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Separation of Radioactive Krypton from Carbon Dioxide and Oxygen with Molecular Sieves

Charles W. Forsberg

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CHEMICAL TECHNOLOGY DIVISION

THORIUM UTILIZATION PROGRAM
Reprocessing Development - Task 200

SEPARATION OF RADIOACTIVE KRYPTON FROM CARBON DIOXIDE AND OXYGEN
WITH MOLECULAR SIEVES

Charles W. Forsberg

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SEPARATION OF RADIOACTIVE KRYPTON FROM CARBON DIOXIDE AND OXYGEN WITH MOLECULAR SIEVES

Charles W. Forsberg

ABSTRACT

In the reprocessing of HTGR nuclear fuels, the off-gas cleanup system generates a stream containing about 1% krypton, 90+% CO₂, and various amounts of O₂, N₂, and xenon. The krypton is radioactive and must be separated from the CO₂ before it is bottled or zeolite-encapsulated for final disposal. A series of theoretical and experimental investigations to find the best method for separating CO₂ and krypton under the required conditions showed that 5A molecular sieves near 0°C and 1.01 x 10⁵ Pa (1 atm) provided the most effective separation. Molecular sieves are powerful solid adsorbents for CO₂ but weak adsorbents for krypton. For a typical expected CO₂-O₂-krypton gas mixture, a molecular sieve bed adsorbs the CO₂, allows the O₂ to pass freely through the bed, and concentrates the krypton before it exits the bed. The process selected and investigated is called frontal analysis gas chromatography.

1. INTRODUCTION, SUMMARY, AND CONCLUSIONS

In the reprocessing of graphite-based nuclear fuels such as those of the HTGR, the uranium and fission products are separated from the graphite by burning the graphite in pure oxygen. The off-gas (primarily CO₂) contains most of the radioactive ⁸⁵Kr. Health regulations limit the amount of ⁸⁵Kr which can be released to the atmosphere. The primary separation of the krypton from the CO₂ is effected with the KALC^{1,2} (Krypton Adsorption in Liquid Carbon Dioxide) process, which removes > 99% of the krypton from the off-gas and concentrates it by a factor of 1000. The resulting krypton-rich gas product contains about 1% krypton, 90+% CO₂, and various amounts of O₂, N₂, and xenon. For

long-term storage and disposal of the krypton, the CO_2 must be removed. This report discusses the theoretical and experimental work in finding and developing a system for this particular separation.

Selective CO_2 freeze-out, reaction of CO_2 with $\text{Ca}(\text{OH})_2$, and adsorption of CO_2 onto molecular sieves were investigated for the CO_2 -krypton separation. Considerations of performance, reliability, remote maintainability, safety, and cost indicated that adsorption on molecular sieves was the optimum separation technique. Therefore, an experimental evaluation of molecular sieves was undertaken.

Molecular sieves are selective adsorbents which strongly adsorb CO_2 , only weakly adsorb krypton, and do not significantly adsorb O_2 . It was calculated theoretically and shown experimentally that if a bed of Linde 5A molecular sieve was fed a gas containing O_2 , krypton, and CO_2 , the CO_2 was totally adsorbed, the O_2 flowed through the bed, and the krypton was concentrated as in a frontal analysis chromatograph. The gas exiting the bed consisted of initially pure O_2 , followed successively by concentrated krypton and the feed gas. The molecular sieve bed can easily be regenerated by heating to 200°C , which drives off the CO_2 .

The following conclusions were drawn from a series of experiments designed to study the operation of a bed of Linde 5A molecular sieve maintained at 0°C and fed a gas composed of 93.09% CO_2 , 5.43% O_2 , and 1.48% krypton:

1. The krypton and oxygen products exiting molecular sieve beds contained < 10 ppm of CO_2 ; in other words, essentially complete separation of CO_2 and krypton is obtained by using molecular sieves.

2. The rate of adsorption of CO_2 onto molecular sieves is very fast; that is, mass transfer does not limit the design and/or performance of a molecular sieve bed.
3. The adsorption of CO_2 releases tremendous amounts of heat. Removal of the heat of adsorption in a molecular sieve bed is the major problem in system design.
4. Desorption of adsorbed CO_2 from a molecular sieve bed is easily accomplished by heating the bed to 200°C .
5. With the above feed gas, the resulting krypton gas product was consistently $> 50\%$ in krypton with the residual being O_2 . The molecular sieve partially separated O_2 and krypton in addition to a total krypton- CO_2 separation.

It is concluded that use of a molecular sieve system is the preferred method for the final separation of CO_2 and krypton under the conditions expected to exist in an HTGR nuclear fuel reprocessing plant.

2. PROCESS SELECTION AND DESIGN

2.1 Introduction

Because of the potential health hazards³ of a worldwide increase in ^{85}Kr , a radioactive gas produced during fission, most of the krypton containing ^{85}Kr must be removed from the off-gas stream of HTGR nuclear fuel reprocessing plants before its release to the atmosphere. The plant off-gas contains $\sim 95\%$ CO_2 , 10 to 15 ppm of krypton, and varying amounts of O_2 , N_2 , and xenon.⁴ It is proposed to use the KALC^{1,2} process to

remove > 99% of this krypton from the off-gas and concentrate it by a factor of 1000. KALC should produce a krypton-rich stream of about 1% krypton, 0 to 3% xenon, traces of O_2 , and 95+% CO_2 . For temporary storage and perhaps disposal, the krypton will be bottled in gas cylinders or encapsulated in zeolites.⁵ Because of economic and safety⁶ considerations, the bottled krypton should have a krypton content of > 10% and contain little or no CO_2 . Removal of CO_2 is desired to avoid the possibility of various chemical reactions activated by the krypton radiation field between the CO_2 , O_2 , and bottle materials. Section 2.2 evaluates alternative processes for this final separation. Sections 2.3 and 2.4 describe the chosen separation processes in detail.

2.2 Process Selection

The following criteria⁷ were applied in selecting the system to be used for the final separation of krypton:

1. The process must concentrate the krypton in the CO_2 gas stream by at least a factor of 10. The nominal krypton feed concentration is expected to be ~ 1%.
2. All the CO_2 should be removed. Conversion of CO_2 to CO, O_2 , and other compounds can occur in the presence of a ^{85}Kr radiation field in storage cylinders.^{6,8} Some of these compounds could accelerate corrosion of the gas cylinders.
3. The materials of construction and any process materials used should be noncombustible. Oxygen will be present, and radiation fields could provide the mechanisms to start combustion.

4. The process must be able to accept highly variable feed gas compositions. Any process upset in other plant off-gas equipment might propagate to this system.
5. The process should be highly reliable and easily maintainable in a radioactive environment.
6. The process should be easily and accurately scalable from bench scale to full size. If we make the assumptions that KALC concentrates the krypton by a factor of 1000 from 10 ppm to 1% krypton, a full-scale plant handles the fuel from power reactors producing 50 GW(e), and the plant operates 300 days per year, then the gas flow rate to this system is 1.83 scfm for a full-scale plant.
7. The process should produce no by-product wastes. Any material of this nature will probably be contaminated with ^{85}Kr and will have to be treated as radioactive waste.

The following types of CO_2 removal systems^{9,10} were evaluated:

1. Carbon dioxide can be removed by reaction with a chemical reagent such as $\text{Ca}(\text{OH})_2$ ^{11,12} to yield a solid reaction product such as CaCO_3 . This approach was considered unacceptable because it either produces an additional solid waste stream with disposal problems or involves a complex system for regenerating the reagents and the CO_2 .
2. Carbon dioxide can be removed by adsorption in a wide variety of solvents. The system involved would be similar to KALC except that a different solvent would be used and CO_2 , not krypton, would

be concentrated. This approach was rejected because of the complexity of the equipment.

3. Carbon dioxide can be removed by selectively freezing the CO_2 out of the gas mixture. If the system is operated at low pressures, the CO_2 is converted from a gas to a solid, which alters the heat transfer coefficient of the cooler. Such devices with variable heat and mass transfer coefficients as a function of time are very difficult and risky to scale up. If the system is operated at high pressures, the CO_2 gas liquefies and the liquid CO_2 dissolves some of the krypton gas, making clean separations of CO_2 and krypton difficult. In either case, this approach was considered unacceptable due to the uncertainties in scaling such equipment up to industrial size.
4. Carbon dioxide can be adsorbed selectively by a variety of adsorbents, including molecular sieves, charcoal, and silica gel. The adsorbents can be regenerated simply by heating. This method was selected as the preferred approach for CO_2 removal. Molecular sieves^{13,14} were chosen as the adsorbent because they are extremely inert, noncombustible, and resistant to damage from high radiation fields.

