UNCLASSIFIED

HW-58587

AEC RESEARCH AND DEVELOPMENT REPORT

MASTER

THE PILOT PLANT DENITRATION OF PUREX WASTES WITH FORMALDEHYDE

T. F. EVANS

FEBRUARY 23, 1959

HANFORD LABORATORIES

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

GENERAL ELECTRIC

UNCLASSIFIED

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

UNCLASSIFIED

HW-58587

UC-4, Chemistry General
(TID-4500, 14th Ed.)

THE PILOT PLANT DENITRATION OF PUREX
WASTES WITH FORMALDEHYDE

By

T. F. Evans

Chemical Development
Chemical Research and Development Operation

February 23, 1959

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. W-31-109-Eng-52 between
the Atomic Energy Commission and General Electric Company

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

Printed in USA. Price \$1.00. Available from the

Office of Technical Services
Department of Commerce
Washington 25, D. C.

UNCLASSIFIED

THE PILOT PLANT DENITRATION OF PUREX
WASTES WITH FORMALDEHYDE

I. INTRODUCTION

The reaction between formaldehyde and nitric acid, in which the acid is destroyed with the production of predominantly gaseous products, has been recognized as of great potential value in the processing of radioactive fuels, particularly during waste treatment. Laboratory studies of the reaction at Harwell and at Hanford have shown that a major fraction of the nitric acid can be readily removed from an acidic solution containing nitrates by the addition of formaldehyde. The process possesses the advantages of low chemical cost; recoverability of nitric acid; and, in the case of waste treatment, the production of a solution relatively low in inert salt concentration suitable for fission product recovery or ultimate disposal.

The primary purpose of the present study was to confirm and extend existing information on the application of the formaldehyde reaction to the destruction of nitric acid in Purex type waste (1WW) through operation of pilot plant scale apparatus. Operational behavior, formaldehyde utilization efficiency, and safety considerations were particular subjects of study. In addition, destruction of nitric acid in a Darex-type dissolver solution was investigated.

II. SUMMARY AND CONCLUSIONS

The continuous denitration of synthetic Purex 1WW solution with formaldehyde was investigated in pilot plant scale equipment. The reaction proceeded smoothly and was easily controlled. The efficiency of formaldehyde utilization depended primarily on the temperature of the acid feed which was introduced at the top of a packed tower in which it contacted vapors from the reaction pot. A temperature approaching the boiling point is necessary for good efficiency. Over 95 per cent of the free acid may be removed at a feed ratio of 3.1 moles of free acid per mole of formaldehyde while simultaneously reducing the 1WW volume by a factor of three.

Formaldehyde in the pot was completely destroyed during a holdup period of less than two hours. Whether the formaldehyde entry line terminated in the liquid or vapor phase was immaterial to the efficiency of the reaction. A residual product acidity of greater than 0.3 molar free acid was required to prevent precipitation, but at the optimum acidity precipitation did not occur until the 1WW volume was reduced by a factor of greater than four. Addition of methanol appeared to cause a small increase in the amount of nitric acid destroyed per mole of formaldehyde but its use in the type of system studied is not considered justifiable.

During special safety tests in which nitric acid and formaldehyde were mixed together and then heated, the maximum pressure developed increased with increasing formaldehyde concentration and with increasing nitric acid concentration up to five molar acid. At higher acid concentrations the reaction usually began before the mixture was heated and sufficiently high concentrations of formaldehyde to cause high pressures could not be accumulated. Pressures up to 47 inches of water were observed. With denitrated 1WW-formaldehyde mixtures, a maximum pressure of 12.3 inches of water was observed from a solution containing 3.3 molar free acid and 1.7 molar formaldehyde. Although a slight pressurization of the process equipment can be brought about by maloperation, the hazards of the process should not cause undue concern.

III. THEORY AND REVIEW

The reaction between formaldehyde and nitric acid has been extensively studied by workers in the British Atomic Energy Research Establishment^(1, 2, 3). They reported the reaction could be represented by the stiochiometry:

Formic acid, produced in reaction (3), will also react with nitric acid in a manner analogous to equations (1) and (2), i. e.

Equations (1) and (2), and (4) and (5) are linked by the reaction

for which the equilibrium is displaced toward the right by increasing the nitric acid concentration and by raising the temperature.

The formaldehyde reaction rate has approximately a third order dependence on the nitric acid concentration and a 1.4 order dependence on the formaldehyde concentration. At 100 C the reaction with eight molar nitric acid is almost instantaneous ($k = 9.1 \times 10^{-4} \text{ liters}^2, \text{ moles}^{-2}, \text{ sec}^{-1}$).

An induction period of up to several hours may precede the reaction, particularly at low acid concentrations and temperatures, since the reaction mechanism seems to involve the nitrite ion. Existence of this induction period has caused fear that a large excess of formaldehyde might be accumulated under some conditions and a dangerous rapid reaction could result. The induction period can be reduced by adding nitrogen dioxide or nitrite ion. Ferric, uranyl, and other salts increase the rate of the reaction and decrease the induction period.

The formic acid reactions are approximately half as fast as the corresponding formaldehyde reactions. Methyl alcohol (present in commercial formaldehyde as a preservative) also reacts with nitric acid but much more slowly than formaldehyde.

