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ISOTOPE SEPARATION BY DISTILLATION: * DESIGN OF A CARBON-13 PLANT

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ABSTRACT

This isotope separating plant has a great height with many long columns in parallel, low process flows compared with its boil-up, and a long time response. All these features result from dealing with a mixture whose separation factor is near unity, the carbon monoxide system. Considering that there are three isotopes of oxygen involved, six molecular species are being separated. Although CO molecules are unreacting within the columns, an exchange reactor is used when the separation is partially complete to assist in obtaining high quality product. These considerations have been formulated in a good theoretical design procedure along with excellent mechanical design, fabrication and assembly to yield a plant of high performance for carbon-13 production.

Separating isotopes is like separating anything else.

Separating isotopes is unlike separating anything else.

Both of these statements are true.

The distinctive thing about isotopic mixtures and their separation is the great similarity which exists in the properties of the components, or put another way, that their separation factor is very close to unity. The implication of this is not that the separations cannot be done, nor that they are only poorly done,

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

nor that a plant to separate isotopes is so much harder to build or to operate than for other separations, it is simply that such plants are different in their design and construction. This paper will attempt to explain how these differences arise and how our group at Los Alamos has tried to solve them. It will be restricted to distillation as the separating technique and will focus particularly on a ^{13}C plant which was completed about 16 months ago. Both the principles which went into its design and its resulting performance will be discussed. However, in keeping with the objectives of this conference, these will be related to more general problems of separation.

As with most separation problems using distillation, we start with the equilibrium relation between the composition of two phases. If a column is necessary for a separation this probably implies a certain similarity of properties for the two components. And if their boiling points are not too different, it is widely true that many systems obey a relationship of constant volatility shown in Fig. 1 and given by

$$\frac{y}{1-y} = \alpha \frac{x}{1-x}$$

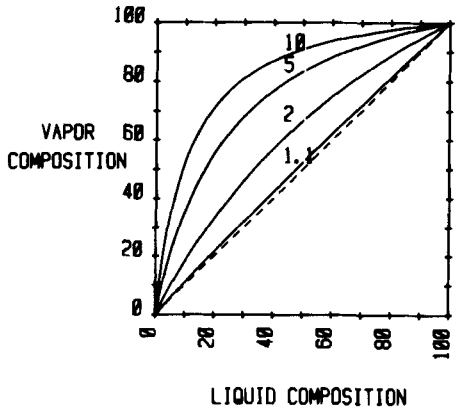


FIGURE 1. The constant volatility assumption - liquid-vapor compositions for several values of alpha.

where x is the mol fraction in the liquid phase and y that of the vapor. For isotopic mixtures, this relationship becomes increasingly valid. The more volatile of the two components concentrates in the vapor phase, but the effect becomes less pronounced as the separation factor approaches one, which is exactly the range for isotopic mixtures. In the case of distillation of carbon monoxide, ^{12}CO has about 0.5% higher vapor pressure than ^{13}CO, or the separation factor for the $^{12}C/^{13}C$ system is 1.005.

The separation factor for carbon monoxide varies with temperature (2) which depends, in turn, on the operating pressure of the distillation column. The resulting function is shown in Fig. 2. In our column the condensers, chilled with liquid nitrogen, operate sub-atmospheric at 570 mm Hg, corresponding to 2 degrees temperature increment across the condenser. The fundamental process in a distillation column is a counter-current movement of liquid

