ORNL-2291
Stable Isotope Separation

Cy. 4

CHEMICAL AND ISOTOPIC STUDIES OF THE NITROX SYSTEM FOR N^{15} ENRICHMENT

G. M. Begun
L. L. Brown
L. B. Yeatts
N. C. Bradley
E. F. Joseph

OAK RIDGE NATIONAL LABORATORY
OPERATED BY
UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide and Carbon Corporation
UCC
POST OFFICE BOX X · OAK RIDGE, TENNESSEE

Printed in USA. Price 25 cents. Available from the

Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

ORNL-2291

Contract No. W-7405-eng-26

CHEMISTRY DIVISION

CHEMICAL AND ISOTOPIC STUDIES OF THE NITROX SYSTEM FOR N^{15} ENRICHMENT

G. M. Begun
L. L. Brown
L. B. Yeatts
N. C. Bradley
E. F. Joseph

DATE ISSUED

JUN 6 1957

OAK RIDGE NATIONAL LABORATORY
Operated by
UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide and Carbon Corporation
Post Office Box X
Oak Ridge, Tennessee

ORNL-2291
Stable Isotope Separation
TID-4500 (13th ed.)

INTERNAL DISTRIBUTION

1. C. E. Center
2. Biology Library
3. Health Physics Library
4-5. Central Research Library
6. Reactor Experimental Engineering Library
7-26. Laboratory Records Department
27. Laboratory Records, ORNL R.C.
28. A. M. Weinberg
29. L. B. Emlet (K-25)
30. J. P. Murray (Y-12)
31. J. A. Swartout
32. E. H. Taylor
33. E. D. Shipley
34. S. C. Lind
35. M. L. Nelson
36. C. P. Keim
37. J. H. Frye, Jr.
38. R. S. Livingston
39. S. J. Cromer
40. F. L. Culler
41. A. H. Snell
42. A. Hollaender
43. M. T. Kelley
44. K. Z. Morgan
45. T. A. Lincoln
46. A. S. Householder
47. C. S. Harrill
48. C. E. Winters
49. D. W. Cardwell
50. E. M. King
51. D. D. Cowen
52. D. S. Billington
53. J. A. Lane
54. M. J. Skinner
55. W. H. Jordan
56. G. E. Boyd
57. R. R. Dickison
58. P. M. Reyling
59. G. C. Williams
60. J. S. Drury
61. A. A. Palko
62. L. Landau
63. A. C. Rutenberg
64. L. L. Brown
65-69. G. M. Begun
70. L. B. Yeatts
71. N. C. Bradley
72. E. F. Joseph
73. C. E. Larson (consultant)
74. P. H. Emmett (consultant)
75. H. Eyring (consultant)
76. G. T. Seaborg (consultant)
77. ORNL – Y-12 Technical Library, Document Reference Section

EXTERNAL DISTRIBUTION

78. R. F. Bacher, California Institute of Technology
79. Division of Research and Development, AEC, ORO
80-577. Given distribution as shown in TID-4500 (13th ed.) under Stable Isotope Separation category (100 copies – OTS)

CONTENTS

CHEMICAL AND ISOTOPIC STUDIES OF THE NITROX SYSTEM FOR N^{15} ENRICHMENT

G. M. Begun
L. L. Brown
L. B. Yeatts
N. C. Bradley
E. F. Joseph

ABSTRACT

The Nitrox system for concentration of nitrogen isotopes has been studied in detail; in this system use is made of the exchange reaction between nitric acid and the oxides of nitrogen. The isotopic separation factor for the system has been found to vary from 1.064 at 1 *M* HNO_3 to 1.020 at 15.5 *M* HNO_3. The conversion of nitric acid to oxides of nitrogen with gaseous sulfur dioxide in the product refluxer has been studied, and suitable refluxers have been designed. A small, two-column enriching cascade has been designed and operated which produced gram quantities of highly enriched N^{15}.

INTRODUCTION

The nuclear properties of N^{15} and N^{14} are entirely different. Nitrogen-15 with an abundance of 0.37 at. % has a cross section for the absorption of thermal neutrons of 8×10^{-5} barn as compared with N^{14}, which has a cross section of 1.78 barns. For this reason, highly purified N^{15} could be considered for use in nuclear devices in which compounds containing natural nitrogen would not be satisfactory.

Chemical exchange has been found to be one of the most attractive means for large-scale production of highly enriched N^{15}. The literature on separation of nitrogen isotopes has been summarized and the problems involved in the operation of a chemical exchange system have been considered in a previous report.[1] While the work described in that report was in progress, a new system for the separation of nitrogen isotopes was suggested at Columbia University.[2,3] This system, in which the exchange reaction between nitric acid and nitric oxide was utilized to effect a concentration of N^{15}, appeared to offer excellent possibilities for the production of highly enriched N^{15} at a lower cost than had been afforded by any previous system. Consequently, research and development work was started at ORNL to gather the data necessary for evaluation of the system.

DESCRIPTION OF THE NITROX SYSTEM

The basic exchange reaction responsible for the isotopic concentration in the Nitrox system is that between gaseous nitric oxide and aqueous nitric acid. The reaction may be written as follows:

$$N^{15}O(g) + HN^{14}O_3(aq) \rightleftharpoons N^{14}O(g) + HN^{15}O_3(aq)$$

When equilibrium is attained, N^{15} concentrates in the nitric acid and N^{14} concentrates in the nitric oxide. In order to attain significant separation of isotopes, it is necessary to carry out this equilibration many times consecutively. This is accomplished by passing nitric acid countercurrently to nitric oxide gas in a packed column. To build up an isotopic gradient, refluxing is required. At the nitric acid or N^{15} end of the column, nitric acid is converted to nitric oxide by the addition of sulfur dioxide gas, which results in the formation of the by-product sulfuric acid. At the nitric oxide or N^{14} end of the column, air or oxygen may be added and the nitrogen dioxide formed absorbed in water to re-form nitric acid. A schematic diagram of the system is shown in Fig. 1. In small-scale operation an infinite feed of nitric acid, which is relatively cheap, can be substituted for the waste refluxer.

SINGLE-STAGE SEPARATION FACTORS FOR THE NITROX SYSTEM

The gas present in the exchange column of the Nitrox system is primarily a mixture of nitric oxide

[1] A. A. Palko *et al.*, *Chemical and Isotopic Studies of the Closed-Cycle Carbonate System for N^{15} Enrichment*, ORNL-2138 (Oct. 24, 1956).

[2] W. Spindel and T. I. Taylor, *J. Chem. Phys.* 23, 981–82 (1955).

[3] W. Spindel and T. I. Taylor, *J. Chem. Phys.* 24, 626–27 (1956).

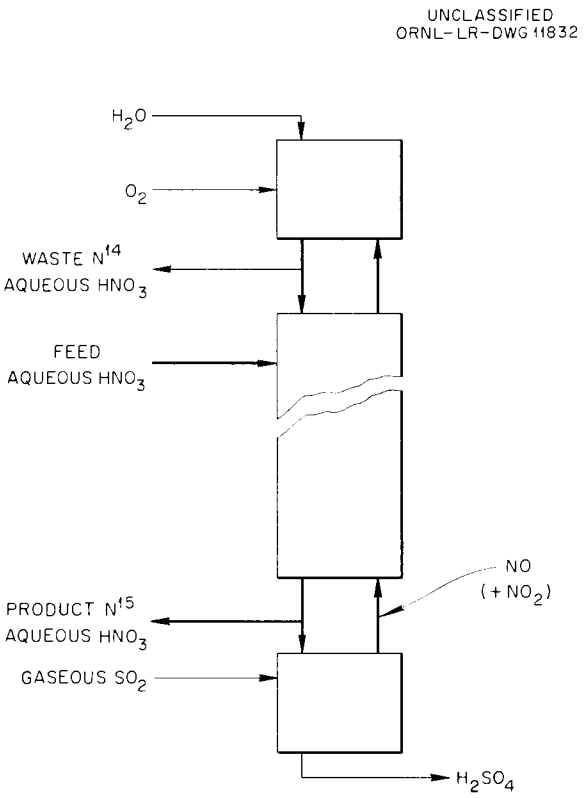

Fig. 1. Schematic Diagram of the Nitrox System for Enrichment of Nitrogen Isotopes.

and nitrogen dioxide. Under equilibrium conditions the composition of this gas mixture is a function of the operating temperature and pressure and of the concentration of the acid used in the liquid phase. The presence of nitrogen dioxide in the gas is necessary to cause sufficiently rapid isotopic exchange for countercurrent operation of the system. However, the effective separation factor for the system is lowered as the amount of nitrogen dioxide in the gas phase increases, since the separation factor for the reaction $NO_2(g)$ vs $HNO_3(aq)$ is considerably smaller than that for the reaction $NO(g)$ vs $HNO_3(aq)$. From this point of view it is desirable to operate the exchange column so that the amount of nitrogen dioxide present in the gas phase is minimized.

To help optimize these opposing effects of nitrogen dioxide on the isotopic enrichment obtainable in the system, a series of runs was made in which the isotopic separation was studied as a function of nitric acid concentration.

Gas-Liquid Contactor

Difficulties were experienced in determining the single-stage separation factor of the Nitrox system in conventional equipment. The reaction must be kept free of air contamination, since oxygen from the air readily oxidizes nitric oxide and therefore upsets the chemical equilibrium of the sample. Atmospheric nitrogen introduces errors in the isotopic analysis of the gas phase. The two phases must be separated at equilibrium without the composition of either phase being changed.

A new type of contactor was developed which handles these problems satisfactorily and is applicable to other systems. Figure 2 is a scale drawing of the contactor, with the finger pump schematically indicated. A gas-handling manifold which had provisions for auxiliaries such as vacuum, helium purge gas, nitric oxide purification, and sample tubes for isotopic samples was connected to the contactor loop.

