**FORMALDEHYDE TREATMENT
OF PUREX RADIOACTIVE WASTES**

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OCTOBER 1963

CHEMICAL PROCESSING

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

GENERAL ELECTRIC

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HW-79622
UC-70, Waste Disposal
and Processing
(TID-4500, 26th Ed.)

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October 1963

FIRST UNRESTRICTED
DISTRIBUTION MADE FEB 28 '64

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. AT(45-1)-1350 between the
Atomic Energy Commission and General Electric Company

Printed by/for the U. S. Atomic Energy Commission

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

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FORMALDEHYDE TREATMENT OF PUREX RADIOACTIVE WASTES

I. INTRODUCTION

Denitration of high-level radioactive wastes with formaldehyde has been successfully accomplished on a full plant scale at Hanford's Purex chemical separations plant. In the Purex plant, plutonium, neptunium, and uranium are recovered from irradiated fuel elements by dissolving the elements in HNO_3 and subjecting the resulting solution to a multistep solvent-extraction process. The plutonium, neptunium, and uranium are decontaminated from radioactive fission products and recovered as separated nitrate product solutions. The bulk of the fission products is contained in a single waste-raffinate stream which is processed for recovery of special materials and by-products, neutralized with NaOH and transferred to storage in large underground tanks.

A key step in the economics of waste handling and storage is removal of HNO_3 from the fission product waste stream and concentration to a minimum volume before neutralization. Thermal concentration of the waste involves volatilization of the HNO_3 and serves as the main volume reduction process. The reaction between formaldehyde and HNO_3 results in formation of gaseous denitration products and was found to be an effective supplement for plant operations. This report describes the laboratory work, semiworks studies, and the design and successful operation of full-scale plant equipment using formaldehyde for the removal of HNO_3 from a highly radioactive waste solution.

Denitration processes using chemicals other than formaldehyde are also being studied at Hanford on a batch and continuous operation basis. Relative effectiveness and costs, however, are not yet firm. Final choice of the process to be used for continued PAW denitration in Purex will be dictated by relative process and economic effects of integrating the denitration step into the overall plant system.

II. SUMMARY AND CONCLUSIONS

Continuous denitration of Purex acid waste (PAW) with formaldehyde has been successfully demonstrated in a full-scale plant prototype unit in the Hanford Purex plant. The reaction is smooth and is easily and safely controlled. Because severe foaming can occur in the reaction vessel, the use of an antifoam agent is required to attain acceptable plant processing rates. Extensive laboratory and pilot plant work, proper equipment design, and satisfactory operating procedures were the bases for developing adequate safeguards that assure complete control of the reaction at all times.

During operation, the formaldehyde and the preheated PAW stream (with 50 to 100 parts antifoam per million parts PAW) are added continuously to the reactor which is maintained at 95 C. From an initial feed concentration of approximately 6.1M, the free acid is reduced to 0.5 to 1.0M in the treated waste. About 2.5 moles of free acid are destroyed per mole of formaldehyde added to the unit for a 60% reaction efficiency. A decontamination factor of 10^4 from feed to recovered acid is typical, which means that the ratio of radioactivity to HNO_3 in the recovered acid has been reduced by a factor of 10,000 when compared to the same ratio in the high activity waste (PAW).

Formaldehyde denitration of the Purex acid wastes reduce the chemical costs of waste treatment and storage. In addition, the process increases the storage capacity of underground tanks because of less salts in the waste, increases the flexibility of waste treatment equipment, and improves the quality of feed for fission product recovery. Formaldehyde denitration is a safe and economical process for supplementing normal waste treatment operations in a Purex-type radiochemical plant.

III. PUREX PLANT OPERATION

The Purex plant process flow is shown in Figure 1 and is described in References (1) and (2). The key steps involve feed preparation; solvent extraction separation of the desired products; and subsequent treatment of the separated products, the solvent, and the waste streams.

