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CURRENT COMMISSION METHODS FOR PRODUCING UO_3, UF_4, AND UF_6

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DISCLAIMER

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PRODUCING UO_3, UF_4, AND UF_6

- Foreword -

The following papers have been prepared at the request of the Atomic Energy Commission with primary reference to its program for encouraging private Industrial Participation in its Feed Materials production operations.

This program has been outlined in press releases of October 27, 1955, and November 18, 1955 and in a "Formal Inquiry for Purchase of Uranium Products from Private Industry" with its appendices and addendum. Briefly, the Commission announced its interest in receiving proposals to be used as a basis for negotiating contracts with qualified firms to process, for a five year period, uranium ores or concentrates to either uranium trioxide, uranium tetrafluoride, or uranium hexafluoride with deliveries to begin about April 1, 1959.

As background for this undertaking requested above, the Technical Information Extension at Oak Ridge has been preparing a Bibliography of Confidential reports on technical aspects of Feed Material process development efforts. Part 1 of this Bibliography, "Uranium Ore Concentrate Refining, Uranium Tetrafluoride Production, and Scrap Recovery" has been issued as TID-3081 and has been sent to all concerns having an approved classified repository under the Civilian Application Program. The reports therein however, were originally prepared only for Commission project distribution. In many cases they are in the nature of interim or progress reports and therefore may be incomplete in that insufficient background or only preliminary and tentative conclusions are presented. These reports cover a period of many years and thus older reports do not reflect the most recent applications of new discoveries and

140 002

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technology. A summary report of the status of Feed Material technology pertinent as of this date to the Commission's Industrial Participation program was seen to be a desirable supplement to these historical documents to interest and aid private firms in the submission of proposals to supply the desired intermediate uranium salts.

The Commission is therefore presenting herein a series of comprehensive technical papers describing the most current production technology and experience of its present operating contractors to accomplish the large-scale processing of uranium bearing material from domestic ores and concentrates to the aforementioned compounds. The objective of these papers is to provide as complete a picture as possible of these production processes and plants within the practical limitations imposed by space, time, and manner of presentation. In general, the principle has been followed of concentrating on those features of the processes, equipment, and plant operation which depend upon, or have evolved from operating experience unique to the uranium industry.

Limited reference is made to historical processes as well as to new developments presently planned for incorporation into the new Feed Materials plant at Weldon Spring, Missouri.

These papers reflect the philosophy, opinion, and experience of the personnel and operating contractor organizations who were responsible for their preparation. In areas of interpretation and evaluation of the existing process technology and experience honest differences of opinion inevitably arise between individuals and between organizations. In no case has the Commission felt it to be wise or proper for it to edit these presentations for the purposes of curtailing arbitrating or reconciling such expressions of opinion.

Of necessity, the various papers and sections and sub-sections within the papers were written simultaneously by different individuals. This has resulted in some variation in method of presentation and in some duplication of the material covered. It is hoped that duplication of coverage and differences in viewpoint between papers will be found to be at least a virtuous fault.

Table of Contents

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SAMPLING

by

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The measurement of uranium content in ores, concentrates, residues, intermediate and finished products is of very great concern to the Atomic Energy Commission and contractors engaged in the production and use of fissionable materials. For this purpose each area performing this work is organized in such a manner that a special group called Accountability is in direct charge of uranium measurements and accounting. Aiding this group on a production basis at Fernald is the Sampling Plant whose distinct and prime purpose is to obtain representative samples by both mechanical and manual methods which have been proven reliable by evaluation.

INTRODUCTION

The Fernald Sampling Plant had as its prototype the U. S. Government owned Sampling Plant in Middlesex, New Jersey, a plant also operated by the National Lead Company.

Although the principal function of the Sampling Plant is one of sampling, and all the operations are directed towards this end, other equally important functions are inherent in the operation to make this plant an integral part of the Feed Materials Production Center which is more commonly designated by the letters F.M.P.C. According to defined process criteria, therefore, the functions of this plant are "to receive, store and sample for assay purposes, and to further store for Refinery feed" such materials as are necessary for the successful operation of the U. S. Atomic Energy program. Primarily, then, the F.M.P.C. sampling operations entail the processing of such uranium bearing materials as virgin pitchblende ore and ion exchange concentrates from the Belgian Congo, ore concentrates from Canada, Australia, Portugal, and the gold fields of South Africa, green salt from the phosphate industries of the southern states, and black oxide and soda salt from the Colorado Plateau. In addition to the above, the Plant is responsible for sampling non-processable low grade residues generated by other operating plants in the area along with feed materials generated by the scrap reclamation plant.

By far the bulk of feed materials sampled concern the off site receipts enumerated above. Pitchblende and ion exchange concentrates, however, are the two materials that give prime definition to the Sampling Plant in terms of process equipment. Feed materials other than these are sampled manually and by procedures that are carefully detailed in order to obtain representative measurements.

Foreign and domestic suppliers have always manifested a keen and active interest in sampling procedures and techniques in order to obtain a just and equitable price for the sale of uranium bearing materials to the U. S. Government. Equally interested is the U. S. Government under the direction of Atomic Energy Commission in unbiased sampling so that the price paid will not exceed the monetary value of the uranium received. Of more immediate importance to the National Lead Company is the fact that the Sampling Plant represents the first stage of a succession of operations towards the production of a finished product. In a very great measure, too, the assays obtained through the sampling procedures will govern the material balances in the rest of the plants or accountability areas, and will measure their operating efficiency in terms of material recovery.

PLANT ORGANIZATION

For purposes of accountability and division of responsibility, the Sampling Plant has been organized into three distinct areas which are designated as the ore storage, ore processing, and sample preparation areas respectively.

STORAGE

The functions of the storage area, while not strictly defined as part of a process, are nevertheless an important adjunct in the proper and efficient operation of the Sampling Plant. Off site feed materials which are packaged in a given number of steel containers of varying sizes are initially stored here. By a system of inspection each shipment is carefully scrutinized. Any discrepancies in lotting and container count or evidences of material losses in transit are immediately noted and reported to the Atomic Energy Commission. Prior to transfer to the Sampling Plant proper, each shipment is segregated into lots which are designated in advance by either the Raw Materials Division in Washington when foreign, or by the producing installations when domestic. Each lot in a shipment is then treated as a distinct entity.

In addition to the identification and storage of off site receipts, the storage area is responsible for the storage of internally generated residues, whether on a long term or interim basis.

ORE PROCESSING AND SAMPLING AREA

The Sampling Plant proper is located in the southwest section of the storage pad and in line with and just north of the Refinery. This is a four story building and in it are housed all the process equipment required for the drying, milling, sampling and weighing of the ores and concentrates. Basically, the building is divided into three sections. The east half of the building is used exclusively for processing pitchblende from the Belgian Congo and has been designed so as to afford the maximum protection to employees against the hazards of radiation either by direct exposure or through the inhalation of air borne dust.

West of the pitchblende area and separated by a radiation barrier is the section for processing ion exchange concentrates also from the Belgian Congo. Although the radiation hazards here are not nearly as great as in the pitchblende line, provisions have also been made to enhance safety by the installation of hoods and dust collector systems.

On the extreme west side of the building is what is commonly referred to as the third system. This was originally designed for processing and sampling non-uranium bearing ores, and is at present being redesigned for sampling small lots of uranium containing materials from both domestic and foreign suppliers. At present these small lots are being sampled manually in this section of the building making use of only the dust collectors of the system.

SAMPLE PREPARATION AREA

The sample processing laboratory is located on the second floor and on the south side of the Sampling Plant. The one section of the laboratory is used exclusively for processing samples of pitchblende ore and radium containing residues. Technicians spend only such time in this area as may be necessary to prepare these samples, and by so doing, limit their radiation exposure time. Adjacent to this area and again separated by a radiation barrier is the section of the laboratory used for preparing all other non-radium bearing samples. Most routine calculations are performed in this room along with the maintenance of laboratory data.

SAMPLING AND SAMPLE PREPARATION

CONGO FEED MATERIALS

As mentioned earlier, pitchblende ore and ion exchange concentrates give prime definition to the Sampling Plant since they are sampled and weighed for official payment purposes. These materials are sold to the United States Government by Union Miniere du Haut Katanga in the Belgian Congo and are controlled in this country by African Metals Corporation, the vendor representatives. Each lot of ore or concentrates to be sampled is processed through the system only in the presence of a vendor representative whose function is to observe that preagreed to processing and sampling procedures are followed without deviation.

PITCHBLENDE PROCESSING

When scheduled for sampling, a complete lot of pitchblende ore is transferred from the storage pad to the Sampling Plant proper. Since the ore is packaged in totally enclosed 55-gallon steel containers, each drum is mechanically deheaded by means of a giant can opener. After deheading and removing the cover, each drum is conveyed to a thawing chamber which is maintained at a temperature of 250° F. during freezing weather and of sufficient surge capacity to accommodate an entire lot. After heating for a period of 24 hours when thawing is required, an operator stationed in a control booth activates the conveyor system and feeds each drum successively to a skip hoist where

140 008

they are elevated to the fourth floor and are automatically dumped onto a vibratory feeder. When emptied, each drum is conveyed through a wash and rinse station where the residual small amounts of ore adhering to the interior of the drum wall are flushed for subsequent recovery by filtration. The cleaned, empty drums exit from the building by means of an enclined belt conveyor and are sent to storage. The ore meanwhile is fed across a magnetic separator for removing tramp iron, then through a jaw crusher for crushing to ½ inch, and finally through a screw conveyor and into a rotary kiln where it is dried to well below 2% moisture content.

As it emerges from the kiln, the dried ore is elevated by means of a bucket elevator and then conveyed through a Natural Frequency conveyor to a surge hopper in preparation for fine grinding. In order to maintain continuity of milling, the surge hopper is initially filled to capacity and then fed continuously after partial discharge.

The milling operation, in addition to being necessary in the preparation of the ore for digestion in the Refinery, also serves to prepare the ore for representative samples. For this purpose a Williams Ring Roll mill is used and is capable of reducing one half inch pieces to a fineness of 95% of the ore passing through a 150 mesh sieve. As the ore is discharged from the surge hopper and milled to rated fineness, it is carried by force, recirculating air to a cyclone where it settles and is discharged to a syntron conveyor which feeds to the first of three Galigher automatic sampling units in series.

At this point the most important operation in the plant takes place. The sampling element in the first unit, and for that matter in all the units, moves back and forth on a track and traverses the ore streams so that an initial 10% portion is uniformly diverted as sample. This 10% portion is next fed to the second sampler which in turn removes a 10% portion. Finally, the 10% portion from the second sampler is fed to the last sampler which removes a 20% portion for an over all gross sample of approximately 0.2%. The reject portion from the first and second samplers merge into a single stream which is conveyed to the drumming station for packaging into pretared 30-gallon drums. The reject portion of the last sampler, on the other hand, is collected directly into a 30-gallon drum and can be used as an auxiliary sample if required, or added to the processed lot. Concurrently with the packout operation, each drum is weighed on two Toledo print weight scales which are maintained in a high degree of calibration and which serve

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as checks on one another to prevent weight discrepancies.

In an operation such as this, dust collectors obviously play an important part in controlling air contamination and in preventing losses of ore. Four dust collectors are part of the system and discharge back to process on a continuing basis.

SAMPLE PREPARATION

Since the total yield of mill sample amounts to only about 0.2% of a lot by weight, the entire quantity is dried for moisture determination. This is accomplished by first blending the total sample in a double cone blender and then drying for a period of not less than 48 hours at a temperature of 235° F. after careful and exact weighing on a Toledo scale graduated in hundredths of a pound. After drying and reweighing for moisture loss calculations, the entire sample is reduced to a 10-pound quantity by successive riffling through a Jones splitter. The 10-pound sample is next passed through a 150 mesh sieve and the oversize milled through a Braun pulverizer until the entire sample is of the desired fineness. After thorough blending on glassine paper, the entire sample is spread out in the shape of a circular disk and by means of a stainless steel spoon transferred to 8-ounce sample bottles in such a manner that all sections of the disk are represented in each bottle prepared. Distribution is now made to the Atomic Energy Commission, New Brunswick, and vendor laboratories for official assaying, to the Company laboratory for accountability assays, and when the agreed to splitting limits are exceeded, to the National Bureau of Standards for umpire assay. Dry basis assays then are applied to the dry weight of material determined by the Sampling Plant weight and moisture determinations as transmitted in official documents to the Commission in Washington, D. C.

ION EXCHANGE CONCENTRATES - INX SYSTEM

PROCESSING

The units of equipment in the INX system are basically identical to those used for pitchblende, but on a reduced and simplified scale. There is no rotary kiln in the system since the concentrates are free flowing and contain no appreciable amount of moisture to interfere with the sampling operation. In place of the fine grinder, a hammer mill located just prior to the sampling units is used for breaking up agglomerates. As in the pitchblende system, three Galigher sampling units in series, automatically withdraw material as sample, but in this case the over all gross sample amounts to 0.1% of an entire lot by weight. Down stream units of equipment for packaging and weighing are the same as those in the pitchblende system which were covered previously.

SAMPLE PREPARATION

Laboratory procedures for the preparation of ion exchange samples represent a departure from the techniques commonly employed. After considerable experimentation it was found that moisture determinations were unnecessary and that assays on an as received basis could be used accurately for measuring the amount of contained uranium in a lot. These procedures have greatly curtailed the large amount of sample work that would otherwise be required, and have resulted in closer agreement between the various assaying laboratories and consequently fewer samples are transmitted to the Bureau of Standards for umpire settlement.

When a lot of concentrates is completed through the process system, the gross sample is immediately transferred to a 2-cubic foot disintegrating blender where it is blended for a period of only five minutes. After blending, a five pound portion is withdrawn from the unit by means of a thief and placed in a four quart Patterson Kelly twin shell blender where it is blended for another five minutes period. Small sample bottles of 35 gram capacity are now filled directly from the blender by means of a stainless steel spoon and transmitted to the various laboratories where the entire quantity in a bottle is dissolved for analysis. The assays again are used for both payment and accountability purposes.

MISCELLANEOUS SAMPLING

By far the greatest amount of work performed by the Plant entails the sampling of feed materials directly from steel drums. Pending design and installation of a third system for automatic sampling, and which to a large extent will eliminate the human element, procedures for sampling directly from drums have been devised and are applied in such a manner as to assure maximum representation.

As in the case of pitchblende and ion exchange concentrates, the two most important aspects of the operation for miscellaneous feed materials entail the functions of weighing and sampling.

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The Toledo print weigh scales used for official and accountability weight data are checked prior to weighing each lot of material. This is done by placing standard weights of 50 pounds. Thereafter the Toledo scales are checked periodically during the operation by employing a standard weight of 500 pounds. In this manner weight discrepancies and malfunctioning of the scales are readily detected and immediately rectified by recalibration and servicing.

When the sampling and weighing operations are intended primarily for official payment to a foreign or domestic supplier, contractual agreements most generally stipulate the determination of gross weights of each lot prior to the withdrawal of material as sample. In this case, and in order to meet accountability requirements, each drum in each lot is also weighed after sampling so that the exact weight of each container is known for transfer purposes. Tare weights of containers are determined after consumption of the material in the Refinery, or in urgent cases by immediately redrumming. When sampling for accountability only, the post sampling gross weights prevail.

Miscellaneous sampling is accomplished by means of slotted pipes of varying diameters which are fabricated from schedule 80, stainless steel, and of sufficient length to reach the bottom of the drums to be sampled. Drum to drum sampling is performed in a random manner by employing a three-hole template and a listing of random numbers which are specifically selected from statistical tables for each lot.

The design of a template is simple and consists of medium gage sheet metal with a radius equal to the radius of either a 30 or 55-gallon steel drum. On the radius of the circular section, three equally spaced holes are cut out with sufficient clearance to accomodate a pipe sampler. Starting at the periphery, the openings along the radius are marked consecutively from 1 to 3. To complete the unit, handles are welded to the top section to facilitate removal.

The listing of random numbers successively applicable to each drum to be sampled are devised in such a manner that the relative occurences of the positions 1, 2 and 3 on the template are in the ratios of 5-3-1 which correspond to the ratios of the areas or volume of the concentric rings formed by a continuance of each opening around the template.

SAMPLING

When ready for sampling, the drum covers are removed singly and replaced with the template. The sample pipe is now placed in the template opening selected from the listing of consecutive random numbers, and by means of an air hammer, driven vertically to the bottom of the drum. For free flowing materials the pipeful of sample is removed only after tilting the drum in a horizontal position. For non-free flowing materials the pipeful of sample is withdrawn vertically. All samples so obtained are immediately placed in a stainless steel container which is fitted with an air tight cover to prevent changes in moisture content due to atmospheric exposure.

SAMPLE PREPARATION

With the wide variety of materials which are currently sampled by means of the slotted pipe, the techniques and procedures for their preparation into assay samples depend on such factors as moisture content, homogeneity, particle size and uranium content. Generally, whenever a material appears uniform and has a particle size in the range of minus 42 mesh, "as is" samples are prepared, following the procedures which were outlined for the ion exchange concentrates. Samples on a dry basis follow the procedures outlined for pitchblende ore, differing only in the fact that they are ground to 80 mesh instead of 150 mesh.

EVALUATION OF SAMPLING METHODS

Acceptance of the Pitchblende and Ion Exchange systems of the Fernald Sampling Plant by the Vendor and the Atomic Energy Commission was contingent upon the successful performance of the process equipment designed to accomplish accurate weighing and sampling. The basic procedures for determining the accuracy and precision of the Fernald system consisted of reprocessing both types of material which were previously sampled officially at the Middlesex installation in New Jersey. A comprehensive comparison of data between the two plants served to measure the reliability of the newly installed systems at Fernald. Since the efficiency of sampling at Middlesex plant had been previously established by an independent program of evaluation, the comparison of Fernald sampling results was recognized to be valid by both the Vendor and the Commission.

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Establishing the reliability of the Ion Exchange system at Fernald was relatively simple, and deemed acceptable for official sampling after five lots of

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material had been processed and evaluated. Samples were taken by means of automatic Galigher units in the system, and in duplicate with the slotted pipe. These were then prepared in the laboratory on both an "as is" and dried basis. Agreement between the two plants was excellent, and established that the "as is" was the preferable method of sample preparation.

On the other hand, the evaluation of the Pitchblende system was more complex and entailed work that extended over the entire year of 1954. As previously noted, the results obtained at the Middlesex Plant were considered reliable standards against which Fernald could be compared with confidence. In evolving a sampling system that would perform with a high degree of acceptability it became necessary to process a total of 35 lots arranged into five distinct groups. Each group was treated as a distinct entity, initially to limit the amount of work that might be required in establishing a successful operation, and after the first group, to measure the effect of mechanical changes necessitated by assay discrepancies between the normal sample and reject portion of the last Galigher sampler which was collected separately.

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Recognizing that the lack of agreement between the normal and reject samples of the system might cause undue delays in obtaining plant acceptance, an auxiliary method of sampling was introduced at Fernald. As a preliminary test, four lots in the second group were sampled in duplicate with a motorized auger and after first processing through the Plant system. Reasonably close agreement between the original and duplicate auger samples was recognized by all parties having an interest in the program, causing this method to become part of the test work with a view to its acceptance as official on an interim basis until such time as the system differences could be rectified.

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Original and duplicate auger samples were then taken from each lot in the third group. Upon receipt of analyses of the lots in this group, and observing the lack of bias between the auger samples, the duplicate sample was discontinued for subsequent test work. Two additional groups of ore lots were next processed and samples prepared by the various method indicated.

At the beginning of the test program, and prior to the introduction of the auger sampling method, initial assays made it apparent that a bias existed between the reject and normal stream of the last Galigher sampler. The

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difference in assay between the two streams amounted to approximately 0.8%. An investigation of the cause of the difference led to the conclusion that the effect of ventilation through the system was biasing the samples by differentially withdrawing the lighter and lower assay fines from the two sample streams. As originally installed, the samplers were directly connected to the down stream units of equipment which were under strong ventilation to prevent plant air contamination. A certain amount of ventiallation was also noted from the rotary feeders discharging the up stream dust collectors and cyclone. The rotary feeders servicing the dust collectors and cyclone were repaired and made dust tight, and the down stream air loading rebalanced so that a reasonably static condition prevailed through the samplers. After making the above changes, the ore lots in group 2 were processed to completion. Results of the first five lots in this group showed closer agreement than previously noted, but reverted to wide differences for the last four lots in the group, pointing out the fact that air equilibrium could not be maintained. To eliminate completely the effect of down stream ventilation, a rotary air lock valve was next installed at the base of the reject chute directly below the last sampler. Two lots of ore from group 3 were then processed in succession. At this point a consultation with a field engineer of the Galigher Company resulted in modifications to the last sampler. The width of the syntron feeder to the sampler was narrowed from 12 to 6 inches in order to increase the cross sectional height of the feed stream which would tend to curtail dusting. To compensate for the change in the feeder width, the stroke of the oscillating element of the sampler was decreased from 18 to 10¼ inches, increasing the instream factor above original design. The effect of the dual change became immediately evident since with the remainder of the lots in the third group the sample size increased by a factor of 50%. The program was continued on this basis, processing the remaining two groups of lots. No further changes or equipment modifications were required to make the pitchblende system function representatively and officially acceptable.

PROJECT WIDE SAMPLING

In addition to the large amount of effort required by the Sampling Plant in determining uranium content in the numerous commodities sampled, other Plants and areas sample extensively at the various stages of the operation and for both process control and accountability purposes. All Plants and areas have the requirement of knowing at

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all times the quantity of uranium handled and on hand. With the exception of the Scrap Plant which transmits samples of finished product to the Sampling Plant for preparation, all other samples taken, whether manually or by automatic samplers, are submitted directly to the analytical group in the Technical Division of the Company where they are analyzed for uranium content and impurities in order to control the rigid specifications required.

SUGGESTED READING

Costa, J. J., *Report on the Evaluation of the INX System of the Fernald Sampling Plant* (1954) (FMPC-421)

Costa, J. J., *Report on the Evaluation of the MGX System of the Fernald Sampling Plant* (1953) (FMPC-332)

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URANIUM OXIDE REFINERY

ETHER PROCESS

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I. INTRODUCTION AND SUMMARY

It is the purpose of this paper to give a basic understanding of the processes used at St. Louis for the preparation of uranium trioxide of nuclear grade from crude uranium chemical concentrates whose composition is approximately uranium oxide or diuranate salts. The underlying reasons for the various steps taken will be explained and the general nature of the equipment used set forth. Operating procedures will be discussed in sufficient detail to make the operation of the process clear. It should be borne in mind that many of the complexities of the equipment and operation are dictated by the extreme health hazard involved in handling the material and by the potential necessity of eliminating virtually all losses.

The raw materials used at the St. Louis refinery are from many sources. Many of these sources now use ion exchange as a method of uranium recovery from acid digestion of low grade ores, followed by precipitation of ammonium diuranate which may be more or less decomposed by heating to crude U_3O_8 (nominal formula). Others precipitate the uranium from acid leaches with sodium, calcium or magnesium hydroxides and ship the dried diuranate salt to the refinery.

These materials dissolve in nitric acid with a relatively small amount of insoluble residue. Such solutions or slurries are used directly for extraction without filtration except in unusual cases. Extraction of the uranyl nitrate from the digest liquor into diethyl ether is accomplished through countercurrent contact in an extraction column. The uranyl nitrate is then re-extracted continuously from the separated ether layer into water in another extraction column. This water layer, containing virtually all of the uranium, is freed from ether, concentrated, and the material put through a second ether extraction step for further purification. The final steps in the process involve concentrating the highly purified water solution obtained from the second extraction, and then thermally denitrating in gas fired kettles. The product is a bright orange powder, UO_3, containing small amounts of residual water and nitrate.

In the following sections the basic chemistry of the process will be discussed and overall material balances given. There will also be presented a description of the plant and equipment and its auxiliaries and a discussion of factors involved in operation.

II. HISTORY AND CHEMISTRY

The large scale production of uranium oxide of nuclear reactor quality was first undertaken in the United States in 1942 by Mallinckrodt Chemical Works, at the request of the OSRD. The process was based on the high solubility of uranyl nitrate in diethyl ether, a property described by Peligot a century earlier and suggested for this purpose by Dr. J. I. Hoffman of the National Bureau of Standards. A production rate of about a ton a day of extremely pure oxide was achieved very early, and such oxide comprised part of the charge of the first successful chain reacting nuclear pile on December 2, 1942.

The first process was a batch operation, employing as raw material a commercially pure black uranium oxide, U_3O_8. This was dissolved in nitric acid and the solution was adjusted to essentially no excess acid over that required for $UO_2(NO_3)_2$, and was boiled down to a very concentrated solution, before contacting the hot solution with pure cold ether. With such concentrated solutions it was possible to extract about 75% of the uranyl nitrate into a large volume of ether, leaving the remainder of the uranium and most of the impurities in a small aqueous layer which could be reworked several times to bring overall recovery up to about 95%. The residual impurities were washed out of the ether layer with successive small portions of distilled water. The uranyl nitrate was then re-extracted almost quantitatively with distilled water by using a water volume equal to the volume of ether extract. This pure aqueous solution was converted into UO_3 by boiling down to drive off all water and eventually all nitrogen oxides.

In 1946, substantial improvements were made in the ether extraction process, both as to the ability to handle lower grade and more complex raw materials, and as to continuous countercurrent operation and larger scale of the plant. These changes were made to accommodate pitchblende ore as a raw material, and were later modified to handle the higher grade concentrates now produced as a result of major developments in the field of raw material recovery. The major chemical change was to precede the "neutral" extraction described above by an "acid" extraction step to insure essentially complete uranium recovery from the ore. For "acid" extraction, the digest liquors are adjusted to 1$\underline{N}$ excess free nitric acid and 4.5$\underline{N}$ (nitrate basis) of salts other than uranyl nitrate. Under such conditions the uranyl nitrate is driven almost quantitatively into ether in about four countercurrent stages, at an ether/aqueous ratio of less than 2. With an acid extraction step for recovery, and a neutral extraction step for final purification, a remarkably efficient and flexible process for refining a wide variety of raw materials was made available, as evidenced by over nine years of successful operation.

The recovery of uranium from low grade ores was originally an acid leach, filtration, caustic precipitation process yielding a product of low assay. Refinements and modifications of this basic process as developed by the vanadium producers of the Colorado plateau and others now yield products assaying 75% U_3O_8 and containing very few troublesome impurities except vanadium. Some of these products are "soda salts" (sodium diuranate) while others are "black oxides" (actually crude UO_2 produced by a reducing carbonate fusion of caustic precipitates). Others are based on a carbonate, rather than an acid, leach of the original ore, while still others are precipitated as a uranous phosphate rather than a sodium diuranate. All of these products have been refined routinely by the two cycle ether process, although occasionally some blending has been necessary.

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With the advent of ion exchange as a recovery method from low grade ores, high assay (75% or more) concentrates are readily attainable, and the presence of troublesome impurities is minimized.

In present refining practice ore concentrates are dissolved in nitric acid, as in these examples:

1) $Na_2U_2O_7 + 6HNO_3 \rightarrow 2UO_2(NO_3)_2 + 2NaNO_3 + 3H_2O$

or 2) $UO_2 + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2NO_2 + 2H_2O$

or 3) $U_3O_8 + 8HNO_3 \rightarrow 3UO_2(NO_3)_2 + 2NO_2 + 4H_2O$

or 4) $U_3(PO_4)_4 + 12HNO_3 \rightarrow 3UO_2(NO_3)_2 + 6NO_2 + 4H_3PO_4$

or 5) $(UO_2)_2(OH)_2SO_4 + 4HNO_3 \rightarrow 2UO_2(NO_3)_2 + H_2SO_4 + 2H_2O$

or 6) $Na_2O \cdot 2UO_3 \cdot V_2O_5 + 6HNO_3 \rightarrow 2UO_2(NO_3)_2 + 2NaNO_3$
$+ 2HVO_3 + 2H_2O$

In all cases it is necessary to use more nitric acid than is called for by these equations in order to provide a sufficient salt background to drive the uranium into the ether, and also in order to hold uranium in solution in the presence of certain impurities. For example, phosphate, vanadate, or molybdate ions tend to precipitate uranium in the absence of excess free acid. The solubility of such compounds as UO_2HPO_4 is a direct function of the acidity, but fortunately considerable attention has been given to this factor both in the raw materials and refining fields, so that this potential source of uranium loss is now well understood. Also, some of the other cations, e.g., ferric iron, form soluble complexes with these same ions in acidic solutions, so a further means of control through choice of composition of the salt background is also available.

Impurities which can be troublesome in a different way are those which form soluble complexes with uranium. These include sulfate and fluoride, and they affect the extraction step by tending to hold uranium in the aqueous phase. This can be seen by the following equilibria:

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(1) $UO_2(NO_3)_2\cdot 4H_2O\cdot 2(Et)_2O + 2H_2O \rightleftharpoons UO_2(NO_3)_2\cdot 6H_2O + 2(Et)_2O$

(2) $UO_2(NO_3)_2\cdot 6H_2O \rightleftharpoons UO_2^{++} + 2NO_3^- + 6H_2O$

(3) $UO_2^{++} + 2NO_3^- + 4H^+ + 2SO_4^= \rightleftharpoons UO_2(SO_4)_2^= + 4H^+ + 2NO_3^-$

In aqueous solution excess NO_3^- from neutral salts will tend to drive more uranium into the undissociated form of uranyl nitrate. This tends to combine with ether, as in the left in (1), and extraction occurs. If an anionic (or neutral) complex is formed, as on the right in (3), there will be less uranium in the nitrate form and extraction will be hindered. This effect, conversely, is useful in ion exchange work, and most uranium recovery by ion exchange is accomplished by means of anionic resins from sulfate solutions. Ferric iron helps extraction into ether from solutions containing sulfate by tying up the sulfate in a ferri-sulfato complex. Similarly aluminum offsets the effect of fluoride on uranium extraction.

Fluoride is a harmful impurity in another way, through its corrosive action on stainless steel. Aluminum is again helpful here, as is iron to a lesser degree with chloride. The limitation on the use of iron with chloride arises from the ether solubility of ferric chloride, so that the chloride content of feed solutions must be carefully controlled.

Other impurities of special significance to this purification system are those with very high neutron cross section and only moderately low distribution coefficient into ether. The most important of these is boron, which is reduced in concentration from feed to product by a factor of only about 1000.

Finally, any extraction system is limited by the physical characteristics of the two liquid phases to be separated. Phase separation can be grossly affected by the character of solids present, and this is exemplified by the effect of gelatinous solids such as silicic acid. Under certain conditions such solids promote the formation of relatively stable emulsions, thereby preventing normal operation of the countercurrent system. Unfortunately the total silica content of the system is not a good measure of the tendency of any given feed solution to form stable emulsions. The "soluble silica", perhaps a colloidal form, is more significant, but a final answer to this problem is yet to be found. Silicic acid is also a scale former in plant equipment, as is calcium sulfate to an even greater extent. Fortunately, raw materials causing such problems of physical operability are becoming less common and can usually be handled by blending of plant feeds.

Extraction alone does not give adequate decontamination of certain of the impurities found in raw materials, especially in a continuous countercurrent system, where phase disengagement is allowed very little time to occur. To remove entrained droplets and to take further advantage of the low distribution coefficient of the impurities, a partial re-extraction, or scrub, of the extract is employed. This results in a great improvement of product purity with the penalty of only a small (e.g., 10%) recycle of uranium in the system. After scrubbing, it is easy to re-extract all of the uranium into a moderate volume of pure water, since the equilibrium favors water in the absence of salting agents. This can be made even more favorable by using warm water for re-extraction, since higher temperature favors the ionic rather than the molecular form of uranyl nitrate (see equilibrium equation above).

The use of two cycles of ether extraction permits some adjustment of chemical conditions so that the net purification is greater than for two duplicate cycles in series. For example, by getting rid of excess nitric acid prior to the "neutral" extraction, corrosion product contamination is markedly reduced. The boil down under netural conditions also converts certain impurities from ether soluble to water soluble forms. Heteropoly acids like phospho-molybdic acid ($H_3PMO_{12}O_{40}$) are ether extractable in the presence of excess nitric acid, but they convert to simple acids ($H_3PO_4 \quad 12MoO_3$) when a stoichiometrically neutral solution of uranyl nitrate is heated. The simple acids are much more soluble in water than in ether, and are therefore left behind during the neutral ether extraction.

Having obtained a uranyl nitrate solution of ultra-high purity, it is necessary to convert it to oxide with a minimum of recontamination. For the anticipated use the product must also be of high density and of a proper crystal structure and particle size to be chemically reactive. Current practice is to boil the solution to the approximate composition $UO_2(NO_3)_2 \cdot 6H_2O$ in conventional stainless steel evaporation equipment, and then complete the dehydration and denitration in stirred stainless steel pots.

$$2UO_2(NO_3)_2 \cdot 6H_2O \xrightarrow{\text{heat}} 2UO_3 + 4NO_2 + O_2 + 12H_2O$$

Overheating produces a reddish-orange material which contains two crystal modifications (by X-ray patterns). Underheating leaves excessive water and nitrate in the product. The proper decomposition sequence produces yellow-orange material which is partly crystalline and partly amorphous, containing some UO_3 hydrate and a little residual nitrate. A reactivity test is described elsewhere.

Most of the metallic impurities are derived from the stainless steel, and these are kept at a minimum by avoiding excess acid in the original "OK liquor". Other impurities may affect the reactivity, and in any case are detrimental to the projected use. It is especially important that elements of high neutron cross-section be very low, and this is checked by means of a neutron absorption test ("shotgun test"). A typical analysis, by chemical and spectrographic methods, follows:

Nitric Insol	10 ppm
Fe	11
Mo	<1
Ag	<0.1
Cr	2
Cu	<1
Ni	3
Pb	<1
Sn	<1
B	<0.15

III. MATERIAL BALANCES AND ENERGY REQUIREMENTS

1. Uranium Material Balance

Because of the monetary value of uranium, all material processed must be accounted for. Current regulations of the AEC require that this be accomplished through the determination of a monthly material balance which is submitted to the accountability group of the supervising operations office shortly after the end of a calendar month. Such a material balance must be based upon auditable basic data which is generated throughout the month. This material balance is made by processing units mutually agreed upon with the operations office. The input to such a processing unit is determined by sampling, weighing, and assaying of all feed material. Product is measured by the same method. The material balance is completed by taking a monthly inventory of work-in-process. Such an inventory requires previous calibration of all vessels containing uranium in solution, thorough preparation to insure accurate measurements, and careful supervision. The size of a processing unit may be any that is convenient and agreeable to the operations office. Subdivision below a certain point is expensive in terms of the accounting and analytical work required to measure liquid flows between processing units. Therefore, in the St. Louis refinery the material balance area has included the complete refinery and has shown good control throughout its history.

At the request of the AEC, statistical evaluation of all measurements has been instituted as a part of the accountability routine. Such statistical evaluation indicates an allowable discrepancy of approximately 1.4% per month varying slightly upon the amount of production. This percentage of allowable discrepancy reduces to .2% for a twelve month period because the effects of the beginning and ending inventory decrease. The .2% value is the difference between the statistical evaluation of the feed material and product measurement methods. During 1954 the discrepancy for this refinery was 2,000 pounds of apparent gain. The discrepancy in the first eight months of 1955 was 3,700 pounds of apparent loss. Such discrepancies are well within the statistical limits described above. No serious discrepancy has developed within the refinery with the exception of a short period when a bias appeared in a vendor's sampling methods. No such bias has ever occurred in the Colorado feed materials, but such a bias is possible as new **sites** with no previous experience in sampling come into production. Some Colorado mills have shipped material containing large amounts of trash which must be separated previous to digestion, and some method of accounting for such inclusions must be provided by the operating contractor.

The actual uranium flow through the refinery process on the basis of an initial digest of 1,000 pounds of Colorado type feed materials is approximately as follows:

Digest input	1,000 pounds
From digest to feed make-up	1,000 pounds
Neutral ether raffinate to feed make-up to be combined with digest product	240 pounds
Total feed to acid extraction	1,240 pounds
Acid extraction product (NOK)	1,236 pounds (Note No. 1)
Neutral wash column raffinate to be combined with NOK	314 pounds
Total feed to neutral extraction	1,550 pounds
From neutral extraction to neutral washing	1,310 pounds
From neutral wash and re-extraction to pot room boil-down	996 pounds
From pot room boil-down to packaged product	995 pounds (Note No. 2)

Note No. 1

Loss from the acid ether extraction appears in the raffinate product which is then precipitated with lime and stored in bulk in the open at a separate site.

Note No. 2

Approximately 0.1% of the total throughput is lost in various exhaust streams such as stack exhausts, water losses from nitric acid concentration, and other miscellaneous processing sewage. These losses are measured intermittently and a general level established to use as a constant loss estimate in the material balance. Continual sampling of such losses has not proven economical.

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The maintenance of the required records for the accountability program requires nine accountants and clerks. Mathematical methods for the statistical applications described are determined by statisticians reporting to other supervisors. At the present time Production Control and Accountability are separate groups in this refinery. However, it is expected that these groups will be combined in the near future with some improvement in communications and amount of records being kept.

2. Chemical Requirements

The process as described previously requires certain chemical reagents to complete the required reactions. The first reagent required is nitric acid for the dissolution of the incoming ores. At present, this refinery uses technical grade 60% acid. Such acid is available from a number of suppliers in tank car quantities. It has been our experience that each 100 pounds of UO_3 product consumes approximately 180 pounds of 60% nitric acid.

Nitric Acid Balance
Per 100 Lbs. Products

Input		Recycle	
Digest	140 lbs.	Absorption	88 lbs.
Adjustment and Salting Agent Dissolution	161 lbs.	Distillation	33 lbs.
			121 lbs.
		Loss	
		Raffinate	172 lbs.
		Absorption (Gas)	7 lbs.
		Product	1 lb.
			180 lbs.
Total	301 lbs.	Total	301 lbs.

Off-gas recovery has varied from approximately 85 to 95% depending upon production load.

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The nitrate values contained in the raffinate are recoverable by denitration of the metal nitrates with heat in a system similar to that used for denitration of uranyl nitrate. At the present time this refinery is operating a denitrator on part of the raffinate produced and precipitating the balance with lime. This lime results in the precipitation of any soluble metal nitrates as the hydrated oxide. This oxide is then filtered and stored in bulk in the open. The neutralizing of these nitrate values requires approximately 50 pounds of lime per 100 pounds of UO_3 produced.

The ether extraction system requires the addition of certain multi-valent ions to the extraction feed solutions to form the proper ionic background for efficient extraction of the uranium. Depending upon the chemistry of the incoming feed material, several such ions can be added. At this refinery we have used iron, magnesium, calcium, and aluminum. Addition of calcium, which is the least expensive salting agent, cannot be accomplished if excessive amounts of sulfate are present due to excessive scaling of the equipment. Iron in the form of scrap, consumes nitric acid and is widely variable in quality and physical form. Magnesium oxide and aluminum hydroxide are currently in use with very good results. Aluminum hydroxide has been added to complex the fluoride ion and it has been found that it serves well as a salting agent and is available at a lower cost than magnesium oxide. These salting agents are required to the extent of approximately 20 pounds per hundred pounds of UO_3 product.

The use of ether as an extracting solvent, though operated completely in a system which is vented to house condensers having good solvent recovery, results in some loss of ether to the atmosphere. The make up of this loss requires approximately two pounds of alcohol free diethyl ether per 100 pounds of UO_3.

Some Colorado feed materials require filtration before introduction to the ether house so as to minimize operational difficulties. To accomplish such filtration it is often necessary to add filter aid in the form of diatomaceous earth. At the present time such filtration requires approximately one pound of filter aid per 100 pounds of UO_3.

At the present time the source of purified water for extraction is city water which has been de-ionized through an ion exchange medium. The cleaning and reactivation of this ion exchange system

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requires about 1/2 pound of sulphuric acid and 1/2 pound of sodium hydroxide per 100 pounds of UO_3 product.

3. Steam Requirements -5,000 t/y U_3O_8 equivalent

Approximately 40,000 pounds per hour of steam is required for the refinery. This steam is used primarily for digestion, boil down at the feed make up area, concentration of the re-extracted uranium solutions before and after the neutral ether extraction. During the cold weather months this amount will increase by approximately 50% as a result of heating requirements. Steam is furnished to the process at 100 pounds gage.

4. Water Requirements -5,000 t/y U_3O_8 equivalent

The operation of this refinery requires water for cooling, washing of solvent streams, and sanitary purposes. Therefore, such water needs to be of three types:

a. Cooling water can be either ground or surface water sufficiently free of solids and precipitating chemicals to avoid fouling of heat exchanger surfaces.

b. As described previously, the uranium extracts are washed and re-extracted with purified water. Purification by distillation or deionization produces water of sufficient purity.

c. Process water is of standard potable purity.

At the present time, this refinery requires approximately the following amounts of these waters:

Purified water	3,500,000 gallons/yr
Cooling water	1,020,000,000 gallons/yr
Process water	320,000,000 gallons/yr

The installation of a cooling tower at this refinery was shown to be economical on the basis of the cost of city water. If this cooling water was not available, the total process water requirement would increase to 1,250,000,000 gallons/yr.

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5. Electricity

In the present refinery, electricity is not used for any process purpose other than motor drives and lighting. It has been our experience that such uses require approximately 1 kilowatt hour per pound of product. Such usage includes the consumption of auxiliary facilities. The gas requirements described below could be replaced by electrical heating if available at a competitive price.

6. Natural Gas

This refinery is equipped with denitration pots heated by natural gas furnaces. These furnaces consume approximately 3,500 cubic feet per thousand pounds of UO_3 produced.

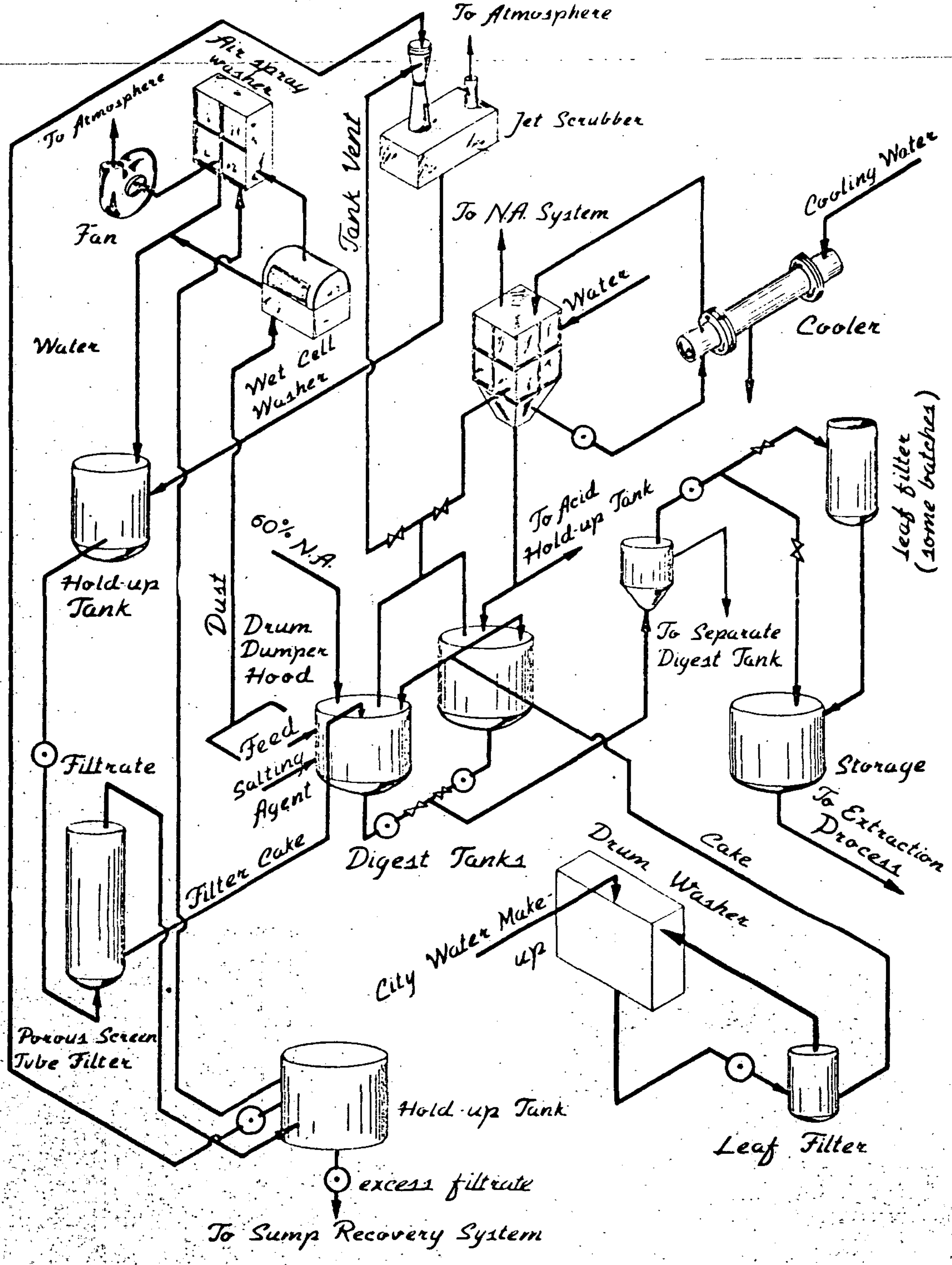
IV. PROCESSES AND ENGINEERING OF PLANT

1. Digestion of Raw Material - Soluble Feed Area

The soluble feed area, used to introduce acid soluble feeds into the refinery, is located as a unit process step in a bay within the main refinery building. This bay has approximately 1,000 sq. ft. of floor space. Operation of the equipment is carried out at three levels: the ground floor, and two deck plate mezzanines. The headroom required for installation and operation of the equipment is approximately 30 ft.

The major elements of the process and principal equipment units are shown diagramatically in Figure 1.

Steel drums (55 gallon) of feed material are brought to the area on pallets by a fork truck and are then set on an enclosed roller conveyor to the drum dumper where the lids are removed and pushed through a slot to the lid washer. The drum dumper, known as a skip-hoist, is a completely enclosed motor driven unit about 4' wide and 5' deep. The drum is clamped in the lifting rig by a pair of steel bands and the drum on the rig is elevated and dumped by means of an overhead 5 H.P. electric motor and drive via a pair of steel cables. The drum rig is mounted on wheels which move inside of a pair of tracks. The wheels and tracks act as guides during the elevation and are arranged so that the rig pivots about the upper wheels when in the uppermost position, thereby inverting the drum. A heavy steel grate is mounted in the drum dumper just below the inverted drum to separate large unwanted foreign objects from the feed; it



Soluble Feed Preparation

FIG. 1

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has openings which are approximately 4" x 4". A manual drum beater operated from the loading position is used to break loose material clinging to the sides of the drum while the drum is inverted. The empty drum is released onto the grate and an air operated level pushes the drum through a side door in the dumper enclosure and onto a continuous linked motor driven conveyor. This conveyor, which is powered by a 1 H.P. motor and speed reducer, is enclosed with bolted steel panels and passes through the drum washer which forms a continuous part of the enclosure. The drum is flushed off by jet nozzles aimed at the inside and side of the drum and is then lowered vertically to the main floor by a cable drawn car housed in a bolted panel enclosure. The washing liquid for both the drum and lid washer consists of recycled (200 gpm) wash water (city water initially) which has been previously used and filtered in a vertical precoat leaf type filter. The recycle system consists of a steel centrifugal pump and steel piping (3" suction, 1 1/2" discharge). The filter cake is flushed off periodically to one of the digest tanks. Both the drum washer and lid washer are vented directly to the atmosphere through mild steel ductwork.

Dust in the drum dumper is controlled by ventilating the enclosure with a 10 H.P. centrifugal fan which removes approximately 3,500 cubic feet of air per minute. The fan pulls the air through a wet cell type separator and then an air spray washer before exhausting to the atmosphere. The water from this operation is filtered in a porous screen tube type filter. The filtrate is recycled to the air washers with a 2" x 2" stainless steel 5 H.P. centrifugal pump. Excess filtrate goes to the sump. The cake is flushed to the digest tank by back washing the filter. The fan, ductwork, and other component parts are constructed of mild steel.

All lines used for handling of fresh acid are of stainless steel Type 347, having welded or flanged connections with Teflon gasket. Wherever possible pipe is bent rather than using fittings to avoid as many points in the system as possible where leakage can occur. A 1 1/2" line is used to pump fresh 60% N.A. to the digest tanks for the initial filling. The volume in the tanks is determined by stainless steel calibrated measuring sticks with the tanks being filled to a predetermined volume corresponding to a measurement on the stick.

Raw material is fed into the acid-filled tanks by a stainless steel screw type conveyor which has a stainless steel housing and which is fitted with a hopper having a volume equivalent to approximately one drum. This screw is located directly below the grate in the drum dumper and discharges from the center to both ends so that it serves both digest tanks. It is powered at one end by a 5 H.P. motor and variable speed drive. The flow of material from the screw can be shut off at either end by means of neoprene sleeve pinch-type valves which are actuated by a 3/4 H.P. motor and speed reducer.

The digest tanks are fabricated from Type 347 stainless steel and are of all welded construction using Type 347 welding rod. The tanks are cylindrical (7'-6" diameter by 7'-6" high) with a bulged bottom and each have a capacity of 2,500 gallons. They are each mounted on the floor with four "I" beam legs resting on individual footings. The design and operating temperatures for these tanks are 300° F. and 275° F., respectively. Heat is supplied to the batch by a 2" diameter Sch. 40 seamless stainless steel Type 347 pipe coil having 6 turns approximately 6' in diameter. The top turn of each coil is approximately one-third of the cylindrical height of the tank from the bottom. The tanks are not insulated. All parts on the tanks are flanged, and each tank has a manhole with swing cover. For momentary inspection these covers have smaller swing type covers mounted on them to prevent the necessity of opening a large port which would permit large amounts of fumes to be discharged into the manufacturing area. Each tank is fitted with a backward discharging turbine type, double impeller agitator driven at 90 rpm by a 15 H.P. motor. Vertical baffles inside the tanks help increase the agitation efficiency. Instrumentation on the tanks consists of temperature indicating controllers which control the flow of steam to the coils.

The vent system for the tanks consists of two alternate systems - a jet scrubber and a fume scrubber - condenser. During digestion of soluble, non-oxidizing feeds, the off-gases and condensables are passed through a 4" venturi jet type scrubber which uses the filtered air spray and wet cell wash water as a scrubbing liquid. The scrubbing liquid is circulated through the jet by a 1 1/2" x 1 1/2" 7.5 H.P. centrifugal pump and this liquid plus the condensed vapors are collected in a 350 gallon separator just below the jet. The liquid from the separator returns by gravity to a 2,000 gallon holding tank. The non-condensable off-gases escape to the atmosphere through a 10" stainless steel duct. An all stainless steel fume scrubber and condenser is alternately used when large amounts of nitric oxide fumes are given off during digestion. This scrubbing system consists of a small jet mounted in the duct work to cool and condense the nitric acid vapors. A separator with a weir overflow is used to receive the recycled water which is continually recirculated through the tube of a shell and tube heat exchanger and back to the scrubber jet. The suction and discharge lines on the recirculation pump are 3" and 2 1/2" Sch. 40 stainless steel lines, respectively. The pump is a cast high alloy pump with a 10 H.P. motor. Tower cooling water is used in the cooler which has a heat transfer surface of approximately 160 sq. ft. Al ductwork in the two venting systems is of heavy gauge stainless steel construction having standard flanged connections with Teflon gaskets. Flanged connections are used to facilitate rapid assembly and disassembly for cleaning. Large flanged plug-type valves in the ductwork determine the direction of flow of the off-gases and fumes.

The process pumping facilities for the digest tanks consist of two pumps so arranged that either pump may serve either tank. These pumps have high Ni-Cr cast alloy bodies which are generally used throughout the process because of their superior corrosion-erosion resistance compared to that of stainless steel. They are powered with 10 H.P. motors. They serve two purposes -- to recirculate the batch while it is digesting in order to aid the mixing action of the agitator and to pump out the batch to storage when digestion is completed. The large amounts of sand and gravel contained in the feed make it necessary to install high throughput stainless steel screens on the suction of the pumps. These screens consist of 1' diameter by 3' long tanks positioned horizontally near the pumps and which have a flanged cover at one end. The screen, which has approximately 1/8" square openings, can be slipped out of the end with the large cover flange when cleaning is necessary. These strainers are connected to the pumps so that each pump can use either strainer. Standard traps are not used because they do not offer enough capacity and restrict the flow. The piping between the pumps, tanks, and strainers and the recirculation and pump-out piping is 2" and 3" diameter Sch. 40 Type 347 stainless steel. Again, all connections and valves are flanged and Teflon gaskets used. Valves are of two types - plug cock and wye type with stainless steel body, plug, and trim and Teflon seats and packing. These type valves are used because they offer fewer pockets and restriction to flow of slurries than do other types. Some of these valves have the high Ni-Cr composition similar to that of the pump casings.

For accountability and housekeeping reasons the digest area has its own floor sump located at the low point in the floor. This sump is approximately 3' in diameter and 6' deep and is covered with a stainless steel grate. The sump has its own stainless steel centrifugal pump (5 H. P.) which is used to periodically pump out the accumulated sump liquor to large sump recovery tanks elsewhere in the refinery. The suction and discharge lines for the pump are 1 1/2" Type 347 stainless steel pipe. The suction line is fitted with a standard stainless steel trap to protect the pump from solids which are flushed into the sump. The top of this trap can be removed and the trap cleaned without removing it from the line.

Because of occasional tank boilover, the presence of acid fumes, and, in general, the necessity for handling nitric acid, special consideration must be given to construction materials other than for process equipment and to electrical fixtures. The main floor of the area is made completely of acid proof brick and mortar including pump bases. To prevent corrosion of the steel channels supporting the pumps on these bases, the top of the channel which protrudes above the acid brick base is covered with a snug fitting light gauge piece of stainless steel. The top of the base is also covered with an acid resistant mastic coating to close the juncture between metal and brick. All external surfaces in the area, including structural steel, steel process equipment, walls, steel pipe, etc. are painted with acid resistant paint. Electrical fixtures are of the vapor-tight class to prevent entrance of acid fumes. Each deck plate mezzanine has its own grate covered drain so that acid and other material spilled on the deck plate can be flushed away. These drains empty by gravity to the main floor sump. For safety, the steel stair steps between levels have abrasive type treads to prevent slippage of the operator's feet; also, access to and from the operating levels is so arranged as to permit rapid movement of the operators.

In general, the modifications to the existing Mallinckrodt plant's digest area to increase its capacity to 5,000 tons per year of U_3O_8 involve those items affecting batch time and not batch size. That is, output could be increased by shortening pumping time for various streams and providing facilities for operations which could be carried on independent of the digest cycle.

2. Feed Preparation

Depending upon the feed being digested several kinds of salting agents are used and are introduced into the digest tanks by different means. For the addition of scrap iron each tank has a hand operated winch with a steel cable. A stainless steel basket is attached to the winch cable to hold the scrap iron. The winch is mounted adjacent to the tank so that it can lower the basket of scrap into the tank through the manhole. The basket is approximately 18" long by 8" deep by 8" wide. A separate winch of the same kind is mounted on the handrail at the edge of the mezzanine to hoist the scrap to the operating platform.

Powdered magnesium oxide is received in drums at the plant and therefore this salting agent can be fed into the tanks using the feed drum dumper described earlier. Another salting agent, aluminum hydrate, is received in drums and can also be fed in this manner.

Before pumping out the digest batch, it is necessary to adjust the acid concentration to the desired value. This is accomplished by draining the necessary volume of 50% nitric acid by gravity from a calibrated overhead holdup tank. The transfer line is 2" Sch. 40 Type 347 stainless steel. The valves on this line are located immediately above the digest tanks for close control of the acid volume delivered to these tanks.

The presence of sand and gravel in the feed requires a settling tank in the pump-out line from the storage area. The digest batch is pumped to the bottom conical section of this tank where the diminishing velocity of the stream as it flows upward permits the solids to settle out. This tank is made of Type 347 stainless steel; it has a height and diameter (top) of approximately 5' and 4' respectively. The sand and gravel are drained from the bottom of the tank and pumped to holding tanks remote from the digest area. The digest liquor overflowing at the top of the tank is conducted to the storage tanks in 2" Sch. 40 stainless steel Type 347 pipe which is manifolded at the storage tanks to permit flow to any tank. These tanks have a total capacity of approximately 30,000 gallons. They are of the same materials and type of design as the digest tanks. So that the digest batch can be concentrated for the following process, these tanks are fitted with steam coils and turbine agitators which are the same as those for the digest tanks.

In the case of digest batches containing acid soluble residues from other parts of the plant, it is necessary to filter the batch through a vertical precoated leaf type filter before pumping to storage. This filter is of the type contained in a small stainless steel tank approximately 3' in diameter and 5' high. The leaves are made of fine stainless steel screens held in stainless steel frames having filtrate passages around the edges.

3. Acid Ether Extraction

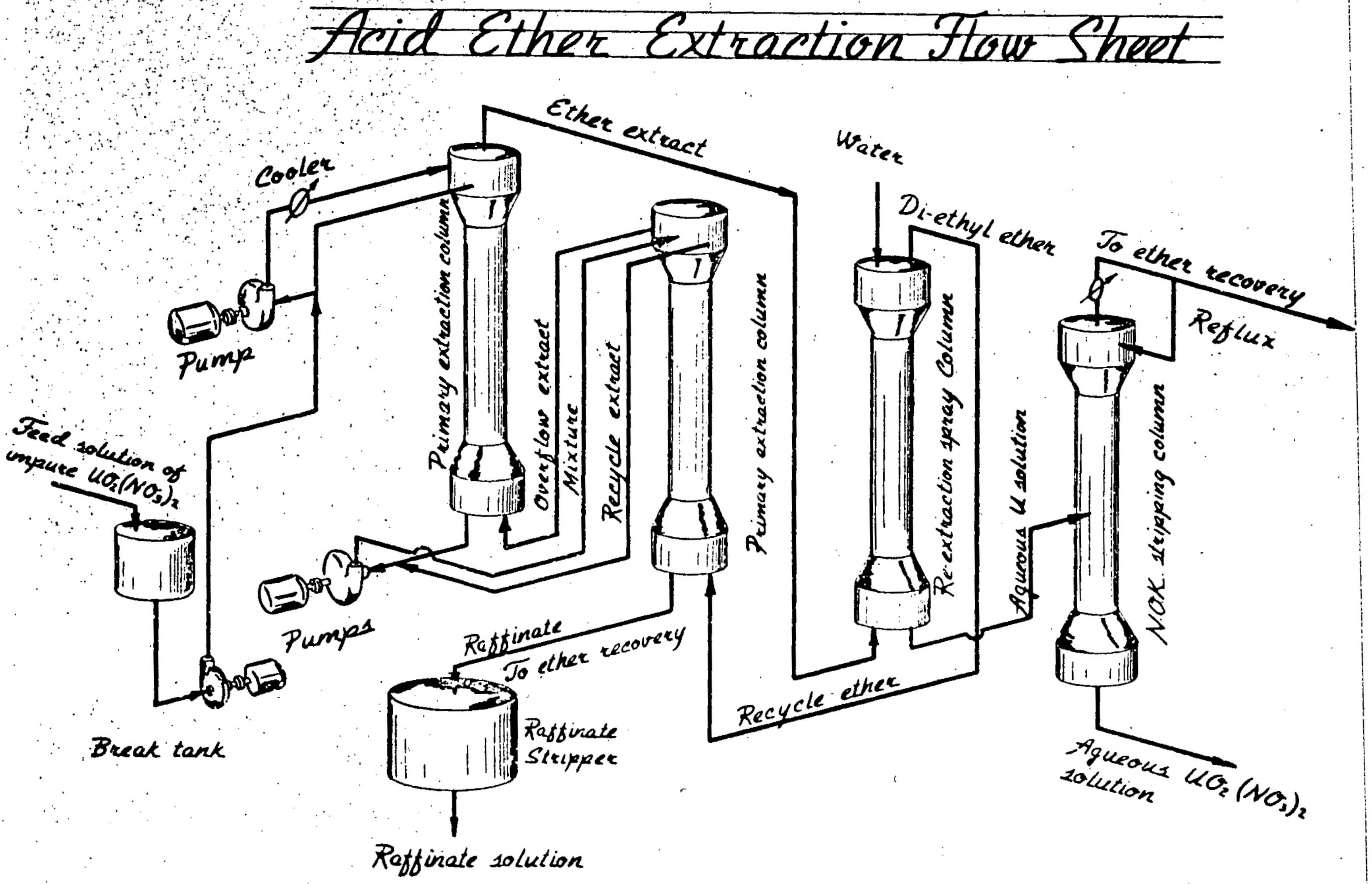
a. Flow Sheet (See Figure 2)

b. Primary Extraction Columns

The purpose of the primary extraction is to separate the uranyl nitrate from gross impurities in the feed solution. Three extraction columns are used for this job with two columns operating in series and the third column as an alternate column for use so that one column can be cleaned while the other two are operating. The columns must be cleaned to remove sludge and scale, primarily $CaSO_4$.

The columns used are open-type columns 14" in diameter by approximately 40' high. Mixing is accomplished by recycle pumps located at intervals of about 4 1/2 feet. With this type column the flooding point is about 750 gallons per hour of feed solution and 1500 gallons per hour of di-ethyl ether. These columns have the advantage of being able to extract viscous slurries at high flow rates and can be relatively easily cleaned of depositing scales and sludge. The columns have the disadvantages of large height required for a theoretical stage and leakage from the pump shafts, creating frequent maintenance problems. Other columns have been tried such as packed columns and columns with beaters for mixing instead of pumps. With the packed column the column floods at much lower rates and cleaning the column is very difficult. Columns with beaters for mixers present the difficult problem of maintenance of the shaft packing unit during operation.

The column operation is controlled primarily by flow meters and level controls. The feed solution comes into the building through a break tank to remove the possibility of ether back-flowing into an area not designed for protection against ether hazards. The feed is then introduced into a pump which recycles ether extract from an enlarged decanter section at the top of the column. A heat exchanger is located in this recycling stream to remove the heat of solution resulting from the exchange into ether. The level is controlled at the base of the column



Acid Ether Extraction Flow Sheet

Fig. 2

with an interface controller and the aqueous solution is pumped along with a recycle extract stream into the decanter section of the second column. The raffinate is removed from the second column through an interface controller at the base of the column. The ether extractant is controlled by a flow meter and is pumped in series through both columns.

c. Re-extraction Column

The ether extract contains impurities, primarily molybdenum, which cannot be removed by solvent extraction techniques in the presence of excess nitric acid. Hence the uranium is transferred again into aqueous solution to prepare for a second ether extraction step which is performed with no excess nitric acid. This operation is done in an open 14" diameter x 20" high column with the extracting water introduced through 21 high velocity jet nozzles. These nozzles are specially designed to give rapid mixing so that the water will extract uranium rapidly; otherwise the water having lower density than the ether extract will flow out with the ether phase. These nozzles have an orifice diameter of 0.06" and are equipped with filters, and are operated at about 60 psig.

The ether extract flows continuously by gravity from the primary extraction column and the water flow is controlled with a flow meter. The temperature of the extracting water is controlled by heating to 90° F. to permit optimum extracting conditions. In this column the ether phase is held continuous by an interface controller at the base of the column. The aqueous solution leaving this column is called an NOK solution.

d. NOK Stripping Column

The dissolved and entrained ether is removed from the NOK solution by distillation in a bubble cap column. This column is 24" diameter by 10' high and contains 13 plates. The solution is heated by an indirect steam calandria and some condensed ether is refluxed to the top of the column to control water content of the distillate.

The NOK solution is fed from a hold tank through a flowmeter. This flowmeter is adjusted to maintain a constant level in the hold tank.

The ether distillate is condensed in an indirect heat exchanger cooled with circulatory brine at approximately 75° F. The liquid temperature in the calandria is maintained at 220° F. with a temperature controller and the product line has a valve which will not open as long as the stripped solution is less than 210° F. This valve is a safety measure to reduce possibility of a solution containing ether getting into an area not protected against ether hazards.

e. Raffinate De-etherizing Equipment

The dissolved and entrained ether in the raffinate solution must be removed before further processing can be done. This is accomplished by batch de-etherization in three turbine agitated 3800 gallon tanks. This operation is done by batch operation instead of continuous column stripping because of scale and sludge problems associated with the slurry feeds and also because with some slurries the solution has to be held hot for several minutes in order to remove the entrained ether.

The raffinate is fed continuously through a hold tank into one of the de-etherizing tanks which has a heel of about 200 gallons of the previously de-etherized raffinate. The tank contents are continuously heated with live steam at about 200° F. while the raffinate slurry is being fed. When the level reaches approximately 2500 gallons the raw raffinate stream is diverted to one of the other tanks. Additional steam is turned on for the de-etherized batch until the temperature reaches 215° F. The slurry is held at this temperature for five minutes and then pumped out. The pump will not operate unless a temperature of 215° F. has been attained. The cycle for this operation is about 2 1/2 hours.

The ether distilled from this operation is condensed in two heat exchangers in series, one is cooled with water and the second is cooled with 15° brine. The water phase of the condensate is separated continuously and returns to the de-etherizing tank and the ether phase is returned to the extracting streams.

f. Ether Processing and Recovery Equipment

The recycling ether streams in the acid ether extraction equipment and condensates from the distillation operations circulate continuously through a central tank. The level is maintained approximately constant in the tank by the addition of fresh ether to make up for evaporative or other losses.

In order to minimize ether losses from the system all tank vents and the vents from stripper condensers, except raffinate strippers, go through one of four additional heat exchangers cooled with 15° F. brine. These additional condensers are called house condensers.

4. Intermediate Liquor Preparation (NOK)

a. Flow Sheet (See Figure 3)

b. NOK Evaporator

The $UO_2(NO_3)_2$ solution (NOK) is concentrated from about 350 gms U/liter to about 1000 gms U/liter in a triple effect evaporator. This is a vertical shell and tube evaporator with pump circulation. The unit is operated with the first effect under a vacuum of about 1"Hg absolute with the vacuum maintained by a steam jet. The transfer surface in each effect is approximately 110 sq. ft. The flow of the solution between the effects is controlled by external level controllers. The concentration is controlled by the temperature in the third effect. The condensate from the condenser and first and second effects is removed by pumping from small tanks in which the level is regulated by level controllers. The condensate from the shell side of the second effect contains about 5% nitric acid so this condensate is retained for concentration and re-use. The condensates from the condenser and shell side of the first effect contain less than 1% nitric acid and are sent to the sewer via a hold tank where the liquid is checked for U values.

Intermediate Liquor Preparation Flow Sheet

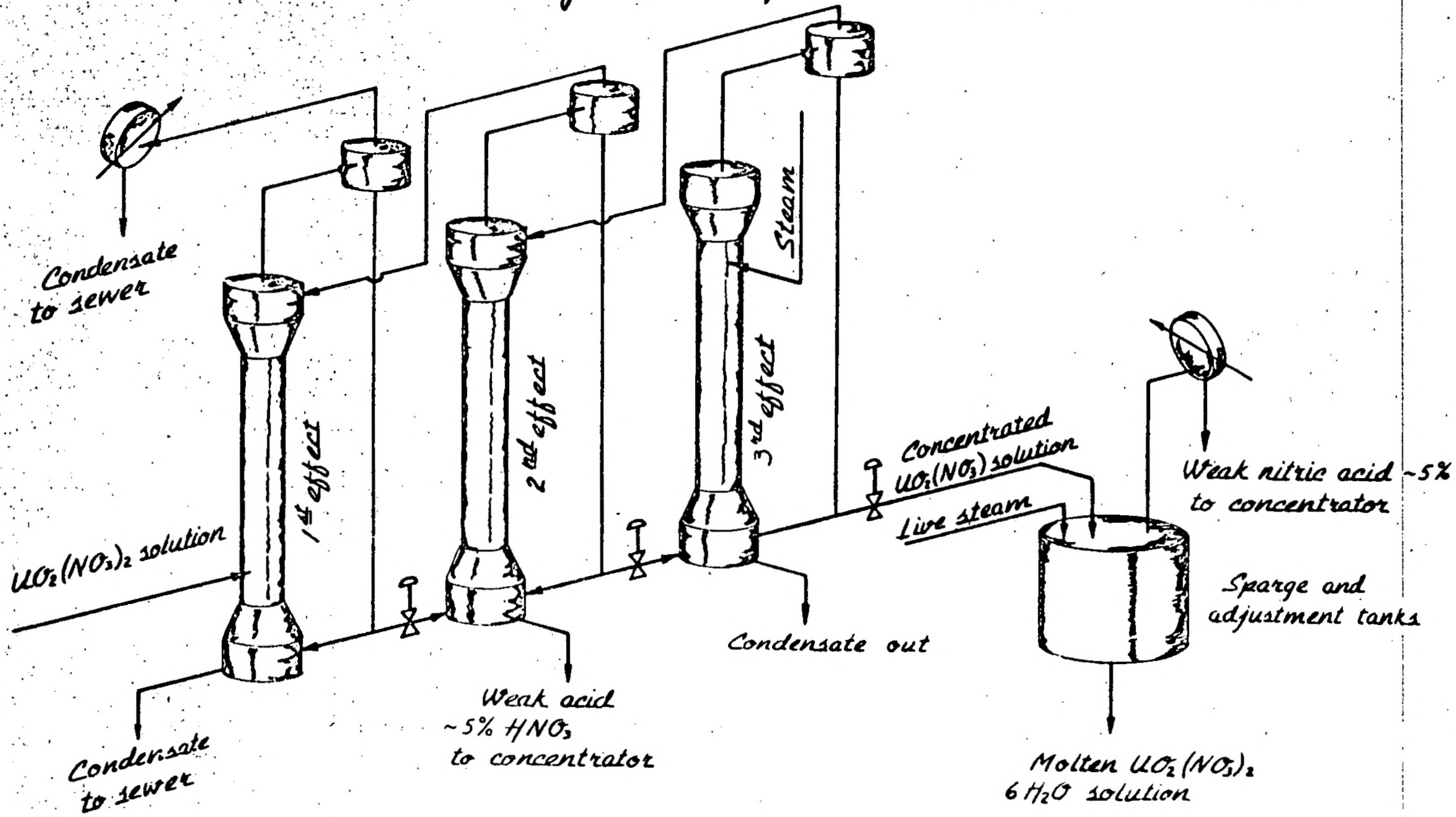


FIG. 3

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If U values are appreciable the material is processed through the central sump recovery system.

The process lines beginning with the third effect are steam traced and insulated to prevent freezing in the lines.

Considerable corrosion is encountered in the third effect resulting in the change of the tube bundle about once every five months. The best materials for construction that have been tried so far are either 347 or 304ELC stainless steels.

c. NOK Tanks

The product from the triple effect evaporator is further concentrated and steam-sparged in order to completely remove any excess nitric acid. This operation is accomplished in five 1200 gallon stainless steel tanks. These tanks are equipped with steam coils, a drilled pipe coil for introduction of live steam, and a propeller type mixer. All U process lines entering and leaving these tanks are either steam traced or steam jacketed to prevent freezing in the lines.

Batch operation is used in these tanks with continuous boiling in the tanks as they are being filled from the triple-effect evaporator. As soon as the tanks are about two-thirds full and have attained a boiling point of 275° F., live steam is introduced for about 30 minutes to remove final traces of nitric acid. The solution is then adjusted with the addition of water to give a molten salt of $UO_2(NO_3)_2 \cdot 6H_2O$. This adjustment is made on the basis of freezing point determination.

During evaporation of the solution and the steam distillation the distillate is condensed in a water cooled shell and tube heat exchanger. The condensate obtained contains about 5% nitric acid which is retained for concentration and re-use.

Corrosion problems are encountered in this operation especially with the steam coils. The coils are fabricated of 347 stainless steel in four bundles which are connected with flanges inside the tank to permit repair and/or replacement of the coils.

5. Secondary (Neutral) Ether Extraction

a. Flow Sheet (See Figure 4)

b. Extractor

The extraction of uranium into di-ethyl ether is accomplished in a one stage mixer decanter. The mixer is 14" diameter by 5' high and the decanter is 34" diameter by 41" high. A pump is used to pump the contents of the mixer through a heat exchanger into the decanter and to recycle about 15 gpm of ether extract into the mixer.

Mixing is accomplished by impinging together the fresh ether feed, the molten salt, and the recycle stream. These flows are controlled by flowmeters and the fresh ether flow rate is varied in order to give an ether extract specific gravity of 1.36 to 1.39. The molten salt is fed at a temperature of about 200° F. Cooling is accomplished through the heat exchanger located in the recycling stream and by evaporation in the mixer. The cooling medium in the cooler is controlled at approximately 60° F. in order to obtain adequate cooling without freezing of the extract in the cooler.

The aqueous phase removal is controlled by an interface controller in the decanter. The extract removal is controlled by a level controller located in the mixer.

c. Spent Aqueous Layer (N. G.) Handling

The spent aqueous phase contains about 17% of the uranium fed to this system. This solution is drained into a hold tank and is pumped continuously with flowmeter control into the primary acid ether extraction column at the primary feed solution entry point.

d. Wash Column

The ether extract from the neutral extraction system is

Neutral Ether Extraction Flow Sheet

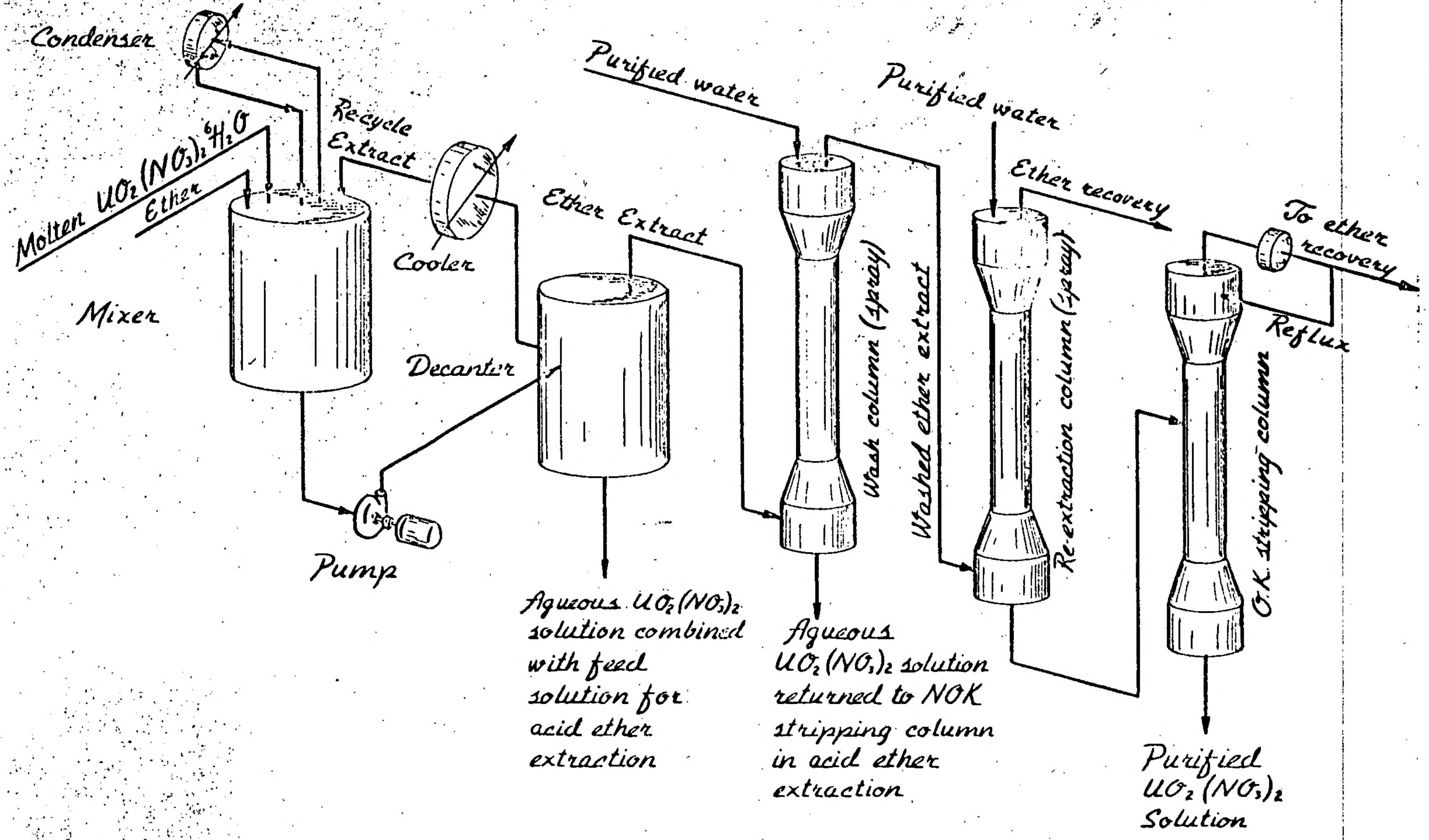

FIG. 4

sent through a wash column for final purification. This column is 14" diameter by 30' high and contains six specially designed high velocity water spray nozzles. These nozzles have an orifice of .036" and operate at about 60 psig. The pure water flow rate is held to about 1/10 the rate of flow of the ether extract by the use of a flowmeter. The extract flow rate is regulated by a flowmeter to maintain a constant level in a holding tank located between the neutral extraction decanter and the wash column.

The ether phase is the continuous phase maintained by an interface controller at the base of the column. The spent wash phase is returned to the holding tank that feeds the NOK solution to the NOK stripper in the acid ether extraction operation.

e. Re-extraction Column

The purified ether extract is sent through a column in which the $UO_2(NO_3)_2$ is re-extracted with pure water. This column is 14" diameter by 20' high and contains 21 high velocity water nozzles. These nozzles have an orifice of 0.042" and operate at about 60 psig. The water rate is controlled by a flowmeter and the water temperature is regulated at 90° F. by a temperature controller. The ether extract is fed continuously by gravity from the wash column. The interface controller is located at the base of the column.

f. OK Liquor Stripping

The aqueous phase from the final re-extraction column is sent to a stripping column for removal of dissolved or entrained ether. The column used is identical in design and operation with the NOK stripping column.