The reaction of formaldehyde with synthetic Purex 1WW was studied by Barton⁽⁴⁾. Seventy per cent of the total nitrate could be destroyed at a feed ratio of four moles of total nitrate per mole of formaldehyde, or

80 per cent of the total nitrate could be destroyed at a total nitrate to formaldehyde mole ratio of two. Decontamination factors of greater than 10^5 for ruthenium and for gross fission products were found between the reaction pot and the recovered acid. The reaction proceeded smoothly and rapidly when the reactants were fed continuously to a reaction pot maintained at greater than 80 C. The product could be concentrated by a factor of three or more before solids began to precipitate. A residence time of about one hour was found to be adequate unless a product acidity of less than 0.5 molar was desired in which case a longer time was required.

IV. APPARATUS AND PROCEDURE

Description of Apparatus

The apparatus was a compromise between available existing equipment pieces and an optimum design based on the previous laboratory data. Special consideration was given to study of the potentially hazardous reaction under abnormal conditions. Figure 1 shows an equipment flowsheet. The reactants were fed through controlling rotameters from head tanks to a reaction pot located inside a 30,000-gallon containment tank for catastrophe control. Also in the large tank were a packed tower and equipment for removal of the product solution. Gases from the pot passed through the packed tower, where they contacted the feed acid, to a downdraft condenser, a backup acid absorber, and the stack.

The reaction pot was a 24-liter stainless steel vessel approximately twelve inches in diameter. It had connections for a steam (or cooling) coil, an air sparger (for agitation), two formaldehyde inlets, water inlet, a temperature bulb, dip tubes, a three-inch safety head, a three-inch flange for the tower, a drain, and a central overflow pipe. For Runs 1-7 the pot overflow volume was 20 liters. For the remainder of the runs this volume was reduced to 8.4 liters by shortening the overflow pipe.

The two formaldehyde feed lines entered the pot through its top. One extended just below the surface of the solution and the other ended in

FIGURE 1
Equipment Flowsheet

the vapor space. Care was taken to ensure a free flow path from the formaldehyde control valve to the pot so as to avoid surges in the formaldehyde flow rate. A pot-pressure-actuated solenoid valve capable of closing the formaldehyde feed line within three seconds in event the pot pressure exceeded three psig was also provided as a safety factor but was never actuated.

The acid feed, which entered the system at the top of the packed tower, was heated by means of variac-regulated electrical heating elements lying along a three-foot section of the feed line.

A 43 psi aluminum safety disc, protected internally by a Teflon (a duPont product) film, was initially installed in the safety head for the first tests of pressure buildup due to abnormal operations. It corroded through after Run 2 and was replaced by a stainless steel safety disc. After Run 7, this was replaced by a blank when a pinhole, probably caused by rough handling, was discovered in the safety disc and subsequent runs were made without safety head protection.

The product solution flowed through a cooler to an overflow vessel which was vented to the atmosphere. From the overflow vessel it was transferred by an air jet to a cyclone separator from which the solution flowed through a conductivity meter to a receiver tank. The reaction pot could be drained by the same air jet used to remove product solution. For batch experiments, temporary piping was added to allow sampling of the pot via the drain line and recirculation from the cyclone through the conductivity meter back to the pot via the normal acid feed inlet point.

The packed tower originally was a two-foot length of three-inch-diameter pipe packed with 1/4-inch stainless steel rings. After Run 3, the packing was replaced with 1/2-inch rings because of high pressure drop in the tower. The change did not correct the difficulty however, and after Run 7 more extensive changes to the tower were made. The tower was replaced by a four-inch pipe and packed with 1/2-inch procelain Intalox saddles. The packing was continued six inches above the four-inch

pipe into a three-inch diameter section to give a total packed height of 2-1/2 feet. At the same time the packing support, a 2-1/2 inch-diameter section of 3/16-inch mesh screen tacked to a stainless steel plate, was replaced by a cone-shaped screen with a maximum opening of 3-1/2 inches. Following these modifications the pressure drop across the tower was normally less than one inch of water. Following Run 15, the acid entry point was raised and the tower was packed to an additional height of 2-1/2 feet in the three-inch vapor line (total packed height = five feet). The acid feed distributor consisted of a splash plate inside a short length of 1-1/2-inch pipe.

Vapors from the tower passed via a vapor line to a downdraft condenser and a bubble-cap absorber. The vapor line was insulated to prevent condensation and reflux of nitric acid prior to the condenser. The condenser was a five-foot length of six-inch pipe inside of which was a cooling coil of 1/2-inch pipe (50 turns) around a core of three-inch pipe (17 square feet). The vapor space was packed with 1/4-inch stainless steel rings. Air, for oxidation of NO, and water for improved scrubbing were metered into the vapor inlet of the condenser. The absorber, incorporated mainly to prevent excessive spread of fumes to the atmosphere, was six inches in diameter. It had four trays with one three-inch bubble-cap per tray and two-foot tray spacing.

Temperatures indicated on Figure 1 were measured with iron-constantan thermocouples welded into stainless steel wells. With this method of construction thermocouples in contact with hot acid were subject to failure because of porous welds. The reaction pot temperature was also measured by a Taylor mercury bulb temperature recorder-controller calibrated to cover the range 90 to 115 C. Steam to the reaction pot coil was controlled by means of this latter instrument.

