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DENITRATION OF PUREX WASTES WITH SUGAR

L. A. BRAY

APRIL 1963

HANFORD LABORATORIES

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

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DENITRATION OF PUREX WASTES WITH SUGAR

By

L. A. Bray

Chemical Laboratory
Chemical Research Operation

Hanford Laboratories

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DENITRATION OF PUREX WASTES WITH SUGAR

INTRODUCTION

Sugar is being used as a denitrating agent for the Purex Solvent Extraction Plant at Hanford. Denitration of the waste stream of a nuclear fuels reprocessing facility, such as Purex, has been investigated for several years.[1-7] The goal is to destroy the original HNO_3 concentration of approximately 5 to 10M to a minimum residual product acidity of about 0.5M free acid. The advantages of an acid destruction would include (1) reduction of the concentration of NaOH ultimately required to neutralize the wastes for long term alkaline storage, (2) a volume reduction of the final stored wastes, (3) an easier and more economical recovery of fission products or other valuable residual trace components due to the decreased acidity and smaller processing volumes, and (4) a reduction of the sodium content in the waste, since sodium adversely affects the efficiency of many of the anticipated fission product recovery processes.

A denitration unit was placed in operation at the Purex plant during 1962 using formaldehyde to treat radioactive acidic wastes. Because of difficulties encountered during initial plant use of formaldehyde, a study of alternate methods of denitration was undertaken. Observations during the ion-exchange strontium recovery program indicated that rapid destruction of HNO_3 occurs in the presence of certain organic complexants plus radiation. This phenomena was accordingly explored further in the laboratory (using a Co^{60} source and synthetic, nonradioactive solutions) for potential application to the denitration of Purex waste (where the fission products would provide the source of radiation). Several reagents, notably critic, ethylenediaminetetraacetic, and tartaric acids were effective in the presence of radiation. Sucrose reacted with HNO_3 in synthetic Purex waste (1WW) at an appreciable rate even in the absence of radiation.[8]

SUMMARY

A process has been developed in the laboratory for the destruction of HNO_3 in Purex-type waste solutions. The denitration process has also

been successfully tested in the high level "hot" cells, the "cold" pilot plant denitration unit, and in the Purex plant. Polyhydroxy compounds such as sucrose, fructose, glucose, and crude syrups such as "black strap" molasses rapidly and controllably decompose HNO_3 in aqueous solutions at temperatures above approximately 85 C. The number of moles of HNO_3 destroyed per mole of sugar fed is a function of the temperature of reaction and the moles of dissolved multivalent metal cations (iron, chromium, etc.). The efficiency of destruction of HNO_3 does not vary with acid concentration over the range of 0.5 to 8M. Destruction of acid does vary with iron concentration. Approximately 12 to 20 moles of HNO_3 are destroyed per mole of sucrose fed as the iron concentration increases from 0 to 1M.

The sugar reaction, although sufficiently rapid for convenient plant time cycles and for continuous or semicontinuous operation, is much less vigorous and exothermic than the formaldehyde reaction and can be safely carried out in large batch equipment, such as the existing Purex plant processing tanks of several thousand gal capacity. The reaction rate is easily controlled by the rate of sugar addition.

The products of the denitration reaction are all gaseous, consisting of oxides of carbon and nitrogen. No residual carbon or organic compounds remain in the treated solutions to complicate further processing or storage. HNO_3 can be regenerated from the off-gasses by use of conventional down-draft condensers.

Economics of denitration of Purex wastes are highly dependent on the cost of sugar. At present prices of 10¢/lb for refined sucrose and 4¢/lb for 37% formaldehyde, reagent costs alone for sucrose denitration are slightly higher than for formaldehyde, based on 18 moles and 2.2 moles of HNO_3 destroyed per mole of the respective reagents. This is equivalent to 3.04¢/lb of acid destroyed using sucrose and 2.37¢/lb of acid destroyed using formaldehyde. The reagent costs using molasses would be 1.17¢/lb of acid destroyed. Total costs for sugar denitration in a new plant might be substantially lower than formaldehyde even with refined sucrose because of the simpler equipment and instrumentation required.

Sugar denitration is not limited to Purex-type wastes but should be applicable to treatment of other HNO_3 solutions, either radioactive or nonradioactive.

EXPERIMENTAL

For laboratory and hot-cell demonstrations, a sugar solution was added either incrementally or batch-wise to synthetic or actual acidic wastes (Table I) and heated. Samples were taken at various time intervals and analyzed for residual carbon, hydrogen ion, and nitrate concentrations. The total nitrate concentration was determined by a phenoldisulfonic acid colorimetric method. The hydrogen ion concentration was determined by complexing the iron in a sample with ammonium oxalate and titrating the resulting solution to the original pH with NaOH. The residual carbon concentration was determined by placing a liquid sample in a platinum boat, drying and heating the resulting product in an oxygen atmosphere to 1000 C, and passing the resulting gas through a standard gas train. The resulting CO_2 was determined by the change in weight of a sodium hydrate asbestos absorbent.

TABLE I

COMPOSITION OF A TYPICAL PUREX ACIDIC WASTE

Constituent	Molarity
H^+	4 to 8
Fe(III)	0.5 to 1.0
Al(III)	0.1
Ni(II)	0.2
Cr(III)	0.1
Na^+	0.68
NO_3^-	5 to 7
$SO_4^=$	0.7
$PO_4^{\equiv}$	0.01
Fission Products	Trace

RESULTS AND DISCUSSION

Denitration Mechanism

The products of denitration of acidic wastes with polyhydroxy compounds such as sucrose ($C_{12}H_{22}O_{11}$) are all gaseous, consisting of oxides of carbon and nitrogen. Sugar (sucrose), upon hydrolysis with acids, yields glucose and fructose in equal amounts. The hydrolysis and oxidation of the glucose portion of the sugar then follows a step-wise reaction sequence[9] similar to that listed in the following set of equations, Figure 1.

