CONF-710417--1

RECEIVED BY OTIE MAY 18 1971

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OPTIMIZED USE OF MULTI-PURPOSE FUEL PROCESSING FACILITIES AT THE IDAHO CHEMICAL PROCESSING PLANT*

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ABSTRACT

Three cycles of solvent extraction are used at the Idaho Chemical Processing Plant (ICPP) for purifying highly-enriched uranium generated from reprocessing highly radioactive fuel elements in various headend facilities. The first cycle of extraction usually employs TBP in this multi-purpose plant, and is followed by two extraction cycles using MIBK. Use of different solvents permits advantage to be taken of their respective characteristics for separating fission products from uranium; MIBK is more effective for zirconium whereas TBP is more effective for ruthenium.

Five headend systems are currently available for dissolving spent fuel elements. Currently, these systems at the ICPP are operated sequentially, along with a waste solidification facility, to permit optimum use of manpower and facilities to result in lowest possible reprocessing costs. For instance, the continuous aluminum process and the first extraction cycle are operated concurrently while the other facilities are in standby and the first cycle product is being collected and stored. Then the second- and third-extraction cycles and product denitration unit are operated concurrently. When these fuel processing facilities are in standby, the waste solidification facility is operated to convert the radioactive waste solutions from the solvent extraction system to a safer, more compact granular solid. This type of alternating operation is believed ideal for a multi-purpose plant and in fact would be highly satisfactory for a single-purpose plant. In such a case, it is highly probable that only the fuel processing and waste solidification facilities would be operated alternately, however, to yield the most efficient-type operation.

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*Work performed under the auspices of the United States Atomic Energy Commission, Contract AT(10-1)-1230.

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INTRODUCTION

Numerous reprocessing plants for spent nuclear fuels will be required in the 1980's to handle the increasing amounts of spent fuel from commercial installations. The U.S.A. already has three commercially-owned reprocessing plants that are operating or being constructed, in addition to three government-owned reprocessing plants being operated for the U.S.A.E.C. by contractor personnel. One of these plants, the Idaho Chemical Processing Plant (ICPP), is a highly versatile multi-purpose plant having a broad range of capabilities to handle many different types of fuel.

Multi-purpose fuel reprocessing plants are designed to maximize flexibility, and a common method to achieve this is to use several headend dissolution systems with common extraction, packaging and waste storage systems. Little has been reported heretofore about how multi-purpose plants are operated to achieve optimized performance.

The ICPP is capable of processing a wide variety of reactor fuels including aluminum, zirconium, and stainless steel alloyed fuels, clad fuels, and thorium fuels containing uranium of various enrichments and concentrations. Furthermore, this plant has facilities to handle special shapes of fuels, to convert waste solutions to solids, and to recover some isotopes and rare gases when desired. Although the plant was

originally designed for high-enriched fuels, modest quantities of low-enriched fuels can be readily processed; however, plutonium can not currently be recovered because the ICPP lacks packaging facilities and ventilation safeguards necessary for this material.

The purpose of this paper is to describe the ICPP and the techniques used in its operation. In brief, sequential-type operation employed at ICPP with various systems permits optimum use of manpower and facilities resulting in lowest possible reprocessing costs. This type of operation also appears ideal for other multi-purpose plants, and should be highly satisfactory for a single-purpose plant.

THE ICPP PROCESSES

During fuel element reprocessing at the ICPP, a series of aqueous processing steps are generally employed, as shown in Figure 1. The first involves dissolution of the fuel in an acid, after which the resulting solution is sent through several cycles of countercurrent solvent extraction to separate and purify the uranium. The product from the final extraction cycle is uranyl nitrate solution with fission products removed almost to background level. This solution is generally denitrated in a fluidized bed to uranium trioxide for shipment.

Usually, but notnecessarily, the first extraction cycle at ICPP employs tributyl phosphate (TBP) in a kerosene diluent as the extractant because the composition requirements of a suitable dissolver product stream for TBP are less stringent than for methylisobutyl ketone (MIBK). This is followed by two extraction cycles using MIBK. Use of different