To determine the separation factor, all portions of the system were purged with helium, and 90 to 100 ml of nitric acid was put in the liquid reservoir with stopcock 1 closed. The apparatus was then assembled, with a light coat of silicone stopcock grease applied to the glass joints. Points A_1 and A_2 were connected by means of a short section of Tygon tubing passing through the finger pump to close the loop completely. By proper use of stopcocks 2 and 3, the whole volume of the loop not occupied by liquid was evacuated, filled with helium, and re-evacuated. Purified nitric oxide was then introduced through stopcock 3 until the manometer pressure was about 2 cm less than atmospheric pressure. Stopcock 3 was turned so as to shut off the manifold and make a path for the gas to flow from the gas reservoir through the pump into the liquid reservoir. The pump was started (set for 450 cc/min) and then stopcock 1 was opened. The pressure in the system began to fall, as some of the nitric oxide was used to form nitrogen dioxide, and so additional nitric oxide was added through stopcock 3. The pressure was kept slightly different from atmospheric so that if a leak developed it could be detected by a pressure change in the system.

The liquid reservoir was temperature-controlled by water from a constant-temperature bath. The Graham-type condenser above the liquid was kept cooler than the reservoir in order to prevent water vapor from circulating with the gas phase and thus, in effect, prevent the formation of nitric acid in

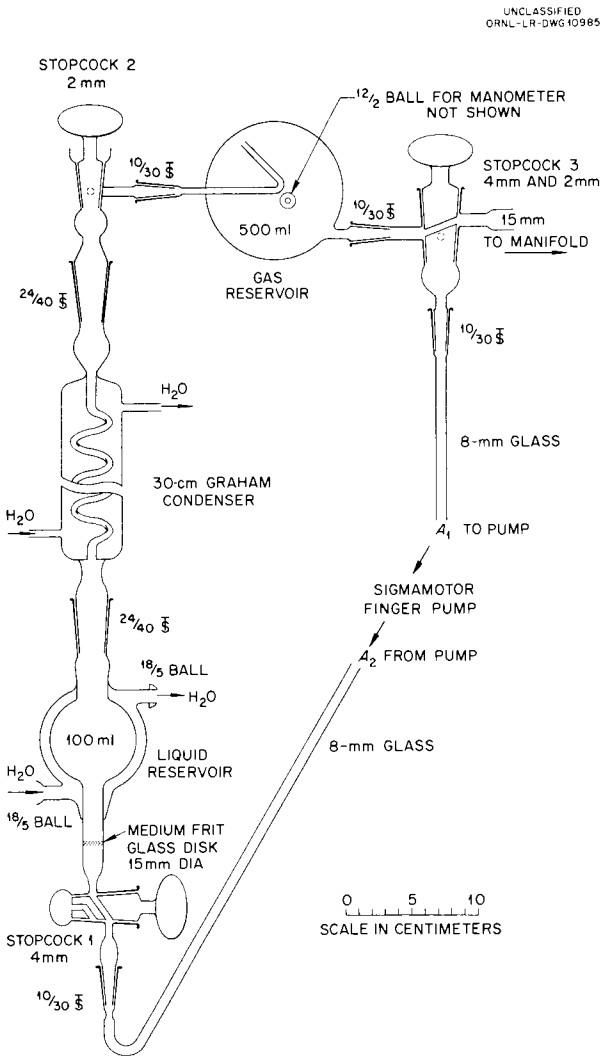

Fig. 2. Gas-Liquid Contact Loop for the Determination of Single-Stage Isotopic Separation Factors.

the gas. The gas was pumped around the loop for 2 hr at constant pressure. To stop the contacting operation, stopcocks 1 and 3 were closed simultaneously, and then the pump was stopped and stopcock 2 was closed. These operations isolated the bulk of the gas from the liquid phase. The liquid phase was left in the liquid reservoir with some gas with which it was already at equilibrium. The gas-phase isotopic samples were taken through stopcock 3 into the manifold and sealed in break-seal tubes. The connection below stopcock 1 was opened to make a sample port for the liquid phase. Helium at atmospheric pressure was run into the system through stopcock 2 to keep a constant pressure over the acid while it was being sampled through stopcock 1 for both chemical and isotopic purposes.

The contactor design is adaptable to other gas-liquid systems. The amount of holdup of either phase can be changed by substituting suitable glassware. Use of other stopcocks will allow pressures greater than atmospheric to be employed. The type of tubing can be changed, depending on the nature of the chemicals to be pumped. However, it is necessary that the tubing have both chemical inertness and mechanical strength.

Determination of the Separation Factor

The starting materials for all determinations in this study were purified nitric oxide and nitric acid solutions. Consequently, some of the nitric oxide had to be oxidized to nitrogen dioxide by nitric acid to establish chemical equilibrium. The gas phase was analyzed for nitric oxide and nitrogen dioxide content for most of the runs to ensure attainment of equilibrium. In every case the ratio of NO_2/NO was slightly greater than that calculated from the data of Abel, Schmid, and Stein,[4] which indicates that, within experimental error, equilibrium was reached during the 2 hr of equilibration. Figure 3 shows the gas-phase partial pressures plotted from the data of Abel, Schmid, and Stein.

Chemical analysis was more difficult for the liquid phase than for the gas. Analyses for NO_3^- and "NO" were made, where "NO" was a measure of the reducing power of the solution. The separation into individual species such as N_2O_3, NO, NO_2, HNO_2, and HNO_3 was not undertaken. Figure 4 shows a curve of the "NO" concentration determined from the reducing power of the solution.

Isotopic samples of the gas phase were prepared by sealing some of the gas in tubes containing pure iron powder. The tubes were heated to 350°C overnight to reduce the oxides to nitrogen. Portions of the liquid phase were neutralized with sodium hydroxide and then evaporated to sodium nitrate. From this point on, quantitative recovery of the nitrogen content from the sample was required in order to preclude additional isotopic

[4] H. E. Abel, H. Schmid, and M. Stein, *Z. Elektrochem.* 36, 692 (1930).

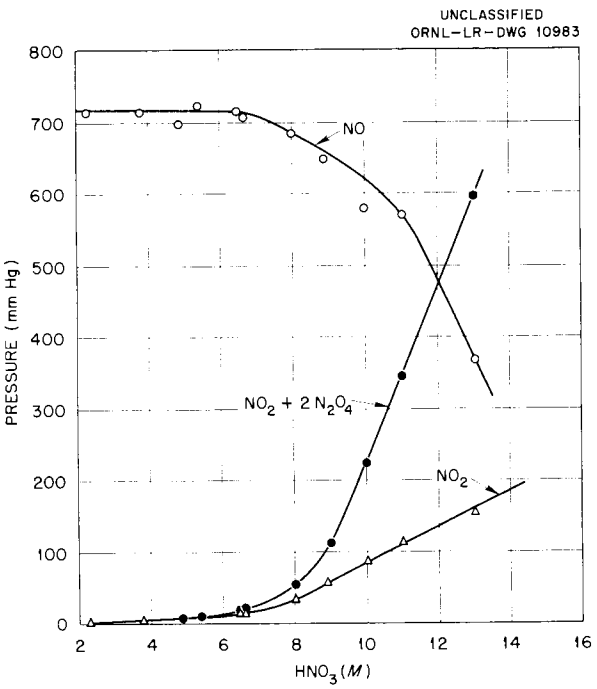

Fig. 3. Gas-Phase Partial Pressures in Equilibrium With Nitric Acid.

fractionation. Each of the following three methods was used:

$$(1)\quad NO_3^- + Hg \xrightarrow[H_2SO_4]{conc} NO(g) \xrightarrow[350°C]{Fe} N_2$$

$$(2)\quad NO_3^- + Fe^{++} \xrightarrow[H_2SO_4]{conc} NO(g) \xrightarrow[350°C]{Fe} N_2$$

$$(3)\quad NO_3^- + Alloy^5 \xrightarrow[NaOH]{conc} NH_3(g) \xrightarrow{H^+} NH_4^+$$

$$NH_4^+ + OBr^- \xrightarrow{OH^-} N_2$$

All three methods are essentially standard for quantitative analysis of nitrate, but the third method was found to be the most reliable. The first two occasionally gave some nitrogen dioxide, which was undesirable since an isotopically homogeneous sample did not result. Six identical samples of each phase were submitted for isotopic analysis. The assays were obtained as the quotient

[5]Devarda's alloy: 50% Cu, 45% Al, 5% Zn.

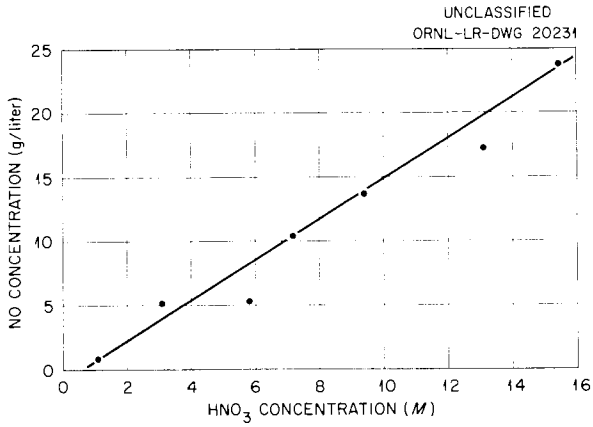

Fig. 4. Dissolved "NO" vs Nitric Acid Concentration for the Nitrox System.

of the N^{15}/N^{14} ratio for the sample to the ratio for a standard nitrogen sample.

The single-stage fractionation factors at 26°C are shown in Table 1 for the equilibrium acid concentrations indicated. Figure 5 shows the same data in graphic form. The 95% confidence interval is calculated from the six replicate mass analyses. The pressure was constant for any single concentration, but over the entire range it varied from 695 to 725 mm Hg.

