination temperature for all the mines investigated, and it can be seen that the results for mine 3 are not necessarily typical of those obtained for the solvent-filter technique. At the present stage of the experimental programme it is not possible to deduce precisely why these specific surface areas

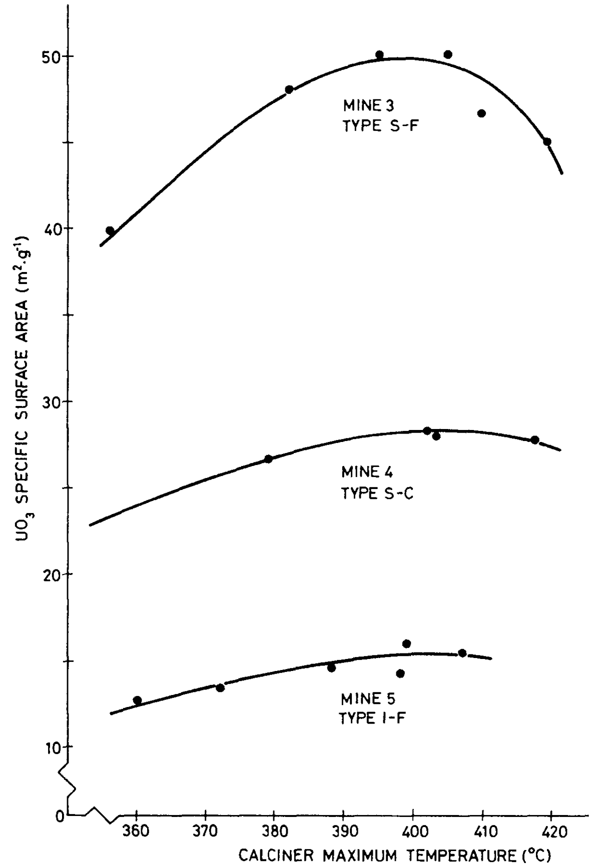

FIG.15. Uranium trioxide specific surface area as a function of calciner maximum temperature.

vary as a function of mine type or indeed as a function of individual mines. It is important to note that mines 3, 4 and 5 all produce uranium from the same geographical area and that the nine mines reported actually represent three different geographical areas. It may therefore be concluded that the geographical area in which the uranium is obtained may also have a considerable influence on the physical properties of the ammonium diuranate slurries prepared.

Subsequent processing of the uranium trioxide to uranium tetrafluoride is hindered by the presence of U_3O_8 in the uranium trioxide and consequently it is desirable to maintain this U_3O_8 content as low as possible. In order to determine the U_3O_8 content the uranium trioxide was analysed for tetravalent uranium and this was found to give a realistic indication of the degree of

TABLE V. URANIUM TRIOXIDE SPECIFIC SURFACE AREA, DRYING AT 280°C, CALCINING AT 400°C

Mine	Type	Area	Specific surface area ($m^2 \cdot g^{-1}$)
4	S-C	A	28.2
9	S-C	B	30.8
10	S-C	C	35.0
7	S-F	C	22.0
6	S-F	C	22.4
11	S-F	B	31.8
3	S-F	A	50.0
5	I-F	A	15.2
8	I-F	B	18.8

calcining to U_3O_8. Thermobalance work indicated that the critical temperature for U_3O_8 production was 413°C and experiments on a limited scale were performed in the drier-calciner unit at temperatures above this value. The results obtained for mines 3, 4 and 5 are given in Table IV and shown in Fig.16. It can be seen that as soon as the temperature increases beyond about 407°C a large percentage of tetravalent uranium is produced.

Despite the wide range in the specific surface area of the uranium trioxide produced, all material has been successfully converted into uranium tetrafluoride and an investigation is presently underway to determine precisely the importance of the various physical characteristics. Clearly the presence of sulphate in the uranium trioxide needs to be thoroughly investigated with respect to its effect upon uranium dioxide production but, at present, results have indicated that no appreciable effects are encountered.

4. SATISFYING NUCLEAR SPECIFICATION

4.1. Impurities

In South Africa the ammonium diuranate slurry delivered to the main processing plant contains a large number of impurities, the major one being ammonium sulphate. The bulk of the ammonium sulphate is lost, being either

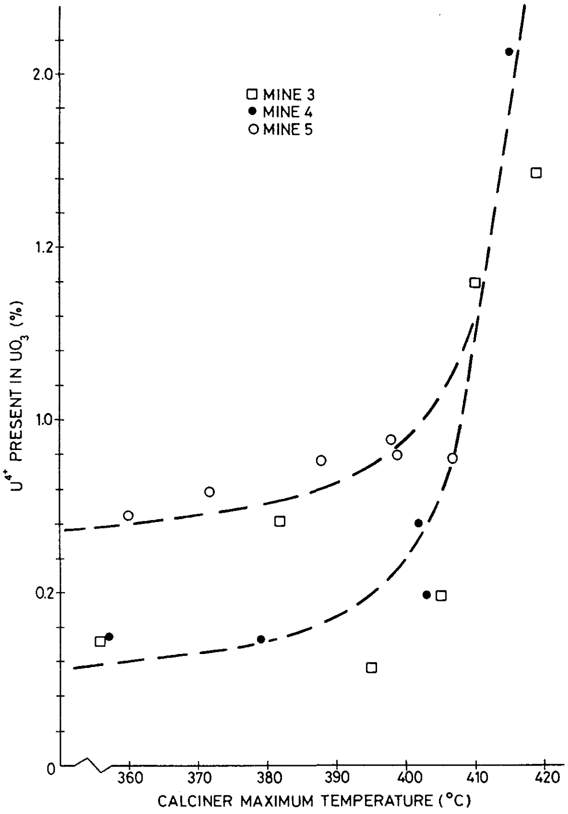

FIG.16. Dryer-calcining results (see also Table IV).

volatilized or decomposed, during the processing steps up to, and including, the reduction stage to uranium dioxide. The concentrations of a large proportion of the other impurities present in the feed material are reduced during the hydrofluorination of uranium dioxide to uranium tetrafluoride and in the processing of uranium tetrafluoride to uranium hexafluoride so that the only significant impurity reporting in the uranium hexafluoride crystallizer is molybdenum.

In general the impurities present in uranium hexafluoride can be divided into two main categories:

(i) Impurities which affect the performance of uranium as a nuclear fuel.
(ii) Impurities which affect the enrichment process.

TABLE VI. CLASSIFICATION OF IMPURITIES IN URANIUM AND TYPICAL VALUES OF SOUTH AFRICAN PRODUCTS – ELEMENTS WITH HIGH NEUTRON CAPTURE

Element	Factor	Typical analysis as ppm on a U basis			Typical UF_6 analysis as ppm boron equivalent on U basis
		ADU	UF_4	UF_6	
Al	0.000 13	50	24	13	0.0016
B	1	1	–	0.2	0.20
C	0.000 004 4	–	–	–	–
Ca	0.000 16	100	67	13.1	0.002
Cd	0.312	<1	–	0.2	0.0624
Co	0.004 9	20	118	17.4	0.0853
Cr	0.000 85	10	27	12.2	0.0104
Cu	0.000 87	10	28	3.0	0.0026
Dy	0.083 7	<0.03	–	–	–
Fe	0.000 67	500	230	61	0.0409
Gd	4.189	<0.1	–	–	–
Li	0.146	–	–	6.7	0.9782
Mg	0.000 041	12	8	19	0.0008
Mn	0.003 5	3	3	1.7	0.0059
Na	0.000 33	100	40	–	–
Ni	0.001 1	3	95	5	0.0055
Si	0.000 082	150	60	15.4	0.0013
Sm	0.533 4	<0.1	ND	ND	
V	0.001 4	–	0.4	0.5	0.0007
				Total	1.4

– Not analysed as consistently acceptable results obtained.
ND Not detected.

Note: The Specification requires that the total of the above impurities, expressed as boron equivalents, should not exceed 8 ppm on a U basis.

TABLE VII. CLASSIFICATION OF IMPURITIES IN URANIUM AND TYPICAL VALUES FOR SOUTH AFRICAN PRODUCTS – ELEMENTS FORMING VOLATILE FLUORIDES

Element	Typical analysis as ppm on a U basis			Specification
	ADU	UF_4	UF_6	ppm on a U basis
Mo	75	8	8.6	<1.4
W	–	0.6	–	<1.4
V	–	0.4	0.5	<1.4
Cr	10	27	12	<10.5
Sb		ND	1	<1
Br	–	–	–	<5
Cl	–	–	–	<100
Nb	10	1.3	–	<1
P	–	–	–	<50
Ru	–	–	–	<1
Si	150	60	15.4	<100
Ta	–	<0.5	–	<1
Ti	–	1	1	<1

ND Not detected.
– Not analysed due to consistently acceptable results.

Impurities which affect the enrichment process can again be divided into two further groups, namely, those metals which form volatile fluorides or oxyfluorides and those metals which form non-volatile fluorides.

The efficiency of nuclear fuel operation is reduced if the fuel contains impurities which capture neutrons. The nuclear specification is based on parts per million boron equivalent, where the capacity for neutron capture is expressed as a function of the absorption cross-section of the element for thermal neutrons as compared with that of boron. Table VI lists the concentrations of the appropriate elements and their boron equivalents.

Due to the fact that enrichment tends to concentrate the volatile impurities in the enriched stream it is desirable to have as few non-uranium volatile fluorides as possible in the uranium hexafluoride feed to the enrichment plant. Of elements forming volatile fluorides or oxyfluorides the concentrations of molybdenum, tungsten, vanadium and chromium are normally specified on a ^{235}U basis, but are shown in Table VII, together with the other volatile fluorides, on a total U basis.

TABLE VIII. CLASSIFICATION OF IMPURITIES IN URANIUM AND TYPICAL VALUES FOR SOUTH AFRICAN PRODUCTS – ELEMENTS FORMING NON-VOLATILE FLUORIDES

Element	Typical analysis as ppm on a U basis		
	ADU	UF_4	UF_6
Al	50	24	13
Ba	<1	–	–
Bi	<1	–	1.2
Cd	<0.3	–	0.2
Ca	100	67	13.1
Cr	10	27	12.2
Cu	10	28	3.0
Fe	500	230	61
Pb	<10	–	2
Li	–	–	6.7
Mg	12	8	19
Mn	3	3	1.7
Ni	3	95	5
K	80	–	–
Ag	–	–	–
Na	100	40	–
Sr	–	–	–
Th	–	–	–
Sn	<3	–	2
Zn	<10	–	12
Zr	500	460	–
Total	1393	982	152

– Not analysed due to consistently acceptable results.

Note: The Specification requires that the total of the above impurities should not exceed 300 ppm on a U basis.

Non-volatile fluorides formed during uranium hexafluoride production may be entrained in the flow of uranium hexafluoride to the enrichment plant and these non-volatile fluorides may then deposit out at various points in the enrichment plant and cause uneven flow characteristics and possible process blockages. Table VIII lists the concentration of the non-volatile fluorides.

Specifications for nuclear grade uranium have been drawn up by various organizations and, although varying in detail, have the same overall structure. The specifications set down for the South African conversion plant are given in Tables VI, VII and VIII and comply with accepted international requirements.

As previously stated, the major significant impurity present in the raw South African uranium hexafluoride produced is molybdenum which is present in the form of molybdenum hexafluoride and molybdenum oxy-tetrafluoride with a total concentration in the range 3 to 10 ppm. This raw uranium hexafluoride is purified to the required nuclear specification by distillation.

4.2. Processing technique

The processing technique adopted for uranium hexafluoride purification is a simple single distillation column. The distillation column is equipped with reboiler and condenser and the material is fed in the liquid phase into the column at a position such that approximately 20% of the total number of theoretical plates are below the feed point. The column is operated under total reflux conditions, with a bleed stream for non-condensables and highly volatile impurities being periodically operated in the vicinity of the condenser, and a bleed stream for the heavy impurities being periodically operated in the region of the reboiler. A side-stream of material of the required purity is extracted continuously from the column. Current indications are that as much as 99% of the feed stream can be recovered as uranium hexafluoride of the required purity while the remaining 1%, corresponding to the impure streams, is processed for the recovery of the uranium and the discharge of the impurities.

5. CONCLUSIONS

The experimental and pilot programmes thus far conducted have provided sufficient information and generated enough confidence that the process involving the direct conversion of mine-produced ammonium diuranate into uranium trioxide will be adopted for the South African refinery. This process has the advantage that the cost, inconvenience and effluent problems associated with the re-dissolution of a uranium concentrate and the resultant re-precipitation of ammonium diuranate are eliminated, but that the uranium trioxide produced does not exhibit consistent chemical and physical properties.

In spite of this variation in the properties of the uranium trioxide, further processing through to uranium hexafluoride can be achieved with only minor adjustments in the appropriate operating parameters.

The entire process for the direct conversion of ammonium diuranate into uranium hexafluoride still requires considerable experimental investigation in order that the physical and chemical properties of the uranium trioxide which are significant in terms of subsequent processing can be identified.

Those operating parameters of the drier-calciner which affect the relevant uranium trioxide properties need to be identified and the dependence of the actual values of these properties on the operating conditions determined, so that uranium trioxide exhibiting more consistent physical and chemical properties may be produced.

ACKNOWLEDGEMENTS

The authors wish to thank staff members of the Process Metallurgy Division of the South African Atomic Energy Board who assisted in the production of this paper.

DISCUSSION

H. PAGE: 1. What is the effect of the high surface area UO_3 on subsequent reactions?

2. Has Dr. Colborn considered establishing conditions for a blended feed of slurry rather than for slurries from individual mines?

R.P.COLBORN: 1. High surface area of the UO_3 requires that care be taken during subsequent processing steps to maintain the material temperature at a value of less than 620°C to prevent material sintering.

2. Yes, blended slurries will be considered once a greater understanding of the drying-calcining mechanism has been obtained. Rightly or wrongly it has been decided that, at present, the product of each mine should be considered independently.

S. SEN: 1. Could the authors please indicate the value of sodium contents in the different grades of concentrates (produced by different process flow-sheets) received in the refinery as well as the sodium contents in the UO_3 and UF_4?

2. Could the authors please indicate the pressure and temperature in the reboiler of the UF_6 distillation unit?

R.P. COLBORN: 1. The actual values of the sodium content obtained in ADU, UF_4 and UF_6 are given in Table VIII. These values apply to a mine using solvent extraction and filtrate for the preparation of the raw ammonium diuranate slurry and are the only values currently available.

2. This question is essentially outside the scope of the paper. However, it can be stated that a temperature of 95°C is used in the reboiler and the pressure obtained corresponds to the actual operating pressure of the column.

A REVIEW AND UPDATE OF REFINING PRACTICE IN CANADA

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Abstract

A REVIEW AND UPDATE OF REFINING PRACTICE IN CANADA.

This paper first reviews the history of the Port Hope uranium refinery of Eldorado Nuclear Limited. The current processes used for the production of UO_3, UO_2 and UF_6 from yellow cake are then discussed. Recent process changes and developments in the areas of solvent extraction and UO_3 production together with new processes for the production of ceramic UO_2 and UF_4, are described. Environmental and waste management problems, progress and solutions are next considered. Finally, some experience in siting a new UF_6 refinery, with respect to Environmental Impact Statements and public hearings, conclude the paper.

1. INTRODUCTION

> *It takes a Philadelphia physicist to understand it but after an hour or so I think I got to understand what was presented ...*
> *George Stapleton, Farmer, Hope Township*

Quoted in ‘ Report of the Environmental Assessment Panel ’, Eldorado UF_6 Refinery, Ontario, February 1979, Fed. Env. Assess. Review Office, Ottawa, Canada.

2. THE PORT HOPE REFINERY

The refinery at Port Hope, located in southern Ontario some 100 km east of Toronto (Figs 1 and 2) first operated as a radium refinery under the ownership of Eldorado Gold Mines Ltd. Radium was mined at the Port Radium mine (Great Bear Lake, North West Territories), concentrated, and the concentrate shipped to Port Hope.

Operations began in 1933, and until 1953 the refinery produced radium products. As a result of an over-abundance of radium, and decreasing prices,

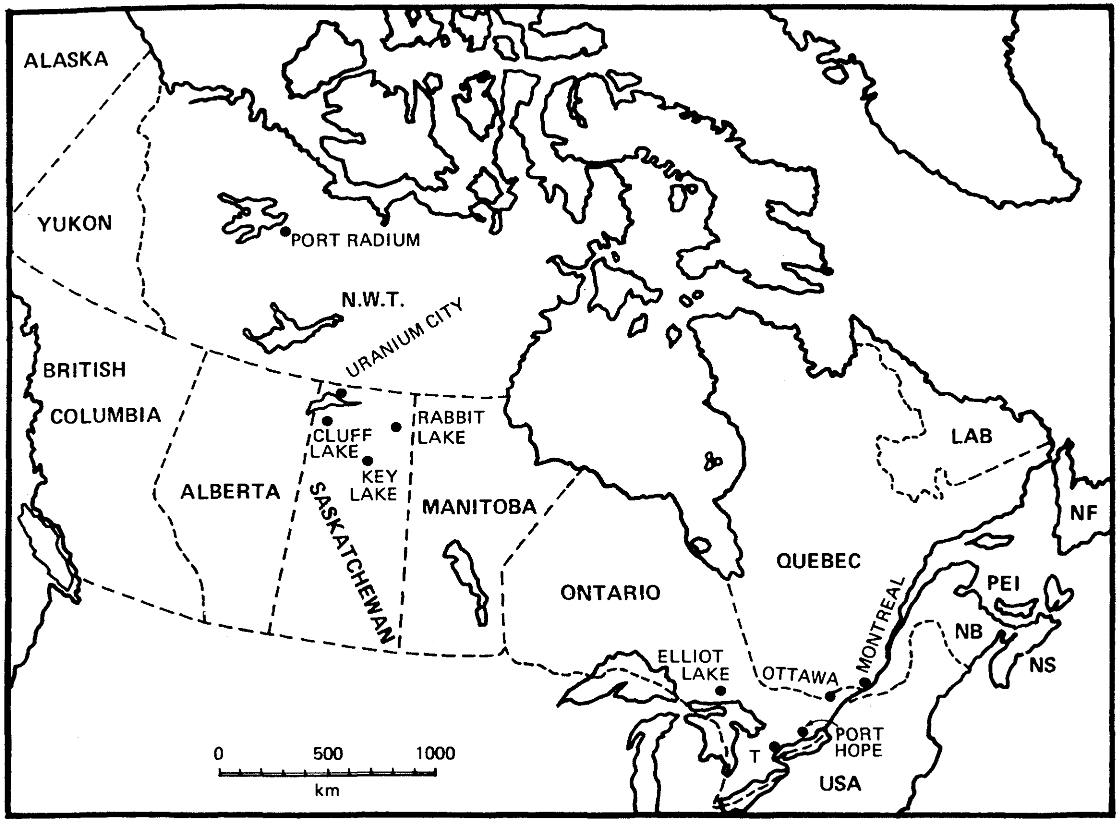


FIG.1. Uranium mining and refinery locations in Canada.

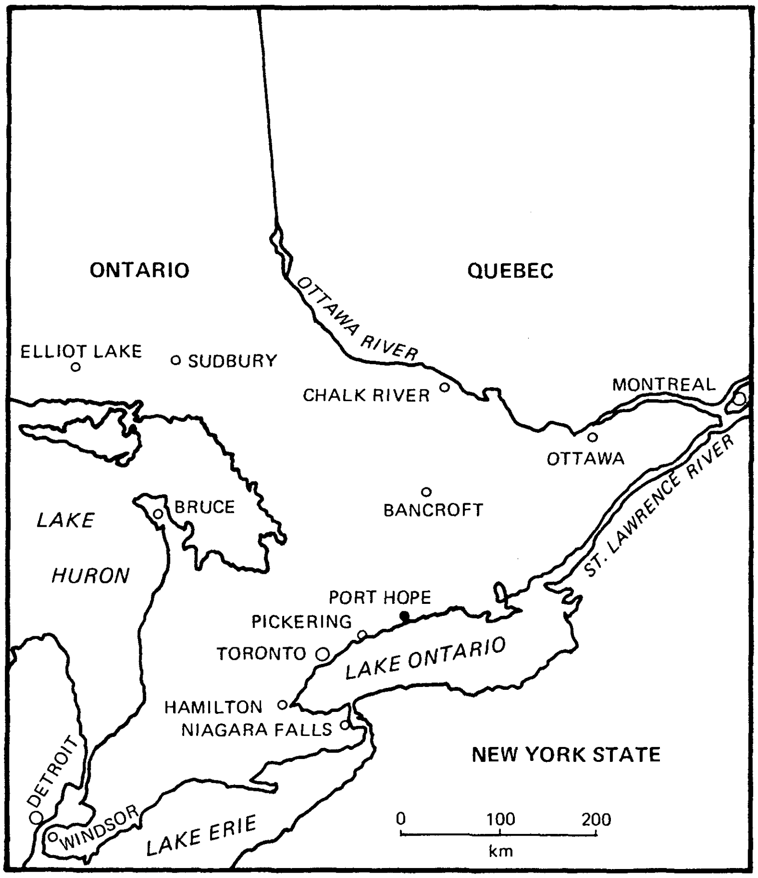


FIG.2. Location of Port Hope refinery in Ontario.

the Port Radium mine was shut down in 1940. It was re-opened in 1942, this time as a uranium mine, to supply uranium to the Manhatten Project in the United States of America.

The Port Hope refinery continued to produce radium products until 1953, but also in 1942 it began to process uranium gravity concentrates from Port Radium.

In 1944, because of the importance of uranium, Eldorado Gold Mines and its assets (mine and refinery) were acquired by the Federal Government of Canada. The name was changed to Eldorado Mining and Refining Ltd, and incorporated as a Crown Corporation.

Since that time, Eldorado (which became Eldorado Nuclear Ltd in 1968) has operated two uranium mines (Port Radium, now closed, and Beaverlodge) and the refinery at Port Hope.

The production of uranium dioxide for use as fuel for the CANDU nuclear reactors began in 1962, and continues. A new UO_2 plant is in the construction stage. Uranium hexafluoride was first produced by Eldorado in 1970 with the commissioning of a new plant.

Current plans are to construct two new UF_6 refineries, one in Ontario and (later) one in Saskatchewan.

In Table I is shown the main historical data on Eldorado Nuclear Limited. Figure 3 shows the production statistics of major uranium products over the last 5 years.

3. CURRENT PROCESSES

The main uranium products, UO_3, UF_6 and UO_2, are produced in three sections of the refinery (Fig.4). In the UO_3 plant yellow cake is converted to purified UNH solution and uranium trioxide. In the UO_2 plant UNH (or UO_3) is converted to ceramic UO_2 for CANDU fuel. In the UF_6 plant, UO_3 is converted first to UO_2, then to UF_4 and finally to UF_6. These three processes are reviewed in the following sub-sections.

3.1. The UO_3 process

Yellow cake (sodium, ammonium and magnesium) from Canadian and off-shore producers is received in 205-ltr steel drums. These are weighed, opened in a drum-opening station, and sampled by an auger process. Ammonium diuranates are fed to a calciner where the ammonia is removed. Both calcined and uncalcined feed is then blended, and goes to the digestion circuit.

3.1.1. Digestion

Digestion of the feed is carried out in four batch digestors, using 13M nitric acid, plus some phosphoric acid to complex thorium. The resulting slurry contains suspended solids (<1%, largely silica), some 2M free nitric acid, and approximately 375 kg/m^3 U as uranyl nitrate. In contrast to operations in the United Kingdom and France the solution is not filtered prior to entering the solvent extraction circuits.

Off-gases from digestion pass through a venturi scrubber. The scrubber liquors are recycled to the digestors, while the treated off-gas goes to nitric acid recovery. Sumpage from the digestion area is fed to the UO_3 plant sump system for recycle.

TABLE I. HISTORICAL HIGHLIGHTS

Date	Event
1926	Eldorado Gold Mines incorporated to develop some gold properties, mostly in Manitoba. They proved to be uneconomic.
1930	Gilbert LaBine and Charles St. Paul discovered pitchblende at Great Bear Lake, NWT, 80 km south of the Arctic Circle – Canada's first orebody of pitchblende.
1933	The first ore was mined for radium at Port Radium and shipped to Eldorado's refinery at Port Hope. The first gram of radium was extracted here in May 1933 from bulk samples. Uranium was virtually a waste product of refining the ore. The commercial product was radium.
1934	Milling operations started at Port Radium.
1935	Extraction of radium and uranium began on a production basis at the Port Hope refinery. Radium was the main product and uranium a by-product with only minor uses, mainly as a ceramic colouring material.
1936	Northern Transportation Company Limited purchased by Eldorado. This Company operates a transportation system on the Mackenzie River from Waterways in northern Alberta to Tuktoyaktuk on the shores of the Arctic Ocean. It remained a wholly-owned subsidiary of Eldorado until September 1975.
1939	It was discovered that the uranium atom could be split, producing unprecedented amounts of energy in the process.
1940	Port Radium mine was shut down because of difficulties of operating in wartime. Refinery was shut down for a 6-week period. Operations at the refinery resumed on a reduced scale, refining concentrates from the Belgian Congo.
1942	The mine at Port Radium was re-opened on a crash basis. A stable source of uranium was required for the Manhattan Project in the USA. The Manhattan Project was in later years to become the United States Atomic Energy Commission. Eldorado began to produce uranium on a larger scale, as well as radium, at the refinery and this continued into the early 1950s.
1944	In the interest of security and control, the Canadian Government acquired the assets of Eldorado and a Crown company named Eldorado Mining and Refining Limited was formed. An aviation division was set up to service Port Radium and Exploration. Since then, Eldorado has remained a federal government Crown Corporation.
1948	Eldorado was appointed the sales agent for all uranium produced in Canada, a practice which continued through the 1950s.
1953	Following Eldorado's development of cobalt beam therapy for the treatment of cancer, there was no longer a market for radium. Consequently, the Company stopped producing radium in 1953, relying on uranium refining. Eldorado started up Canada's second uranium producing mine in the Beaverlodge area of northern Saskatchewan, which still operates today. A research and development division was formed with headquarters in Ottawa.
1955	Port Hope Refinery was converted to the solvent extraction process to produce nuclear grade uranium trioxide or orange oxide.

