

COMPUTER SIMULATION OF A NITROGEN OXIDES ABSORPTION COLUMN AT  
THE SAVANNAH RIVER SITE\*

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**COMPUTER SIMULATION OF A NITROGEN OXIDES ABSORPTION  
COLUMN**

**AT THE SAVANNAH RIVER SITE\***

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ABSTRACT:

A computer model of a nitrogen oxides absorption column has been constructed for the purpose of testing process control strategies in a time- and cost-effective manner. The model consists of a simplified physical and chemical scheme that approximately matches real column behavior. Various feedback, feedforward, and recycle strategies have been tested, and an optimum combination selected. This combination will be tested in the plant in the near future. The overall project goals, the behavior of the real column, and how the model has been applied to process control research and development will be discussed.

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## COMPUTER SIMULATION OF A NITROGEN OXIDES ABSORPTION COLUMN AT THE SAVANNAH RIVER SITE

### INTRODUCTION

The Savannah River Site is a production complex for the U. S. Department of Energy. The major facilities at the site are: fuel and target fabrication facilities; nuclear reactors; chemical separations plants, and a defense waste processing area. In the chemical separations facilities, irradiated materials are dissolved and the desired products separated from waste materials.

Large quantities of oxides of nitrogen (NO<sub>x</sub>) are routinely emitted from the dissolution process and from a denitration operation in the separations facilities. These gases are routed through a nitrogen oxides absorption column located adjacent to the separations building. This column, referred to as the F-8 Column, removes NO<sub>x</sub> from the offgas streams of the dissolvers and denitrators and generates nitric acid. The nitric acid is recycled to the dissolvers.

Because of continually more stringent environmental emission restrictions, control of the F-8 Column has become increasingly more difficult. The Savannah River Site has initiated a project to improve operation and control of the column. The project objectives are to use improved control to produce 50 (weight) percent nitric acid while limiting the instantaneous NO<sub>x</sub> emission rate to maintain opacity from the separations area stack to less than 40 percent. (A further goal is to reduce the yearly average NO<sub>x</sub> emissions to less than 20 pounds per hour.)

The Savannah River Laboratory chartered a task team to collect and study F-8 Column performance data and to recommend appropriate process control strategies. The task team constructed and installed an instrumentation package on the F-8 column which would record normal performance data. Simultaneously, an effort was mounted to construct a computer model of the column which would be used to test candidate process control strategies prior to actual Plant testing. This report describes that model.

### PROCESS BACKGROUND

The F-8 column is a 44 tray bubble cap column 6 feet in diameter and 60 feet tall. Gas flow into the column is derived from two sources that are combined just before entering the column. The major source of nitrogen oxides (NO<sub>x</sub>) is two chemical dissolvers, which produce offgas composed of up to 70-80% NO<sub>x</sub> at approximately 100-400 scfm. The second source of NO<sub>x</sub> gases is thermal denitrators, which produce 0-10% NO<sub>x</sub> at 300-400 scfm.

Normal column operation when only the denitrators are functioning consists of allowing the denitrator offgas to flow through the F-8 column when the minimum volume of liquid is present. No acid is produced then, except on the trays themselves, and no emission problems have been tied to this type of operation. When a dissolver is operating however, additional water is sent to the column to capture the extra NO<sub>x</sub> and make concentrated nitric acid. Emission problems have been experienced during dissolver operations and weak acid is often produced.

A complete dissolver run will take approximately 60 hours. The dissolutions are manually operated batch processes and show the typical type of variability that would be

expected. In addition, the operation of the F-8 column is also manual, with the exception of a flow controller on the inlet water feed line, and also shows manual operation variability.

There are two main chemical operations in the reactor fuel dissolution process: removal of the aluminum cladding with sodium hydroxide, and dissolution of the uranium fuel with nitric acid. The de-clad fuel is heated in 50% acid, dissolving the uranium and fission products. The acid dissolution is accomplished in two separate steps, called cuts, each of which can take 10 to 14 hours to complete. The two cuts are normally separated by 2 to 5 hours, during which time the dissolved metal solution is removed and sent on for further processing and fresh acid is added.