Table 1. Single-Stage Fractionation Factors for the Nitrox System

HNO_3 Concentration (M)	α^* (95% C.I.)
1.084	1.064 ± 0.001
3.08	1.057 ± 0.005
5.82	1.060 ± 0.002
6.10	1.062 ± 0.003
7.20	1.053 ± 0.005
9.40	1.053 ± 0.002
10.20	1.040 ± 0.003
13.10	1.018 ± 0.003
14.20	1.027 ± 0.001
15.45	1.020 ± 0.001

$$*\alpha = \frac{(N^{15}/N^{14})_{liquid}}{(N^{15}/N^{14})_{gas}}.$$

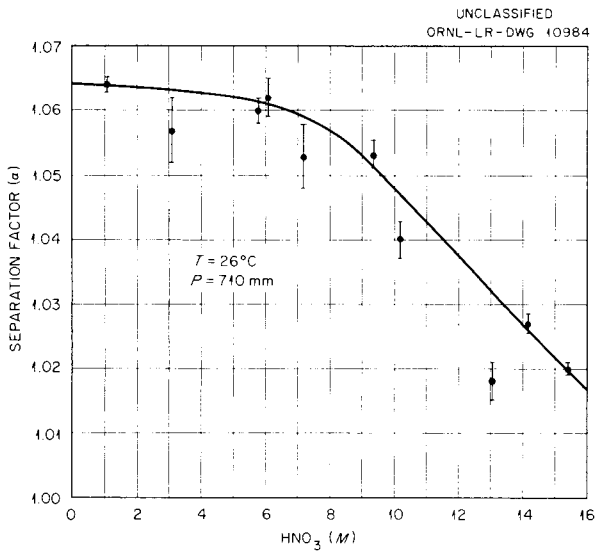

Fig. 5. Nitrox Isotopic Separation Factor vs Nitric Acid Concentration.

Calculation of the Separation Factor

The Nitrox system contains many chemical species, and therefore estimation of the separation factor as a function of nitric acid concentration is difficult. The gas phase consists primarily of NO, NO_2, and N_2O_4, with small amounts of N_2O_3 also present. The liquid phase contains NO_3^-, dissolved NO, undissociated HNO_3, HNO_2, NO_2^-, and probably other ions and molecules. As a first approximation the gas phase can be considered as consisting of NO, NO_2, and N_2O_4 in the proportions given by Abel, Schmid, and Stein.[4] The liquid phase will be treated simply as NO_3^- with dissolved "NO" as determined experimentally by the reducing power of the solution (see Fig. 4). In this simple picture the reactions responsible for isotopic concentration are

(1) $N^{15}O + N^{14}O_3^- \rightleftharpoons N^{14}O + N^{15}O_3^-$

(2) $N^{15}O_2 + N^{14}O_3^- \rightleftharpoons N^{14}O_2 + N^{15}O_3^-$

(3) $N_2{}^{15}O_4 + 2N^{14}O_3^- \rightleftharpoons N_2{}^{14}O_4 + 2N^{15}O_3^-$

In the estimation of the separation factors for the above reactions, the separation factors for the following reactions can be used:

(4) $N^{15}O + N^{14}O_2 \rightleftharpoons N^{14}O + N^{15}O_2$

(5) $2N^{15}O_2 + N_2{}^{14}O_4 \rightleftharpoons 2N^{14}O_2 + N_2{}^{15}O_4$

The isotopic separation factor for reaction 1 is the isotopic ratio of N^{15} to N^{14} in the NO_3^- ion divided by the N^{15}-to-N^{14} ratio in the gaseous nitric oxide:

$$\alpha_1 = \frac{(N^{15}/N^{14})NO_3^-}{(N^{15}/N^{14})NO} .$$

The isotopic separation factors for the other reactions defined similarly will be designated as α_2, α_3, α_4, and α_5, respectively.

The separation factor for reaction 1 may be estimated from the Nitrox data at low acid concentrations, where the phases are nearly pure NO and NO_3^-. Correction for dissolved "NO" gives a value of 1.065. The separation factor for reaction 4 has been determined by Begun and Melton[6] to be 1.028, and that for reaction 5 has been estimated by Begun[7] to be approximately 1.023. From these values the separation factor for reaction 2 may be calculated to be 1.036 and that for reaction 3 to be 1.013. It should be realized that these values may vary by ±0.002 because of uncertainties in the determinations.

For low concentrations of N^{15} it can be shown that

$$(\alpha - 1) = M_1(\alpha_1 - 1) + M_2(\alpha_2 - 1) + M_3(\alpha_3 - 1) ,$$

where

α = the effective over-all separation factor measured for the system,

M_1 = the fraction of the total N as NO,

M_2 = the fraction as NO_2, and

M_3 = the fraction as N_2O_4.

Table 2 shows the results of calculations made in this manner. Dissolved "NO" was assumed to have the same isotopic concentration as the gaseous nitric oxide, and a correction of the separation factor was made for this quantity.

Considering the approximations made, the calculated and observed values agree quite well. The decrease of nitric oxide and the increase of nitrogen dioxide and nitrogen tetroxide in the gas-phase quilibrium mixture are largely responsible for the reduced separation factor at the higher acid concentrations.

---

[6] G. M. Begun and C. E. Melton, *J. Chem. Phys.* 25, 1292 (1956).

[7] G. M. Begun, *J. Chem. Phys.* 25, 1279 (1956).

Table 2. Calculated and Observed Separation Factors for the Nitrox System

Molarity of HNO_3	Fraction of Gas Phase N as			Calculated Separation Factor*	Experimental Separation Foctor**
	NO_2	N_2O_4	NO		
2	0.000	0.000	1.000	1.064	1.064
4	0.007	0.001	0.992	1.064	1.063
6	0.014	0.004	0.982	1.061	1.061
8	0.041	0.027	0.932	1.059	1.057
9	0.078	0.065	0.856	1.056	1.054
10	0.101	0.161	0.738	1.051	1.049
11	0.121	0.258	0.621	1.046	1.044
12	0.150	0.348	0.502	1.040	1.038
13	0.173	0.440	0.387	1.035	1.033

*Corrected for dissolved "NO".

**$\dfrac{(N^{15}/N^{14})_{liquid}}{(N^{15}/N^{14})_{gas}}$.

PRODUCT REFLUX STUDIES

In order to produce highly concentrated N^{15}, the conversion of nitric acid to nitric oxide and nitrogen dioxide in the reflux reaction at the product end of the system must be highly quantitative. This requirement is imposed by the high reflux ratios (of the order of 7000/1) that must be employed to produce N^{15} enrichments of 95% or greater. It is desirable to cut the losses of enriched nitrogen to 1 part in 20,000 or less; therefore a study was made of the continuous reaction of sulfur dioxide with nitric acid to form nitric oxide plus nitrogen dioxide in order to design an efficient refluxer. Since it is also desirable from an economic standpoint to produce sulfuric acid of as high concentration as possible, studies were made of this factor.

The two predominant reactions which take place between the sulfur dioxide and nitric acid are

(1) $3SO_2 + 2HNO_3 + 2H_2O \rightleftharpoons 3H_2SO_4 + 2NO$

(2) $SO_2 + 2HNO_3 \rightleftharpoons H_2SO_4 + 2NO_2$

The composition of the gas mixture leaving the refluxer is a function of the concentration of nitric acid entering the refluxer, the temperature of the reaction, and the degree of equilibration above the reaction zone. When the gas mixture entering the exchange column contained more than the equilibrium amount of nitric oxide, it was found to equilibrate quite rapidly. However, when the refluxer produced more than the equilibrium percentage of nitrogen dioxide, equilibration in the opposite direction was found to be relatively slow. Since it is desirable for the column to operate under chemical equilibrium, excess nitrogen dioxide formation in the refluxer should be minimized.

Spindel and Taylor[8] found that the excess nitrogen dioxide in the gas produced by the refluxer could be reduced by diluting the nitric acid with water before the acid entered the refluxer. This dilution has two effects: It speeds the chemical equilibration by lowering the acid concentration and lowers the temperature of the reaction zone, which results in production of less nitrogen dioxide.

Figure 6 shows a diagram of a typical test refluxer. A water inlet, a nitric acid inlet, and a gas sampling port were provided at the top of the refluxer. A sulfur dioxide inlet and a sulfuric acid outlet through a gravity leg were located at the bottom of the unit. Glass helices were found to be an effective packing. A cooling jacket and an internal cooler were found to be necessary to

[8]W. Spindel and T. I. Taylor, *J. Chem. Phys.* 23, 981–82 (1955).

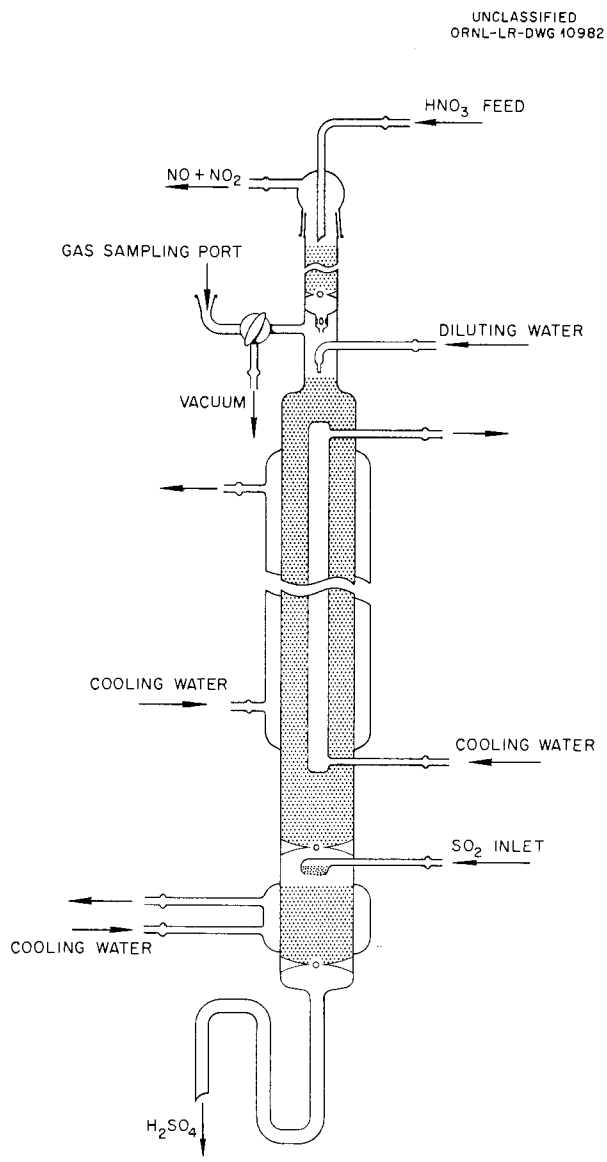

Fig. 6. Nitrox System Product-End Refluxer.

remove the heat of reaction in a satisfactory manner.

