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-1-

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TO: W. M. Harty

FROM: R. J. Sloat and R. E. Smith

ACUUM NITRIC ACID FRACTIONATION IN THE PUREX PLANT

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GENERAL ELECTRIC
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-2-

H-30600

VACUUM NITRIC ACID FRACTIONATION IN THE PUREX PLANTINTRODUCTION

The TBP Plant nitric acid fractionator was designed to operate at atmospheric pressure to produce 60% nitric acid. Operating at these conditions, excessive corrosion has resulted in those regions of the fractionator which are in contact with boiling concentrated acid (e.g., the reboilers and lower trays of the tower). Frequent shutdowns have been required for maintenance and repair of the reboiler unit. Since the Purex fractionator is located in the canyon and is not accessible for contact maintenance, frequent shutdowns for repairs would be costly and could seriously limit the processing capacity of the Purex Plant. Consequently a study has been conducted to determine the preferred method of minimizing corrosion in the Purex nitric acid fractionator and its reboiler. This document formalizes information which has already been transmitted informally to the Design Section, and which is being used as the basis for Design studies to convert the Purex Plant nitric acid fractionator from atmospheric to vacuum operation.

SUMMARY AND CONCLUSIONS

Several different ways of minimizing the corrosion in the nitric acid fractionation equipment of the Purex Plant have been evaluated. Although alternate approaches, such as construction of portions of the fractionator from corrosion resistant materials have been considered, it is concluded from this study that the nitric acid fractionator tower and its reboiler in the Purex Plant should be redesigned to operate under vacuum.

Several alternative vacuum installations have been considered. The installation recommended as a basis for design studies produces 60% nitric acid in two steps. As is indicated on the flowsheet on Figure 2, the vapor from the No. 2 Purex concentrator is fed to a bubble-cap absorption tower which operates at atmospheric pressure to produce 30% acid liquid bottoms. The 30% nitric acid solution is fed to a bubble-cap vacuum fractionation unit which produces the 60% acid. Pertinent preliminary specifications and operating conditions for the vacuum fractionator are listed below:

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GENERAL ELECTRIC
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-3-

H4-30600

Liquid Feed	30 wt. per cent HNO_3 ($\sim 5.6 \text{ M}$)
Bottoms	60 wt. per cent HNO_3 ($\sim 13 \text{ M}$)
Overhead	0.1 M HNO_3
L/V (top section)	0.25
Operating Pressures (at 16.7 Tons U/Day processing rate -- superficial column velocity at top of column = 20 ft./sec.)	
Top	Approx. 50 mm. Hg absolute
Bottom	Approx. 150 mm. Hg absolute
Theoretical Plates:	
Upper Section	1-1/2
Lower Section	2-1/2
Actual Bubble Cap Trays:	
Upper Section	5 or more
Lower Section	6 or more
Diameter	6 to 8 ft.

DISCUSSION

A number of methods have been suggested for minimizing the corrosion of the Purex fractionator. Among the solutions evaluated are the following:

- 1) Construction of those portions of the fractionator which are in contact with concentrated boiling nitric acid from non-corrosive materials such as tantalum, stoneware and glass.
- 2) Reduction of the concentration of acid produced to reduce the corrosion rates of equipment fabricated from stainless steel.
- 3) Operation under vacuum to reduce the operating temperature of the fractionation equipment, thereby reducing corrosion rates.

Order of magnitude calculations indicate that a fractionator reboiler tube bundle fabricated from tantalum would cost \$150,000 to \$200,000. Although these costs would not alone rule out further consideration of a tantalum reboiler, other factors such as (1) the development program required to confirm the feasibility of such a unit for use at Purex operating conditions (e.g., electrolytic corrosion of dissimilar metals),

GENERAL ELECTRIC
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-4-

HW-30600

(2) the lack of fabrication know-how for making a process vessel of this type and size, and (3) the favorable evaluation of vacuum fractionation as an answer to the excessive corrosion have led to the conclusion that these alternate materials should not be considered further.

In Document HW-30246, "Recovered Acid Use in Radox and Purex", it was concluded that the minimum concentration of recovered acid usable in the Purex Plant would be approximately 50 wt. per cent. Since an appreciable portion of the Purex recovered acid must be used in the dissolvers and for butting up the 2AF solution the use of lower concentrations would result in reduced dissolution rates and possible processing limitations in the 2A Column. Although reduction of the HNO_3 concentration to approximately 50% would reduce the corrosion rates slightly (a maximum of a factor of 1.5 to 2), the extent of the reduction is not great enough to be considered a solution to the corrosion problem.