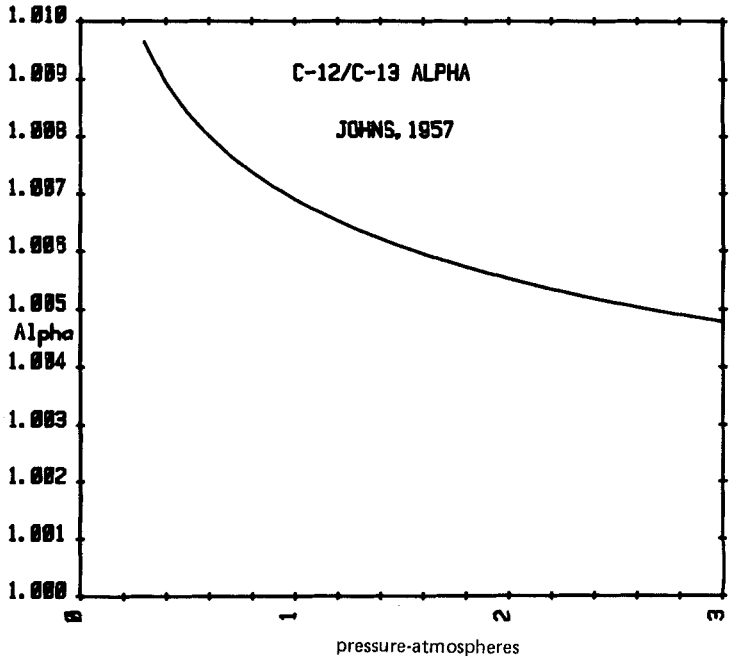


FIGURE 2. Alpha for $^{12}CO/^{13}CO$ versus pressure.

draining down through packing material and of vapor percolating upward through the same pathway, so that the carbon-13 concentrates in the liquid. Hence the isotopic abundance of carbon-13 is richer down the column than at the top. By making a column long enough, one can get a good grade of carbon-13 (see Fig. 3). The measure of length of interest here is the height equivalent to a theoretical plate (HETP), a concept which loosely equates the performance of a packed column to a column made of many phase-contacting plates of perfect efficiency. For carbon-13 a thousand or so theoretical plates are required, so that even with high efficiency packing an isotope separating plant must be very long. A plant which we built a decade ago with a theoretical plate height of 2 cm was over 40 meters long (1). Our more recent plant is over 200 meters long and is the longest distillation column ever built.

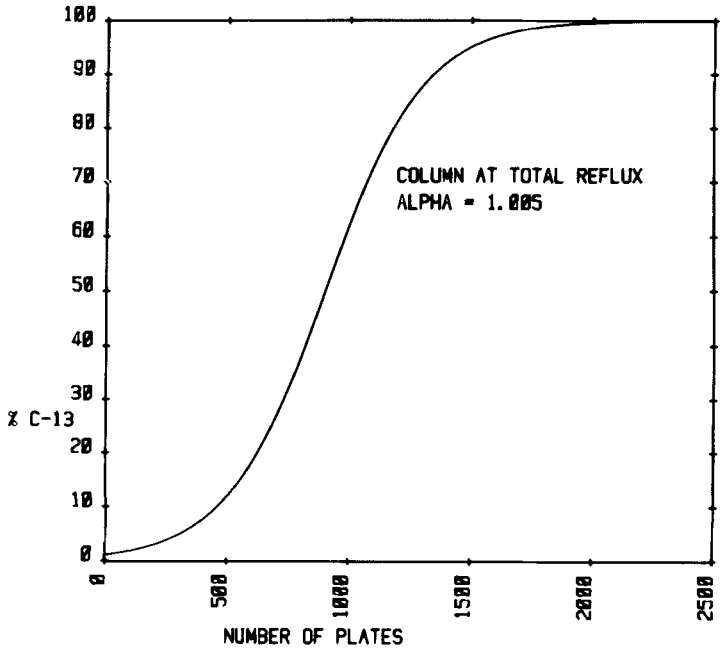


FIGURE 3. Separation of carbon-13 by distillation without draw-off (total reflux).

This length corresponds to nearly 3000 theoretical plates as compared to a hundred or so for most laboratory or industrial distillations. We have named this plant the COLA column, not in honor of any beverage, but from the Spanish word for tail. A small parasitic column is contained in the same vacuum jacket, and its name is unavoidably COLITA.

If a column with a few thousand plates is maintained at normal abundance at the top (i.e., 1.11% ^{13}C), carbon monoxide drawn off from the bottom is enriched in carbon-13, as shown in Fig. 4. But the more rapidly withdrawn, the worse is the quality of the product. To some extent, one can help matters out by adding length to the column, that is, more plates. One can make a column indefinitely long but if the draw-off is as much as 0.01% of the boil-up, the product will be limited to around 50% ^{13}C. Ten times this draw-off will reduce the quality of the product to about 10% and so on, until one is finally faced with the normal abundance he started with. Or, put another way, to yield a given flow rate of good grade product, the column needs ten or twenty thousand times that flow rate for its boil-up.