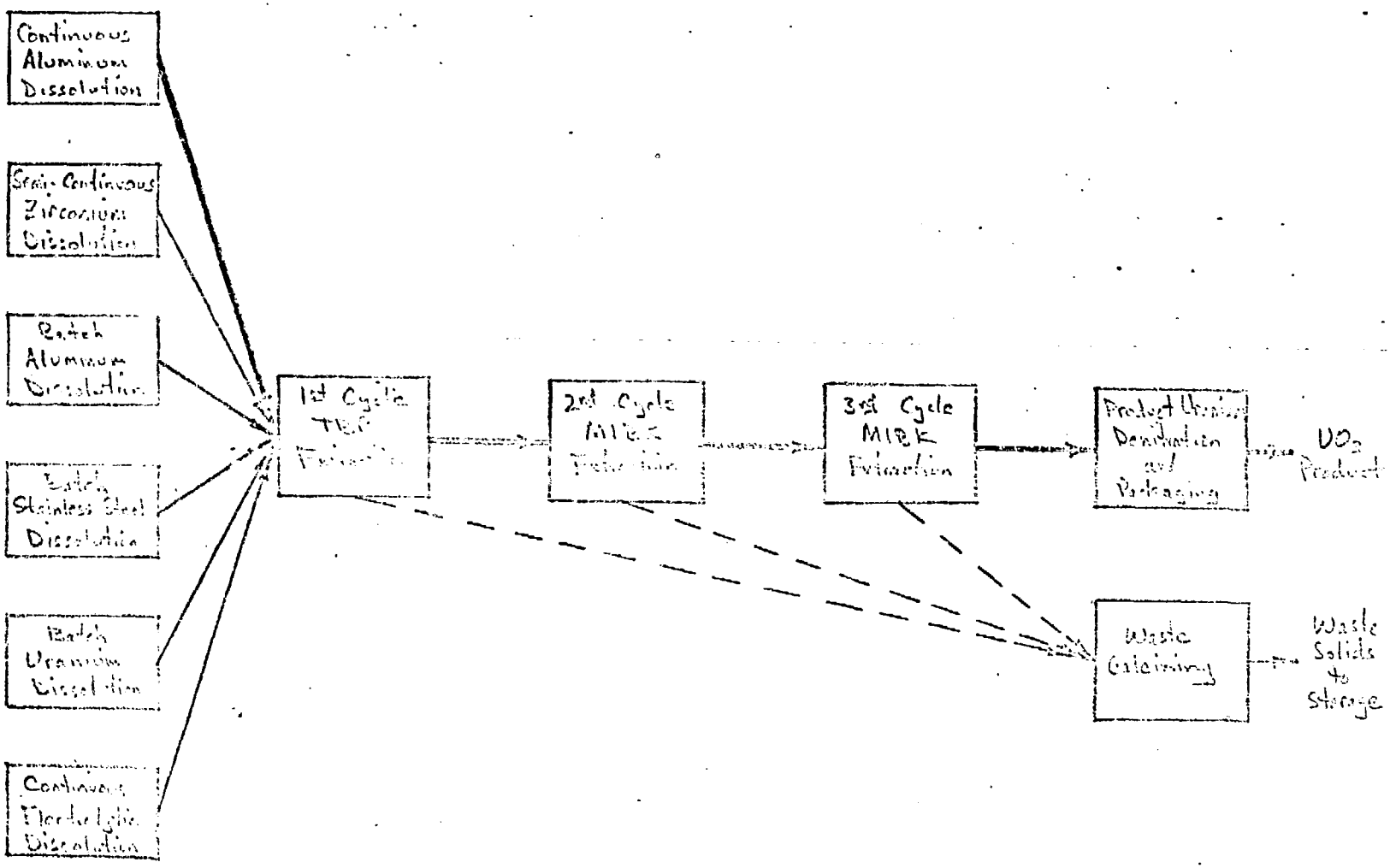

Fig. 1. Schematic diagram of ICPP Fuel and Waste Processes

solvents permits advantage to be taken of their respective characteristics for separating fission products from uranium; MIBK is more effective for zirconium, whereas TBP is more effective for ruthenium.

Dissolution

Dissolution requirements, reagent compositions, and dissolving conditions are highly dependent on the metals used in the fuel element cladding and matrix; the metals generally consist of aluminum, zirconium, or stainless steel. Five headend systems are available at the ICPP for dissolving spent fuel elements. The most commonly used is the continuous nitric-acid system having a capacity of 500 kilograms of aluminum per day. The other dissolver systems include an hydrofluoric-acid system (600 kg of zirconium per day), a sulfuric-acid system (50 kg of stainless steel per day), a nitric-acid system (5 kg unalloyed uranium per day), and a second (noncontinuous) aluminum alloy-nitric acid system. A sixth headend system currently being installed is an electrolytic dissolution process for stainless steel-clad or matrix fuels. A seventh system, which is a non-aqueous headend process for graphite-based fuels, is in the development stage.

First Cycle Extraction

The uranium in the dissolver product solution, which in the case of aluminum fuels consists of uranyl nitrate, aluminum nitrate, and fission product nitrates, is isolated by contacting the liquid with TBP

in countercurrent extraction columns. The liquids from the hydrofluoric and sulfuric acid dissolutions are complexed with aluminum nitrate and nitric acid, respectively, so that they may be processed without excessive corrosion through the same stainless steel extraction system. The uranyl nitrate is preferentially dissolved in the organic material which is subsequently contacted with water to remove the uranyl nitrate. A schematic diagram of this extraction cycle is shown in Figure 2.