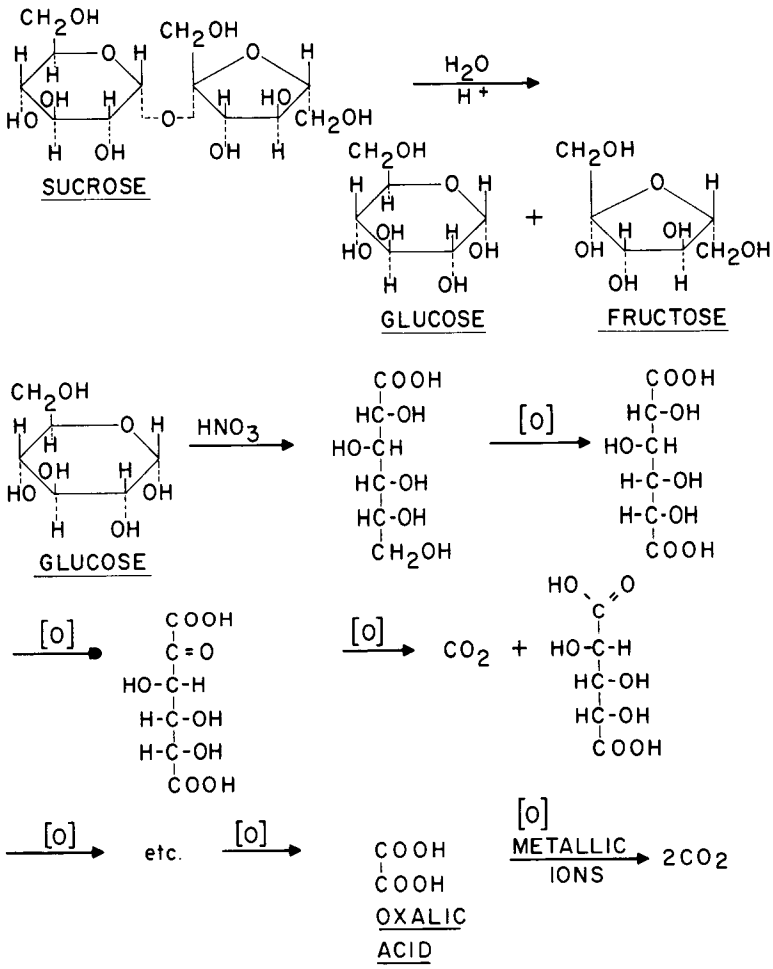

FIGURE 1

Oxidation of Sucrose

The oxidation of the fructose moiety follows a reaction sequence similar to that of the glucose portion. From these equations, it can be seen that two hydrolysis reactions and at least three oxidation reactions are required before any evolution of gaseous CO_2 will occur. It is not surprising therefore that a relatively long induction period of from 6 to 10 min has been noted for this oxidation reaction.

$$12\ HNO_3 + C_{12}H_{22}O_{11} \rightarrow 12CO + 6N_2O_3 + 17H_2O \qquad (1)$$

$$12\ HNO_3 + 6NO \rightarrow 18NO_2 + 6H_2O \qquad (2)$$

$$24\ HNO_3 + 12CO \rightarrow 24NO_2 + 12\ CO_2 + 12H_2O \qquad (3)$$

$$C_{12}H_{22}O_{11} + 48HNO_3 \rightarrow 48NO_2 + 12\ CO_2 + 35H_2O \qquad (4)$$

According to these reactions, the observed efficiency could range from 12 to 48 moles of HNO_3 destroyed per mole of sucrose consumed.

Denitration as a Function of Acid Concentration

The use of sucrose for the destruction of HNO_3 has been suggested as an alternate for the current formaldehyde procedure. It is therefore necessary to compare the two processes. The British Atomic Energy Establishment[1-3] has investigated the formaldehyde reaction extensively and found that 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, a different mechanism comes into play. As the HNO_3 concentration decreases, the reaction finally approximates a 1:1 ratio. The destruction of HNO_3 with sucrose is not similar but is linear with acid concentration, i.e., the sucrose reaction destroys the same number of moles of acid at all acid concentrations.

The destruction of HNO_3 was determined as a function of acid concentration by adding increments of sucrose equivalent to approximately 0.03M of sucrose per liter of synthetic 1WW, to a solution containing an original 8M

HNO_3. Each increment added to the acid solution was refluxed (95 to 105 C) for 4 to 6 hr. Samples were taken after each reflux and analyzed for the concentration of the remaining undestroyed HNO_3 before each additional sucrose addition. Figure 2 shows that the destruction of HNO_3 is linear with acid concentration, implying that the same mechanism exists over this range of acid concentrations.

Denitration as a Function of the Metallic Salt Concentration

T. V. Healy[1, 3] noted that the presence of ferric or uranyl nitrates found in fission product solutions catalyzed the reaction of both concentrated or dilute HNO_3 with both formic acid and formaldehyde. The stoichiometry of the sucrose denitration reaction (moles of HNO_3 destroyed per mole of sucrose fed) and the speed of the reaction with added metal salts were briefly studied.

Results for the sucrose denitration of several HNO_3 solutions were obtained in which the ferric salt concentration was varied from 0 to 1M. Table II and Figure 3 show the results for hydrogen ion, nitrate, and residual carbon concentrations after the sucrose and acid reacted at 100 C for approximately 24 hr.

The moles of HNO_3 destroyed per mole of sucrose fed varied from 11.5 to 20.5 with 0 to 1M ferric salt. Figure 3 shows that the residual carbon remaining after 24 hr is also a function of the iron concentration in the initial acid solution.