In operation a refluxer liberated heat in a rather sharp reaction zone. The lower portion of this reaction zone was defined by the white color of the packing below, contrasted with the intense brown nitrogen tetroxide color where the reaction began. The reaction zone with the intense brown color was generally about 1 in. long but became considerably longer when the water-cooled area of the refluxer was reduced or eliminated. Above the reaction zone the nitric acid was emerald green in color, due to dissolved oxides of nitrogen. The color intensity of the gas decreased as the gases proceeded up the refluxer. The color intensity of the brown gas mixture leaving the top of the refluxer varied with the concentration of nitric acid, the area of the cooling surface, and the distance of the reaction zone from the top of the refluxer. Three refluxers of this type were studied. They differed mainly in the placement of the water-cooling devices and in the length of the packed section. Refluxer A was 46 cm long, with an inside diameter of 2.5 cm, had an internal spiral cooling coil, and was packed with $\frac{1}{16}$-in. glass helices. Refluxer B had a 30-cm-long packed section which, through the use of three concentric tubes, had both internal and external cooling surfaces. The packing material was $\frac{1}{32}$-in. glass helices. Refluxer C (shown in Fig. 6) had a 44-cm-long section, was 2.5 cm in inside diameter, and was packed with $\frac{3}{32}$-in. glass helices. Table 3 shows data obtained by operating refluxers A and B at nitric acid flows of 80 ml/hr. In the runs made with water addition the rate of water addition was 37 ml/hr.

It was found that the nitrogen dioxide content of the gas from refluxer B was lower than that of the gas from refluxer A. This lower content resulted from better cooling of the reaction zone. Water addition to refluxer B gave a large increase in the ratio $NO(g)/NO_2(g)$. Addition of this much water, however, was found to increase appreciably the losses of nitrogen in the waste sulfuric acid. Table 4 shows additional results of operating refluxer B at a constant nitric acid flow rate of 85 ml/hr. Runs were made at various nitric acid feed concentrations and with two different lengths of packed column above the reaction zone.

The data illustrate the decrease in reaction rate of the reaction

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$$

as the nitric acid concentration is increased. The effect of increased column length was to decrease the excess nitrogen dioxide in the gaseous mixture, as is illustrated in run 4. Refluxer C was found to operate very successfully at a flow rate of 240 ml of 7 *M* HNO_3 per hour. Reaction with the sulfur dioxide occurred just below the inside cooling condenser. Under these conditions the mole ratio of NO/NO_2 was nearly the equilibrium value for 7 *M* HNO_3, and the total nitrogen losses

Table 3. Effect of Cooling Methods and Water Dilution on the Product-End Reflux Reaction

	HNO_3 Feed (*M*)	Mole Ratio, NO/NO_2	Effluent		
			H_2SO_4 (*M*)	SO_2 (*M*)	Total Nitrogen (ppm*)
Refluxer A	10.1	1.09	10.1	0.46	64
	10.1		9.8	0.57	58
	10.1	0.89	9.6	0.58	67
	10.1		10.0	0.45	
Refluxer B	10.1	1.6	10.6	0.44	32
Refluxer B with	6.8	5.8	9.7	0.37	136
water dilution	6.8	5.4	9.5	0.45	121

*Calculated on the basis of gram atoms of nitrogen.

Table 4. Effect of Nitric Acid Concentration and Gas Path Length in Product Refluxer

Experiment No.	HNO_3 Feed (*M*)	Gas Path Length (cm)	Mole Ratio, NO/NO_2	Effluent		
				H_2SO_4 (*M*)	SO_2 (*M*)	Total Nitrogen (ppm*)
1	6.1	8	9.2	8.0	0.68	90
2	8.1	8	3.2	9.5	0.71	121
3	10.1	8	1.9	10.3	0.64	116
4	6.1	20	44.6	8.0	0.57	97
5	8.1	20	5.7	9.6	0.47	96
6	10.1	20	1.8	10.6	0.47	27

*Calculated on the basis of gram otoms of nitrogen.

were reduced to 15 ppm. Approximately 9 *M* H_2SO_4 with a sulfur dioxide content of 0.36 mole/liter was produced.

The cost of producing enriched N^{15} by the Nitrox system can be lowered by the sale of the sulfuric acid produced in the product reflux reaction.[9] A series of experiments were performed to determine the relation between the concentration of sulfuric acid produced by the Nitrox product-end refluxer and the concentration of nitric acid fed to the system. Since the separation factor for the Nitrox system decreases with an increase in nitric acid concentration, the relation between the separation factor and the concentration of sulfuric acid produced by the refluxer can be maximized from such data.

The product refluxer was operated for 3 to 5 hr at each nitric acid concentration. Three sulfuric acid samples were taken for each experiment at intervals after the first hour of operation. The experimental results are presented in Table 5 and plotted in Fig. 7.

From these data it is apparent that the highest concentration of sulfuric acid which can be produced by this reflux is approximately 11 *M*, or 68%. The leveling off in sulfuric acid concentration as the nitric acid concentration becomes greater than 9 *M* is caused by the change in the stoichiometry

[9] B. B. Klima *et al.*, *Estimate of the Cost of Producing Nitrogen-15 by Chemical Exchange: Nitric Acid–Nitric Oxide System Using Sulfur Dioxide Reflux*, ORNL CF-55-1-22 (Jan. 14, 1955).

Table 5. Effluent Data for Product-End Reflux

Average HNO_3 Concentration in Feed (moles/liter)	Average Concentration (moles/liter) in Effluent	
	H_2SO_4	SO_2
15.4	11.0	0.26
13.9	10.9	0.31
11.9	10.9	0.35
9.4	10.7	0.37
7.0	9.0	0.31
4.7	6.5	0.41
2.8	4.1	

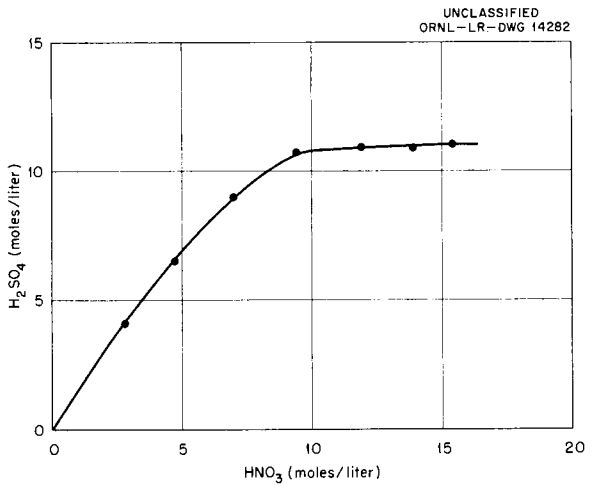

Fig. 7. Concentration of Waste Sulfuric Acid as a Function of Nitric Acid Molarity for the Nitrox System.

of the reaction as shown by Eqs. 1 and 2 and by the sulfuric acid produced from the higher concentrations of nitric acid occupying an appreciably smaller volume than the nitric acid solution from which it was made. By using the equations for the net reactions that occur in the product refluxer along with the data of Abel, Schmid, and Stein[4] and the specific gravity data from the *Handbook of Chemistry*,[10] it can be shown that the volume change and the change in the stoichiometry are compensatory as the concentration increases.

[10]N. A. Lange, *Handbook of Chemistry*, 8th ed., p 1180, Handbook Publishers, Sandusky, 1952.

COLUMN ENRICHMENT STUDIES

In order to evaluate further the isotope separation potentialities of the Nitrox system and to provide design data for larger units, a small laboratory column was operated to enrich N^{15}. This unit was designed to operate continuously, with attention given to it only during the day shift. Figure 8 shows a schematic diagram of the apparatus. The 15-mm-ID water-cooled exchange column was 7 ft long and was packed with Podbielniak stainless steel Heli-Pak, 0.03 × 0.070 × 0.070 in. The product refluxer with internal and external cooling was packed with $\frac{3}{32}$-in. glass helices for about 12 in. above the sulfur dioxide inlet. A short section at the bottom of this refluxer, serving to cool the hot sulfuric acid effluent, was also packed with this material. The water-cooled waste-end refluxer was 3.5 ft long, with an inside diameter of 1 in., and was packed with $\frac{3}{32}$-in. glass helices. The exchange column and both refluxers were constructed of glass. The delivery lines were, for the most part, $\frac{1}{4}$-in.-OD stainless steel tubing. Glass-to-stainless steel connections were made with heavy-walled Teflon tubing.