Dissolver solution from the various headend systems enters the top of the first extraction column where the uranium and some acid are extracted away from the aluminum and the bulk of the fission products. For MTR-type aluminum fuels the extractant is five percent TBP in a kerosene diluent. The organic stream, containing the uranium, flows to the scrubbing column where it is contacted with aluminum nitrate solution to remove fission products and nitric acid. The spent scrubbing stream, containing a small amount of uranium, is recycled to the extraction column feed. Uranium in the organic stream leaving the scrubbing column is back-extracted into the aqueous phase in the stripping column with a dilute nitric acid stream. Prior to concentration, the stripping column product stream is washed in a fourth column with kerosene to remove dissolved TBP. The concentrated product from the evaporator may be fed directly to the second extraction cycle or placed in intercycle storage.

Nuclear safety is maintained in the first extraction cycle by making frequent rate checks of the organic stream to the extraction column, limiting the U-235 throughput to 1.6 kg/hr (before burnup basis), and

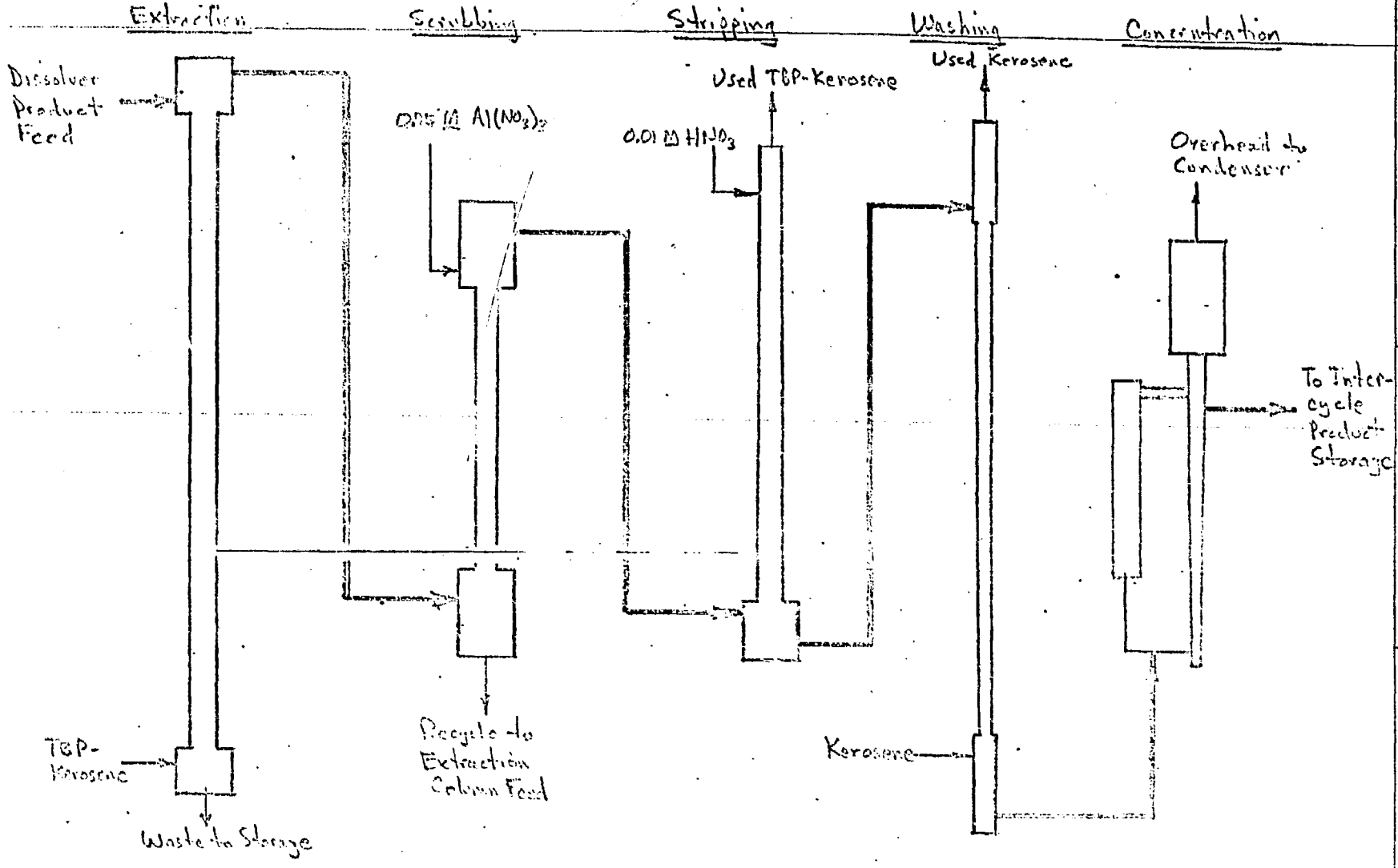

Fig. 2. Schematic diagram of first (TBP) extraction cycle.

limiting the TBP concentration. The controlling item is the head of the extraction column which has a minimum critical U-235 concentration limit of approximately 26 g/l. This is based on an eight-inch thick layer (approximately 60 l) of solvent in the head. The solubility of U-235 in five percent TBP in kerosene is approximately 20 g/l so safety is assured.