2.3 Process Flowsheets

2.3.1 System location

Figure 2.1 is a simplified front-end flowsheet of the HTGR fuel reprocessing plant, showing the location of the krypton removal equipment.¹⁵ The CO_2 removal equipment is located in such a way that, if

Fig. 2.1. Flowsheet of off-gas system of HTGR fuel reprocessing plant.

the CO_2 removed from the krypton-rich gas stream (1% krypton) is contaminated with krypton, it can be recycled to the front end of the main krypton removal equipment. The flow rate of the CO_2 removal system is only about one-thousandth that of the main off-gas stream; hence total recycle of this CO_2 will not significantly change the size of the major equipment items.

2.3.2 Process flowsheet No. 1

The simplest flowsheet for the continuous separation of krypton and CO_2 is shown in Fig. 2.2. The process consists of two columns filled with molecular sieves,¹⁴ which are aluminosilicate crystals that can adsorb CO_2 up to 20% of their own weight. This material is chemically inert and can be heated to several hundred degrees Centigrade without damage.

Some types of molecular sieves, such as Linde 4A, adsorb CO_2 but not krypton.^{16,17} Other molecular sieves, such as Linde 5A, adsorb both CO_2 ^{17,18} and krypton;¹⁹⁻²⁶ however, the CO_2 is more strongly adsorbed and displaces the krypton held by the molecular sieve. Molecular sieves such as type 5A may be used in preference to type 4A because of their faster adsorption kinetics and higher adsorption capacities.²⁷ Molecular sieve 5A adsorbs about 17.5% of its own weight in CO_2 ¹⁸ in the presence of a gas mixture containing 95% CO_2 at 1 atm and 0°C. At 1 atm and 200°C, it adsorbs only 1% of its weight in CO_2 . Such characteristics allow molecular sieves to be used for selectively adsorbing CO_2 out of a gas stream at low temperatures and to be regenerated at high temperatures. The adsorption of CO_2 releases large amounts of heat; hence

Fig. 2.2. Simple flowsheet for separation of CO_2 and krypton.

it is necessary to cool the bed continuously when adsorbing CO_2 and to heat the bed continuously when desorbing CO_2 .

The actual separation process, as shown in Fig. 2.2, works as follows: The feed gas is admitted through valve A into column 1, a clean molecular sieve bed maintained at 1 atm of pressure and 0°C . The CO_2 is adsorbed on the bed, and the krypton and other gases exit the bed through valve D to the krypton product line. As the CO_2 adsorption front approaches the top of column 1, the exit gas from this column is diverted through valves E and G into column 2, which also contains clean molecular sieve. The krypton product exits from column 2 via valve I. After column 1 becomes saturated with CO_2 , the feed gas is diverted directly to column 2 through valve F while valves E and G are closed. At this time, valve C is opened and column 1 is heated to at least 200°C . The adsorbed CO_2 is drawn off the column, valve C is then closed, valve D is opened, and the column is cooled to 0°C . When the CO_2 adsorption front in column 2 approaches the top of column 2, valve I is closed and valves B and H are opened. This diverts the flow from the top of column 2 to the bottom of column 1. When column 2 is saturated with CO_2 , the feed gas is sent directly to column 1 via valve A, and valves B, H, and F are closed. At this time, valve J is opened and column 2 is heated to at least 200°C to regenerate the molecular sieve. After regeneration, valve J is closed, valve I is opened, and the column is cooled to 0°C . At this point, the two columns have gone through one complete cycle, separating CO_2 from krypton.

The instrumentation and controls for such a system are simple. Because of the large amounts of heat released during the adsorption of

CO_2 , the adsorption front in each column can be followed by thermocouples. Alternatively, the undiluted krypton with CO_2 removed is much more radioactive than the feed gas; hence radiation detectors can easily determine the location of the CO_2 adsorption front which divides the krypton product gas from the feed gas. Either thermocouple or radiation detector readings can be used to trigger the opening and closing of the individual valves.

Various types of molecular sieves could be used; experimentally, both Linde 4A and 5A molecular sieves are satisfactory. The system pressure should be $\sim 10^5$ Pa (~ 1 atm). The adsorption of CO_2 increases with pressure up to slightly above 10^5 Pa (1 atm). Colder temperatures also increase CO_2 adsorption in molecular sieves, but the increase tends to level off around 0°C ; thus little advantage is gained by operating below 0°C .

2.3.3 Process flowsheet No. 2

An alternative molecular sieve process flowsheet (Fig. 2.3) permits separation of a gas stream of O_2 , krypton, and CO_2 into a pure O_2 stream, an O_2 -krypton stream, and a pure CO_2 stream. At the cost of greater complexity, this flowsheet produces a more highly concentrated stream of krypton. It is based on the particular characteristics of molecular sieve 5A, which strongly adsorbs CO_2 ,^{17,18} weakly adsorbs krypton,¹⁹⁻²⁶ and does not significantly adsorb O_2 .²⁸

Let us assume that a single column of 5A molecular sieve is fed a mixture of O_2 , krypton, and CO_2 . As the feed gas enters the column, the krypton and CO_2 are adsorbed; the O_2 , on the other hand, is unadsorbed and flows directly through the column. As more feed gas enters,

Fig. 2.3. Process flowsheet No. 2.

the CO_2 , which is more strongly adsorbed, displaces the krypton from the molecular sieve bed. After a few minutes of operation of a single bed, three zones are noted: a zone of clean bed near the gas exit with oxygen in the gas phase, a zone of krypton adsorbed on the bed with O_2 and krypton in the gas phase, and a zone with CO_2 on the bed and feed gas in the gas phase. Analysis of the gas leaving the bed with time shows pure O_2 initially, followed successively by a krypton- O_2 gas mixture and the feed gas when the molecular sieve is saturated with CO_2 . This process is described as frontal analysis chromatography in the literature.^{29,30} It has been investigated but apparently has not been used on any significant scale.

Let us consider one complete cycle for bed I. Feed gas is fed into a clean column, first via valve 32 from bed III and then via valve 10 from the main feed gas line. Valve 13 is opened to allow the oxygen from the feed gas to flow directly through the column to the O_2 product line while the krypton and CO_2 are adsorbed. The bed is constantly cooled to remove the heat of adsorption of CO_2 and krypton. As the process continues, krypton adsorbs onto the top portion of the bed and CO_2 adsorbs on the bottom portion. When the krypton approaches the top of the column, valves 12 and 23 are opened while valve 13 is closed. The transition zone of gas leaving column 1, where the gas goes from pure O_2 to a constant O_2 -krypton mixture, is sent to column 2. After it has been determined that a constant-composition mixture of O_2 -krypton is leaving column 1, valve 12 is closed and valve 14 is opened; this diverts the gas mixture to the krypton product line. As the second gas transition region between the

krypton- O_2 mixture and the feed gas approaches the top of column 1, valve 14 is closed and valve 12 is opened, diverting the gas to column 2. After the gas transition zone has passed into column 2, valve 10 is closed while valve 20 is opened. This diverts the feed gas to column 2. Valve 15, which supplies pure CO_2 to column 1, is then opened to allow just enough CO_2 sweep gas through column 1 to push the feed gas present in the pipes and between the molecular sieve particles out of the bed. At this time, valve 12 is closed, valve 11 is opened, and the bed is heated to at least $200^\circ C$, driving the pure CO_2 off the molecular sieve to the CO_2 product line. A small compressor lowers the gas pressure, resulting in very little residual CO_2 on the molecular sieve. Valve 11 is closed, valve 13 is opened, and the bed is subsequently cooled back to $0^\circ C$ from the bottom of the column to the top. This procedure ensures that the small amount of CO_2 remaining in column 1 will be readsorbed on the molecular sieve near the bottom of the column so that, when feed gas enters, there is no risk of CO_2 existing with the initial O_2 product. With this final cooling, bed 1 is ready to begin its cycle again. The other columns go through an identical cycle, yielding pure O_2 , CO_2 , and an O_2 -krypton product mixture.

This process can be used both to purify krypton and, possibly, to remove krypton from the off-gas directly without the use of the KALC system. This second alternative will be discussed in Sect. 5. If xenon is added to the feed gas, the result is a gas mixture of O_2 -krypton and xenon exiting each bed after the O_2 -krypton mixture but before the feed gas leaves it.

3. THEORY

3.1 Adsorption Data

Large amounts of data have been collected, and extensive theoretical analysis^{14,31-33} has been made of the adsorption of various gases on molecular sieves. This section reviews the data and describes the method of analysis used to predict experimental behavior.