The procedure was to deliver approximately 7 *M* HNO_3, by means of a microbellows pump, from an "infinite reservoir" to the top of the exchange column. As the acid passed down the column it exchanged with a countercurrent stream of nitric oxide containing a small fraction of nitrogen dioxide. In the product refluxer the nitric acid, enriched in the N^{15} isotope, reacted with sulfur dioxide to produce oxides of nitrogen and sulfuric acid saturated with sulfur dioxide. The latter mixture flowed from the bottom of the refluxer, and the oxides of nitrogen passed up the refluxer and into the exchange column. By the time that these gases had proceeded a few inches into the exchange column, chemical equilibrium had been established with the 7 *M* HNO_3. Therefore mainly nitric oxide, with a low concentration of nitrogen dioxide, contacted the downward flowing nitric acid. After leaving the exchange section, the nitric oxide reacted with oxygen to produce nitrogen dioxide, which then passed countercurrently to water in the waste-end refluxer. The reaction which takes place between the water and this particular nitrogen oxide is

$$3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$$

The reaction was carried out in the presence of

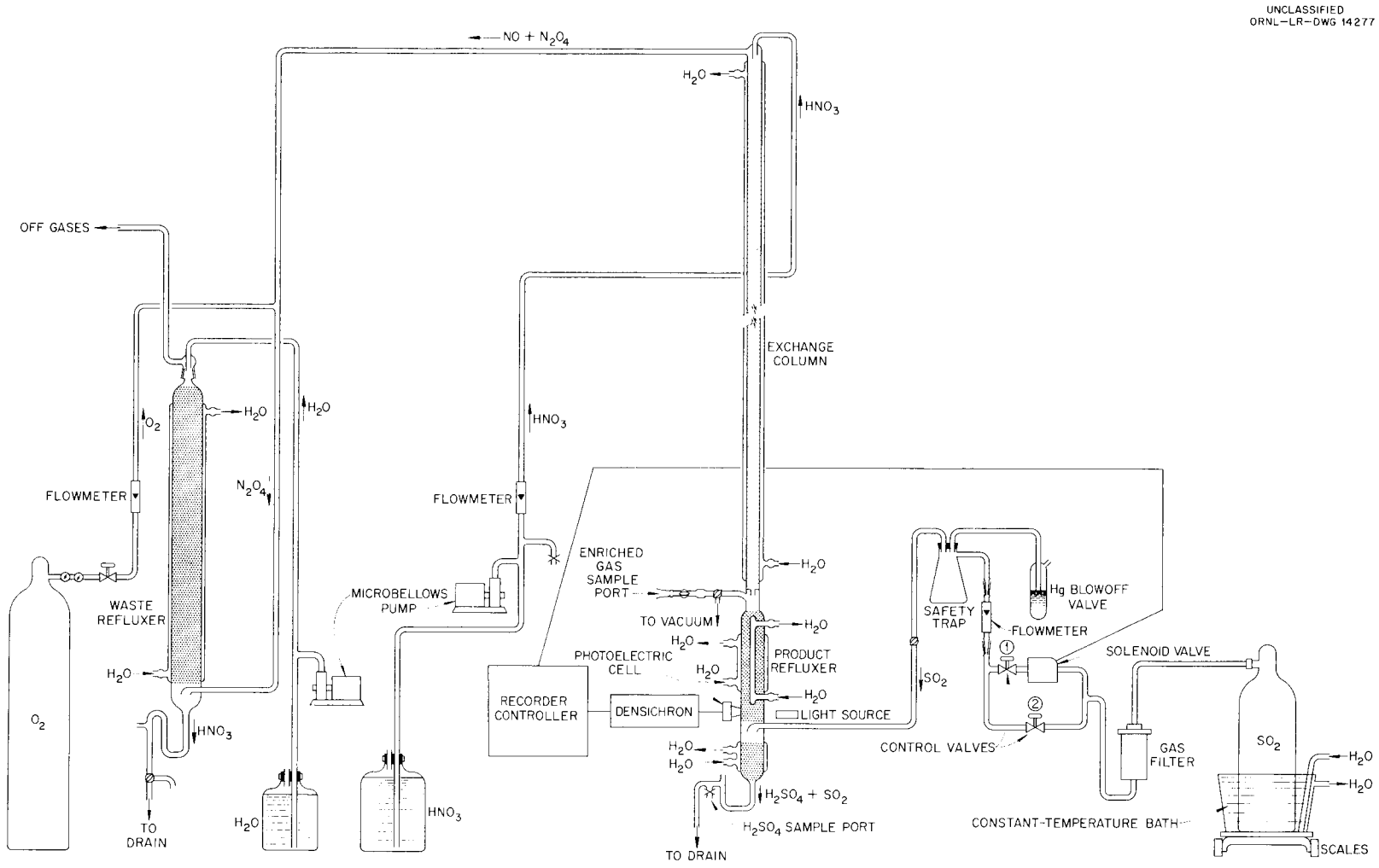

Fig. 8. Schematic Diagram of Laboratory Column and Equipment for Study of the Nitrox Process.

excess oxygen in order to convert all the nitric oxide to nitrogen dioxide. In large-scale operation, where chemical costs are of major importance, a high percentage of this re-formed nitric acid would be returned to the system as feed material. However, in this operation the nitric acid formed was sampled and discarded.

An automatic control of the flow of the sulfur dioxide was utilized to minimize the shifts in the isotopic gradient caused by the movement of the reaction zone in the product refluxer. Control was based upon the fact that there is a sharp color difference at the reaction zone – red-brown nitrogen dioxide above the reaction interface and clear solution below. The intensity of the light transmitted horizontally by the refluxer depends upon whether the clear solution or the red-brown solution intercepts the light beam. A light source was placed on one side of the refluxer, directly opposite a photoelectric cell whose electrical output was rectified and amplified by a Densichron unit. The output of this unit was fed to a recorder which controlled a normally closed solenoid valve (see Fig. 8). During column operation a constant flow of sulfur dioxide to the product refluxer was maintained through control valve 2. This flow was slightly less than the stoichiometric flow of sulfur dioxide required to hold the reaction zone at a constant level; hence the red-brown color moved downward in the refluxer and finally intercepted the light path. The solenoid valve then opened, increasing the flow of sulfur dioxide until the red-brown color moved up. The solenoid then closed and the cycle was repeated. This sensitive device functioned well and resulted in smooth column operation.

Enriched gas was sampled periodically at the head of the product refluxer. Approximately 5 ml of gas at 300 mm pressure constituted a sample, and it was captured in an evacuated break-seal tube containing a small quantity of pure iron powder. The samples were heated overnight at 350°C to reduce the oxides of nitrogen to molecular nitrogen. A mass analysis was then made of the samples. Samples were also taken for chemical analysis of the sulfuric acid effluent from the product refluxer and of the nitric acid produced by the waste refluxer. Operational data for three runs made with this equipment are summarized in Table 6. Cooling water temperatures varied from 23 to 31°C during the runs.

At the start of run 2 the relative flow of oxygen to the waste refluxer was increased, which resulted in a higher recovery of the oxides of nitrogen. After 18 hr of operation in run 2 the sulfur dioxide flow was insufficient for a short time, resulting in some losses through the product refluxer and a slowing down of the increase in isotopic concentration. In preparation for run 3, the holdup in the product refluxer was reduced by approximately one-half to reduce the equilibrium time. The holdup reduction was effected by reducing the diameter of the refluxer and the amount of packing. With this reduction in holdup, chemical equilibrium between the oxides of nitrogen and the nitric acid

Table 6. Operational Data for Runs 1 to 3

Run No.	Feed HNO_3		Product Reflux Effluent			Total Time in Continuous Operation	Final Total Separation[a]
	Moles per Liter	Cubic Centimeters per Hour	H_2SO_4 (moles/liter)	SO_2 (moles/liter)	N (ppm)		
1	7.10	210	9.1	0.22	10	7 hr	3.05
2	7.10	390	9.1	0.29	5	60 hr	11.0
3	6.97	360 164[b]	9.0	0.31	8	9 days	31.8[c] 52.1

[a] Total separation $= \dfrac{(N^{15}/N^{14})_{product}}{(N^{15}/N^{14})_{initial}}$.

[b] Changed to 164 ml after seven days.

[c] After seven days.

was no longer achieved in the refluxer, but at the base of the column. At the same time, the sulfur dioxide tank was placed in a constant temperature bath at 32°C, and heating tape was placed on the sulfur dioxide lines to keep them above 32°C. This resulted in a smoother flow of sulfur dioxide.

Figures 9 and 10 show plots of the isotopic analyses from runs 1 and 2. Here, total separation is defined as

$$\frac{(N^{15}/N^{14})_{product}}{(N^{15}/N^{14})_{feed}} .$$

The product samples were taken at time intervals from the bottom of the exchange column. Figure 11 shows the results of isotopic analyses made on the samples from run 3.

If a separation factor of 1.055 is assumed, the stage height can be calculated for the two flow rates used in experiment 3. At a flow rate of 360 ml of nitric acid per hour, there were approximately 65 stages in the column at equilibrium, yielding a stage height of 1.3 in. At a flow rate of 164 ml/hr, the number of stages increased to 74 and the stage height was reduced to 1.1 in.

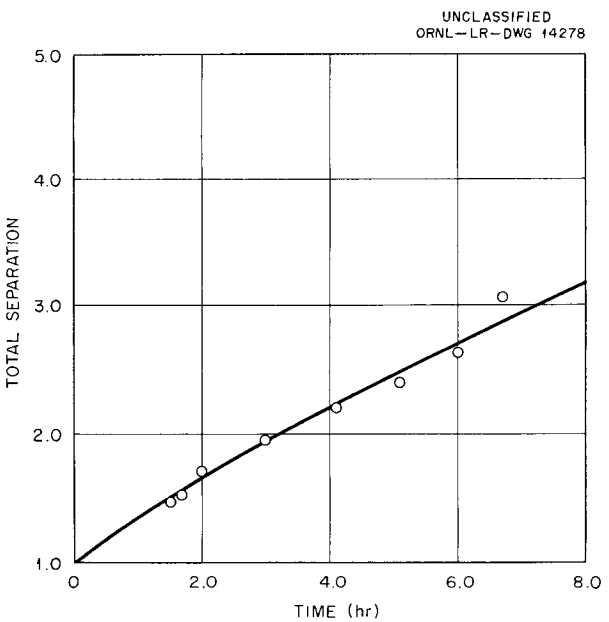

Fig. 9. Time vs Total Separation Curve for Run 1.