6. Other Extraction House Equipment

a. Pure Water Preparation

The present facilities have two acceptable methods of obtaining pure water for use in the extraction operation, i.e. distillation and ion exchange. Approximately 12,000 gallons of water having a specific resistance greater than 50,000 ohms is used.

The de-ionized water is produced in a Model 1953, Size 18" x 72" unit made by Elgin Softener Corporation.

The distilled water is produced in a triple effect evaporator that has copper for heat exchanger surfaces and stainless steel piping for the flow of the purified water.

b. Deluge System

The building housing the ether house operations has a Grinell deluge system for protection against fires. The system used will deliver about 5,000 gpm and is a dry system which can be manually started or may be started by HAD (heat activated) heads. If this system is activated, the fire department alarms are also activated.

c. Electrical System

The electrical system used in the ether house operation must conform to Class I, Group C rating, as applied to motors, switches, lights, etc. In the present plant most of the starters and push buttons are located in the hazardous area. In the newer installations the starters are remotely located and only the push buttons are located in the hazardous area. The latter method is preferable from initial cost and maintenance standpoints.

d. Ventilation System

Forced ventilation is provided by introduction of temperature regulated heated air or fresh air and by an exhaust system. The exhaust system has pick up points located throughout the building and is designed to pick up near each floor level. The ventilation system produces about 15 air changes per hour.

e. Spillage Collection

All material draining to the floor is collected in a stainless steel pot located at the lowest point in the floor. The liquids are pumped from this sump into a 1,000

140 046

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gallon stainless steel tank. This tank is equipped with a steam coil for distillation and a shell and tube heat exchanger cooled by 15° F. brine for condensing ether. This tank is operated batchwise to remove ether from aqueous solutions. After de-etherization these solutions are pumped to the central sump recovery system for further processing.

f. Refrigeration System

The condensing and cooling units in the ether house operation require approximately 125 tons of refrigeration operating at a temperature level of about 15° F. An inhibited ethylene glycol-water system is used for the circulating brine. A five ton refrigeration unit is also installed to maintain cold temperatures in the house condensers during periods when the plant is not operating.

7. Evaporation and Denitration of Pure Uranyl Nitrate

The purified uranyl nitrate solution as produced from the extraction operations contains about 500 gms of U/liter. This solution is evaporated with steam coils to about 1200 gms U/liter and then thermally decomposed in twenty gas-fired kettles to uranium trioxide.

a. Boildown Tanks

The concentration of the solution is performed in five batch operated boildown tanks. Each tank is equipped with a steam coil. The operation is manually controlled to give a solution with a boiling point of 248° F.

b. Distribution System to Denitrators

The concentrated solution is held at about 210° F. during the transfer to the decomposition kettles. This transfer is accomplished by pumping the solution. The pumping system is a complete circulating system with draw off valves at each kettle and each tank. The entire system is steam traced and insulated to prevent freezing and each line is properly sloped and fitted to permit adequate draining and flushing as required for shutdown.

c. Denitration Kettles

The denitration kettles are dished bottom pots with an I. D. of 30" a vertical side wall of 18" and dish radius of 30". The pot walls are 1/2" thick and are made of 347 stainless steel. The pot is gas heated in a ceramic furnace with four gas burners located tangentially along the pot.

The pot is agitated with a 7 1/2 H. P. vertical gear head drive with an output speed of 36 RPM. The agitator is designed to fit the contour of the pot and is horizontally and vertically braced for strength. The agitator blades are made from 1/2" x 4" stainless steel bar stock. The agitator clears the bottom of the pot by about 1/8" and the sides by about 3/16". The pot has a close-fitting half circle removal lid for removal of product and each pot is connected through stainless steel ductwork to the nitric acid absorption system.

The pot cycle must be carefully controlled because this step influences the reactivity of the product in subsequent processing.

The pot cycle is controlled by having fixed gas pressure to the calibrated burners and utilizing varying numbers of burners during the cycle.

d. Product Collection and Drum Loading

The uranium trioxide product in the denitration pots is unloaded pneumatically with a 40 H. P. vacuum producer. This unit includes a cyclone collector for primary collection and reverse jet cleaning bag collector for final collection. The entire unit with piping is made of stainless steel.

The product from the collection system is screened through a 20 mesh vibrating sifter. The undersize material goes directly to the final product hopper and the oversize is crushed through a hammer mill which discharges to the final product hopper.

The finished product is drummed in 30 gallon specially lined steel drums which hold about 900 pounds each. The drum loading system is designed with good seals and dust collection equipment to prevent dusting into the atmosphere.

8. Raffinate System

a. The de-etherized raffinate from the extraction house is pumped to three raffinate precipitation tanks (2,300 gallons) equipped with heating and cooling coils and backward discharging turbine type agitators. The tanks are 8'0" diameter x 5'6" high with standard dished bottoms and fabricated of Type 304 stainless steel (heat treated) and Type 347 stainless steel. The tanks are equipped with temperature indicator controllers, atmospheric vents through a central absorption system and are piped through a common header to a pair of pumps, with one being a standby spare. All pipe lines, stacks and pumps are of the 300 series stainless steel.

Lime slurry for precipitation is made up in a 1,000 gallon steel tank equipped with a propeller type agitator and a dumping hood which is vented through an exhaust fan to the atmosphere. It is then pumped to a 1,000 gallon steel lime slurry storage tank. A continuous recirculating system is used for transferring to the raffinate precipitation tanks.

The filtration equipment consists of a rotating disc type filter with six leaves of 6' diameter, a vacuum compressor and positive pressure blower which supplies air for cake blow-off. The normally open section of the filter is enclosed by a counterbalanced steel hood which is exhausted to atmosphere through an exhaust fan in order to reduce the alpha radiation exposure hazards of the operators.

The precipitated raffinate is pumped to the filter bowl at 40 gpm through a stainless steel centrifugal pump. The filtration rate is approximately 20 gpm with the excess overflowing back to the feed tank. The cake is discharged through chutes into Roura hoppers, sampled and transferred to dump trucks and then hauled to a central storage area. The filtrate is collected in filtrate hold tanks, either a 5'6" diameter x 5'6" tank (Type 304 stainless steel) or an 8'0" diameter x 5'6" tank (Type 347 stainless steel) equipped as are the raffinate precipitation tanks. After sampling for U analysis - U must be less than 1 lb/1000 gallons - the filtrate is either dumped to the sewer or recycled as salting agent. If the filtrate is to be recycled, it is concentrated in the 2,300 gallon tank to 45° Be and the nitric acid content is adjusted by addition of 60% HNO_3 from a 2'6" diameter x 3'0" measuring tank. This tank is equipped with a vent, calibrated gage glass and a float actuated level control valve. After adjustment, the liquor is pumped to two 5'6" x 5'6" (Type 304 stainless steel) hold tanks, from which it is pumped to the feed adjustment area as needed.

b. Raffinate Denitration

At present, investigation is under way on a process of continuous raffinate denitration to recover the nitric acid values in the raffinate. The de-etherized raffinate is concentrated in a tank which is the exact duplicate of the raffinate precipitation tanks, with the offgas discharged through the central absorption system. From the concentrator the raffinate is pumped, through a recycle line, to the continuous raffinate denitrator. The denitrator is an externally heated, closed trough in which a hydraulically driven paddle agitator is rotated. The trough is fabricated of Type 309 Cb stainless steel and the agitator of Type 347 stainless steel.

The offgases from the denitrator are first filtered through a stainless steel pressure type filter with cylindrical tubes made of stainless steel cloth. The dust collected at this point is re-combined with the metal oxides. The fumes then pass through a jet type fume scrubber before going on to the nitric acid absorption system for final recovery. The product from the denitrator discharges into a cooling screw and is then packaged in drums for storage.

9. Nitric Acid Recovery System

The nitric acid recovery system has a two fold function:

1. to recover for re-use the nitrogen oxides and dilute nitric acid given off by various processes in the plant, and

2. to prevent air pollution inside and outside the plant.

a. Absorption System

There are two main sources of nitrogen oxides -- the digestion tanks and denitration pots -- with a combined output of 15-18 pound moles total oxides per hour. The gases are exhausted through jet type fume scrubbers from the source of generation by the suction created by Nash Hytor compressors. These compressors then compress the gases to 30-32 psig before pumping to the absorption towers.

Five Nash Hytor compressors are operated in parallel with a recirculating, cooled liquid seal system. The compressed gases and seal liquor pass through a separator, with an internal float control valve. The excess acid from the liquid separator is pumped to one of the center trays of the bubble cap absorption tower and the gases pass through a gas cooler into the absorption tower. The ducts to the compressors are valved, so that any compressor or compressors can be separated from the system. The compressors are made of cast Type 347 stainless steel, and require overhauling about once a year to maintain the close tolerances necessary for maximum compressor capacity.

The absorption tower is a twelve tray bubble cap column with cooling coils on each tray. The off-gases from the tray column then pass through six packed towers in series with countercurrent flow of gas and liquid. A pressure controller on the lean end packed tower controls the pressure of the system at 30 psig. The liquid overflow from the tray column is collected in intermediate storage tanks before being pumped to the recovered acid storage tank for re-use in the refinery. The liquid overflow from the packed towers is used as feed to the nitric acid concentrator.

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b. Nitric Acid Concentrator

Dilute nitric acids of varying strength are collected from concentrators, condensers and scrubbers throughout the plant. Two tanks, 8'6" diameter x 34'0", of stainless steel are used for storage of dilute acids, one for acids of less than 2% HNO_3 and one for acids of greater than 2% HNO_3.

For recovery of weak acids a vacuum concentrator is used. This consists of a packed rectifying column about 4' diameter by 10' high with a forced circulation external shell and tube calandria. Vacuum is produced by a barometric condenser. Product draw-off from the rectifier is manually controlled through a rotameter.

Either Type 347 stainless steel seamless or Type 309 Cb stainless steel welded tubes are used in the calandria, since these types have been found to give the best service life.

10. Sump Recovery System

Large volumes of low solids content liquors from various plant sumps are handled in this system. The sumps are 50 gallon stainless steel pots set into a concrete pit and sealed in with acid resisting sealing compound. The pots are covered with a stainless steel bar grate with a stainless steel backing screen (1/4" mesh) to keep large foreign objects out of the sumps. All floors are sloped to drain to these sumps. Each sump has a manually operated stainless steel self priming pump to pump the liquors to the recovery system.

These sump liquors, along with the de-etherized sump liquors from the ether extraction house, are collected in three tanks. These tanks are fabricated of Type 304 stainless steel (heat treated) and are 7'0" diameter x 7'0" with standard dished bottoms and a capacity of 2,150 gallons. They are fitted with Type 347 stainless steel coils with a surface area of 120 sq. ft., Type 347 stainless steel backward discharging turbine type agitators and are vented to atmosphere through a central absorption system fabricated of Type 347 stainless steel. Two of the tanks are used for receiving and concentrating liquors, which are then pumped via a stainless steel centrifugal pump to the third tank for final adjustment. Here the liquors are concentrated to a U content of approximately 3.0 lb/gallon, and the nitric acid content is adjusted by adding 60% HNO_3 from the nitric acid measuring tank. The resulting concentrate is then pumped via centrifugal pump to the feed adjustment tanks.

This system has a capacity of 20,000 gals/day and the load varies with spillage, pump leakage, boilovers, and plant housekeeping.

11. Dust Collection System

a. Raw materials such as lime, magnesium oxide, and aluminum hydrate are bagged materials and are normally added to the system as slurries. The dry materials are slurried in tanks equipped with dumping hoods which are exhausted to atmosphere. Exhaust fans in the vent stacks provide a face velocity at the dumping point adequate to handle all dust generated in the process.

b. The orange oxide produced in the pot rooms is pneumatically conveyed from the pots to the packaging station. The entire system operates under 10" Hg vacuum. The dust collector is of the Hersey Reverse-Jet type and because of the possibility of bag leakage or bag bursting, the exhaust gases from the vacuum producer are discharged to a low pressure Hersey type filter for final polishing before discharge to the atmosphere. The material collected in the high vacuum collector is added to the storage hopper, while that from the polishing filter is packaged in drums and reintroduced into the feed at the digesters.

c. In the packaging of finished materials or dust collector dusts, which are packaged in 30 gallon drums, the drum is raised by hydraulic jack to a sponge rubber gasketed cover plate attached to the filling spout. An exhaust vent coming off the cover plate exhausts all dusts that are generated into a reverse jet type filter.

12. Mist Elimination

One of the major problems in the plant is the elimination of nitric acid mist from the atmospheric vent stacks on the process tanks. Various means have been tried to solve this problem among those being:

a. Use of a water curtain type unit on a single stack.

b. Use of a jet type fume scrubber on a single stack.

c. Use of a central absorption system for a group of tanks.

Of the three systems, the central absorption system has been most effective. In this system vent stacks from a number of tanks are tied into a common discharge stack with a separation chamber and exhaust fan on the tail end. Mounted vertically in the common stack are three or four spray nozzles with a capacity of 50 to 75 gpm each. The flow of water to the nozzles is controlled by a temperature controller which measures the temperature of the offgas from the exhaust fan. The control valves are operated stepwise from the output air pressure of the controller.

13. Tank Farm

Nitric acid is received in tank car quantities as 60% by weight nitric acid. The cars are unloaded by self priming pumps through top connected piping fitted with swivel joints and pumped to a series of storage tanks. There are two stainless steel tanks 8'6" diameter x 34' 0" long with a capacity of 13,800 gallons each, saddle mounted with a 4' poured concrete dike around them. In addition, there are four 10' diameter x 14' 0" Type 347 stainless steel tanks with a capacity of 8,200 gallons each and these also have a dike around them. The vertical tanks are equipped with bubbler type (static pressure) level indicators. Two centrifugal pumps handle the transfer of acid into the plant. The 50% by weight nitric acid from the acid recovery system is stored in an 8' diameter x 21' stainless steel tank with a capacity of 8,500 gallons, and is pumped through two centrifugal pumps into the plant measuring tanks as needed.

Diethyl ether is received in tank car quantities and is pumped to a 10' diameter x 25' high, steel storage tank with a capacity of 13,750 gallons. The pipe lines are equipped with connections to ground for this operation. The storage tank is equipped with a combination vacuum-pressure relief valve with a lightning arrestor grid, a series of spray heads around the top of the tank, with water flow regulated by a temperature controller for use only during the summer months, and a bubbler type (static pressure) level indicator with calibrated manometer. The ether is pumped to an intermediate storage tank of 2,300 gallon capacity and from here is pumped into the ether extraction house as needed.

V. AUXILIARIES

Auxiliary facilities at the St. Louis plant serve the refinery and also other plants and pilot plants operating on other phases of uranium production in the same area. For this reason they will have to be described as they exist in their entirety with suitable indications where pertinent of their relationship to the refinery operations.

1. Warehouse Facilities

Warehouse facilities presently comprise about 12,500 sq. ft. of inside space for the storage of finished products, uranium bearing residues and other chemicals requiring covered storage. About 20,000 sq. ft. of outside space have been provided for the storage of ore drums and empty drums.

The warehouse is a ventilated one story building with a reinforced concrete floor having a high load bearing capacity. Loading docks are provided for handling materials brought in by railroad cars and trucks. Decontamination facilities are provided at the railroad and truck loading docks. Large fans and ventilators in the warehouse roof provide for circulation of air in bays where uranium bearing residues are stored.

Finished products are stored in the warehouse in 30 gallon drums, 5 drums to a pallet, four pallet loads high. Ores are generally stored outside in 30 gallon drums, 4 drums to the pallet, but only three pallet loads high. Drums are transported to and from the warehouse by means of fork trucks. At the present time

140/ r55

15 fork trucks are used in addition to dump trucks, pick up trucks and other vehicles. Certain contaminated residues are taken by dump truck to an area provided for this purpose at a remote location. This warehouse is practically entirely for the refinery.

2. Stores

About 14,000 sq. ft. have been provided for the storeroom facilities. Of this, about 6,000 sq. ft. are needed for the issuing storeroom where the smaller parts and fittings are kept, and about 8,000 sq. ft. are used for the storage of larger pieces of equipment such as pumps, motors and fans. All materials in the storeroom are stored in shelves, bins and bays for ease in issuing and the bays have adequate space for the passage of fork trucks.

Receiving and shipping presently require about 150 sq. ft. for office space and approximately 600 sq. ft. for temporary inside storage including a shipping and receiving dock. The dock is located just off a concrete driveway and provides loading space for delivery trucks. Approximately one-half of the stores facility is used for refinery service.

3. Boiler House

A boiler house of approximately 9,000 sq. ft., including a basement area, supplies steam for the refinery, the green salt plant, laboratories and other facilities in the plant area. Steam is generated at 115 psi by three coal fired boilers, each having a rated capacity of 42,000 pounds per hour. Approximately 65% of the steam generated is used by the refinery for chemical processing, tanks and evaporators.

In addition to supplying steam for the plant, the boiler house furnishes refrigeration, compressed air, instrument airs, cooled water, and softened water. Compressed air facilities include three small horizontal reciprocating units and one large V-type unit.

A 4,500 gpm cooling tower on the boiler house roof supplies cooled water for condensers, heat exchangers and other plant requirements. In addition to the above services, the boiler house also provides for emergency power in case of power failure.

140 / 56

4. Analytical Laboratory

The analytical laboratory is a one story building having a floor space of approximately 7,600 sq. ft. It contains all necessary equipment for testing samples of finished material, for control of the materials in the refinery and other plants, for special analysis for research and production, for spectrographic analysis and for tests of material accountability. A separate laboratory of about 740 sq. ft. has been provided for testing the neutron absorption of orange oxide.

The control section of the analytical laboratory is operated 24 hours per day and performs control tests on all plant materials at each stage of the operation. About 40% of this space is devoted to refinery testing.

5. Maintenance Shops

Maintenance shop work, about 150,000 man hours per year on the refinery, includes adjustment and repair of equipment, renewal of parts, cleaning, painting and upkeep of plant buildings and manufacture of certain pieces of new equipment for plant usage.

Maintenance shops require a total of about 10,200 sq. ft. of floor space. This area includes approximately 2,400 sq. ft. for a machine shop, 1,200 square feet for a millwright shop, 1,600 sq. ft. for a welding and pipefitting shop, 1,500 sq. ft. for a sheet metal shop, 1,000 sq. ft. for an electrical shop, 600 sq. ft. for a vehicle repair shop, and about 300 sq. ft. for office space.

Machine shop equipment includes four lathes the largest of which is 25" x 72", two shapers, two drill presses, two milling machines, tool grinders, key cutters and a 300 cfm fume collection system. Other shops provide normal equipment and facilities usually installed in plant shops.

A separate instrument shop is provided of about 2,500 sq. ft.

6. Service Facilities

Locker rooms and clothes change space have been provided for all employees. In order to fulfill health requirements, employees going into the plant are required to change into plant clothes, and for this reason lockers have been assigned to each employee. Locker and change space presently utilize about 3,400 sq. ft. The shower room and lavatories require approximately 900 sq. ft. of space.

Plant clothes must be washed after each use and for this purpose a laundry facility has been installed. About 3,600 sq. ft. of space have been allotted to the laundry for the installation of washing machines, hot water tanks, driers, pressing machines, and sewing machines.

The plant cafeteria has a seating area of about 1,500 sq. ft. and a food preparation and dishwashing area of approximately 800 sq. ft.

The health physics office has an area of approximately 1,500 sq. ft. and contains, in addition to office space, electronic testing rooms and equipment.

The medical office is composed of a dispensary having an area of about 700 sq. ft. and a doctor's office and examination room of about 300 sq. ft.

About 50% of all of the above is related to refinery operation.

7. Offices

The accounting office comprises about 3,500 sq. ft. and is, at present, composed of two sections. One section, having an area of about 3,000 sq. ft. handles general cost accounting and payroll and contains desk space for about 15 people. The other section, of about 500 sq. ft., has desk space for about five persons and handles material records and costs.

The accountability office has desk space for ten persons and is presently allotted approximately 600 sq. ft. of space.

Engineering has desk space for 14 engineers and drawing board and table space for 11 draftsmen. The engineering office has an area of about 2,000 sq. ft.

Production supervision offices are assigned to each major production facility. At present, the refinery has about 800 sq. ft. allotted for office space.

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VI. OPERATION OF PLANT

The operation of the plant will be discussed under five major headings. The first operation is digestion.

1. Digestion

Ore and concentrates are generally received in 30 gallon clamp top drums. Occasionally the drum handling system must handle 15, 50, 60, and other non-standard drum sizes. These drums are palletized for easy handling. A fork truck is used to remove the drums from a pallet and place them on the conveyor leading to the drum dumping mechanism.

In preparation for the drum dumping the operator introduces the required amount of nitric acid into the tank to which the uranium bearing ore or concentrate will be added, opening the connection from the fume scrubbing system to the tank. After the required amount of acid has been added to the tank the agitator on the tank is started and the introduction of the drums of feed material begins. It should be noted that the amount of nitric acid used for any particular batch depends largely on the nature of the material being dissolved. For sodium uranate, for example, as much as 6,500 pounds of dry salt might be added to 1,500 gallons of nitric acid to make a single batch in a 2,500 gallon dissolving tank.

The drum handling equipment described in Part IV will handle approximately 20 drums of feed material per hour. The operator introduces these drums after removing the lids by simply releasing a stop mechanism on the conveyor allowing the drum to move forward to the drum dumper. When the drum is positioned on the dumper the operator actuates a mechanism which grasps the drum firmly to the dumper, then actuates a second mechanism which moves the drum up into the dumping position. Since the material has a tendency to cake inside the drum it is necessary to strike the sides of the drum several sharp blows to be sure that the major part of the uranium bearing material falls out. A screw mechanism is actuated to deliver this material to the proper tank. In some cases, as for example, in the introduction of uranium oxide, care must be taken in this introduction because of the heavy evolution of nitric oxide fumes in the dissolution process. After the drum has been dumped it is moved through the drum washing mechanism to remove as much as possible of the remaining uranium from the interior of the drum and to wash any unhealthy dust from its exterior. Great care must be exercised during this operation in as much as some feed batches react violently and may foam over, causing the tank contents to spill out on the floor. Particular care should be used in the introduction of any feeds which contain carbonates, sulfides, or other gas evolving constituents.

After the required amount of feed has been added the operator allows the tank to stir and then draws a sample for nitric acid and uranium analysis.

In addition to the feed materials, salting agent may be required, particularly when uranium oxide and other high assay materials are being introduced. These salting agents are normally introduced by dumping drums of the salting agent into the tank. However, in the case of iron, which is used as a complexing agent, the iron is introduced in a basket which is lowered through the manhole in the tank and allowed to dissolve slowly. Great care must be used in this operation to avoid exposure of the operator to the toxic nitric oxide fumes.

After all of the required materials are added and the operator has determined, by inspection, that no further reaction is taking place, the tank is allowed to agitate an additional 15 minutes and a sample is then taken for uranium and nitric acid analysis. The uranium analysis is made on a composite sample of all the batches dissolved during a particular day for material balance and inventory purposes. The nitric acid analysis, however, must fall between the limits of 0.5 to 0.7 pounds per gallon of 100% nitric acid. Use of charts at his disposal if the nitric acid limits fall outside these two control points permits the operator to adjust by adding more nitric acid or more feed material or some neutralizing agent.

When the analysis is satisfactory the tank is pumped out through the cone tank, which removes heavy gravel, into a storage tank. Solid materials and other foreign substances which are insoluble in nitric acid frequently block the outlet and discharge tank lines from these tanks. To overcome this the operator uses a back flush of water and air as needed. However, in some cases the lines must be disassembled to unplug the tank.

The cone tank used here is drained once a week to remove the heavy solids. The traps, on the other hand, on each of the two digester tanks are cleaned after each batch. The solids from these traps are neutralized, dried, and ground and introduced back into the digester tanks. The cell washer used to scrub dust from the drum dumping operation is cleaned into a tank provided for this purpose once every month. Normally, liquor from this tank is circulated through an Adams filter into the cell washer. The same liquor can be used for drum washing. The adams itself must be cleaned approximately every three days by being "blown back" into the digestion tank. It should be noted that prior to filtration through the Adams this liquor must be neutralized by the addition of magnesium oxide.

In this digestion operation the most troublesome operating problem is the tendency of the tanks to run over or so-called "wild" feed batches. In addition, occasional difficulties occur with the screw feeding mechanism and it generally has to be repaired about once a month. The drum washing system, including the lowerator, is particularly troublesome and very difficult to keep in satisfactory operating condition. The screen used to sift out foreign material presents a difficult dust sealing problem as does the packing glands on the feeding screws. The primary safety hazards in this area result from the boilover of tanks and the evolution of noxious fumes. The dust evolved from the dumping operation presents a serious health hazard if not controlled. The limit established by our Health Department for nitric oxide concentration is 25 ppm. The radioactive dust concentration limit is set at 70 alpha D/min/M^3.

Two chemical operators per shift are required for this job in addition to a fork truck operator.

2. Feed Storage

Feed from the digestion area is stored until ready for extraction. In addition, liquors from the plant recovery system (see Section 6 in this part) are adjusted for nitric acid concentration of .5 to .7 pounds per gallon and a uranium content not to exceed 2.7 pounds uranium per gallon. Nitric acid concentration is adjusted by chart through the addition of acid or magnesium oxide. The solution is further adjusted by the addition, if necessary, of magnesium oxide, nitric acid, and water, or, if the material is low in sulfate, calcium nitrate from the raffinate precipitation area. After these adjustments have been completed this material may be run directly in the extraction plant or blended with other materials in the event that such blending is helpful to the extraction.

Both in making up composites and in blending feed materials the plant operator must keep in mind the necessity of obtaining a feed to the ether extraction system which will run reasonably well with minimal uranium losses to the raffinate. In some cases, for example, where low assay feeds are available it may be well to blend such feeds with high assay feeds in making up a digestion batch so as to minimize the use of magnesium oxide and other materials as salting agents. Also, some very low assay materials because of the foreign substances they contain tend to emulsify in the extraction process themselves, or to extract poorly. Blending is very helpful in these cases. Where high concentrations of vanadium, phosphates, or sulfates are present, the proper compositing may minimize the adverse effects such as scaling, high uranium loss, and emulsions. In controlling, blending and handling of the feeds, one chemical operator per shift has been used. No unusual maintenance problems have been found in this area which is a relatively trouble free operation in itself.

3. Extraction Operation

Because of the complexity of the extraction operation it is advisable to consider the area as broken into four parts.

a. Acid Extraction

The first part is the so-called acid extraction. Before starting a particular feed batch into the extraction area the operator measures out an aliquot of feed into an aliquot of standard base. When a precipitate forms, the batch is considered satisfactory for extraction operation. This test, it should be noted, is a safety test to prevent the accidental introduction of very high acid material into the extraction plant. The reaction between nitric acid and ether is extremely violent to the point of being explosive if it occurs within a closed vessel and every precaution must be taken to prevent such an occurrence.

If satisfactory feed is available the operator sets the valves so as to set up the circulation of ether from the ether hold tank into the bottom of the second extraction column, from the decanter atop the second extraction through the recirculation pump back to the decanter. Also, he sets the valves so that as the second column is filled it overflows ether into the bottom of the first column. After the first column is filled the circulation of ether out of the decanter and back is also started. After both columns are full the column pumps are started in operation. The ether flow continuing, ether extract flows from the first column into the re-extraction column. This in turn fills and overflows into the ether hold tank. When the ether flow has thus been established the acid stage mix cooler brine is turned on. The feed is pumped into the "T" section from the cooler permitting the ether feed to mix intimately and proceed to the decanter.

By means of the rotameter controllers, the ratio of feed introduced to ether flow is maintained at 1 to 2. It is important wherever aqueous layers come in contact with ether that this ratio not be exceeded, since a greater proportion of feed in excess of perhaps 1 to 1.5 will usually result in the formation of relatively stable emulsions. These stable emulsions defeat the extraction process and can cause serious losses of production and contamination of product.

As the system fills with uranium, the extract flows from the top of the No. 1 column into the re-extraction column. At this point the water should be started through the heater to maintain the temperature at 80° F. and into the jets of the re-extraction column. This water flow is set manually at a rate which gives an ether gravity of 0.714 or less. It is important that this water ratio be maintained sufficiently high to remove all the uranium since uranium that is not removed at this point will be lost into the raffinate as the ether recycles back into the bottom of the second column. Conversely, if excessive water is used the water extract will be too dilute which will result in overloading concentrating capacity of the NOK system causing a loss of production. Care should also be taken in the operation of this column to avoid flooding as a result of excessive water or extract flows. As raffinate accumulates at the bottom of the second extraction column the valves protecting the level controls should be open permitting raffinate to flow into the raffinate stripper feed tank and NOK liquor to flow from the bottom of the re-extraction column into the NOK

c63

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stripper feed tanks. When 100 to 200 gallons of liquor has been accumulated in each of these hold tanks the strippers should be started. Starting the NOK stripper, brine should be started circulating into its condenser and it would be well at this time to also check that brine is going through the house condenser system, steam block valves are open on the NOK stripper, and the temperature controller set at 210° F. on the outlet and a temperature of 130° F. at the top level. The pressure controller should be set at approximately 15 inches of water. When the temperature at the bottom of the stripper rises above 210° F. the feed pump to the stripper may be started and feed gradually introduced into the stripper until full rate operation is obtained.

In starting the stripper it should be remembered that it is necessary that a fluid be in the stripper to its outlet level. If the stripper is empty it should be filled with water before starting. This is preferably done during the prior shutdown of the stripper. Next, when 100 to 200 gallons of raffinate is accumulated in the raffinate stripper feed tank, the raffinate stripper should be started. This is done by heating the seal in the stripper to a temperature of 215° F. and turning on both the water and the brine condensers above the stripper tank to be used. The pressure kick-off should be checked to be sure that it is in operation and feed started into the stripper. This stripper is operated on a batch basis with one tank receiving while another tank is pumping out. When one stripper is full and de-etherizing, the flow should be switched to the second stripper which should be hot and ready, and the first stripper pumped out into the raffinate area for further treatment as provided in Section 5 of Part IV.

The NOK liquor which has been de-etherized is delivered to the triple effect evaporator feed tank which will be considered in the next section of this part. The primary difficulties experienced in the operation of this first extraction result from a precipitation of numerous scales within the extraction apparatus itself. Calcium sulfate and other soluble salts precipitate out as the uranium content is reduced in the aqueous layer by the extraction apparatus itself. Calcium sulfate and other soluble salts precipitate out as the uranium content is reduced in the aqueous layer by the extraction process. Salting-in effect of the uranium is well-known. In order to overcome this problem a spare column was installed in the extraction plant so that one column could be cleaned while the other two were in operation. This cleaning is done mechanically by disassembling the column and scoring the inside with appropriate scrapers through the ports on the column. The auxiliary piping on the column is also reamed out when necessary. Before opening these columns for cleanout, however, the operators empty the columns of their normal contents and fill them with hot water at a temperature of 180-190° F. and drive off any ether vapor which may be within the columns. The columns are then flushed and checked for ether vapor with an explosimeter. If ether is still detected in the column the process of filling it with hot water is repeated until no ether is detected. This practice of de-etherizing is followed everytime it is necessary to open a vessel which contains or has contained ether. It can be expected that when high sulfate or other difficult feeds are encountered the columns will need to be switched and cleaned as much as once a week and adequate provision should be made for this operation. The same scaling problems present some difficulties with pumps. Scaling on mechanical seals or on impellers can and does lead to maintenance problems. The maintenance of the column pumps is a particularly expensive proposition and provision should be made for easy removal to the shop for repair.

One chemical operator is sufficient to operate this first extraction stage exclusive of the stripper operations. Stripper operations both for this stage and the neutral system are handled by a single operator. There are within the extraction plant a total of four operators per shift. The other two operators are engaged in the operation of the NOK system, which will be described next, and the neutral system.

The primary safety hazards in this extraction operation result from the inflammability of ether and the decomposition reaction with nitric acid. To take care of the problem of the inflammability of ether any leaks which occur are promptly fixed and the ventilating equipment regularly inspected to be sure that no concentration of ether vapor in excess of the explosive limits can occur in the room. In order to avoid the reaction of nitric acid and ether, nitric acid is kept out of the building and special precautions as noted previously are taken to be be sure that no feed batches contain excessive amounts of nitric acid. The problem of the reaction of nitric acid and organics occurs in all uranium extraction systems and must be dealt with with care.

b. <u>NOK System</u>

When approximately 100 or 200 gallons of de-etherized NOK liquor has accumulated in the evaporator feed tank the evaporator may be started into operation. To start the evaporator the water is turned on the condenser and cooler. The steam is then turned on the tracing lines and the ejector. The valves are then set on the evaporator to permit the pumping of liquor from one effect to the other. Liquor is drawn up by vacuum into the first effect until a liquor level shows midway on the sight glass with the by-pass valve open. The pump is then started so that liquor is carried over into the second effect. This process is repeated until all the effects have liquor levels midway on their sight glasses and the product pump is in operation to delivery liquor to the NOK tanks. Steam is then turned on to the third effect and the temperature controller is set at 240° F. Care must be taken to maintain the levels, using the by-passes if necessary, during the initial operation of the evaporator. As the evaporator operation reaches steady state the by-pass valves should be closed. If the evaporator is in good mechanical condition, i.e., no leaks, the operation is relatively troublefree, however, when the evaporator is shut down and the liquor pumped out it should be remembered that it is necessary to flush out with water those portions of the evaporator where heavy concentrations of uranium were present to prevent freezing while the evaporator is down. The product from the evaporator is collected in one of the several NOK tanks. As soon as the coil is covered the steam is turned on in the NOK tank to boil the liquor down to a boiling point of 275° F. When approximately 500 gallons have been accumulated in a tank the product from the evaporator is switched to another tank and the steam sparge is started on the full tank. During any operation on the NOK system water should be on the NOK tank condenser so that the acid boiled off may be recovered by the nitric acid concentrator. The steam sparge is continued full for approximately 45 minutes at which time a sample is taken and diluted 1 to 1. This sample is submitted to the laboratory for nitric acid analysis. If the sample is 7.5-10.5 gms/l acid deficient it is satisfactory. If the acid content is higher than this, as is normally the case, additional sparging should be done at the rate of three to four minutes per gm/l of excess acid to be removed. If the acid content is lower than the value indicated it may be necessary, under special conditions, to bring a small amount of acid into the area to add, but it is preferable to add, where space allows, more evaporator product.

When the acid concentration is correct the tank may be diluted to a boiling point of 257° F. After this dilution has been made with water, the operator conducts a so-called NG test. In this test 50 ml of the adjusted feed is added and shaken with 100 ml of ether. If, after shaking and separation, 15 to 17 ml. of aqueous layer is present the batch is satisfactory for introduction into the neutral system. If the water layer should fall outside of these limits the batch should be adjusted by dilution or concentration as required. It should be emphasized at this point that the batches should not be adjusted until within five or six hours of usage since the batch will have to be readjusted if allowed to set for a longer period of time. This operation is conducted by one operator as mentioned in the preceding section. In addition to operating the NOK tanks and the evaporator this operator is charged with the responsibility of taking care of the deionized water system, which will be described later, or the distilled water evaporator.

In these operations difficulties arise as a result of the extensive corrosion which occurs in the third effect of the evaporator or upon the coils of the NOK tanks. Because of the continuing difficulties with this corrosion, both the tank coils and the evaporator tubes are designed for easy replacement. The most recent information indicates that the tube bundle in the third effect will need to be replaced every six months and the steam coils in the NOK tanks on a semi-annual basis. In addition to the maintenance difficulties great care must be exercised in the operation of these tanks and the evaporator to avoid freezing of the uranyl nitrate salts. Also, care must be taken during evaporation to avoid any boilovers of the tank.

The principal hazard in this operation is that of scalding.

c. Operation of Neutral Stage

The operation of the neutral stage is started in much the same manner as that of the first extraction; that is, the ether cooler is turned on and the flow of ether is started from the ether hold tank into the neutral mixer, from the neutral mixer into the decanter, from the decanter through the recycle line back into the neutral mixer. When the level fills up in this system ether is permitted to overflow from the top of the neutral decanter into the extract hold tank from which it is fed into the wash column. Ether, after filling the wash column, overflows into the re-extraction column by gravity and then flows out of the re-extraction column by gravity into the ether hold tank, completing the cycle. After the ether flow has been started and the ether cooler is on, the flow of primary brine is started into the primary cooler, then the secondary brine is started through the neutral mix cooler. It is important that the temperature of the secondary brine flowing into the neutral mix cooler be controlled so that it does not fall below 60° F. With the cooler in operation the flow of uranyl nitrate may be started into the mixer. This flow should be controlled so that the gravity of the cooled extract does not exceed 39° Be. As the uranium flow starts in the block valve on the decanter level control should be open, permitting the flow of NG back to the NG hold tank for flow into the acid stage mix. As the extract begins to come off the decanter and accumulate in the extract hold tank the flow into the wash column of distilled or deionized water should be started through the water cooler with the brine on from the water storage tank and into the wash column at a ratio of one gallon of water for every nine gallons of extract, and the water should be started to the re-extraction column and operated in the same manner as the re-extraction column on the first extraction. As the OK liquor accumulates at the bottom of the re-extraction column it should be allowed to drain by gravity through the level control valve into the OK stripper feed tank.

The OK stripper can be started after 100 to 200 gallons of OK liquor has been accumulated and its operation is very similar to the NOK stripper described previously. The wash water from the wash column should be allowed to flow through the level control valve into the NOK stripper feed tank. This operation of the neutral system is relatively trouble-free except for the constant danger of freezing. It is particularly important that frequent checks be made on the gravity of the extract and the temperature of the coolant to the neutral cooler because of the constant danger of the system freezing. If the gravity becomes too great or the temperature of the secondary coolant should fall too low, either condition may be sufficient to freeze the system solid and necessitate an arduous thawing procedure. It is also very important that in the event of a failure of the ether pump that the feed flow be shut off immediately in the event that the interlock should fail. In addition to freeze-up difficulties, operational problems arise because of the difficulty of maintaining a free flow of uranyl nitrate into the system. It is particularly difficult to get this flow when changing NOK tanks.

Although normally little or no scaling is experienced in the neutral system, under special circumstances involving unusual feeds the deposition of uranyl vanadate on the surface of the neutral system equipment has required special physical cleanouts on a frequent basis. Also, in regular operation, great care should be taken that no water phase is carried with the extract into the wash column or beyond.

This operation, with the exception of the OK stripper, is conducted by one man.

d. Operation of Other Extraction Facilities

Within the ether house, wash waters and sump liquors are collected and pumped into a special closed de-etherizing tank called the sump tank. When 600 to 700 gallons of sump liquor have been accumulated in the sump liquor hold tank it is pumped into the sump de-etherizing tank and the valves on this tank are closed. Brine should be flowing through the sump tank condenser with the tank open to this condenser. The steam flow is started into the coils of the sump de-etherizing tank and the ether gently boiled off and heating continued until a temperature of 205° F. is attained at which point the valve to the condenser is closed and the contents of the tank are pumped out to the sump recovery system described in Section 6.

In addition to the sump tank, the NOK tank operator controls the operation of the deionizer. This unit is a standard two chamber resin unit and is operated in accordance with the manufacturer's recommendations. As a secondary supply of water in the event the resin treatment fails the triple effect evaporator is available for the production of distilled water. This still is operated in a manner similar to that of the NOK triple effect evaporator except that the bottoms from the third effect are discarded and the condensate from each effect except the third effect shell side are collected after condensation as distilled water. The water to be used in the neutral system, whether produced by the deionizer or the still, is continuously monitored by an electronic system which measures the conductivity. The specific conductivity limit has been set at 7 micromhos.

Two operational difficulties arise in the production of pure water. Experience has shown that to maintain a very high quality of water frequent regeneration of the resin bed is necessary. In the operation of the evaporator on the other hand, de-scaling is required on a periodic basis about once every six weeks during continuous usage.

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4. Trioxide Operation

The uranyl nitrate from the OK stripper is collected in the OK liquor boildown tanks. When the coils of these tanks are covered, steam is turned on and left on until the tank is full and at a boiling point of 245° F. under atmospheric conditions. This liquor is sampled and submitted to the laboratory for an iron determination. After the full batch has been accumulated it is circulated through the OK liquor piping system.

When a pot needs to be charged the valves above that pot are opened and 50 gallons of liquor is allowed to drain into the pot. The lid is placed securely on the pot and the damper opened to connect it with the nitric acid fume recovery system. At this point, the No. 1 burner is lit. Ten minutes later the No. 2 burner is lit and then after an additional ten minutes the No. 3 burner is lit. The fourth burner is lit 20 minutes after lighting the third. Forty-five minutes after lighting the burners the agitator is turned on. When the liquor within the pot becomes turbid (approximately 1 1/4 hours after the burners are lit) the gas is shut off to the No. 3 and No. 4 burners; 25 minutes later the gas is turned off to the No. 2 burner. As soon as the liquor converts into powder the remaining burner is shut off and the powder allowed to cool with agitation for about 2 1/2 hours.

After the powder has cooled the required amount of time it is unloaded into the pneumatic system. This is done by attaching a metal hose to the outlet nearest the pot to be unloaded and starting up the vacuum producer and vacuuming out the powder from the pot. Normally in a pot load, a certain amount of hard cake, called mill cake, remains adhered to the stirrer. This cake is smashed with a stainless steel rod and vacuumed up with the powder. When the pot has been emptied the vacuum producer to the pneumatic system is shut off, the powder having been discharged automatically into the orange oxide storage bin. The pot is then ready for refilling to start its cycle over. The total cycle time is approximately seven hours. In unloading the pot care should be taken that the air temperature from the dust collector does not exceed 150° F.

As part of the pneumatic system, a sifter-crusher arrangement has been incorporated so that the powder falling into the storage hopper is ready for packaging for shipment. The powder from this hopper is simply discharged into an empty 30 gallon drum resting on a roller conveyor. This roller conveyor has a hydraulic actuating device which forces the drums up tight against the dust seal while the drum is filling. After the drum has been filled it is lowered, lidded, weighed, and sent to the warehouse for storage. During this filling operation an automatic sampler samples the drums. Individual drum samples are submitted to the laboratory for complete chemical analyses on a lot composite basis. In this operation four men are required; three men to tend the pots and the boildown tanks while the fourth takes care of the packaging operation.

One of the primary difficulties experienced in this operation is frequent bag failure on the pneumatic system. In addition to delaying the operation for repairs, the actual repair itself is somewhat difficult because of the hazardous dust problem that is encountered on opening the dust collector to replace the broken bag. In handling the bag, entries for replacement must all be handled under very careful conditions to prevent undue exposure to a dust hazard. As mentioned before, the radioactive dust limit is 70 alpha D/min/M^3. Special arrangements should be made to have expert health-physics advice during such repair work. Our recent experience has indicated that these bags must be replaced on a monthly basis.

Considerable difficulty has also been experienced with the packaging system primarily because drums are occasionally filled too full and variations in the density of the powder make it difficult to determine when the drum is full.

From a safety point of view, two major hazards exist. One hazard is the molten uranyl nitrate hexahydrate salt as an acidic molten salt. Uranyl nitrate hexahydrate is thought to be a dangerous splash hazard and all operating personnel in this area are required to wear goggles during the filling of the pots as a result. The second serious hazard is represented by the nitric oxide fumes evolved when the uranyl nitrate is converted to the trioxide. From the health-physics point of view, the primary hazard from this area is the uranium trioxide dust which is extremely difficult to contain.

5. Raffinate Area

The raffinate from the raffinate stripper is received in the raffinate precipitation tanks. When 1,300 gallons have been received the operator checks to be sure that the temperature is below 170° F. and takes a sample for uranium determination. If the temperature is suitable he starts the introduction of a lime slurry made up with five pounds of lime added per gallon of water used. Approximately 500 gallons of this previously prepared lime slurry is used to neutralize a batch to a pH of 10 on Hydrion paper. After precipitation, the batch is pumped continuously to the Peterson filter from which the excess overflows back into the precipitation tank. When the bowl level is above the point of overflow the operator starts the vacuum pump with the barometric legs protecting the pump and opens the vacuum lines to the filter. The filter is started in rotation, the air blow turned on, and the cake discharges to a portable hopper situated below the filter. This operation continues until the tank is empty at which time the operator switches over to the next tank which is usually ready to follow through. The hoppers underneath the filter are removed by the fork truck operator. In addition to his services, this area requires two production operators to handle this operation and the triple effect evaporator which is situated in this area. The filtrate from the Peterson filtration is sampled for uranium concentration and either concentrated for use as salting agent in the feed storage area or discarded to the sewer as the need and the uranium analysis indicate.

The primary hazard in this area is radiation from the raffinate, from which the operator should be shielded. Where raffinate is permitted to dry a dust hazard arises.

The primary operating difficulties in this area are centered in the Peterson filter. Difficulties arise in pumping the heavy slurries to the Peterson and obtaining a good discharge from the Peterson and in maintaining the bag life on the Peterson itself. It is necessary, for example, as a minimum to change all of the Peterson bags on a weekly basis. Failure to do so results in greatly reduced filtration rates and bottlenecks the plant. No special maintenance problems exist in this area except those that could normally be expected in a chemical plant operation utilizing filters, pumps, and agitators.

In this area also the salting agent makeup tanks are situated, where the operators of this area makeup synthetic salting agent by adding 1,000 gallons of 60% nitric acid, 500 pounds of magnesium oxide, and 2,500 pounds of lime to the tank and mixing. This salting agent is than available for pumping to the feed storage area as needed.

It should also be pointed out that an experimental continuous raffinate denitrator is under development in this area. This involves the use of a screw type reactor containing a bed of heated denitrated raffinate to which concentrated raffinate is continuously being added.

It is thought that perhaps this development might lead to the recovery of the nitric acid values from the raffinate and avoid the use of lime for neutralization.

6. Nitric Acid Recovery

The nitric acid recovery system for this plant consists of two basic units. The first is the absorption unit.

a. Absorption Unit

Fumes from the decomposition of uranyl nitrate hexahydrate and the uranium octaoxide are collected in ductwork and pumped by the use of stainless steel Nash Hytors into a system of absorption towers. This unit is a commercially designed nitric oxide recovery unit and is operated reasonably in line with the manufacturer's recommendations. The primary duties of the operator, in addition to tending the pumps, is to be sure that the proper amount of water or weak acid is introduced into the system and strong acid is drained countercurrently as produced. The primary operating problems of this area occur in the Nash Hytors which, because of the hot operating temperatures and the possibility of dust carryover, are difficult to maintain. It should be appreciated that a Nash Hytor is a close tolerance machine and any abrasion or corrosion would greatly reduce efficiencies. As a result, a considerable part of the maintenance effort of this plant is spent in the overhauling and adjustment of the Nash Hytors. In the wintertime some difficulties occur because the absorption towers and some of the auxiliaries are externally located. As a result freezeups must be guarded against. All of the other units of the plant are internally located because of the relatively low freezing points of uranium solutions. The pumps, particularly the hytors, are difficult to keep sealed and the continual drippage corrodes away pump bases, making a difficult pump base maintenance problem throughout the area.

b. Concentrator

Weak acid is collected from the condensers on the triple effect evaporator and the NOK tanks as well as from

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several other small sources into a storage tank. From this storage tank these acids are fed into a packed vacuum rectifier. This operation is started by opening the inlet to the rectifier and feeding in acid and then turning on the water supply to the barometric leg producing a vacuum of about 15 inches on the rectifier. Acid is circulated out of the rectifying unit into a heat exchanger and back into the unit. The present unit produces a 15° Be acid which is fed into the first absorber of the fume recovery system for fortification.

Throughout this nitric acid system and the tank farm, which this operator also controls, concentrated nitric acid itself is the primary hazard and represents a grave danger where splashing or squirting is possible. Any fume leaks or any attack of nitric acid upon iron would also represent a serious hazard.

7. Sump Recovery System

As is mentioned elsewhere, no direct sewers are permitted in the refinery and where sewers are necessary they are on elevated locations so that any drainage to the sewer system can be controlled. Wash liquors, drippings, etc., are collected in sumps which are pumped as they fill to the central sump recovery system. From the central sump recovery system all the waste liquors of the plant are collected and continuously concentrated by the use of a steam coil while being collected. When approximately 1,300 gallons have been collected the recovery liquors are switched to the second tank for collection and the concentration in the first tank is continued until it reaches a concentration of 3 pounds per gallon of uranium by batch analysis. When this uranium concentration is achieved the acid content is checked and adjusted to .5-.7 pounds HNO_3 per gallon or this adjustment is done optionally in the feed storage area. Both this area and the raffinate area in addition are served by fume scrubbers, the operation of which consists merely of turning on the blower and the scrub water. The recovery system is operated by one man per shift.

TBP EXTRACTION PROCESS
FERNALD REFINERY

by

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The TBP extraction process as presently in operation at the Feed Materials Production Center located at Fernald, Ohio, is the product of approximately six years of extensive laboratory and pilot plant investigations and plant operating experience. The result of this effort has been the development of a new process for the recovery of uranium in a pure state from uranium-bearing ores and concentrates. It incorporates the most recent advances in uranium recovery technology that have come to light in the various Atomic Energy Commission's operations. The process offers the advantages of (1) a high uranium recovery, (2) direct extraction from a slurry feed, (3) a single solvent extraction process and (4) a high degree of product purity. A general discussion of the process fundamentals, process design, and operating plant size and facilities requirements are presented.

INTRODUCTION

Upon the decision of the Atomic Energy Commission to undertake the expansion of the feed materials processing facilities in 1950, a survey was begun to select a suitable process for the Refinery which ultimately was to be located at Fernald and operated by the National Lead Company.

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In the course of this survey, the New York Operations Office requested the recommendations of the Oak Ridge National Laboratory concerning a suitable solvent extraction process to handle uranium recovery from slurry-type ore feeds. In the course of this survey, tributyl phosphate was compared with diethylether, pentaether and hexone, using samples of actual refinery feeds from the St. Louis plant(1) and recommendations were made that tributyl phosphate be considered as the most desirable solvent. Arrangements were subsequently made whereby a process flowsheet prepared by ORNL was jointly evaluated with the Mallinckrodt Chemical Works in its pilot plant in St. Louis.(2)

Subsequently, additional work by Mallinckrodt Chemical Works and the Catalytic Construction Company verified the results of the Oak Ridge group. The TBP process was chosen for the Fernald plant on the basis of its higher recoveries from low-grade feeds as compared with diethylether and because the high flash point of the solvent rendered it less of an explosion hazard than diethylether. It was further demonstrated that adequate uranium purity could be obtained in a single solvent extraction cycle using tributyl phosphate whereas it appeared that at least two cycles would be required with ether.

In the fall of 1951, the Atomic Energy Commission completed construction of a full-scale pilot plant at Fernald and studies were undertaken to establish the type of Columns that would be selected for the Refinery and to establish optimum operation conditions for the types of ore feeds that were expected at the National Lead plant. On the basis of some small-scale work carried out by the Oak Ridge National Laboratory in two-inch columns, and on the basis of the larger pilot plant-scale tests by National Lead at Fernald,(3,4,5) pulse columns were chosen as the most desirable type of contacter over jet-mixer columns, spray columns and Schaibel columns that were also considered.

The National Lead pilot plant was also used to develop suitable piping arrangements to handle slurries, pumps, pump packings, and slurry metering equipment and satisfactory materials of construction to contain the process. The Fernald refinery began operations in January, 1954, and has now been on-stream approximately 24 months. The process and equipment, as presently operated, presents the combined efforts of the Technical and Production groups and incorporates the most recent advances in technology that have come to light in the various Commission operations.

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The process has yielded material of satisfactory purity and has demonstrated the ability to recover uranium to the extent of 99.8% or greater from almost all available feed materials.

In presenting the following data on the process and equipment at Fernald, in most cases, no effort has been made to present the personal recommendations of the authors. It is felt that the Fernald operation as presently practiced is in itself the best recommendation for what is good in the way of equipment or process.

PROCESS FUNDAMENTALS

Uranium trioxide (UO_3, orange oxide) is produced from uranium ores and concentrates at the Fernald refinery using a three-step process. The uranium values in the raw feed material are first converted to uranyl nitrate by dissolution in concentrated nitric acid. By preferential extraction using an organic extractant, the uranyl nitrate is removed from the feed slurry in a pure form. Following re-extraction from the organic phase with water, the aqueous uranyl nitrate is evaporated to dryness and calcined to yield a pure uranium trioxide. The uranium depleted slurry from the extraction process is evaporated and calcined to recover the nitric acid which is reused, and the oxides of the other elements initially present in the concentrate are stored. A schematic diagram covering this process is presented in Figure 1. The prior ore sampling and subsequent green salt production operations have been included. Each operation in the production of UO_3 is presented in detail with a flowhseet of the system.

DIGESTION FLOWSHEET (Figure 2)

The uranium concentrate is received at the digestion area in 55-gallon drums which have been previously sampled for assay and weighed in the Sampling Plant. On the receiving pad the concentrate is segregated into batches, each batch containing sufficient uranium for a single digester loading. The drums are transferred by roller-conveyer to the bucket elevator where they are dumped manually. A view of the ore receiving station and bucket elevator is shown in Figure 3. The bucket elevator carries the ore to the top of the digestion building and from there it is conveyed by screw conveyer to a surge hopper. From the surge hopper the material is carried again by screw conveyer to the individual digesters. There is essentially no solids hold-up in the ore feed system. The digestion area control center is shown in Figure 4.

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PROCESS FLOWSHEET

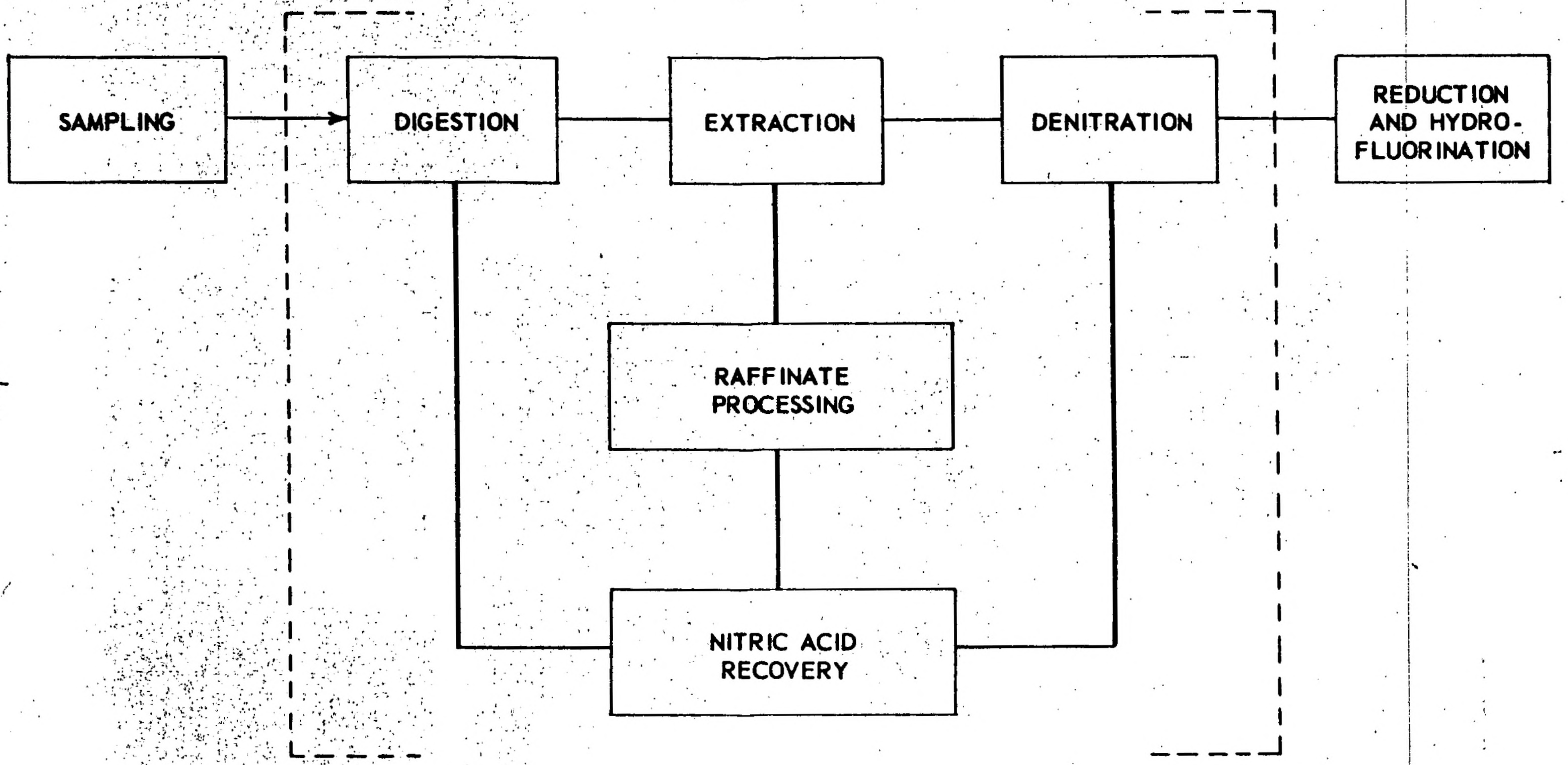

FIGURE 1

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FEED SLURRY PREPARATION SYSTEM

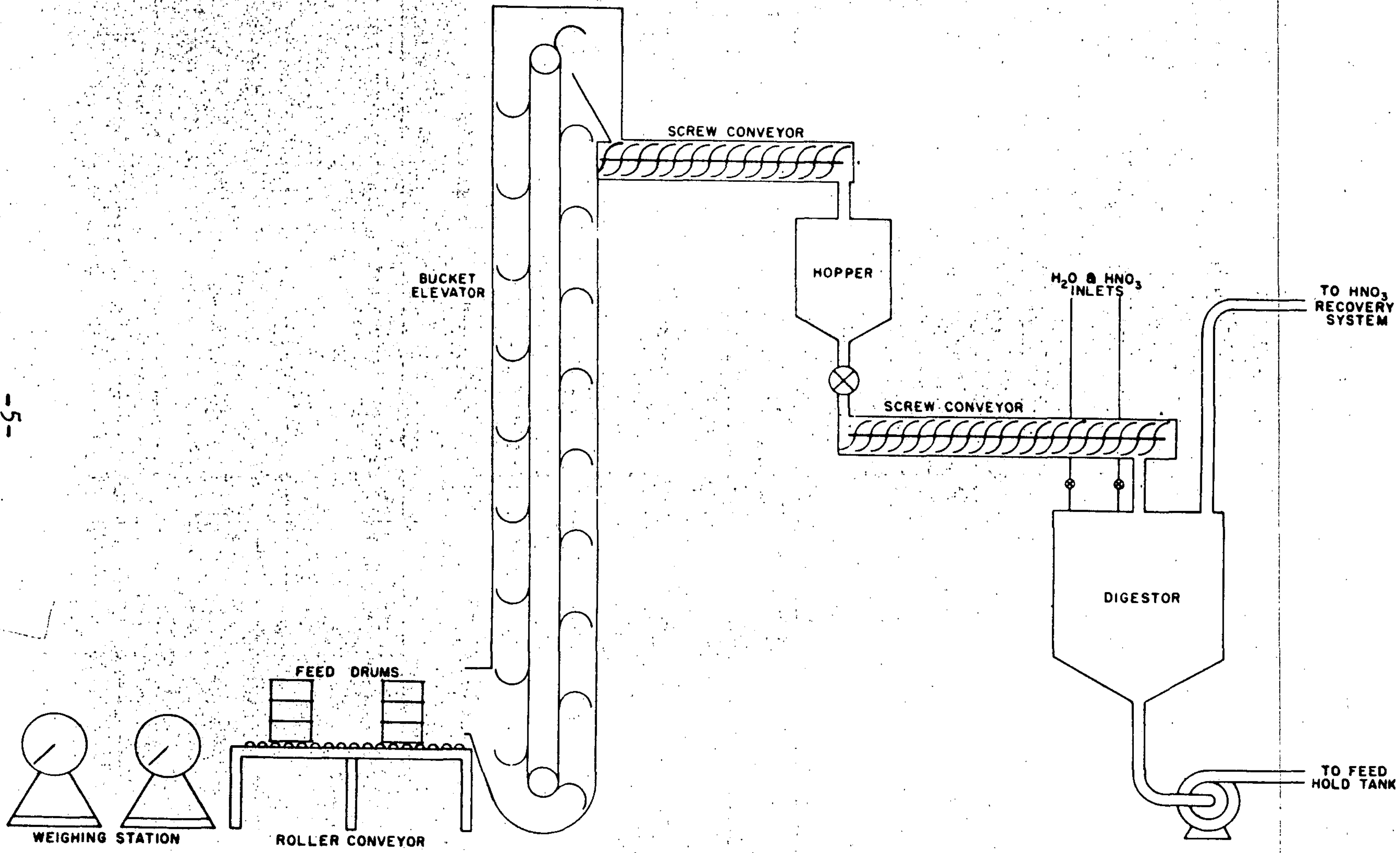

FIGURE 2

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ORE RECEIVING AREA

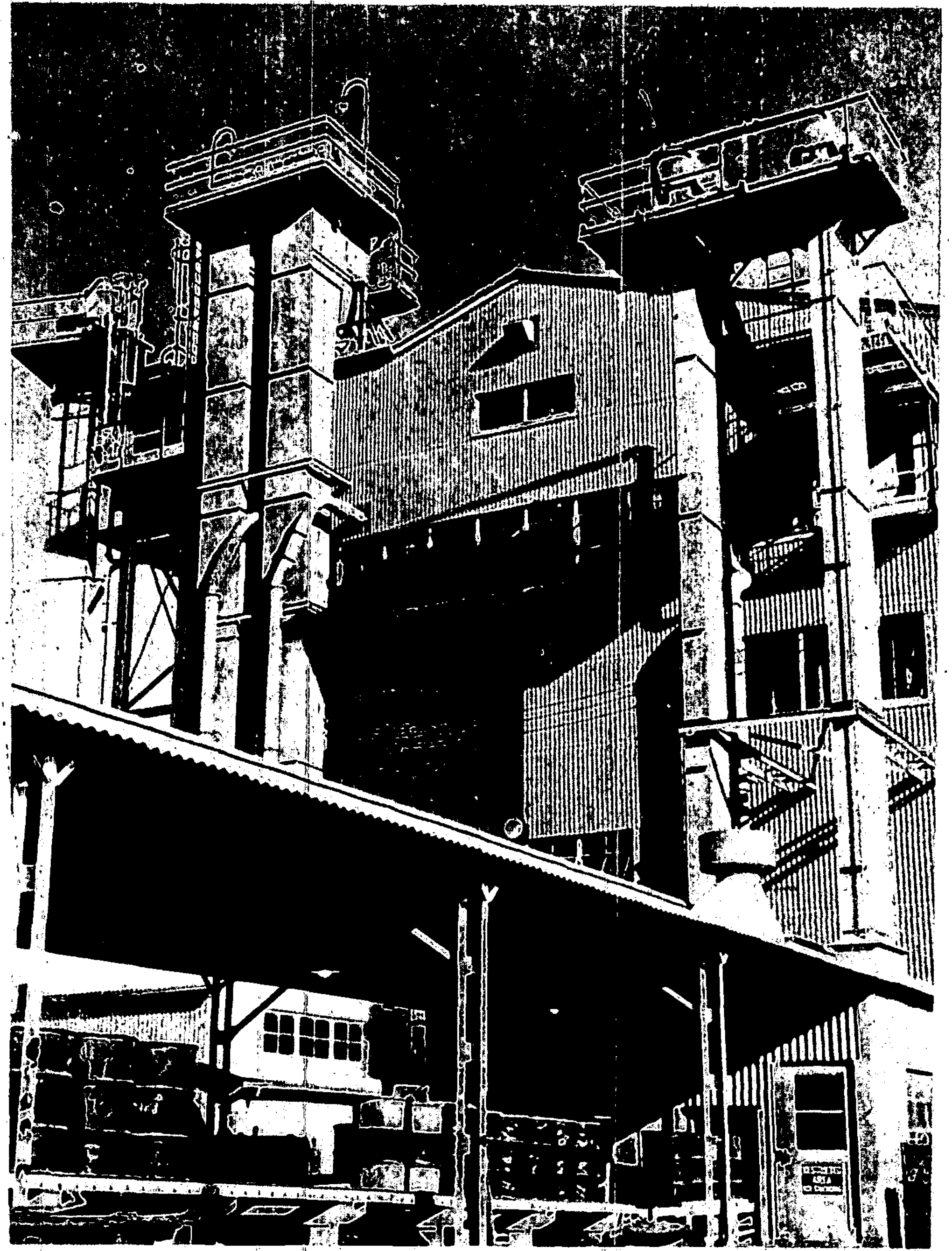

FIGURE 3

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DIGESTION AREA CONTROL PANEL

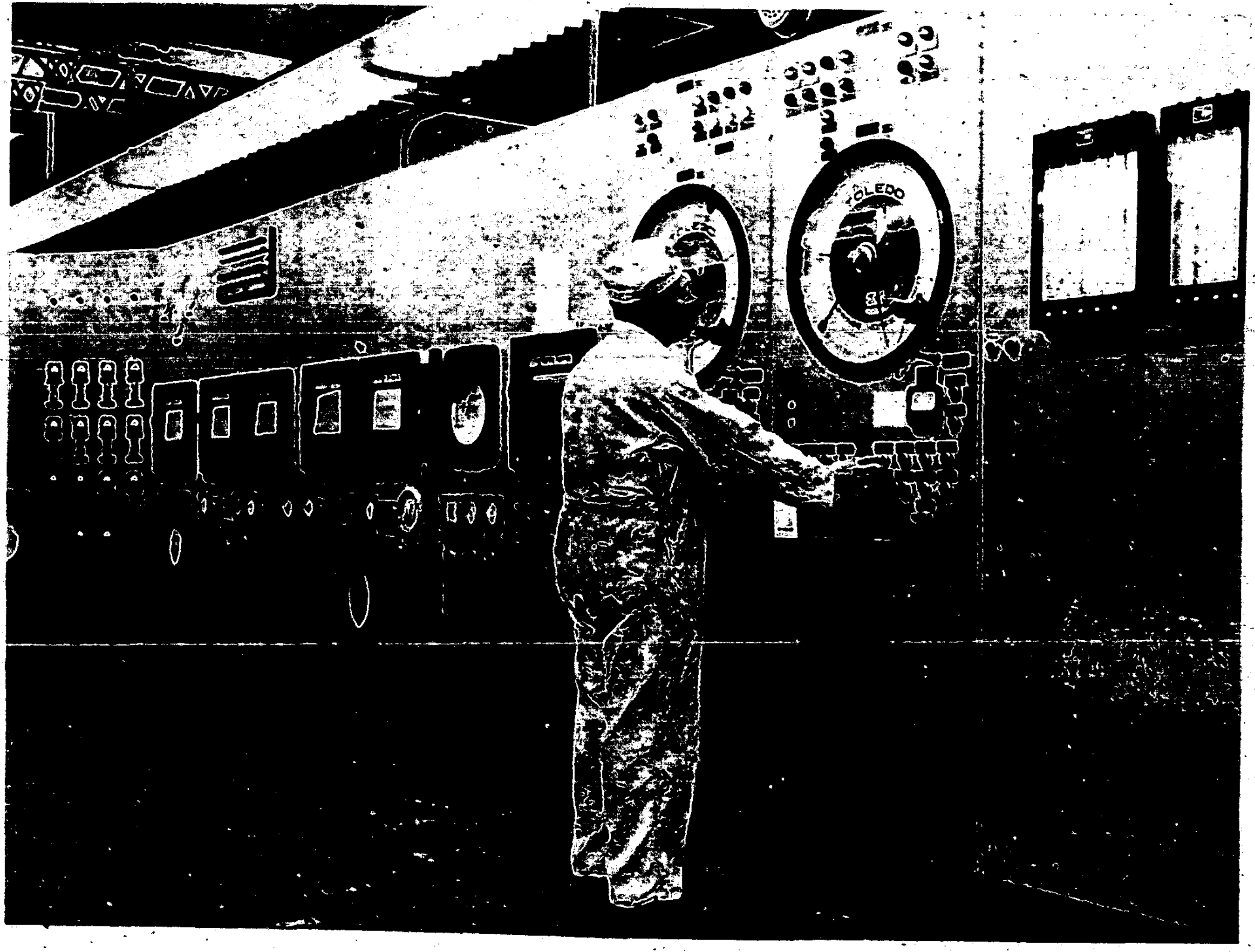

FIGURE 4

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The required volumes of acid and water to yield a final feed slurry concentration of 200 g/l uranium and 3N nitric acid are calculated from the acid consumption and volume change factors supplied by the laboratory for the particular type of concentrate being processed. After the acid and water have been metered into the digester tank the dry feed is added. The rate of the digestion reaction is controlled by the rate of ore addition and the temperature of the digest batch. Each digester is equipped with internal coils which can either be used for heating or cooling and with heavy duty agitators. Any water vapor, nitric acid or oxides of nitrogen evolved during the digestion reaction are conveyed through a vent line system to the nitric acid recovery area. Figure 5 shows the top of one of the digesters. The agitator, ore and acid addition lines and off-gas lines can be seen. Dust collectors located in the vent lines trap any fine solid material carried from the digester. A three-hour digestion cycle is required to produce a 2500-gallon digest batch. After digestion is completed, the feed slurry is sampled for uranium and nitric acid and if necessary, the concentrations are adjusted by the addition of ore, acid or water to meet the 200 ± 10 g/l uranium and 3.0 ± 0.2N nitric acid specification. The slurry is then pumped to the extraction area.

EXTRACTION FLOWSHEET (Figure 6)

The digest slurry is received from the digestion area into the feed hold tank. The feed system is designed to handle slurries containing a relatively high solids content and which have a high settling rate. Slurries containing up to 15% solids by settled volume, have been handled successfully in this system. The feed tank is equipped with an agitator and a recycle loop extending to the top of the extraction columns. A high velocity centrifugal pump continuously circulates the slurry through the loop at a rate sufficient to keep the solid particles suspended, thereby supplying a relatively homogeneous feed stream to the columns. The slurry is fed to the extraction columns through a take-off line located at the top of the recycle loop, the flow rate being controlled by an air operated, diaphragm valve.

The extraction system is composed of five columns: two extraction columns operating in parallel with a single scrub column and followed by two re-extraction columns. All the columns are perforated-plate, pulsed units. The pertinent specification for each column is presented in Figure 7. Figures 8 and 9 are photographs of a 6-inch-

BATCH DIGESTER - TOP VIEW

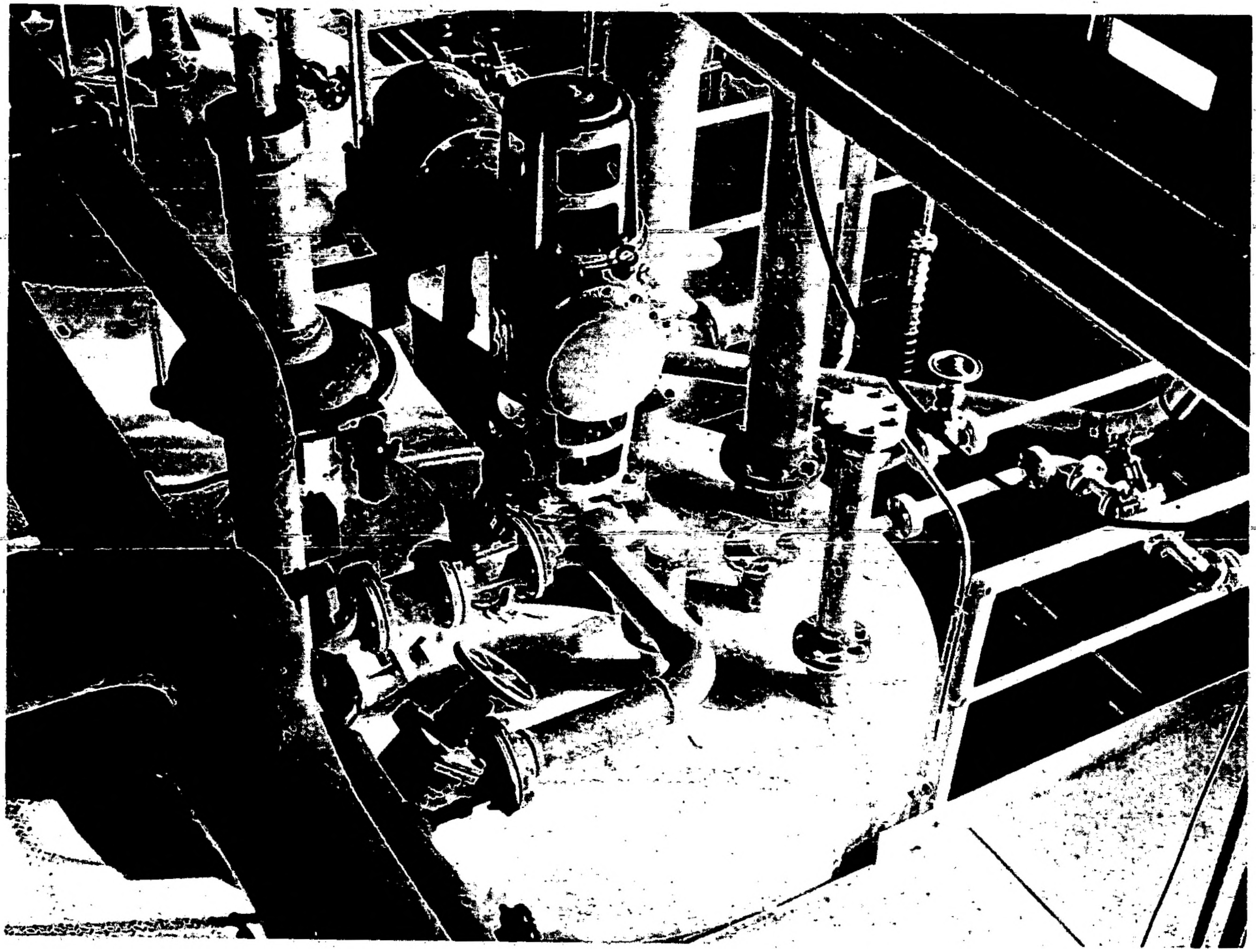

FIGURE 5

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SLURRY EXTRACTION SYSTEM

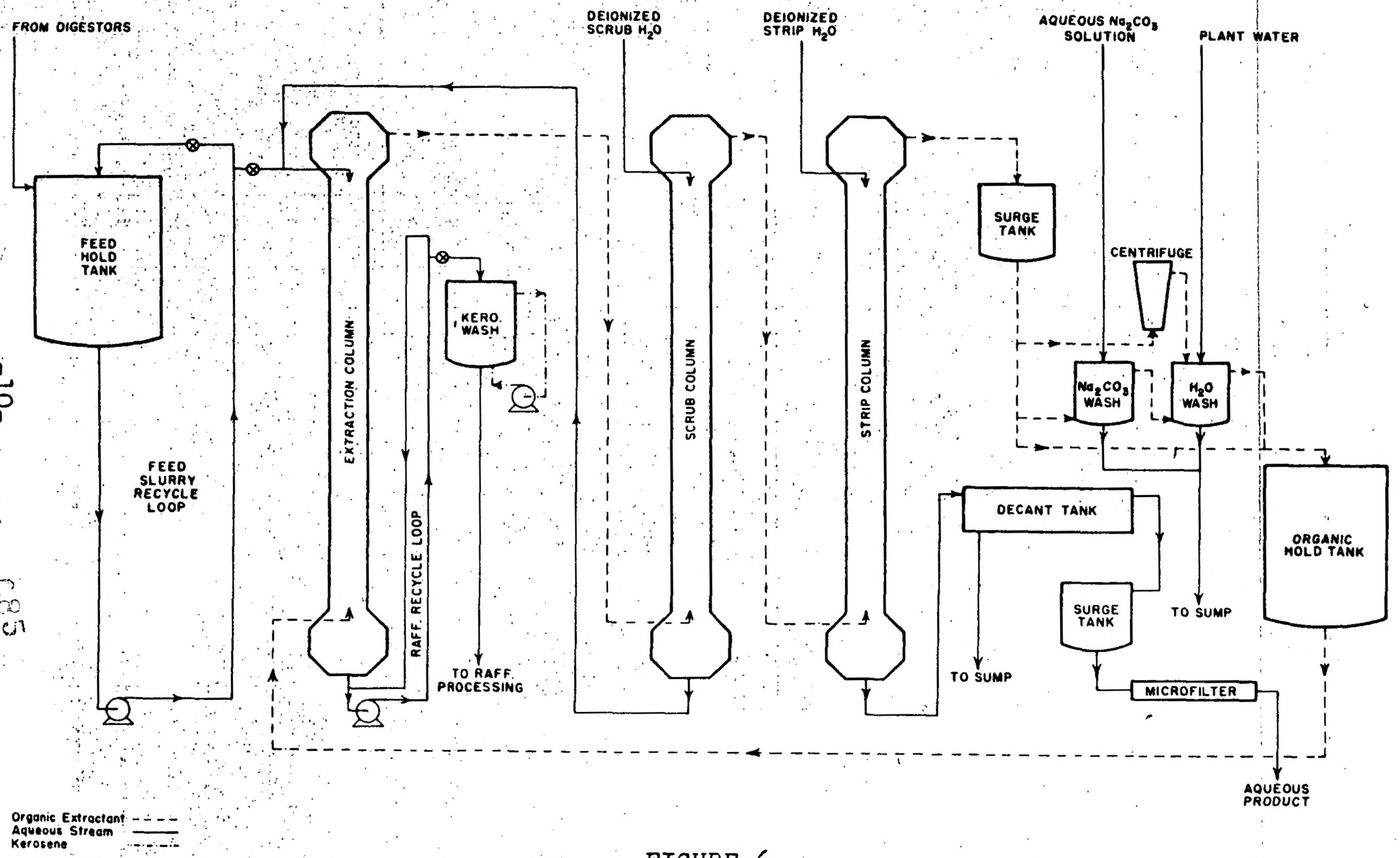

FIGURE 6

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COLUMN SPECIFICATIONS

FERNALD REFINERY

	EXTRACTION COLUMN	SCRUB COLUMN	RE-EXTRACTION COLUMN
COLUMN DIMENSIONS:			
COLUMN HEIGHT - TOTAL	36 FT.	35 FT.	35 FT.
PLATED HEIGHT	25 FT.	25 FT.	25 FT.
COLUMN DIAMETER	18 IN.	22 IN.	26 IN.
DISENGAGEMENT CHAMBER DIA.	36 IN.	44 IN.	52 IN.
DISENGAGEMENT CHAMBER VOL. (EFF.)	19.5 $FT.^3$	118.5 $FT.^3$	160 $FT.^3$
PLATE GEOMETRY:			
PLATE SPACING (BETWEEN CENTERS)	2 IN.	2 IN.	2 IN.
PLATE THICKNESS	1/16 IN.	1/16 IN.	1/16 IN.
PLATE HOLE DIAMETER	3/16 IN.	1/8 IN.	1/8 IN.
PLATE FREE AREA	23%	23%	23%
HOLE SPACING (BETWEEN CENTERS) EQUILATERAL TRIANGLE CONFIG.	3/8 IN.	1/4 IN.	1/4 IN.

