MASTER MCW-1441

CONTRACTOR FOR U.S. ATOMIC ENERGY COMMISSION

DEVELOPMENT OF THE TBP-HEXANE PROCESS FOR URANIUM PURIFICATION

February 1, 1960

Mallinckrodt®

WELDON SPRING PLANT

This document is
PUBLICLY RELEASABLE
David Hamrin OSTI
Authorizing Official
Date 9/7/2016

MALLINCKRODT CHEMICAL WORKS
URANIUM DIVISION

Contract No. W-14-108-Eng-8

Printed in USA. Price $ .75 Available from the
Office of Technical Services, Department of
Commerce, Washington 25, D.C.

Date of Issue: February 1, 1960

Report Number: MCW-1441
Subject Category: Technology-Feed Materials

TOPICAL REPORT

DEVELOPMENT OF THE TBP-HEXANE PROCESS FOR URANIUM PURIFICATION

by

W. C. Philoon
R. M. Edwards
R. H. Farris

This paper was presented at the 135th National Meeting of the American Chemical Society, Boston, Massachusetts, April 1959.

Mallinckrodt Chemical Works
St. Louis, Missouri

Date of Issue: February 1, 1960

Report Number: MCW-1441
Subject Category: Technology - Feed Materials
(TID-4500, 15th Ed.)

Internal Distribution

	No. of Copies
Mr. B. J. Buntz	1
Mr. K. J. Caplan	1
Dr. P. J. Fain	1
Dr. J. A. Fellows	1
Dr. C. D. Harrington	1
Mr. R. F. Hartmann	1
Dr. J. A. Kennelley	1
Mr. H. C. Kloepper	1
Dr. C. W. Kuhlman	1
Mr. G. P. Lang	1
Dr. J. P. Morgan	1
Dr. D. E. Morris	1
Mr. E. N. Nelson	1
Dr. N. F. Neumann	1
Mr. W. G. Petty	1
Dr. W. C. Philoon	1
Mr. R. D. Piper	1
Dr. W. J. Robertson	1
Mr. A. E. Ruehle	1
Mr. E. F. Sanders	1
Dr. J. U. Shepardson	1
Mr. J. W. Stevenson	1
Mr. E. K. Teter	1
Mr. L. G. Weber	1
Mr. S. W. Weidman	1
Mr. J. H. Yeager	1
Dr. W. A. Ziegler	1
Technical Editor	1
Technical Library	2