TABLE I (cont.)

Date	Event
1958	Plant-scale facilities were added for the production of uranium metal and natural ceramic oxide powder.
Early 1960s	World demand for uranium virtually ceased in the early 1960s as the US and UK governments stopped stock-piling uranium for military uses. The Port Radium mine, discovered in 1930, was shut down due to lack of economic ore reserves.
1961	Vacuum furnace was installed for the melting and casting of uranium metal and alloys of uranium metal.
1962	In order to help sustain the Port Hope operations, Eldorado began producing ceramic uranium dioxide or UO_2 at the refinery to fuel the Canadian nuclear energy programme. Since that time all the UO_2 fuel for the remarkably successful CANDU reactors has been processed at Port Hope and sent to fuel fabricators in Toronto, Peterborough, Port Hope and, more recently, Moncton.
1968	Plant was constructed for the production of nuclear pure zirconium billets from zircon sand. Design was begun on a 2200 ton/year production facility to produce uranium hexafluoride (UF_6).
1970	Based on its UO_2 experience, Eldorado entered the world market for nuclear reactor fuels in 1970 with the start-up of uranium hexafluoride or UF_6 operations. UF_6 capacity has been increased steadily during the 1970s. Today, about 23% of the nuclear reactor fuel processed at this refinery is UO_2 for CANDU reactors and 77% is UF_6 for foreign-designed light water reactors.

3.1.2. Solvent extraction

From the digestion circuit the feed is pumped to the solvent extraction (SX) circuit, the flow being controlled by a rotary dip feeder. Contactors used in the SX circuit consist of a 76 cm diameter Mixco column (extraction), and 56 cm pulse columns for scrubbing and stripping.

Eldorado uses 25 vol.% TBP in Exxon DX3641 as the solvent. After contacting the aqueous and organic phases in the Mixco extraction column, at an A:O ratio of 1:4, the loaded solvent phase contains about 100 kg/m^3 U. This is discharged from the top of the column and cascades into the bottom of the scrub (pulse) column. Raffinate from the extraction column goes to the raffinate treatment circuit where it is treated prior to drumming (discussed further in subsequent paragraphs).

In the scrub stage, the loaded solvent is contacted with a small flow of pure water or pure uranyl nitrate solution (OK liquor), at an A:O ratio of 1:15, to remove co-extracted impurities and free acid. Aqueous discharge from the scrub stage is recycled to the digestion circuit.

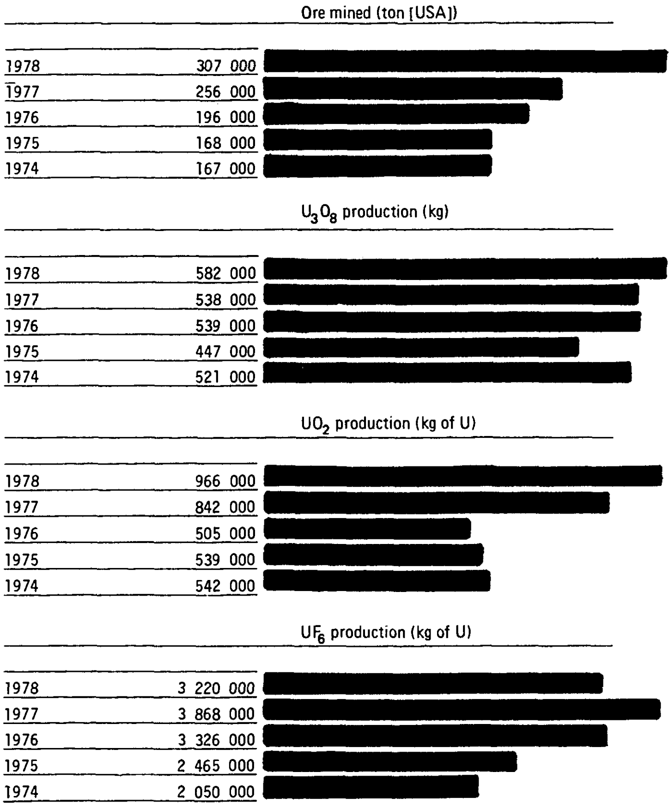


FIG.3. Production statistics 1974 to 1978.

Scrubbed solvent from the top of the scrub column flows into the bottom of the strip (pulse) column, where it is contacted with pure water, at an A:O ratio of 1:1.5, to strip the uranium. The uranyl nitrate solution produced goes to a skimmer to remove any entrained solvent, and then to an evaporation stage.

A portion (bleed) of the stripped solvent is contacted with a sodium carbonate solution (50 kg/m^3) to remove 'unstrippables' and other deleterious components and, together with the rest of the stripped solvent, is recycled to the uranium extraction stage. Aqueous wastes from this treatment operation, plus general area sumpage, are treated in the UO_3 plant sump treatment system for recycle.

The pure OK liquor (~130 kg/m^3 U) is concentrated to about 1300 kg/m^3 U in two evaporation stages. Vapours from evaporation are partially condensed and sent to the process condensate tank for recycle. Approximately 80% of the vapours are vented to atmosphere. Sumpage goes to the plant treatment system for recycle.

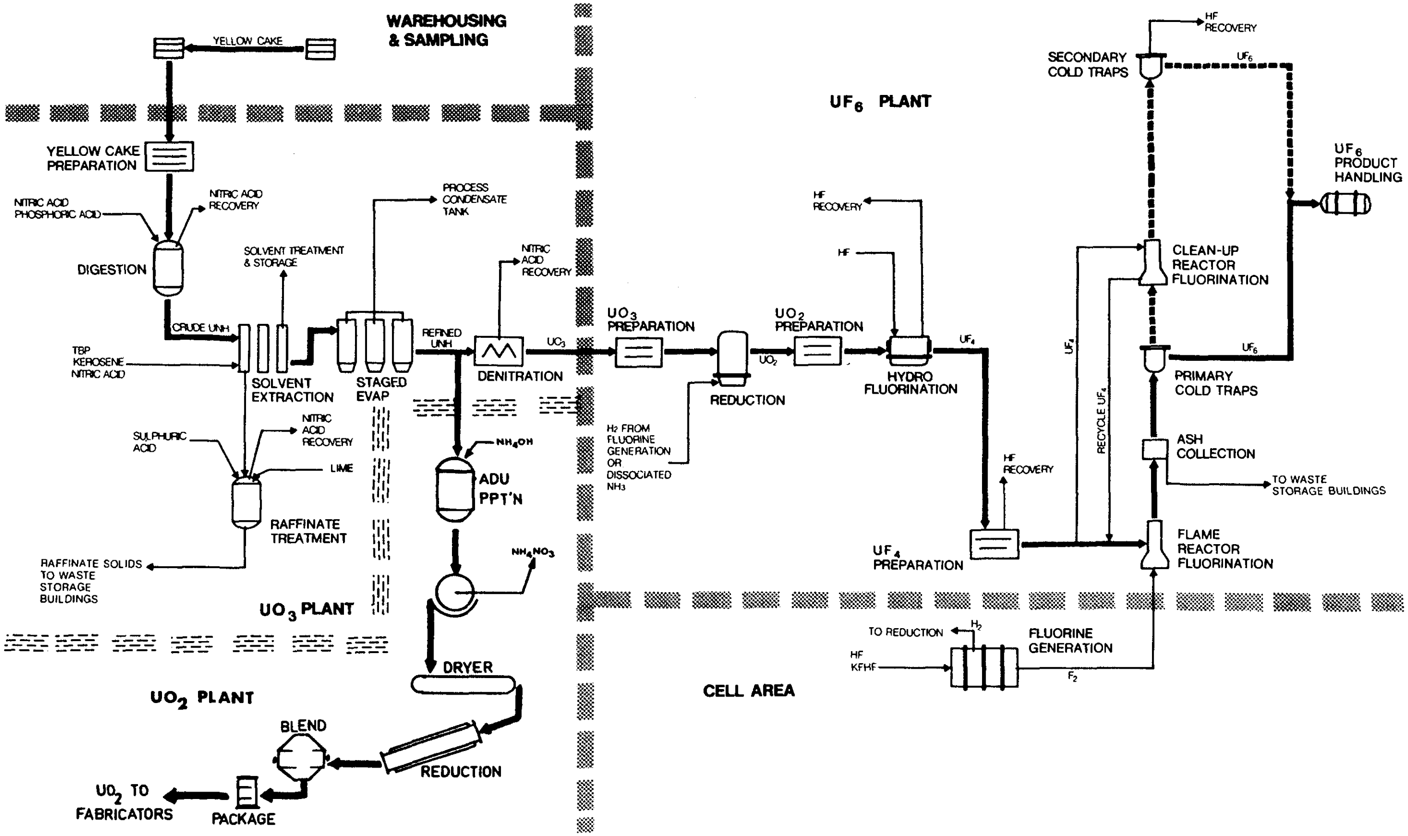


FIG.4. Schematic diagram of Port Hope refinery processes.

Following evaporation, the concentrated uranyl nitrate hexahydrate (UNH) is thermally decomposed in continuous pot denitrators to UO_3. Off-gas from this stage is scrubbed and fed to the nitric acid recovery circuit for recycle to digestion.

3.2. The UF_6 circuit

3.2.1. Uranium dioxide

Product from the denitration pots is pulverized and 'airveyed' to the UF_6 plant, where the UO_3 is formed into briquettes and reduced by dissociated ammonia to UO_2 in moving bed reactors. Reduction is by hydrogen, usually as dissociated ammonia but hydrogen generated in the fluorine cells has also been used in the reactor for UO_3 reduction.

Both UO_3 and UO_2 feed transfer and preparation stages have bag-houses for dust collection. Reduction reactor off-gases are passed through a packed tower KOH scrubber prior to discharge to the atmosphere.

3.2.2. Uranium tetrafluoride

The UO_2 briquettes are fed to four vertical hydrofluorination reactors and reacted with gaseous hydrogen fluoride to produce uranium tetrafluoride. Reactor off-gas is scrubbed in packed tower columns with KOH solution.

3.2.3. Uranium hexafluoride

UF_4 from the hydrofluorination reactors is pulverized and fed to the fluorine flame reactors, where it is reacted with fluorine to produce uranium hexafluoride. Ash from the flame reactors is drummed and stored. Some ash is recycled to the flame reactors.

After filtering, the gaseous UF_6 is cooled and condensed as solid UF_6 in weighed cold traps, and then melted prior to transferring to shipping cylinders.

3.2.4. Fluorine cells

There are 44 cells each of 6000 A, including eight new cells recently commissioned. All the cells have series rectification, by two rectifiers. The base electrolyte is KHF_2, with gaseous HF input to maintain about 41 wt.% HF concentration. Temperature in the cells is maintained at 95 ± 5°C by internal water cooling.

Fluorine production is on a demand basis, production being sufficient to produce some 22 000 kg of UF_6 per day.

3.3. The UO_2 circuit

This circuit is used for the production of ceramic natural uranium dioxide, which is converted into fuel bundles for the CANDU nuclear reactors. Eldorado does not manufacture the fuel bundles, this is carried out by Canadian General Electric, Westinghouse Canada Ltd, and Combustion Engineering.

3.3.1. The ADU process

This process has been employed almost exclusively since 1962 for the production of ceramic UO_2.

Feed to the ADU circuit is uranyl nitrate solution from the SX circuit, containing some 400 kg/m^3 U, 200 kg/m^3 NO_3^-, and at a pH of about 2. The solution is diluted to approximately 200 kg/m^3 U before adding aqueous ammonium hydroxide to pH 8 at about 80°C, to precipitate ammonium diuranate (ADU) in a batch operation. After settling, the thickened ADU is filtered and washed on a drum filter. The moist ADU is fed through an extruder onto a belt dryer. Drying of the resultant 'spaghetti' is done at about 120°C.

The dried material then goes to reduction to ceramic grade UO_2, by either batch or continuous reduction modes.

Batch operations employ vertical furnaces of either 50 or 500 kg capacities. Dissociated ammonia is used as the reductant, and 'exalene' (burned natural gas) as the inert gas. Continuous operations employ rotary kilns, either 23 or 36 cm diameter. Again, dissociated ammonia is used as the source of hydrogen.

Product from the kilns and batch furnaces is blended and packaged for shipment to the fuel fabricators.

Gaseous and solid products from the operation are treated and recycled as necessary. The major by-product, ammonium nitrate solution from the precipitation of ADU, is evaporated to 550 to 600 kg/m^3 NH_4NO_3 and pumped to storage. The problems associated with this by-product are discussed in sub-section 5.3.

4. RECENT PROCESS CHANGES

Some process changes, current and planned, are briefly described in the following sub-sections.

4.1. Mixco column

As noted in section 3 under the UO_3 plant description, the extraction stage of the SX circuit now employs a 76 cm diameter by 920 cm high Mixco column (Fig.5). This column employs an axial shaft on which are attached turbine

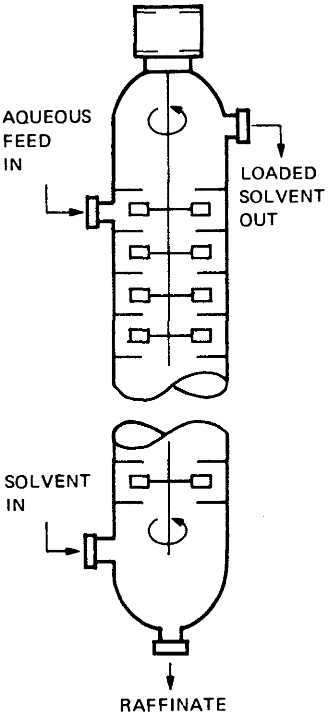


FIG.5. Mixco column.

impellors at appropriate intervals, alternated with stage separators. A single motor drive provides the necessary energy input. The column is operated in the countercurrent mode.

Throughput is approximately 0.5 m^3 per square metre (10.2 gal/ft^2). The column has operated well, and can readily handle the solids ($<1\%$) in the feed liquor, and requires less frequent cleaning than the pulse column.

4.2. Denitration of uranyl nitrate (UNH)

In the past, batch pot denitrators were used for the denitration of UNH to UO_3. Recently, most of the pots have been converted to the continuous mode of operation (Fig.6).

Trough denitration has also been investigated over the past year or two. To date, however, this operation has not been thoroughly de-bugged and is still in the commissioning stage.

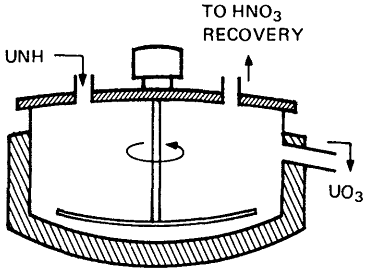


FIG.6. Continuous pot denitrator.

4.3. The AU/uranium dioxide process

Because of the environmental/waste management problems associated with the ADU process (described in sub-section 3.3.1), the AU process was developed, mainly to eliminate the large ammonium nitrate waste liquor and the accompanying disposal problems. The AU process is described briefly in the following paragraphs.

In this process (Fig.7), UO_3 rather than ADU is used as the feed material. The UO_3 is fed to a feed tank where it is slurried with ammonium nitrate solution (about 200 kg/m^3). The slurry can be pumped via a shear pump to a 100 mesh screen, the oversize being returned to the slurry tank. This operation is not required if the UO_3 feed is of less than 100 mesh size.

The UO_3 is metathesized in three continuous (gravity flow) tanks at about 80°C, with a retention time of 4 h, and at pH 2.9 to 3.0. After metathesis, the uranium in solution at this stage (resulting from the formation of nitric acid in the metathesis) is precipitated as ADU by the addition of ammonium hydroxide to pH 8. The slurry is then pumped to a drum filter where it is filtered and washed with water. Following washing, the AU is extruded, dried at 110 to 120°C on a belt dryer and reduced to UO_2 as in the ADU process.

The filtrate from precipitation and washing is recycled through a make-up tank where the NH_4NO_3 concentration is adjusted to the required strength by the addition of suitable reagent.

By recycling NH_4NO_3, rather than the single-use operation in the ADU process, the amount of NH_4NO_3 requiring treatment is minimal. The process is thus essentially free of environmental and waste disposal problems.

The process makes use of an almost stoichiometric ammonium uranate intermediate, as indicated by the following equations which represent its formation:

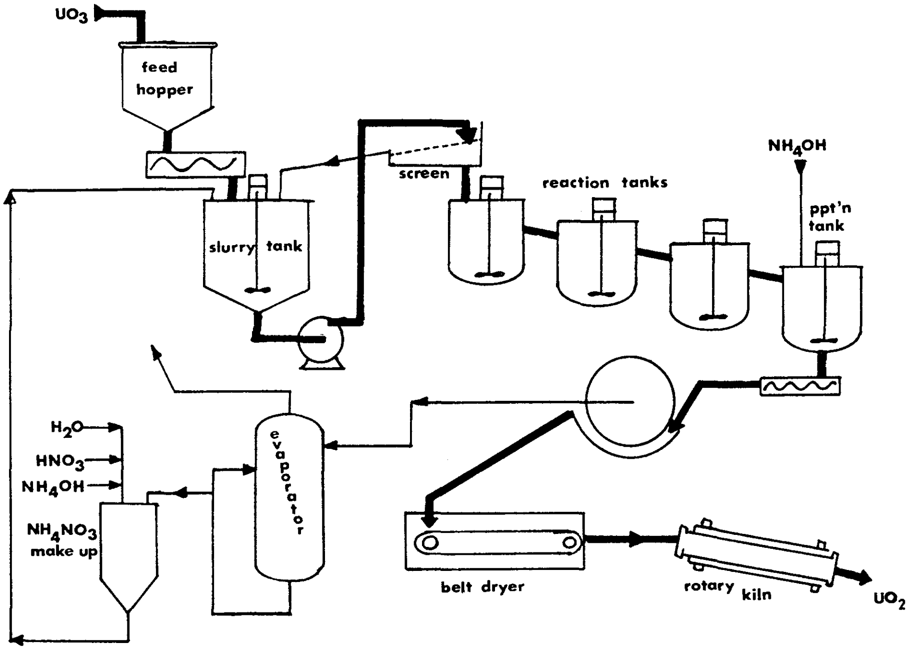


FIG. 7. The Eldorado AU process.

$$6UO_3 + 2NH_4OH + nH_2O \xrightarrow{80^\circ C} 6UO_3 \cdot 2NH_3 \cdot xH_2O + 2HNO_3 + (n-x)H_2O$$

$$6UO_3 \cdot 2NH_3 \cdot xH_2O \xrightarrow{120^\circ C} 6UO_3 \cdot 2NH_3 \cdot 5H_2O + (x-5)H_2O\uparrow$$

Analytical data support the formula given above for AU.

4.4. New UO_2 facility

The present ceramic UO_2 facility at the refinery has grown with the increasing demand for natural UO_2 for the Canadian nuclear programme. Consequently, the operation is spread throughout the refinery. As a result, there is the need to drum handle a dusty product. To minimize the handling of UO_2, to better contain uranium dust and to meet its future contractual obligations it was decided in December 1976 to consolidate the ceramic UO_2 operations in a single plant on the present refinery site. Upon qualification of the product from the new UO_2 plant the existing plant is to be phased out of production.

The new UO_2 plant will have a 'nameplate' capacity of 2820 ton (2558 t) U/year, based on a 7 day/week, 325 day/year operation. It is expected to begin operating in January, 1980.

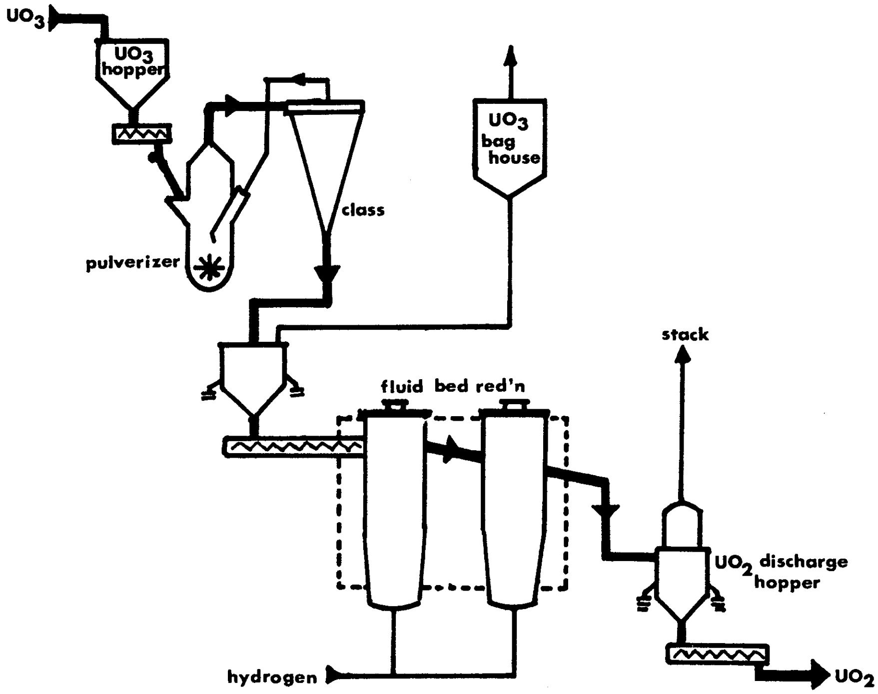


FIG.8. Wet-way UF_4 process: Hydrogen reduction in fluid beds.

The plant was originally designed to convert UO_3 to an ammonium uranate and thence to uranium dioxide. By following this route the generation of ammonium nitrate is avoided. The new plant has a capability to produce ceramic UO_2 by both the ADU and AU routes.

4.5. Wet-way UF_4 process

A wet-way process for the production of UF_4 is currently undergoing commissioning, and should be in production by the autumn of 1979. This process is intended for use in the new UF_6 refinery, rather than the dry-way process currently in use at the Port Hope refinery.

Feed to the process is UO_3 which is reduced to UO_2 by hydrogen reduction in fluid beds (Fig.8). The UO_2 is then reacted with aqueous hydrogen fluoride at 100°C to produce UF_4 (Fig.9). The UF_4 slurry so produced is dried on a drum dryer (Fig.10), and is then fed to a calciner to complete the water removal. It then goes to the UF_6 flame reactors. All hydrogen fluoride is recovered and recycled, eliminating the production of calcium fluoride resulting from the treatment of hydrogen fluoride wastes with lime, and the subsequent disposal problem.

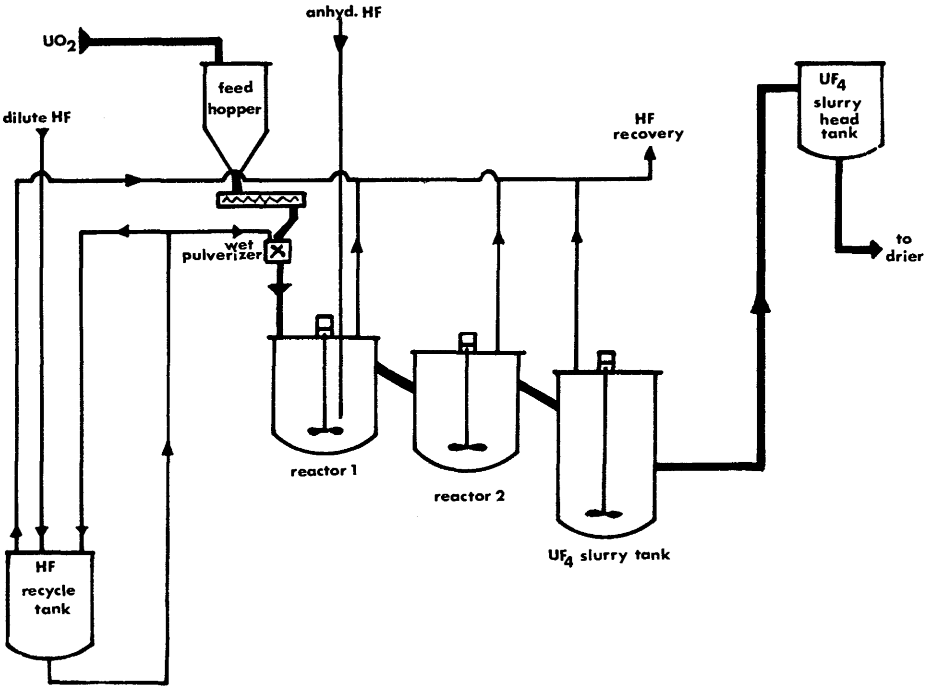


FIG.9. Wet-way UF_4 process: Reaction with aqueous hydrogen fluoride.

5. ENVIRONMENT/WASTE MANAGEMENT

Several sites around the refinery have been used in the past for the disposal of solid and aqueous wastes resulting from refinery processes. The use of these sites is shown schematically in Fig.11.

Currently Eldorado has only one dumpsite available for the disposal of waste and this is located at Port Granby, approximately 20 km from Port Hope. Refinery residue has been taken by road transport to this site for land burial since 1955. Because of the proximity to good farmland, and erosion from the lake, this site is now considered unsuitable for residue burial; it is planned to relocate the residue already buried there after a dumpsite is approved for the disposal of low-activity waste. As there is little room left for further burial at Port Granby, the current residue at the refinery is put into drums. Over a 4-month period approximately 8000 forty-five gallon (205 ltr) steel drums have been filled with residue and stacked in a warehouse on the refinery site. The calcium fluoride generated in the UF_6 plant continues to be buried at the Port Granby burial site.

