NITROGEN TETROXIDE SCRUBBER DATA ANALYSIS

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ABSTRACT

A major difficulty in the analysis of scrubber data is that of separating the physical effects, such as mass transfer, from the physico-chemical effects, such as reaction rates. This is especially true for the absorbtion of nitrogen tetroxide in the various liquids that were tested in the NASA-Kennedy Space Center Hypergolic Toxic Vapor Scrubber Program. A fruitful approach to correlating the data for outlet concentrations was to treat the overall absorbtion as a pseudo first-order absorbtion equation. This approach provided a method for normalizing the data to constant inlet concentration, constant sump liquor condition, and constant scrubbing time, and permitted evaluation of the test and fluid parameters that affected both absorbtion rate and scrubbing time. The analysis indicated that scrubber performance may be improved by optimizing liquor concentrations and liquor flowrate distributions.

1.0 INTRODUCTION

The absorbtion of gases in liquids with which they react can be extremely complex with regard to the chemical reactions in the liquid. This is especially true for the absorbtion of nitrogen tetroxide in the various liquids that we tested (References 1 and 2).

A schematic diagram of the scrubber is shown in Figure 1. Nitrogen tetroxide vapor mixed with nitrogen gas enters the inlet vent on the right. Two modes of scrubbing were tested.

The operative mode is counter-flow scrubbing of the vapor with circulating liquid in packed towers. The inoperative mode scrubbing is vapor bubbling through a liquid.

In the operative mode, the gas-vapor mixture sequentially enters the bottom of the towers and flows out the top, finally exiting from tower 4 outlet vent. During this mode of operation, liquor from the storage tank is pumped to the top of each tower to wet the packing (ceramic saddles); the liquor then drains back into the storage tank.

In the inoperative mode, the gas-vapor mixture enters the diffuser pipe in the bottom of the storage tank, bubbles up through the liquor to flow through tower 4 and exits from the outlet vent. Liquor is not pumped to wet the towers for inoperative mode scrubbing.

Test data were obtained for nitrogen flow rates of 10, 50, 100, 200 and 400 standard cubic feet per minute. The nitrogen was mixed with nitrogen tetroxide vapors to produce inlet vapor concentrations ranging from hundreds to hundreds of thousands parts per million. Three different sump liquors were tested; sodium hydroxide in water, sodium sulfite in water, and a mixture of sodium hydroxide and sodium sulfite in water. The tests are described in detail in Reference 2.

2.0 ANALYSIS

A fruitful and apparently uncommon approach to correlating the data for outlet concentrations was to treat the overall absorbtion as a pseudo first order absorbtion equation,

$$\frac{dc}{dt} = -kc$$

The integrated form of the pseudo first-order absorbtion equation is

$$\log C_{out} = \log C_{in} - kt$$

where

C_{out} = outlet concentration

C_{in} = inlet concentration

k = average absorbtion rate

t = scrubbing time

If the reaction is truly a first-order reaction, the absorbtion rate k will not vary with species concentrations (Reference 3). If the reaction is not first order, k will vary with concentration of the scrubbed species or of other species. It is also possible for k to vary with the condition of the tower packed bed and with flowrate of the gases through the tower packed bed. This could result from poor wetting of the packed bed, either because of a too low liquid flowrate or because of poor liquid distribution within the packed bed (Reference 4).

Plotting outlet concentrations versus inlet concentrations on log-log graph paper permits evaluation of the test and/or fluid parameters that affect either absorbtion rate k or scrubbing time t. Such a plot provides a method for normalizing the data to constant inlet concentration, constant sump liquor condition or constant scrubbing time. Examples will be given in the data that follows.

The gas concentrations that will be shown in the figures are determined by the wet chemistry method (Reference 2). No estimates of the uncertainty of the measurements were made in this analysis. The individual shaded areas represent a sequential set of runs for which the flow control valve settings were constant. The numbers next to the shaded areas are run numbers as described in the test report (Reference 2). Test data from each of the three sump liquors will be discussed.

2.1 Sodium Hydroxide in Water

Figure 2-1 shows the performance of the N_2O_4 scrubber with sodium hydroxide (NaOH) in water as the sump liquor. Scrubbing performance ranges from good (runs 23, 24 and 25) to poor (all runs near the kt = 0 line). The inoperative data correlate with nitrogen flowrate. The operative data imply poor or marginal tower wetting and/or saturated liquid in the towers.

An example of normalizing the inoperative data to explicitly show the correlation of outlet concentration with nitrogen flowrate is given in Figure 2-2. The data were normalized to an inlet concentration of 10,000 PPM by translating the inoperative data points parallel to lines of constant kt in Figure 2-1. The added scrubbing obtained by wetting tower 4 is also shown.

Figure 2-3 shows the relative contributions of each tower to overall scrubbing. The data were normalized to an inlet concentration of 10,000 PPM. Note the larger amount of scrubbing in tower 1 and the nearly uniform scrubbing contributions of the remaining towers. A possible explanation is that tower 1 scrubs the easily absorbed N_2O_4 while the remaining towers are scrubbing the more difficult NO_2.

Figure 2-4 shows the product of absorbtion rate times scrubbing time for the tower data and the inoperative mode data. Note that tower 1 scrubs twice as well for the nitrogen flowrate of 50 scfm than for the 100 scfm flowrate. This implies that the absorbtion rate is the same for both flowrates since the scrubbing time of the 50 scfm flowrate is twice that of the 100 scfm flowrate. Towers 2, 3 and 4 scrub equally well at both flowrates. The average of absorbtion rate times dwell time for the inoperative mode data were normalized to an inlet concentration of 10,000 PPM and then normalized again to $k \quad t = 1.0$ for a nitrogen flowrate of 50 scfm. Since this is data for gas-vapor diffusion through a given depth of liquid, the product $k \quad t$ may also be proportional to a gas-liquid surface area to volume ratio for diffusion. As the flowrate increases from 10 to 200, the ratio decreases. At higher flowrates, the increased agitation in the liquid may cause the ratio to increase. The added contribution to scrubbing with tower 4 wet is also shown. This increment corresponds to the scrubbing of NO_2 in a single tower for operative mode.

The effect of liquor flowrate to the towers is shown in Figure 2-5. Scrubbing improves with higher liquid flowrate to the towers and with increased dwell time, i.e., lower gas flowrate.

2.2 Sodium Sulfite in Water

Figure 3-1 shows the performance of the N_2O_4 scrubber with sodium sulfite (Na_2SO_3) in water as the sump liquor. These data show outlet concentrations ranging from complete scrubbing (0 PPM) to little scrubbing (outlet concentration nearly equal to inlet concentration). Outlet concentrations of from 0 to 0.1 PPM are shown on Figure 3-1 as 0.1 PPM. The data show the effects of probable poor tower wetting and saturated liquid. Runs 25 through 30 show scrubbing performance for the 25% sodium sulfite liquor as the total amount of N_2O_4 absorbed approaches 600 lbs. Run 31 shows the outlet concentration return to 0 PPM for a fresh sump liquor of 10% sodium sulfite. These data do not permit determination of optimum sump liquor concentrations. Runs 36 and 37 show nearly the same scrubbing performance even though tower 4 was not wetted for run 36. The liquor flowrate through the wetted towers was the same, i.e., total liquor flow for run 36 was 3/4 of the flow for run 37. This shows that tower 4 did not contribute to scrubbing. The lack of scrubbing could be due to an improper distribution of liquor to the towers.