External Distribution

External distribution according to TID-4500, 15th Ed.	490

DEVELOPMENT OF THE TBP-HEXANE PROCESS FOR URANIUM PURIFICATION

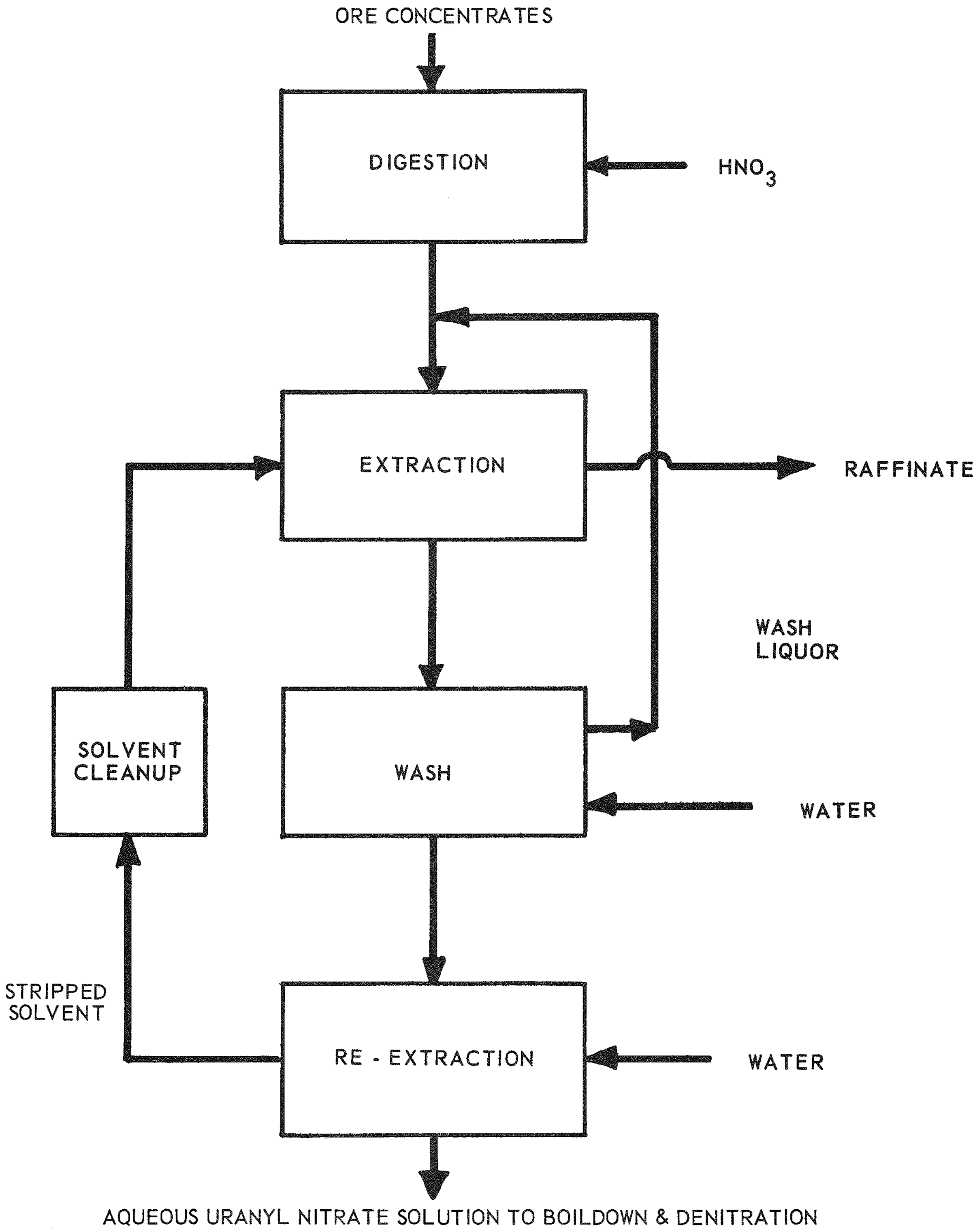
In 1954 the Atomic Energy Commission decided upon the construction of a new uranium purification plant to be located at Weldon Spring, Missouri, and operated by the Mallinckrodt Chemical Works. Solvent extraction was chosen as the method of purification because of its proven flexibility, economy, and applicability to a wide variety of feeds. A two-year pilot plant study was undertaken, first to provide a basis for the initial selection and sizing of the extraction equipment, and secondly through exploration of variations in certain equipment, construction and operating conditions to develop a flowsheet permitting a substantial increase in plant capacity.

Feed materials cover a wide variety of ore concentrates from domestic and foreign sources with uranium content from 50 to 75% with most averaging 60-65%. The end products of the plant are uranium metal, salts and oxides of nuclear purity for use in either plutonium production or isotope separation.

A flowsheet of a generalized uranium extraction process is as follows (Figure 1): the ore concentrates are digested with nitric acid to convert the uranium to soluble uranyl nitrate, and the resultant slurry is then contacted with solvent. The uranyl nitrate is almost quantitatively extracted, leaving a raffinate very low in uranium to be neutralized and discarded. Uranium-bearing solvent is then passed through a wash step where it is contacted with a small amount of pure water to remove dissolved and entrained impurities passing through the extraction step. Since the aqueous stream from this step contains significant quantities of uranium, it is recycled to the extractor. The uranyl nitrate is then stripped from the solvent with demineralized water, producing an aqueous stream of highly purified uranyl nitrate ready for boildown and denitration to uranium trioxide. The stripped solvent is returned to the extraction step after a clean-up treatment.

FIGURE 1

GENERALIZED FLOW SHEET: URANIUM PURIFICATION
BY
SOLVENT EXTRACTION



SOLVENT CHOICE

Limitations of time necessitated an early selection of solvent, thereby restricting the choice to the two solvents then in commercial-scale use, diethyl ether and diluted tributyl phosphate (TBP).[1] Mallinckrodt experience since 1942 had proven the ether process to be satisfactory, but somewhat complex, since two extraction cycles were required for adequate purity. Several years of plant experience of the National Lead Company of Ohio using TBP diluted with kerosene in a single cycle operation demonstrated high recoveries, acceptable product purity and stable operation with a wide variety of feeds. Characteristics of this process have been discussed by Arnold.[2] In addition, the TBP system is free from the potential hazards present in the handling of large volumes of ether. For these reasons, therefore, TBP diluted with kerosene was originally chosen for the Weldon Spring plant and the plant equipment selected and sized on this basis.[3]