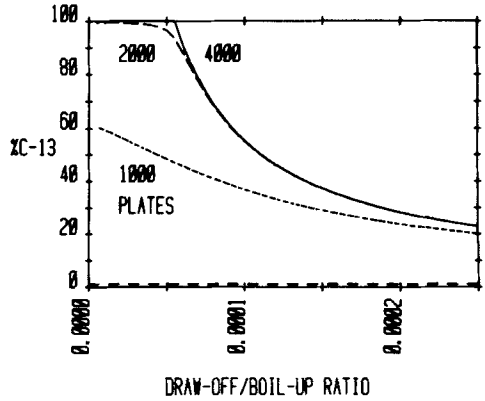


FIGURE 4. Product quality versus production rate of ^{13}C. This figure and Fig. 3 consider only two isotopic components with $\alpha = 1.005$.

A small 25 mm laboratory distillation column boiling CO with a good quality packing can typically handle 1000 moles per day of upstreaming vapor counter-current with down-trickling liquid and without the two phases interfering with the motion of each other. So, one could obtain about 0.1 mole per day of good grade product with such a column. Now 0.1 M/D probably exceeded the world's production of carbon-13 when our laboratory began the ICONs program ten years ago. But today we produce 25 to 50 times that and we look to still larger requirements. The usual chemical engineering solution to the matter of an increased production requirement for a distillation problem is to build a "fatter" column, one with larger diameter. And what with area scaling, a doubling of the diameter results in a four-fold increase in the boil-up and, thus, in available draw-off, up to a point. Even before this point, this height of a theoretical plate increases roughly proportional to the diameter, so that the long column becomes even longer (Fig. 5). Eventually, the fat column ceases to work at all!

What is involved here has to do with the mechanics of liquid percolating downward through the packing material and its selective tendency to migrate to the wall. J. G. Montoya in our laboratory made some studies several years ago on columns which were 150 mm (6 inch) diameter using nitric oxide - another cryogenic fluid for isotopic separation. These large columns were able to accept the very large predicted boil-up flows and would sometimes yield very good plate heights. But again, a similar length, when refilled, would be very poor. The use of recommended redistributors did not help much. The most discouraging experiment occurred when a good section and a moderately good one were connected atop each other. The combination was worse than either alone.

Our approach to this design problem has been a compromise between both approaches as seen in Fig. 6. Starting with 25 mm tubing to form our fundamental column unit ten years ago, we have progressed to using a 50 mm column as our building block. In

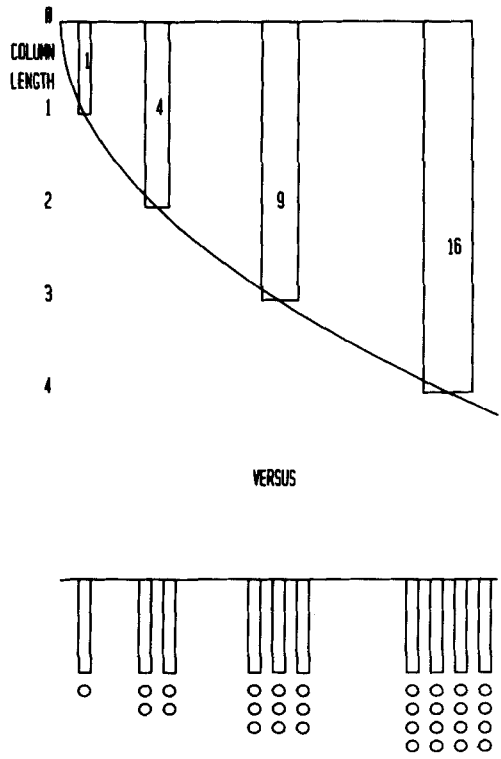


FIGURE 5. Two methods of increasing production of high quality product. In the first method the columns have increasing diameter while in the second there is an increased multiplicity of columns.

addition, by using a different type packing we have been able to increase the boil-up capacity not only by the factor of four from area considerations but by another factor of two due to openness of the packing, resulting in a full factor of eight in throughput. This has decreased by a factor of 2.5 the number of plates, so the columns must be longer. But this is as far as we have been willing to go in this direction. Since this is still short of our needed production capacity, we have recently been building plants with six of these larger tubes operating in parallel. In the COLA plant these six 50-mm columns are each 100 meters long.