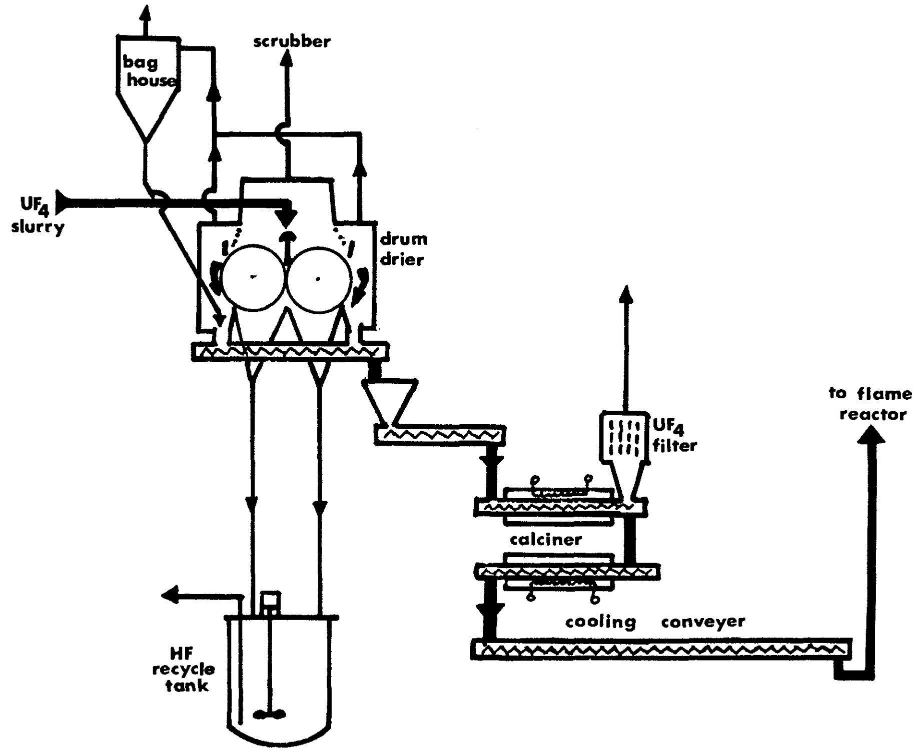


FIG.10. Wet-way UF_4 process: Drum drying and calcining.

5.1. Raffinate

Attempts are underway at Eldorado to reduce the mass of waste material (Figs 12 and 13) to a minimum. The main waste stream from the TBP solvent extraction process is the so-called raffinate stream containing the impurities that enter the refinery in yellow cake. This raffinate stream is approximately 1.5N in free nitric acid. Since the inception of the TBP SX process, attempts have been made to recover this nitric acid by evaporation, and to recover some of the combined nitrates by sulphuric acid springing. The waste from the refinery operation was thus concentrated as a mixture of sulphate and nitrate salts. This material was neutralized with a lime slurry, filtered and the filter cake taken by road transport to an Eldorado dumpsite for burial in pits. At one time, the clarified filtrate which met the environmental standards of the day was discharged to the Port Hope harbour on Lake Ontario. As environmental regulations tightened

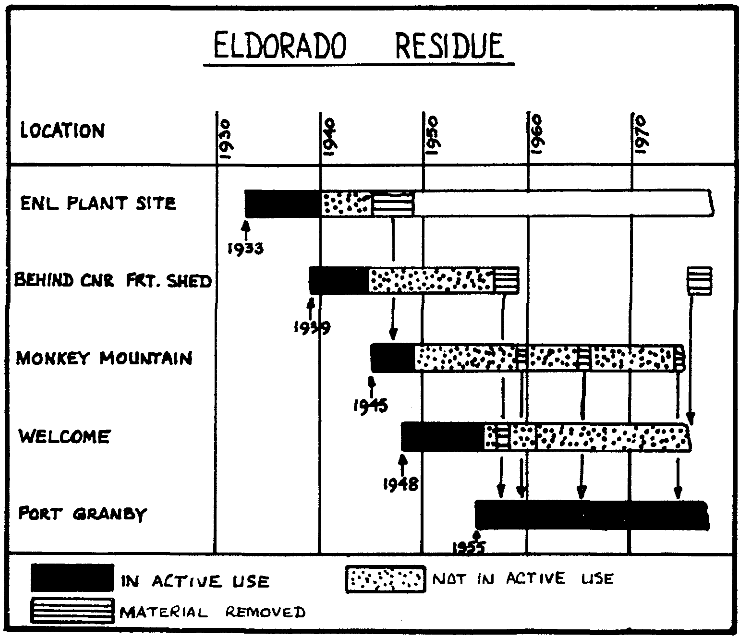


FIG.11. *Waste disposal sites.*

in the late 1960s it became apparent that Eldorado would no longer be permitted to discharge the clarified filtrate to the lake because of nitrate and ammonia levels. The radium content of this stream was in the order of 0.01 μCi/ltr, which was sufficiently high to prevent its use as a fertilizer without first removing the radium. For an interim period this stream was acidified and evaporated for further nitrate recovery and the residue combined with the solids that were taken to the Eldorado dumpsite for burial.

From January 1, 1979 Eldorado is no longer burying the residue at the dumpsite but instead is storing it as a dry residue in drums. To reduce the mass of residue the ammonium diuranate yellow cake arriving at the refinery is calcined at 450°C for ammonia elimination. The ammonium-free raffinate stream continues to be evaporated with increased sulphuric addition for increased nitric acid recovery. At this time the evaporator bottoms are mixed with slaked lime powder in a paddle blender and the product discharged into drums for permanent storage. As might be surmised, this is a labour-intensive and expensive operation.

As an alternative to this method of waste management, development work has been carried out on returning the acid evaporator bottoms to the uranium producers for uranium recovery, and combining the waste from the refining operation with the waste from the mining and yellow cake production operation.

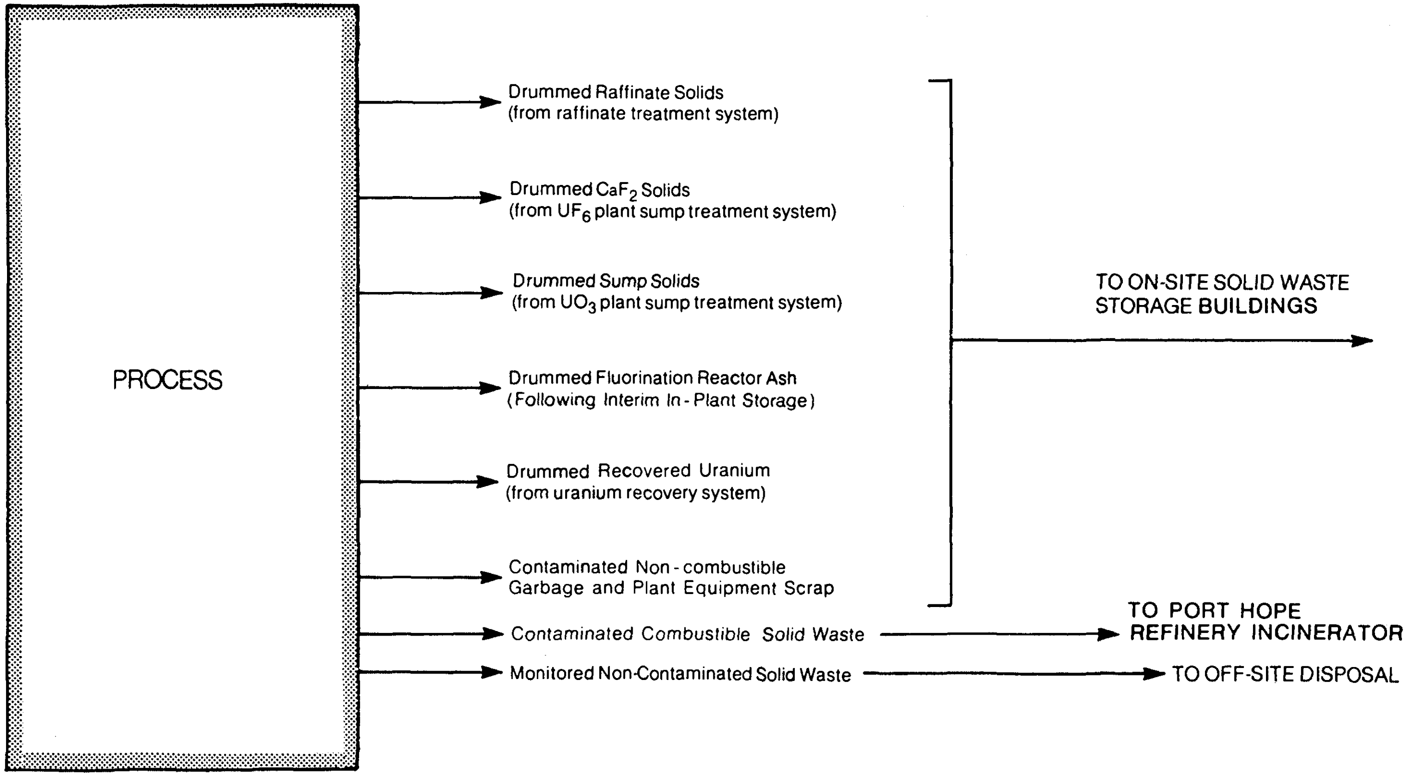


FIG.12. Process solid waste sources.

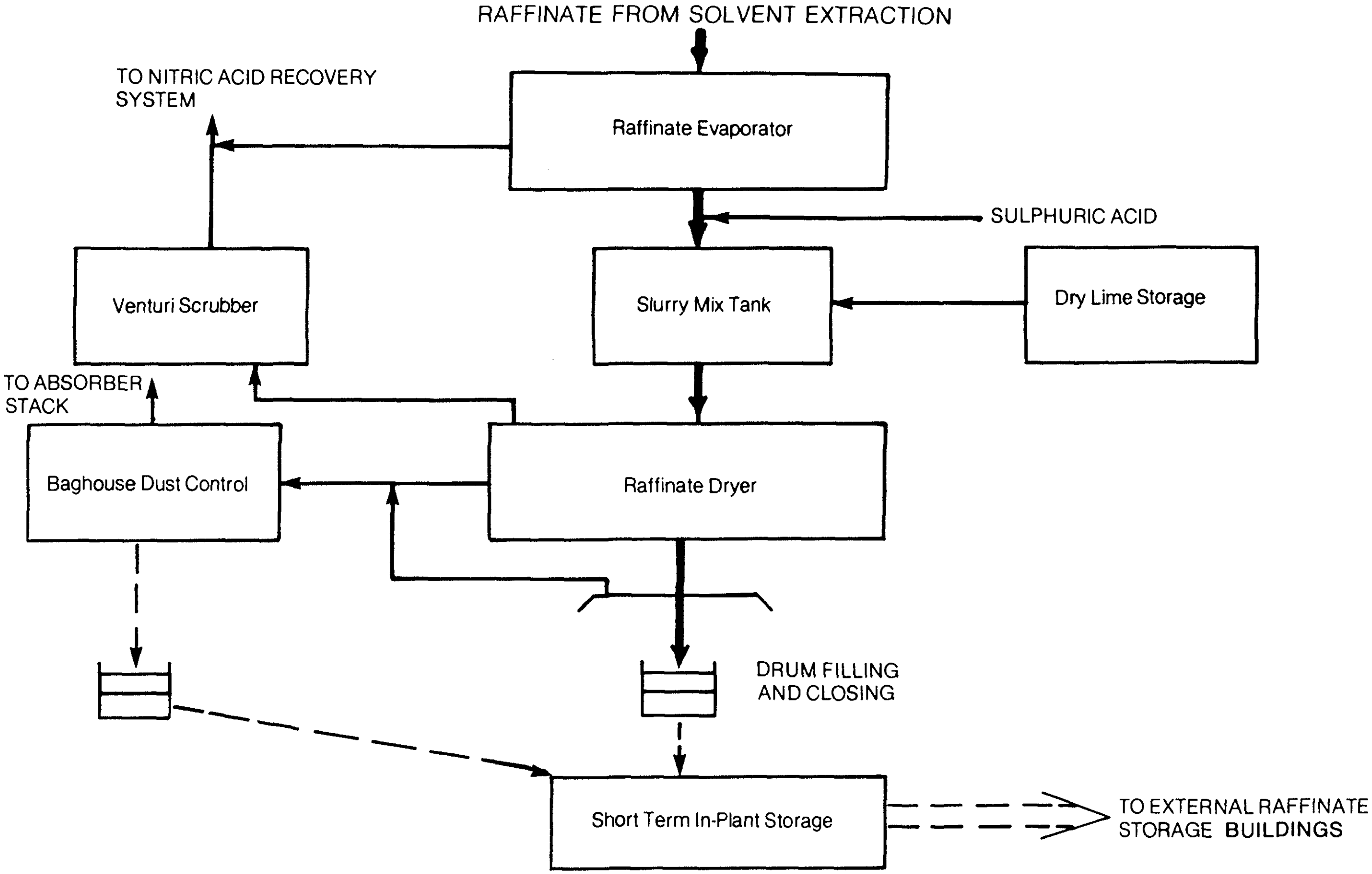


FIG.13. In-plant raffinate treatment.

Approval has been obtained from the Atomic Energy Control Board and from the Ontario Ministry of the Environment to ship the acidic raffinate evaporator bottoms to a yellow cake producer at Elliot Lake over a 6-month period for uranium recovery. Over this period of time Eldorado is to demonstrate that both the ammonium and nitrate levels in this waste can be reduced to less than 100 lb/day. The shipments to Elliot Lake will be made in 22 700 ltr-capacity road tankers containing approximately 38 000 kg of the concentrated acidic waste. Approximately 450 000 ltr of acidic waste have already been shipped to the Elliot Lake region in this manner. The initial shipments contained high nitrate values, presenting problems to the mill. Equipment is now being installed to overcome this problem, and Eldorado is also looking at methods of reducing the nitrate level in the shipments primarily to satisfy environmental regulations but also to further help eliminate the problems in the uranium recovery operation.

Should the project for the return of the yellow cake impurities to a yellow cake producer not be successful, the next plan is to convert the acidic residue to solids by calcining at 500°C. Until a better method of storing these solids becomes available, it is planned to store this material in drums, and store the drums in warehouses. It is estimated that this technique will reduce the quantity of waste to approximately 20% of the weight of yellow cake processed at the refinery. Needless to say, further purification of yellow cake that can be accomplished at the mine and mill site would be welcomed by Eldorado from the point of view of waste management.

5.2. Calcium fluoride

A second waste stream produced at the refinery results from the excess hydrogen fluoride that is used to convert UO_2 to UF_4 and thence to UF_6. The current practice at Eldorado is to neutralize the excess hydrogen fluoride with a potassium hydroxide solution.

In the regeneration of the potassium hydroxide solution, uranium is first removed as potassium diuranate and the clarified solution of potassium fluoride treated with powdered quicklime. The resulting calcium fluoride is separated by filtration and sent to an Eldorado dumpsite for burial. For the present 5000 t/a UF_6 plant located in Port Hope the quantity of wet calcium fluoride cake produced is approximately 200 t/month. To avoid production of this waste, Eldorado has undertaken to develop a UF_6 process that will use hydrogen fluoride more efficiently and avoid the production of this large quantity of waste which does pose a disposal problem.

5.3. Ammonium nitrate

In the ADU process for the production of UO_2 for the Canadian nuclear programme, ammonium nitrate is produced as a by-product (Fig.4). This is a

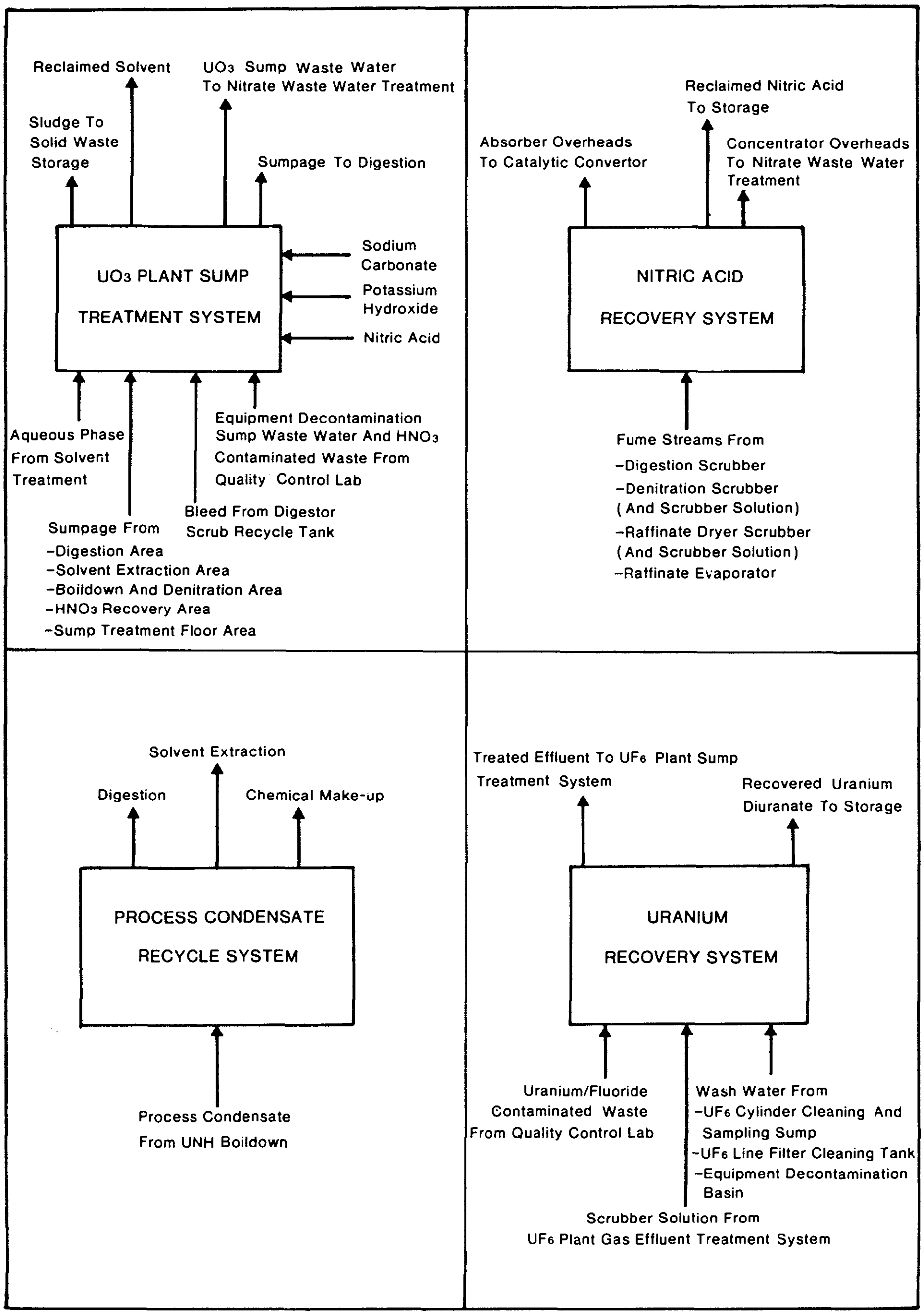


FIG.14. Internal recycle process.

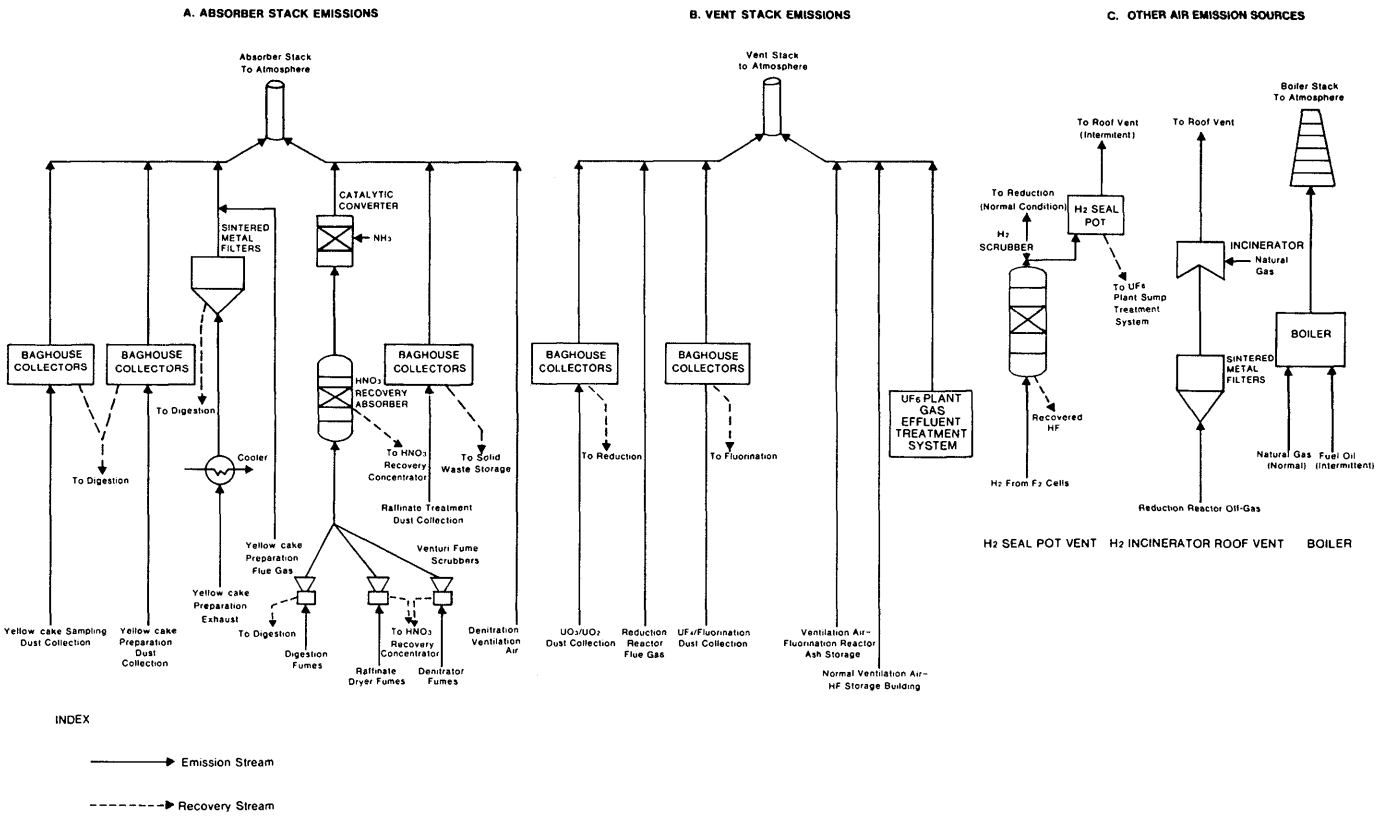


FIG.15. Air emission control schematics.

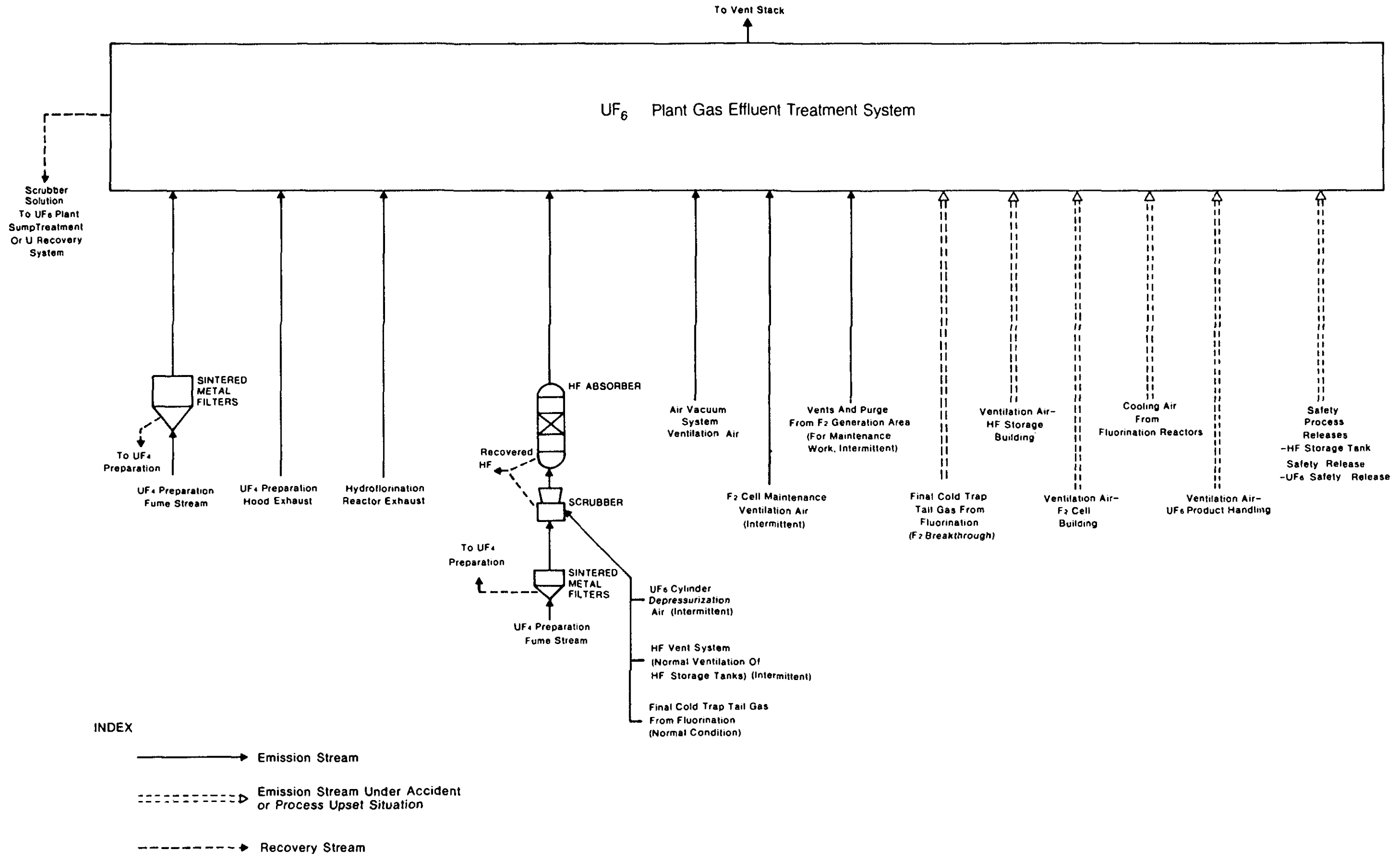
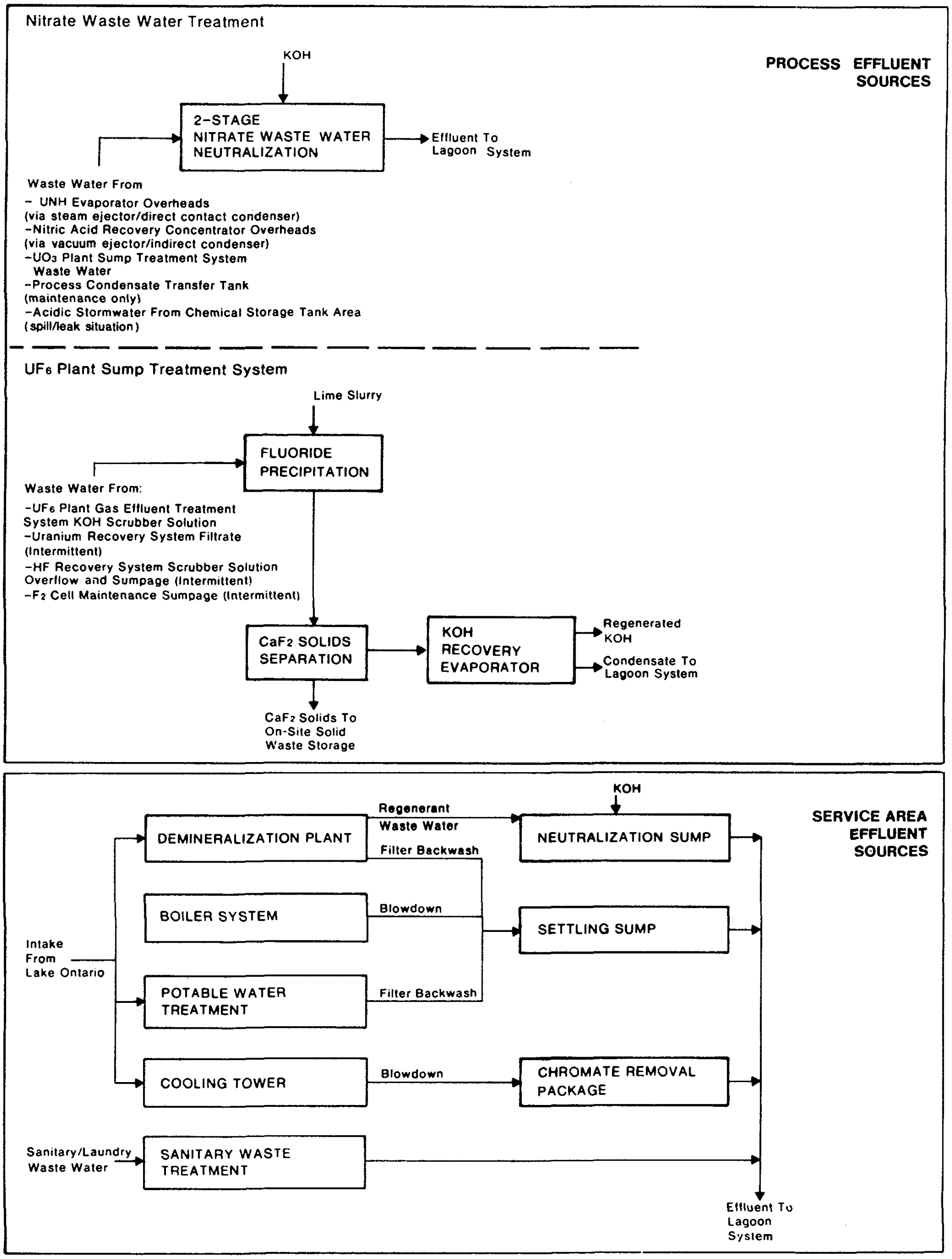


FIG.16. UF_6 plant gas effluent treatment system.


