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PILOT PLANT DENITRATION OF PUREX WASTE WITH SUGAR

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PILOT PLANT DENITRATION OF PUREX WASTE WITH SUGAR

INTRODUCTION

Recent laboratory studies by L. A. Bray, Chemical Laboratory, have indicated that sugar (sucrose) reacts with nitric acid in synthetic Purex waste (1WW) at an appreciable rate. The studies have also shown that a major fraction of the nitric acid can be destroyed by the addition of sugar. Thus, denitration of Purex 1WW with sugar may be an attractive alternate to denitration with formaldehyde. An experimental program was undertaken to provide information on denitration of Purex 1WW with sugar in pilot-plant-scale equipment. This report describes the experimental program and presents the experimental results.

SUMMARY

Batch denitration of Purex 1WW was investigated in 12 batch runs in the pilot plant denitration unit. Sugar was continuously added to 25 liters of hot 1WW. After sugar addition was complete, the hot solution was digested for several hours. The reaction proceeded smoothly and was easily controlled. About 19 to 22 moles of nitric acid were destroyed per mole of sugar with a reaction pot temperature of 100 C and a digestion period of 12 hours. About 17 moles of nitric acid were destroyed per mole of sugar when the reaction pot temperature was reduced to 95 C.

A possible plant flowsheet for batch denitration with sugar was developed. This flowsheet presumes batch denitration of large 2,500-gallon batches of 1WW in a standard 5,000-gallon Purex Plant tank and incorporates 12 hours of sugar addition and 12 hours of digestion. The flowsheet was successfully demonstrated in the pilot plant equipment. A 1.4 M sugar solution was added to 25 liters of hot (100C) 1WW for 12 hours and the mixture was digested for 18 hours. The initial nitric acid concentration was 6.14 M. The residual nitric acid concentration was 0.94 M and 0.90 M after 12 and 18 hours of digestion, respectively. A residual carbon content equivalent to 1.9 and 0.4 percent of the total carbon fed as sugar was present after 12 and 18 hours of digestion, respectively. About 19 moles of nitric acid were destroyed per mole of sugar fed.

Foaming was produced during batch denitration with sugar by addition of 0.4 gram of DBP per liter of synthetic 1WW. The addition of 0.2 gram of Dow Corning Antifoam B per liter of 1WW reduced foam levels by about a factor of two.

An induction period of about six to nine minutes was observed before the reaction started. The length of the induction period increased as initial sugar addition rates were reduced. Gentle air sparging reduced the induction period by about a factor of two. Attempts to use sodium nitrite as a means of decreasing the induction period were not successful.

Sugar solution was added to cold 1WW and the mixture was heated to determine the pot pressures and tower pressure drops that could be developed under abnormal conditions. A decrease in pot vacuum of 30 inches of water and a tower pressure drop of eight inches of water were observed when 20 liters of 1WW and 2.7 liters of 2.5 M sugar solution were mixed together and rapidly heated to 100 C.

EQUIPMENT AND MATERIALS

Description of Equipment

The equipment consisted of the denitration unit and necessary auxiliaries to handle the off-gas, feed the reactants, and receive the condensate. This equipment was not an optimum design for batch denitration with sugar but was available from previous studies of continuous denitration with formaldehyde. An equipment flowsheet is shown in Figure 1. Because of the potential hazards of the reaction during abnormal conditions, the denitration unit was enclosed in a stainless steel hood with a Plexiglas® front.

The denitration unit was made of sections of glass pipe. It consisted of a 6-inch-I.D. by 9-foot-high reaction vessel surmounted by a 4-inch-I.D. by 8.5-foot-high tower. Beginning 2 feet 8 inches above the reaction pot, a 4-foot section of the tower was packed with 1/2-inch porcelain Intalox® saddles. The top and bottom packing supports consisted of 4-inch-diameter sections of 1/4-inch mesh screen welded to flanges that were inserted between sections of the glass tower. The 1WW entered the unit six inches above the packing.

The reaction pot contained a steam coil, two sugar feed lines, two thermocouples, an alternate 1WW feed line, and an air sparger. The bottom of the unit was a blind pipe flange with connections for the steam coil, thermocouples, air sparger, a deluge water inlet, and a drain or sampler line. The 4-1/2-inch-diameter steam coil consisted of 22-1/2 turns of 5/8-inch-O.D. tubing (10 BWG). Steam flow was controlled manually with a valve on the steam inlet.

