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NO_x REACTIONS AND KINETICS

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NO_x REACTIONS AND KINETICS

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NO_x REACTIONS AND KINETICS

INTRODUCTION

Partial neutralization of the Hanford waste liquors requires injection of nitric acid into the recirculation loop of the evaporator-crystallizer. Process testing of partial neutralization, as a viable means of further residual liquor volume reduction, indicated a definite need for an understanding of NO_x chemistry, since NO_x was observed in the vessel vent piping. By developing an understanding of the kinetics and reaction mechanisms of NO_x, potential corrosion difficulties in the carbon steel off-gas lines can be reduced or eliminated before operation of the partial neutralization prototype begins.

The purpose of this report is to present the pertinent reactions dealing with NO_x; thermodynamic, equilibrium and kinetic calculations with the postulated reactions; and interpretation and application of data to the 242-S evaporator-crystallizer system. This report also defines the need for experiments to determine the specific liquid phase reaction mechanisms.

SUMMARY

The evaporator-crystallizer system was divided into liquid and gas phase reaction zones. The dimers and alternate forms of NO₂ and NO were neglected as reaction forms, because they exist in low concentrations and rapidly reach equilibrium with NO and NO₂.

The NO_x content in the concentrated acid is limited by purchase specifications to 300 ppm. Solubility and thermodynamic calculations identified NO₂ as the primary NO_x form in the concentrated acid. Dilution of the acid before injection into the recirculation loop chemically converts a large part of the dissolved NO₂ to NO in a 3:1 stoichiometric considerations dictate that the NO will flow into the gas phase system.

Reactions of any NO₂ remaining in the diluted acid with nitrate and caustic in the slurry further reduces the probability of NO₂ evolution into the gas phase. Of the five possible acid-slurry reactions, the law of mass action implies that a 1:3 yield of NO per mole of NO₂ is expected in the system.

From NO chemistry and the NO₂ acid-slurry reaction, NO will be essentially the only form of NO_x flowing into the gas phase reaction zone.

The actual gas phase formation of HNO_3 , which can take place above the gas phase dew point, is a two step process in which the oxidation of NO to NO_2 is rate determining. Less than 0.1 percent conversion of NO to NO_2 occurs before EC-3. An approximate NO oxidation of one-sixth is noted between EC-3 and the 200 CFM vessel vent air bleed.

REACTIONS

The possible NO_x reactions in the liquid and vapor phases differ; and the product(s) of the liquid phase reaction are able to flow into the off-gas line to become the reactants in the gas phase. The dimers or alternate forms of NO and NO_2 , such as N_2O_4 , N_2O_3 and N_2O_5 , were neglected, since these compounds represent only a small fraction of the total oxides at room temperature and rapidly reach equilibrium with NO and NO_2 (reference 7).

Liquid Phase

The zone between the acid storage tank and the vapor liquor interface in the main evaporator-crystallizer body constitutes the reactor volume for the liquid phase reactions of NO_x . Since the slurry is continuously exposed to extremely low pressures, NO_x cannot remain dissolved in solution. Therefore, any NO_x in the liquid phase could only have come from the injected acid or side reactions between the nitric acid and some component of the feed or slurry.

The concentrated acid (12M, 57 percent by weight) has a purchase specification of 300 ppm NO_x^* . The relative compositions of NO and NO_2 in the 300 ppm NO_x determines the liquid phase reactants in NO_x production. The solubility of NO in HNO_3 was assumed to be no greater than the solubility of NO in H_2O (0.05 ppm). The basis for this assumption is observation of the relatively few liquid substances in which NO can be dissolved, and the inability to find a thermodynamically acceptable reaction between any form of NO and HNO_3 . NO_2 is readily soluble in both HNO_3 and H_2O , and the entering 300 ppm NO_x can reasonably be assumed to be essentially NO_2 .