FIGURE 7

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diameter perforated-plate and a section of the glass, six-inch Pilot Plant column showing the plate bundle construction. Since the number of columns employed in each of the three extraction operations (extraction, scrubbing and re-extraction) is unimportant in describing the system, a simplified three-column system will be discussed. A view of the refinery showing portions of the scrub and strip columns is presented in Figure 10.

EXTRACTION COLUMN

The aqueous feed slurry is introduced into the extraction column at a point just above the center of the top perforated-plate. Past experience has shown that specially designed spray nozzles are not required on the slurry inlet, therefore to minimize feed line plugging, a straight pipe inlet is used. The scrub recycle stream from the scrub column is combined with the feed stream as it enters the column. The organic extractant (33.5 volume per cent tributyl phosphate in an inert purified kerosene diluent) is introduced through the pulse generator transfer line into the top of the lower disengagement chamber. By adding the organic stream in this manner the pulse generator cylinder and transfer line is kept filled with the non-acidic phase, thereby minimizing corrosion in the generator.

The extraction column is operated with the organic phase continuous and the aqueous phase dispersed to avoid deposition of solids on the plates. Attempts have been made to operate slurry extraction columns with the aqueous phase continuous but to date there is no report of successful operation. The combined liquid phases are pulsed through the stationary perforated-plates, with the aqueous phase passing down and the organic phase up through the column. Both vertical, piston-type generators (Figure 11) and Teflon bellows-type pulse generators (Figure 12) are presently in use in the Fernald refinery. Although the bellows-type units are inert to nitric acid corrosion, they have been found to possess a shorter life span as they tend to fail mechanically under extended operation. Modification of the bellows design from saw-tooth to wave-form has resulted in units which have tested between five and six million cycles before rupturing. A pulse amplitude of 3/4-inch and a frequency of 60 cycles per minute are used.

The extraction columns are operated with a carefully controlled organic extractant flow rate and the feed stream flow rate is regulated so as to maintain a constant uranium saturation level in the organic product stream. Since the nitric acid and other impurities which follow the organic

PULSE COLUMN PERFORATED PLATE (SIX-INCH COLUMN)

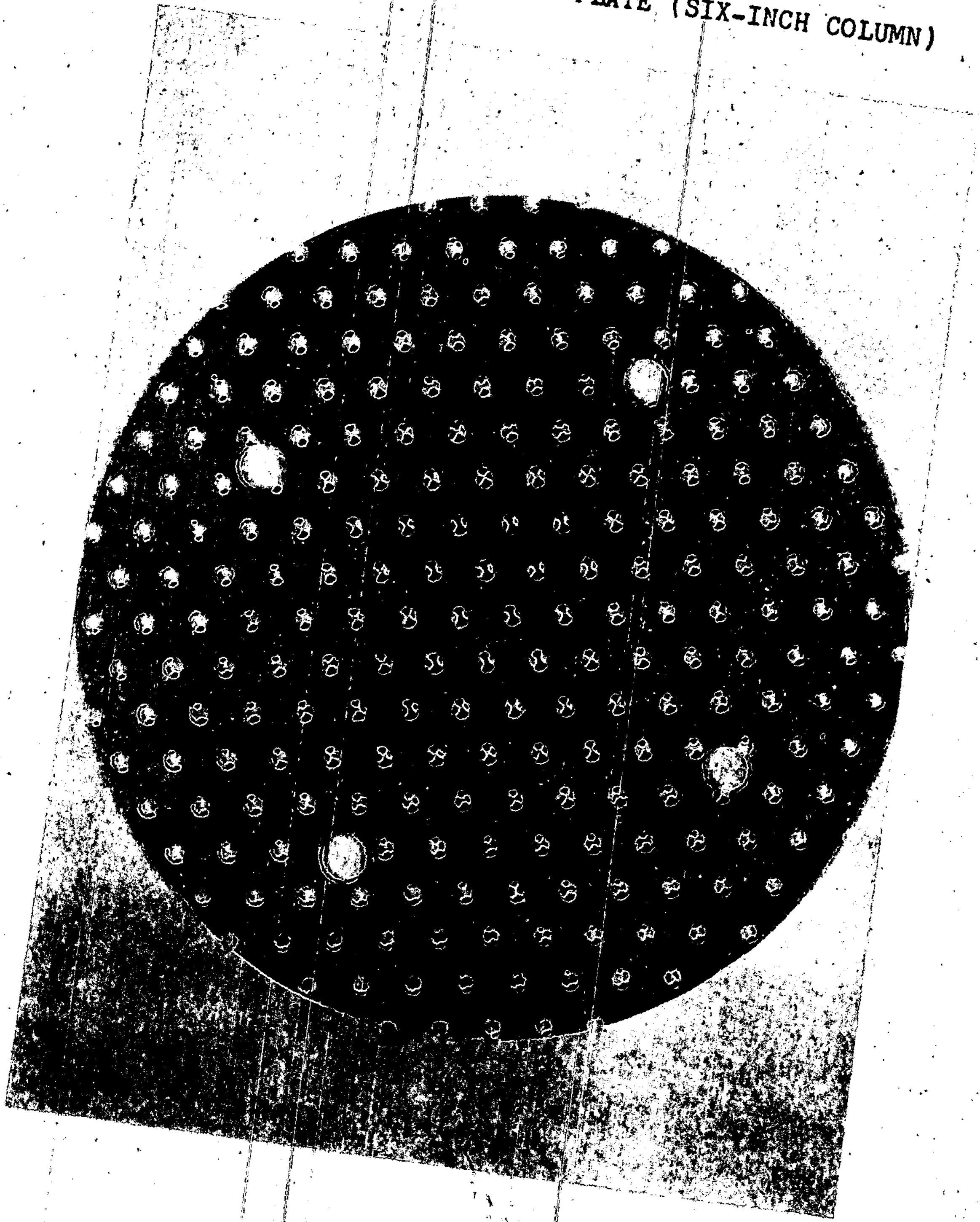

FIGURE 8

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PILOT PLANT COLUMN SECTION

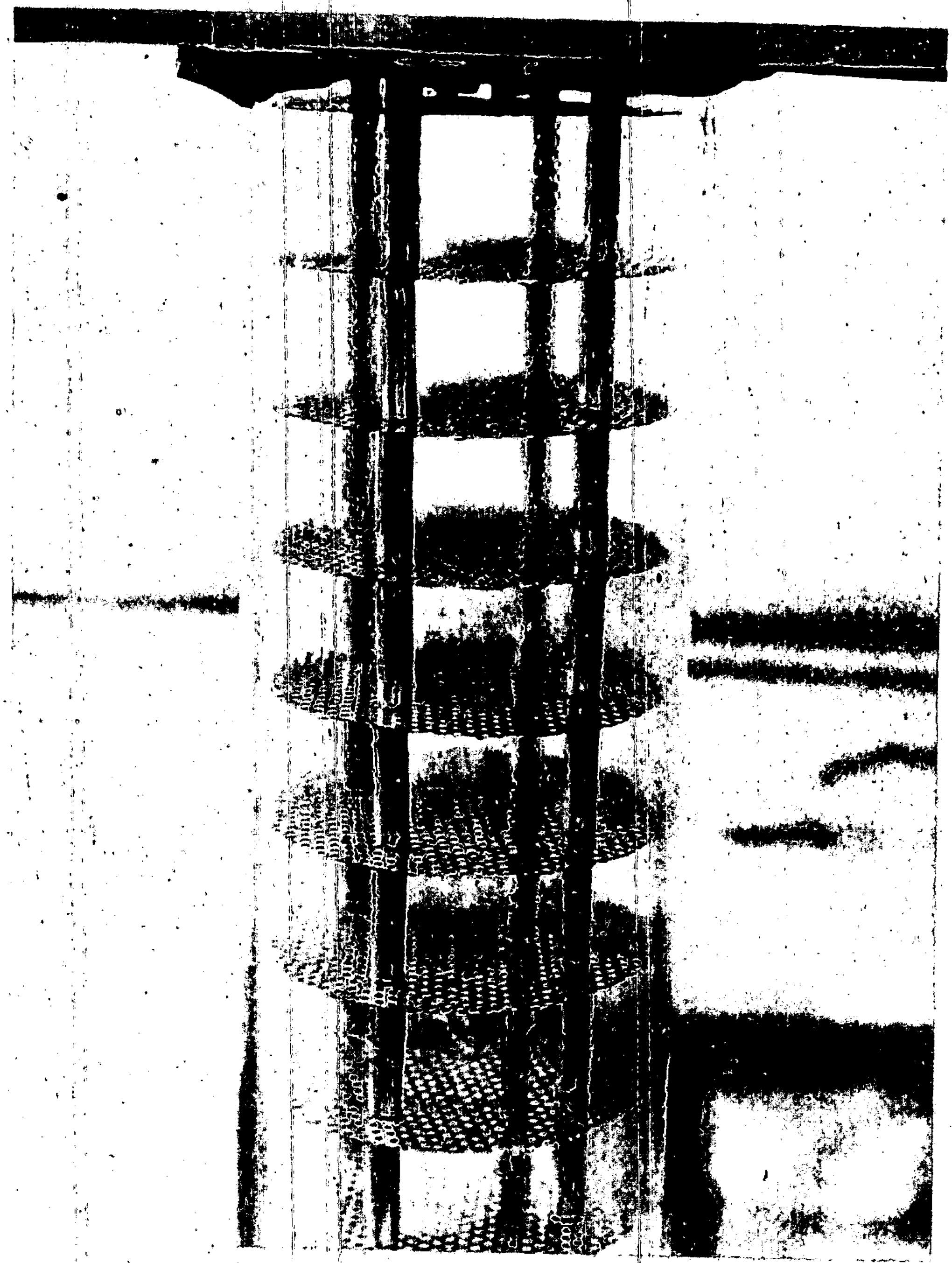

FIGURE 9

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REFINERY COLUMNS

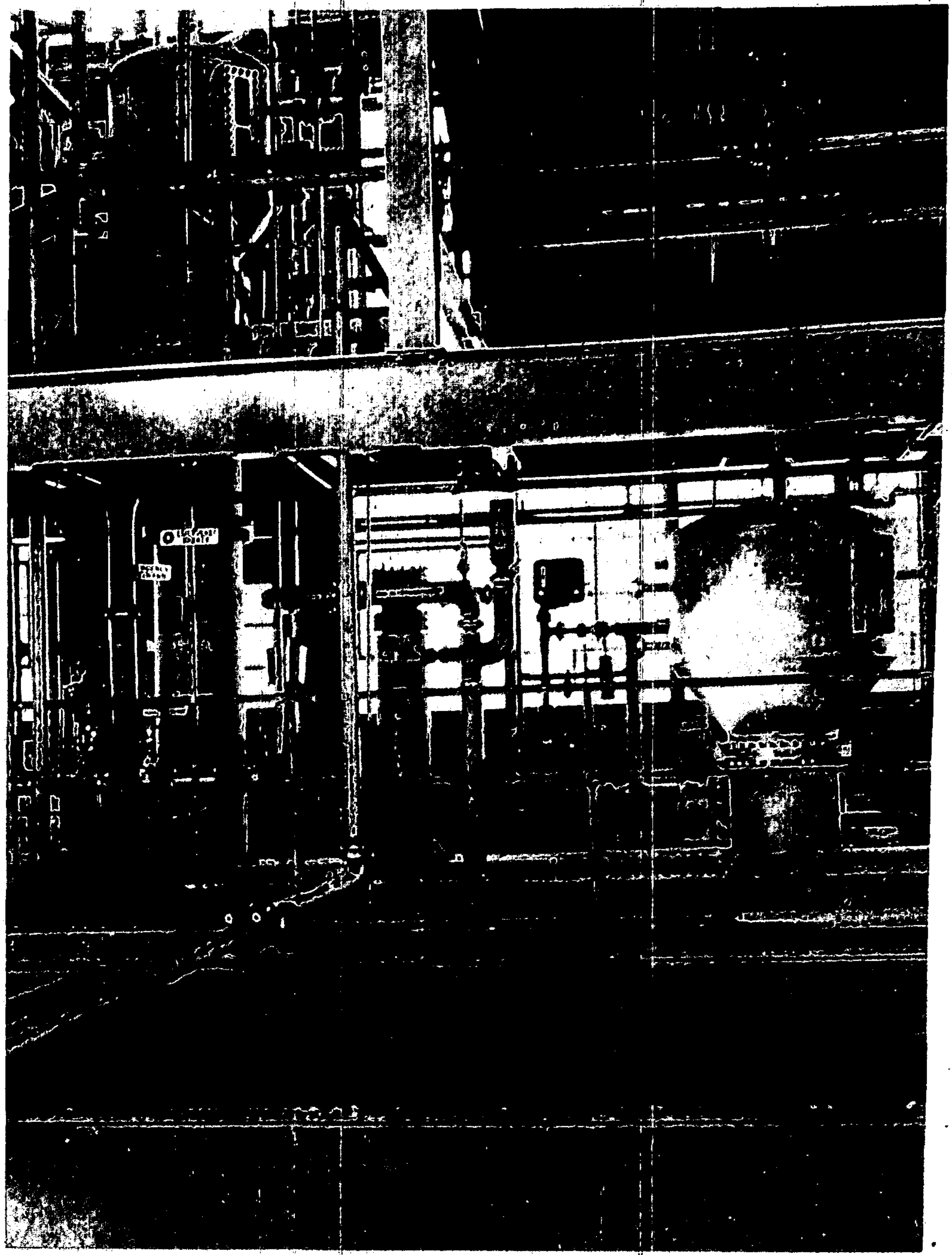

FIGURE 10

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PULSE GENERATOR - PISTON TYPE

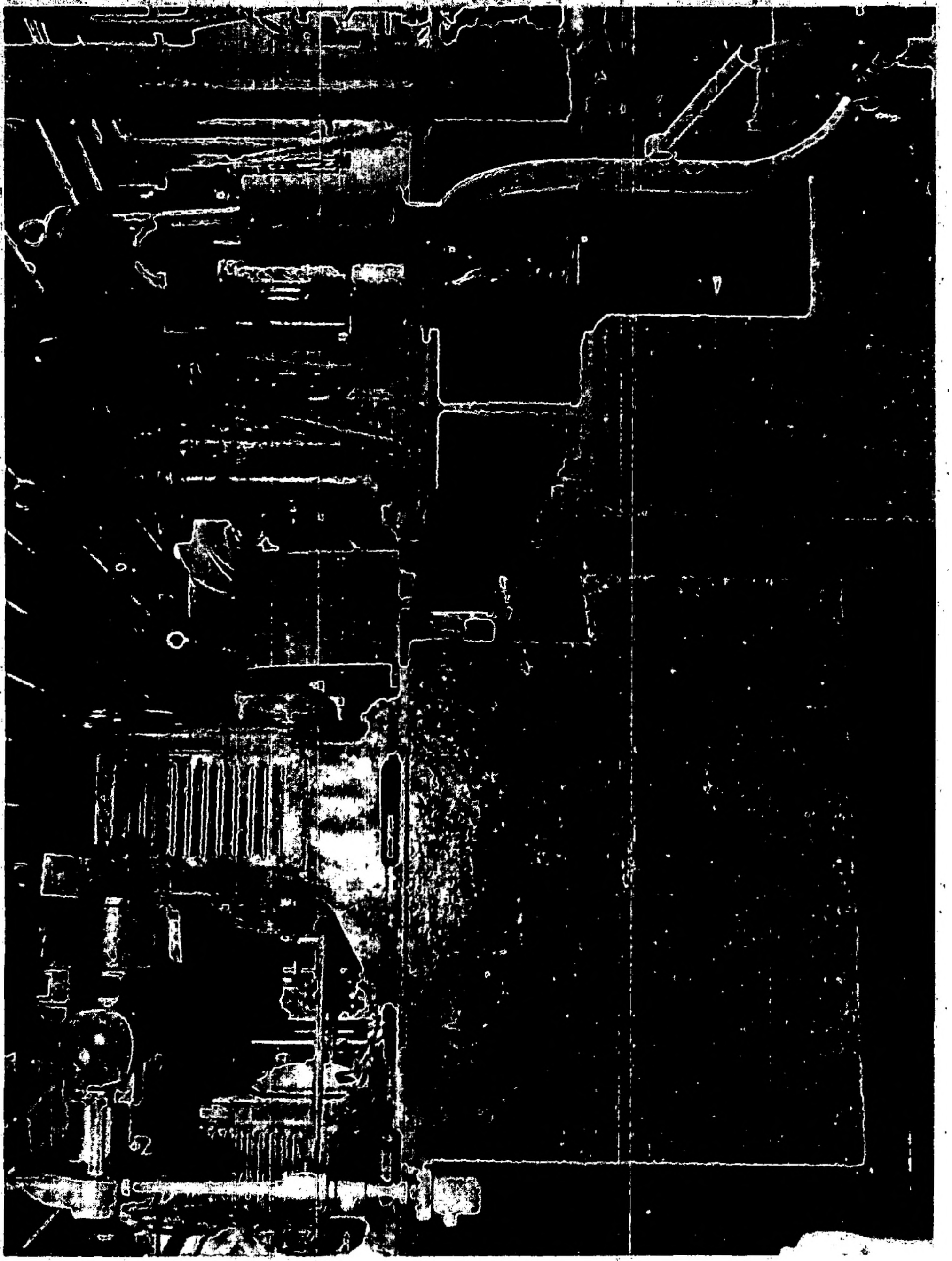

FIGURE 11

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PULSE GENERATOR - BELLOWS TYPE

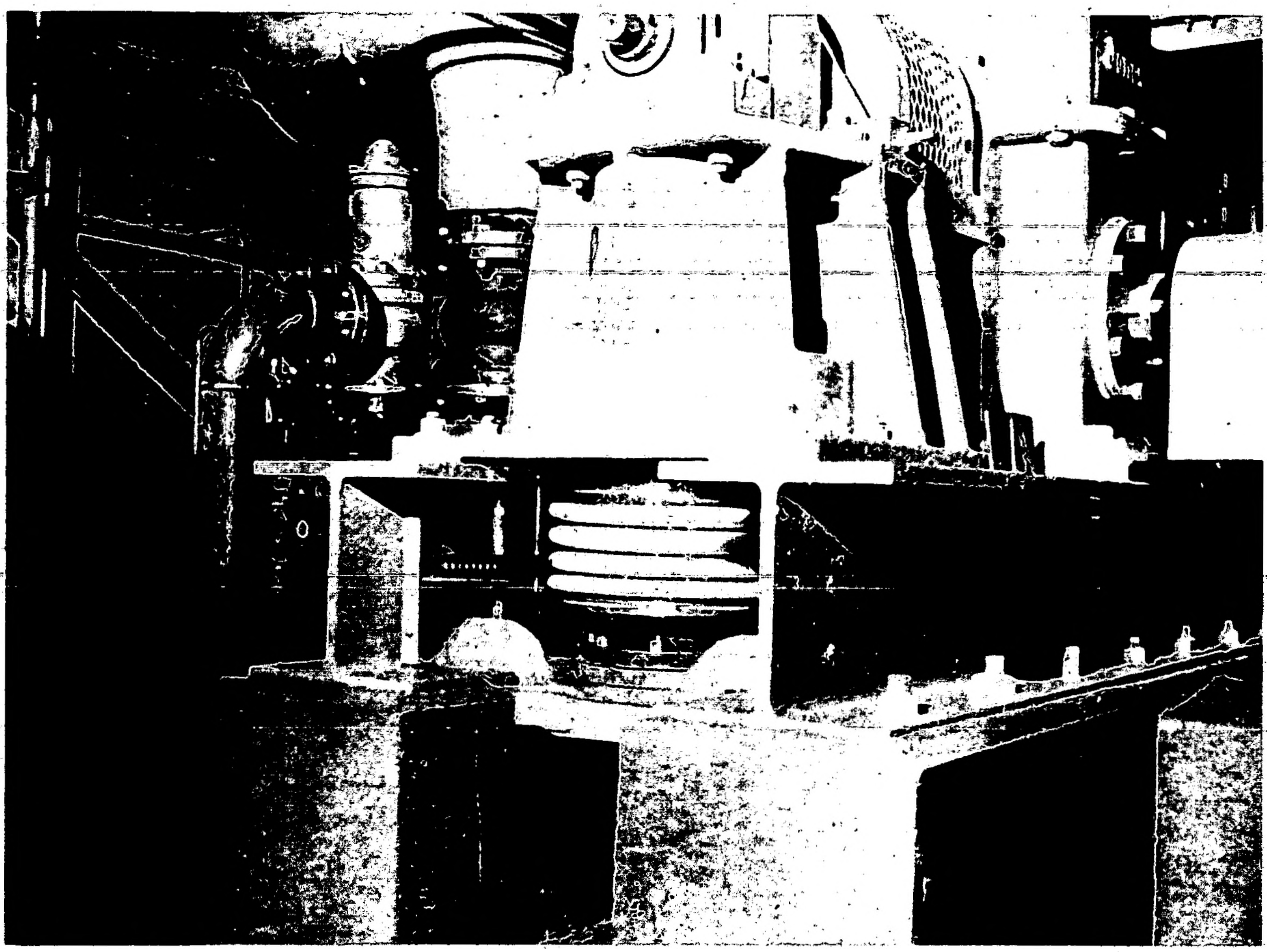

FIGURE 12

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phase contribute little to the specific gravity of the product stream in comparison to that contributed by the extracted uranium, it is possible to maintain a constant uranium saturation level in the product stream by monitoring and controlling its specific gravity. The system is instrumented to automatically control the feed stream flow rate so as to maintain an extract of uniform uranium concentration. (A specific gravity of 0.995 to 1.000 which is equivalent to 95 to 110 g/l uranium is the normal saturation level employed.)

A differential pressure cell located in the organic phase in the top disengagement section senses and continuously records its specific gravity. Any variation from the density control set point automatically changes the feed stream flow rate by operating the air control valve on the feed line and brings the uranium concentration in the organic stream to the desired level. The feed stream flow rate is continuously measured and recorded. Both venturi and induction-type flow meters are in use. To date, the automatic instrumentation on the extraction columns has not proved entirely satisfactory. There is a considerable time-lag between the time that a variation in the product stream density is sensed and the time that the corrective change takes effect. This results in over-compensation and continuous cycling in feed flow rate and product saturation. It has been found through experience that variations in the specific gravity of the organic product are generally caused by fluctuations in the uranium concentration in the feed slurry. These can be better compensated for by manual adjustment of the flow rate. An experienced operator at the panelboard can maintain a more uniform operation by manual control than can be maintained by the present automatic instrumentation. A view of the extraction system control center showing the organic product stream density, feed slurry flow rate, and column interface recorders (right to left) is presented in Figure 13. Considerable effort is being made to develop a successful automatic feed control system.(4,6,7,8)

The system is normally operated at a feed slurry to organic extractant flow ratio of 5 to 9 with a scrub recycle flow to organic flow of 1 to 9.

Extraction of the uranium from the feed slurry is essentially complete in the extraction column. The depleted raffinate containing less than 0.05 g/l uranium is freed of the organic phase in the bottom disengagement chamber. There is, however, a considerable quantity of entrained TBP remaining in the raffinate leaving the column which repre-

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EXTRACTION AREA CONTROL PANEL

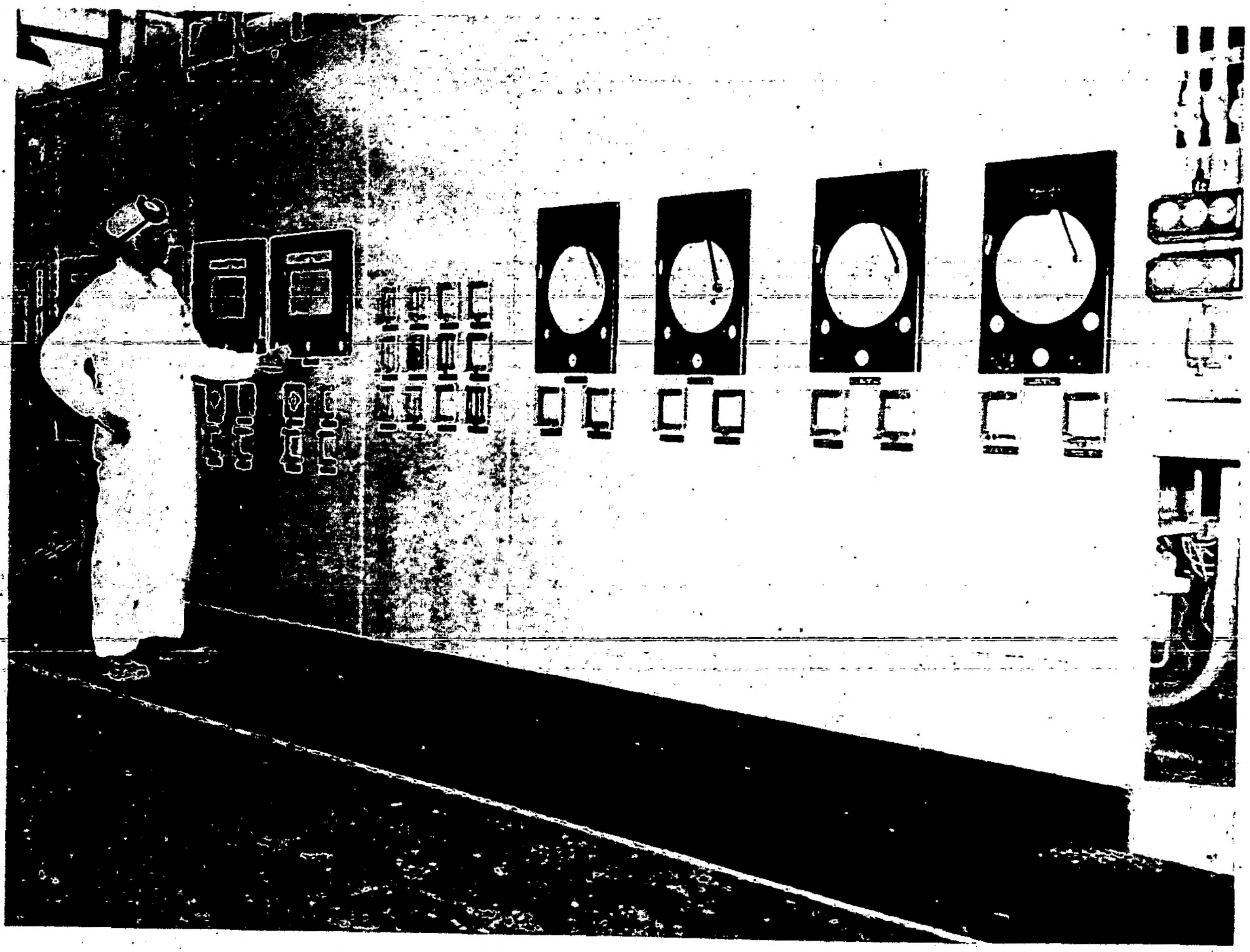

FIGURE 13

sents a loss of extractant and could cause an explosion during the subsequent high temperature raffinate processing. To reclaim the entrained TBP, the raffinate stream is contacted countercurrently with continuously recycled kerosene in a single-stage mixer-settler. When the kerosene wash liquor reaches a TBP concentration of approximately 10%, it is withdrawn and fresh kerosene is charged to the washing system. The dilute TBP-kerosene mixture is decanted to remove entrained raffinate solids, and introduced with the required additional TBP to raise the concentration to 33.5% into the organic extractant system. After kerosene washing, the raffinate stream contains less than 0.2 g/l of TBP.

The washed raffinate stream is handled in a manner similar to the feed slurry stream. To prevent settling of the solids in the pipe lines, the slurry is pumped at high velocities through a recycle loop equipped with a take-off line to convey the material to the raffinate area. In the raffinate area the slurry is stored in hold tanks under constant agitation to prevent settling until it is processed to recover the nitrate values.

SCRUB COLUMN

Although in the TBP extraction system, as outlined, the TBP is relatively specific toward uranium, other compounds (nitrates) do extract or are physically entrained in the organic product stream. Therefore, while the extraction column does eliminate practically all of the impurities with the exception of nitric acid, an additional purification step is required to bring the contamination level to within the imposed product purity specifications. This operation is performed in the second pulse column or scrub column.

The scrub column differs physically from the extraction column only with respect to column diameter and plate geometry (Figure 7); however, the operation of the column differs considerably. As in the extraction column the organic stream (product stream from extraction column) enters at the bottom through the pulse generator transfer line and passes up the column. It is contacted with a downward flow of deionized water. The flow ratios used are dependent upon the amount of impurities in the original feed material and the amount of impurities carried with the organic stream from the extraction column. In the case of low impurity concentrates (high assay), a scrub water to organic stream flow ratio of 1 to 9 is used. This ratio is frequently increased to 1 to 6-7 to meet purity specifications. The combined phases are pulsed at an amplitude of 1/2 inch and a frequency of 50 cycles per minute. The column is operated with the aqueous phase continuous and the organic phase dispersed.

During the scrubbing operation, essentially all of the residual acid and metallic impurities are transferred to the aqueous phase together with a small quantity of the uranium. The aqueous stream leaves the bottom disengagement chamber of the scrub column and is recycled to the extraction column where the uranium values are again extracted.

Certain impurities are more easily scrubbed out using warm water, others can be removed more completely with cold water. It has been found by experience that the scrub column operates effectively at ambient temperatures (approximately 85°F).

RE-EXTRACTION (STRIPPING) COLUMN

The re-extraction system is essentially the same as the scrubbing system. Whereas in the scrub column the organic phase is contacted with water at a flow rate just sufficient to remove essentially all the impurities and a small amount of uranium, in the re-extraction column the aqueous to organic flow ratio is increased to the point where all of the uranium values are removed from the now, purified organic stream. The columns employed in the two operations are the same with respect to plate geometry, differing only in diameter (Figure 7). An aqueous to organic flow ratio of 1 to 1 is used, the aqueous phase being preheated (150°F) deionized water. The pulse conditions required are a frequency of 50 cycles per minute at an amplitude of 1/2 inch. After being essentially depleted of uranium, the organic phase leaves the top of the column and is pumped to the solvent clean-out system where it is treated, pumped to the organic hold tank and returned to the extraction cycle.

The aqueous uranyl nitrate product stream (OK liquor) after leaving the bottom of the strip column is pumped to an auxiliary decant chamber where additional phase separation is accomplished. This step is introduced as a safety measure to avoid the possibility of excessive quantities of organic being entrained and carried into the evaporation and calcination system. From the decant tank, the aqueous product passes through 20 micron, sintered, stainless steel filters (Figure 14) to remove the last traces of suspended solid impurities. The combination of the auxiliary decant tank and the filter are a vital part

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PRODUCT STREAM MICRO FILTERS

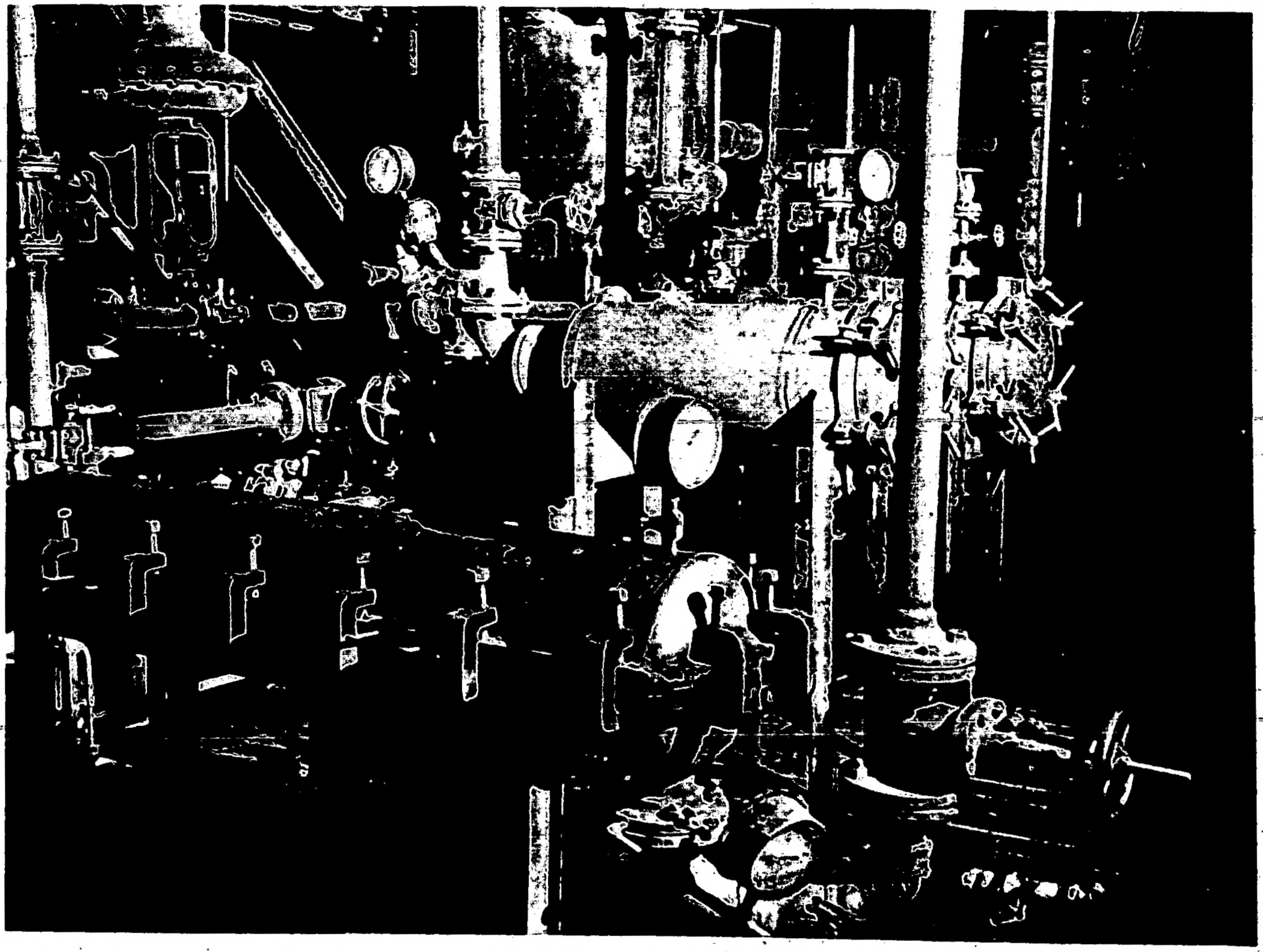

FIGURE 14

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of the system. Finely divided, low density solids such as are found in ore slurries (i.e., silica and carbon) are readily transferred between the aqueous and the organic phases in the pulse columns and are therefore carried across the column interfaces and through the system. Not only are silica and carbon impurities in themselves but they are excellent adsorbers of other metallic impurities. These final treatment steps are sufficient to remove essentially all of these physically entrained impurities. The filters are installed in parallel with a stand-by spare unit. When the on-stream unit begins to load up, as can be noted by observing the increase in pressure drop across the filter, the stream is switched to the spare unit and the first unit is opened and cleaned by flushing.

After passing through the filters, the OK liquor is pumped to the denitration area where it is stored in stainless steel tanks for further processing. The solution is sampled at this point and analyzed both chemically and spectrochemically for total impurities.

SOLVENT CLEAN-UP FLOWSHEET (Figure 15)

The organic phase from the re-extraction columns contains many impurities, which have been introduced during the extraction process, and which must be removed prior to recycling to the extraction system. The residual uranium must be removed to prevent its later loss through the raffinate stream from the extraction column; the hydrolysis products of the tributyl phosphate, namely the di and mono derivatives, which will hinder the extraction process if present in greater than trace concentrations, must be removed; and the residual entrained solids must be removed to prevent excessive build-up and resulting product contamination. The solvent clean-up system has been designed to meet these requirements.

The solvent clean-up system consists of a two-stage mixer-settler system for first, washing the solvent with aqueous sodium carbonate and then with plant water and a high-speed centrifuge for removing residual entrained solids. The equipment sizing and design prohibits washing and centrifuging the entire solvent stream, hence the stream splits as noted in Figure 14. A 1% sodium carbonate solution is used in the first mixer at a 1 to 3 aqueous to organic flow ratio. This operation neutralizes the residual acid, converts the uranium to an organic insoluble form and thus removes it from the organic phase and from the water soluble sodium salts of the degradation products of the TBP and the kerosene diluent. In the second mixer-

SOLVENT CLEAN-UP SYSTEM

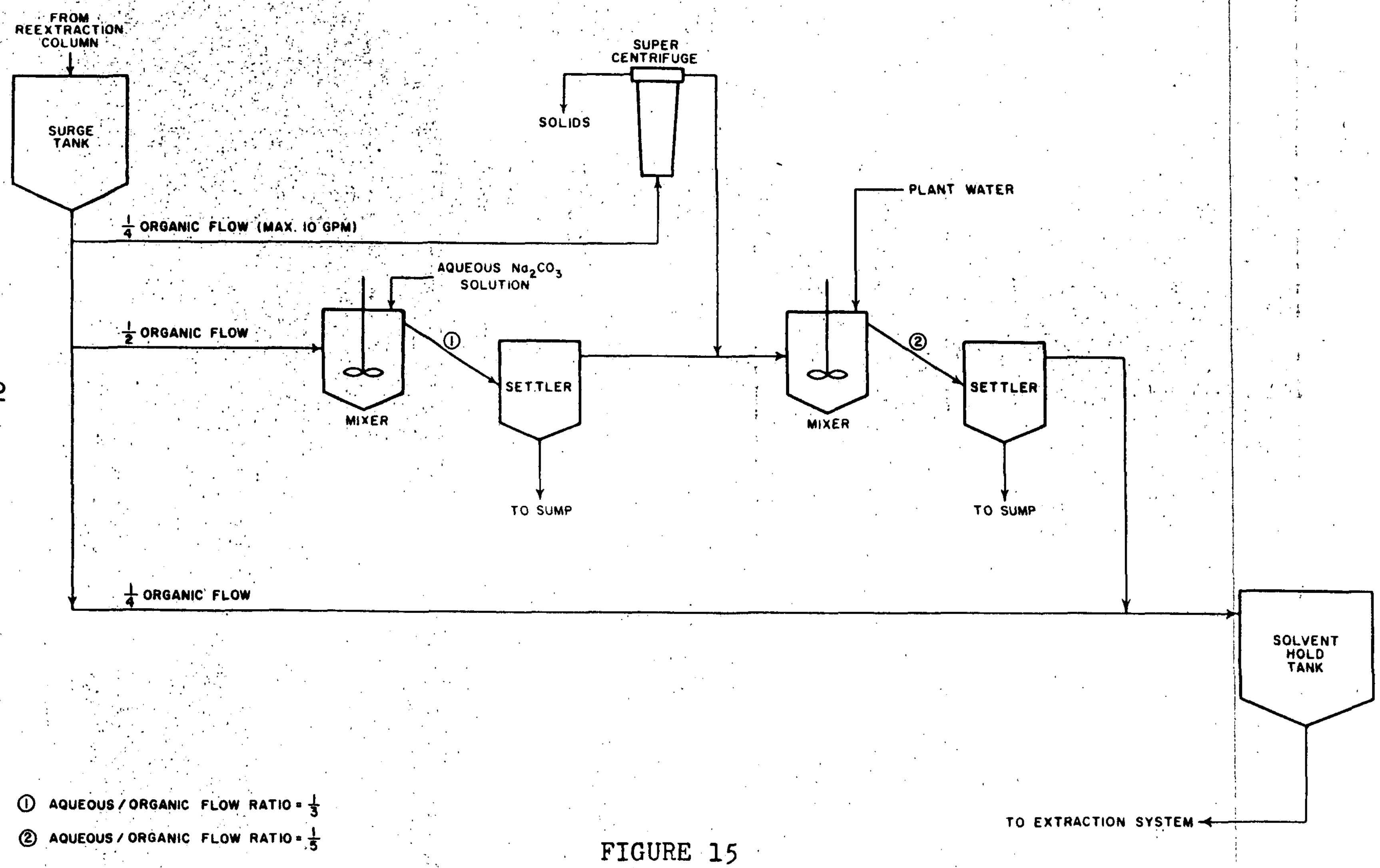

FIGURE 15

settler unit a 1 to 5 ratio, aqueous to organic water wash is used to remove the now water-soluble impurities. Approximately 10 gpm of the unwashed solvent is diverted to a high-speed centrifuge(9) where the entrained solids (notably finely divided carbon and silica) are removed. This operation was introduced into the clean-up system to reduce the solids content of the solvent inventory thereby reducing the accumulation of solid material at the column interfaces. The interfacial "crud" band tends to reduce the operational efficiency of the columns and tend to increase impurity carry-over through the system. Plant-scale tests have shown that the centrifuge removes approximately 50% of the entrained solids. After leaving the centrifuge the clarified organic enters the water wash mixer.

The combined organic streams after leaving the solvent clean-up system, enter the organic hold tank from where it is recycled to the extraction column.

DENITRATION SYSTEM FLOWSHEET (Figure 16)

The aqueous uranyl nitrate product from the extraction area is stored in the OK liquor tanks located in the denitration area. At this point in the process, the stream contains 90 to 100 g/l uranium, 0.04 to 0.05N HNO_3 and is at a temperature of approximately 100°F. The solution is pumped at a constant rate (50-60 gpm) through a preheater to a vertical-tube evaporator where it is concentrated to 350-370 g/l uranium at a constant temperature of 220°F. The evaporators are located on the roof of the denitration building (Figure 17) which permits the concentrated solution to flow by gravity from the evaporator to the stream-heated boildown tanks. Here, it is further evaporated to 1150 to 1200 g/l uranium; essentially a molten uranyl nitrate hydrate. In order to maintain a constant composition feed to the denitration pots, the boildown operation is conducted at a closely-controlled temperature (260°F) and at a constant temperature. The operation is monitored by product density measurement. From the boildown tanks, the molten salt cascades to a sparge tank which is at present used only as a surge tank. Up to this point the operation is continuous. The vapor streams from the evaporator, boildown tank and sparge tank after passing through entrainment filters to remove any entrained organic material are condensed, cooled and sent either to the sump or nitric acid recovery area.

The denitration operation is conducted batch-wise in a series of gas-fired denitration pots. During denitration,

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DENITRATION SYSTEM

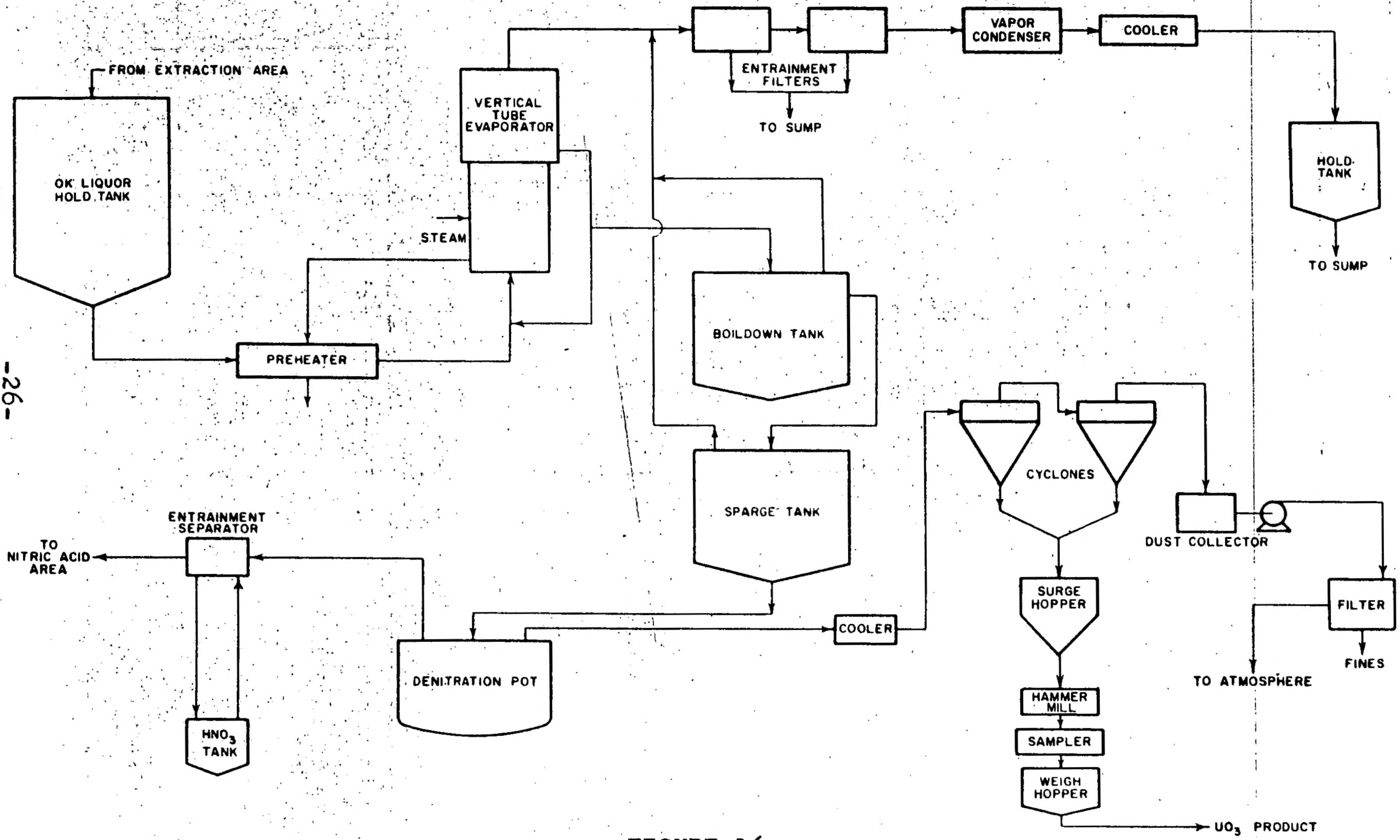

FIGURE 16

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URANYL NITRATE EVAPORATORS

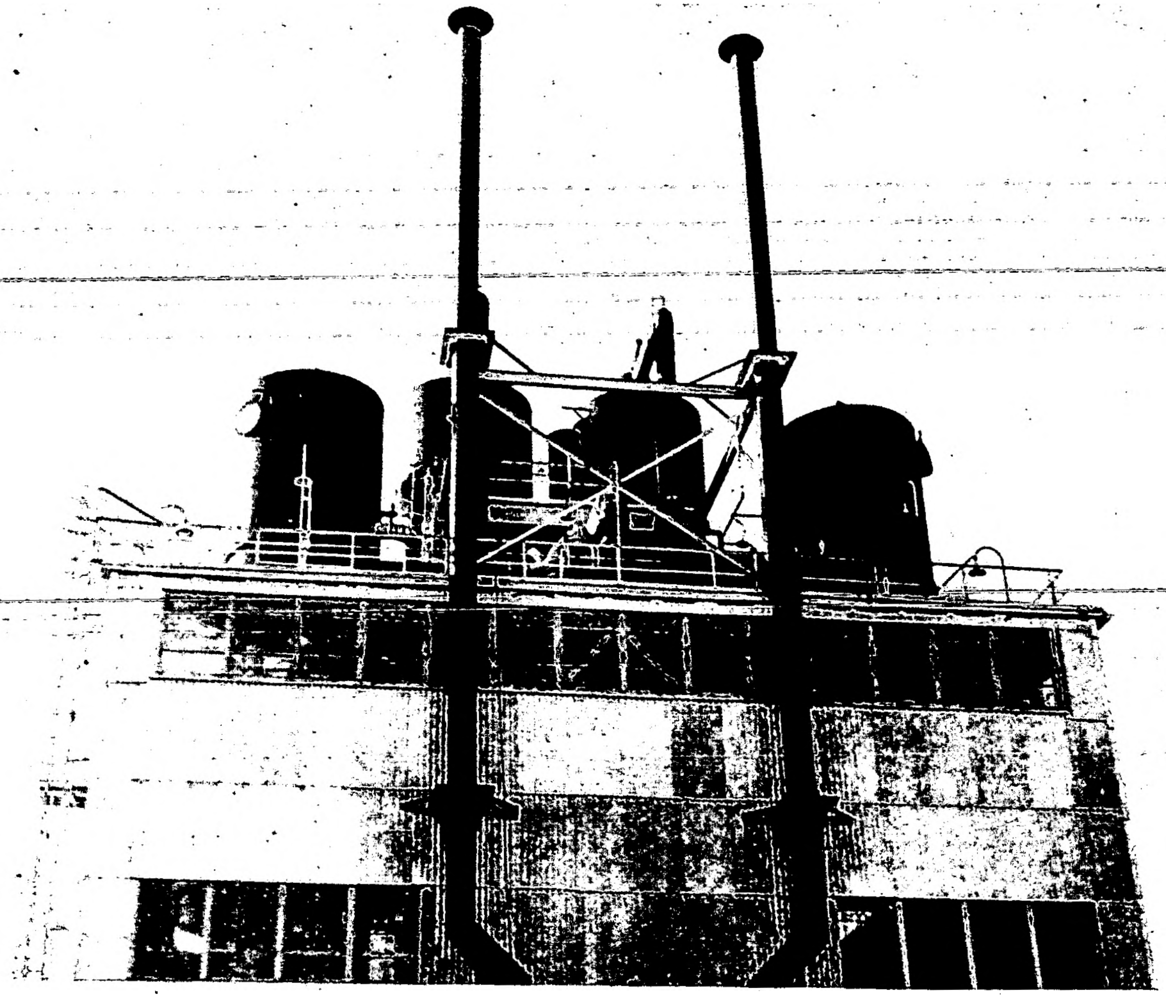

FIGURE 17

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the pot charge is continuously stirred to prevent caking. Caking on the walls is prevented by setting the agitator blades close to the inner surface of the pot. This prevents conversion of the UO_3 to U_3O_8 by overheating.

Each pot receives a charge of molten uranyl nitrate at a temperature of approximately 250°F. The denitration operation is broken down into four cycles: a one-hour heat-up period, a 4.5-hour denitration period (500°F), a 1.5-hour cooling period and a 1/2-hour degassing period, make a total of 7.5 hours for the entire cycle. The oxides of nitrogen evolved during the process pass through an entrainment separator to remove uranium oxide dust and sent to the nitric acid recovery area.

After cooling and degassing, the UO_3 powder is removed from the pots by a vacuum "gulping" system. The UO_3 is manually "vacuumed" from the pot using flexible metal hoses. Cyclones remove the solids from the air stream and convey them to a surge hopper. The fine material is removed by dust collectors and finally a plate and frame air filter. These fines are contaminated and are returned to the digestion area. From the surge hopper, the product UO_3 is sent by screw conveyer to a hammer-mill where it is powdered to meet specification, sampled for purity analysis and charged to the hoppers. After weighing the hoppers are sealed and stored pending shipment to the green salt plant.

RAFFINATE PROCESSING FLOWSHEET (Figure 18)

The raffinate, after leaving the extraction system area is pumped to one of a series of hold tanks located in the raffinate processing area. While in the tanks the raffinate is continuously agitated to prevent the solids from settling. After being analyzed for uranium and TBP content, the material is pumped to the evaporator. If the uranium concentration exceeds 0.2 g/l it is returned to the digestion area for reprocessing. If the TBP concentration exceeds 0.20 g/l it is washed with kerosene and decanted before it is further processed.

The evaporator (forced circulation) consists of a two-pass, horizontal shell and tube exchanger, a centrifugal pump and a flash chamber. Approximately 90% of the total volume is vaporized in this unit with the remaining 10% withdrawn as a raffinate concentrate. Since the raffinate pumping rate varies with the hydrostatic head in the hold tanks, the evaporator is operated at constant temperature and liquid level. The temperature employed depends upon

RAFFINATE PROCESSING SYSTEM
EXISTING SYSTEM

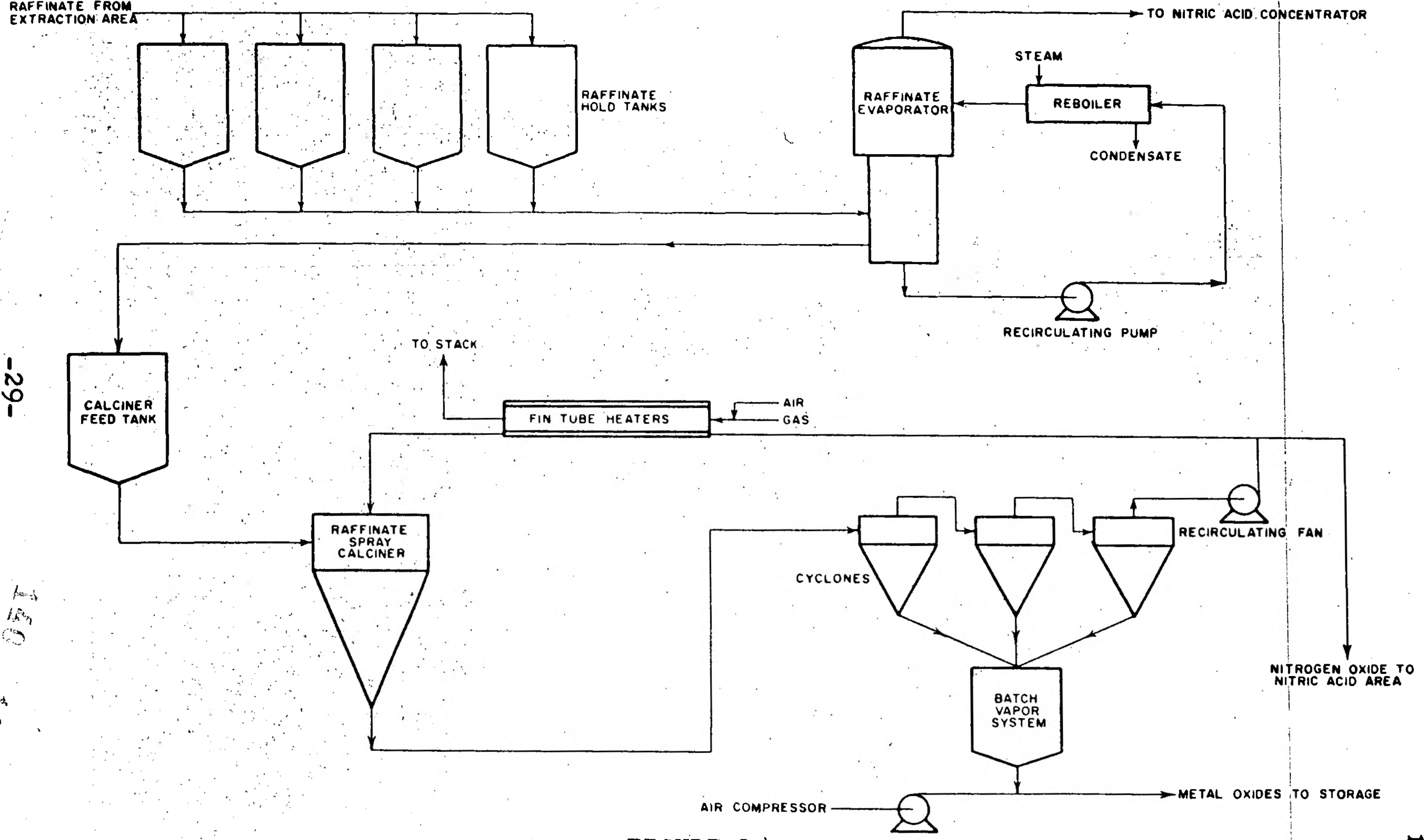

FIGURE 18

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the type of raffinate (solids and soluble salt content). Because of the variation in raffinate components, the volume reduction affected varies from 10-15 to 1. Evaporator temperatures range from 250° to 280°F. The vapor stream from the evaporator is sent to the nitric acid concentrator.

The evaporator product flows by gravity to the calciner feed tank from where it is pumped to a spray calciner. In the calciner, the metal nitrates are converted to oxides and the evolved oxides of nitrogen, together with any residual nitric acid is sent through a series of cyclones to separate the entrained solids to the absorbers in the acid recovery area. A portion of the vapor stream is recirculated through indirect fired fin-tube heaters back to the calciner. The calciner operates at inlet temperature of 950°F. The finely powdered metal oxides from the cyclone separators are drummed and stored. A general view of the raffinate processing area is given in Figure 19.

The spray calciner has proved unsatisfactory. Entrained solids in the recycle gas stream deposit on the heat exchange surfaces of the fin-tube heaters where they act as an insulator, resulting in frequent heater-tube burn-outs. In addition, clogging of the calciner spray nozzles occurs. The maintenance requirements to keep the unit on stream is prohibitive.

In view of the above difficulties, an alternate calcining method has been developed and designed and is at present under construction. The new system (Figure 20) will incorporate the same evaporation step as described above. The evaporator product will then be dried on a drum drier, the vapor stream going to the acid recovery area. The dry solids (approximately 10% residual moisture) will be fed by screw conveyer to a rotary calciner where the nitrate values will be removed as oxides of nitrogen and sent to the nitric acid absorbers. A pilot drum-drier and calciner has recently been installed, however, operating data are not available.

The present method of raffinate processing is dictated by the local restrictions on waste disposal and is not necessarily the most economical method. Local waste disposal facilities will be a consideration in chosing the location for a new refinery and will influence the raffinate processing system design.

RAFFINATE PROCESSING AREA

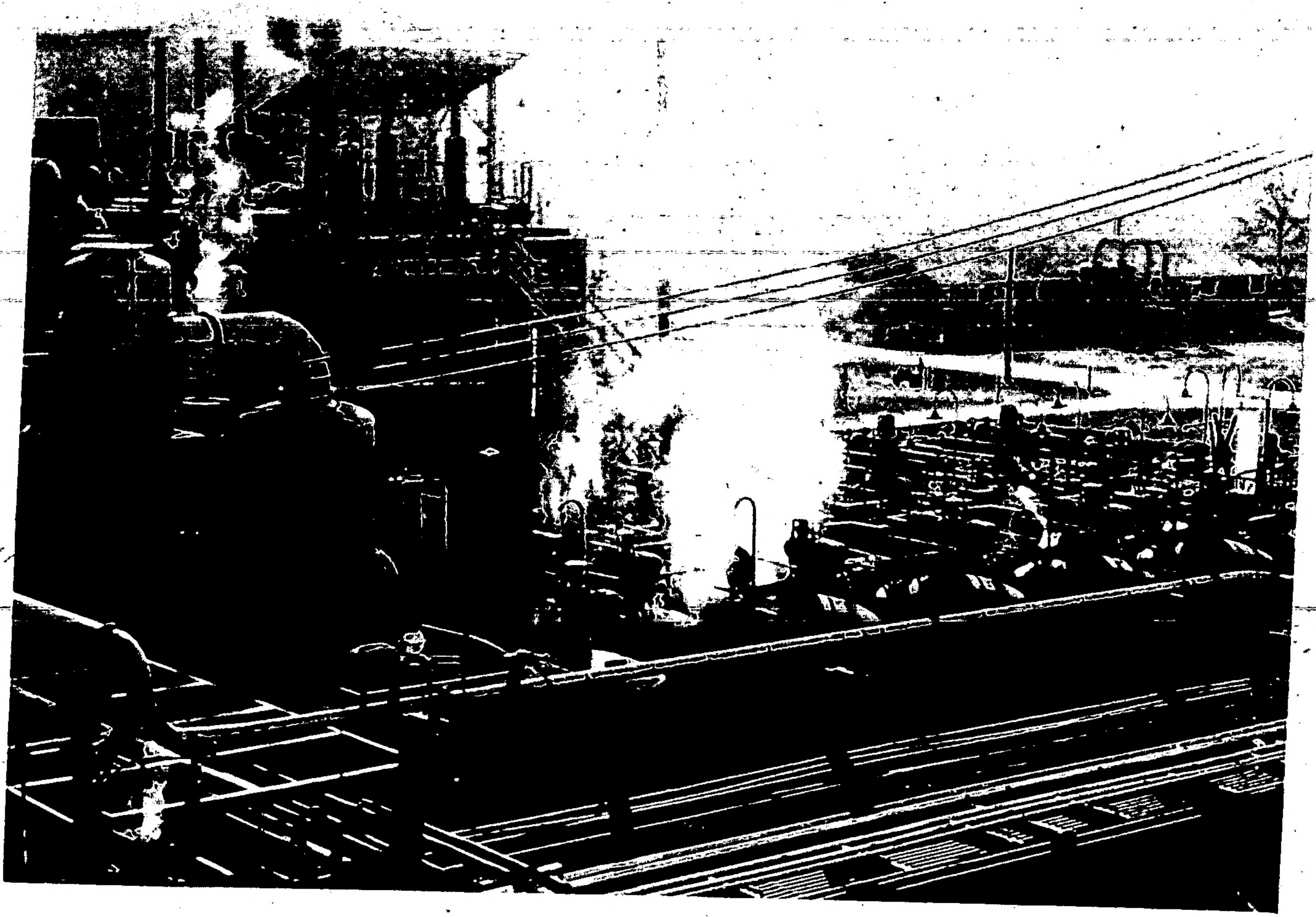

FIGURE 19

RAFFINATE PROCESSING SYSTEM
PROPOSED SYSTEM

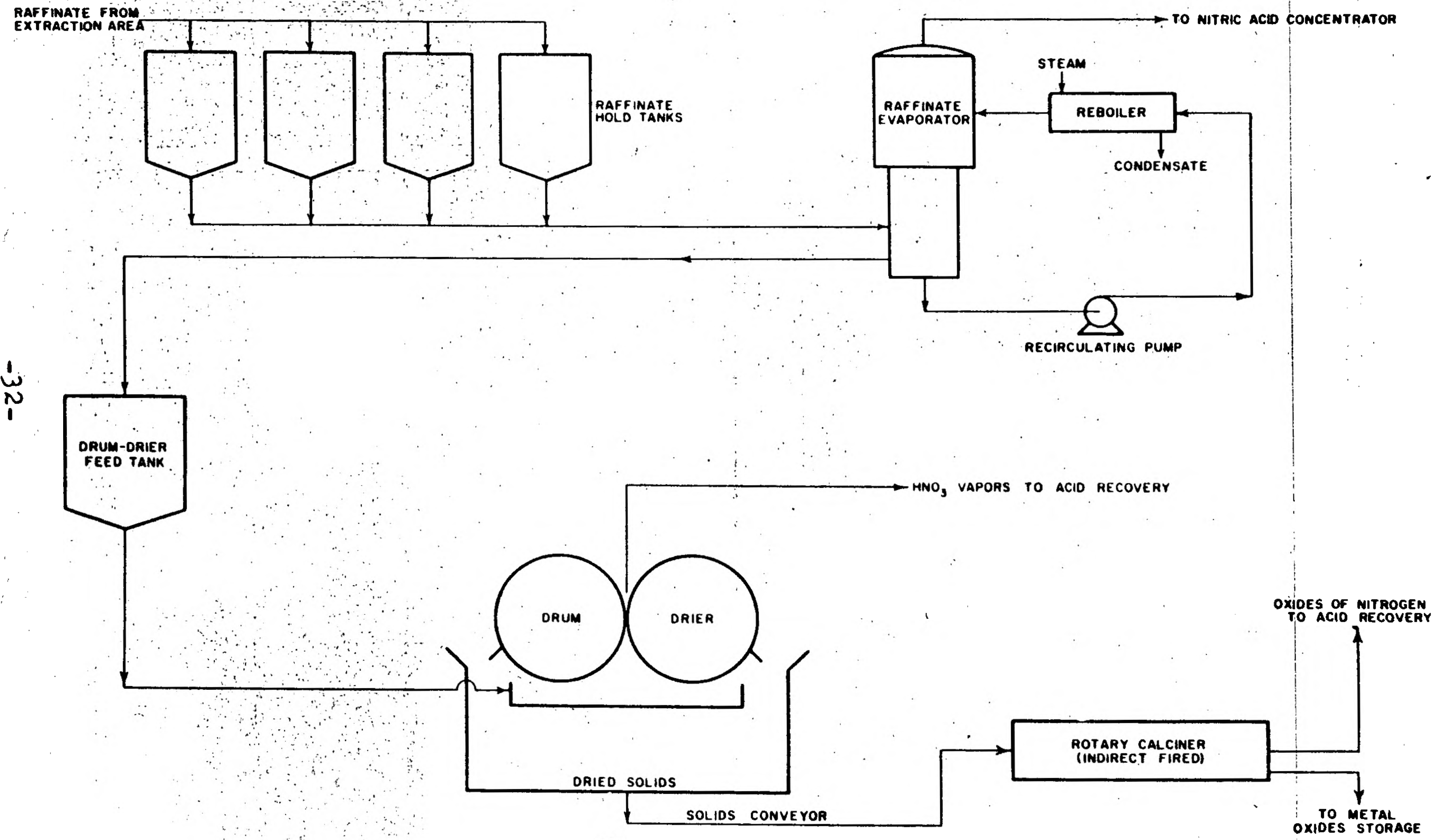

FIGURE 20

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NITRIC ACID RECOVERY FLOWSHEET (Figure 21)

The combined vapor streams from the digestion area, denitration area and the raffinate spray calciner pass through a scrubber system in which the nitric acid and part of the water vapor is condensed and sent (as weak acid) to the concentrator. Any entrained solids are removed by a filter in the dilute acid stream and returned to the raffinate area. The oxides of nitrogen are passed through an oxidation chamber to the absorption towers where they are converted to dilute nitric acid and sent to the concentrator. Nitric acid vapors from the raffinate evaporator are sent directly to the acid concentrator. All of the dilute nitric acid is concentrated to 55 to 60 per cent acid and returned for use in the digestion system.

The concentrator is a twelve-plate bubble-cap tower equipped with a steam heated external reboiler and with a surface condenser. Overall column efficiencies up to 54% have been found by testing.

Small but significant quantities of chlorides and fluorides are volatilized from the raffinate during evaporation and calcination and are carried by the vapor streams to the acid concentrator. They are concentrated together with the nitric acid and at the operating temperatures employed promote severe equipment corrosion. Evaporator tests have shown that approximately 50% of the chloride present in the raffinate passes to the concentrator and are accumulated in the middle of the tower. Chloride removal (7,10) is accomplished by withdrawing the acid from the ninth plate of the concentrator to an ozone sparge tank where it is contacted with ozone (Welsbach Ozone Generators). The chlorides are removed by oxidation according to the equation:

$$2H^+ + 2\,Cl^- + O_3 \dashrightarrow O_2 + H_2O + Cl_2$$

The free chlorine is dissolved and removed by the sparge air and the chloride-free acid is returned to the eighth concentrator tray. Sparging tests indicate 160° to 170°F to be the optimum temperature for removal of chlorides from a 15 to 20% nitric acid using a 1% ozone-in-air mixture.

Fluoride control(10,11) is accomplished by addition of aluminum oxide to the digestion batch to form the $AlF_3^{\equiv}$ complex which has a much lower volatility in acid solution than the free fluoride ion. This procedure results in the retention of over 90% of the fluorides in the metal oxide product, 10% going to the acid recovery system. A ratio of

NITRIC ACID AREA

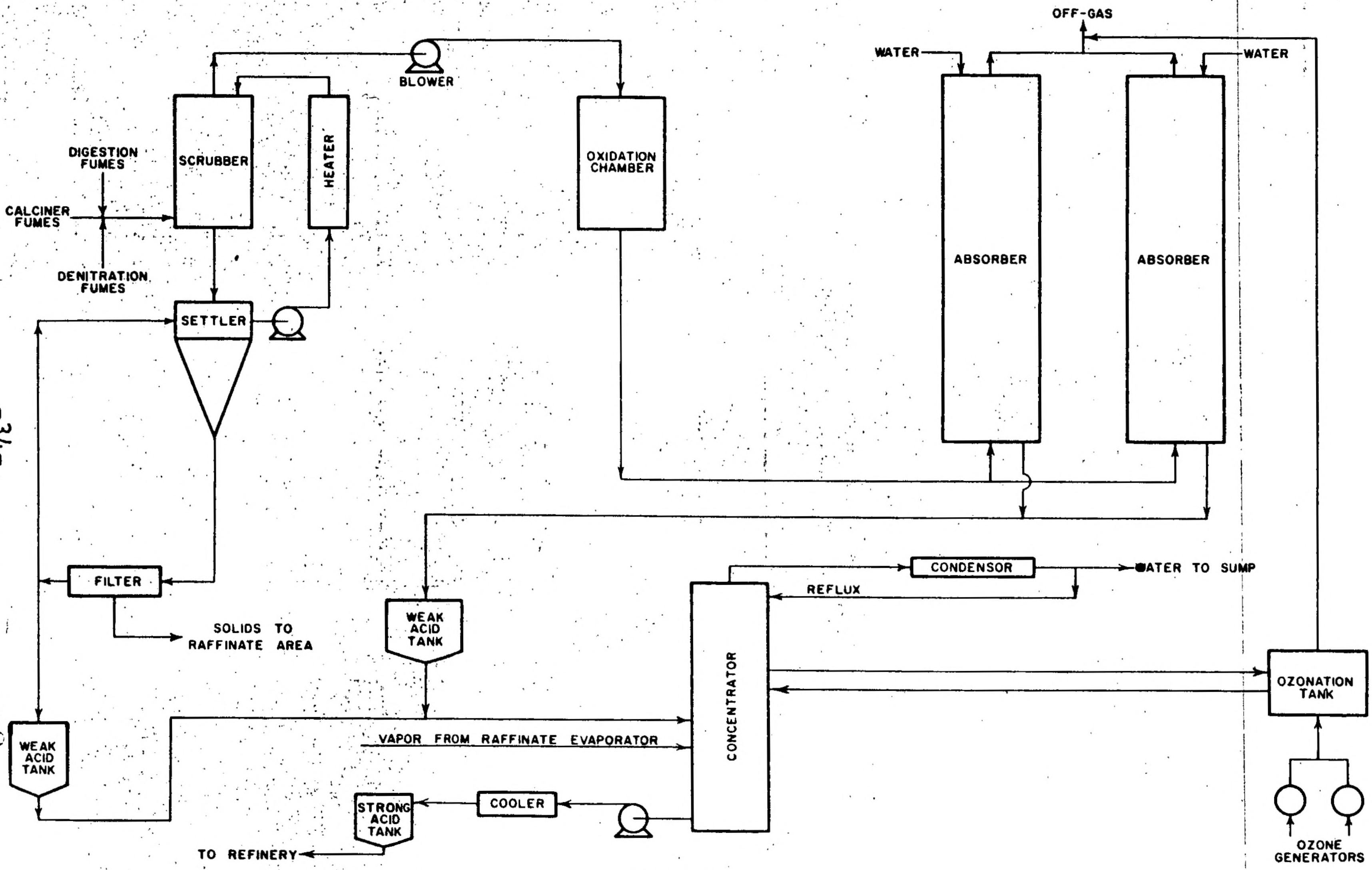

FIGURE 21

five parts of aluminum (as Al_2O_3) per part of fluoride (by weight) has been found sufficient to suppress the fluoride volatility.

A photograph of the nitric acid recovery system showing the absorbers, concentrator, ozonation tank and acid storage tanks is included (Figure 22).

PROCESS CHEMISTRY

The following discussion of the chemistry involved in processing uranium concentrates to UO_3 must, of necessity, be brief. Only the chemistry which most directly affects the process will be covered.

DIGESTION

The chemical reactions involved in the conversion of the uranium values in the feed material to uranyl nitrate depend upon the form in which the uranium exists in the ore or concentrate. In the case of high-grade ores or concentrates with which we are presently concerned, the uranium will most probably exist in one of the following compound forms. If it is a naturally occurring high-grade ore which required only mechanical up-grading at the mine, the uranium most probably exists as U_3O_8 (black oxide) or as a mineralogical combination of the U_3O_8 and other metal oxides. However, in most cases chemical up-grading of the uranium assay is required, especially in the case of the domestic ore deposits. In these cases, the final concentrate, as received at the refinery, is either (1) a magnesium diuranate $Mg_2U_2O_7$, (2) an ammonium diuranate $(NH_4)_2U_2O_7$ or (3) a calcined ammonium diuranate which, depending upon the temperature at which it was calcined, is a variable mixture of the diuranate and ill-defined uranium oxides. Figure 23 presents the stoichiometric digestion reactions for a black oxide ore and diuranate concentrate.

Using these reactions, it is possible to make a rough calculation of the nitric acid requirements for the conversion to uranyl nitrate, however, the presence of other elements which react with acid will increase the requirements.(12,13)

The reaction involved in the conversion of the diuranate (Mg or NH_4) to the nitrate is the one with which the commercial producer will be concerned. It should be noted that in these concentrates the uranium exists in the VI valence state which eliminates the acid requirements for oxidation (as in the conversion of U_3O_8). It can be added

NITRIC ACID RECOVERY AREA

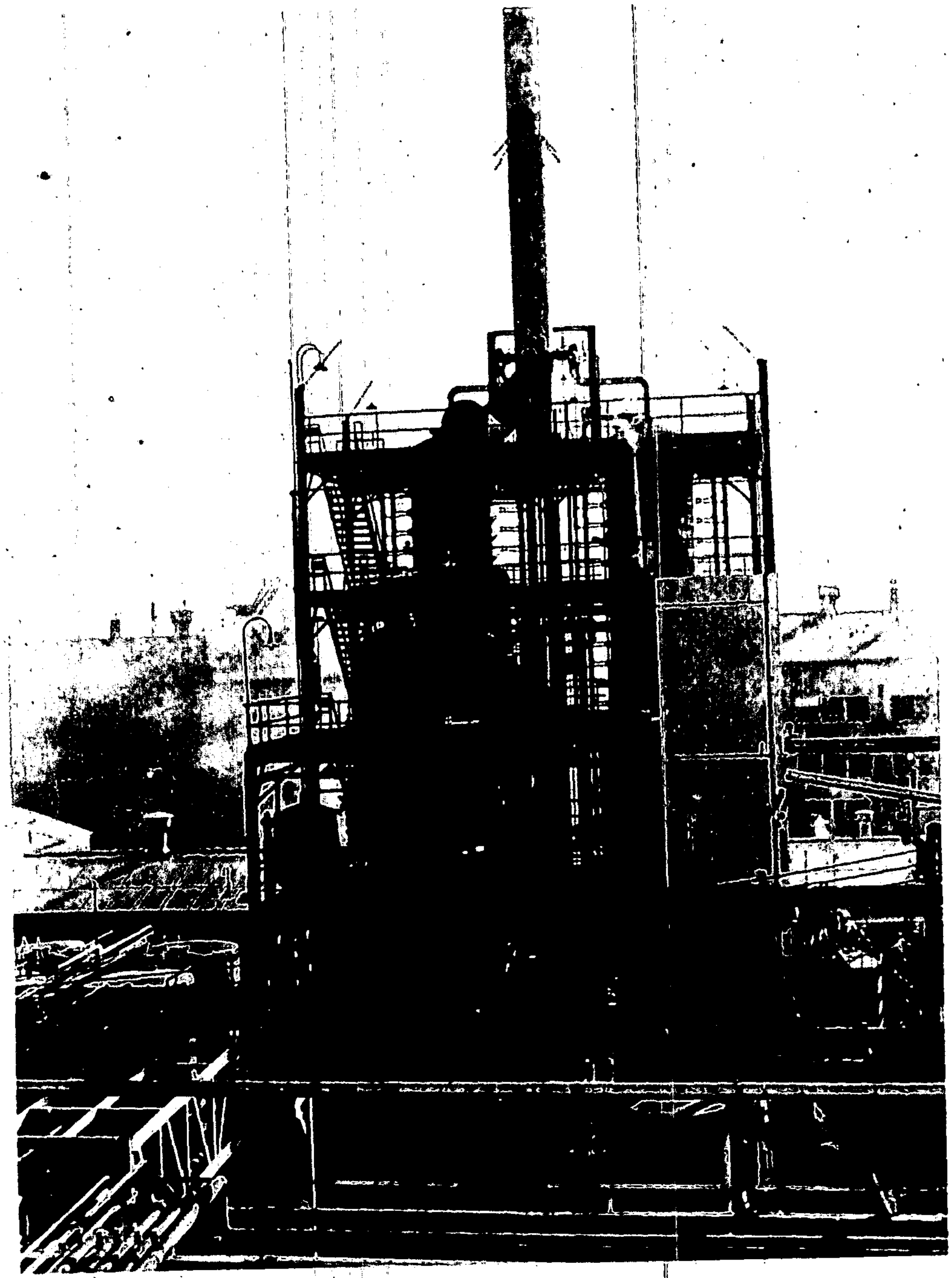

FIGURE 22

CHEMISTRY OF THE DIGESTION PROCESS

GENERAL PROCESS:

$$\text{URANIUM ORES OR CONCENTRATES} \xrightarrow[\Delta]{\text{CONC. } HNO_3} \text{AQUEOUS URANYL NITRATE}$$

SPECIFIC REACTIONS:

$$U_3O_8 + 8HNO_3 \longrightarrow 3UO_2(NO_3)_2 + 2NO_2 + 4H_2O$$

$$MgU_2O_7 + 6HNO_3 \longrightarrow 2UO_2(NO_3)_2 + Mg(NO_3)_2 + 3H_2O$$

FIGURE 23

that in concentrates of this type, the other metals probably exist in their higher valence state and therefore do not consume excess acid through oxidation.