Aluminum nitrate is used as a scrubbing agent in the scrubbing column rather than nitric acid, equally suitable for scrubbing fission products, because it is desirable to minimize the amount of uranium that is recycled and acid that is carried over by the organic stream to the stripping column (the presence of significant quantities of acid in the column would make it difficult to strip uranium into the aqueous phase and the capacity of the existing stripping column is marginal for existing processes). Separate extraction and scrubbing columns are used rather than a single combined extraction-scrubbing column because of limited cell heights. Pulsed sieve plate columns are used although mixer-settlers and other contactors would also be applicable. Calculated and actual lengths for the columns are given in Table I.

Plutonium and neptunium present in the dissolver product stream in the tetravalent state are extractable under the TBP first cycle conditions. These materials are reduced with ferrous sulfamate in later extraction cycles and are partitioned from the uranium at that time.

Aluminum nitrate waste solution from the TBP extraction column is stored for eventual calcination. The TBP in kerosene from the stripping column is continuously washed in three mixer-settlers for recycle to the process. The first and third washes use 0.04 M nitric acid; the second

TABLE I

CALCULATED AND ACTUAL LENGTHS OF ICPP SOLVENT EXTRACTION (TBP) COLUMNS

Column	Calculated Height of a Transfer Unit (HTU), feet	Active Length of Column, feet	I.D., Inches
Extraction	<2.1	23	10
Scrubbing	>2.3	10	8
Stripping	<1.3	14	9

wash uses 0.5 M sodium carbonate. The contact time in each mixer-settler is about 30 minutes. Spent kerosene from the wash column and spent TBP-kerosene from extraction are steam-stripped to remove fission products and plutonium, and then they are burned in an incinerator.

Intercycle Product Storage

Intercycle storage for the TBP cycle product is composed of geometrically-safe vessels (12.7 cm I.D.) for aqueous uranium solutions. The storage capacity is approximately 4800 liters which is equivalent to about 50 days of holdup based on processing MTR-type aluminum fuel and storing intercycle solution at a uranium concentration of 200 g/l. Solution from this storage is fed to the MIBK extraction system.

Second and Third Cycles of Extraction

The second and third extraction cycles at ICPP utilize MIBK as the extractant. The aqueous product stream from intercycle storage is fed

to the first column of the second cycle at about midheight, as shown in Figure 3. The aqueous stream then flows down the column countercurrent to a stream of MIBK flowing up the column and extracting the uranium. The MIBK stream entering the bottom of this compound column passes first through an extraction section and then a scrubbing section. A relatively large volume of scrubbing solution introduced at the top of the column provides a salting agent, aluminum nitrate, to force the uranium in the extraction section of the column into the organic phase. Also entering with the scrubbing solution is sufficient ammonium hydroxide to create an acid-deficient condition in the extraction part of the column for improving decontamination of uranium from fission products. The uranium in the MIBK phase leaving the first column flows to a stripping column. Here, the uranium is back-extracted into an aqueous phase with a dilute nitric acid stream. Feed is prepared for the third extraction cycle by concentrating the aqueous stream in an evaporator. The third extraction cycle is similar in most respects to the second cycle and includes an evaporator in which the product solution is concentrated to about 1.5 M uranyl nitrate for convenience in shipping and denitration.

Plutonium and neptunium follow a path similar to that of the fission products in the second and third extraction cycles. Ferrous sulfamate is added to the second cycle scrubbing stream to reduce the plutonium and neptunium to relatively inextractable valence states. Similar reducing agents may also be used in the third extraction cycle for the same purpose if additional alpha decontamination is required to meet uranium