Standard operating procedures call for the F-8 column operators to use a fixed water flow profile in all cases unless emission problems are encountered. If emissions problems are experienced the operators increase the water flow arbitrarily in an attempt to control emissions. In addition, prior to each cut, the operators attempt to develop the normal column operating differential pressure by adding water to the column at or near the maximum rate of 4 GPM. Of four monitored dissolver runs, none used the prescribed profile exclusively.

### CONTROL PROBLEM

Fundamentally, each run will be slightly different due to differences in amount of fuel added to the dissolvers, random temperature variations, etc. However, to obtain exactly 50% acid, an exact amount of water must be used. The fixed flow profile strategy then is doomed to consistent failure on either the acid strength goal or the emissions level goal. The process control problem thus becomes how to determine the correct amount of water necessary and how to add it so that emissions are always at acceptable levels.

The problem is an inherently difficult one. Current data suggests that the NO<sub>x</sub> emission level at the top of the F-8 column averages near 1% by volume at a flow of perhaps 600 scfm. F-8 emissions are mixed with filtered separations building emissions before atmospheric release. Typical separations building air flows are 180,000 scfm. Thus the NO<sub>x</sub> emissions are diluted to near .0033 volume percent or approximately 30 ppm by volume.

In practice, emission control is accomplished by increasing the water flow and washing out the NO<sub>x</sub> more completely. However this adds additional water to the column and produces weak acid. The optimal process control strategy would hold the emissions at the maximum acceptable level while producing acid of the appropriate strength, barring any thermodynamic limitations on acid strength.

It should be obvious that trying to determine the optimal process control strategy via real-world testing would be both cost and time prohibitive, as well as causing unacceptable atmospheric releases. Computer modeling becomes the only viable rapid way to screen options. This is the justification of the ADS modeling effort, and it in turn places some minimum requirements on the model so developed. Most importantly, the model should mimic F-8 column behavior when varying NO<sub>x</sub> feeds are sent to it. Secondly, the model should run somewhat faster than at real-time speeds.

This report describes an empirical F-8 computer model. The model assumptions are described and calculations based on real data are compared to actual performance.

Limitations of the model are discussed and a pathforward to an improved version of the model is outlined.

## DISCUSSION

### Summary

The F-8 computer model began as an attempt to maintain first-principles accuracy while minimizing software development time. A results-oriented emphasis was desired. Because of such considerations, simplification of first-principle models was required. The resultant model became essentially fully empirical and therefore modeling outside normal operating conditions should be considered highly suspect. In fact, oversimplification causes any results of this model to be suspect and requires all conclusions be verified by real world testing. However even with this caveat, the model does remarkably well at predicting column performance features from real data.

Two versions of a FORTRAN computer model of the F-8 column were constructed. The first used internal code to calculate feed flows and compositions while the second read data files for that information. The second version was used to verify model performance relative to the real world and the first will be used to test process control strategies.

The model mimicked F-8 behavior sufficiently well that it could be used to screen process control strategies. When the model was run on the VAX.8550 and no other users were present, 36 hour dissolver runs were simulated in 5 minutes. The same model was run on a MicroVax II with simulation times of 30 minutes.

The model is highly empirical and contains severe approximations and assumptions. Some of these are:

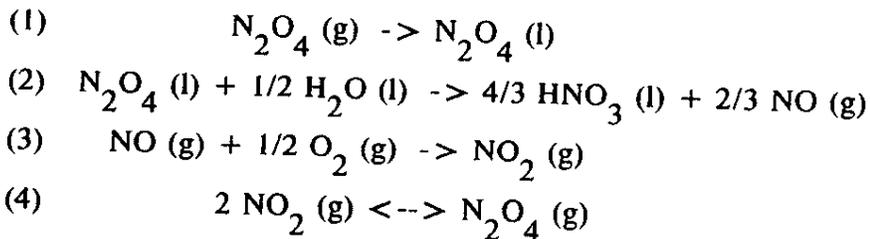
- Minor chemical reactions are ignored.
- Rate constants, equilibrium constants, and reaction extents are empirically adjusted.
- Differential expressions are either integrated or approximated.
- Flows do not experience any holdups.
- Isothermality (mass balance only, no heat balance)

Each of these limitations is discussed below.