TABLE II

DESTRUCTION OF NITRIC ACID AS A FUNCTION OF IRON CONCENTRATION

Conditions: 400 ml of 6M HNO_3, varying $Fe(NO_3)_3$
40 ml of 2.5M Sucrose (14.4 grams of carbon)
Temperature, 100 C

Reaction Time, hr	Fe M	H^+ M	NO_3^- M	Residual Carbon, %[a]	Volume, ml	Moles HNO_3 Destroyed per Mole Sucrose Fed (b)	(c)
-	-	6.27	5.9	-	400	-	-
24		3.36	2.8	2.09	405	11.5	12.3
-	0.1	6.18	6.0	-	400	-	-
28		2.25	2.4	4.9	400	15.7	14.4
-	0.5	6.19	7.2	-	400	-	-
19		1.60	3.1	3.4	374	18.8	17.2
23.5		1.61	3.0	0.69	374	18.8	17.6
-	1.0	6.15	8.8	-	400	-	-
19		1.09	3.9	0.63	379	20.5	20.4
24		1.14	3.9	0.21	379	20.3	20.4

(a) Based on percent of total carbon fed as sucrose
(b) Based on free acid analyses
(c) Based on $NO_2^- + NO_3^-$ analyses

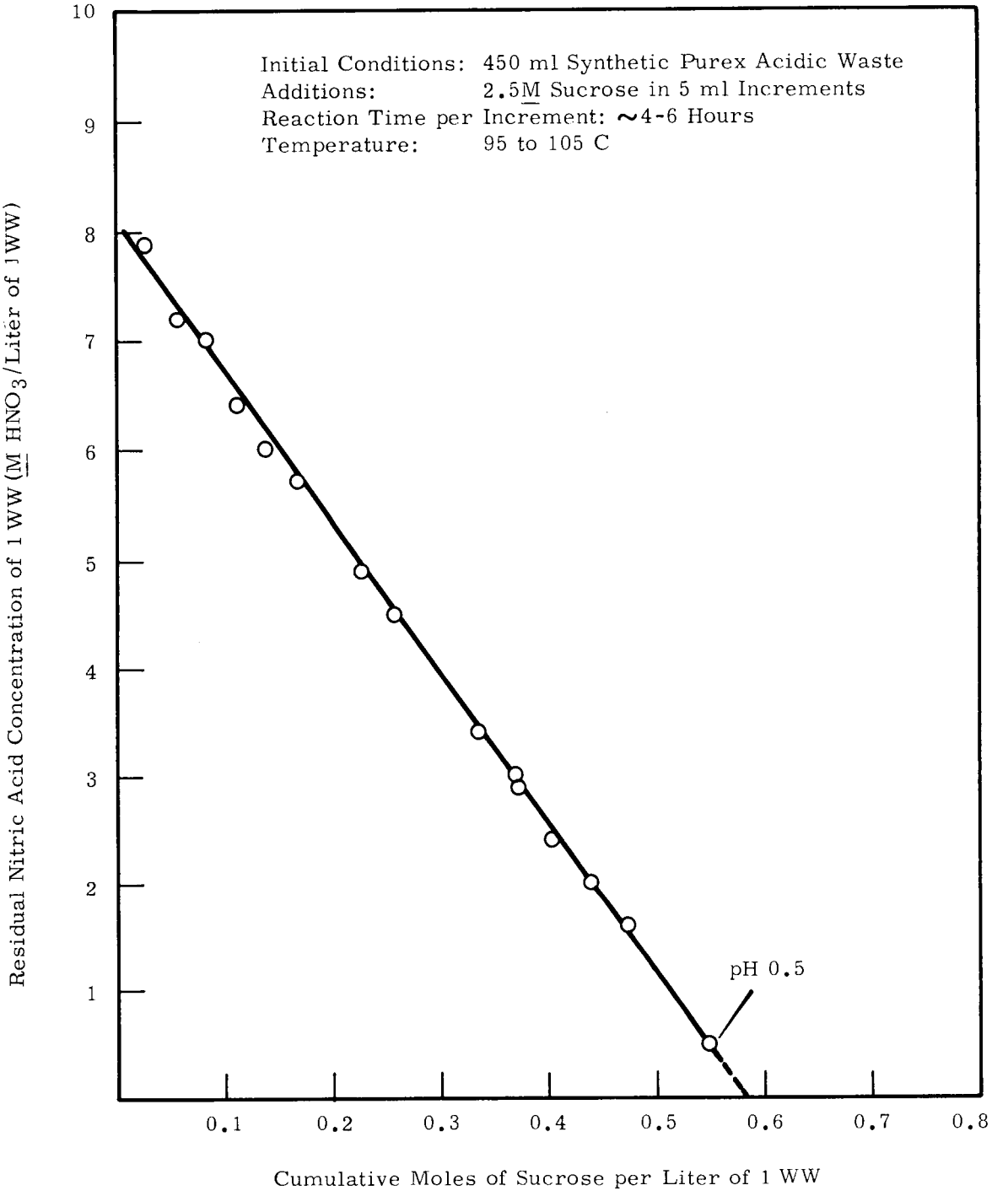

FIGURE 2

Destruction of HNO_3
(1WW with Sucrose as a Function of Acid Concentration)