Gases from the tower passed to a downdraft condenser, a caustic scrubber, and a stack. The condenser was a 5-foot length of 6-inch pipe. It contained a cooling coil of 1/2-inch pipe (50 turns) around a core of 3-inch pipe. The caustic scrubber, incorporated to prevent excessive spread of fumes to the atmosphere, was an 18-inch-diameter by 3.6-foot-high tank equipped with a cooling coil. The gas inlet line entered at the top of the tank and terminated in a sparger ring located four inches above the bottom. Gases from the sparger ring passed through a 20-inch height of 5 M sodium hydroxide to the vapor space and outlet line. Vacuum for the off-gas system was provided by an air jet in the off-gas line just beyond the scrubber.

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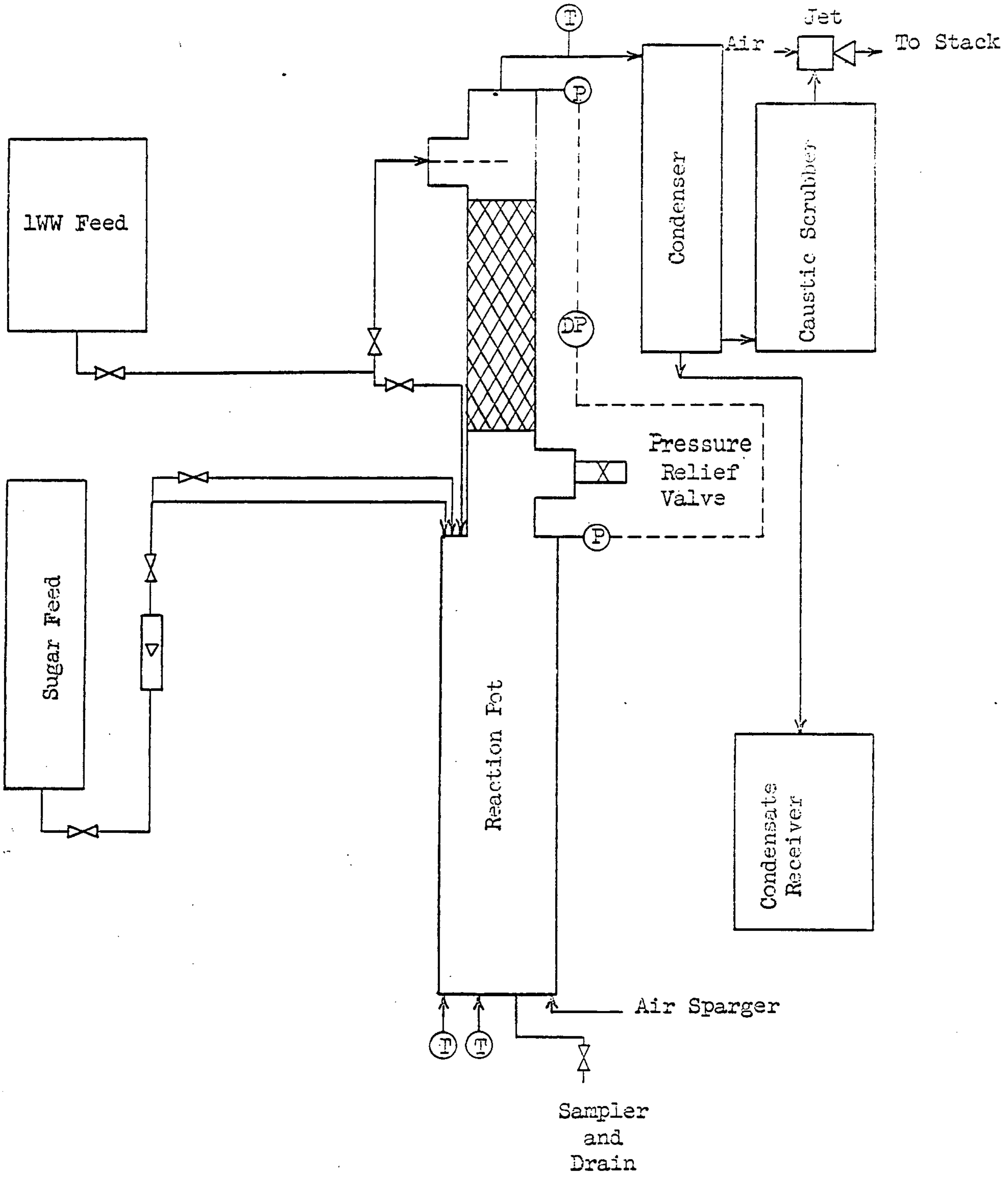
FIGURE 1
EQUIPMENT FLOWSHEET



The temperature of the gases leaving the tower was measured by a Weston thermometer. Reaction pot temperature was measured with chromel-alumel thermocouples enclosed in stainless steel sheaths. The thermocouple signal was received by a Brown indicator-recorder calibrated to cover the range 0 to 150 C.

The two sugar feed lines, an alternate 1WW feed line, and a pot pressure tap entered the pot through a flange between the tower and reaction pot. The sugar solution was metered into the unit through a rotameter.

