Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Mills, T. R. , Garcia, M. G. , Vandervoort, R. C. and McInteer, B. B.(1989) 'A Chemical Exchange System for Isotopic Feed to a Nitrogen and Oxygen Isotope Separation Plant', Separation Science and Technology, 24: 5, 415 — 428
To link to this Article: DOI: 10.1080/01496398908049778
URL: http://dx.doi.org/10.1080/01496398908049778

SEPARATION SCIENCE AND TECHNOLOGY, **24**(5 & 6), pp. 415–428, 1989

A Chemical Exchange System for Isotopic Feed to a Nitrogen and Oxygen Isotope Separation Plant

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Abstract

A process has been developed to provide isotopic feed to a nitric oxide isotope distillation plant. Central to the process is the isotopic chemical exchange of NO and nitric acid in countercurrent flows in a 3-in. diameter packed column. An isotopically depleted stream of NO is reenriched to natural isotopic abundances by the exchange and is recycled as feed back to the distillation columns. Makeup NO is generated in another column from sulfur dioxide and nitric acid. Multistage gas purifiers reduce condensible impurities in the nitric oxide below 10 ppm. The process operates unattended at flow rates of 0.5 to 2 mol/min. The new NO recycle-enrichment and generation processes have successfully provided the feedstock for the NO isotope separation columns for over 6 years.

INTRODUCTION

Cryogenic NO distillation columns of great length (50 to 100 m) have been built and continuously operated at the Los Alamos ICON Facility (Isotopes of Carbon, Oxygen, and Nitrogen) for over a 25-year period (*1*, *2*). These columns are the heart of the ICON nitrogen and oxygen isotope separation system, which is based upon isotope effects on the vapor pressure of nitric oxide. The columns operate under automatic control around the clock with relatively little requirement for operator intervention. This facility has been responsible for providing the major fraction of the world's supply of ^{15}N and ^{18}O for research in recent years (*3–8*).

Because the system is a cryogenic operation, the nitric oxide feed to the columns must be of exceptionally high purity (about 99.999% excluding light gases) to avoid plugging the columns with condensed gases. For many years the NO was purchased in tube trailers and was further purified by various cryogenic purifiers designed and constructed by ICON personnel.

In 1980 the sole American bulk supplier of nitric oxide chose to discontinue production of NO for safety and economic reasons. With no supplier of feed material, Los Alamos considered a number of schemes for producing NO before developing a totally new method for obtaining NO feed. This new approach combines recycling an NO effluent stream with a process for NO generation to make up for isotopic product withdrawal and handling losses.

ISOTOPE SEPARATION PROCESSES

The most abundant isotopes of nitrogen and oxygen have atomic masses 14 and 16, respectively. The natural abundances of the rarer, heavy isotopes are ^{15}N, 0.365%; ^{17}O, 0.037%; and ^{18}O, 0.204%. All these isotopes are stable, and there are no long-lived radioisotopes of nitrogen or oxygen. Isotope separation processes used to enrich the heavy isotopes for a large variety of research uses include NO distillation, NO/HNO_3 chemical exchange, and water distillation.

The NO distillation process makes use of the higher vapor pressures of the light isotopes of nitrogen and oxygen in liquid nitric oxide. The relative volatilities are 1.027 for ^{14}N vs ^{15}N and 1.036 for ^{16}O vs ^{18}O at 120 K (*9*). The NO distillation columns take NO gas feed of natural isotopic composition and produce a bottom drawoff of NO gas enriched in the heavy isotopes. A top product from the columns consists of gas from which nearly all the heavy isotopes have been stripped (^{15}N, ^{17}O, $^{18}O \approx 0.01\%$). This stream is normally a waste stream, but it can be also used to provide chemicals depleted in the heavy isotopes. Presently four such NO distillation columns are in operation at the ICON facility. The total NO feed and waste streams for these columns are about 2 mol/min each.