3.2 Fundamental Data

A search of the literature reveals extensive data concerning the adsorption characteristics of O_2 ,²⁸ CO_2 ,¹⁶⁻¹⁸ and krypton¹⁹⁻²⁶ on molecular sieves. Figure 3.1 shows the adsorption curves used for CO_2 and krypton on Linde 5A molecular sieve at 0°C and 200°C in most calculations. The CO_2 adsorption curve was provided by the Linde Division of Union Carbide Corporation.¹⁸ The krypton adsorption curve is the one reported by Kitani.¹⁹

Extreme care must be taken in using literature values of adsorption in the design of industrial equipment. Linde 5A molecular sieve, like other commercial molecular sieves, contains about 80 wt % active crystals and 20 wt % inert clay binder to hold the crystals together.³¹ Many of the data reported in the literature were obtained on pure molecular sieve crystals. The value of 0.8 in the equation for krypton adsorption in Fig. 3.1 is included to correct for the difference between literature values and commercial products.

Figure 3.1 appears to show adsorption linear with pressure. This is true for a reasonable range of pressures; however, as shown for CO_2

Fig. 3.1. Adsorption of carbon dioxide and krypton on Linde 5A molecular sieve.

at 0°C, adsorption begins to approach a limit as loading of the molecular sieve proceeds.

3.3 System Analysis

If a molecular sieve bed could be sectioned along its major axis and the gas analyzed at each location, the results for an oxygen-krypton-CO₂ system would be similar to those shown in Fig. 3.2. As explained earlier in Section 2.3.3, three distinct zones are apparent: a feed gas zone, a krypton-rich zone, and an oxygen zone separated by two transition regions. As feed gas is fed to the system, the oxygen zone is pushed out by an expanding krypton zone, which in turn is displaced by the feed gas zone. Note that the expanding krypton zone implies a longer section of molecular sieve bed with adsorbed krypton but does not alter the maximum krypton concentration.

For engineering and design calculations, three factors in Fig. 3.2 could be of interest: the variation of gas composition as a function of distance in transition region 1, the maximum concentration of the krypton at quasi-steady-state conditions in Zone B, and the variation of gas composition as a function of distance in transition region 2. Experiments, which are discussed in Section 4, clearly show that the gas transition regions 1 and 2 are very narrow compared to the bed length due to very fast mass transfer. As a consequence, the details of what occurs in these transition regions can be neglected for a practical bed design. For this reason, a simple, iterative numerical procedure was developed to determine only the maximum krypton concentration in Zone B without

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Fig. 3.2. Gas composition vs molecular sieve bed position.

going into the complexities of transient mass transfer. The calculated results obtained from this simplified numerical procedure, which totally ignores kinetics, are in agreement with experiments as discussed in Section 4.

The computer program, which is listed in Appendix A, requires the following as input data: (1) temperature of the molecular sieve, (2) pressure of the molecular sieve, (3) feed gas composition, and (4) adsorption isotherms as a function of temperature and partial pressure for each gas for each type of molecular sieve considered.

Adsorption isotherm data are available both in the literature and from manufacturers in the form of graphs and equations for O_2 ,²⁸ CO_2 ,¹⁶⁻¹⁸ krypton,¹⁹⁻²⁶ and other gases.

The iterative numerical procedure (Fig. 3.3) to find the maximum krypton concentration in Zone B is based on following the progress of 1 cm^3 of feed gas in the molecular sieve bed. As an example, let us assume that a feed gas composed of 93.09% CO_2 , 1.48% krypton, and 5.43% O_2 , by volume, is introduced into a bed of 5A Linde molecular sieve maintained at a constant temperature of 0°C and 1 atm of pressure. This volume of gas is unaffected and unadsorbed as it passes through the first part of the bed, which has been saturated with CO_2 . However, it soon reaches a transition zone, where CO_2 is adsorbed on the bed while krypton is desorbed. At this point, the CO_2 in the feed gas, 0.9309 cm^3 , is adsorbed onto the bed, thereby displacing the previously adsorbed krypton.

Fig. 3.3. Iterative numerical procedure for calculating krypton product concentration.

Isotherm adsorption charts for 5A molecular sieve show that, at 0°C and a CO₂ partial pressure of 0.9309 atm, 89.15 cm³ of CO₂ is adsorbed per gram of molecular sieve; that is, 0.9309 cm³ of CO₂ would be totally adsorbed onto 0.010442 g of molecular sieve (Fig. 3.3, step 1).

Now the initial composition of the remaining gas without CO₂ but including the krypton displaced by CO₂ adsorption can be calculated (Fig. 3.3, step 2). The feed gas without CO₂ consists of 0.0148 cm³ of krypton and 0.0543 cm³ of O₂ and hence has a krypton concentration of (0.0148)/(0.0148 + 0.0543), or 21.4%. At 1 atm of pressure, the partial pressure of krypton is therefore 162.77 torr (Fig. 3.3, step 3).

The equation given by Kitani and Takada¹⁹ for determining the volume of krypton that is adsorbed on 5A molecular sieve is:

$$V = \frac{0.8 * 0.0007 * P}{T^{1/2}} \exp \left[\frac{3500}{1.9872 * T} \right], \quad (3.1)$$

where

P = pressure, torr,

T = temperature, °K.

This equation implies that 3.482 cm³ of krypton per gram can be adsorbed on 5A molecular sieve at 0°C and 162.77 torr of krypton partial pressure.

Consequently, the CO_2 which was adsorbed onto 0.010442 g of molecular sieve displaced 0.0363573 cm^3 of krypton from the molecular sieve that was in equilibrium with the krypton gas above it (Fig. 3.3, step 4).

Some oxygen is coadsorbed with the krypton and also pushed off the bed with CO_2 ; however, this amount is so small that it can be ignored.

With the krypton from the feed gas (0.0148 cm^3), the krypton desorbed from the molecular sieve (0.0363573 cm^3), and the oxygen from the feed gas (0.0543 cm^3), the new krypton product is calculated to have a krypton concentration of 48.51% (Fig. 3.3, step 5). Based on this concentration and 1 atm of pressure, the partial krypton vapor pressure is calculated to be 368.68 torr (Fig. 3.3, step 6).

The final calculated krypton product partial pressure (368.68 torr) differs from the estimated krypton vapor pressure (162.77 torr) used to calculate the amount of krypton that was displaced from the molecular sieve by the CO_2 . If these two values had been identical, the final krypton product concentration would have been known. Clearly, the original estimate of the partial pressure of krypton over the molecular sieve saturated with krypton was low because it did not account for the increase in krypton partial pressure caused by the krypton displaced with CO_2 . The calculations from step 4 (Fig. 3.3) onward, which include calculation of the amount of krypton desorbed from 0.010442 g of molecular sieve, must be repeated using the new higher vapor pressure, 368.68 torr (step 7). This iteration procedure (Fig. 3.3, step 7) is repeated until the partial pressure of krypton used to calculate the amount of krypton displaced by the CO_2 gives the final concentration

of krypton to the desired degree of accuracy. For this example, the final gas composition upon convergence of this numerical technique is 71.49% krypton and 28.51% O_2 .

There are other formulations on how to solve this particular problem, which is known in the literature as a frontal analysis problem. Noniterative methods of solution have been developed to describe the process by Claesson.²⁹

4. EXPERIMENTS

4.1 Experimental Goals

A series of experiments was designed to investigate the feasibility of separating krypton from CO_2 with molecular sieves. These experiments had three goals:

1. To experimentally verify that the process is workable.
2. To obtain sufficient information to enable design of a full-scale system. The information would be sufficient to design a system with conservative design margins but not sufficient for a highly optimized design with only small design margins.
3. To investigate the effects of gaseous components such as xenon and oxygen on system performance.

4.2 Conceptual Experimental Design

This experiment consisted basically of measuring the composition, pressure, temperature, and flow rate of the gases entering and leaving

a single molecular sieve bed as a function of time. Figure 4.1 shows the basic design. The following experimental parameters could be varied: gas composition, type of molecular sieve, gas flow rate, molecular sieve bed temperature, and system pressure.

4.3 Experimental Design

The experimental apparatus evolved throughout the experiment, attaining the final configuration described below. Since much of the piping and apparatus was used only for instrument calibration purposes, the final design appears complex.

4.3.1 Molecular sieve column

The design of the molecular sieve column is shown in Fig. 4.2. A narrow column (3/4 in.) was initially designed to permit the molecular sieve to be easily kept at a constant temperature and to ensure that any effects of uneven gas distribution across the column would be small. Experiments later showed that the heat generated by the adsorption of CO_2 on molecular sieves is so great that a full-scale system must be composed either of many narrow columns placed in a parallel arrangement or fewer, larger columns containing provisions for internal cooling.

4.3.2 Molecular sieves

Two types of molecular sieves, 4A and 5A, were chosen for evaluation. Their characteristics are summarized in Table 4.1. The choice of molecular sieves was based on best estimates of the materials that were commercially

Fig. 4.1. Conceptual experimental design.