Pot pressure was indicated on a water manometer which had its zero in the center of the scale and could indicate either a vacuum or pressure of 0 to 30 inches of water. The pressure at the top of tower was indicated on an identical manometer. The difference in the reading on the two manometers gave the pressure drop across the tower.

A pressure relief valve was installed at the bottom of the tower for safety purposes. This valve was adjusted to open if the pot pressure exceeded five psig but it was never actuated. Also, the steam inlet line, sugar addition line, and deluge water line were equipped with ball valves to permit rapid shutdown and rapid water quenching of the reaction in the event of abnormal conditions.

Materials

An aqueous solution of refined sugar was used for the program. The sugar concentration was 2.5 M for Runs 1 through 11 and 1.4 M for Run 12.

The synthetic Purex 1WW for Runs 1 through 11 was made up to approximate the target composition given in Table I. For Run 12, the target concentrations of free acid and nitrite plus nitrate were increased to 6.1 M and 8.35 M, respectively. Laboratory analyses for specific components in each batch are also listed. Analyses for the other components were not performed. Each batch of synthetic 1WW contained a small amount of free-settling sediment but the 1WW was filtered prior to use in the denitration unit.

EXPERIMENTAL RESULTS

The major portion of the experimental program was directed at obtaining information on batch denitration of 1WW with sugar. Foaming was induced in several runs by the addition of dibutyl phosphate (DBP) to the 1WW and the effect of Dow Corning Antifoam B was studied. In other tests, attempts were made to pressurize the system by deliberately initiating an abnormally rapid reaction. Also, the induction period before the reaction started was studied and attempts were made to reduce it. Details of the results are discussed in the following sections.

TABLE I

SYNTHETIC 1WW COMPOSITION

Component	Molarity				
	Target(*)	Batch 1 (Runs 1 to 4)	Batch 2 (Runs 5 to 9)	Batch 3 (Runs 10 and 11)	Batch 4 (Run 12)
H^+	5.1	5.2	4.9	5.1	6.14
Na^+	0.68				
Fe^{+++}	0.80				
Al^{+++}	0.10				
Cr^{+++}	0.10				
Ni^{++}	0.02				
$NO_2^- + NO_3^-$	7.35	7.0	7.4	7.2	8.2
SO_4^{--}	0.72				
PO_4^{---}	0.01				

*Target composition in Runs 1 through 11. Target H^+ and $NO_2^- + NO_3^-$ concentrations for Run 12 were 6.1<u>M</u> and 8.35<u>M</u>, respectively.

Batch 1WW Denitration

Twelve batch runs were performed in the denitration unit to study denitration of 1WW with sugar under a variety of conditions. Sugar was continuously added to 25 liters of hot 1WW in each run. The 1WW was held at 95C in Run 11 and at 100 C in all other runs. After sugar addition was complete, reaction pot temperature was maintained and the solution was digested for several hours. The solution in the pot was sampled immediately after sugar addition was stopped and periodically throughout the digestion period to follow the reaction. After the digestion period, the solution was cooled and the volume was measured to determine the volume reduction.

Table II shows the operating conditions during the sugar-addition portion of each run and also shows the volume reduction that was measured after completion of the digestion period. Information on sugar utilization, residual carbon, and compositions during the digestion period is shown in Table III. Data on Runs 6 and 7 are not shown in Tables II and III because they were short runs with incomplete sugar addition. They were performed to study foaming and are discussed later.

In general, the runs were smooth and easily controlled. Once the pot temperature was adjusted to the desired temperature, no further adjustments were required to maintain the temperature regardless of the sugar addition rate. During sugar addition, the solution in the pot was vigorously agitated by reaction gases that were dispersed throughout the pot and the solution was raised above the initial liquid level. Solution agitation, liquid level rise, and pressure drop across the tower increased as sugar addition rates were increased. For example, the height of the solution above the initial liquid level was 10 and 32 inches in Run 4 at sugar addition rates of 10.8 and 120 ml/minute, respectively. At the highest sugar addition rate attained (120 ml/minute or 2.6 pounds of sugar per minute per square foot of tower cross section), the pressure drop across the tower was 1.5 inches of water and a decrease in pot vacuum of eight inches of water was noted. When sugar was added rapidly as in Runs 1 through 5, the maximum pressure drop, most vigorous agitation, and greatest liquid level rise occurred simultaneously with the end of sugar addition.