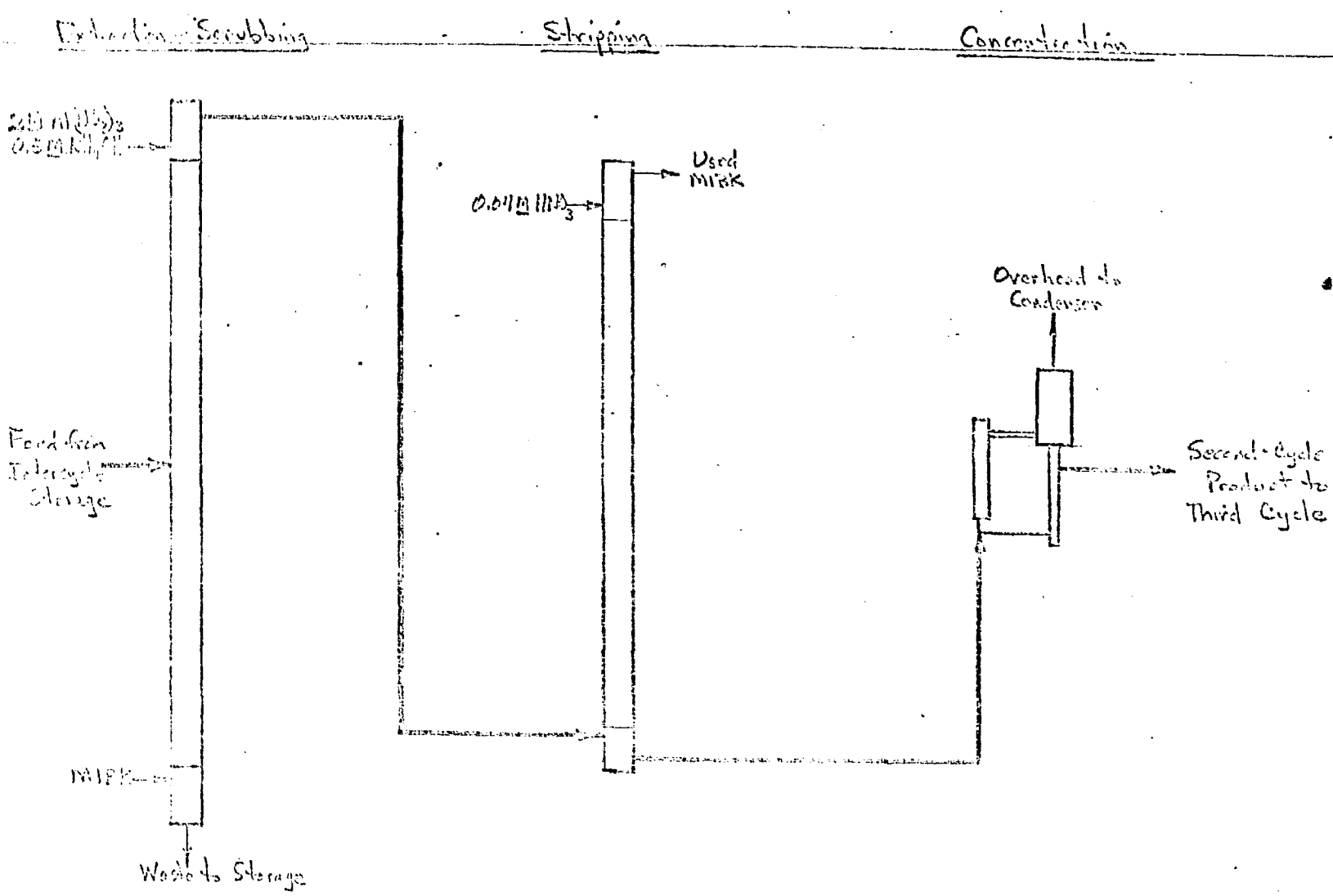

Fig. 3. Schematic diagram of the second (MIBK) extraction cycle.

product specifications; however, an available fourth extraction cycle free of ferrous ion is necessary in this case to prevent the product from being contaminated with iron.

Spent MIBK from the columns is treated with a small volume of 3.0 M sodium hydroxide and then steam distilled to remove decomposition products and fission product contamination. The solvent is then recycled to the process.

The columns in the second and third cycles are packed with 3/8-inch by 3/8-inch stainless-steel raschig rings. All of the columns are 5-inch O.D., small enough in diameter to be nuclearly safe under all operating conditions. Calculated and actual lengths of the columns are given in Table II. Aqueous outflow from the columns is controlled by air pressure applied to a discharge loop on each column.

TABLE II

CALCULATED AND ACTUAL LENGTHS OF ICPP SOLVENT EXTRACTION (MIBK) COLUMNS[a]

Column	Calculated Height of a Transfer Unit (HTU), feet	Active Length of Column, feet
Extraction/Scrubbing	2.75	31
Stripping	1.75	21

(a) The second and third cycles are essentially identical.

Waste Storage

Aqueous waste solutions from the extraction cycles and other fuel processing operations are transferred to large volume stainless steel tanks for interim storage of three to five years before being calcined to a solid. The high-activity-level waste solutions from the first extraction cycle are kept separated from the low-activity-level waste from the second and third cycles. Various types of wastes are further segregated according to the acid type, ie, nitric acid, hydrofluoric acid, and sulfuric acid.

Waste Calcination

At the ICPP, the Waste Calcining Facility (WCF) is used to convert radioactive waste solutions into solids which are more economical and significantly safer to store. Solution storage is now viewed as an interim means of storing wastes, and calcination is viewed as a means of converting fission products to a form desirable for long-term storage. The heart of the WCF is a well-fluidized, heated bed of granular solids. The waste solution is sprayed into the fluidized bed and coats the particles; water vapor and volatile gases flash from the spray droplets leaving the residual metal oxides uniformly deposited on bed particles. The spheroidal granular particles, ranging in diameter from 0.1 to 1.5 mm, are continuously removed from the calciner and pneumatically transported to storage facilities. With calcination, waste volumes are consistently decreased by a factor of about ten. Net processing rates are usually around 250 to 350 liters per hour.