Experience with the TBP-kerosene process demonstrated, however, certain areas in which improvements might be made both in the process and the equipment.[3]

Tributyl phosphate is an excellent solvent for uranyl nitrate, having high capacity, selectivity and stability to nitric acid. It is normally diluted with an inert diluent, however, to minimize the adverse effects of high specific gravity (0.98) and viscosity on phase separation and mass transfer rates. The lower paraffin hydrocarbons in general are suitable diluents and refined kerosene has been used extensively in the past. Early in the development program it appeared that the use of a lighter diluent should, however, further lower the specific gravity and viscosity of the solvent, thereby improving phase separation and mass transfer. N-hexane, with a specific gravity of 0.69 (compared to 0.80 for kerosene) appeared satisfactory and was recommended for use in the Weldon Spring plant instead of kerosene.[4]

Experimental studies with varying solvent concentration indicated that satisfactory operation was possible with values as high as 50% TBP in hexane. Start-up and emulsification problems arose, however, and product purity suffered. The bulk of the experimental program was conducted with a solvent concentration of 25-30% with 30% recommended for plant design as a compromise between the capacity increase resulting from high TBP concentrations and ease of operation that is achieved with a more dilute solvent.[5]

SLURRY EXTRACTION

Pulse columns, spray columns and mixer-settlers of various types were tested using 25% TBP in kerosene for the extraction of the feed slurry and rejected largely because excessive emulsification occurred when agitation was vigorous enough to permit good phase contact. The unit found most satisfactory and adopted for plant use was the pumper-decanter, a type of mixer-settler in which the two phases are mixed externally in a centrifugal pump and allowed to separate in a tank or decanter.[1, 3] The design evolved as the result of several experimental observations:

1. Vigorous agitation of course is necessary to obtain the good phase contact required for high extraction efficiency. The liquids involved, however, exhibit a strong tendency to emulsify unless a ratio of solvent to aqueous of at least 10/1 is maintained.

2. There was substantially less emulsification when the system was operated with the less viscous fluid (solvent) as the continuous phase.

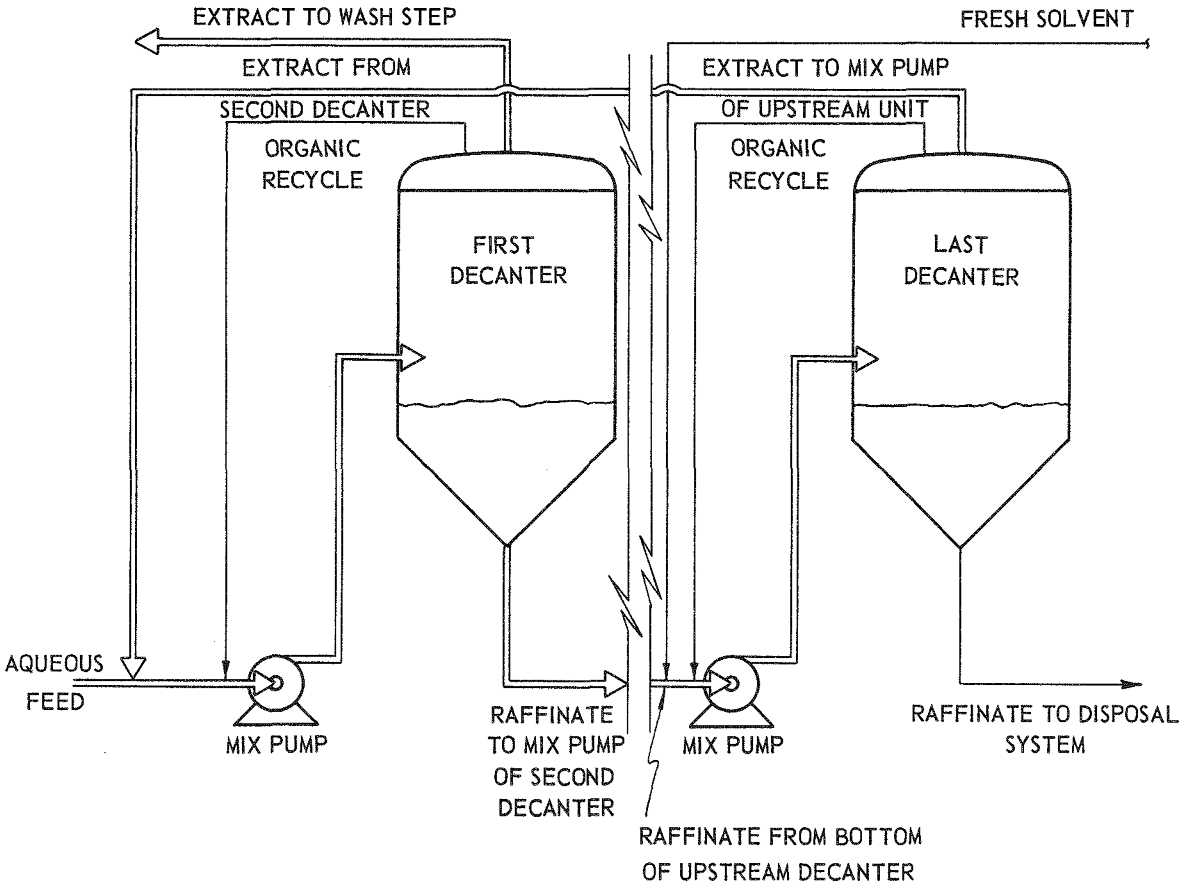
3. Separation of the two phases after mixing took place much more readily with the continuous phase in rotary motion.