### **Chemical Reactions and Rate, Equilibrium, and Mass Transfer Constants**

Steady-state computer models of nitrogen oxides absorption columns abound as this process is a major way of producing concentrated nitric acid (1, Chilton). These models simulate the chemistry of several nitrogen species, such as NO, NO<sub>2</sub>, N<sub>2</sub>O<sub>3</sub>, and N<sub>2</sub>O<sub>4</sub>, all being present in the gas and liquid phases. Mass transfer coefficients, equilibrium constants, and rate constants are thus necessary for all possible reactions. A good overview of this is given by Counce (2).

The calculational complexity of these models makes them inherently difficult to use in a dynamic sense, especially when rapid modeling turnaround is desired. Thus the chemistry normally included in column models was here simplified to include only four chemical reactions which are:



The first equation (1) represents the net mass transfer of nitrogen species from the gas phase to the liquid phase. Real data show an approximately constant reduction in NOx concentration between feed and offgas concentrations. This suggested a fixed plate efficiency was required for accurate modeling. Steady-state models use this formalism as well.

However, thermodynamic limitations do exist and are typically included via an equilibrium state calculation. When this standard method was tried, oscillatory behavior was encountered. Therefore an empirical approximation was used. This approach consisted of a variable plate efficiency where either a low and fixed efficiency was used when far from equilibrium levels or a smaller, smoothly decreasing plate efficiency was used when near to thermodynamic limits. Changes to the empirical plate efficiency factors substantially affected the ultimate acid strength obtained when testing process control strategies. Usually the real runs did not approach acid concentrations where the form of the approximation mattered, thus the actual value and form of this approximation cannot be tested.

The second equation (2) above was assumed to go to completion.

Equation (3) represents the rate-limiting gas phase reaction. The model uses an integrated expression taken from Chilton (1) that calculates the fraction of NO oxidized based on initial NO and O<sub>2</sub> partial pressures. The Chilton expression for the rate constant was used, although there are several others available. The calculated extent of oxidation never seemed correct, however, and empirical corrections were applied to the rate constant and the fraction oxidized. The quadratic expression in fraction oxidized was solved via the quadratic formula and the positive root was shown to give unreal solutions, thus only the negative root is calculated in the model.

The Chilton reference was later found to have a typographical error in the integrated expression that transformed it from a quadratic in fraction oxidized to a cubic. This was not corrected in the model as an empirical fit was obtained. Perhaps one of the cubic roots would have more accurately calculated the fraction NO oxidized.

The fourth equation (4) was assumed to be a fast equilibrium. The equilibrium constant expression was taken from Miller (3) and was not modified. The quadratic equilibrium expression in pressure was solved via the quadratic formula and the positive root was shown to always require more NO<sub>2</sub> than was available. Thus only the negative root was used in the model.

The order in which the equations are listed represents the calculational order used in the model as well. Prior to calculating the chemical reactions, gas flow was simulated, and after the chemistry, liquid flow was simulated.

## Gas and Liquid Flow

Simplistic gas and liquid flow expressions were used. For the liquid, flow onto a tray usually produced an equivalent off-flow. It was found necessary to limit off-flow to a maximum of 2.5 gallons/minute to match a breakpoint in the acid concentration curves however.

Maximum tray liquid volumes were fixed by an assumed linear distribution of the nominal 20" of water differential pressure. Varying the amount and distribution of water on the column within the limits of normal operating differential pressure did not affect the results greatly.

Liquid flow is normally expressed as a differential equation. This implies a holdup time which is characterized by a time constant. The F-8 model assumes this constant to be zero under normal flow conditions. The model also uses a fixed operating differential pressure. The inclusion of differential equations into the model would allow these restrictions to be dropped, but this would also require the determination of the column time constant.