Run 32 demonstrates the dramatic effect of poor tower wetting and/or saturated liquid. The scrubber was set in the operative mode at a nitrogen flowrate of 50 scfm and a nominal inlet concentration of 27,000 PPM. Outlet concentration was 0 PPM. Then the sump liquor pump was shut off. The outlet concentration rose to 30 PPM at 5 minutes, 9,100 PPM at 10 minutes, 10,600 PPM at 15 minutes and 10,900 PPM at 20 minutes. Thus, the low outlet concentrations on the order of 0 PPM are representative of good scrubbing, i.e., well-wetted towers, sufficient dwell time and an unsaturated liquor. The higher outlet concentrations that occurred with the pump off are the result of poor tower wetting and/or saturated liquor.

Figure 3-2 shows the time history of scrubbing for run 32. The data is normalized to an inlet concentration of 10,000 PPM. Note the initial rapid decrease in scrubbing. This indicates that a relatively small change in liquor flowrate could affect scrubbing. The nominal liquor flowrate is 160 GPM.

Figure 3-3 shows the effect of liquor flowrate on scrubbing performance.

2.3 Mixture of Sodium Hydroxide and Sodium Sulfite in Water

Figure 4-1 shows the performance of the N_2O_4 scrubber with water and a mixture of 18% sodium sulfite - 5% sodium hydroxide as the sump liquor. These data show the effects of poorly wetted towers and/or insufficient dwell times for pump-off data, high flowrate data and for runs 10 through 20 with the exception of the low nitrogen flowrate runs 12 and 18. Post test examination revealed that for these runs (10 through 20), ceramic saddles had been conveyed in the sump liquor flow to deposit at the shower heads in the towers which probably caused flow distortion and poorly wetted towers. The data show no effects of sump temperature changes from 83 to 135°F. Since pH was constant and no species concentrations in the sump liquor were measured, the data could not be normalized to show optimum liquor concentration.

Figure 4-2 shows the pump-off data of run 4. Since the degradation in scrubbing performance with time is even more rapid than the previous pump-off data with sodium sulfite alone in the sump liquor, it is expected that the sensitivity of scrubbing performance to liquor flowrate and distribution should also be greater. This is partially confirmed by the impaired spray nozzles of runs 9-20.

Figure 4-3 summarizes the effects of tower wetting and/or saturated liquor. The data do not permit separating the two effects.

3.0 CONCLUSIONS

Analysis of the scrubber test data in terms of a pseudo first-order absorbtion equation provides a powerful method for separating physical effects from physico-chemical effects. Analysis of chemical reactions in terms of a pseudo first-order reaction equation is a common approach in theoretical chemical kinetics but apparently has not been applied previously to the analysis and correlation of absorbtion data.

The wide variations of outlet concentrations for the same nominal run conditions suggests that the tower conditions of wetting and/or liquid saturation are marginal. This is supported by the pump-off data which show outlet concentrations increasing greater than 3 orders of magnitude when the liquid flow was stopped.

The upper limit for the scrubbing capacity of the sodium hydroxide/ sodium sulfite sump liquor was not determined. The reduced performance of the later capacity runs may be due only to impaired liquid distribution in the towers resulting from the ceramic saddles that migrated to the shower heads.

Although this scrubber was designed to reduce outlet concentrations to 150 or less PPM N_2O_4, maximum permissible outlet concentrations will likely be reduced in the future. Optimization of the scrubber will permit more stringent outlet concentations to be met. The optimization of liquor concentrations requires detail species concentration measurements rather than simply pH determinations.

4.0 RECOMMENDATIONS

It is recommended that additional analyses and tests be conducted to extend and/or verify the conclusions of this report. This would develop additional information on the order and sensitivities of the chemical reactions and produce suggestions for optimum operation of the scrubber system such as feedback control of the sump liquor, corrections of liquid and gas flow patterns and distribution schedules, and dwell times. The tests would include the effect of geometry changes on flow patterns and distributions, measurements of performance in regions not covered by present tests, use of feedback control and finally, confirmation of performance predictions when operated in a predicted optimum configuration.

5.0 REFERENCES

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3. Laidler, K.J.: Chemical Kinetics, McGraw-Hill Book Company, Inc., 1950.

4. Danckwerts, P.V.: Gas-Liquid Reactions, McGraw-Hill Book Company, 1970.

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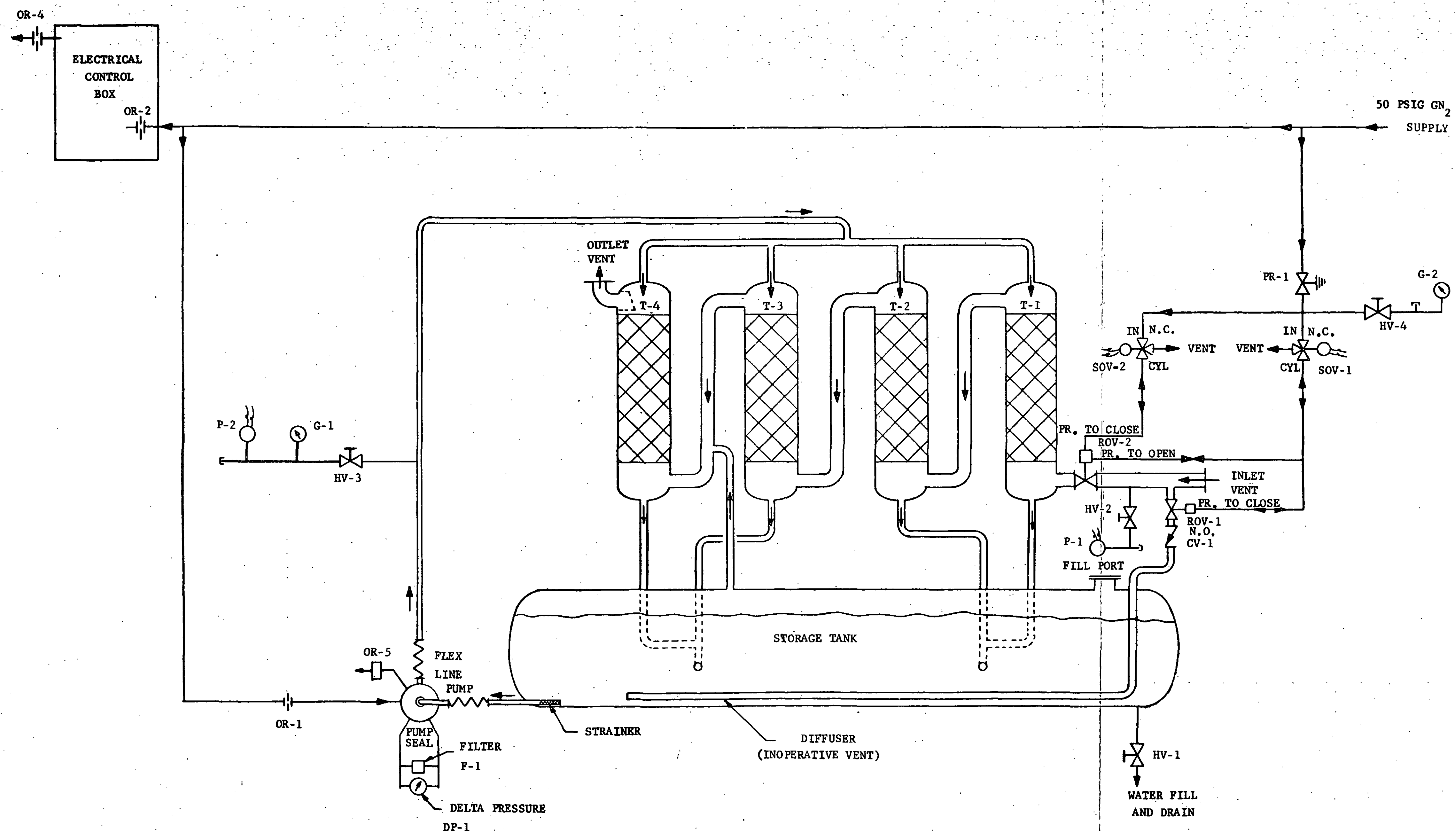