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PART	DESCRIPTION
1	1/4" O.D. tubing x 0.035" W x 8" Lg — 304 L SST.
2	Upper cap.
3	3/4" dia. perforated disc — 316 SST.
4	"O" ring vacuum coupling for 3/4" tubing, Cajon 316 SST body with Viton A "O" ring.
5	3/4" O.D. tubing x 0.065" W x 36" Lg — 304 L SST.
6	Lower cap.
7	1/4" O.D. tubing x 0.035" W x 52" Lg — 304 L SST.
8	1/8" O.D. copper constantan thermocouple.
9	Thermocouple tee — 304 L SST.

Fig. 4.2. Molecular sieve column.

Table 4.1. Characteristics of molecular sieves used

	Type of molecular sieve	
	4A ^a	5A ^a
Manufacturer	Union Carbide Corporation, Linde Division	Union Carbide Corporation, Linde Division
Form	Beads	1/16-in. pellets, ~3/16 in. long
Composition	Sodium form of aluminosilicate crystals, Type A	Calcium form of aluminosilicate crystals, Type A
Analysis	~80% active crystalline material, ~20% inert clay binder	~80% active crystalline material, ~20% inert clay binder
Density (bulk)	42 lb/ft ³	40 lb/ft ³ (minimum)
Heat of adsorption for krypton		3720 cal/mole ^b
Heat of adsorption for H ₂ O		18,000 cal/mole (maximum)

^aCommercially produced form.

^bData taken from ref. 19.

available and applicable for use in a full-scale system. The physical form of the molecular sieve is important because it partially determines mass transfer rates and system pressure drops.

4.3.3 Experimental flowsheet

Figure 4.3 shows the flowsheet of the experimental apparatus. The dark line indicates the gas flow during a normal experimental run. All piping was constructed of 1/4-in. 316 stainless steel tubing with 0.035-in.-thick wall. Gas sample lines to the mass spectrometer and some pressure gauges were constructed of 1/16-in. 316 stainless steel capillary tubing with an internal diameter of 0.030 in. Whitney valves with compression fittings (Swagelok) were used throughout. In-line heating and cooling coils were made by coiling the tubing and placing it in a constant-temperature bath.

The constant-temperature bath for the molecular sieve consisted of a 4-ft section of 8-in. pipe with a flat plate welded on one end. Calrod heaters were bent around the pipe and secured to the pipe. The molecular sieve bed was located in the center of the bath (pipe), and insulation was placed around the bath. For experiments at temperatures below 100°C, the bath was filled with water; for those at 0°C, it was filled with ice and water. An air bath is used for experiments above 100°C. The constant-temperature bath contained several thermocouples and thermometers. Constant temperature was maintained by manually adjusting the rheostat, which provided power for the Calrod heaters.

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Fig. 4.3. Flowsheet of the experimental apparatus used in molecular sieve study.

4.3.4 Instrumentation

Various instruments and techniques were used to obtain the data from each experiment. The primary instruments are described below.

The composition of the inlet gas was determined by mixing various quantities of pure gases. In most experiments, a gas mixture of the composition 93.09% CO₂, 5.43% O₂, and 1.48% krypton, contained in a single cylinder, was used as the feed gas. The individual gases used in preparing this mixture were specified to be of high purity with very low water concentrations. The final product was analyzed repeatedly over a period of several weeks by several different techniques. Thus this particular gas composition was considered as a known quantity in the various experiments.

Gas flow rates were measured with standard laboratory rotameters which were calibrated with a volume displacement meter. These rotameters had a range of about 0 to 150 cc per minute at standard conditions of temperature and pressure.

System pressure was measured with various pressure gauges having a range from -15 in. Hg to 60 psig. (System pressure could be varied over this entire range.) The system had a vacuum pump for low pressures, while high pressures were obtained via the feed gas cylinders. The pressure was regulated via a pressure control valve (Model 75B, Research Controls, Inc.) with a Foxboro controller.

Temperature measurements throughout the system were made with copper constantan thermocouples and recorded on a 12-point temperature recorder with a temperature range of -50 to 200°C. The temperature

of the constant-temperature bath was controlled manually via rheostats that supplied the power to various Calrod heaters.

The measurement of the volume of gas exiting the molecular sieve bed during an experiment, as well as the calibration of rotameters, was achieved with a Vol-u-Meter.* This is a standard volume displacement meter, which consists of a clear tube and a piston with mercury seals.

The krypton in the feed gas was spiked with ^{85}Kr , a radionuclide which emits beta rays. Since ^{85}Kr has a half-life greater than 10 years, no corrections for its decay needed to be made during an experimental run. The krypton gas concentrations as a function of time were then measured with a beta-radiation cell and counter. This counter was designed to measure ^{85}Kr in the KALC³⁴ process. At a constant temperature and pressure, a doubling of the radiation count rate after correction for background count rate and instrument dead time implies that the concentration of krypton has doubled. After calibration with the standard feed gas, this detector gave very accurate krypton gas analyses. The measurements of the percentage of krypton in the gas streams as a function of time made with this system are believed to be the most accurate analyses performed during experimental runs.

Carbon dioxide concentrations were measured with a Beckman Model IR 315 infrared analyzer. Because of range limitations, this instrument

* Manufactured by the Brooks Instrument Co.

was used only to measure low concentrations of CO_2 . With proper calibration, it can measure levels as low as 10 ppm.

All other on-line gas analyses were conducted with a UTi Model 100 C Precision Mass Analyzer.* This mass spectrometer was used primarily for xenon analysis and to verify that no gas impurities leaked into the system.

4.4 Experimental Work

4.4.1 Experiments with Linde 4A molecular sieve

Linde 4A molecular sieve was used in the first series of scoping experiments. Not all the instrumentation was fully operational during these experiments, nor were the techniques fully developed; hence the accuracy of the raw data is somewhat less than in later experiments. Only a few experiments were done with Linde 4A molecular sieve because scoping studies with Linde 5A molecular sieve gave better results.

Figure 4.4 plots the krypton concentration of the gas leaving the Linde 4A molecular sieve bed as a function of time for three experimental runs. In each case, a constant flow of feed gas was fed to a molecular sieve in a 0°C ice bath. The conditions for these experiments are detailed in Table 4.2, while some of the calculated results are listed in Table 4.3.

Three conclusions were drawn from the experimental data:

1. Linde 4A molecular sieves adsorb CO_2 but do not adsorb significant amounts of krypton or O_2 . Total removal of CO_2 from a feed

*Built by Technology International, Sunneyvale, Calif.

Fig. 4.4. Krypton content of gas leaving 4A molecular sieve bed vs cumulative volume of feed gas admitted to molecular sieve bed.

Table 4.2. Constant parameters in experiments
with 4A molecular sieve

Feed gas analysis		
CO ₂ , %		93.09
O ₂ , %		5.43
Kr, %		1.48
Average molecular wt. of feed gas, g/mole		43.93744
Type of molecular sieve		Linde 4A beads
Molecular sieve temperature, °C		0
Molecular sieve bed cross section, cm ²		1.94778
Molecular sieve bed inside diameter, cm		1.57 (0.62 in.)
Molecular sieve bed length, cm		94.62 (37.25 in.)
Weight of molecular sieve (dry), g		131.5

Table 4.3. Experimental results using Linde 4A molecular sieves

Parameter	Expt. A	Expt. B	Expt. C
Bed temperature, °C	0.0	0.0	0.0
Bed pressure, 10^5 Pa (psia)	1.01 (14.7)	1.70 (24.7)	2.39 (34.7)
Feed gas flow rate/unit bed area, $\text{cm}^3(\text{STP})/\text{cm}^2\text{-min}$ ($\text{g}/\text{cm}^2\text{-min}$)	7.224 (0.01416)	10.32 (0.020234)	9.417 (0.01846)
Length of mass transfer zone, ^a O_2 peak to krypton peak, cm	21.7	30.97	-- ^b
Length of mass transfer zone, ^a krypton peak to feed peak, cm	11.8	4.3	-- ^b

^aThe length of the mass transfer zone is defined as the minimum distance through the bed where the concentration of krypton changes by 80% of the difference between one quasi-steady-state concentration of krypton exiting the bed and another quasi-steady-state concentration of krypton exiting the bed.

^bPeak value not obtained; bed insufficient length to obtain steady-state krypton-oxygen gas composition.

gas composed of 93.09% CO_2 , 5.43% O_2 , and 1.48% krypton yields a gas containing 21.4% krypton and 78.7% O_2 . The maximum krypton concentration obtained, as shown in Fig. 4.4, is about 20% (i.e., the concentration of krypton expected if only CO_2 is adsorbed).

2. The optimum operating pressure for molecular sieves is near 10^5 Pa (14.7 psia) for operating temperatures in the vicinity of 0°C . The operating pressures for this series of experiments varied from 1.01×10^5 Pa (14.7 psia) in experiment A to 2.39×10^5 Pa (34.7 psia) in experiment C. As the results of these experiments show, in the delay of the krypton breakthrough at higher pressures, the advantage of higher operating pressures is that the molecular sieve can adsorb more CO_2 . Unfortunately, the molecular sieve begins to saturate in CO_2 slightly above 1 atm, with less and less CO_2 being adsorbed for each increase in system pressure.