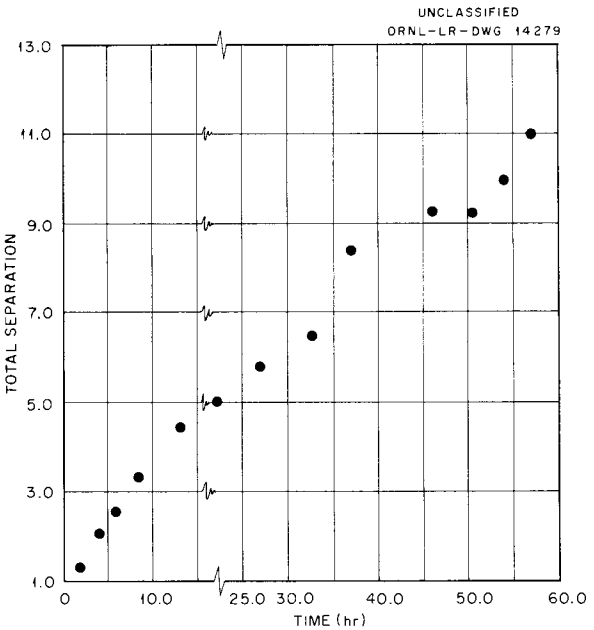

Fig. 10. Time vs Total Separation Curve for Run 2.

NITROX PRODUCT UNIT

In order to provide scale-up data and to further evaluate the Nitrox system, it was decided to construct a small unit that would produce high purity N^{15} in gram quantities. Accordingly, a two-column cascade was designed, along with the associated refluxers and control equipment needed.

Design Considerations

The normal abundance of N^{15} is 0.37 at. %. This low starting concentration makes it necessary to process large quantities of nitric acid to produce appreciable amounts of N^{15}. Figure 12 shows a plot of x_n on a logarithmic scale vs V_{min}/D, where x_n is the mole fraction of N^{15} in the gas phase at stage n, V is the interstage flow, and D is the product withdrawal rate. The formulas of Shacter and Garrett[11] were used to make the calculations, and the product was assumed to contain 99.38% N^{15}. The smallest reflux ratio that can be used to produce the required product assay if an infinite number of stages are used is represented by V_{min}/D. In actual practice, 1.1 to 1.4 V_{min}/D is used. The minimum number of stages required to

[11] J. Shacter and G. A. Garrett, *Analogies Between Gaseous Diffusion and Fractional Distillation*, AECD-1940 (April 7, 1948).

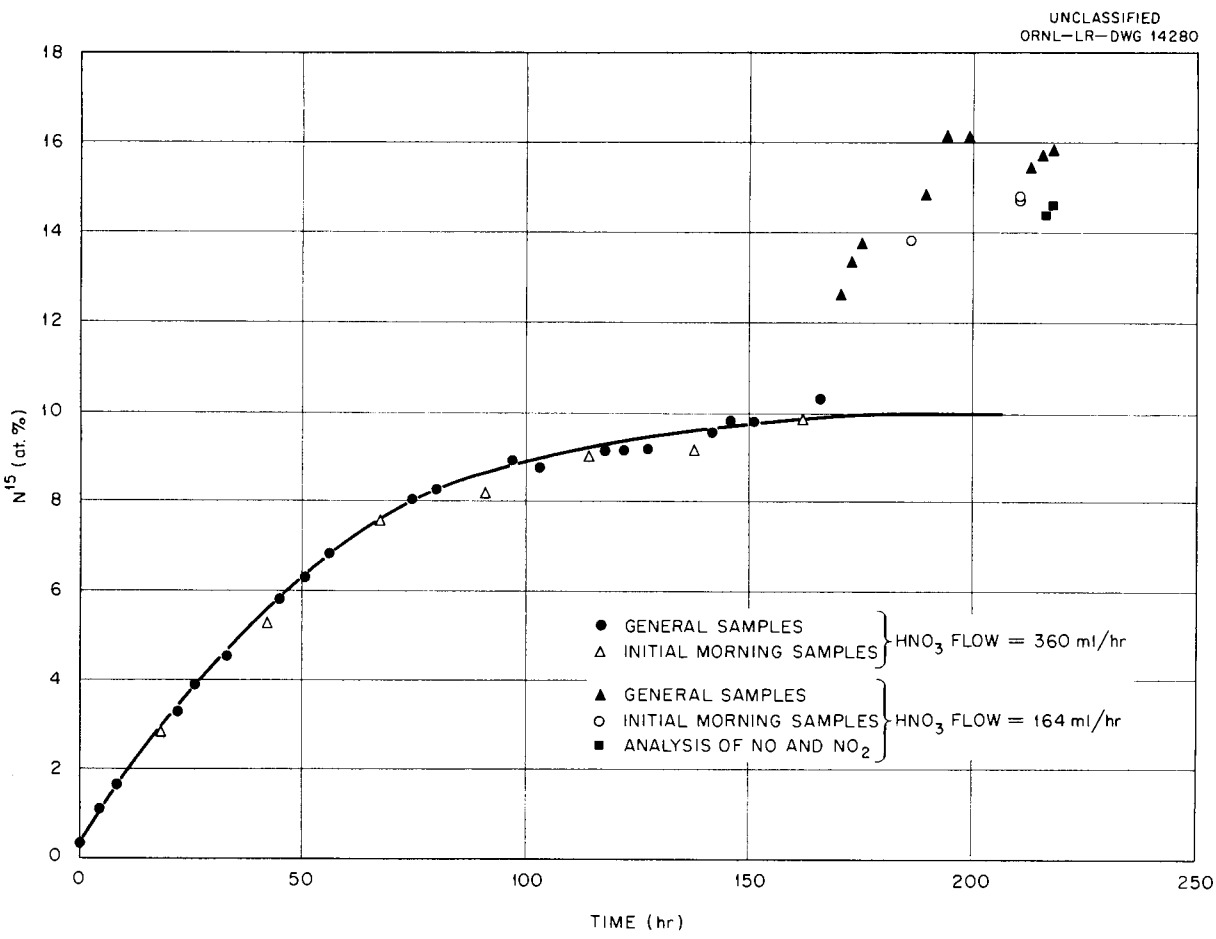

Fig. 11. Time vs Per Cent of N^{15} from Run 3.

produce 99.38% N^{15} under total reflux conditions, with a separation factor of 1.055, is 200.

From Fig. 12 it can be seen that a square cascade (that is, one where the interstage flow needed at the feed point is maintained all the way through the system) would contain an excessive holdup of enriched N^{15} in the latter part or top of the cascade. Equilibrium time calculations showed that at least a month would be required for the gradient to be established in such a cascade. In addition, since the stage efficiency of large columns is poorer than that of small columns, some 70 to 80 ft of 2-in. column would be required to produce 99.38% N^{15}. If, however, the cascade is broken into two units or tapered, the total length of column required and the equilibrium time can be reduced. Figure 12 shows that if the first column is designed to produce 5 to 10% N^{15}, the second column can be quite small, since most of the separation work will be accomplished in the first column. Thus it was decided that the cascade should consist of two columns in series. For the first column a 2-in.-ID glass pipe 20 ft long was chosen, and for the second column a ½-in.-ID glass pipe 20 ft long was selected. It was estimated that the equilibrium time for this entire system would be between five and ten days, depending upon the holdup in the refluxers, and that the 5 to 10% N^{15} produced in the first column would be enriched to better than 99% N^{15} in the second column. The apparatus was designed with the objective of making operation nearly automatic so that manpower requirements would be kept to a minimum.

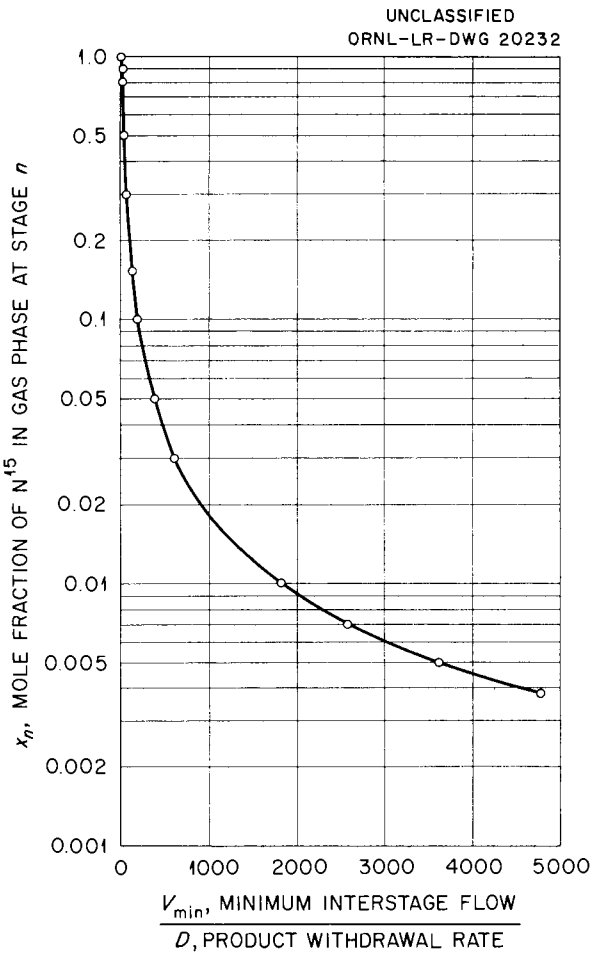

Fig. 12. Plot of x_n vs V_{min}/D for a Product Concentration of 99.38 % N^{15}.