The principles of operation of the resulting design are shown in Figure 2, which illustrates schematically the end stages in a series of several countercurrent units.

Recycled solvent from the top of each decanter is mixed in a pump with the raffinate from the bottom of the previous unit (or with the aqueous feed) and the extract from the next unit. The pump discharge enters the body of the decanter tangentially and the phases disengage. An interface is maintained in each decanter body by a float control.

The pilot plant system consisted of four pumper-decanters arranged for countercurrent flow of organic and aqueous streams as described.

FIGURE 2
SCHEMATIC FLOW DIAGRAM OF PUMPER-DECANTERS
END STAGES



The extraction of uranyl nitrate by tributyl phosphate is thought to follow the equation: $UO_2^{++} + 2NO_3^- + 2TBP \rightleftarrows UO_2(NO_3)_2 \cdot 2TBP$

$$K = \frac{UO_2(NO_3)_2 \cdot 2TBP}{(UO_2{}_{aq}^{++})(NO_3^-)^2(TBP_{org})^2}$$

with the formation of a definite complex of uranyl nitrate and tributyl phosphate in the organic phase. As indicated by the equilibrium constant, uranium extraction is favored by excess nitrate ion in the aqueous phase, nitric acid usually being added for this purpose. Thus, it may be seen that a given amount of solvent has a capacity for uranium indicated by the stoichiometry of this reaction apart from any considerations of equilibrium between the phases. The degree to which the available tributyl phosphast is complexed in this reaction is termed "saturation." Certain impurities of importance as well as nitric acid are extracted but to a much lesser degree than uranium, and it is possible by operating with high degrees of extract uranium saturation to limit the extraction of impurities. The theoretically calculated relationship between the number of extraction stages, the extract concentration, the phase flow ratio, and the relative impurity level indicated that the advantage gained by the use of more than five stages would be quite marginal.[6]

In the four pilot plant pumper-decanters, operating at close to 100% stage efficiency, uranium recoveries as high as 99.99% were demonstrated with various feeds and blends and extract saturation in the range of 96-99%.[7] Five stages were therefore recommended for the plant to allow for feed variations and scale-up uncertainties. Throughput capacity was limited by entrainment of aqueous droplets in the extract stream. Control of the flow ratio based on the density of the extract in the second decanter proved satisfactory since the density at this point is quite sensitive to changes in concentration.[6]

Limitations of auxiliary equipment made it impossible to determine the ultimate capacity of the pumper-decanters with 25% TBP in kerosene and digestion slurries. Tests with water and solvent, however, indicated a top throughput rate of about 70 gal/hr/sq. ft., a figure probably higher than that attainable with slurries.[3] Later modifications of the auxiliaries permitted capacity measurements with TBP in hexane. Using a clear solution of 200 gU/l, a rate of 96 gal/hr/sq. ft. was observed with 25% TBP in hexane, and 73 gal/hr/sq. ft. with a digest slurry of the same uranium content.[6] Thus the capacity improvement resulting from substitution of hexame for kerosene can be seen.