The pot pressure was measured through Republic differential pressure transmitters and recorded on a dual-pen Foxboro pressure recorder. The two pens were calibrated to record the ranges 0 to 30 inches of water

and 1 to 15 psi. The maximum rate of pressure change encountered was of the order of 10 inches of water per second, which was within the response limits of the recorder.

The conductivity cell was a seven-inch length of polyethylene, 1/4-inch inside diameter, with two 0.2- by 0.2-inch platinum electrodes oriented parallel to the line of flow and spaced 3-1/4 inches apart. The resistance was measured on an Industrial Instruments Conductivity Bridge, Model RC 16B1, using 1000 cps input and a 0.1 mf external capacitor. The cell and bridge were provided by the Process Control Development Operation.

Materials

The formaldehyde used was the common commercial grade methanol-stabilized 37 per cent solution. It analyzed 13.5 molar formaldehyde and 10.5 per cent methanol. For Run 18, the composition was altered by the addition of 1.2 liters of reagent grade methanol to eight liters of formaldehyde to increase the methanol concentration to approximately 20 per cent.

The synthetic Purex 1WW acid feed was made up to approximate the target composition given below. Laboratory analyses for specific components used in subsequent calculations are also given; analyses for the other components were not performed. Batches two and three contained a small amount of free-settling sediment contributed by the technical grade ferric sulfate used to provide the ferric ion. It is unlikely the differences in composition would materially affect the application of the results to similar solutions.

Component	Target	Molarity		
		Batch 1 (Runs 1 to 9)	Batch 2 (Run 10)	Batch 3 (Runs 11 to 18)
H ⁺	6.2	6.7	6.1	6.1
Na ⁺	1.0	0.94	0.76	0.90
Fe ⁺⁺⁺	0.2			
Al ⁺⁺⁺	0.1			
Cr ⁺⁺⁺	0.01			
Ni ⁺⁺	0.006			
NO ₃ ⁻	7.08	7.4	7.0	7.6
SO ₄ ⁼	0.5			
PO ₄ [≡]	0.02			

Normal Procedure

During normal operation readings of tank liquid levels; product conductivity; and product, condensate, and absorbate specific gravity were made at half-hour intervals. Runs were continued for at least two hours after the conductivity readings became constant. Samples of the flowing streams taken during this period were used for subsequent calculations. Free acid, sodium, total nitrate, and formaldehyde concentrations were normally determined in the product stream and the total nitrate concentration was determined in the condensate and absorber acid.

The normal startup procedure was as follows:

1. Check head tanks to determine that no large amount of either reactant had leaked to the reaction pot and that sufficient feed was available for the run.
2. If heel from previous run had been removed, fill pot to the overflow point with 1WW.
3. Heat the pot to near boiling.
4. Start the reactant flows, acid preheater, and auxiliary water and air flows.

5. Adjust the pot temperature control point to provide the desired volume split between overflow and condensate.

Shutdown normally consisted merely of stopping the reactants and then all other flows to the equipment and recording the head tank liquid levels. After some runs a simmer period of up to an hour at 95 C was allowed after shutting off the reactants to determine whether a longer holdup time in the pot would have had any effect on the overflow composition.

V. DISCUSSION OF RESULTS

The major portion of the studies was directed at the continuous destruction of nitric acid in synthetic Purex 1WW solution. Other tests included batch destruction of nitric acid in the Purex 1WW and in Darex dissolver solution and attempts to pressurize the system by deliberately initiating an abnormally rapid reaction. Results of the continuous runs are given in Table I and of the pressurization tests in Table II.

Continuous 1WW Denitration

Results of the continuous runs are tabulated in Table I, however the data relating to the efficiency of denitration prior to Run 8 are not representative of practical operational conditions because of flooding in the packed tower. Results from Runs 8 through 18 are plotted in Figures 2 and 3 and compared with Barton's laboratory results.

The most pronounced effect noted is the strong dependence of efficiency on the temperature of the acid feed. The efficiency of formaldehyde utilization is measured by the closeness of approach to the line representing four moles of nitric acid destroyed per mole of formaldehyde reacted - characteristic of the stoichiometry in the presence of 8 to 16 M HNO_3 . Minor discrepancies between the two figures arise from the fact that points in Figure 2 were calculated from total nitrate analyses whereas those in Figure 3 were calculated from free acid analyses. Both figures confirm that a high feed temperature is desirable.

