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NO–HNO$_3$ Exchange System for Production of ^{14}N Highly Depleted of ^{15}N

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Abstract

The isotopic exchange reaction between NO and HNO$_3$ was used to prepare ^{14}N highly depleted ^{15}N. This required an efficient reflux system of low hold-up to convert oxides of nitrogen to nitric acid by reaction with oxygen and water. A study of the characteristics of the one constructed showed that less than 1 part in 32,000 of the nitric acid was lost from the refluxer as oxides of nitrogen. ^{14}N with an atom fraction of less than 0.00004 of ^{15}N was prepared at the rate of 46.0 g/day. The application of the refluxer to a system for producing ^{15}N is discussed.

INTRODUCTION

^{14}N highly depleted of ^{15}N has several applications in nuclear physics, chemical research, and industrial research (*1–3*). A relatively pure ^{14}N could be prepared by a chemical exchange method that has been successfully used to concentrate ^{15}N having isotopic concentration over 99.5%. The chemical exchange method involves the exchange reactions between nitric acid and nitric oxide. The major reactions are (*4–7*):

Exchange

$$^{15}NO + H^{14}NO_3 \rightleftarrows {}^{14}NO + H^{15}NO_3, \qquad \alpha = 1.055 \tag{1}$$

Product reflux

$$3SO_2 + 2HNO_3 + 2H_2O \rightleftarrows 3H_2SO_4 + 2NO \tag{2}$$

$$SO_2 + 2HNO_3 \rightleftarrows H_2SO_4 + 2NO_2 \tag{3}$$

Waste reflux

$$2NO + O_2 \rightleftarrows 2NO_2 \tag{4}$$
$$3NO_2 + H_2O \rightleftarrows 2HNO_3 + NO \tag{5}$$

As seen from the above, in the preparation of ^{15}N Reactions (1) through (3) are of prime importance, while Reactions (4) and (5) are secondary. Since ^{14}N becomes concentrated in the gas phase, contrary to the earlier case, Reactions (1), (3), and (4) are of great importance. In the present investigation attempts are made to develop refluxers to obtain quantitative conversion of oxides of nitrogen to nitric acid and obtain the ^{14}N isotope highly depleted of the ^{15}N isotope.

EXPERIMENTAL

In order to test the operation of the refluxer to convert oxides of nitrogen to nitric acid, preliminary experiments were carried out with a 157-cm long × 2.2 cm i.d. column packed with HeliPak 3013. A typical experimental setup is shown in Fig. 1. The oxides of nitrogen that are formed according to Reactions (2) and (3) rise upwards in the column (C) and enter into the product refluxer (P) where they are quantitatively converted into nitric acid. Several modifications of this refluxer were tested and the design shown in Fig. 2 was found to be satisfactory for the experimental conditions used in the present studies. It consists of a jacketed glass column packed with 3/32 in. glass helicies in two sections with a space between them. Excess oxygen is introduced into this space where the oxides of nitrogen leaving the exchange column are mixed, and part of the NO is oxidized to NO_2. The lower packed section prevents these gases from going back into the exchange column. As the partially oxidized gases pass through the upper packed section, they react with water that is introduced from the top to form nitric acid. The NO formed according to Reaction (5) is reoxidized by excess oxygen.

The oxidation of nitric oxide by oxygen in the gas phase by Reaction (4) is kinetically of the third order:

$$\frac{d(P_{NO})}{dt} = \frac{-k(P_{NO})^2}{(P_{O_2})} \tag{6}$$

and unlike most of the homogeneous gas reactions, the rate constant decreases with increasing temperature (*8*, *9*). In a packed column with an excess of oxygen and no other inert gas, a part of the nitric oxide may also be oxidized in the solution phase. Although the absorption of NO_2 and N_2O_4 in water to form nitric acid has been investigated extensively

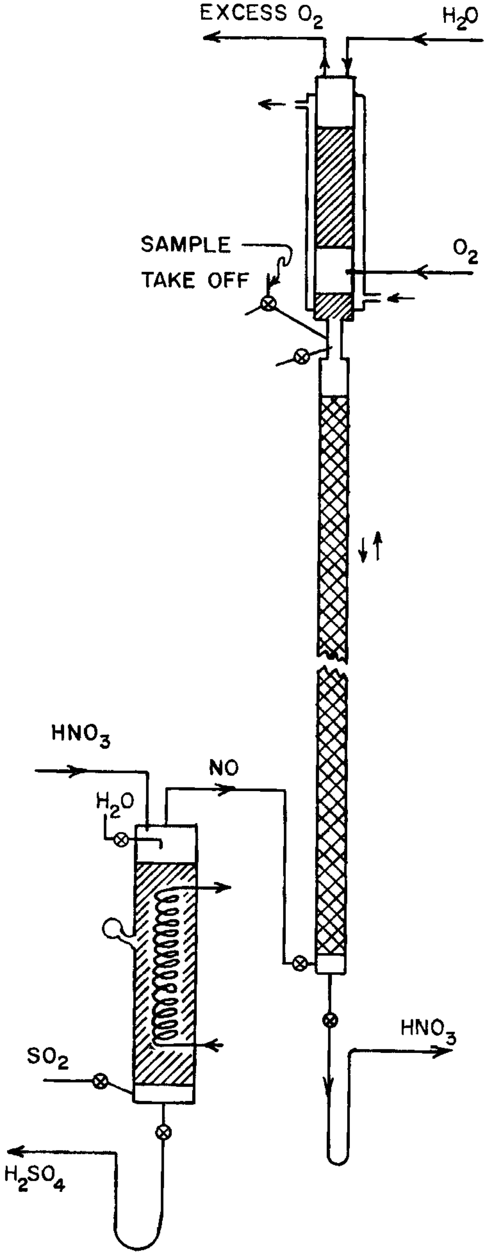

FIG. 1. Exchange system with a short column to test designs for the upper refluxer.