WASH AND RE-EXTRACTION

Pilot plant studies were also conducted to determine the best type of equipment for the wash and re-extraction steps. Operation with water to organic ratios approaching the theoretical minimum is desirable to minimize the introduction of impurities as well as the amount of water removal required in the subsequent boildown step. Equipment containing a large number of transfer stages was therefore indicated. Pilot plant studies with TBP-kerosene showed pulse columns to be the most suitable of various equipment types tested.[4, 6]

Preliminary pilot plant studies in 4-inch pulse columns were made with TBP-kerosene, using a plate design and configuration which had been found satisfactory elsewhere. Since more stable operation was obtained with the aqueous phase continuous, this manner of operation was adopted as standard.[6] Based on these studies, a single column was chosen for washing, but the calculated number of transfer stages required for re-extraction would be too great for the use of one column in view of the practical limitations on column height. The use of two columns in series was therefore recommended.[6] The adoption of hexane as diluent and the resultant capacity increase of the pumper-decanters made it desirable to increase the throughput capacity of the pulse columns to achieve a balance between extraction and re-extraction. Since the two re-extraction columns in series would contain more stages than actually necessary it appeared that the design of the column internals could be modified to permit increases in capacity at the expense of some mass transfer efficiency.[6] Since the capacity of a pulse column is usually set by emulsification which is the result of excessively fine dispersion of one phase within the other, capacity increases were realized by decreasing the degree of dispersion of the organic within the continuous aqueous phase.

Table I shows the effect of several variables. Initially stainless steel plates were used with 1/8-inch holes, 23% free area and a 2-inch plate spacing. Data for early TBP-kerosene runs show flooding rates of 600 to 700 gal/hr/sq.ft.[1] The substitution of hexane for kerosene increased the figure to 1050,[8] as a consequence of improved phase separation. As can be seen, increasing the hole diameter from 1/8 to 1/4 inch raised the capacity of the re-extraction column to 1560. Three-eights-inch holes effected a still further improvement to 1800. Increase in the number of holes to allow 33% free area gave an additional increase to 1990. In general, performance of packed extraction columns has been found to improve when the packing is wetted by the dispersed phase. In line with this experience, plates of solid Teflon were substituted, using 3/8-inch holes and 33% free area. A capacity increase to 2880 gal/hr/sq.ft. was observed here, apparently the result of increased coalescense of the organic phase below the plates. In all cases up to this point, a 2-inch plate spacing was maintained. Four-inch spacing was then tried, a substantial increase to 3300 resulting. Eight-inch spacing was tried, but showed no improvement. Operating conditions for all of these runs included a 1-inch sinusoidal stroke in the column, 80-85°F operating temperature, aqueous to organic ratios of 0.1/1 in the wash column and 1/1 in the re-extractor. Each capacity value was measured at the optimum pulse frequency generally in the range of 30-50 cy/min. It should be noted that because of height limitation in the available pilot plant columns a higher ratio of aqueous to organic was necessary than would be required in the plant where greater column height could be used. Operations were also conducted at room temperatures, whereas in plant practice a temperature of 130-135°F would be used in re-extraction since elevated temperature shifts the equilibrium in favor of the aqueous phase. Thus it was possible in the pilot plant approximately to triple the throughput capacity of the re-extraction column and increase between four and five times the capacity of the wash column.

These results, of course, deal only with throughput capacity, the maximum total volume of both phases which can be made to flow through the column under conditions of stable operation. Since most of the changes tend to decrease the degree of dispersion of one phase within the other, inevitably some decrease in mass transfer efficiency resulted. It was found, however, that by changing the pulse stroke length from 1 inch to 1.8 inches, thereby increasing the energy input to the column, the net effect on the re-extraction column was a loss in efficiency requiring the use of about 6% more water for re-extraction, an increase tolerable in plant operation.[8] Stainless steel plates with a thin coating of Teflon were found to be equally as effective as solid Teflon and were therefore recommended for plant use in the interests of economy.[9]

TABLE I

Effect of Plate Design on Pulse Column Capacity

Plate Condition				Organic Composition	Wash Column Capacity	Re-extraction Column Capacity
Mat'l	hole dia. ins.	Free Area Percent	Spacing ins.		gal/hr/sq.ft.	gal/hr/sq.ft.
S.S.	1/8	23%	2	28% TBP-kerosene		600-700[1]
S.S.	1/8	23%	2	25% TBP-hexane	750	1050[8]
S.S.	1/4	23%	2	25% TBP-hexane	1290	1560[8]
S.S.	3/8	23%	2	25% TBP-hexane	1540	1800[8]
S.S.	3/8	33%	2	25% TBP-hexane	1890	1990[8]
Teflon	3/8	33%	2	25% TBP-hexane	2650	2880[8]
Teflon	3/8	33%	4	25% TBP-hexane	3600	3300[8]

