Written: February 18, 1970

Distributed: April 10, 1970

LA-4391

UC-22, ISOTOPE SEPARATION

TID-4500

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

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Using Carbon Monoxide Distillation

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Dale E. Armstrong
Arthur C. Briesmeister
B. B. McInteer
Robert M. Potter

This work supported by the Divisions of Biology and Medicine
and Military Application.

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The Los Alamos carbon-13 plant.

A CARBON-13 PRODUCTION PLANT USING CARBON MONOXIDE DISTILLATION

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ABSTRACT

A fractional distillation plant using carbon monoxide with an isotope separation capacity of approximately one mole per day of carbon-13 at 95% concentration has been built, and has been operated for eight months. The distillation column is 140 ft long, has a single 1-in.-diam column for the bottom 80 ft, 20 ft of four 1-in. columns in parallel in the middle, and a top section of 40 ft of 12 columns in parallel. It is packed with wire helices. The column is fed at the 120-ft level; in the top 20 ft, 135 moles of CO per day are stripped to 0.5% carbon-13 from the natural abundance of 1.1%. The HETP is about 1 in. The column is enclosed in a 6-in.-diam Dural vacuum jacket, using Styrofoam spacers and aluminized Mylar film insulation, and is situated in a 125-ft-deep hole in the ground that has an 18-in.-diam steel liner extending 15 ft above ground into a second-story control room. The plant uses about 1 kW of heat, and about 1000 liters per day of liquid nitrogen, of which about half is used to condense the carbon monoxide.

I. Introduction

Isotope separation processes take advantage of differences in physical and chemical properties between isotopes to effect separation. One such difference is in vapor pressure: liquid carbon-12 monoxide has a vapor pressure 0.8% greater than that of carbon-13 monoxide. Fractional distillation would therefore concentrate the heavier isotope in the liquid phase. A fractional distillation plant has been built that is capable of separating nearly one mole per day of carbon-13 at 95% concentration as carbon monoxide.

The production of carbon-13 by low-temperature distillation of carbon monoxide is not a new process. Johns and London¹ completed such a plant in 1949. A more recent installation has been constructed at Mound Laboratory.² The LASL plant is distinguished by a higher production level, 4 kg of carbon-13 annually; by its use of multiple parallel columns for the early stages; and by its novel housing, a hole in the ground.

In August 1968, the Los Alamos Scientific Laboratory (LASL) was requested by representatives of the Division of Biology and Medicine of the Atomic Energy

Commission to build and operate a facility to produce "a few kilograms of carbon-13 over the next few years" as part of a program to stimulate use and production of this isotope for chemical and biological research throughout the scientific community. We had had experience with low-temperature distillation plants for other isotopes,³ and had planned to construct a more modest carbon monoxide distillation plant to provide carbon-13 for general research at LASL. The first carbon monoxide was admitted to the completed plant in July 1969.

An unforeseen difficulty arose in September 1969 just as the product concentration began to approach 95% carbon-13; undetected carbon dioxide condensed and plugged the 12 small feed lines, thereby seriously unbalancing the matched flows to the column. After a few weeks of token production, the column was warmed and the CO₂ was pumped away. More carefully purified gas at 1 ppm CO₂ was then flowed into the column and, alerted now, we detected incipient plugging after a few weeks. The column was closed off, and the techniques were developed for obtaining our ultimate purity of 0.05 ppm

CO₂ as described in this report. With gas feed of this purity, the column no longer plugged, and the pestiferous feed lines opened up. At the time of this report, the plant has been operating continuously, as designed, with no further trouble.

Complete engineering drawings of the essential parts of this facility are available from the Clearinghouse for Federal Scientific and Technical Information, National Bureau of Standards, U. S. Department of Commerce, Springfield, Virginia, 22151, as CAPE-1970.

II. Design Considerations

A. General. A distillation column for isotope separation operates on the small differences in the vapor pressure of the isotopic species of the substance being distilled by repeated exchange between liquid and vapor. In a packed column, the packing material forms an evenly distributed, highly dispersed surface over which the liquid flows downward from the condenser to the boiler where it is converted into vapor. The counter-current motion of these two phases plus the considerable contacting surface area between them effects the desired separation.