UNCLASSIFIED

TABLE I

DESTRUCTION OF NITRIC ACID IN PUREX 1WW

Run No	Tower	H ₂ CO Entry		1WW		Air Rate % of Stoich	H ₂ O Rate			Liquid Volume Liters	Pot		Condensate			Product		Hold up hrs	Residual Nitrate-%			Residual H ₂ CO %	Residual Free Acid %	(Free Acid H ₂ CO) Mole Ratio		Material Balance			
		Pt	Rate	Temp	Air		Conden- ser	Absorber	Temp		Press	Rate	Conc	Recovery	Conc	Overflow	Nitrate-%		Residual H ₂ CO	Free Acid	NO ₂ /H ₂ CO Mole Ratio			Fed	Reacted	Fed	NO ₃ -	Vol	
		(1)	(2)	mi/min ° C	SCFM		mi/min	mi/min	° C		in H ₂ O	mi/min	H ⁺ M	% (3)	Sp Gr	H ⁺ M	%(4)		% (5)	(6)	(7)			(8)	Fed	Reacted	Ratio Fed	NO ₃ -	Vol
1	1	V	195	85	2 0	184	--	100	20	103 9	18	7 9	57	1 26	3 6	70	53	3 2	43	32	0	5 0	3 4	4 5					
2	1	L	187	60	2 0	220		150	20	103 9	10	58	7 1	57	1 28	64	64	2 8		47	1 0	5 6	3 0	5 0	82	95			
2-A	1	L	194	26	2 0	200		150	20	103 9	14	60	8 3	56	1 28	65	58	3 0		38	1 4	5 2	3 4	4 7	79	89			
3	1	L	193	23	2 0	160	--	200	20	107 0	20	30										4 2		3 8					
4	1	L	170	28	2 0	288	-	100	20	104 5	25	43	7 5	54	1 27	76	62	3 2		53		6 7	3 2	6 0	88	80			
5(10)	1	L	105	25	2 0	316	--	100	20	104 2	24	44			1 30							4 5		4 0		54			
6	1	L	106	24	1 5	228		100	20	104 2	17	44	6 1	53	1 30	4 6	54	46	5 7	43	34	0 2	37	4 4	2 9	4 0	83	85	
6-A	1	V	107	24	1 5	210	--	100	20	104 2	19	92	3 8	66	1 29	4 4	53	57	5 5	41	32	0 1	37	4 1	2 8	3 7	91	126	
7	1	V	106	25	1 5	132	-	200	20	101 8	28	45			0 7			62	5 1				2 6		2 3		86		
8	2	V	103	80	1 5	169		100	8 4	99 5	1 8	45	6 2	28	1 24	1 3	60	61	2 2	20	19	0 2	12	3 2	2 6	2 9	58	89	
9	2	V	103	79	1 0	70		150	8 4	100 0	3 6	81	3 9	46	1 33	0 0	40	33	4 1	9	10	7 0	0	1 9	1 9	1 7	66	87	
10	2	V	214	80	1 0	54	-	200	8 4	99 0	4 5	88	6 8	48	1 19	0 8	63	61	1 1	20	18	0 1	9	3 1	2 5	2 7	73	87	
11	2	V	211	81	1 5	101	--	200	8 4	98 8	3 6	54	9 3	28	1 20	2 0	79	96	0 7	42	30	1 0	27	4 0	2 9	3 2	68	106	
11 A	2	L	216	79	1 5	100		200	8 4	98 8	3 6	41	9 7	35	1 20	2 0	77	75	0 9	41	30	0	26	4 0	2 8	3 2	71	82	
12	2	V	207	79	1 0	133	--	200	8 4	101 0	3 5	27	10 8	41	1 24	4 0	81	91	0 7	64	54	0	56	7 8	3 6	6 2	85	97	
13	2	V	215	25	1 0	105	100	200	8 4	98 8	3 5	107	4 3	70	1 23	3 7	100	79	0 8	70	60	56	0	63	6 3	2 6	5 0	100	83
14	2	V	211	94	1 0	115	50	200	8 4	100 0	3 9	111	5 2	64	1 25	3 4	71	67	1 0	53	43	0	41	6 8	3 9	5 4	89	91	
14-A	2	V	216	94	1 0	114	50	200	8 4	103 0	3 9	132	4 9	65	1 28	3 4	57	54	1 2	47	39	37	0	32	6 8	4 2	5 4	88	87
15	2	V	201	92	1 0	65	50	200	8 4	101 5	4 5	174	4 0	56	1 29	1 4	41	43	1 6	29	18	19	0	10	3 7	3 0	2 9	96	92
16	3	V	187	93	1 5	120	150	200	8 4	101 0	5 1	221	3 3	66	1 24	1 3	54	54	1 4	29	23	23	0	12	4 2	3 3	3 4	86	89
17	3	V	186	93	1 5	103	150	200	8 4	101 2	5 4	260	3 1	66	1 30	0 1	38	36	2 1	20	14	14	0	0	3 6	3 1	2 9	86	89
18(9)	3	L	188	93	1 5	107	150	200	8 4	101 7	5 3	238	2 7	56	1 30	1 7	38	45	1 7	28	19	19	0	11	4 3	3 5	3 4	75	88

NOTES

- (1) See 'Description of Apparatus' Tower 1 - Flooded Tower 2 = 2-1/2 feet of 1/2 inch Intalox Saddles Tower 3 = 5 feet of 1/2 inch Intalox Saddles
 (2) V Vapor space L Liquid phase
 (3) Fraction of destroyed nitrate recovered in condensate
 (4) Overflow rate relative to 1WW feed rate By sodium balance
 (5) Overflow rate relative to 1WW feed rate By overflow accumulation measurement
 (6) Weight of nitrate in overflow relative to weight in 1WW feed By 'Free' acid analysis and sodium balance
 (7) Weight of nitrate in overflow relative to weight in 1WW feed By total nitrate analysis and sodium balance
 (8) After one half- to one hour summer at 95 °C By total nitrate analysis
 (9) Methanol content of formaldehyde 20 per cent
 (10) Large leak in vapor line