EXTRACTION

The proposed mechanisms(14) for the TBP extraction of uranyl nitrate and nitric acid are given in Figure 24. These involve: (1) a primary ionization of the uranyl nitrate in the aqueous phase, (2) mass transfer of the nitrate ion across the aqueous-organic interface followed by complexing of the nitrate ion with TBP in a one to one mole ratio and (3) mass transfer of the uranyl ion across the phase boundary followed by complexing of the uranyl ion with two nitrate-TBP complexes. Essentially, the same mechanism applies to the TBP extraction of nitric acid with the exception that the final HNO_3-TBP complex has a 1 to 1 mole ratio.

Tributyl phosphate as an extractant exhibits the high degree of specificity for the uranyl ion. It is important to note that although nitric acid also exhibits an affinity for TBP, it has an equilibrium constant of the order of one-fortieth of that of uranyl nitrate (assuming the proposed mechanism). Other extractable metallic nitrates exhibit still lower affinities for TBP. The relative order of the equilibrium constants permits effective separation in the extraction column. It is doubtful whether the amount of contamination in the organic product stream from the plant extraction columns is the result of true TBP extraction of impurities. Probably physical entrainment of the aqueous phase and slurry solids contribute greatly to the total contamination level. The view is supported by laboratory data which show that under carefully controlled extraction conditions, followed by complete phase separation, a more complete separation is possible.

The presence of nitric acid and nitrate salts other than uranyl nitrate affects the extraction of uranium by increasing the nitrate ion concentration in the aqueous phase and by changing the activity coefficient of the salts which are extracted by TBP. The extraction reaction of uranyl nitrate is dependent on the second power of the nitrate ion coefficient. In general, it can be stated that the distribution coefficient (organic/aqueous) of uranyl nitrate is dependent on the total nitrate ion concentration (activity) in the aqueous phase regardless of its origin (nitric acid or metal nitrates). In the use of feed slurries from the digestion of uranium concentrates, sufficient nitrate strength is present for efficient

CHEMISTRY OF THE EXTRACTION PROCESS

PROPOSED MECHANISM

URANIUM EXTRACTION

$$\mathrm{UO_2(NO_3)_2}\ \text{(AQUEOUS)} \xrightleftharpoons{\text{IONIZATION}} \mathrm{UO_2^{++}}\ \text{(AQUEOUS)} + \mathrm{2NO_3^-}\ \text{(AQUEOUS)}$$

$$\mathrm{2NO_3^-}\ \text{(AQUEOUS)} + \mathrm{2TBP}\ \text{(ORGANIC)} \rightleftharpoons \mathrm{2(NO_3 \text{-} TBP)}\ \text{(ORGANIC)}$$

$$\mathrm{UO_2^{++}}\ \text{(AQUEOUS)} + \mathrm{2(NO_3 \text{-} TBP)}\ \text{(ORGANIC)} \rightleftharpoons \mathrm{UO_2(NO_3)_2 \text{-} 2TBP}\ \text{(ORGANIC)}$$

$$\mathrm{UO_2(NO_3)_2}\ \text{(AQUEOUS)} + \mathrm{2TBP}\ \text{(ORGANIC)} \xrightleftharpoons[\text{SCRUBBING AND RE-EXTRACTION}]{\text{EXTRACTION}} \mathrm{UO_2(NO_3)_2 \text{-} 2TBP}\ \text{(ORGANIC)}$$

NITRIC ACID EXTRACTION

$$\mathrm{HNO_3}\ \text{(AQUEOUS)} + \mathrm{TBP}\ \text{(ORGANIC)} \xrightleftharpoons[\text{SCRUBBING}]{\text{EXTRACTION}} \mathrm{HNO_3 \text{-} TBP}\ \text{(ORGANIC)}$$

FIGURE 24

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extraction. Extraction is further enhanced by the free acid (3N) in the feed slurry.

It should be noted that the presence of large concentrations of anions (sulfate and phosphate) other than the nitrate ion, tends to reduce the extraction efficiency by forming non-extractable uranium compounds.(8) The uranyl ion is extracted only as the nitrate in the TBP system.

The scrubbing and re-extraction mechanisms are merely the reverse of the extraction mechanism. In the scrub column, the organic phase is relatively low in acidity. When contacted with a small volume of water, the nitric acid and metallic impurities are transferred to the aqueous phase since they have a low distribution coefficient (organic to aqueous). The resulting aqueous solution has a relatively low nitrate salting strength, therefore, a portion of the uranyl nitrate is also transferred to the aqueous phase. In the re-extraction column the organic phase which is now almost free of nitric acid is contacted with an equal volume of water at a temperature of 150°F, which results in essentially complete reversal of the extraction mechanism and all of the uranyl nitrate transfers to the aqueous phase.

A pure uranium nitrate distribution curve between a 3N aqueous nitric acid solution and a 33.5% TBP organic phase is presented in Figure 25.(15) A distribution curve for a typical uranyl nitrate feed slurry (also 3N HNO_3) is presented for comparison. It will be noted that the feed slurry exhibits greater uranium distribution coefficients than the pure uranyl nitrate solution illustrating the effects of the excess nitrate salting strength in the former.

Figures 26 and 27 are a representation of the equilibrium conditions existing in the extraction and scrub columns as shown by a plot of the equilibrium data taken from a laboratory batch-countercurrent extraction test. (5,14) These tests are routinely run on new feed materials in order to be able to predict their behavior in the plant columns. The complex nature of the competing reflux of uranium, nitric acid and metallic impurities in the TBP system requires close inspection for an estimation of its behavior. The data also aids in predicting steady-state conditions and are the basis for establishing refinery flow ratio and column throughput.

The "profile" (Figure 27) of the extraction and scrub column equilibrium conditions is a diagrammatic presentation of the uranium and nitric acid concentration in the

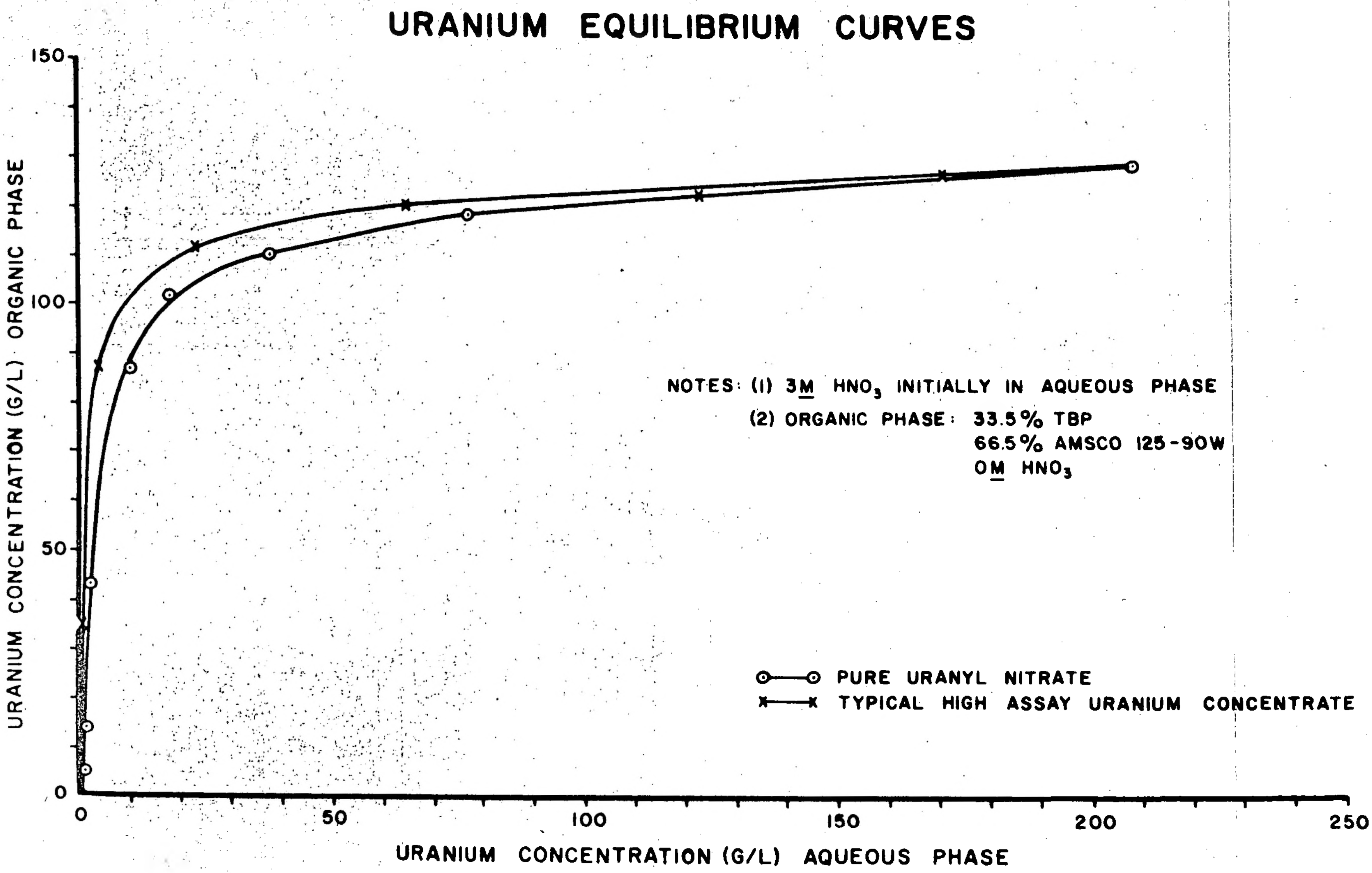

FIGURE 25

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LABORATORY BATCH COUNTERCURRENT EXTRACTION STAGE DATA (PURE UNH)

FEED: 0.849$\underline{M}$ (210 Mg/Ml) URANIUM; 3.10$\underline{N}$ NITRIC ACID
DENSITY – 1.364 g/Ml @ 25 °C; VISCOSITY – 16.2 Millipoise @ 25 °C
ORGANIC: 33.5% TBP; 0$\underline{N}$ HNO_3; 66.5% AMSCO 125
SCRUB: DEIONIZED WATER (Recycled to Extraction Section)
PHASE VOLUME RATIO: FEED/ORGANIC/SCRUB = 5/9/1
FEED/ORGANIC = 1/1.8
ORGANIC/SCRUB = 9/1
ORGANIC/AQUEOUS (TOTAL) □ 3/2 EXTRACTION SECTION
DATA TAKEN AFTER THREE VOLUME CHANGE IN SYSTEM

STAGE		ORGANIC PHASE				D.C.'S (ORG/AQ)		E.F.'S (ORG/AQ)		AQUEOUS PHASE			
		URANIUM		HNO_3 ($\underline{N}$ eq)^b	TOTAL^a (eq)^b	U	HNO_3	U	HNO_3	URANIUM		HNO_3 ($\underline{N}$ eq)^b	TOTAL^a (eq)^b
		(Mg/Ml)	($\underline{N}$ eq)^b							(Mg/Ml)	($\underline{N}$ eq)^b		
SCRUB SECTION	4	104.0	0.87	0.030	8.1	0.853	0.517	7.68	4.65	121.9	1.02	0.058	1.08
	3	122.2	1.03	0.039	9.6	0.663	0.275	5.97	2.48	184.0	1.55	0.142	1.69
	2	129.0	1.08	0.043	10.1	0.804	0.111	7.24	1.00	159.3	1.34	0.386	1.73
	1	127.5	1.07	0.063	10.2	0.807	0.052	7.26	0.47	158.0	1.33	1.20	1.53
EXTRACTION SECTION	1	124.6	1.05	0.124	10.6	1.99	0.035	2.99	0.053	62.6	0.53	3.52	24.3
	2	44.0	0.37	0.614	8.9	~81	0.158	~120	0.237	0.545	0.005	3.89	23.4
	3	0.345	0.003	0.877	7.9	~350	0.224	~525	0.336	0.001	<0.001	3.92	23.5
	4	0.008	<0.001	0.869	7.8	> 8	0.226	> 12	0.339	<0.001	<0.001	3.84	23.0
	5	<0.001	<0.001	0.835	7.5	~ 1	0.234	~ 1.5	0.351	<0.001	<0.001	3.57	21.4
	6	<0.001	<0.001	0.653	5.9	~ 1	0.245	~ 1.5	0.368	<0.001	<0.001	2.66	16.0

"a" – PRODUCT OF PHASE VOLUME RATIO AND SUM OF THE URANIUM AND NITRIC ACID EQUIVALENTS.
"b" – EQ □ EQUIVALENTS
D.C. = DISTRIBUTION COEFFICIENT = CONC. IN ORGANIC PHASE CONC. IN AQUEOUS PHASE
E.F. = EXTRACTION FACTOR = D.C. MULTIPLIED BY THE PHASE VOLUME RATIO

FIGURE 26

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LABORATORY BATCH COUNTERCURRENT EXTRACTION AND SCRUB SECTION PROFILES
33.5 % TBP FLOWSHEET; URANYL NITRATE-NITRIC ACID FEED

FEED STREAM: 0.840 M (200 G/L) URANIUM; 3.0 M NITRIC ACID
DENSITY = 1.364 G/ML AT 25°C.; VISCOSITY = 16.2 MILLIPOISE AT 25°C.
ORGANIC STREAM: 33.5 VOLUME % TBP; 66.5 % AMSCO 125-90W; NON-ACIDIFIED
SCRUB STREAM: DEIONIZED WATER; 0 M NITRIC ACID
FEED/ORGANIC/SCRUB PHASE RATIO: 5/9/1 TEMPERATURE = 25°C.

DATA TAKEN AFTER THREE COMPLETE VOLUME CHANGES

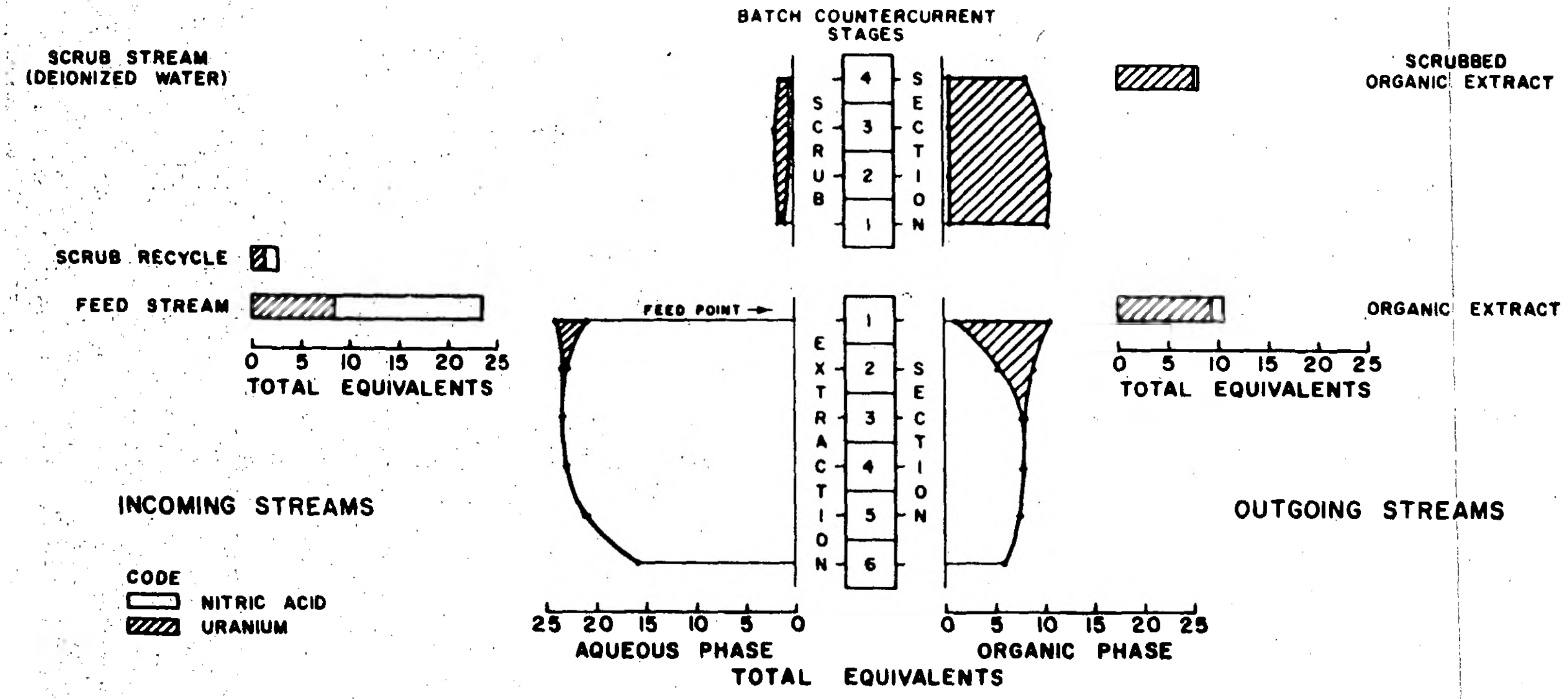

FIGURE 27

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individual stages as shown in Figure 26. Since both uranium and nitric acid complex the TBP, the representation of the concentrations of these materials by convention, is plotted additively on the horizontal axis. The nitric acid content is represented by the distance from the vertical axis to the first curve and the sum of the uranium and nitric acid concentrations is represented by the distance from the ordinate to the outer curve. The horizontal distance between the curves is therefore the uranium concentration.

One of the important requisites of an organic extractant is that it be stable at the temperatures and acid concentrations existing in the process. Tributyl phosphate is relatively stable at 150°F (temperature of the re-extraction column) in contact with 3N nitric acid (acid concentration in the extraction column) as indicated in Figure 28. The first hydrolysis step to the dibutyl phosphate has the lowest reaction rate and is therefore the rate determining step.

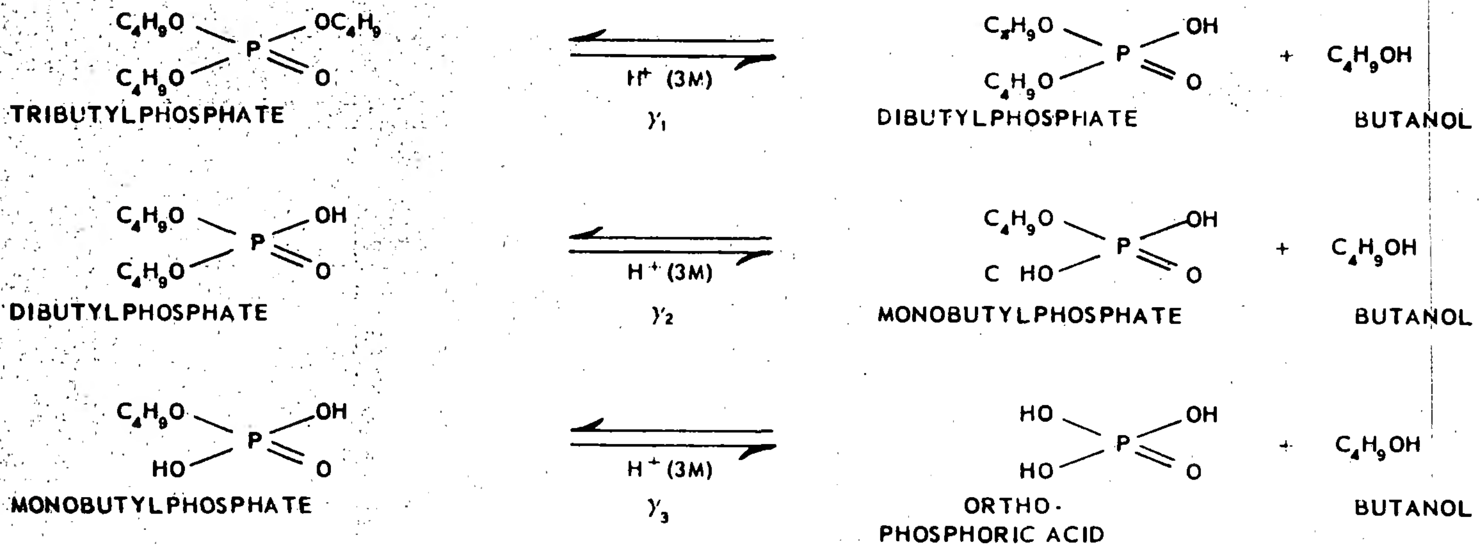
A build-up of the di and mono butyl phosphate and phosphoric acid must be avoided, since each degradation product has a detrimental affect on the efficiency of the extraction process. Dibutyl phosphate forms an aqueous insoluble complex with uranyl nitrate which, however, is quite soluble in the organic phase. A build-up of this material would result in a uranium loss from the re-extraction column. The mono derivatives forms an organic insoluble complex with uranyl nitrate which would result in uranium loss through the raffinate stream. This complex is soluble to some extent in 3N nitric acid. Ortho phosphoric acid forms the aqueous insoluble, non-extractable uranyl phosphate. By washing the uranium depleted organic stream from the strip column with sodium carbonate the di and monobutyl phosphate are converted to the water-soluble sodium salt and removed from the extractant.

DENITRATION

In the evaporation and boildown operations the OK liquor (aqueous solution containing 95 to 100 g/l uranium) is converted to a molten uranyl nitrate hydrate. The exact degree of hydration varies depending upon the temperature and retention time in the boildown and sparge tanks. The reported boiling point for the hexahydrate is 248°F (as shown in Figure 29). At the Fernald plant the operation is controlled on an indicated temperature of 260° ± 2°F which yields a product containing 1150 to 1200 g/l uranium and having a density of 2.54 at 260°F. This

HYDROLYSIS OF TRIBUTYLPHOSPHATE

(ACID HYDROLYSIS IN 3M HNO_3 SYSTEM)*



HYDROLYSIS RATE CONSTANTS:*

γ_1 : 76°C – 0.045%/DAY ; 105°C – 0.23%/DAY

γ_2 : 76°C – 50%/8 DAYS

γ_3 : 25°C – 50%/300 DAYS ; 46°C – 50%/22 DAYS ; 76°C – 50%/18 DAYS

FIGURE 28

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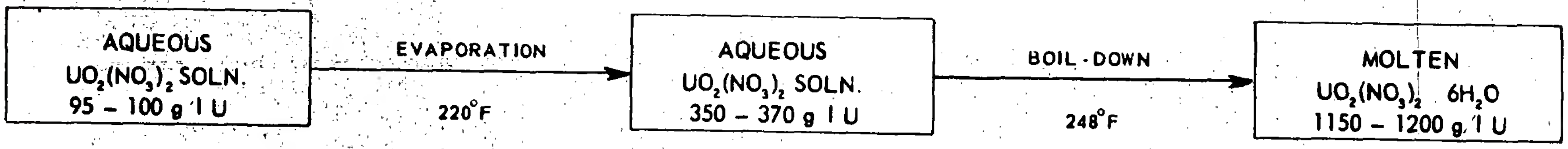
CHEMISTRY OF THE DENITRATION PROCESS



$$2UO_2(NO_3)_2 \cdot 6H_2O \text{ (MOLTEN SALT) } \xrightarrow[450°F]{\text{DENITRATION}} 2UO_3 + 4NO_2 + O_2 + 6H_2O$$

FIGURE 29

corresponds to a somewhat lower hydrate than the hexahydrate.

At a temperature of 450°F, the molten uranyl nitrate hydrate is thermally denitrated to UO_3. If this temperature is exceeded, the UO_3 is converted to U_3O_8 (black oxide). A hard scale sometimes collects on the inner walls of the pot where the agitator blades cannot remove it. Probably at the relatively high skin temperature of the pot there is some conversion to U_3O_8, however, this must not exceed 1.0%.

MATERIAL BALANCES

Two material balance flowsheets are presented in Figures 30 and 31. The extraction system balance sheet has been calculated from plant-scale test data and reflects actual on-stream operating performance, with the exceptions as noted below. The total refinery process material balance was calculated from plant-scale test data with adjustments made based on certain assumptions with regards to the type of concentrate processed.

EXTRACTION SYSTEM MATERIAL BALANCE FLOWSHEET (Figure 30)

The extraction system as originally designed included five pulse columns; two extraction columns, two scrub columns and a single re-extraction column. It was on this column distribution basis that the column diameters (Figure 7) were selected. A later modification (15) of the extraction flowsheet (the TBP content of the organic stream was increased from 22.5% to 33.5%) necessitated the use of two re-extraction columns in parallel. To do this one of the scrub columns was converted to a strip column. The column arrangement as now used is: two extraction columns (18-inch diameter) operating in parallel with a single 22-inch-diameter scrub column, and two re-extraction columns, one 22 inches in diameter, and one 26 inches in diameter. With this column order the aqueous raffinate from the scrub column is split in half and recycled to the two extraction columns and the organic product from the scrub column is split so as to send approximately 40% to the 22-inch and 60% to the 26-inch re-extraction column. The stream concentrations (uranium, nitric acid and flow rates) used are averages taken from actual plant data. The material balance is based on a feed slurry concentration of 200 g/l uranium and 3N nitric acid. TBP distribution data (raffinate and product stream losses) have not been included.

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EXTRACTION SYSTEM FLOW SHEET

MATERIAL BALANCE

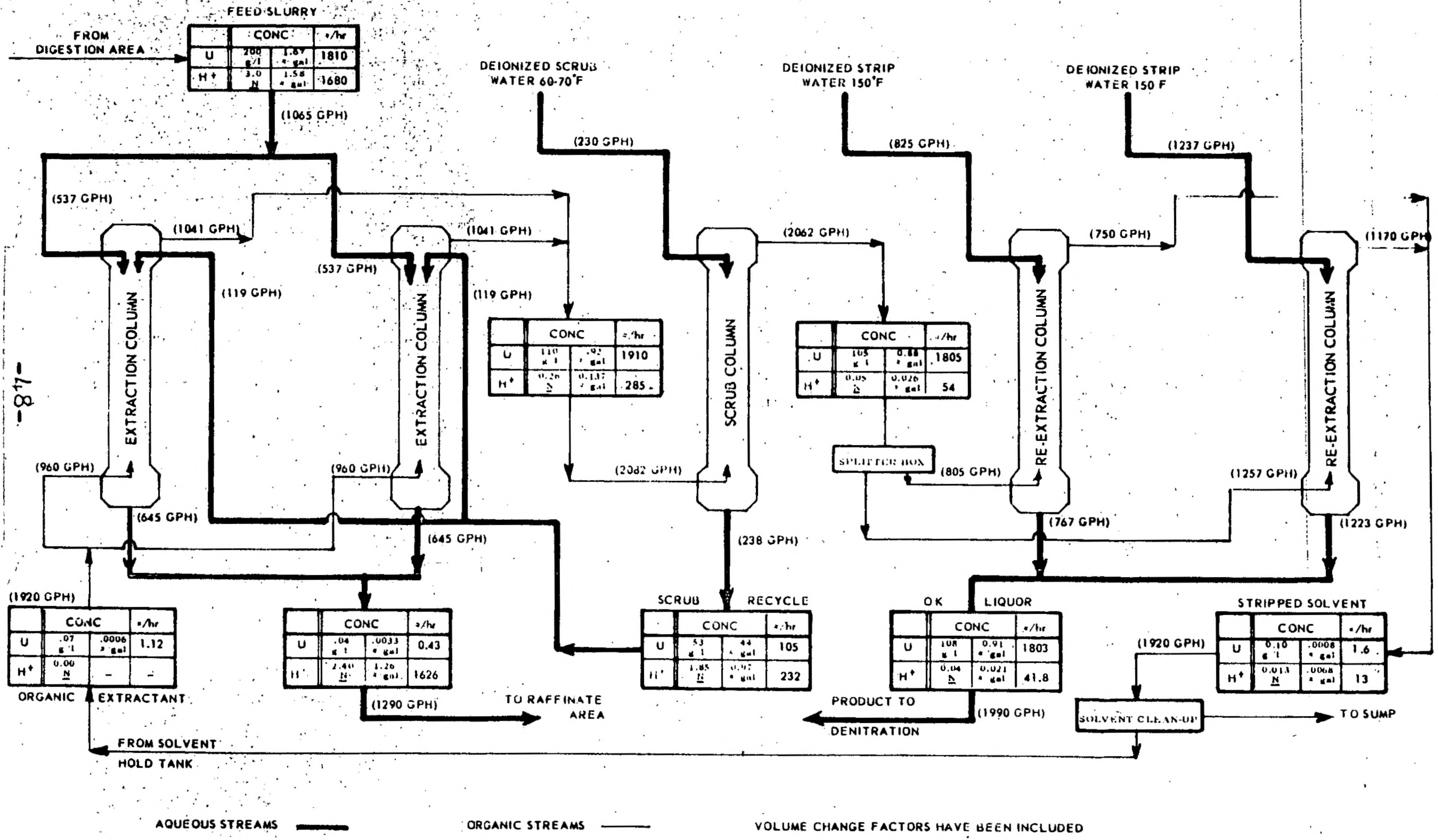

FIGURE 30

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REFINERY PROCESS MATERIAL BALANCE (Figure 31)

The refinery material balance flowsheet covers the process from ore digestion through UO_3 production including raffinate processing and acid recovery. Uranium, nitric acid, water and chloride balances are included. The chloride balance has been presented in order to show its distribution and the effect of ozonation on chloride removal. Calculations have been based on the processing of one ton of concentrate assaying 60% uranium and 0.1% chloride on a uranium basis (0.06% on an as received basis). The acid used for digestion is 12$\underline{N}$ (56%) and the dilution liquor is considered to be water. No allowance has been made for recycle of waste streams containing small quantities of uranium and water, such as results from pump leakage, etc. It was further assumed that a diuranate concentrate was being processed, therefore digestion at a low temperature would result in no appreciable quantity of water, nitric acid or oxides of nitrogen being sent from the digestion to the acid recovery area. The remaining 40% by weight (800 lb) of the original concentrate was carried independently as metal oxides to storage.

A 100% uranium balance has been assumed and the nitric acid recovery calculated using plant-test data is 92.5%. Chloride removal by ozonation is 58% of the chloride entering the system.

FEED MATERIALS SPECIFICATIONS

In view of the rigid purity specifications imposed on the UO_3 product, it is necessary that the maximum tolerable concentrations of the interfering elements present in the feed material be predetermined. A considerable amount of laboratory, pilot plant and plant-scale investigations have been accomplished toward developing a set of feed material specifications for the TBP extraction process.(7,8) The results of these investigations are presented in Figure 32. The list is by no means complete, plant-scale evaluations are continually in progress.

The major impurities normally encountered in uranium-bearing materials can be capitalized into three groups depending upon their affect on (1) the physical extraction system, (2) the efficiency of the extraction process and (3) the purity of the product.

Those impurities which affect the physical extraction system are the scaling agents and those ions which promote excessive corrosion of the equipment in a nitric acid

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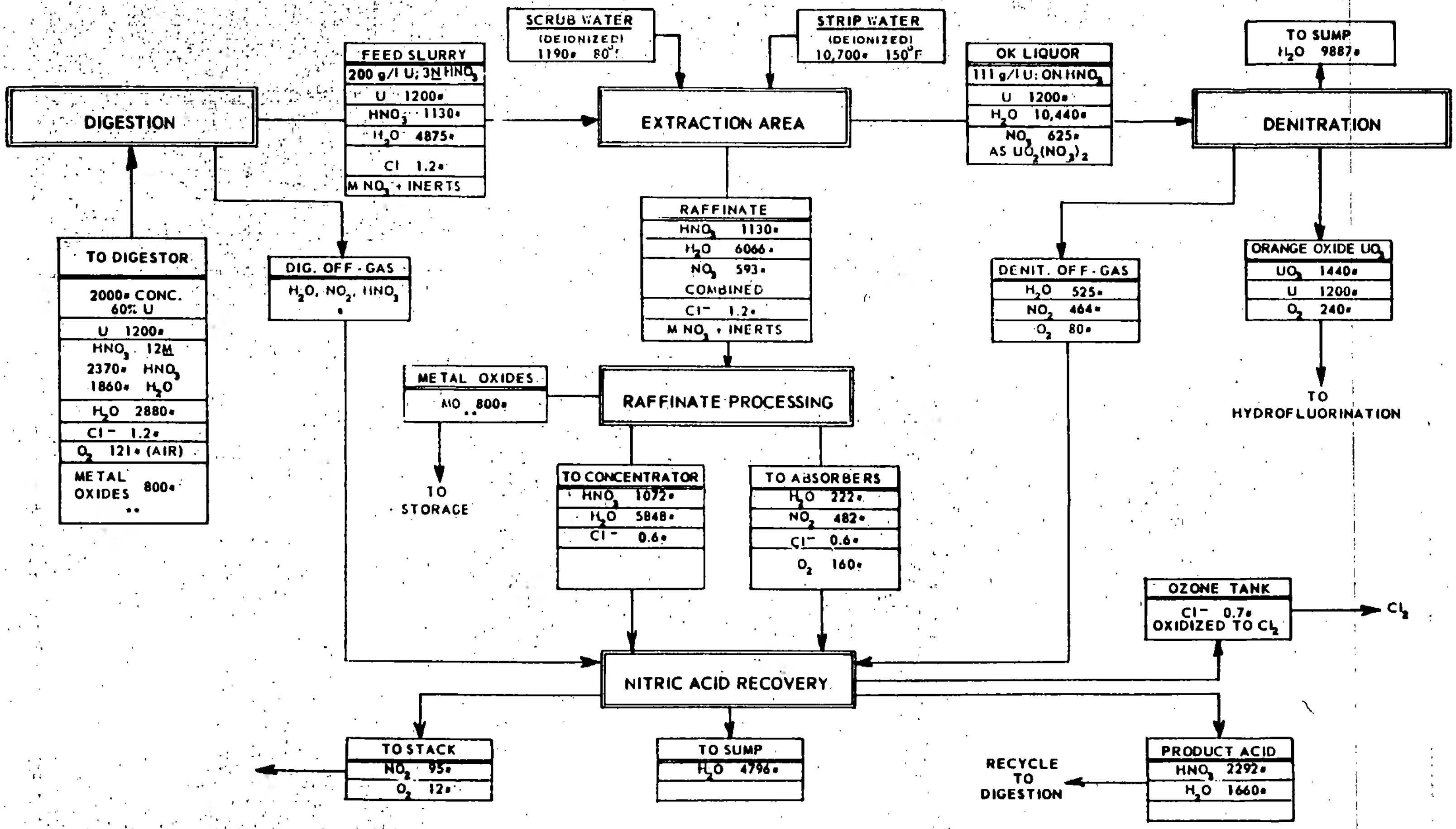
REFINERY PROCESS (ORE TO UO_3) MATERIAL BALANCE



BASIS FOR CALCULATIONS:
- a) 1 TON URANIUM CONC. (TYPICAL DIURANATE PPT.) 60% U, 0.1% Cl (U BASIS)
- b) 12M HNO_3 USED IN DIGESTION
- c) FRESH WATER FOR DILUTION

* LOW TEMP. (~150°F) DIURANATE DIG. – NO APPRECIABLE OFF-GAS
HIGH TEMP. (~200°F) U_3O_8 DIG – APPRECIABLE OFF-GAS

** METAL OXIDES AND INERTS ESTIMATED - CARRIED INDEPENDENTLY OF CALCULATIONS

FIGURE 31

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FEED MATERIAL SPECIFCATIONS

COMPONENT	SPECIFICATION (MAX.)
U_3O_8	$\geq 75\%$
V_2O_5	20% (U_3O_8 BASIS)
PO_4	6% (U_3O_8 BASIS)
SO_4	30% (U_3O_8 BASIS)
$PO_4 + SO_4$	$\frac{5\ (\%PO_4) + (\%SO_4)}{35} \leq 1$
$Ca + SO_4$	$(\%Ca) \times (\%SO_4) \leq 40$
Mo	0.6% (U_3O_8 BASIS)
Cu	4% (U_3O_8 BASIS)
Fe	30% (U_3O_8 BASIS)
As	0.8% (U_3O_8 BASIS)
CO_3	1% (U_3O_8 BASIS)
Cl, Br, I (AS Cl)	0.10% (U_3O_8 BASIS)
F	0.20% (U_3O_8 BASIS)
B	0.7% (U_3O_8 BASIS)
Cd	●
RARE EARTHS	●
Th	●
MOISTURE	$\leq 10\%$
PARTICLE SIZE	−¼ INCH

● FIRM SPECIFICATIONS (MAX) ARE NOT AVAILABLE. DEVELOPMENT WORK NOW IN PROGRESS TO DETERMINE THESE.

FIGURE 32

medium. Calcium sulfate tends to deposit on the walls and plates in the extraction columns, necessitating operational shutdowns for cleaning. A continuous scale build-up would result in changes in the column characteristics and overall reduction in extraction efficiency and production capacity. In extreme cases, scale deposition may extend to pipe lines and pumps. In the case of those feed materials which contain high percentages of insoluble silicates as well as calcium sulfate, secondary silicate deposition has been noted. Fluorides and chlorides in the presence of nitric acid, present a serious corrosion problem in the raffinate processing and nitric acid recovery areas. Although corrosion has been successfully controlled by the addition of aluminum oxide to the digestion batch to complex the fluoride ion and by the use of ozonation to remove the chloride ion from the nitric acid concentrator, a careful control on the halide concentration in the feed slurry is necessary.

There are a number of impurities, generally present in the form of anions, which tend to reduce the efficiency of the extraction process. Predominant among these are sulfate and phosphate. When present in sufficient quantity, these ions associated with the uranyl ion yielded compounds which are not extracted by the TBP. When this occurs, the extraction column efficiency is greatly reduced. The arsenic and vanadate ions have the same effect, but to a lesser extent. The detrimental affects of some of these ions can be reduced by the addition of metals with which they preferentially combine, thereby freeing the uranyl ion. The addition of iron, for example, results in the formation of ferric phosphate which has no affect on the extraction system. In border-line cases increasing the free nitric acid content in the feed slurry compensates for the presence of interfering ions.

The last of the major impurities are those which directly affect the purity of the final uranyl nitrate product. These are carried through the refining process either by TBP extraction or by physical entrainment. The latter can occur in the form of solids entrained in the organic stream or in the case of soluble impurities through aqueous carry-over from the extraction and scrub columns. These impurities can be divided into four subgroups. Of primary importance are elements of high cross-section for thermal neutrons which therefore must be held to an absolute minimum in the product. These include: boron, cadmium, the rare earths, lithium, arsenic, etc. A second subgroup is made up of those elements which affect the physical structure of the uranium metal product and stability of the fuel element while in the reactor. The group includes sulfur, carbon, phosphorus, and the halides.

The third subgroup includes a large group of elements which have a special affinity for tributyl phosphate and its hydrolysis products, and therefore tends to follow the uranium through the extraction system. In general, they are the elements which possess high oxidation states. Chromium, vanadium, thorium, zirconium, cerium, molybdenum, lead, ruthenium, palladium, zinc and tin fall in this category. The presence of these impurities either affects the metallurgical processing of the uranium metal or the reactor efficiency. The final subgroup is composed of those elements which form volatile fluorides and therefore must not be present in the products scheduled for conversion to UF_6 and subsequent introduction into gaseous diffusion plants.

In the case of high grade uranium concentrates (those which assay greater than 50% U) the above mentioned impurities are not generally present in concentrations great enough to affect the extraction process; however, it is important that a number of these impurities be continually monitored in the incoming feed material. This is especially true in the case of those elements which directly affect product purity and/or whose presence promote equipment corrosion.

In addition to the chemical impurities mentioned above, refinery operational difficulties are encountered in processing feed slurries containing large quantities of nitric acid insolubles. The presence of these solids increased the difficulties in pumping and metering the feed slurries to the columns, the raffinates from the columns and in processing the raffinate for nitric acid recovery. It has been found that a maximum solids concentration not exceeding 5 per cent by volume can be processed without difficulty. The presence of solids in the raffinate stream tends to increase solvent losses by physical entrainment. To reduce this loss to a minimum, the raffinate stream is washed with kerosene to recover the tributyl phosphate.

The uranium concentrates tentatively scheduled for processing in the proposed refineries are for the most part, high assay materials. Chemical analyses of some of the typical high assay uranium concentrates which have been successfully processed in the FMPC refinery are presented in Figure 33. It should be noted that in most cases the impurity concentrations meet feed material specifications with the possible exception of the halide

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CHEMICAL ANALYSES* OF TYPICAL HIGH ASSAY URANIUM CONCENTRATES

COMPONENT	SOUTH AFRICAN	AUSTRALIAN	CANADIAN	DOMESTIC
U_3O_8	75	65	70	65
SO_4	7	1	1.5	0.01
PO_4	0.06	1	1.5	0.08
SiO_2	1.2	3.5	5.4	1.7
CaO	0.4	0.8	0.5	0.3
MgO	0.4	5.5	0.2	0.2
V_2O_5	0.3	0.02	0.5	5.2
MoO_3	0.01	<0.001	<0.001	<0.001
Fe	0.25	2	0.4	0.03
Al_2O_3	0.30	1	1	0.04
Ni	0.33	0.2	.05	–
Cr		0.5	–	–
Na		0.2	8	7.7
NH_3	1-3	0.01	–	0-3.5
MOISTURE (120° C, 2 HRS.)	2-5	7	0.8	14
Cl	1.16	1	.04	0.03
F		0.03		0.06
LOSS ON IGNITION (150° C)	15-25	15	5.8	16.8
LOSS ON IGNITION (1000° C)	15-26	16	6.1	16.8

* SELECTED AVERAGE ANALYSES – PERCENT ON AS RECEIVED BASIS.

FIGURE 33

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content. The analyses presented in the table are averages over all of the shipments received from the various geographical locations.

PRODUCT (UO_3) SPECIFICATIONS

A compilation of the chemical and physical specifications for the orange oxide product are given in Figure 34. Under normal operating conditions these specifications are easily attained in the TBP extraction system when processing average and high-assay concentrates.

The assay figure of 81.5% is self-explanatory. The nitrate and HNO_3 concentrations are a measure of the completeness of denitration and must be kept low to minimize corrosion in subsequent processing steps. The rare earths, boron and cadmium, since they must meet rigid specifications in the metal, must be kept at a minimum to maintain low neutron absorbance. Corrosion contamination during the denitration process is reflected in the iron, nickel and chromium specifications.

The density specifications have been established since the apparent density of the UO_3 is directly reflected in the apparent density of the UF_4 product. A low density at this stage in the processing reduces the weight of the charge that can be placed in the reactor vessel used for reduction to metal and affects production capacity. In addition, there is evidence that the reactivity of the UO_3 in the subsequent reduction and hydrofluorination processes is related to the density of the oxide.

Since a certain amount of corrosion contamination(9) is inevitable in the high temperature denitration step, it is important that internal specifications be placed on the iron content of the aqueous uranyl product from the extraction plant so that the UO_3 specification will not be exceeded. These have been set locally at 10 ppm (U basis) which added to the normal 15 ppm pick-up during denitration resulted in a total iron content of 25 ppm. There is no appreciable chromium or nickel pick-up through denitration. Maintaining the nitric acid normality below $0.04\underline{N}$ is important in order to meet these specifications.

PROCESS DESIGN

CRITICAL CONTROL POINTS

The digestion operation is a standardized batch-wise leaching process involving no particularly critical points

PRODUCTION PURITY SPECIFICATIONS – UO_3

	MIN	MAX
TAP DENSITY gm cc	3 5	
BULK DENSITY gm cc	2 4	
U %	81 5	
C ppm		100
NO_3 %		0.85
HCl INSOLUBLE (U_3O_3) %		1.0
H_2O (DIRECT DETERMINATION), %		1.0
F (NON VOLATILE) TOTAL, ppm		250
Ag ppm		1
B ppm		0 20
Cd ppm		0.20
Cr ppm		10
Cu ppm		50
Fe ppm		30
Mn ppm		5
Mo ppm		1
Ni ppm		15
P ppm		50
Si ppm		20
S ppm		50
Th ppm		50
V ppm		30
Gd ppm		0.05
Dy ppm		0.10

FIGURE 34

of control with regards to equipment operation. A possible exception is the ore addition system. Some low-grade ores react violently with nitric acid and require a carefully controlled rate of addition to prevent digester boil-over and excessive uranium carryover through the vent system. In the case of high-grade concentrates this difficulty is not encountered.

Accurate analyses of the uranium content of the concentrate and of the concentration of the nitric acid are required for correct batch make-up and subsequent constant feed slurry composition. Frequent feed slurry concentration adjustment after digestion results in increased analytical and operator manpower and necessitates additional surge capacity in the area. Efficient column operation in the extraction system depends greatly upon a constant uranium and acid concentration in the feed slurry. This is especially important when operating near the equipment capacity limits. The use of large volume feed hold-tanks tends to minimize sudden concentration and flow rate fluctuations.

There are a number of critical control points in the extraction system. All of the process streams must be delivered at a constant flow rate to and from the columns in order to maintain column equilibrium. This implies rigid interface control as well. The clarified streams, both aqueous and organic, offer no problem and can be controlled by using conventional flow control equipment and instrumentation. The feed slurry and extraction column raffinate streams which may contain a high percentage of heavy solids are difficult to handle. The use of high velocity recycle loops on both streams have proved satisfactory. By maintaining a constant back-pressure on the air-operated flow control valves in the recycle loop take-off lines, fairly constant flow rates to and from the extraction column are achieved. The valve in the raffinate line is automatically controlled by the interface level controller (air-operated, float-type) located in the bottom disengagement section of the column. The same system is used in the aqueous recycle line from the scrub column to the extraction column and on the aqueous product line from the re-extraction column. Since the aqueous waste stream from the bottom of the scrub column is recycled to the feed point of the extraction column, these two columns operate as a closely integrated unit and therefore rigid flow and interface control is essential. The liquid levels in the columns are maintained by gravity over-flow (all columns operate at atmospheric pressure).

In the slurry extraction system considerable "crud" build-up occurs at all of the column interfaces, due to finely divided solids (carbon and silica) being carried through the system. The crud frequently interferes with the operation of the interface-controller float, resulting in variations of the interface position. Water lines have been installed for flushing out the float chambers. Level control recorders are located on the control panel so that any fluctuation in the interface level can be observed and the condition corrected.

The organic product density control system has been previously discussed.

In order to attain complete conversion of the UO_3 to UF_4 at a high production rate, it is important that close control be maintained throughout the denitration process. Variation in the feed rates and operating temperatures of the evaporator and boildown tank, result in varying degrees of hydration in the molten salt charge to the denitration pots. This in turn results in variations in the completeness of denitration, state of oxidation and density of UO_3 product.

The uranyl nitrate evaporator is operated so as to maintain a constant temperature in the recycled product. A temperature controller in the recycle line varies the steam pressure to the evaporator. In the boildown tank, the bulk liquid temperature is held constant by controlling the steam pressure to the unit. The product overflows by gravity to the sparge tanks. The hold-up time in the sparge tanks is kept to a minimum and heat is added only to maintain the uranyl nitrate in a liquid state. Density recording instruments in the sparge tank are used as a check on the product. Close control of the denitration pot heating-cycle yields a product having a fairly constant chemical and physical composition.

MATERIALS OF CONSTRUCTION AND CORROSION PROBLEMS

The entire system from digestion through denitration, including raffinate processing and nitric acid recovery, is constructed of stainless steel. The ore-handling system is mild steel. All of the digestion, tankage, columns, acid pumps, denitration equipment and raffinate processing equipment are constructed of 304 ELC. The feed slurry and raffinate pumps are made of Durimet-20. The tube bundle in the OK liquor evaporator is 309 Cb steel. Except at points where frequent modifications are contemplated, welded joints are used. Where vapor-phase corrosion (high temperature) is a problem, Heliarc welding is used.

There are no serious corrosion problems in the digestion, extraction and denitration process areas from the point of view of equipment failure. However, the rigid specifications on the iron, cobalt and nickel content (measured in ppm) of the product requires the use of highly corrosion-resistant equipment. Relatively serious erosion problems are encountered in the feed slurry and raffinate-handling equipment. Pump and control valves must be repaired or replaced at frequent intervals.

The presence of the fluoride and chloride ion in the raffinate processing and nitric acid recovery process streams result in a high corrosion rate in the equipment in these areas. Aluminum addition and ozonation has aided in reducing corrosion control problems. Replacement of the present nitric acid concentrator with one which will operate under reduced pressure is expected to reduce the rate of corrosion considerably in this area.

MAINTENANCE EXPERIENCE

Maintenance requirements in the digestion and extraction areas can be considered as normal for a process involving the use of concentrated nitric acid and the handling of high-solids content slurries. Stand-by pumps have been installed on all process lines to reduce downtime for maintenance to a minimum. With slurries containing 3% or less of silicious solids, good service life is reported. Difficulties are encountered when the solid content reaches about 15%. Processing high-assay concentrates offers no problems.

A considerable amount of maintenance has been required on the dust collection, gulping system and off-gas lines, located in the denitration area. Frequent line-plugging caused by solids entrainment and solidification of uranyl nitrate in the lines has been experienced. The heavy load imposed on the agitators and drive mechanism during the denitration operation necessitates frequent repair of this equipment.

A considerable amount of maintenance is required in the raffinate processing area with the present equipment. The main difficulties encountered are tube-plugging in the raffinate evaporator, erosion of the raffinate circulating pump and the burning-out of the fin-tube heaters in the spray calciner. The latter difficulty will be eliminated when the raffinate drum-drier-calciner system is installed.

Excessive corrosion in the nitric acid concentrator and re-boiler due to the presence of halides is the cause of high maintenance requirements in the acid recovery area.

ON-STREAM FACTORS

As originally designed and constructed, the total refinery capacity was limited by the capacity of the denitration equipment (number of denitration pots). This situation is in the process of being remedied by the installation of additional pots. Past operating experience indicates that with the expanded facility, a 90% refinery on-stream factor will be realized.

PLANT SIZE CONSIDERATIONS AND SUPPORTING FACILITIES

MANPOWER REQUIREMENTS

The manpower requirements (Figure 35) as discussed in this paper include the operating personnel for digestion, extraction, denitration, refinery sump, raffinate processing and nitric acid recovery and are based upon plant design similar to that at the Fernald site. They do not include administrative, general service, laboratory, cafeteria, utilities, maintenance and transportation. These figures are based on a 7-day, 4-shift work week.

Supervision is divided so as to have one area foreman in charge of the main process which is located in the refinery building and the other area foreman in charge of the raffinate processing and acid recovery areas located outside the refinery building.

The manpower requirements are entirely dependent upon the plant design, raffinate processing requirements, degree of instrumentation, etc.

Assuming that the proposed 5,000 ton/year plant is also operated on a 7-day, 4-shift work week, a rough estimate of the operating manpower requirements can be made. These figures are based on a plant employing the same technology and basic equipment. Operation of the digestion area would require 24 persons. Twenty-four operators would be required in the extraction area and 12 in the denitration area. The raffinate processing and nitric acid recovery areas would require essentially the same number of personnel as at present, namely 24. Administrative and

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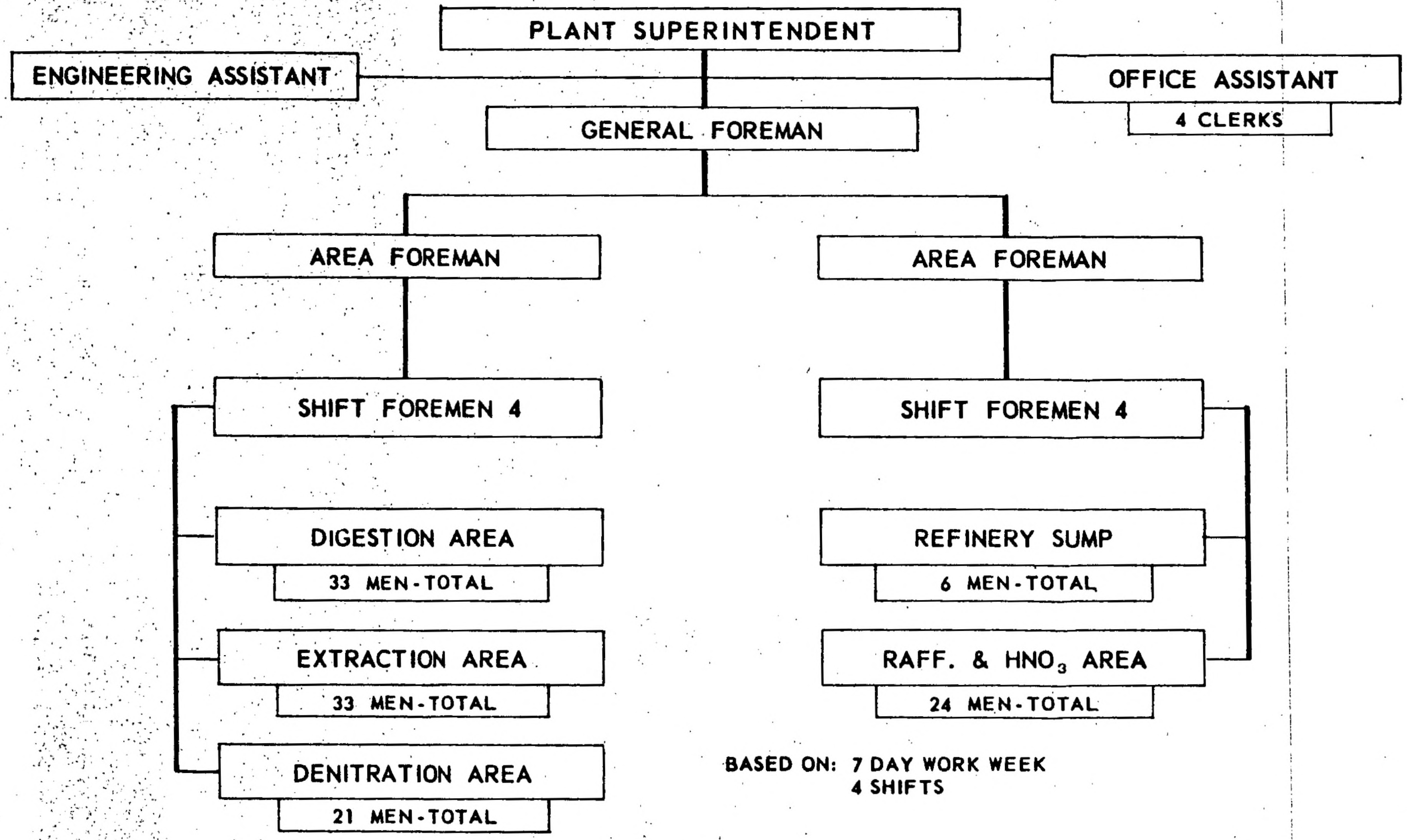
OPERATING PERSONNEL REQUIREMENTS



BASED ON: 7 DAY WORK WEEK
4 SHIFTS

FIGURE 35

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supervision, since they depend upon company practice may vary widely and cannot be estimated.

BUILDING AND PLANT AREA REQUIREMENTS

The building and plant area requirements (Figure 36) presented here are estimated figures for a 5,000 ton/year plant employing the technology now existent at the Fernald site. These figures are for the production area only and do not include administration, maintenance and general services.

Approximately 12,500 sq. ft. of building area are required to house the digestion, extraction and denitration operations. With the exception of the control center for the nitric acid recovery system, the remainder of the installation, i.e., feed material storage, product storage, raffinate processing and the nitric acid plant do not require buildings. The feed material and orange oxide storage area requirements are the same as those presently used at Fernald. The raffinate processing area would be somewhat smaller than the Fernald area because less raffinate storage space is required for a 5,000 ton/year plant. It is estimated that essentially the same plant area would be required for nitric acid recovery as is presently in use.

Additional space would be required for power generation and water treatment facilities.

UTILITIES AND DIRECT MATERIAL REQUIREMENTS

The utilities and direct material requirements per ton of uranium processed from concentrate to UO_3 are presented in Figures 37 and 38. The utilities consumption have been prorated from total consumption figures and are not absolute. The figures are based on Fernald operation experience. Assuming the same technology for the 5,000 ton/year plant, these figures can be used for estimating as presented.

ANALYTICAL REQUIREMENTS

Rigid analytical control over the entire process from raw material testing through product analysis is required in order to produce an orange oxide which meets the established purity specifications. In addition to what might be considered as a normal analytical load, as dictated by the basic processes involved, there are the additional problems resulting from variations in feed materials, a rigid accountability program and a rigid

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BUILDING AND PLANT AREA REQUIREMENTS

PRODUCTION AREAS *

PROCESS	BUILDING AREA (FT^2)	PLANT AREA (FT^2)
REFINERY (TOTAL)	11,000	24,000
FEED MATERIAL STORAGE		6,000
DIGESTION	4,500	5,000
EXTRACTION	4,000	4,500
DENITRATION	2,500	2,500
PRODUCT (UO_3) STORAGE		6,000
RAFFINATE PROCESSING		6,000
NITRIC ACID RECOVERY	1,500	12,000
TOTAL	12,500	42,000

- ESTIMATED FIGURES FOR 5000 TON URANIUM/YEAR PLANT
PRORATED FROM FERNALD BUILDING AND PLANT AREAS
FIGURES DO NOT INCLUDE POWER GENERATION, WATER TREATMENT, ADMINISTRATIVE, ETC. FACILITIES.

FIGURE 36

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UTILITIES REQUIREMENTS

(PER TON OF URANIUM)

AREA	FUEL GAS (CUBIC FEET)	ELECTRICITY (KILOWATT HOUR)	STEAM (POUNDS)
GENERAL		17.3	
DIGESTION		329.0	9,832
EXTRACTION		476.2	
DENITRATION	3229.5	171.0	55,419
RAFFINATE PROC.	4111.9	166.0	17,042
ACID RECOVERY		166.0	4,260

ESTIMATED WATER CONSUMPTION (GAL)

PER TON OF URANIUM

PROCESS WATER	: ALL AREAS	3,060
DEIONIZED WATER	: EXTRACTION AREA	4,760
COOLING WATER	: DENITRATION AREA	362,000
	: ACID RECOVERY AREA	362,000
	: ALL OTHER AREAS	49,000

FIGURE 37

[redacted]

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DIRECT MATERIAL REQUIREMENTS

PER TON OF URANIUM PROCESSED

MATERIAL	DIGESTION AREA	EXTRACTION AREA	
		EXTRACTION	SUMP PROCESSING
NITRIC ACID (42° BE)	148 GAL.		
TRIBUTYLPHOSPHATE		1.7 GAL.	
KEROSENE		7.5 GAL.	
ALUMINA (Al_2O_3)*	50 LB.		
SODA ASH**		60 LB.	
SULFURIC ACID (66° BE)***		0.5 GAL.	
CAUSTIC SODA (FLAKE)***		14 LB.	
MAGNESIUM OXIDE			130 LB.
FILTER AID			40 LB.
LIME			160 LB.

* FLUORIDE CONTROL ** SOLVENT CLEAN-UP *** DEIONIZER REGENERATION

FIGURE 38

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139

corrosion control program. At the Feed Materials Production Center at Fernald, all of the production analyses are conducted by the Analytical Department with the exception of a few on-the-spot tests conducted by the Refinery operators. Sampling is accomplished by the operating personnel and the samples are sent either to the central analytical laboratories, or in the case of the more direct control samples, are sent to the laboratory situated in the Refinery area.

All incoming lots of uranium concentrate are checked for uranium, fluoride and chloride content before entering the digestion process. The uranium assay is required in order to calculate the weight of ore and acid for the digestion batch, the halide analysis is required in order to maintain corrosion control in the raffinate and nitric acid processing areas. In the case of feed materials from new sources, a more complete analysis is made to determine whether it meets the feed material specifications.

In the digestion area, each digest batch is checked for uranium and free-nitric acid content and adjusted to meet specifications before pumping to the extraction system. As an additional safety measure the feed slurry is again checked for fluoride and/or chloride content. All recycle streams to the digestion area are analyzed for uranium, acid and halide content.

The heaviest analytical load is from the extraction area. A rigid sampling schedule is adhered to covering all of the process streams which are important toward maintaining operational control. The extraction column feed, organic extractant and raffinate streams, the extraction column recycle stream, and the re-extraction column product and stripped organic streams are sampled each hour routinely. All streams are sampled at least once each shift. A close check of the raffinate stream for uranium and TBP content is required to minimize uranium losses. The TBP analysis is used as an indication of the total organic (TBP plus kerosene) content of the raffinate. Frequent testing (hourly) of the extraction column organic product stream for specific gravity is done in order to maintain the required uranium saturation and resultant product purity. The organic stream from the re-extraction column is monitored for its uranium content to avoid a possible build-up and subsequent raffinate losses.

The aqueous product stream (OK liquor) is grab-sampled each hour and analyzed for uranium, nitric acid, iron and TBP. The uranium analysis is used as a check on the re-extraction column performance, the nitric acid as an indication of corrosion impurity pick-up during the subsequent processing steps, the iron content as a general indication of the product purity of the OK liquor and the TBP as a safety measure to avoid a possible organic explosion hazard in the high temperature boildown and denitration process. A continuous sample of the product stream is taken and submitted each day for a complete chemical and spectrochemical analysis to determine the total impurity content (acceptance analysis).

In the denitration area, the OK liquor and boildown tanks are sampled at regular intervals to maintain a control on product purity. Each hopper of orange oxide is sampled and submitted for complete chemical and spectrochemical analyses for product purity, before releasing for processing to green salt.

Process-control sampling is also done throughout the raffinate processing and nitric acid areas.

A summation of the analytical manpower requirements and the sample receipts are presented in Figure 39, with a breakdown as to the processing area from which the samples originate. The sample load is dependent on the uranium tonnage being processed, only if a multiple extraction column system is involved. In this case, the number of process stream samples would depend upon the number of columns in operation. If raffinate processing and/or acid recovery operation are not included, the number of samples per day would decrease by approximately thirty. With additional instrumentation and operator experience, a considerable portion of the analytical control analyses could be conducted by the production personnel in the production area (approximately 25%). A number of the analyses must be performed by laboratory technicians, using specialized equipment (fluorimeters, spectrometers, etc) which must be isolated from the production operation.

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ANALYTICAL REQUIREMENTS

ANALYTICAL FUNCTION	PERSONNEL REQUIREMENTS*	NO. OF SAMPLES PER DAY	NO. OF ANALYSES PER DAY
SUPERVISORY AND CLERICAL	2		
REFINERY LABORATORY**	16	168	580
DENITRATION LABORATORY	4	12	36
SPECTROGRAPHIC LABORATORY	1	12	12
SAMPLE RECEIVING ROOM	1	192	
TOTAL	24	192	628

* BASED ON 7 DAY WORK WEEK; 3 SHIFTS

** INCLUDES DIGESTION, EXTRACTION, RAFFINATE AND NITRIC ACID AREAS

FIGURE 39

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URANIUM OXIDE REFINERY

TBP HEXANE PROCESS

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I. INTRODUCTION AND SUMMARY

It is the purpose of this paper to describe the design and projected operation of the extraction-purification section of the new uranium refinery being built at Weldon Spring, near St. Louis, Missouri. A basis of 5,000 tons per year of U_3O_8 equivalent has been assumed and raw material feed as for the ether and TBP kerosene plants as noted in other papers in this report.

The Weldon Spring Refinery is believed to incorporate the best features of the two plants already in existence, and is expected to combine the unusually high uranium recovery with extremely high product purity. Major new features to aid in accomplishing these purposes are included in the process flow sheets and the equipment design.

The following sections are devoted to a discussion of the reasons for these changes, a description of the major and auxiliary equipment, and a discussion of the plan of operation of this equipment. The general extraction process is represented in Figure 1, while Figure 2 is a more detailed look at the pumper decanters.

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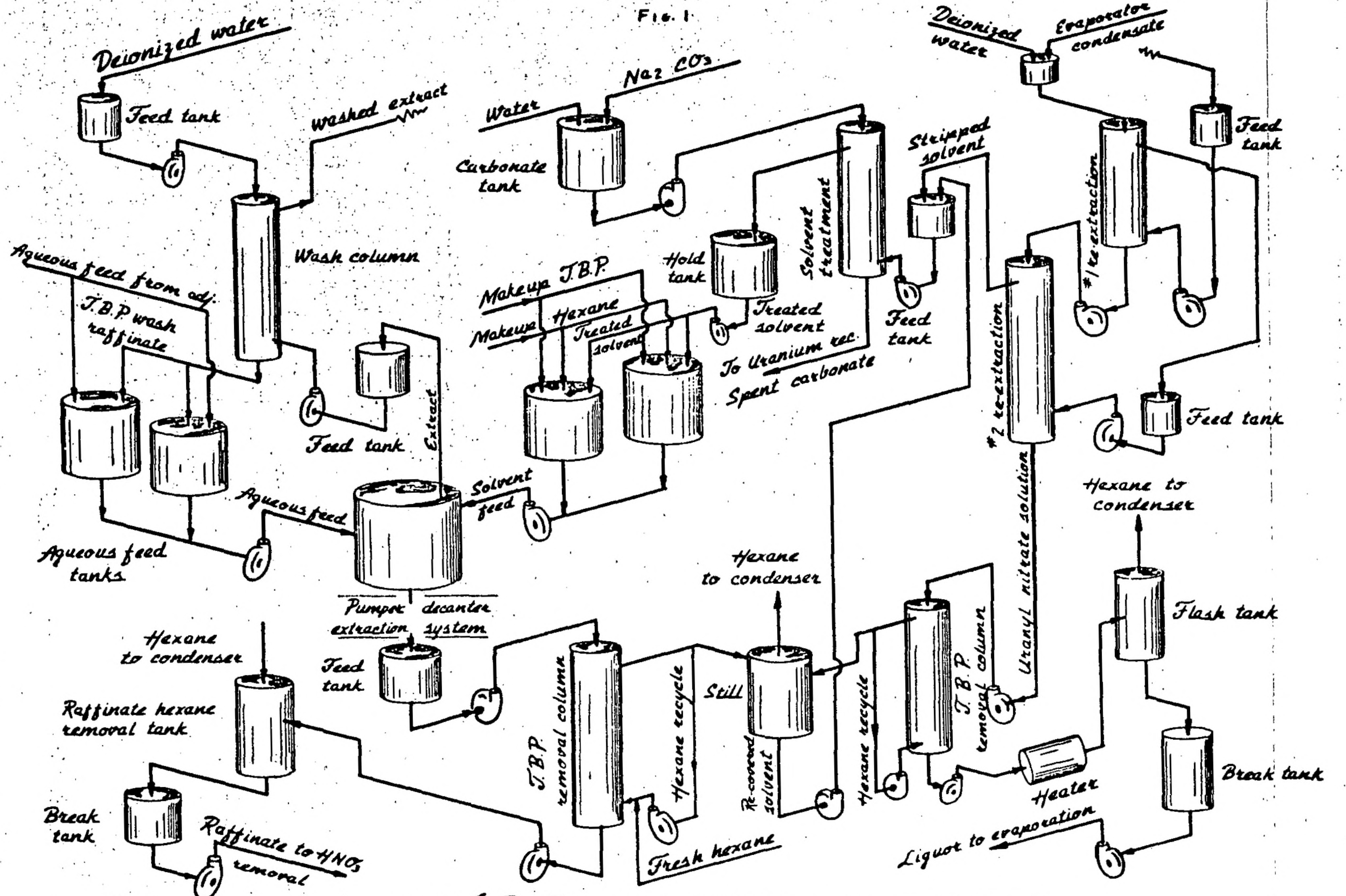
Fig. 1



T.B.P. Extraction System

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Pumper Decanter Extraction System

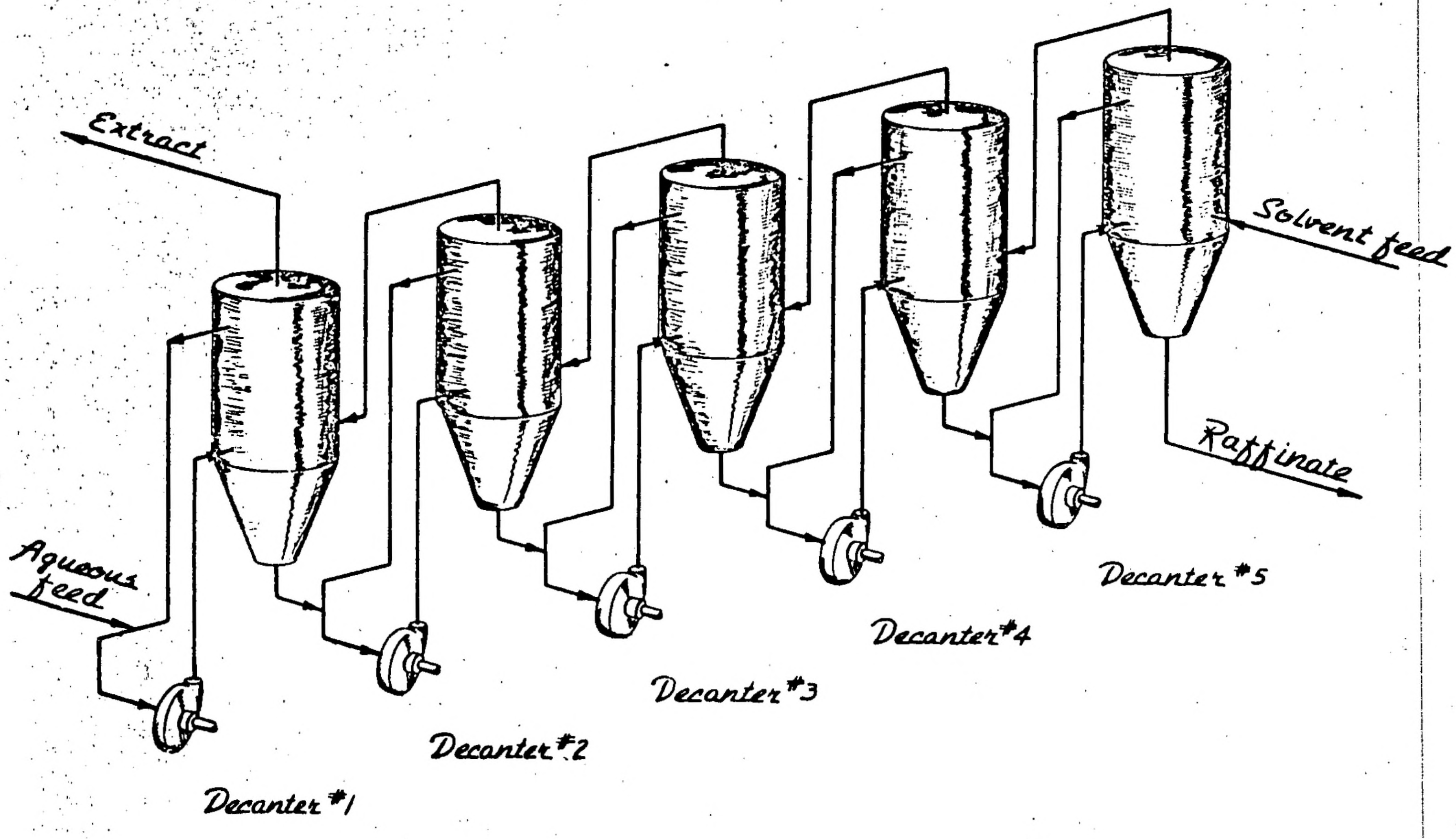

FIG. 2

II. HISTORY AND CHEMISTRY

In 1949, a pilot plant was established at Mallinckrodt to investigate the use of a different solvent for the extraction and purification of uranium from high grade ores and ore concentrates, namely, tributyl phosphate (TBP) diluted with an inert solvent such as kerosene. This method had already been shown to be applicable to uranium extraction from other systems, by work at Iowa State College and at Oak Ridge National Laboratory, and appeared to offer distinct advantages with respect to better recovery and less fire or explosion hazard. These expectations were realized in the pilot plant work, and a production plant operated by National Lead Company of Ohio was based on this process (described elsewhere).

Uranium is extracted by TBP through the formation of a stable TBP complex:

$$UO_2 + 2NO_3 + 2TBP \longrightarrow UO_2(NO_3)_2 \cdot 2TBP$$

Nitric acid and other metal nitrates, such as thorium and rare earths, also form organic soluble complexes with TBP, but these complexes are not as stable as that with uranium. By saturating the organic phase with uranium, this difference in stability can be used to reduce the impurity level in the uranium product. The stability of the uranium complex allows essentially complete extraction of uranium, which results in very low uranium losses.

In comparing an all ether system with an all TBP-kerosene system, certain advantages are evident for each:

Relative Advantages of Two Refinery Processes

Ether	TBP-Kerosene
Purity of product	Very high recovery of uranium
High saturation capacity	Stability to strong oxidants at high acidity
Low viscosity	High flash point
Low specific gravity	Low solubility in water

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Relative Advantages of Two Refinery Process (Cont.)

Ether	TBP-Kerosene
Ease of removal from aqueous solutions	
Stability to hydrolysis	
Ease of re-extraction	

Some of these advantages are mutually incompatible, hence cannot be realized in a mixed system. However, the dual-solvent two-cycle system at Weldon Spring will combine the very high recovery of TBP with the very high purity of ether extraction. The stability of TBP to oxidizing acids will permit the use of 3N or higher excess free acid in the recovery cycle, as compared to the 1N limit imposed by the sensitivity of ether to HNO_3, thereby easing the restrictions on raw materials with respect to phosphate, vanadium, molybdenum, arsenic, and sulfate plus calcium. Through the use of hexane as a diluent, the physical properties of the mixed solvent will approach those of ether, promoting complete separation of organic and aqueous liquids. The change in chemical environment in going from first to second cycle, described in the discussion of the ether process, will again aid in decontamination of important impurities.

On the other hand, the dual system will be approximately as subject to fire hazard as the all-ether system. Close control of the aqueous-organic flow ratio will be required to obtain saturation and at the same time to prevent uranium losses, but by exercise of such control the recovery will be higher than with ether because of the stronger complex. On the other hand, re-extraction from the stronger complex is more difficult, resulting in more dilute solutions and more boildown after the first cycle. The higher acidity itself is not an unmixed benefit, because it enhances corrosion, especially in the presence of halides.

Nevertheless, the dual solvent two-cycle system, which has now been subjected to extensive pilot plant study, appears to incorporate the best features of uranium refining technology to date.

140 148

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III. OUTLINE OF PROCESS

1. Feed Preparation

The Weldon Spring refinery incorporates in the current design a sampling plant wherein feed material received in drums will be put through grinding, blending, and sampling equipment to obtain as accurate analyses of plant feed as possible. The material will be packaged in large hoppers of two to four ton capacity. These hoppers will be transferred to the feed makeup area and the material fed directly from the hoppers into the nitric acid digestion tanks. 60% nitric acid will be used to dissolve the feed material and sufficient feed will be added to produce approximately 200 g/l uranium solutions at 3N nitric acid excess. Material will be sampled at this point for total acid and uranium content. Upper and lower limits have not as yet been established. These solutions will contain 1 1/2 to 2 pounds per gallon of suspended solids depending upon the quality of the feed material received. The problems in ore digestion will be essentially the same at Weldon Spring as they are at the St. Louis Plant and control will be maintained on the rate of ore addition to minimize excessive fuming. The temperature of the digest liquors will be controlled at around 190°F to insure rapid solution. Failure to control either the temperature or the addition of the ore can lead to foaming, boil-overs, and the associated excess fume liberation which could get severe enough to overload the fume duct capacity and flood the area around the digest tanks with poisonous NO_2.

2. Solvent System

The hexane tributyl phosphate solution used to extract the aqueous feeds is a circulating system which will be checked periodically to determine that the tributyl phosphate content is within the acceptable range. The nominal tributyl phosphate concentration which will be used at Weldon Spring is 26% - 30% by weight in n-hexane of narrow boiling range. This is the same hexane that is commercially used for the extraction of soy bean and cotton seed. The solvent system undergoes some chemical decomposition during its use which is primarily hydrolysis of tributyl phosphate to the dibutyl and monobutyl esters. These hydrolysis products remain soluble in the hexane phase whereas the complete decomposition produces butyl alcohol and phosphoric acid which are continually washed out by contact with the aqueous phase. The mono- and dibutyl esters exhibit greater complexing action with the impurities contained in the feed solutions, particularly the rare earths and iron, and therefore if not removed from the solvent system cause a gradual deterioration of product purity. The removal is accomplished by a sodium carbonate wash. The sodium carbonate combines chemically with the acid phosphate ions producing sodium butyl phosphates which are removed from the tributyl phosphate hexane stream. When using kerosene as a diluent rather than the hexane proposed for Weldon Spring, there is a further complication inasmuch as kerosene often contains compounds which are susceptible to oxidative decomposition when contacted with nitrate solutions. This oxidation produces compounds which can, and have, caused considerable difficulty in uranium refining. Hexane on the other hand, has been used for many months in pilot plant operation at St. Louis with no trouble that we have attributed to the hexane diluent.

3. Uranium Extraction

A five stage pumper decanter system is planned for this extraction which is designed to recover 99.95% of the contained uranium and produce an organic phase which is nearly saturated (95% or more) with respect to uranium. As one approaches the 100% saturation goal, the danger is always present that uranium will be rejected in the aqueous raffinate causing low recoveries. Because of this latter contingency, it is planned to run slightly below 100% saturation since maximum recovery is of utmost importance in the primary extraction operation.

When operating below saturation, the remainder of the TBP is complexed with nitric acid. This nitric acid, if allowed to remain with the uranium solution to the boil down operation, would cause considerable corrosion of the equipment, and, therefore, some pick-up of impurities. To prevent this, the extract solution will be washed at Weldon Spring in a pulse column using deionized water to achieve maximum removal of nitric acid. A pulse column is used in this operation because there is no danger of scaling, only a remote possibility of emulsions, and maximum stage contacting can be achieved by this system with minimum control. As the water descends in the pulse column, it is equilibrated with the rising extract and because the extraction coefficients favor the removal of nitric acid, a greater portion of the acid is removed than the uranium. Careful operation of the washing step is critical to reduce succeeding corrosion and maintain the purity of the product achieved in the primary extraction units. The water phase is recycled to the feed system so that no loss of uranium occurs as a result of the washing operation. The overall capacity of the primary extraction system is definitely controlled by the degree of washing that is necessary or desired. For the proposed Weldon Spring operation approximately 10% of the uranium will be removed by the wash step and recycled. The extraction and washing operation complete the purification and recovery operations in this part of the process. The remainder is merely the removal of the uranium from the organic phase into water and the treatment of the effluent water streams from the operation to remove solvents without further purification.