Other conditions:
pulse frequency 30-50 cy/min
1'' stroke length
80-85°F
0.1/1 A/O ratio in wash
1/1 A/O ratio in re-extraction

HIGH URANIUM, LOW ACID FLOWSHEET

Up to this point, all work had been done with a feed slurry containing 200 gU/1 and 3N nitric acid, conditions chosen largely as a result of experience at other sites.[6] The ability of the pumper-decanters to handle feed slurries with high solids content suggested the possibility of increasing the uranium concentration and lowering the acid level in the feed. Since the throughput capacity of the pumper-decanters is largely determined by the aqueous stream, an increase of uranium concentration in this stream could cause an almost proportional increase in uranium extraction capacity. A decrease in the concentration of free nitric acid could be made without adversely affecting extraction since at the resulting higher solvent rate increased nitric acid extraction from the raffinate would take place maintaining the high level of acid in the pumper-decanters required for good uranium extraction.[10]

Since the free nitric acid required per pound of uranium could be substantially diminished, substantial economic savings could be realized if the raffinate could be neutralized and discarded instead of processed for acid recovery. In addition, the lower acid strength required for digestion would eliminate the need for reconcentration of acid regularly recovered from other plant sources.

Solubility studies made on a variety of ore concentrates using 1N free nitric acid showed a uranium solubility in excess of 440 g/1 at 100°F in all cases.[11] Several pilot plant runs were then made with feed slurries containing 400 gU/1 and 1N free nitric acid. Operation was in general quite satisfactory. Some scaling in the pumper-decanters was observed although not enough to cause trouble. It was necessary to increase the organic recirculation ratio from 10/1 to 20/1 to attain satisfactory mass transfer without emulsification but extract saturations in the range of 96-99% were attained and uranium losses in the raffinate ran as low as 0.01% with good feeds.[10] In some cases, raffinate losses as high as 0.6% were observed with feeds of high slurry viscosity. Such feeds could be handled in the plant by blending with better quality materials. Some evidence of sodium leakage through the pumper-decanters was observed, proved by later investigation to be the result of entrainment of aqueous droplets. Slight changes were necessitated in the operation of the wash column but there was, of course, no effect on the re-extraction column. A typical product liquor analysis is shown in Table 2.

SOLVENT TREATMENT

Tributyl phosphate is subject to slow decomposition in an acid environment. The decomposition products form stable complexes with uranium in the organic phase from which the uranium cannot be readily re-extracted by water, and if allowed to build up in the solvent will eventually cause the non-re-extractable uranium to rise to a level where it will interfere with extraction. In addition, impurities in the hexane apparently react with nitric acid to form unknown compounds which upset the uranium-solvent equilibrium in a similar manner. Since many of these decomposition products are acidic, they can be removed by scrubbing the stripped solvent with sodium carbonate solution. The uranium is extracted as the soluble tricarbonate complex and can be later recovered by precipitation with caustic and filtration. Pilot plant studies led to the recommendation of an open spray column as a suitable contacting device.

TBP-RECOVERY

The aqueous raffinate and product uranyl nitrate liquor both contain small amounts of entrained TBP, the recovery of which is important for economy. In addition, organic matter in the product liquor must be removed before the boildown operation to avoid a dangerous reaction with nitrates at elevated temperature. Pilot plant studies showed that washing with hexane in an open spray column reduced the TBP level in the aqueous product to about 0.02%.

TABLE 2

Spectrographic Analysis of Pilot Plant Product Liquor[10]
Feed Slurry: 400 gU/1, 1M HNO_3

Impurity	Concentration PPM, U Basis
Na	78
Fe	4
Si	17
Mg	10
V	$<$ 9
Zn	10
Pb	1
Cu	1
Co	2
B	$<$ 0.1
Mo	$<$ 1
U	126 g/1
HNO_3	0.002 g/1

SUMMARY OF RECOMMENDED FLOWSHEET

Based on the development program described, the operating conditions recommended for plant operation are shown in Table 3.[14] The indicated variances in the flow ratios were determined experimentally to be the maximum allowable with satisfactory recovery and product purity.[15] The complete flowsheet is shown in Figure 3.[10]

The Weldon Spring refinery started operation in June 1957, and operation since that time has satisfactorily borne out the predictions of the pilot plant program.