The rate of flow, called the boil-up, determines the rate of effective production. If CO of normal 1.1% carbon-13 abundance, is fed to a plant having Q moles/day of boil-up, then the ultimate production capability, σ , is given approximately by (see Sec. III)

$$\sigma = \epsilon Q c_0 \quad (1)$$

where ϵ is the aforementioned vapor pressure difference of 0.008 and c_0 is the natural abundance of 0.011. Hence each mole/day of boil-up allows only 0.000088 mole/day of carbon-13 production, or 1 mole/day of carbon-13 production requires at least 11,400 moles/day of boil-up. This relates directly to the consumption of liquid nitrogen and the boiler power requirements for such a plant, 420 liters of liquid nitrogen daily for 800 W of heater power. These values may be compared with our final design of 0.89 mole of carbon-13 per day, 960W, and 520 liters of liquid nitrogen, with additional losses causing perhaps 1000 liters total daily consumption.

The second major design consideration has to do with the length of the plant and the number of simple single-stage separations necessary to achieve good enrichment. If the plant were designed to just attain 95% carbon-13 from natural abundance, the number of stages would be given by

$$N = \frac{1}{\epsilon} \ln \frac{c_f (1 - c_0)}{(1 - c_f) c_0} \quad (2)$$

where c_f is the desired product concentration. For $c_f = 0.95$, this expression predicts 930 stages. By rule of thumb, a production system is twice as long as the minimally designed system, or 1860 stages. With 1 in. required per stage, the HETP (height equivalent of a theoretical plate), the resulting plant length is 155 ft from

these simple considerations; the final design was 140 ft long.

Finally, naive considerations may be applied to the CO requirements. A mole production of carbon-13 requires approximately 100 mole/day of completely stripped feed. This would create a formidable separation job, especially in boil-up requirements. We compromised, devoting the upper 20 ft to this stripping function, which allowed stripping to 0.5% carbon-13 while using a feed of 135 moles of CO daily.

A 3-ft-diam hole, 125 ft deep, was drilled through the soft tuff (compacted volcanic ash) at a site where a one-story laboratory addition was planned. The 18-in.-diam steel liner of this hole extends upward through this structure, terminating 15 ft above ground level. The prefabricated metal control room for the carbon-13 plant, including a tower and hoist capable of lowering 20-ft-long column sections was placed on the roof of the one-story addition. A 50-gal storage Dewar for liquid nitrogen, open to the atmosphere, is mounted on the side of the control room. The hydrostatic head of liquid in this automatically filled Dewar maintains equal liquid levels in the column condenser and in all other auxiliary equipment requiring liquid nitrogen. The hole liner and control room have the capacity for several other such columns for production of either carbon-13 or other isotopes.

Liquid nitrogen is stored in a primary supply Dewar located approximately 200 ft from the control room. On demand, the liquid nitrogen flows through a vacuum-insulated 1-in.-diam transfer tubing surrounded by aluminumized Mylar film.

Carbon monoxide is supplied from a tube trailer or 20,000 standard cubic feet capacity located 600 ft from the control room, in a marked, unfrequented area. All operations near the trailer are performed with gas masks because of carbon monoxide's hazardous nature. For the same reason the control room is well ventilated, and all potentially dangerous lines and equipment are inside a separate hooded and ventilated area. A continuous CO detector samples the air in these regions, with an alarm at 50 ppm CO. It has been estimated, however, that the average carbon monoxide flow through this plant is equivalent to the exhaust of a single, poorly tuned automobile.

Eleven vacuum systems are required for this plant. We have located all the mechanical forepumps together in a separate room approximately 30 ft from the control room with 1-5/8 in., or smaller, copper lines for piping. Chilled circulating water, compressed air, helium, nitrogen, oxygen, and propane services are supplied, as well as heated air, air conditioning, and electrical power.

Two special instruments are a helium-type leak detector and an analytical mass spectrometer, located in the control room.

(a)

(b)

(c)

Early construction phases of the carbon-13 plant. After the hole was drilled (a), the steel liner was lowered, its joints were welded, and it was cemented and packed into place (b). The column vacuum jackets were then lowered into the hole in 20-ft sections, with mechanical vacuum joints between them (c).