4. Re-extraction into Water

Following extraction and washing, it is necessary to remove the metal ions from the organic phase in order to recycle the solvent as well as to be able to concentrate the uranium for the subsequent neutral ether extraction. Re-extraction will be accomplished at Weldon Spring in pulse columns using deionized water. Pulse column operation for this step makes possible the attainment of maximum uranium concentration in the water re-extraction phase. Since high temperatures favor the distribution of uranium into the water phase, the re-extraction column will be operated slightly below the boiling point of the hexane diluent, between 120 and 140°F. This is contrasted to lower temperatures which will be maintained in the pumper decanters to favor the transfer of the uranium into the organic. It is essential in the re-extraction operation to achieve maximum removal of the uranium from the organic phase. The recycle solvent contacts the effluent aqueous phase in the primary extraction and any uranium remaining in the organic would tend to increase the raffinate uranium content. Careful control of uranium content (density, light transmission) must be maintained on the solvent leaving the re-extraction column to achieve this goal. The selection of the control system to be used is largely a matter of preference.

5. Removal of Solvent From Aqueous Streams

The final processing operation of the extraction plant is the preparation of the aqueous streams, both extract and raffinate, for removal from the explosion-proof area. This processing is carried out in two steps. The first operation is a wash with hexane. This washing accomplishes a double purpose. First, it removes the entrained droplets of TBP hexane solution that are invariably carried over from any liquid-liquid contacting process. Secondly, it extracts any dissolved TBP in the water phases. Our primary reason for hexane wash is safety, since it has been determined that TBP in contact with strong nitrate solutions at high temperature can lead to

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explosive reactions. It should be pointed out that we feel that this is one of the advantages of using hexane as the diluent as contrasted to the use of kerosene. It is only possible to employ the hexane wash because the dilute solution of TBP in hexane that results from the washing operation can be recovered and reused whereas if kerosene were used, the temperatures necessary to distill the kerosene from the dilute TBP solutions would cause decomposition of the TBP.

After the hexane wash, both the raffinate and extract are subjected to high temperature stripping which volatilizes the entrained hexane. By proper temperature control, essentially 100% removal of hexane can be accomplished. The raffinate and extract streams are then completely safe to handle in non-explosion-proof equipment.

IV. DESCRIPTION OF EQUIPMENT

1. Preparation of Uranyl Nitrate Feed Solutions

The preparation of uranyl nitrate feed solutions consists of four basic steps: transfer of ore to digesters, digestion in nitric acid, adjustment of digest liquor composition, and transfer of the adjusted liquor to the extraction area.

The major raw materials used as a source of uranium for the plant are dry solids passing a 1/4 inch screen and consisting chiefly of uranates and uranium oxides with a uranium assay of 55-75%. This ore concentrate is transported in portable hoppers by fork trucks from a storage pad. The hoppers are lifted into position on a scale by a monorail hoist. When the hopper is in position, a portable vibrator is mounted on the hopper cone to facilitate removal of ore to a rotary feeder. The ore feed rate is controlled by varying the speed of the rotary feeder. The ore is conveyed to either of two batch digestion tanks by a screw conveyor.

Nitric acid (50-60%) is fed by gravity to a digestion tank from an acid measuring tank prior to ore addition. A coil is provided in each tank with steam and water connections for maintaining the tanks at proper temperature (150-220°F). Intense agitation is required to keep the larger ore particles suspended during digestion because of the high density (up to 7.5 g/cc). A fume scrubbing unit, consisting of spray jet, separator, jet pumps, and recirculating cooler is provided for cooling the fumes evolved during digestion, condensing water vapor, and scrubbing approximately half of the nitrogen oxides from the fumes before the fumes go to the nitric acid plant for absorption. The condensate from the spray jet is returned to the digester. Excellent fume and dust control is essential not only for uranium retention and nitric acid economy, but to protect operating personnel from the hazard of inhaling uranium-bearing dusts and/or nitrogen oxides.

In addition to the feed-digestion system described above, which is one of two duplicate lines, a separate tank equipped with drum washing and handling facilities and a sieve plate is available for digestion of refinery sludges, and mud from sumps and traps, or those ore concentrates which are too wet or non-homogeneous for processing in the sampling plant.

The liquor from the digesters is pumped to one of four adjustment tanks for blending with recycle uranyl nitrate liquor from the ether extraction cycle and concentrated sump liquor. Adjustment of the solution composition is accomplished by addition of nitric acid, water, prepared solutions of iron or aluminum nitrates, or boiling down. Each tank is equipped with an agitator and coils for steam and cooling water. After proper adjustment, the liquor is pumped to one of two break tanks.

The slurry from the feed adjustment break tanks is pumped batchwise to one of two aqueous feed tanks located in the solvent area. These tanks also receive a continuous recycle stream of TBP wash raffinate from the wash column. Agitators are provided in these tanks to obtain a uniform feed stream to extraction and to prevent solids from settling. A seal loop is provided in the line from feed adjustment to the aqueous feed tanks to insure against solvent vapor backing up through this line into a non-solvent area.

2. Pumper-Decanter Extraction Step

In the extraction operation, aqueous feed and solvent are contacted countercurrently in five pumper-decanter units. A feed mixture from one of the aqueous feed tanks is pumped continuously to decanter No. 1, and solvent (26-30% TBP in hexane) is pumped continuously to decanter No. 5. The flow rate of the solvent is controlled at a constant value determined by the desired production rate of the system. The flow rate of the aqueous stream is controlled by a flow ratio recording controller reset by a specific gravity recording controller. The specific gravity is measured in the organic overflow stream from either decanter No. 2 or decanter No. 3.

The aqueous feed enters the suction side of a centrifugal pump where it is dispersed in a recycling solvent stream from decanter No. 1. The mixed phases are pumped into decanter No. 1 where the heavier aqueous phase settles out. Solvent overhead from decanter No. 2 enters the bottom of decanter No. 1 and a portion of it rises up through the decanter countercurrent to the falling aqueous droplets. This solvent overflows from decanter No. 1 to the TBP extract pump tank which feeds the wash column. The remainder of the solvent flows out the bottom of decanter No. 1, along with the dispersed aqueous phase, and is mixed in another centrifugal pump with recycling solvent from decanter No. 2.

In a similar manner the dispersed aqueous phase proceeds through the decanter system until it coalesces as raffinate at the bottom of decanter No. 5 below the level at which solvent feed from solvent adjustment is introduced. The raffinate layer discharges by gravity through a control valve actuated by a raffinate-solvent interface level controller in decanter No. 5 to the raffinate pump tank. All decanters are operated as closed vessels so that the net flow of solvent through the system results from the pressure developed by the solvent feed pump.

3. Pulse Column Washing and Re-extraction

Three pulse columns are used in the washing and re-extraction operations - one for washing and two in series for re-extraction. All three columns contain horizontal stainless steel plates spaced at two inch intervals. Column contents are pulsed by reciprocating pistons to give a sine-type displacement curve having an amplitude of 1/2 - 1 inch and a frequency of 30-60 cycles per minute.

In all three cases the solvent phase is pumped from a tank into the bottom of the column and dispersed to rise countercurrent to the aqueous flow. The solvent coalesces at the top of each column and overflows to a tank feeding the next column. Aqueous discharge from each column is by gravity through a control valve actuated by a solvent-aqueous interface level controller near the top of the column.

Deionized water is used for washing. The rate of water input is regulated by a flow ratio controller to give the desired ratio of wash water to extract. The water used for re-extraction is a combination of deionized water and condensate from the condenser and first effect of the triple effect evaporator used for concentrating the uranyl nitrate product from the TBP extraction. The flow rate of the mixed water to re-extraction is controlled by the specific gravity of the aqueous stream leaving the second re-extraction column and going to the first. Both water and extract feeds to re-extraction are preheated to permit column operation at elevated temperatures (120-140°F).

4. Solvent Treatment and Adjustment

The stripped solvent overflowing from the last re-extraction column is treated with 5% sodium carbonate in the solvent treatment column. This column contains no plates or packing and operates with the stripped solvent being dispersed at the bottom through vertical 1/2" pipes. The solvent rises through the column and coalesces at the top before overflowing to a hold tank. From the hold tank the solvent is pumped to one of two batch solvent adjustment tanks, equipped with agitators, where TBP or hexane is introduced as required for makeup or to correct the TBP-hexane ratio. These adjustment tanks serve as feed tanks for the solvent going to the pumper-decanter extraction system.

Sodium carbonate is pumped to and drained from the solvent treatment column in a batchwise manner. Spent carbonate batches are collected in a tank equipped with a steam coil and agitator. The carbonate is heated to remove hexane, and then 50% sodium hydroxide is added to precipitate any uranium present. When precipitation is complete, as indicated by sample analysis, the slurry is filtered and the cake recovered for reprocessing.

5. Removal of Organic Material from Aqueous Product Streams

Organic material in aqueous product streams consists of TBP and hexane, and its removal is accomplished in two steps: (1) scrubbing with hexane to remove TBP, and (2) heating to volatilize and remove the hexane. Three columns are used for treating separately the raffinate from the pumper-decanters, the aqueous product from re-extraction, and TBP area sump liquors. Each column is operated in a continuous manner with a continuous aqueous phase and with hexane dispersed through vertical 1/2" pipes at the bottom. No plates or packings are used in the columns. The hexane rises through each column countercurrent to the aqueous phase and coalesces at the top of each column. Hexane is drawn off near the top and pumped again into the bottom of each column as a recycle stream along with fresh hexane. Hexane contaminated with small amounts of TBP overflows from the top of each column to a hexane recovery still. The aqueous phases discharge through control valves regulated by aqueous-

155

solvent interface controllers located in the upper part of each column. Fresh hexane is introduced to the columns only when the TBP content of the recirculating hexane gets too high.

The uranyl nitrate product stream from the TBP removal column flows through a seal loop, designed to prevent hexane flow in case of interface control failure in the column, to pumps which put it through a heater and into a flash vaporizer for hexane removal. The steam rate to the heater is controlled by the aqueous stream discharge temperature. The flashed liquor flows out of the vaporizer by gravity through a seal loop, which maintains a level in the vaporizer, to a break tank. The vaporizer is equipped with steam coils below the liquor level. Low temperature and/or high pressure in the vaporizer stops the vaporizer discharge, admits steam to the vaporizer coil, and by an interlock system shuts down that part of the extraction system which feeds the vaporizer. Similar shut down occurs when a hexane analyzer in the break tank indicates an unsatisfactorily high hexane level.

Raffinate from the raffinate TBP removal column is continuously pumped to the raffinate stripping tank. This tank is provided with steam coil and agitator, for continuously boiling off hexane. The stripped raffinate is withdrawn from the stripping tank and passes through a low temperature cut-off and break tank system similar to that employed with the uranyl nitrate liquor. The sump liquor is handled after TBP removal by a system similar to that used on raffinate.

6. Recovery of Solvents

All tanks normally containing hexane are vented to a house condenser operated on tempered water (65°F) for recovery of hexane. The mixture of hexane and water from the condenser is drained to a work tank for decantation to separate the two phases.

Hexane from the TBP removal columns overflows continuously to the hexane recovery still, where it is continuously boiled to concentrate the TBP to a useable level. The still is provided with steam coils and agitator. Steam is introduced at a constant rate unless cut off to prevent coil exposure. Vapors from the still go to a hexane condenser. When the desired TBP concentration is reached, the TBP-hexane mixture in the still is pumped to the tank feeding the solvent treatment column.

7. Other Facilities and Requirements

The TBP extraction process is housed in an area separated from other areas by a fire wall and equipped with a deluge system. All equipment in the area is explosion proof. Every effort is made to prevent sparking in the area or transfer of organic material out of the area.

Stainless steel (#347 or equivalent) is used throughout for handling acidic nitrate solutions. Due to the reduction of stainless steel corrosion resistance by halide ions, feeds containing large amounts of halide must be avoided or worked off by employing aluminum or iron nitrates in the feed solutions. The complexing action of iron and aluminum counteracts the halide effect.

All areas must be provided with sumps to avoid loss of uranium. A separate sump collection system is provided for the TBP area. Sump liquors, after TBP removal, are concentrated by boiling in tanks. Each tank contains steam coils which are fed with steam at a constant rate. Completeness of concentration is determined by the temperature of the boiling liquor.

Steam condensate and cooling water are directed to a flash tank and are sampled by a continuous sampler (for accountability) before being discharged from the plant.

All tanks and decanters in the TBP area are equipped with emergency vents consisting of a rupture disc, pressure indicator, and a relief valve.

Because a portion of the ore concentrate is usually insoluble in nitric acid, many of the process streams contain appreciable quantities of solids which vary greatly in character and amount from day to day. Sanding and plugging of lines is minimized by proper piping design, including the establishment of minimum velocity requirements, but provisions must be made for frequent flushing of lines.

V. OPERATION

The digestion and adjustment areas will normally operate to supply an aqueous feed to the TBP area containing approximately 210 g/l uranium and 210 g/l excess nitric acid. This feed, when combined with the TBP wash raffinate from the wash column, should yield a feed mixture for extraction having about 200 g/l uranium and 3 M excess nitric acid. These composition specifications have been chosen largely to reduce the chances of scaling in the pumper-decanter extraction step. About 20% of the uranium is expected to come from the recycle liquor from the ether extraction system; the balance should come from the digesters.

The aqueous flow to the pumper-decanters will be regulated to hold the uranium level in the solvent overhead from the #3 decanter at about 30 g U/l. Under these conditions adequate saturation of the extract and recovery of uranium from the raffinate should be achieved. The total solvent recycle rate on each decanter will be held at about ten times the aqueous rate, with half of the solvent recycle going through the bottom of the next decanter. This recycle ratio is sufficient to avoid emulsification and provide satisfactory stage efficiency without excessive pumping costs.

The wash step will be carried out with a water:extract ratio of 1:10. At lower water rates insufficient washing is accomplished; higher rates yield little washing improvement and result in excessive uranium recycle.

The re-extraction step will be operated at a temperature of about 130°F. The water rate will be controlled so that about 30% of the re-extraction will occur in the second column. Under these conditions adequate stripping of uranium should be accomplished with a water rate about 10% greater than the theoretical minimum.

The following table shows approximate flow rates and compositions of various streams in the extraction area:

Basis: 1 gph Aqueous Feed to Decanters

Stream	Type	Rate, gph.	U, g/l	HNO_3, g/l	Density, g/cc
Aqueous Feed	Aqu.	1.0	200	189	1.4
Raffinate	Aqu.	1.0	0.05	173	1.2
TBP Feed	Org.	2.0	0.01	0	0.75
TBP Extract	Org.	2.0	100	8	0.9
Wash Raffinate	Aqu.	0.2	160	80	1.2
Washed Extract	Org.	2.0	84	0	0.9
Product UN Liquor	Aqu.	1.5	112	0	1.15

Basis: 1 gph Aqueous Feed to Decanters

Stream	Type	Rate, gph	U, g/l	HNO_3, g/l	Density, g/cc
Stripped Solvent	Org.	2.0	0.03	0	0.75
Dumped Carbonate*	Aqu.	0.006	10	0	1.1

The TBP removal columns will be operated with a limit of 5% TBP on the recirculating hexane. Under these conditions the TBP content of hexane-treated streams should be less than 0.2 g/l. The maximum TBP load on the removal system is expected to be 5 ml/l TBP in raffinate and sump liquors, and 1 ml/l TBP in the uranyl nitrate liquor.

The hexane content of the aqueous streams going to the vaporization facilities is expected to be less than 1%. Minimum temperature for vaporization will be set at 175°F, which is about 20°F above the boiling point of hexane.

VI. AUXILIARIES

Auxiliaries required for the TBP-hexane plant are similar to those for an ether plant, although, of course, storage must be provided for two different solvents. There is some difference in the manner in which the aqueous streams leaving the TBP area are treated.

The uranyl nitrate product, at 112 g U/l, is somewhat more dilute than the product from an ether cycle. As a consequence, steam requirements for concentration are higher than in the ether system.

The raffinate contains approximately 1.5 lb/gal of excess nitric acid. This acid may be largely recovered by boiling the raffinate, and it is economically advisable to do so. The ether system raffinate contains very little recoverable acid.

The following table shows estimated process requirements in the digestion, adjustment, and TBP areas per pound of uranium in the ores handled. These figures do not include requirements for concentrating the product uranyl nitrate liquor.

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*Batch operation

Material	Amount per lb. U.
60% Nitric Acid	1.2 lb.
125 psig Steam	10. lb.
Hexane	0.03 lb.
TBP	0.01 lb.
Sodium Carbonate	0.01 lb.
50% Sodium Hydroxide	0.01 lb.
Deionized Water	1.0 gal.
Cooling Water	120. gal.

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CONVERSION OF URANIUM TRIOXIDE TO URANIUM TETRAFLUORIDE IN VIBRATING TRAY REACTORS

by

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ABSTRACT

Vibrating trays are employed to convert uranium trioxide to uranium tetrafluoride in a two-step reduction-hydrofluorination process. The design of the reactors is similar to that employed for commercially available, mechanically oscillated conveyors, but the units are strengthened to meet the stringent process requirements of high vibrational frequency and high temperature. The trays are operated at resonant frequency to minimize stresses in the supporting framework and drive assembly. Vibration isolation from connecting piping and other equipment is accomplished by means of flexible bellows assemblies.

The uranium trioxide is first reduced to uranium dioxide with a large excess of hydrogen gas (ca. 1000%). A gas recycle system is employed and both concurrent and countercurrent flow of reactants produce good results (i.e., 98% conversion). The reactor tray wall temperatures are held at 1200°F. and the oxide is kept in the reaction zone for about one hour. The reaction is rapid and exothermic and temperatures substantially higher than 1200°F. are reached in the powder bed. A reactor, which is 15 feet long and 2 feet wide, will handle at least 500 pounds per hour of uranium trioxide.

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Conversion of the uranium dioxide to uranium tetrafluoride is accomplished in two 40 feet long by 2 feet wide vibrating trays connected in series; preheated hydrogen fluoride gas is fed counter-current to the flow of powder. With a material equivalent to standard oxide in productivity, a single line of equipment can produce 95% uranium tetrafluoride at a rate of 300 pounds per hour and 90 to 92% uranium tetrafluoride at a rate of 400 pounds per hour. Reactor wall temperatures are graded from 650°F. at the powder feed end to 1050°F. at the product take-off to obtain maximum conversion. A powder retention time of about four hours is employed and the hydrogen fluoride excess is held at about 100%. The reactor exit gases are condensed and the 70% acid which is recovered is sold.

INTRODUCTION

The uranium tetrafluoride, used in the manufacture of the uranium hexafluoride feed for the gaseous diffusion plants, was originally prepared batchwise in stationary pan reactors. The low production capacity of these units and the lengthy cycle required for complete conversion of the powder to uranium tetrafluoride resulted in a high operating cost, however, and the manual handling of uranium powders in open pans presented a serious contamination problem. For these reasons, a program for the development of a continuous process for the preparation of uranium hexafluoride from uranium trioxide was authorized and work was started at the Oak Ridge Gaseous Diffusion Plant in early 1948.

At this time, joint investigations of two possible processing methods, employing either fluidized bed or vibrating tray reactors, were initiated. It was soon shown, however, that fluidization of the available uranium oxides was not feasible and the entire development effort was centered on the vibrating trays. This process was then proven on a pilot plant scale and production facilities were installed at the Oak Ridge and Paducah plants.

A description of these facilities and a discussion of the operating experience follows.

PROCESS DESCRIPTION

The preparation of uranium tetrafluoride from uranium trioxide in the vibrating trays is accomplished in two separate steps according to the following chemical reactions:

1. $UO_3 (S) + H_2 (g) \rightarrow UO_2 (S) + H_2O (g)$ + 40,000 Btu./lb. mol

2. $UO_2\ (S) + 4HF\ (g) \rightarrow UF_4\ (S) + 2H_2O\ (g) + 80{,}000\ \text{Btu./lb. mol}$

A simplified flow diagram of the process is shown as figure 1.

In operation, the raw uranium trioxide is fed from a hopper and screw conveyor into the reduction tray and is contacted with about 1000% excess of preheated hydrogen, which can be introduced either concurrent or countercurrent to the flow of solids. The wall temperature of the reactor is held at 1200°F. and the powder velocity is adjusted to give a residence time of 1/2 to 1-1/2 hours, dependent on the type of oxide being processed. The powder is conveyed through the tray at the desired rate by regulating the frequency and time of oscillation; normally, a vibrating frequency of about 800 cpm. is applied for about 1/2 minute every 15 minutes.

The major portion of the hydrogen gas for the reduction process is supplied by the available fluorine generators, and the remainder is produced in standard electrolytic hydrogen generators*. For gas economy, the hydrogen leaving the tray reactor area is cooled to remove the water produced by the reduction reaction and then recycled to the tray with a positive displacement blower. Both the pressure and the hydrogen concentration in the system are automatically controlled.

The uranium dioxide product is discharged from the reduction tray into a hopper in which the powder serves as a gas seal between the reduction and hydrofluorination systems. The oxide is then screw fed into the hydrofluorination tray reactors and is moved through the two vibrating trays arranged in series. Here, it is contacted with preheated anhydrous hydrogen fluoride which is fed countercurrent to the flow of solids. A hydrogen fluoride excess of 105% is maintained so that a saleable mixture of 70% hydrogen fluoride and 30% water is condensed from the outlet gases.

The wall temperatures are graded from 650 to 900°F. on the first tray and from 850 to 1050°F. on the second tray. This temperature profile is necessary not only to prevent caking of the powder, but to attain the maximum conversion of the uranium dioxide to uranium tetrafluoride. Powder residence times of 1-1/2 to 2 hours are employed on each tray and, as in the reduction system, intermittent vibration is applied to the reactors.

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*A large quantity of fluorine is required for the conversion of uranium tetrafluoride to uranium hexafluoride in the feed plants. Actually, the amount of hydrogen produced in the fluorine generators is sufficient to reduce all of the uranium trioxide but a supplementary supply is required since some gas must be vented to maintain the desired hydrogen concentration in the recycle system.

The uranium tetrafluoride product is discharged into a hopper from which it is either conveyed to the fluorination system or loaded into drums.

PLANT DESCRIPTION

The uranium tetrafluoride production plant is composed of the following areas: central control room, reduction, hydrofluorination, powder handling, hydrogen production and storage, hydrogen fluoride storage, hydrogen fluoride vaporization, and miscellaneous maintenance, office and locker rooms. Physically, the plant layout is such that the reduction and hydrofluorination areas are adjacent to the control room. The powder handling area is located near the tray reactor area and includes equipment for handling both the feed oxide and the uranium tetrafluoride product as well as dust collection systems which serve both areas. The hydrogen production cells are installed in a separate room and the gas holder is placed outdoors. The hydrogen fluoride storage area consists of a tank farm located away from the building for safety reasons and the hydrogen fluoride vaporizers are in a small room adjacent to the reactor area. A description of the individual facilities follows.

Control Room

Sufficient instrumentation is provided in the central control room to allow monitoring and adjustment of critical process variables in the reduction and hydrofluorination steps from that point.

Reduction

Each reduction line consists of a uranium trioxide storage hopper and feed screw, a heated vibrating tray reactor, a uranium dioxide product hopper and conveyor, and a recirculating gas system which includes a recycle pump*, an inlet gas preheater, and outlet gas filter, and an outlet gas cooler. With the exception of the reactor, standard equipment is used.

The uranium trioxide hopper is sized to hold about a 6-hour supply of powder and is equipped with an electromagnetic vibrator to assure continuous feeding. The powder is fed from the hopper to the tray by a variable speed screw conveyor.

The reactor is similar in design to commercially available, mechanically oscillated conveyors, but the unit has been strengthened to meet the stringent process requirements of high vibrational

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*The recycle pump is common to all lines.

frequency and high temperature. The design of the reactor is shown in figure 3 and a photograph of one of the production units is presented as figure 4.

The 15 feet long by 2 feet wide tray reactor trough is fabricated from 1/2-inch thick Inconel or 347 stainless steel and is slightly domed to add strength. The tray is mounted on horizontal 4-inch schedule 40 Inconel or 347 stainless steel pipe support arms which extend through slots in the furnace enclosure and are welded to a pipe frame on both sides of the tray reactor. Each pipe frame is fastened to rocker arms which are connected to a heavy concrete inertia block. This block is separated from the floor with springs to prevent the transmission of vibration to the building. The rocker arms are connected to torsion bars which act as springs and remove most of the load from the drive unit. The tray reactor assembly is designed to operate at the resonant frequency to minimize stresses in the supporting framework and drive mechanism.

Motion is imparted to the reactor by an eccentric shaft which is rotated by a variable speed drive and is connected to the tray framework. The angle at which the tray is moved is controlled by the angle of the rocker arms which are usually adjusted at either 50 or 60° to the horizontal. A drive stroke of 1/8-inch is employed for the tray reduction reactor.

Gas and powder connections to the reactor are made through flexible bellows assemblies. The connector shown in figure 5 has proven satisfactory for the conditions met in the feed plants.

The trays are heated with conventional electric resistance wire furnaces which are isolated from the vibration as much as possible. It was found, however, that a small amount of vibration was transmitted to the furnaces and it was necessary to use a heavy element wire, about 1/4-inch in diameter. The furnaces are divided into three control zones along the length of the tray reactor and the top and bottom heaters in each zone are controlled separately.

Hydrogen is recycled through the system with a Nash Hytor-type K pump. The inlet hydrogen is passed through a trombone pipe coil, which is heated by an electric furnace, and the outlet gases are cooled in a water-jacketed pipe heat exchanger. The water produced in the reduction reaction is exhausted with the water furnished to the pump. Entrained solids are removed from the gases by a porous carbon tube filter installed directly above the tray gas outlet.

A continuous gas analyzer is used to control the concentration of hydrogen in the recycle stream. When the hydrogen content falls below the desired value, gas is automatically vented from the system. Pure hydrogen is admitted through a control valve which is actuated by the system pressure.

Hydrofluorination

The hydrofluorination line contains two vibrating trays arranged in series. The tray reactors are similar in design to the reduction trays, but are 40 feet in length by 2 feet wide and employ a drive stroke of 1/4 inch. The original hydrofluorination tray reactors used at Oak Ridge were unsatisfactory from the standpoint of mechanical strength and will not be described. Design changes which were made before the reduction trays and the Paducah hydrofluorination trays were installed adequately reinforced the oscillating assemblies.

The hydrogen fluoride gas, fed to the tray from the vaporizers, is passed through an electrically heated superheater and preheater. The hydrogen fluoride-water mixture in the reactor off-gases is removed by a water-jacketed heat exchanger. Any solids entrained in the outlet gases are removed by a porous carbon tube filter. The small amount of hydrogen fluoride in the gas leaving the condenser is stripped by a water scrubber.

Powder Handling

Mechanical transport of powder is used wherever possible, both for economy and to minimize contamination problems. The incoming oxide is received in 5-ton containers which are hoisted by a crane and attached to the top of the reduction reactor feed hoppers as required. Provision is also made for the transferring of material from 30-gallon drums into the large containers. This is accomplished mechanically in a closed housing by inverting the drum using a skip hoist. The drum is then automatically washed and dried in a closed system while the next drum is being dumped.

The uranium tetrafluoride product is collected from the tray reactor line product hoppers and moved by continuous flow conveyors into a large product storage hopper. The powder is then either loaded into product drums or fed to the fluorination system feed hoppers by continuous flow conveyors if uranium hexafluoride is being made at the same plant.

Powder spilled in the reactor and powder handling areas is removed by vacuum cleaning. There are several collection systems, each of which includes a cyclone, blow ring bag filter, paper-asbestos polishing filter, and centrifugal exhauster. The collected powder usually contains enough dirt and impurities to make chemical purification necessary.

Hydrogen Production and Storage

Most of the hydrogen for the reduction process is furnished by the fluorine generators. A 15-cell electrolytic hydrogen facility is

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provided, however, to supplement this gas supply and to allow operation if the fluorine cells are off-stream. The hydrogen cells are connected in series and require about 40 volts. The production rate at the maximum current of 7,500 amperes is approximately 4.6 pound mols per hour. A 200 cu. ft. moving piston, dry seal gas holder is installed in the hydrogen supply line to provide storage capacity.

Hydrogen Fluoride Storage Area

Anhydrous hydrogen fluoride is received in railroad tank cars containing about 75,000 pounds (10,000 gallons) of material. The liquid is stored in 12,500-gallon steel tanks and is transferred to the vaporizer area according to demand. Dry air is used to pressure the acid from the tank cars and from the storage tanks to the plant.

Aqueous acid is drained from the plant area into tanks similar to those used for anhydrous acid storage and then transferred with air into tank cars.

Hydrogen Fluoride Vaporization

Anhydrous hydrogen fluoride is transferred from the tank farm into a 750-gallon steel tank which furnishes liquid to the vaporizers. The flow of hydrogen fluoride is controlled by the liquid level in the vaporizer and heat is furnished by a steam flow which is regulated by the hydrogen fluoride gas pressure.

OPERATING EXPERIENCE

Reduction System

The performance of the reduction systems in both feed plants has been excellent. Greater than 97% conversion of the uranium trioxide to uranium dioxide has been attained consistently with powder feed rates of at least 500 pounds per hour per line and few operating difficulties have been encountered. Leaks, plugged lines, and failures of the flexible connectors and powder conveyors have been the causes of the small amount of downtime.

Studies of the trays have shown that essentially no reaction occurs until the temperature of the powder is increased to about 1000°F. After this temperature has been reached, however, the reduction reaction progresses rapidly, and a sharp rise in the temperature of the powder bed is noted. As can be seen in figure 6, the temperature of the powder during the reduction step is directly proportional to the bed depth and is not affected significantly by tray reactor wall temperature changes of 100°F. Temperatures as high as 1700°F. were reached in the deepest bed tested, while increases to only 1200 to 1400°F. were experienced in the shallow beds. These tests were made with the same feed rate and the different bed depths were attained by varying the powder residence time. In all cases, at least 97% conversion to uranium dioxide was realized until the powder residence time was decreased to less than 0.4 hour (bed depth of 0.4 inch under the test conditions).

It has been estimated that temperatures of about 2000°F. are reached in the deep beds of the reduction screw reactors with feed rates of about 300 pounds per hour of uranium trioxide. Under these conditions, it appears that little or no sulfate activation of the uranium trioxide can be tolerated, and it is possible that screw flight failures due to the high temperatures alone will occur with higher oxide feed rates. With the trays, however, shallow beds of powder can be processed and the temperatures should be no greater than 1400°F.

Hydrofluorination System

The operation of the 40-foot long hydrofluorination trays installed at the Oak Ridge facility was unsatisfactory in that mechanical failures of the eccentric drives and the framework of the trays occurred frequently. The design of the oscillating assembly was modified, however, for the 15-foot long reduction trays and the Paducah hydrofluorination trays, and few difficulties have been encountered with these units. The hydrofluorination trays at the Oak Ridge plant have been replaced with screw reactors.

The conversion of uranium dioxide to uranium tetrafluoride is normally somewhat lower in the tray reactors than in the screw reactors. With a material equivalent to standard uranium trioxide in reactivity, a single line of tray equipment can convert 95% of the uranium dioxide to uranium tetrafluoride at a rate of 300 pounds of uranium dioxide per hour. If the feed rate is increased to 400 pounds per hour, the percentage conversion drops to 90 to 92%.

It appears from the above data that the percentage conversion to uranium tetrafluoride on a vibrating tray is significantly decreased when the depth of the powder bed is increased. When the powder on a tray is examined, the material at the bottom of the bed is much darker than at the top, and little agitation or mixing of the powder is noted when the tray is vibrated. Operation with various oxides in both the production facilities and the pilot plant has shown this bed depth effect in varying degrees. Essentially no change in conversion was noted with feed rates of 200 to 450 pounds per hour of standard uranium trioxide, while a decrease of about 20% occurred when the feed rate of another pot-calcined oxide was increased from 200 to 300 pounds per hour.

The reactivity of the uranium trioxide feed also has a great effect on the conversion to the tetrafluoride. Under the optimum operating conditions, conversion values of 95, 90, and 83%, respectively, were obtained with sulfate activated pot-calcined oxide and two different untreated pot-calcined oxides at a feed rate of 300 pounds per hour of uranium trioxide. With oxide activated by the "wet slurry" process, 97% conversion was realized with a feed rate of 600 pounds per hour. This latter material was processed with a low residence time, about 1 hour, and the bed depth was relatively shallow. On the basis of these tests, it appears that the vibrating trays may be equal or superior to the screws if a very reactive feed material is used. With the unreactive oxides, however, better conversion will be obtained with the screw reactors.

In hydrofluorinating the various oxides on the trays, it has been found necessary to adjust the tray reactor temperatures to compensate for the rapid initial reaction rate. This is accomplished by grading the temperatures from about 650°F. at the feed point to 1050°F. at the product discharge. The optimum temperature gradation must be determined for each oxide, however, and is dependent to some degree on the reactivity of the material. For example, with a very reactive material, such as the slurry activated oxide, the starting temperature is lowered to 400°F. and the maximum temperature is about 800°F. If the temperature is too high at any point, the powder will either cake on the tray and eventually plug the reactor, or partial sintering and poor conversion to tetrafluoride will occur.

The hydrogen fluoride excess for the vibrating tray hydrofluorination process is lower than that employed with the screw reactors. The hydrogen fluoride flow is adjusted to give an outlet gas composition of 70% hydrogen fluoride and 30% water (105% excess) and the gas is completely condensed in a single water cooled condenser. No beneficial effects of higher gas excesses have been noted with untreated pot-calcined oxide.

Powder Movement

As an aid in determining the operating conditions for the feed plant trays, a study of the effect of the length of stroke and the vibrational frequency on the powder velocity was made. The results of tests with nominal strokes of 1/8 and 1/4-inch are presented in figure 7. As can be seen, the frequency with the 1/8-inch stroke must be about 150 cpm. greater than with the 1/4-inch stroke to obtain the same powder velocity. It should also be noted that the powder velocity is slightly lower when hydrogen fluoride is passed over the tray. In the plant facilities, the longer stroke is used in the hydrofluorination trays while the stroke of the reduction units is 1/8 inch.

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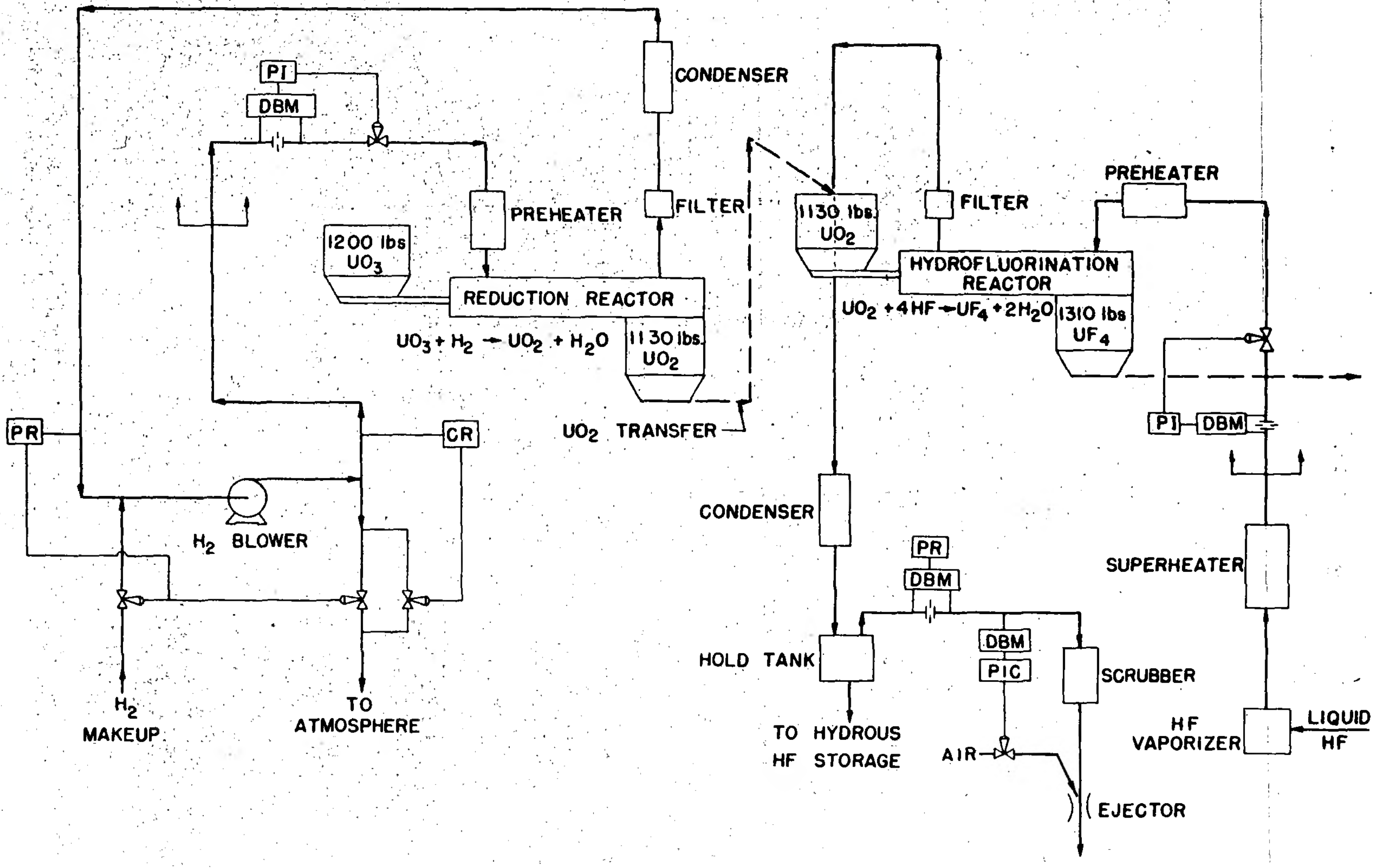
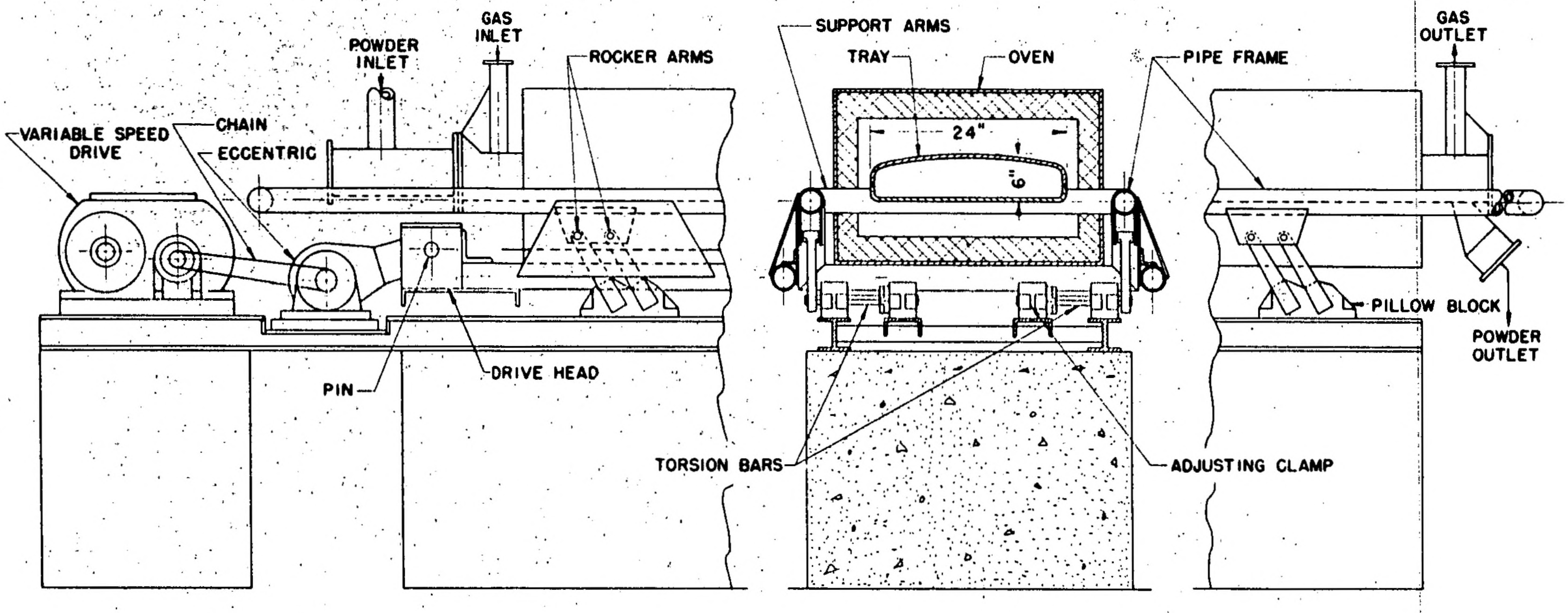


Figure 1
SCHEMATIC FLOW DIAGRAM UF_4 PRODUCTION



TYPICAL SECTION

Figure 3
15' REACTOR TRAY

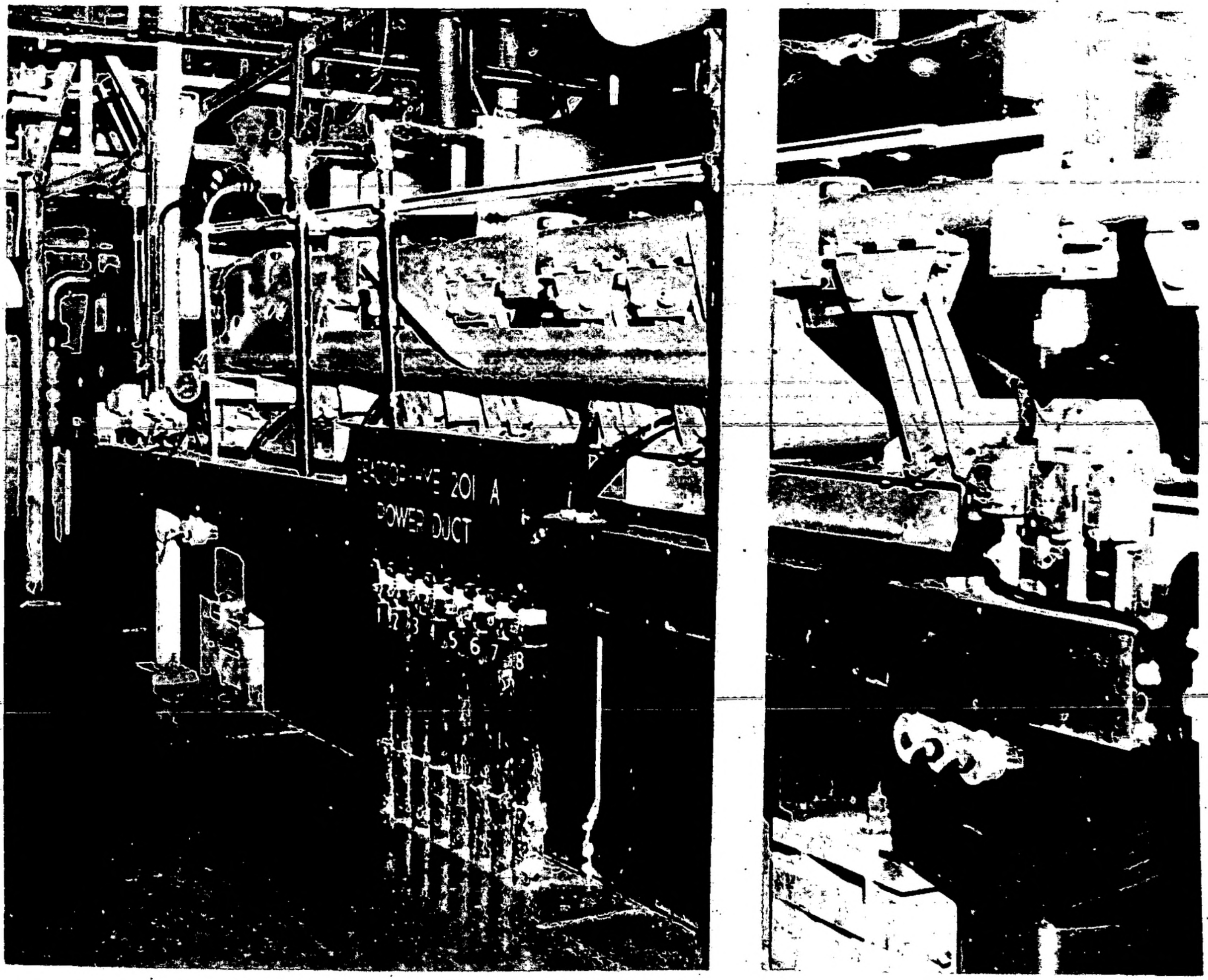


Figure 4
VIBRATING TRAY REACTOR - SIDE VIEW

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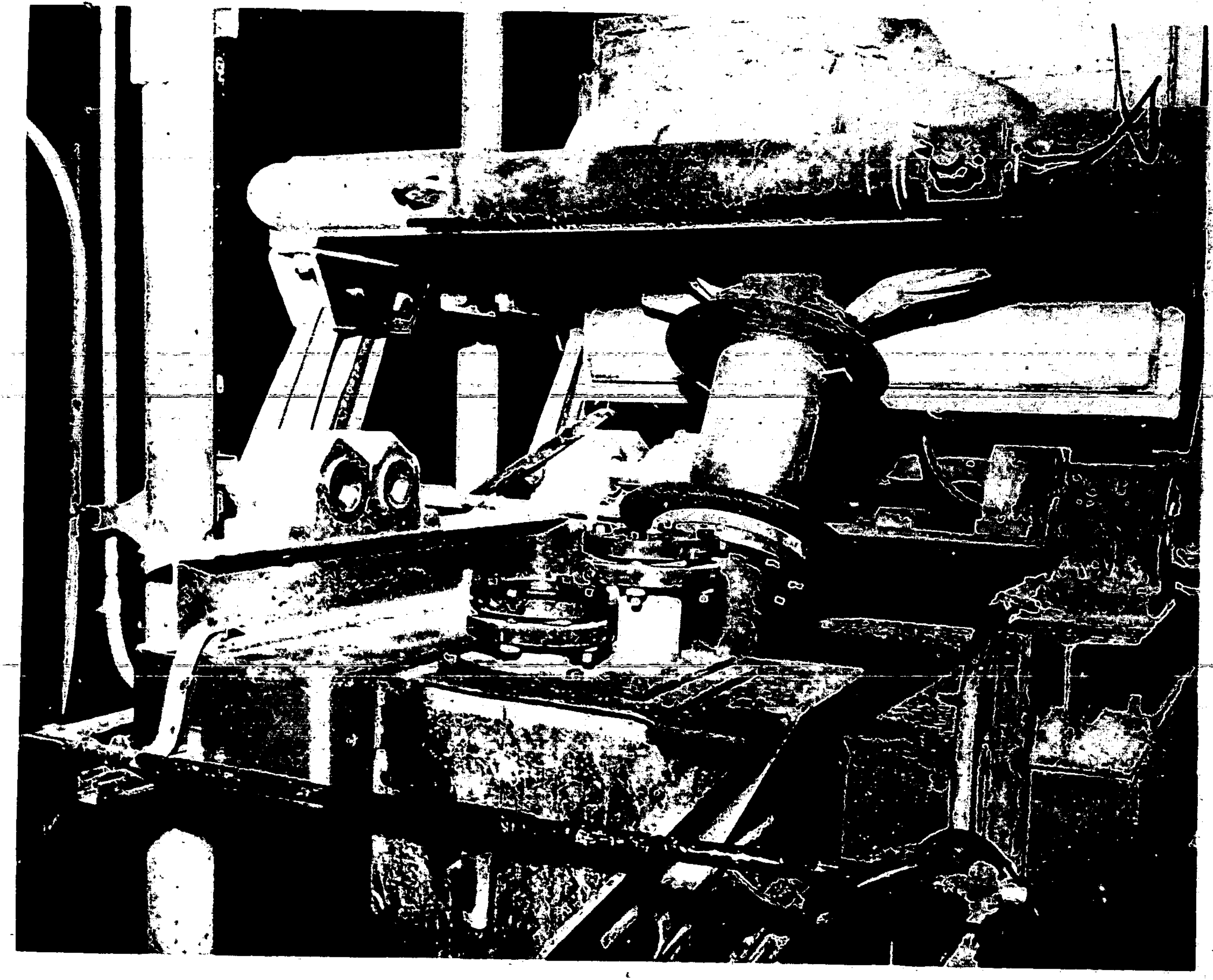

Figure 5
VIBRATING TRAY REACTOR - POWDER DISCHARGE

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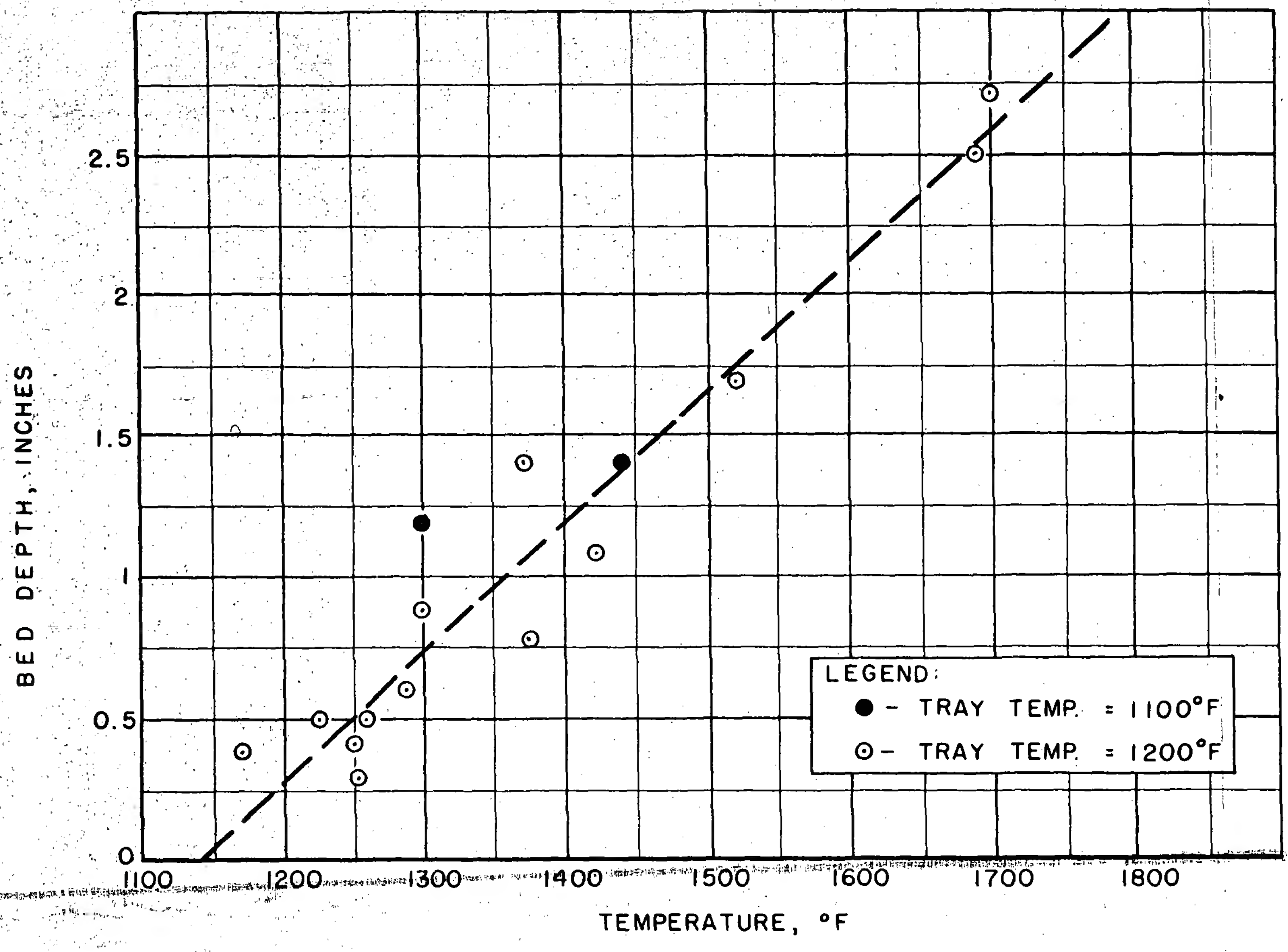

Figure 6
REDUCTION OF UO_3 ON A VIBRATING TRAY-EFFECT OF BED DEPTH ON POWDER TEMPERATURE

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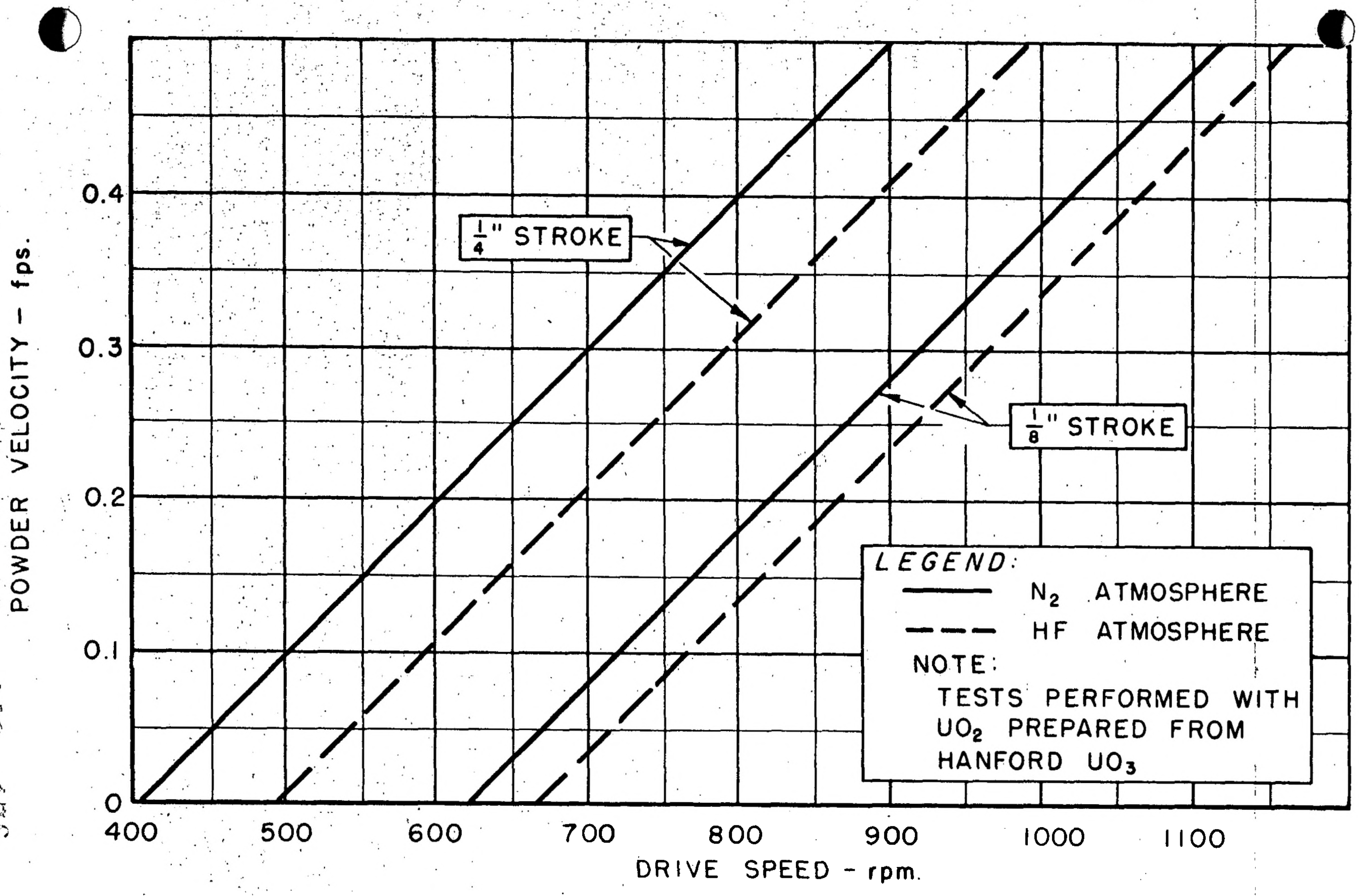

Figure 7
POWDER VELOCITY VS. TRAY FREQUENCY

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URANIUM TETRAFLUORIDE PLANT

Mallinckrodt Chemical Works
St. Louis, Missouri

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I. INTRODUCTION AND SUMMARY

Uranium tetrafluoride as produced at Mallinckrodt is a dense, bright green powder -- normally referred to as "Green Salt". There are three major parts to the green salt process. They are (1) the reduction of uranium trioxide to uranium dioxide by means of a high temperature reaction with hydrogen, (2) the conversion of uranium dioxide to uranium tetrafluoride by means of a high temperature reaction with hydrofluoric acid, and (3) the recovery of hydrofluoric acid partially as 70% acid, which is sold as such, and partially as anhydrous acid, which is recycled to the process.

It is the purpose of this paper to outline in as much detail as is practicable those points which would be most important in the construction and operation of a plant to carry out the functions mentioned above. In order to carry out this purpose, the following subjects are covered:

1. History and basic chemistry of the process starting with the early manufacture of uranium tetrafluoride in 1942 and including the latest thermodynamic and chemical information on the process reactions.

2. Material balance on the process including uranium losses, power and raw material consumption.

3. Equipment and engineering of plant describing in general the major pieces of process equipment.

4. Auxiliary equipment describing in general the major pieces of auxiliary equipment used in the green salt process.

5. Operation of the process as currently practiced at Mallinckrodt.

II. HISTORY AND BASIC CHEMISTRY

When it became necessary in 1942 to prepare large quantities of UO_2 and UF_4, most of the small scale laboratory methods of preparation, which were described in the literature, were tested and evaluated for production use. Mallinckrodt, duPont, Harshaw, and Linde were among the companies active in this work. It was found that H_2, H_2 plus water vapor, NH_3, cracked NH_3, and illuminating gas can be used to reduce UO_3 or U_3O_8 to UO_2. Aqueous HF can be used to precipitate hydrated UF_4 from solutions of tetravalent uranium. Either anhydrous HF or NH_4HF_2 can be used at high temperatures to convert UO_2 to UF_4.

The plant processes used from 1942 to 1949 were batch type processes. The quality of product was good and the processes were quite satisfactory from technical and cost aspects. UO_3 was reduced to UO_2 with H_2 or cracked NH_3 in stainless steel trays in electrically heated muffles at 1500°F for 6 to 8 hours. The product was cooled in H_2 or cracked NH_3, packaged, and transferred to the hydrofluorination process. UO_2 was converted to UF_4 with HF in monel trays in gas heated steel or monel muffles at 1070°F for 20 to 30 hours. Several muffles were connected in series to take advantage of countercurrent gas flow for reduction of HF consumption. The offgas was neutralized and discarded. The finished UF_4 was cooled in N_2, then in air, packaged and transferred to the next process. Magnesium is suitable for trays providing the temperature is kept low, 1000°F. Graphite is also suitable for trays and muffles.

In 1949, development was started at Mallinckrodt on continuous processes for the production of UO_2 and UF_4. These developments were successful. The quality of the product is equal to that of the batch process, and the operation is cheaper and safer.

Almost concurrently, Carbide and Carbon Chemical Company developed horizontal vibrating tray reactors for both the reduction and hydrofluorination steps. The solids are moved countercurrent to gas flow by vibrating the tray for 10 to 30 seconds every 10 to 15 minutes. Residence times and temperatures are about the same as for the screw reactors.

Since 1952, Catalytic Construction Company, New Brunswick Laboratory, and National Lead of Ohio have been developing a moving bed reactor. Pellets of UO_3 move by gravity down a vertical furnace tube countercurrent to a stream of H_2 and NH_3, or cracked NH_3 and steam. The reduced pellets are contacted with HF and steam in a lower section of the reactor, or in another reactor, to produce UF_4. The reactor has the advantages of high capacity, low cost and low HF consumption. Development work has been encouraging but the moving bed reactor is not yet an established process.

All of these continuous processes are based on chemistry studied at Mallinckrodt, Carbide, and Los Alamos between 1945 and 1949, and later re-examined more extensively at New Brunswick Laboratory.

For the reaction,

$$UO_{3(s)} + H_{2(g)} \longrightarrow UO_{2(s)} + H_2O_{(g)},$$

ΔF^o is -15 kcal/mol at 77°F and ΔH is -26 kcal/mol at the same temperature. The equilibrium is so strongly in favor of UO_2 and H_2O over the range of operating temperatures that the reaction is practically irreversible.

The rate of reaction varies with the type of UO_3, the particle size of the UO_3, the hydrogen content of the gas phase, the rate of supply of H_2 to the UO_3, and perhaps other variables not yet defined. With plant-prepared, pot type, UO_3, reaction becomes rapid at about 900°F, small samples reacting completely with a large excess of H_2 in about 40 minutes. For this type oxide the fraction unreacted, F, varies with time according to the equation

$$\frac{-dF}{dt} = kF.$$

These values of k can be represented by the equation

$$\log k = \frac{-35{,}000}{2.303\ RT} + 9.28,$$

where R is the gas constant and T is the absolute temperature, i.e., the activation energy is 35,000 calories.

The heat of reaction is sufficient to raise the temperature of small samples 50 to 100° F. The temperature of the reacting powder in screw reactors is not known but there is evidence which indicates that temperatures as high as 1700° F. may be attained.

For the reaction

$$UO_{2(s)} + 4HF_{(g)} \rightleftharpoons UF_{4(s)} + 2H_2O_{(g)},$$

the free energy change reverses sign over the operating temperature range so that the reaction is reversible. The data from the various laboratories are not in quantitative agreement on the values of the equilibrium constants. Thus for the equilibrium constant at 500° C., $K_p = (P_{H_2O})^2 (P_{HF})^4$, values have been reported which range from about 30 to 400. These constants correspond to a variation in the equilibrium HF content of the gas phase of from 37% to 20% by weight. Data from the various laboratories give roughly the same value of ΔH, -47,000 cal/mol, when plotted according to the equation

$$\log K_p = \frac{-\Delta H}{2.303\ RT} + C.$$

The rate of reaction varies with the temperature at which the UO_2 was prepared, with the HF content of the gas phase, and probably with such operating variables as bed depth, efficiency of mixing of gas and solid, and particle size.

For a given sample of UO_2, in a large excess of gas, the fraction unconverted can be represented by

$$\frac{-dF}{dt} = kP^nF^m$$

where F = the fraction of UO_2 unreacted at time t
P = partial pressure of HF
n = order of reaction with respect to gas (= O for a large gas excess).
m = order of reaction with respect to solid (= 1, approximately).

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These values of k can be represented by

$$\log k = E/2.303RT + C$$

E = apparent activation energy = 13,000 cal.
R = gas constant
T = absolute temperature
C = constant of integration = 1.74

As examples of laboratory experience small samples react almost completely in 5 hours at 900°F with large excesses of anhydrous HF. Under the same conditions reaction is complete in 2 hours at 1100°F.

In plant practice the reduction process is operated with a 1.5 times theory flow of cracked NH_3 and the excess is burned. Under these conditions the product is usually 97 to 98% UO_2. The remainder is at least partly present as interstitial oxygen in the UO_2 crystal lattice and is thought to be of some importance in its effect on the rate of reaction with HF during hydrofluorination. This oxygen appears as UO_2F_2 content of UF_4. This is reported as water soluble uranium on the analysis sheets.

The hydrofluorination is also incomplete so that small amounts of UO_2 remain in the finished product. The product must contain at least 97% UF_4, not more than 2% ammonium oxalate insoluble (AOI), chiefly UO_2.

It has been found necessary to carry out the reaction slowly in the initial stages to avoid caking. This caking can cause incomplete reaction, as well as mechanical difficulties in the operation of a stirred reactor.

Corrosion can be a severe problem in high temperature reactors, particularly with hydrofluoric acid. This is especially important from the contamination standpoint, even mild corrosion causing serious difficulty in producing specification material. Some stainless steels have been found suitable for the reduction reactor, while Inconel, Hastelloy C, Monel, and even silver are used for construction of equipment exposed to HF-H_2O mixtures at elevated temperatures.

III. MATERIAL BALANCES

The product contains 99.5% of the total uranium in the feed to the plant. Dust collector and other residues contain approximately 0.5% of the uranium. Apparent losses are less than 0.1%. The uranium unaccounted for is 0.58% for any one month or 0.09% for any year. The uranium in process is equal to that produced in 12 to 18 hours of operation.

Ammonia consumption for reduction is 0.054 lb NH_3/lb UF_4. Of 100 lb of HF entering the plant 45 lbs leave as UF_4, 53 lbs leave as 70% HF and 2 lbs are lost to the scrubbers.

A total of 1 KWH/lb UF_4 is required for the process. Water requirements are small 0.5 to 0.7 gal/lb UF_4. Steam consumption is approximately 3 to 8 lb steam/lb UF_4. Ammonia is cracked and burned to provide a source of inert gas for purging. The reagent consumption for scrubbers is 0.007 lb 45% KOH/lb UF_4 and 0.019 lb $Ca(OH)_2$/lb UF_4.

IV. EQUIPMENT AND ENGINEERING OF PLANT

1. General Layout

The green salt process is housed in a steel and concrete building approximately 120' x 160'. About one-half of the building is 55' high; one-third about 16' high; the remainder about 32' high. Storage space is included inside the building for a reasonable amount of uranium trioxide feed as well as uranium tetrafluoride product. Also inside the building are offices for all the foremen and technical staff connected with the plant and a small maintenance shop and mechanical storeroom; lavatories and smoking areas are also included. Storage tanks outside of the main building are provided for the storage of anhydrous hydrofluoric acid, 70% hydrofluoric acid, and anhydrous ammonia. A small building approximately 60' x 30' houses auxiliary equipment. Three tank car unloading spots are available adjacent to the building, a railroad car unloading dock takes up most of one side of the building and a truck unloading dock is adjacent to the inside storage area of the building. Figure 1 is a schematic flow diagram of the reduction and hydrofluorination process.

2. Reduction Equipment

Uranium trioxide enters the building in thirty gallon drums.

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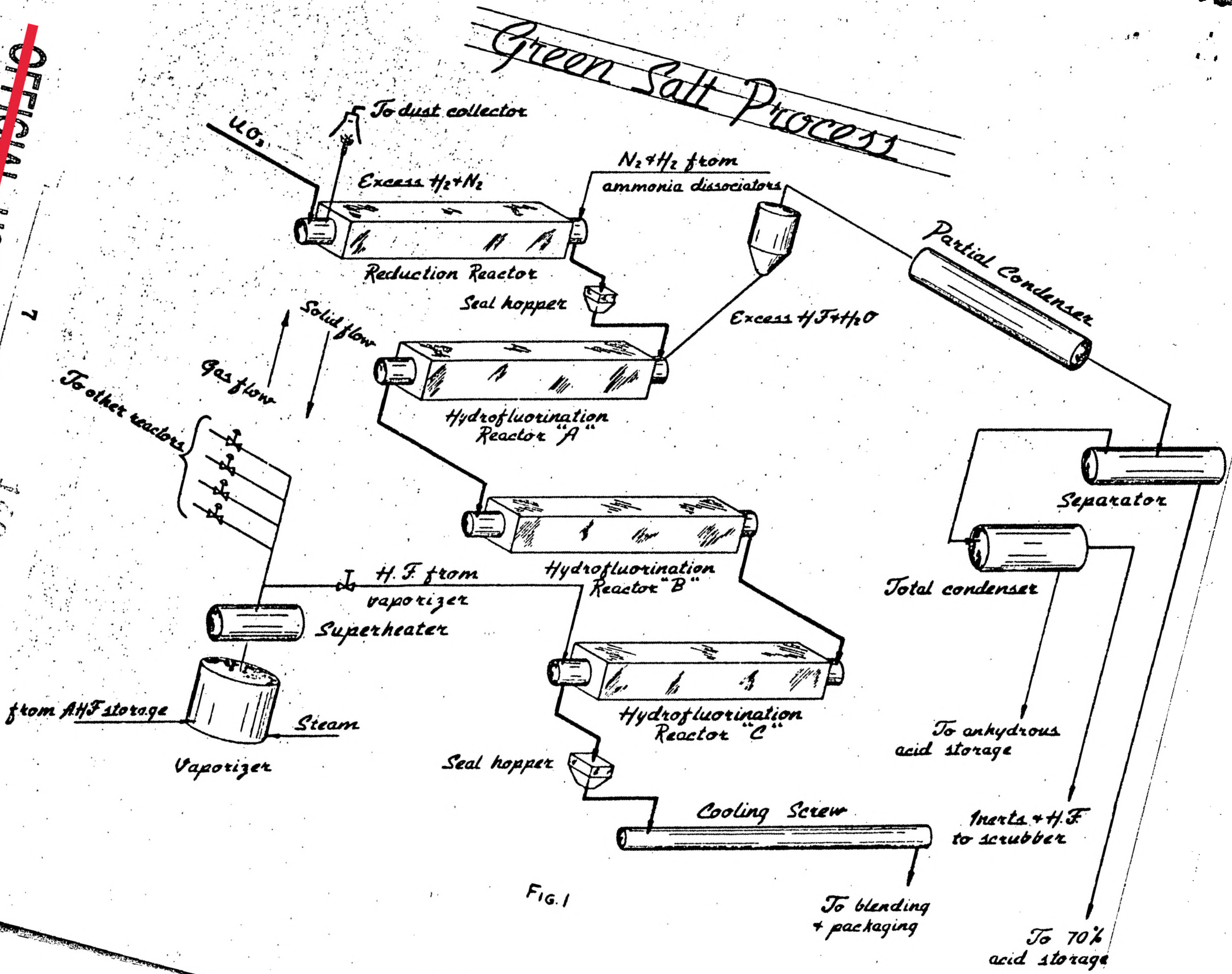

Fig. 1

These drums are first placed in a totally enclosed skip-hoist and upon signal from the operator the drums are hoisted to a level of about 16' above the floor, dumped, returned to a lower level, inverted, and then sent through a drum washer and dryer. This totally enclosed system also includes the washing and drying facilities for the drum lids which are removed by hand inside the skip-hoist before the drum is elevated to the 16' level. The uranium trioxide which is dumped falls through a grate into a large hopper which in turn feeds the material by means of a screw conveyor through a crusher into a 6" Hapman conveyor. This conveyor elevates the goods to the very top of the building and distributes it to the five individual reduction reactor feed storage hoppers. The Hapman conveyor mentioned here is a 'disc-in-tube' type conveyor. This Hapman, which is typical of all Hapmans in the plant, consists of a stainless steel tube surrounding a chain made up of circular discs linked together which are drawn slowly along through the tube. All the Hapman conveyors in the plant have discs made of magnesium. The five hoppers fed by this Hapman conveyor are individually mounted on scales and each one feeds by means of a screw feeder, an intermediate seal hopper and an additional screw feeder into its own reduction reactor. Each one of the weigh hoppers will contain approximately one day's feed to the reactor. The material fed out of these hoppers is controlled by the level in the small feed hopper below it. Paddle type level indicators in these small reactor feed hoppers signal the screw feeder in the weigh hopper above in such a manner that a level and a seal is maintained in the small reactor feed hopper. The reactor itself, which is fed by this feed hopper, consists of a 16" diameter horizontal tube approximately 22' long made of 1/4" 309 stainless steel. Inside this tube is a specially designed agitator-conveyor which rotates slowly at a constant speed. The agitator-conveyor is a lawn mower type rotor made of 309 stainless steel with a 6" pipe shaft supported in bearings on each end of the reactor tube. The outside diameter of the rotor is about 14". Since this reactor is operated with an internal temperature of something like 1200 to 1500°F, the agitator-conveyor must be designed in such a way that the sag caused by its own weight at these temperatures is not enough to allow the rotor to touch the tube. If there is any contact between the rotor and the tube, contaminated goods will result. The rotor is driven by means of a variable volume hydraulic system. A 15 H.P. electric motor drives two hydraulic piston pumps, each with variable displacement. The hydraulic fluid is piped from the pump on the first floor of the building up to a hydraulic motor driving a 164:1 gear reducer. This gear reducer in turn drives a 4" diameter shaft which enters the reactor tube through a Teflon packed gland and is then coupled to the rotor. The hydraulic motor and gear reducer are both mounted in a drive box which is attached to the end of the reactor tube. This equipment is designed so that the rotor may be adjusted to speeds varying from 2 to 20 rpm. The maximum hydraulic pressure which may be applied to this rotor is 2,000 psi. The reactor tube is encased in an electric resistance furnace about 18' long, overall. The heating elements are placed along the sides of the furnace in such a way that temperature may be controlled in four separate zones longitudinally along the reactor. These furnaces have a rating of 38 kilowatts.

A mixture of hydrogen and nitrogen gas is passed through the reactor countercurrent to the flow of uranium trioxide. The hydrogen-nitrogen mixture is manufactured from anhydrous ammonia in a standard ammonia dissociator operating at about 1600°F. There are five dissociators, each one rated at 2000 standard cfm of dissociated gas per hour. Anhydrous ammonia is stored outside the building in two 8' diameter, 44' long steel tanks. Liquid ammonia is drawn off directly to the dissociators. The flow of the hydrogen-nitrogen mixture is automatically regulated by a Fisher Porter rotameter type flow controller. The effluent gas from the reactor containing excess hydrogen, nitrogen, and the water formed in the reaction is burned immediately above the outlet from the reactor. The flame is maintained by an automatic sparking device. Over the top of the flame is a hood and dust collector connection so that the uranium-containing dust leaving the system at this point is picked up along with the burned gases and drawn through a reverse-jet, bag type dust collector. Enough air is also drawn in at this point so that the temperature of the gases entering the dust collector does not exceed 190°F. A thermocouple in the flame senses a flame failure and automatically shuts off the hydrogen gas to the system. If the dust collector fails for any reason, the exhaust gases from the reactor are automatically diverted to the atmosphere through a stack.

Of the five reduction reactors in the plant, four can feed their product only to a hydrofluorination reactor bank immediately below them. The fifth reduction reactor can, in addition, by means of a replaceable spool piece, feed its product into a cooling screw about 6" in diameter and 10' long and from there into a blending and packaging system. This cooling screw is horizontal and is partially immersed in a trough containing cooling water. Cooling water is also supplied to the hollow shaft of the screw conveyor.

3. Hydrofluorination Equipment

The product from the reduction reactors is uranium dioxide.

This product falls out of the reactors through a rotary valve into a small seal hopper and is fed from the seal hopper by means of a screw conveyor into the top one of a series of three hydrofluorination reactors. Each of these reactors is a 16" diameter horizontal tube about 22' long made of 1/4" Inconel. Each of these reactors has in it a lawn mower type agitator-conveyor similar to those in the reduction reactors except that, in this case, the agitator-conveyor is supported at only one end and rests on the tube for a good part of its length. These rotors have either a very small shaft in the center or else none at all, and hence, are quite flexible. The primary material of construction of these rotors is Hastelloy C. The ribbons making up the outer framework of the rotor are formed of 1/4" by 1 3/4" Illium R flat stock formed to a 9' pitch. The outer diameter of these screws is about 15 3/8". The bottom reactor of the three has in it a rotor which is slightly different from the other two in that it is quite a bit stronger mechanically and has no internal shaft. The material passing through these reactors drops freely from one to the other through a 10" diameter Monel expansion joint about 3' long. Each of the agitator-conveyors is driven in exactly the same way as the reduction rotor. Similarly, these hydrofluorination reactors are encased in electric furnaces; the top hydrofluorination reactor having four temperature control zones, the next reactor having three temperature control zones, and the bottom reactor having two temperature control zones. Temperature is controlled in these furnaces by means of a thermocouple inserted through the side of the furnace with its junction immediately below the center of the reactor tube. These thermocouples are located in the center of each control zone.

Anhydrous hydrofluoric acid is metered into the bottom reactor and travels countercurrent to the flow of uranium dioxide. It leaves the top hydrofluorination reactor at the feed end through a 10" diameter Monel riser. This riser goes immediately into the bottom of an Adams carbon tube filter made of Monel. This filter has in it fifteen carbon tubes with a total filtering area of 52.5 square feet. The hydrofluoric acid vaporizing and recovery system is described elsewhere. It should be noted here that a very serious corrosion problem results if hydrofluoric acid gas is allowed to condense at any given point in the reactor or filtering system. In order to make sure that condensation does not occur, extensive steam tracing and steam jacketing, where necessary, are employed. The ends of the reactor tubes which extend out of the furnace have been protected from cooling by placing small Calrod heaters at critical points. This normally is necessary only at the feed end of the top hydrofluoric reactor where the hydrofluoric acid gas concentration is at its lowest point in the reactor system.

160 186

The product from the bottom hydrofluorination tube is uranium tetrafluoride, or "green salt". The green salt falls from the bottom reactor into a small seal hopper and is sent from there through a screw conveyor into a 4" diameter cooling screw. A definite amount of green salt is maintained in the seal hopper by an automatic pneumatic weighing device which regulates a small screw feeder to the cooling screw. This cooling screw has a conventional screw conveyor through it and is 4" in diameter and 9' long. A very small flow of nitrogen is introduced through this cooling screw countercurrent to the flow of material. The nitrogen leaves the feed end of the cooling screw and goes through a small, one tube carbon filter to a low pressure scrubbing system. The material discharged from the cooling screw falls directly into a green salt storage hopper on scales. This hopper will contain about one day's production of green salt.

Instrumentation in the reactor section of the plant, not mentioned above, includes tachometers on each individual rotor drive, high pressure cut-offs which will stop the flow of hydrofluoric acid gas to a reactor bank in the event of high internal pressure, an additional thermocouple in each control zone of each reactor which is recorded separately, and recording and indicating instruments on the hydraulic pressure on each hydraulic motor driving a rotor. Most all of these instruments have their control points or indicating points on the first floor.