To simulate gas flow a linear pressure profile across the column that distributed the 20" of water differential pressure equally on each tray was assumed. Then the amount of gas injected onto the column in one time step was calculated and added to the gas space above tray 1. A pressure was calculated from this and compared to the 'ideal' pressure and any excess gas was moved up to the next tray. This was repeated for all trays. Next, the chemistry calculations were done, followed by the liquid flow. If enough NO<sub>x</sub> was present and moved to the liquid phase, gas flow could potentially be precluded in the next time step. In practice this never occurred when conditions approximating real ones were simulated.

The minimum liquid tray volume was set at 23 gallons and the tray gas volume was set at 35.34 cubic feet. The use of the 20" of excess water during operation was not accounted for in the gas volume which is a hidden approximation.

The bottom of the column has an approximate capacity of 360 gallons. This volume serves to hold up changes in product acid concentration. The flow out of the column bottom is controlled by a level controller changing a valve opening. In simulations, it was found that an assumed volume of 180 gallons reproduced actual measured data reasonably well.

## Isothermality

Liquid on the column trays is cooled by circulating chilled process water through cooling coils located in each tray. No information was available for cooling water temperature or tray temperatures, so the determination of actual heat transfer characteristics was impossible. Thus the decision to build a model based solely on mass balance.

While the oxidation rate constant and the equilibrium constant contained temperature dependence, the mass transfer coefficient did not. Also reaction (2) was assumed to go to completion. Thus temperature effects were not explicitly included in two of the four chemical reactions. Actual field data showed product acid temperature variations of 15 to 20 degrees Centigrade. Therefore the isothermality assumption may also be severe, at least for the lowest few trays.

### Initial Conditions

The initial conditions used to start a simulation are always critical. This model used the following assumptions:

- 79% N<sub>2</sub> and 21% O<sub>2</sub> gas composition
- Gas pressure in each tray given by a linear decrease in pressure from the inlet pressure of 1.4 atm. totaling 20" of water (.05 atm.)
- Liquid volume on each tray equal to 23 gallons plus the linearly distributed excess volume equivalent to 20" of water.
- Acid on trays 1 to 12. Trays 1, 2, and 3 would have the same concentration with subsequent tray concentrations decreasing linearly to zero at Tray 13. Actual concentration on Tray 1 was determined by either matching real data initial product acid concentration or choosing an appropriate value for simulated feeds.
- Column bottom acid equal to Tray 1 acid concentration.

### Other Assumptions

Other implicit and explicit assumptions include:

- No reactions occur in pipes.
- Complete mixing in gas and liquid phases.
- Remaining gas volume are made up by air (79% N<sub>2</sub> / 21% O<sub>2</sub>).
- No other gases are present.

### Model Verification

In the context of the F-8 model, verification means the process whereby the model was shown to simulate F-8 behavior within the limits required to accomplish the Savannah River Laboratory program objectives. This was done by feeding the computer program real data collected via the F-8 instrumentation package and modifying both the model and the data until acceptable results were obtained.

Data manipulation was found to be necessary to make the model act like the F-8 column. Approximate mass balance calculations on the raw data showed disagreements of up to 35% of the incoming material. This fact suggested potential absolute calibration errors in flows, as the NO<sub>x</sub>, acid, and O<sub>2</sub> monitors were externally calibrated with recognized standards and methods.

Thus the overall verification process consisted of (1) selecting 'modelable' runs (a judgment decision which attempted to balance data problems with modeling results), (2) determining the extent the real data had to be adjusted, and (3) comparing the calculated output profiles with observed column data.

Information from one of the modelable runs is presented in Figures 1 - 6. The measured NO<sub>2</sub> profiles are presented in Fig. 1 and the measured NO profiles in Fig. 2. (Measured inlet concentrations from both the dissolver and denitrator sources are shown in both figures, along with the measured column outlet concentration.) Measured acid concentration data are presented in Figure 5.

Figures 3, 4, and 5 present the 'best' simulation results of this run. The actual data are shown as solid or dashed lines while the simulations are shown as dotted lines. The most severe failure of the model in exactly matching the actual data is with regards to the acid composition profiles. Unexplained dips are present, and both simulations seem to lag the

real data. However, the purpose was not to fit the data, but to mimic it within limits sufficient to determine the effects of process control strategies.