Corrosion data from various sources (Ind. and Eng. Chemistry, November 1952, and the Du Pont Company) indicate that for any given HNO_3 concentration stainless steel corrosion rates decrease appreciably as the temperature of the acid decreases. Although the data used in plotting Figure 1 do not fall on smooth curves, the general trend of the data indicates that a two-fold reduction in corrosion rate is achieved with a 20°F . decrease in HNO_3 temperature. Since the operating temperature may be reduced 60°F . or more by operating the nitric-acid fractionator under vacuum it appears that corrosion rates may be reduced by from 6 to 10 fold. Although the above corrosion data are average surface corrosion rates and do not necessarily represent the change in corrosion which might be expected in weld craters and crevices, the data are sufficiently encouraging to indicate that vacuum fractionation equipment may be designed which is capable of operating for extended periods with little maintenance required. (The most recent reboiler installed in the Mallinckrodt HNO_3 vacuum fractionation unit has operated without maintenance for over a year.)

Alternate Vacuum Fractionation Methods

Several possible methods have been considered for incorporating a vacuum fractionation unit in the Purex Plant. Among the schemes considered are the following:

1. Scheme 1, a single vacuum fractionator capable of producing 60% acid directly from the overhead of the No.2 Purex Concentrator. This unit would be designed to fit in the present Purex fractionator location.
2. Scheme 2, a single vacuum fractionator capable of producing 60% acid directly from the overhead of the No.2 Purex Concentrator. This unit would be designed for installation in a new fractionation area adjacent to the 202-A Building.

GENERAL ELECTRIC
COMPANY

-5-

HW-30600

3. Scheme 3. Sixty per cent acid is produced in two steps. Acid in the overhead from the No 2 Concentrator is absorbed in a bubble-cap tower designed to operate at atmospheric pressure to produce approximately 30% HNO_3 bottoms. The 30% acid is then fed to a fractionation unit which operates under vacuum to produce 60% acid. Both units are to be designed to fit in available space within the 202-A Building.

Calculations made to determine the diameter of the Scheme 1 fractionator required to handle potential future Purex processing capacities (as high as 16 to 25 tons U/day) indicate that the upper section of a conventional bubble-cap tower would be too large (approx. 13 ft. diam. for 16.7 tons U/day) to fit in the available cell space. Other types of fractionation towers (e.g., Turbogrids sieve plate towers) capable of operating at higher throughput rates than conventional bubble-cap tower could conceivably be designed to fit in the cell. Such designs were not considered desirable for inclusion in the plant because of their limited rangeability (stable operation range not greater than a factor of two).

Although it would be possible to design a conventional bubble-cap fractionation unit to be installed in a new fractionation area outside the 202-A Building (Scheme 2) the additional construction cost, design and construction delay, and the inconvenience resulting from a new isolated operating area dictated the choice of an "inside-the-building" scheme.

Discussion of Scheme 3 - Preferred Installation

The schematic flowsheet on Figure 2 indicates the operating conditions which would be employed in the nitric-acid-recovery system for Scheme 3, the two-step absorption-fractionation method of operation. As is indicated on Figure 2 the 0.1 M HNO_3 distillate from the 60% vacuum fractionation unit is routed to the Purex No. 1 Acid Concentrator. This distillate HNO_3 concentration was selected as a design basis for the vacuum unit for the following reasons:

- 1) The volume of acid back-cycled is not great enough to significantly affect the processing capacity of the other concentration units. Material balance calculations around the concentration and fractionation facilities indicate the following flow variations with increased HNO_3 concentration in the vacuum fractionator overhead.

60% HNO_3 Vacuum Fractionator Overhead HNO_3 Conc., M	60% HNO_3 Vacuum Fract. Overhead Flow (SAF = 100)	No. 2 Acid Concentrator	
		Overhead Flow	Overhead HNO_3 Conc., M
0.1	126	643	1.93
0.5	133	651	1.93
1.0	148	665	2.05
2.0	186	700	2.23

Note: Feed concentration to the 60% Vacuum Fractionator is assumed 30% HNO_3 for each of the above cases.