Slower sugar addition rates were employed in Runs 8 through 12 to simulate sugar addition over a period of several hours to a large plant-scale tank. At these slower rates, the tower was greatly oversized and little or no pressure drop across the tower was observed. The temperature of the gases leaving the tower slowly increased during each run and the maximum temperature listed in Table II was attained during the last hour of sugar addition. Solution agitation and liquid level rise reached a maximum about one hour after sugar addition was started. Thereafter, liquid level and solution agitation appeared to remain essentially constant until sugar addition was stopped. Evidence of a decrease of the reaction rate as sugar addition progressed was provided by a significant color change in the tower. The color of the fumes in the vapor space of the tower changed from almost black during the first two hours of sugar addition to a pale amber when sugar addition was completed.

TABLE II

OPERATING DATA FOR BATCH DENITRATION

		Sugar Addition(1)				
Run No.	Sugar Added, Moles	Time at Rate, Min.	Rate, Ml/Min.	Tower ΔP, In. of H_2O	Maximum Off-Gas Temp, C(2)	Volume Decrease, %
1	8.37	60	10.8	0	90	16
		72	14.8	0		
		80	20.4	0		
2	8.37	50	11.6	0	90	11
		10	24.0	0.2		
		62	40.7	0.3		
3	8.37	15	18.8	0	93	15.1
		13	34.1	0.2		
		15	54.7	0.3		
		27	66.7	0.8		
4	8.37	10	10.8	0	94	20.7
		6	66.8	-		
		8	100.0	0.8		
		17	120.0	1.5		
5	4.37	8	16.2	0.1	92	8.6
		19.5	83.1	1.1		
8	5.12	195	4.1	0.1	48	6.0
		120	4.66	0.1		
		60	5.16	0.1		
		30	7.0	0.1		
		15	11.3	1.3(3)		
9	5.12	380	4.71	0.1	91	8.0
		39	6.6	0		
10	6.40	245	10.45	0	95	25.4
11	5.12	277	5.56	0	65	5.3
		51	10.0	0		
12	6.84	720	6.79	0	85	0.3

(1) Sugar concentration 2.5 M in Runs 1 through 11 and 1.4 M in Run 12.
(2) Maximum temperature of gases leaving tower.
(3) Foam above lower pressure tap.

TABLE III

SUGAR UTILIZATION

Run No.	Digestion Time, Hrs(1)	Product Concentration H+, M	Product Concentration NO_3^-, M	Product Concentration Residual Carbon, %(2)	Moles HNO_3 Destroyed Per Mole Sugar Fed (3)	Moles HNO_3 Destroyed Per Mole Sugar Fed (4)
1	4.25	0.38	1.5	-	14.6	17.1
2	4.5	0.72	1.3	-	13.6	17.4
3	0	2.5	3.0	-	9.2	13.3
	5	0.09	1.3	35.2	15.3	17.6
4	0	1.8	2.0	-	11.3	16.2
	3	0.54	1.1	48.3	14.2	18.3
	6	-0.1	0.97	29.7	15.9	18.6
5	0	3.7	5.2	-	8.7	15.1
	3	2.0	3.9	31.6	17.6	21.9
	6	1.6	3.7	16.3	19.7	23.0
	11	1.3	3.8	1.5	21.2	22.5
	16	1.3	-	0.7	21.2	-
8	0	2.5	3.8	31.5	12.5	18.7
	6	1.4	-	-	17.5	-
	9	1.3	3.3	5.0	17.9	21.0
	12	1.2	3.3	1.4	18.4	21.0
9	0	2.3	3.7	-	13.6	19.5
	6	1.3	3.5	5.0	18.1	20.4
	9	1.3	3.4	4.0	18.1	20.8
	11	1.1	3.4	2.7	19.0	20.8
10	0	1.9	3.2	-	14.4	18.8
	3	0.72	2.5	-	17.8	20.8
	6	0.27	2.5	14.8	19.1	20.8
	12	0.06	2.5	6.1	19.7	20.8
11	0	3.1	4.2	-	10.6	15.7
	6	2.1	3.9	-	15.2	17.1
	9	1.9	3.9	8.2	16.1	17.1
	12	1.8	3.8	4.2	16.5	17.6
12	0	2.0	3.4	-	15.1	17.6
	3	1.4	2.8	-	17.3	19.7
	6	1.1	2.9	7.8	18.4	19.4
	9	1.0	2.8	4.0	18.8	19.7
	12	0.94	2.9	1.9	19.0	19.4
	15	0.96	2.9	1.06	18.9	19.4
	18	0.90	2.9	0.38	19.2	19.4

(1) Time after sugar addition complete.
(2) Percent of total carbon fed as sugar.
(3) Based on free acid analyses.
(4) Based on NO_2^- + NO_3^- analyses.