The primary alternative process for separation of nitrogen isotopes utilizes the ability of nitric acid and nitric oxide to come to isotopic equilibrium:

$$^{15}NO + H^{14}NO_3 \leftrightarrow {}^{14}NO + H^{15}NO_3 \qquad (1)$$

Called the Nitrox process, this system makes use of an isotope effect ($\alpha = 1.035$) which concentrates ^{15}N in the liquid phase (*10*). The oxygen isotopes also come to exchange equilibrium, and the Nitrox process has been used for oxygen isotope enrichment (*11*). Typically a Nitrox plant has a packed column with countercurrent flows of gas and liquid. Equivalent plate heights in a Nitrox column are small (7 cm), which indicates rapid isotopic equilibration between gas and liquid (*10*).

FEED EXCHANGE SYSTEM

This rapid isotopic equilibration between nitric acid and nitric oxide suggests the possibility of using this effect to reenrich the NO waste stream back to normal isotopic abundances. The NO containing little ^{15}N, ^{17}O, and ^{18}O in the column top flows could be equilibrated with HNO_3 containing natural abundances of these isotopes, and the equilibrated NO could be recycled back to the distillation columns as feed. If countercurrent flows are used in a packed bed, a roughly constant concentration difference driving force in the bed transports the ^{15}N from the HNO_3 to the NO (Fig. 1). Because of the molar excess of oxygen in Eq. (1), the HNO_3 stream from the exchange bed is only partially depleted in heavy oxygen isotopes.

When pure nitric oxide gas and nitric acid solution are mixed and come to phase equilibrium, the resulting liquid and gas each contain NO, NO_2, N_2O_3, N_2O_4, H_2O, HNO_2, and HNO_3 (*12*). In particular, NO_2 is instrumental in permitting the isotopic exchange between HNO_3 and NO by means of the N_2O_3 formed by combining NO and NO_2. As the nitric acid concentration increases, the gas-phase composition of NO_2 increases rapidly (5 mol% at 8 N acid), which in turn facilitates rapid isotopic exchange (*12*).

Since the NO feed to the isotope separation columns must contain no more than ppm levels of impurities, the NO_2 must be removed from the gas stream. A solution to this problem is to feed the concentrated HNO_3 to the middle of the packed column and feed water at the top. The top half of the column acts as a scrubber to convert the NO_2 in the NO stream to NO via the reaction

$$3NO_2 + H_2O \rightarrow NO + 2\ HNO_3 \qquad (2)$$

Because N_2O_3 is a mixture of NO and NO_2, and N_2O_4 is a dimer of NO_2, these other higher nitrogen oxides are also reduced to NO via Reaction

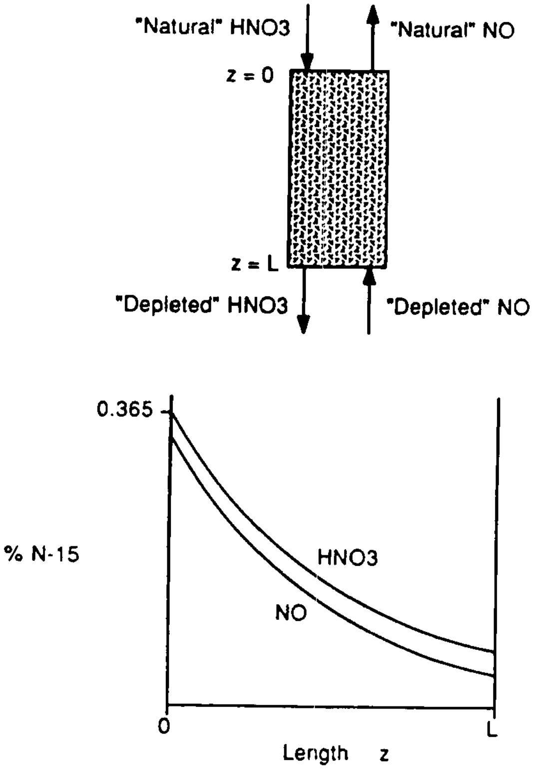

FIG. 1. Countercurrent flow, packed bed exchanger.

(2). A side benefit of Reaction (2) is that no nitrogen is lost from the system in the purification.

The central piece of apparatus which has been developed employs countercurrent gas and liquid flows to obtain NO of natural isotopic abundance. In the lower half of the packed column (the exchanger), the NO and HNO_3 solution exchange isotopes to yield "normal" NO as in Fig. 1. In the upper half of the column (the scrubber), the higher oxides of nitrogen are reduced to NO by Reaction (2). The HNO_3 concentration in the exchanger is determined by the ratio of acid to water flow rates.