In the first step, caustic solution is used to remove the aluminum jacket surrounding the uranium in the irradiated fuel element. The metallic uranium is dissolved in HNO_3 to form an acid-uranium nitrate solution containing plutonium, neptunium, and fission products. The feed solution is then contacted by an organic base (30 vol% tributylphosphate, 70 vol% diluent similar to kerosene) in a pulsed solvent extraction column under the proper chemical and flow conditions so that the plutonium, neptunium, and uranium transfer into the solvent leaving the fission products in the aqueous phase. Subsequent processing separates the plutonium and neptunium from the uranium in the Partitioning and Second Uranium Extraction Columns by proper adjustment of the plutonium and neptunium valence states. The three products leave the First Cycle as aqueous streams and each is subjected to a second transfer into the solvent (leaving the fission products in the aqueous phase) for additional fission product decontamination. The fission product streams from the First Cycle and the three Second Cycle operations are combined, concentrated and introduced into the first column to recover any plutonium, neptunium and uranium that may have remained with the fission products. Thus virtually all of the fission products (greater than 99.9%) leave the separations equipment in the HNO_3 effluent from the first column.

The raffinate waste stream, Purex high-activity waste (PAW), is thermally concentrated to recover HNO_3 and reduce the volume; about 90 to 95% of the HNO_3 in the waste stream is recovered. The remaining 5 to 10% of the HNO_3 is neutralized during and immediately after the waste is processed for recovery of desirable fission products. Neutralization of acid is required to permit storage of the waste in carbon steel-lined concrete tanks. The radioactivity content of this waste stream is such that the solution is self-boiling and requires that the material be adequately contained for hundreds of years. Consequently, construction of suitable storage space is costly and the incentive is great to reduce the stored waste volume to a minimum compatible with safety and the required high storage integrity.

IV. EARLY LABORATORY WORK ON THE HNO_3 -FORMALDEHYDE REACTION

The reaction of formaldehyde and HNO_3 has been known for years as a method of reducing the concentration of HNO_3 and nitrates from solutions without adding undesirable nonvolatile materials to the system. However, the reaction was pictured as violent and difficult to control mainly because of its induction period. Very little information was reported in the literature until T. V. Healy of the United Kingdom Atomic Energy Research Establishment published his work in 1957.⁽³⁾ His studies of the reaction were conducted at 100 C, and demonstrated that at this elevated temperature, the induction period is negligible. His work also included a laboratory demonstration of the feasibility of using a continuous formaldehyde addition to a vessel containing HNO_3 (3 to 20M) at 100 C.

The reaction was represented by Healy as different equations depending upon concentration of HNO_3 reacting. The equations are:

If formaldehyde is added to concentrated HNO_3 , initially 4 moles of HNO_3 are destroyed per mole of formaldehyde; but, as the acid concentration decreases, the reaction finally approximates a one-for-one ratio with formic acid and NO_2 as the products.

Barton tested in the Hanford Laboratories the feasibility of applying the formaldehyde reaction as a means of reducing the HNO_3 concentration in the high-activity waste (PAW) from the Purex separations plant.⁽⁴⁾ The reaction between formaldehyde and the HNO_3 in synthetic PAW proceeded smoothly when formaldehyde was added to the solution at a temperature greater than 80 C. Up to 75% of the formaldehyde was utilized at the stoichiometric ratio of 4 moles of HNO_3 destroyed per mole of formaldehyde added.

Volatilization of fission products did not appear to be a problem. Treated synthetic acid waste could be concentrated by a factor of three or more before solids began to precipitate.

V. SEMIWORKS DEVELOPMENT DATA

When laboratory studies showed potential application for the reaction between formaldehyde and HNO_3 in the Purex high-activity waste, pilot plant studies were initiated to confirm and extend existing laboratory information.⁽⁵⁾ Equipment design, operational behavior, formaldehyde utilization efficiency and safety considerations were the particular subjects of study. Figure 2 is a process flow chart showing the different equipment pieces.

The results from these studies confirmed the feasibility of continuous denitration of synthetic Purex plant PAW. Specific information obtained from these studies included:

- (1) The efficiency of formaldehyde utilization depended primarily on the temperature at which the acid feed was introduced into the system; a temperature near boiling was required to obtain good efficiency.
- (2) Over 95% of the free acid* was removed at a ratio of about 3 moles of free acid per mole of formaldehyde added.
- (3) The residual free acid must be greater than 0.3M to prevent solids precipitation.
- (4) Discharge of the formaldehyde either above or below the surface of the liquid was immaterial to the efficiency of the reaction.

