



**PEACEFUL USES
OF ATOMIC ENERGY**

Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy

Held in Geneva

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Volume 17

Processing Irradiated Fuels and Radioactive Materials



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PREFACE

More than 2,100 papers were submitted by the nations, the specialized agencies, and the International Atomic Energy Agency, which participated in the Second United Nations International Conference on the Peaceful Uses of Atomic Energy. The number of papers was thus about twice that involved in the First Conference. Provision was therefore made to hold five concurrent technical sessions in comparison with the three that were held in 1955. Even so, the percentage of orally presented papers was less in 1958 than in 1955.

In arranging the programme, the Conference Secretariat aimed at achieving a balance, allowing adequate time for presentation of as many papers as possible and, nevertheless, leaving time for discussion of the data presented. Three afternoons were left free of programme activities so that informal meetings and discussions among smaller groups could be arranged. No records of these informal meetings were made.

A scientific editorial team assembled by the United Nations checked and edited all of the material included in these volumes. This team consisted of: Mr. John H. Martens, Miss L. Ourom, Dr. Walter M. Barss, Dr. Lewis G. Bassett, Mr. K. R. E. Smith, Martha Gerrard, Mr. F. Hudswell, Betty Guttman, Dr. John H. Pomeroy, Mr. W. B. Woollen,

Dr. K. S. Singwi, Mr. T. E. F. Carr, Dr. A. C. Kolb, Dr. A. H. S. Matterson, Mr. S. Peter Welgos, Dr. I. D. Rojanski and Dr. David Finkelstein.

The speedy publication of such a vast bulk of literature obviously presents considerable problems. The efforts of the editors have therefore been primarily directed towards scientific accuracy. Editing for style has of necessity been kept to a minimum, and this should be noted particularly in connection with the English translations of certain papers from French, Russian and Spanish.

The Governments of the Union of Soviet Socialist Republics and of Czechoslovakia provided English translations of the papers submitted by them. Similarly, the Government of Canada provided French-language versions of the Canadian papers selected for the French edition. Such assistance from Governments has helped greatly to speed publication.

The task of printing this very large collection of scientific information has been shared by printers in Canada, France, Switzerland, the United Kingdom and the United States of America.

The complete Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy are published in a 33-volume English-language edition as follows:

Volume No.		Sessions Included
1	Progress in Atomic Energy	1, 2, 23a, 23b, 23c
2	Survey of Raw Material Resources	E-5, E-7b, E-9
3	Processing of Raw Materials	E-10, E-6 and E-7a
4	Production of Nuclear Materials and Isotopes	E-11, E-12, C-14, C-15
5	Properties of Reactor Materials	E-14, E-15
6	Basic Metallurgy and Fabrication of Fuels	E-13, E-17, E-18
7	Reactor Technology	E-19, E-21, E-22
8	Nuclear Power Plants, Part 1	3, 6, 7
9	Nuclear Power Plants, Part 2	B-9, B-10, B-11
10	Research Reactors	B-5, B-12
11	Reactor Safety and Control	B-13, B-14a, A-14
12	Reactor Physics	B-17, B-18, B-21
13	Reactor Physics and Economics	B-19, B-15, B-14b
14	Nuclear Physics and Instrumentation	A-18, A-19
15	Physics in Nuclear Energy	A-21, A-22

**Volume
No.**

**Sessions
Included**

16	Nuclear Data and Reactor Theory.....	A-11, A-12, A-13
17	Processing Irradiated Fuels and Radioactive Materials.....	C-17, C-18, C-19
18	Waste Treatment and Environmental Aspects of Atomic Energy	C-21, C-22, D-19
19	The Use of Isotopes: Industrial Use	5b, D-7
20	Isotopes in Research	D-6
21	Health and Safety: Dosimetry and Standards.....	5a, D-15
22	Biological Effects of Radiation	D-9, D-10
23	Experience in Radiological Protection.....	D-11, D-12
24	Isotopes in Biochemistry and Physiology, Part 1	D-13
25	Isotopes in Biochemistry and Physiology, Part 2	D-14
26	Isotopes in Medicine	D-17, D-18
27	Isotopes in Agriculture	D-21, D-22
28	Basic Chemistry in Nuclear Energy	C-9, C-10, C-11
29	Chemical Effects of Radiation	C-12, C-13
30	Fundamental Physics	15, A-17
31	Theoretical and Experimental Aspects of Controlled Nuclear Fusion	4, A-5, A-6
32	Controlled Fusion Devices	A-7, A-9, A-10
33	Index of the Proceedings	

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TABLE OF CONTENTS

Volume 17

Session C-17: Processing Irradiated Fuels, Part I		Page
P/307	Howells <i>et al.</i> Chemical Processing of Fuels	3
P/82	Buck <i>et al.</i> Chemical Processes at Dounreay	25
P/2182	Shevchenko <i>et al.</i> Treatment of Irradiated Fuel Elements.....	46
P/536	Bruce <i>et al.</i> Experience with Pilot Processing Plants	49
P/1172	Regnaut <i>et al.</i> Fuel Processing at Fontenay-aux-Roses	73
P/1171	Prevot <i>et al.</i> Final Plutonium Treatment at Fontenay-aux-Roses..	96
P/585	Barendregt and L. Koren Lund A Fuel Reprocessing Plant	107
P/137	Carleson Extraction of Plutonium	111
P/31	Brown <i>et al.</i> Complexes of Ru, Ni, Zr and U in Plant Processes .	118
P/2143	Zvyagintsev <i>et al.</i> Chemistry of Radioruthenium	130
P/1915	Ryan, Wheelwright..... Anion Exchange in the Processing of Plutonium	137
P/526	Reid <i>et al.</i> Reprocessing of Fuel Containing Zirconium	145
P/2429	Swanson Selective Dissolution of Cladding Containing Zirconium	154
P/2100	Vesely <i>et al.</i> Extraction of Irradiated Uranium.....	162
P/530	Winchester, Maraman Aqueous Recovery of Plutonium from Alloys	168
P/2412	Branica, Bona Partition of Uranium and Thorium	172
P/2206	Vdovenko Fission Products in Ether Extraction	175
P/1173	Durandet <i>et al.</i> Pulsed Columns in Solvent Extraction	180
P/515	Geier Improved Pulsed Extraction Column Cartridges	192
P/502	Mason, Parsi Ion Transfer Membranes in Chemical Processing	200
P/30	McIntosh, Evans Effect of Metal Species on Stainless Steel Corrosion...	206
P/1458	Nairn <i>et al.</i> Extraction of Actinide Elements	216
P/537	Lewis Americium and Neptunium Recovery Processes	236
P/1883	Higgins, Crane Production of Curium-242.....	245
Record of session		252
Session C-18: Processing Irradiated Fuels, Part II		
P/1930	Culler, Blanco Feed Preparation for Aqueous Separation Processes...	259
P/2409	Cooper, Walling Jr. Aqueous Separation and Decontamination Processes .	291
P/144	Hultgren, Haeffner Plutonium Separation Using a Silica Gel Column....	324