(a)

(b)

The prefabricated control room was brought out (left) and lowered into place (right).

The carbon-13 plant control room. Vacuum lines and exhaust ventilation enter from the left. On the right at the roof edge is the 50-gal storage Dewar. Atop the control room are the tower and hoist for lowering column sections; for this operation a hatch in the roof of the control room is opened, as well as the full-height door.

The 4000-gal primary storage Dewar is regularly filled with liquid nitrogen. A pressure-control switch ordinarily opens a solenoid-operated vent gas valve, releasing the vapors through the opening on the upper part of the tank, and maintaining 8-psia liquid pressure. During filling, the vapors are diverted and the pressure is manually controlled. The vertical riser carries liquid nitrogen to the carbon-13 plant.

An expansion joint for a 150-ft straight run of transfer tubing. This design with three different sets of sliding O-ring seals permits all the seals to be at ambient temperature and allows the outer tube of the vacuum jacket to be rigidly held, while the inner tube that conducts the liquid nitrogen is free to shrink more than 2 in.

Liquid nitrogen is delivered to the secondary 50-gal Dewar through the vertical transfer line above it. A phase separator permits the vapors to exhaust to the air. The Dewar and all transfer lines are vacuum pumped for insulation. Liquid nitrogen is supplied to the plant and auxiliary equipment through the horizontal transfer tubing.

Cold nitrogen vapor is boiled off the column condenser. To prevent ice formation which might block this flow or upset the liquid level, a vent tube heater maintains a warm exit. The large valves that admit the liquid nitrogen to the column or other equipment are encased in Styrofoam, then wrapped with weatherproof tape.

Immediately inside the control room those vacuum systems that require diffusion pumps are connected to this bank. Also visible are shut-off valves and pneumatic vacuum valves, as well as thermocouple- and ionization-type vacuum gauges.

SIX-INCH VACUUM JACKET COUPLING

The couplings between the 20-ft-long sections of Dural vacuum jackets are mechanical seals with triple O-rings. All seven sections were lowered and connected in one day. Later testing with a helium leak detector showed all the seals to be tight.

B. The Column. The column was constructed of 20-ft-long unit tubes of 1-in.-o.d. by 0.035-in.-thick stainless steel seamless tubing. Seven sections, designated A through G were assembled and lowered into the vacuum jacket, with G lowermost. They are described in Table I. The typical sequence of operations was as follows.

1. One-inch tubing was cleaned and cut to length to form the unit tubes.

2. Heaters, thermocouples, and small tubing for gas leads were attached.

3. Unit tubes were inserted in Styrofoam spacers at 3-ft intervals. These spacers serve as insulators and help maintain structural rigidity of the assembled section.

4. Electrical power leads and heater interconnections were attached.

5. The assembly was wrapped with 40 layers of aluminized Mylar film.

6. Binding wires were wrapped around each Styrofoam spacer, anchoring the thermocouple and power leads, gas lead tubes, and four guide tubes of 1/4-in.-o.d. stainless steel tubing, all attached to the periphery of the Styrofoam.

7. The completed assembly was attached to a lowering clamp and transferred to a semicircular carrying

cradle, which was carried to the assembly tower. Here the assembly was lifted to a vertical position above the hole.

8. The unit tubes, gas lead tubes, thermocouples, power leads, and guide tubes were connected to the previously assembled lower sections.

9. All column and gas leads were tested for leaks with a helium leak detector. A resistance check was made on all electrical connections. Gas lead tubes were checked for flow impedance to detect partial plugs. Heaters were briefly energized, and thermocouple response was noted.

10. Electrical connections were insulated and checked for shorts, and packing was loosely poured into the unit tubes. A mechanical vibrator was used to settle the packing, and the weight of packing in each section was recorded.