Particular attention was given to studies involving pressurization of the equipment due to possible inadvertent addition of formaldehyde to HNO_3 at low temperatures followed by heating. Tests showed that when cold HNO_3 and formaldehyde were mixed and heated, the subsequent pressure increased with HNO_3 concentration until 47 in. H_2O pressure

* Free acid (dissociated hydrogen ions) analysis is determined by a coulometric titration that generates a free base by the constant current electrolysis of a dilute sodium bromide solution. The results are reported as free acid molarity.

was generated at 5M HNO_3 . At higher acid concentrations, the reaction usually started before the mixture was heated or before the concentration of formaldehyde could be increased sufficiently to produce a pressure above 47 in. of water.

VI. APPLICATION TO THE PUREX PLANT

Successful pilot plant denitration of simulated Purex plant PAW prompted further evaluation as to the application of the reaction to the Purex plant.⁽⁶⁾ A reduction in the HNO_3 concentration of the PAW before neutralization would reduce the amount of NaNO_3 in the final waste in proportion, and thus the volume of the final stored waste could be reduced significantly without precipitating additional solids. Not only would the reduced volume contribute to reduced waste storage costs, but sludge temperature control problems produced by precipitated sludge would be reduced. In addition, at normal production rates, the value of the HNO_3 recovered and the savings from reduced caustic consumption would result in a net essential material saving of approximately \$2/ton of uranium processed through the Purex plant.*

The reaction between formaldehyde and HNO_3 was recognized as an exothermic reaction with a possible induction period, and under certain conditions could be quite violent. The use of this reaction to treat high-activity waste in the processing plant meant that the reaction must be under control at all times. When handling highly radioactive fission products, loss of control cannot be tolerated. Based on laboratory work and the results of the semiworks tests, control could be assured under proper operating conditions. Accordingly, the decision was made to install formaldehyde denitration equipment as a prototype system with all the necessary safety features engineered into it which would prevent losing control of the reaction. Installation of one system as a prototype recognized the need for in-plant test studies to develop and establish final process and safety controls before placing the unit into routine operational use.

* All materials costs and flowsheet volumes are stated in terms of dollars or gallons per ton of uranium processed through the Purex plant.

VII. PUREX PLANT EQUIPMENT DESIGN

A. Process Equipment Description

The plant process flowsheet and prototype equipment design⁽⁷⁾ were patterned after that developed for the semiworks studies as shown in Figure 3. A controlled flow of PAW is pumped from the Concentrator Overflow Tank through a preheater into a packed tower mounted above the reactor. The heated PAW travels downward through the tower counter-current to the hot gaseous products from the reaction and is at or near the boiling point when it drops into the reactor. Formaldehyde is metered into the reactor and is discharged onto the surface of the liquid.

The products of the reaction, CO_2 , H_2O and oxides of nitrogen, travel upward through the packed tower and are deentrained in the packed section above the PAW inlet and by the tantalum mesh deentrainment pad mounted above the packed section of the tower. The deentrained off-gases are blended with air to oxidize the NO to NO_2 and routed into the bottom portion of a packed tube and sheet condenser provided with a downward flow of reflux water. The water vapor is condensed on the outside of the tubes and the oxides of nitrogen, except NO, are absorbed by the condensed vapor and reflux water to form recovered HNO_3 . About 60% of the oxides of nitrogen present are recovered in this step.

Depending upon its radioactivity content, the recovered acid can be recycled to the Purex Acid Waste Concentrator for additional decontamination by evaporation, or it can be routed directly into the Purex plant recovered acid system. The recovered acid is used in the process throughout the plant.

The formaldehyde is stored outside in a 5000 gal tank and is pumped from the tank through an all-welded line and a flow control system directly into the reactor by a canned motor pump. This design eliminates the hazards of storing formaldehyde inside the building with the accompanying special requirements for fire and ventilation control.

Safety considerations were designed into the equipment wherever possible. To locate the denitration equipment adjacent to the vessels handling the PAW, the reaction vessel was inserted inside a 5000 gal tank and the additional equipment was mounted on or above the tank. The tank-within-a-tank concept provides a safety feature which was not included as a design requirement but which could provide an additional margin of safety. The small size of the reaction vessel (20 in. diameter by 8 ft high) was selected to limit the amount of formaldehyde and PAW reacting at one time on the premise that a large tankful of reacting formaldehyde and HNO_3 out of control would be more hazardous than a small tankful. Other safety controls are described in the section concerning safety instrumentation.