The reaction slowed rapidly and the liquid level steadily receded after sugar addition was stopped. Within 30 to 50 minutes after sugar addition was stopped, the liquid level was at or below the initial level and the solution was bubbling gently with about 0.5 to 2 inches of foam. The amount of reaction decreased further with continued digestion and the thermometer in the vapor line indicated a steadily declining temperature. After 12 hours of digestion, the reaction was essentially complete. Only a very few bubbles were observed in the solution and most of these appeared to be the result of vapor formation on the steam coil. Only a faint yellow color was visible in the vapor space in the tower and the thermometer in the vapor line indicated a temperature less than 10 C above the ambient temperature.

The operating conditions of Runs 1 through 4 and Run 10 are not representative of practical operating conditions because too much sugar was added. The sugar-treated waste from Run 4 was acid deficient six hours after sugar addition was stopped and still contained 29.7 percent of the total carbon added as sugar. The solution from Runs 1, 2, 3, and 10 would also have become acid deficient if the digestion period had been continued.

After nine hours of digestion in Run 10, a yellow precipitate began to adhere to the wall of the reaction pot and samples of the solution contained about 10 percent solids (wet settled volume). When the pot was drained after the run, the precipitate was observed to be about 1/2-inch deep on the bottom of the pot and about 1/4-inch deep on the coil and bottom two feet of the vessel wall. Contact with boiling water for four hours had no visible effect on the precipitate. Contact with 1WW at 100 C for three hours removed the material on the wall and bottom of the pot but had no visible effect on the material adhering to the coil. Contact with 1 M HNO_3 at 100 C removed the material on the coil in two hours. Presumably, the material was ferric sulfate. The typical dark brown color of ferric hydroxide resulted upon contact with sodium hydroxide. Similar solids were not observed in Runs 1 through 4 in which the digestion period was six hours or less.

A volume reduction was achieved in each run. Volume reduction was greatest for Runs 1 through 4 and Run 10 in which an excess of sugar was added rapidly to the reaction pot. The greatest volume reduction occurred in Run 10 even though a smaller amount of sugar was added more slowly than in Runs 1 through 4. The larger volume reduction is attributed to the installation of lagging on the tower after Run 8. As a result, heat losses were reduced, the tower heated more rapidly, and condensate reflux was decreased.

Sugar Utilization

About 19 to 22 moles of nitric acid were destroyed per mole of sugar fed with a reaction pot temperature of 100 C and digestion periods of 12 hours or more. About 17 moles of nitric acid were destroyed per mole of sugar fed when the reaction pot temperature was reduced to 95 C in Run 11. Destruction of about 19 moles of nitric acid per mole of sugar occurred when sugar addition rates were decreased to allow longer sugar addition periods. At the lower sugar addition rates, tower heat-up was slower and the gases leaving the tower were cooler. These data suggest that the reduced sugar utilization was partially the result of increased condensate reflux and increased scrubbing of oxides of nitrogen from the gas. Considerable reflux was observed in every run and the gases in the tower were visibly lighter in the top foot of the packed section during Run 8. As mentioned earlier, the tower was lagged for all runs after Run 8. The gases leaving the tower were hotter in Run 9 than in Run 8 and a slight improvement in sugar utilization resulted on the basis of free acid analyses even though the digestion period was one hour shorter. Further improvements could be achieved by externally heating the tower.

Early in the digestion period of each run, sugar utilization was appreciably lower when free acid analyses were used as the calculation basis instead of nitrate analyses. As the digestion period progressed, this discrepancy decreased until, after 11 hours of digestion, sugar utilization was about the same on the basis of either free acid or nitrate analyses. Most of the small difference after 11 hours of digestion is attributed to small discrepancies between the free acid and nitrate analyses. Possible explanations of the apparent anomaly during early stages of digestion are that (1) some of the organic by-products from breakdown of the sugar may be complexing the metallic cations and the free acid analysis is, in part, sulfuric acid and/or (2) the free acid analysis is, in part, organic acids. The color of the sugar-treated waste gave further evidence in support of organic complexes. The waste was a dark brownish-red color during the first seven hours of digestion in Runs 5, 8, 9, 10, and 12. Thereafter, the brownish-red color steadily diminished and the waste returned to the typical dark blue-green color after 11 hours of digestion.

Organic complexes may also explain why a precipitate was observed in Run 10 but not in Run 4. The residual carbon concentration was 7.1 grams per liter in Run 10 when the precipitate was first observed after nine hours of digestion. The residual carbon concentration was still 18.1 grams per liter in Run 4 even though the waste was acid deficient.

Foaming and Antifoam Agent

Severe foaming was produced in Runs 6 through 9 by the addition of 0.4 gram of DBP per liter of 1WW. Once foaming was produced, the effect of Dow Corning Antifoam B was studied. Both the DBP and antifoam agent were added to the 1WW head tank and mixed with the 1WW by air sparging before the 1WW was transferred to the denitration unit. The DBP was added as an aqueous solution of sodium dibutyl phosphate.