11. The section was then lowered to flange level and blocked in place, freeing the hoist for the next section.

Whenever gas lead tubes, warm throughout most of their path, connected to the cold column it was necessary to provide for contraction of the column when cold. This amounted to 4-in. shrinkage at the lowermost point. Because all such tubes were made of 1/8-in.-o.d. tubing, a simple spiral coil sufficed. However, where the 12 feed tubes connected at the A-B interface it was necessary to wind these spirals loosely around the individual unit tubes. Even so, the clearance between these tubes was so

TABLE I
THE SEVEN COLUMN SECTIONS

Section Designation	Nominal Length (ft)	Active Length (ft)	No. 1-in. Tubes	No. Heaters	Power Added (W)	Total Boil-up (W)	Gas Leads ^a	Thermocouples ^b	Mass of Packing (kg)
G (bottom)	20	18.9	1	2 ^c	26.6	26.6	3 at bottom 1 36" from bottom	3 at bottom 2 36" from bottom	3.40
F	20	20.7	1	1	26.6	53.3	---	1 at bottom	3.76
E	20	20.2	1	1	26.7	80.0	---	1 at bottom	3.24
D	20	20.0	1	---	---	80	---	1 at bottom	3.31
C	20	20.0	4	4	240	320	1 at bottom	2 at bottom	12.63
B	20	20.0	12	24	640	960	1 at bottom	2 at bottom	37.94
A	20	20.0	12	---	---	960	12 at bottom 12 at top	1 at bottom 1 6" below top	37.20

^aAll gas leads of 1/8-in.-o.d. by 0.035-in.-thick stainless steel tubing except the 12 top leads of the A-sections which are of 3/8-in.-o.d. tubing to allow column evacuation.

^bAll thermocouples are 20 gauge copper-constantan.

^cIf the bottom temperature exceeds 0°C, the power for section G is automatically transferred from the bottom 26.6-W heater to a similar stand-by heater located 36 in. higher.

small that the spirals intermeshed with their neighbors.

At the B-C transition, the 12 B tubes reduce to four C tubes. This is accomplished by four hollow manifolds allowing three of the B tubes to communicate with one of the C tubes. No packing support screens were used at these points; the transition manifolds were themselves filled with packing. A similar situation occurs at the C-D transition where the four C tubes reduce to the single D tube.

The condenser unit was connected to the column by inserting conical screen holders above the packing in the A tubes and reducing the 1-in.-o.d. tubing to a short 3/4-in.-o.d. length communicating to the 3/4-in.-o.d. copper condensers surrounded by liquid nitrogen.

All field connections were silver soldered, whereas welding was used wherever possible in assembled, externally fabricated units such as the transition manifolds and the condenser head.

A tribute to the excellence of these techniques is the uneventful, if tedious, assembly operation. Thermal insulation was excellent, with only 35-W stray heat leak, and no gas leaks appeared when the column was cooled. Apparently every connection was made properly.

(a)

(b)

(c)

(d)

Assembly of column G. (a) A strip heater is soldered and clamped to a copper boiler unit. Power leads and thermocouples are attached. (b and c) Styrofoam spacers are slid into place, and the column is wrapped with 30 layers of aluminized Mylar film. (d) The Teflon base support is ready to receive the four $\frac{1}{4}$ -in.-o.d. guide tubes.

Column G is transferred to a cradle and attached to the hoist preparatory to lowering into the hole.

The twelve-to-four tube transition between sections B and C. Note heaters attached to the 12 B tubes.

Details of the four-to-one tube transition between sections C and D.

Feed lines connected to the A-B interface. They spiral around the columns to accomodate to the relative expansion.

The condenser head is connected atop the entire assembled column.

The Styrofoam spacers were machined to receive 1, 4, or 12 tubes and were placed every 36 in. along the length of each section. The packing material, Heli-Pak 3013, manufactured by Podbelniak, Inc., Bensenville, Ill., is made of stainless steel wire.

The assembled column during operation.

Details at the column top. . .

12 TO 4
TRANSITION

4 TO 1
TRANSITION

BOTTOM
HEATER
UNIT

...and on to the bottom.

An overall view of the column.

C. Flow Control. The sequence of events for the gas fed to the plant is as follows.

1. Raw CO is supplied from a 22-tube trailer initially pressurized to 1500 psi.

2. After passing a pressure regulating valve (PRV) set for 50 psia, the gas is piped through a 600-ft-long, heavy wall, stainless steel, welded line to the control room.