FIGURE 1 SCHEMATIC - OXIDIZER TOXIC VAPOR SCRUBBER

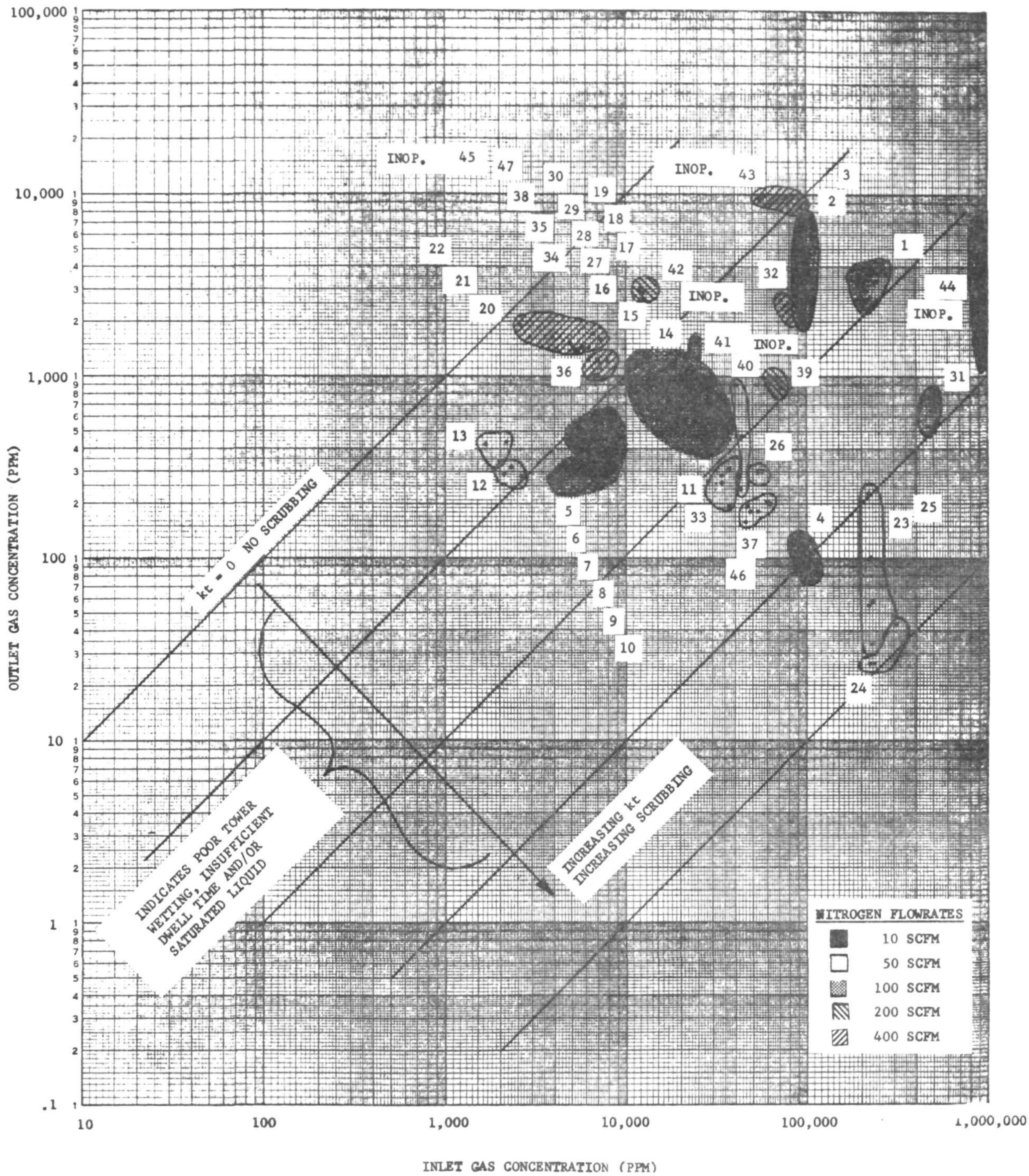


Figure 2-1
N_2O_4 Scrubber with NaOH Sump Solution Inlet Gas Concentration (PPM) vs Outlet Gas Concentration (PPM) for Various Nitrogen Flowrates