Results of the foaming studies are shown in Table IV.

TABLE IV

INDUCED FOAMING DURING BATCH DENITRATION WITH SUGAR

Run No	DBP Conc., g/l 1WW	Dow Corning Antifoam B Conc., g/l 1WW	Time at Rate, Min.	Rate, Ml/Min.	Maximum Foam Rise, Inches
6	0.4	0	50	9.8	53
7	0.4	0.2	65	5.5	6
			105	11.8	37
8	0.4	0	195	4.1	19
			120	4.66	27
			60	5.16	35
			30	7.0	41
			15	11.3	53
9	0.4	0.2	380	4.71	15
			39	6.6	23

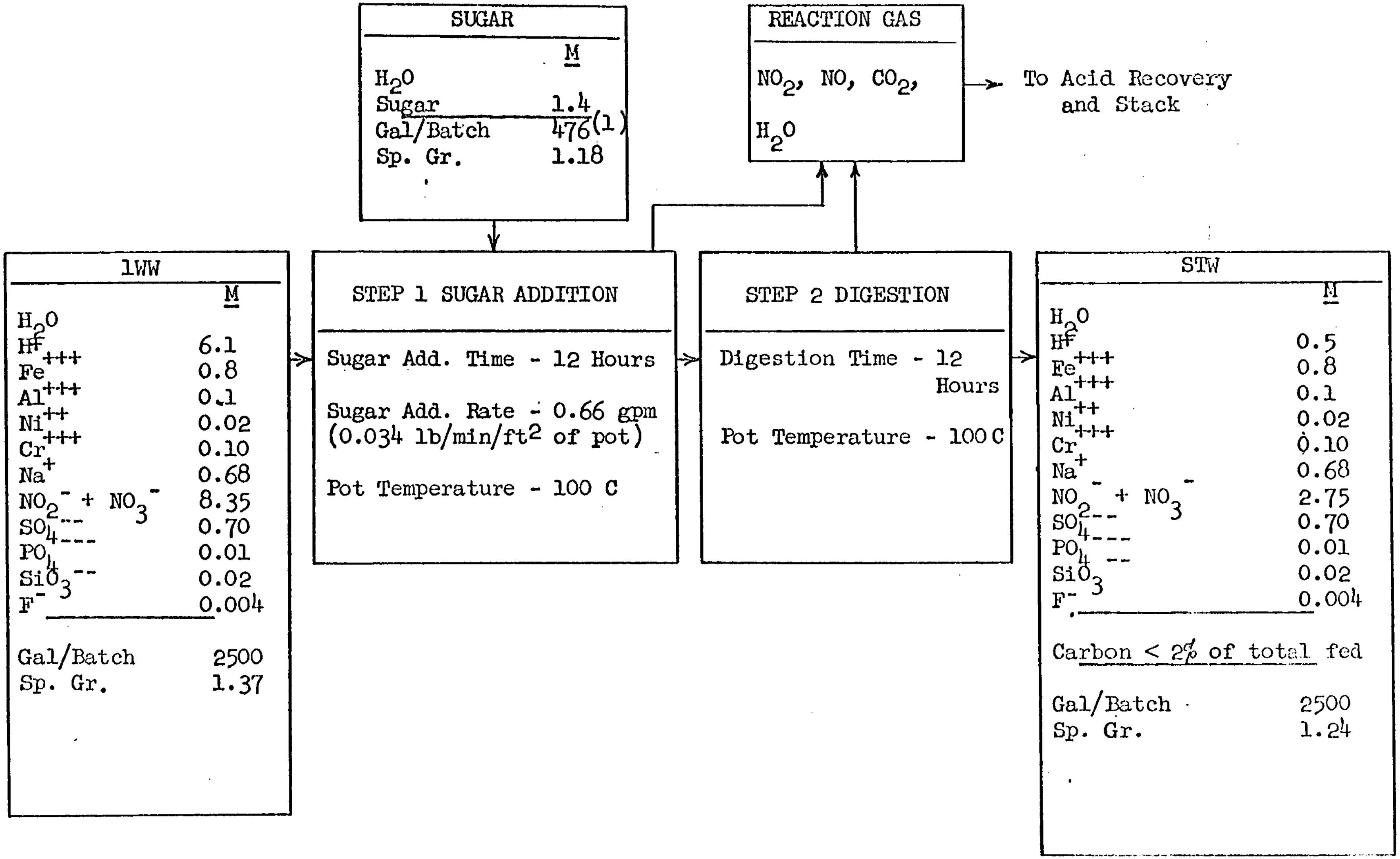
The maximum height of the foam layer increased as sugar addition rates were increased. Foam height was reduced by about a factor of two by addition of 0.2 gram of Dow Corning Antifoam B per liter. The data further show that, for 1WW with a tendency to foam, the sugar addition rate must be restricted to keep the foam below the top of the reaction vessel. In the present runs with 25 liters of 1WW, the initial liquid level was 48 inches below the top of the pot. Thus, in the pilot plant unit without antifoam agents, restriction of the sugar addition rate to about 0.07 pounds of sugar per minute per square foot of pot cross section was required to keep the foam below the top of the pot.