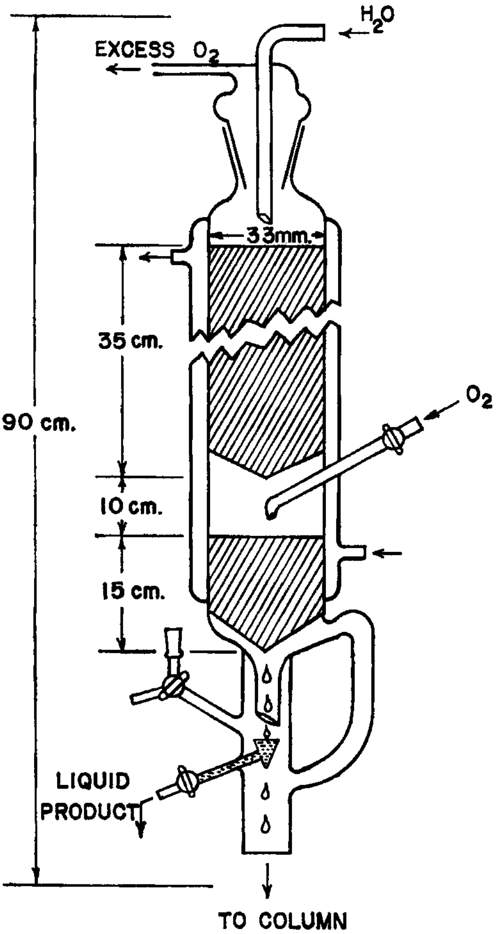

FIG. 2. Details of the design of the upper refluxer for converting oxides of nitrogen to nitrogen to nitric acid.

(*10–15*), there is no general agreement on the details of the mechanism of the reaction. However, it is significantly influenced by the concentration of nitric acid and the composition of the gas phase. In the present case the situation is more complicated due to the concentration gradient present along the refluxer. For the preparation of either ^{15}N or ^{14}N, the exchange system is to be operated at 10 *M* HNO_3. In order to obtain this concentration of HNO_3, precalculated water was supplied from the top of the refluxer. For approximately 10 *M* HNO_3, which is in equilibrium with the oxides of nitrogen, the mole fractions of the gas phase components are: 0.81 NO, 0.083 NO_2, 0.051 N_2O_4, 0.041 N_2O_3, and 0.15 H_2O (*16*, *17*). Using these values for a flow of 10 ml HNO_3/min of 10 *M* HNO_3, which corresponds to 100 mmoles nitrogen/min, the flow of each species in mmoles/min is NO = 75.2, NO_2 = 7.7, N_2O_4 = 4.75, and N_2O_3 = 3.8. By combining the reactions proposed by Verhoek and Daniels (*18*) with those in the literature (*19*, *20*), the overall reactions and the oxygen requirement can be calculated. The following are the reactions:

$$2NO_2 \rightleftarrows N_2O_4 \tag{7}$$

$$NO + NO_2 \rightleftarrows N_2O_3 \tag{8}$$

$$NO + \tfrac{3}{4}O_2 + \tfrac{1}{2}H_2O \rightleftarrows HNO_3 \tag{9}$$

$$NO_2 + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2 \rightleftarrows HNO_3 \tag{10}$$

$$N_2O_4 + \tfrac{1}{2}O_2 + H_2O \rightleftarrows 2HNO_3 \tag{11}$$

$$N_2O_3 + O_2 + H_2O \rightleftarrows 2HNO_3 \tag{12}$$

The oxygen requirement thus calculated is 64.5 mmoles/min for a flow of 10 ml HNO_3/min. The water requirement for the refluxer to form nitric acid is 50 mmoles/min plus the amount that is required to make 10 ml/min of 10 *M* HNO_3. Since 10 *M* HNO_3 is 48.6% by weight HNO_3 and its density is 1.259 g/cc at 25°C, 6.6 g of water will be needed.

Exchange System for ^{14}N

After preliminary experiments had shown that the product refluxer operated satisfactorily, sufficient data was obtained with a 157-cm long × 2.2 cm i.d. column to design an exchange system to obtain relatively pure ^{14}N. In this column a steady-state overall separation of 9.4 was attained in about 13 to 14 hr. Using a value of 1.055 for the single stage separation factor (α), a HETP of 3.8 was obtained this value is in approximate agreement with the values obtained by Taylor and Spindel (*5*) for the concentration of ^{15}N. Due to greater values of overall separation and uncertainty about the hold-up in the product refluxer, it was not possible to estimate the rate of approach to steady state using the equations proposed by Cohen (*21*). However, it was evident from the relatively short time required to attain steady-state overall separation that the hold-up in the product refluxer would not in any way affect the operation of the larger system.

A reduction of the ^{15}N content of normal nitrogen by a factor of 100 was considered adequate for most of the applications of ^{14}N. The minimum number of theoretical plates required for this separation is 86 as calculated from the relation $n = \log S/\log \alpha$, $\alpha = 1.055$. Using the value of 3.8 cm for HETP as measured earlier by Ghate and Taylor (*22*), the minimum length of the packed column would be 327 cm. Usually, for production, one provides 1.5 to 2 times the minimum number of theoretical plates so that an exchange column of 500 to 650 cm long would be suitable.