FIGURE 2-2: EFFECT OF NITROGEN FLOWRATE ON OUTLET CONCENTRATION

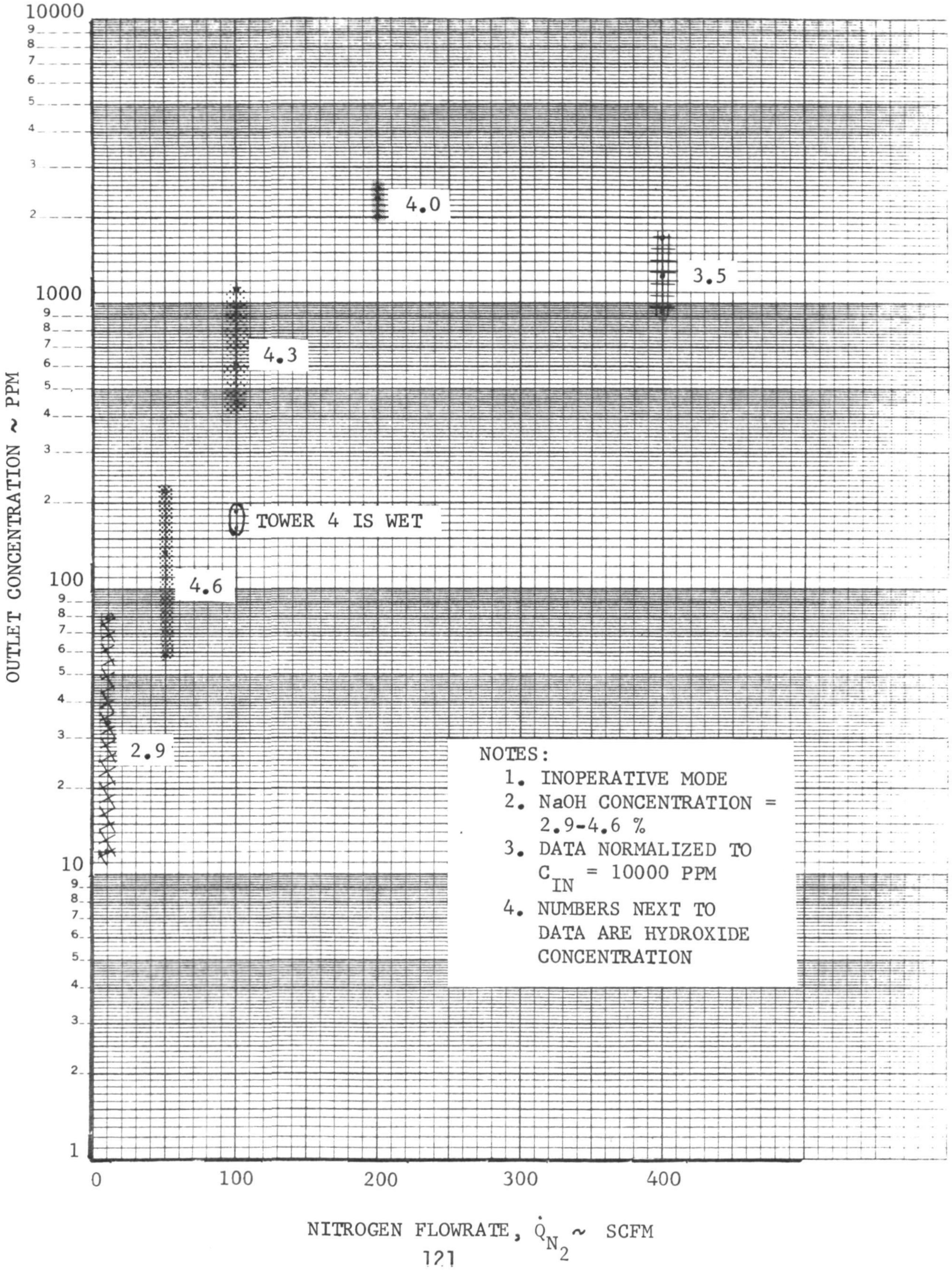


FIGURE 2-3: EFFECT OF NUMBER OF TOWERS ON OUTLET CONCENTRATION

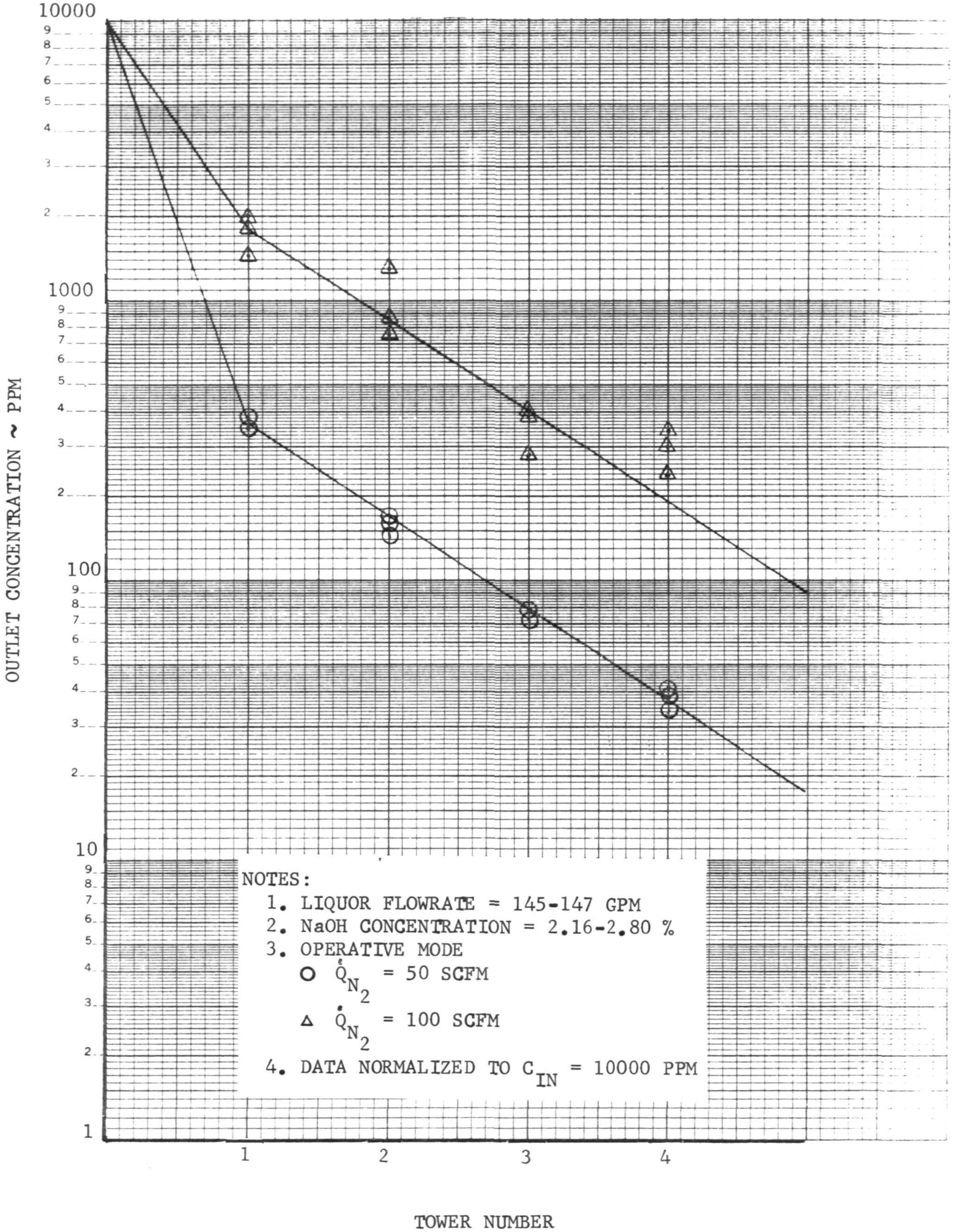
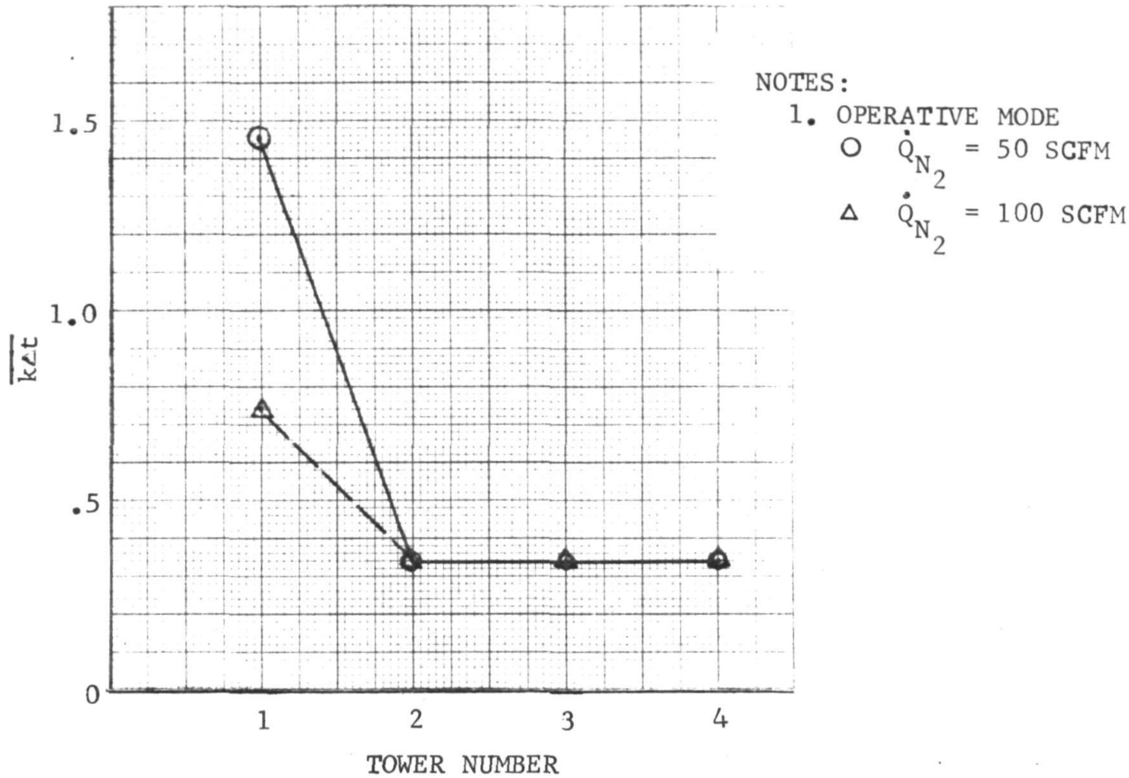