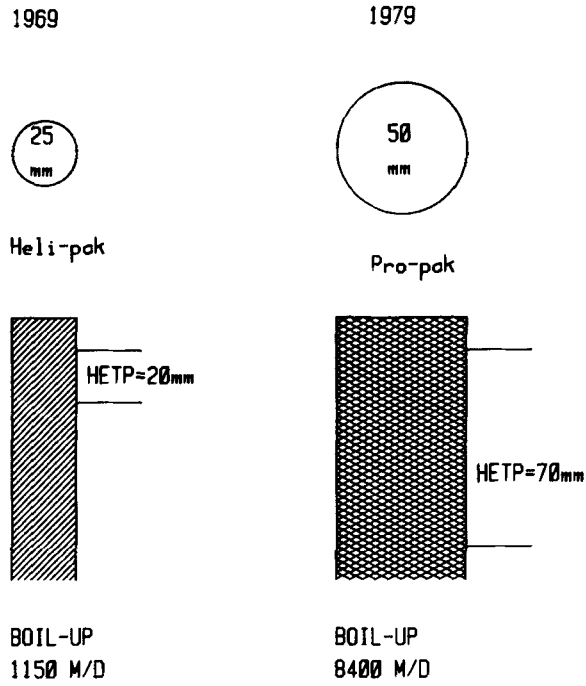


FIGURE 6. The fundamental column unit in 1969 and 1979. Heli-pak is 1.3 x 2.5 x 23 mm wire forms manufactured by Podbelniak, Inc., 341 East Ohio Street, Chicago, IL. Pro-pak is produced by Scientific Development Co., State College, PA.

But what, we may ask, do we mean by six columns, or, for that matter, by two columns in parallel? If a column is a unit going between a boiler and a condenser, then two in parallel might be two columns between the same boiler and the same condenser, as in Fig. 7a. But this arrangement simply does not work either in theory or in practice. The flaw is that the condition of equal counter-current streams of liquid and vapor is violated. With care, one might expect to achieve a uniformity of, say, 1% in vapor and liquid streams in one of these columns. But as we just saw, a draw-off of only 0.01% of the boil-up is a typical operating condition. Thus, the column would behave as though it were

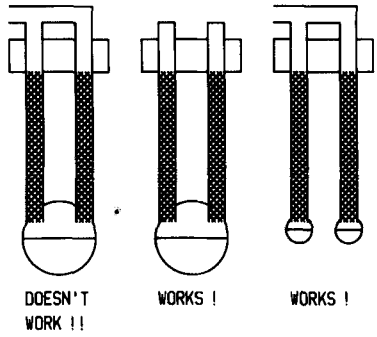


FIGURE 7. Parallel distillation columns. The first arrangement permits cross-circulation between the two columns so that their counter-current streams are unequal. The separating process behaves then as though there were a draw-off the size of the discrepancy.

being drained, and no appreciable separation would be observed. Either separate condensers (Fig. 7b) or separate boilers (Fig. 7c) would alleviate this problem.

Such considerations lead to the general flow pattern shown in Fig. 8. Six columns, each with its own condenser, arise from a common boiler. Each column has its own feed line and its own top draw-off line for carbon monoxide which is depleted in carbon-13. But from the main boiler a liquid overflow also runs down through another identical column which is about 100 meters long and which has its own boiler at the bottom. From this Boiler #2, the main column product is withdrawn at a rate of a few moles per day.

The detailed design of this set of columns required recognition of the isotopes of oxygen as well as of carbon in the natural abundance supply gas. This results in six different isotopic forms of carbon monoxide, each with its own abundance and its own separation factor shown in Table 1. At column temperatures, the carbon monoxide molecule is so stable that the rate of exchange reaction is negligible. One simplification which we adopted for design purposes was to neglect the presence of both oxygen-17 molecular forms. They are scarce and should never become appreciable. The problem was thus reduced to four components.