3. It encounters two 2½-in.-o.d. by 4-ft-long tubes in series, each filled with Ascarite (a granulated material consisting of NaOH on a matrix of asbestos) for removing CO₂.

4. It is reduced to 30-psia pressure by another PRV, and passes, in turn, through two chilled stainless steel filters at -181°C for final getting of condensible impurities.

5. It is again reduced by a PRV to 28 psia, and passes through one arm of the electric flow meter and then through the thermal control valve. Impedance of this valve reduces the pressure to 20.5 psia.

6. It then subdivides into 12 parallel paths. The flow impedance of each path is a combination of the feed line impedance itself (more than 30 ft of 1/8-in.-o.d. tubing) and a metering needle valve that comprises the dominant impedance of the combination. The feed gas then enters the column at 12.5 psia.

The major portion of this gas flow exits from the top of the plant. The sequence for this top flow is as follows.

7. The 12 top flow gas streams exiting at 10.5 psia first encounter one of a set of 12 matched fixed flow-impedances made of flattened 1/8-in.-o.d. tubing. They are then manifolded into a single stream at 6.0-psia pressure.

8. This top flow stream then passes through the second arm of the electric flow meter.

9. The stream then encounters a floating ball flow meter and a throttle valve that sets the net level of flow rate. The gas pressure is less than 1.0 psia at this point.

10. This gas is then pumped by a mechanical vacuum pump and is vented into a site ventilation system. Ultimately it issues from a stack highly diluted.

The far smaller flow of product gas from the bottom of the plant is as follows.

11. Issuing from the plant at 18.0 psia, the gas is

periodically admitted to a metering volume of 165 cm³ every 10 min by means of a timer-controlled solenoid valve.

12. During alternate portions of this timed cycle, the metering volume is connected to a cryogenic storage trap immersed in liquid nitrogen, which reduces the metering volume pressure to 6.0 psia. This 700-cm³ volume trap is able to store 3 weeks' production, if necessary.

In practice, the trap is warmed on a weekly schedule, and the product material is temporarily transferred to another cryogenic trap on the final product manifold.

13. If the product is desired as CO₂, it is passed through a tube containing CuO at 400°C, and the converted gas is trapped cryogenically in a final pressure cylinder. This cylinder, when warm, then contains liquid CO₂ at 750-psi pressure.

14. Otherwise, the product is packaged into 20-liter gas storage cylinders at 300-psi pressure by warming the temporary cryogenic trap.

Diagnostic data are obtained from the pressure gauges, flow meters, and mass spectrometer sampling points located throughout the plant. A multipoint recorder maintains a continuous record of 16 thermocouples. The feed flow and product flow are automatically controlled by the electric flow meter network and by a timer cycle, respectively. The secondary liquid nitrogen supply is controlled by a liquid level control that opens the transfer line from the primary storage dewar on demand. The temperature of the copper oxide furnace is also automatically controlled.

Emergency controls include heater protection overrides for the four column heaters and for the two electric flow meter heaters to prevent burnout. A relay interlock causes all three column flows to be interrupted if the electric flow meter protection circuit is energized. Relief valves throughout the plant protect against overpressuring damage to the equipment. However, should the final product trap pressure become excessive, its contents would transfer to a dump tank. In the event of power failure, the insulating vacuum of the column jacket is isolated. Meanwhile, an auxiliary emergency power supply is automatically started up to supply the entire room. Additional emergency protection is obtained from a central switchboard continually maintained by the Los Alamos Scientific Laboratory for all strategic equipment emergencies, of which the carbon-13 plant has a circuit. Staff personnel are called immediately if a signal is received. This occurs if there is a power failure, if the secondary supply of liquid nitrogen becomes too low, if the primary liquid nitrogen pressure becomes too low to transfer, if the column vacuum is lost, or if either of the main flows to or from the column ceases.

Starting such a plant is tedious, and restarting it is at the sacrifice of 6 weeks' steady production. It is particularly important that emergencies involving loss of power to the column heaters, loss of column vacuum, and loss of liquid nitrogen refrigerant supply be as infrequent as possible, because they may require that the column be preflooded again. Power outages of less than 10 sec have been sufficient to deflood the column.