FIGURE 2-4: EFFECT OF NUMBER OF TOWERS AND GAS FLOWRATE ON EFFECTIVE ABSORBTION



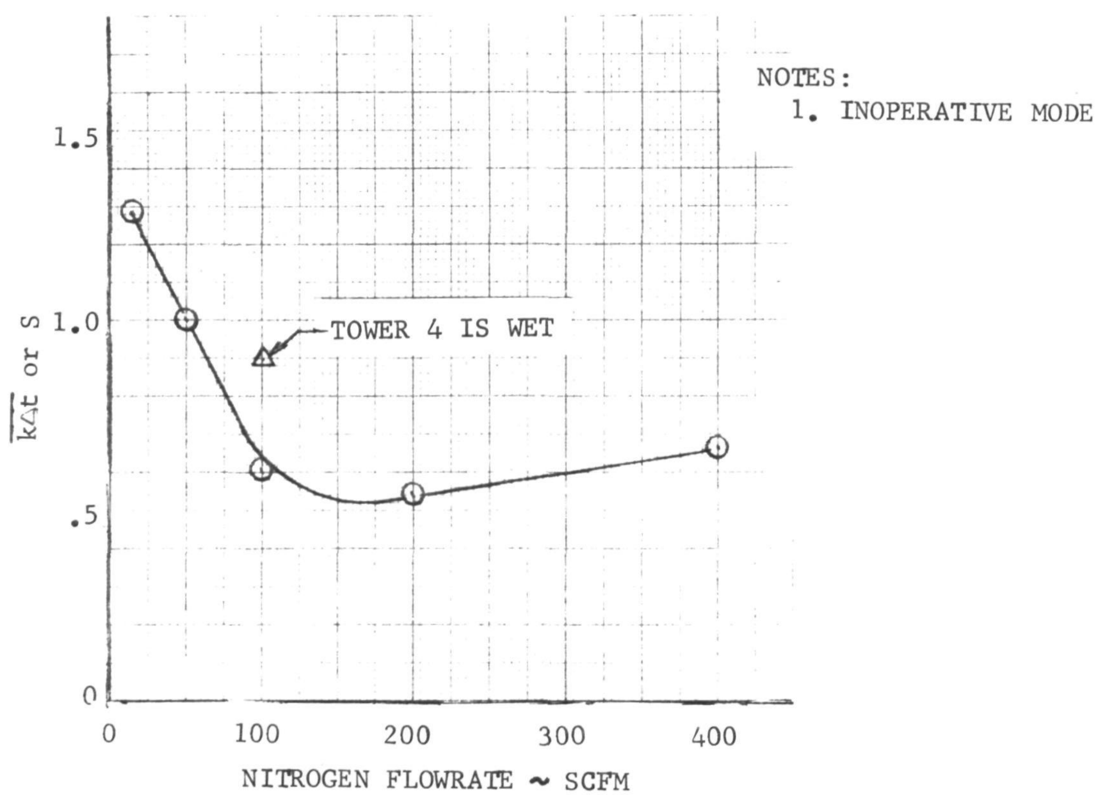
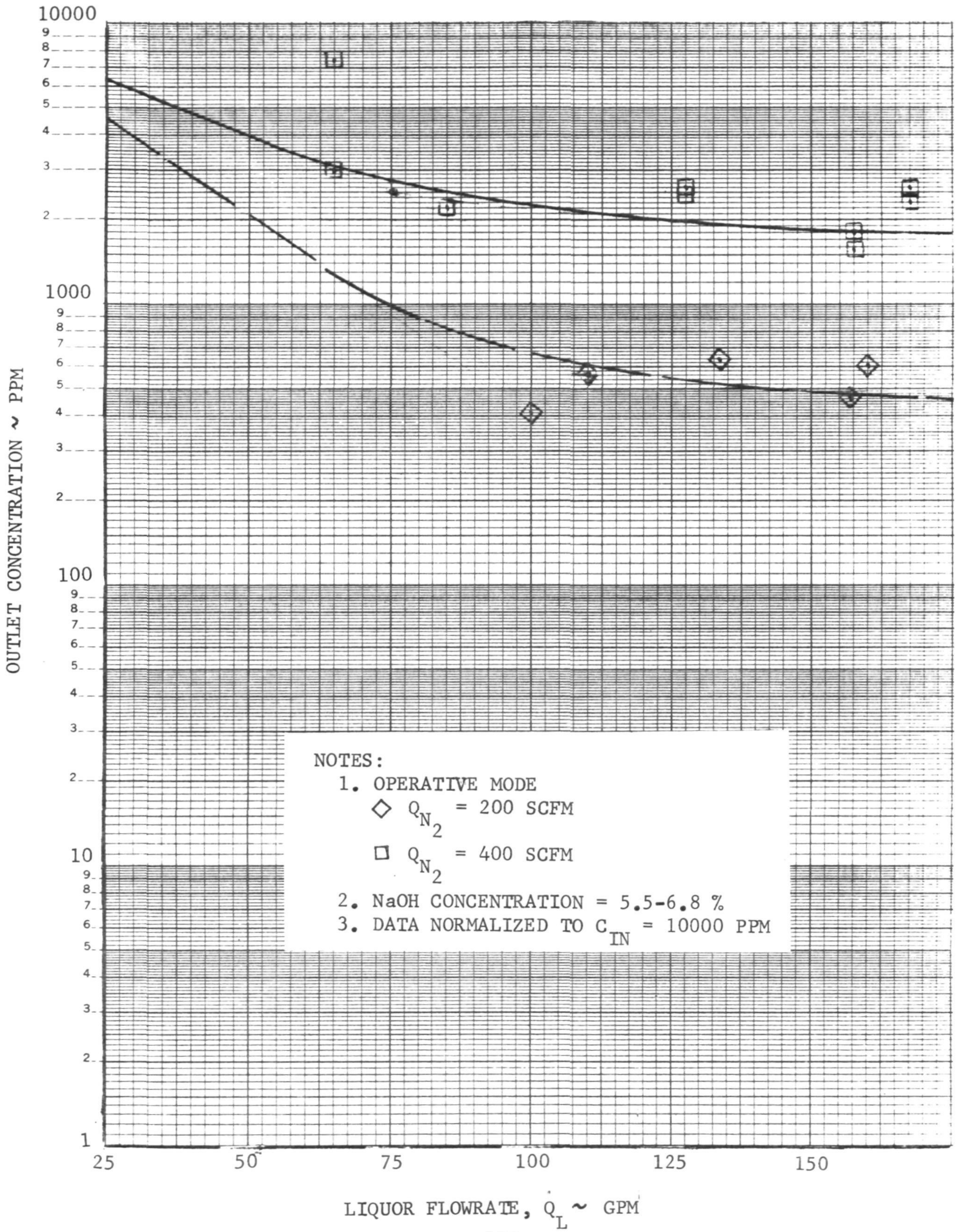