Dilution of the 12M acid has been proposed as a means of controlling the side reactions between nitric acid and sodium nitrite. Upon dilution, a chemical reaction occurs in which the NO_2 converts to NO and nitric acid.

- * While 300 ppm is only 0.03 weight percent, if no NO_x conversion occurs in the evaporator system, an NO_x concentration of 45,000 ppm exiting EC-3 results. The calculated concentration of 45,000 ppm NO_x is considered over 45 times too great for problem free operation in the vessel vent system.

Concentrated acid dilution occurs prior to injection into the evaporator-crystallizer recirculation loop, therefore, 1:3 stoichiometric ratio of NO yield to NO₂ in the concentrated acid should be observed in the diluted acid. It should be pointed out that the acid injected during process testing had been sparged after dilution and before injection into the recirculation loop. No provisions have been made for sparging or NO_x removal during prototype operation. Consequently, the prototype NO_x concentrations should be expected to be higher than those reported in the process tests. The incoming NO cannot react with the caustic (NaOH) or water in the slurry because of solubility and thermodynamic information previously cited. NO will, therefore, pass from the liquid phase to gas phase unimpeded.

NO₂ has a considerable possibility for reaction within the caustic slurry. The following four reactions describe alternate reaction paths and are presented with the reference number and the standard Gibb's free energy. Please note that all of the reacting materials below are in the liquid phase, except for the NO and NO₂ dissolved in solution.

Standard free energy values were found in reference 4. The stoichiometric yield of NO per mole of initial NO₂ ranges from 0 for reaction 4 to 1 for reaction 5. Reactions 2 and 3 have a 1:3 ratio. The free energy change indicates reactions 3 and 4 will occur most readily. Laboratory study applying similar operating conditions is required to determine the actual NO yield.

The law of mass action is utilized to predict which of the four liquid phase NO_x reactions would most likely occur. This statement implies that the concentrations of products or reactants tend to drive a reaction in the forward or reverse direction. The concentrations of some of the pertinent compounds in the slurry line are:

<u>Component</u>	<u>Concentration (moles per liter)</u>
H ₂ O	~ 30
NO ₂ ⁻	~ 3
OH ⁻	~ 3
NO ₃ ⁻	~ 3

The relatively high water concentration will tend to drive reactions 3 and 4 in the reverse direction for HNO_3 generation, and reaction 2 will have the greatest nitric acid formation driving force. The expected quantitative yield of NO per NO_2 injected in the liquid system is 1:3. Laboratory study can confirm this supposition.

The neutralization reaction between nitric acid and sodium nitrite can potentially produce NO_2 and NO. These reactions as described in reference 1 (p. 14) are:

At equilibrium, the neutralization reactions greatly favor product formation. However, reaction 7 is spontaneous only in an acidic medium. The processing slurry is definitely caustic. Therefore, NO and NO_2 will not be evolved into the gas phase via the neutralization reaction, except for that region near the point of acid injection where the acid and the caustic-nitrite slurry mix.

The NO_x in the gas stream leaving the evaporator body will essentially consist of NO. Both the NO injected with the diluted acid and the NO evolved from liquid phase conversion of NO_2 to NO will pass into the gas phase system.

Gas Phase

The system from the vapor-liquor interface to the exhaust stack composes the reactor vessel for the gaseous formation of nitric acid. A wide range in partial pressures and relative compositions exists within the gas system since the system pressure and temperature varies between 40-760 torr and 130°-70°F respectively.

An entirely gas phase reaction between NO_2 and water vapor has been found to appreciably contribute to the formation of nitric acid vapor. A mist existing below the gas phase dew point, containing upwards of 40 percent HNO_3 is definitely present in any system in which chemical or physical disturbances occur. (reference 2). This nitric acid mist is generated because the vapor pressure of nitric acid is very much lower than the vapor pressure of water.

