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INVENTION REPORT
USE OF SUGAR TO NEUTRALIZE NITRIC ACID WASTE LIQUORS

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DESCRIPTION OF INVENTION

INTRODUCTION

Destruction of nitric acid in the waste stream of a nuclear fuels separations facility, such as the Purex Solvent Extraction Plant at Hanford, has been under investigation for several years[1][2][3]. The goal of such a process would be to destroy the original concentration of approximately 5 to 10 molar nitric acid to a minimum residual product acidity of about 0.5M free acid. The advantages of such a process would include, 1) an economical way to reduce the concentration of sodium hydroxide ultimately required to neutralize the wastes for long term alkaline storage, 2) reduction of the salt content in the stored wastes, 3) a 60 percent volume reduction of the final stored wastes, 4) easier and more economical recovery of fission products or other valuable residual trace components, due to decreased acidity and smaller processing volumes, and 5) reduction of the sodium content in the waste, since sodium adversely affects the efficiency of many of the anticipated fission product recovery processes.

A prototype denitration unit has been placed in operation at the Purex separations plant using formaldehyde to treat radioactive acidic wastes. The reaction vessel is only approximately 2 feet in diameter by 4 feet tall and is surmounted by a packed tower 1 foot in diameter by 6 feet tall. The efficiency of formaldehyde

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1) G.B. Barton, "The Removal of Nitric Acid from Purex Plant First Cycle Acid Waste (1WW) by Reaction with Formaldehyde", HW-55941, May 2, 1958.

2) T.F. Evans, "The Pilot Plant Denitration of Purex Wastes with Formaldehyde", HW-58587, February 23, 1959.

3) G.C. Oberg, "Denitration of Purex Plant 1WW", HW-60161, May 1, 1959.

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utilization depends primarily on the temperature of the acid feed which is introduced at the top of the packed tower in which it contacts formaldehyde vapors and lower oxides of nitrogen from the reaction pot. Because of its violent chemical reaction with nitric acid at elevated temperatures, formaldehyde must be carefully controlled. The Purex denitration plant was therefore designed as a continuous operation carried out in a small unit with a short hold-up time. Formaldehyde would be unsuitable for large-scale batch-type operation due to the danger of violent explosions.

Difficulties have attended the use of the Purex formaldehyde unit. With actual plant waste, as contrasted to the synthetic solutions used in the laboratory and semi-works development, the process has proven ineffective due to foaming of solution up into the packing, loss of temperature control, plugging of in-concrete transfer lines, resultant efficiencies of at best approximately one-half that predicted from laboratory studies, and maintenance problems due to in-line polymerization of formaldehyde solutions. Expensive anti-foams have been required for even nominal operation. There are the further minor operation drawbacks that formaldehyde is extremely irritating to mucous membranes, is a powerful reducing agent and must be treated with great care. Handling of the formaldehyde in a plant therefore requires special storage and handling facilities.

Because of the difficulties which have attended the use of formaldehyde, other organic compounds have been tested as reagents for the destruction of nitric acid.

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Several (notably citric, oxalic and tartaric acids) were found to be effective in the presence of radiation. Sugar (sucrose) reacted with nitric acid in synthetic Purex waste (1WW) at an appreciable rate even in the absence of radiation. The use of sugar for the destruction of nitric acid is the basis for the disclosure of this report of invention. Advantages are that the reaction is inherently safe, can be carried out batch-wise in large (existing) tanks, and (because of the ample head room in these tanks) should not require use of anti-foaming agents. Other advantages are lower reagent cost and ease and safety of handling and storage.

EXPERIMENTAL

For laboratory and hot-cell demonstrations, a sucrose solution was added either incrementally or batch-wise to synthetic or actual acidic wastes (Table I) and heated. E. A. Coppinger, Chemical Research and Development, has demonstrated the process on a large scale in a semi-works unit in the 321 Building, 300 Area.[4]

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4) W. H. Reas, (E. A. Coppinger), "Chemical Research and Development Operation Monthly Report - October, 1962", HW-75376C.

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TABLE I

COMPOSITION OF A TYPICAL PUREX ACIDIC WASTE

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

RESULTS

Laboratory results in which the sucrose was added batch-wise to synthetic acidic waste solutions indicate that:

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1) The efficiency of the destruction of nitric acid (moles of nitric acid destroyed per mole of sucrose) does not vary appreciably with acid concentration. A series of acid solutions containing from 8M to 0.5M nitric acid were tested by adding sucrose and determining the efficiency of the sucrose-nitric acid reaction. The efficiency and rate are, however, a function of iron concentration, both increasing with concentration of iron (which is believed to function as an oxidation-reduction catalyst).