This is illustrated in Figure 6, where an additional simulation has been conducted on the run. In this simulation, a water flow control strategy based on a feedforward technique was used. Specifically, a theoretical equation relating the NO<sub>x</sub> feed to water addition under the assumptions that all NO<sub>x</sub> would be absorbed and 50 weight percent acid would be produced was used to calculate water flow to the column. No emission control strategy was employed here, but a restriction of water flow if acid strength was less than 40% was employed.

Obviously, this control strategy has radically altered the profile. Compared to the change in profile, the mis-match of the simulation to the data becomes secondary. Similar effects are seen in the NO<sub>x</sub> emission profiles when emission control strategies are tested.

In conclusion, the modeling program goal was to quickly build a computer model of the F-8 column and use it to screen candidate process control strategies. The model described in this paper satisfies that goal.

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Figure 1. NO<sub>2</sub> Composition Profiles from a Typical Dissolver Run

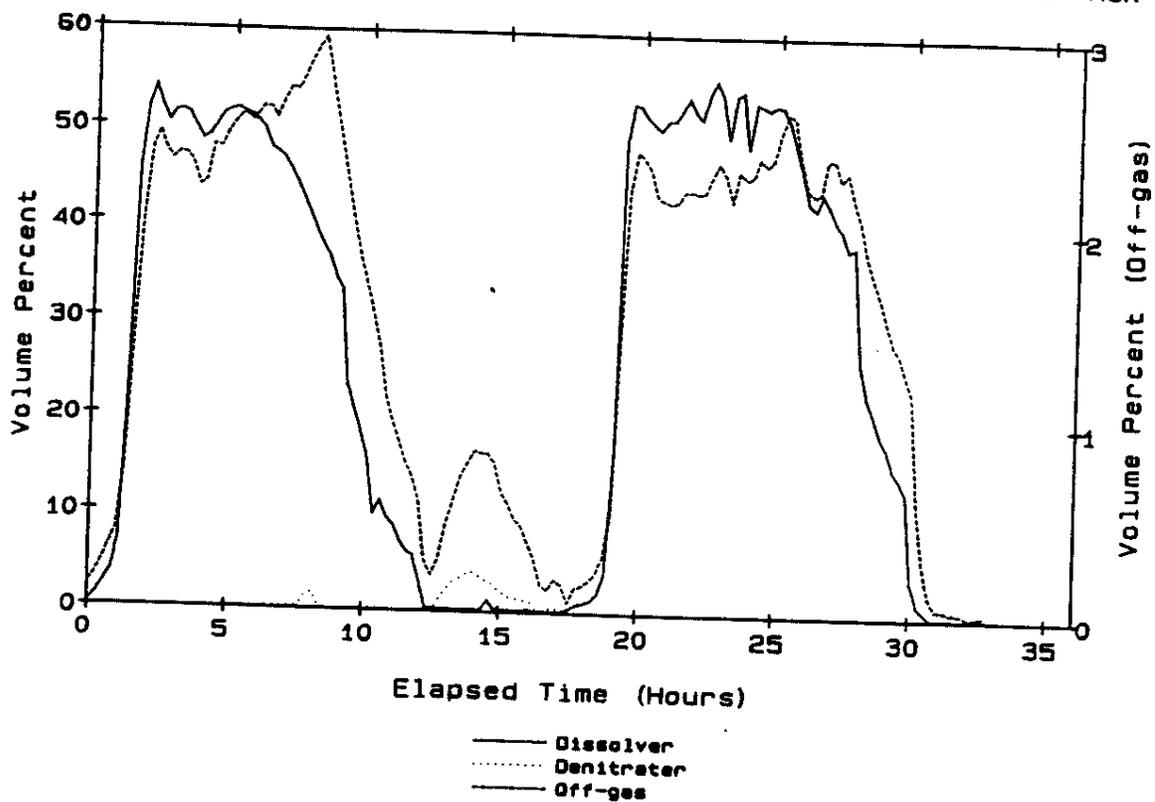


Figure 2. NO Composition Profiles from a Typical Dissolver Run

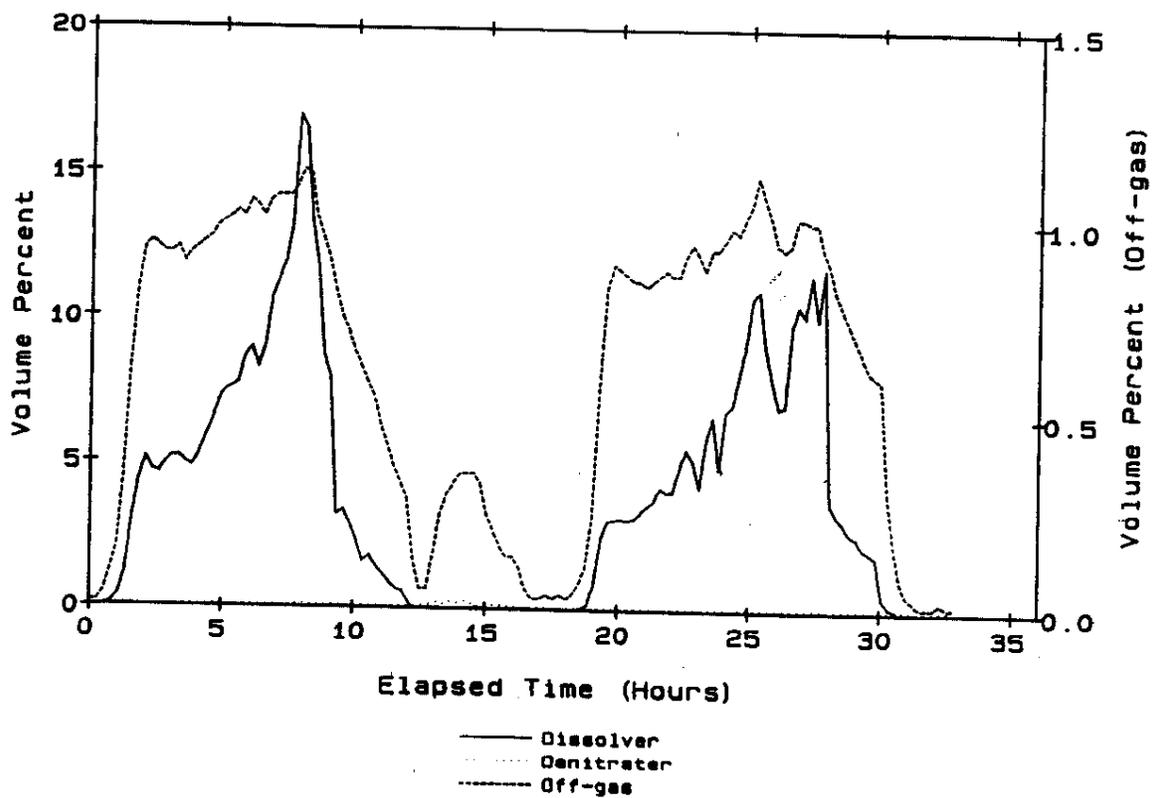


Figure 3. Comparison of Actual and Calculated NO<sub>2</sub> Composition Profiles from a Typical Dissolver Run