An extensive dust collection system operates in conjunction with the reactor banks. The major points of dust collection are:

1. Vents on all green storage hoppers.

2. Vents on all hoppers feeding uranium trioxide to the system.

3. Dust hoods around the end of each reactor tube. These hoods are used only when it becomes necessary to remove a rotor from the tube. At this time a large black iron tube which is big enough to hold the rotor is placed immediately adjacent to the end of the reactor tube and the rotor pulled into it. The end of the black iron tube is then closed and the rotor removed to another area for cleaning.

Teflon gasket material and packing material is used extensively throughout the hydrofluoric acid system.

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Almost all screw feeders and all of the cooling screws are driven through small, variable speed hydraulic transmission. This provides the necessary flexibility required to handle changes in the bulk density of the material being handled as well as changes in throughput rates which may occur from time to time.

IV. BLENDING AND PACKAGING EQUIPMENT

Immediately below the five green salt storage hoppers is a Hapman conveyor which in turn feeds additional Hapman conveyors. This system of conveyors picks up the green salt from each individual storage hopper as desired, carries it to the top of the building, and dumps it through a hammer mill into a weigh hopper. This weigh hopper is designed to hold one blender charge. The blender is immediately below the weigh hopper and is a rotating drum batch type machine driven by a 20 H.P. motor. The feed and discharge for this blender are integral one with the other. A large specially designed enclosure is fitted around the feed-discharge opening in order to make this a dustless installation. When the material is discharged from the blender it falls through a continuous sampler into a packaging hopper. This packaging hopper also holds one blender charge. Material is drawn from this packaging hopper through a vibratory feeder into 9 gallon drums on an automatic scale. This scale allows a drum to be filled to a particular weight within very close limits. The feeders above are operated by the automatic scale. When a drum has been filled it is closed and rolled out of the packaging enclosure onto an additional scale wheer the gross weight is printed. The tare weight of each drum is printed on another print weigh scale before it is placed in the packaging enclosure.

If the one reduction reactor previously mentioned is manufacturing uranium dioxide for packaging, the discharge from its cooling screw drops into a Hapman conveying system which delivers the material to a large weigh hopper at the top of the building. This weigh hopper is immediately above a blender quite similar to the green salt blender. This blender feeds a continuous sampler and packaging station also. In this case, however, the packaging station is not designed with automatic feeding and weighing. Rather, the 30 gallon drums packaged here are fed by a rotary valve immediately below the packaging hopper. This rotary valve is operated merely by a timer which is set by the operators based on previous experience. The drum is then rolled out of the enclosure onto a print weigh scale. In this case one scale is used printing both tare and gross weights. There are two complete green salt packaging lines and one uranium dioxide packaging line.

It might be mentioned here that throughout the green salt plant all conveyors, hoppers, feeders, and duct work which carries dust of good quality (i.e., low impurity level) are made of stainless steel. In those hoppers, feeders, etc., where there may also be hydrofluoric acid gas present, the material of construction is Monel.

Both electrical and air operated vibrators are used extensively in the plant. Practically all hoppers including dust collector hopper-bottoms have some vibrating device installed on them permanently. Most vibrators are connected electrically with the feeder at the discharge of a given vessel and operates only when the feeder operates.

V. HYDROFLUORIC ACID SYSTEM

Anhydrous hydrofluoric acid is stored in 34' by 8' diameter steel tanks in refrigerated concrete vaults outside of the building. These tanks are pressurized slightly in order to feed liquid anhydrous hydrofluoric acid to vaporizers inside the building. These vaporizers are about 3' in diameter, 6' tall, and steam jacketed. The liquid acid enters the bottom of a vaporizer so that excess pressure (which may occur when the HF gas flow is throttled for any reason) merely forces the acid back into the storage tank. This also serves to regulate automatically the heat transfer area available for vaporization. The vaporizers are made of ASTM 285 steel. This is a fully-killed steel which is necessary in order to handle the corrosion problem at this point. In order that there may be no large variations in the molecular weight of the gas with small changes in temperature, the gas leaving the vaporizer passes through an Inconel sheel and tube superheater, where it is heated with low pressure steam to about 200°F. From the superheater, the gas enters a header and is divided through automatic control instruments and fed to the individual reactor banks.

The effluent gas from the Adams filter immediately following each reactor bank consists of about 80% hydrofluoric acid, 20% water with a small percentage of inerts. This gas enters a header and is joined by the offgases from all other reactors. The combined gas stream then flows through two Adams filters in parallel. These Adams filters are exact duplicates of the individual Adams filters on each reactor bank. Following the two "clean-up" Adams filters, there is a small Monel hair filter box. This is designed to prevent small particles of carbon from entering the recovery system. After reaching the Monel hair filter the gas travels through three shell and tube partial condensers. The tubes, tube sheets and head liners of these condensers are made of silver. These partial condensers are maintained at about 140°F by means of a tempered water system. The condensed liquid and uncondensed gas from the partial condensers goes through a silver lined separator which is a vessel about 1' in diameter by 2' long. The liquid collected in the separator is approximately 70% acid and flows through a seal leg into one of two 70% run down tanks. These tanks are 4' in diameter by 6' high and are made of steel. They are equipped with agitators and sampling devices. After the acid has been checked for assay it is then dropped by gravity to the 70% storage tanks outside the building. These storage tanks are also 8' in diameter by 34' long and are located in the concrete vaults along with the anhydrous storage tanks. All of the anhydrous and 70% storage tanks are set on scales.

The gas that leaves the silver separator is essentially anhydrous hydrofluoric acid. This gas passes through a shell and tube cupro-nickel and monel condenser operating at about -15°F. The condensed liquid drops out of the condenser through a seal leg into one of two steel anhydrous run-down tanks. The material collected in these run-down tanks is periodically dropped back to one of the three anhydrous storage tanks in the vault. The noncondensables from the final condenser are drawn through an 8" Monel Schutte-Koerting fume scrubber. The scrubbing liquid in this condenser is potassium hydroxide. The potassium hydroxide solution enters the scrubber at about 50 pounds pressure. The gas pressure at the inlet to the scrubber varies from 2" to 4" of water, vacuum. The pressure of the hydrofluoric gas at the entrance to the reactors varies from 1/2 to 1 pound per square inch gage. The gas pressure in the reactors cannot be allowed to exceed 2 pounds per square inch gage, otherwise seal hoppers and packing glands will cease to operate.

V. AUXILIARIES

Necessary to plant operations are auxiliary units which supply power, refrigeration, dust control, steam, compressed air, and water.

Two complete refrigeration units are needed for the handling of hydrofluoric acid. One unit is used for the condensing of the anhydrous hydrofluoric offgas from the partial condensers. The other unit provides refrigeration for cooling lines during unloading of tank cars of anhydrous hydrofluoric acid and also for refrigeration necessary to keep the anhydrous hydrofluoric acid tank storage vaults at 60°F.

The first mentioned refrigeration unit consists of a six cylinder, two stage, Freon twelve compressor which has a rated capacity of 15.4 tons at -30°F suction and 105°F condensing temperature operating in conjunction with a shell and tube type water cooled condenser, an eight inch by eight foot receiver, and a four foot long heat exchanger. The second unit for refrigerating the vaults and unloading lines is a four cylinder compressor of a 25.9 tons capacity at a suction temperature of 40°F and a 105°F condensing temperature.

Power for the plant is provided from its own substation consisting of three 500 KVA transformers and one 750 KVA transformer providing a capacity of 650 KW at 480 volts and 1300 KW at 208 volts. For emergency use there are two gasoline driven generators on standby.

Nitrogen is used as the inert gas in the plant and is manufactured in an inert gas generator which receives its feed from the ammonia dissociators. The unit has a rated capacity of 2000 cubic feet of nitrogen per hour. Normally this fully automatic unit burns the cracked ammonia at a production rate of 350 cubic feet per hour of dry nitrogen. The specifications for use calls for a maximum allowable oxygen and hydrogen content of 1/2% each by volume. To maintain the required assay, the burned dissociated ammonia passes through a condenser and then through activated alumina for final water removal. The nitrogen which is sampled regularly has such uses as: a pressure pad in the anhydrous hydrofluoric acid tank to provide positive flow from these tanks, inert gas for purging anhydrous hydrofluoric acid lines and tanks, purging of reactors, and for maintenance of pressure seals to prevent leakage of hydrofluoric acid.

One of the major operation problems is proper ventilation and dust control of the working areas and equipment. Each operating unit is fully provided with dust and fume collecting units for safe operation. In addition to the dust control system there are two vacuum systems for collection of process material. These vacuum systems, one for contaminated green salt and brown oxide and the other for uncontaminated material, have a 600 cfm capacity at a vacuum at 8 to 9 inches of mercury. They are used in instances where it is necessary to vacuum out reactors or for cleaning up after maintenance work.

Besides the above auxiliaries such necessities as instrument air, compressed air, and cooling water are provided by the central plant's power facilities.

VI. OPERATION

1. Operation of Reduction Reactor

The reduction reactor is operated at a furnace temperature of 1200°F and is capable of producing 500 lbs/hr of UO_2, but except in the event of producing UO_2 as a finished product, the normal rate of production is approximately 300 lbs/hr. Feed material is uranium trioxide which is an average 200 mesh size. The UO_3 is hoisted by a Hapman conveyor to storage hoppers for feed to these brown reactors. These hoppers feed automatically and the weights discharged are checked hourly. This material is then fed to the brown reactor via seal hoppers. The eight hour discharge rates of these hoppers are carefully checked in order to maintain a constant feeding rate to the brown reactors. Besides constant feeding, the seal hoppers maintain a seal to prevent the escape of hydrogen to the atmosphere. It is necessary for the operator to be vigilant to prevent the loss of this seal.

The speed of the brown screw is normally 3 to 4 rpm with infrequent difficulty with respect to driving power. 1 1/2 to 3 H.P. is required to drive this screw. The reactor operates at a normal bed depth of 1 to 2 inches and little difficulty is experienced in conveying this material through the reactor.

Close attention is necessary to the recording and controlling temperature instruments in order to maintain their proper functioning. If the latter do not check within 30 degrees, this calls for immediate action. It is possible to affect the reactivity of UO_2 and later conversion to UF_4 if proper temperature control is not maintained. Occasionally there is a build up of pressure and an automatic shut off of the hydrogen supply. This may be traced to difficulty in the dust collection system which will automatically cut off the hydrogen supply or it might mean a build up of dust in the off-gas exhaust system or an actual build up of material in the reactor tube. If the hydrogen flow cuts off, immediate remedial action is necessary. There are recording charts and alarms to indicate such stoppage of hydrogen, and upon such a stoppage, nitrogen automatically purges the reactor.

Preventive maintenance as well as quick service and spare parts are necessary for proper operation of the feed screws and mechanical equipment of the weigh hopper and feeding seal hopper. It is the weekly procedure to clean out the effluent gas lines to prevent build up of dust.

2. Operation of the Hydrofluorination Reactor

Each reduction reactor is followed by three hydrofluorination reactors in series. The UO_2 discharged from the reduction reactor is received via a seal hopper as feed for the first hydrofluorination reactor. The feed is converted in three countercurrent stages until its final discharge of a minimum acceptable assay of 96% of UF_4. The first of the three hydrofluorination reactors converts approximately 75% of the UO_2 to UF_4 while the second brings the assay up to approximately 90% and the third to at least a minimum of 96% UF_4.

In many respects the three hydrofluorination reactors are independent of each other. While each of these reactors operates on the same feed and the same source of anhydrous hydrogen fluoride, the operating procedure is different in respect to temperatures, screw speed, and hydraulic pressures. As in the reduction reactor, the hydrofluorination reactors are divided into zones for heating and temperature control. The following are the normal temperatures, screw speeds, and driving horsepower maintained in the reactors. It is noted that reactor A receives its feed from the reduction reactor and reactor C produces the final UF_4.

Reactor	Zone 1	Zone 2	Zone 3	Zone 4	Screw rpm	Driving H.P.
A	670°F	790°F	915°F	975°F	7-8	1 1/2-3
B	860	980	1045		10	3-3 1/2
C	1070	1100			14-15	3-3 1/2

The major operational controls are based upon the above plus the amount of anhydrous hydrogen fluoride input and the pressure of the input and effluent gas. These controls are those which indicate the character of the operation before receipt of control sample results. Considering the number of controls and the complexity of the operation, there is no normal pattern that might be considered as a standard operating one, other than constant control.

Besides the above stated controls, there are certain other procedures necessary to operations such as the "blow back" of the Adams filters every three hours to clean the carbon tubes, the use of nitrogen during the blow back and the purging of the reactors with nitrogen before mechanical work and inspection. Therefore, in order to

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properly integrate the factors involved, constant attention is the rule due to the nature of the equipment and the reaction that is occuring. There is a tendency for the UF_4 to cake as it is being formed and this necessitates adjustment of the temperatures of the various zones. In addition to temperature adjustment of the heating units, other adjustments such as opening or closing the end of the furnaces is sometimes needed. The same caking or clogging of the tubes quite often calls for manipulation of the speed of the screw in the effort to push or break up a mass of material in a reactor or a downcomer between reactors. In this respect there is a limit to what can be accomplished since the screws are of flexible design and can withstand only a limited driving force.

As indicated, the normal procedure is to manipulate screw speeds and temperatures in the event of blocking, or high horsepower requirements in the screw drives. When this method fails, tubes must be opened after thoroughly removing hydrogen fluoride from the tubes. The UF_4 must then be vacuumed out in order to get at the source of difficulty. At times the caked area may necessitate probing with rods to loosen it. Extensive rigging is necessary to pull screws for replacement or repair and depending on the reactor it may mean removing the drive mechanism before pulling the screw.

As briefly mentioned, the material handled is of such a nature in the various stages of operation that the seal hoppers can be a source of difficulty both from the maintenance point of view and the feeding requirements. The seal hoppers have a tendency to feed erratically, because of bridging of material and density variations which in turn cause periodic surges. Feed screws in these hoppers must be watched as well as the units containing these screws. Without attention, surges can disrupt the smooth flow of material through the reactors and this in itself can cause masses that will jam the screws and downcomers. In this regard, vibrators are carefully maintained in all available places where there is a possibility of bridging or build up.

Control sampling is standard procedure on a scheduled basis. Twice daily control samples are obtained both of the UF_4 product of the hydrofluorination reactor and the UO_2 from the reduction reactor. These samples are important as an added means of interpreting the operation of the reactors. To all appearances, it is possible to have good physical operation of a reactor only to have below assay material. Sampling itself requires techniques that must be carefully standardized and maintained in respect to health hazards and affect on the samples themselves and the material in the reactors. Double sealing mechanisms are used in the sampling apparatus to prevent air intake by the reactors as well as the escape of dangerous gases. When sampling UO_2, a special technique of preventing reoxidation of the UO_2 sample is required which is accomplished by using dry ice to cool the sampling vessel before and after receiving the sample. While taking hydrogen fluoride samples, special techniques and equipment are used to insure complete collection of the gas from the viewpoint of collecting accurate samples as well as the protection of personnel.

Because of the hazardous nature of hydrogen fluoride and the necessity of maintaining a completely sealed operational unit, maintenance and careful inspection are continual. A leak, no matter how minute, calls for tracing down and repairing. Complete, and at times, cumbersome safety equipment is necessary both for maintenance work and sampling.

3. Operation of the HF System

Anhydrous hydrogen fluoride is received in tank cars and stored in tanks in refrigerated vaults. The flow of the AHF to an individual bank of reactors is regulated by a series of units which have to be carefully controlled. Individual rotameters control the flow of the HF gas from the vaporizer to each of the reactors. This gas is controlled in temperature and pressure before metering to give constant conditions. These units are balanced to regulate the gas used to an even flow and a constant amount.

In the operation of the reactors themselves, the adjustments made on the AHF used are limited to cutting off the supply during purging of the reactors and during "blow back" of the Adams filters to remove the excess dust collected in the filter. The off-gas from these Adams filters is approximately 80% HF and this is filtered three times before condensing in two stages: partial giving 70% acid; and total, giving AHF. Careful attention by production is maintained on the recovery of AHF and the production of 70% HF. The condensing temperatures are important in order to control the assay of the products. Poor control results in below minimum assay. An extensive system of temperature indicating and recording records as well as pressure records are maintained. Daily assays are also used to evaluate efficiency as well as for monthly production controls.

A neutralizing scrubber is used in conjunction with the hydrogen fluoride recovery system. The inert gas and dust from the final

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condensers used in the condensing of the anhydrous hydrogen fluoride is fed to a potassium hydroxide neutralizing scrubber. The product of the scrubber is a neutralized uranium-containing precipitate which is treated by two stage filtering in Niagara filters plus centrifuging before ultimate shipment in drums for treatment in the refinery. Lime scrubbers are used in the purging of all HF systems not having uranium present. The slightly alkaline product of this scrubber is dumped to the sewer. Such systems that are purged to the lime scrubbers are pipe lines, tanks; and tank cars. Operation control is necessary on the scrubbers as well as a thorough preventive maintenance program.

4. The "Re-Run" Reactor

At times during operation, a series or a combination of operational difficulties can result in low assay material caused by incomplete conversion of UO_2 to UF_4. Such material is processed in the "Re-run" Reactor.

The "Re-run" consists of two 12" diameter, 22 foot long, Inconel reactors in series. The temperature of the first tube is controlled in four zones progressing in 100°F increments from 700°F to 1,000° controlled in similar manner to the main furnaces. The second tube is controlled from 950°F, to about 1,100°, and to a final zone temperature of 1,150°F at the discharge end. Anhydrous hydrogen fluoride is fed to this reactor countercurrently. The amount of anhydrous hydrogen fluoride used is based upon the assay of the feed. The normal feed rate of this reactor is based upon the assay of the feed. The normal feed rate of this reactor is approximately 120 lbs/hr. For driving the re-run screw, a Reeves mechanical drive is used and the power consumption is recorded by ammeters. Occasional difficulties are experienced due to jamming of the screws and corrosion.

5. The Revertor

The revertor is an 8" diameter, 10 foot long, Inconel reactor used to revert contaminated UF_4 to black oxide (U_3O_8). The source of feed is material vacuumed from the operational areas during maintenance work, cleanout of screws and appurtenances, and the break down of equipment.

The reactor is driven by a Reeves mechanical drive at 5 rpm. The furnace temperature is controlled similarly to the other reactors by setting its four zones to 1,250°F. The feed rate is approximately

40 lbs per hour. Since the operation is opposite to the hydrofluorinating reactions, this reactor is fed with steam and air to convert the fluoride to the oxides of uranium. The steam used in this reactor is fed countercurrently at a rate of 45 lbs/hr and air is bled in with the steam at 0.5 cfm.

Care is necessary in temperature control and feed gases; yet due to the presence of steam and hydrogen fluoride, a strong corrosive action is always present in spite of temperature control. The drive end is most seriously attacked because of some condensation of weak hydrofluoric acid solution. Attention is always the rule in cognizance of this corrosion potential.

The combination of dust load and the acid-steam produced create a problem in the offgas lines. The average on-time of the reverter is 90% and the down-time is, in the majority of cases, due to corrosion and plugging of the effluent gas lines. The offgases are filtered and passed on to the hydrogen fluoride recovery system.

6. Sump System

The sump system is used to accumulate and prepare for transfer to the refinery all the residues produced in the plant during washing and cleaning of equipment and transfer drums plus the product of the scrubber used in the treatment of hydrogen fluoride gases containing uranium.

The contaminated wash waters plus the slurry from the KOH scrubbers are received in storage tanks prior to filtering and centrifuging as noted previously. All clear, uncontaminated liquors are dumped into the sewers.

Control is maintained on the KOH slurries both on the pH of the slurry and the pounds per gallon of KOH contained. Fluoride is checked on the final cake from the sump system. If control of the system is not carefully maintained from the operation and preventive standpoint, the cake product can be sufficiently contaminated with fluoride to prevent its used in the refinery.

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THE USE OF THERMOBALANCE AND REACTIVITY TESTS IN THE EVALUATION OF URANIUM TRIOXIDES

by

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ABSTRACT

The wide variation in the physical and chemical characteristics of uranium trioxide feed materials which results from differences in production methods currently being investigated has necessitated the development of test methods (1) to predict whether or not a given oxide will process satisfactorily under reasonably standardized feed plant conditions and, if not, (2) to establish what changes in processing conditions will be necessary.

Thermobalance and modified Fox reactivity tests which aid in establishing whether a given oxide has suitable reaction characteristics or reactivities are described. Test data are presented which show that materials having high reactivities under certain conditions cannot be expected to behave properly in present plant equipment. The tests are essentially use tests and are valid only to the extent that the conditions selected for the tests are representative of the conditions which will be encountered in actual operations. Data are also presented which show that thermobalance continuous behavior profiles, particularly when used in combination with knowledge of other physical and chemical characteristics, are useful in estimating the optimum conditions for converting a given oxide to uranium tetrafluoride.

INTRODUCTION

The wide variations in the physical and chemical characteristics of uranium trioxide feed materials which result from difference in production

140 198

methods has necessitated the development of test methods (1) to predict whether or not a given oxide will process satisfactorily under reasonably standardized feed plant conditions and, if not, (2) to establish what changes in processing conditions will be necessary. Since feed plant conversion of uranium trioxide to uranium tetrafluoride involves separately a hydrogen reduction step and a hydrofluorination step, tests have been devised to evaluate (a) the behavior of an oxide under standardized reduction conditions from thermobalance data and (b) the behavior on hydrofluorination from data obtained by the use of the thermobalance as well as reactivity equipment for making direct comparison tests.

THERMOBALANCE TESTS (1)

The thermobalance test as employed at the Oak Ridge Gaseous Diffusion Plant measures conversion at essentially zero bed depth as a function of time under the conditions selected for the run. If a series of tests is performed in which the conditions of reduction and hydrofluorination are varied over a wide range, data are obtained which not only permit determination of whether an oxide will reduce and hydrofluorinate properly in process equipment, but also permit estimation of the optimum conditions for the conversion.

A schematic diagram of the thermobalance employed is shown in figure 1. Essentially, it consists of a means for periodically weighing a solid sample of material which is undergoing reaction with a gas under controlled thermal conditions. Gas flows are adjusted and controlled so that the reactant gas is preheated to the desired temperature before coming in contact with the sample after which the excess and the product gases are withdrawn through a nitrogen gas seal. A flow diagram of the equipment is shown in figure 2. The seal arrangement prevents the entrace of air to the reactor or the escape of exhaust gases into the room. Experience has shown that uranium trioxide which reduces satisfactorily in the feed plant will require no longer than 10 minutes for 97% reduction with hydrogen in the thermobalance reactor at a temperature of 560°C.

To begin such a thermobalance test, a 0.5 g. sample of the uranium trioxide is weighed into the sample boat on an auxiliary balance, the sample and boat are then suspended in the heated reactor from the thermobalance, the reactor is closed and the sample is allowed to reach reaction temperature in a flowing stream of helium. When the system reaches thermal equilibrium (usually 10 minutes is sufficient), the initial net weight of the sample is obtained by weighing in helium and correcting to the corresponding weight in hydrogen. At zero time, the helium flow is replaced with a flow of hydrogen of 1500 cc. per min. Weighings are made at one-minute intervals until the weight remains constant over a 5-minute period. Fractional conversions to uranium dioxide for each of the interim weights are calculated by considering the total weight change to represent complete reduction.

The data thus obtained may be plotted in a number of ways. The semilogarithmic plot employed for first order reactions is generally acceptable although the reaction does not appear to be strictly one of first order. Typical reduction curves for five different uranium trioxides are shown in figure 3. These data show that all except experimental oxide number 3 will reduce satisfactorily in the feed plant.

Following demonstration of satisfactory reduction behavior of the uranium trioxide, the resulting uranium dioxide may then be subjected to hydrofluorination with anhydrous hydrogen fluoride at some predetermined temperature. In order to parallel more closely the temperatures prevailing in feed plant reductions, it is sometimes desirable to perform the reduction at 925°C. prior to the hydrofluorination test. Hydrofluorination data for a typical pot oxide reduced at two different temperatures and hydrofluorinated at various temperatures are shown in figure 4 plotted on the same basis as the reduction data. These results show that both the temperature of reduction and the temperature of hydrofluorination have an important influence on the amount of conversion to be expected. Figure 5 shows a similar plot for an experimental oxide having a satisfactory reduction rate. Again, the behavior shows dependence on both the temperature of reduction and the temperature of hydrofluorination, but the degree and nature of the dependence are obviously different from those of the pot oxide. The interpretation and use of these data will be examined later when they are discussed in conjunction with the results of the reactivity test.

REACTIVITY RATIO TEST (2)

The reactivity ratio test was developed primarily to obtain a quick index to the probable behavior of a subject oxide on hydrofluorination compared directly to that of a selected standard oxide known to process satisfactorily in the feed plant. The test is essentially a use test and is valid only to the extent that the conditions selected are representative of the conditions which will be encountered in actual operations. The reactivity ratio or index is defined as the ratio of the conversion to uranium tetrafluoride of the unknown material to that of the standard oxide under identical conditions.

The equipment required for this test is shown schematically in figure 6. The reactivity measurements are made in an Inconel reactor which is heated by a standard tube furnace, capable of sustained operation at 925°C. In addition to the heated reactor, a temperature recorder, a small condenser, and sources of hydrogen, hydrogen fluoride and nitrogen are required. In operation, duplicate samples weighing

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about 10 g. each of the subject oxide and the standard uranium trioxide are loaded at room temperature into Inconel boats and slipped into position under the thermocouple well in the Inconel reactor. Hydrogen is passed at a rate of about 5 standard cubic feet per hour over the samples while the reactor is heated to the desired temperature after which the hydrogen flow is maintained for 2 hours. With the hydrogen still flowing, the reactor is adjusted to the hydrofluorination temperature. The hydrogen flow is then replaced with hydrogen fluoride passing over the sample at such a rate that 1 cc. of condensate per minute is collected from the exhaust gases. In present practice, the hydrofluorination is continued for three hours since shorter periods sometimes have lead to erroneous predictions of plant performance. At the conclusion of the hydrofluorination, the hydrogen fluoride supply is cut off and the reactor is purged with nitrogen while being cooled to 120°C. The samples are removed and analyzed for uranium tetrafluoride and the reactivity ratio is calculated. Typical reactivity ratios for a series of oxides compared with pot-calcined oxide A under several different sets of conditions are shown in table I. The value of the ratio is clearly a function of the test conditions. Obviously the nature of the dependence is not the same for all oxides, but all the pot oxides examined behave similarly at the two highest hydrofluorination temperatures.

DISCUSSION OF THE TESTS

The utility of any test depends upon the general validity of the results and the ease with which the result can be obtained. Thermobalance data give an accurate evaluation at essentially zero bed depth of the behavior of an oxide throughout the conversion period under the conditions selected either for reduction of the uranium trioxide or the hydrofluorination of uranium dioxide. The reactivity ratio test described is capable, in a single test, of giving information for only a single time after the hydrofluorination has begun. By plotting a thermobalance run under the selected set of conditions on both the subject oxide and the standard oxide on a single graph and taking the ratios of the conversions at various times, one obtains an approximation of the results of a series of reactivity tests run for these various periods of time. One pair of such comparison plots is given in figure 7 for pot-calcined oxides A and B. A second pair of such plots under the same sets of conditions for an experimental oxide and pot-calcined oxide A is given in figure 8. The pot-calcined oxides show some similarity in their behavior in that the reactivity ratios, regardless of the time for which they are computed, are greater than 1.00 under both sets of test conditions using oxide A as the comparison oxide. The experimental oxide behavior is such that the reactivity ratios computed under the milder conditions increase rapidly with time whereas under the more stringent conditions the computed reactivity ratios actually reverse and then decrease rapidly with time.

TABLE I

TYPICAL REACTIVITY RATIO TEST RESULTS

	Reactivity Ratio							
Material	590°C. H_2 410°C. HF*	590°C. H_2 550°C. HF	590°C. H_2 600°C. HF	760°C. H_2 550°C. HF	760°C. H_2 600°C. HF	925°C. H_2 410°C. HF	925°C. H_2 550°C. HF	925°C. H_2 600°C. HF
Pot Oxide A	1.00 (70-75%)**	1.00 (95%)**	1.00 (>99%)**	1.00 (97%)**	1.00 (>99%)**	1.00 (80%)**	1.00 (93%)**	1.00 (>95%)**
Pot Oxide B	1.27	1.00	1.00	1.03	0.98	-	1.03	0.99
Pot Oxide C	1.25	1.02	-	1.01	0.97	1.15	0.99	1.00
Pot Oxide E***	1.15	1.01	1.01	1.01	0.99	-	1.03	1.00
Experimental Oxide-3	1.20	-	-	-	-	-	0.90	-
Experimental Oxide-11	1.38	0.92	-	-	0.68	-	0.78	0.73

*Hydrofluorination for 30 minutes instead of 3 hours.

**Per cent of pot oxide A converted to uranium tetrafluoride.

***Same as pot oxide B without addition of sulfate.

Obviously, it is imperative that the reactivity ratio measurement be made under conditions approximating those to be encountered in feed plant processing and that the desired conversion range be attained in the test if this measurement is expected to predict accurately feed plant performance of an oxide.

The data given in table II also confirm this observation. Whereas the reactivity ratios shown in the first column are significantly different from those indicated by pilot plant tests, there is at least a qualitative agreement between the corresponding ratios shown in the last three columns. This difference is due primarily to the lower temperature and the shorter time selected for making the first comparison. Statistically, the percentage conversion as determined from a single hydrofluorination run of pot-calcined oxide A at 550°C. after reduction at 925°C. is 93.2 ± 2.7% at the 95% confidence level. Reproducibility becomes better with higher conversions and somewhat worse with lower conversions.

The profiles obtained from thermobalance data, while providing the means of making a reactivity ratio comparison for any desired degree of conversion, allow direct prediction of plant performance with a given oxide only to the extent that plant reaction temperatures are duplicated. Nevertheless, the profiles are useful in detecting which oxides will process unsatisfactorily under normal operating conditions and when used in combination with knowledge of other physical and chemical characteristics, e.g., surface area, particle size, crystal structure, and chemical purity, indicate rather reliably the optimum conditions for attaining the desired degree of conversion of a given oxide to uranium tetrafluoride. However, these optimum conditions for conversion may be impossible to achieve in any of the present processing plants. Actually this is the case for certain experimental oxides; and if the experimental oxides 5 and 11 were to be processed in present equipment, production would be reduced by at least 50%.

The properties of uranium trioxide are dependent on the method of preparation as shown by the data in figure 8 and tables I and II. Minor variations in a manufacturing process sometimes have been found to make small but important changes in the ease of processing; e.g., the addition of a few hundred parts per million of sulfate to pot-calcined oxide has resulted in a significant increase in production at the Paducah and Oak Ridge Gaseous Diffusion feed plants. However, corrosion difficulties associated with the action of sulfur on the materials of construction make the large scale employment of sulfated oxides of doubtful value.

The nature of the thermobalance test makes it especially suitable for measurement of the reactivity of uranium trioxides toward reduction while the reactivity ratio test is more suitable for the production control testing of the hydrofluorination reaction. Therefore, the proposed reactivity specifications for uranium trioxide consist of a combination of the two tests; i.e., a thermobalance test to check the reactivity on reduction and a reactivity ratio determination to check

TABLE II

REACTIVITY RATIO MEASUREMENTS ON VARIOUS OXIDES

	Reactivity Ratio			
Material	590°C. Reduction 410°C. Hydrofluorination	925°C. Reduction 550°C. Hydrofluorination**	925°C. Reduction 600°C. Hydrofluorination	Predicted From Plant or Pilot Plant Tests
Pot-Calcined Oxide A	1.00	1.00	1.00	1.00
Pot-Calcined Oxide B	1.25	1.03	0.99	0.99
Pot-Calcined Oxide C	1.25	0.99	1.00	0.96
Pot-Calcined Oxide D	1.20	0.97	-	0.99
Pot-Calcined Oxide E*	1.15	1.03	1.00	0.95
Experimental Oxide-5	1.04	0.82	-	0.77
Experimental Oxide-11	1.38	0.78	0.73	0.68

*Same as pot-calcined oxide B without sulfate addition.
**Hydrofluorination for 30 minutes instead of 3 hours.

the acceptability of the rate of hydrofluorination. While work which will determine the ultimate reactivity specification is in progress, the following tests, based on the data obtained to date, appear to give reactivity ratios in reasonable agreement with plant experience.

(a) The Reduction Test. The representative sample of uranium trioxide shall be at least 97% converted to uranium dioxide when reduced in hydrogen in a thermobalance for 10 minutes at 560°C. The sample dispersed to effectively zero bed depth shall be introduced into the furnace at 560°C. and preheated in helium for 10 minutes before introducing the hydrogen.

(b) The Hydrofluorination Test. The representative sample of uranium trioxide shall have a reactivity ratio, determined at 600°C., of at least 0.97 compared to the selected standard oxide.

The hydrofluorination test equipment and procedure will be that presented in a report now in preparation entitled

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"Equipment and Procedures for Testing Uranium Trioxides." The test conditions are the following:

1. The sample of uranium trioxide in the hydrofluorination test shall be reduced for 2 hours at 925°C.
2. The reduced sample shall be treated with anhydrous hydrogen fluoride at 600°C. for 3 hours.
3. For the tests to be valid, the standard oxide must be at least 95 per cent converted to uranium tetrafluoride by the test.

The data in figure 3 indicate that 4 of the 5 oxides examined in that study meet the requirements of the reduction test. The data in table II indicate that materials which will meet the requirements of the reduction and the hydrofluorination tests will process satisfactorily in the feed plant and that a number of uranium trioxides which meet these requirements have been prepared.

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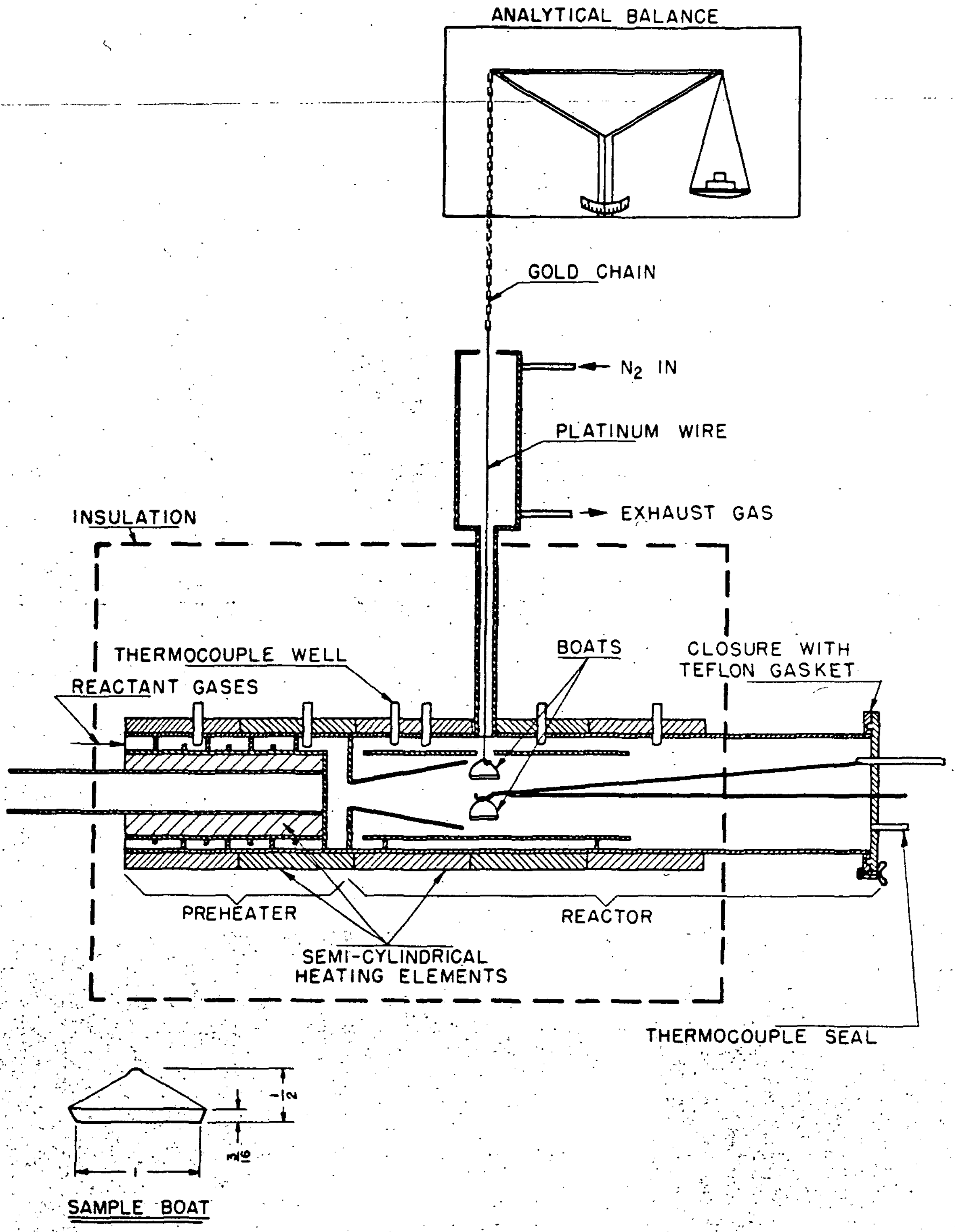
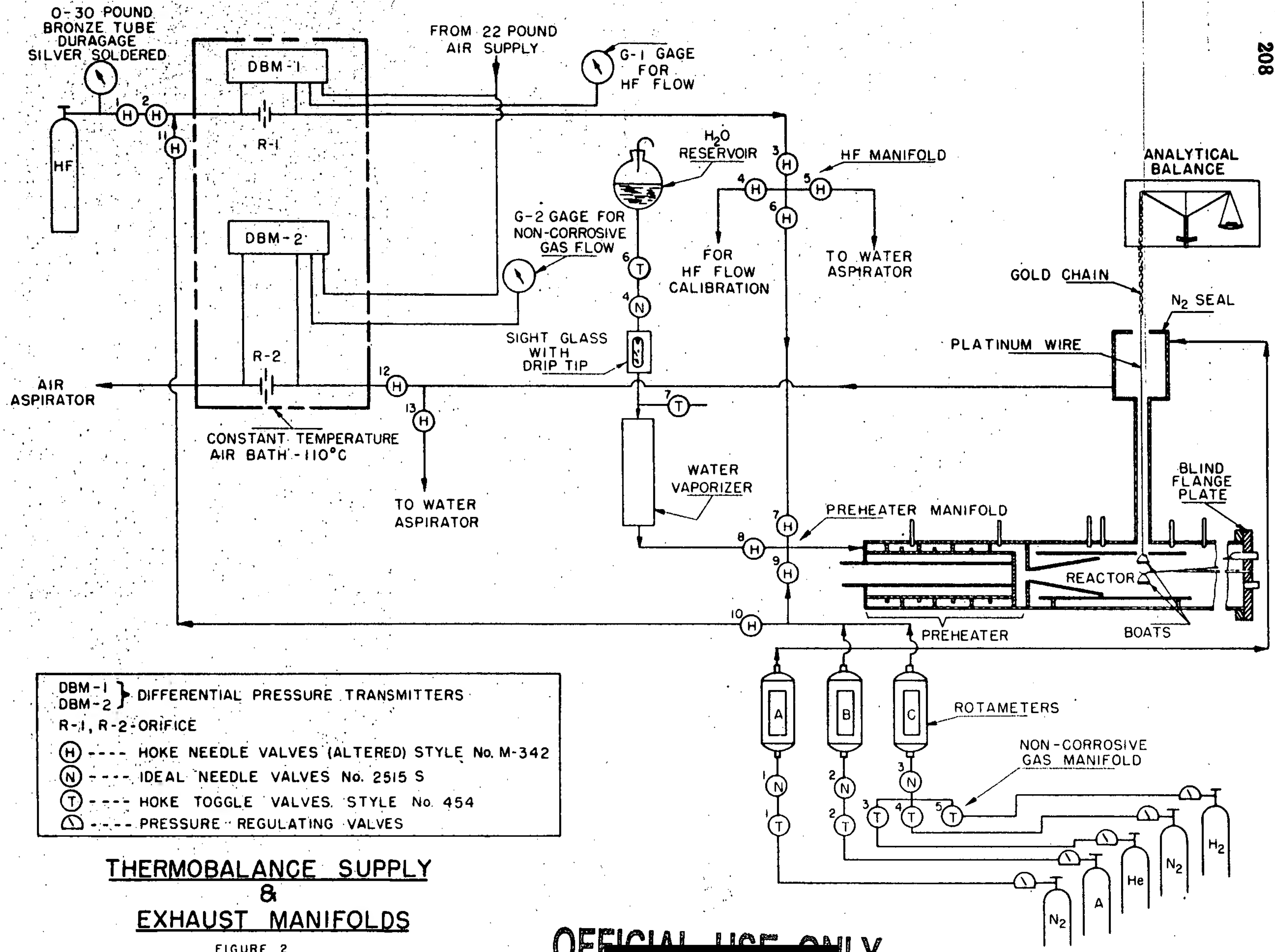


THERMOBALANCE

FIGURE 1



THERMOBALANCE SUPPLY & EXHAUST MANIFOLDS

FIGURE 2

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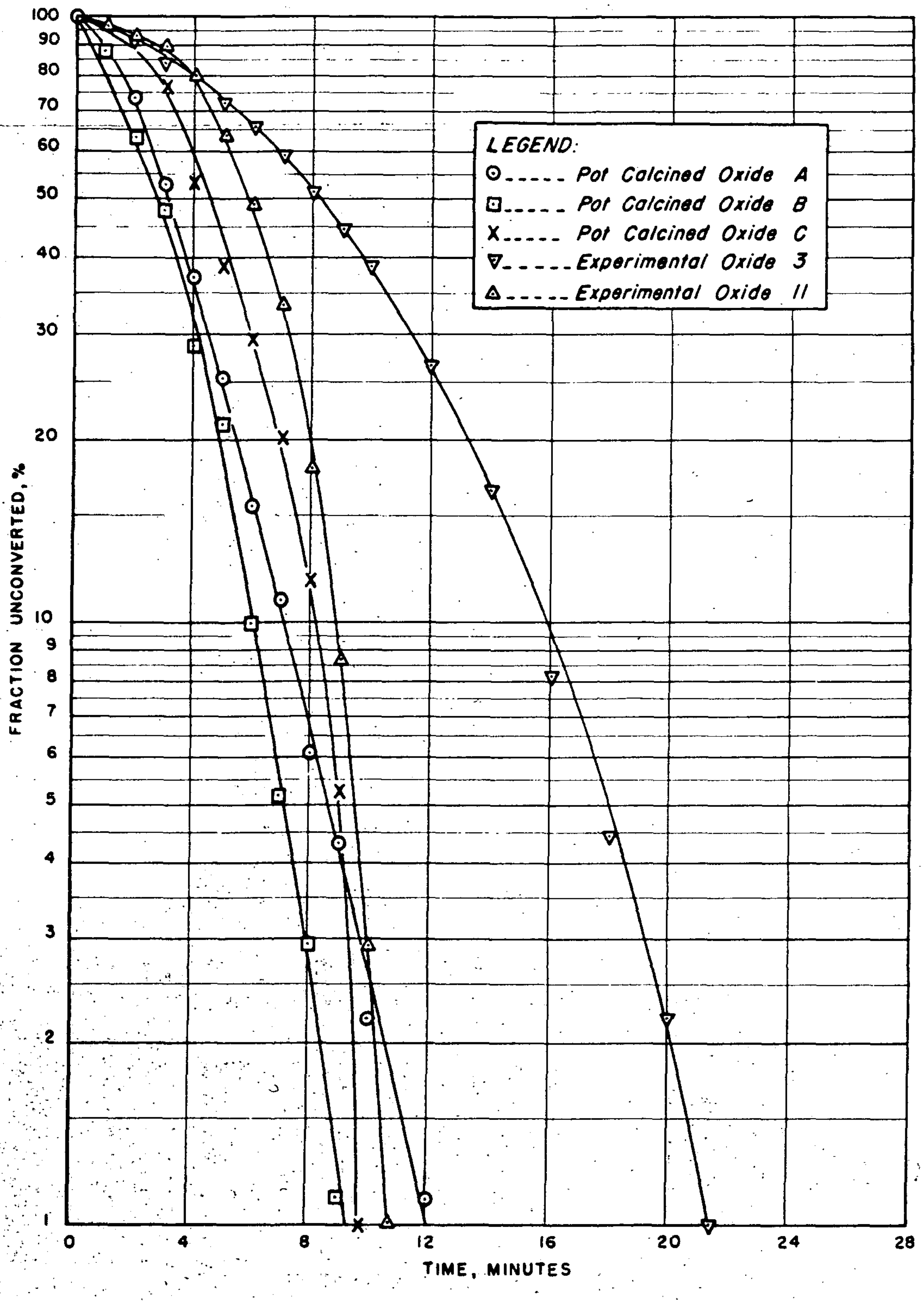

REDUCTION OF UO_3 IN HYDROGEN AT 560° C.

FIGURE 3

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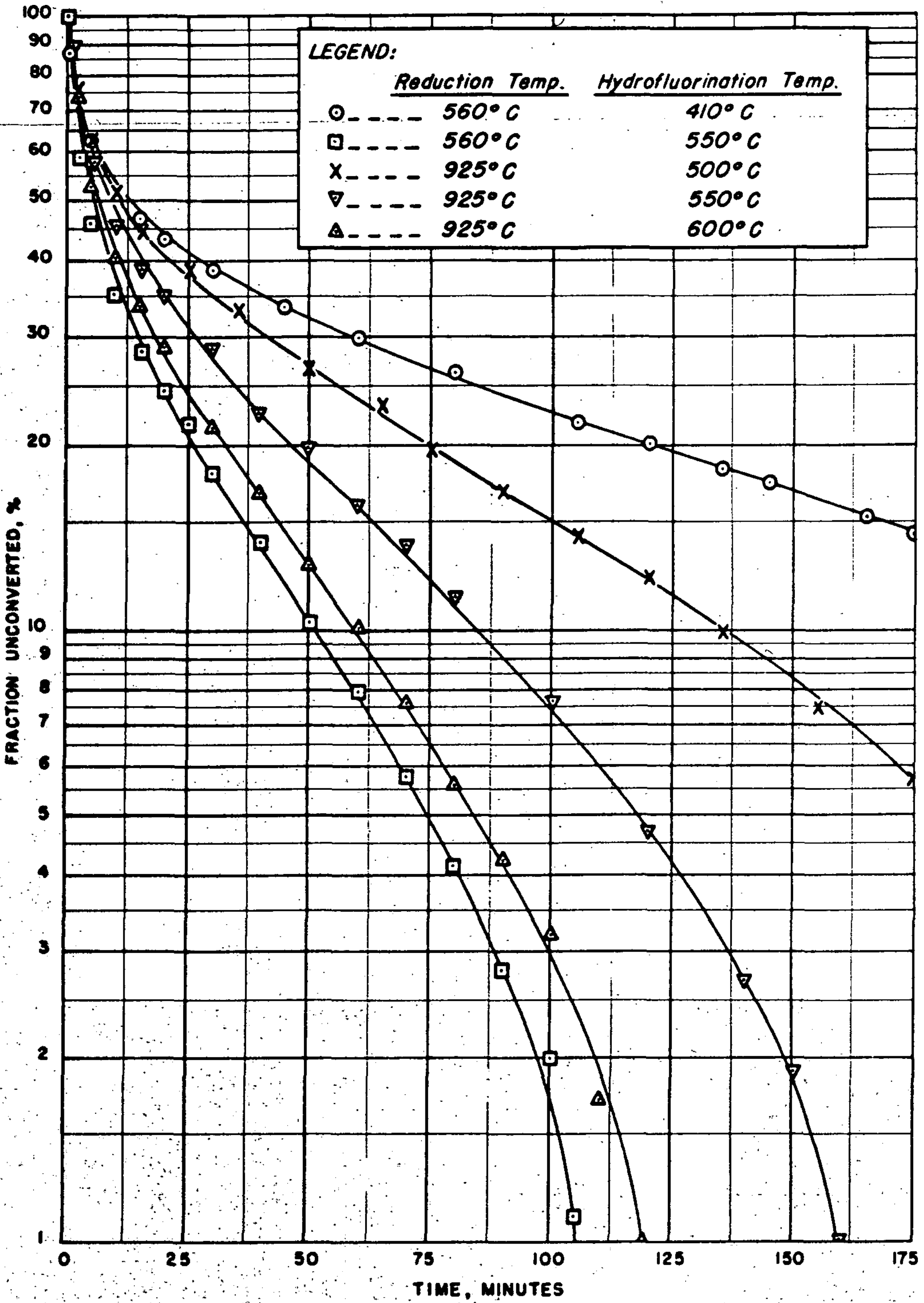

HYDROFLUORINATION OF UO_2 FROM REDUCTION OF POT CALCINED UO_3 (A)

FIGURE 4

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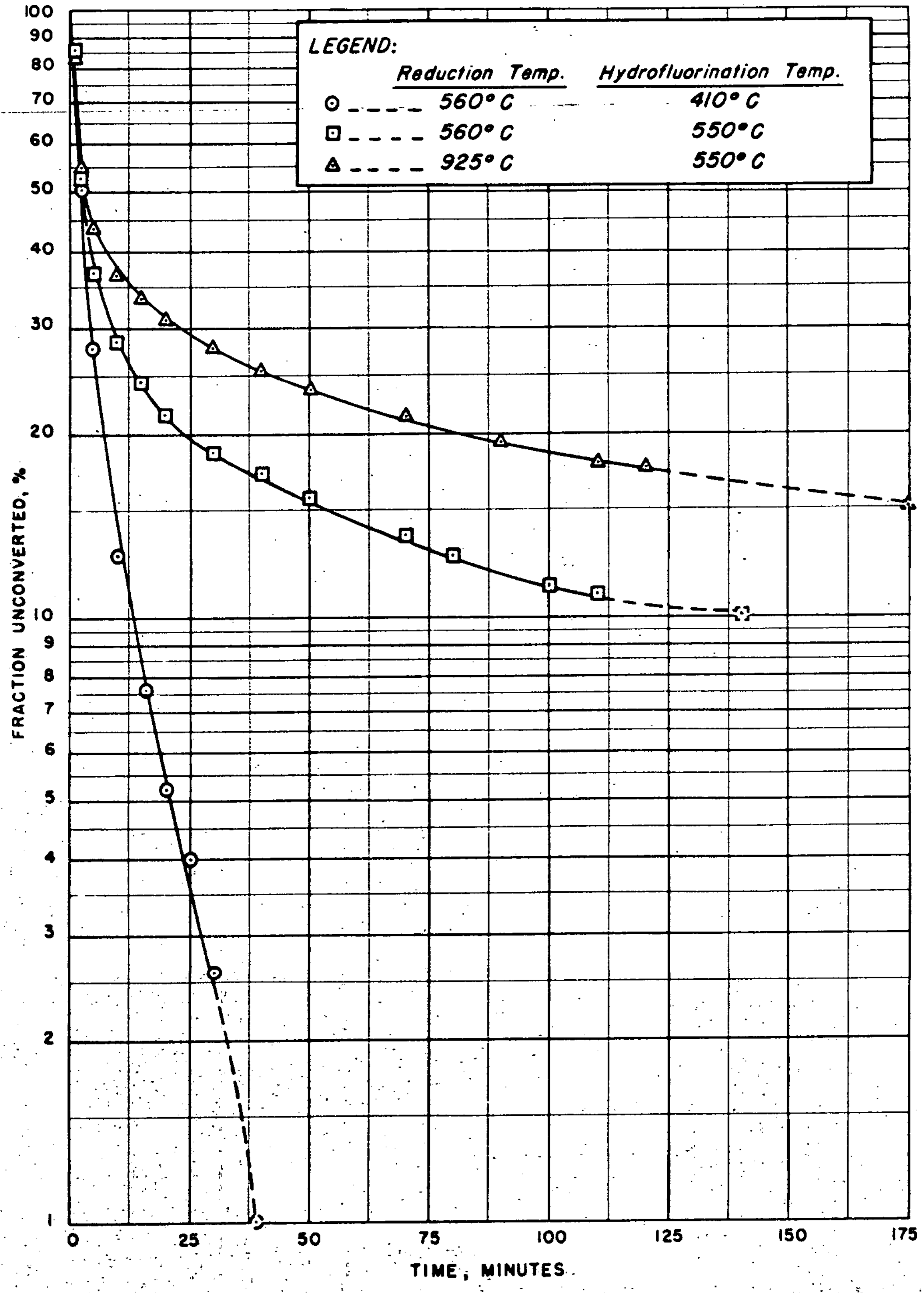

HYDROFLUORINATION OF UO_2 FROM EXPERIMENTAL UO_3 (II)

FIGURE 5

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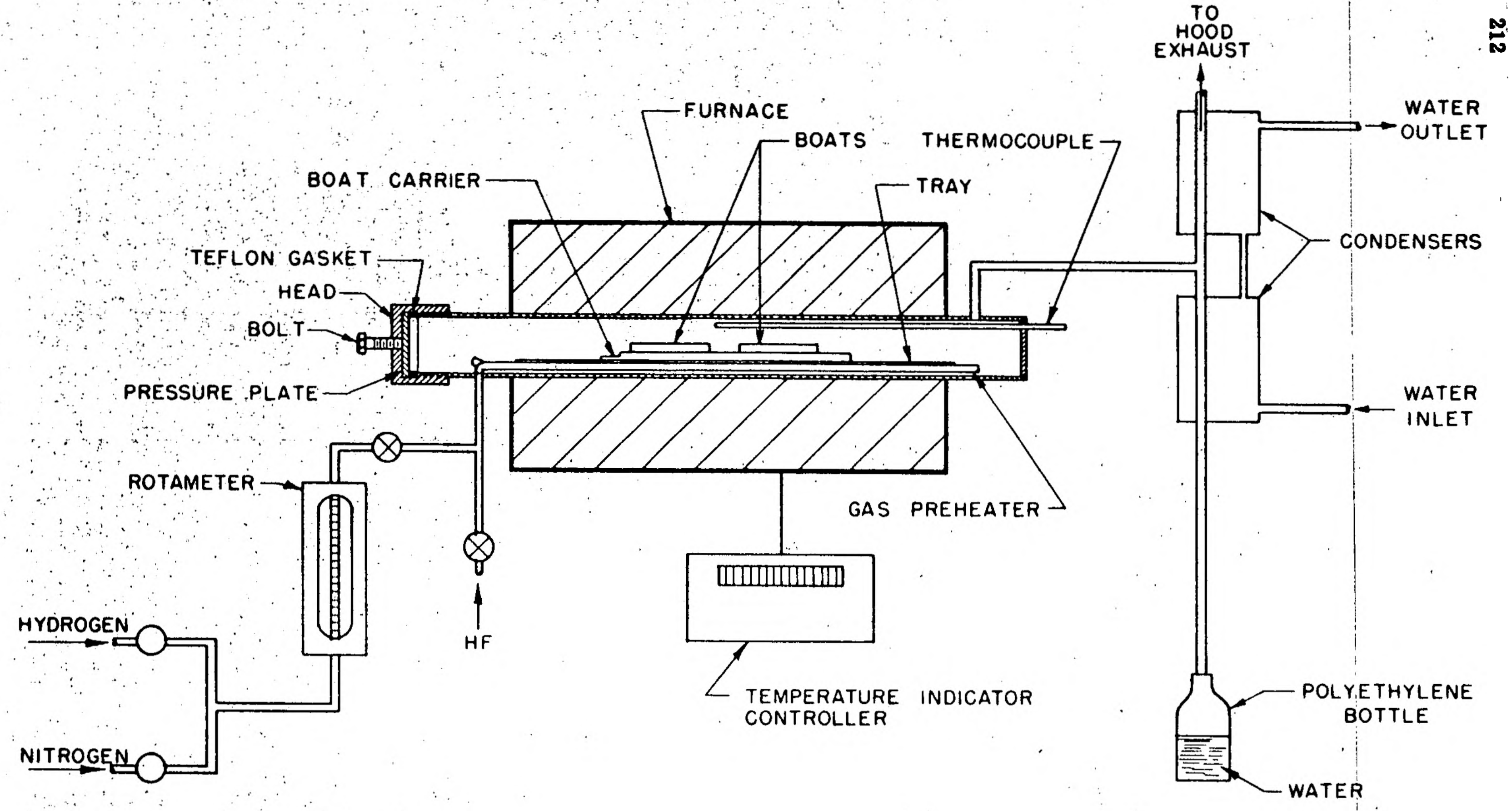
[redacted]



○ -- HOKE VALVE No. 413 (MONEL)

⊗ -- HOKE VALVE No. 342 (MONEL)

UO_3 REACTIVITY APPARATUS

FIGURE 6

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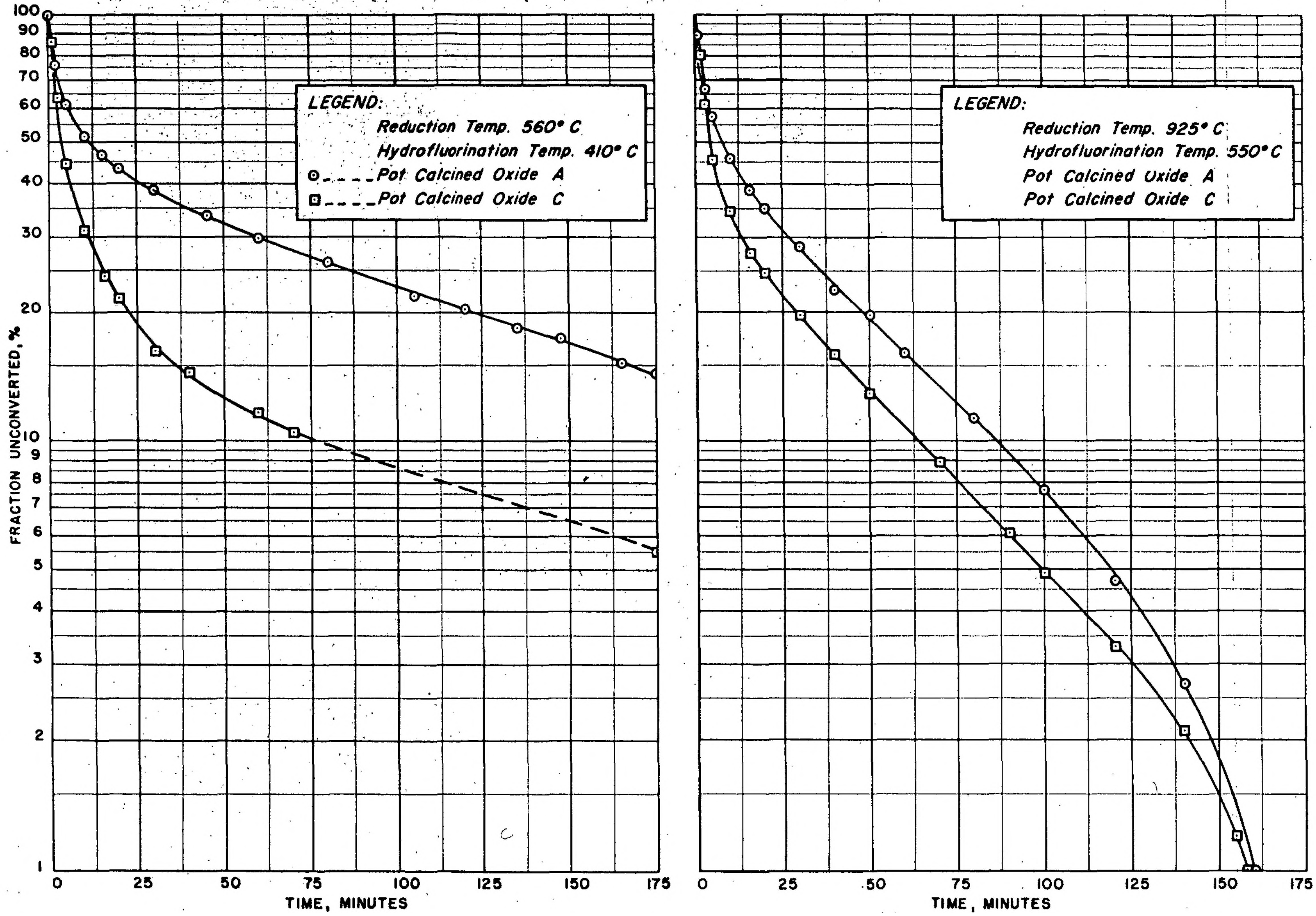

ESTIMATION OF PLANT PERFORMANCE BY COMPARISON OF HYDROFLUORINATION REACTIVITIES

FIGURE 7

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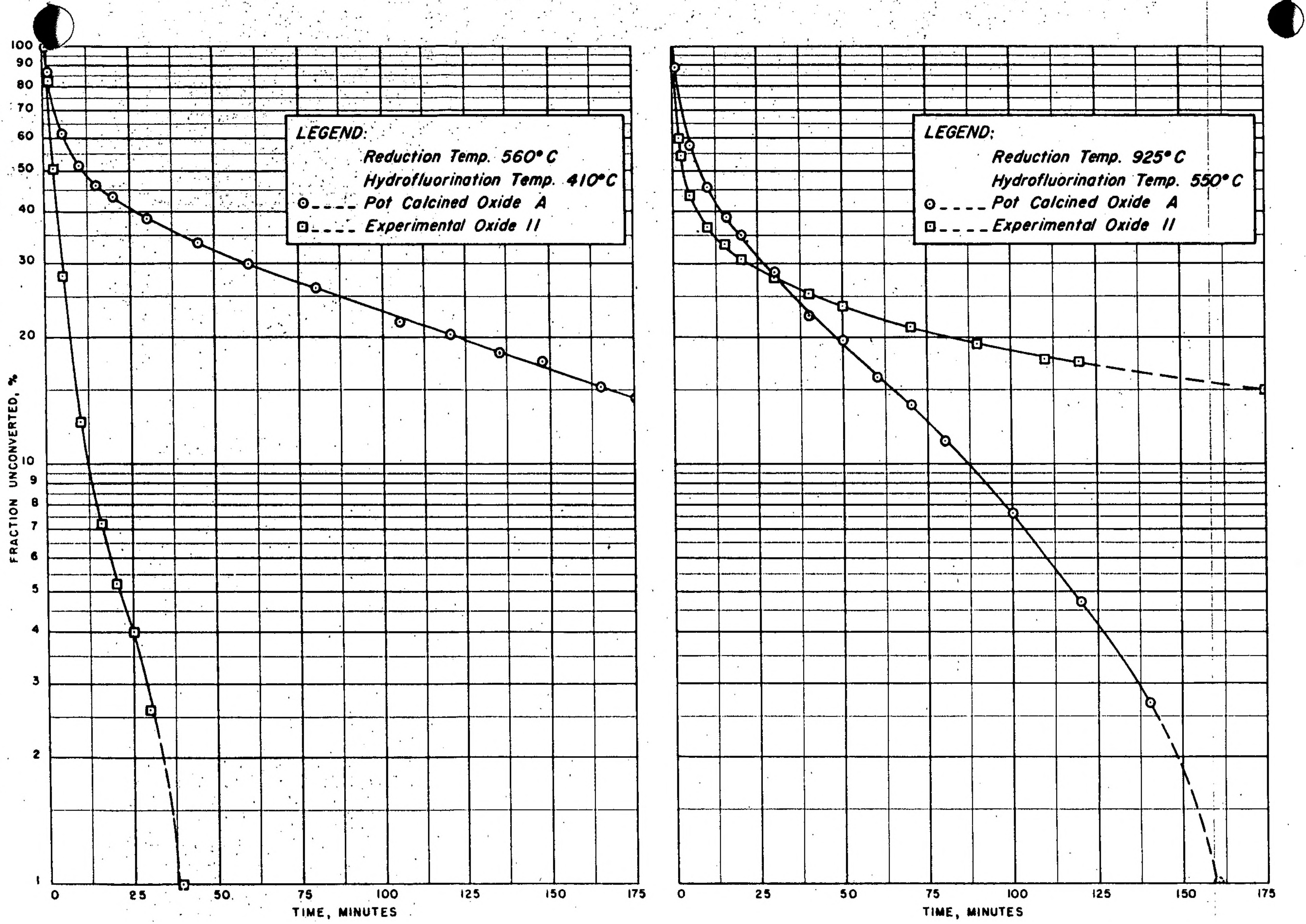

ESTIMATION OF PLANT PERFORMANCE BY COMPARISON OF HYDROFLUORINATION REACTIVITIES

FIGURE 8

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ANALYTICAL CHEMISTRY CONSIDERATIONS

by

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Soon after the end of the war, statements were made that ton quantities of uranium of atomic weight purity were manufactured on a production basis. Although this statement may be a bit on the drastic side, it nevertheless gives an indication of the purity of materials needed for the atomic energy program. To obtain this purity, constant control by analysis is required.

Since it may be necessary to analyze for most of the elements found in nature, the problem at first appears formidable. Early in 1942 it was found that many of the required elements could be determined by spectrochemical means. By the end of the war, methods had been developed for essentially all of the elements required, and many of these methods were published in the National Nuclear Energy Series.[1] A compendium of analytical procedures in present use has been compiled. The specifications for UO_3, UF_4, and UF_6 are given in Table I.

The analyses required are divided into the determination of macro constituents and the determination of micro constituents. The determination of the macro constituents such as total uranium, nitrate content, etc., are simple chemical operations which can be performed in any modern analytical chemistry laboratory.

The analysis for micro constituents is an entirely different problem. Here it is necessary to determine certain elements in the parts per million range or less to a precision which is generally not considered possible by usual analytical chemistry methods. The need for analyses in this range is because of the absorption of neutrons by many elements, the effect of certain impurities in the gaseous diffusion plant, and the effect that certain trace elements have on uranium metal made from the products under consideration. In some instances the presence of very small amounts of impurities make a material worthless for use in reactors. Tables II and IIA show the neutron absorbing effect of some of the most important elements.

TABLE I

PROPOSED SPECIFICATIONS FOR UO_3

Item	No.	Specifications
Assay (on sample basis)	1.	81.5 wt. % Total uranium minimum
	2.	1.0 wt. % HCl insoluble maximum
	3.	0.85 wt. % NO_3 maximum
	4.	1.0 wt. % water maximum
Physical Properties (on sample basis)	5.	Free flowing, uniformly mixed powder with bulk density of 2.4 and tap density of 3.5 gm./cc. minimum
	6.	Minimum of 98% thru 40 mesh screen Minimum of 80% thru 80 mesh screen From 45 to 70% thru 325 mesh screen
Maximum Impurity Levels (on U basis)	7.	Gd at 0.05 ppm maximum
	8.	Dy 0.10 " "
	9.	B 0.20 " "
	10.	Th 50 " "
	11.	Cd 0.20 " "
	12.	Ag 1 " "
	13.	V 30 " "
	14.	Cu 50 " "
	15.	Ni 15 " "
	16.	Cr 10 " "
	17.	Fe 30 " "
	18.	C 100 " "
	19.	Si 20 " "
	20.	Mn 5 " "
	21.	Mo 1 " "
	22.	P 50 " "
	23.	S 50 " "
	24.	A maximum of 250 ppm is allowed for elements forming non-volatile fluorides (which are defined as those having a vapor pressure of 1 atmosphere at or above 300°C) such as Na, K, Ca, Mg and Al.
	25.	In addition to the above specifications, undue contamination will constitute a basis for rejection or renegotiation of price.
Other	26.	Nominal lot size for sampling recommended at 10,000 pounds.

Table I contd.   PROPOSED SPECIFICATIONS FOR UF_4

Item	No.	Specifications
Assay (on sample basis)	1.	96.0 wt. % UF_4 minimum
	2.	1.9 wt. % AOI maximum
	3.	1.0 wt. % UO_2F_2 minimum
	4.	2.5 wt. % UO_2F_2 maximum
Physical Properties (on sample basis)	5.	Free flowing, uniformly mixed powder with tap density of 3.0 gm./cc. minimum
	6.	Minimum of 98% thru 40 mesh screen Minimum of 80% thru 80 mesh screen From 45 to 70% thru 325 mesh screen
Maximum Impurity Levels (on U basis)	7.	Gd at 0.05 ppm maximum
	8.	Dy 0.10 " "
	9.	B 0.20 " "
	10.	Th 50 " "
	11.	Cd 0.20 " "
	12.	Ag 1 " "
	13.	V 30 " "
	14.	Cu 70 " "
	15.	Ni 65 " "
	16.	Cr 20 " "
	17.	Fe 60 " "
	18.	C 100 " "
	19.	Si 20 " "
	20.	Mn 10 " "
	21.	Mo 1 " "
	22.	P 50 " "
	23.	S 100 " "
	24.	A maximum of 250 ppm is allowed for elements forming non-volatile fluorides (which are defined as those having a vapor pressure of 1 atmosphere at or above 300°C) such as Na, K, Ca, Mg, and Al.
	25.	In addition to the above specifications, undue contamination will constitute a basis for rejection or renegotiation of price.
Other	26.	Nominal lot size for sampling recommended at 10,000 pounds.

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TABLE I contd.

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8. All analyses shall be performed on representative samples withdrawn in the liquid state from each cylinder.

TABLE II

THERMAL NEUTRON ABSORPTION BY IMPURITIES

	Specification Impurities	
Element	Danger Coefficient[a] K(U)	PPM for 0.01% A[b]
Gd	9090	0.011
B	2160	0.046
Cd	703	0.14
Dy	210	0.48
Ag	18	5.6
Mn	7.4	13.5
Ni	2.6	39
V	3.1	32
Cu	1.8	56
Fe	1.4	71
Cr	1.7	57
Th	0.94	107
Mo	0.81	124
S	0.47	211
P	0.19	526
Si	0.14	699
C	0.008	1130

[a] Absorption of neutrons by the impurity compared to the absorption by an equivalent amount of uranium.

[b] Parts per million of impurity in uranium which gives a thermal neutron absorption of 0.01%.

TABLE IIA

THERMAL NEUTRON ABSORPTION BY IMPURITIES
(Not considered in Specifications for UO_3 and UF_4)

Element	Danger Coefficient $K(U)^a$	PPM/0.01% A^b
Li	310	0.3
Ir	69	1
In	51	2
Rh	45	2
Co	19	5
Hf	18	6
Sc	17	6
Au	15	6
Re	14	7
Cs	6.8	15
Se	4.6	22
Ta	3.6	28
Ti	3.6	28
Os	2.4	42
Pd	2.3	43
W	3.2	31
As	1.7	59
Pt	1.3	78
Ga	1.2	81
Ge	1.0	100
Ru	0.75	133

a. Absorption of neutrons by the impurity compared to the absorption by an equivalent weight of uranium.

b. Parts per million of impurity in uranium which gives a thermal neutron absorption of 0.01%.

H, N, Cl, K, Br, I, Hg with K(U) 10, 4, 27, 2, 3, 2 and 59 respectively, and elements with K(U) less than one, not listed.

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Tables III and IIIA show the proposed specifications for trace elements in UO_3, UF_4 and UF_6.

TABLE III

MAXIMUM IMPURITY OF TRACE ELEMENTS IN UO_3 AND UF_4

Element	Method of Analysis	Parts per Million
Gd	(1)	0.05
Dy	(1)	0.10
B	(4)	0.20
Th		50
Cd	(4)	0.20
Ag	(4)	1
V	(4)	30
Cu	(4)	50
Ni	(3)	15
Cr	(4)	10
Fe	(3)	30
C		100
Si	(4)	20
Mn	(4)	5
Mo		1
P	(4)	50
S		50

TABLE IIIA

MAXIMUM IMPURITY OF TRACE ELEMENTS IN UF_6

Element	Method of Analysis	Parts per Million
B		1
V		1
Cr	(4)	25
Si	(4)	100
Mo	(2)	1
P	(4)	50
Br	(2)	1
Cl	(2)	100
Ru	(1)	n.d. Limit 1
Nb	(1)	" 3
Ta	(1)	" 40
Ti	(1)	" 3

(1) Analyzed spectrographically on chemical concentrates.
(2) Chemical Analysis.
(3) Chemical or spectrographic analysis.
(4) Spectrographic Analysis.

Some of these elements are unfamiliar to many chemists. Fortunately, spectrographic methods have been developed for the determination of most of these elements. Some of these elements may be determined directly while others have to be concentrated before analysis.

Uranium is characterized by exceedingly complex spectra derived from a multiplicity of electron configurations in both the neutral and ionized atoms. The ionization potential is low, probably near that of cesium, consequently it is difficult to separate the spectra arising from neutral and ionized atoms. The rich line spectrum is further confused by a heavy background attributed to unresolved, weak lines and to continuous radiation of solid particles, characteristic of the spectra elements forming refractory oxides. As a result of these properties, the direct excitation of uranium materials by the common methods, employing the d.c. arc, the a.c. arc, and higher-energy, condenser discharges, produces highly complex spectra. Thus, little or no choice is offered for the simplification necessary to the observation of impurity lines at low impurity concentrations. The possibility of employing a spectrograph of very high dispersion, for example, 1 A per mm or better, to resolve the thousands of lines and reduce the background is not a practicable solution for most laboratories in view of the space requirements for the equipment and the large number of photographic plates or films necessary to cover the spectral range for a variety of impurity elements. For the majority of analytical laboratories, the practical limitation of dispersion is represented by that available in the large commercial instruments, for example, grating spectrographs having a dispersion of 5 A per mm in the first order and 2.5 A per mm in the second order. With an instrument of this type it is possible, by direct arcing of a uranium oxide sample, to determine calcium with a limit of detection of two parts per million. However, this is an exceptional case; for the majority of elements the dispersion is far from that necessary for the direct observation of impurities at the low concentrations desired in the analysis. The alternative to direct observation of the spectrum is the separation of the impurities from the uranium matrix, followed by spectrographic determination. The system of methods to be described includes four concentrational in which 33 volatile impurity elements may be separated from the uranium matrix by fractional distillation, using gallium oxide, and their arc spectra simultaneously recorded to permit spectrographic determination. The three remaining methods provide chemical separation of three groups of the more refractory elements, namely, the rare earth concentrate, the zirconium-group concentrate and the platinum-group concentrate. These methods, combined with direct determination of calcium in the analytical scheme, permit the determination of 63 chemical elements in uranium-base materials in most cases of a few parts per million and extending in important cases to the order of 0.01 part per million.

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Chemical methods are the basis for the above spectrographic methods. Some of these chemical methods are time consuming and all require strict adherence to detail in order to obtain satisfactory results.

In order to check chemical and spectrographic procedures, reference samples have been prepared. Reference samples of UF_4 and UO_3 are available. These samples are materials of regular production which have been analyzed for the constituents usually found in these materials. Table IV shows analyses of such materials.

TABLE IV

ANALYSES OF TYPICAL PLANT PRODUCTS

UO_3	
Total Metal	82.19%
HCl Insoluble	0.36%
UO_3 Assay (calculated)	98.51%
Chromium	< 4 ppm
Nickel	a 4 ppm
Iron	10 ppm
Boron	< 0.2 ppm

UF_4	
Total Metal	75.93%
Tetra Assay (U^{+4})	74.83%
Ammonium Oxalate Insoluble (UO_2)	0.98%
Uranyl Fluoride (Water Soluble) (Calculated)	1.41%
UF_4 Assay (Calculated)	97.57%
Iron	13 ppm
Copper	< 2 ppm
Nickel	10 ppm
Chromium	4 ppm

Spectrographic analysis relies on samples of U_3O_8 containing varying amounts of added impurities. Table V shows standards used in the analysis of an uranium oxide matrix.

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TABLE V

U_3O_8 STANDARDS FOR SPECTROSCOPIC ANALYSIS

Values in ppm
Based on metal

	A	B	C	D	E	F	Standard Matrix X
Element	B-135	B-136	B-137	B-138	B-139	B-140	B-441
Al (a)	500	200	100	50	20	10	-
Fe (c)	491	216	93	44	22	19	< 5
Mo (c)	689	190	94	112	19	9	-
P (c)	474	208	101	50	21	11	-
Si (a)	500	200	110	60	30	20	e 10
V (c)	584	237	114	57	25	13	-
Zn (p)	507	165	106	55	20a	10a	-
Bi (a)	50	20	10	5	2	1	-
Co (a)	50	20	10	5	2	1	-
Cu (p)	66	28	11	6	3	2	e 1
Mg (a)	50	20	10	5	2	1	< 1
Mn (c)	496	209	100	53	22	11	-
Ni (p)	42	19	11	6	2a	1a	-
Pb (p)	66	30	9	5	2a	1a	-
Sn (a)	50	20	10	5	2	1	-
Ag (a)					e5	e3	< 0.1
B (c)	13	3.4	2.7	2.0	0.7	0.35	< 0.2
Cd (p)	9	2.4	2.4	0.6			

Note:-	(a)	element added to matrix
	(c)	element chemically determined
	(p)	element polarographically determined
	e	estimated
	-	not detected

Since rare earths such as gadolinium and dysprosium are not determined direct but on a chemically prepared concentrate using lanthanum as a carrier, these elements are not included in the above. Table VI shows standards used for such determinations.

TABLE VI

RARE EARTH STANDARDS

Element	Microgram Equivalent (Microgram R.E./1 mg La)						
	Std.	A	B	C	D	E	Blank
Gd		100	50	20	10	5	0
Eu		100	50	20	10	5	0
Dy		100	50	20	10	5	0
Er		100	50	20	10	5	0
Sm		100	50	20	10	5	0

$$\text{part per million of R.E.} = \frac{\text{Microgram equivalents}}{\text{wt. of sample in grams}}$$

It is expected that some quantities of the above reference samples and standards can be made available for sale by the New Brunswick Laboratory on a continuing basis, in addition to some quantities of gallium oxide for carrier purposes on an interim basis.

In addition to the analyses required for the final product in any plant, there is a certain amount of analysis for process control.