In this feed exchange process some NO is lost due to dissolved nitrogen oxides in waste HNO_3. In addition, NO is removed from the isotope separation process due to product withdrawal and losses due to generation of impurities in the isotope separation columns. Due to these losses, it is necessary to generate small amounts of NO to achieve a material balance for the plant. This is done by reacting HNO_3 with sulfur dioxide in a packed bed, countercurrent flow reactor using the reaction

$$2H_2O + 3SO_2 + 2HNO_3 \rightarrow 2NO + 3H_2SO_4 \qquad (3)$$

Reaction (3) is used to provide the product-end reflux for the Nitrox process (*12*). The fact that the Nitrox process produces enriched ^{15}N is proof of the ability of Reaction (3) to completely reduce nitric acid. Approximately stoichiometric flows of SO_2 and HNO_3 are assured by the control system described below.

APPARATUS

A schematic diagram of the feed exchange process is given in Fig. 2. Two exchanger/scrubber column are used. The nitric oxide gas from the top of the four NO distillation columns is fed into the bottom of the exchangers, concentrated HNO_3 is fed to the top of the exchangers, and deionized water is fed to the top of the scrubbers. The exchanger/scrubbers are 73 mm i.d. (3 in. × 0.065 in. wall) stainless steel columns filled with 4 mm Propak stainless steel packing (Scientific Development Co., State College, Pennsylvania). The packed heights of the exchanger and scrubber portions of the columns are 152 and 122 cm, respectively. Regions at the top, middle, and bottom of the exchanger/scrubbers are left unpacked to permit phase separation where there are flows to and from the column. The exchanger and scrubber sections have cooling coils of copper tubing or water jackets on the exterior walls. A copper-constantan thermocouple measures the temperature of the exchanger wall 30 cm above the bottom of the packing. Technical grade HNO_3 is pumped from a 750-liter holding tank into the exchangers by diaphragm pumps, and the waste HNO_3 flows through a U-trap to a 19,000-liter waste acid tank. The waste HNO_3 passes through heated gas desorbers on the process side of the U-trap.

The NO gas exiting the scrubbers passes through a condenser cooled with 5°C water from a circulating refrigerator. Condensate flows under gravity to a glass reservoir which is drained periodically. Nitric oxide is further dryed in one of two drying beds, 2.7 m by 10 cm diameter, packed with silica gel. A hygrometer continuously monitors moisture in gas exiting the drying bed. A stainless steel bellows pump (Metal Bellows Co.)