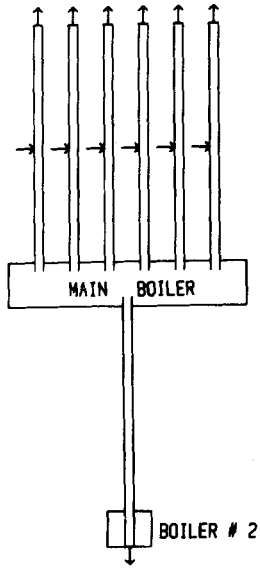


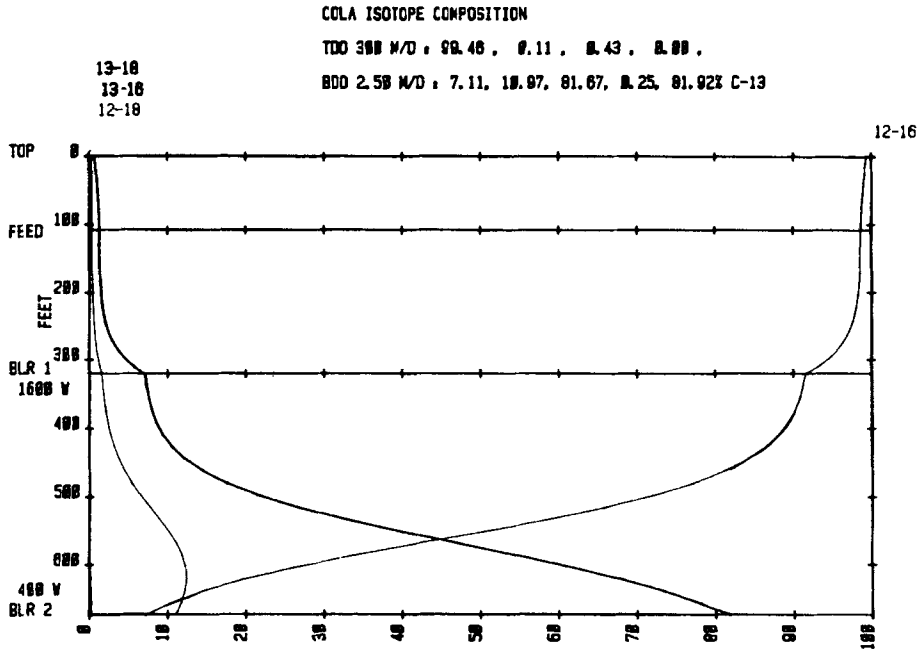
FIGURE 8. The flow pattern for the COLA column.

TABLE 1
Isotopic Forms of Carbon Monoxide

CARBON		
^{12}C		98.89%
^{13}C		1.11%
OXYGEN		
^{16}O		99.76%
^{17}O		0.04%
^{18}O		0.20%

FORM	MASS	NAT.ABUND.	Alpha
$^{12}C^{16}O$	28	98.65	1.0000
$^{12}C^{17}O$	29	0.04	0.9925
$^{12}C^{18}O$	30	0.20	0.9950
$^{13}C^{16}O$	29	1.11	0.9932
$^{13}C^{17}O$	30	0.00	0.9907
$^{13}C^{18}O$	31	0.00	0.9882

Computer calculations were made for the distributions of these four components as shown in Fig. 9. This presents graphically the abundance of each component from the top of the column to the feed point to Boiler #1 to the bottom. This figure shows the $^{13}C^{16}O$ increasing throughout the column, while the $^{12}C^{16}O$ decreases from top to bottom. However, the $^{12}C^{18}O$ displays a maxi-



HOLD-UP, moles

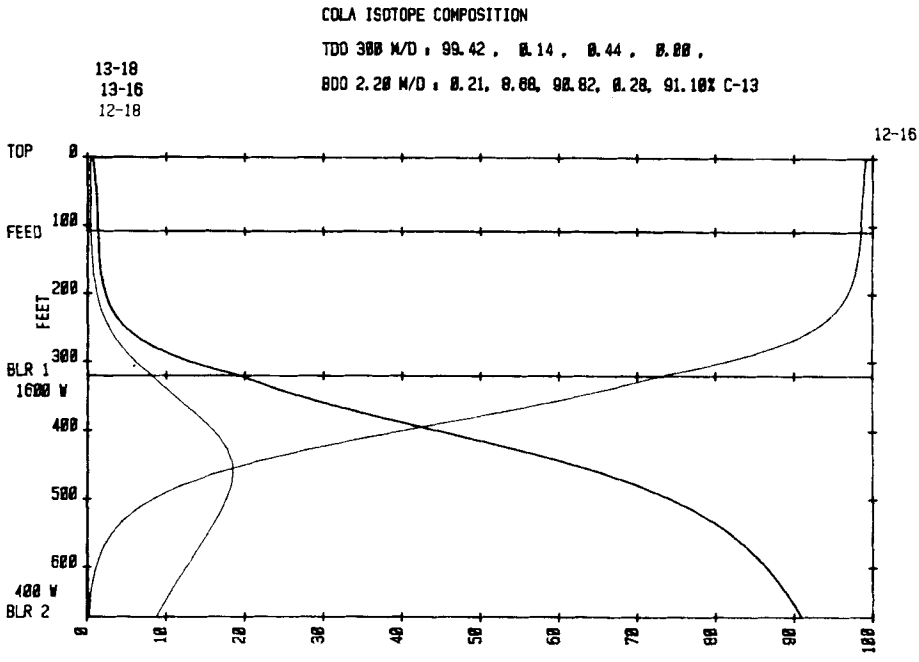
	1	2	3	
12-16	349	1616	834	2800
12-18	37	8	2	46
13-16	160	34	8	210
13-18	0	0	0	0