As was discussed in the Liquid Phase section, NO has by far the greatest probability of passing through the vapor-liquor interface and entering the gas phase. NO does not react directly to form HNO_3 under the conditions in the gas phase. Therefore, NO must first form NO_2 before HNO_3 generation occurs. The chemical reactions describing NO_2 and HNO_3 formation are given below with their standard Gibb's free energy and reference number. All of the reactants and products are in the gas (or vapor) phase.

The rate of NO oxidation is characterized as being slow, continuing until completion is reached. On the other hand, kinetic data indicates that the gas phase formation of nitric acid vapor (Equation 9) is quite rapid, having an equilibrium half time of much less than a minute. NO oxidation must be the rate determining or limiting step in HNO_3 production. An analysis of NO oxidation kinetics was undertaken using the equations presented in reference 6 (See Appendix). Approximately one-sixth of the initial NO was converted to NO_2 between the vapor-liquor interface and the 200 CFM air bleed prior to the deentrainment pad (DU-C-1).

The low pressures (near full vacuum) practically rule out the possibility of NO oxidation in either the primary or inter-condenser. The NO that entered the gas phase system flows without changing form until O_2 and NO partial pressures are great enough for NO oxidation to occur. The after condenser (EC-3) is the point that NO oxidation is first initiated. (reference 6)

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Date: August 26, 1976
To: J. O. Honeyman
From: K. L. Monohan *K.L. Monohan*
Subject: RESIDENCE TIME, PARTIAL PRESSURE AND CONVERSION
STUDY OF THE 242-S EVAPORATOR-CRYSTALLIZER OFF-
GASES DURING PARTIAL NEUTRALIZATION

- References:
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Room Section"
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INTRODUCTION

The partial neutralization process tests demonstrated a need for an in-depth kinetic study of NO_x generation, in that varying concentrations of NO_x were observed and monitored in the 242-S Vessel Vent System while testing.

During process testing, leaks were detected within several tubes in the EC-3 condenser. The failure appears to have occurred prior to the test, but it does raise the question as to the corrosion potential in the remaining condensers. A study of residence times, partial pressure of NO_x and oxygen, and expected conversions of NO_x to nitric acid was undertaken to define those pieces of process equipment which have the highest likelihood of nitric acid corrosion.

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Residence Times

The residence time study was based on flow rates given in the Vacuum Evaporator-Crystallizer Flowsheet (reference 1). The flowsheet specified the condensation rate in EC-1 as being 40 GPM, an air inleakage of 2 CFM, and a 2 CFM gas flow rate at the EC-3 output. The assumptions of a saturated vapor entering EC-1, exiting temperatures at the EC-1 and EC-2 condensers of 86°F, and an estimated pressure of 76 mm Hg at the steam jet between the primary and inter-condensers are made. Calculations proceeded from the nitric acid injection point and continued to the top of the exhaust stack.

The total residence time in the liquid phase, i.e., the injection point to the vapor-liquor interface in the evaporator body, was found to be 4.335 seconds with equal percentages of the time being spent in the recirculation loop pipe and the reboiler body.

Of more importance to the corrosion susceptible piping in the condensers and venting system, is the residence time in the vapor phase - from the 42" vapor line to the exhaust stack. The total residence time through the off-gas lines amounted to 124 seconds, approximately 77 percent of the total residence time being spent in the vessel vent line between EC-3 and the deentrainment pad (DU-C-1). It should be noted that the residence times through EC-1, EC-2 and EC-3 are two percent, five percent and nine percent of the total time respectively. Figure 1 is a plot of the residence time as a function of position in the system.

After the liquid and gas phase residence times were computed, an investigation was made to determine the effect 1) opening of the air bleed (DOV-EC1-2) to allow entry of 20 CFM of air and 2) relocation of the 200 CFM air bleed from near DU-C-1 to the EC-3 output would have on residence times. It should be noted that the original calculations specified DOV-EC1-2 as being closed.