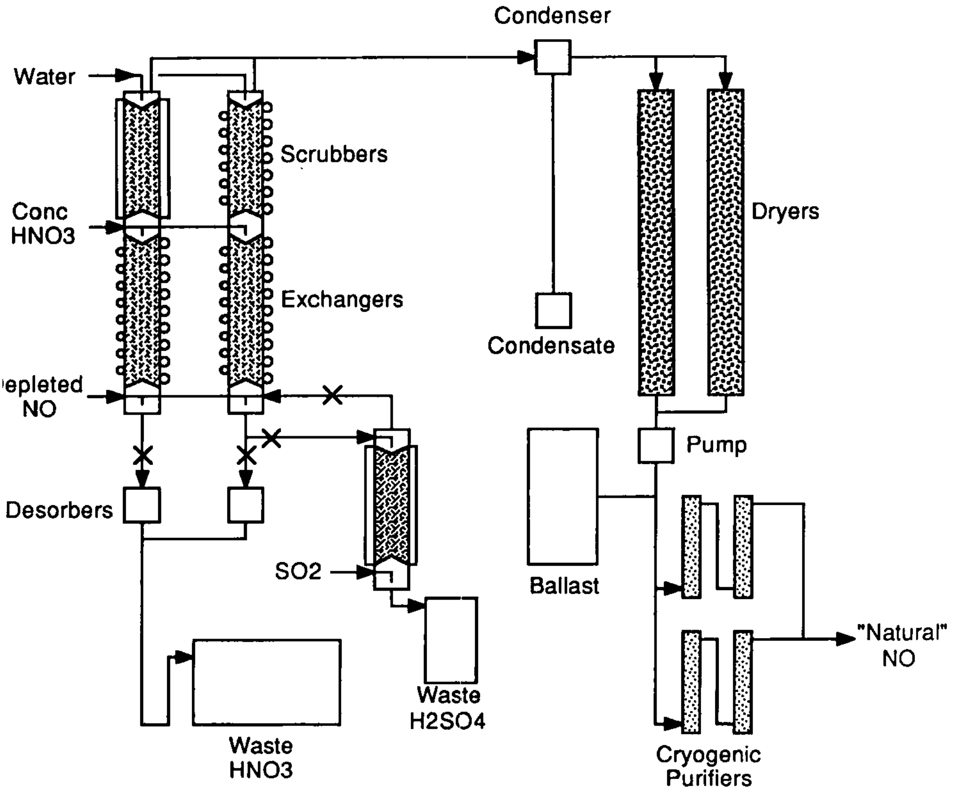

FIG. 2. NO isotope feed exchange system.

compresses the NO into a 12,000-liter ballast tank. Final purification of the nitric oxide is done by flowing the column feed gas through a pair of cryogenic purifiers, maintained at −140°C, just above the NO liquefaction temperature. The cryogenic purifiers each have two beds, 30 cm by 2.4 cm diameter, filled with partially oxidized copper wires.

Makeup NO is generated in a stainless steel packed column filled with 1 cm ceramic Raschig rings. The packed region is 91 cm by 7.3 cm diameter. A water jacket surrounds the packed region to remove heat generated by Reaction (3), which has a heat of reaction of 72.5 kcal/mol of NO at 25°C. Thermocouples in Pyrex wells measure the bed temperature for reaction control purposes at 30, 45, and 61 cm from the bottom of the bed. When the makeup apparatus is in operation, HNO_3 is diverted from bottom of the exchanger to the top of the packing, and SO_2

(99.98% purity) is fed to the bottom of the packing. Waste sulfuric acid is collected in a 100-liter holding tank which is drained manually. The weight of H_2SO_4 in the holding tank is measured using load cells.

SYSTEM OPERATION

Automatic controls permit unattended, 24-h operation of the exchange and scrubbing system. Both regulating and protective shutdown controls are included. Operators are in attendance only during a normal 40-h week, but a number of key parameters (pressures, temperatures, flows) are continuously monitored by a computer which generates telephone calls to operators in the event of malfunctions.

Nitric oxide flow rates from the four distillation columns to the exchange system are controlled by gas mass flow controllers (Tylan Corp.). The deionized water to the scrubbers is controlled by throttle valves and measured by rotameters. Concentrated HNO_3 flow is controlled by adjustable stroke diaphragm pumps and is measured by Teflon rotameters. The waste HNO_3 is heated to 77°C in the thermostatically controlled desorbers to return dissolved NO_x gases back to the process.

Since the waste nitric acid goes through a U-trap to a waste holding tank at atmospheric pressure, the liquid level on the process end of the trap is dependent on the exchanger pressure. The exchanger operating pressure is controlled to avoid blowing the liquid seal in either direction. Exchanger pressure controls include a liquid level control in the acid drain line and a pressure switch. If the exchanger pressure rises, the pressure switch closes the NO feed valve to the exchanger. If the pressure falls, the liquid level in the drain line rises, and the level control closes the NO exit valve from the exchanger system.

The condenser normally drains under gravity, and a liquid level control shuts down the entire process if it senses a liquid pool in the condenser. Bulk liquid in the condenser could be due to flooding of the scrubber or a plugged liquid drain line. Either of these situations could lead to damage to the silica gel in the drying bed and lack of proper drying. When the drying bed is loaded with sufficient water that the NO is no longer dry (about 10 ppm water), the hygrometer triggers a signal for operators to switch drying beds.

Normally both cryogenic purifiers are used to clean the feed to the four NO distillation columns. Each stage of each purifier has individual heaters and temperature controls to keep the temperature slightly above the NO liquifaction temperature (−140°C). If the temperature of the second stage of either purifier rises above −100°C, the valve at the exit of that purifier closes automatically to prevent passage of volatile impurities. Mass flow controllers regulate the feed flows to each of the columns from the purifiers, and the computer generates a callout signal if the flows fall below preset levels.