B. Instrumentation

1. Process Control

Process control instrumentation centers mainly around flow and temperature of the reacting solutions. The PAW flow is controlled by a flow pot that is a piece of 5 in. pipe 24 in. long having an inlet and an outlet chamber separated by a baffle containing two orifices located at different heights. As the hydrostatic head on the lower orifice increases, as measured by a static pressure instrument (weight factor), the flow through the orifice increases. Eventually the liquid level reaches the second orifice and at this point the flow increases appreciably with a minor increase in liquid height within the pot. The PAW flow into the pot is controlled by a diaphragm-operated valve, actuated by the weight factor controller set to control the pot liquid level at a height which will deliver the prescribed flow. This type of control was selected instead of a rotameter to avoid plugging problems associated with the fine solids suspended in the PAW. Formaldehyde flow control is accomplished by an electronic rotameter actuating a diaphragm-operated valve through a recorder-controller.

The temperatures of the preheated PAW, the reaction vessel contents and the recovered acid receiver are measured by thermohms. The measured temperature is recorded by a recorder-controller which actuates a steam control valve to maintain the desired temperature. The pressure within the reactor and the differential pressures across the reactor tower and the packed condenser are measured and recorded.

2. Safety Instrumentation (Figure 4)

The condition that must be avoided during the operation of the formaldehyde unit is the addition of formaldehyde to the reaction vessel before the solution temperature in the vessel reaches 80 C. For this reason, an interlock exists between the temperature recorder-controller for the reaction vessel and the electrical circuit for formaldehyde pump. If the pot temperature falls below 90 C, the controller shuts off the formaldehyde pump if it is running or prevents its being started if it is not running. In either case, the pot temperature must exceed 90 C before the pump can be started. Thus at all times of formaldehyde addition, the temperature is sufficiently high to prevent an induction period which could result in a delayed reaction and pressurization within the equipment. If for any reason a vigorous reaction takes place in the reaction pot, and the operating pressure in the pot which is normally negative becomes positive and exceeds 2 in. water pressure, an interlock shuts off the formaldehyde pump automatically to prevent further formaldehyde addition to the reacting mixture. After a negative pressure has been reestablished and not before, the pump may be restarted.

The solvent used in the Purex process may become degraded and nitrated if allowed to remain in contact with concentrated HNO_3 solutions at elevated temperatures. The most likely location for forming nitrated, degraded solvent is in the waste concentrator, where the HNO_3 concentration ranges from 5 to 7M and the holdup time is greater than 50 hr. Nitrated solvent is unstable and could produce a violent chemical reaction if heated to a temperature greater than 130 C in the presence of heavy metal salts or if heated to greater than 150 C in the presence of PAW. (8)

To insure a temperature of less than 150 C at all times (in case some degraded solvent should enter the denitration equipment), the steam pressure to the coils of the PAW preheater and the reaction vessel is limited to a maximum pressure of 39 lb/in.² by the installation of properly selected control and pressure relief valves.

Since heavily nitrated and degraded solvent is heavier than the aqueous phase, it accumulates on the bottom of vessels. To prevent the introduction of degraded solvent and solids into the formaldehyde denitration reactor, the suction of the pump in the feed tank is located 12 in. off the bottom. Possible accumulations of nitrated solvent and solids are periodically purged from the feed tank by steam ejector transfer of the bottoms directly into the neutralizer tank, bypassing the denitration equipment.

C. Remote Maintenance Concept

Processing highly radioactive materials not only requires remote operation of the equipment, but also dictates remote maintenance capabilities if failed equipment is to be replaced or repaired within a reasonable time. Usually, failed equipment must be replaced because high radiation dose rates prevent maintenance personnel from approaching and repairing it. Certain types of equipment pieces have sufficient value or require long enough delivery time to warrant their decontamination and repair; however, this is a lengthy procedure.