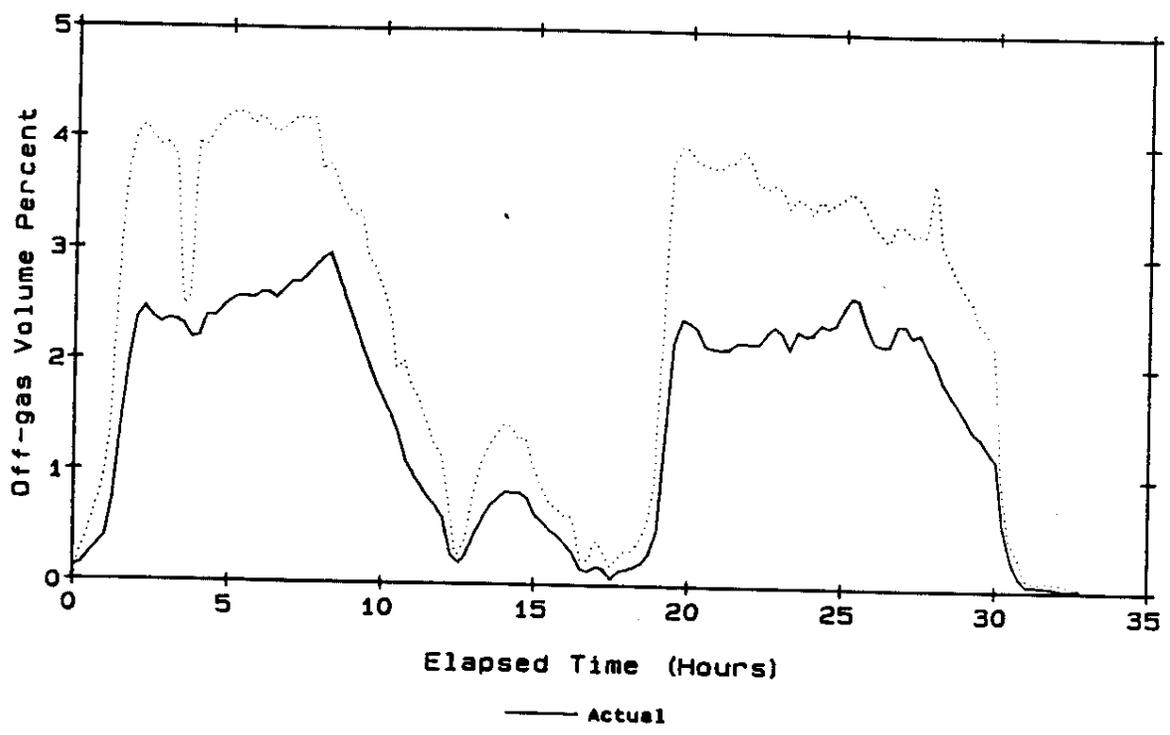


Figure 4. Comparison of Actual and Calculated NO Composition Profiles from a Typical Dissolver Run