The start-up of this plant proceeds as follows. With the warm column evacuated, liquid nitrogen is admitted to the condenser and a flow of purified CO gas is begun to the plant. Approximately 24 h is required for the entire column to be cooled by the liquid. Continuing the inflow, one watches the liquid head appear at the various levels of the column on the system of pressure gauges until the C-section is full. We have at this point used two different procedures successfully. The first and simplest is to continue the inflow until the B-section is full. All column heaters are then turned on. The resulting boiling liquid then nearly fills the entire column, possibly requiring topping out until strong pressure surges indicate that even the condenser tubes are full of liquid. One then begins withdrawing CO gas from the column through the top flow network, and the flood begins to subside. Finally, after several weeks, the liquid level reaches the bottom of the column as indicated by a slow rise in the bottommost thermocouple. When the flooding is done entirely with normal material, one finds the enrichment to be about 50% carbon-13 at this point, and several more weeks are required to attain 90 to 95% carbon-13 and begin production. The second procedure involves admitting sufficient liquid to fill under boiling one tube of the A and B sections. All 12 tubes are then pressurized with helium gas to 25 psi, and, one by one, this helium pressure is reduced in a selected tube, causing the liquid to be pushed up into this tube from the others. Slowly

(over a 30-min period) this reduced pressure is increased to its original value, thereby wetting the packing of the selected tube. This is repeated for each of the 12 tubes, and the helium is then slowly and uniformly removed, and CO withdrawal continues as before. This procedure involves about one-third as much liquid as the other.

It is found that a weekly check for feed line clogging and cleanout of any plugged lines is desirable. This necessity arises from the trace amounts of CO₂ carried into the plant at levels of 0.05 ppm or less in the purified gas. Apparently short plugs of solid CO₂ form slowly in these lines where they enter the A-section. The plugs are detected by flowing at 21.0 psia to one tube at a time. A comparative flow meter, constructed of a short flattened length of tubing in the feed line, is read, and a 0- to 4-in. H₂O differential pressure gauge registers the pressure drop. The total time for determining how well the feed lines are matched in their overall flow impedance is less than one-half hour. If one of the lines shows a markedly lower flow, it is possible to remove the plug as follows. The throttle valve for this line is opened wide, and 30 psia of feed gas is applied to the plugged line. After 5 min the flow increases to a maximum steady value. This large flow, about ten times the normal flow rate for one line, is continued for another 5 min, and the throttle valve is reset. This plugging check and cleanout procedure involves less than 1 h of down-time for the column flows.

Less frequent maintenance procedures involve removing and replacing the spent Ascarite and mechanical maintenance of the vacuum pumps and instruments. When operating steadily, the plant requires only a few hours per day of an operator's time. No attendance is ordinarily required for a weekend.

All control lines of the plant lead first to this upper panel of isolating valves. Also shown is the assembly of pressure gauges at the various process points.

Flow meters and control valves for flow control throughout the plant are mounted in the lower panel. Pilot lights indicate operation of solenoid valves. The switch control panel at the bottom is used to place heaters and solenoid valves under automatic or manual control.

Incoming lines from the column connect in the rear of the upper panel. Feed lines in the top row have adjustable needle valves for matching the 12 feed flows. Lines from the top of the column are connected to the middle row of valves which are connected to fixed matched-flow impedances made of flattened tubing and finally to the draw-off manifold. The valves in the bottom row serve various other functions.

This maze of lines is necessary for the lower valve control panel.

Control instrumentation for the plant.

Through two separate networks, the feed flow to the column and the top draw-off flow are passed through this electric flow meter. Each stream is brought to the same reference temperature with cooling water and is then subjected to a small fixed matched heater power while thermally isolated, increasing the gas temperature to approximately 80°C . The increased temperature of the two streams is sensed by a pair of thermocouples in a differential network, thereby allowing controls to match the two flows and prevent either excess or deficiency of liquid in the column.

A -1 - to $+1$ -mV on-off controller causes power to be applied to the heater of the thermal control valve for the feed flow shown wrapped in asbestos tape above the Lucite protective box. This thermal valve is simply a flattened length of tubing bound to a cartridge heater. Its impedance variation is caused by the changes in the density and viscosity of the flowing gas, being 40% greater at 85° than at 25°C .