This single advantage of high system pressure is outweighed by three disadvantages. Two of these are associated with all molecular sieves, whereas the third is specific to 4A molecular sieves.

- (a) As system pressure increases, the width of the krypton peak leaving the molecular sieve bed (see Fig. 4.4) decreases.

The total amount of krypton leaving the bed is about the same in each experiment; however, at higher pressures, the krypton gas volume is less. At the high pressure used in experiment C, the volume of krypton generated in about 1 m of bed is insufficient to allow the peak krypton concentration to be attained. Removal of the krypton from the gas flow as it leaves the bed is desirable so that it can be sent to a

bottling station. High pressure narrows the peak and thereby increases the difficulty of removing krypton alone; hence high pressure should be avoided.

- (b) As the system pressure increases, proportionally more of the gas is present in the gas phase between the molecular sieve particles than is adsorbed by the molecular sieve (because molecular sieve adsorption levels off). As shown earlier in Fig. 2.2, a large amount of krypton present in the feed gas in the void space between particles cannot be separated from the CO_2 . The problem is intensified as the pressure increases.
 - (c) At high system pressures, 4A molecular sieves can begin to adsorb krypton but the kinetics of krypton adsorption and desorption are so slow that practical system designs are not possible.
3. The kinetics of CO_2 adsorption by Linde 4A molecular sieve, although reasonably fast, are, as shown later, relatively slow compared with alternative molecular sieves such as 5A. Table 4.3 gives the length of the mass transfer zone between the CO_2 and the krypton. (The mass transfer zone is defined as that minimum length through the molecular sieve bed where the concentration of krypton varies by 80% of the difference between the peak krypton concentration in the bed and the krypton concentration in the feed.) The measured mass transfer length is as high as tens of centimeters. The mass transfer length for 5A molecular sieves, on the other hand, does not exceed a few centimeters, implying much faster mass transfer.

4.4.2 Series A experiments with Linde 5A molecular sieve

Linde 5A molecular sieve strongly adsorbs CO_2 and weakly adsorbs krypton; however, it does not adsorb O_2 significantly. Consequently, when a feed gas composed of 93.09% CO_2 , 5.43% O_2 , and 1.48% krypton is fed to 5A molecular sieve, it is separated into CO_2 , krypton, and O_2 . Figure 4.5 shows the results of a typical experimental run. The separation of the various gases is sharp, in contrast to the experimental results shown in Fig. 4.4 with 4A molecular sieve.

The results of ten experimental runs are given in Table 4.4. Throughout these runs, the molecular sieve was kept in a constant-temperature bath at 0°C . The composition of the feed gas was 93.09% CO_2 , 5.43% O_2 , and 1.48% krypton with ^{85}Kr tracer. The system pressure was varied from 1.01×10^5 Pa (1 atm) to 2.53×10^5 Pa (2.5 atm), while the feed gas flow was varied from 1.494×10^{-2} g per minute per square centimeter of molecular sieve bed cross section [7.62 cm^3 (STP)/ $\text{cm}^2\text{-min}$] to 29.964×10^{-2} g/ $\text{cm}^2\text{-min}$ ($152.86 \text{ cm}^3/\text{cm}^2\text{-min}$). When it was desired to strip the molecular sieve of CO_2 , the bed was heated to at least 150°C for 8 hr under vacuum provided by a mechanical vacuum pump and was purged with oxygen several times during bakeout. The following results were obtained:

1. In each run where the bed was carefully desorbed of CO_2 , the concentrations of CO_2 in the oxygen product and in the oxygen-krypton product were below the limit of CO_2 detection (10 ppm) by the instrumentation being used.
2. No krypton was detected in the pure oxygen exiting the bed before the krypton. The krypton detector can detect krypton concentrations

Molecular Sieve: Linde 5A
 Feed Gas: 93.09% CO₂, 5.43% O₂, 1.48% Kr
 Bed Conditions: 0°C, 1.14 atm
 Feed Gas Flow: 48.9 cm³(STP)/cm²-min
 Bed Length: 94.6 cm (37.25 in.)

Fig. 4.5 Gas composition from molecular sieve bed vs time.

Table 4.4. Experimental results

Run number	Pressure (atm)	Flow rate (cm ³ /cm ² -min) ^a	Length of mass transfer zone (cm)	Max. krypton concentration (%)	Implied temp. difference (°C)	CO ₂ adsorbed (cm ³ /g) ^b
1	1.0	7.6	1.0	52.3	30	89.8
2	1.0	34.1	2.3	55.6	25	93.9
3	1.0	49.9	1.0	58.0	21	103.5
4	1.0	76.2	1.4	56.2	24	93.5
5	1.0	91.7	1.5	55.5	25	99.6
6	1.14	48.0	1.1	58.6	--	87.9
7	1.14	48.9	1.1	58.2	--	93.8
8	2.36	50.3	2.1	51.6	--	94.6
9	2.36	96.4	3.1	61.8	--	96.6
10	2.36	152.9	2.3	57.4	--	93.1

^aGas at standard temperature and pressure, corrected by using ideal gas law.

^bGas at standard temperature and pressure adsorbed per gram of molecular sieve.

about one-thousandth that of the feed gas; this implies that the krypton concentration in the oxygen is not more than 0.001 the krypton concentration in the feed gas.

3. The mass transfer between CO_2 , krypton, and the adsorbing surface is very rapid and does not limit the performance of a molecular sieve bed under reasonable operating conditions. Table 4.4 shows the length of the krypton- CO_2 mass transfer zone within the molecular sieve bed. The mass transfer length is defined as the minimum distance through the bed where the concentration of krypton changes by 90% of the difference between the maximum krypton concentration and its value in the feed gas. Note that the length of the mass transfer zone is only about three times that of the molecular sieve pellets (0.5 cm). A mass transfer zone, at most a few centimeters long in a bed that is several meters long, does not limit bed performance or operation. Mass transfer should not be a limiting factor in equipment design or performance.
4. When a feed gas containing 1.48% krypton was used, the concentrations of krypton in the product streams of all experiments exceeded 50%. This implies total CO_2 removal and significant separation of O_2 from krypton since the maximum krypton concentration possible by removal of CO_2 only is 21.4%. Table 4.4 shows the krypton product concentrations. According to theory, a krypton concentration of 71.5% would be expected at 0°C and 1 atm of pressure with the feed gas previously described. Note that the predicted krypton concentration is higher than the experimentally determined concentration.

Adsorption of CO_2 releases large amounts of heat (12,500 cal/mole), which results in a decrease in the adsorption of krypton. This decrease, according to the model, results in a decrease in the maximum krypton concentration. As shown in later experiments, the rising internal bed temperature caused this difference between theory and experiment. The column labeled "Implied Temperature Difference" in Table 4.4 shows to what temperature the bed must be heated above 0°C in order for the model to fit experimental results. As a point of comparison, the heat of adsorption of the CO_2 on the molecular sieve would be sufficient to increase the temperature of the bed to 240°C if there was no cooling and if higher temperatures did not desorb CO_2 and thereby reverse the heat effects. This temperature effect indicates that the limiting design condition for a molecular sieve bed in the proposed process is the rate at which heat of adsorption can be removed from the bed.

5. The capacity of the molecular sieve to adsorb CO_2 , using the manufacturer's data,¹⁸ was found to be $94.2 \text{ cm}^3/\text{g}$ for a temperature of 0°C , a pressure of $1.01 \times 10^5 \text{ Pa}$ (1 atm), and a gas composed of 93.09% CO_2 . This value agrees with the experimental results presented in Table 4.4. The experimental data show considerable scatter because the amounts of CO_2 entering and leaving the experimental apparatus are simply measured by rotameters over a period of several hours, a technique which is not designed to obtain accurate values. At these CO_2 partial pressures, the molecular

sieve is approaching saturation and small changes in pressure have little effect on the amount of CO_2 adsorbed.

6. The preliminary molecular sieve bed desorption runs were made by heating the bed to 150°C . The results indicate that the CO_2 evolved from the bed contained less than one-fiftieth of the krypton that the feed contained. The krypton that is evolved is primarily krypton released from the gas spaces between molecular sieve particles, above the bed, and in the piping. The krypton concentration in the desorbed CO_2 can be decreased by minimizing open gas volumes or purging the bed with small amounts of CO_2 to displace the krypton-containing feed gases from the gas spaces in the bed.