Two years of intensive pilot plant development work led to a flexible plant design. Even though equipment design and sizing were frozen at an early stage, subsequent systematic studies of operating conditions made it possible approximately to triple the capacity of the plant without additional major capital expense. The plant operating economies resulting from these developments played a substantial part in making it possible for the AEC to close down the older and obsolete ether process refinery with a resultant saving in direct operating cost of about $1,000,000 per year.

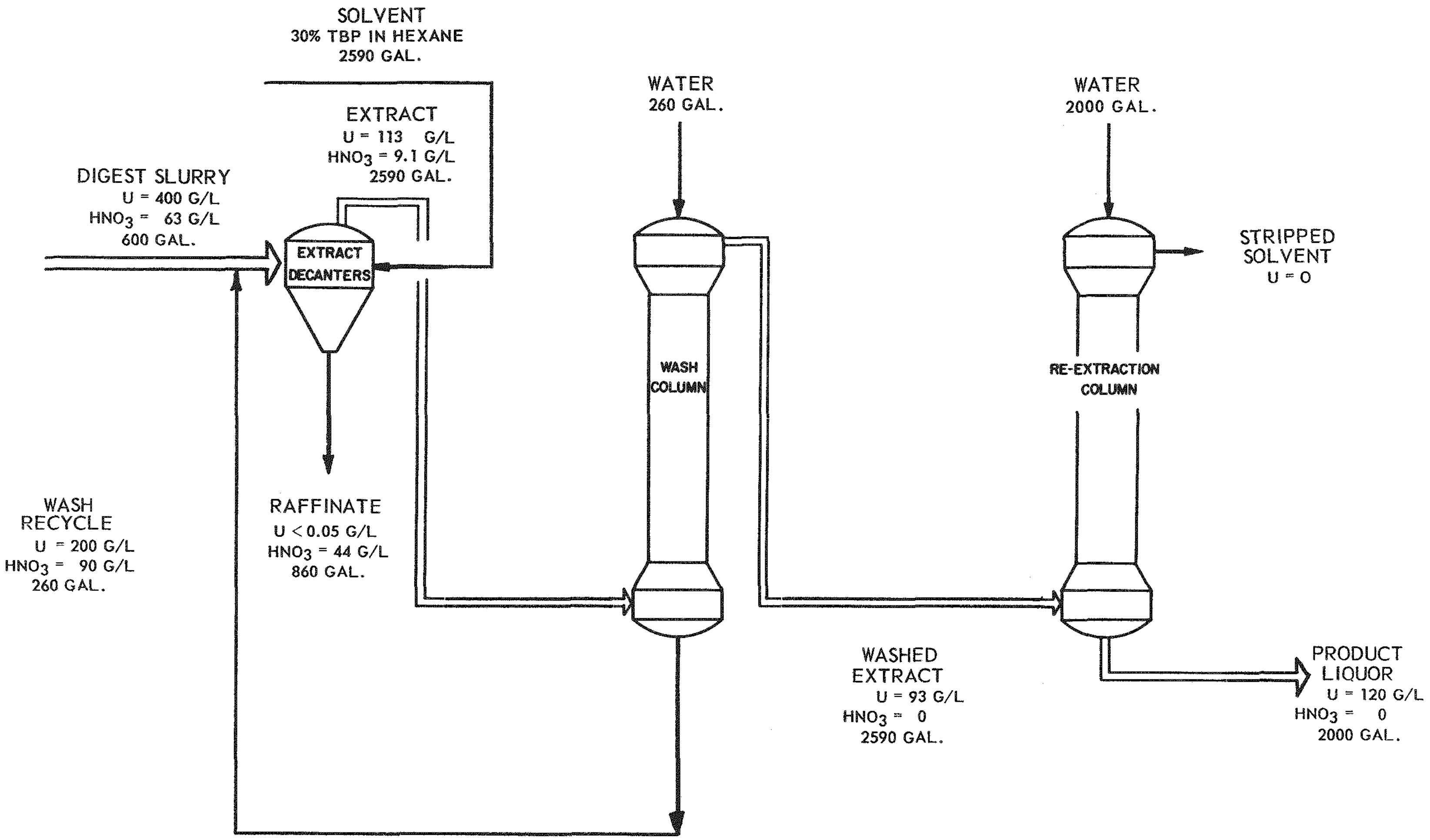
TABLE 3

Summary of Recommended Plant Operating Conditions for Extraction System

1. Feed slurry concentration	400 gU/1, 1N HNO_3
2. Solvent composition	30% TBP in N-hexane
3. Organic to aqueous ratio in pumper decanters	3.0 ± 0.15
4. Organic to aqueous ratio, wash column	10 ± 0.5
5. Organic to aqueous ratio, re-extraction columns	1.36 ± 0.06

