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TECHNOLOGY—FEED MATERIALS

Date: November 13, 1951

SUBJECT: Denitration of Uranyl Nitrate
QUARTERLY REPORT for Period 8/10-11/10/5

To: F. L. Steahly

From: V. J. Reilly

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To: F. L. Steahly

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Chemical Technology Division
Laboratory Section

From: V. J. Reilly

Problem No. TDSI-

Part

Q U A R T E R L Y R E P O R T

Title: Denitration of Uranyl Nitrate

Work by: V. J. Reilly and E. M. Sampson

Secret Notebook No. 1079

Introduction

In order to simplify equipment it was found desirable to concentrate uranyl nitrate solution prior to denitration by removal of water only. Since this stream contains small amounts of nitric acid, fractionation of the vapors is indicated. This work was initiated to determine how far the concentration may be carried by removal of water only, that is, at what point the vapors have the nitric acid-water azeotrope composition. Short of this concentration, the boiling and freezing points, as well as vapor composition, were desired to determine a practical limit for this evaporation.

Summary

The composition during IEU boildown where vapors of the azeotropic composition come off is at 85% UN and 4.1% HNO_3 .

The freezing and boiling points for compositions near the end of the boil-down have been determined. The freezing point rises much more rapidly than

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the boiling point; at 85% UN and 4.1% HNO_3 , the solution is metastable, as after cooling to seed, reheating to the boiling point did not redissolve the solid phase.

Vapor-liquid equilibria have been obtained for compositions near the end of the boildown. From these data the number of theoretical plates for removal of water has been obtained.

Discussion:

The goal of the pre-concentration was tentatively placed at 78.9% UN ($\text{UO}_3(\text{NO}_3)_2$). We have found that, from the standpoint of freezing point and vapor composition, that this concentration can be attained and probably exceeded. The limit for removal of water only from this system, is ultimately at the point where vapors of the azeotropic composition come off of the pot. We found the liquid composition at this point to be 85% UN and 4.1% HNO_3 . This liquid, however, was metastable, as after cooling down to crystallize and reheating to the boiling point, two phases (crystal and solution) co-existed. Therefore, a practical limit in the concentration step appeared to depend on the freezing point of the solution. Freezing points and boiling points were determined for a series of compositions obtained by distilling water only from a UN- HNO_3 solution. These are shown in Table 1. There was no difficulty due to return of liquid from the column onto the (hotter) pot solution. The condensate appeared to mix in, rather than flash distil on

UO₃(NO₃)₂

The effect of phosphate on foaming in the pot was investigated. A solution containing 79% UN and roughly 4% HNO_3 was refluxed with 100, 200, and 400 ppm of phosphorus, added as Na_2HPO_4 . No effect on foaming was noted. At the 400 ppm level, a precipitate was present. Inorganic orthophosphate was used for additive, as it is believed that the phosphate present will be due to hydrolysis of TBP, the end-product of which is orthophosphoric acid. The intermediates are believed to hydrolyze faster than does TBP.

In order to determine the number of theoretical plates required to effect the removal of water only from this system, it was necessary to determine the vapor composition in equilibrium with the uranyl nitrate solution. For this purpose a modified Othmer equilibrium still was used. A nichrome heating ribbon was used to prevent condensation of the vapors between the liquid in the pot and the condenser. The results of these experiments are given in Table II. Also indicated are the number of theoretical plates required at various vapor compositions, reflux ratios assuming the product composition to be .001 wt. % HNO_3 (0.000286 mol % and 0.000213 thole %).

In these experiments only the composition expected near the end of the preconcentration was studied, as this will give the highest HNO_3 concentration, and accordingly will indicate the maximum number of theoretical plates required for the batch distillation.

The McCabe-Thiele method was employed to graphically determine the number of theoretical plates. In so doing the difference in molar heats of vaporization ($\text{H}_2\text{O}:\text{L} = 9720 \text{ PCU/lb. mol.}$ and $\text{HNO}_3:\text{L} = 7250 \text{ PCU/lb. mol.}$) were accounted for by using a thermal mol basis (1 Thole = 10000 PCU). As a result, this graphical method is a good approximation.

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Table I

Freezing and Boiling Temperatures for Concentrated UN Solutions

Liquid Composition				Freezing Point °C	Boiling Point °C
% UN		% HNO3			
Calc. ¹	Det'd.	Calc. ²	Det'd. ³		
77.0	80.4	4.40	3.80	83	129
78.4	79.5		5.18	95	130.5
79.8	80.8		5.23	106	134.5
81.0	82.2		4.47	113	137.5
82.3	83.5		4.32	122	140

- Note: 1 % UN calculated from % UN in UNH started with (anal. of batch) and amounts of water and sample removed each time. It may be noted that the calculated value is uniformly low by about 1%, except in case of 1st sample, where analysis is obviously out of line. The batch anal. undoubtedly is incorrect; the correct % UN in the first line is more nearly 78%.
- 2 % HNO₃ calculated from the amounts of materials charged to pot.
- 3 The values of % HNO₃ determined are believed to vary due to the variation in the composition of the hold-up in the column.

Table II

Vapor-Liquid Equilibrium in the UN-HNO₃-H₂O System

Composition of Sol'n. Wt. Percent		Composition of Vapor Percent HNO ₃			Minimum Reflux Ratio	No. of Theoretical plates at Reflux (Ratio(reflux:product))	
UN	HNO ₃	Wt.	Mole	Thole*		One	Two
80.2	4.0	23.7	8.22	6.19	0.57	4.9	3.9
74.4	7.6	35.4	13.6	10.5	1.03	∞	4.0
76.6	5.9	27.7	9.85	7.53	0.70	7.9	3.9
80.3	2.0	24.3	8.36	6.38	0.59	4.9	3.9
80.2	2.5	22.3	7.54	5.74	0.53	4.9	3.9
85.0**	4.1	68.0	37.8	31.6			

** This result obtained by fractionating until fairly concentrated nitric acid refluxed at top of column (under total reflux).

* Thole = Thermal Mole = 10000 PCU = 18000 BTU

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