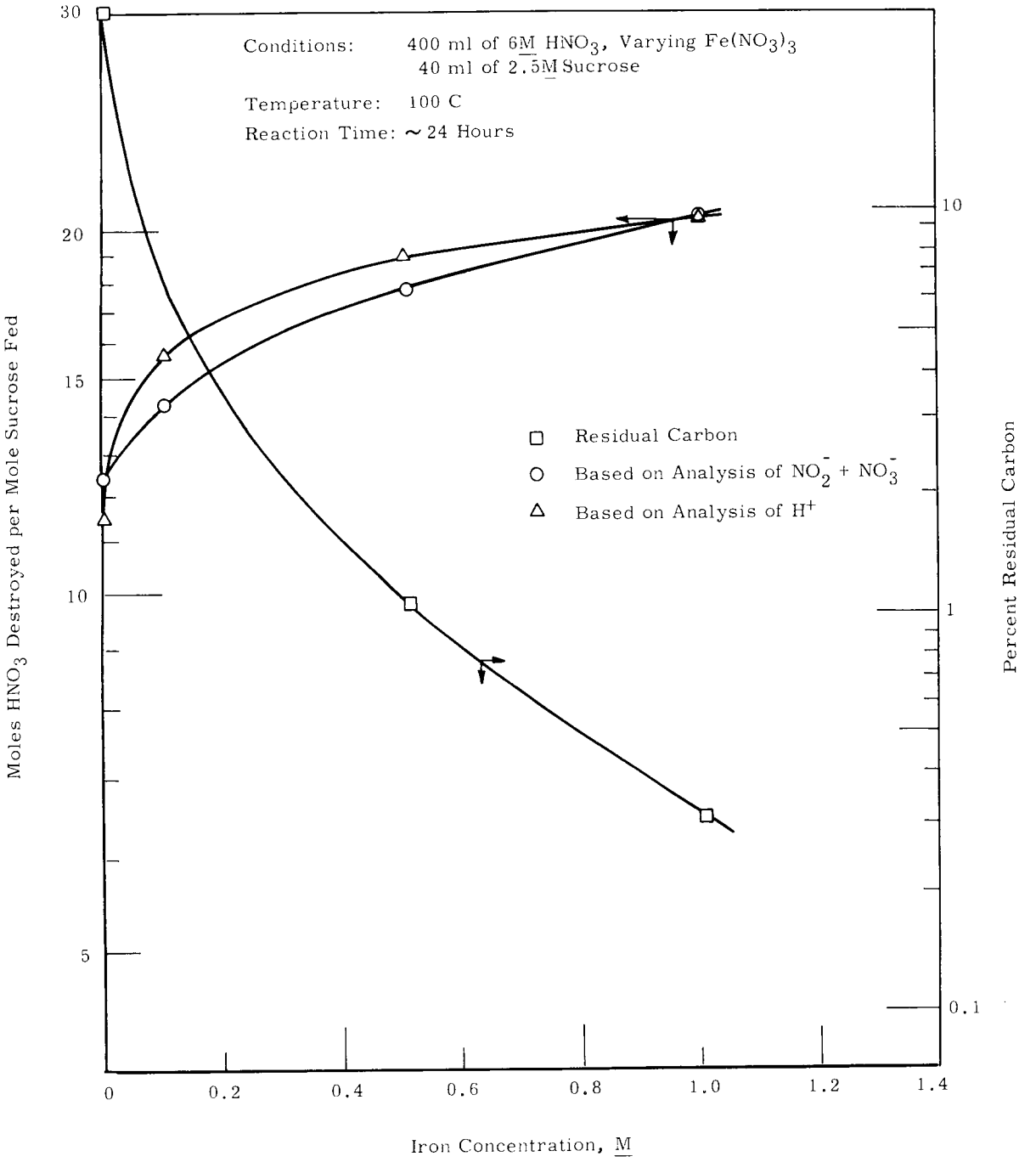

FIGURE 3

Denitration as a Function of Iron Concentration at a Constant Reaction Time

The destruction of HNO_3 with sugar will proceed with or without a catalyst such as iron, chromium, or other catalytic ions associated with fission product wastes. However, the catalytic effect, i.e., the change in reaction rate in the presence of or lack of such ions, should be taken into consideration as future waste concentrations change and for applications involving the denitration of purified fission product solutions.

Denitration as a Function of Time

The sucrose-HNO_3 reaction was studied to determine some of its properties. The reaction is easily controlled by rate of sucrose addition. The rate of gas evolution is a function of the catalyst, the reaction temperature, and the sucrose addition rate. The initial reaction temperature for rapid acid destruction is approximately 85 C, although it has been noted that once the reaction has started and then stopped, the restart temperature is much lower (approximately 50 C) and is probably due to the formation and catalytic effect of oxides of nitrogen such as nitrite.

The moles of HNO_3 destroyed per mole of sucrose fed improved approximately 10% by increasing the reaction temperature from 85 to 100 C. The acid destruction was not improved with the use of a reaction tower above the reaction vessel, such as that required in the formaldehyde procedure. The initial induction period is only 6 to 9 min after the initial addition of sugar (before visible evidence of oxides of nitrogen), and air sparging reduced this period by a factor of 2 to 4.

A number of laboratory batch denitration studies were performed to determine the acid destruction as a function of time. The results provided the technical basis for further testing of batch, semicontinuous and continuous denitrations in both the cold Semiworks and Purex plants. Typical results for the denitration of synthetic acidic waste (0.8M Fe) with time are shown in Table III and Figure 4. The reaction temperature was held constant at 100 C. Samples were periodically analyzed for residual carbon, hydrogen ion, and nitrate. Residual nitrate and hydrogen ion concentrations are shown in Figure 4 in terms of acid destruction, i.e., moles

TABLE III

DENITRATION OF ACIDIC WASTE AS A FUNCTION OF TIME

Conditions: 400 ml Synthetic Purex Waste (0.8M Fe)
40 ml of 2.5M Sucrose

Temperature, 100 C

Reaction Time, min	H^+ M	NO_3^- M	Residual Carbon, %[a]	Volume, ml	Moles HNO_3 Destroyed per Mole Sucrose Fed (b)	(c)
0	6.49	8.0	----	400	----	----
10	3.74	4.1	96.2	440	9.7	14.2
30	3.44	3.8	50.5	430	11.4	16.0
100	2.78	3.5	37.6	415	13.8	17.8
300	1.84	3.5	9.61	395	19.1	18.5
655	1.65	3.5	3.22	380	20.1	19.1
1250	1.61	3.5	0.37	370	20.4	19.4