GENERAL ELECTRIC
 COMPANY

-6-

HW-30600

- 2) The desired separation in the 60% vacuum fractionation unit may be attained with a reasonable number of bubble-cap trays. As is indicated below, an eleven-tray tower is required. If tray efficiencies are greater than those used in the design calculations, the overhead concentration during actual operation would be lower than the nominal 0.1 M.
- 3) The amount of acid in the 0.1 M overhead is small enough to permit discharge to cribs (after pH adjustment) if later plant considerations should indicate that backcycling of the vacuum fractionator overhead to the No. 1 Concentrator should be discontinued.

30% Atmospheric Pressure Absorption Unit

The design for the absorption unit may be quite similar to that employed in the upper portion of the fractionator designed for atmospheric pressure operation (H-2-5237). However, since relatively high corrosion rates (i.e., 2 or 3 times rates in upper portion of column) are expected in the lower section of the column which is subjected to condensing 20 to 30% HNO_3 the tower should be lengthened enough to permit inclusion of a 5-ft packed section. In passing through this packed section the nitric acid vapors will be de-superheated and reduced in HNO_3 concentration (from 30 to approximately 10%) thereby lengthening the expected life of the bubble-caps in the atmospheric absorption tower. The packing used should be thick-walled so that appreciable corrosion may occur before the efficiency of the packed section is reduced. The 2 in. long by 2 in. diameter Raschig rings should be fabricated from stainless steel (e.g., thick-walled pipe) or other HNO_3 resistant material. Ceramic-type packing is not considered desirable because of spalling and cracking.

A liquid distributor should be included in the tower just above the packed section.

60% Vacuum Fractionation Unit

Tray Requirements. As is indicated on Figure 2, the vacuum fractionation unit should be designed to produce 60% HNO_3 bottoms and 0.1 M HNO_3 overhead from the 30% liquid feed supplied by the absorber unit. An operating diagram was developed to determine the reflux conditions to be employed in the fractionator and the number of theoretical plates required above and below the feed point to achieve the desired separation. Using the reduced pressure HNO_3 - H_2O equilibrium data from Perry and the Ponchon-Savarit calculation method it is determined that 1-1/2 and 2-1/2 theoretical plates are required in the top and bottom of the vacuum fractionator, respectively, when the column is operated at 50 mm. absolute pressure (150 mm. at the bottom of the tower). Assuming a 30% overall tray efficiency in the top section and approximately 50% in the bottom section, 5 and 6 actual bubble-cap trays are recommended for the top and bottom sections, respectively. The liquid-to-vapor reflux ratio (L/V) in the top section is approximately 0.25.

GENERAL ELECTRIC
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-7-

HW-30500

Tower Diameter. Order-of-magnitude calculations indicate that a 6 to 8 ft. diameter tower would be capable of processing HNO_3 at 16.7 tons U/day plant rates at the above processing conditions. Superficial column velocity at the top of a 7 ft. diam. column (50 mm. Hg pressure) at an 8.33 ton U/day processing rate would be approximately 9 ft./sec.

Reboiler. Although the temperature of the boiling 60% HNO_3 will be reduced considerably by operating under vacuum (reduced from approx. 250°F. boiling point at 760 mm. pressure to approx. 175°F. at 150 mm.), the skin temperature of the reboiler tubes will be somewhat higher than that of the boiling liquid and high corrosion rates may be obtained. The skin temperature is dependent upon the steam temperature. This is in turn dependent upon the design of the reboiler heat-transfer surface and the boil-up requirement of the unit. If the reboiler is designed so that 20 lb./sq.in. gauge steam may be used, the skin temperature would be approximately 260°F. Although reboiler tubes may be thick walled and optimum welding techniques should be employed in fabrication, repair or replacement of the reboiler heating element may be expected every 1 to 3 years. Consequently, it would be desirable to design the reboiler tube bundle or bundles in the vacuum fractionator for replacement by remote means. If sufficient space is available in the canyon, replaceable tube bundles similar to those designed for the Purex Concentrators, would be desirable.

GENERAL ELECTRIC
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-8-

HW-30600

FIGURE 1

NITRIC ACID CORROSION OF STAINLESS STEEL
(DATA FROM IND & ENG CHEM. NOV. 1952)

Figure 2

NITRIC ACID BALANCE AROUND THE PUREX CONCENTRATION AND FRACTIONATION FACILITIES (30 to 60% HNO_3 Vacuum Fractionator)