Since about 100 g of ^{14}N depleted of ^{15}N was desired, the size of the exchange system to obtain this quantity in a reasonable time was arrived at as follows: The maximum mmoles HNO_3/min of product P with a mole fraction N_p of ^{14}N that can be withdrawn for a given interstage flow, L, in mmoles HNO_3/min is (*5*)

$$P = \frac{LN_0(1 - N_0)(\alpha - 1)}{N_p[1 + (\alpha - 1)(1 - N_0)] - N_0} \tag{13}$$

The mole fraction $(1 - N_0)$ of ^{15}N in the feed material is 0.00365 so that N_0 is 0.99635, and since the desired concentration of ^{15}N in the product is 0.0000365, the mole fraction N_p of ^{14}N is 0.9999635. For $\alpha = 1.055$ and interstage flow $L = 100$ mmoles/min, the maximum withdrawal rate P is calculated to be 5.24 mmoles HNO_3/min or 106 g/day of nitrogen at the specified concentration. This would correspond to the maximum P/L ratio 70.052. This maximum withdrawal rate applies only to a column with an infinite number of stages. In order to account for the losses and fluctuations, the practical withdrawal rate is usually 30 to 40% lower than the minimum. That is, it should be possible to withdraw 64 g of nitrogen per day at an overall separation of about 100.

Based on the above estimates, the exchange system shown diagrammatically in Fig. 3 was constructed. Because of the limited height of the room, it was necessary to make the exchange column in two sections. The two sections, I and II, were intercoupled through a bellows pump (P_3). Both these sections provided a total of 525 cm of packed length, packed with HeliPak 3013. The product reflexer (B) at the top of Column II is supplied with a precalculated amount of oxygen and water to obtain

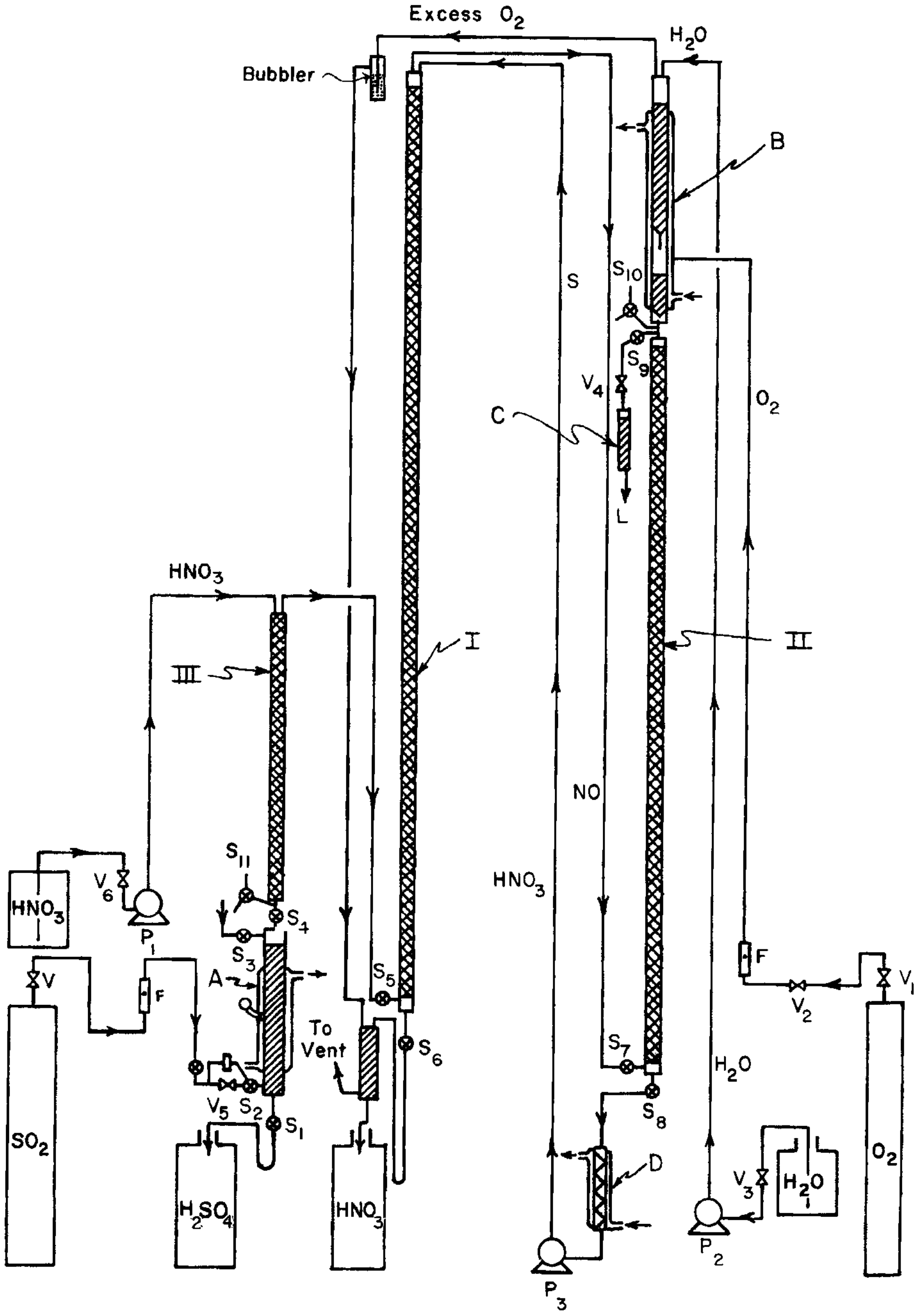

FIG. 3. Exchange system for the preparation of ^{14}N highly depleted of ^{15}N.