Nitrate Waste Water Treatment
KOH
2-STAGE NITRATE WASTE WATER NEUTRALIZATION
Effluent To Lagoon System
PROCESS EFFLUENT SOURCES
Waste Water From
- UNH Evaporator Overheads (via steam ejector/direct contact condenser)
-Nitric Acid Recovery Concentrator Overheads (via vacuum ejector/indirect condenser)
-UO3 Plant Sump Treatment System Waste Water
-Process Condensate Transfer Tank (maintenance only)
-Acidic Stormwater From Chemical Storage Tank Area (spill/leak situation)
UF6 Plant Sump Treatment System
Lime Slurry
FLUORIDE PRECIPITATION
Waste Water From:
-UF6 Plant Gas Effluent Treatment System KOH Scrubber Solution
-Uranium Recovery System Filtrate (Intermittent)
-HF Recovery System Scrubber Solution Overflow and Sumpage (Intermittent)
-F2 Cell Maintenance Sumpage (Intermittent)
CaF2 SOLIDS SEPARATION
KOH RECOVERY EVAPORATOR
Regenerated KOH
Condensate To Lagoon System
CaF2 Solids To On-Site Solid Waste Storage
KOH
SERVICE AREA EFFLUENT SOURCES
DEMINERALIZATION PLANT
Regenerant Waste Water
Filter Backwash
NEUTRALIZATION SUMP
BOILER SYSTEM
Blowdown
SETTLING SUMP
Intake From Lake Ontario
POTABLE WATER TREATMENT
Filter Backwash
COOLING TOWER
Blowdown
CHROMATE REMOVAL PACKAGE
Sanitary/Laundry Waste Water
SANITARY WASTE TREATMENT
Effluent To Lagoon System

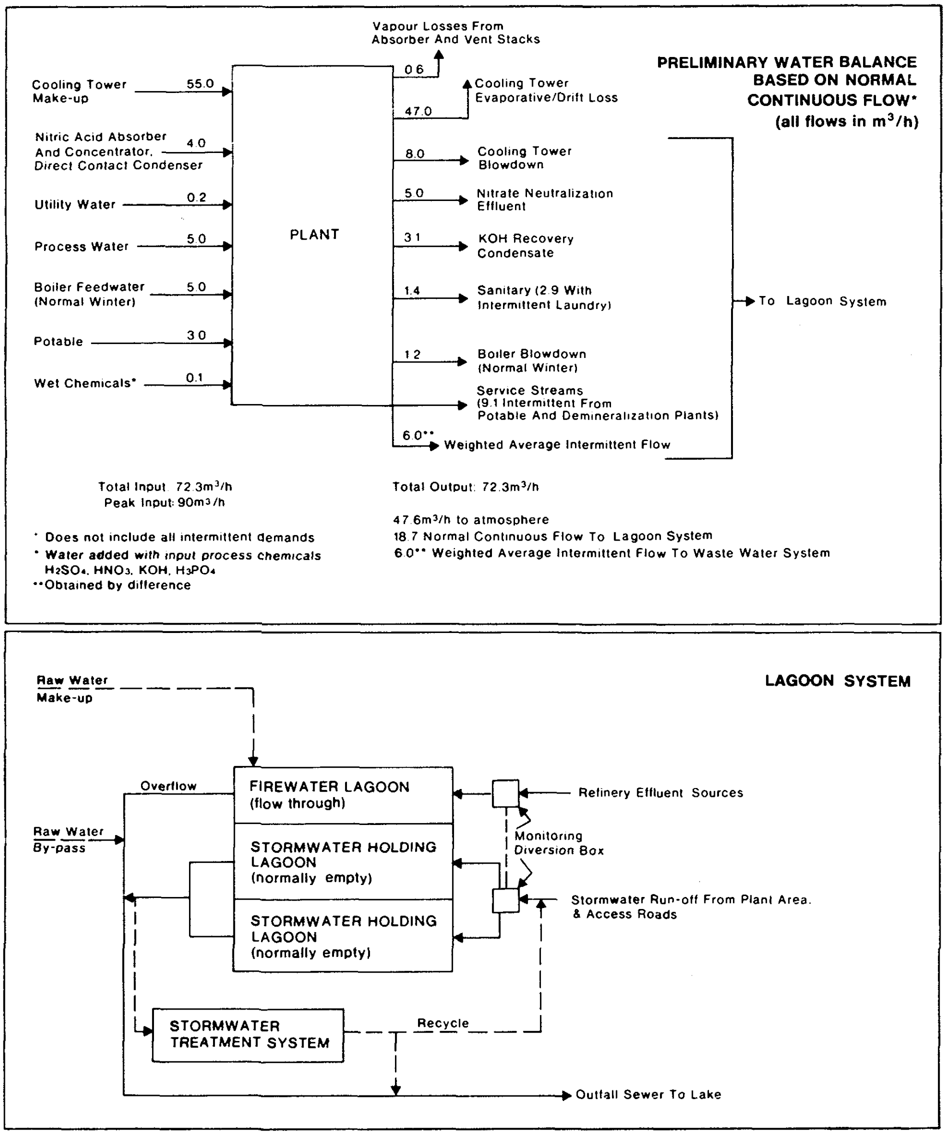


FIG.17. Waste water management schematic.

relatively pure stream that has recently been approved for agricultural use, providing that the radium level in a 50% solution of ammonium nitrate is below 10 pCi/ltr. However, the Eldorado philosophy on waste management continues to favour recycling on the same site as the preferred method of waste management (Fig.14), as in the case of effluents from the UF_6 plant. A process was developed whereby the ammonium nitrate waste stream has been eliminated. This is the AU process described in sub-section 3.3.1. The ADU process, as noted previously, uses ammonium hydroxide addition to uranyl nitrate to produce ammonium diuranate and ammonium nitrate. With a production rate of 1 136 300 kg of uranium it is now necessary to dispose of 818 200 kg of ammonium nitrate per year. With the new AU process the production of this by-product will be essentially eliminated, removing the necessity to store it for 11 months of the year, and then dispose of it.

5.4. Other emissions

Stack emissions have, and can, be kept under control by the efficient use of scrubbers, bag-houses, and sintered metal filters. Figures 15 and 16 are schematic diagrams showing Eldorado's approach to eliminating stack emission problems.

Waste water management utilizes accepted chemical industry practices, and is shown schematically in Fig.17.

6. EXPANSION PLANS: NEW UF_6 REFINERY

Eldorado has been planning to build a new refinery, with a capacity to process 9000 t of uranium from ore concentrates, since 1975. Although not required, ENL decided to refer the project to the Federal Environment Assessment Review Office for a panel review, as it was realized that the proposed refinery and associated waste management area could have significant environmental impacts. After hearings held in September–October 1977 and February 1978, the Environmental Assessment Review Panel reached a decision in May 1978. The Panel found the refinery and plant process to be acceptable if a number of conditions were met. The Panel also found the proposed waste management system unsuitable as a means of storage because of unknown reliability, costs, engineering difficulties and the need to retrieve the stored material. The Panel concluded that the Port Granby site would not be acceptable for the project, because the net effect on the local area would be negative.

Following rejection of the Port Granby site Eldorado was encouraged by citizens groups in the Port Hope area to seek an alternative site in the area, and a site was recommended in neighbouring Hope Township. Eldorado then decided to prepare environmental impact statements for this site, and for sites located in Blind River and Dill Township (Sudbury) (Fig.2). Hearings were held in November and December 1978. In March 1979, all three sites were approved by the Environmental Assessment Review Panel for the construction of a new uranium hexafluoride refinery. The Government of Canada must now rule on which site the refinery is to be built. Plant construction is expected to begin early in 1980, and plant operation in mid-1982. The plant was originally designed to receive ammonium diuranate concentrates produced in the Province of Ontario. Because of the desire to reduce levels of ammonia in the lakes and rivers of Northern Ontario, the uranium producers have been requested to lower the quantity of ammonia discharged in their effluents. As a result of these latest regulations, there is a good possibility that a magnesium diuranate will be the feed material for the new refinery. Consequently, new specifications for yellow cake have been drafted and are currently under review by the producers and the refinery.

DISCUSSION

H. PAGE: 1. Will the product of the new UF_6 process be hydrated?

2. Will there be any tendency to pyrohydrolysis in the subsequent drying and calcining stages?

A.W. ASHBROOK: 1. We will produce an intermediate hydrate assumed to be $UF_4 \cdot \frac{3}{4} H_2O$ from TGA studies. This material is further dehydrated in a two-stage stirred bed calciner to reduce the total H_2O to less than 0.05%.

2. There is a tendency towards pyrohydrolysis, and this can be minimized by careful control of temperature in the calcining stage. We have not finely tuned the process, but at this time we are obtaining UO_2 values in the calcined product below 0.5%.

D.W. BOYDELL: How many compartments are there in the mixco unit and how many theoretical stages is this equivalent to? That is, how many mixer settlers units would be required? Has the experience with the mixco unit been satisfactory in this application?

A.W. ASHBROOK: There are 28 compartments in the mixco extraction column. This number is equivalent to approximately four stages of mixer settlers based on a McCabe-Thiele diagram. However, this relationship is hypothetical only, since the uranium concentration along the column is not linear. We have had very good experience with this type of column for this particular application.

UNITED KINGDOM EXPERIENCE OF PRODUCTION OF URANIUM FLUORIDES

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Abstract

UNITED KINGDOM EXPERIENCE OF PRODUCTION OF URANIUM FLUORIDES.

The paper gives an account of the development of the technology and a description of the processes used at the Springfields Works of British Nuclear Fuels Ltd, in refining uranium concentrates and producing uranium fluorides.

1. INTRODUCTION

Preparation of uranium hexafluoride began in the United Kingdom in 1940, in the Research Department of the former General Chemicals Division of Imperial Chemical Industries (ICI). By 1944 the scale of preparation had moved from the original gram quantities to ~200 kg/year at which time the UK 'Tube Alloy' project had been absorbed into the United States of America 'Manhattan Project' [1].

United Kingdom interest in the production technology of uranium fluorides resumed almost immediately after the war and since that time has been centred at the Springfields Works of British Nuclear Fuels Limited (BNFL) and some general comments on the site are relevant.

Springfields Works is located on a 220 acre[1] site near to the estuary of the River Ribble between the towns of Preston and Blackpool in the North West of England. The principal production-scale activities on the site are:

(a) manufacture of all the UK requirements for Magnox (natural metal) and AGR (enriched oxide) nuclear fuel together with their associated fuel element components;

(b) toll conversion of customer's uranium to nuclear fuel or intermediates such as uranium hexafluoride or ceramic grade uranium dioxide.

Site back-up services for these production activities include sophisticated Development, Design, Analytical, Training and Health Physics and Safety facilities.

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[1] 1 acre = 4047 m^2.

The total manning complement comprises 2000 blue collar and 1000 white collar workers. Springfields differs from most yellow cake convertors in that the conversion service forms only part of the comprehensive fuel service provided on site.

In the remainder of the paper, a brief history of the development of the conversion process at Springfields will be given together with an outline of the current technology and comments on the influence of yellow cake quality on the hexafluoride production process.

2. PROCESS DEVELOPMENT BACKGROUND

As is well known, BNFL in common with most convertors operate what has been termed head-end refining, that is purification of uranium using solvent extraction as distinct from fractional distillation of uranium hexafluoride. At BNFL, purified uranyl nitrate is then converted to uranium tetrafluoride and subsequently to uranium hexafluoride to make a three-stage conversion sequence. While fluorides of uranium have been made at Springfields since the late 1940s, the development of the three stages of the conversion sequence proceeded with some measure of independence and the history of these developments will be dealt with separately, beginning first with uranium purification.

2.1. Uranium purification

The first requirement for large-scale quantities of nuclear-grade uranium in the UK occurred in 1946 in order to fuel the first reactors at Windscale and to provide uranium hexafluoride, a few years later, for the Diffusion Plant at Capenhurst. At this time the feed uranium consisted of pitchblende from Shinkolobwe in the Belgian Congo. The purification process, which was designed, built and brought into operation very quickly, involved crushing, wet ball milling, leaching, precipitation, redissolving, and solvent extraction using diethyl ether to produce pure uranyl nitrate solution which then constituted the feed to the UF_4 process. This very long sequence of operations comprised a multiplicity of low-volume batch operations, one of which, the purification stage using diethyl ether, was extremely hazardous and in total gave rise to a bewildering variety of liquid and sludge recycles. Although this process met the original requirement, of the order of several hundred tonnes of U per year, it rapidly became apparent that it did not make economic sense when set against the demands of the first phase of the UK nuclear energy programme being planned in the early 1950s. What was needed were higher volume, lower cost, environmentally more acceptable continuous plants, designed for a feed of the new high-grade yellow cake concentrates starting to be produced in South Africa and elsewhere. To meet this need, considerable development work was done in the early 1950s at Harwell, Windscale and Springfields which culminated in the choice of continuous counter-current box mixer settler contactors using 20% by volume of tributyl phosphate in odourless kerosene as solvent, for the first production scale plant at Springfields which was commissioned in 1956. A further three larger units of purification plant were brought on line in 1958 [2] and continue in use, with refurbishing and uprating [3], to the present day. Testimony to the wisdom of the original choice has been the reliability of the contactor over many years of operation and its flexibility and adaptability when dealing with a variety of yellow cakes from all parts of the globe.

2.2. Uranium tetrafluoride production

The original technology for UF_4 production first introduced at Springfields in 1946 comprised precipitation of ammonium diuranate from uranyl nitrate, followed by calcination, reduction, and hydrofluorination, all stages being carried out in batches in small-volume static bed convertors. This process was extremely uneconomic in labour and raw materials, and gave rise to significant quantities of nitrate-containing effluent. In order to eliminate these undesirable features it was replaced in 1958 with the first fluidized bed hydrofluorination plant. As the gas/solid reactions at the denitration, reduction and hydrofluorination stages involved high heats of reaction, whether endothermic or exothermic, the process called for contacting systems with good heat transfer characteristics to avoid plugging, local hot spots leading to deactivation, or in the case of UF_4, sintering and lump formation. These considerations led to the choice of three fluidized bed stages for denitration, reduction and hydrofluorination. Four lines of plant were installed in 1960 [4] and, while somewhat under-used in the lean years of the early 1960s, have continued in operation to provide, until very recently, all natural tetrafluoride requirements at BNFL.

However, by the late 1960s it had become apparent that uranium fluoride production capacity at Springfields which was surplus to internal demand in the UK could be sold to overseas organisations wishing to purchase toll processing facilities. The initial success in this new venture together with predictions of future market growth coincided with the formation of British Nuclear Fuels Limited, an independent company ‘hived-off’ from the parent UKAEA to operate in the total nuclear fuel cycle both in the UK and overseas. Estimates of market growth and future market share led BNFL to conclude in the late 1960s that further expansion at the UF_4 stage could be justified and considerable attention was given to the form that the expansion should take. At this time the experience of fluidized bed hydrofluorination with its multiple reactors, the need for HF recycling to reduce AHF costs, and the consequent high plant corrosion rates and maintenance cost, pointed in the direction of continuous counter-current reaction systems with high reaction rates and high HF utilisation. Feasibility studies of the various options available led to the choice of rotary kilns for the reduction and hydrofluorination contacting systems, a choice which was fortified by the experience, already available at Springfields, of production operations of rotary kilns for conversion of uranium hexafluoride to ceramic grade uranium oxide by the short dry route (IDR), now in operation both at Springfields and, under licence, overseas.

An expansion in fluidized bed hydrofluorination involving replication of the standard reactors was brought on line in 1975 as a holding operation while rotary kiln UF_4 development was completed and the production-scale rotary kiln plant was commissioned in 1978. Thermal denitration of uranyl nitrate followed by rotary kiln reduction and hydrofluorination represents the current state of production technology in the UK for the uranyl nitrate to uranium tetrafluoride stage.

2.3. Uranium hexafluoride production

Springfields became interested in uranium hexafluoride production in the late 1940s and by the early 1950s a plant comprising several small-scale stirred batch reactors was in operation fluorinating a feed of UF_4 with purchased chlorine trifluoride.

The original attraction to fluidized bed technology at Springfields was in connection with the development and design of a contactor to replace the initial batch reactors. However, because the first stage of the UK nuclear energy programme was based on natural uranium fuel, UK demand for uranium hexafluoride was easily accommodated by the original 'hex' plant until 1962 [1] when a prototype fluidized bed hex plant was commissioned. This prototype served both as a production facility and development tool until 1968 when the first production scale fluid bed hex plant contactor and site-operated fluorine generation unit was commissioned. A second larger contactor was commissioned in 1973 and increments of fluorine generating capacity have been progressively added to match the increase in market growth. The staging of fluorine capacity expansion has provided the opportunity to introduce several recent developments in this very important feature of the UF_4 to UF_6 conversion stage.

3. PROCESS DESCRIPTION

3.1. Uranium purification

For twenty years yellow cake was delivered to Springfields as loose loads of 45-gallon drums. As a consequence two or three times a year a drum spillage incident occurred when a drum fell into a dock or onto public roadways. When the practice of shipping drums in ISO containers was adopted the occurrence of such incidents was virtually eliminated.

On arrival at Springfields and after sorting into lots each drum in each lot is weighed and then sampled by the auger method. Proposals to introduce the falling stream method of sampling have been considered on frequent occasions over the years, but experimental comparison between the falling stream and the auger method always demonstrated that the auger method is equal to the falling stream from the point of view of sampling, and in our view much more desirable from a cost and safety viewpoint, control of airborne contamination being of dominant concern until the uranium is in solution.

After sampling, the drums of yellow cake are emptied, inside a ventilated cabinet, into the dissolver feed hopper. If the concentrate contains 'tramp' material such as nuts, bolts, gloves, etc., then it is necessary to sieve this material before it enters the dissolver.

Yellow cake is fed at a controlled rate into a four-stage continuous dissolver co-current with nitric acid, either purchased or recovered, and recycled washwaters. Continuous on-line measurements of uranium concentration and free acidity of the product allows automatic control of the dissolving process to yield a slurry of 45% of uranium wt/vol. and 8% free acid with respect to nitric acid.

After cooling the slurry, nitric acid insoluble material such as sand or silica is removed by filtration on precoated continuous rotary vacuum filters. The filtrate, together with recycle washings, yields a crude uranyl nitrate solution containing ~35% of uranium wt/vol. together with nitric soluble impurities. Removal of these soluble impurities is performed by continuous counter-current solvent extraction in mixer/settler contactors using 20% by volume of tributyl phosphate in odourless kerosene as solvent. Each solvent extraction unit comprises eight stages of extraction and eight stages of scrub followed by twelve stages of strip, yielding product solutions containing 11% of uranium wt/vol., which is then stored in a battery of large storage tanks to await the results of the quality control analysis. From a final product purity viewpoint the analysis at this point is all important. The range and frequency of impurity determination varies with the yellow cake being processed but the object is to prevent uranium which will not meet the hex specification being fed forward.

By replication or modification of the basic process units the capacity at the yellow cake purification stage has been expanded to the present level of ~ 12 000 t of U per year with some 3000 to 6000 t of U per year of 'stretch' capacity remaining. The plant, most of which is constructed of stainless steel, has given continuous reliable service for more than 20 years, with energy and raw material utilizations which are acceptably low.

3.2. Uranium tetrafluoride production

3.2.1. Evaporation

Pure uranyl nitrate at 11% of uranium wt/vol. is evaporated to a molten concentrate containing 110% of uranium wt/vol. in a battery of four effect climb-

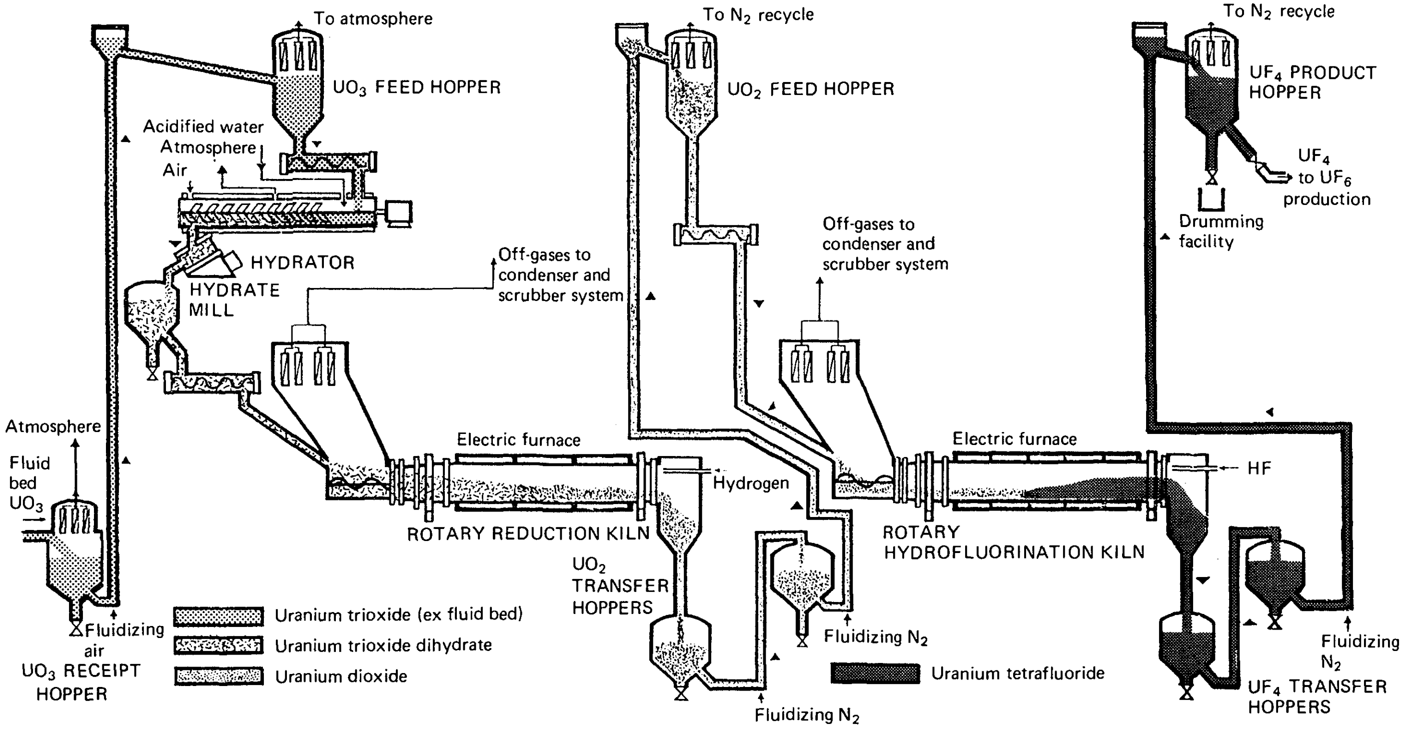

FIG.1. UF_4 kiln plant.

ing film evaporators. Product concentration, as measured by the boiling point elevation, is automatically controlled, as are the levels of liquor in each effect. Steam condensate from the first effect and condensed distillates from the remaining three effects is used for pre-heating the uranyl nitrate feed to the evaporators and then recycled for use as a source of distilled water at the purification stage.