Figures I and II show the control points and the analyses made at these points in a representative ether extraction type of plant. Figure III, IV, V and VI show similar points used in a representative tributyl phosphate type of plant. In addition there are several other points dealing with recovery problems where control analyses are made. These are indicated in Table VII.

LEGEND FOR FIGURES 1 AND 2

Ⓢ = sampling point
D = days
A = acid normality
G = specific gravity
AOI = ammonium oxalate insoluble
A-1 = nitric acid insoluble

The remaining are as indicated such as: U, UF_4, Fe, Ni, U^{+4}, UO_2, HF, O_2, H_2, Mo, and pH.

LEGEND FOR FIGURES 3, 4, 5 AND 6

Ⓢ = sampling point
D = days
M = months
A = acid normality
F = fluorides
G = specific gravity
T = Tributyl phosphate
S = spectrographic analysis
A-1 = nitric acid insoluble
BD = bulk density
R = reactivity
AOI = ammonium oxalate insoluble
PS = particle size

The remaining are as indicated such as: U, Fe, Ni, CO_2, O_2, H_2, U^{+4}, UO_2, UO_2F_2, UF_4, KOH, HF, NO_3, UO_3 and screen.

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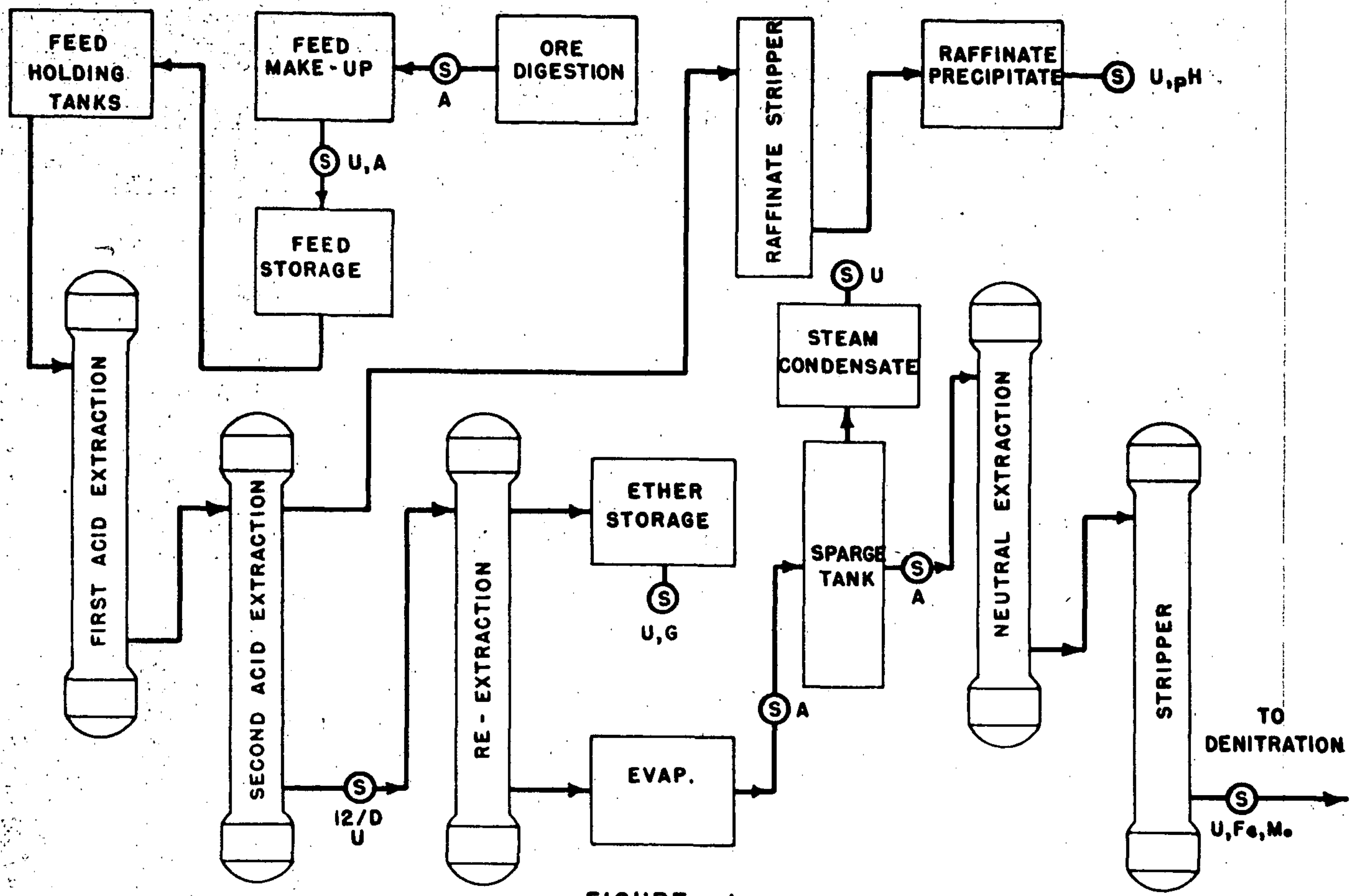

FIGURE - I
DIGESTION AND EXTRACTION SECTIONS

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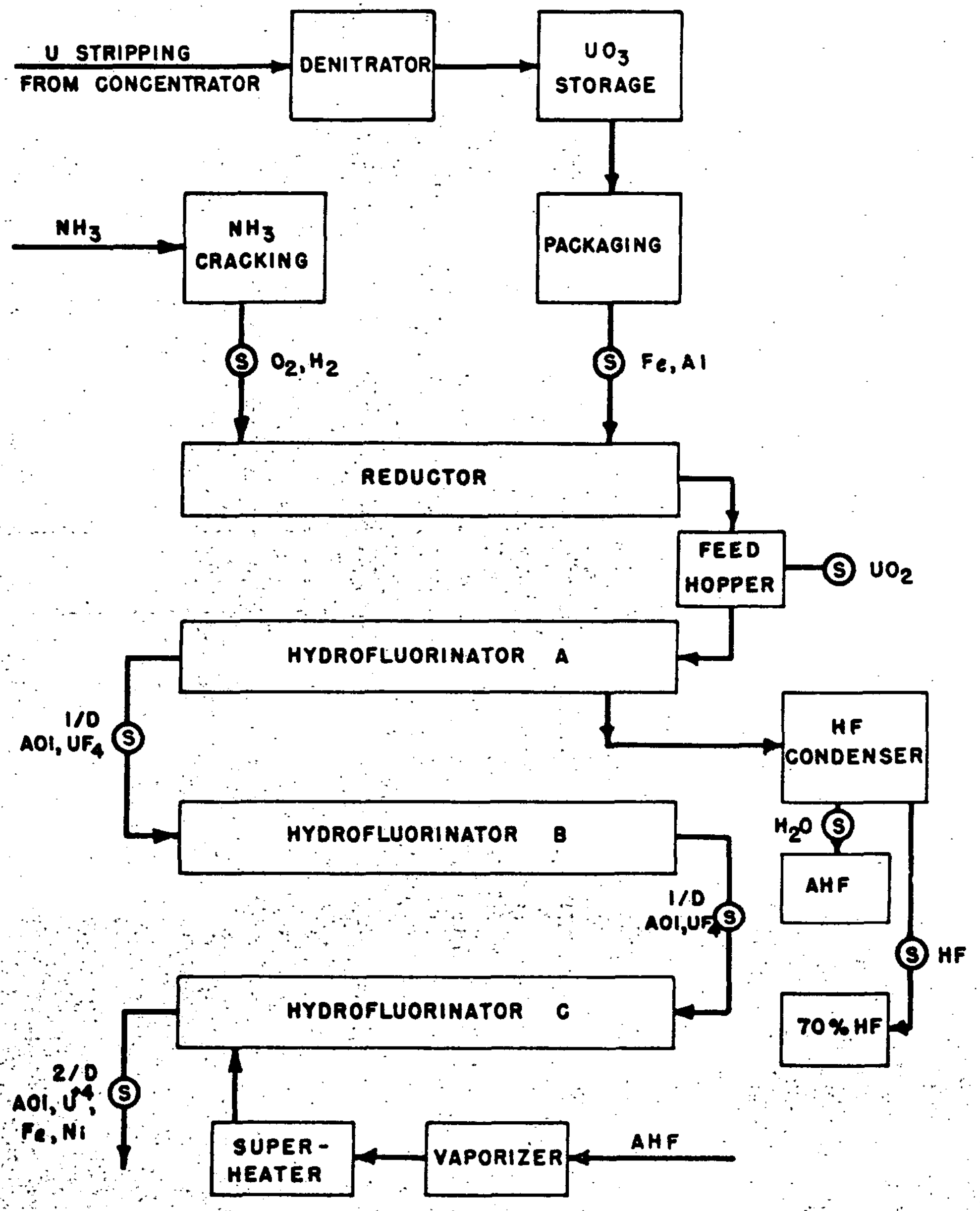

FIGURE - 2
DENITRATION, REDUCTION & HYDROFLUORINATION SECTIONS

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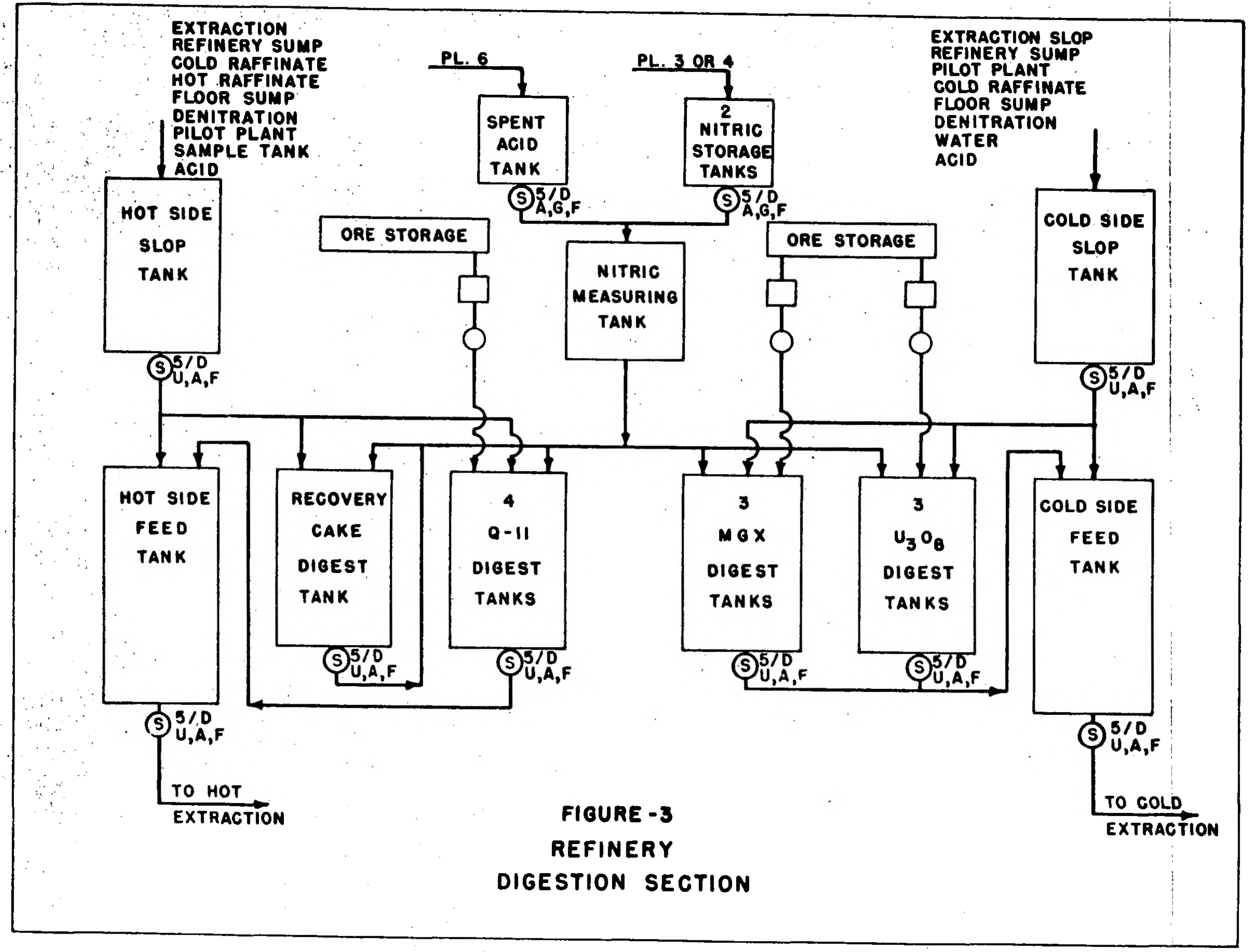

FIGURE - 3
REFINERY
DIGESTION SECTION

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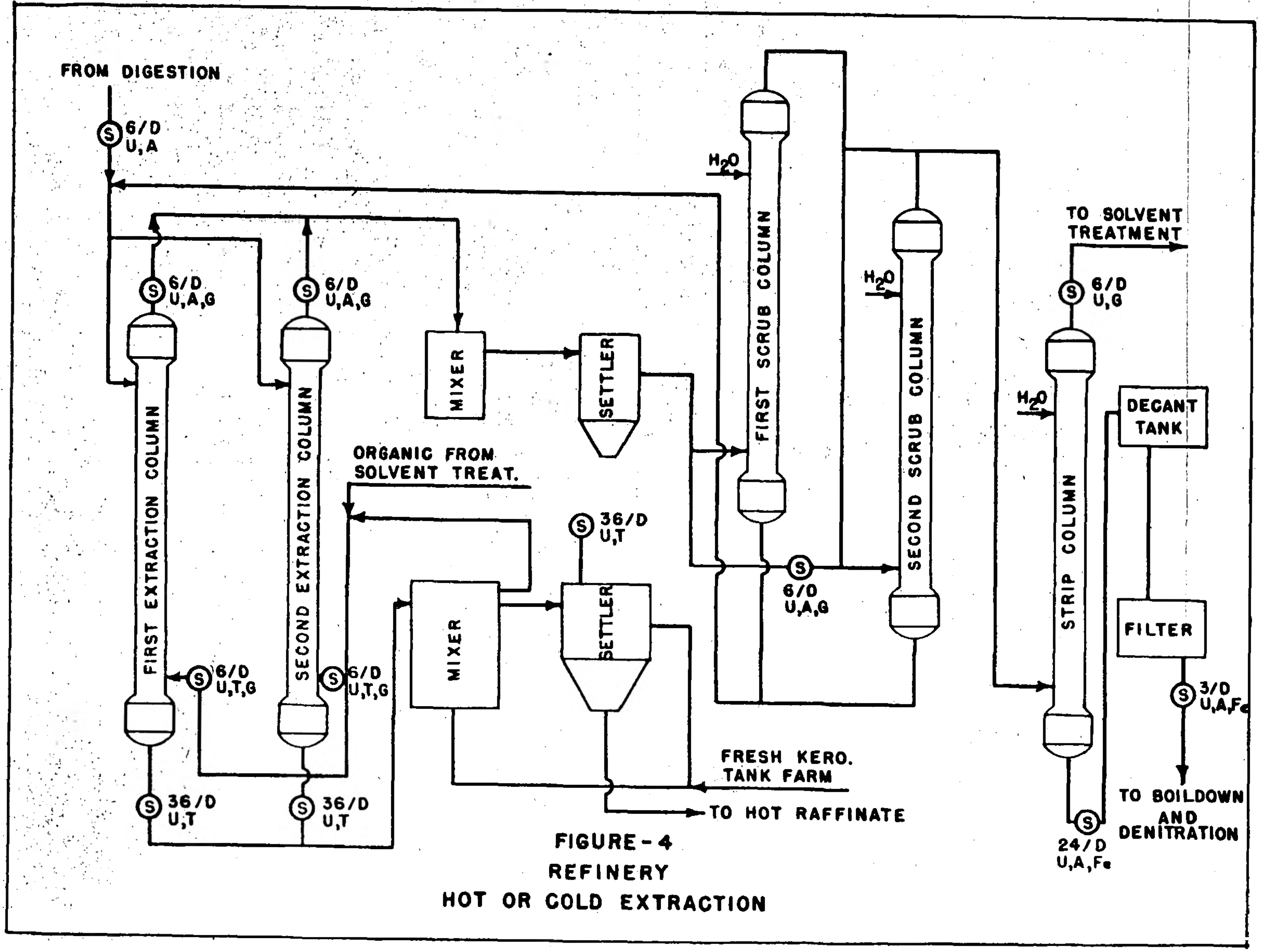

FIGURE - 4
REFINERY
HOT OR COLD EXTRACTION

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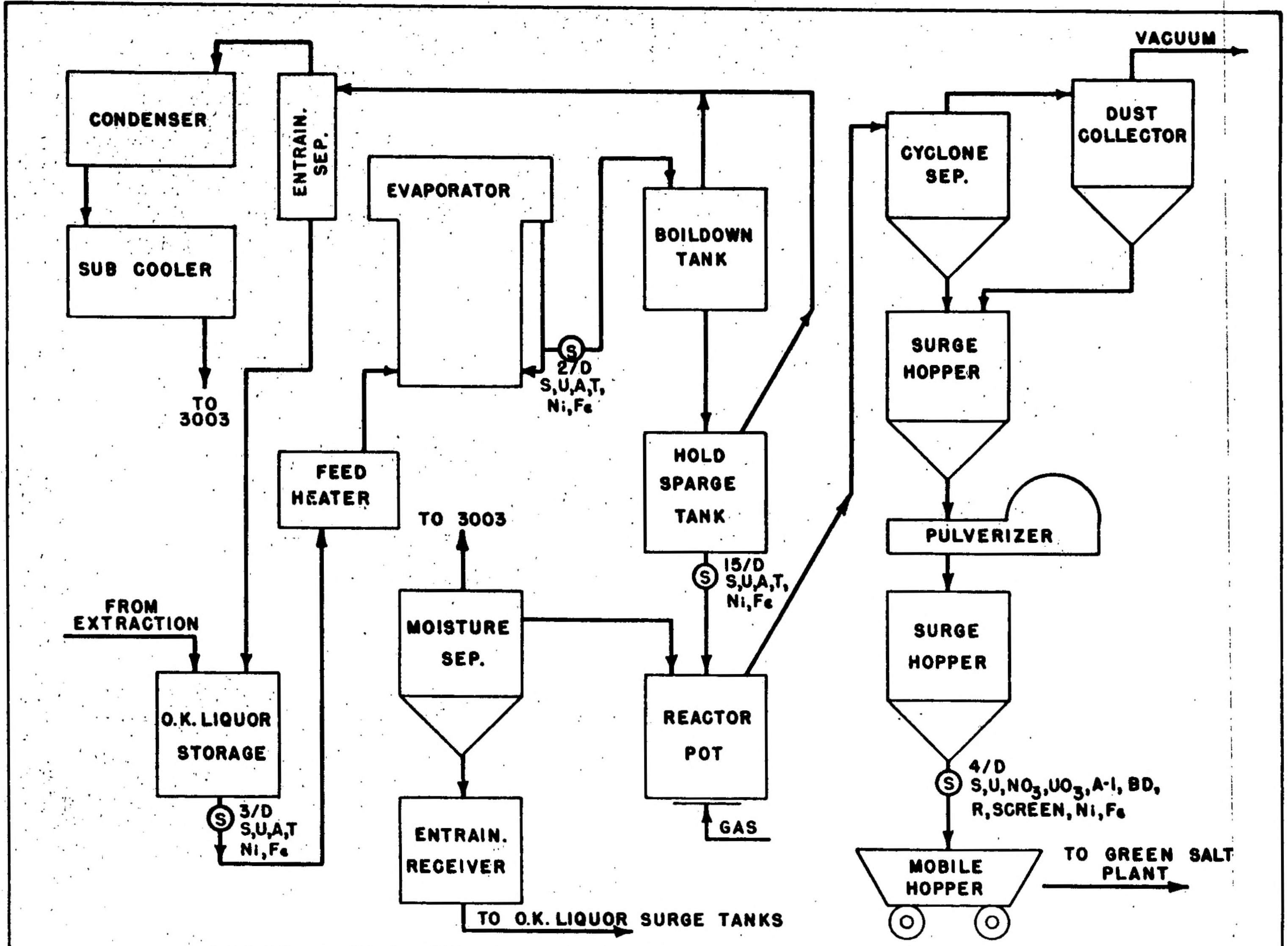

FIGURE - 5 BOILDOWN & DENITRATION SECTION

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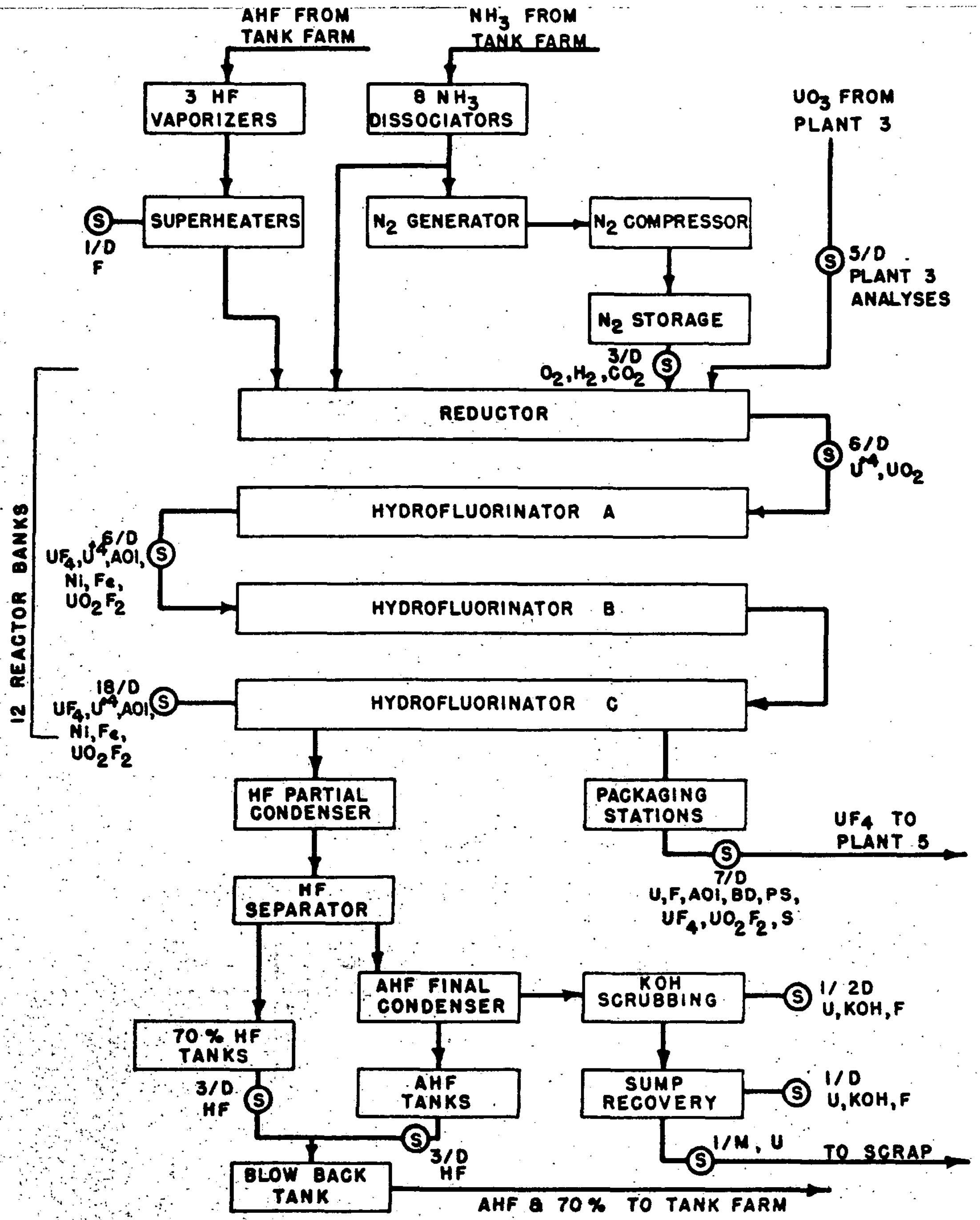

FIGURE - 6

REDUCTION AND HYDROFLUORINATION

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TABLE VII

WASTE RECOVERY ANALYSES

Type of Sample	Analyses	Frequency of Sampling
Hot Raffinate Section		
Hot raffinate	U, TBP	6 per day
Raffinate filtrate	U, TBP, Ra	3 per day
Clear liquor	U, Ra	1 per 2 days
Filtrate	U, Ra	1 per 2 days
Cake slurry	Ra, Au, Wgt. % solids, U	1 per 2 days
Refinery Sump		
Sump effluent	U, NO_3, pH	9 per day
Neutralizer tank	U, NO_3, Ni, Co, Fluorides	3 per day
Cake slurry	U, pH, Fluorides	3 per day
General Sump		
Hold tank	U, NO_3, Fluoride	3 per day
Hold tank	U, NO_3, Fluoride	3 per day
Hold tank	U, NO_3, Fluoride	3 per day
Hold tank	U, NO_3, Fluoride	3 per day
Combined Raffinate		
Hold tank (top)	U, TBP, Cl, Insol. solids	8 per day
Hold tank (bottom)	U, TBP, Cl, Insol. solids	8 per day
Calciner feed	Acid normality, NO_3, H_2O Sp.G., Insol. solids, Fe	3 per day
Nitric Acid Recovery		
Concentrator series	HNO_3, Cl, Fluoride	6 per day
Ozone tank	HNO_3, Cl, Fluoride	1 per day
Acid storage	HNO_3, Fe, Ni, Fluoride	1 per day
Acid storage	HNO_3, Fe, Ni, Fluoride	1 per day
Gas sample	Oxides of nitrogen, O_2, N_2	1 per week
Gas sample	Oxides of nitrogen, O_2, N_2	1 per week
Gas sample	Oxides of nitrogen, O_2, N_2	1 per week
Gas sample	Oxides of nitrogen, O_2, N_2	1 per week
Absorber	HNO_3, Cl, Fluoride	1 per day
Acid storage	HNO_3	1 per day

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RECLAMATION OF URANIUM SCRAP MATERIALS RESULTING FROM UO_3 AND UF_4 PRODUCTION

by

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The types of uranium bearing scrap materials generated during the production of UO_3 and UF_4 at the AEC's Feed Materials Production Center at Fernald, Ohio are listed and their points of origin, uranium assays and methods of treatment for uranium recovery are discussed. An estimate of the quantities of the various scrap materials to be expected during the operation of a UF_4 production plant (5000 tons U_3O_8/year) is given.

INTRODUCTION

The relative economic success of many industrial processes is often contingent on the recovery of valuable constituents from waste or scrap materials. Such is the situation in the refining and fabrication of uranium metal where sizable quantities of scrap materials are generated and the need for an extremely pure product causes a certain amount of off-specification materials to be produced. The high monetary value of uranium has necessitated an extensive recovery program in uranium refining operations. The National Lead Company of Ohio, in its operation of the AEC's Feed Materials Production Center (FMPC) at Fernald, Ohio has become intimately involved in this type of activity. The FMPC Metal Recovery Plant recovers uranium from the various scrap materials generated in its own refining and fabrication operations and from essentially all of the scrap materials produced by the various AEC sites throughout the country. However, only a minor per cent of the total uranium tonnage recovered from the internal scrap at FMPC, results from the production of UO_3 and UF_4, the bulk of the scrap emanating from metal production and fabrication. It is the purpose of this paper to review in detail the generation of off-specification and scrap materials during the production of UO_3 and UF_4 based upon the experience obtained during similar operations at Fernald.

SCRAP GENERATION AS RELATED TO UO_3 AND UF_4 PRODUCTION

At Fernald, the production of uranium metal begins with the receipt and sampling of uranium ore concentrates. These concentrates are sent to the ore refinery where they are digested in nitric acid and the uranium, in the form of uranyl nitrate, is extracted from the resulting slurry by means of a mixture of tributyl phosphate and kerosene in perforated-plate pulse columns. The uranyl nitrate is then re-extracted from the organic phase with water and the resulting aqueous solution is evaporated. The concentrated solution is thermally decomposed, or denitrated, to uranium trioxide in gas-fired denitration pots. This material constitutes the feed for the UF_4 or Green Salt Plant. In this plant the UO_3 is reduced to uranium dioxide by hydrogen and hydrofluorinated to uranium tetrafluoride by anhydrous hydrogen fluoride in electrically-heated reactor banks.

In the course of the production of UO_3 and UF_4, several uranium-bearing scrap materials are generated which are reprocessed by one of several methods for recovery of the contained uranium. Following is a list of these materials, their average assay, their point of origin in the UO_3 and UF_4 processes, and an estimate of the tonnages of each scrap to be expected during the operation of a plant producing 5000 tons of U_3O_8 per year as specification UF_4.

TYPES OF SCRAP RESULTING FROM UO_3 PRODUCTION

Off-Specification UO_3 - is material which does not meet finished product specifications with respect to contaminants and which cannot be blended with good product to yield a mixture which meets specifications. This material has been found to have an average assay of 65 per cent uranium.

Metal oxides - result from the evaporation and calcination of solvent extraction raffinates during the

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recovery of nitric acid. This material contains an average assay of <0.2 per cent uranium.

Contaminated sand and soil - results from the excavation of outside ground areas where uranium bearing materials have been spilled. The uranium assay of this type of scrap varies markedly - averaging 2 per cent.

Contaminated kerosene - results from the treatment of solvent extraction raffinates for the removal of traces of tributylphosphate. This material averages 0.035 g/l. uranium.

Sump liquors - result from equipment cleanup processing spills and pump seals. The uranium content of these liquors range from 1 to 5 g/l.

TYPES OF SCRAP RESULTING FROM UF_4 PRODUCTION

Scrap UF_4 - is material averaging 78 per cent uranium and consists of (1) floor sweepings, (2) clean-out from reactor tubes when removing the flight screws for repair, (3) reblend material which has subsequently been declared scrap due to high metal contamination, UO_2F_2 content or ammonium oxalate insoluble (AOI), and (4) dust collector residues consisting of UO_2, UO_3, and UF_4.

Sump cake - results from the filtration of building sump liquors and spent, contaminated KOH scrubbing liquors. This material contains fluorides and averages 3 per cent uranium.

Carbon tubes - This material consists of broken and damaged porous carbon tubes removed from the Adams filters, which are used to remove entrained UF_4 dust from reactor off-gases. This material averages 5 per cent uranium.

Contaminated cloth - results from broken or damaged dust collector bags which contain an average of 8 per cent uranium.

Metal filters - this material, averaging 33 per cent uranium, consists of fine monel hair removed from hair filters. These filters are located in the reactor off-gas lines downstream of the Adams filters to insure complete removal of entrained UF_4 dust from the reactor off-gases prior to KOH scrubbing.

ESTIMATED SCRAP GENERATION

The quantities of the various scrap materials estimated to result from the production of 5000 tons of U_3O_8 per year as specification UF_4 are presented in Table I. These figures were estimated from the information available from similar operations conducted at FMPC during fiscal year 1955.

TABLE I

GENERATION OF URANIUM BEARING SCRAP MATERIALS DURING THE PRODUCTION OF UO_3 AND UF_4

(Basis: 5000 tons U_3O_8/year as specification grade UF_4)

Scrap Material	Quantity Produced (lbs U/year)	Average Assay (% U)
UO_3 Production		
Contaminated Kerosene	100	.035 gms/liter
Contaminated Sand and Soil	900	2.0
Metal Oxides	3,500	<0.2
Off-specification UO_3	5,600	65
Sump liquors	No available estimate	1-5 gms/liter
UF_4 Production		
Scrap UF_4	406,000	78
Sump Cake	900	3
Contaminated Cloth	50	8
Carbon tubes	200	5
UF_4 and Metal Filters	12	33

RECLAIMING PROCESSES

It is the purpose of the uranium reclaiming operation (as employed at FMPC) to convert the uranium in the various scrap materials into a form which can be reintroduced into the refining operations. In the case of the scrap materials resulting from the production of UO_3 and UF_4, the uranium is converted into a form suitable for use as a feed material, i.e., containing no contamination which is detrimental to refinery processing from either corrosion or extraction standpoints.

DIRECT REFINERY PROCESSING

Several of the scrap materials produced are recycled directly as a feed material without any prior treatment (other than occasional grinding) as they contain no contamination which is detrimental to refinery processing. Materials that are processed directly as a feed material are (1) off-specification and scrap UO_3, (2) sump cake (halide free) and (3) spills and washings not processed to sump cake.

PYROHYDROLYSIS

Off-specification UF_4 and scrap materials containing UF_4 (such as dust collector residues and floor sweepings) are treated by a high temperature hydrolysis to convert the contained UF_4 to U_3O_8. This reaction is represented by the following equation:

$$3UF_4 \ / \ O_2 \ / \ 6H_2O\ (g) \xrightarrow[1\ \text{hr.}]{1500\ \text{F}} U_3O_8 \ / \ 12HF$$

It has been found that this reaction is essentially quantitative.[1]

In practice, the pyrohydrolysis operation has been conducted in two different units. These are described below:

<u>Muffle Furnace</u> - The muffle furnace and auxiliaries illustrated in Figure 1, are used in the pyrohydrolysis of UF_4 and scrap materials containing a high percentage of UF_4.

This is a single hearth furnace consisting of a steel shell lined with Mullite refractory brick, and a muffle dome constructed of 3/8" Inconel. The furnace is heated by means of two burners; one installed above the dome

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MUFFLE FURNACE LAYOUT FOR THE PYROHYDROLYSIS OF UF$_4$

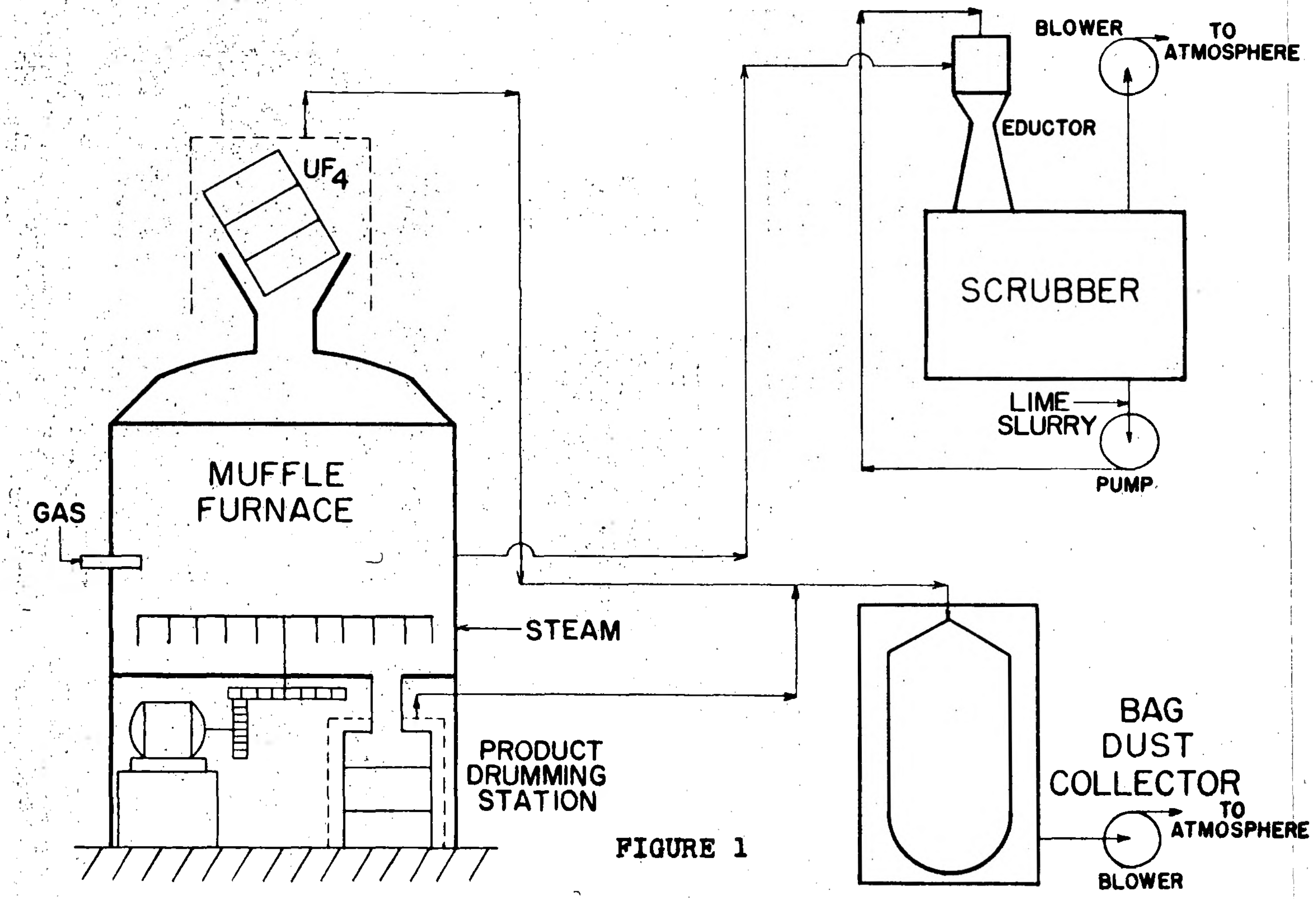

FIGURE 1

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and the other just above the hearth.

Scrap material is fed to the furnace through an Inconel feed chute. The material is rabbled back and forth across the hearth by means of a rabble arm (20% chromium, 3% nickel, 77% iron alloy) whose drive mechanism causes it to change direction every few minutes. Steam is introduced into the furnace through a line in the side of the hearth. After the necessary reaction time has elapsed, the material is rabbled out of the furnace through a discharge port and into a product drum. The off-gases from the furnace pass through a 304 ELC stainless steel flue to a lime slurry scrubber (Schutte-Koerting) where the HF is neutralized. The scrubbed gases are then vented to the atmosphere through a blower. Dusting which occurs in the drum dumper and product drumming station is controlled by venting these units to a bag-type dust collector (Day). The collected dust is drummed and recycled to the furnace.

Screw Reactor - A technique used for continuously pyrohydrolyzing materials containing UF_4[2], consists of contacting the material with steam countercurrently in a screw reactor (Figure 2). Drummed scrap material is dumped into a feed hopper and passes over a vibrating screen. The oversize is collected in a drumming station and is pulverized and recycled. The undersize material is fed to the reactor by means of a small screw conveyor. The reactor shell is constructed of Inconel. The screw, constructed of Hastelloy "C", is of the ribbon-type to reduce the resistance to the passage of reactant and product gases. Heating is effected by nichrome strip heaters located on both sides of the reactor. Superheated steam is introduced at the discharge end of the reactor, passing countercurrently to the direction of solid flow. The material is discharged from the reactor through a port in its base and is transferred to a product drumming station by means of water cooled screw conveyor. The off-gases are conveyed to a cast iron scrubber (Schutte-Koerting) through a monel line and then vented to the atmosphere through a blower. Here again the dust produced by the drum dumping and the oversize product drumming stations is collected in a bag-type dust collector (Amerjet) and drummed for return to the reactor.

OTHER

The uranium present in contaminated soil, sump cake (containing halides) and ashes from the incineration of contaminated cloth is recovered in the form of a uranium

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SCREW REACTOR LAYOUT FOR THE PYROHYDROLYSIS OF UF_4

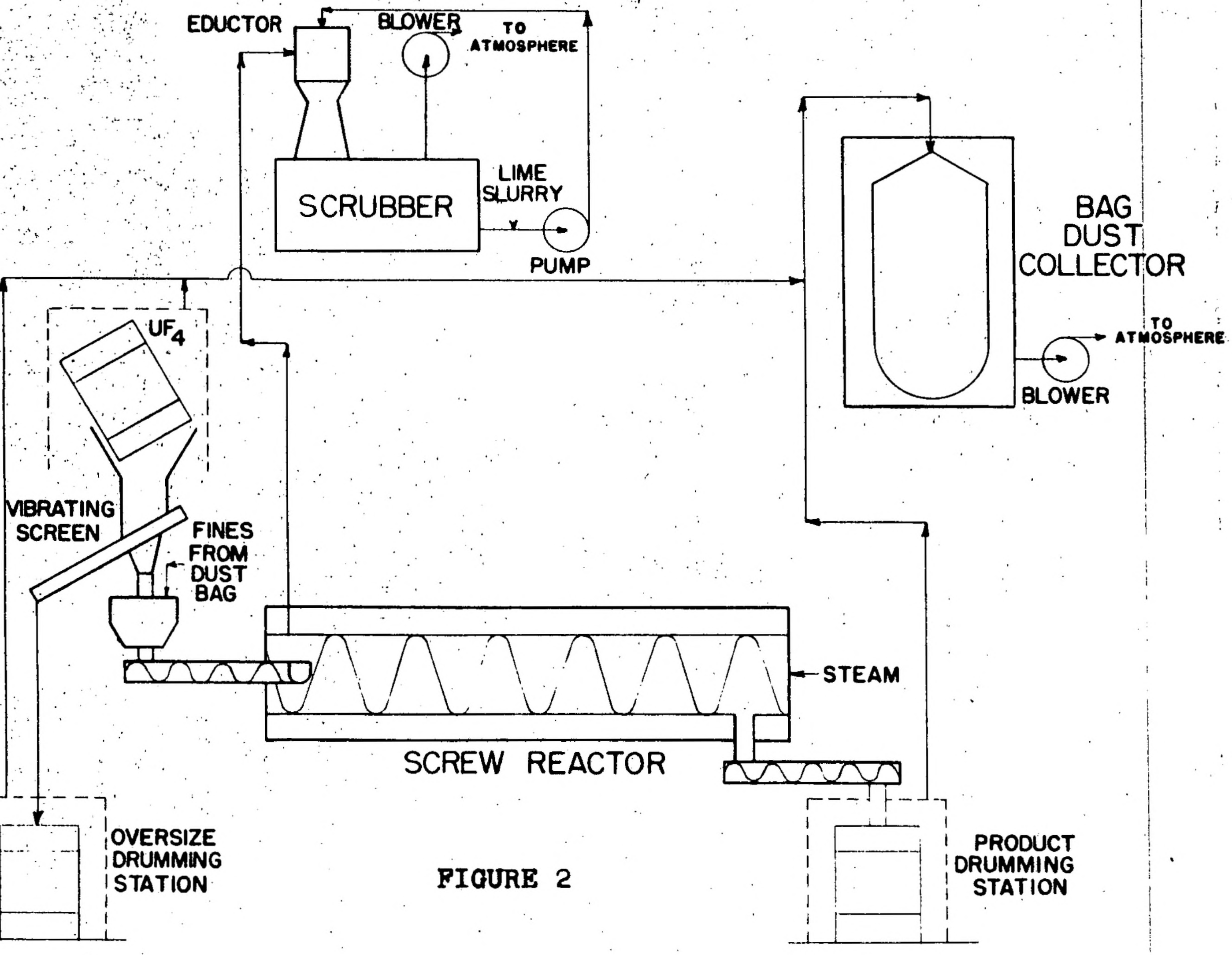

FIGURE 2

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concentrate by dissolution in hydrochloric acid followed by precipitation of the filtered liquors with ammonium hydroxide (pH 6.0). The Fernald plant produces sizable tonnages of scrap in other operations which are processed in this manner. The uranium bearing scrap generated during UO_3 and UF_4 production represents only a very small percentage of the total scrap handled by this technique.

The sump liquor resulting from UO_3 production is neutralized to pH 8.0 with MgO and filtered. The resulting filter cake is sluiced back into the nitric acid digestors in the ore refinery for processing with incoming feed materials.

No attempt has been made to recover the uranium from contaminated kerosene, metal oxides or metal filters.

SUMMARY

The uranium present in the majority of the scrap materials resulting from the production of UO_3 and UF_4 at FMPC are recovered by (1) recycling directly to the nitric acid digestion - solvent extraction system and by (2) subjecting materials containing UF_4 to a pyrohydrolytic treatment prior to introduction into the latter system.

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(2) Teter, E. K., Final Report of Pilot Plant Work Done on the Reversion of UF_4 to UO_2 by Continuous Methods, NYO-1321, March 8, 1951.

THE CONTINUOUS CONVERSION OF URANIUM TETRAFLUORIDE TO URANIUM HEXAFLUORIDE WITH FLUORINE IN TOWER REACTORS AND THE DESIGN AND OPERATION OF A MULTIPLE CELL FLUORINE PLANT

by

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ABSTRACT

Uranium tetrafluoride is converted to uranium hexafluoride in a tower reactor which is designed to burn a finely divided powder in a stream of fluorine. The uranium tetrafluoride is screw fed and falls through a vibrating baffle assembly which tends to disperse the powder by breaking up agglomerates and soft lumps. This finely divided uranium tetrafluoride is easily ignited by preheated fluorine which is introduced through four jets surrounding the powder feed point. The outlet gas from the tower passes through (a) a cooler which removes a large part of the heat evolved in the reactor; (b) a filter which separates any entrained dust from the stream; (c) a recirculating gas blower which repasses excess fluorine to the tower to obtain maximum combustion and minimum ash rates; and (d) cold traps which remove the uranium hexafluoride product. The system is pressure and concentration controlled and any inleakage of non-condensable gases through pump seals and gas buffers is removed continuously. A specially designed fluorine clean-up reactor converts the fluorine in this stack stream to uranium hexafluoride which is recovered in cold traps. An alternate fluorination system design eliminates the gas recycle. Successful operation depends upon close control of gas and powder feed rates and efficient burn-up of excess

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fluorine from the tower reactors in a fluorine clean-up unit.

Fluorine is prepared by electrolysis in a multiple cell plant and each cell is capable of producing about 150 pounds of fluorine per day. Cells are normally operated at 8 to 10 volts and about 4,000 amps. without interruption until breakdown; the current efficiency is about 90%. The electrolyte is KF·2HF and the operating temperature is about 215°F. Auxiliaries to the banks of cells include a tempered water system, a direct current supply system, a large capacity ventilation system, a waste hydrogen fluoride disposal system, a dry nitrogen supply, a steam supply, and a process control laboratory. Important design considerations for a fluorine plant are that (1) a minimum of impurities be contained in product gases, (2)control be centralized, (3) production and using processes be linked, (4) cells be operated electrically in series, (5) long continuous operation be possible, (6) some capacity to store fluorine be provided, (7) the plant be safe to operate, and (8) raw materials be used efficiently. The principle routine maintenance consists of cell rebuilding and replacement, leak repair, pump and valve repair and replacement, and instrument calibration.

INTRODUCTION

Uranium hexafluoride is the stable gaseous compound used in the gaseous diffusion process for the separation of the isotopes of uranium. It is actually a solid at 70°F. with a vapor pressure of 1.5 psia.; at 133°F., the sublimation pressure of uranium hexafluoride reaches 14.7 psia. The vapor pressure curve is steep and at minus 55°F., the vapor pressure of uranium hexafluoride is 0.003 psia. The triple point of uranium hexafluoride is 147.3°F. and 22.7 psia.

Ruff, who had previously studied the volatile heavy metal fluorides, molybdenum and tungsten hexafluorides, suspected the existence of an analogous compound of uranium and, with Heinzelmann in 1909, succeeded in preparing it by the reaction of fluorine with uranium metal, uranium carbide, or uranium pentafluoride. For almost thirty years after Ruff's investigation, uranium hexafluoride received little attention and the few recorded preparations were all made according to his method. The fluorination procedure was substantially improved by Abelson who, about 1941 at the National Bureau of Standards, introduced the use of uranium tetrafluoride as the material to be exposed to elemental fluorine. He recommended a temperature of 525°F. and used fused sodium chloride as a catalyst. Both British and American workers found shortly thereafter that a catalyst was unnecessary and even detrimental to successful fluorination.

The first uranium hexafluoride feed for the Oak Ridge Gaseous Diffusion Plant was prepared by a batch process. Uranium tetrafluoride powder was loaded into Monel metal pans, and these pans were placed in furnaces operating at about 570°F. In the interests of gas economy, the furnaces were arranged in series; thus, fluorine admitted to the system had a long gas path and was completely consumed. Reaction rates were low since uranium tetrafluoride powder beds were deep (about 1 to 2 inches), and the bed surfaces rapidly became glazed from the formation of low melting intermediates UF_5, U_2F_9, and U_4F_{17}, which were stable at the operating conditions employed.[7] Many hours were normally required to complete the consumption of the powder charge. Additional handling problems developed from beta and gamma radioactive residues, as well as from uranium contamination resulting from the spread of the finely divided uranium tetrafluoride powder during loading operations.

Uranium hexafluoride continued to be produced by this batch process until 1950 when a feed plant was installed at the Oak Ridge Gaseous Diffusion Plant. Carbide engineers, during 1949 to 1950, had developed a continuous process for the production of uranium hexafluoride and the heart of the process was the tower reactor. It was found that finely divided uranium tetrafluoride powder and fluorine gas preheated to about 1000°F. would burn as a flame, and conversion would be essentially complete if a small fluorine excess were maintained and if the finely divided powder were well dispersed in the gas stream. It was also shown that the fluorine concentration was not critical and that efficient burning would occur with fluorine concentrations of 30 to 100 mol percent (the remainder being hydrogen fluoride, oxygen, and nitrogen). A 6-inch diameter tower, 10 feet high, was capable of converting at least 500 pounds of uranium tetrafluoride per hour to uranium hexafluoride.

A necessary auxiliary of a uranium hexafluoride plant is a fluorine manufacturing plant. Fluorine is produced in an electrolytic cell from a fused salt of KF•2HF by the electrolytic dissociation of hydrogen fluoride. The fluorine cells used at Oak Ridge and Paducah are of the medium temperature type[2-7]. The cells operate at 210 to 220°F. Fluorine is liberated at a carbon anode and hydrogen is liberated at a steel cathode. The first fluorine cells in Oak Ridge were constructed for 2,000 ampere operation. As production demands were increased, the cell was modified to extend heat transfer area and to enlarge carbon anode area. This new cell, which contained larger anodes, allowed operation up to 4,000 amps[8,9]. During the past year, considerable experience has been gained in the performance of a still larger cell having additional anodes which can operate well in excess of 4,000 amps. Average life before requiring maintenance overhaul of both the 4,000 ampere cell and the larger one is now approaching 10 million ampere-hours.

FLUORINATION SYSTEM

PROCESS TECHNOLOGY

The conversion of uranium tetrafluoride to uranium hexafluoride with elemental fluorine is a highly exothermic reaction as shown in the following equation:

$$UF_4 + F_2 \rightarrow UF_6 + 108{,}000 \text{ Btu./lb. mol } UF_6 \qquad (1)$$

Figure 1 is a simplified flow diagram of the process. The reaction proceeds almost instantaneously and to completion when a finely divided, well dispersed stream of powder is contacted by an excess of preheated fluorine in a vertical tower reactor. Virtually all of the reaction takes place in the first two feet of the tower; thus, it is necessary to provide cooling by means of continuously welded coil attached to the outside wall. Water and steam are circulated through the coil and the tower wall temperature is maintained at about 1000°F. The outlet gas from the tower, which is at a temperature of about 1200°F., is cooled to about 300°F. and then filtered to remove entrained dust. The dust is a combination of unburned uranium tetrafluoride and non-volatile impurities that were present in the powder feed. The gas stream, which contains uranium hexafluoride, fluorine, hydrogen fluoride, oxygen, and nitrogen, is admitted to a refrigerated heat exchanger (cold trap) operating at about 10° F. and most of the uranium hexafluoride is removed by condensation as a solid; the vapor pressure of uranium hexafluoride at this temperature is 0.13 psia. The gas leaving the heat exchanger is returned to the reactor to supply a 25 to 50% excess of fluorine gas relative to the stoichiometric requirements of the uranium tetrafluoride feed so that maximum conversion to uranium hexafluoride is obtained. Recycling can be accomplished by means of a positive displacement, lobe-type pump. The recommended fluorine feed concentration is 50 mol percent although complete burning is obtained with concentrations as low as 30%. The other non-condensable gases enter the process through pump seals, impurities in the fluorine (the major source of hydrogen fluoride), in-leakage through buffered valves, partially open or faulty purge valves, etc. Oxygen is also liberated when fluorine reacts with the small quantities of uranium dioxide and uranyl fluoride present in the uranium tetrafluoride.

$$UO_2 + 3\,F_2 \rightarrow UF_6 + O_2 + 445{,}000 \text{ Btu/lb. mol } UF_6 \qquad (2)$$

$$UO_2F_2 + 2\,F_2 \rightarrow UF_6 + O_2 + 220{,}000 \text{ Btu/lb. mol } UF_6 \qquad (3)$$

Gas inventory and concentration control are accomplished by means of remotely operated control valves which admit fluorine to the process and release gas from the system to the stack. Efficient utilization of the fluorine is obtained by passing the bleed gas to a clean-up reactor. This unit

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operates with an excess of uranium tetrafluoride (20 to 50%) and, for all practical purposes, is able to convert all of the fluorine in the gas stream to uranium hexafluoride over a wide range of fluorine concentrations. Approximately 10% of the plant production is accomplished in this reactor. The uranium hexafluoride in the vent stream is removed by refrigerated heat exchangers operating at about minus 55°F. and product losses are negligible.

The primary tower reactor operates at atmospheric pressure and the recirculating blower, located directly after the gas filter, discharges at about 18 psia. to the cold traps. This arrangement is desirable to prevent any atmospheric wet air inleakage to the cold traps; uranium hexafluoride hydrolyzes easily to solid uranyl fluoride and hydrogen fluoride, and serious line and heat exchanger plugging would result if water were allowed to enter the process.

The small amount of unburned uranium tetrafluoride powder from the primary reactor, i.e., less than 2% of the feed, is collected in a receiver located directly under the tower. The ash which is removed is allowed to cool since it contains a high concentration of beta and gamma radioactive UX_1 and UX_2 (thorium and protoactinium); it is refed to the process at a later date.

An alternate fluorination system eliminates the gas recycle and operates with close to stoichiometric quantities of reactants. The outlet gas from the primary reactor passes through a cooler, filter, and 10°F. cold trap before admittance to the clean-up reactor. Although some of the operating flexibility is lost and ash rates are generally higher, ca. 5%, because of the lower excess of fluorine used as compared to the system described above, the need for a recirculating pump, the highest maintenance item in the cycle, is eliminated.

Both systems are monitored by specially designed analyzers which continuously measure and record the concentrations of uranium hexafluoride and fluorine at the critical points of the process.

The uranium hexafluoride product is liquefied in the heat exchangers by heating to about 200°F. At this temperature, uranium hexafluoride liquid has a vapor pressure of approximately 50 psia. The contents of the exchangers are drained into a 10-ton cylinder. Once an exchanger has been emptied, it is recooled and, thus, made ready for re-use. The heating, draining, and cooling cycle requires about 12 hours.

PLANT LAYOUT

The plant may be considered to be divided functionally as well as physically into the following areas: (1) central control room and office; (2) fluorine production; (3) powder handling; (4) fluorination; (5) cold trapping; (6) hydrogen fluoride storage; (7) refrigeration;

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(8) maintenance areas; (9) laboratory; (10) power substation and load center; and (11) locker rooms. All except the hydrogen fluoride storage area are located in or close to the main process building. The hydrogen fluoride storage area is ordinarily located at some distance from the main plant for safety reasons, and must also be situated at a railroad siding. The remaining areas are grouped around the central control room in the most economical way so as to minimize process piping and conveyor runs, and personnel traffic through the various areas. In general, this amounts to placement of the fluorination and cold trapping areas adjacent to the control room with the powder handling facilities off to one side and the fluorination plant off to the other. The refrigeration area should be located between the fluorine plant and the cold trapping area. The remaining areas can be located where convenient.

The detailed functions of the areas listed as numbers 2 through 6 are discussed in the technology sections, and areas 7 through 11, in the section covering building services.

The central control room, although not mentioned in the later descriptions, may be considered to be the nerve center of the overall process, particularly for the fluorination reactor and fluorine cell operations. Main process variables, such as temperatures, pressures, flows, hopper inventories, fluorine cell voltages, electrolytic current, and stream concentrations, are constantly monitored in the central control room with a minimum of operating and supervisory labor. Provision is also made for the control of other process variables such as powder feeds and gas flows to the reactor equipment.

The graphic panel shown is of considerable advantage in the visualization of the process and facilitates application of corrective control measures.

EQUIPMENT FUNCTION AND DESCRIPTION

Powder Handling

The functions of the powder handling systems are the distribution and metering of the uranium tetrafluoride to the reactor systems, the collection and reprocessing of unreacted material, and the recovery of uranium salts from venting and vacuum cleaning operations. Minimization of manual operations has been found desirable from the standpoint of economy and decreased contamination.

Uranium tetrafluoride is received in 30-gallon drums containing about 750 pounds of powder. The powder is dumped from the drums and the drums are washed free of residual material. This entire operation is performed mechanically in a closed system shown in figure 3 in which the drums are first dumped into a hopper using a skip hoist and then conveyed through a washing system. The tetrafluoride is fed by a rotary valve to a continuous flow conveyor system which distributes it to the reactor feed hoppers as required. Receivers, which are placed at the bottom of the tower reactor and the filter to collect the unreacted powder are replaced when full. A large part of the radioactive contamination is collected by the filter and this material is transferred to a solvent extraction facility for purification and recovery of the uranium. The tower ash is stored for about two months to allow the decay of UX_1 and UX_2. These receivers are then unloaded in equipment similar to that used in the uranium tetrafluoride handling and the material is ground, screened, and collected in a storage hopper from which it is fed by a rotary valve into the uranium tetrafluoride conveyor.

The clean-up reactor system is supplied with uranium tetrafluoride by the same conveyor used for the primary reactors, and the equipment used for powder feed is identical. Instead of being collected in batch receivers as in the primary system, the unreacted material is screw fed from a collection hopper at the bottom of the equipment to a continuous flow conveyor and returned to the screening station. Because of the large excess of uranium tetrafluoride used in the clean-up reactor, the penetrating radiation level of the unreacted material is low and does not interfere with processing in the primary reactors.

The dust collection system used in conjunction with the vacuum cleaning operation consists of a cyclone, a bag filter provided with blow rings, and a paper asbestos-type polishing filter. A multi-stage centrifugal exhauster is used to provide the motive power. The discharged powder is collected in drums and because the contamination with miscellaneous dirt must ordinarily be processed chemically for purification. The philosophy of placement of the vacuum cleaning outlets is discussed under utilities and building services.

A second type of exhaust system, provided on evacuation connections to the reactors and closely associated equipment, includes an inertial separator to remove solids followed by a water scrubber which traps any uranium hexafluoride present and the remainder of the solids.

Tower Reactor and Associated Units

Fluorine Preheater. The incoming gas to the tower reactor must be preheated to approximately 800°F. The gas preheater is a 2-inch IPS schedule 40, seamless, soft annealed Monel trombone enclosed in an electric furnace.

Disperser. The disperser is mounted directly over the tower reactor and is designed to even out the stream of powder coming from the screw feeder and to break up any soft lumps. Two acceptable designs are shown in figure 4. The baffle assembly requires a vibrator attached for proper dispersion; the rotating disperser is complete as illustrated. Sectioned Graphitar rings with dry air buffering seal the process from atmosphere. Monel is the material of construction.

Jet Assembly. The fluorine enters through the Monel jet assembly to the tower proper. Four demountable jets, 90° opposed, direct the gas at the uranium tetrafluoride.

Reactor Proper (Figure 4). The fluorine and uranium tetrafluoride react in the tower to form uranium hexafluoride. The reaction produces a bright flame and a considerable amount of heat. The reactor proper is a 6-inch IPS schedule 40 Monel pipe, 12 feet long. To prevent the tower from melting, water and/or steam flow through cooling coils welded to the outside wall. Three sets of coils are used since the amount of cooling required is different for each zone of the reactor. The tower is not insulated, and a large portion of the heat of reaction is dissipated into the surrounding air. The reactor wall is kept below 1000°F. by varying the flow of cooling water and steam to the coils. The lower zones of the reactor should be held above 800°F. to prevent the formation of solid intermediates UF_5, U_2F_9, and U_4F_{17} which would stick to the walls and plug the tower. The reactor just described has a capacity of about 500 pounds of uranium tetrafluoride per hour.

Tower Expansion Bellows. The Monel tower expansion bellows, located at the bottom of the reactor, absorbs thermal expansion and permits accurate weight indications on the tower ash receiver scales.

Ash Receiver. The ash receiver is located at the base of the tower to collect any non-volatile impurities or unconsumed uranium tetrafluoride. Steel drums, specially shaped for easy filling and clean dumping, are used. Toggle action C-clamps facilitate connecting and removal of drums. The receiver capacity is about 30 gallons.

Since the hot gases from the tower do not circulate through the ash receiver, the walls of the vessel may cool down sufficiently to condense uranium hexafluoride. To prevent this, a removable heater should surround the receiver.

The ash receiver is mounted on a scale or load cells to chart the rate of ash build-up.

Cooler

The exit gas from the tower passes through a section of steam cooled pipe. The steam in the outer jacket cools the gas to approximately 350°F. Three-inch IPS schedule 40 Monel pipe in a 4-inch steel jacket is employed.

Filters

A dust filter follows immediately after the cooler to remove any non-volatile fluorides and unburned uranium tetrafluoride carried by the gas stream. A back-up filter follows the primary filter as an additional safety factor. Sintered nickel tubes are the filtering media; a steel filter jacket is employed.

Compressor

The compressor returns the unused fluorine to the tower. A positive displacement, Monel lobe-type pump is utilized. There are four shaft seals each buffered with dry air through a packing ring; braided copper-Teflon packing is employed. The required compression ratio is about 1.3 to 1.4.

Primary Cold Trap (Figure 6)

The primary cold traps are refrigerated to about 10°F. and remove practically all of the uranium hexafluoride in the gas stream by condensation as a solid. The units are of tube and shell construction. Twelve-foot long hairpin tubes are employed and are arranged in rows and passes. Heating and cooling is accomplished by circulating cooled liquid or steam through the tubes. Baffling across rows increases the gas path and large fins, which are spaced closer and closer together as the trap outlet is approached, produce about a 9:1 fin to massive surface area ratio. The fins are brazed to the tubes. A holding capacity is about 10 tons of uranium hexafluoride. Monel-clad steel is employed for the shell and tube sheet; cupro-nickel, Monel, copper, and nickel, for tubes and fins.

Clean-Up Reactor (Figure 8)

The clean-up reactor removes the fluorine in the vent gas by reaction with uranium tetrafluoride to produce uranium hexafluoride. Approximately 10% of the plant production is accomplished in this unit. Unlike the primary tower, the clean-up reactor operates with an excess of uranium tetrafluoride. The unburned uranium tetrafluoride is conveyed back to the main uranium tetrafluoride feeding facility. The gas preheater, powder disperser, and jet assembly are identical to the equipment used with the primary tower. Figure 9 is a photograph of the feed assembly, powder disperser, and part of the tower proper.

Reactor Proper. The reactor proper consists of a shortened tower, about 8 feet long. The top 5 feet is 6 inches in diameter, and the bottom 3 feet is 12 inches in diameter. Coils are welded to the tower for cooling, as described previously, and are arranged in four zones.

In addition, electric furnaces which enclose the unit assure a minimum temperature of 800°F. at any point on the reactor walls. The problem of intermediate fluoride formation is considerably more serious here than in the primary reactor because of the presence of a large excess of uranium tetrafluoride.

Cooling Screw. The cooling screw cools the gases leaving the tower to below 350°F. to prevent the filter from burning and conveys the excess uranium tetrafluoride to the ash hopper. The unit is seal welded to the tower; it is 16 inches in diameter and about 10 feet long. A cooling coil for water and/or steam is attached to the outside shell. The screw flight, which is driven by a 7.5 hp. motor, is designed to prevent intermediates from sticking to the vessel walls; the design was arrived at by experimentation and scale-up. The construction is all Monel.

Filters. The filter is located directly over the end of the screw flight and the ash hopper. Thus, any powder collected in the filter falls into the ash hopper. A bump tank is a necessary auxiliary; its purpose is to blow back the filter at regular intervals to prevent pressure build-up in the system. The filter design is similar to that employed for the primary filters. A back-up filter follows the primary filter as in the primary tower cycle.

Ash Hopper and Screw. This unit discharges to a conveyor which returns the unburned uranium tetrafluoride to the central supply point. Either a cone-shaped or a trough-shaped hopper is used. Steel is the material of construction. The hopper is heated to about 500°F. to discourage condensation of uranium hexafluoride on the powder.

Conveyor. The conveyor is of standard commercial design as described earlier with regard to uranium tetrafluoride distribution.

Secondary Cold Trap (Figure 10)

The secondary cold traps which follow the clean-up reactor are designed to remove virtually all of the uranium hexafluoride from the vent gas stream. They are refrigerated to minus 55°F. and are heated with steam to liquefy the contents for drainage. Tube and shell heat exchangers, similar in design to the primary traps, are employed except that the refrigerant and steam are piped into separate coils. The holding capacity is 2,000 pounds of uranium hexafluoride.

Chemical Traps

Steel chemical traps follow the secondary cold traps and remove the small quantities of uranium hexafluoride which remain in the gas stream, ca. 0.06 mol percent. A bank of six traps, one foot in diameter and designed for about a two-minute hold-up per trap, is employed. The charge is activated alumina. A dual air ejector system in the vent line is an aid in removing the vent gas. The uranium is removed from the alumina by acid leaching.

Drain Cylinders

After the cold traps (both primary and secondary) are filled, they are heated to about 200°F. Uranium hexafluoride liquefies and drains into a 10-ton capacity steel cylinder. The gross weight, full, is close to 15 tons. Accurate scales are required for inventory purposes. The particular scales in use at Oak Ridge and Paducah are able to weigh with an accuracy of about 0.02%. A water protection system should be provided at each drain station to freeze down the drain valve in the event of a release. It is imperative not to exceed the safe weight of 10 tons in filling cylinders since the density of liquid uranium hexafluoride is about 25% lower than the density of the solid; thus, overfilling could cause a hydrostatic rupture of the cylinder.

FLUORINE PLANT

Fluorine is produced by electrolysis of hydrogen fluoride in an anhydrous electrolyte, $KF \cdot 2HF$ (m.p. = 160.7°F.). When a direct current is passed through the electrolyte, both fluorine and hydrogen are evolved. The fluorine collects in the anode compartments and hydrogen in the cathode compartments above the electrolyte surface. These gases are removed through separate piping systems; and the hydrogen fluoride, which is consumed, is replaced continuously. Anhydrous liquid hydrogen fluoride is shipped to the fluorine plant in 8,000 to 10,000-gallon tank cars; dry, oil-free air is used to transfer the hydrogen fluoride to storage tanks. From these tanks, the hydrogen fluoride is transferred to steam-heated vaporizers and then, through a metering station, is introduced as a gas to each fluorine cell.

The fluorine and hydrogen streams are piped to electrolyte entrainment separators necessitated by electrolyte carry-over due to minor explosions in the cell, pressure surges, and a small amount of mist normally entrained. The gases are then admitted to steel surge tanks which dampen pressure fluctuations resulting from the operation of lobe-type positive displacement blowers that compress each gas to about 2 psig. At this point in the system, the fluorine and hydrogen gases each contain about 15 mol percent hydrogen fluoride. Most of the hydrogen fluoride is recovered by condensation utilizing a minus 118°F. refrigeration system; even at this temperature, the equilibrium concentration of hydrogen fluoride is about 2 mol percent. From the heat exchangers, the fluorine is piped to the fluorination towers or to the fluorine storage facility; the hydrogen is scrubbed with water and vented.

A 36-cell fluorine plant is described in this paper. The principal components of the plant are presented in figure 11. The fluorine cell area is divided into two rooms, each containing 18 cells, so arranged that one room may be in operation while major maintenance work is performed in the other. The hydrogen fluoride condensers are located above the cell floor; the associated refrigeration equipment for the condensers is in an annex to the main building. The electric substation and rectifying equipment is in a basement room below the cell rooms. The main control board is in the central control room and is operated in conjunction with the other processes in the building. The maintenance area is above the cell floor adjacent to the condensers. The anhydrous hydrogen fluoride and fluorine storage areas are located remotely from the main building for safety reasons; similarly, the hydrogen fluoride vaporizer and pumping is located in specially ventilated rooms exhausted to a disposal stack. An acid neutralization building affords facilities for neutralizing acid drained from the vaporizers and from the maintenance area. A discussion of the various plant units follows:

HYDROGEN FLUORIDE SYSTEM

The liquid hydrogen fluoride, 99.95% pure, is shipped to the fluorine plant in 8,000 to 10,000 gallon tank cars. Forty-five psig. dry, oil-free air is used to transfer the liquid hydrogen fluoride to either of two 12,500 gallon tanks. Each tank is mounted on a scale framework equipped with a strain gage weight sensitive unit and recorder to give a continuous record of the hydrogen fluoride in storage. Figure 12 shows the steel piping system for the storage tanks arranged so hydrogen fluoride can be transferred by dry air under pressure to either storage tank or from one storage tank to the other, or several hundred feet to an 800 gallon day tank which leads directly to the fluorine cell feed supply system. The storage tanks are located in a concrete catch basin which drains to a dilution pond. A sheet metal roof built over the storage tanks prevents the heat of the sun from unduly increasing the vapor pressure of the hydrogen fluoride. Each storage tank is equipped with two fluorothene-coated Monel rupture disc assemblies to protect them against excess pressure. A remotely controlled water spray system is installed to cool these storage tanks, to dilute leaking hydrogen fluoride, or to prevent fuming. All liquid hydrogen fluoride and vapors are transferred by dip legs or openings in the top of the tanks.

The day tank is mounted on a scale platform equipped with a continuous weight recording system; by this means, the total weight of hydrogen fluoride fed, the rate of feed to the hydrogen fluoride vaporizer and the hydrogen fluoride distributing system is measured. The day tank pressure is maintained in the range of 13 to 15 psig. by means of automatic pressure controllers which supply dry nitrogen. Excess pressure in the day tank, especially during hot weather, is avoided by use of a cool water spray. Additional protection from excess pressure in the day tank is provided by a fluorothene-coated Monel rupture disc assembly followed by a relief valve and discharge line to a disposal stack. The vaporizer is a steam-jacketed tank, and although only high purity hydrogen fluoride is used for cell feed, small quantities of some impurities, including water, will accumulate in the bottom. Since these impurities can cause operational difficulties in the cells, the hydrogen fluoride fed to the vaporizer is cut off once a day and the residue is drained to waste.

Vaporized hydrogen fluoride passes to a heated feed distribution and control manifold located adjacent to the fluorine cell room. An automatic control valve in the hydrogen fluoride feed line is used to maintain 5 psig. pressure in the manifold. Nitrogen is introduced automatically if the pressure drops so that electrolyte from the fluorine cells is not forced into the hydrogen fluoride feed system. Control of the feed of hydrogen fluoride to a single cell is regulated manually with a needle valve and the feed rate is measured by an orifice. Block valves on either side of the metering assembly allow repairs to be made when necessary.

Vent gases released by the vent control valves on the day tanks and from the hydrogen fluoride transferring operation contain valuable amounts of hydrogen fluoride and are passed through a cold trap cooled by liquid carbon dioxide to minus 55°F. to recover hydrogen fluoride before being vented to the disposal stack.

FLUORINE AND HYDROGEN SYSTEMS

Cell Design and Assembly

The fluorine cells used in the program are of the medium temperature types noted earlier. The cells operate at 210° to 220°F. The fluorine is liberated at the carbon anode and hydrogen at the steel cathode. The characteristics of the cell are shown in table I.

Cell Body. The cell body consists of a welded Monel tank with a steel water jacket for cooling and heating (figure 13). Additional heat transfer capacity is provided by installation of baffles in the water jacket and water recirculation tubes in the center of the tank. Wheels are attached to the cell body to facilitate transfer during installation and removal of cells from the fluorine plant.

Cell Head. The cell head (figure 14) consists of a steel plate with fluorine and hydrogen compartment Monel separating skirts, externally threaded packing glands for support of anodes and cathodes, fluorine and hydrogen gas outlet pipes, nitrogen purge and hydrogen fluoride feed lines, electrolyte thermocouple wells, and an electrolyte sample well. The cell head is attached to the cell body with a bolted flange and sealed with a rubber gasket.

TABLE I

CELL CHARACTERISTICS

Maximum Current, amperes		4,000
Voltage, volts		8 to 10
Effective Anode Area, sq. ft.		32
Current density, amps./sq.ft.		125
Size, inches	Length	68
	Width	32
	Height	30
Anodes	Number	24
	Dimensions, inches	1.25 x 8 x 18
Operating temperature, °F.		210 to 220
Hydrogen Fluoride in Electrolyte, percent		41
Life, ampere-hours	Anodes	5,000,000(a)
	Diaphragms	40,000,000(a)
	Cell Bodies	40,000,000(a)

(a) Average of a large number of cells over a 3-year period.

Anode Assembly. The anode assembly (figure 15) consists of twelve carbon anodes arranged in two parallel rows of six each. Two assemblies totaling twenty-four anodes are used in each cell. Each assembly is suspended by two copper rods brazed to the chrome-molybdenum steel solid anode support bar; the bars, which also serve as electrical conductors, are projected through insulating packing glands in the cell head. Carbon anodes of the GAA and YAA grade are used, and sets of anodes for a cell are chosen on the basis of resonant frequency.

Cathodes. The cathode assembly (figure 16) consists of three vertical parallel steel plates welded (stress relieved) to cross plates at the ends and suspended through the cell cover by steel rods through insulating packing glands.

Screen Diaphragms. The diaphragm assembly (figure 16) is six mesh woven Monel screen attached to an angle frame. It bolts to the gas separation skirt head through an electrically insulating Teflon gasket and acts to divert the hydrogen gas into the hydrogen gas chamber of the cell. The diaphragms also serve as a barrier preventing broken anodes from making direct contact between adjacent active anodes and the cathode thus shorting out the cell.

Cell Cleaning and Drying. All cap screws, anode support bars, diaphragms, and gaskets are thoroughly cleaned and degreased with trichloroethylene before assembly. The entire cell including anodes is then dried for 16 hours after assembly with an air purge at 180 to 210°F. before charging with electrolyte. Approximately 2000 pounds of electrolyte containing 41 weight percent hydrogen fluoride is then added to the cell.

Cell Instrumentation

A number of instruments permit the control room operator to monitor the condition of each cell. Pressure switches attached to the hydrogen and fluorine exit gas lines actuate alarms in the control room to indicate pressures greater than 2 inches of water in the cell. The most common causes of this type of trouble are plugged gas lines and explosions in the cell. The latter is the result of either low electrolyte levels or holes burned in the gas separation skirt. In addition to the pressure switches, a cell pressure indicator is used by the operator as an aid in determining incipient plugging conditions.

The temperature of the cell is measured by a thermocouple in the electrolyte and is recorded in the control room and also on the cell room panel. Variations in temperature are caused by cooling system difficulties and high voltage operation. It is normally desired to maintain the cell at 210 to 220°F. Lower temperatures may cause solidification of the electrolyte, and higher temperatures may result in an excessive amount of hydrogen fluoride carryover with the hydrogen and fluorine and will increase the corrosion of the cell parts.

The cell voltages are recorded in the control room. Since all the cells are electrically connected in series, a single recording ammeter in the control room suffices to measure the current flow.

Cell Connections

Each cell is mounted on a support stand that is electrically insulated from the floor, and all connections from the cell to the gas headers or service line have insulating gaskets and bolts. Through the use of double throw switches, it is possible to connect the cell either to the 400 volt, 4,000 ampere operating bus or to the 60 volt, 2,000 ampere conditioning bus. The voltage and amperage of the conditioning bus can be adjusted for depolarization.

An isometric drawing showing the piping to an individual fluorine cell is shown in figure 17.

The two banks of 18 cells have separate process piping systems which join in common headers for carrying the gas flows to the fluorination towers. A similar system of fluorine and hydrogen vent headers is provided for purging and maintenance.

Some electrolyte is transported as a mist with the fluorine and hydrogen. The use of entrainment separators in the gas outlet lines directly above the cells, followed by catch-alls in the vertical lines leading to the headers, have been only partially effective in trapping the mist.

Hydrogen fluoride is continuously added to the cell through a dip pipe in the electrolyte. Cooling water or steam is supplied to each cell jacket through a flexible rubber hose.

A header extends the length of each cell room to supply nitrogen for purging to connections on the anode and cathode compartment of each cell.

Fluorine Piping

The fluorine and vent headers are piped in the form of an H, as shown in figure 18, each quadrant serving nine cells. Valves permit any quadrant to be isolated from the rest of the system, and the fluorine and vent headers are cross connected for flexibility of operation.

The fluorine is piped into a 500 cubic foot steel surge tank located on the mezzanine above the cell room. The surge tank dampens pressure fluctuations resulting from blower operation. The fluorine flows from the surge tank to either of two positive displacement lobe type blowers. There are four shaft seals on each pump buffered with nitrogen through a lantern ring and utilizing copper impregnated Teflon packing. The fluorine is discharged from the blower at 2 psig. to the hydrogen fluoride removal system.

To remove hydrogen fluoride from fluorine effectively, it was necessary to install a refrigeration system capable of cooling the gas below minus 110°F. Even at this temperature, the equilibrium concentration of hydrogen fluoride in fluorine is about 2%. The fluorine, laden with hydrogen fluoride, enters a series of three heat exchangers where it is cooled by the exit fluorine stream from the condenser. From the heat exchanger, the fluorine enters the condenser which is maintained at minus 118°F. by evaporating Freon-13. Two sets of heat exchangers and condensers are provided, one being a spare. From the condenser, the fluorine is piped to the fluorination towers or to the fluorine storage facility.

Normally, 800 pounds of fluorine is stored in three 1,000 cubic foot steel storage tanks located in a small building adjacent to the main plant. A 2 cfm., double diaphragm compressor[10] supplies fluorine to the tanks at a maximum of 60 psig. One diaphragm is actuated by a hydraulic oil unit, which transmits power through an inert liquid fluorocarbon to the second diaphragm which pulsates and compresses the fluorine.