In any event, replacement or repair requires removal of the equipment piece from the processing area remotely. At Hanford, remote maintenance is accomplished by a shielded-cab crane that has appropriate hooks and electrically operated impact wrenches attached to cables on drums. The operator views the work area from inside the shielded cab through a monocular periscope. Equipment pieces and piping sections are fabricated with connector nozzles which can be "made up" by turning the head of a single bolt. These connector heads are used on piping called "jumpers" to transport steam, water, process solutions, condensate,

process and instrument air, instrument signals, electrical power, and any other kind of services required to operate the plant within the remotely maintained process areas. Design and construction are based on tolerances of $\pm 1/16$ in. to insure reproducibility of location and a tight fit. To provide complete flexibility, all process piping and equipment pieces can be replaced remotely.

Figures 5, 6, 7, and 8 show the process vessels in the formaldehyde denitration system. Each vessel is equipped with special nozzles to accept the connector heads attached to the piping jumpers. The reaction vessel bolts to the ring flange of the tank into which it fits, while the tower bolts to the reaction vessels. A total of 40 jumpers connect the various equipment pieces to each other or to adjacent tanks and service connections. The equipment and piping were designed to permit a sequence schedule of installation to avoid interferences.

VIII. DEMONSTRATION OF PLANT-SCALE OPERATION

A. Early Operating Experience

Early operating experience with the prototype system in the plant demonstrated that safe control of the reactor operation was practical. The response of the safety features and the individual capacities of the system components were established during a series of preliminary operability tests and initial test operation with plant solutions. The reaction was found to start within 1 to 3 min after the initial addition of formaldehyde to the heated PAW solution. Operation appeared smooth and controllable although mechanical equipment difficulties did not permit good operating continuity.

Process efficiencies realized during early test operations with the prototype unit, however, were disappointingly low. Allowable throughput rates and denitration efficiencies appeared to be less than half that expected on the basis of seimworks data. Although the unit was operated at less than half the design rate, the pressure drop across the reaction tower frequently exceeded 50 in. of water, which caused the reactor to

operate slightly pressurized. During initial operation, instrumentation showed that the reactor liquid level dropped off rapidly until only 10 to 20% of the normal level remained. Even so, the pot contents continued to overflow into the receiver tank. In addition, the radioactivity in the recovered acid was thousandfold higher than desired. The behavior indicated that one or both of two probable conditions were occurring: (1) the HNO_3 and formaldehyde were reacting in the tower, and (2) excessive foaming in the reaction vessel extended into the tower.

Mechanical difficulties were also encountered, such as: (1) the formaldehyde flow was frequently two to three times the flowsheet value because of an oversized rotameter; (2) a failed thermohm erroneously indicated the maximum obtainable reactor temperature to be 95 to 100 C when the temperature was actually higher; (3) the gasket between the reaction vessel and the tower did not seal tightly and allowed highly radioactive vapor and liquid to leak into the cell if the system was slightly pressurized; and (4) a section of the transfer line between the PAW feed tank and the reactor plugged during a shutdown period.

By proper maintenance and equipment modifications plus continued operation of the plant prototype, the equipment difficulties were resolved. However, because remote operation of the unit prevented a diagnosis and because experimental operations interfered with production requirements, a rapid and exact definition of the process problem was impossible in the plant unit. Consequently, further laboratory and semiworks studies were initiated.

B. Scale Model Operation ⁽⁹⁾

Construction and operation of a one-tenth scale glass model denitration unit showed that the principal difficulty observed with the plant prototype unit was associated with severe foaming in the reactor pot. Two major test study areas were investigated in the scale model; operation without organic materials in the feed and operation with organic materials in the feed. In addition, the probability of prereaction in the tower was evaluated and batch versus continuous operation was tested.

The operating difficulties that had been experienced in the plant unit were not encountered in scale model operation during initial tests using synthetic PAW that had not been contacted with solvent. The unit operated smoothly and the reaction was easily controlled. The pressure drop across the tower was less than 1 in. of water at all flows tested and no difficulty was experienced in maintaining 10 to 20 in. of vacuum in the reaction pot. No flooding or excess reaction in the tower packing was observed even at rates equivalent to the plant flowsheet rate.