	Page
P/2216 Vdovenko, Kovalskaia	Purification by Dibutyl Ether Extraction..... 329
P/519 Karraker	Temperature Effects on Solvent Extraction..... 333
P/521 Siddall III	Solvent Extraction Recovery of Uranium and Thorium 339
P/544 Wilson	Tertiary Amine Extraction of Plutonium..... 348
P/32 Martin <i>et al.</i>	Processing of Reactor Fuels by Liquid Metals..... 352
P/1830 Baker, Leary	Plutonium Processing in the United States..... 356
P/1795 Schraidt, Levenson	Developments in Pyrometallurgical Processing..... 361
P/517 Chiotti, Voigt	Pyrometallurgical Processing..... 368
P/529 Leary <i>et al.</i>	Pyrometallurgical Purification of Plutonium Fuels... 376
P/540 Feder, Teitel	Reactor Fuel Purification by Crystallization..... 383
P/538 Burris <i>et al.</i>	Melt Refining of Reactor Fuels..... 401
P/1780 Brand <i>et al.</i>	Low Decontamination Processing of Nuclear Fuels... 407
P/541 Levenson <i>et al.</i>	A Pyrometallurgical Process and Plant..... 414
P/1434 Wiswall <i>et al.</i>	Chemistry of Liquid Metal Fuel Reactors..... 421
P/1781 Dwyer <i>et al.</i>	Continuous Processing of a Liquid Fuel..... 428
P/2388 Steunenbergh, Vogel	Survey of Fluoride Volatility Processes..... 438
P/539 Steunenbergh <i>et al.</i>	Fluoride Volatility Processing of Fuels..... 452
P/2253 Prusakov <i>et al.</i>	Fluorination Treatment of Irradiated Uranium..... 468
P/535 Cathers <i>et al.</i>	A Fused-salt Fluoride-volatility Process..... 473
P/932 Bernhardt <i>et al.</i>	Basic Studies of Uranium Hexafluoride Separation.. 480
P/542 Lawroski <i>et al.</i>	Fluidization Techniques in Fuel Processing..... 485
Record of session	492

Session C-19: Handling Radioactive Materials

P/1174 Curillon, Cœure	Problems Raised in Building the Marcoule Plant 496
P/516 Oberg, Sloat	Experience with a Solvent Extraction Pilot Plant... 505
P/514 Schwennessen	Survey of Processing Plant Design and Operation... 514
P/1903 Wick, Thomas	Plutonium Metallurgy Installations at Hanford..... 531
P/531 Morgan <i>et al.</i>	The Los Alamos Plutonium Metal Production Plant . 537
P/88 Ford, Walford	Critical Assembly Experiments at Dounreay..... 545
P/518 Colven	Critically Safe Equipment for Aqueous Processing... 555
P/427 McLendon <i>et al.</i>	Nuclear Safety in Processing of Enriched Uranium.. 564
P/520 Tober	Purification of Uranium, Plutonium and Neptunium. 574
P/1796 Goertz	Recent Developments in Active-handling Installations . 585
P/1459 Bown, Hyam	High-activity Handling Cells in the United Kingdom . 597
P/2026 Yakovlyev, Dedov	Remote Operations in Radiochemical Laboratories... 652
P/543 Goertz	Installation for Irradiated-plutonium Measurements.. 659
P/532 Peterson <i>et al.</i>	Plutonium Fuel Handling Cells..... 664

TABLE OF CONTENTS

ix

Page

P/528	Cramer, Schonfeld	Plutonium Metallography Techniques	668
P/1829	Maraman	Recent Developments in Handling Alpha Sources ...	676
P/533	Metz	Plutonium Analytical Chemistry Laboratories	681
P/1629	Hall, Sharma	A Tropical Radiochemistry Laboratory	691
P/2095	Macháček <i>et al.</i>	Design of a Radiochemical Laboratory	696
Record	of session		707

Session C-17

PROCESSING IRRADIATED FUELS, PART I

LIST OF PAPERS

	Page
P/307 The chemical processing of irradiated fuels from thermal reactors G. R. Howells <i>et al.</i>	3
P/82 Chemical processes at U.K. Atomic Energy Authority Works, Dounreay..... C. Buck <i>et al.</i>	25
P/2182 Problems in the treatment of irradiated fuel elements at the first USSR atomic power station..... V. B. Shevchenko <i>et al.</i>	46
P/536 Operating experience with two radiochemical processing pilot plants F. R. Bruce <i>et al.</i>	49
P/1172 The processing of irradiated uranium in the Fontenay-aux-Roses pilot plant P. Regnaut <i>et al.</i>	73
P/1171 Final treatment of plutonium at the end of the Fontenay-aux-Roses pilot plant I. Prevot <i>et al.</i>	96
P/585 The fuel reprocessing plant at the Joint Establishment for Nuclear Energy Research T. J. Barendregt and L. Koren Lund	107
P/137 The extraction of plutonium at various oxidation potentials G. Carleson	111
P/31 The significance of certain complexes of ruthenium, niobium, zirconium and uranium in plant processes P. G. M. Brown <i>et al.</i>	118
P/2143 Chemistry of radoruthenium O. E. Zvyagintsev <i>et al.</i>	130
P/1915 Application of anion exchange to the reprocessing of plutonium J. L. Ryan and E. J. Wheelwright	137
P/526 Reprocessing of fuel containing zirconium D. G. Reid <i>et al.</i>	145
P/2429 The selective dissolution of zirconium or zircaloy cladding by the Zirflex process J. L. Swanson	154
P/2100 The extraction of irradiated uranium by methylcyclohexanone V. Vesely <i>et al.</i>	162
P/530 Aqueous recovery of plutonium from alloys containing fission product elements R. S. Winchester and W. J. Maraman	168
P/2412 Partition of uranium and thorium between nitric and perchloric acids and four organic solvents M. Branica and E. Bona	172
P/2206 Distribution of fission products in the ether extraction process V. Vdovenko	175
P/1173 A study of pulsed columns in solvent extraction J. Durandet <i>et al.</i>	180