-12-

HW-58587

UNCLASSIFIED

TABLE II
PRESSURIZATION TESTS

Initial Pot Composition			Formaldehyde Total Gram Moles	Maximum Press. -in. H ₂ O
Composition	Free Acid			
	Conc. -M	Total Gram Moles		
HNO ₃	2.0	20	2.5	0.3
HNO ₃	2.0	20	9.8	2.1
HNO ₃	2.4	20	24.6	18.6
HNO ₃	5.1	48	2.5	0.2
HNO ₃	5.1	48	6.3	2.4
HNO ₃	5.1	49	12.5	36
HNO ₃	5.1	48	14.3	47
HNO ₃	7.7	75	3.4	2.4
HNO ₃ (1)	7.7	72	5.9	<12
HNO ₃ (2)	7.7	72	8.9	0.8
HNO ₃ (2)	7.7	72	9.1	4.5
1WW product from				
Run 12	4.0	34	6.8	8.4
Run 13	3.8	26	13.5	12.3

NOTES:

- (1) Maximum pressure occurred prior to heating while sparge air for mixing was on.
- (2) Maximum pressure occurred prior to heating.

FIGURE 2
Denitration of Purex 1WW

FIGURE 3
Denitration of Purex 1WW

The effect of feed temperature is primarily a reflection of the effect of temperature on the reaction in the packed tower:

A high temperature shifts the equilibrium to promote the reaction of NO (characteristic of the less efficient formaldehyde reaction, Equation 2) with nitric acid to form NO₂ (characteristic of the more efficient reaction, Equation 1); thus, effectively increasing formaldehyde utilization. The formaldehyde utilization efficiency which would be observed if the vapors from the top of the packed tower were in equilibrium with the feed acid at the temperature of the feed, was calculated theoretically for nitric acid solutions with no added salts. The calculations are outlined in the Appendix and the results are shown in Figure 4. The strong effect of feed temperature is evident.

Deviations of the experimental data from the curves shown in Figure 4 are due to several competing causes. The presence of salts in the feed acid increases the relative volatility of nitric acid from a solution of a given acid concentration and shifts the effective feed composition to a higher acidity. The fact that the tower is of finite length and is not perfectly efficient naturally should cause the experimental efficiency to be lower than that calculated because of incomplete attainment of the equilibrium. Attainment of efficiencies higher than those calculated theoretically is attributed primarily to the normal operational procedure of evaporating water from the reaction pot simultaneously with the reaction. Although an increase in the partial pressure of water vapor should promote the formation of NO (lower efficiency), rather than NO₂ apparently the effective tower temperature was raised sufficiently by an increased boilup rate to more than compensate for the adverse effect of water vapor on the equilibrium.

The effect of increasing the tower height reflects the degree to which equilibrium at the top of the tower was approached. Runs 16 and 17 with a packed height of 5.0 feet were more efficient than Run 15 with a

FIGURE 4
Equilibrium Formaldehyde Utilization

height of 2.5 feet under otherwise similar conditions, but the difference in formaldehyde utilized was only about 10 per cent. The tendency for the points at high nitrate to formaldehyde feed ratios to approach the 4:1 ratio more closely than those at lower feed ratios suggests the tower was adequate to achieve essentially equilibrium conditions when the oxide vapors from the pot were predominantly NO_2 but that it was incapable of completing the conversion of NO to NO_2 by the nitric acid reaction when the vapors were mainly NO . Although a taller tower would probably be a little more efficient than those used, the formaldehyde savings to be anticipated through its use are not great. Another reason for lower efficiencies at the lower feed ratios is the possible formation of N_2O or N_2 rather than NO and NO_2 under the stronger reducing conditions present at low feed ratios. The reaction gases were not analyzed to check for these products.

The holdup time required to complete the pot reaction, even at a residual acidity of less than 0.1 molar, is less than two hours. The most severe conditions investigated in the present experiments were Runs 10 (0.8 M residual acidity at 1.1 hours holdup) and 16 (0.1 M residual acidity at 2.1 hours). Essentially no formaldehyde remained in the product in either of these runs. The absence of residual formaldehyde or formic acid is confirmed by the absence of further reduction of nitrate in the product during an additional simmer period of up to one hour. Only in Run 9 in which the product was reduced to zero free acid was a significant amount of formaldehyde left in the product. A holdup time of one to two hours (based on overflow rate) corresponds to a sufficiently small vessel that the equipment changes necessary for investigation of shorter holdup times was judged not worthwhile in the present series. A baffle in the liquid phase between the overflow point and the feed inlets, while not present in the pilot plant reaction pot, would decrease the likelihood of by-passing unreacted formaldehyde to the product.