3.2.2. Denitration

The denitration reactor consists of a vertical cylinder of stainless steel with a conical base through which pass 21 fluidizing air nozzles. The bed of uranium trioxide is maintained at 300°C by electrically-heated elements inside 21 tubes protruding through the conical base, and by electrically-heated jackets on the surface of the cylinder.

Molten uranyl nitrate concentrate is pumped into the fluidized bed where it decomposes into uranium trioxide, oxides of nitrogen, oxygen, and steam. The uranium trioxide overflows continuously from the denitrator and is transported pneumatically to storage hoppers. Fluidizing air and exhaust gases are first filtered and then directed to a nitric acid recovery plant, where acid is recovered by condensation followed by continuous counter-current absorption. Recovered acid is recycled to the dissolution stage of the process to realize the double benefit of cost reduction and reduction of nitrate level in effluent.

Existing capacity at the evaporation and denitration stage amounts to ~10 000 t of U per year. Should demand require 'stretching' of existing units the capacity can be increased to ~12 500 t of U per year with space available in the existing building for installation of additional units.

3.2.3. Hydration of uranium trioxide

Uranium trioxide as prepared by fluidized bed denitration, consists of hard spherical particles with a low surface area and low internal porosity. To increase surface area and internal porosity and thus ensure rapid diffusion of gases in subsequent reactions, the uranium trioxide is hydrated under conditions which lead to the formation of low-density high-surface-area dihydrate particles.

Hydration takes place in a stainless steel trough containing an interrupted screw conveyor fed with metered quantities of uranium trioxide and hydrating fluid. Control of temperature along the trough ensures the formation of a dry, free-flowing hydrate which discharges into a stock hopper.

3.2.4. Reduction of uranium trioxide

Uranium trioxide dihydrate is screw-fed at the required rate into a stainless steel rotary kiln where it contacts metered quantities of hydrogen counter

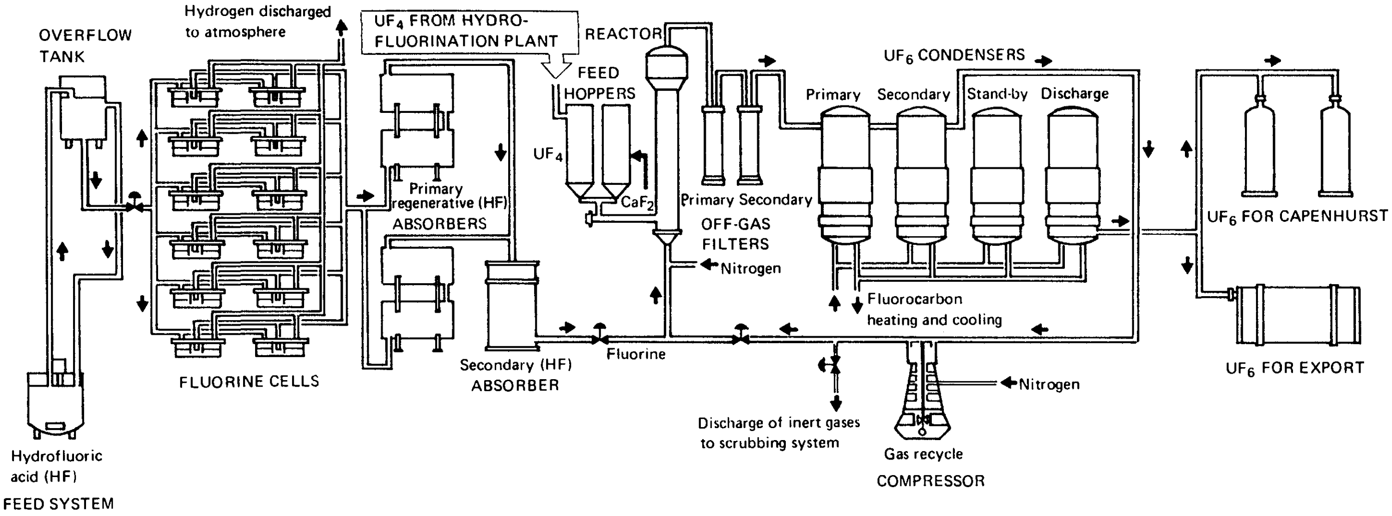

FIG. 2. UF$_4$ to UF$_6$ production at Springfields.

currently (see Fig.1). A system of flights and dam rings within the kiln provides the necessary gas/solid contact and residence time, and the product uranium dioxide is transported pneumatically on nitrogen to the feed hoppers of the hydrofluorination kiln.

Exhaust gases containing nitrogen, steam, and surplus hydrogen pass through filters suspended above the powder feed end and are then vented to atmosphere via a water-cooled condenser and caustic scrubber. The precise temperature control of the kiln contents required to achieve complete reduction without loss of reactivity is obtained by means of a combination of three independently-controlled electric muff heaters and forced-air cooling of sections of the barrel.

3.2.5. Hydrofluorination of uranium dioxide

Hydrofluorination takes place in an inconel rotary kiln where controlled quantities of anhydrous hydrofluoric acid and uranium dioxide are contacted counter currently (see Fig.1). Dam rings and flights similar to those used in the reduction kiln provide the residence time and gas contact required to ensure complete conversion to uranium tetrafluoride.

Because thermal damage of the basic particle can lead to deactivation and incomplete conversion or, in the most extreme instance, sintering of the bulk material, careful control of powder temperatures in the reacting zones is essential. This control is achieved automatically using a combination of independent electrically-heated muffs and forced-air cooling for removal of exothermic heat. Exhaust gases containing steam, nitrogen and the small amount of unused HF are filtered, condensed, and finally scrubbed before discharge to atmosphere.

A year's operating experience has confirmed the economic advantages of the kiln route for tetrafluoride production and it is the intention to replace the fluidized bed plant by a second kiln plant unit in the near future.

3.3. Uranium hexafluoride production

3.3.1. Fluorine generation

The fluorine generation cells in use at Springfields are derived from the basic design developed by ICI and described by Rudge [1]. Fluorine is produced from cell-grade anhydrous hydrofluoric acid in batteries of cells (see Fig.2) by the electrolysis of the molten salt $KF \cdot 2HF$ at 80°C using mild-steel cells and amorphous-carbon anodes. The HF content of the electrolyte is maintained at the desired level of ~42 wt% by the automatic addition of AHF. HF in the fluorine product is removed by absorption on sodium fluoride to give a gas containing less than 0.2% of HF wt/vol. Hydrogen evolved at the cathode is scrubbed with caustic potash solution before discharge to atmosphere via a flame trap.

Automatic control of a slight positive pressure in the fluorine cell header is achieved by a control valve in the line to the reactor circulating system, while a lute at the inlet to the hydrogen scrubber provides a slight positive pressure in the hydrogen header.

Existing fluorine generation capacity is equivalent to ~7500 t of U per year as hexafluoride, with a further bank of cells currently being installed which will raise total capacity ~9500 t of U per year as hexafluoride by December 1979.

3.3.2. Hexafluoride production

Two contactors are currently in use at Springfields with a combined capacity of ~9500 t of U per year as hexafluoride. Uranium tetrafluoride is fed at a controlled rate into an inert fluidized bed of calcium fluoride maintained at ~450°C in a monel reactor fluidized with a mixture of nitrogen and fluorine and operating at a negative pressure (see Fig.2). The fluorine reacts instantaneously with the tetrafluoride to form gaseous uranium hexafluoride, which is first filtered to remove entrained solids and then condensed. The incondensable gases containing nitrogen and unused fluorine are recycled, using a reciprocating compressor, to the base of the reactor where fresh fluorine is introduced at a rate equivalent to its usage. Control of reaction temperature within the desired range is achieved by a combination of electric-muff heating or forced-air cooling.

Hexafluoride is removed from the condenser by liquefaction and gravity run-off into the appropriate transfer cylinders from where a 'gassing back' operation is performed to eliminate light gas contamination. Banks of condensers are provided to operate as cooling and liquefying units in turn using a fluorocarbon liquid at −40°C when on primary or secondary cooling duties, and fluorocarbon vapour at ~105°C for liquefaction of hexafluoride.

3.4. Residues recycle

Solid and liquid residues containing uranium are recycled to recover uranium values. Examples of such residues are:

(a) potassium diuranate scrubber cakes from the hex plant scrubbers
(b) hex reactor filter residues
(c) floor sweepings arising from spillages
(d) liquor spillage

The recycling of residues involves dissolution by batches in nitric acid, followed by filtration and purification in a mixer-settler contactor operating under conditions suitable for a dilute uranyl nitrate feed. Purified uranyl nitrate arising from uranium recycle is then absorbed into the uranyl nitrate stream derived from yellow cake processing.

3.5. Effluent treatment and disposal

All effluents arising from the process are discharged in accordance with authorizations issued by independent government-controlled regulating agencies.

3.5.1. Liquid effluents

(1) Raffinate from the purification stage is neutralized with lime slurry and the neutral solution discharged along a pipe into a local estuary. Continuous sampling demonstrates that the discharge is routinely well within authorization levels.
(2) Solutions containing fluorine are treated with lime slurry to precipitate calcium fluoride. The solid residue after filtration is disposed of by burial and the filtrate discharged to the estuary.
(3) Nitric acid recovered from the denitration stage is recycled to the dissolution stage.

3.5.2. Solid effluents

Insoluble residues from the yellow cake or residue leaching stages are washed free of uranium and placed in drums for burial at a local disposal site.

3.5.3. Gaseous effluents

Elimination of particulate uranium from the gaseous discharge of plants handling uranium powder is effected by a combination of primary filters or cyclones backed up by absolute filters. All such discharges are via stacks of the appropriate height.

Discharges which might contain noxious gases such as fluorine, HF, oxides of nitrogen, etc., are passed through scrubbing towers irrigated with an appropriate absorbing solution.

3.6. Safety

While attention to safety has received a high priority at Springfields since its early beginnings, in recent years safety issues at Springfields, as in all nuclear installations in the United Kingdom, have been formally regulated by issue of a statutory licence which is monitored by the independent Nuclear Installation Inspectorate, whose inspectors have free and unlimited access to all operations. Additionally, a permanent monitoring and advisory service for dealing with radiological, chemotoxic and other hazards is provided on site by the Health Physics and Safety Department, which is responsible directly to the General Manager.

The essence of the safety policy is that no activity is undertaken until its safety implications, whether radiological, chemotoxic or otherwise, have been considered and detailed formal instructions, approved by the appropriate level of authority, made available to the shop floor operators. Formal approval for modifications of equipment or procedures is likewise required before their introduction.

For new plants the safety policy requires the involvement of experienced safety advisors at the design stage, who then assist the operating department in the preparation of safety submissions to the Nuclear Installation Inspectorate requesting approval to proceed. Before new plant is brought on stream detailed schedules and instructions for pre-commissioning, commissioning and operation require Inspectorate approval under the terms of the operating licence.

While nuclear hazards, in the criticality sense, are absent the radiological and chemotoxic hazards associated with yellow cake conversion processes cannot be ignored.

External exposure hazards are, in general, insignificant but considerable attention is given to control of airborne uranium contamination at all stages of the conversion process, and particularly where the uranium is in the form of powder or hexafluoride. By total enclosure of potentially dusty operations inside ventilated cubicles and provision of adequate ventilation in general areas, the continuously-monitored airborne contamination is kept well below recommended occupational levels. Confirmation of the effectiveness of airborne contamination control procedures is obtained by routine urinalysis and whole-body monitoring of all operators in active areas.

Concern for the chemotoxic hazards attendant on processes involving anhydrous hydrofluoric acid, fluorine, uranium hexafluoride, etc., begins at the design stage in the choice of design principles, materials of construction, jointing materials, etc. This concern is carried over into the operational phase by repeated emphasis in operator training, both off plant and on plant, of the paramount importance of safety. In recent years, increased shop floor involvement and participation in safety issues has been achieved by the election of shop floor representatives who co-operate with management in a formally co-ordinated joint approach to hazard elimination.

4. INFLUENCE OF YELLOW CAKE QUALITY

An important feature of the interface between the mill operator and the yellow cake convertor is the question of yellow cake quality, a question complicated in the past by the variety of specifications in circulation. The recent exercise performed under the aegis of the American Society for Testing and Materials (ASTM), aimed at defining a standard specification for uranium ore

TABLE I. MAXIMUM LEVEL OF IMPURITIES IN YELLOW CAKE PROCESSED AT SPRINGFIELDS WORKS

Specified impurities				Non-specified impurities	
Impurity	Proposed limits (wt % U basis)		Maximum level (wt % U basis)	Impurity	Maximum level (ppm U basis)
	Normal	Maximum			
Arsenic	0.05	0.10	0.120	Aluminium	29 000
Boron	0.005	0.10	0.029	Silver	100
Calcium	1.0	5.0	4.72	Barium	310
Carbonate	2.0	4.0	4.72	Bismuth	240
Halides*	0.10	0.30	1.00		
Fluorine	0.10	0.30	0.33	Cobalt	710
Iron	0.15	1.0	1.08	Chromium	80
Magnesium	0.02	0.5	5.96	Copper	3 070
				Thorium-230	11
Molybdenum	0.10	0.30	0.50	Lithium	8
Phosphorus	0.16	0.32	14.40	Manganese	2 770
Potassium	0.2	3.0	1.90	Niobium	750
Silicon	0.5	2.5	4.88	Nickel	900
Sodium	0.5	7.5	10.00	Lead	7 000
Sulphur	1.0	4.0	6.13	Antimony	290
Thorium	1.0	2.5	3.52	Tungsten	700
Titanium	0.01	0.05	0.26	Zinc	340
Vanadium	0.1	0.70	2.51	Rare earths	35 400
Zirconium	0.10	0.50	2.60		

* Exclusive of fluorine.

concentrate, goes some way towards removing confusion in that it provides a specification that all convertors are prepared to accept. However, some impurities such as sodium, potassium and magnesium, specified with rigour in the ASTM draft might cause problems to certain mill operators yet present no problems to most convertors.

TABLE II. YELLOW CAKES PROCESSED AT SPRINGFIELDS

Australian	Rum Jungle, Northern Territory Radium Hill, South Australia South Alligator, Northern Territory United Uranium, Northern Territory Mary Kathleen, Queensland
Canadian	Rio Algom, Elliot Lake, Ontario Macassa, Bancroft, Ontario Beaverlodge, Saskatchewan Denison, Elliot Lake, Ontario Dyno, Bancroft, Ontario Faraday, Bancroft, Ontario Gunnar, Saskatchewan Milliken Lake, Elliot Lake, Ontario Northspan, Elliot Lake, Ontario Rayrock, Elliot Lake, Ontario Stanleigh, Elliot Lake, Ontario Stanrock, Elliot Lake, Ontario
American	Cotter, Canon City, Colorado Susquahanna, Falls City, Texas Susquahanna, Edgemont, South Dakota Susquahanna, Three Rivers, Texas Western Nuclear, Jeffrey City, Wyoming Utah, Gas Hills, Wyoming Utah, Shirley Basin, Wyoming Anaconda, Bluewater, New Mexico Petrotomics, Shirley Basin, Wyoming Federal American Partners, Riverton, Wyoming
African	Nufcor Palabora Games Estates Somaire
Miscellaneous	Belgian Ionex Swedish Spanish Yugoslavian Argentinian Portuguese German

TABLE III. HEXAFLUORIDE QUALITY

	Specification limits	Typical Springfields quality
Maximum vapour pressure of filled container at 200°F, in pounds per square inch, absolute	73	57
Minimum weight per cent of UF_6 in material	99.5	99.98
Maximum mol per cent of hydrocarbons, chlorocarbons, and partially-substituted halohydrocarbons	0.01	< 0.005
Maximum number of parts of elements indicated per million parts of total uranium:		
Antimony	1	< 0.5
Bromine	5	< 5
Chlorine	100	< 25
Niobium	1	< 0.7
Phosphorus	50	< 10
Ruthenium	1	< 0.4
Silicon	100	< 20
Tantalum	1	< 1
Titanium	1	< 0.4
Total number of parts of elements forming non-volatile fluorides (having a vapour pressure of one atmosphere or less at 300°C), per million parts of total uranium, e.g. Al, Ba, Bi, Cd, Ca, Cr, Cu, Fe, Pb, Li, Mg, Mn, Ni, K, Ag, Na, Sr, Th, Sn, Zn, and Zr	300	< 110
Maximum number of parts of elements or isotopes indicated per million parts of ^{235}U		
Chromium	1500	< 300
Molybdenum	200	< 40
Tungsten	200	< 100
Vanadium	200	< 60
Uranium-233	500	< 500
Uranium-232	0.110	< 0.01
Maximum thermal neutron absorption of total impurity elements as equivalent parts of boron per million parts of total uranium	8	< 2

However, while specifications for yellow cake can provide a general description of its quality and an indication of its suitability as feed to a particular conversion process, it has long been recognized at BNFL that most specifications are not completely comprehensive with respect to the definition of all unwelcome elements or species. To take two examples:

(1) Zirconium, an element notorious for creating problems at solvent extraction, was not included in yellow cake specifications until quite recently.

(2) Thorium-230, which frequently appears in yellow cake prepared by routes which do not include solvent extraction or ion-exchange, rarely appears in yellow cake specifications despite the handling and processing inconveniences occasioned by its presence in yellow cake.

To check whether yellow cake from a new source contains impurities which might create problems in, or add to the cost of, BNFL's conversion process, the practice of obtaining a pre-delivery sample has been adopted. This sample is analysed comprehensively and subjected to laboratory-scale dissolution, filtration and purification tests, the results of which are used to predict plant-scale performance.

As a consequence of identifying problems at the laboratory-scale level, plant-scale processing of normal concentrates has presented few problems and a measure of the plant's adaptability can be seen from a study of Table I showing the highest level of a particular impurity over the whole range of BNFL's experience of yellow cake.

Over the wide variety of yellow cakes processed at Springfields (Table II), precise control of conditions at the solvent extraction stage has been sufficient to ensure that the pure uranyl nitrate can be converted to hexafluoride meeting the American, Russian and British specifications. As an added precaution, before the pure uranyl nitrate is released for downstream processing bulk samples are analysed for impurities relevant to the hexafluoride specification and for impurities likely to influence subsequent reactions. The scope of the analysis at this stage is governed by experience of the yellow cake being processed and if none is available, by the results of the tests on the pre-delivery sample.

Although hexafluoride purity is principally determined at the solvent extraction stage, in the BNFL process some further purification takes place at the hydrofluorination and fluorination stages and analysis of contractual samples of hexafluoride consistently demonstrates its high quality. A measure of this quality is given by comparison of specification requirements with achieved purity for typical hexafluoride production (Table III).

REFERENCES

[1] RUDGE, A.J., "Production of elemental fluorine by electrolysis", Industrial Electrochemical Processes, Elsevier (1971).

[2] PAGE, H., et al., Processing of Uranium Ore Concentrates and Recycle Residues to Purified Uranyl Solution at Springfields, Br. Nucl. Energy Conf. J. 5 4 (1960) 272.

[3] PAGE, H., "Optimization of the main line uranium purification plant at Springfields Works", Solvent Extraction and Ion Exchange (Symp. Springfields Works, May 1974), British Nuclear Fuels Ltd, Preston (1974).

[4] HAWTHORN, E., et al., Fluidized-Solids Dryway Process for the Production of Uranium Tetrafluoride at Springfields, Br. Nucl. Energy Conf. J. 5 4 (1960) 285.

DISCUSSION

S.A. YOUNG: Is there any significant purification of UF_6 at the stage of condensation and transfer from condensers into transport cylinders, and if so what impurities are reduced?

H. PAGE: In the BNFL process hexafluoride quality control is established at the purification stage and monitored by chemical analysis of all pure uranyl nitrate before it is released for subsequent processing. Any contamination arising out of the subsequent processing which could influence hexafluoride quality, for example pick-up of chromium, is checked by chemical analysis of the uranium tetrafluoride before it is fed to the 'hex' plant. Because of the high quality of the UF_4 feed with respect to the species defined in the hexafluoride specification, most of which are present below detection level, it is not possible to determine the decontamination which occurs at the hexafluoride stage, but a study of the fluoride chemistry of, for example, chromium, implies that some decontamination occurs in the BNFL process. The condensation, liquifaction, and gassing back sequence referred to in the paper does of course reduce the level of light gas contamination from contaminants such as nitrogen and hydrogen fluoride.

S. SEN: You are removing hydrogen fluoride from the fluorine gas by absorption on sodium fluoride in contrast to other converters who use refrigeration at $-120°F$. Did you consider refrigeration for your process, and if so what are the advantages of the process adopted by you over one involving refrigeration?

H. PAGE: Recovery of hydrogen fluoride by refrigeration was considered at the design stage, but the vapour pressure of hydrogen fluoride is significant even at the low temperatures attainable with refrigeration equipment. BNFL concluded that to achieve the desired low levels of hydrogen fluoride carry over, it would be necessary to provide a combination of refrigeration and absorption or a process based solely on absorption. In the event it was decided to provide a hydrogen fluoride recovery stage based on absorption on, and regeneration from, sodium fluoride.

P.G. ALFREDSON: In your fluidized bed plant for conversion of UO_3 to UF_4 you required the addition of sulphate at the denitration stage to activate the material for subsequent reactions, whereas in the rotary kiln plant you described the use of hydration. Have you stopped adding sulphate for the rotary kiln plant?

H. PAGE: The product of the denitration stage consists of hard, dense spherical particles which are ideal for fluidizing or pneumatic transport, but lack the surface area and internal porosity required for subsequent gas/solid reactions. Addition of a modest quantity of sulphuric acid to the concentrated uranyl nitrate before denitration improves the reactivity of the uranium trioxide without impairing its fluidizing properties, but a balance has to be struck between the improved reactivity and the increased corrosion of nickel-based alloys which results from the increased sulphide present after the reduction stage. Because good fluidization properties are not a requirement for the rotary kiln plant the uranium trioxide can be activated after its formation, and this is carried out in a simple hydration step to yield uranium trioxide di-hydrate. It is thus unnecessary to sulphate material destined for the rotary kiln plant.

P.G. ALFREDSON: In your paper you referred to the product purity from solvent extraction which is required for hexafluoride production, but only in general terms. Would you please give examples of the elements and concentrations which are of concern. Obviously elements forming volatile fluorides will be of interest. Are there others?

H. PAGE: Product quality is a function of, and is controlled by, the degree of solvent loading in the region of the crude uranyl nitrate feed stage. By saturating the solvent with uranium in this region impurities which also have an affinity for tri-butyl phosphate are excluded from the solvent. Automatic measurement of the specific gravity and temperature of the settler No.7 solvent phase and integration of the signals provide a means of control of the aqueous feed to achieve a solvent loading commensurate with adequate purification and low uranium levels in the raffinate. Beta-counting of the loaded solvent to detect the uranium daughter ^{232}Th is also used for on-line control when processing yellow cake containing thorium. In addition, to check for elements which feature in the hexafluoride specification the purification stage product is, from time to time, monitored for impurities which can affect down-stream plant or reactions. Sodium can occasionally appear as a result of using demineralized water for backwashing at plant start-up and will affect the speed of the hydrofluorination reaction at levels much in excess of 20 ppm U basis. The free acidity and chloride level is routinely checked to avoid concentrations which could lead to corrosion of stainless steel. Concentrations in a typical product are 0.2% of nitric acid wt/vol. and less than 20 ppm chloride. Special care is taken to detect and prevent carry over of entrained solvent into the evaporation stage, to avoid the risk of the explosive reactions reported from other plants as a result of heating mixtures of TBP/OK/uranyl nitrate/nitric acid to temperatures in excess of 120°C.

A. ABRÃO: You mentioned that sulphur compounds increase the corrosive action of hydrogen fluoride on the nickel-based alloys used in the tetrafluoride plant. How is the rate of Monel corrosion affected by the quality of the anhydrous hydrogen fluoride?

H. PAGE: The corrosion of Monel by hydrogen fluoride is dramatically enhanced by sulphur compounds, particularly sulphur dioxide, which can enter the system as impurities in hydrogen fluoride. To keep corrosion rates within tolerable levels it is necessary to limit the sulphur dioxide content of hydrogen fluoride to less than 0.02 wt% and the sulphuric acid content to less than 0.04 wt%.

STUDIES FOR PRODUCING UF_6 FROM $UF_4 \cdot nH_2O$ IN JAPAN

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Abstract

STUDIES FOR PRODUCING UF_6 FROM $UF_4 \cdot nH_2O$ IN JAPAN.

Test plant operation for industrialization of the Power Reactor and Nuclear Fuel Development Corp. (PNC) wet process which consists of ore leaching, solvent extraction (Amex chloride conversion), electrolytic reduction, and UF_4 hydrate precipitation has been carried out for over 10 years at the Ningyo-Toge mine with several technical developments and improvements. At the end of 1977 a conversion test facility was set up at the mine site and experiments on the dehydration and fluorination step from $UF_4 \cdot nH_2O$ to UF_6 were started and the results of the experiments are described. The water of crystallization in the $UF_4 \cdot nH_2O$ ($n = 1 \sim 1.2$) is removed by dehydration; about 75% is removed at around 200°C and the remainder at about 350°C. Through the study of the dehydration rate of these two kinds of water of crystallization, the reactor-grade UF_4, containing less than 0.1% H_2O, about 1% UO_2, and 0.3% UO_2F_2 by weight, was obtained under the conditions of dehydration of 1 hour at 350°C in an atmosphere of nitrogen by operation in batches of a 3-in diameter fluidized-bed dehydrator. Through the study on the fluorination rate obtained from batch and continuous experimental operation of the 3-in diameter fluidized-bed reactor, high fluorine utilization efficiencies, over 99.9% (less than 0.1% of fluorine unreacted) were obtained at 380°C with 40% fluorine content in N_2 gas and a feed rate of 5 kg UF_4/h.