(a) Based on percent of total carbon fed as sucrose
(b) Based on free acid analyses
(c) Based on $NO_2^- + NO_3^-$ analyses

of nitrate or hydrogen ion destroyed per mole of sucrose fed. In the first 10 min of the batch reaction (after evolution of oxides of nitrogen) the results were 14 and 10 respectively. These results show that 49% of the original nitrate and 37% of the hydrogen ion were destroyed during the first 10 min, but only 4% of the total carbon content had been evolved as an oxide. The difference noted between the hydrogen ion and nitrate destroyed during the initial reaction is assigned to the intermediate formation of organic acids.

To define more fully the rate of sucrose (or residual carbon) destruction, several other batch denitration studies were performed; the results are shown in Figure 5. In these studies, the acidic waste was again mixed with sucrose, heated at 100 C, and periodically sampled to determine residual carbon as a function of time. The results show 60% of the sucrose destroyed after 60 min, 75% after 120 min, and 99% after approximately 20 hr. In actual radioactive wastes, any remaining carbon should be destroyed by radiation.

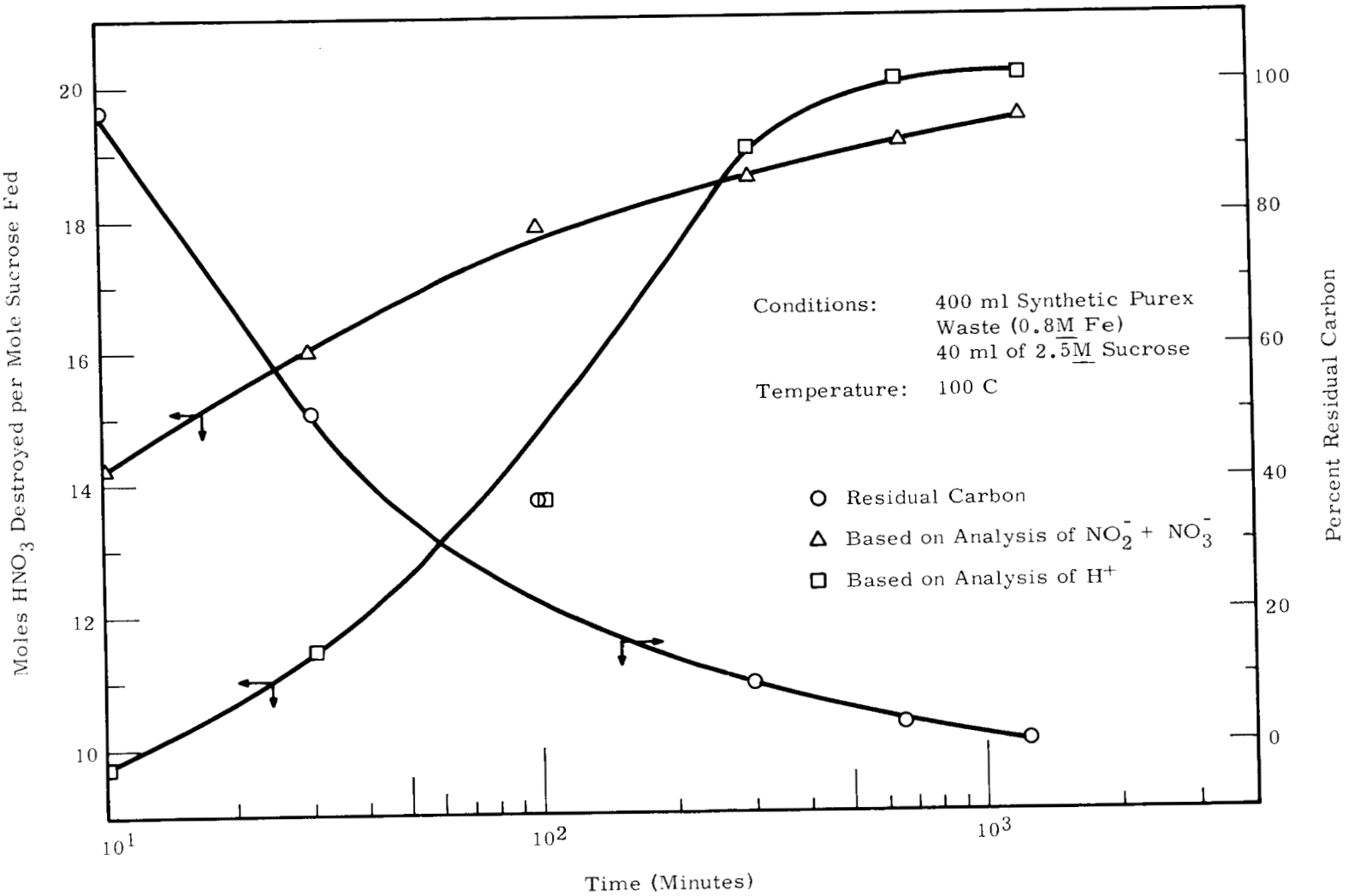

FIGURE 4

Denitration of Acidic Waste as a Function of Time

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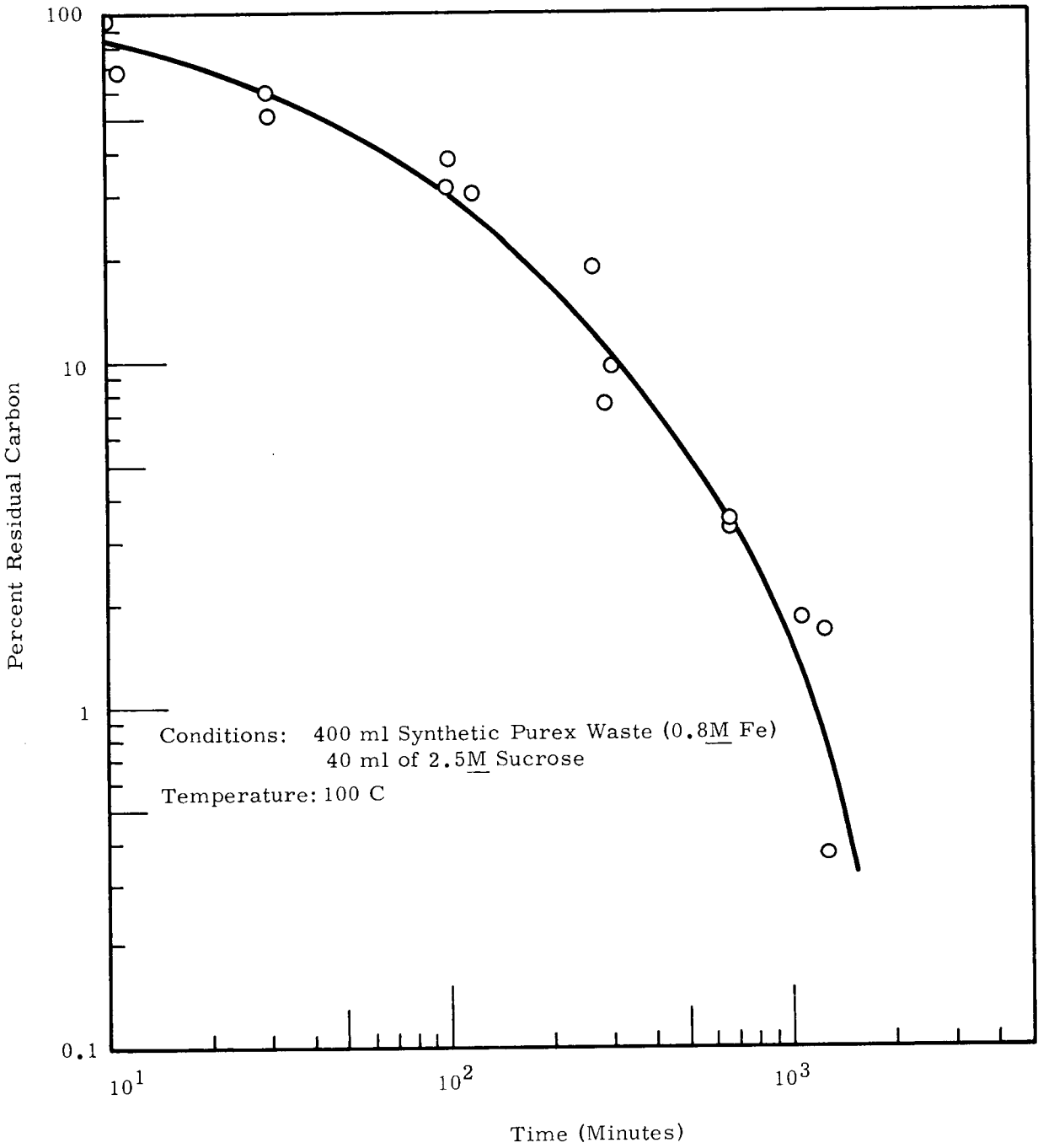

FIGURE 5

Residual Carbon as a Function of Time

Process Denitration