2) The sugar-nitric acid reaction is very "smooth" and easily controlled. Sugar, unlike formaldehyde, may be added to the reaction vessel either continuously or batch-wise, i.e. it has been demonstrated that addition of all of the sugar at the beginning of the reaction is not catastrophic, assuming of course that the equipment is properly sized. With initial addition of all of the sugar and heating to ca. 100 C, the reaction is vigorous - but not explosive - and can be readily controlled by controlling the temperature.

3) The reaction can be very nearly stopped by reducing the input heat, although nitric acid has been slowly destroyed at laboratory room temperatures over a period of several weeks while in contact with sucrose.

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4) The approximate initial temperature for rapid destruction of nitric acid is 85 C, although it has been noted that once the reaction has started and then been stopped, the re-start temperature is much lower (approximately 50 C).

5) The efficiency of the destruction of nitric acid is improved with the addition of certain dissolved metal cations such as iron. In a series of experiments in which the iron concentration was varied from 0 to 1 mole per liter of 6 molar nitric acid, the efficiency varied from 14.5 to 20.6 moles of acid destroyed per mole of sugar consumed.

6) The efficiency of the destruction of nitric acid is slightly improved with increased reaction temperature. (From 85 C to 100 C, approximately 10 percent).

7) The reaction tower required in the formaldehyde process is not required and does not improve the sugar-nitric acid destruction efficiency.

8) The sugar-nitric acid reaction taken to completion is free of all carbonaceous products and the sugar and nitric acid have been converted to gaseous products.

9) The sucrose-nitric acid reaction has an induction period of only four to six minutes (after initial addition of sugar before visible evidence of reaction is noted). Gentle air sparging or addition of sodium nitrite

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appears to reduce the induction period by a factor of two to four.

10) If for some operational error, i.e. the digestion period was not completed, experiments with a cobalt-60 source show that any carbonaceous products remaining in solution will be readily destroyed by radiation and converted to gaseous products.

These results may be illustrated by the following examples taken from numerous laboratory, hot-cell and semi-works demonstrations.

Example I

In a hot-cell demonstration, using actual Purex radioactive acidic waste (1WW), 500 milliliters of 1WW were heated with 40 milliliters of 2.5M sucrose for 2.5 hours. To simulate a worst possible case, all of the sugar was added initially and the solution 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 one-half inch). The nitrate concentration was reduced from 5.3 M to 1.06 M in 2.5 hours for an 80 percent over-all denitration and an efficiency of 21 moles of nitric acid per mole of sucrose.

Example II

In a laboratory test, 400 milliliters of synthetic 1WW (0.5 M Fe^{3+}, 4.4 M NO_3^-) were heated with 40 milliliters of 2.5 M sucrose for 24 hours at 95 C. The nitrate, hydrogen ion and carbon contents of the solution were analyzed periodically as shown:

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Time (Minutes)	Nitrate (M)	H^+ (M)	Carbon (g/l)
0	4.0	3.6	33
20	2.4	2.6	32
60	1.3	2.2	20
300	0.86	1.3	13
480	0.76	1.0	9.4
1440	0.56	0.2	1.9

The batch-type experiment shown indicates an over-all destruction of 15 moles of nitrate per mole of sucrose. Similar laboratory experiments indicated that increased temperature (95 to 107 C) and an increase in metal cations, such as iron, will increase the efficiency of the denitration reaction.

Example III

A sucrose denitration production test at the Purex plant, using 3000 gallons of 1WW, is scheduled for early in 1963. To define a flowsheet for the plant test, denitration studies have also been investigated in the "cold" semi-works pilot plant in the 300 area. Thirteen detailed runs have been completed by E. A. Coppinger using simulated feeds. A proposed flowsheet has resulted from laboratory, hot-cell and these semi-works studies. Other batch, semi-continuous, and continuous schemes have also been suggested for further laboratory and engineering study.

A possible plant flowsheet[5], for batch denitration with sucrose, was successfully demonstrated in the pilot plant unit. As shown in Figure 1, a 1.4 M sugar solution was added to a batch of heated (100 C) 1WW for 12 hours. The initial nitric acid concentration of the 1WW was 6.14 M. After completion of the sugar addition, samples were analyzed periodically to determine residual carbon, total nitrate and hydrogen ion concentrations as shown:

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Time (Hours)	H^+ (M)	Nitrate (M)	Carbon (% Residual)
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 length of 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 sugar fed. The hydrogen ion and total nitrate concentrations were nearly uniform after 24 hours with a residual carbon content of less than 2 percent.

CLAIMS

1) A process has been suggested for the destruction of nitric acid. Polyhydroxy compounds such as sucrose, frutose and glucose were found to rapidly decompose nitric acid in aqueous solutions at elevated temperatures. 2) The

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5) E. A. Coppinger, Monthly Progress Report, December, 1962.