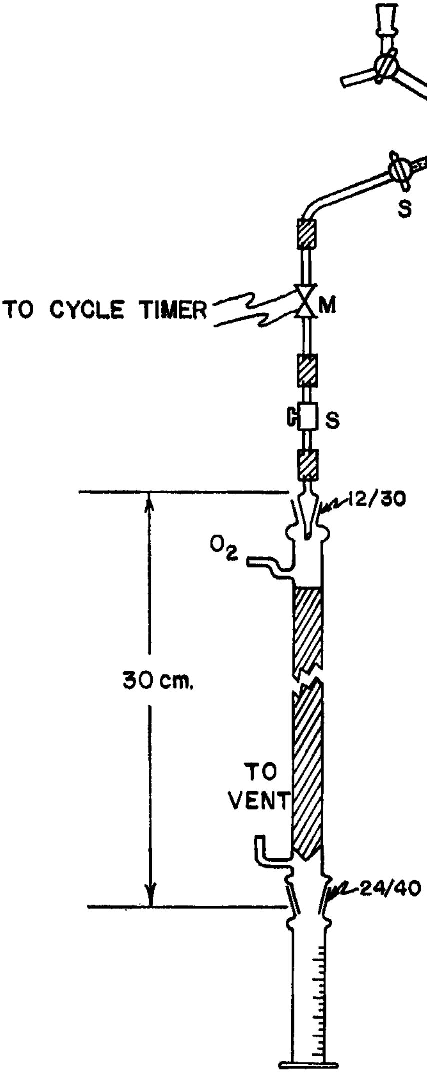

FIG. 4. Details of product withdrawal system.

10 *M* HNO_3 at the rate of 10 ml/min. A withdrawal system was connected at the bottom of this refluxer product, the details of which are shown in Fig. 4. To withdraw the liquid product (HNO_3) at the desired rate, a solenoid valve (M) was connected to the cycle timer which controlled the percentage of time the valve was open. The liquid product is then passed countercurrently with a small stream of oxygen over a section packed with glass helicies. In this manner dissolved oxides of nitrogen were oxidized and a clear product was obtained.

Start-up Procedure

Before starting operation of the exchange system, columns were flooded with 10 *M* HNO_3 to ensure proper wetting of the packing. Then columns were drained slowly with a flow of 10 ml of 10 *M* HNO_3/min to Column III and 7.5 ml H_2O/min to the product refluxer. When the columns were free from excess liquid, SO_2 was passed through the bottom refluxer (A) to generate oxides of nitrogen according to Reactions (2) and (3). These oxides then rise countercurrently through Columns III, I, and II, and finally enter into the product refluxer where they are mixed with oxygen and absorbed into water to produce nitric acid.

The progress of the separation was followed by isotopic analyses of gas and liquid samples withdrawn from the top of Column II, Fig. 3. Since direct introduction of oxides of nitrogen into the mass spectrometer is unsatisfactory because of their reaction, decomposition and adsorption in the ion source (*23–25*), it was necessary to convert them to nitrogen (*26*). The conversion to nitrogen was accomplished by passing the oxides of nitrogen through a Cu/CuO furnace maintained at 750°C (*5*). In the case of liquid samples the nitric acid was first converted to nitric oxide by reaction with Hg and H_2SO_4 (*27*) and then it was converted to nitrogen as described above.

The isotopic analyses of the nitrogen samples were made with a single collector Nier-type mass spectrometer (*28*).

RESULTS AND DISCUSSION

The progress of overall separation with time is shown in Fig. 5. After about 49 hr of operation under total reflux an overall separation of 192 was obtained. A typical spectra of ^{14}N highly depleted of ^{15}N is given in Fig. 6. In calculating the ratio of mass 28 to mass 29, a lot of difficulty was encountered due to uncertainty in the contribution of mass 29 background. However, attempts were made to estimate the mass 29 background