Hydrogen Piping

The hydrogen and fluorine pressures in the fluorine cells must be maintained equal to each other to prevent the electrolyte level from moving below the gas separation skirt and thereby allowing explosive recombinations of the gases. This pressure control system is shown in figure 19. The pressure equalizing is accomplished by regulating the suction pressure on the hydrogen and fluorine pumps through recycle valves. The suction pressure of the hydrogen pump is used as the datum for the fluorine system.

The production rate is controlled by regulating the amperage to the cells from the control room. Since the demand for fluorine is usually constant, it is not necessary to change the operating rate frequently.

Vent systems have been provided for the hydrogen, fluorine, and hydrogen fluoride gases. All or any portion of the hydrogen may be vented through a flame arrestor on the roof. The fluorine may be vented through an 80-foot stack when purging a cell or piping, or occasionally when conditioning a cell. The hydrogen fluoride is vented to the disposal stack; such venting is necessary when transferring liquid hydrogen fluoride to the day tank, and to relieve high pressures in the hydrogen fluoride storage and feed systems.

ELECTROLYTE PREPARATION

Electrolyte is prepared by adding hydrogen fluoride gas to potassium bifluoride powder in the electrolyte make-up tanks. The hydrogen fluoride gas is introduced below an agitator through a dip leg. The tanks are jacketed so that they can either be cooled with hot water to remove the heat of solution or heated with steam to prevent solidification of the electrolyte after it has been prepared. Fluorine is then bubbled through the electrolyte to react with traces of water which may be present.

When cells are removed from production for maintenance, the reusable electrolyte is stored in tanks where products of cell corrosion will settle to the bottom and can be separated from the clean electrolyte above it.

AUXILIARIES

Tempered Water System

Cooling water at 100 to 120°F. is supplied at 10 psig. to the cells from a treated water system. Flow control to the cells is achieved by sizing the supply header so that the only appreciable pressure drop in the system is due to the piping and valves at the cells. The warmed water from the cells flows to a 1,000-gallon tank where the temperature is lowered by the addition of colder water. When all of the cells are down for maintenance, steam is admitted to the 1,000-gallon tank to raise the water the water temperature to 180°F. to maintain the electrolyte fluid during the shutdown period.

When an individual cell is removed from the bus, the flow of cooling water is stopped, and steam is supplied to keep the electrolyte fluid.

Electrical

The direct current power supply for the fluorine cells consist of two 2,000 amperes, 400 volt ignitron tube rectifier units connected in parallel to supply 4,000 amperes, 400 volts on the operating bus. The output may be varied to any voltages between 60 and 400 by a combination of phase control of the rectifiers and by a 32 tap autotransformer in the primary supply to the rectifiers.

Two 30 volt, 2,000 ampere selenium oxide rectifiers are provided for cell conditioning. These rectifiers may be connected either in series to supply 60 volts, 2,000 amperes, or in parallel to supply 30 volts, 4,000 amperes on the conditioning bus. In either case, the voltage may be varied from zero to full voltage by means of variable autotransformers in the primary supply.

A ground detecting and locating device, connected to the 400 volt direct current bus, actuates an alarm when the ground current exceeds a set value.

Ventilation and Stack

Special precautions are taken to keep the cell room, hydrogen fluoride vaporizer room and pump rooms ventilated. Two ducts run the full length of the cell room to exhaust the air through an 80-foot stack. Fresh air from the supply duct is admitted through louvers in the wall.

Ventilation is provided for the fluorine storage building making it possible to vent the fluorine gradually to the stack when a storage tank rupture disc fails.

OFF~~ICIAL USE ON~~LY

Aqueous Hydrogen Fluoride

A small building containing a lime neutralization system is provided for the disposal of waste aqueous hydrogen fluoride. A pit adjacent to the building holds the neutralized waste until it can be sampled and drained.

Nitrogen Supply

Dry, oil free nitrogen, piped into the building at 100 pounds pressure, is reduced to supply pressures of 50, 10, and 2-1/2 psig. The nitrogen is used primarily for cell purging and pressure regulation in the hydrogen fluoride vaporization systems.

OPERATION

Plant operations are centered in the control room and on the cell floor. Prior to start-up of the plant, the rectifier reset switches and cell temperatures are checked in the control room, and the fluorine is valved to process and the hydrogen to vent. In the control room, the rectifiers are then activated and the fluorine pump started when the pressure approaches the operating range; the cooling water temperature is simultaneously adjusted.

When single cells are installed in position, the hydrogen and fluorine gas chambers are purged with dry nitrogen for 1 hour, then the cell is electrically connected to the conditioning bus and given a high voltage depolarization. When the cell is operating at normal voltage, it is switched to the operating bus. Positioning of electrical switches in the cell room is performed with an electrician's hot stick; the exact sequence is marked for each operation.

The instruments are monitored at least hourly to maintain normal amperage, voltage, cell temperature, cooling water temperature, and pressure for each cell as shown in tables I and II. If pressure extremes are noted on cells or in the gas headers, instrument control settings are changed or other corrective action is taken. Cells operating at excessive temperature or voltage, but not polarized, can be checked electrically on the operating bus. Broken anodes are often discovered by measuring the cell voltage from anode to ground and cathode to ground; a fluctuation of voltage indicates that one or more anodes are broken. If the anodes appear intact, the electrolyte level and analysis is verified. If high temperatures occur without an increase in voltage, the water circulation system may be at fault. If the presence of moisture is suspected, five pounds of lithium fluoride is added, and the cell is operated on the conditioning bus at low and slowly increased amperage.

TABLE II

NORMAL FLUORINE PLANT OPERATING CONDITIONS

Cooling water inlet temperature	90 to 120°F.
Cooling water outlet temperature	110 to 140°F.
Cell pressure	
Hydrogen side	0 to 2 inches water (signal at 2 inches)
Fluorine side	0 to 2 inches water (signal at 2 inches)
Fluorine pump suction pressure	0 to 1 inches water (pump cuts off at ± 4 inches water)
Hydrogen pump suction pressure	0 to 1 inches water (pump cuts off at 2 inches water differential from fluorine pump suction pressure)
Hydrogen pump discharge	2.0 psig.
Fluorine pump discharge	2.0 psig.

MAINTENANCE

Routine maintenance involves cell rebuilding, installation, and removal; leak repair; and pump replacement. Cell rebuilding, consisting of dismantling and reassembly, is done in the maintenance area. After the cells are reassembled, they are lowered via elevator to the main floor. Here they are filled with electrolyte from the electrolyte make-up tank and moved to the vacant position in the cell room and connected to the system. A dolly and track system permit ease of movement and accurate placement of the cells. Acid cleaning, replacement of gas separation skirts and tanks, and renewing of anode bus contact surfaces are considered major repairs and are performed in the various service shops. When a cell is removed from position, all connecting lines are checked for restrictions and the mist traps are steam-cleaned and dried.

Shutdown maintenance occurs when a main line valve, pipe, or other piece of equipment develops a leak that cannot be repaired during operation, or when a general cleanout of lines is necessary. Leaks most often occur in the cell hydrogen fluoride connections. Cleanout shutdowns are planned and coordinated with other maintenance requirements to keep the over-all downtime to a minimum.

The headers, mist traps, pump suction headers, and certain valve spools are disassembled before cleaning. The smaller removable pieces are steam cleaned; the others are cleaned by means of a commercial vacuum cleaner using long lengths of hose, or if necessary, by brushing or scraping. It is helpful to work rapidly since the electrolyte dust is hydroscopic and becomes sticky in contact with air. On reassembly, new gaskets are used, and all gaskets and contact surfaces are degreased with trichloroethylene. On-stream efficiency varies from 90 to 97%. Cell replacement and the periodic cleanout (approximately monthly) account for most of the 3 to 10% plant downtime.

IMPROVEMENTS

Recently, a bank of larger fluorine cells (figure 20) has been put into operation. Each cell has a 42 sq. ft. effective anode area, 32 anodes, and operates at 4,500 to 5,000 amperes. Heat transfer in the cell has been improved by decreasing the jacket space for cooling water circulation thus increasing the velocity, by adding cooling surface to the center of the cell by replacing the former three 3-inch tubes with twelve 1-1/4 inch cooling tubes, and by improving the over-all heat transfer coefficient by raising the inlet water temperature. Another change increases the lateral spacing between anodes to about 3/4-inch and this modification might also improve the heat transfer. Latest results indicate that a large increase in cell life is being attained. Some cells have had 18,000,000 ampere-hours accumulated before failure, and there is evidence that the average cell life will exceed 10,000,000 ampere-hours.

Summarizing advances made in recent years in cell performance, it can be stated that major gains have resulted from selection of better metal alloys for cell parts, improved methods of fabrication, high purity of raw materials, an improved hydrogen fluoride continuous feeding system, an improved pressure balancing system between anode and cathode compartments and exercising rigorous care in cell maintenance and assembly.

MATERIALS OF CONSTRUCTION

Fluorine and uranium hexafluoride do not present a corrosion problem from an operating standpoint if the proper procedures in design and fabrication of systems are followed. Steel is used for construction of systems designed to operate below 400°F. Monel is generally used for higher temperatures up to about 1200°F. although it is desirable to limit operating temperatures to below 1000°F. because of increased corrosion from air as well as the process fluid and decreased strength above this temperature. Cold drawn annealed Monel is used for this purpose. Although nickel is somewhat more resistant to the process fluids, it has not been used as widely because of the greater cost and because Monel has been easier to obtain. Either Monel or nickel is used in contact

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with the process fluid in cold traps, shells and heads and in drain piping to minimize formation of corrosion products which tend to plug drain piping. Bundle tubing baffles and fins may be copper, cupronickel (70 to 30), nickel, or Monel. A special bellows sealed valve having a cast Monel body and brass or Monel bellows is employed throughout the process. Welding of Monel is accomplished by the metal arc process and for thin sections by the Heli-arc method. Monel and copper may be soldered using ASTM grade 7 silver solder. Teflon, which is sometimes diluted with 30% by weight of calcium fluoride to improve resistance to fluorine, and copper are employed for gasketing materials. Use of gaskets is limited as far as possible to connections which must be broken frequently.

Since fluorine and uranium hexafluoride both might react violently with foreign matter, especially grease or oil, cleanliness of equipment and piping is mandatory. Degreasing with chlorinated solvents such as trichloroethylene is standard practice. Systems must be leak tight not only to avert the hazard and loss associated with the release of process chemicals but also to prevent inleakage to wet air since the contained moisture will react with the uranium hexafluoride to form solid uranyl fluoride which will plug lines.

UTILITIES AND BUILDING SERVICES

A summary of utility requirements and expected uses follows:

DRY AIR

The dew point must be less than minus 60°F. and the air must be substantially oil and dust free. The building supply pressure should be no less than 95 psig. Dry air is used for purging and buffering except in the fluorine plant, for instrument air supply, and for forcing hydrogen fluoride from the storage area. The maximum instantaneous use rate is estimated to be 1200 scfm.

DRY NITROGEN

The dew point should be less than minus 60°F. and the gas must be absolutely free of dust and oil. Oxygen content is less than 100 ppm. The building supply pressure must be no less than 40 psig. Dry nitrogen is used for purging and buffering in locations where oxygen is not permitted such as in hydrogen containing systems in the fluorine production plant.

STEAM

The building supply pressure is at least 100 psig. and the steam should be dry but with negligible superheat. The main process uses are

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heating cold traps, injection into tempered water systems, vaporization of hydrogen fluoride, line tracing, and cooling of fluorination equipment. The estimated maximum instaneous use rates are 10,000 pounds per hour for process uses and 40,000 pounds per hour for wintertime heating, based on 0°F. outside, 70°F. inside.

SANITARY WATER

Sanitary water is used for fire water as well as for safety showers and customary uses.

COOLING WATER

The maximum instantaneous rate is 1600 gpm. The cooling water should be filtered supply water equivalent to sanitary water in solids content. If the water is very hard, steam condensate should be substituted for use in the fluorination reactor coils.

MISCELLANEOUS SERVICE AREAS

Refrigeration

The refrigeration area contains equipment with a capacity of about 50 tons at 0°F. and 25 tons at minus 55°F. to be used in cold trapping of the uranium hexafluoride and 15 tons at minus 118°F. used in the condensers which remove hydrogen fluoride from the electrolytic fluorine and hydrogen streams.

Maintenance

The maintenance area is used for the rebuilding and repair of fluorine production cells and the making of submajor repairs on other equipment. If not provided in other locations, equipment for the removal of uranium salts and electrolyte from used equipment is required.

Laboratory

A small laboratory is provided in the process building so that prompt analysis of electrolyte acid content, fluorine purity, and fluorination system gas compositions can be obtained.

Power Distribution

The power distribution system consists of an outdoor substation to reduce incoming three phase power to 460 volts, a load center which contains the transformer breakers and the main feederbreakers for the various pieces of equipment. These breakers are used to allow positive disconnection of electrical equipment for repair. Starting

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and stopping of equipment is accomplished from push button stations or control instrumentation either locally or in the central control room. The magnetic contactors are grouped for convenience in maintenance and are located outside of the processing area if required for protection against damage in the event of a chemical release.

The distribution of the installed capacity which totals 4400 kva. for the uranium hexafluoride production plant is: fluorine production electrolytic power, 3500 kva.; ventilation, 350 kva.; furnaces, 150 kva.; miscellaneous process motors, 300 kva.; and building lighting, 100 kva.

Locker Rooms

Because of possible exposure to uranium bearing materials, operating and maintenance personnel are required to wear coveralls. Two locker rooms, one for changing into work clothing and the other for the street clothes are provided with a shower room between the two rooms.

GENERAL BUILDING SERVICES

General building services include heating and ventilating, vacuum cleaning, and crane service.

Ventilation

Ventilation requirements are such as to require high air change rates in several areas of the process considered to be critical in the event of process chemical leakage. These areas are maintained at negative pressure with respect to their surrounding so any chemical releases may be localized and withdrawn with the exhaust air to be discharged through an adequate stack. These areas, the normal and emergency air change rate per hour and heat load, if any, are as follows: tower pit area - 60/60, 1,200,000 Btu. per hour; cell neutralization room - 50/100; fluorine cell room - 30/60, heat load 800,000 Btu. per hour; electrolyte make-up room, hydrogen and fluorine pump rooms, hydrogen fluoride vaporizer room - 25/50; cold trap area - 12/30; hydrogen fluoride condenser room - 6/20; and powder handling and reactor areas - 6/12. In addition, spot ventilation and hoods are provided as required for example at reactor flanges where uranium hexafluoride might escape, an exhaust is taken through a water scrubber to catch any escaping uranium.

Vacuum Cleaning

Vacuum cleaning piping with multiple outlets located to allow easy clean-up of spills is provided in powder handling areas. The dust collection equipment was previously described under powder handling.

Crane Service

A crane with 15-ton capacity minimum is required for handling the uranium hexafluoride product cylinders. A smaller crane is required for handling of powder drums. An electric chain hoist of one-ton capacity is used to raise the ash receivers from the pit to the main floor.

HEALTH AND SAFETY

Health and safety problems in the fluorine production and fluorination systems may be divided into three general classes: (1) electrical and mechanical; (2) chemical release; and (3) radiation, including exposure, inhalation, and ingestion. Despite the extreme reactivity and poisonous nature of the chemical materials handled, health and safety problems present no unusual difficulties when proper safety precautions and procedures are intelligently followed.

Problems in the first classification are common to most chemical plants and do not warrant an extensive discussion; however, it should be mentioned that since the fluorine cells are operated in series with relatively large current and system voltage differential, careful adherence to procedure is required when removing a cell from production and electrically by-passing it. The system is such that a single accidental ground will not result in current flow to ground in order to provide additional safety for operating personnel.

Process chemicals which can produce severe burns both externally and in respiratory passage, as well as poisoning, are fluorine, hydrogen fluoride, and uranium hexafluoride. The maximum allowable concentrations in air for these materials in effect at the Oak Ridge plant are, respectively, 1 ppm. fluorine, 3 ppm. hydrogen fluoride, 0.25 mg./cu. m. of uranium tetrafluoride, and 0.05 mg./cu. m. of uranium hexafluoride.

Concentrated fluorine gas and liquid anhydrous hydrogen fluoride are two of the most dangerous chemicals from a personnel safety standpoint. Both of these materials in concentrated form produce immediately, painful and severe burns which require instantaneous antidotal treatment. Exposure to aqueous hydrofluoric acid is especially insidious in that severe burns may be produced by a contact with the acid, which may go unnoticed until some time later. With prolonged inhalation of moderate amounts of fluorine or hydrogen fluoride vapor, there is also a serious hazard of lung edema.

Ingestion of uranium salts causes problems both from a radiological and chemical standpoint. Water soluble materials such as uranyl fluoride, which may be produced by the hydrolysis of uranium hexafluoride, tend to pass out of the body in the urine, but in the process of elimination from the body, damage to the kidneys may result. Inhalation of small amounts of relatively insoluble materials such as uranium tetrafluoride will result in deposition in the pulmonary system where the short range but powerful alpha radiation may be harmful to the lung tissues. Radioactive contaminants present in natural and reprocessed uranium salts must also be considered in evaluating health problems. Personnel working in uranium salt processing areas are given an industrial health recheck every two months.

Problems concerning external radiation in the fluorination system are limited to those encountered in the handling of ash which contains most of the radioactive uranium decay products in concentrated form. Even here, the problem is ordinarily not severe except when ash-containing equipment must be opened or in an area where a large number of ash containers are stored. Since ash radiation is mostly of the beta type, it is almost completely absorbed by the metal walls of the containers.

Processing areas are checked regularly by safety inspectors to insure maintenance of safe working conditions. Routine air-monitoring is considered to be a necessary adjunct of the over-all safety program.

Protective clothing such as Neoprene gloves, suits, gas masks and oxygen masks, protective goggles or face shields, and footwear are available where needed for both routine and emergency operation. With regard to fluorine cell operation, acid-proof goggles or safety glasses and a face shield are worn when electrolyte levels or samples are being taken or when cells are being filled. Purging and testing of equipment contents before opening is standard procedure.

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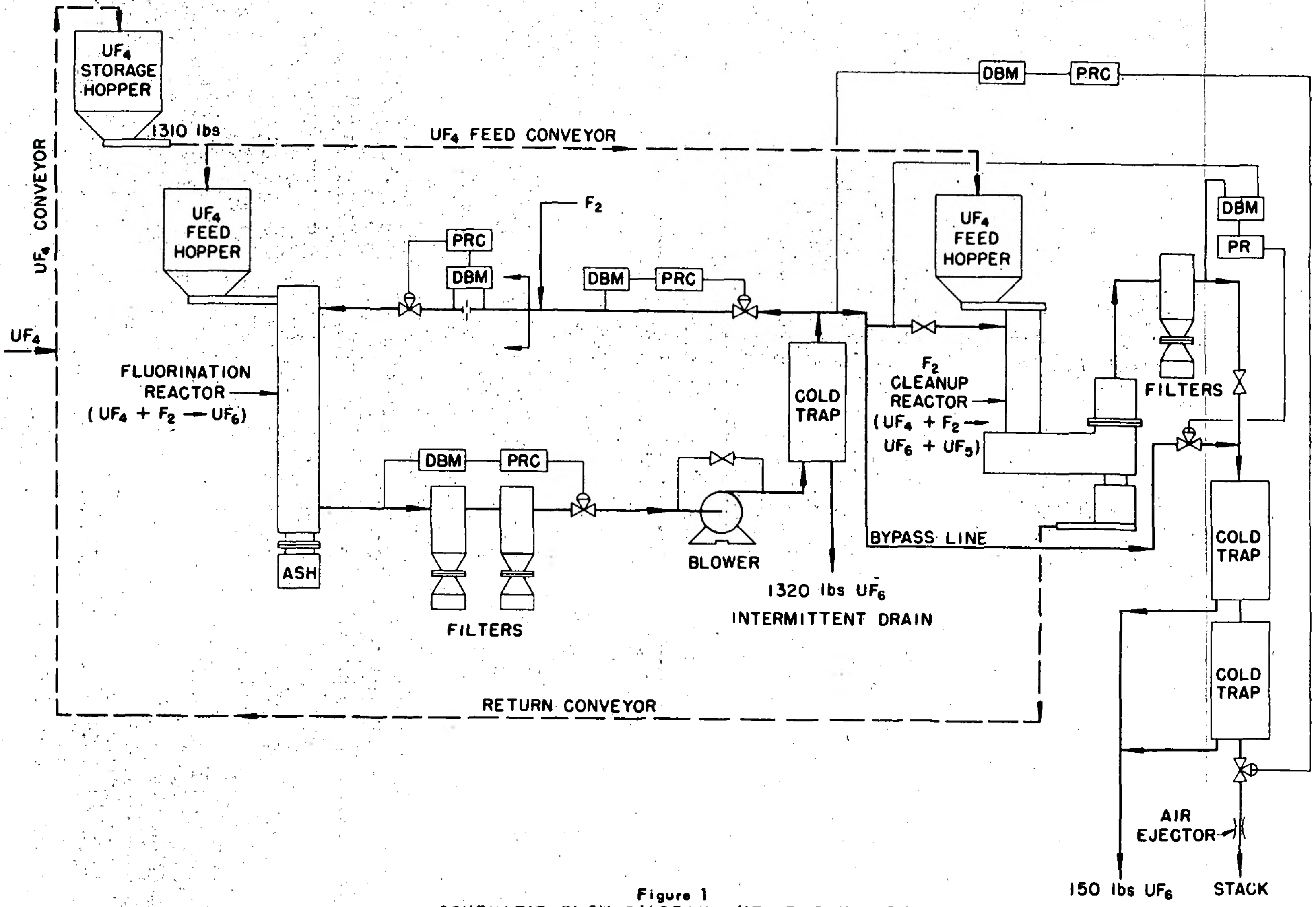

Figure 1
SCHEMATIC FLOW DIAGRAM – UF_6 PRODUCTION

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Figure 3
POWDER HANDLING FACILITY

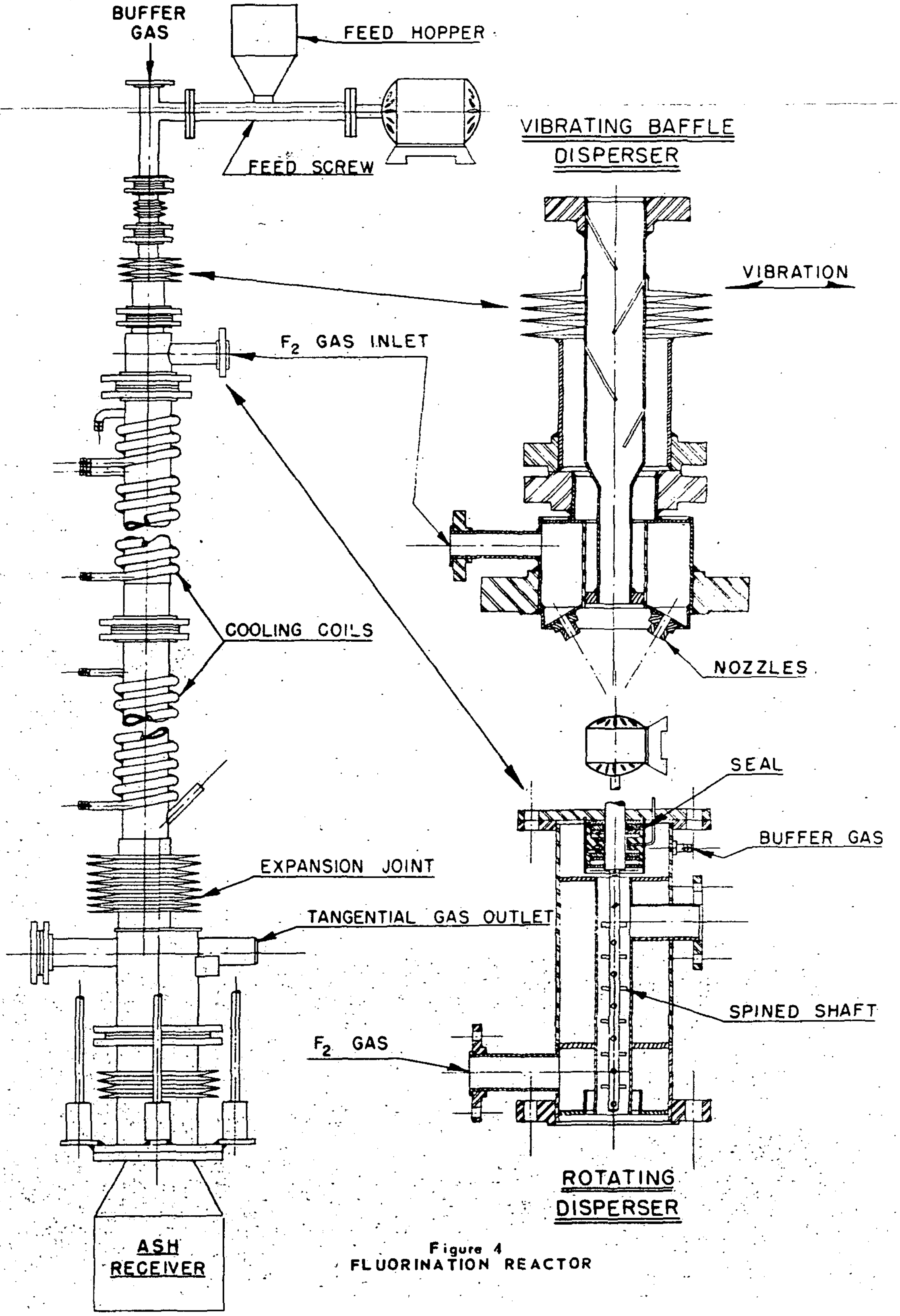

Figure 4
FLUORINATION REACTOR

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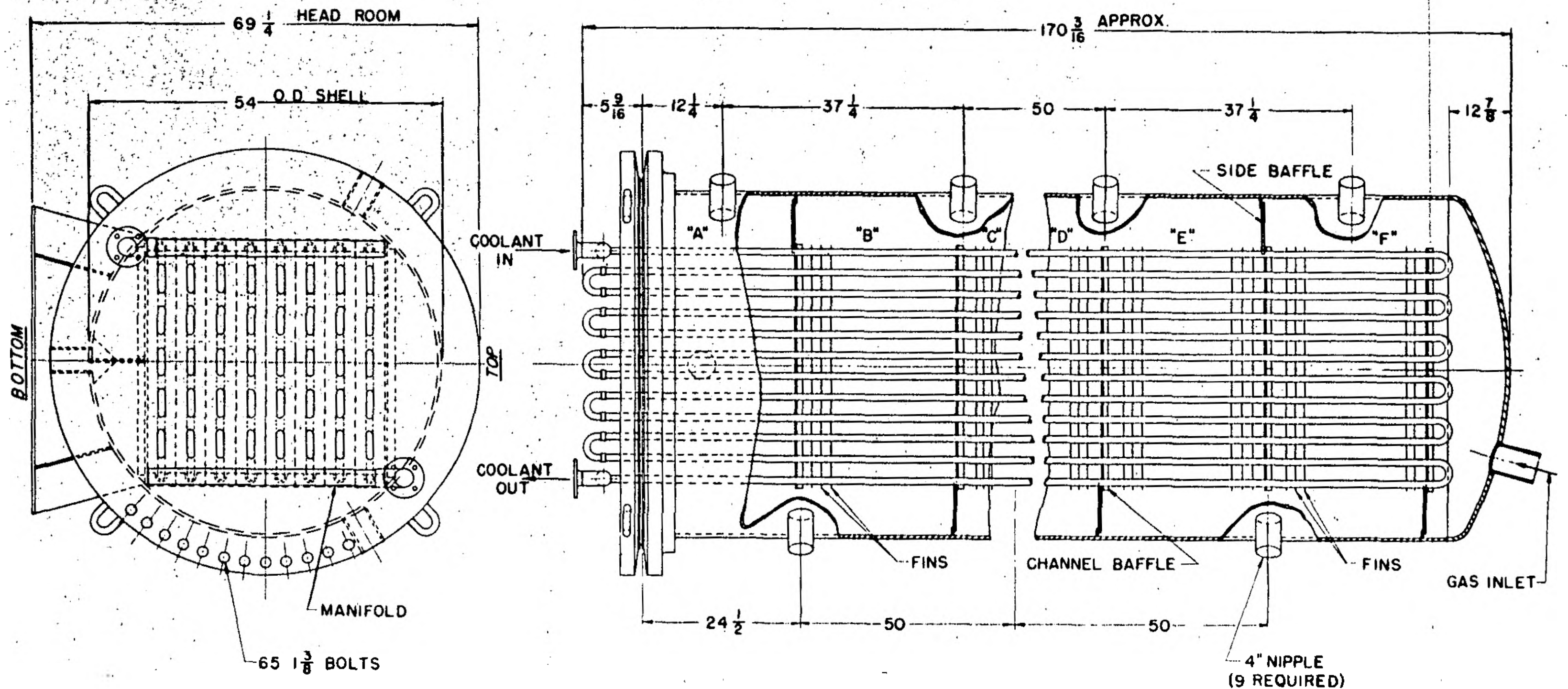

SECTION	FINS REQUIRED
A	47
B	38
C	30
D	23
E	17
F	11

Figure 6
ROUGHING COLD TRAP

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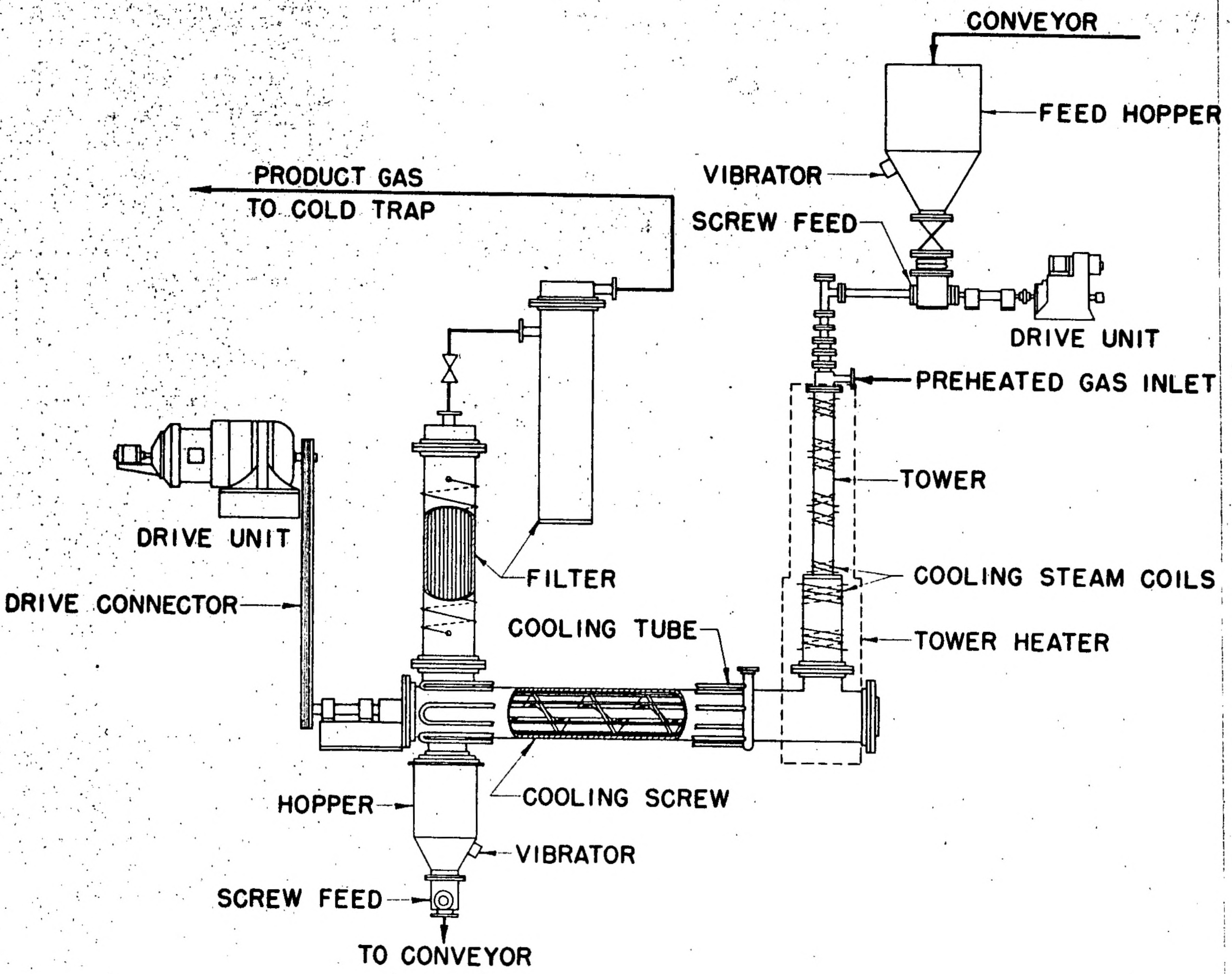

Figure 8
CLEAN-UP REACTOR SYSTEM

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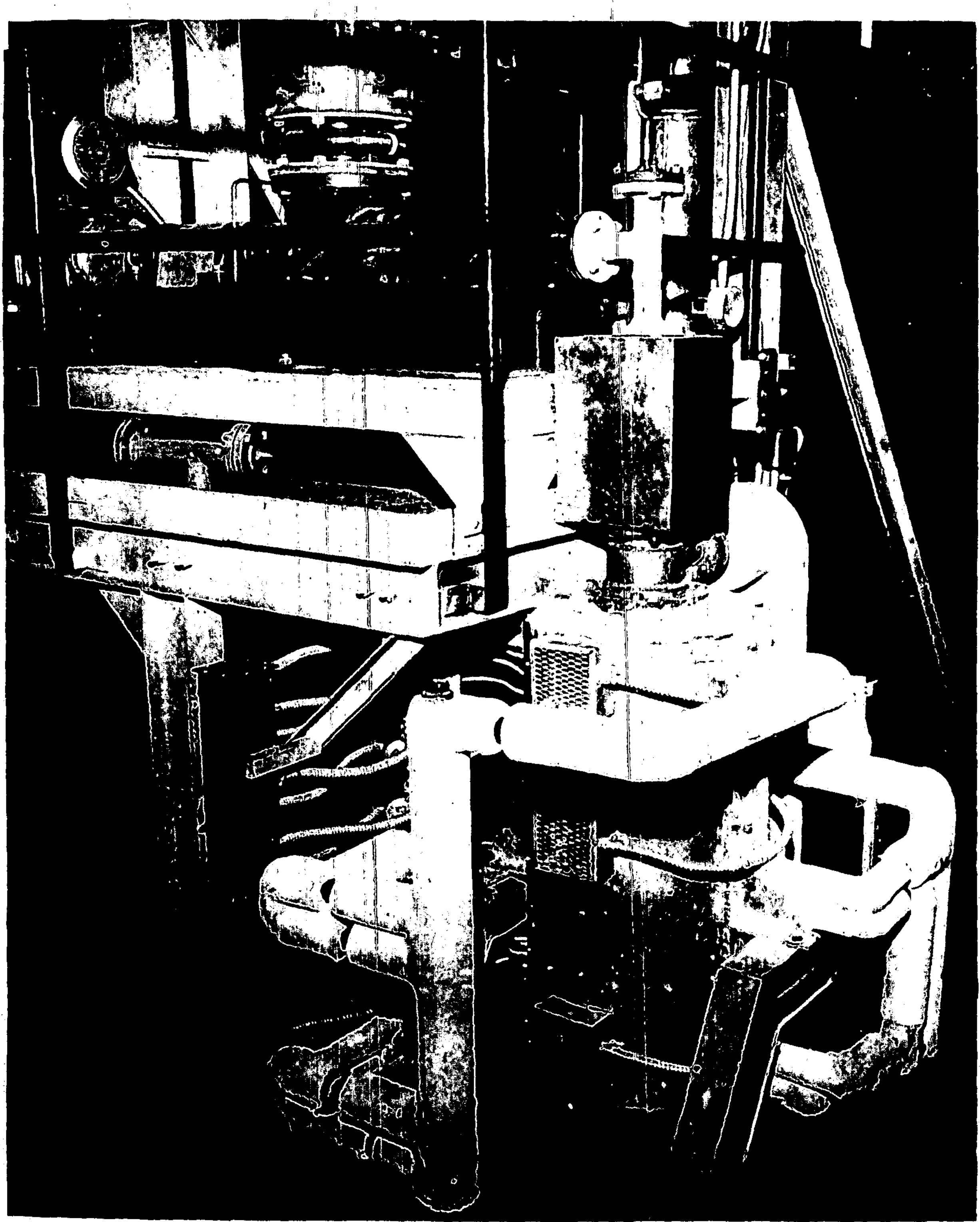

Figure 9
FLUORINE CLEAN-UP REACTOR

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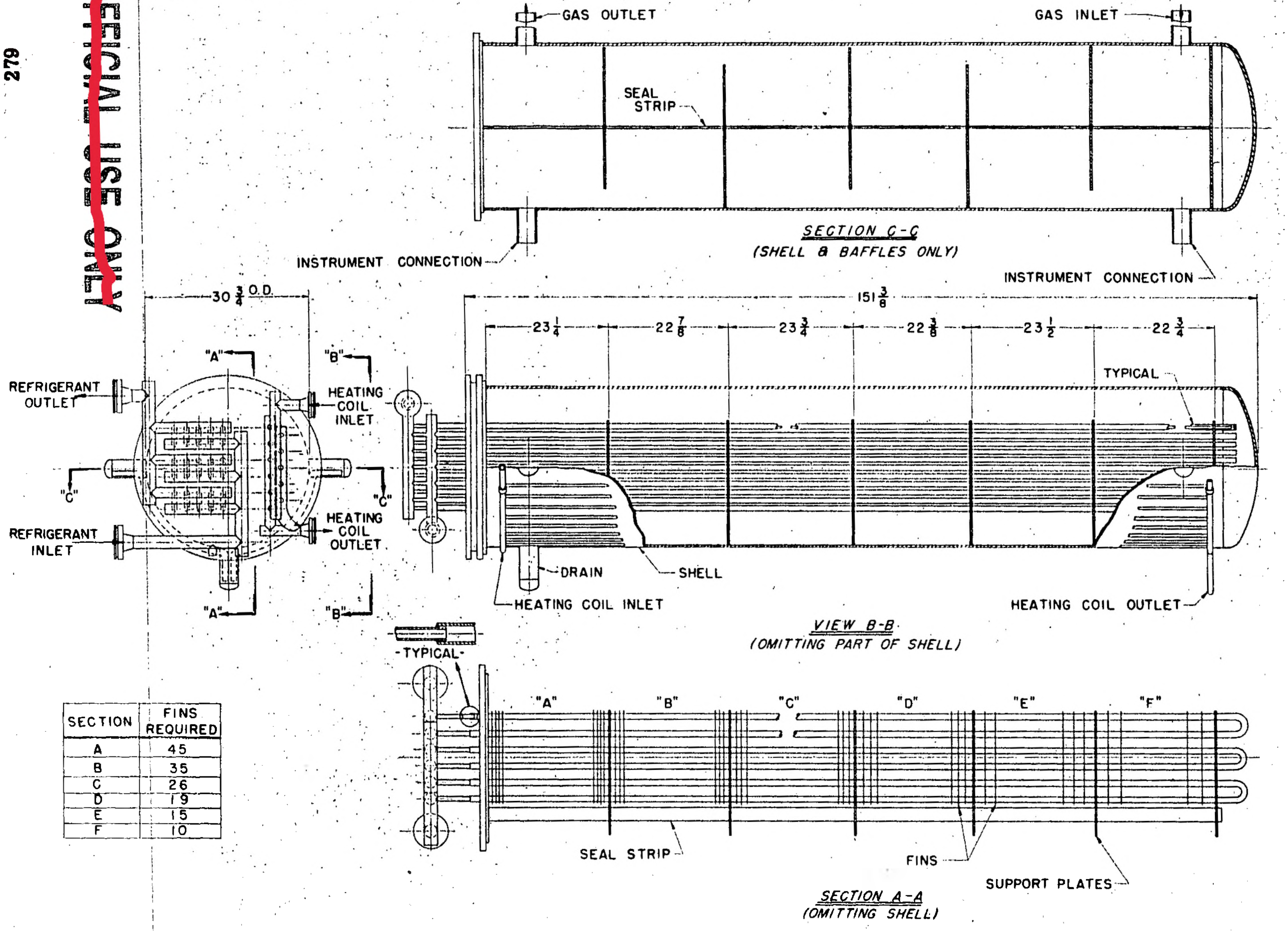

SECTION	FINS REQUIRED
A	45
B	35
C	26
D	19
E	15
F	10

Figure 10
SECONDARY COLD TRAP

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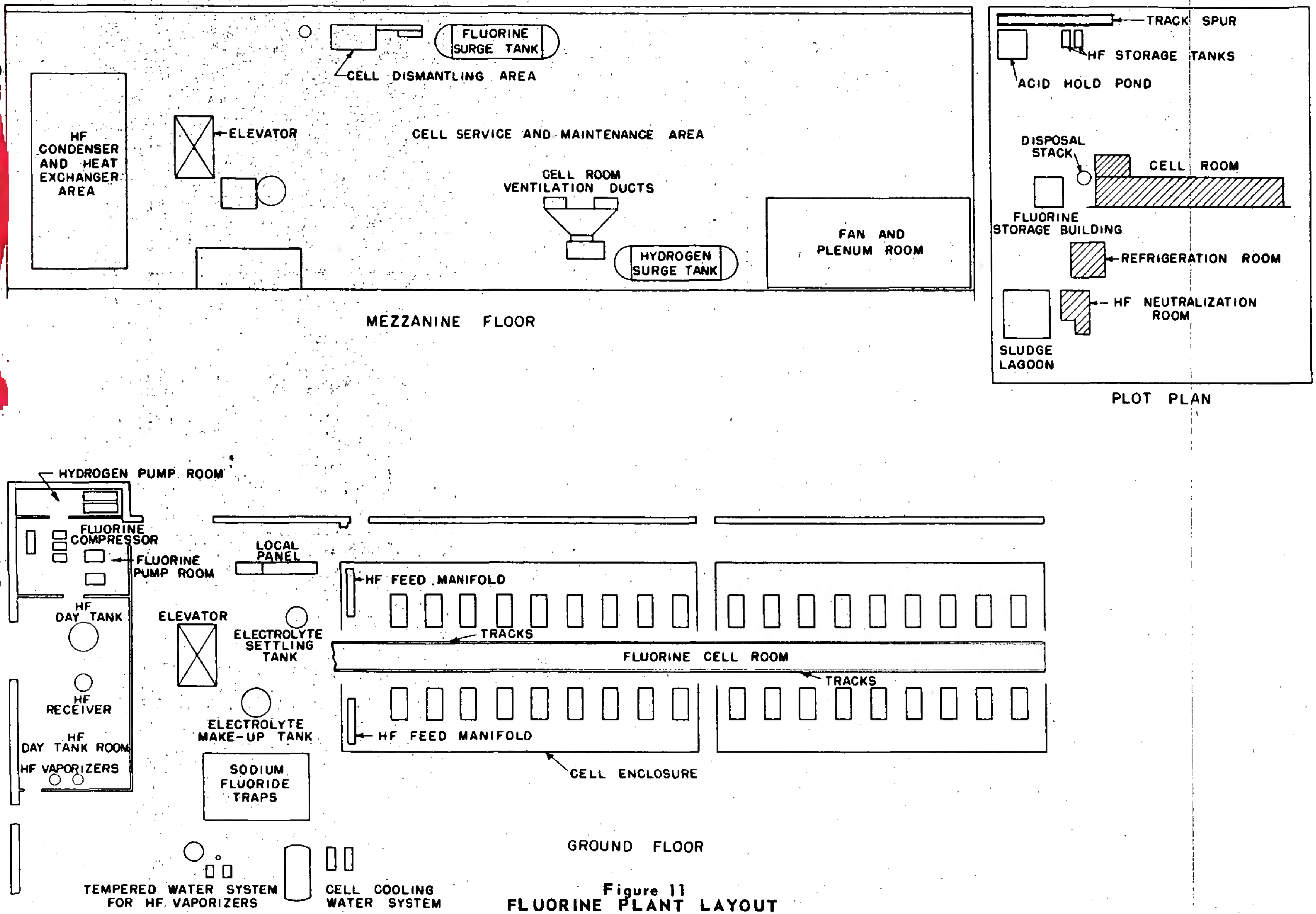

Figure 11
FLUORINE PLANT LAYOUT

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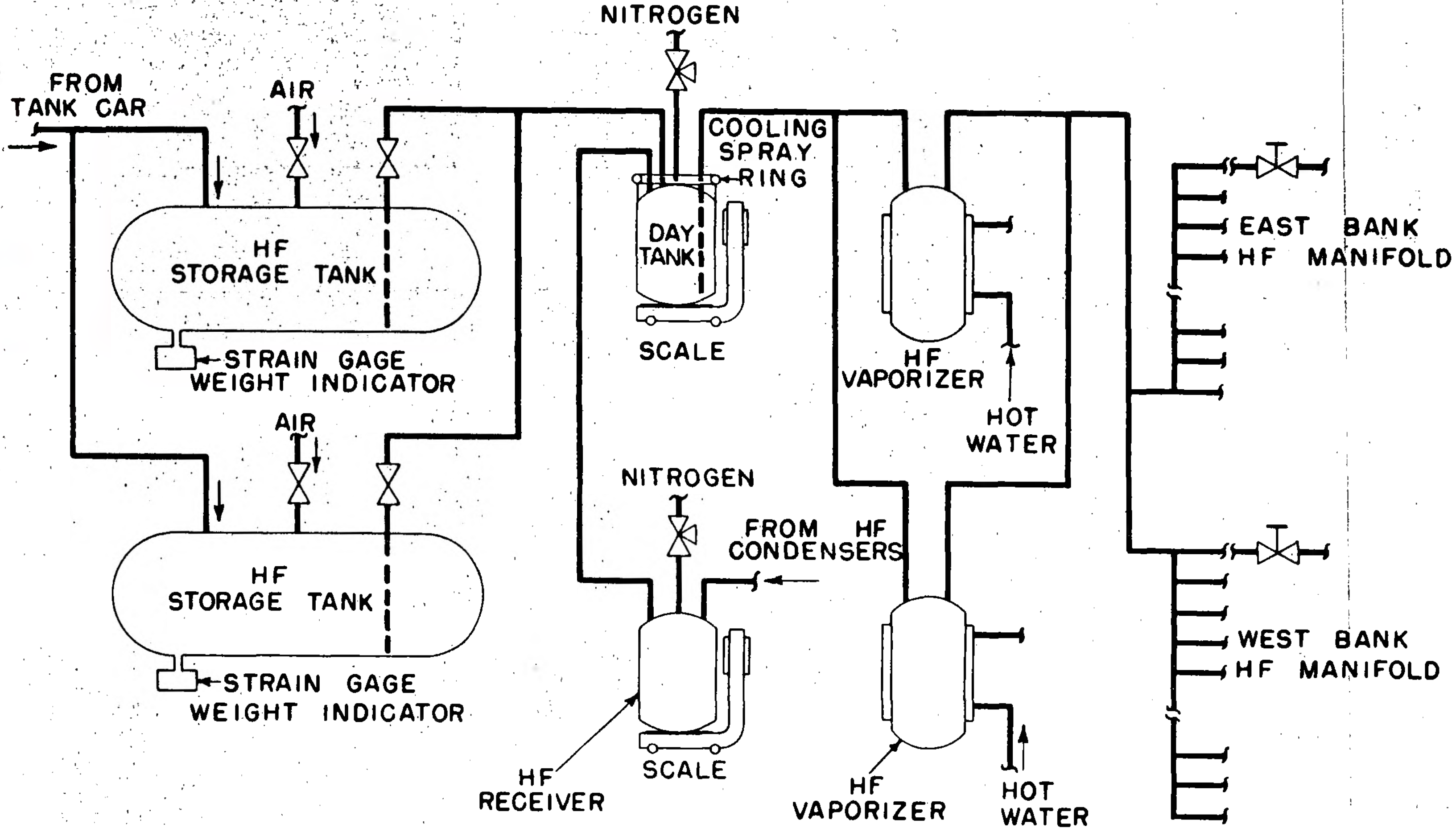

Figure 12
HYDROGEN FLUORINE FEED SYSTEM

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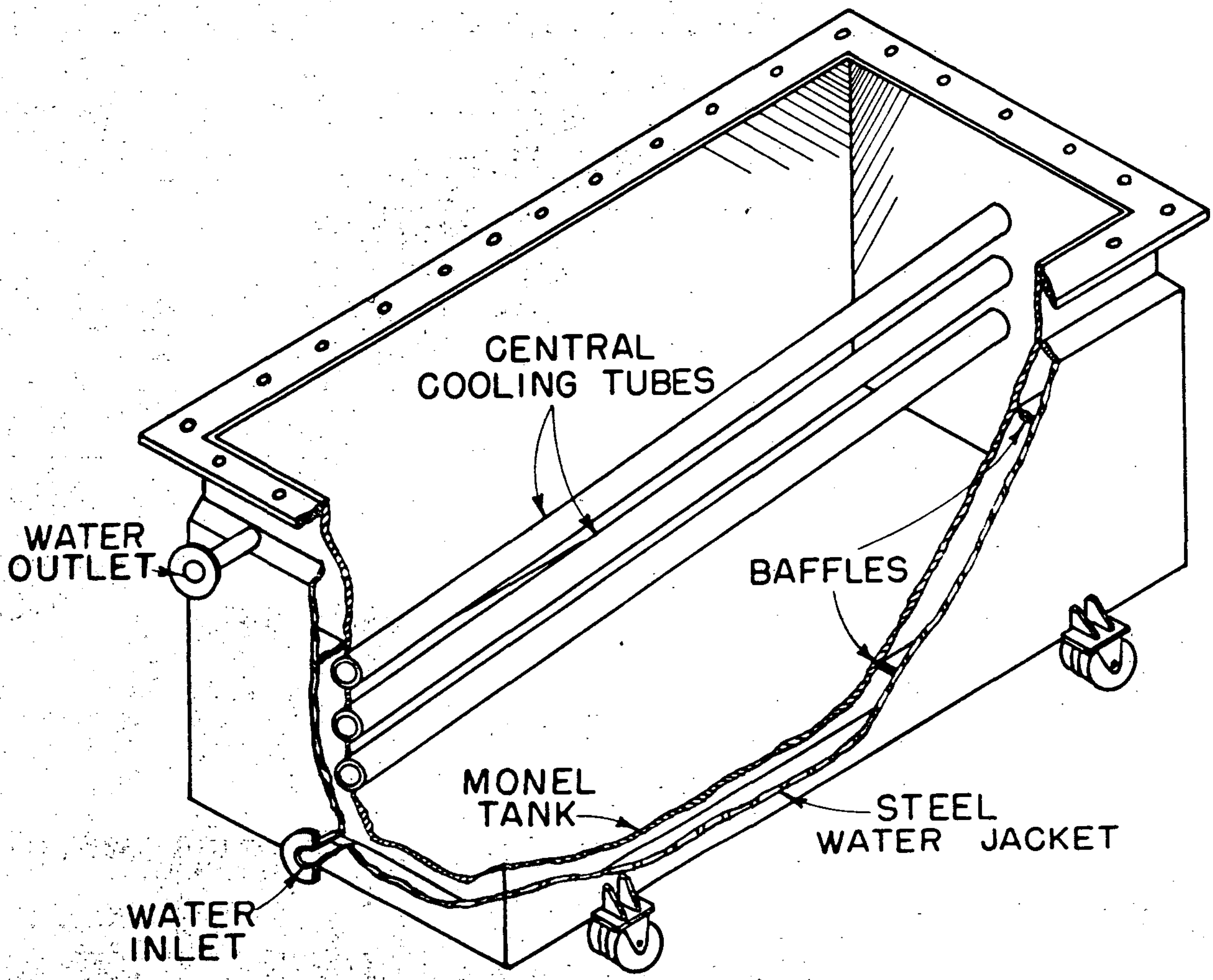

Figure 13
CELL BODY

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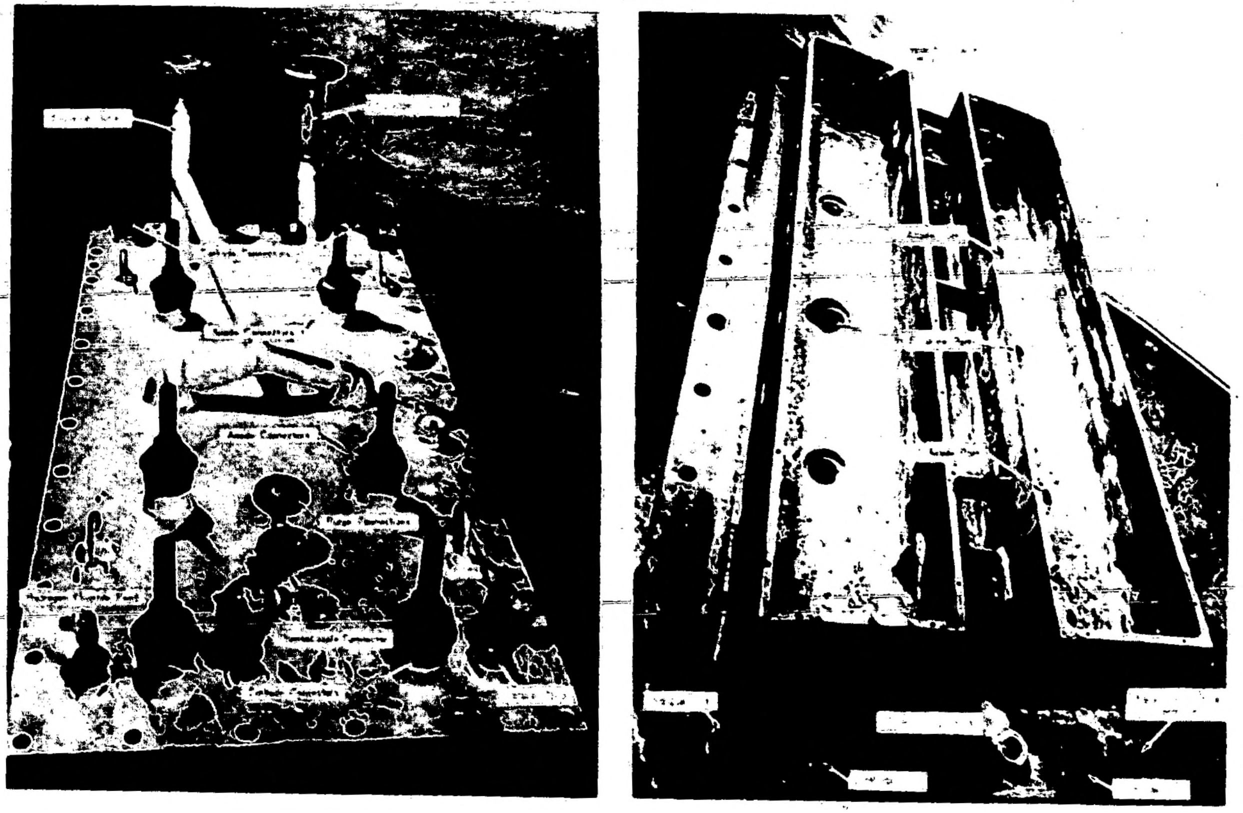

Figure 14
FLUORINE CELL HEAD-
TOP AND BOTTOM VIEWS

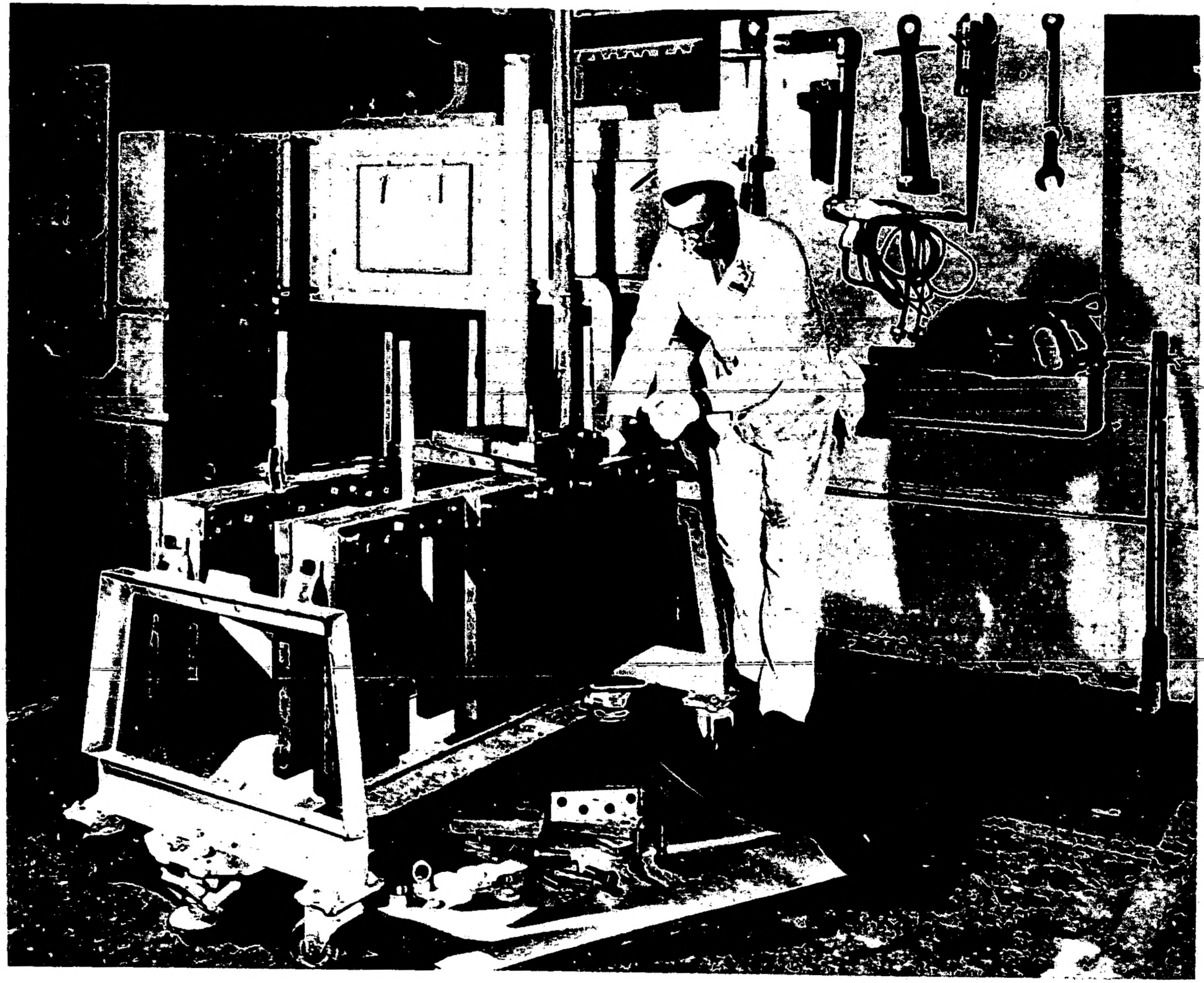

Figure 15
ASSEMBLY OF ANODES FOR FLUORINE CELL

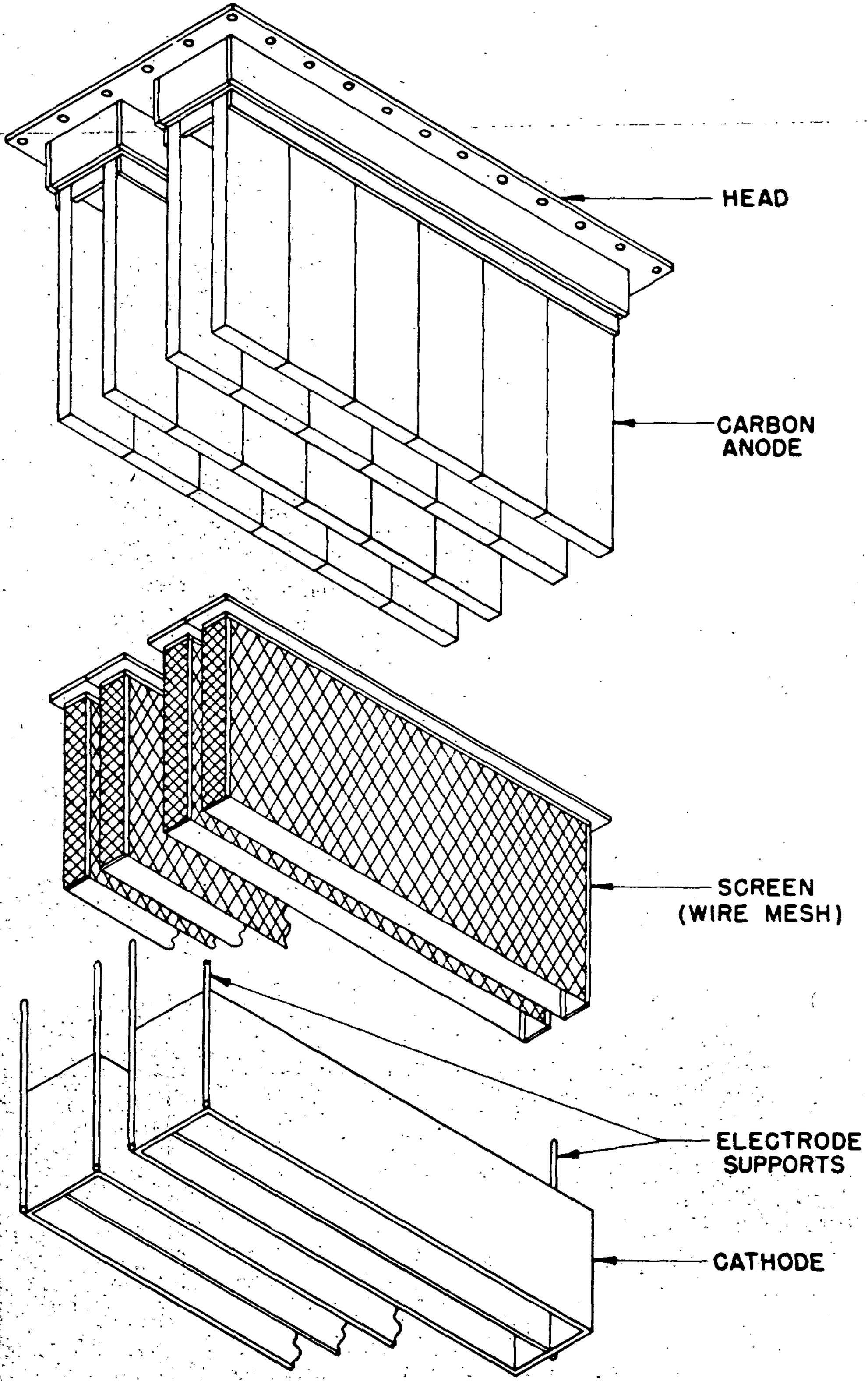

Figure 16
FLUORINE CELL HEAD ASSEMBLY

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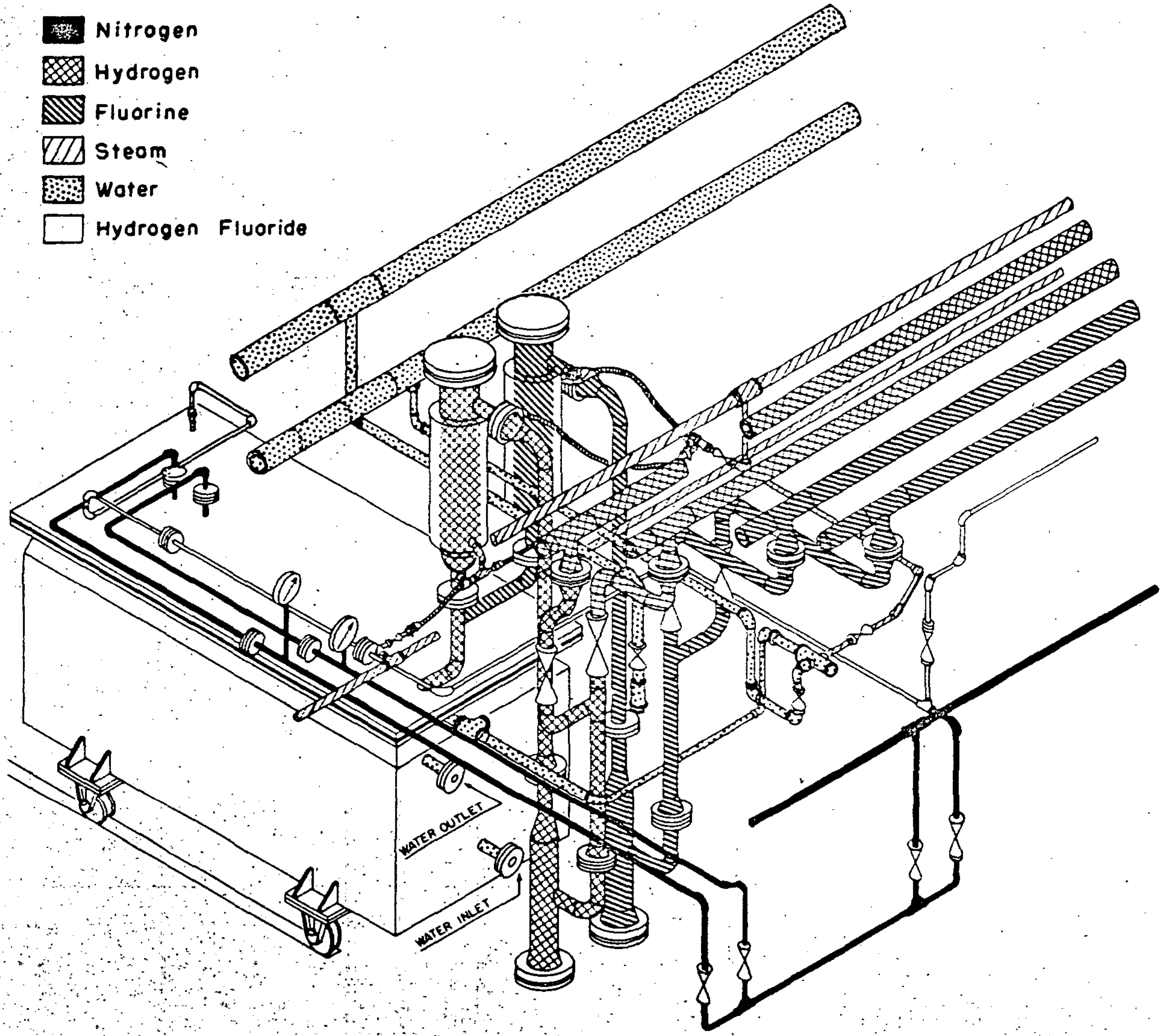

Figure 17
FLUORINE CELL PIPING

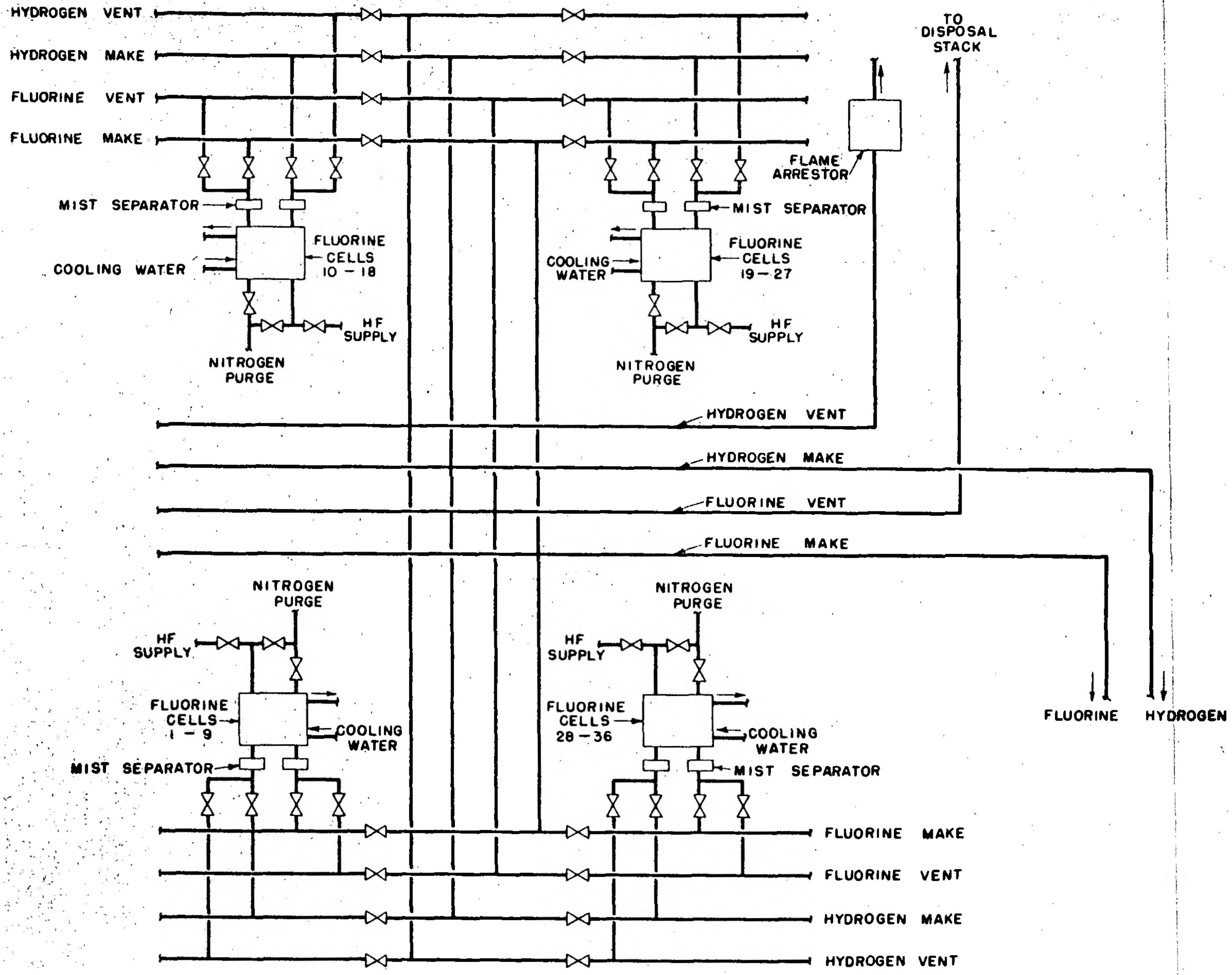

Figure 18
PROCESS GAS FLOW

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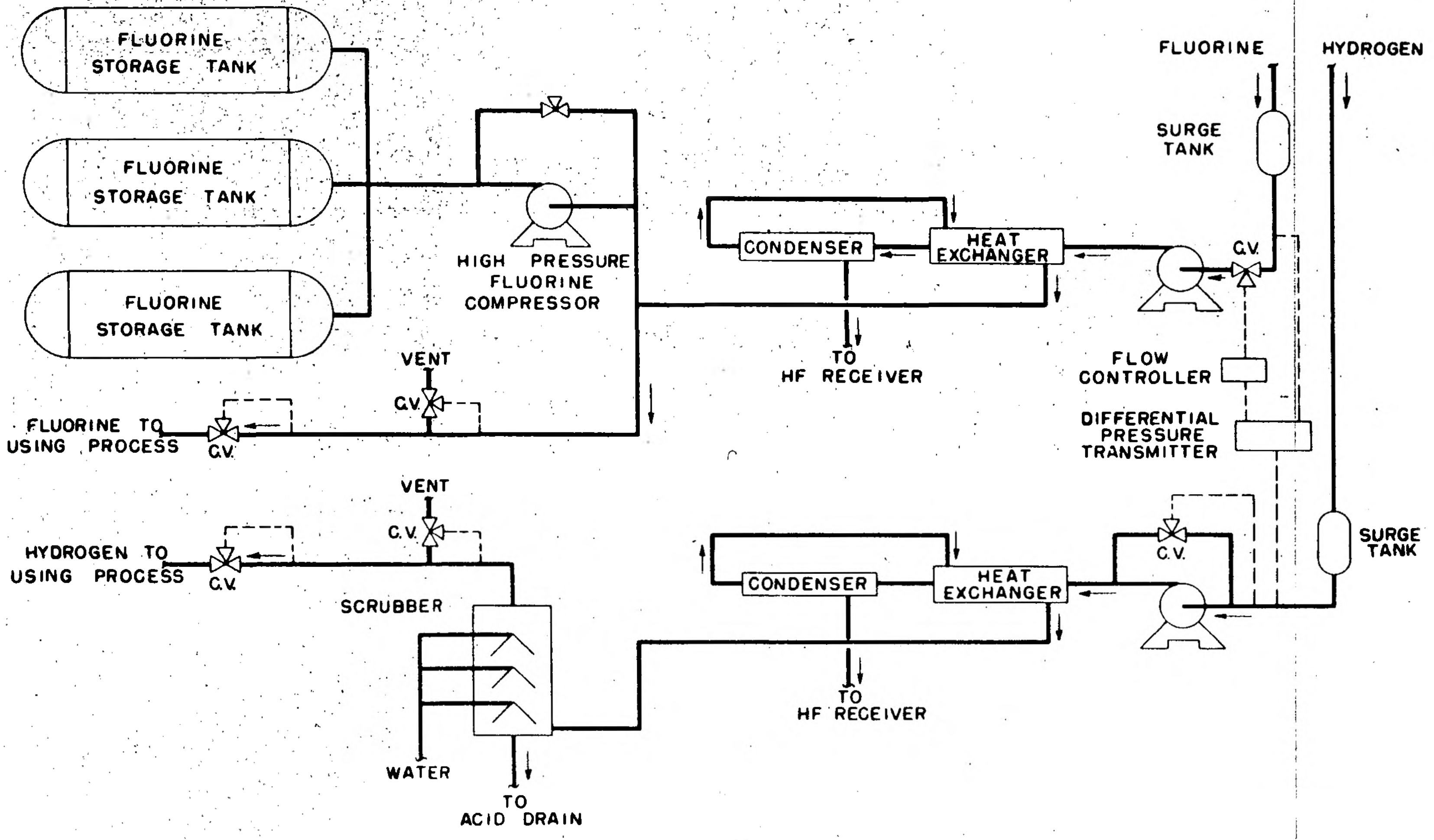

Figure 19
PRESSURE CONTROL SYSTEM

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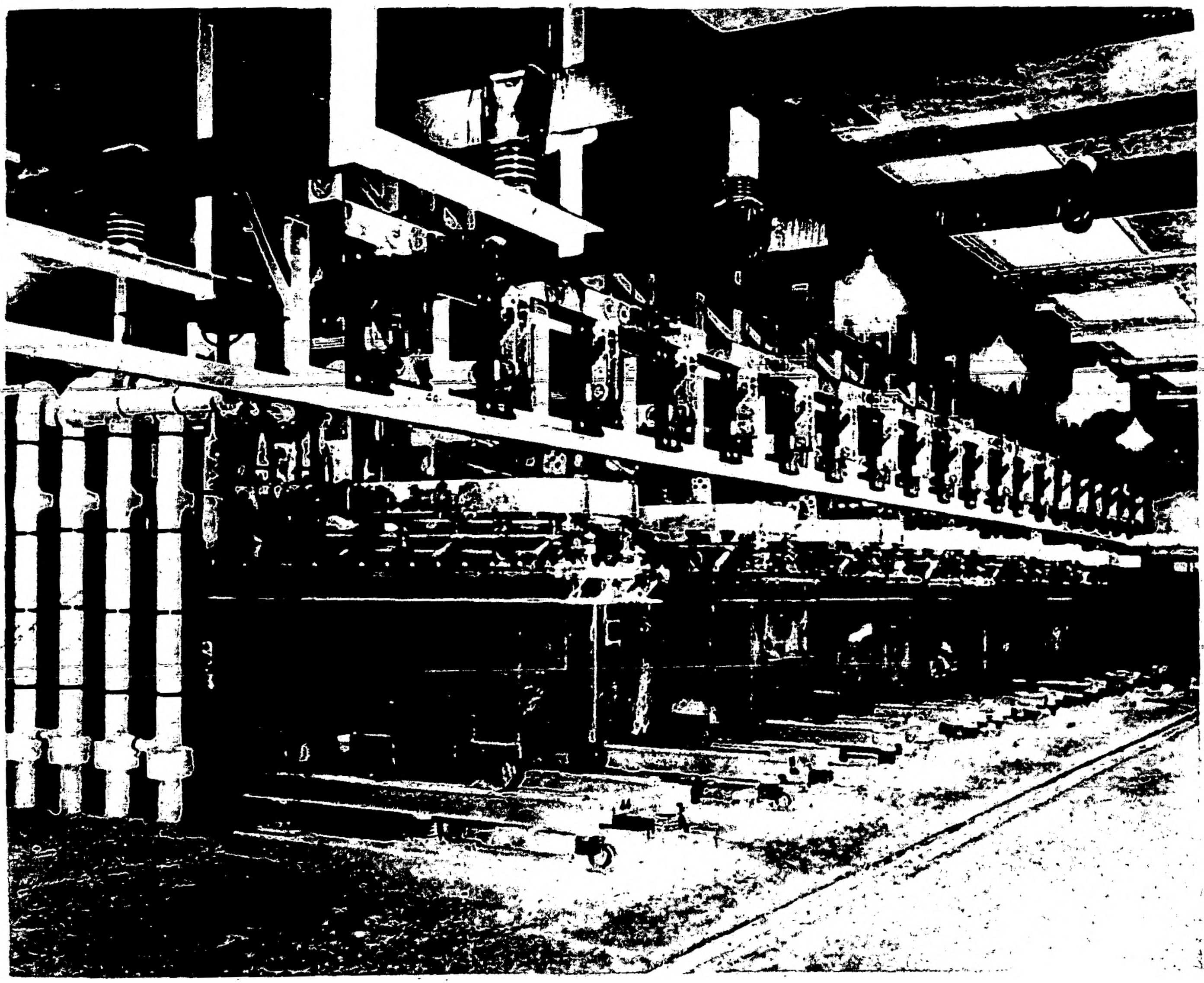

Figure 20
BANK OF LARGE FLUORINE CELLS

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