Plant operating difficulties were closely duplicated when severe foaming was induced in the glass scale model by the addition of solvent degradation product (dibutyl phosphate) to the synthetic PAW. At low formaldehyde rates, operation was essentially unchanged from earlier runs conducted without dibutyl phosphate present. At flowsheet rates, however, foam rose 76 in. above the overflow and 14 in. into the packed tower. Whenever the foam layer covered the pressure tap at the bottom of the tower, the pressure drop across the tower rose (up to 23 in. of water) and pot pressure increased (up to 15 in. of water).

The foam problem was alleviated in the scale model by the addition of antifoam agents to the synthetic PAW. Of the three antifoam agents tested, antifoams containing silicone in an emulsifying agent were the most effective. When antifoam was added to the PAW, foam height was reduced by a factor of two, and the tower differential pressure dropped from 23 to 5 in. of water. In addition, the appearance of the foam and solution in the reaction pot at normal flowsheet rates was changed when antifoam agents were added to PAW. The definite interface between the foam layer and reacting liquid ordinarily seen near the overflow disappeared but streams of foam permeated the liquid in the pot to within 28 in. of the bottom. After the addition of an antifoam agent, the maximum foam height was 37 in. and maximum differential pressure across the tower was only 5 in. of water, compared to 76 in. and 23 in., respectively, at the same rates without antifoam.

Test runs with the formaldehyde added below the surface of the liquid in the reactor (vice vapor space addition) did not show any change in operating characteristics of the test unit.

Although operation of the scale model unit during batch denitration tests was comparable to continuous operation, the formaldehyde utilization was lower. Approximately 1.4 to 2.0 moles of nitrate were destroyed per mole of formaldehyde added to test batches vs. 2.0 to 2.4 moles of nitrate destroyed per mole of formaldehyde added to PAW on a continuous basis.

C. Successful Plant Operation

After the scale model tests, continuous denitration of Purex high level waste with formaldehyde was successfully demonstrated in the plant prototype unit. Operation of the prototype unit is based upon the Formaldehyde Denitration Flowsheet outlined in Figure 9. Temperatures of the preheater and reaction vessel are maintained at 95 C by automatic controllers during the entire operating period. The PAW feed which contains approximately 6.1M HNO_3 is pumped at a controlled rate through the flow pot through the preheater and into the packed section of the reactor tower. An antifoam (10% silicone in an emulsifying agent) is added to the PAW in the flow pot to control foaming during the reaction. A 37 wt% formaldehyde solution stabilized with 6.5 to 7.5% methanol is pumped at a controlled rate into the vapor space of the reaction vessel. The formaldehyde-treated waste continuously overflows into the receiving vessel. The off-gases containing oxides of nitrogen, water vapor, and carbon dioxide are deentrained in the tower, and then mixed with air before entering the updraft condenser where HNO_3 is recovered for reuse in the Purex plant.

When antifoam is used to minimize foaming in the reaction vessel, the reaction is smooth and easily controlled at flowsheet rates. Without antifoam addition, the formaldehyde flow rate must be limited to 50% of flowsheet rate to prevent the foam created in the reactor from entering

the tower and pressurizing the unit. Addition of the antifoam agent directly into the PAW stream at concentrations of 50 to 100 ppm reduces reactor foaming sufficiently to allow processing at flowsheet rates.

Acid concentrations of the PAW stream vary somewhat depending upon operating conditions in the plant solvent extraction section and waste concentrator; however, concentrations as determined by the free acid analysis currently average 6.1M HNO_3 as shown in the flowsheet, Figure 9. Free acid concentrations of formaldehyde-treated waste ranged between 0.5 and 1.0M .^{*} Calculations indicate 2.5 moles of acid are destroyed per mole of formaldehyde fed to the unit. Complete destruction of any residual formaldehyde in the waste is assured by a residence time in excess of 1 hr at 95 C in the reaction vessel and an additional residence time in excess of 24 hr at 70 to 90 C in the waste batch collection tank.