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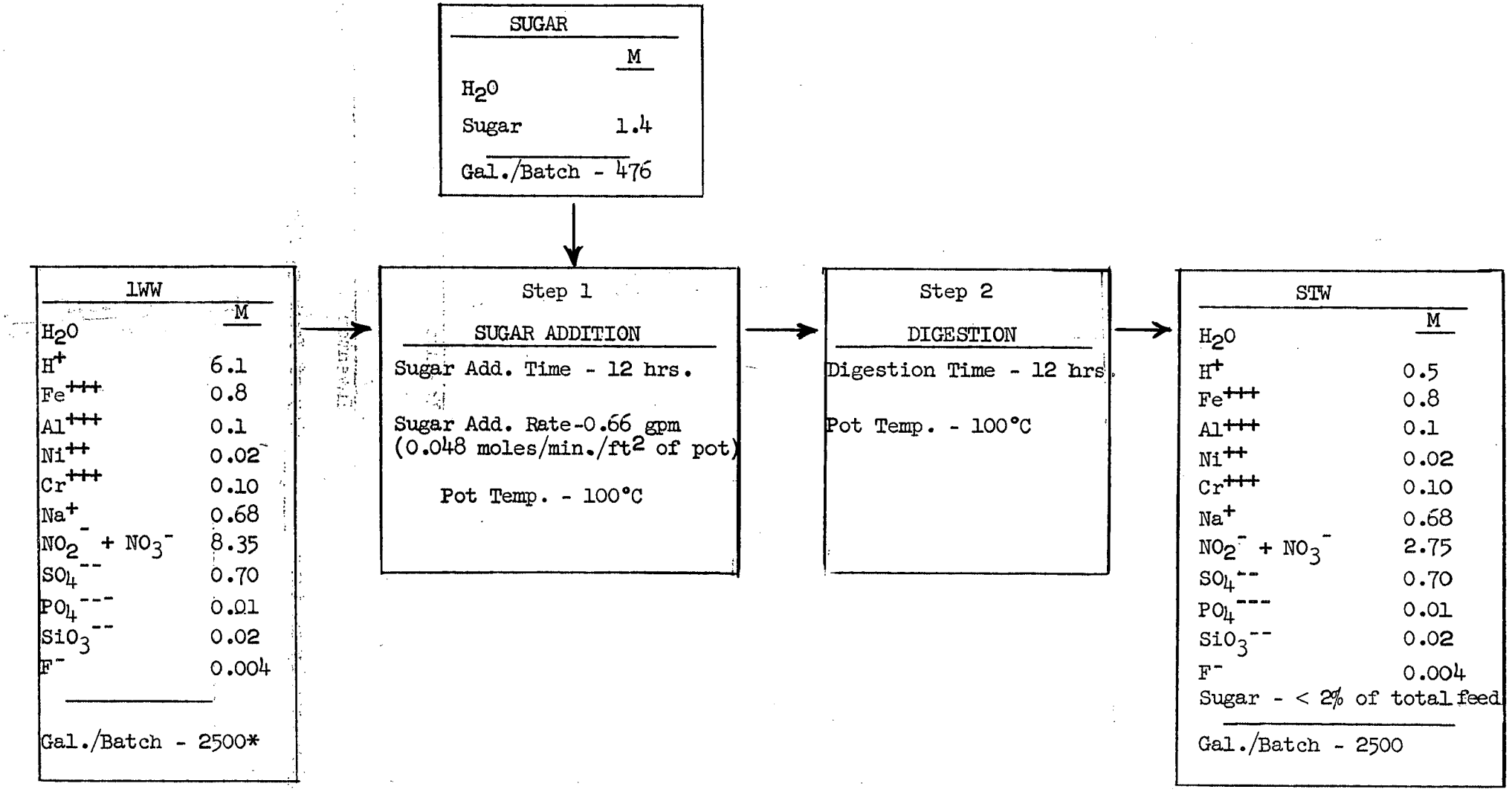
FIGURE 2. PUREX SUGAR TREATED WASTE FLOWSHEET



*Based on the 5000 gal. tank which will be used in the plant.

efficiency (moles of nitric acid destroyed per mole of sugar) of the denitration is a function of temperature and moles of dissolved metal cations (iron, chromium, etc.). 3) Sugar is easily handled without hazard, may be used in either a batch or continuous process, does not require addition of costly anti-foam agents, and has been estimated to reduce the chemical costs of the present denitration operation by 50 percent. 4) The use of sugar for the denitration of aqueous solutions is not limited to highly radioactive waste solutions from chemical separation plants. The use of sugar for denitration of highly radioactive wastes is however significant to the atomic industry in that it will reduce the cost of waste handling, storage, solidification, and fission product recovery. The gaseous oxides of nitrogen resulting from the denitration of aqueous wastes can be also recovered and reused. 5) Although sucrose has been used for these studies because of its low cost and availability, other related polyhydroxy or carbohydrate compounds should behave similarly.

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