The calculations based on a 20 CFM air bleed (DOV-EC1-2 being ~ 10% open) yield a reduction in gas phase residence time from 124 seconds to 16 seconds. An approximate ten fold reduction in the time spent in-line between EC-3 and the 275 CFM air bleed was observed - 78.3 seconds for the 2 CFM flow rate versus 7.12 seconds for the 20 CFM bleed.

The relocation of the 200 CFM air bleed in-line immediately after the EC-3 condenser reduces the gas phase residence time by a factor of 5. The majority of the 24.5 second total residence time has also shifted from the vessel vent line to the EC-3 condenser system with 45 percent or 11.3 seconds being spent in that system. Table I lists the three different residence time studies for comparative purposes.

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Partial Pressures

From the experience gained during process testing of the partial neutralization process, calculations of NO_x , H_2O vapor, O_2 and N_2 partial pressures were based on a NO_x concentration of 1000 ppm (mole percent) exiting the after condenser (EC-3). The assumptions of an ideal gas and a gas operating temperature of 77°F exiting EC-3 were made.

Again applying these conditions - a 20 CFM valve opening and a 200 CFM relocated air bleed, partial pressures can now be calculated and compared to those partial pressures in the current evaporator system - 2 CFM exiting EC-3. The 2 CFM values, as reported above, were assumed to contain 1000 ppm NO_x exiting EC-3. This same mass flow rate of NO_x was used as a common basis for comparison of the differing air bleeds. Negligible differences in O_2 , N_2 , and H_2O vapor partial pressures were noted between the three different conditions. Table II lists NO_x partial pressures for the different conditions.

A slight lowering, 20 percent on the average, of the NO_x partial pressure is evident in the off-gas system for the 20 CFM air bleed, except in EC-2, EC-3, and the vessel vent line. A 4-, 5-, and 10-fold decrease in NO_x partial pressure was calculated in those lines respectively.

The substitute 200 CFM air bleed yields a substantial lowering of the NO_x concentration in the line from EC-3 to DU-C-1. A reduction of 100-fold is observed in-line. Refer to Table II for NO_x partial pressures at 2 CFM, 22 CFM, and 202 CFM exiting EC-3.

Percent Conversions

The gas phase formation of nitric acid has been documented to consist of 1) the oxidation of NO to NO_2 and 2) reaction of the formed NO_2 with water vapor to yield gaseous HNO_3 , which is expected to condense promptly to form a mist of dilute nitric acid. The chemical reactions are:

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Reaction 1 must be substantially underway before any HNO_3 can be formed. Kinetic studies of HNO_3 formation have found reaction 1 to be the rate determining or limiting step in HNO_3 manufacture (reference 2). The operating conditions of the evaporator system have been postulated to allow only NO to exit the evaporator body with the other non-condensable gases. Therefore, kinetic analysis of equation (1) should yield valuable conversion information which will help to define those process areas containing appreciable nitric acid. If the rate equation, defined by reaction 1, is integrated with respect to time, assuming the O_2 concentration constant, a relationship between residence time, concentration, and conversion results:

$$t = \frac{1 - F_R}{F_R} \left[\frac{1}{[\text{NO}]_0} \times \frac{1}{K[\text{O}_2]} \right] \quad (3)$$

where t = residence time
 F_R = fraction of NO remaining
 $[\text{NO}]_0$ = initial NO concentration
 $[\text{O}_2]$ = oxygen concentration
 K = oxidation rate constant ($\frac{1^2}{\text{mol}^2 \text{ sec}}$)

A K value of $7.5 \times 10^3 \text{ l}^2 / \text{mol}^2 \text{ sec}$ at 77°F was used in calculations.

Substitution of the residence times in the vessel vent line, NO concentration, and O_2 concentration for the three different air bleed-ins produces three divergent conversions. Using the flow sheet conditions of 2 CFM air in-leakage and 2 CFM at EC-3, the percent conversion was found to be 16 percent. Values for the 20 CFM value air bleed and the 200 CFM reoriented air bleed were .18 percent and .002 percent respectively.