The NO generation system operates under automatic control, but is run only when operators are present. A fixed flow of HNO_3 solution goes to the NO generator. One thermocouple in the reactor bed senses the heat of Reaction (3) and controls the SO_2 flow between two settings to keep the reaction zone stationary. Typically the reaction zone operates at about 96°C. A second thermocouple, higher in the bed, closes the SO_2 valve in the event the reaction zone starts moving upwards. If the reaction zone moves into the exchanger, a thermocouple on the exchanger wall will stop all flows. Holding the reaction zone stationary assures that the flows of SO_2 and HNO_3 approach the required 3:2 stoichiometric ratio.

Routine work done by process operation personnel includes isotopic analyses of gas streams, regeneration and cleanout of the dryers and purifiers, filling and draining of supply and waste acid tanks, and monitoring of the various process parameters for unusual trends. Isotopic analyses of the NO gas are done on a CEC-621 cycloidal mass spectrometer using the NO^+ ion peaks. The HNO_3 supply tank is filled from drums using barrel pumps. The waste HNO_3 and H_2SO_4 are emptied into portable tanks for transport to another location where the acids are neutralized with caustic solution before disposal.

PERFORMANCE

Over the 6 years the process has been used, the apparatus and process have evolved toward a more efficient and reliable system. Although the portions of the entire system clearly interact with each other, it is useful to consider the basic isotopic exchange and the purification apparatus separately.

The operating total pressure in the exchangers is roughly one standard atmosphere; in Los Alamos atmospheric pressure is 590 torr, and the process pressure is about 150 torr positive relative to ambient. Typical flows to each of the exchanger/scrubbers are 18 STP liter/min of NO, 1.5 mL/s of deionized water, and 1.1 mL/s of concentrated HNO_3. With these flows the molar flow rate of nitric acid is about 25% in excess of the NO molar flow. The actual water and acid flows are routinely adjusted to maintain an acid concentration of 7 *N*. The NO entering the exchanger has an isotopic composition which varies depending upon operation of the various NO isotope distillation columns. A typical composition of the heavy isotopes is 0.04% ^{15}N, 0.01% ^{17}O, and 0.02% ^{18}O. The NO leaving the exchanger has a typical composition of 0.32% ^{15}N, 0.04% ^{17}O, and 0.20% ^{18}O. This exchange does not make use of the isotope separation effect; in fact, the separation effect somewhat hinders attainment of natural isotopic abundances. The waste acid has 0.09% ^{15}N and approximately natural oxygen isotopic composition due to the large molar excess of oxygen in the HNO_3/H_2O solution.

During the early years of use of the exchange process, difficulty was encountered in obtaining proper isotopic exchange and avoiding flooding in the exchange column. Various sizes of Propak, both single sizes and mixed, were used in exchangers and scrubbers. Good performance has been obtained with the 4 × 4 mm Propak presently in use. Both 2- and 3-in. diameter exchange columns were used to obtain liquid and gas rates recommended for Propak (*13*). The most important step in avoiding flooding problems was to support the packing with a conical-shaped stainless steel screen (105° included angle, 10 mesh). Separating the scrubber and exchanger sections by an unpacked region has also helped prevent column flooding due to heat generated by dilution of HNO_3 at the feed point. The water and acid flows are directed onto packing holddown screens on the column axis. The pointed end of the conical screen, whether supporting or holding down, always points toward the packing.

At the bottom of the exchanger, where pure NO contacts the acid solution, local cooling occurs due to some NO going to higher oxidation states. The temperature rises at the top of the exchanger packing due to mixing of water and HNO_3 and the exothermic Reaction (2), which occurs in the scrubber. The efficiency of renormalizing the isotopic abundances in the exchanger is minimally affected by temperature, thus the exchanger is not cooled and runs at room temperature. This is consistent with the observation that 25 to 50°C temperatures were optimal for the Nitrox process (*12*).

Improvements were also made in vessels for desorbing dissolved gases from the waste nitric acid. With early desorbers (drain lines wrapped with heat tape), as much as 10% of the circulating NO was lost and dissolved gases. With the prsent pool boiler desorber, the fraction of lost gas is as low as 1% of the circulating NO flow. In addition to the lower duty cycle on the NO makeup apparatus, the waste acid is handled more safely without dissolved gases. The waste nitric acid is normally quite clear; a blue color to the acid is a sign of dissolved gases such as N_2O_3. Some leak problems at fittings developed with the hot acid (77°C), but these have been addressed by replacing fittings with welded joints.