FIGURE 9. A performance chart for the COLA column yielding 82% grade product.

mum in the lower section due to the build-up of the less volatile $^{13}C^{16}O$. That is, the $^{12}C^{16}O$ pushes it down, so to speak, while the $^{13}C^{16}O$ pushes it up and it is caught in the middle. The fourth component, $^{13}C^{18}O$, is of no appreciable size on this graph. Above the graph the two exit streams are described by the stream flow rate in moles per day and the abundance of the four components. The sum of the last two yields the total ^{13}C abundance, as shown for the bottom draw-off. Below the graph is a calculation of the hold-up of each species. Thus, the total chart displays the operating characteristics for a set of input parameters. In this example the heaters in Boiler #1 are dissipating 1600 W into the liquid CO in that boiler: Boiler #2 is set for 400 W. There is a bottom draw-off of 2.5 M/D and a top draw-off of 300 M/D, so that the feed flow is 302.5 M/D. With this condition the plant yields about 82% ^{13}C in the bottom stream while the top stream has been depleted from 1.1% to 0.43%.

The program which was used for calculating these performance charts makes a preliminary computation from the power level and the known condenser dimensions to give a top pressure. It then computes the pressure distribution for the three sections and the corresponding temperature distributions and finally a set of alphas for all four components. These are averaged for each section so that calculations are made for a constant alpha in each section for each component. Calculations are made iteratively by the so-called θ-method (3) until convergence is obtained. Hold-up is assumed to be proportional to the boil-up power in a column section. However, our assumed constant of proportionality for packing hold-up proved to be smaller than was observed in practice. About 50% should be added to the calculated figures. In this example, the ^{13}C hold-up is calculated to be 200 moles, but a more accurate value would be 300 moles of ^{13}C. If the plant will produce only 2 moles per day of contained ^{13}C, an estimate of the build-up time to get on stream would be 150 days, or about five months.