1. INTRODUCTION

Using domestic uranium ore as feed material, PNC has been developing the uranium processing technology which produces UF_4 and UF_6 directly from ore instead of through the yellow cake production since 1964. This process consists of direct uranium processing from ore to UF_4 by the wet process and the succeeding UF_6 production from UF_4.

The research and development of the process up to the $UF_4 \cdot nH_2O$ precipitate has already been reported at the previous IAEA Advisory Group Meeting held in Washington in 1975 [1], therefore the dehydration of the precipitate of UF_4 hydrate ($UF_4 \cdot nH_2O$) and conversion of dehydrated UF_4 to UF_6 will be reported here.

$UF_4 \cdot nH_2O$ is dehydrated in a fluidized-bed reactor at about 400°C. A fluidized-bed reactor has some excellent properties such as high heat transfer which leads to uniform bed temperature and reduces the formation of UO_2.

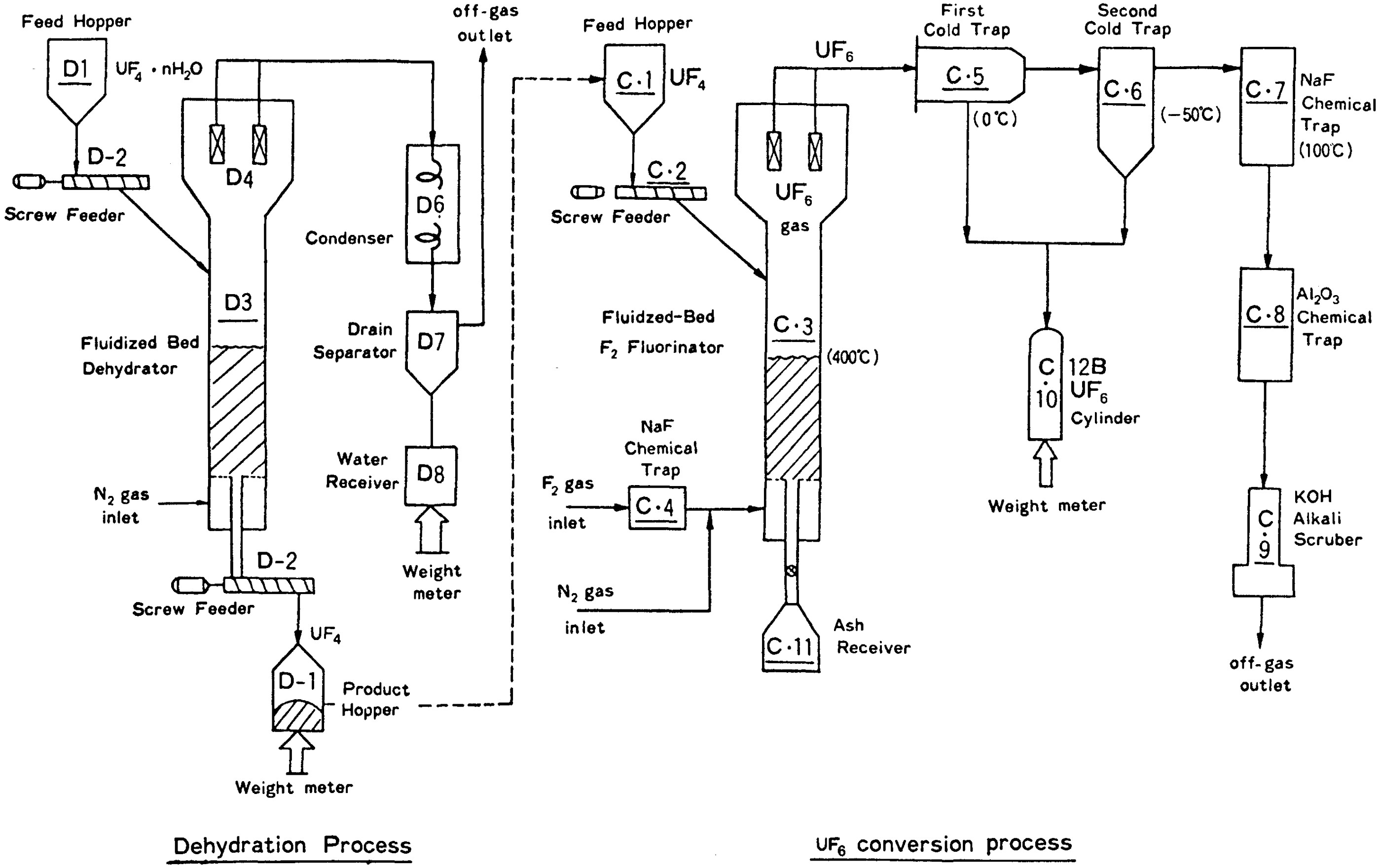


FIG.1. Process flow sheet of UF_6 conversion from $UF_4 \cdot nH_2O$.

On the other hand, the rapid mixing property of powder in the fluidized bed may lead to undehydrated $UF_4 \cdot nH_2O$ remaining in the product, therefore the operational conditions which ensure the specification of water content and reduce the formation of UO_2 must be carefully studied.

The water in the product is converted to HF in the subsequent fluorination step and reduces the purity of UF_6. Taking into consideration the fact that the US Energy Research and Development Administration (ERDA) specification of UF_6 purity is more than 99.5wt% and assuming that no other impurities than HF are contained in the UF_6, the specification of water content in UF_4 is less than approximately 0.25 wt%. Taking into account the other impurities, it should be less than 0.1 wt%.

Dehydrated UF_4 is converted to UF_6 by reaction with elemental fluorine. Fluidized-bed reactors or flame-tower reactors are usually used for this reaction. A fluidized-bed reactor has a disadvantage in that its production capacity is limited compared with a flame-tower reactor with the same diameter because of its limited gas velocity. But a fluidized-bed reactor was selected because of the following advantages:

(a) Not only UF_4 but also UO_2 and UO_3, etc., can be converted directly to UF_6 because of the easy removal of their high reaction heat release.
(b) Bed temperature can be controlled uniformly.
(c) The residence time in the bed is not limited so that the feed can be converted completely.
(d) Elemental fluorine can be completely utilized in the bed.

2. EXPERIMENTAL EQUIPMENT

The conversion test facility constructed in the autumn of 1977 at Ningyo-Toge Mine consists mainly of a fluidized-bed dehydrator and a fluidized-bed fluorinator of 3-in diameter, cold traps, chemical traps, and an alkali scrubber. Many tests for UF_6 conversion have been carried out, using UF_4 produced from domestic uranium ore. The process flow sheet of the UF_6 conversion equipment is shown in Fig.1.

The feed $UF_4 \cdot nH_2O$ is charged into a fluidized-bed reactor (D3) from an upper feed hopper (D1) through a screw feeder (D–2). The reactor is heated to about 400°C and the dehydration reaction takes place.

The product UF_4 is removed from the reactor through a lower screw feeder (D–2) and placed in a product hopper (D–1) which is used as a feed hopper for the subsequent process (C·1).

N_2 gas is used as the inert fluidizing gas, and dehydration water containing HF is condensed in a condenser (D6) and weighed for analysis.

TABLE I. FLUIDIZING PROPERTY OF UF_4 AND Al_2O_3

Measuring items \ Samples		Hydrated UF_4	Dehydrated UF_4	Sintered Al_2O_3
Bulk density	(g/cm^3)	2.051	2.23	1.89
True density	(g/cm^3)	5.0	5.0	3.76
Average particle size	(μm)	72	65	169
Minimum fluidizing velocity (air)	(cm/s)	1.5 ~ 3.0	1.5 ~ 3.0	5.0

The dehydrated UF_4 is charged into a 3-in diameter fluidized-bed reactor (C·3) from a feed hopper (C·1) through a screw feeder (C·2). Sintered Al_2O_3, which does not react with fluorine, is charged into the reactor as the bed material, and charged UF_4 is mixed and diluted with this Al_2O_3.

Fluorine gas is diluted with N_2 gas and then introduced into the reactor from the bottom.

A NaF chemical trap (C·4) is set before the reactor to remove a small quantity of HF in the F_2 gas and prevent the back flow of UF_6 gas.

UF_4 is converted to UF_6 gas by reaction with fluorine gas in the fluidized bed at 400°C.

After reaction the UF_6 gas is cooled and trapped in cold traps.

The first cold trap is cooled to about 0°C and the second to about −50°C. The off-gases from the cold traps contain a small quantity of UF_6 and F_2, therefore these gases are treated by a NaF chemical trap (C·7) which absorbs UF_6 gas, an activated Al_2O_3 chemical trap (C·8) which absorbs F_2 gas, and an alkali (KOH) scrubber (C·9) which absorbs a little residual UF_6 and F_2.

The solid UF_6 trapped in the cold traps is warmed with hot water at about 80°C to melt it and it is then run off into a 12B cylinder (C·10) set under the cold traps.

Some non-volatile fluorides are accumulated in the fluidized bed together with Al_2O_3 and removed into an ash receiver (C·11) at intervals.

To provide against the accidental release of UF_6 gas, the equipment is set in a hood which is ventilated through an alkali (KOH) scrubber and high efficiency particulate air filters.

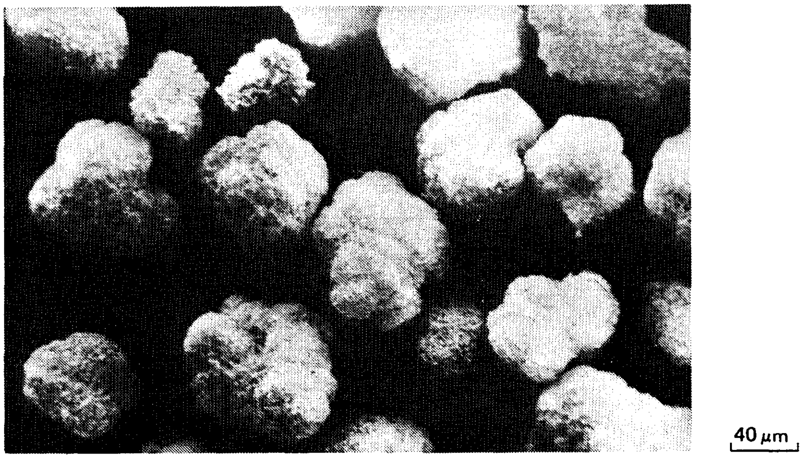


FIG.2. Scanning electron micrograph of hydrated UF_4 (scale 40 µm).

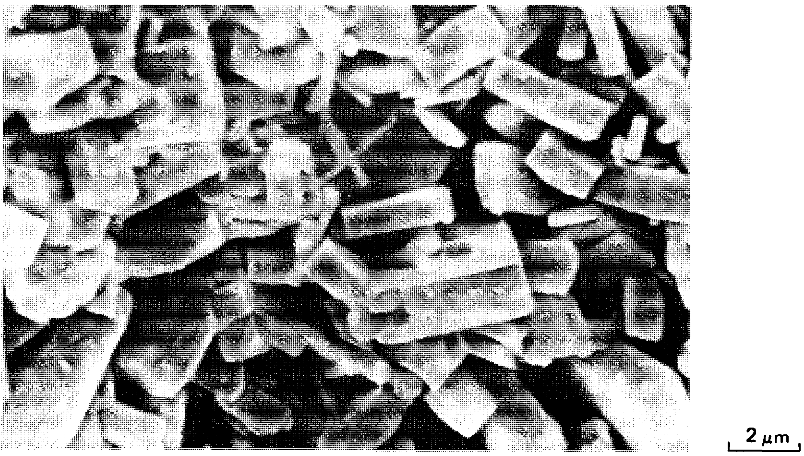


FIG.3. Scanning electron micrograph of hydrated UF_4 (scale 2 µm).

3. THE RESULTS OF EXPERIMENTS AND DISCUSSION

3.1. Fluidizing properties of feed powders

The properties of powders have very important effects on the operation of a fluidized-bed reactor. The properties of the powders used in the experiments are summarized in Table I. Scanning electron microscopic photographs of UF_4 powders are shown in Figs 2, 3 and 4.

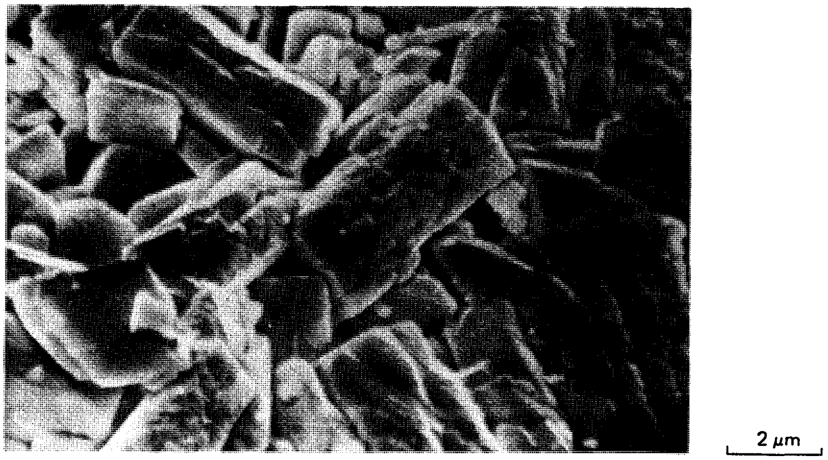


FIG.4. Scanning electron micrograph of dehydrated UF_4 *(scale 2 μm).*

$UF_4 \cdot nH_2O$ produced by the hydrofluorinate precipitation process is a fine powder, so that the fluidizing velocity is low as shown in Table I. After dehydration in the fluidized-bed reactor the product becomes finer as shown in Table 1.

3.2. Dehydration rate of $UF_4 \cdot nH_2O$

The water of crystallization in $UF_4 \cdot nH_2O$ is removed by dehyration in two stages at about 200°C and 390°C as shown in Fig.5.

The results of experiments show that the dehydration proceeds with the first-order kinetics for both the first and the second stage water of crystallization and the water content wt% X(t) of the product can be approximately represented, as follows:

$$X(t) \fallingdotseq X_{F_1} e^{-k_1(T)t} + X_{F_2} e^{-k_2(T)t} \tag{1}$$

where

t is the dehydration time (min)
X_{F_1} is the weight of the first stage water of crystallization, in per cent
X_{F_2} is the weight of the second stage water of crystallization, in per cent
$k_1(T)$ is the first stage dehydration rate constant at temperature T K (ltr/min)
$k_2(T)$ is the second stage dehydration rate constant at temperature T K (ltr/min)

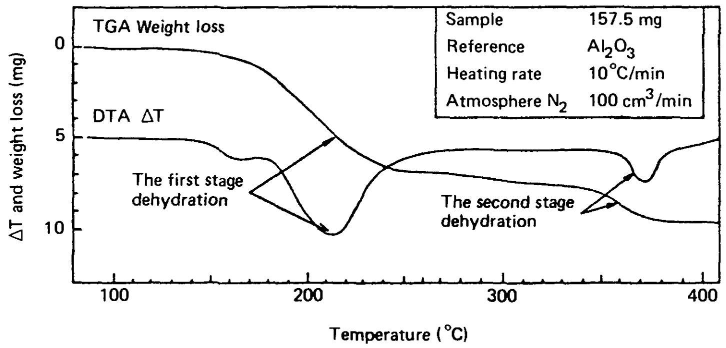


FIG.5. DTA and TG curves of $UF_4 \cdot nH_2O$.

and $k_1(T)$, $k_2(T)$ are represented as follows:

$$k_1(T) \fallingdotseq 1.32 \times 10^9 \exp\left[-\frac{11\,000}{TK}\right] \quad \text{(ltr/min)} \tag{2}$$

$$k_2(T) \fallingdotseq 4.157 \times 10^{11} \exp\left[-\frac{18\,120}{TK}\right] \quad \text{(ltr/min)} \tag{3}$$

From these empirical formulas, if the dehydration time is longer than 30 min at 350°C, the water content of the product shall be less than the specification of 0.1 wt%.

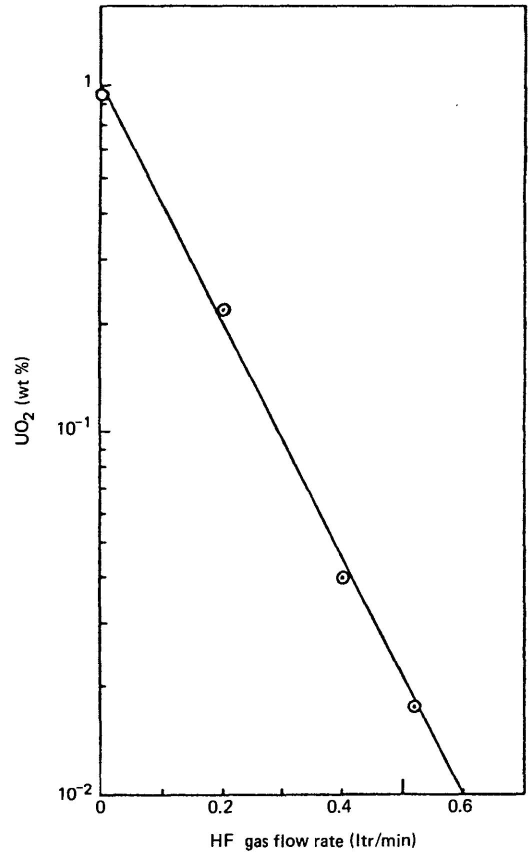
3.3. The continuous dehydration treatment of feed

Theoretical analysis on the continuous treatment of a solid feed, with an assumption of complete mixing of solids in the bed, is described precisely in Ref.[2], so that only the resultant semi-theoretical equations for the continuous dehydration of $UF_4 \cdot nH_2O$ with multi-stage fluidized beds are shown, as follows:

$$\overline{X}_{np} = X_{F_1}\left[\frac{S}{k_1(T)+S}\right]^n + X_{F_2}\left[\frac{S}{k_2(T)+S}\right]^n \tag{4}$$

where

n is the number of stages of multi-stage fluidized beds
$\overline{X}_{np}$ is the average water content of the product (wt%)
S = F/W, reciprocal mean residence time (ltr/min)
F is the feed rate (g/min)
W is the weight of the bed inventory (g).



Experimental condition

Bed inventory
5.0 kg UF_4

N_2 gas flow rate
10 ltr/min

Reactor temperature
410 °C

FIG. 6. Decrease of UO_2 formation by adding HF gas.

Actually discrepancies from the theory were found and may be caused by the fluidizing state, such as short pass or piston flow of UF_4 through the bed without complete mixing.

3.4. The formation of uranium oxides

With the dehydration of $UF_4 \cdot nH_2O$, the oxide UO_2 is formed according to the following reactions:

$$UF_4 \cdot nH_2O \xrightarrow{400°C} UF_4 + nH_2O \qquad (5)$$

$$UF_4 + 2H_2O \overset{400°C}{\rightleftharpoons} UO_2 + 4HF \qquad (6)$$

The addition of HF gas prevents the formation of UO_2. The experimental data shows that the formation of UO_2 can be reduced exponentially by increasing the addition of HF as shown in Fig.6. When the dehydration was performed in an atmosphere of N_2 gas only, the formation of UO_2 was about 0.8 ~ 1 wt% for the batch treatment and 1 ~ 3 wt% for the continuous treatment at a temperature between 300 and 400°C.

The formation of UO_2F_2 is about 0.25 ~ 0.5 wt% after dehydration.

It is important to mention that the formation of UO_2 is lower for batch treatment than for continuous treatment and may become even lower at some optimum temperature.

3.5. The reaction between the dehydrated UF_4 and F_2

The experiment was performed using the fluidized-bed reactor previously described, charging constant weight of UF_4 and sintered Al_2O_3 into the bed, making up the bed at constant temperature, sending F_2 and N_2 gas mixture from the bottom of the reactor and measuring the UF_6 gas product and F_2 with a thermal conductivity cell.

It has been said that usually the reaction between the UF_4 particles and the F_2 gas proceeds according to the 'diminishing-sphere-model' [3]. But the experiments for dehydrated UF_4 showed that the reaction proceeds according to the following zero order rate equations:

$$-\frac{dm}{dt} = K(T) = CNu \tag{7}$$

where

t is the time (min)
m is the amount of feed UF_4 in the reactor (g)
K(T) is the rate constant at temperature T K (g/min)
Nu is the UF_6 production rate (mole UF_6/min)
C is the factor which converts UF_6 mole to g weight of UF_4 feed and is given as follows:

$$1/C = \frac{A}{270} + \frac{B}{308} + \frac{1-A-B}{314} \tag{8}$$

where

A is the weight fraction of UO_2 impurity in the UF_4 feed
B is the weight fraction of UO_2F_2 impurity in the UF_4 feed.

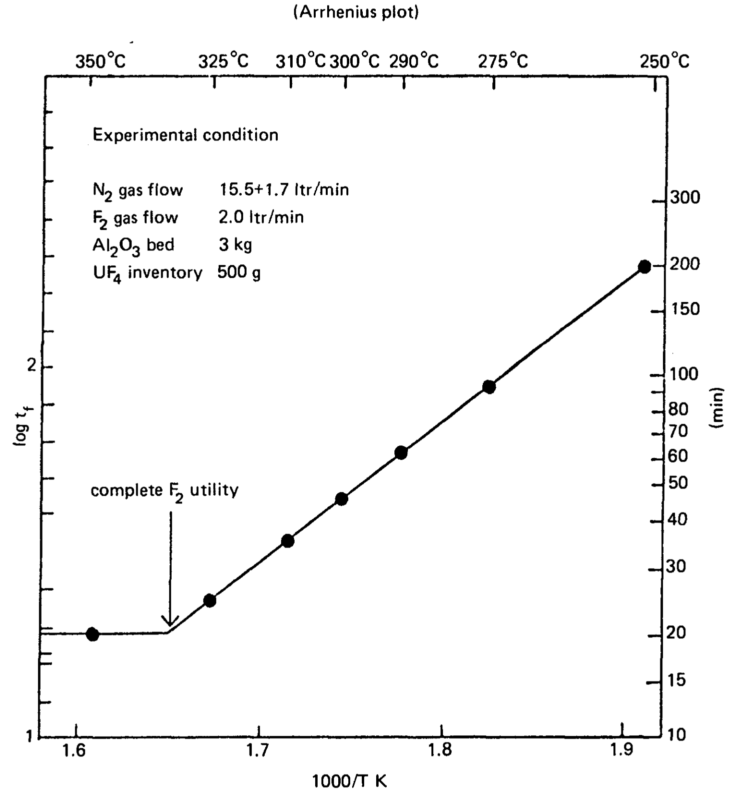


FIG. 7. Effect of bed temperature on reaction time.

The solution of equation (7) is as follows:

$$m = m_0 - K(T)\, t \tag{9}$$

and

$$t_f = m_0/K(T) \tag{10}$$

where

m_0 is the initial amount of feed UF_4 in the reactor (g)
t_f is the reaction time (min).

The UF_6 production rate is constant during the reaction period, and the reaction time t_f is proportional to the initial feed inventory m_0. From the

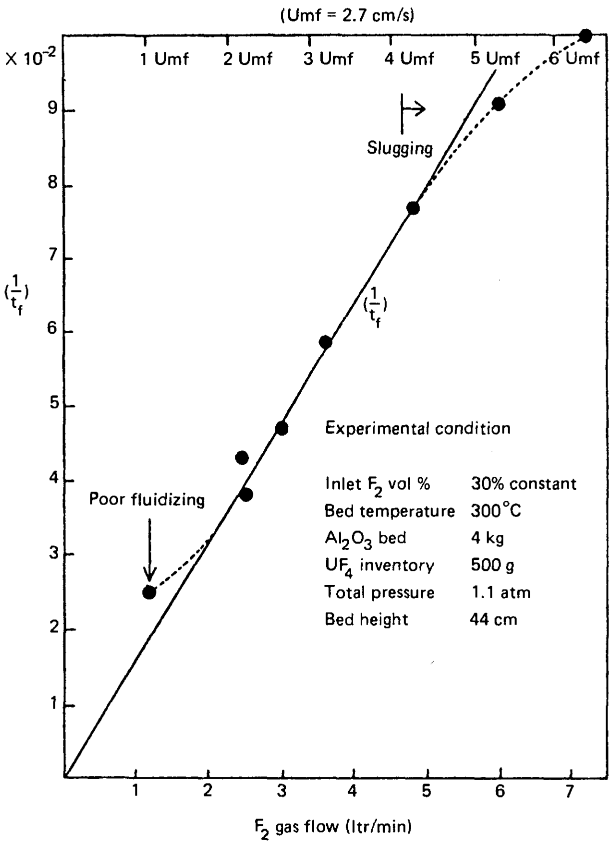


FIG.8. Effect of gas velocity on reaction in fluidized bed.

experimental results, the rate constant K(T) which is proportional to $1/t_f$ can be summarized as follows:

(a) Temperature dependence shows that K(T) has excellent fit with the Arrhenius equation shown in Fig.7 and the activation energy is 17.83 kcal/mole.

(b) K(T) is proportional to fluorine partial pressure and bed height of the reaction zone.

(c) The higher the dehydration temperature rises, the lower the reactivity becomes.

(d) Reaction becomes weak when total gas velocity exceeds slugging velocity [4], about 4 U_{mf} as shown in Fig.8.

From these experimental results, the UF_6 production rate by reaction between UF_4 and F_2 can be represented by the following experimental equation:

$$-\frac{dm}{dt} \doteqdot 1.14 \times 10^6 \, N_F{}^\circ Lm \exp\left[-\frac{9.03 \times 10^3}{T\,K}\right] \tag{11}$$

for $2\, U_{mf} < U_0 < U_c$

where

$N_F{}^\circ$ is the inlet F_2 gas flow rate (ltr/min)
Lm is the bed height at zero gas flow (cm)
U_0 is the superficial gas velocity (cm/s)
U_c is the slugging velocity $\cong 4\, U_{mf}$
Umf is the superficial gas velocity at minimum fluidizing conditions (cm/s).