LIST OF PAPERS

(Continued)

		Page
P/515	Improved pulsed extraction column cartridges..... R. G. Geier	192
P/502	Applications of ion transfer membranes in nuclear chemical processing E. A. Mason and E. J. Parsi	200
P/30	The effect of metal species present in irradiated fuel elements on the corrosion of stainless steel in nitric acid A. B. McIntosh and T. E. Evans	206
P/1458	The extraction of actinide elements from wastes J. S. Nairn <i>et al.</i>	216
P/537	Americium and neptunium recovery processes W. H. Lewis	236
P/1883	The production and chemical isolation of curium-242 in thousand-curie quantities G. H. Higgins and W. W. T. Crane	245

The Chemical Processing of Irradiated Fuels from Thermal Reactors

By G. R. Howells, T. G. Hughes, D. R. Mackey and K. Saddington *

The chemical plants located at the Windscale Works of the United Kingdom Atomic Energy Authority are designed to process natural or slightly enriched uranium fuels after irradiation.^{1,2} The object is to separate the uranium and plutonium, initially from the associated fission products and subsequently from each other, in a pure condition. The depleted uranium in the form of uranyl nitrate solution is returned to the Springfields factory for re-enrichment and refabrication. The plutonium is converted into billet form.

Liquid-liquid extraction methods are used in a variety of contactors for the separation and purification processes. The aqueous phase derives from the dissolution of the fuel elements in nitric acid. Two organic solvents are used in different stages of the process. The first is $\beta\beta'$ dibutoxy diethyl ether (Butex), used for the primary separation and for uranium purification; the second, tributyl phosphate diluted with odourless kerosene, is used for plutonium purification. Conversion of the pure plutonium nitrate solution to metal is carried out in a number of steps, *viz.* conversion to solid oxalate, decomposition to oxide, conversion to tetrafluoride and finally reduction of the fluoride with metallic calcium.

The paper describes the underlying chemistry of the process, gives chemical flowsheets for each stage and deals with the engineering and chemical engineering aspects of the plant. The instrumental and general control of the plant is described and the experience of some six years' continuous operation is reviewed with particular mention of any points of unusual interest.

PROCESS CHEMISTRY

The basic chemistry was first investigated by a group of workers under Dr. R. Spence^{3,4} at Chalk River, Ontario, during 1947. On the basis of this work the design of the Primary Separation Plant was started and a further detailed study of this process, and also the development of additional uranium and plutonium purification processes, was continued at

A.E.R.E. Harwell and the Widnes Research Laboratory of Imperial Chemical Industries Ltd. During the initial work a number of other processes apart from solvent extraction (distillation, precipitation and adsorption processes) were considered. The solvent extraction method was finally selected because of its greater efficiency and because far more information was available in this field than in any other.

The process is based upon the fact that uranium and plutonium can be efficiently extracted from a solution of their nitrates by organic solvents, the fission products, with a few exceptions, remaining virtually inextractable. Ketones generally give the most efficient extraction, followed by ethers, ether-esters, esters, alcohols, aldehydes and nitro paraffins in descending order of efficiency. Hydrocarbons and halogenated hydrocarbons give negligible extraction. During the early work on the primary separation process the number of solvents considered was reduced to four: ether, hexane, butex and triglycol dichloride. Butex was finally selected since it gave, under the appropriate reducing conditions, the best separation of uranium and plutonium by a single solvent process. Butex was preferred to hexone since the latter is less stable to nitric acid and it was found possible to use butex in a primary separation process using only nitric acid as salting-out agent, thus allowing a high ratio of evaporation for the highly active aqueous raffinate.

Butex has a high flash point (low fire hazard) and a low solubility in water. Its disadvantages are its high viscosity, its density (near to that of water) and the formation with uranyl nitrate, under certain conditions, of crystalline complexes, *viz.* $\text{UO}_2(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} \cdot \text{C}_{12}\text{H}_{26}\text{O}_3$ in the presence of nitric acid and $\text{UO}_2(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} \cdot 2\text{C}_{12}\text{H}_{26}\text{O}_3$ in the absence of acid. Butex is decomposed by heating with nitric acid. The reaction is a stepwise oxidation of the solvent molecule, ultimately to CO_2 and water, accompanied by reduction of the nitric acid. Aliphatic acids such as oxalic and butyric are intermediate products. Radiation appears to cut down the initiation period and triggers off a reaction indistinguishable from the thermal reaction. A mixture of gases (NO_2 , NO , CO_2 , CO , H_2 etc.) is evolved. At acidities used in

* United Kingdom Atomic Energy Authority, Industrial Group, Risley, Warrington, Lancashire, England.

extraction processes (up to 20% w/w HNO_3) the extent of the decomposition is negligible and does not interfere with normal operation. However at higher acidities (50–60% w/w HNO_3) the reaction may become violent with rapid gas evolution. This is important in high ratio evaporation processes where the final product acidities are high. Such processes can be made safe by prior removal of organic matter from the aqueous feed solutions. Butex and volatile degradation products can be effectively removed from aqueous solutions by steam stripping before evaporation. Commercial butex, however, can introduce non-volatile organic impurities which have to be removed by a pretreatment of the solvent. Washing the raw solvent with 57% w/w nitric acid followed by a wash with 20% w/w acid is effective.

Uranium metal is readily dissolved by nitric acid, the rate of solution being roughly proportional to the acid concentration. Ordinary batch dissolving of uranium may be approximately represented by the following equation:



In practice 5–6 moles of nitric acid are used per mole of uranium.

Acid economy can be achieved by the introduction of oxygen into the dissolving process (fumeless dissolving⁵). This oxidises nitrogen oxide fumes which are then reabsorbed in weak nitric acid. Fumeless dissolving has a further advantage in reducing the volume of the off-take gases with consequent simplification of scrubber design.