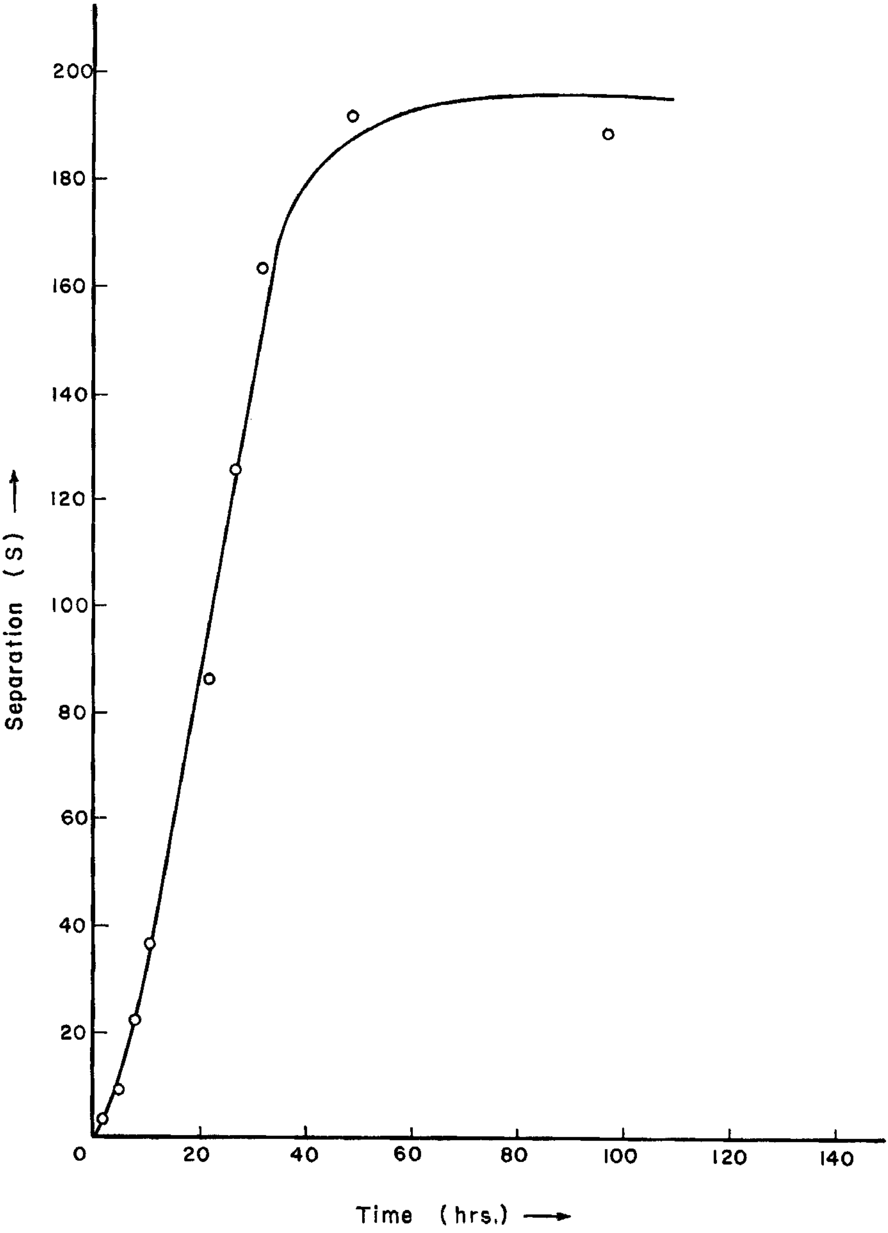

FIG. 5. Overall separation, S, as a function of time.

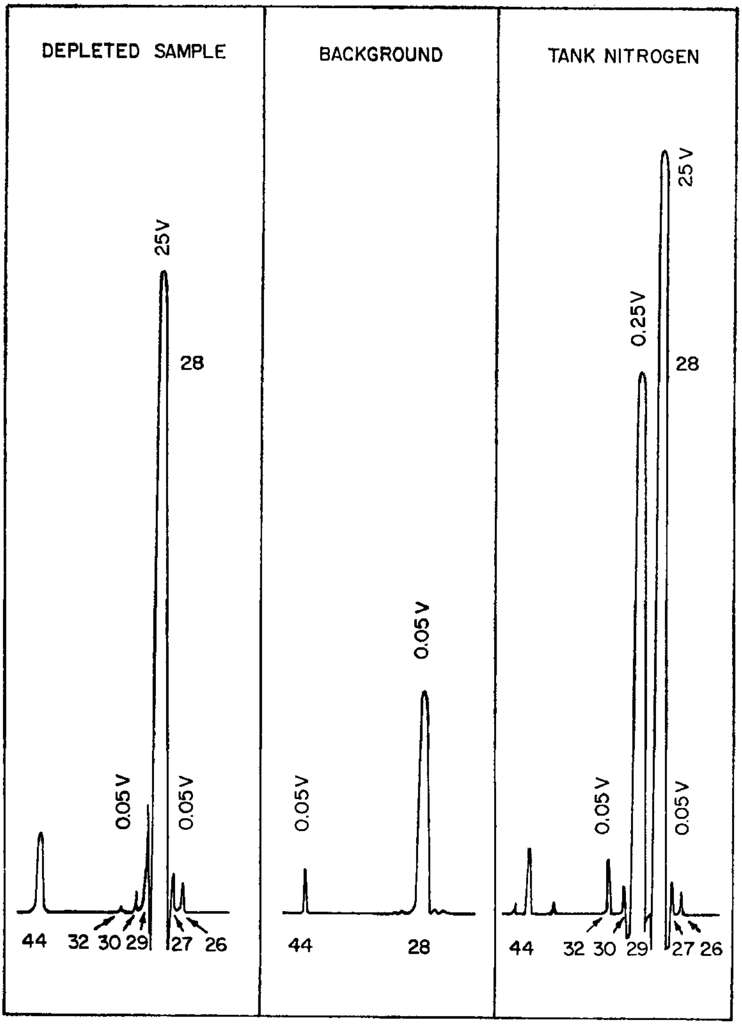

FIG. 6. Mass spectrometer record showing the mass 29 peak in the product relative to that in tank nitrogen.

contribution using gases other than nitrogen, but the results were not consistent. Using the approximate value of 2.5 divisions as the contribution of mass 29 background to the peak at mass 29 in the sample ratio, R_p 24.800 of mass 28 to mass 29 was obtained. The average value of the similar ratio R_0 for tank nitrogen with the particular settings of the ion source controls was 142. The overall separation is then $S = 24{,}800/142 = 174.6$. Since

$$S = \frac{R_p}{R_0} = \frac{N_p}{1 - N_p} \Big/ \frac{N_0}{1 - N_0} \tag{14}$$

where N_p is the atom fraction of ^{14}N in the product and N_0 is atom fraction of ^{14}N in the feed. Using the value of 0.99635 for N_0, a value of 0.999979 for N_p when $S = 174.6$ is obtained.