3.6. Fluorine utilization

The amount of F_2 consumed by reaction with UF_4 which contains UO_2 and UO_2F_2 as impurities can be estimated by the following equation:

$$N_F = \frac{1}{100}\left[\frac{3A}{270} + \frac{2B}{308} + \frac{100-A-B}{314}\right]\left(-\frac{dm}{dt}\right) \times 22.4 \quad \text{(ltr/min)} \tag{12}$$

The fluorine utilization efficiency f can be defined as follows:

$$f = N_F/N_F{}^\circ \tag{13}$$

Usually

UO_2 wt% $A = 1$ $\qquad$ UO_2F_2 wt% $B = 0.5$

and bed height Lm = 43 cm for 4 kg Al_2O_3 + 500 g UF_4, so that f can be represented as follows:

$$f \doteqdot 3.60 \times 10^6 \exp\left[-\frac{9.03 \times 10^3}{T\,K}\right] \tag{14}$$

For continuous fluorination of UF_4 with constant bed inventory, the experimental data are compared with equation (14) and shown in Fig.9.

The discrepancies from equation (14) may be due to the difference in gas velocity. The higher the gas velocity becomes, the more the fluorine passing

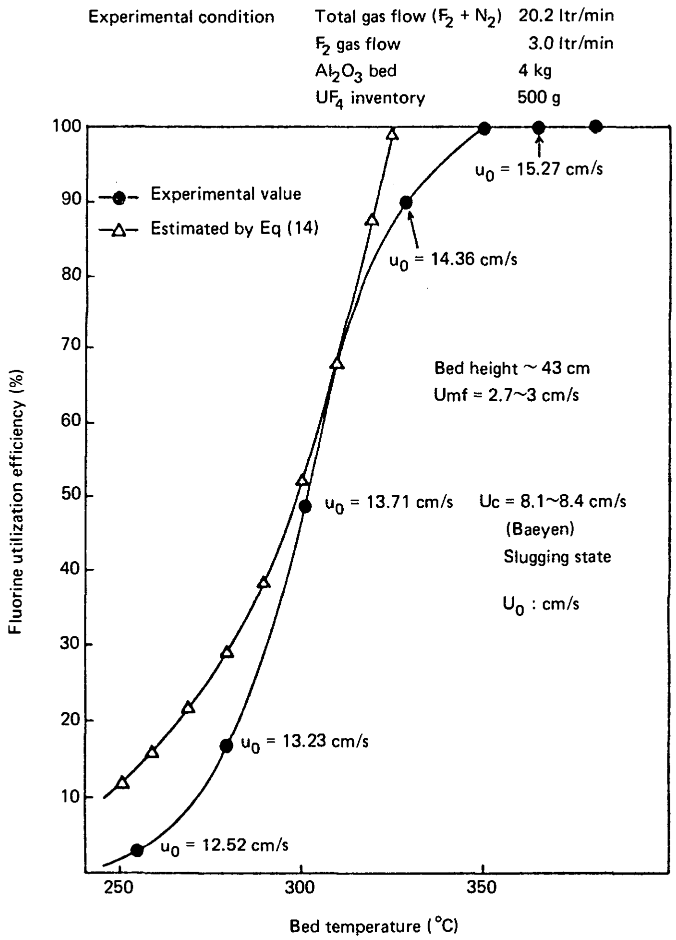


FIG.9. Effect of temperature on utilization of fluorine.

through without reacting with the UF_4 increases, and fluorine utilization efficiency falls as shown in Fig.8. As the UF_4 content in the bed increases, the fluorine utilization efficiency rises.

3.7. Some problems on operation of fluidized-bed fluorinator

3.7.1. Caking and channelling

As mentioned by many authors [5] the caking of the bed, which is usually caused by the formation of intermediates such as UF_5, is a serious problem.

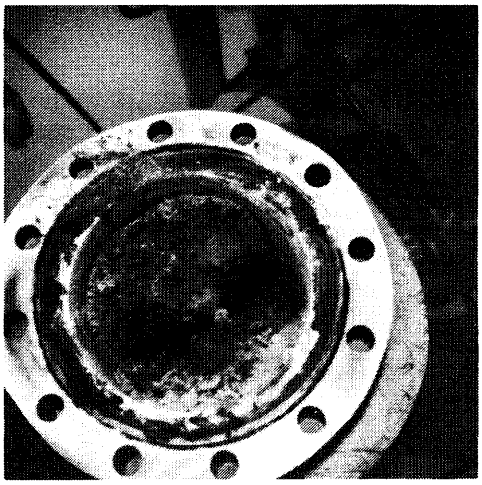


FIG.10. Caking of bed material in the upper cone part of the reactor.

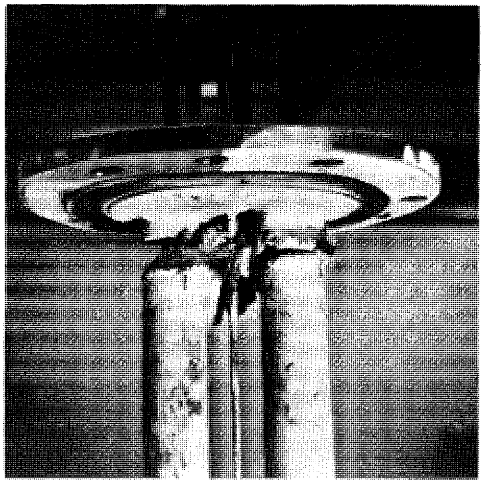


FIG.11. Caking of bed material attached at sintered metal filters in cone part.

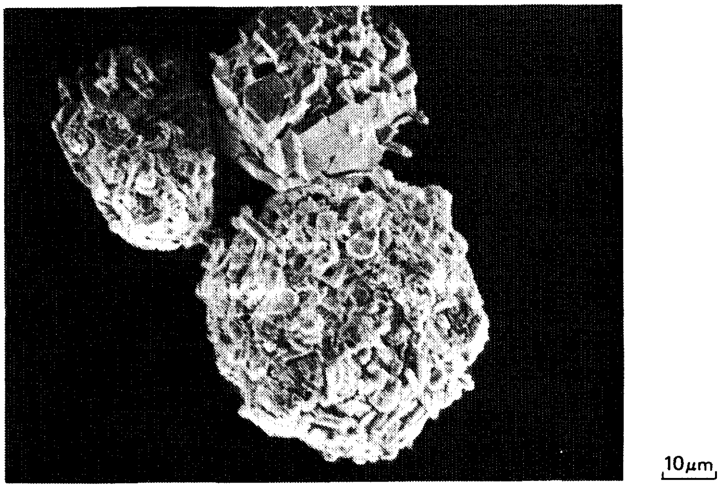


FIG.12. Scanning electron micrograph of the caking material U_2F_9.

Figures 10 and 11 show the caking in the upper cone part of the reactor. Releasing UF_6 gas, UF_5 has changed to black U_2F_9. Figures 12, 13 and 14 show scanning electron microscopic photographs of the U_2F_9.

Such formation of the caking may depend on the properties of the UF_4 powder, F_2 inlet pressure, UF_4 content in bed, total gas velocity, bed temperature and other causes.

3.7.2. Corrosion of fluorinator

The lower part of the reactor being used as a preheater was suffering remarkable corrosion by F_2 gas. The compound made by the corrosion of the reactor (Inconel 600) is NiF_2 and it had been stripped from the inside of the wall, forming thin ring plates just like the annual rings of trees, as shown in Fig.15.

The thickness of the corrosion plates, ξ_n, depends on the wall temperature, as shown in Fig.16.

The parabolic low of corrosion represented by the following equation was examined:

$$\xi_n^2 = 2\,k_1\,e^{-\frac{E_1}{RT}}\,t_0 \qquad (15)$$

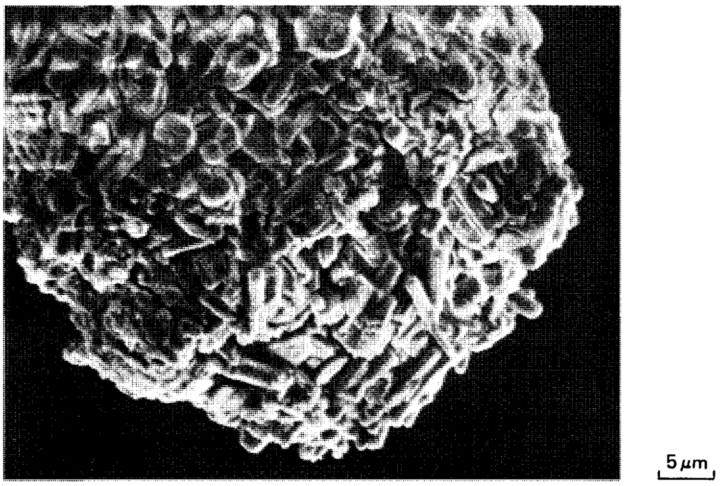


FIG.13. Enlarged photograph of Fig.12.

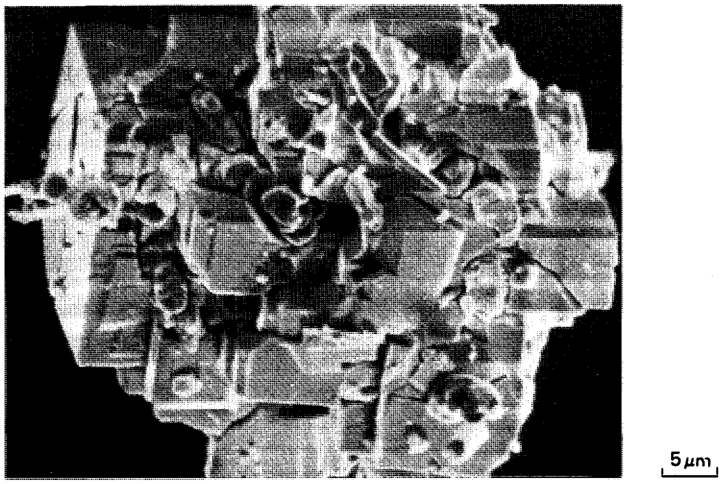


FIG.14. Enlarged photograph of Fig.13; U_2F_9 crystal structure is cubic.

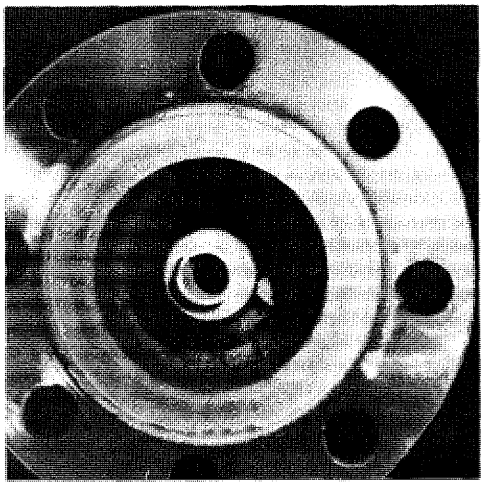


FIG.15. Corrosion of preheater part of fluorination reactor.

where ξ_n^2 is the thickness of a single corrosion layer at exposure time t_0. If the stripping of a corrosion layer occurs by n times in time t at every constant period t_0, equation (15) becomes as follows:

$$\xi_n^2 = (n\xi_n)^2 = (2\,k_1\,e^{-\frac{E}{RT}}\,nt_0)n = n\xi^2 \qquad (16)$$

where ξ is the thickness of a single corrosion layer and ξ_n is the thickness of multiple corrosion plates at exposure time t.

The corrosion is promoted by the stripping of the corrosion layer by n times. From our observations, the number of the plates, n, is about 56, and total exposure time, t, is about 750 h. Using these data in equation (16) and comparing with Fig.16, the following experimental equation without stripping can be derived:

$$\xi_0 \doteqdot \left[6.08 \times 10^4\ t_0(s)\ \exp\left(-\frac{10\,013}{TK}\right)\right]^{\frac{1}{2}}\ (\mu m) \qquad (17)$$

at F_2 vol.% ≒ 30% and 1 atm.

The inside of the wall of the fluidized bed was being scraped by the bed material (Al_2O_3) with the corrosion rate about 1.87 μm/h.

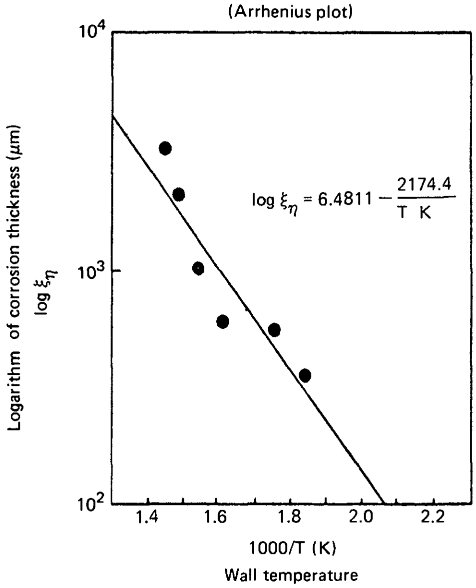


FIG.16. Effect of temperature on corrosion thickness.

The change of temperature may cause the stripping of the corrosion plates, or high temperature may be undesirable against corrosion, and a strong material against fluorine attack, such as Ni or Monel, may be desirable for the fluorinator as mentioned by many authors [5].

3.7.3. The accumulation of ^{234}*Th*

Since the feed UF_4 had been kept for about a year before UF_6 conversion, ^{234}Th in the UF_4 had accumulated up to the secular equilibrium content. Thorium-234 accumulated as ThF_4 in the Al_2O_3 bed of the fluorinator, owing to the use of such a feed, so that the gamma radioactivity of the bed increased.

The rising rate of radioactivity at a point 16 cm from the centre of the reactor was about 0.15 (mR/h)/h for the processing rate 4 kg UF_4/h. From this fact, the radioactivity C(t) (mR/h) at a point 16 cm from the centre of the reactor is estimated by the following equations:

$$C(t)_{\gamma=16\ \mathrm{cm}} = 2.14 \times 10^{12}\ \frac{\lambda_0}{\lambda_1} \cdot F\,(1-e^{-\lambda^1 t_s})\,(1-e^{-\lambda^1 t})$$

$$= 31.2\ F\,(1-e^{-1.2\times 10^{-3}\,t_s})\,(1-e^{-\lambda^1 t}) \qquad (18)$$

where

t_s is the storage time of the UF_4 (h)
t is the fluorination time (h)
F is the UF_4 feed rate (kg UF_4/h).

4. CONCLUSIONS

The UF_6 conversion tests, using $UF_4 \cdot nH_2O$ produced by the wet process have been carried out, and successful results have been obtained.

For the dehydration of $UF_4 \cdot nH_2O$ with the fluidized-bed reactor, batch operation may be preferable to continuous operation, because the formation of UO_2 was lower for the former than the latter, and a completely dehydrated product was obtained.

As the experiments with the fluidized-bed fluorinator show, the UF_4 produced in this way has a high reactivity with F_2, and almost 100% fluorine utilization can be attained with complete conversion of UF_4 to UF_6, so that the clean-up reactor to remove fluorine will be saved.

On the other hand, maximum UF_6 production capacity with a 3-in diameter fluidized-bed reactor is 6.6 kg UF_6/h and is lower than that of a flame-tower reactor.

This may be improved by enlarging the diameter of the reactor and in this way the fluidizing state will be stabilized.

Based on these experimental results, the UF_6 conversion pilot plant of 200 t U/year is now under design to promote further industrialization and to supply UF_6 to the enrichment pilot plant in Japan.

The construction will start in August 1979, and test operation will be started in the latter half of 1980.

REFERENCES

[1] TAKENAKA, S., KAWATE, H., "Some recent improvements in a uranium processing pilot-plant at the Ningyo-toge mine", Uranium Ore Processing (Proc. Advisory Group Meeting Washington, DC, 1975), IAEA, Vienna (1976) 55.
[2] KUNII, D., LEVENSPIEL, O., Fluidization Engineering, John Wiley and Sons, New York (1969).
[3] LABATON, V.Y., JOHNSON, K.D.B., J. Inorg. Nucl. Chem. **10** (1958) 74.
[4] BAEYEN, J., GELDERT, D., Chem. Eng. Sci. **29** (1974) 255.
[5] SMILEY, S.H., BRATER, D.C., LITTLEFIELD, C.C., PASHLEY, J.H., Union Carbide Nuclear Corp., Oak Ridge, TN, Rep. K1518 (1966).

DISCUSSION

S. SEN: Could the authors give the details of passivation treatment given on nickel surface before exposure of the surface to corrosion by F_2 and UF_6?

T. NAGASAKI: Material is not Ni but Inconel 600. Before fluorination, the inside of the fluorinator is cleaned of all grease and oil with trichloroethylene. After that the inside wall of the reactor is treated with F_2 diluted with N_2 through low F_2 vol.% (5%) to high vol.% (30%) at a temperature between 25 and 400°C. Small metallic, inorganic and organic dirt is burned up by F_2 gas slowly and gently, and a protection layer of fluoride may be formed inside the wall.

H.E. JAMES: I wish to refer to the paper on the PNC UF_4 process that was presented at the IAEA meeting in Washington in 1975 (Table VI, page 12). In particular, the Mo content of the UF_4 was quoted to be 2 ppm on a U basis. The UF_6 produced from this UF_4 also contained 2 ppm Mo on a U basis, which is above the ERDA specification for UF_6 of 1.4 ppm Mo on a U basis. I should like to ask the authors whether they can report any new data on the purities with respect to Mo of the UF_6 produced by PNC?

S. TAKENAKA: Using a spectrophotometric method for the analysis of Mo (ASTM C-761-73 150-161), the Mo content in $UF_4 \cdot nH_2O$ and UF_6 was determined to be 0.4 ~ 0.6 ppm (U base). This value was below ERDA's specification of 1.4 ppm (U base). The condition of the hydrofluorinate precipitation stage in the PNC process was improved so that Mo was removed.

REFINING OF YELLOW CAKE BY SOLVENT EXTRACTION

Pakistan Status Report

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Abstract

REFINING OF YELLOW CAKE BY SOLVENT EXTRACTION. PAKISTAN STATUS REPORT.

The paper describes the pilot-plant studies made at the Pakistan Institute of Nuclear Science and Technology, Rawalpindi, on refining yellow cake. The process units mainly consist of digestion and filtration, solvent extraction, precipitation and filtration, and calcining and reduction. Extraction parameters, such as free acidity in terms of nitrate ion concentration, throughputs and AF index, have been studied in some detail. Product of satisfactory chemical purity, as confirmed by spectrochemical analysis, was produced by this method.

1. INTRODUCTION

In Pakistan a modest effort has been made to become familiar with the existing uranium extraction technology. A pilot plant for the refining of uranium has been installed at the Pakistan Institute of Nuclear Science and Technology at Rawalpindi.

After successful commissioning of the plant a study was initiated to gain operational experience and to develop technical know-how on the refining of yellow cake (U_3O_8) by solvent extraction. A flow diagram of this pilot plant is shown in Fig.1 and its main process units, with their batch capacities, are:

Digestion and filtration,	5.0 kg U per operation
Solvent extraction,	1.0 kg U per hour
Precipitation and filtration,	1.0 kg U per hour
Calcination and reduction,	0.5 kg U per hour.

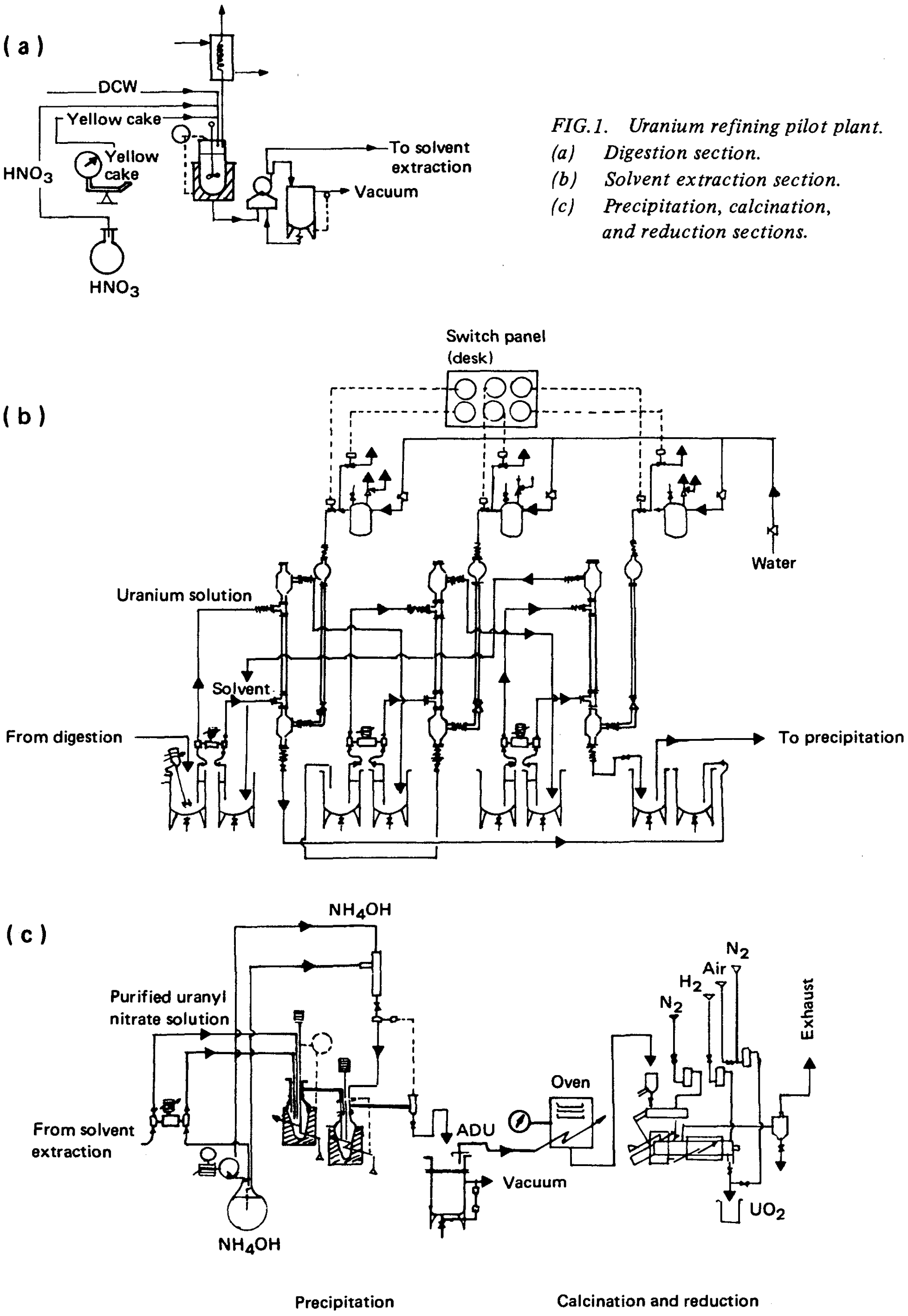

FIG. 1. Uranium refining pilot plant.
(a) Digestion section.
(b) Solvent extraction section.
(c) Precipitation, calcination, and reduction sections.

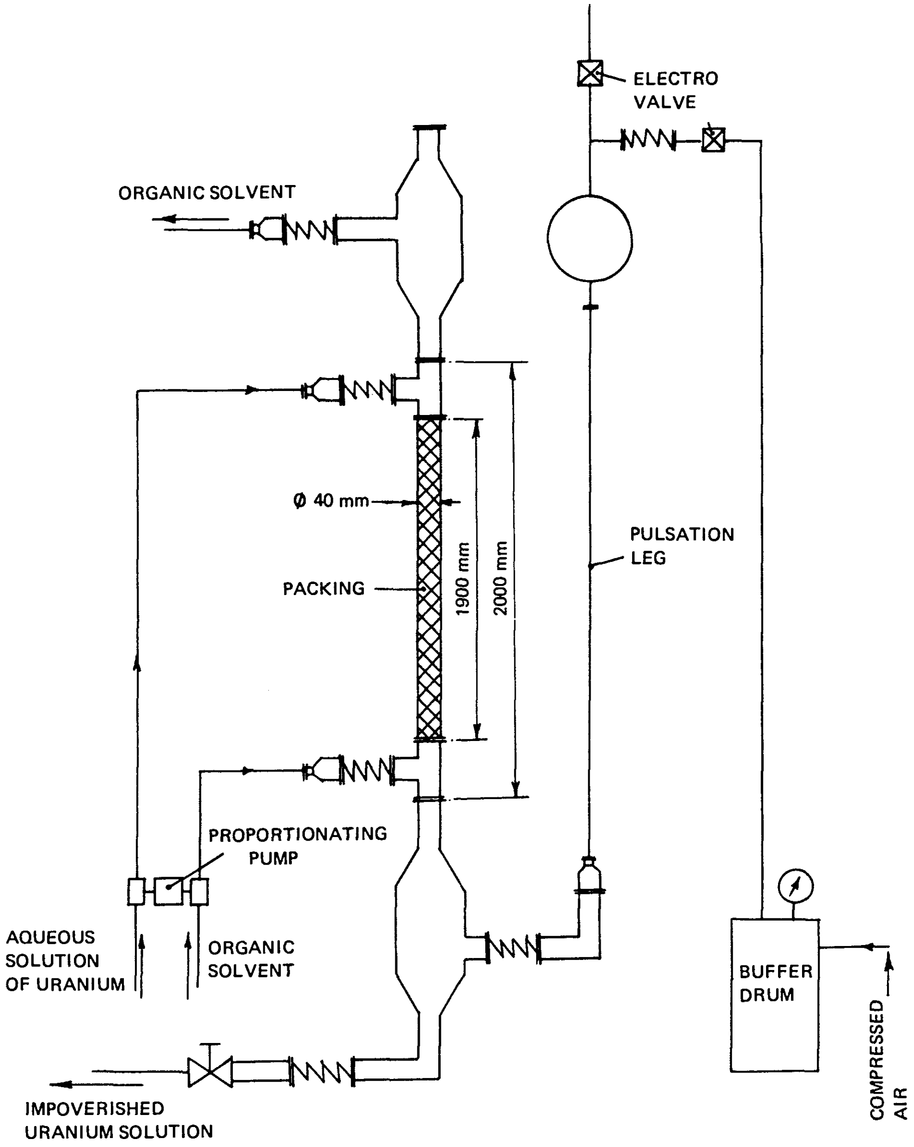

FIG. 2. Column arrangement.