Figure 10 is a similar performance chart for a somewhat re-



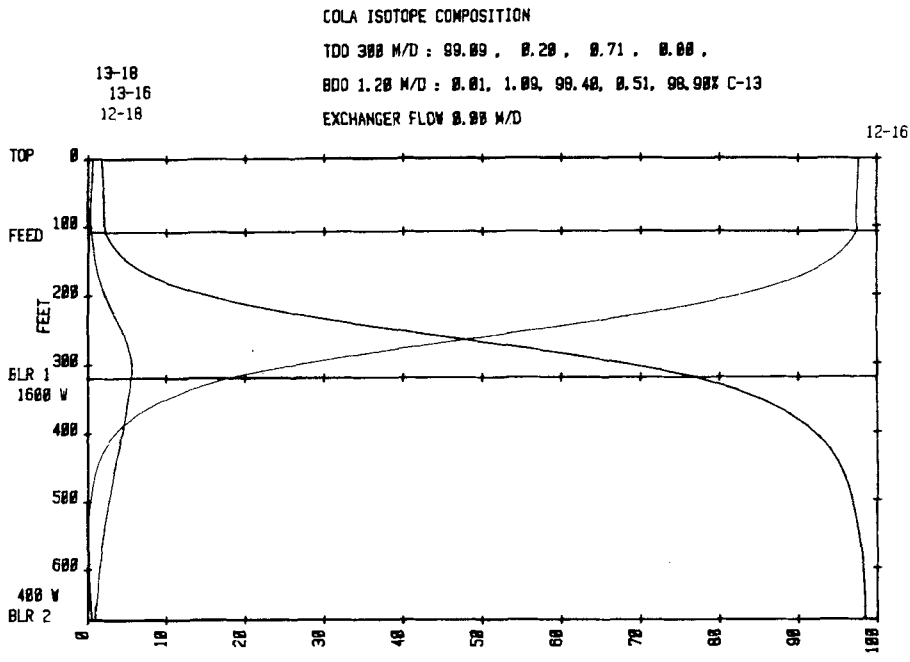
HOLD-UP, moles

	1	2	3	
12-16	120	1551	833	2505
12-18	79	35	2	116
13-16	**354**	**73**	**0**	**435**
13-18	**0**	**0**	**0**	**0**

FIGURE 10. A performance chart for the COLA column yielding 90% grade product.

duced bottom flow rate, so that the product is over 90% ^{13}C. The shape of the curves has changed, the maximum of the $^{12}C^{18}O$ curve is more pronounced, and the production rate of the contained ^{13}C is about the same. But the hold-up figure for ^{13}C is a factor of two larger than before which means another five months of waiting.

To carry this type of consideration to an extreme, we may consider Fig. 11 for which the bottom draw-off rate has been re-



HOLD-UP, moles

	1	2	3	
12-16	16	1173	823	2012
12-18	18	48	4	70
13-16	519	438	16	973
13-18	0	0	0	1

FIGURE 11. A performance chart for the COLA column yielding 99% grade product.

duced to 1.2 moles per day, so that the column is producing nearly 99% pure product. The $^{12}C^{16}O$ has nearly disappeared and the $^{12}C^{18}O$ is the chief contributor of carbon-12. At this flow rate a small amount of $^{13}C^{18}O$ may be seen. But the hold-up is up another factor of two. Although it is possible at steady state to produce 99% ^{13}C, it would take years to reach steady state.

One result of the long build-up periods which is characteristic of isotope separating plants is that once started they should

be kept going. If one must run them for five months just to begin production, then he must either keep them going or start over again. For cryogenic columns this means continuing a rather expensive liquid nitrogen usage rate. It also implies that a high level of reliability engineering is desirable. One tries to avoid any type of failure which would mean shutting down the columns or, worse, rebuilding the columns which are down in a hole and inaccessible. It also means that the columns and their associated equipment must be well protected so that plants can be left with confidence overnight and for weekends. There is an alarm system which calls out operating personnel for any serious malfunctions, but this is now highly infrequent.

To return to the problem indicated in Figs. 9-11, how should one produce a good grade ^{13}C, better than 80%? It seems that the problem lies in the interaction of the $^{12}C^{18}O$ molecules with the $^{13}C^{16}O$; they are nearly identical in their vapor pressure so they are very hard to separate from each other. If this is so, one could promote the exchange reaction in carbon monoxide. Then the $^{12}C^{18}O$ molecules would become very scarce with the resulting mixture being easier to separate.

If there is a mechanism at the molecular level whereby the carbon and oxygen atoms can change partners, i.e., if one can promote the reaction

$$^{12}C^{18}O + {}^{13}C^{16}O \rightleftharpoons {}^{13}C^{18}O + {}^{12}C^{16}O$$

and if, furthermore, there is no isotopic selectivity, then the probability for a given isotope to be attached in a molecule is equal to the atom fraction of that isotope in the total mixture. Thus from probability theory