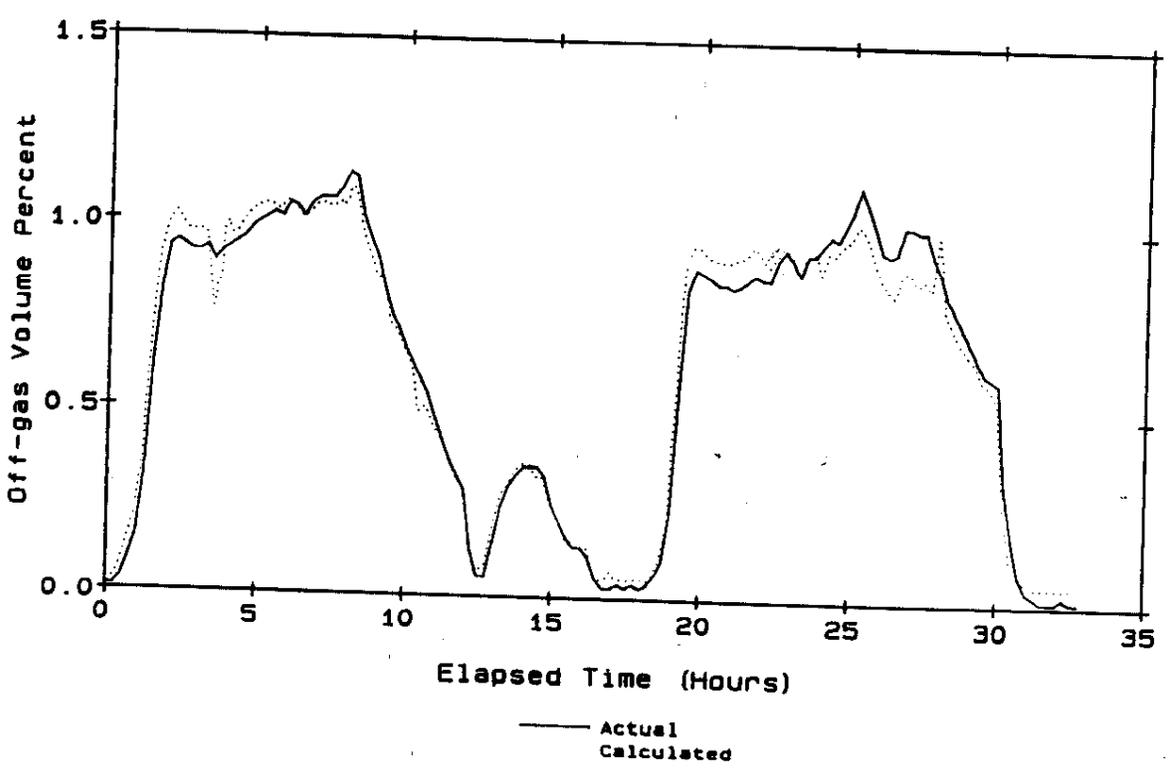


Figure 5. Comparison of Actual and Calculated Nitric Acid Composition Profiles from a Typical Dissolver Run

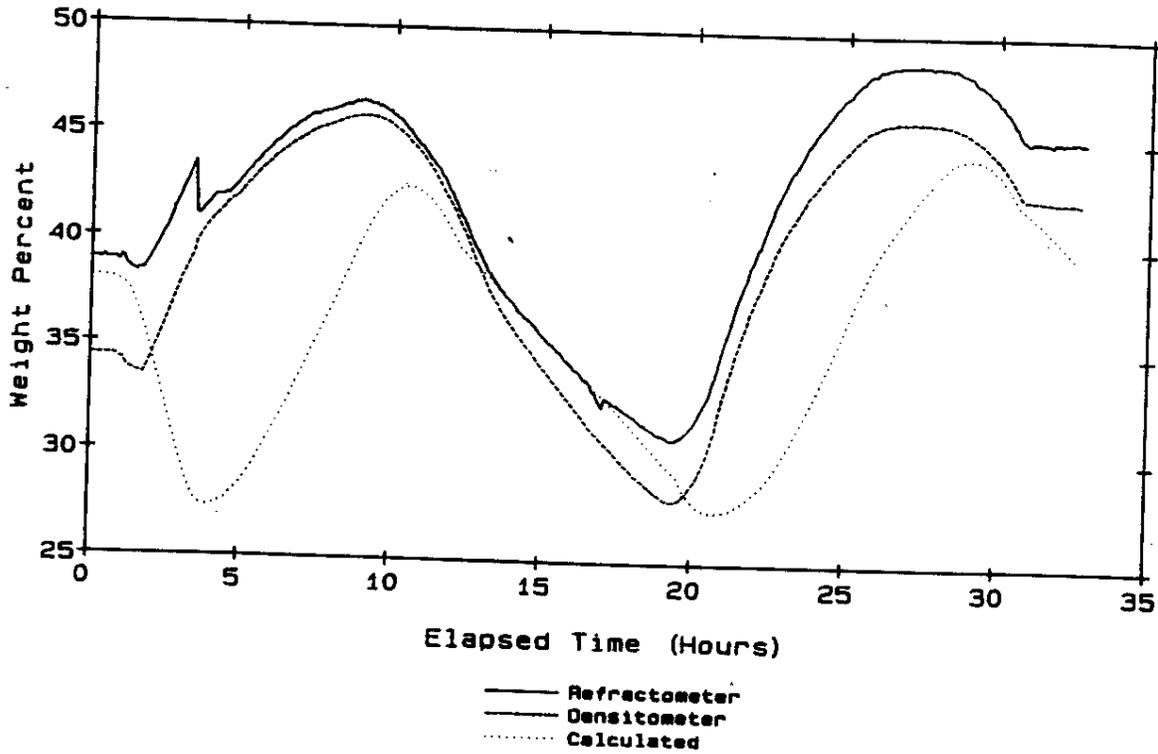


Figure 6. Comparison of Actual and Calculated Nitric Acid Composition Profiles from a Typical Dissolver Run (Using Actual Plant Water Flow and NOx Feed-Driven Feedforward Water Flow)