The unit used for the digestion of yellow cake is a 20-ltr glass reactor, enclosed in a three-zone electrically-controlled furnace with an adjustable speed agitation unit.

The solvent extraction unit consists of three identical pulsed columns each for extraction, scrubbing and re-extraction. The columns are packed with Raschig rings and pulsation is created by compressed air and electrovalves. Liquid streams to the columns are fed through proportionating pumps. A typical arrangement of the columns is shown in Fig.2.

The precipitation unit operates continuously and consists of two 2.5-ltr glass vessels placed in electrically-heated jackets where the solution can be agitated by electric stirrers.

Both calcination and reduction operations are carried out in an electrically-heated vibrating-type furnace having a 900-mm long inconel reaction tube. The furnace has three independent heating zones with automatic powder feed and gas introduction systems.

2. PROCESS AND OPERATION

2.1. Digestion and filtration

As a standard practice yellow cake is dissolved in nitric acid according to the reaction

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

and the concentration of uranium for purification is fixed at 300 g of U per litre. The dissolution temperature is maintained at 80°C throughout the reaction, which takes about 3 h to complete. The solution is allowed to cool, filtered and transferred to a storage tank where its free acidity is adjusted to between 2 and 3N with nitric acid prior to solvent extraction treatment.

2.2. Solvent extraction

Greater emphasis was laid on studies to establish solvent extraction parameters that govern the purification of yellow cake using TBP as solvent. Trials were carried out using 22.5% TBP in dodecane by volume as solvent.

2.2.1. Extraction

The uranium-bearing aqueous phase is fed from the top and the organic phase from the bottom of the column to effect a counter-current flow system.

Thorough intermixing of phases is achieved owing to the presence of the packing and the air pulsation. The organic phase rich in uranium leaves at the top and is retained in a tank. The depleted aqueous phase coming out at the bottom is frequently checked for uranium content. If the uranium is less than 0.5 g/ltr, the solution is sent to the waste storage area, otherwise the uranium is recovered by precipitation with sodium hydroxide from the waste solution.

The following conditions have been found to give 99.9% extraction efficiency and were used for the normal operation of the extraction column:

Aqueous flow-rate	2.2 ltr/h
Organic flow-rate	6 ltr/h
Pulse frequency	40
Pulse height	30 cm

2.2.2. Scrubbing

The uranium-enriched organic phase is scrubbed with refined uranyl nitrate solution in the next column. The following optimum conditions have been established, so that no emulsion formation takes place:

Aqueous flow-rate	0.9 ltr/h
Organic flow-rate	9.1 ltr/h
Pulse frequency	40
Pulse height	10 cm

The aqueous phase was analysed for its uranium content. A number of experiments were carried out using 2, 4 and 6M HNO_3, demineralized water (DMW) and refined uranyl nitrate solution for scrubbing. It has been found that the best results are obtained when refined uranyl nitrate solution is used for scrubbing as the uranium losses from the organic phase are relatively low, though acid removal is high when DMW is used.

2.2.3. Re-extraction

Demineralized water is used for the re-extraction of uranium from the organic phase. The scrubbed organic phase containing about 100 g of U per litre is fed in at the bottom and DMW at the top of the column, the organic phase moves upward and becomes depleted in uranium. The aqueous phase containing 70 to 80 g of uranium per litre is stored in a tank.

After washing with 0.2% sodium carbonate solution the organic solvent is re-used. The effects of pulse frequency and pulse height on re-extraction

TABLE I. URANIUM MATERIAL BALANCE: SOLVENT EXTRACTION CYCLE

Stage	Liquid	Flow-rate (ltr/h)	U concentration (g/ltr)	
			Feed	Discharge
Extraction	Organic phase	6	0	110
	Aqueous phase	2.2	300	0.5
Scrubbing	Organic phase	9.1	110	101
	Aqueous phase	0.9	0	9
Re-extraction	Organic phase	5.5	101	10 ± 5
	Aqueous phase	7.5	0	75 ± 5

efficiency have been studied. The following working conditions for the re-extraction column have been found to give maximum efficiency:

Aqueous flow-rate	7.5 ltr/h
Organic flow-rate	5.5 ltr/h
Pulse frequency	50
Pulse height	20 cm

Table I shows the overall material balance in terms of uranium content in both the organic and aqueous phase for the complete solvent extraction cycle.

2.2.4. Precipitation

Uranium is precipitated as ammonium diuranate with ammonia solution

$$2UO_2(NO_3)_2 + 6NH_4OH \longrightarrow (NH_4)_2U_2O_7 + 4NH_4NO_3 + 3H_2O$$

Precipitation is carried out in two stages with different pH values and the flow-rates of pure uranium and ammonia solution are so adjusted that 70% of the uranium is precipitated in the first stage. Generally, the following conditions are used to precipitate uranium as ADU:

TABLE II. SPECTROCHEMICAL ANALYSIS

Element	Feed material (yellow cake)	Refined uranyl nitrate	UO_2 powder final product
Al	500	20	10
B	5	1	0.3
Cd	1	1	0.2
Ca	–	–	–
C	–	–	–
Cr	–	–	–
Cu	10	3	–
Dy	–	–	–
F	–	–	–
Gd	–	–	–
Fe	500	5	10
Pb	–	2	–
Mg	–	5	2
Mn	20	2	–
Mo	20	N.D.	–
Ni	100	N.D.	3
Si	250	20	20
Na	N.D.	N.D.	–
Th	–	–	–
V	5	N.D.	–
Zn	100	N.D.	–

Concentration of uranium solution	70 g U/ltr
Strength of ammonia solution	5.5N
Flow-rate of uranyl nitrate solution	9.0 ltr/h
Flow-rate of ammonia solution	1.3 ltr/h
Temperature	70°C
pH in first reactor	3.5 ± 0.2
pH in second reactor	7.0 ± 0.1.

After washing and drying, the ADU is crushed to 160 mesh size and heated at 300°C for 6 to 8 h to obtain orange-coloured UO_3.

TABLE III. EFFECT OF THROUGHPUT ON EXTRACTION

Free acid	Flow-rate through column (aq.+org.) (ltr/h)	Average efficiency (%)
2N	3.72	99.0
	7.44	99.0
	11.16	88.3
2.5N	7.44	99.5
	11.16	97.5
3N	3.72	99.9
	7.44	99.9
	11.16	95.3

2.2.5. Calcination

The UO_3 powder is fed to the furnace at 600°C at a flow-rate of 500 g/h where dried air or N_2 gas is passed counter-currently at the rate of 200 ltr/h. As a result, U_3O_8 is formed according to the reaction

$$6UO_3\ \tfrac{1}{2}\,H_2O \xrightarrow{600^\circ C} 2U_3O_8 + O_2 + 3H_2O$$

Different combinations of calcination temperature (between 400 and 600°C) and powder flow-rates were tried. At a lower temperature the flow-rate of powder has to be reduced considerably to achieve complete conversion of UO_3 to U_3O_8. Therefore, all calcination runs were carried out at 600°C.

2.2.6. Reduction

U_3O_8 powder is recharged in the furnace and reduced in a hydrogen atmosphere according to the reaction

$$U_3O_8 + 2H_2 \xrightarrow{600-700^\circ C} 3UO_2 + 2H_2O$$

A number of reduction runs have been carried out at different temperatures and powder flow-rates to observe the effect of these parameters on the physical

TABLE IV. EFFECT OF AF INDEX ON EXTRACTION AND RE-EXTRACTION EFFICIENCY

Frequency (counts/min)	Amplitude (cm)	Average efficiency (%)	Frequency (counts/min)	Amplitude (cm)	Average efficiency (%)
Extraction			**Re-extraction**		
Aqueous flow-rate 2.2 ltr/h Organic flow-rate 6.0 ltr/h			Aqueous flow-rate 7.5 ltr/h Organic flow-rate 5.5 ltr/h		
30	30	99.1	25	25	Not feasible
35	30	99.4	30	25	87.2
40	30	99.9	35	25	Column flooded
45	30	99.6	40	25	Column flooded
50	30	Emulsification	50	25	Column flooded
55	30	Emulsification	30	20	79.7
45	25	99.8	35	20	82.8
50	25	99.5	40	20	94.3
55	25	Emulsification	45	20	95.6
60	25	Emulsification	50	20	97.0
			35	15	79.0
			40	15	78.8
			45	15	Column flooded
			50	15	Column flooded
			55	15	Column flooded

characteristics of the UO_2 powder, i.e. bulk density, surface area, and O/U ratio. A powder flow-rate of about 250 to 300 g/h gives a good quality UO_2 at a reduction temperature of 700°C.

3. RESULTS AND CONCLUSION

In general, the experience and results on purification of impure yellow cake in the laboratories have been quite satisfactory. This conclusion can be

TABLE V. OPTIMUM OPERATING CONDITIONS FOR SOLVENT EXTRACTION OF URANIUM

Column	Aqueous flow-rate (ltr/h)	Organic flow-rate (ltr/h)	Pulse frequency	Pulse height (cm)
Extraction	2.2 (3N HNO_3, 300 g U/ltr)	6.0 (22.5%)	40	30
Scrubbing	0.9 (uranyl nitrate solution 70 g U/ltr, 0.1N HNO_3)	9.1 (22.5%)	40	10
Re-extraction	7.5 (demineralized water)	5.5 (22.5%)	50	20

drawn from Table II which shows the spectrochemical analysis of the feed material, the refined uranium after solvent extraction, and the UO_2 produced.

With the efforts to achieve maximum extraction efficiency in the refining of yellow cake, emphasis was laid mainly on the following parameters that could possibly affect the extraction process:

Free acidity in terms of NO_3^-
Throughputs
AF index (where AF index = amplitude (counts/s) X frequency (cm)).

A number of experiments were devised at a fixed AF index (20) to study the effect of free acidity and throughput on uranium extraction efficiency. These results are shown in Table III. It was observed that when the throughput is between 4 and 8 ltr/h, the uranium extraction efficiency is above 99.0%. In the same range of throughputs, the extraction efficiency is also at its maximum when the free acidity is between 2 and 3N.

The effect of variation of AF index on extraction showed that with an increase in AF index at constant throughputs, the extraction efficiency also increases. This effect was, however, limited as at higher AF indices, emulsification starts. A similar trend was noticed when dealing with the re-extraction operation where column flooding took place with increased AF index (Table IV).

As a result, optimum operating conditions for the solvent extraction of uranium in the pilot plant were determined and are shown in Table V.

TABLE VI. EFFECT OF CHANGING PARAMETERS ON THE QUALITY OF UO_2 POWDER

Serial No.	Bulk density		Reduction temperature (°C)	UO_2		
	UO_3	U_3O_8*		Bulk density	O/U	Surface area
1	0.706	0.810	700	1.225	2.09	3.33
2	0.760	0.823	700	1.235	2.13	3.80
3	0.763	0.847	700	1.290	2.10	4.80
4	0.771	0.852	700	1.310	2.11	4.01
5	0.809	0.968	700	1.307	2.05	3.08
6	0.820	0.978	750	1.385	2.10	3.90
7	0.824	0.978	750	1.450	2.06	3.41
8	0.824	0.978	650	1.390	2.10	4.10
9	0.824	0.978	600	1.352	2.10	5.78
10	0.860	1.02	650	1.620	2.11	3.14

* Calcined at 600°C.

In order to produce UO_2 powder of desired specifications from the refined yellow cake, the physical characteristics of UO_2 powder in general were also determined. Some of these results are shown in Table VI.

4. FUTURE PROGRAMME

The pilot-plant facility was essentially planned to familiarize the engineers with the current techniques for the refining of uranium from concentrate. It is planned to extend the studies to the behaviour of other solvents and diluents for the refining of uranium. At present, small quantities of UO_2 can be produced to meet the demands for specific powders required for research and development work.

Theoretical studies are in progress to adapt the pilot plant for the extraction and refining of zirconium and other nuclear materials.

Investigations on the pilot plant will also assist in the design and installation of refining plant on a larger scale.

YELLOW CAKE PRODUCED FROM SWEDISH URANIUM ORES

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Short Communication

INTRODUCTION

Two types of uranium ores have been found in Sweden, both relatively low grade. These are alum shales and vein-type ores in Precambrian rocks.

In this short communication the uranium extraction principles for these ores and the yellow cake assays are presented.

URANIUM ORES IN SWEDEN

In Sweden uranium mineralizations have been proven in alum shales and in Precambrian rocks.

Large but low-grade uranium ore reserves are found in the extensive formations of alum shale in Sweden. The highest uranium grades have been indicated at Ranstad in the southern part of the country where the alum shale is a part of the practically horizontal series of sediments belonging to the upper Cambrian era. The uranium-carrying horizon is 2.5 to 4.0 m thick with a grade varying between 250 and 325 g/t U. The total uranium content in the Randstad area is over 1 Mt of which it should be possible to recover at least 300 000 t on a purely technical and economic basis.

A small uranium mill was constructed at Ranstad and put on stream in 1965. The plant operated at reduced capacity for 3 years producing about 300 t of yellow cake. Due to the low demand for uranium at that time, caused by delays in the nuclear power programmes, the plant was closed down in 1969.

Since this time the facilities at Ranstad have been used for pilot plant testing, developing more efficient technology for the processing of shale-type ores. Process development for new uranium ores is also conducted on a laboratory and pilot scale.

In northern Sweden vein-type uranium mineralizations have been found. At Pleutajokk 3000 t of uranium have been indicated. Depending on selectivity

TABLE I. YELLOW CAKE ASSAYS FROM RANSTAD

Constituent	Production period Sodium uranate (%)	Pilot plant Sodium uranate (%)	Pilot plant Ammonium uranate (%)
U	72.0	70.7	73.3
Moisture	0.5	1.2	2.0
As	0.001 0	<0.000 5	0.002
B	0.000 05	<0.000 05	0.000 1
Br	<0.000 5	<0.000 5	0.000 4
Ca	0.15	0.03	0.011
Cl	0.0005	0.000 5	0.000 5
CO_3	1.90	1.3	0.10
F	<0.000 7	<0.000 5	0.009
Fe	0.05	0.02	0.07
I	<0.005	<0.001	<0.001
K	0.03	0.01	0.005
Mg	–	–	0.000 7
Mo	0.015	0.03	0.01
Na	7.4	7.6	0.008
NH_4	–	–	3.5
PO_4	0.010	0.12	0.04
SiO_2	0.02	0.02	0.2
SO_4	0.03	0.10	3.2
Th	<0.005	<0.005	<0.000 5
Ti	–	–	0.000 3
V	<0.000 5	<0.000 5	0.000 1
Zr	–	–	0.006

Assays for As–Zr are per cent of dry concentrate weight.

TABLE II. AMMONIUM URANATE FROM PLEUTAJOKK

Constituent	Content (%)
U	74.6
Moisture	2.0
As	0.000 3
B	0.000 2
Br	0.000 4
Ca	0.04
Cl	0.000 5
CO_3	0.15
F	0.004
Fe	0.02
I	<0.001
K	0.005
Mg	0.001
Mo	0.04
Na	0.000 8
NH_4	2.0
PO_4	<0.01
SiO_2	0.15
SO_4	2.5
Th	0.008
Ti	0.003
V	0.01
Zr	0.025

Assays for As–Zr are per cent of dry concentrate weight.

difficulties and choice of mining methods the average grade of the ore body is expected to be between 250 and 700 g/t. The uranium occurs as uraninite in thin veins irregularly distributed in the ore zones.

Flow sheets for the processing of this ore have been worked out and tested on a laboratory and pilot scale. Conventional acid leaching followed by solvent extraction yielded high uranium recoveries.

Uranium mineralizations associated with phosphorite have also been found in a number of locations. No feasible methods for commercial processing of these ores have yet been suggested.

RANSTAD ALUM SHALE

Uranium is extracted from the alum shale at Ranstad by vat leaching with sulphuric acid.

In the full-scale operation uranium was recovered from the leach liquor by ion exchange. IRA 400 and IRA 405 from Rohm & Haas was used as a resin. Elution was carried out with sulphuric acid and the eluate treated by solvent extraction with EHPA (the Elux process). Uranium was stripped with sodium carbonate, and sodium uranate was precipitated by raising the pH with sodium hydroxide. The sodium uranate was produced in a coarse, heavy form.

In pilot-scale testing uranium has been recovered from the leach solution by solvent extraction with amines. Stripping has been carried out with both sodium carbonate and ammonium sulphate. The sodium sulphate circuit requires a second solvent extraction circuit for molybdenum separation.

Assays of these three types of yellow cake from the Ranstad plant are shown in Table I.

PLEUTAJOKK ORE

Recovery of uranium from the Pleutajokk ore body has been tested in a pilot plant. Conventional slurry leaching with sulphuric acid can be applied and uranium recovered from solution by amine extraction. Uranium is stripped with ammonium sulphate and precipitated as ammonium uranate. The analysis of yellow cake from the pilot plant is shown in Table II.

A NOTE ON URANIUM IN THE UNITED STATES OF AMERICA

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Short Communication

I should like to offer a few remarks to clarify the record of these proceedings, and to present for inclusion in the record information and data on the status of uranium production in the United States of America.

First, a reference was made early in this meeting to USAEC uranium concentrate specifications. For the record, USAEC uranium concentrate purchases ceased at the end of 1970. Since then, all uranium production has been for sale in the commercial market and producers must meet concentrate specifications set by the commercial conversion facilities such as those of Kerr-McGee, which were described by J.W. Craig, by Allied Chemical Corporation at Metropolis, Illinois, and by Eldorado and British Nuclear Fuels, both of which receive, or have received, concentrates from producers in the United States of America.

The USAEC was abolished as an agency in January 1975 and its functions transferred to the Energy Research and Development Administration, which was referred to in T. Nagasaki's paper. ERDA was abolished in October 1977. The activities of both the AEC and ERDA now reside in the US Department of Energy, for example, the operation of the uranium enrichment facilities.

Regarding the status of uranium production in the USA, I should like to point out that the past year (1978) was a record year. Uranium concentrate production of 14 200 tonnes U was more than produced during the prior peak years of 1960, 1961, and 1962 when annual production was about 13 600 tonnes.

Two mills, one new and one renovated, began processing uranium ore in 1978, making a total of twenty conventional mills in operation at the end of the year. Another new mill is ready to begin processing ore, and two others are under construction.

Production increased at most in situ or solution mining operations, and considerable progress was made in the commercial recovery of uranium from copper leach liquor and from wet-process phosphoric acid. Two new facilities for recovering uranium from wet-process phosphoric acid commenced operation in 1978, and several other plants were in the design or construction stages.

Since ore for the uranium mills in the USA comes from approximately 250 underground mines and about 35 open-pit mines, and because of the variety in mill flow-sheets, it can be understood why there is not more uniformity in the quality of concentrates produced. With further anticipated expansion of the industry, perhaps a doubling of capacity in the next 10 years, plus expansion of production by solution mining and from wet-process phosphoric acid and copper leach liquor, it might be expected that there will continue to be considerable variability in uranium concentrates produced in the USA.

Another aspect of future ore processing in the USA that should be considered is that the average grade of ore processed is gradually decreasing. For example, since 1972 the average millfeed grade has dropped from about 0.21 per cent U_3O_8 to an average of 0.13 per cent in 1978. With the increased sales price for uranium, producers are looking at more vigorous extraction techniques to recover a greater percentage of the uranium, such as longer leach times, elevated temperatures, and even acid pressure leaching. Such leaching techniques would be expected to solubilize more impurities in the ore and hence affect the quality of concentrates produced. Additionally, other low-grade resources are being investigated as future sources of uranium. Processing of such materials also would lead to concentrates of somewhat different quality than produced today.

In summary, I can only suggest that there needs to be a continuing dialogue and understanding between the concentrate producers and conversion and refinery plant operators. This meeting has been an excellent step in that direction.

As a side issue and final remark, I would like to suggest that this might be a suitable forum to correct, or attempt to correct, misunderstandings or misuse of the term ‘yellow cake’. So often the expression ‘yellow cake’ is used in the press as a synonym for U_3O_8. Perhaps this does not bother others as much as it does me but I ask, should we strive for clarification? In my opinion one buys or sells U_3O_8 or U in uranium concentrate and not ‘yellow cake’.

PANEL SUMMARY

At the conclusion of the technical sessions the participants met for a panel discussion. The chairman of the panel, Dr. H. Page, called on the other session chairmen Dr. A.W. Ashbrook, Mr. J.W. Craig, Mr. G. Lyaudet and Dr. S.A. Young to summarize highlights from the meeting. This was followed by a discussion of several specific topics. The following is a summary of the meeting including the discussions of the final panel session.

The ore leaching process was not a subject for in-depth review at this meeting. However, it was appropriate that the first papers included accounts of ore leaching studies. The mineralogy of the ore is the fundamental factor determining the nature of the leaching recovery problem, the composition of the leaching solution and any subsequent problems in the concentration and purification processes. There is a continuing need for research into the recovery of uranium from sources with difficult mineralogy such as refractory uranium minerals, of which one is monazite, as described in one paper, and reactive gangue minerals such as apatite, problems with which are outlined in two papers. The application of heap leaching was especially discussed. This technique remains an attractive low-cost alternative for recovering uranium from ore bodies containing limited reserves. However, there remains the uncertainty of the fraction of uranium available which can be recovered and the problem of rehabilitation after leaching.

One paper described work on the extraction and concentration of uranium from copper leach solutions. The winning of uranium from such solutions containing only 10 to 15 ppm of uranium presents a particularly challenging problem to the concentration process and tends to focus on the advances and changes taking place in this area.

Thus, since the late nineteen fifties solvent extraction (SX) using tertiary amines tended to replace resin ion exchange (IX) in new installations and also in many established operations. Because of the inherent advantages from its truly continuous nature and from the greater selectivity of the tertiary amines, SX produces a steady stream of more highly concentrated and purer uranium solution for precipitation.

IX retained its economic advantage for the treatment of solutions of low uranium concentration and for that purpose SX was introduced as a second concentration and purification stage resulting in the eluex processes. However, in the last few years there has been the successful demonstration in industrial uranium extraction plants of continuous resin ion exchange processes (CIX). These share with SX the advantages of a lower inventory of exchange medium and the ability to produce a steady stream of high grade eluate. At this meeting one paper described a proposal to introduce a type of reflux in the elution process in order to achieve very high concentrations of high purity uranium solutions for precipitation. Developments in this whole technology of CIX will be watched with interest.

The next stage in the overall process is to produce the intermediate uranium concentrate or yellow cake from the strip or eluate solutions. It is noteworthy that the several papers describing aspects of this process are the first publications devoted specifically to this subject. This information represents the accumulation of many years' experience and will make a most useful contribution to the documentation of the uranium fuel cycle technology. It is apparent that important properties of yellow cake such as the sulphate content, the alkali and alkaline earth elements content, the degree of hydration, and physical properties affecting dewatering and later reactivity in the dissolution process, are profoundly affected by each of the precipitation process variables such as (a) temperature, (b) type, concentration and rate of addition of precipitant, (c) whether continuous or batch operation is used, and (d) the pH or pH range throughout the operation. There is still much to be learnt of the fundamental processes involved but it appears to be an area where a considerable degree of automation can be applied.

The description of the NUFCOR operation is unique, representing over 20 years' experience with the handling and transportation of yellow cake slurries and the precise sampling and accounting procedures, as well as the subsequent dewatering, drying and packing operations. This will be a most valuable contribution in the light of a possible trend to slurry transport in other countries.

Finally, there is the group of papers describing relevant facets of the processes used to refine the yellow cake and convert the uranium to tetra and hexa fluorides. Of particular interest was the data presented examining the differences in behaviour of yellow cake concentrates produced from various sources and from various process flowsheets. Data was presented in several papers directly relating the effect of various impurities in the refining process and this will be a useful reference for future consideration of product specification.

Many of the papers whether dealing with ore processing, yellow cake preparation, refining, or fluoride production, discuss problems associated with and means used to minimize the discharge of effluents. Indeed this became the first of three topics which were particularly discussed by the Panel.

All industry is under public scrutiny for the control of effluents. However, the uranium industry is expected to demonstrate a particularly high level of responsibility in this aspect of their operations. This is not only with respect to the discharge of uranium, the control of which is maintained at very low to negligible levels, but also to the various elements derived from the process reagents. Thus, an example was cited during the discussion of one paper of a new installation where 5 to 10% of the cost had been on a process to control the concentration of sodium ion to less than about 300 mg/ltr. These considerations therefore play a significant role in the selection of reagents used in various of the processes described at this meeting. There is a need also to examine and carry out research in methods of reagent recovery and recycle with the ultimate goal of total containment.

A second subject for particular discussion was the matter of yellow cake product specification for sales contracts to refineries.

Much useful data emerged from the meeting, which also provided a rare opportunity for yellow cake producers and refiners to communicate. There has been a tentative but explicit suggestion to prepare a uniform specification for uranium concentrate with standardized accounting techniques. However, it is believed that there requires to be very careful consideration of the problems of individual producers who are faced with intrinsic fundamental differences in source materials, differences in the economy of raw material supply, and differences in environmental demands both from natural causes and regulatory legislation.

There is therefore a need to discuss this matter in much greater detail and to include the important contribution the analyst could make on this subject.

A final subject for discussion was the related consideration of producing uranium tetrafluoride or a nuclear grade oxide product at the ore processing site in order to bypass some of the refinery operations. One paper at the meeting in fact described the extension of studies of such a process by PNC in Japan. However, the general conclusion was that especial circumstances would be required to motivate the yellow cake producers to proceed beyond the present type of product when that product was going to a 'toll' refinery. In addition it was thought that the 'tolling' refineries would be reluctant to offer economic encouragement to such a move because of the likely difficulty of obtaining such products with a consistently high quality from a multiplicity of sources. However, for a fully integrated, non-tolling arrangement, processes of the type under study in Japan can offer certain advantages:

(a) variations in quality and the effect on the conversion process,
(b) environmental pressures and problems, and
(c) the potential for alternative mill products, e.g. UF_4.

The meeting concluded by recommending that these stages of the fuel cycle of yellow cake preparation, its refining and conversion, should not be neglected for so long again and should be the subject either of further special meetings or made a specific part of future meetings, conferences or symposia on ore processing or uranium extraction. It was also pointed out that aspects concerned with sampling and analysis remained to be discussed as a most relevant and important part of the operation.

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