FIGURE 2-5: EFFECT OF LIQUOR FLOWRATE ON OUTLET CONCENTRATION



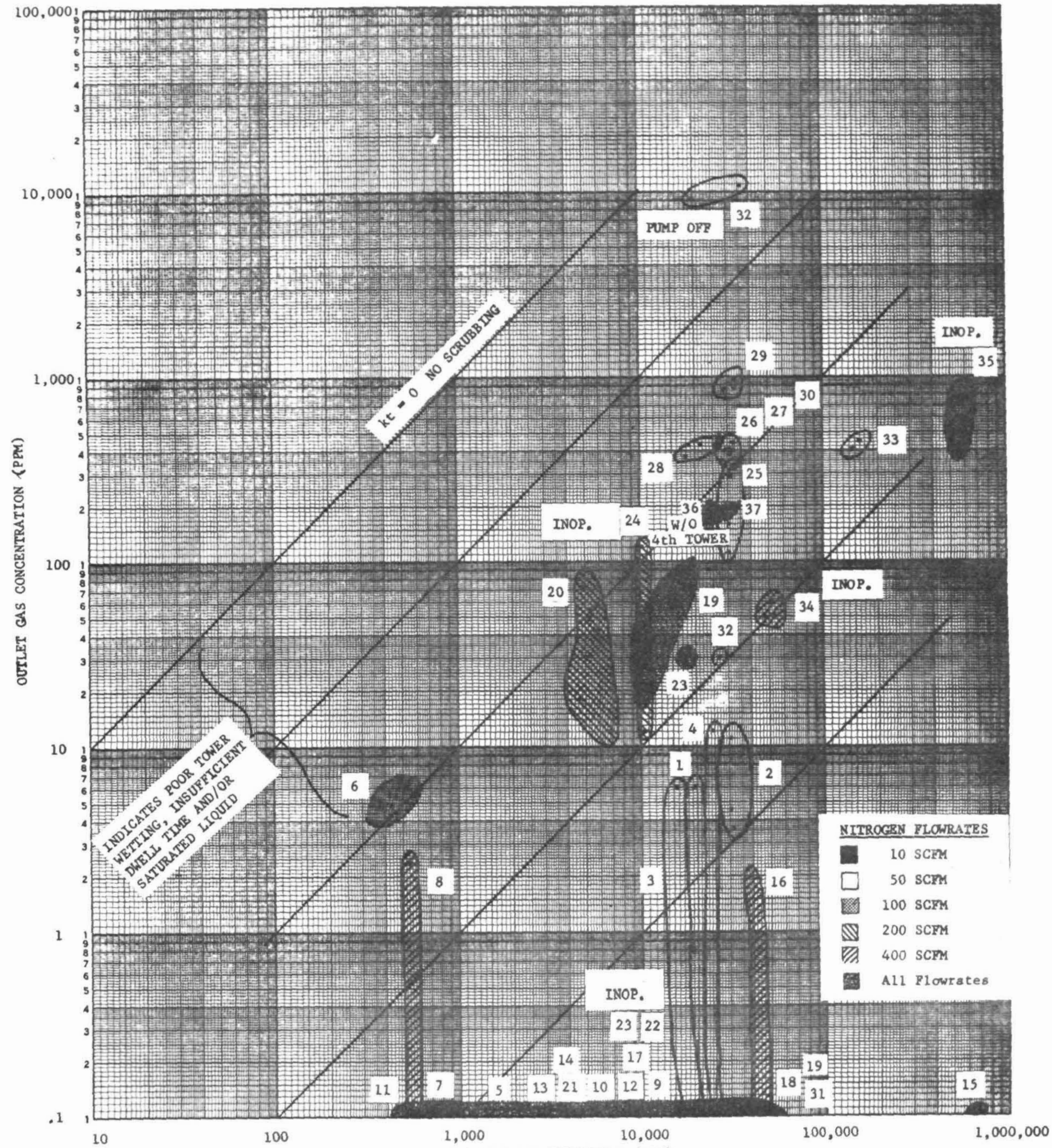


Figure 3-1
N_2O_4 Scrubber with Na_2SO_3 Sump Solution Inlet Gas Concentration vs Outlet Gas Concentration for Various Nitrogen Flowrates