The NO makeup reactor bed is operated when the pressure in the ballast tank falls below 39 psig (2600 torr). The NO flows from the columns to the exchangers are interrupted because the entire apparatus is run at a higher pressure during NO generation. The HNO_3 flow is maintained slightly in excess of the stoichiometric amount for Reaction (3) to help prevent SO_2 passing into the exchanger. The production rate of NO is typically 0.7 to 0.8 mol/min. The waste H_2SO_4 concentration is 14 *N*, and it has up to 5% HNO_3 in it.

Although the superficial liquid volumetric flow in the scrubber is about half that in the exchanger, there are no signs of significant channeling. Apparently all NO_2 is removed by Reaction (2). The gas in sight glasses at the top of the scrubbers is totally colorless while the gas in the exchanger is notably brown. The scrubbers are operated with 5°C cooling water in the coils or jacket to remove the heat of Reaction (2) and to lessen the load on the condenser.

The condenser removes about 2 L of water per day from a 2 mol/min NO stream. The measured pH of the condensate water in air is 2.5. Using a Henry's law constant of 1.93×10^4 atm for NO at 5°C (*14*), the mole fraction of NO in water is 5×10^{-5} at the system operating pressure. When the condensate water is exposed to air, oxygen begins dissolving in the water, the O_2 oxidizes the NO to HNO_3 (via NO_2), and this mole fraction of NO yields 0.003 *M* HNO_3. The close agreement of this concentration with the measured pH is further evidence of good scrubbing of the gas stream.

Each dryer handles the full NO flow and reduces the water content below 10 ppm for 5 to 7 days before regeneration. The regeneration cycle requires 2 days of purge with nitrogen while the dryer is heated to 150°C, which is followed by cooling and evacuation of the dryer. After perhaps 10 cycles, the silica gel exhibits an increasing pressure drop (>100 torr) or requires more frequent regeneration, and the silica gel is replaced with fresh material.

The cryogenic purifiers remove condensible impurities to an extent such that no plugging of the NO distillation column feed lines occur. Each purifier operates 7 days before it is warmed for a preventive cleanout. If this is not done, the purifier runs well until it removes about 3 STP liters of condensible gases, at which time the flow becomes restricted or stops. A purifier cleanout requires 16 h of purge with nitrogen at room temperature followed by evacuation. On occasion a short cleanout (3 h) is done; however, impurities are not totally removed from the purifier.

Although the copper wires in the purifiers were intended primarily for thermal mass, a green material, presumably a chloride, forms on the pellets. This coating eventually causes flow restriction even when the purifier is warm. When this occurs, the purifier is rinsed thoroughly with water, then dryed and evacuated.

Direct quantification of impurity levels in the NO fed to the isotope columns has been difficult. Water content can be directly measured by the hygrometer. The lower limit of sensitivity of the CEC mass spectrometer is about 100 ppm, and sensitivity to NO_2 is extremely poor on this spectrometer. Samples analyzed on a Nuclide 12-90-GQ mass spectrometer show peaks at masses 44 (N_2O) and 46 (NO_2), but extremely pure NO from the tops of the isotope columns shows similar magnitudes of the same peaks. Such peaks in the mass spectrometer are due to molecular reactions in the spectrometer. Samples analyzed on a Digilab FTS-40 FTIR spectrometer show very small indications of impurities, but the results are mostly qualitative—the impurity levels are well below 100 ppm. Mass spectrometric analyses of final isotopic products show evidence of some SO_2 passing through the entire purification process and through the isotope columns. Based upon the observed SO_2 compositions and the enrichment of the SO_2 in the columns, the estimated maximum level of SO_2 in the feed is a few ppm.

What one is left with is indirect indication of impurity levels. At the temperature of the cryogenic purifiers, −140°C, the vapor pressures of water and NO_2 are sufficiently low to predict sub-ppm concentrations. The fact that the feed lines on the NO isotope columns have not plugged in over 6 years of continuous operation at −150°C is supportive of very low feed impurity levels.