4.4.3 Series B experiments with Linde 5A molecular sieve

The first series of experiments outlined the basic adsorption characteristics of Linde 5A molecular sieve for the proposed process. This second series was undertaken to address four specific questions:

1. Does the heat of adsorption of the CO_2 on a molecular sieve bed present a real design limitation for building full-scale equipment?
2. How does xenon in the feed gas affect the proposed process?
3. How is the proposed process affected by lower-than-expected concentrations of krypton?
4. Are there any problems in desorbing CO_2 from the molecular sieve bed?

The apparatus used for this set of experiments was the same as that used in earlier experiments except for two modifications of the molecular

sieve bed: thermocouples were installed, and the length was doubled by placing two identical beds in series.

The installation of thermocouples revealed that the adsorption of CO_2 produces so much heat that even cooling of the narrow 0.75-in.-OD molecular sieve bed used in these experiments with an ice bath cannot keep its temperature at 0°C . The corrected temperature and krypton concentration measurements from a single experimental run are plotted in Fig. 4.6. Other experimental parameters and results of this experiment are shown in Table 4.5. The krypton measurements are from a detector downstream of the bed, while the thermocouple is located in a region of the bed near the exit. Two expanded scales show the breakthrough of krypton and CO_2 out of the bed. There are two temperature peaks; the smaller peak is from the heat of adsorption of krypton (3720 cal/mole), while the larger one is from the heat of adsorption of CO_2 . Carbon dioxide heated the center of the bed to nearly 40°C before the ice bath recooled the bed back to 0°C . The large temperature transient of the bed in a constant-temperature bath shows conclusively that the major design limitation will be in finding methods to cool the bed adequately. The large temperature transient also suggests the possibility of determining the location of the CO_2 adsorption front in a molecular sieve bed by the use of thermocouples.

A series of experiments was made with xenon added to the standard feed gas. Figure 4.7 shows the results of one of these experiments, whereas Table 4.6 lists the conditions and some of the results of the experiments. Like Fig. 4.6, Fig. 4.7 plots both the temperature of

Fig. 4.6. Krypton concentration and molecular-sieve-bed thermocouple readings vs time.

Table 4.5. Conditions for the experimental data shown in Figure 4.6

Type of molecular sieve	5A
Feed gas composition, %	
CO ₂	93.09
O ₂	5.43
Krypton	1.48
Bed temperature, °C	0
Bed pressure, Pa (psia)	1.10 x 10 ⁵ (15.9)
Gas flow rate (constant), cm ³ /min-cm ² bed (STP) (g/cm ² bed-min)	52.58 (0.1031)
Maximum krypton concentration, %	59.5

Fig. 4.7. Krypton concentration and molecular-sieve-bed thermocouple readings vs time.

Table 4.6. Conditions and selected results
of experiments made with feed gas
containing xenon

Type of molecular sieve	5A
Feed gas composition, %	
CO ₂	90.82
O ₂	5.30
Xenon	2.44
Krypton	1.44
Bed temperature, °C	0
Bed pressure, Pa (psia)	1.01 x 10 ⁵ (14.7)
Gas flow rate, cm ³ (STP) min-cm ² bed cross section	53.0
Maximum krypton concentration, %	57.54
Maximum xenon concentration, %	67.0

the molecular sieve near the exit of the bed and the krypton gas concentration exiting the bed as a function of time since the experiment started. The experiment had a constant flow of feed gas; hence the time since the start of the experiment is proportional to the cumulative feed gas admitted to the bed. The following observations were made about xenon:

1. The xenon gas concentrates between the krypton gas peak and the feed gas as detected by the mass spectrometer.
2. Adsorption of xenon on the 5A molecular sieve produces heat¹⁹ (5250 cal/mole), which causes a significant rise in bed temperatures (Fig. 4.7).
3. The xenon does not appear to totally displace all krypton, as seen by the higher-than-feed concentration of krypton in the xenon gas between the krypton gas peak and the feed gas.
4. The peak xenon gas concentration measured was 67%. However, this value has a very large degree of uncertainty associated with it because of mass spectrometer calibration problems, very long sample lines to the spectrometer, and the semibatch analysis by the spectrometer for xenon.
5. Xenon does not significantly affect the product concentration of krypton.
6. The CO₂ content of the concentrated xenon exiting the molecular sieve bed is below 10 ppm; 10 ppm was the lowest concentration detectable with the instrumentation used.

Several experiments were conducted using a feed gas low in krypton to observe the effect of varying gas compositions. The only major

result of these experiments was to narrow the width of the krypton peak leaving the molecular sieve bed. Figure 4.8 shows the results of a typical run. In this particular case, the krypton content in the feed was insufficient to produce a peak krypton concentration $> 41\%$. Variations of krypton concentrations in the feed gas should not affect system operation or performance.

A set of experiments was conducted to determine whether any problems existed in desorbing CO_2 from Linde 5A molecular sieve by heating the bed to 200°C . None was found. In some experiments, the heating rate (70°C/hr) was sufficient to cause a pressure rise in the bed because CO_2 could not escape fast enough through the piping network. In any design work where a fast desorption cycle by heating is used, the rate of gas evolution should be calculated to ensure sufficient piping size.

In most experiments, the bed was heated to 200°C , the CO_2 was driven off, and oxygen was allowed to flow over the exit of the bed. The bed was then cooled from the bottom to allow any residual CO_2 to adsorb onto the portion of the bed near the gas feed point. Oxygen blanketed the bed as the CO_2 was adsorbed. In such cases, no problems were seen in the adsorption part of the cycle. For example, Fig. 4.5 shows an adsorption cycle where the above procedure was used with no difficulty. Any real design problems with desorption are likely to be related to heat transfer.

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Fig. 4.8. Krypton gas concentration exiting the molecular sieve bed vs time.

5. DESIGN CONSIDERATIONS AND RECOMMENDATIONS

5.1 Design Recommendations

The results of the experiments and analyses conducted, along with the preliminary flowsheets of the full-scale off-gas system,^{35,36} allow four recommendations for design to be made:

1. Linde 5A molecular sieve, or the equivalent, should be used for separating krypton and CO_2 because it only slightly adsorbs krypton but strongly adsorbs CO_2 . This is desirable for the following reasons:
 - (a) The krypton will separate from lighter gases. Some types of plant upset conditions result in large quantities of light gases. The proper choice of molecular sieve eliminates this problem.
 - (b) Slight krypton adsorption provides a sharp separation between O_2 and krypton fronts and krypton and CO_2 gas fronts. Such a separation makes location of the gas front by either thermocouple or radiation detection instruments easier due to the strong temperature and gas gradients in the bed.
 - (c) Higher krypton concentrations can be obtained.
2. The molecular sieve columns should be arranged so that all of the gas zones leaving one column enter directly into the next column; with such an arrangement, the column has infinite length from the standpoint of the gases. The oxygen, krypton, and other gases can be withdrawn in the piping between beds, simply narrowing the width of the respective gas zone as it passes between beds. This

approach is desirable if there is a low krypton concentration.

The krypton gas zone can be cycled through several columns, building up the length of the krypton gas zone until it is easy, by valving, to remove only the krypton gas without O_2 or CO_2 . Processes such as those described in Fig. 2.2, while feasible, should be avoided if high krypton concentrations are desired.

3. The major design constraint is cooling the molecular sieve bed. As discussed earlier, the adsorption of CO_2 releases very large quantities of heat. In addition, in actual facilities, the krypton may contain up to 6% ^{85}Kr . The decay of this radioactive isotope will provide a very high heat load. Any design must recognize that most of this heat is being dumped into the small krypton gas zone and the nearby CO_2 adsorption zone; consequently, heat transfer calculations must be based on the active zone instead of the whole bed. It is recommended that the bed be designed very similar to a vertical tube-and-shell heat exchanger. No molecular sieve in the bed can probably be more than a few centimeters from the heat transfer surface.
4. The cross-sectional area of the bed depends on the gas velocity in the bed. A reasonable range of gas velocities is from 50 to 100 $cm^3/min-cm^2$ of bed cross section. Slower gas velocities increase the bed size. Faster gas velocities cause excessive pressure drops and create cooling problems. Molecular sieve manufacturers³⁷ provide correlations to calculate pressure drop. If bed cooling is insufficient, the temperature rises and krypton adsorption decreases, resulting in a decrease in krypton concentrations.

5.2 System Design and Sizing

No effort was made to prepare a detailed design for a krypton-CO₂ separation system placed after KALC for a full-scale plant for reprocessing HTGR fuel elements. A preliminary design was made using the assumptions listed in Table 5.1 and the process flowsheet shown in Fig. 2.3. The results of this design are listed in Table 5.2. The most important conclusion obtained is that the actual system could be built with three molecular sieve columns 20 in. in diameter and 8 ft long. Careful design and process modification could probably reduce the size of the system by one-half.