In this single liquid nitrogen container are three chilled line filter units, a cycling cryogenic pump, no longer used, and the cryogenic trap for product storage. Each filter (for 7- μ m particles) is maintained at -181°C by an individual bath of pressurized liquid nitrogen at 60 psia. Prepurified feed gas is flowed successively through two of these filters with the third on stand-by. Prior to each filter the gas is completely chilled by a 6-in.-long region packed with copper wool.

Surrounding the cryogenic product trap is a metal shroud, open at the bottom. When this region is open to the atmosphere it fills with liquid nitrogen, but pressurizing it with helium displaces the liquid and the trap may be warmed electrically *in situ*.

The gauge above the flattened tubing is used to measure the 12 individual feed-flow rates. Normally the feed gas passes through the unflattened branch.

This furnace, maintained at 400°C , surrounds a 2-in.-i.d. by 12-in.-long stainless steel tube filled with copper oxide. It is used for converting CO to CO_2 as final product.

Twelve separate locations throughout the plant are available for mass spectrometer analysis for isotopic abundance of the molecules of CO formed by ^{12}C , ^{13}C , ^{16}O , and ^{18}O . Gross impurity gases of over 100 ppm abundance, including CH_4 , Ar, O_2 , CO_2 , and $\text{Fe}(\text{CO})_5$, may also be measured.

Trace amounts of condensible impurities are measurable with this addition to the mass spectrometer sample inlet system. A 0.2-liter/atm sample is condensed in the small length of capped tubing. The line filter immediately above it is then also chilled with the liquid nitrogen, and the CO is removed by pumping through this filter. The system is then warmed to room temperature, and the impurities are released into the mass spectrometer sample inlet. This allows detection of 0.02 ppm CO_2 , which concentration may be decreased tenfold for a larger sample.

III. Performance

When first embarking on the design of this plant, having no experience in distillation of CO, we attempted to guess the safe level of boil-up for this material in a 1-in.-o.d. column. As mentioned in the Introduction, this figure is intimately related to the ultimate production level of the plant. Our guess was 40 W, but the British experience with CO distillation¹ was at a lower power level as well as with different packing material. It became mandatory that preliminary experiments be done to determine if such power was safely away from the flood point, as well as to determine HETP, holdup, pressure drop, and condenser performance and to gain experience in small-scale distillation and isotopic analysis of CO.

A 120-cm-long experimental column quickly showed that flood conditions occurred only above 100 W (approximately 105 W). Near this operating point all other parameters become worse: the holdup, the HETP, and the pressure drop all increase. Somewhat arbitrarily, we selected 80 W as our design operating power. Other measured parameters were an HETP of 2.0 cm, and holdup of 0.4 STP liter per cm. The column's pressure drop was 37 mm Hg at 700-mm-Hg operating pressure.

With this factor of two increase in power, our original 1 kg/yr plant design was doubled in production capability. By increasing the number of top stage tubes from 6 to 12, we attained another doubling. Such was the genesis of the final design.

The production period chosen for this analysis was the two weeks from February 1 to 15, 1970. A comparatively steady state had been attained before this, although the operational history had not been outstandingly smooth. In particular, a somewhat dubious preflood operation had been performed 6 weeks previously, and, furthermore, a very short power outage had occurred on January 26. Thus, these performance data are conservative and realistic, rather than display items. Data were taken daily during this period, and those shown in Table II represent an average.

Table II A shows the observed performance characteristics of the plant during this period. The temperatures given are on the basis of the carbon monoxide vapor pressure. Analyses were obtained mass spectrometrically from the peaks at mass numbers 28, 29, 30, and 31 assuming these to arise from combinations of ¹²C, ¹³C, ¹⁶O, and ¹⁸O, thereby neglecting all contributions of ¹⁷O. Values given for ϵ are from Johns' measurements⁴ according to his formula,

$$\epsilon = (78.2/T^2) - (0.394/T) \quad (3)$$

for the vapor pressure differences of ¹³C¹⁶O and ¹²C¹⁶O. Two general remarks are, first, that the feed material is slightly lower in its abundance of both heavy isotopes than is usually assumed for normal abundance: namely, 1.11% for ¹³C and 0.204% for ¹⁸O. Second, the production rate of 18.2 liters/day of CO which is 92.76% ¹³C corresponds to an annual production of 3.6 kg of contained ¹³C.