Fumeless dissolving may be represented as follows:



The dissolution of irradiated uranium rods in hot nitric acid produces a solution containing uranium as U(VI) and Pu mainly as Pu(IV) and some Pu(VI).

The metal ions which are extracted by butex form, in the aqueous phase, nitrate complexes which are soluble in the solvent; e.g., in the case of uranium, in addition to the presence of hydrated UO_2^{2+} ions there is also a series of hydrated nitrate complexes,⁶



which are in equilibrium, the higher complexes having the greater tendency to solvate with the organic phase to form compounds of the type $\text{UO}_2(\text{NO}_3)_2 \cdot x\text{H}_2\text{O} \cdot y$ (butex).

The following ions are readily extracted into butex:



whereas Pu(III) and the remaining fission products transfer only to a small extent or are completely inextractable.

The partition coefficients (K = ratio of equilibrium concentrations of species between solvent and aqueous phases) of the former group are greatly affected by the concentration of nitrate ions in the system, so that it is possible, using the necessary number of

extraction stages, to quantitatively extract uranium or plutonium into a solvent phase at high nitrate concentrations and to subsequently remove them again by back-extraction into an aqueous phase at low ion concentrations. The success of the extraction process is largely dependent upon the efficiency and ease with which these transfers can be accomplished.

The partition coefficient for plutonium is also dependent upon its valency state. The value of K for Pu(III) is much lower than those for Pu(IV) and Pu(VI). It is also much lower than that for U(VI) at all nitrate concentrations and this provides a basis for the separation of uranium and plutonium. Approximate values of the partition coefficients are given in Table 1. From these it is clear that by converting the plutonium to the Pu(III) form a good separation of uranium and plutonium can be readily achieved.

Table 1. Approximate Partition Coefficients of U and Pu in Butex

	3N nitric acid in aqueous phase	8M ammonium nitrate and 0.2N nitric acid in aqueous phase
	K	K
U(VI)	1.5	3
Pu(VI)	1.8	2.5
Pu(IV)	7	7
Pu(III)	< 0.01	< 0.002

Pu(VI) and Pu(IV) can be reduced to Pu(III) by a number of agents, e.g., hydroxylamine, hydrazine, ferrous ion and sulphur dioxide. The reducing agent finally chosen for the process was ferrous sulphamate since this effects a rapid reduction and can be easily destroyed later in the process when it is desired to reoxidise the Pu(III). The ferrous ion and the sulphamate ion act separately. The ferrous/ferric couple reduces the Pu(IV) and Pu(VI); the sulphamate ion stabilises the ferrous ion in nitric acid solutions by destroying nitrous acid which would otherwise oxidise the Fe^{++} ion and so interfere with the formation of Pu(III).

Pu(III) is oxidised rapidly and completely in the cold to Pu(IV) and Pu(VI) by dichromate ion. Ammonium ceric nitrate could be used, but dichromate is preferable by reason of its availability and since, unlike the ceric salt, it does not oxidise the fission product ruthenium to the volatile tetroxide.

As noted earlier, fission product ruthenium forms a complex $(\text{RuNO}(\text{NO}_3)_3)$ which is easily extracted by butex. Hence, in a multicycle process using butex as solvent throughout, this species would be carried forward with the uranium and plutonium streams and although present only in minute amounts would prejudice the high degree of decontamination required. There are a number of ways of overcoming this. One is to modify the forms of the highly extractable fission product species by chemical treatment, converting them to relatively inextractable forms

before the later extraction cycles. In the case of $[\text{RuNO}](\text{III})$ this can be accomplished by a hot hydrazine treatment followed by the addition of ferrous sulphamate. This is used as a preliminary step in the uranium purification process. Another method is to use a two-solvent process in which the second solvent has a lower affinity for radicals extracted by the first. In this way the degree of decontamination in a given number of cycles can be improved. In the plutonium purification process 20% tributyl phosphate in odourless kerosene (20% TBP/OK) is used as the second solvent.

The partition coefficients (Table 2) of U(VI), Pu(VI), Pu(IV), Pu(III) and fission products into 20% TBP/OK (as with butex) permit efficient extraction of uranium and plutonium, a high decontamination from fission products, and subsequently, under suitable back-wash conditions, an efficient separation of uranium and plutonium.

Table 2. Approximate Partition Coefficients of U, Pu and Fission Products in 20% TBP/OK

	6N nitric acid in aqueous phase
	K
U(VI)	30
Pu(VI)	3
Pu(IV)	20
Pu(III)	0.01
Ru	Low for mixed species (< 3)
Zr(IV)	1
Ce(IV)	0.2
Nb	0.01
Y(III)	0.02

The use of 20% TBP/OK results in a much higher decontamination from ruthenium than with butex, whilst the latter solvent gives better zirconium decontamination. Ruthenium is stripped most efficiently from 20% TBP/OK at high acidities whereas low acid stripping is most effective for zirconium removal. The above chemical considerations have been combined in the following integrated process flowsheet.

FLWSHEETS

As a basis for description the flowsheet refers to the processing of 1 tonne of uranium metal which has been irradiated to 1000 Mwd/t and cooled for 100 days. The approximate composition of this fuel is given in Table 3.

Continuous Fumeless Dissolving and Conditioning

The uranium rods, 6N nitric acid and oxygen are fed continuously to the dissolver to produce a uranyl nitrate solution approx 3N in nitric acid (Fig. 1). The acid feed absorbs the nitrogen oxide gases evolved. 3N nitric acid dissolving conditions were chosen as the optimum on the following considerations:

Table 3. Composition of 1 Tonne U Fuel After 1000 Mwd/t Irradiation, Cooled for 100 Days (Irradiation time 300 days)

Element	Approx. weight, g	Activity $\beta + \gamma$, curies*
U	998×10^3	—
Pu	800	—
Cs	110	13,100
Sr	40	41,500
Ba	40	4,200
Y	20	51,000
La	40	—
Ce	100	174,000
Pr and other rare earths	155	15,000
Zr	115	112,000
Nb	5	203,000
Mo	85	—
Tc	25	—
Ru	55	37,000
Rh	12	—
Other elements	40	2,000
Total activity		652,800

* The activity from short-lived daughters of Cs^{137} , Sr^{90} , Ce^{144} , Ba^{140} and Ru^{106} is included with the parents.