Workers at ORNL⁽⁵⁾ have reported that nitric acid will react with methanol, as with formaldehyde, but at a slower rate. Since methanol would

be a cheaper reductant than formaldehyde, one experiment, Run 18, was carried out in which the concentration of methanol in the formaldehyde was increased from 10.5 per cent to 20 per cent. A small increase in the amount of nitrate destroyed (about five per cent) may have resulted, but it was too little to warrant the extra effort and hazard associated with adding methanol. The excess nitrate destroyed corresponded to less than 0.7 mole per mole of methanol fed.

Precipitation of salts from the product solution depends on the final free acid concentration and the degree of concentration. The solution of Run 9 contained 60 per cent solids (wet settled volume) as it overflowed the pot and had the consistency of a thick mud. On a dry basis the solid analyzed 53 per cent sulfate and 13 per cent iron. The solution of Run 17, initially clear, precipitated 40 per cent solids upon standing for several days. An earlier sample from the same run with 0.2 M free acid and the same degree of concentration was stable for at least three weeks, but formed a precipitate similar to that of later samples from the same run when concentrated to 65 per cent of its original volume. The solutions from other runs were stable indefinitely with little or no precipitation. When the solution from Run 15 was concentrated to 28 per cent of the original 1WW volume no solid precipitated. Further concentration to 19 per cent of the original 1WW volume caused precipitation of a coarse crystalline solid (soluble in excess water) unlike the finely divided precipitates from low-acid solutions. A final acidity of about 0.5 M and an overflow volume of 33 per cent of the initial feed volume (for the 1WW composition used in these experiments) appear to be reasonable product objectives. Differences in the salt content of the 1WW would be reflected in the allowable degree of concentration, but the optimum free acid concentration from the standpoint of solids precipitation would probably be about 0.5 M regardless of salt composition.

A major fraction of the nitric acid destroyed was recovered in the condenser. Figure 5 shows the relationship between acid recovery and condensate concentration achieved with the pilot plant condenser. Three

FIGURE 5
Acid Recovery in the Condensate

runs in which less than the stoichiometric air requirement was added showed poorer than average acid recovery. Stoichiometric air requirements were calculated, on the basis of no residual formaldehyde, by the equation

The reason for the poor recovery in Run 8 is unknown.

In order to achieve maximum recovery of acid in the condensate, supplementary water was required to increase the condensate flow rate.

An alternate condenser design, not tested in these experiments, would be an up-draft condenser with additional water for scrubbing. In such a unit higher recovery at low condensate concentrations might be anticipated, but high condensate concentrations could only be obtained with low boilup rates.

Operational Behavior

The equipment was characterized by smooth, uneventful operation with a pressure drop from pot to packed tower effluent of the order one inch of water or less. Pressure fluctuations within a run were 0.5 inch of water or less. With an absorber water flow rate of 200 ml/min the principal pressure drop (3.5 inches of water) was across the absorber. When the absorber water flow rate was 100 ml/min the pressure drop across the absorber was lower (Run 8) because this rate was insufficient to maintain the normal liquid level on the absorber trays (the weep holes were too large). Prior to Run 8, high pot pressures (28 inches of water maximum) were encountered which were apparently caused by floods in the packed tower initiated by the packing support screen.

On the basis of Runs 11 and 11-A, the location of the formaldehyde entry point (above or below the liquid level) appeared to be unimportant to the operation. During Run 18, in which the methanol concentration of the formaldehyde was doubled, and unexplained pressure cycle was observed while formaldehyde was being fed to the vapor space. The pressure averaged 7.5 inches of water with a cycle of ± 2.7 inches and a period of

about five minutes. Switching to the liquid phase feed point eliminated the cycling and reduced the average pressure to 5.3 inches of water. No similar difficulty was observed during any of the other runs. Formaldehyde was normally fed to the vapor space to minimize the possibility that liquid from the reaction pot might be forced back through the formaldehyde feed line to the head tank in the event of maloperation.

Control of the degree of concentration in the pot was satisfactorily achieved by control of the pot temperature. The temperature required to yield a specified overflow concentration was sensitive to other operating variables however and had to be empirically determined for each set of conditions used. The pot temperature could be maintained within ± 0.2 C.

An alternate control system is that in which the coil steam and boilup rate are controlled through the specific gravity of the overflow solution. Use of the specific gravity of the solution in the pot, as determined by dip tubes, for control of the coil steam was attempted during the present experiments. This simple method of detection was seriously affected by the large fluctuations in pot pressure encountered during the early runs however, and control was impossible. When the pot solution volume was reduced after Run 7, the upper specific gravity dip tube was uncovered and no alternate specific gravity meter was added since pot temperature had been found to provide adequate control. The relationship between degree of concentration and specific gravity of the cooled overflow solution is shown in Figure 6. Within the limitations of the experimental precision, the points confirm the expected dependence of the solution specific gravity on the degree of concentration and the residual acidity. Control of the steam flow through a more refined specific gravity sensing element may result in a system less influenced by changes in process variables than the temperature control system used here.

Over-all material balances indicate a small loss of both nitrogen oxides and total volume. Since the acid absorber was relatively inefficient and oxides of nitrogen were visible in the stack off-gas, the loss of nitrogen

FIGURE 6
Specific Gravity of Product Solution

values is understandable. A loss of 10 to 15 per cent in over-all volume was normally observed. Barton⁽⁴⁾ also observed a loss of about 15 per cent in volume, presumably because of the destruction of nitric acid (which he did not recover). In the present experiments, any volume loss attributable to the volume occupied by the nitric acid destroyed should be much reduced because of the recovery of most of the acid in the condensate. Condensate temperatures were sufficiently low to prevent loss of water as vapor and the loss of entrained condensate is unlikely in view of the low absorber acid concentrations obtained (about one molar). Error in measurements of the condensate flow rate is the most probable cause of the discrepancy.