The foam layer can be characterized as a mass of tightly-packed brownish bubbles approximately 1/8-inch to 1/4-inch in diameter. The bubbles appeared to be relatively stationary with little agitation at the sugar addition rates employed. Foam build-up was slow and an operating period of about 30 minutes was required before the maximum foam height was attained for a given sugar addition rate. There was a definite interface between the solution and the foam layer. This interface fluctuated erratically from about two inches below to about seven inches above the normal liquid level at the sugar rates employed. Below the interface, the solution was vigorously agitated by the reaction gases.

Flowsheet Development

On the basis of the data from Runs 1 through 11, a possible plant flowsheet for batch denitration with sugar was developed. This flowsheet is shown in Figure 2. It presumes batch denitration of large 2,500-gallon batches of 1WW in a 24 hour time cycle in a standard 5,000-gallon Purex Plant tank.

FIGURE 2
PUREX SUGAR TREATED WASTE FLOWSHEET



SUGAR

	M
H_2O	
Sugar	1.4
Gal/Batch	476(1)
Sp. Gr.	1.18

REACTION GAS

NO_2, NO, CO_2,

H_2O

To Acid Recovery and Stack

1WW

	M
H_2O	
H^+	6.1
Fe^{+++}	0.8
Al^{+++}	0.1
Ni^{++}	0.02
Cr^{+++}	0.10
Na^+	0.68
$NO_2^- + NO_3^-$	8.35
SO_4^{--}	0.70
PO_4^{---}	0.01
SiO_3^{--}	0.02
F^-	0.004
Gal/Batch	2500
Sp. Gr.	1.37

STEP 1 SUGAR ADDITION

Sugar Add. Time - 12 Hours

Sugar Add. Rate - 0.66 gpm (0.034 lb/min/ft^2 of pot)

Pot Temperature - 100 C

STEP 2 DIGESTION

Digestion Time - 12 Hours

Pot Temperature - 100 C

STW

	M
H_2O	
H^+	0.5
Fe^{+++}	0.8
Al^{+++}	0.1
Ni^{++}	0.02
Cr^{+++}	0.10
Na^+	0.68
$NO_2^- + NO_3^-$	2.75
SO_4^{--}	0.70
PO_4^{---}	0.01
SiO_3^{--}	0.02
F^-	0.004
Carbon < 2% of total fed	
Gal/Batch	2500
Sp. Gr.	1.24

(1) Assumes 21 moles nitric acid destroyed per mole of sugar

A 12-hour sugar addition period is specified in the flowsheet. This addition time results in a sugar addition rate of 0.034 pounds of sugar per minute per square foot of pot cross section. This rate is below the rate of 4.1 ml/minute or 0.04 pounds of sugar per minute per square foot of pot cross section in Run 8 which resulted in a foam height of 19 inches when DBP was present in the 1WW. Unless plant 1WW has an appreciably greater tendency to foam, the foam level should stay well below the top of the tank without the use of antifoam agents.

Assuming use of the existing plant tower from the formaldehyde denitration unit (13.25-inch I.D.), the specified sugar addition rate corresponds to 2.8 pounds of sugar per minute per square foot of tower cross section. This rate is only slightly higher than the maximum rate attained in Run 4 in which a pressure drop of 1.5 inches of water was observed across the tower. This indicates that the tower from the formaldehyde denitration unit should be adequate during normal operation at the specified sugar rate.

A 12-hour digestion period is also specified in the flowsheet. Observations during the pilot plant runs indicate that the reaction is essentially complete after 12 hours of digestion. Residual carbon analyses predict a residual carbon content of less than two percent of the total carbon fed as sugar. If a lower carbon content is desired, a longer digestion period can be used.

The specified compositions of both the 1WW and sugar solution are changed from those used in Runs 1 through 11. A nitric acid concentration of 6.1 M is specified to reflect current practice more closely. A sugar concentration of 1.4 M instead of 2.5 M is specified since it appears desirable to use a more dilute solution for plant operation. With the more dilute solution, viscosity variations arising from changes in ambient temperature are decreased and flow control should be improved. The additional water in the 1.4 M solution essentially compensates for the six to eight percent volume reduction achieved in Runs 8 and 9.