FIGURE 3-2: EFFECT OF TOWER DRYING TIME ON OUTLET CONCENTRATION

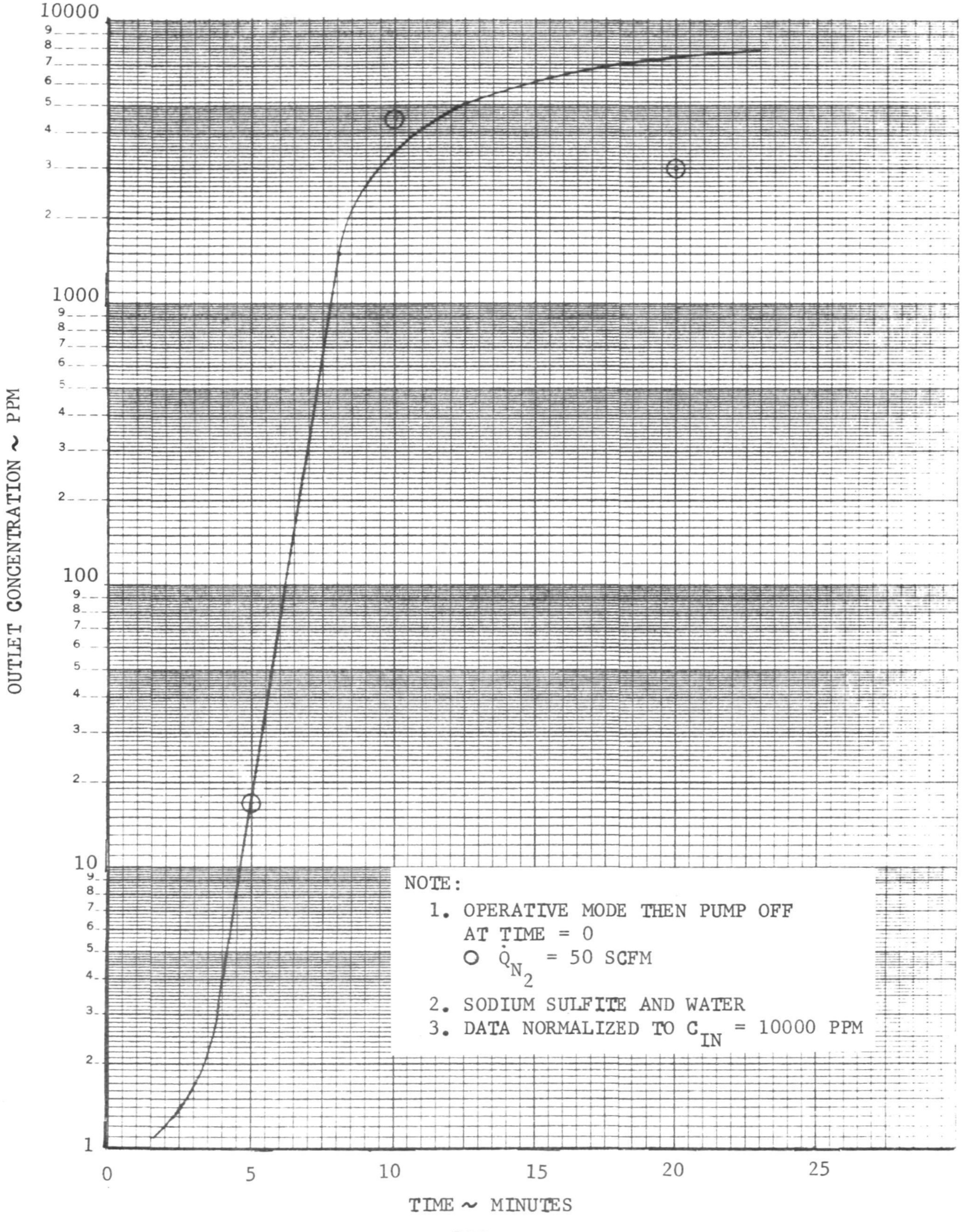
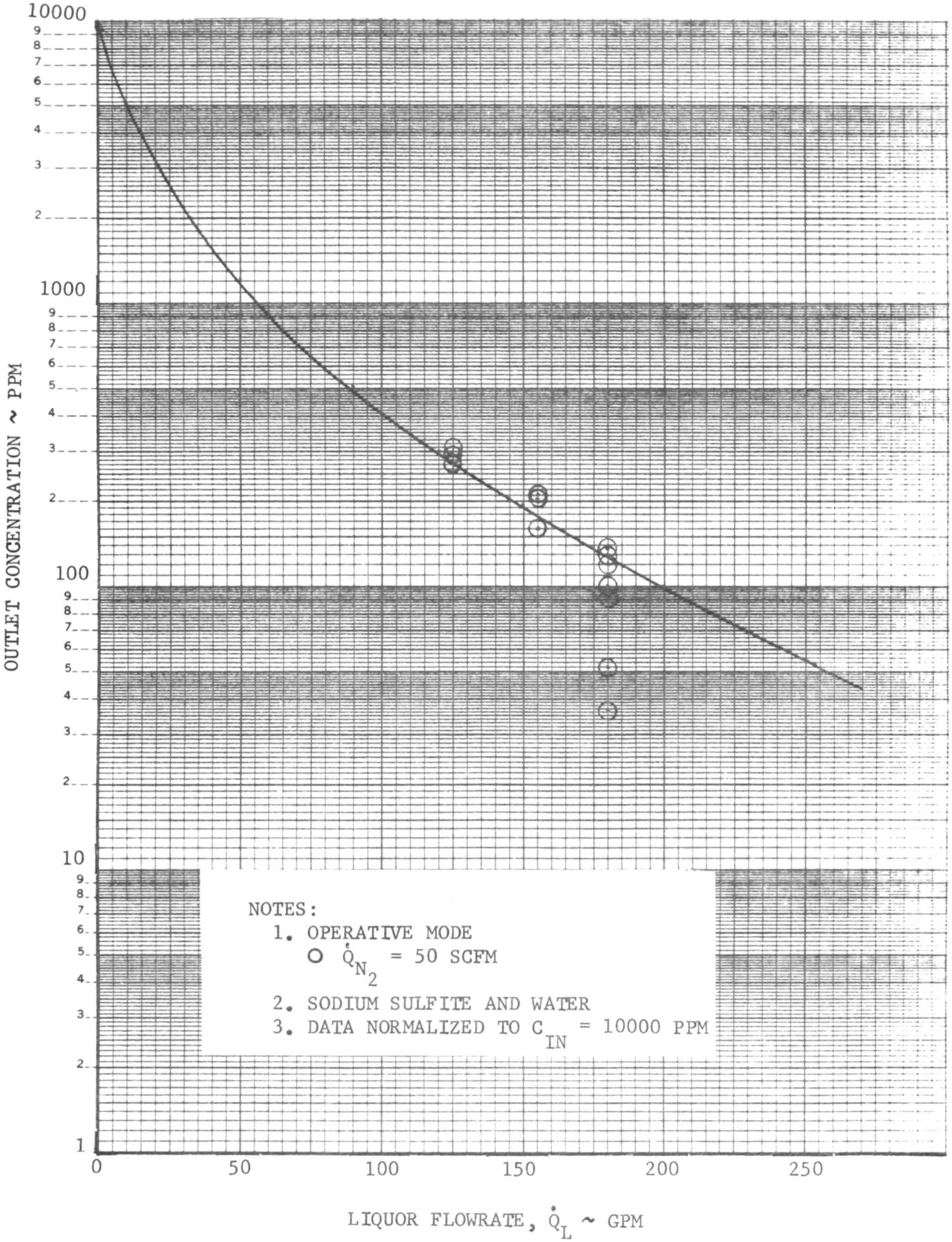