The Enriching Unit

A schematic drawing of the enriching unit is shown in Fig. 13. The apparatus used and the operating procedure were as follows: Seven molar nitric acid was metered from a 1000-gal feed tank by a Lapp Pulsafeeder proportioning pump into the top of column I, which consists of 20 ft of 2-in.-ID glass pipe packed with 0.05 × 0.05 × 0.10 in. stainless steel Heli-Pak. Nitric acid from the bottom of column I flowed into refluxer I. This all-glass unit was 3 in. in diameter and 78 in. long. An internal cooling coil $1\frac{7}{8}$ in. in diameter extended down 38 in. from the top. A cooling jacket 4 in. in diameter extended 36 in. down from the top, except for a 2-in. unjacketed portion 28 in. from the top for interface control. Below the cooling coils a 34-in. unjacketed section provided a stripping section above the sulfur dioxide inlet. Sulfur dioxide gas from a 1-ton cylinder of liquid sulfur dioxide passed through a pressure-regulating valve, a surge tank, a control system, and into the refluxer 72 in. from the top. The refluxer was packed with $\frac{3}{16}$-in.-dia glass helices. The sulfuric acid produced in the refluxer passed from a gravity leg through a neutralizing bed to the drain. The nitric oxide and nitrogen dioxide produced by the refluxer passed up the exchange column. Water could be metered into the refluxer if desired, and a gas sample port was provided.

A portion of the flow in column I (~5%) was withdrawn and pumped by a microbellows pump to the top of column II. Column II consists of 20 ft of $\frac{1}{2}$-in.-ID glass pipe packed with 0.030 × 0.030 × 0.070 in. stainless steel Heli-Pak. Refluxer II at the bottom of the column was of all-glass construction and was $1\frac{1}{2}$ in. in inside diameter and 27 in. long. A 0.4-in.-dia cooling tube extended 10 in. down from the top, and a cooling jacket extended 7 in. from the top. The sulfur dioxide inlet was 22 in. from the top. The refluxer was packed with $\frac{1}{8}$-in. glass helices. The interface operating level was 1 in. below the cooling jacket. The nitric oxide plus nitrogen dioxide produced in the refluxer passed up exchange column II, out the top of the column, and into the bottom of column I. A means of metering water into the refluxer was provided. Provision was made for withdrawal of samples of gaseous nitric oxide plus nitrogen dioxide and for removing product nitric acid at intervals.

Waste nitric oxide plus nitrogen dioxide from column I entered refluxer III 4 ft from the bottom. This refluxer consisted of 12 ft of 6-in. glass pipe packed with $\frac{1}{2}$-in. Berl saddles and was used to absorb the nitric oxide and nitrogen dioxide. Air entered the bottom of the refluxer to convert nitric oxide to nitrogen dioxide, and water was metered into the top of the column. The nitric acid formed was passed to the drain through a neutralizing bed of limestone.

Stainless steel tubing was used for all sulfur dioxide, nitric acid, and vent lines. Teflon or Kel-F gaskets were used for all flange joints, and Koroseal tubing was used for the gravity legs. Polyethylene tubing was used for drain lines to the neutralizer. The nitric acid and sulfur dioxide were both filtered through micrometallic stainless steel filters. Spare nitric acid pumps were provided because of the necessity of continuous operation.

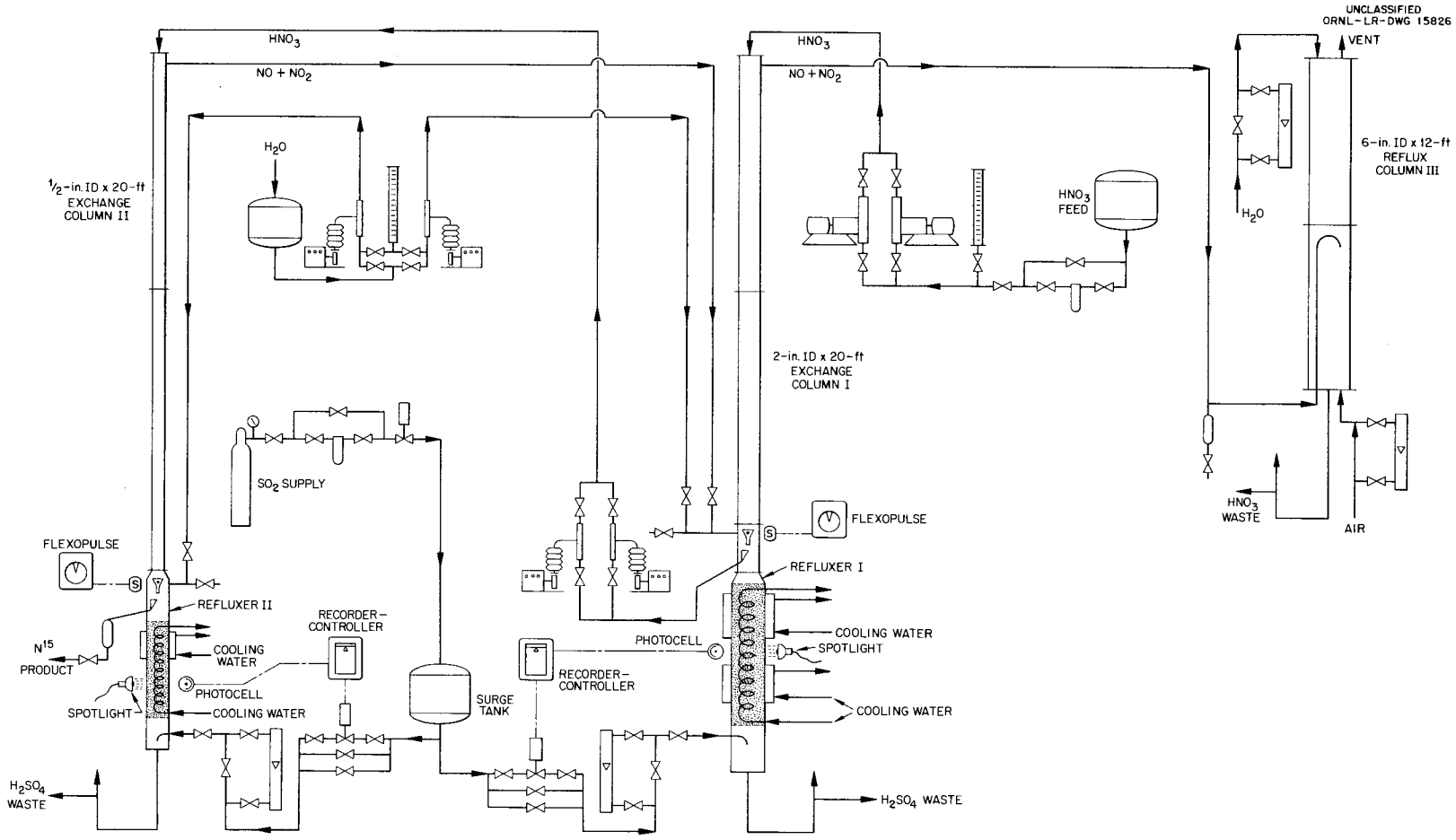

Fig. 13. Schematic Diagram of Nitrox Enrichment Unit.

In order to produce highly enriched N^{15} it is necessary to operate the unit continuously. Approximately five to ten days are required to build up an isotopic gradient before the product can be removed. Automatic operation and control of the apparatus are therefore advantageous. In operation the nitric acid flow to column I was metered at a constant rate. Sulfur dioxide flow to the refluxer was varied in order to maintain the reaction interface at a constant level in the refluxer. A definite color interface existed in the refluxer between the brown nitrogen dioxide color and the colorless sulfuric acid below. A spotlight which shone through the column and registered on a photocell on the opposite side of the refluxer was placed at the desired operating level. The photocell output was amplified by a Densicron photometer, and the output was fed to a Brown recorder-controller. When the interface turned brown, the controller operated a solenoid valve on a bypass sulfur dioxide line, which remained open until the interface color became light again. Each refluxer had its own control system. Spare lights were provided which went on automatically when a bulb burned out. By proper adjustment of the main and bypass flows of sulfur dioxide, good control was obtained. In order to protect the stainless steel packing and other parts from attack by sulfuric acid and sulfur dioxide in the event of a power failure, a normally open solenoid valve was placed in the sulfur dioxide supply line. A time-delay circuit was installed which shut down the pumps and the sulfur dioxide supply when the power failure lasted for more than 30 sec.

At the bottom of column I a deflecting funnel diverted a small portion of the acid, which was then pumped to the top of column II. The funnel was deflected by an electromagnet energized periodically by an electronic timer, enabling any constant fraction of the flow in column I to be diverted to column II. The product-removal device at the bottom of column II was of a similar type but with a much slower timer, as only a very small fraction of the flow was withdrawn.

Operation of the Cascade

Operation during the first run was erratic, and numerous difficulties had to be overcome. The Lapp pumps were rebuilt to give constant flow rates, and the control circuits for the sulfur dioxide supply were made more dependable. It was found that the initial design of both refluxers I and II was not entirely satisfactory and that further refluxer development work was necessary. This was especially true of refluxer I, the large unit. Experience with several designs showed that the diameter of the refluxer, the diameter of the packing, and the cooling area available were important. Fine packing ($\frac{1}{8}$-in. glass helices) produced a very sharp interface with good control features. However, when the reaction was carried out in a short band, the overheating which resulted made operation difficult. It was also found that too much cooling produced a solid formation in the refluxer.

The following criteria must be considered in refluxer design:

1. A stripping section is necessary below the interface to ensure low nitrogen losses.
2. The packed section above the control interface should be long enough to bring about equilibrium between "NO" and nitric acid, or else water must be added to the refluxer. Excess nitrogen dioxide, above the equilibrium mixture, should not be allowed to enter the exchange column, because heating of the column will result.
3. Cooling of the refluxer should be sufficient to produce a gas mixture rich in nitric oxide. Excess cooling results in a solid formation in the refluxer.
4. The cross-sectional area of the refluxer must be kept small to ensure turbulent sulfur dioxide flow and a sharp interface.
5. Holdup of nitric acid in the refluxer must be kept as low as possible to minimize isotopic equilibrium time.