Denitration of solutions may be accomplished by (1) slowly adding sucrose to a full batch tank, (2) simultaneously filling the tank and adding sucrose during the same period, or (3) adding sucrose and fresh acidic waste continuously to a denitrated solution which is continuously being dumped as new material is added.

A laboratory test was run (simulating a proposed plant test) to evaluate the simultaneous addition of both sucrose and acidic waste into a heated reaction tank over a period of 50 hr. Major uncertainties were (1) whether the residual carbon content would be excessive, and (2) whether the acid destruction (moles of HNO_3 destroyed per mole of sucrose fed) would be adequate. The test simulated the coaddition, to a 3000 gal tank, of 1 gal of acidic waste per minute and the required amount of sucrose to denitrate that gallon. Table IV shows that at the end of 50 hr approximately 19 moles of HNO_3 were destroyed per mole of sucrose fed and that the residual carbon content was a negligible 3%. The success of this test indicates that the denitration of large quantities of waste may be accomplished as the waste is collected rather than after the reaction vessel is filled with waste.

Other Potential Sources of Sugar

Batch denitration tests were performed to evaluate other potential sources of sugar. A "standard liquor" and a "thick juice" were obtained from the Utah-Idaho Sugar Company, Moses Lake, Washington. In addition, a supply of Hawaiian "black strap" molasses was obtained from the Pacific Molasses Co., Portland, Oregon.