FIGURE 3-3: EFFECT OF LIQUOR FLOWRATE ON OUTLET CONCENTRATION



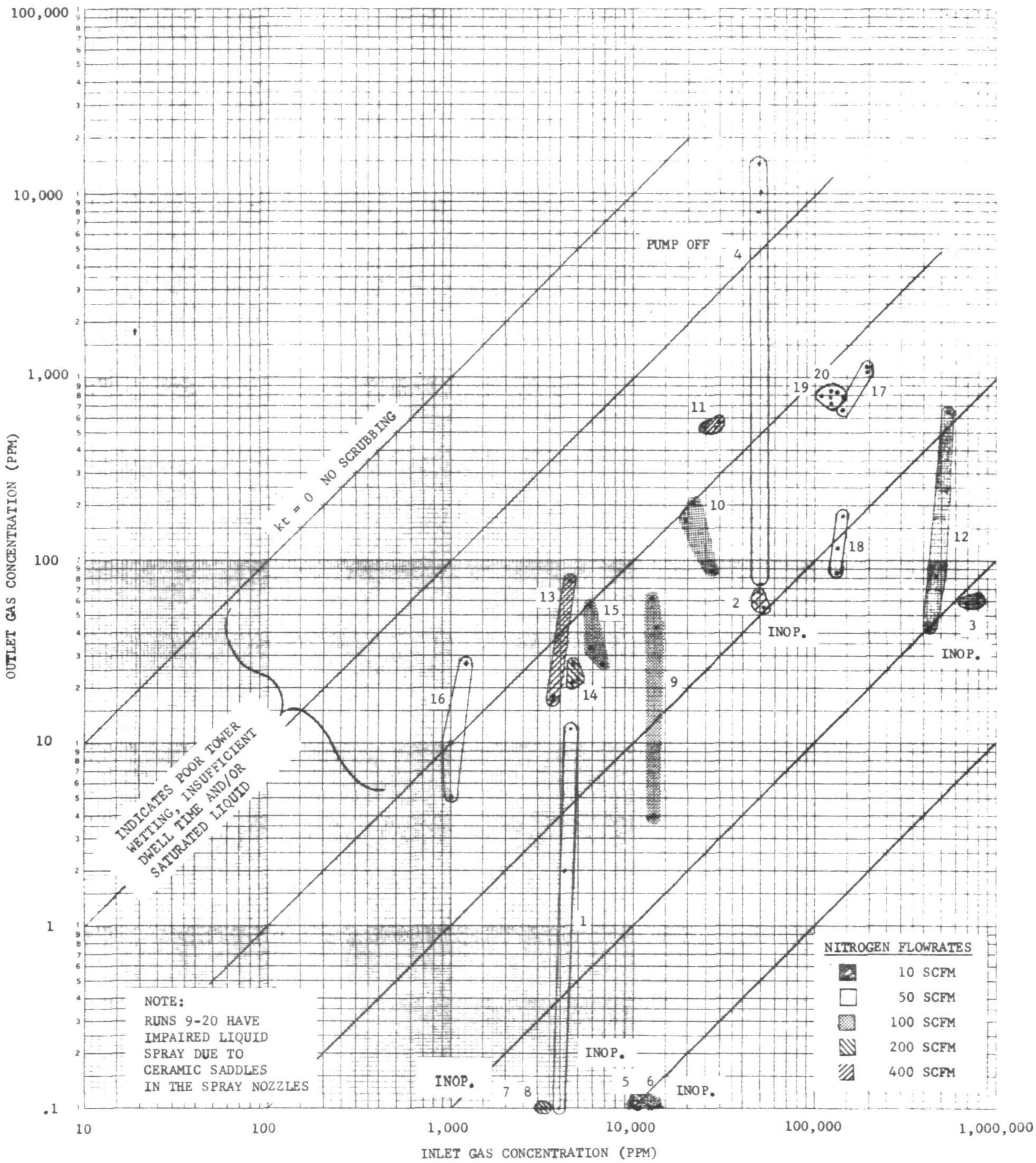


Figure 4-1
N_2O_4 Scrubber with $NaOH/Na_2SO_3$ Sump Solution Inlet Gas Concentration (PPM) vs Outlet Gas Concentration (ppm) for Various Nitrogen Flowrates

FIGURE 4-2: EFFECT OF TOWER DRYING TIME ON OUTLET CONCENTRATION

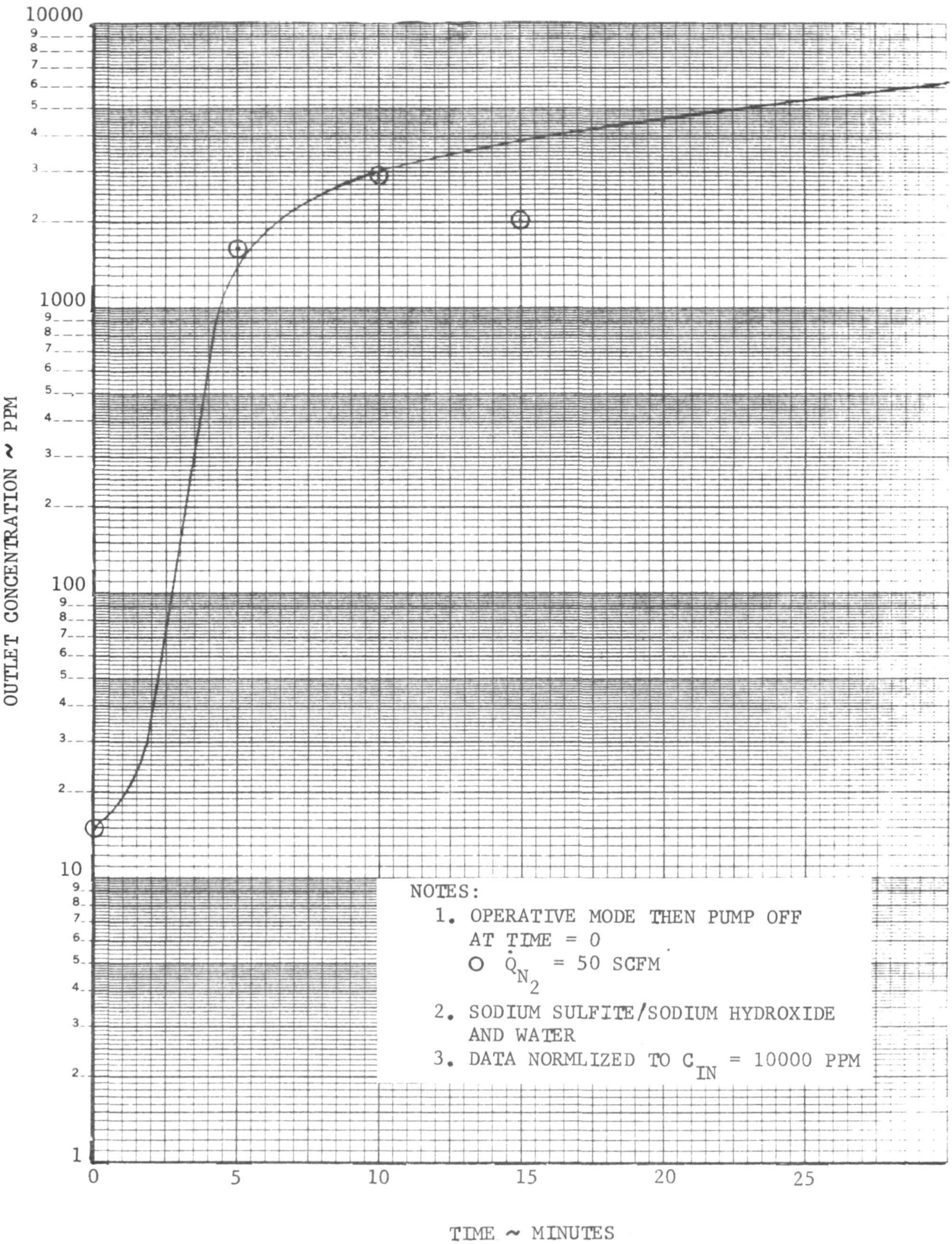


FIGURE 4-3: EFFECT OF TOWER/LIQUOR CONDITION ON OUTLET CONCENTRATION

NOTES:

1. SODIUM HYDROXIDE/SODIUM SULFITE AND WATER
2. DATA NORMALIZED TO C_{IN} = 10000 PPM