5.3 Alternative Uses for the CO₂-Krypton Separation System

The experiments performed to date indicate that this molecular sieve system can separate krypton from CO₂ at almost any krypton concentration. It is therefore reasonable to ask if the KALC system could be replaced with this system. While technically feasible, the preliminary evidence suggests that this would be uneconomical for two reasons:

1. If the molecular sieve columns were sized for a full-scale plant to replace KALC, using the assumptions of Table 5.1, each column would have a diameter of 50 ft. Although careful design and engineering could greatly reduce this size, the volume of the equipment would still be large. Since the off-gas contains radioactive ⁸⁵Kr, the system would contain a large inventory of ⁸⁵Kr. Radiation shielding requirements and requirements to protect equipment against external damage imply thick, reinforced concrete walls. The cost of containment structures around the

Table 5.1. Assumptions used in preliminary design of krypton-CO₂ separation system using molecular sieves

Plant capacity	50,000 HTGR fuel blocks/year [50 GW(e) equivalent]
Plant operating schedule	300 days/year
Total system off-gas flow/HTGR fuel block	$4.5 \times 10^8 \text{ cm}^3$ ($1.6 \times 10^4 \text{ scf}$)
Off-gas composition	CO ₂ : 95% Kr: 15 ppm Other: 5%
Type of molecular sieve	Linde 5A
CO ₂ adsorption (200-0°C)	0.174 g CO ₂ /g molecular sieve
CO ₂ heat of adsorption/desorption	12,500 cal/mole (max.)
Density of molecular sieve	0.64 g/cm ³ (40 lb/ft ³)
Heat capacity of molecular sieve	0.21 cal/g·°C (0.21 Btu/lb·°F)
Heat of adsorption of other gases, heat leakage, krypton heating, other losses	50% of heat of adsorption of CO ₂
Bed pressure	$1.01 \times 10^5 \text{ Pa}$ (1 atm)
Bed adsorption temperature	0°C
Bed desorption temperature	200°C
Bed heat capacity (internal)	Equivalent to molecular sieve heat capacity
Ratio of molecular sieve cross-sectional area to total system cross-sectional area	0.5
Heat capacity of gases in molecular sieve bed	0.0
Bed design gas flow rate	$50 \text{ cm}^3/\text{min}\cdot\text{cm}^2$ bed cross section
KALC system concentration of krypton	1000
Ratio of flow rate of molecular sieve system to total system flow rate	1000
Off-gas volume to molecular sieve system/HTGR fuel block	$4.5 \times 10^5 \text{ cm}^3$ ($1.6 \times 10^1 \text{ scf}$)
Gas composition to molecular sieve system	
CO ₂	95%
Kr	1.5%
Other	3.5%

Table 5.2. "Design" of Kr-CO₂ sorption system
for full-scale plant

Krypton product concentration	+50%
Number of columns	Three
Diameter of columns	51.4 cm (20.2 in.)
Height of columns	243.8 cm (8 ft)
Adsorption cycle time	292 min
Desorption cycle time ^a	292 min
Average cooling capacity required for adsorption cycle	2.877 kW at 0°C (9.82 x 10 ³ Btu/hr at 0°C)
Heat required to desorb column	25.2 kWhr (8.60 x 10 ⁴ Btu)
Cooling required to cool column from 200°C to 0°C	15.9 kWhr (5.413 x 10 ⁴ Btu at 0°C)
Amount of molecular sieve per column	1.62 x 10 ⁵ g (358 lb)

^aOne column always ready to start adsorption cycle.

equipment would become excessive because of large column sizes and probably exceed the cost of the actual equipment.

2. The equipment costs are significant. Although no detailed design or cost calculations were made, a system designed by using the assumptions of Table 5.1 would require 1.07×10^6 lb of molecular sieve. At a current price of \$1.47/lb for large quantities,³⁸ the cost of the molecular sieve alone would amount to \$1.58 million.

While replacement of the KALC process by this molecular sieve process is unlikely, the latter process, because it can accept various concentrations of krypton in its feed gas, does allow the KALC designer considerable leeway in his design. Trade-offs in the size and complexity of KALC with this system are possible.

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APPENDIX A: COMPUTER PROGRAM TO DETERMINE MAXIMUM
KRYPTON PRODUCT CONCENTRATION³⁹

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OS/360 FORTRAN H

DATE 77.126/09.27.49

COMPILER OPTIONS - NAME= MAIN,OPT=00,LINECNT=60,SIZE=0000K,
SOURCE,EBCDIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,NOID,NOXREF

C DEFINITION OF TERMS
C AC02=SUBROUTINE TO CALCULATE CC CO2 ADSORBED PER GM MOLECULAR SIEVE
C AKR=SUBROUTINE TO CALCULATE CC KR ADSORBED PER GM MOLECULAR SIEVE
C AKRA=VOLUME KR ADSORBED, CC/GM
C A02=SUBROUTINE TO CALCULATE CC O2 ADSORBED PER GM MOLECULAR SIEVE
C AXE=SUBROUTINE TO CALCULATE CC XE ADSORBED PER GM MOLECULAR SIEVE
C P=PRESSURE IN MMHG
C PCO2=PARTIAL PRESSURE CO2 IN MMHG
C PKR=PARTIAL PRESSURE KR IN MMHG
C PO2=PARTIAL PRESSURE O2 IN MMHG
C PXE=PARTIAL PRESSURE XE IN MMHG
C T=TEMP IN DEGREES CELSIUS
C TK=TEMP IN DEGREES KELVIN
C TX=TEMP, WHICH KR ADSORBED, VARIABLE USED TO INVESTIGATE EFFECT
C OF LOCAL HEATING DUE TO KR AND CO2 HEAT OF ADSORPTION
C VCO2A=VOLUME CO2 ADSORBED, CC/GM
C VCO2Z=VOL OF GAS IN CO2 ADSORPTION ZONE,CC
C VKRZ=VOL OF GAS FLOWING THROUGH KR ADSORPTION ZONE,CC
C VO2Z=VOL OF GAS FLOWING THROUGH O2 ADSORPTION ZONE,CC
C VXE=VOLUME XE ADSORBED, CC/GM
C VXEZ=VOL OF GAS FLOWING THROUGH XE ADSORPTION ZONE,CC
C XCO2=MOLE FRACTION CARBON DIOXIDE
C XO2=MOLE FRACTION OXYGEN
C XO2CO2=MOLE FRACTION CO2 IN GAS PHASE ABOVE O2 ADSORPTION ON BED
C XO2O2=MOLE FRACTION O2 IN GAS PHASE ABOVE O2 ADSORPTION ON BED
C XO2KR=MOLE FRACTION KR IN GAS PHASE ABOVE O2 ADSORPTION ON BED
C XO2XE=MOLE FRACTION XE IN GAS PHASE ABOVE O2 ADSORPTION ON BED
C XKR=MOLE FRACTION KRYPTON
C XKRCO2=MOLE FRACTION CO2 IN GAS PHASE ABOVE KR ADSORPTION ON BED
C XKRKR=MOLE FRACTION KR IN GAS PHASE ABOVE KR ADSORBED ON BED
C XKRXE=MOLE FRACTION XE IN GAS PHASE ABOVE KR ADSORPTION ON BED
C XXE=MOLE FRACTION XENON
C XXECO2=MOLE FRACTION CO2 IN GAS PHASE ABOVE XE ADSORBED ON BED
C XXEKR=MOLE FRACTION KR IN GAS PHASE ABOVE XE ADSORBED ON BED
C XXEO2=MOLE FRACTION O2 IN GAS PHASE ABOVE XE ADSORBED ON BED
C XXEXE=MOLE FRACTION XE IN GAS PHASE ABOVE XE ADSORBED ON BED
C PROGRAM BASIS
C PROGRAM IS BASED ON FOLLOWING THE PROGRESS OF A KNOWN VOLUME OF
C GAS THROUGH A MOLECULAR SIEVE BED. THE INITIAL VOLUME OF GAS
C WAS CHOSEN FOR CALCULATIONAL EASE. IT EQUALS THE AMOUNT OF
C OFFGAS NEEDED SO THE CO2 IN THE FEED GAS CAN BE ADSORBED ONTO ONE
C GRAM OF MOLECULAR SIEVE GIVEN INPUT TEMPERATURES, PRESSURE AND
C FEED GAS COMPOSITION.
C INPUT DATA