Effect of Product Withdrawal Rate

The exchange system was operated for about 96 hr and then the product was withdrawn at several different rates to determine the effect on the concentration of ^{15}N in the product. Figure 7 shows the change in the concentration of ^{15}N when the product was withdrawn at different rates. It is apparent from the plot that even the highest withdrawal rate has little or no effect on the concentration of ^{15}N in the product. However, a more sensitive measure of the effect of product withdrawal rate is obtained from the values of overall separations. Table 1 summarizes the results on this basis. In Fig. 8 the overall separation S is plotted as a function of P/L; that is, the fraction of the interstate flow that is drawn off as a product. At a value of 0.023 for P/L, which corresponds to 2.3 mmoles HNO_3/min or 46.0 g nitrogen/day, the overall separation was reduced to 100, which reduced the ^{15}N concentration by a factor of 100 from its natural abundance. The rate of 46.0 g/day at which the product was

TABLE 1

Effect of Product Withdrawal Rate on Overall Separation

Rate			R_p	S	Atom fraction
$\frac{\text{mmoles HNO}_3}{\text{min}}$	$\frac{\text{g Nitrogen}}{\text{day}}$	P/L	$\frac{\text{Mass 28}}{\text{Mass 29}}$	$\frac{R_p}{R_0}$	^{15}N
0	0	0	27,300	192	0.000019
1.38	27.8	0.0138	21,300	150	0.000024
2.40	48.4	0.0240	13,700	96	0.000038
3.65	73.6	0.0365	10,800	76	0.000048

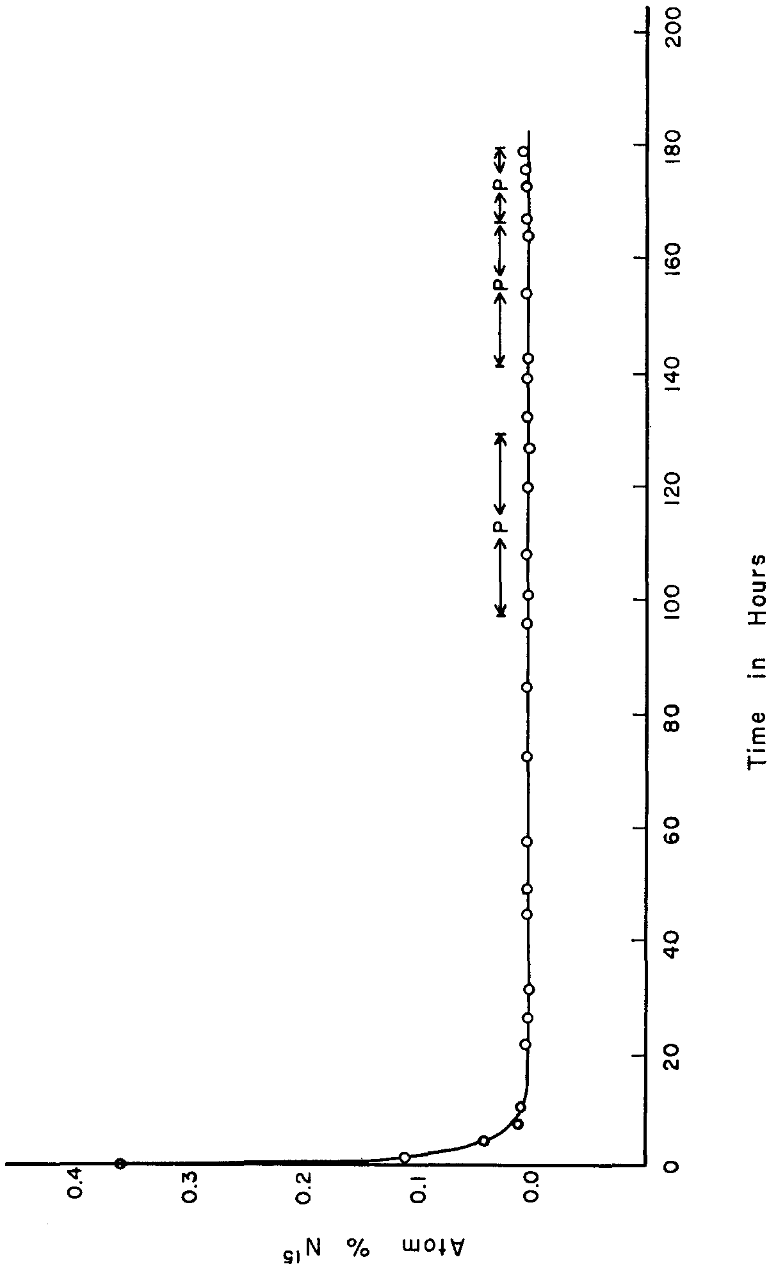

FIG. 7. Atom fraction of ^{15}N during the operation of the system. *P* indicates the periods during which product was withdrawn.