To analyze the distribution of isotopic composition numerically, we renormalized the observed concentrations for simplicity to include only the three major molecular forms ¹²C¹⁶O, ¹²C¹⁸O, and ¹³C¹⁶O whose mole fractions are denoted by c_1 , c_2 , and c_3 , respectively, and shown in Table II B. The equations that were numerically integrated are

$$\frac{dc_2}{d\lambda} = (\epsilon' - \epsilon'c_2 - c_3 + \frac{\sigma}{\epsilon Q})c_2 - \frac{\sigma c_2^*}{\epsilon Q} \quad (4)$$

and

$$\frac{dc_3}{d\lambda} = (1 - \epsilon'c_2 - c_3 + \frac{\sigma}{\epsilon Q})c_3 - \frac{\sigma c_3^*}{\epsilon Q} \quad (5)$$

where $\lambda = \epsilon N$ is a dimensionless length variable; ϵ' is the ratio of the ¹⁸O separation factor to that for ¹³C, assumed constant at 0.7; σ is the withdrawal rate; c_2^* and c_3^* are the withdrawal compositions; and N is the number of theoretical plates. First the integration is performed from the product end to C, to B, and finally to the feed point. A new integration is then performed from the top draw-off to the feed point. This calculation gives the composition distribution throughout the plant and the number of plates for each section, which allows computation of the HETP parameter. As shown in Table II-B, the large HETP for the upper sections indicates incomplete preflooding. It is estimated that with HETP values of 2.0 cm throughout, at least 10% higher production rate should be attainable.

References

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3. B. B. McInteer and Robert M. Potter, Ind. Eng. Chem. Process Design Develop. 4, 35 (1965).
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TABLE II
PLANT PERFORMANCE
Feb. 1 - 15, 1970

A - As observed

Feed Flow 3700 liters/day
Bottom Flow* 18.2 liters/day
Top Flow 3680 liters/day

	p, psia	Temp, °C	Isotopic Composition, %				
			¹² C ¹⁶ O	¹² C ¹⁸ O	¹³ C ¹⁶ O	¹³ C ¹⁸ O	
Condenser	—	-198.0	—	—	—	—	
Top of Plant	10.6	-194.5	99.20	0.166	0.631	—	(Raffinate Stream)
Bottom A	12.1	-193.2	98.45	0.272	1.27	0.003	
Bottom B	13.2	-192.7	95.28	0.81	3.89	0.02	
Bottom C	14.5	-191.7	82.87	2.70	14.40	0.03	
Bottom G*	18.0	-189.6	1.89	5.35	92.46	0.30	(Product Stream)
Feed	—	—	98.72	0.197	1.084	0.002	(Feed Stream)

B - Adjusted and calculated

Feed Flow 3700 liters/day
Bottom Flow 18.2 liters/day
Top Flow 3680 liters/day

				Q (boil-up), liters/day	ε, %	λ	Calculations	
	c ₁ , %	c ₂ , %	c ₃ , %				N, No. plates	HETP, cm
Top of Plant	99.20	0.166	0.631					
				308,500	0.751	1.6	213	2.86
Bottom A (Feed Point)	98.45	0.272	1.274					
				308,500	0.718	1.9	265	2.30
Bottom B	95.28	0.81	3.89					
				102,800	0.706	2.2	312	1.96
Bottom C	82.90	2.70	14.40					
				25,700	0.671	3.7	7.7	2.12
				17,800	0.671	2.0		
				8,900	0.671	2.0		
Bottom G	01.90	5.37	92.73					

*After subtracting CH₄ impurity present to ~3%.

Mass spectra of plant CO compositions during operation.

Computed profile of isotopic compositions during production period. For computational purposes $^{13}\text{C}^{18}\text{O}$ was neglected and the data were renormalized to a three-component mixture. Values of λ , the dimensionless height variable, were determined from the observed $^{13}\text{C}^{16}\text{O}$ concentration. Points shown are the observed data for $^{12}\text{C}^{18}\text{O}$.