$$P[^{i}C^{j}O] = P[^{i}C] \cdot P[^{j}O]$$

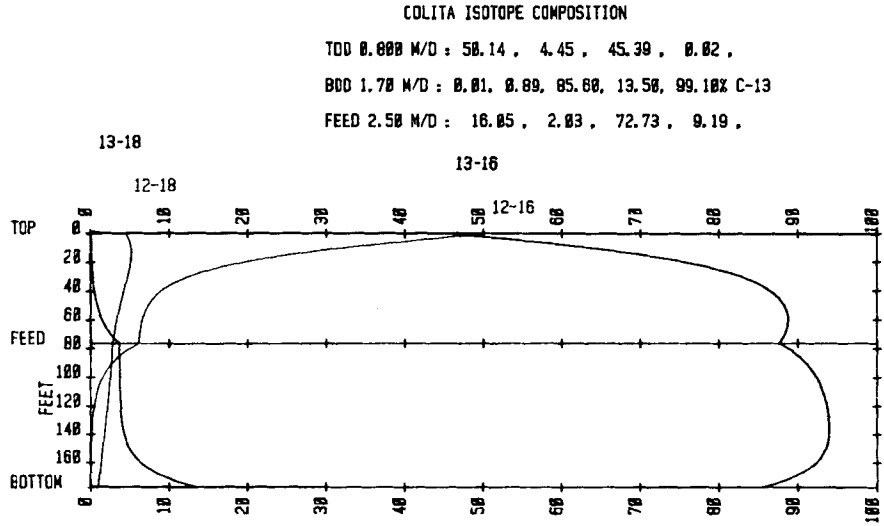
Using as an example the ~80% ^{13}C product shown in Fig. 9, the resulting mixture is shown in Table 2. The molecular distribution has changed considerably in this example. The most dramatic effect is in the $^{13}C^{18}O$ abundance, although probably the reduction in the unwanted $^{12}C^{18}O$ is the more beneficial result.

TABLE 2
Typical COLA Product

	Before	After Exchange
$^{12}C^{16}O$	7.11%	16.05%
$^{12}C^{18}O$	10.97%	2.03%
$^{13}C^{16}O$	81.67%	72.73%
$^{13}C^{18}O$	0.25%	9.19%
Atom Abundances		
^{12}C		18.08%
^{13}C		81.92%
^{16}O		88.78%
^{18}O		11.22%

The result of using a second column to perform a final separation is shown in Fig. 12 which is a performance chart for COLITA. Using this exchanged material as a feed this chart predicts a good 99% quality product to be attainable, with a top stream of 45% material to be reworked or saved. The hold-up calculations show less than 200 moles of ^{13}C to be held up in this column.

These performance charts become important when the design problems become more complex and it is less clear that there are simple principles to guide one. A particular instance of this is the possibility that one might simply exchange the COLA product and return it to the COLA column. It is an attractive idea, entirely avoiding the construction and operation of a second column. However, the computer analysis of this option fails to confirm such a benefit, at least if the product is returned to the same bottom draw-off point. It seems possible still that there might be a withdrawal made above the bottom, the stream to be then exchanged and returned possibly to some still different level with benefit. Such a system presents one with sufficiently complicated operating difficulties that the auxiliary column may be preferable. To repeat, one is dependent upon the computer analysis of the problem and is no longer guided by simple principles.



HOLD-UP, moles

	1	2	
12-16	1	7	7
12-18	1	2	3
13-16	50	32	82
13-18	3	0	3

FIGURE 12. A performance chart for the COLITA column.

These calculations have worked well in practice. An exchanger using a water-cooled tungsten tube vacuum furnace was designed by our group at Los Alamos. It ran at around 1200°C and promoted the exchange reaction to near completion for long periods in a reliable fashion. A small amount of carbon dioxide was sometimes present so that the resulting exchanged gas was purified cryogenically before being fed to COLITA. But recent work at Los Alamos has shown that passing carbon monoxide over ruthenium catalyst dispersed on alumina successfully promotes the isotopic exchange reaction at 400°C. This new development has permitted much simpler equipment for the exchange reaction unit. It is easy to tell whether the exchanger is doing its job by measuring the mass spec-

trum of the resulting gas. The large mass-31 peak and the greatly reduced mass-30 peak are clear landmarks.

Upon first measuring the COLITA product we were alarmed that the mass-30 peak was not really clearing out as predicted in the supposedly 99% product. We kept finding only about 98.8%. And then we realized that the computerized performance charts had tricked us, and we remembered the neglected oxygen isotope ^{17}O and that there could be a contribution to the mass-30 peak from $^{13}C^{17}O$. So for these high enrichment samples, we started measuring the atomic ion C^{+} peaks at mass-12 and mass-13 and were reassured that the material was above 99% ^{13}C.

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ACKNOWLEDGMENTS

Apart from the theoretical design of the COLA system reported here, many others contributed to the total project. The mechanical design was handled by Dale E. Armstrong, engineering design by T. R. Mills, chemical problems were handled by Maxwell Goldblatt, the construction and fabrication under the supervision of J. G. Montoya was performed by R. Romero, M. G. Garcia, and A. Romero, and operating design matters were considered by R. C. Vandervoort and C. E. Lehman. The recent work on catalysis of CO exchange was by David C. Moody.

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