Denitration comparative tests were obtained by mixing known volumes of sugar with a synthetic acid waste, heating to 100 C and sampling at various time intervals. Analyses were obtained for hydrogen ion and residual carbon concentrations as shown in Table V. All sugar sources tested compared favorably with refined sucrose. Calcium and strontium impurities

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TABLE IV

SUCROSE DENITRATION TEST

To Simulate Addition of 1 gal/min to Purex 5000 gal Tank

Goal: 1500 ml 1WW added in 3000 min
Destruction of ~ 20 moles of NO_3^- per mole of sucrose
Residual carbon < 2% at end of 3000 min

Conditions: 0.5 ml 1WW/min, 0.089 ml 1.4M sucrose/min
Assume volume of pot equal to 1WW added

Time, min	Temp, C	Sample No.	Volume Sucrose, ml	Volume 1WW, ml	Carbon g/liter	Carbon % Residual	Total NO_3^- M	H^+ M	Moles NO_3^- Destroyed per Mole of Sucrose fed, based on: NO_3^-	H^+
0	102	1	--	100	0.01	--	7.2	6.34	--	--
300	100	2	26.7	150	1.1	3.1	3.4	2.94	15.2	13.6
629	100	3	54.5	315	0.82	2.3	3.2	2.53	16.5	13.0
809	101	4	70.0	405	0.96	2.8	2.7	2.34	18.6	16.5
1309	100	5	94.5	655	0.41	1.4	3.3	2.51	19.3	19.0
1594	100	6	104.5	750	0.20	0.7	3.8	2.87	17.4	17.8
1834	101	7	164.5	890	1.20	3.2	2.6	2.12	17.8	16.3
2074	102	8	184.0	1035	0.44	1.2	3.1	2.03	16.5	17.3
2134	103	9	189.4	1065	0.63	1.8	3.1	2.11	16.5	17.0
2254	103	10	200.3	1135	0.52	2.5	3.3	2.15	15.8	17.0
2734	103	11	227.8	1455	0.71	2.2	3.3	2.15	17.8	19.1
2794	100	--	246.5	1485						
2854	100	--	268.0							
2914	100	12	--	--	1.1	3.0	2.5	1.80	20.2	19.5
2974	100	13	--	--	0.9	2.5	2.9	1.70	17.0	18.4
3034	100	14	--	--	2.0	3.4	2.9	1.60	17.0	18.8
3094	100	15	--	--	1.4	3.8	2.8	1.50	17.4	19.2
3154	100	16	--	--	1.0	2.7	2.8	1.50	17.4	19.2
3214	100	17	--	--	0.6	1.6	2.7	1.49	17.8	19.2
3424	101	18	--	--	0.2	0.5	2.7	1.44	17.8	19.4
3634	102	19	--	--	0.2	0.5	2.8	1.42	17.4	19.5

Final Volume: 1485

TABLE V

DENITRATION OF ACIDIC WASTE IN VARIOUS SUGARS

	Reaction Time, hr	Volume, ml	H^+, M	Residual[a] Carbon, %	Acid[b] Destruction
STANDARD LIQUOR*					
Conditions	0	400	6.4	-	-
[400 ml IWW (0.8M Fe)	1	425	2.9	55.8	10.8
50 ml Standard Liquor]	7.75	360	0.8	11.6	18.5
	15.75	360	0.41[c]	2.8	19.6
Conditions	0	400	6.4	-	-
[400 ml IWW (0.8M Fe)	1.4	450	3.7	40.6	14.6
25 ml Standard Liquor]	7.2	425	3.0	5.6	20.9
	22.7	415	2.9	1.3	22.1
THICK JUICE*					
Conditions	-	400	6.4	-	-
[400 ml IWW (0.8M Fe)	2	460	3.7	41.7	15.7
25 ml Thick Juice]	7.7	425	3.1	5.9	22.7
	23.7	400	3.2	1.2	23.4
BLACK STRAP MOLASSES*					
Conditions	0	400	6.4	-	-
[400 ml IWW (0.8M Fe)	1	440	4.2	51.9	24.2
15 ml Black Strap]	24	425	4.1	3.7	27.9
SUCROSE*					
Conditions	0	400	6.4	-	-
[400 ml IWW (0.8M Fe)	1.75	450	4.5	31.6	15.3
25 ml of 1.4M Sucrose]	4.75	435	4.2	7.5	21.0
	18	415	4.2	1.8	23.3

*

STANDARD LIQUOR		THICK JUICE		BLACK STRAP MOLASSES		SUCROSE	
Dry Substance, %	68.0	Dry Substance, %	64.1	Assume 48% Sugars		Sucrose Concentration	1.4M
Sugar, %	63.6	Sugar, %	47.8	SpG	1.4	Strontium, ppm	1
pH	7.9	pH	7.8	Sugar Concentration, M (Supplier's anal.)	~1.96	Calcium, ppm	8
SpG	1.32	SpG	1.30	Strontium, ppm	100		
Sucrose Concentration, M	~2.46	Sucrose Concentration, M	~2.19	Calcium, g/liter	1.8		
Strontium, ppm	18	Strontium, ppm	22	Obtained from:	Pacific Molasses Co.		
Calcium, g/liter	0.6	Calcium, g/liter	1.0	Approximate cost:	$39.25/ton		

(a) Based on percent of total carbon fed as sugar
(b) Based on moles of destroyed H^+ per mole of sugar fed
(c) Precipitate formed was very fine and hard to dissolve

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found in the various sources of sugar are reported because of their potential contamination to the fission product recovery program. The percent residual carbon and the moles of hydrogen ion destroyed per mole of molasses fed after 24 hr of reaction both appear high as compared to the other sugars tested. This is probably due to the presence of other reactive carbonaceous materials in molasses, but not reported as sugar.

Hot Cell, Semiworks, and Purex Plant Demonstrations

In a hot-cell demonstration, using actual Purex radioactive acidic waste (1WW), 500 ml of 1WW were heated in an open beaker with 40 ml of 2M sucrose for 2.5 hr. To simulate a worst possible case, all of the sucrose was added initially, and the solution was quickly heated to 100 C. Evolution of oxides of nitrogen was initially vigorous, but controllable, and there was little or no tendency to foam (foam height less than 1/2 in.). The nitrate concentration was reduced from 5.3M to 1.06M in 2.5 hr for an 80% overall denitration or an efficiency of 21 moles of HNO_3 per mole of sucrose fed.