A gamma activity decontamination factor of 10^4 has been obtained between the PAW and the recovered acid. This means that the ratio of fission product activity to HNO_3 concentration in the recovered acid is a factor of 10,000 smaller than the same ratio in the PAW. However, under current operating conditions, the radioactivity is a factor of 10 greater than that acceptable for direct reuse in the Purex plant; thus, return of the acid to the waste concentrator for additional decontamination by evaporation is required before plant usage. Approximately 40% of the acid destroyed by the formaldehyde is recovered as 20 wt% HNO_3 in the condensate receiver tank. An estimated 50% of the acid that escapes from the denitration prototype unit via the condenser vent system is recovered in the plant backcycle waste system. Tests are scheduled to determine the optimum air flow needed for oxidation of the nitric oxide and the optimum reflux water flow required to produce maximum acid absorption at a reasonable concentration. Recovery in

* In this range, the coulometric method used to date for determining free acid (disassociated hydrogen ion concentration reported as free acid) produces higher results than pH measurements of the denitrated wastes. Plant experience indicates the free acid is actually less than reported; hence, efficiency calculations are biased low.

the prototype condenser is expected to increase to a nominal 55 to 60% of the HNO_3 destroyed by the reaction. Approximately 15% additional acid will be recovered in the normal plant condenser vent system.

Every precaution is taken to insure complete control of the reaction by equipment design and administrative procedures. The Hazards Control diagram (Figure 4 and Section VII. B. 2) locate and describe the primary equipment controls installed to assure safe operation of the prototype unit. After temperatures and liquid levels are adjusted to runsheet values, the PAW is started and maintained at 95 C for a minimum of 30 min before the formaldehyde flow is started at 10 to 20% of the flowsheet value. If the reaction does not begin within 3 min, the formaldehyde flow is stopped until the reason for nonreaction can be determined. Plant experience has shown the reaction starts within 1 to 3 min and is easily detected by fluctuations in the reactor liquid level and specific gravity readings in the reactor and increased off-gas temperatures.

After start of the reaction is assured, the formaldehyde flow is slowly increased to flowsheet rate. As the reaction becomes increasingly vigorous, the reactor pressure recorder and the reactor tower differential pressure recorder indicate the extent of the reaction. During normal operation, the tower differential recorder registers 40 to 45 in. of water vacuum when the condenser vent system registers 50 in. of water vacuum. The reaction vessel pressure recorder usually indicates a vacuum of greater than 15 in. of water.

IX. ADVANTAGES OF FORMALDEHYDE TREATMENT

Formaldehyde treatment of Purex radioactive wastes offers economic and operational advantages in terms of reduced essential materials costs, improved waste storage capability and increased plant flexibility. The relative effects of treating and not treating Purex acid wastes with formaldehyde are summarized in Tables I and II.

TABLE I

EFFECT OF DENITRATION OF VOLUME AND CHEMICAL CONSUMPTION

(The comparative information given in this table is based upon the chemicals and/or volume required per ton of uranium processed in the plant.)

	Without Formaldehyde Treatment	With Formaldehyde Treatment
Volume of PAW from Concentrator, gal	40	40
Amount of HNO ₃ Removed, lb	--	104
Amount of HNO ₃ Recovered, lb	--	83
Amount of HNO ₃ in Final Waste, lb	124	20
NaOH Required to Neutralize Waste, lb	78.7	12.7
Amount of Sodium Added, lb	45.2	7.3
Minimum Safe Storage Volume Required for Sodium Added, gal	29.5	4.8

TABLE II

DENITRATION ECONOMICS

(To determine the economic value of the formaldehyde denitration process, the following basis was used for delivered costs of chemicals as 100% usable materials.)

Assumed Cost*

NaOH	2.96 ¢/lb
HNO ₃	2.64 ¢/lb
Formaldehyde	10.05 ¢/lb
Underground Tank Storage**	45.00 ¢/gal

Direct Neutralization

Cost of NaOH	\$2.32/T
Net Cost	<u>\$2.32/T</u>

Formaldehyde Treatment Plus Neutralization

Cost of Formaldehyde Used	2.08/T
Cost of Antifoam	0.02/T
Cost of NaOH	0.38/T
Total Cost	\$2.48/T
Value of HNO ₃ Recovered	<u>2.20/T</u>
Net Cost	<u>\$0.28/T</u>

Savings

Chemical	\$2.04/T
Waste Storage 24.7 gal (From Table I) x 45 ¢/gal	<u>11.12/T</u>
Total Savings	<u>\$13.16/T</u>

* A flowsheet value of 40 gal of PAW/ton of uranium produced was assumed for calculating the costs of materials and storage.

** If underground storage tank replacement costs were used, storage costs would be approximately a factor of two greater than the figures in this table.