FIGURE 3

TBP-HEXANE PROCESS FOR URANIUM PURIFICATION
HIGH-URANIUM, LOW ACID FLOWSHEET
BASIS 1 TON U



BIBLIOGRAPHY

1. R. H. Fariss, C. S. Powell, J. E. Spooner, and R. S. Summers, Uranium Extraction with Diluted Tributyl Phosphate, "Process Development Quarterly Report, Part II," February 1, 1955, p. 8-41. Report MCW-1372, Mallinckrodt Chemical Works.
2. D. S. Arnold, B. E. Ryle, J. O. Davis, Chemical Engineering Progress, 54, p. 90-95 (1958)
3. R. H. Fariss, J. E. Spooner, C. S. Powell, and R. S. Summers, Uranium Extraction with Diluted Tributyl Phosphate, "Process Development Quarterly Report, Part II," May 1, 1956, p. 8-47. Report MCW-1376, Mallinckrodt Chemical Works.
4. R. H. Fariss, C. S. Powell, Uranium Extraction with Diluted Tributyl Phosphate, "Process Development Quarterly Report, Part II," August 1, 1955, p. 8-55. Report MCW-1378, Mallinckrodt Chemical Works.
5. R. H. Fariss, et al., Pilot Plant Operation of a TBP-Hexane Extraction Cycle for Purification of Uranyl Nitrate, "Process Development Quarterly Report, Part II," November 1, 1956, p. 19-52. Report MCW-1398, Mallinckrodt Chemical Works.
6. R. H. Fariss, et al., Uranyl Nitrate Purification by Extraction with Tributyl Phosphate in Hexane, "Process Development Quarterly Report, Part II," November 1, 1955, p. 9-102. Report MCW-1381, Mallinckrodt Chemical Works.
7. R. H. Fariss, L. H. Krone, and D. J. Nerrow, Pilot Plant Operation of a TBP-Hexane Cycle for Uranyl Nitrate Purification, "Process Development Quarterly Report, Part II," August 1, 1956, p. 17-54. Report MCW-1393, Mallinckrodt Chemical Works.
8. R. H. Fariss, et al., Pilot Plant Operation of a TBP-Hexane Extraction Cycle for Uranyl Nitrate Purification, "Process Development Quarterly Report, Part II," February 1, 1956, p. 49-89. Report MCW-1383, Mallinckrodt Chemical Works.
9. R. H. Fariss, L. H. Krone, and D. J. Nerrow, Pilot Plant Operation of a TBP-Hexane Cycle for Uranyl Nitrate Purification, "Process Development Quarterly Report, Part II," August 1, 1956, p. 17-54. Report MCW-1393, Mallinckrodt Chemical Works.

10. J. T. Krieg, et al., Pilot Plant Testing of a Low Acid Flowsheet for the TBP-Hexane Extraction Process, "Process Development Quarterly Report, Part II," May 1, 1957, p. 55-72. Report MCW-1402, Mallinckrodt Chemical Works.

11. J. T. Krieg and R. H. Fariss, Gross Solubility of Uranium in Digest Liquors, "Process Development Quarterly Report, Part II," May 1, 1957, p. 13-20. Report MCW-1402, Mallinckrodt Chemical Works.

12. J. T. Krieg and R. H. Fariss, Gross Solubility of Uranium in Digest Liquors, "Process Development Quarterly Report, Part II," May 1, 1957, p. 13-20. Report MCW-1402, Mallinckrodt Chemical Works.

13. J. T. Krieg and J. A. Soukup, Impurity Leakage Through the TBP-Extraction Process by Entrainment, "Process Development Quarterly Report, Part II," November 1, 1957, p. 25-31. Report MCW-1409, Mallinckrodt Chemical Works.

14. R. H. Fariss, J. T. Krieg, and J. A. Soukup, Pilot Plant Studies of Variables Affecting Uranium Purity in a TBP-Hexane Extraction Cycle, "Process Development Quarterly Report, Part II," May 1, 1957, p. 21-54. Report MCW-1402, Mallinckrodt Chemical Works.

15. J. T. Krieg, et al., Sensitivity of the Weldon Spring TBP-Extraction System to Process Flow Rates, "Process Development Quarterly Report, Part II," August 1, 1957, p. 43-52. Report MCW-1404, Mallinckrodt Chemical Works.