1. K_U and K_{Pu} in column PS.1 are high enough for efficient extraction at this acidity without the addition of a salt. This allows the column PS.1 aqueous raffinate to be evaporated to small bulk.
2. Corrosion rate of the stainless steel dissolver at boiling temperature is low enough to be acceptable at this acidity.
3. The metal (and therefore activity) hold-up in the dissolver is not excessive for continuous operation at this acidity.

The continuous overflow from the dissolver is cooled to 25–30°C and conditioned with acid (as required) before feeding to column PS.1. Cooling is used to maintain the higher values of K_U and K_{Pu} obtained at lower temperatures. The extraction process in column PS.1 is exothermic so that prior cooling is also useful to reduce the temperature attained in the column and thus inhibit solvent-acid interaction.

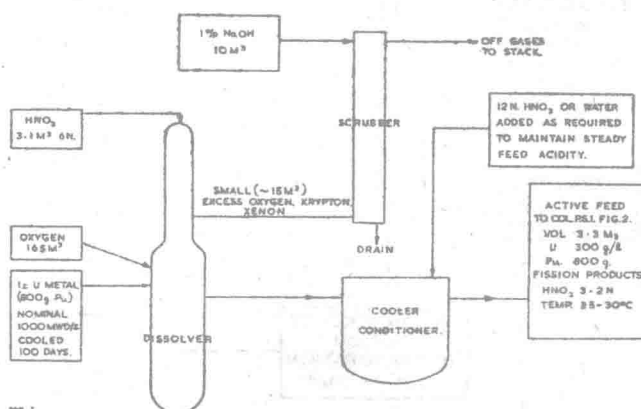


Figure 1. Continuous fumeless dissolving and conditioning

The uranium concentration in the active feed (300 g/l U) is the maximum concentration (avoiding crystallisation) compatible with the acid conditions and allowing a margin for operational variations. This keeps the volume of the highly active aqueous raffinate from column PS.1 to a minimum.

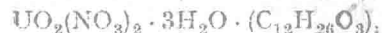
Primary Separation of U, Pu and Fission Products

The active feed from the cooler is extracted with butex in column PS.1 (Fig. 2). Over 99.9% of the uranium and 99.98% of the plutonium leaves with the solvent phase and 99.5% of the fission product activity is contained in the aqueous raffinate stream.

The fission product activity which follows the uranium and plutonium stream is mainly due to ruthenium with small amounts of zirconium, cerium and niobium. The decontamination factors (DF, defined as the ratio of the amounts of the species in the feed and product solutions) for these are approximately 10 , 4×10^3 , 1×10^5 and 4×10^2 respectively. The low value obtained for DF_{Ru} is due to the fact that the ruthenium in the feed solution exists in the form of a number of species. Whilst some of these are virtually inextractable by organic solvents, or have only low partition coefficients, the trinitrato form is highly extractable. Though this form, δ^0 , is slowly changed in the presence of nitrous acid to less extractable species, the time of contact in the plant

is insufficient to permit significant conversion. The strip serves to remove entrained fission products from the solvent stream but is ineffective in stripping ruthenium which has partitioned into the solvent. A 3N nitric acid strip is used to retain the uranium and plutonium in the solvent phase.

The solvent/aqueous ratio used ensures that the uranium concentration at the feed plate is less than 150 g/l U at which concentration there arises the possibility of crystallisation of the butex/U complex:



The acidity of the solvent extract from PS.1 is adjusted to 0.5N HNO₃ with ammonia and ferrous sulphamate solution added to reduce the plutonium to Pu(III). This reduction is satisfactory in the presence of Fe⁺⁺/Fe⁺⁺⁺ ratios in excess of 10:1. The purpose of column PS.2, which is operated as a low acid - high salt system, is to separate the uranium and plutonium. About 0.01% of the uranium and one third of the activity follow the plutonium stream, and about 0.02% of the plutonium and two thirds of the activity follow the uranium from this column.

Concentration and Storage of Highly Active Liquor

The raffinate from PS.1 is steam stripped (Fig. 3) to remove organic volatiles and is then evaporated semi-continuously under vacuum (to reduce corrosion