COMPARISON WITH ALTERNATIVES

Prior to development of the feed exchange system, NO was purchased and used in a single pass through the isotope columns. At the final cost of $12/lb (1981 dollars), the feed was costing approximately $35 K/mo based on the flow of the single NO column existing then. The commercially produced NO had a 0.5% N_2 impurity. Although other impurities were initially quite small, NO disproportionates at a significant rate in the gas phase to other oxides:

$$3NO \rightarrow N_2O + NO_2 \qquad (4)$$

Two cryogenic distillation column purifiers were needed to remove these various impurities from the tube trailer NO. The purifiers were automated, but they required frequent cleanouts and significant operator attention. Since NO in the condensed state is a shock-sensitive, detonable high explosive (*15*), it was necessary to have the purifiers operate behind barricades.

It would be possible to produce NO via Reaction (3) and use it in a single pass through the isotope separation columns as was done previously. The amount of required supply HNO_3 would be the same as with the present system (about 95 L/d per exchanger), but the SO_2 useage would be 138 kg/d, up to 100 times that at present. The waste H_2SO_4 would require 50% more equivalents of caustic to neutralize. The $^{14}N^{16}O$ stream was a useful by-product and was converted to labeled compounds in the past, but recent demand for these compounds has been relatively small. As a result, the isotopically depleted NO would have to be converted to some innocuous chemical forms.

Various other NO production methods which have been considered include reaction of $NaNO_2$ with SO_2 (*16*) and oxidation of ammonia. The first method is reputed to produce very pure NO; however, the $NaNO_2$ is not as standard an industrial chemical as are other potential feedstocks. Waste products would include Na_2SO_4 and other sodium compounds. Catalytic NH_3 oxidation to NO is a widely used reaction, but it is almost exclusively used as the first step in production of HNO_3. Stopping this reaction at NO would require rapid cooling and significant purification of product.

A generic process for producing NO would be any one which had the net reaction

$$4HNO_3 \rightarrow 4NO + 2H_2O + 3O_2 \qquad (5)$$

This would most likely be an indirect process which has several reactions and chemical intermediates which are recycled. Reaction of copper or zinc with HNO_3 followed by electrolytic reduction of the metal ions back to the elemental state was suggested (*17*), but this method has not been actively pursued. Ishida and coworkers have investigated chemical systems which could accomplish Reaction (5) as part of their work to eliminate the need for supply chemicals and waste disposal in the Nitrox process. Their systems include a Fe(II)/Fe(III) closed-cycle process (*18*) and a process for reconverting H_2SO_4 to SO_2 (*19*).

Each of the alternative processes has major disadvantages compared to the feed exchange method for NO feed to the isotope separation columns.

When NO was purchased the cost of NO was extremely high, and the amount of purification and operator attention required was as high as with the exchange method. Use of Reaction (3) to produce NO would greatly increase the need for chemical supplies and waste disposal; purification of NO would be no less easy than at present. The other methods considered may be useful, but much development would be required to obtain a reliable process. The magnitude of purification problems associated with these methods is unknown.

CONCLUSIONS

An isotope exchange feed process for a NO isotope distillation plant has been designed, constructed, and operated for over 6 years. The process recycles isotopically depleted NO by reenriching the NO to natural isotopic abundances via chemical exchange and by returning the NO to distillation columns as feed material. To the first approximation, the exchange process allows conservation of the NO inventory within the isotope plant. Multiple purification stages reduce impurity levels to less than 10 ppm of condensibles in the recycle NO. The system is fully automated for unattended operation. A subprocess is used to generate NO to make up for small losses in the exchange system, in the isotope columns, and product withdrawal.

The NO exchange and generation processes have achieved the goal of providing isotopic feed to the NO isotope separation columns in a smooth and continuous manner. Over 35 kg of ^{15}N and 30 kg of ^{18}O have been produced by the isotope columns since the feed exchange process was put on stream.

Acknowledgments

The authors wish to acknowledge significant contributions by C. A. Lehman, J. G. Montoya, T. A. Nothwang, and R. Romero in the construction, operation, and maintenance of the feed exchange process.

This work was performed under the auspices of the U.S. Department of Energy.

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Received by editor May 13, 1988