To define a flowsheet for a Purex plant test, denitration studies have also been investigated in the cold Semiworks plant. Thirteen detailed runs have been completed by E. A. Coppinger[10] using simulated feeds. Several proposed flowsheets have resulted from laboratory, hot-cell, and these semiworks studies. A possible plant flowsheet was successfully demonstrated. As shown in Figure 6, a 1.4M sucrose solution was added to a batch of heated (100 C) 1WW over a period of 12 hr. The initial HNO_3 concentration of the 1WW was 6.14M. After completion of the sucrose addition, samples were analyzed periodically to determine residual carbon, total nitrate, and hydrogen ion concentration as shown in Table VI.

The digestion time was extended in this test only to determine how the trace carbon was destroyed with time. About 19 moles of nitrate were destroyed per mole of sucrose fed. The hydrogen ion and total nitrate concentrations were nearly uniform after 24 hr with a residual carbon content of less than 2%.

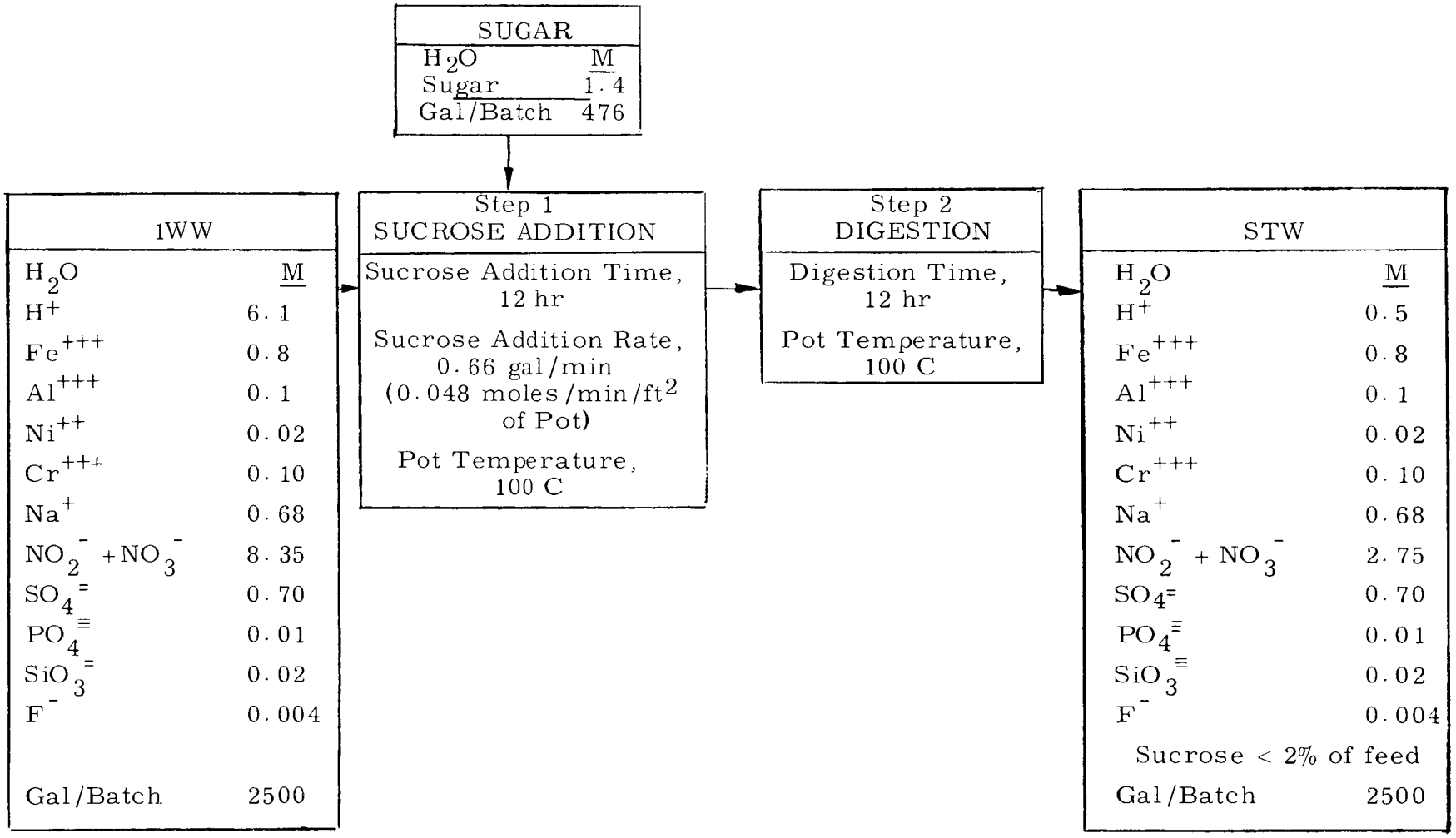

FIGURE 6

Purex Sucrose Treated Waste Flowsheet

TABLE VI

SAMPLE ANALYSIS AFTER SUCROSE ADDITION

Time, hr	H^+, M	Nitrate, M	Residual Carbon, %
0	6.14	8.2	-
12	2.0	3.4	-
15	1.4	2.8	-
18	1.1	2.9	7.9
21	1.0	2.8	4.1
24	0.94	2.9	1.9
27	0.96	2.9	1.1
30	0.90	2.9	0.4

The sucrose process for the denitration of Purex waste was successfully tested[11] in the plant during February, 1963, culminating the laboratory and semiworks development. A 2500 gal batch of 1WW, initially 4.5M H^+, was heated, and 1600 lb of sucrose slowly added. The final hydrogen ion concentration was 0.68M or 18.2 moles of HNO_3 destroyed per mole of sucrose fed. Sugar has been adopted for routine plant use.

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