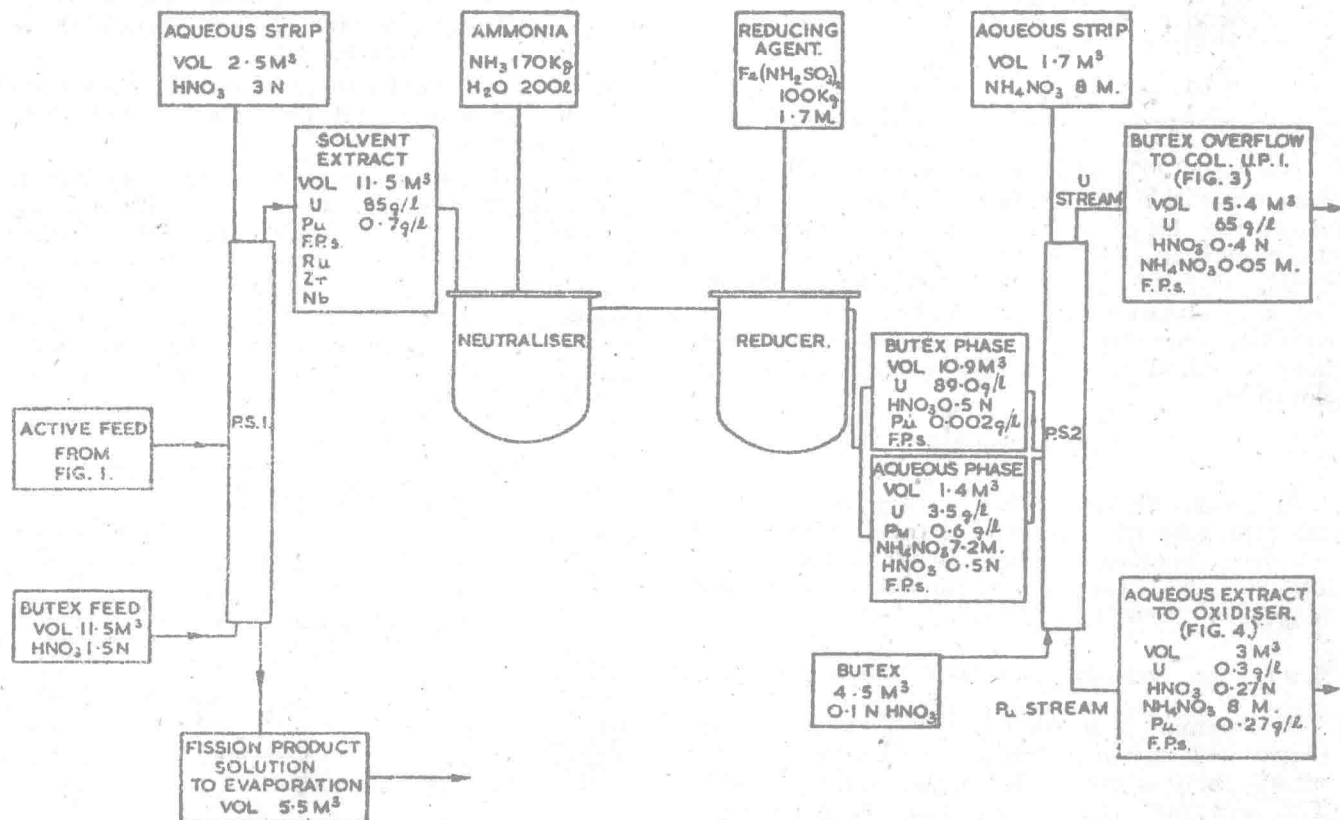


Figure 2. Primary separation of uranium, plutonium and fission products

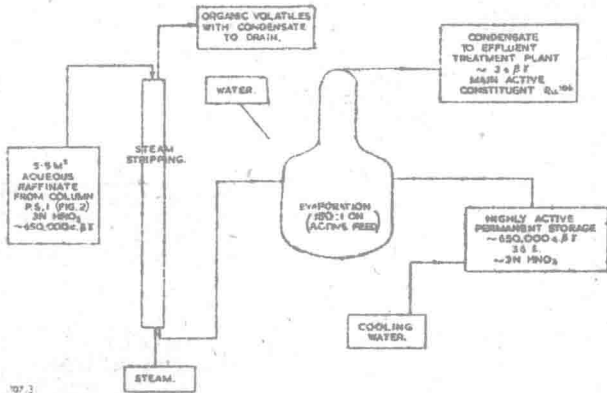


Figure 3. Concentration and storage of highly active liquors

of the stainless steel evaporator). The maximum acidity in the evaporator is about 9N nitric acid and under these conditions there is no significant formation of volatile RuO_4 . Water is added intermittently to reduce the acidity to below 3N nitric acid to prevent the precipitation of fission products in the concentrate. This is stored underground in stainless steel tanks with water cooling.

Uranium Purification

The solvent extract from PS.2 is backwashed with dilute nitric acid in UP.1. The product is then

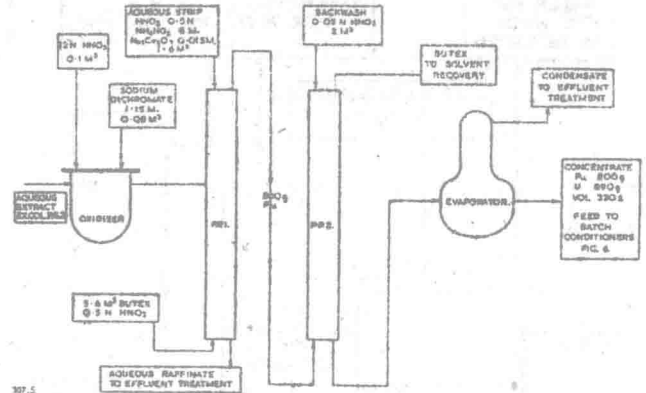


Figure 5. First cycle plutonium purification

evaporated to reduce the volume handled in later equipment and to provide a concentrated feed of uranium which will aid decontamination from ruthenium in the following extraction stages (Fig. 4). The Pu(III) present is oxidised to Pu(IV) and Pu(VI) during the evaporation. The concentrate is stored for 6 months to obtain additional ruthenium decontamination by decay before further processing.

The aged solution is adjusted with caustic soda to 0.5N nitric acid and heated with hydrazine and ferrous sulphamate for 2 hours at 80°C. This treatment reduces the plutonium to Pu(III) and modifies the