CONCLUSIONS

Three major conclusions can be drawn from the residence time and partial pressure study.

First, the carbon steel piping and vent lines, primary and inter-condensers are likely safe from nitric acid corrosion. This conclusion was indicated by, 1) the residence time throughout the primary and inter-condensers and related piping being only 6.9 percent of the total residence time, and 2) the concentrations (or partial pressures) of O_2 and NO_x are so low that no appreciable amounts of HNO_3 could be formed and 3) the percent conversion of NO to NO_2 is only .00018 percent in EC-2.

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Secondly, the vessel vent line from EC-3 to the current 200 CFM air bleed has the greatest potential for nitric acid corrosion. The residence time as well as the NO_x and O_2 partial pressures show a definite peak while in the vent piping. Therefore, the possibility of forming HNO_3 vapor is higher in this vent piping than at any other point in the system.

Lastly, for the 20 CFM and 200 CFM cases, the shorter residence times and lower NO_x partial pressures result in a significantly lower conversion of NO_x to nitric acid indicating the advantages of decreased residence time and NO_x concentration. Relocation of the 200 CFM air bleed from the vessel vent line to the EC-3 outlet produces a 5-fold reduction in residence time, a 100-fold diminishment in NO_x concentration, and only a .002 percent conversion of NO to NO_2 . Pressure drop calculations further establish the advisability of decreased residence time. Pressure drops were computed to be .0001" H_2O for 2 CFM at EC-3, .0135" H_2O for 22 CFM at EC-3, and 1.14" H_2O for 202 CFM at EC-3. Of the three conditions studied, the 200 CFM relocated air bleed realizes the goal of minimal nitric acid formation the best.

KLM:bac

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FIGURE 1
RESIDENCE TIMES

FIGURE 2
PRESSURE TRAVERSE

TABLE I

RESIDENCE TIMES: GAS PHASE (SECONDS)

Position	Flow Rate		
	2 CFM	22 CFM	202 CFM
Evaporator - EC-1	.14	.14	.14
EC-1	2.24	2.24	2.24
EC-1 - jet ₁	.03	.03	.03
Jet ₁ - EC-2	.19	.04	.19
EC-2	5.7	.65	5.7
EC-2 - Jet ₂	.02	.02	.02
Jet ₂ - EC-3	.26	.19	.26
EC-3	11.3	1.07	11.3
EC-3 - Vessel Vent Air Bleed	78.3	7.12	.775
Vessel Vent Air Bleed - Exhauster	7.2	5.0	5.5
Exhauster - Stack	1.7	1.7	1.7

TABLE II

PARTIAL PRESSURES (mm Hg)

Position	FLOW RATE		
	2 CFM	22 CFM	202 CFM
Evaporator - EC-1	1.1×10^{-5}	1.1×10^{-5}	1.1×10^{-5}
EC-1	1.5×10^{-4}	1.5×10^{-4}	1.5×10^{-4}
EC-1 - Jet ₁	7.9×10^{-4}	6.3×10^{-4}	7.9×10^{-4}
Jet ₁ - EC-2	5.0×10^{-4}	4.7×10^{-4}	5.0×10^{-4}
EC-2	1.1×10^{-2}	2.3×10^{-3}	1.1×10^{-2}
EC-2 - Jet ₂	5×10^{-2}	6.55×10^{-3}	5×10^{-2}
Jet ₂ - EC-3	6.6×10^{-3}	6.1×10^{-3}	6.6×10^{-3}
EC-3	1.6×10^{-1}	2.6×10^{-2}	1.6×10^{-1}
EC-3 - Vessel Vent Air Bleed	7.6×10^{-1}	6.89×10^{-2}	7.52×10^{-3}
Vessel Vent - Exhauster Air Bleed	7.5×10^{-3}	5.12×10^{-3}	7.5×10^{-3}
Exhauster - Stack	3.8×10^{-3}	3.8×10^{-3}	3.8×10^{-4}