SEQUENTIAL OPERATION

For a number of years the ICPP extraction facilities have been operated sequentally to achieve optimum use of manpower. With sequential operation, the continuous aluminum dissolution process and the first extraction cycle (TBP), for instance, are operated concurrently until the intercycle product storage tanks are filled. Then the second and third extraction cycles (MIBK) and product denitration and packaging are operated concurrently until the intercycle storage is emptied. During this time, the dissolution systems and first extraction cycle are in standby. When a fuel processing campaign is completed by alternate operation of the dissolution-TBP extraction and the MIBK-product packaging systems, the WCF is operated to convert waste solution to solids. This type of alternating operation, depicted schematically in Figure 4, is believed ideal for a multi-purpose plant because maximum use is made of manpower; the operating crew is sized solely for sequential-type operation of the fuel processing facilities.

During operation of the WCF, extra operations people are usually available. During this time, casual fuel processing operations can be accomplished. At ICPP, casual fuel processing can involve the dissolution of significant quantities of fuel that require special handling because of hazardous or insoluble additives, special accountability requirements, or slow reaction rates. Batch dissolver systems as well as a hot cell with remote manipulators and shielding windows can be used at ICPP for fuels requiring special handling. The resulting dissolver

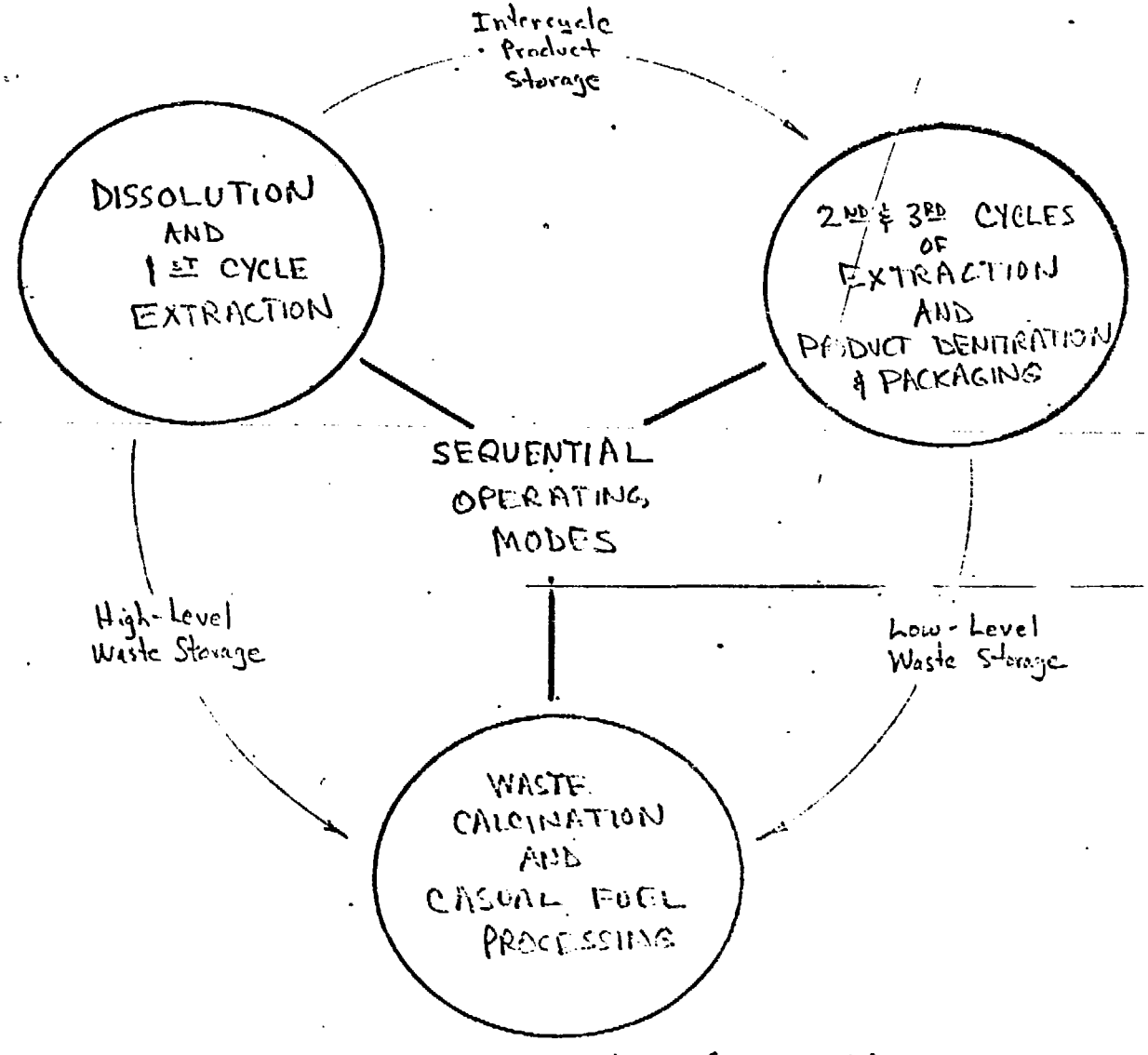

Fig. 4. Sequential operating modes for ICPP

solutions and salvage solutions from decontamination operations can be processed through the necessary extraction cycles as part of the casual operations or stored for a regular extraction campaign. In addition, the extraction systems might be operated on a casual basis to recover Np-237 from waste raffinate solutions.

At some point in time, the anticipated fuel load and waste inventory at ICPP will be sufficiently large to make concurrent operation of the fuel and waste processing facilities necessary to keep waste inventories within bounds. At that time, the operating crew will be enlarged sufficiently to permit operation of the WCF simultaneously with sequential operation of the fuel processing facilities. Thus, a dissolution head-end and the first cycle extraction systems could be operated simultaneously with the WCF until the intercycle storage was filled. Then, the WCF operation would continue while the MIBK extraction and product packaging systems were operated.

Sequential operation of a single-purpose plant is possible also. In this case, it is highly probable that only the fuel processing and waste solidification facilities would be operated alternately, however, to yield the most efficient-type operation. In this case, the waste solidification facility would probably be designed to process the necessary waste solution in about two months time; during waste processing, necessary maintenance, repairs, and modifications to the plant facilities could be made.

Commercially-owned fuel reprocessing plants for power reactor fuel must be designed and built with over-capacity to eventually be economic. Thus, for a time, they will have to be operated at a reduced rate until a sufficient fuel load is available for full rate. During this early

period, sequential-type operation of the extraction and dissolution facilities could be economically advantageous because manpower could be minimized.