Estimation of the residual free acid concentration in the product was very satisfactorily accomplished with the conductivity meter previously described. Figure 7 shows the data from both continuous and batch experiments. The conductivity bridge was difficult to read closely and it is likely that another bridge, specifically designed for high conductivities, would provide a better correlation. Conductivity measurements were very helpful for observing the approach to constant conditions during the pilot plant studies. They should prove equally valuable for monitoring or control in conjunction with production plant equipment.

The possibility of corrosion of stainless steel equipment was investigated by measuring the weight loss of two 304-L stainless steel coupons added to the pot before Run 8. They were removed at the end of the study after about 80 hours at 95 C or above (including five hours in Darex feed solution). They showed no evidence of attack and an insignificant increase in weight.

Batch 1WW Denitration

Two experiments were performed to determine the formaldehyde utilization efficiency under batch conditions. For this purpose, the equipment was modified so solution from the pot could be routed through the conductivity meter, sampled and returned to the pot via the normal acid feed line.

FIGURE 7

Conductivity of Denitrated Synthetic Purex 1WW Concentrates

UNCLASSIFIED

In each experiment formaldehyde was added continuously to fifteen liters of 1WW held at 95 C. In the first experiment, the formaldehyde rate was 20.5 ml/min and its flow was interrupted twice for half-hour periods to observe whether unreacted formaldehyde or formic acid was present in the solution. In the second experiment, formaldehyde was added at 40.0 ml/min with no interruption. Solution from the pot was circulated through the conductivity meter and sampled at 30- and 15-minute intervals, respectively. Figure 8 shows the results for the second experiment. In each, the formaldehyde addition was stopped after the conductivity readings indicated the acid had been largely destroyed. The pot was allowed to simmer at 95 C for 30 minutes after the addition was completed, but little additional reaction took place. Sodium analyses indicated no significant volume change during the course of the reaction; the formaldehyde solution added exactly compensated for the volume loss due to nitrate destruction and evaporation. The over-all efficiency was respectively 1.81 and 1.91 moles of nitrate destroyed per mole of formaldehyde reacted in the two experiments. There was essentially no change in efficiency during the course of the reaction until the acid concentration had been reduced to less than one molar free acid.

Darex Dissolver Solution Denitration

Two experiments, similar to the batch 1WW denitration experiments just described, were performed to determine the feasibility of destroying nitric acid in Darex dissolver solution prior to solvent extraction.

The stock solution, a composite from current Darex experiments being carried out in Chemical Engineering Development Operation, had the composition

<u>Component</u>	<u>grams/liter</u>
U	198
Fe	33.6
Free Acid	2.67
Cl	1.08

FIGURE 8
Batch 1WW Denitration

It was butted to 6.5 and 8.6 molar free acid respectively with 60 per cent acid for the two experiments. Formaldehyde was added at about 40 ml/min to 15 liters of the resulting solution with the pot maintained at 95 C. After reaction, the volume in the pot was approximately 80 per cent of the initial volume. The over-all efficiencies were respectively 1.77 and 1.89 moles of nitric acid destroyed per mole of formaldehyde in the two experiments. The initial ratio was about 2.3. The final acidity was 0.07 molar in both cases and the final formaldehyde concentration was 0.20 and 0.05 molar, respectively. The final solutions contained too little free acid to prevent precipitation. Earlier cessation of formaldehyde addition followed by a simmer period of about an hour should result in a stable product solution with a lower formaldehyde concentration. Approximately 50 per cent of the chloride disappeared from the pot in each experiment.

Conductivity measurements provided a convenient means of following the course of the reaction, however, the curve of resistance vs free acid concentration is appreciably different from that for 1WW solutions as shown in Figure 7.

Pressurization Tests

Tests to determine the maximum pressure which might be generated under abnormal conditions through operational error consisted of adding formaldehyde to a cold acidic solution followed by heating. The results obtained are given in Table II.

The initial experiments, performed prior to the series of continuous denitration studies, were with nitric acid alone in the reaction pot. With two and five molar acid the maximum pressure increased with increasing acid and formaldehyde concentrations as would be expected from the previous kinetic studies^(1, 2, 3). The maximum pressure occurred during heating after the temperature had risen to 40 C or higher. The duration of the pressure surge was dependent on the total amount of reactants present. With 7.7 molar acid the reaction began before the pot was heated and a high formaldehyde concentration could not be built up since it reacted

as rapidly as it was added. In all the nitric acid tests a free space of about sixteen liters existed above the solution in the pot. The tower off-gas system was the same as during the early runs reported above.