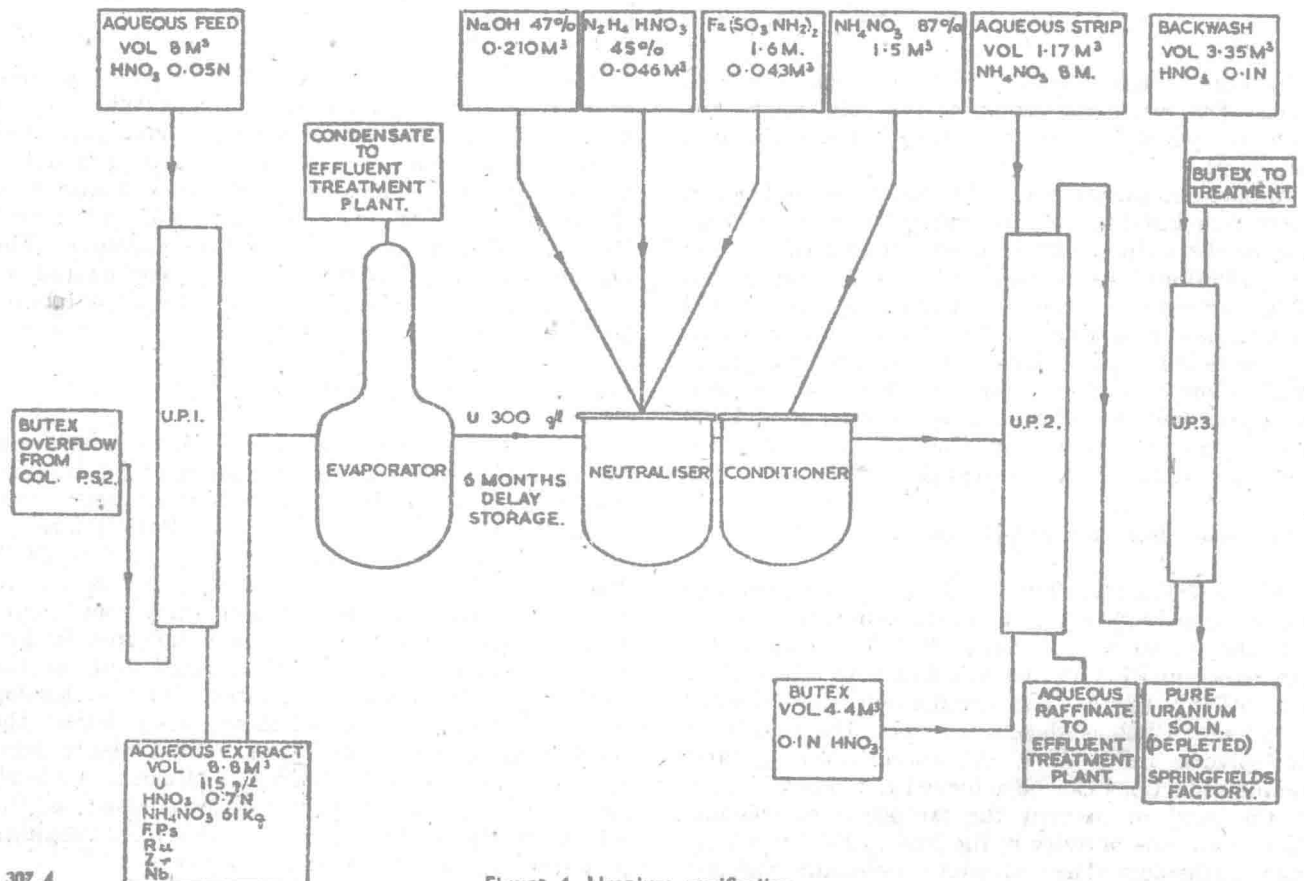


Figure 4. Uranium purification

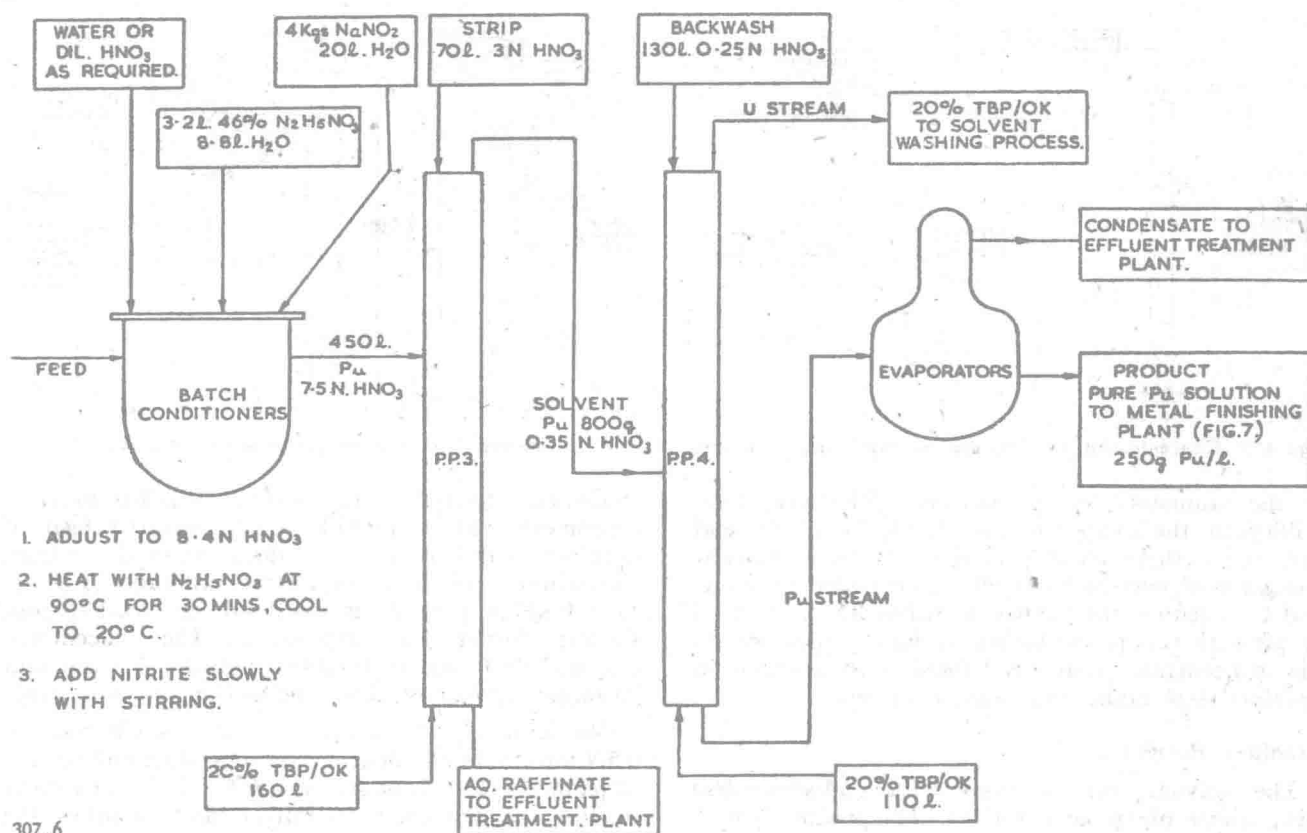


Figure 6. Second cycle plutonium purification

ruthenium species present to relatively inextractable forms. The hydrazine stabilises the sulphamate but its main purpose is associated with the ruthenium treatment.

Ammonium nitrate is added to make the conditioned liquor 6 molar. This salt concentration, together with that of the sodium nitrate present (from the caustic soda addition), ensures efficient uranium extraction.

The uranium is extracted into butex in UP.2 and backwashed into dilute acid (250 g/l U) in UP.3. The ruthenium, zirconium plus niobium, and plutonium decontamination factors are about 200, 200 and 40 respectively in UP.2, and the product from UP.3 is pure enough to allow handling of metal produced from this liquor at the Springfields factory.