The proposed flowsheet was successfully demonstrated in Run 12. A 1.4 M sugar solution was added to 25 liters of hot (100 C) 1WW for 12 hours. The initial nitric acid concentration was 6.14 M and the average sugar addition rate was 6.79 ml/minute or 0.036 pounds of sugar per minute per square foot of pot cross section. After sugar addition was complete, the solution was digested at 100 C for 18 hours and sampled periodically.

Results have been summarized earlier in Table III. The residual nitric acid concentration was 0.94 M and 0.90 M after 12 and 18 hours of digestion, respectively. A residual carbon content equivalent to 1.9 and 0.4 percent of the total carbon fed as sugar was found after 12 and 18 hours of digestion, respectively. About 19 moles of nitric acid were destroyed per mole of sugar fed. The sugar utilization was slightly lower and the final acidity was higher than predicted in the flowsheet. This data suggests that the volume of 1.4 M sugar solution should be increased to about 520 gallons in the flowsheet in Figure 2. However, since sugar utilization is affected by tower conditions (temperature, heat losses, and condensate reflux), the flowsheet conditions should be a reasonable starting point until sugar utilization is established for the plant equipment.

Pressurization Tests

Tests were made to determine the pot pressures and tower pressure drops that could be developed under abnormal conditions. These tests consisted of adding sugar solution to cold 1WW in the denitration unit and then heating the mixture. In one series of tests, the mixture was heated to 100 C at a rate of about 10 C per minute. Results of these tests are shown in Table V.

TABLE V

PRESSURIZATION TESTS

Reactants				Reaction	Maximum Pot	Max. Tower
1WW		Sugar		Initiation	Vacuum Decrease,	ΔP, Inches
Vol., L	H^+, M	Vol., L.	Sugar, M	Temp., C	Inches of H_2O	of H_2O
6.5	5.2	0.87	2.5	93	11	0.3
10	5.2	1.34	2.5	86	13	1.5
15	5.2	0.05	2.5	100	7	0.1
15	5.2	0.50	2.5	88	8	0.4
15	5.2	1.0	2.5	84	15	1.4
15	5.2	2.0	2.5	85	19	6.0
20	5.2	2.7	2.5	85	30	8.0

The total pot volume was 46.4 liters in each of these tests. The free space above the solution can be determined by subtracting the total volume of reactants from the total pot volume. The tower and off-gas system were the same as described earlier. The manometer indicating pot vacuum was adjusted to 25 inches of water before each test and the maximum decrease in pot vacuum was observed during each test. Actually, a positive pressure of five inches of water was observed when 20 liters of 1WW was used. The total change was listed in Table V as a vacuum decrease of 30 inches of water for simplicity. As would be expected, the increase in pressure drop across the tower and decrease in pot vacuum were dependent on the the total amount of reactants present and on the sugar concentration in the mixture. These data indicate the need for adequate operating procedures and safeguards to prevent the attainment of abnormal conditions.

In one final test, two liters of 2.5 M sugar solution were added to 15 liters of 1WW (5.2 M H^+). The mixture was rapidly heated to 70 C and then heated at a rate of about 1 C per minute until the reaction started at 83 C. The steam was turned off immediately after the reaction started but the temperature continued to rise. Twelve minutes after the reaction started, the solution reached a temperature of 89 C which was maintained for 15 minutes. Thereafter, the temperature slowly dropped as the reaction slowed.

The 1WW contained 0.4 gram of DBP per liter of 1WW in the final test. Foam rose into the tower immediately after the reaction started even though there was about 68 inches of freeboard in the pot. The maximum foam height could not be observed because the tower was lagged but the foam was in the tower for 17 minutes after the reaction started. During this period the foam level fluctuated erratically above and below an opening in the lagging 10 inches above the bottom of the tower. Simultaneously, the pressure drop across the tower fluctuated from about 0.2 to 20 inches of water. A decrease in pot vacuum of 24 inches of water was observed when the pressure drop was a maximum.

Induction Period Tests

In each batch run, an induction period was observed before the reaction started. The length of the induction period was observed to be six and nine minutes at sugar addition rates of 10 and 5 ml/minute, respectively. Tests were made to confirm this induction period and to check the effect of agitation. These tests consisted of adding 2.5 M sugar solution at rates of 5 and 10 ml/minute to 25 liters of 1WW that was held at 100 C. Without agitation the induction period was identical to that observed during the batch runs. With gentle air sparging, the induction period was three minutes at a sugar addition rate of 10 ml/minute.

Attempts to use sodium nitrite as a means of decreasing the induction period were not successful. These tests consisted of adding 2.5 M sugar solution at a rate of five ml/minute to 25 liters of 1WW that was held at 100 C. In one test the sodium nitrite concentration was 0.01 M in the 1WW. In other tests the sodium nitrite concentration was varied from 0.01 to 0.1 M in the sugar solution. The induction period was unchanged or about nine minutes in each test.