Immediately prior to Runs 13 and 14 formaldehyde was added to the product from the previous run in the reaction pot while at ambient temperature. Steam was then turned on to the coil and the maximum pressure observed. While the resulting pressures of 8.4 and 12.3 inches of water indicate a significant pressure surge can be produced by such maloperation, these values are not high enough to be alarming. The acid concentration in the pot prior to heating was 4.0 and 3.8 molar, respectively. Both feed acid and formaldehyde would, prior to heating, have to be added to the low-acid product normally present in the pot, in order to generate pressures of this magnitude.

VI. APPENDIXTOWER EQUILIBRIUM CALCULATIONS

Basis: Equilibrium between feed acid and off-gas at the temperature of the feed at the top of the packed tower. No salts present.

The equilibrium involves the reactions:

$$K_1 = \frac{(p_{\text{NO}}) (p_{\text{HNO}_3})^2}{(p_{\text{NO}_2})^3 (p_{\text{H}_2\text{O}})} \quad (2)$$

$$K_2 = \frac{(p_{\text{N}_2\text{O}_4})}{(p_{\text{NO}_2})^2} \quad (4)$$

From the data of Forsythe and Giaugue⁽⁶⁾, K_1 was calculated to be

$$\log K_1 = 2028/T - 8.7895$$

in the temperature range 25 C to 100 C.

T = absolute temperature, ° K

From thermodynamic data⁽⁷⁾, K_2 was calculated to be

$$\log K_2 = 3032/T - 9.2231$$

The vapor in equilibrium with the incoming acid feed was assumed to satisfy the equation:

$$1.00(\text{atm}) = p_{\text{CO}_2} + p_{\text{NO}} + p_{\text{NO}_2} + p_{\text{N}_2\text{O}_4} + p_{\text{H}_2\text{O}} + p_{\text{HNO}_3} \quad (5)$$

Air leakage was neglected.

CO₂ and nitrogen oxides are formed by the reactions (in the reaction pot):

Substituting equations (2), (4), and (8) into (5) gives

$$4(1.00 - p_{\text{H}_2\text{O}} - p_{\text{HNO}_3}) = 7 K_1 \frac{(p_{\text{NO}_2})^3 (p_{\text{H}_2\text{O}})}{(p_{\text{HNO}_3})^2} + 5(p_{\text{NO}_2}) \left(1 + \frac{6}{5} K_2 p_{\text{NO}_2}\right) \quad (9)$$

Partial pressures of water and nitric acid above nitric acid solutions were interpolated from data in Perry⁽⁸⁾. Equation (9) was then solved by trial and error for p_{NO_2} for each condition of temperature and acid concentration.

The formaldehyde utilization efficiency was calculated by the equation:

$$\frac{\text{HNO}_3}{\text{H}_2\text{CO}} \text{ (mole ratio reacted)} = \frac{p_{\text{NO}} + p_{\text{NO}_2} + 2 p_{\text{N}_2\text{O}_4}}{p_{\text{CO}_2}} \quad (10)$$

using partial pressures calculated from equations (2), (4), (8), and (9). The results are shown in Figure 4.

LITERATURE CITED

1. Healy, T. V. and B. L. Ford (Miss), AERE-C-R-1339, April 2, 1954 (Confidential).
2. Morris, J. G., The Reaction of Nitric Acid with Formaldehyde, AERE-CE-R-1490, October 12, 1954 (Official Use Only).
3. Healy, T. V. and B. L. Davies (Mrs.), The Destruction of Nitric Acid by Formaldehyde. Parts II, III, and IV, AERE-C-R-1739, February 22, 1956.
4. Barton, G. B., HW-55941, May 2, 1958 (Confidential).
5. Dean, O. C., Monthly Progress Report for Chemical Development Section B, August 1958, CF-58-8-91, August 27, 1958.
6. Forsythe, W. R. and W. F. Giauque, "The Entropies of Nitric Acid and Its Mono- and Tri-hydrates. Their Heat Capacities from 15 to 300 ° K. The Heats of Dilution at 298.1 ° K. The Internal Rotation and Free Energy of Nitric Acid Gas. The Partial Pressures over Its Aqueous Solutions." J. Am. Chem. Soc. 64,48(1942).
7. Latimer, W. M., The Oxidation States of the Elements and Their Potentials in Aqueous Solutions, 2nd Ed. New York:Prentice-Hall (1952).
8. Perry, J. H., Chemical Engineers' Handbook, p 169, 3rd Ed. New York:McGraw-Hill (1950).

UC-4, Chemistry General
(TID-4500, 14th Ed.)

INTERNAL DISTRIBUTIONCopy Number

1	G. J. Alkire
2	G. B. Barton
3	L. P. Bupp
4	R. E. Burns
5	V. R. Cooper
6	T. F. Evans
7	J. B. Fecht
8	C. T. Groswith
9	K. M. Harmon
10	M. K. Harmon
11	O. F. Hill
12	H. H. Hopkins
13	E. R. Irish
14	P. R. MacMurray
15	L. H. McEwen
16	R. L. Moore
17	A. M. Platt
18	W. H. Reas
19	H. P. Shaw
20	R. J. Sloat
21	R. E. Smith
22	H. F. Tew
23	R. E. Tomlinson
24	E. E. Voiland
25	M. T. Walling
26	300 Files
27	Record Center
28 - 30	Extra
31 - 34	G. E. Technical Data Center, Attn: A. Cohen