ISN 0002 50 T=0.0
ISN 0003 51 TK=273.16+T
ISN 0004 52 P=760
ISN 0005 53 XCO2=.9309
ISN 0006 54 XXE=.0000
ISN 0007 55 XKR=0.0148
ISN 0008 57 XO2=0.0543
C
ISN 0009 200 PCO2=P*XCO2
ISN 0010 201 CALL AC02(PCO2,TK,VCO2A)
ISN 0011 202 PXE=P*XXE/(XXE+XKR+XO2)
ISN 0012 203 VCO2Z=VCO2A/XCO2

```

ISN 0013 210 DO 220 I=1,10
ISN 0014 211 CALL AXE(PXE,TK,VXEA)
ISN 0015 212 VXEZ=VXEA*VC02Z*(1.0-XC02)
ISN 0016 213 XXEXE=(VXEA+XXE*VC02Z)/VXEZ
ISN 0017 214 IF(XXE) 221,221,215
ISN 0018 215 IF(ABS((PXE-XXEXE*P)/(XXEXE*P))-0.001) 230,220,220
ISN 0019 220 PXE=XXEXE*P
ISN 0020 221 PRINT 222
ISN 0021 222 FORMAT(5X,'XENON QUESTION XXE=0.0R ITERATION PROBLEM')
ISN 0022 230 XXEC02=0
ISN 0023 231 XXEKR=XKR*VC02Z/VXEZ
ISN 0024 232 XXE02=X02*VC02Z/VXEZ
C CALCULATION GAS FLOW THROUGH XE ADSORPTION ZONE
ISN 0025 300 PKR=P*XXEKR/(XXEKR+XXE02)
ISN 0026 310 DO 320 I=1,100
ISN 0027 311 TX=TK+0.0
ISN 0028 312 CALL AKR(PKR,TX,VKRA)
ISN 0029 313 IF(XXE-.0001) 316,316,314
ISN 0030 314 W=VXEZ*XXEXE/VXEA
ISN 0031 315 GO TO 317
ISN 0032 316 W=1.0
ISN 0033 317 VKRZ=W*VKRA+VXEZ*(1.-XXEC02-XXEXE)
ISN 0034 318 XKRKR=(VKRA+XXEKR+VXEZ)/VKRZ
ISN 0035 319 IF(ABS((PKR-XKRKR*P)/(XKRKR*P))-0.0001) 330,320,320
ISN 0036 320 PKR=XKRKR*P
ISN 0037 321 PRINT 322
ISN 0038 322 FORMAT(5X,' KRYPTON QUESTION')
ISN 0039 330 XKR02=0.0
ISN 0040 331 XKRXE=0
ISN 0041 332 XKR02=XXE02*VXEZ/VKRZ
C CALCULATION GAS FLOW THROUGH KR ADSORPTION ZONE
ISN 0042 400 P02=P
ISN 0043 410 CALL A02(P02,TK,V02A)
ISN 0044 411 W=VKRZ*XKRKR/VKRA
ISN 0045 412 V02Z=W*V02A+VKRZ*(1.0-XKR02-XKRXE-XKRKR)
ISN 0046 413 X0202=1.0
ISN 0047 414 X02C02=0.0
ISN 0048 415 X02XE=0.0
ISN 0049 416 X02KR=0.0
C OUTPUT OF RESULTS
ISN 0050 900 PRINT 901
ISN 0051 901 FORMAT(50X,'BED CONDITIONS')
ISN 0052 902 PRINT 903
ISN 0053 903 FORMAT(5X,'GAS ABOVE ADS ZONE',22X,EX,'CO2',18X,'XE',18X,'KR',
218X,'O2')
ISN 0054 904 PRINT 905,XC02,XXE,XKR,X02
ISN 0055 905 FORMAT(5X,'CO2 ZONE MOLE FRACTIONS',17X,4(5X,F10.8,5X))
ISN 0056 906 PRINT 907,XXEC02,XXEXE,XXEKR,XXE02
ISN 0057 907 FORMAT(5X,'XE ZONE MOLE FRACTIONS',17X,4(5X,F10.8,5X))
ISN 0058 908 PRINT 909,XKR02,XKRXE,XKRKR,XKR02
ISN 0059 909 FORMAT(5X,'KR ZONE MOLE FRACTIONS',17X,4(5X,F10.8,5X))
ISN 0060 910 PRINT 911,X02C02,X02XE,X02KR,X0202
ISN 0061 911 FORMAT(5X,'O2 ZONE MOLE FRACTIONS',17X,4(5X,F10.8,5X))
ISN 0062 912 PRINT 913,VC02Z,VXEZ,VKRZ,V02Z
ISN 0063 913 FORMAT(5X,'GAS VOL INTO ADSORPTION ZONE,CC',6X,4(5X,F10.5,5X))
ISN 0064 914 PRINT 915,VC02A,VXEA,VKRA,V02A
ISN 0065 915 FORMAT(5X,'ADSORPTION CC/CM',21X,4(5X,F10.5,5X))
ISN 0066 916 PRINT 917,T

```

```

ISN 0067      917 FORMAT (20X,'BED TEMPERATURE =',2X,F10.5,2X,'DEGREES C')
ISN 0068      918 PRINT 919,P
ISN 0069      919 FORMAT (20X,'BED PRESSURE   =',2X,F10.5,2X'TORR')
ISN 0070      920 PRINT 921
ISN 0071      921 FORMAT (20X,'BED MATERIAL   =',2X,'SA MOLECULAR SIEVE')
ISN 0072      922 PRINT 923,TX
ISN 0073      923 FORMAT (20X,'KR  TEMPERATURE =',2X,F10.5,2X,'DEGREES K')
ISN 0074      STOP
ISN 0075      END

```

```

          COMPILER OPTIONS - NAME= MAIN,OPT=00,LINECNT=60,SIZE=0000K,
                           SOURCE,EBCDIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,NOID,NOXREF.
ISN 0002      SUBROUTINE AXE(PXE,TK,VXA)
ISN 0003      VXA=0.8*0.00019842*PXE*EXP(4900./((1.9872*TK))/SQRT(TK)
              C   BASED ON GRAPH S. KITANI AND J. TAKADA ADSORPTION OF KRYPTON
              C   AND XENON ON VARIOUS ADSORBANTS J. NUCLEAR SCIENCE AND
              C   TECHNOLOGY 2,NO 2,PG. 51-56 FEB.1965
              C   0.8 FACTOR IN EQUATION BECAUSE MS IS 0.2 INERT CLAY BINDER
ISN 0004      RETURN
ISN 0005      END

```

```

          COMPILER OPTIONS - NAME= MAIN,OPT=00,LINECNT=60,SIZE=0000K,
                           SOURCE,EBCDIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,NOID,NOXREF
ISN 0002      SUBROUTINE AKR(PKR,TX,VKRA)
ISN 0003      VKRA=0.80*0.0007*PKR*EXP(3500./((1.9872*TX))/SQRT(TX)
              C   EQUATION IN S. KITANI AND J. TAKADA ADSORPTION OF KRYPTON
              C   AND XENON ON VARIOUS ADSORBANTS J. NUCLEAR SCIENCE AND
              C   TECHNOLOGY 2,NO 2,PG. 51-56 FEB.1965
ISN 0004      RETURN
ISN 0005      END

```

```

          COMPILER OPTIONS - NAME= MAIN,OPT=00,LINECNT=60,SIZE=0000K,
                           SOURCE,EBCDIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,NOID,NOXREF
ISN 0002      SUBROUTINE ACO2(PCO2,TK,VCO2A)
ISN 0003      VCO2A = 51.4300 + 6.86185*ALOG(PCO2)
              C   ASSUMES 0 DEGREES C BED, 200 DEGREES C BAKEOUT AT BELOW 10 TORR
              C   DATA FROM LINDE ISOTHERM DATA SHEET 22
ISN 0004      RETURN
ISN 0005      END

```

```

          COMPILER OPTIONS - NAME= MAIN,OPT=00,LINECNT=60,SIZE=0000K,
                           SOURCE,EBCDIC,NOLIST,NODECK,LOAD,MAP,NOEDIT,NOID,NOXREF
ISN 0002      SUBROUTINE AO2NPO2,TK,VO2A)
ISN 0003      VO2A=5.6
ISN 0004      RETURN
ISN 0005      END

```

XENON QUESTION XXE=0 OR ITERATION PROBLEM

		BED CONDITIONS				
GAS ABOVE ACS ZONE		CO2		XE	KR	O2
CO2 ZONE MOLE FRACTIONS	0.93089998		0.0	0.0	0.01483000	0.05430000
XE ZONE MOLE FRACTIONS	0.0		0.0	0.0	0.21418214	0.78581738
KR ZONE MOLE FRACTIONS	0.0		0.0	0.0	0.59524223	0.30475771
O2 ZONE MOLE FRACTIONS	0.0		0.0	0.0	0.1	1.00000000
GAS VOL INTO ADSORPTION ZONE,CC	103.61530		7.15982		13.46158	11.98615
ADSORPTION CC/GM	96.45549		0.0		11.30176	5.60000
BED TEMPERATURE =		0.0	DEGREES C			
BED PRESSURE =		750.00000	TOFR			
BED MATERIAL =		SA MOLECULAR SIEVE				
KR TEMPERATURE =		273.15991	DEGREES K			

IHC002I STOP 0

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