Run 2 was made with the refluxers that were developed in the testing period and which have been described previously. The nitric acid flow rate was 4 liters/hr in column I and 190 ml/hr in column II. Operation was continued for 19 days. Termination of the run took place because of an operational error. A maximum product enrichment of 96.7 at. % N^{15} was attained, and product was withdrawn for two days which totaled 15 ml of 7 M HNO_3 containing 95% N^{15}.

Figure 14 shows the isotopic gradient during the run. The first partial drop in concentration was due to loss of nitric acid caused by failure of a bellows on the feed pump to column II. The second drop in concentration was caused by the controlling-recorder pen for column II catching in the chart paper, with a resulting loss of product nitric acid to the drain.

The flow rate in column I was increased to 4.5 liters of nitric acid per hour for run 3. With this

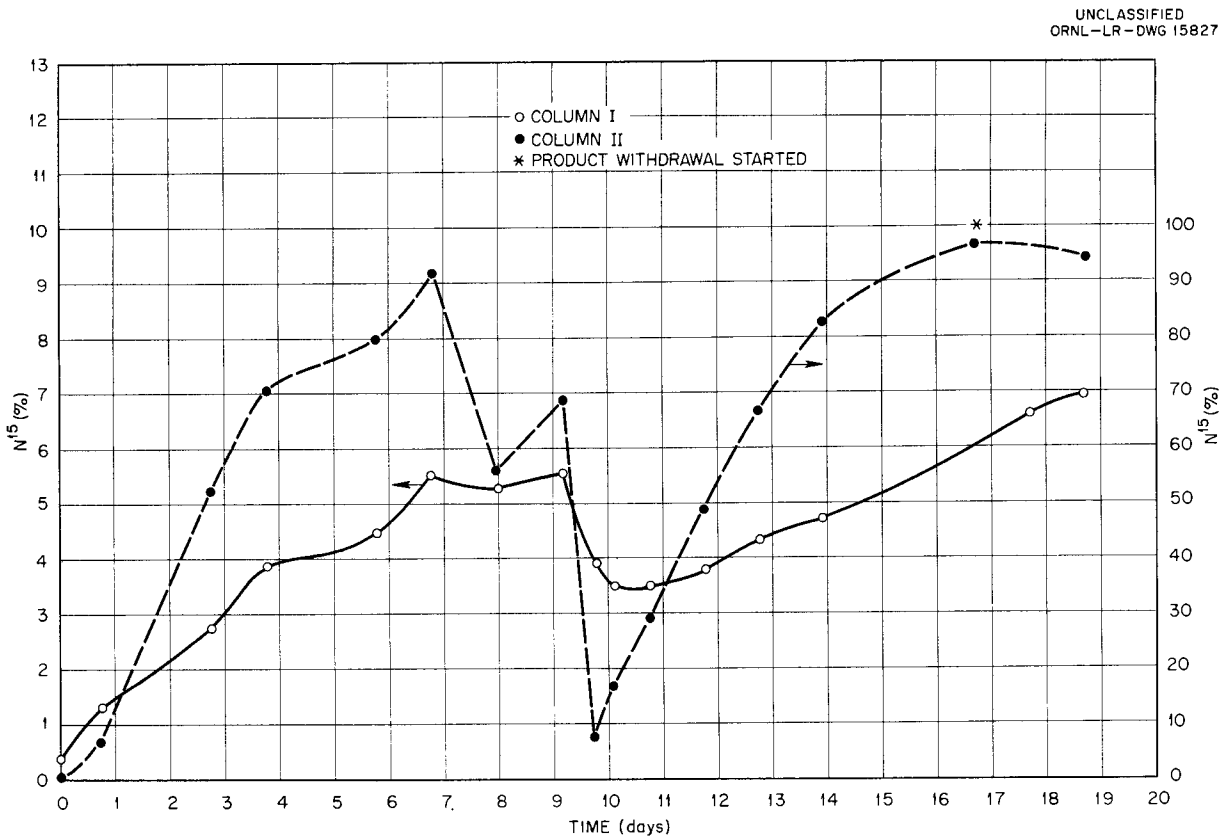

Fig. 14. Buildup of Isotopic Gradient During Run 2.

increased flow rate it became necessary to add 350 ml of water per hour to refluxer I. The flow rate in column II was 200 ml/hr. Isotopic data from run 3, which lasted for 28 days, are shown in Fig. 15. The drop in isotopic concentration shown after five days of operation was due to loss of product from refluxer II during the night. This took place because of a sulfur dioxide pressure drop during this time. Product removal was started after nine days of operation and was continued until the final shutdown. The rate of production of high purity N^{15} was approximately 1.2 g/day. Operation of the system was stopped because of erratic performance of refluxer II – accumulation in the refluxer of a small quantity of grease or oil-like material prevented wetting of the packing. Channeling of the unit was beginning when operation was stopped.

Table 7 shows the averages of the analyses made upon the sulfuric acid produced by the two product refluxers. The concentration of the sulfuric acid produced was about 9.0 M. The average nitrogen loss in the discarded sulfuric acid ran from 12 to 24 ppm, which was considered to be satisfactorily low for the production of 99% N^{15}.

Table 7. Average Data from Product Refluxers

	Refluxer I		Refluxer II	
	Run 2	Run 3	Run 2	Run 3
Waste H_2SO_4, moles/liter	8.92	8.60	8.86	9.20
Dissolved SO_2, moles/liter	0.63	0.38	0.50	0.26
Nitrogen loss, ppm of feed	12	13	24	14

The equilibrium time for the system to attain the 95% N^{15} level was six to seven days. There was, however, a slow increase in the concentration of N^{15} in column I which apparently was still going on after 27 days of operation. The only explanation

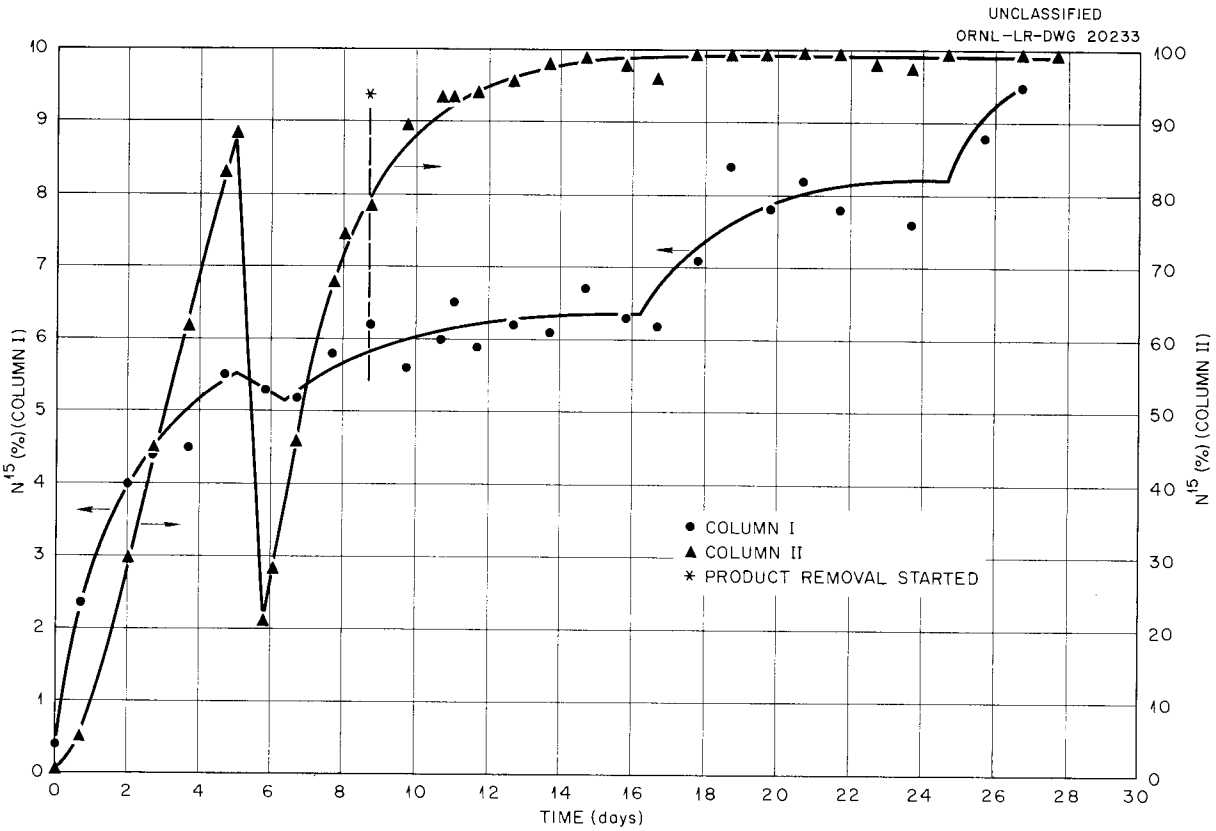

Fig. 15. Buildup of Isotopic Gradient During Run 3.

for this increase is that there was a slow increase in the efficiency of the packing which led to a shorter stage height in the large column as time went on. This could have been caused by a cleaning action of the solution or by a slight etching of the packing. Since the system was not allowed to come to equilibrium at total reflux but only with product removal, the maximum value possible for N^{15} enrichment was not attained. The stage height for the large column was less than 4 in. and was less than 1.6 in. for the small column.

It is believed that the experience with the Nitrox system has shown it to be the most promising system known at present for the concentration of nitrogen isotopes. The apparatus described operated unattended at night, with observation and adjustment at intervals on the day shift. It has been found to be entirely feasible to operate a Nitrox cascade to produce high-purity N^{15} continuously with automatic controls.