A. Reduced Essential Materials Costs

Denitrating the wastes with formaldehyde reduces the NaOH required for neutralization of the PAW solution before transfer to underground storage from 78.7 lb/ton to 12.7 lb/ton of uranium processed. Assuming caustic costs of 2.96 ¢/lb, this reduces the flowsheet chemical cost by \$1.94/ton of uranium processed.

Approximately 83 lb of HNO_3 per ton of uranium processed are recovered from the PAW solution by formaldehyde treatment. Acid is returned to the recovered acid system of the plant for reuse. Assuming acid values of 2.64 ¢/lb, the flowsheet return is \$2.20/ton of uranium processed.

After deducting the formaldehyde costs from the combined savings resulting from reduced caustic consumption and increased acid recovery, formaldehyde treatment offers a net savings in chemical costs of \$2.04/ton of uranium processed through the plant.

B. Improved Waste Storage Capability

Treatment of acid in PAW solution with formaldehyde reduces the sodium salt content of the neutralized waste during its storage in underground tanks and thereby improves waste sludge control. The bulk of the heat generating fission products in the waste precipitates in alkaline solutions and tends to settle on the bottom of the tanks in a layer of sludge. Dissipation of heat generated in the sludge is affected by the amount of solids deposited which is influenced by the circulation rate and salt content of the supernatants. Uncontrolled precipitation and settling out of solids could result in temperatures considerably exceeding the control limit of 300 F. The sodium salt concentration in the tank is therefore limited to less than 8M to prevent excess salt precipitation and sludge temperature increases.

Removal of HNO_3 before neutralization by formaldehyde reduces the sodium added during neutralization from 45.2 to 7.3 lb/ton of uranium processed. The minimum waste storage volume of the NaOH added during

neutralization is therefore reduced from 29.5 to 4.8 gal/ton of uranium processed. As indicated in Tables I and II, this volume reduction is equivalent to storage space savings of \$11.12/ton of uranium processed. Since construction costs are continually increasing, savings based upon current or future tank replacement costs would be significantly higher.⁽¹⁰⁾

C. Improved Plant Flexibility

Experience has shown that the recovery efficiency of the acid absorber in the Purex plant waste treatment system may be increased by minor changes in the operating procedure. One such change involves adjusting the rate of waste solution boil-off so as to provide a near optimum absorber vapor throughput; thus, the overhead acid losses are reduced. However, to provide minimum neutralized waste storage volumes, the rate of waste solution boil-off in the past has been controlled to minimize the bottoms acid concentration rather than to optimize absorber acid overheads efficiency. With formaldehyde treatment available to recover HNO_3 from the PAW solution, absorber efficiency may be increased with no increase in neutralized waste storage requirements.

A lower acid concentration in the formaldehyde-treated PAW reduces the amount of caustic required during acidity adjustments in the Fission Product Recovery process.⁽¹¹⁾ The lower salt content improves the feed quality and the smaller overall volume reduces both the chemical consumption and the processing time cycle. Some difficulties have been noted in the plant in maintaining stable precipitate-free solutions of the low free acid concentrations possible with formaldehyde denitration.

Current plans for long-term management of high level waste at Hanford are based on processing the raffinate solutions for removal of long-lived isotopes and interim storage of the short-lived and inert residues until the material can be immobilized as a salt cake.⁽¹²⁾ The process flowsheets developed for waste extraction require a slightly acid solution for good separation and benefit by a low salt content. Thus

denitration with formaldehyde provides a feed material better suited to waste extraction than neutralization with caustic.

Other waste management plans under consideration for off-site Purex type plants include calcination and long-term storage as an acid solution. Both types of storage would benefit by a formaldehyde denitration process; the former in terms of a more suitable feed stock and the latter in terms of lower tank corrosion.

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FIGURE 1
Purex Process Flowsheet

FIGURE 2

Semiworks Denitration Flowsheet

FIGURE 3
Formaldehyde Denitration Equipment

FIGURE 4
Formaldehyde Denitration Flowsheet

FIGURE 5
Formaldehyde Reactor

FIGURE 6
Formaldehyde Reactor

FIGURE 8

Formaldehyde Reaction Tower

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FIGURE 8
Updraft Condenser

FIGURE 9
Formaldehyde Denitration Flowsheet

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