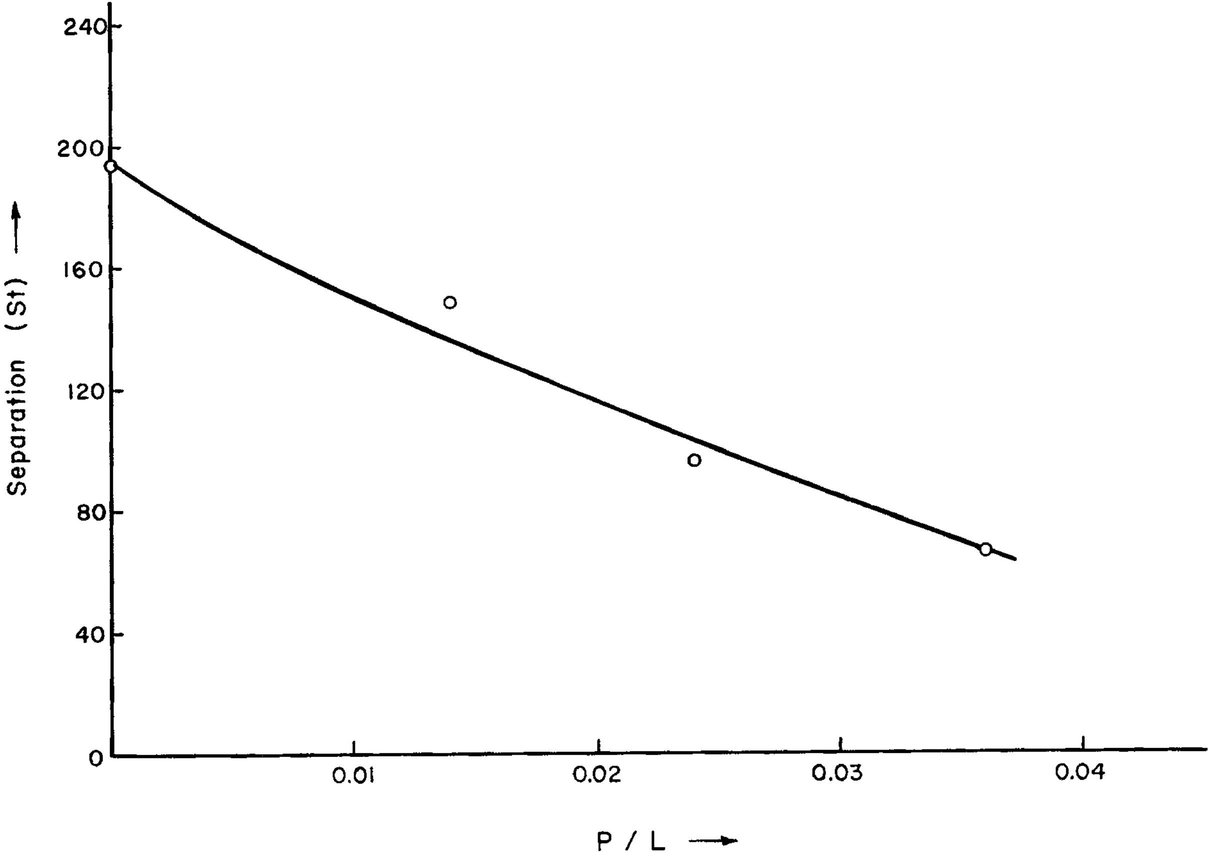

FIG. 8. Overall separation as a function of the fraction of the interstage flow drawn off as product.

withdrawn was about 19% less than the 64.0 g/day arrived at in the design calculations. This indicates that an exchange column 2 to 2.5 times longer than the minimum length would probably have improved the agreement.

Performance of the Product Refluxer

A decrease in the production rate could result from the loss of oxides of nitrogen from the top of the refluxer. The extent of loss was measured by allowing the gases that leave the product refluxer to pass through 230 ml of water in a 250-ml graduated cylinder. After 10 to 40 hr the solutions were titrated with standardized sodium hydroxide using chlorophenol red indicator. The ratio of losses to the interstage flow during the collection time was in the range of 1 part in 2,900 to 1 part in 33,000. This would be equivalent to a P/L ratio of 0.00034 to 0.00003 compared to a ratio of 0.0365 for the maximum product withdrawal. These observations indicate that the refluxer was quite efficient in converting the oxides of nitrogen into nitric acid.

Another indication of the reliable operation of the refluxer was the constancy of the concentration of the nitric acid produced. As shown in Table 2, the concentrations of various samples were in the range 10.1 to 10.8 *M* with an average of 10.45 *M*. This is slightly higher than 10.0 *M* because it includes the dissolved oxides of nitrogen withdrawn with nitric acid and oxidized by oxygen in the product withdrawal system.

The rate of production of nitric acid by this refluxer is 281 moles HNO_3/day/liter of volume. This is significantly greater than the 32 moles HNO_3/day/liter of volume produced in commercial 60 ton/day high

TABLE 2

Concentration of Nitric Acid Produced by Product Refluxer During Initial Part of the Experiment

Product No.	Volume (ml)	*M* (moles/liter)	Product No.	Volume (ml)	*M* (moles/liter)
1	25.0	10.10	8	50.0	10.22
2	29.0	10.22	9	40.0	10.80
3	31.0	10.22	10	44.8	10.80
4	36.0	10.50	11	45.0	10.80
5	31.0	10.80	12	36.0	10.10
6	35.0	10.80	13	37.0	10.10
7	23.5	10.80	14	47.0	10.80
			Av.	—	10.40 ± 0.3

pressure nitric acid plants using air for oxidation (*14*). However, per unit cross-sectional area, the refluxer used here produced only 17 moles HNO_3/day-cm^2 compared to 42 moles HNO_3/day-cm^2 for the commercial plants. Apparently the use of oxygen in the arrangement used as in the present work results in a much greater rate of oxidation and absorption of the oxides of nitrogen to form nitric acid.

APPLICATION TO PRODUCTION OF ^{15}N

The product refluxer discussed in the previous section has an important use in the production of ^{15}N. As an example, the use of the refluxer for preparing 1 g/day of 99% ^{15}N is illustrated in Fig. 9. The minimum interstage flow rate L at the feed point where the atom fraction of ^{15}N is 0.00365, as calculated by Eq. (13), is 243 mmoles/min. This is usually increased by 20 to 40% to take care of losses, fluctuations, etc., so that a flow of about 300 mmoles/min would be used. Previous experience of Taylor and Spindel (*5*) and the present work show that HETP values of about 4.0 cm can be obtained with HeliPak 3013 at flow rates as high as 3.0 ml/min-cm^2. On this basis the diameter and length of the first enriching column should be 3.5 and 550 cm, respectively. The second enriching column, which receives about 4% of the flow in the first column, is filled with HeliPak 3012 and operates at about 1 ml/min-cm^2, so that its diameter should be 1.2 cm with a length of about 600 cm. The lengths indicated would provide 1.8 times the minimum number of stages required to produce 99% ^{15}N. Similarly, the diameter of the stripping section should be the same as the first enriching column since it has the same interstage flow. If it is desired to recover about 70% of the ^{15}N from the nitric acid, the atom fraction in the waste would be 0.0012, so that the stripping column should operate at an overall separation of 3.1 for ^{14}N. With $\alpha = 1.055$ the minimum number of stages would be 21.0, and twice this number should be provided for production. Using a value of 4.0 cm for HETP, the length of the stripping section should be 200.0 cm.