First Cycle Plutonium Purification

The Pu(III) and ferrous sulphamate in the aqueous stream from PS.2 are oxidised with sodium dichromate and the plutonium (mainly PuVI) is extracted into butex in PP.1 and backwashed with dilute nitric acid in PP.2 (Fig. 5). The volume reduction achieved in column PP.2 is dependent upon the acidity of the solvent from PP.1. At lower acidity greater volume reductions can be achieved but this is limited by the need to prevent the formation of colloidal plutonium. The activity in the feed to PP.1 is mainly due to ruthenium. The ruthenium, zirconium, niobium

and cerium decontamination factors are approximately 15, 30, 130 and 10 respectively. With a lower acid strip in PP.1 the ruthenium, zirconium and cerium decontamination factors are increased (DF_{Nb} is reduced) but there is a simultaneous lowering of the plutonium extraction efficiency. 0.5N nitric acid has been found to be the best compromise. The aqueous product from PP.2 is concentrated to 2-3 g/l Pu for feeding to the second plutonium purification cycle.

Second Cycle Plutonium Purification

The object of this cycle is to purify further the plutonium stream from fission products and uranium (Fig. 6). The plutonium is completely converted from a mixture of valency states to the Pu(IV) form to obtain a high K_{Pu} and extraction efficiency in PP.3. This is carried out by first adjusting the acidity to 8.4N nitric acid, adding hydrazine nitrate and maintaining a temperature of 90°C for 30 minutes. Reduction of plutonium to Pu(III) is rapid and, as the hydrazine is destroyed by the nitric acid, re-oxidation to Pu(IV) occurs. To complete the re-oxidation, the solution is cooled to 20°C and sodium nitrite solution, which destroys the residual hydrazine, is added. 20% TBP in odourless kerosene is used as the solvent in this cycle, the change of solvent resulting in improved decontamination factors.

In PP.3 the plutonium and uranium are extracted into the solvent phase and stripped with 3N nitric acid. The principal fission products present are ruthenium and zirconium and the decontamination factors obtained for these are about 2000 and 10 respectively. The relatively high acid strip (3N), which is not optimum for zirconium removal (K_{Zr} is lower at lower acidities), is necessary to ensure that the solvent feed to PP.4 is about 0.35N in nitric acid. This is essential, since the separation of uranium and plutonium in PP.4 is sensitive to acidity changes. U(VI) and Pu(IV) are separated in PP.4 by virtue of the difference of their partition coefficients at low acidities. The efficiency of separation and the plutonium loss (with the uranium stream) in PP.4 is dependent upon the acidity in the backwash section, the acidity in the stripping section (lower portion of column) and the uranium concentration in the feed. The decontamination factor for uranium is normally over 1000 with the flowsheet U/Pu ratio, the backwash 0.23–0.25N and the aqueous product 0.55–0.63N nitric acid. The product from PP.4 is concentrated by evaporation before the metal finishing process.

Plutonium Metal Finishing

The solution obtained from the purification plant is conditioned with hydrogen peroxide to ensure that the plutonium is in the Pu(IV) state. This permits a high efficiency of precipitation on the addition of oxalic acid. The oxalate is dried, calcined at 475°C in an atmosphere of oxygen, converted to PuF_4 with anhydrous HF at 475°, and the fluoride reduced with calcium to form the metal billets (Fig. 7).

PLANT LAYOUT

The diagrammatic plan of the plant layout required for the processing of uranium cartridges according to the chemical flowsheets above is shown in Fig. 8. The key plant is obviously the Primary Separation Plant, in which the initial purification stages are carried out and the uranium is separated from the plutonium. The complexity of the processes and equipment in all other plants depend on the effectiveness

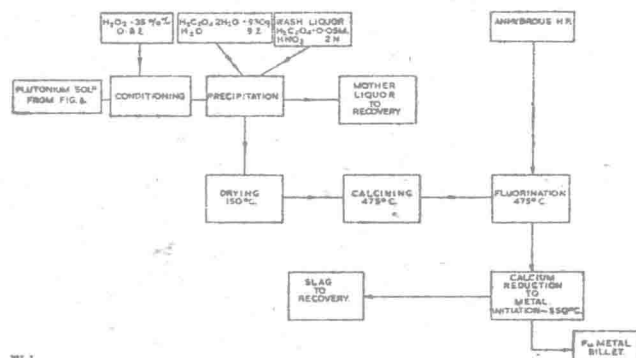


Figure 7. Plutonium metal finishing

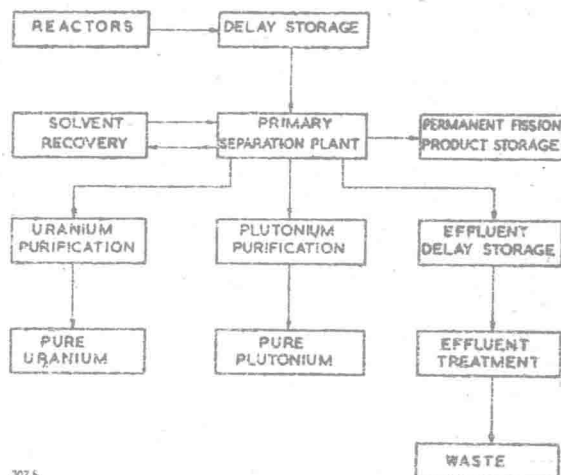


Figure 8. Diagrammatic plan of plant layout

with which the Primary Separation Processes are carried out.

Can Removal

The uranium is irradiated in the reactors in the form of rods of varying length and diameter and is contained in either an aluminium or a Magnox can. After discharge from the reactor, the rods are stored under water so that short-lived activity may decay. Immediately prior to chemical treatment, the cans are removed from the uranium rods, by a mechanical method, in an annex to the delay storage pond. The operation is carried out under 4 ft 6 in. of water, each rod being placed in 'V' block guides and forced through a die by means of a hydraulic ram. The die is sized so that the uranium rod will pass through whilst the can will not, the operation being facilitated by fins carried on the canned surface and the fact that the cans are not bonded to the rod. After passing through the die, the rods fall into a shielded container suitable for transport to the Chemical Plant.

The Primary Separation Plant

The Primary Separation Process comprises the following unit operations:

- The dissolution of uranium in nitric acid.
- The initial purification from fission products.
- Separation of plutonium and uranium.
- Primary purification of the plutonium.

The simplified Plant Flow Diagram for the Primary Separation Process is shown in Fig. 9. The shielded containers are lifted to the top of a tall building (Fig. 10) and placed in a water reservoir. The rods are removed and are fed, one at a time, through the shield by mechanical means, lifted through a water seal and fall continuously into a dissolving unit. The dissolver is a welded cylindrical vessel, the lower portion of which is steam-jacketed and forms the dissolving section and the upper portion is water-