OTHER STRATEGIES

In addition to sequential operation and casual processing, various other strategies are used to maximize output at ICPP. The techniques include (1) testing dissolver solutions for extraction behavior, (2) preparing individual dissolution and extraction flowsheets for each type of fuel, (3) clarifying extraction feed solutions, (4) co-processing fuels, (5) minimizing non-scheduled maintenance, and (6) preparing long-range planning and operating schedules.

Testing for Extraction Behavior

At the ICPP, fuel processing campaigns are characterized by frequent variation in the activity level and composition of the solvent extraction feed solution, due in part to the non-uniform nature of the fuels and the frequency with which unusual fuels are processed. Two simple and inexpensive tests have been used to study those feed solutions which cause difficulties in the pulsed solvent extraction columns and to predict operating problems prior to processing "off-spec" solutions.

The first of these tests is designed for the detection and diagnosis of the various forms of flooding of the pulsed sieve plate columns. This test is known as a dispersion-coalescence test and involves mixing equal aliquots of the aqueous feed and organic extractant by means of

a perforated plate agitator, which moves vertically across the interface. The quantitative measurement consists of observing the time required to achieve a given degree of dispersion of both phases. In general, the time for coalescence is of greater sensitivity and significance than the dispersion time. Usually it is equally valuable to be able to see the nature of the emulsion that may be formed in the columns, and to observe the effect of any solids which may be present in the solutions. The most frequent application of the dispersion-coalescence test occurs when a column gives evidence of flooding. Then, dispersion-coalescence characteristics of the feed-solvent system from the plant are determined. If stable emulsion formation is experienced--indicative that flooding is actually occurring in the plant column--gelatin treatment is tried in the test. If the results are favorable, gelatin is added to the plant feed.

The second test is designed to detect a marked reduction in the distribution coefficients for either extraction or stripping of actual process solutions. In general, two stages of extraction and two stages of stripping are performed in a test using appropriate plant feed, solvent, and scrubbing and stripping reagents. The phase ratio of the second extraction or stripping stage is adjusted until the uranium loss is less than one percent as indicated by the uranium distribution coefficient. If the distribution coefficients for both stages of extraction and stripping are as predicted by basic equilibrium data for the processes, no serious loss of uranium due to chemical interference

is indicated. This test is particularly useful for the detection of a pinch in the operating diagram for the stripping operation; such a pinch is often caused by dibutyl phosphate or a similar complexing substance. Based on the results of this test, suitable process flowsheets are prepared and plant operating conditions are adjusted to achieve an optimum recovery of uranium.

These two tests have been routinely used in conjunction with normal plant control and continuing surveillance of the fuels being processed, as well as with special analyses of any "off-spec" solutions or precipitates. In this manner, these two simple tests offer valuable diagnostic help in minimizing plant operating difficulties.