To convert the oxides of nitrogen to 10.0 M nitric acid, the size of the refluxer can be calculated by using a proportional scaling factor. Since our present refluxer operated satisfactorily for a rate of 100 mg atom nitrogen/min, for a feed of 300 mg atom nitrogen/min the diameter of the refluxer would be about 5.8 cm i.d. and the total length about 100 to 120 cm. The water and oxygen flows should be 22.7 ml/min and 4.73 liters/min, respectively. The heat generated would be about 9.47 kcal/min. Adequate cooling should be provided.

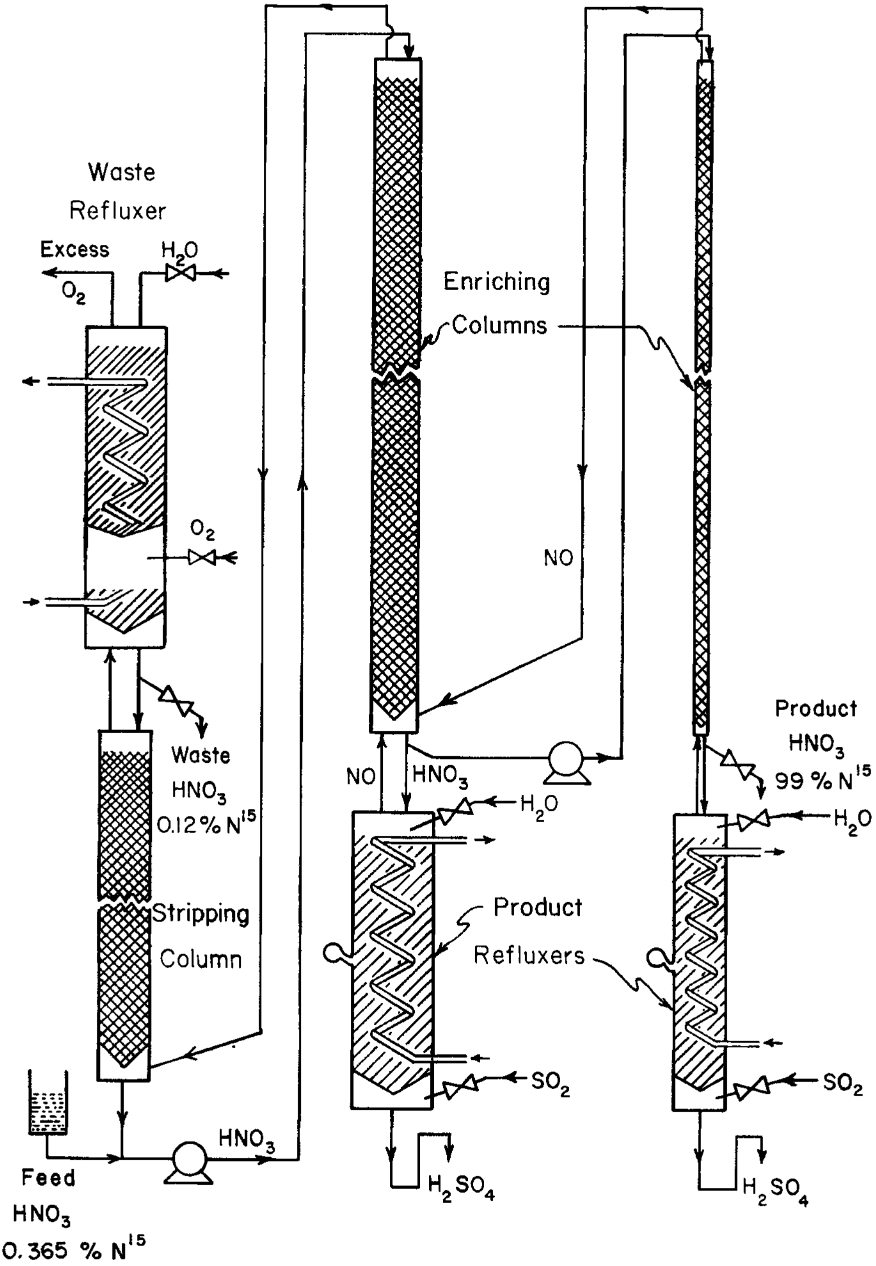

FIG. 9. System for the production of 1 g/day of 99% ^{15}N using a waste refluxer for recovery of 70% of the ^{15}N in the nitric acid.

The rate of withdrawal W of waste nitric acid and the feed flow F can be arrived at by material balance calculations for nitric acid, $P = F - W$, and a material balance on ^{15}N, $PN_p = FN_0 - WN_w$ where $N_p = 0.99$, $N_0 = 0.00365$, and $N_w = 0.0012$. Solving for F and W, one obtains $F = 18.87$ mmoles HNO_3/min and $W = 18.82$ mmoles HNO_3/min, i.e., 1.88 ml 10 M HNO_3/min. Thus the feed and waste flows of nitric acid are essentially the same. This value of 1.88 ml 10 M HNO_3/min is required when the stripping section and the refluxer to convert oxides of nitrogen to nitric acid are not used. Such an arrangement would mean a requirement of 2.7 liters of HNO_3/day as against 43.2 liters/day otherwise. Previous experience shows that use of the stripping section does not add any complications to the system. There is a savings in construction costs because the nitric acid is produced at atmospheric pressure, and the use of nitric acid partially compensates for the cost of the oxygen used. In addition, the removal of oxides of nitrogen from the waste gases would reduce pollution problems.

Acknowledgments

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