Separate Flowsheets

Because of the diversity of aluminum and zirconium type fuels processed at ICPP, a custom flowsheet is prepared for each fuel to guarantee complete safety while minimizing processing costs and uranium losses. Separate chemical flowsheets for the first cycle of extraction are necessary to increase the extraction, scrubbing, and stripping efficiencies while staying within the operating limits of the equipment. In addition, waste solution volumes and uranium losses can be minimized by preparing separate flowsheets.

Clarification of Extraction Feed

Refractory zirconium dioxide from the surface of zirconium-clad fuel elements and insoluble surfactant materials such as silica from aluminum-alloy fuels have been a troublesome source of solids in extraction feed solutions. About a year ago a solid-bowl centrifuge was installed to

remove the larger solids from the dissolver solution upstream of the TBP extraction system. The solids have caused significant downtime because of plugging in the feed lines to the extraction columns and flooding in the columns. Operation has been noticeably improved since the centrifuge was installed.

Co-Processing

Several years ago it was recognized that processing of fuel at ICPP could be improved by operating the aluminum and zirconium headend dissolution systems simultaneously and mixing the resulting dissolver solutions. The dissolver product from aluminum fuel can be used to complex and adjust the zirconium-fuel dissolver product. Previously, aluminum nitrate solution and nitric acid were purchased and used for complexing and adjusting the zirconium dissolver product prior to extraction. Thus, with co-processing, less operating time is required and much less chemicals are required; the latter in turn reduces the amount of waste produced and hence the WCF operating time and the required storage volume for radioactive waste solids. An added improvement resulting from co-processing is that the fluoride in the zirconium dissolver product prevents surfactancy caused by insoluble silica (from aluminum dissolver product) in the extraction columns.

Minimizing Non-Scheduled Maintenance

Non-scheduled maintenance has been minimized at ICPP, which uses a direct maintenance philosophy, by replacing or modifying mechanical or poorly designed equipment and by installing critical equipment items (such as jets and transfer lines) in pairs. Where possible, air lifts and

jets are used in place of pumps, eductors in place of blowers, and pneumatic pulsers in place of mechanically-operated pulsers. Equipment with a high maintenance potential is placed in shielded cubicles outside hot cells to limit the decontamination efforts when maintenance is required. The design of all new processes or modifications to existing processes is critically examined for simplicity, reliability, and decontaminability; in addition, intensive nonradioactive testing and operation are employed, and this has resulted in minimum equipment failure during initial radioactive operation. Process downtime and personnel exposure are also kept in check, and direct maintenance, when required, is accelerated by employing (1) in-cell photographs of equipment to orient maintenance personnel with cell layout, (2) mockups for training maintenance personnel, (3) permanently installed ladders and platforms around process equipment, (4) unattended automatic saws for cutting in-cell piping, and (5) using leakproof, quick-disconnects in shielded cubicles.

Long-Range Planning

Through effective long-range planning, it will be possible to make better use of available capacity at the ICPP to permit the reprocessing of many problem-type nuclear fuels for which there are no existing processing facilities in the U.S.A. The fuels involved are the wide varieties of reactor fuel elements that are being used or planned for use. Most of these fuels will become available in quantities economically justifying recovery of residual fissionable material, but in quantities too small to justify individual processing facilities. When examined

individually, the reprocessing economics are marginal, at best; however, on a collective basis when capital, research and development, and operating costs can be prorated against several fuels, the economic picture at ICPP is very attractive. This is true, in part, because the versatile solvent extraction and other equipment, cell space, and manpower can be used to advantage for problem-type fuels to produce a more attractive cost situation than would otherwise exist. In order to produce an attractive cost situation, however, it is also imperative to employ effective long-range planning techniques.

To determine a near optimum operating schedule, as well as to determine the priority for processing any particular fuel load, the economics of fuel reprocessing and waste disposal for numerous alternative cases, in which a ten-to-fifteen year period is considered, are being examined using a cash flow technique. With the cash flow technique, total yearly expenditures--capital, operating, research and development, and any other costs related to a program--are subtracted from the gross annual receipts to yield a cash flow. All cash flows are discounted--put on a present value basis--so that the net effect of various program perturbations can be interpreted in terms of today's dollars. The discounted cash flow concept places a greater value on current than on future dollars in accordance with an assumed interest rate. In this way, dollars to be received or spent in the future are discounted to their lower equivalent value as of today. These present worth values then can be compared directly with dollars to be received or spent today.

In addition to and as part of the economic analysis, the total program is reviewed to determine the long range needs for research and development efforts. Each fuel that might be processed is reviewed for any special requirements, such as new or modified headend or extraction facilities.

CONCLUSIONS

The ICPP uses sequential-type operation, whereby only a portion of the plant extraction and other facilities are operated simultaneously, and other strategies to permit optimum use of available time, manpower, and facilities. This type of operation is believed ideal for a multi-purpose plant and could also be highly satisfactory for a single-purpose plant.