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PROPOSED HELIUM PURIFICATION
SYSTEM FOR THE EXPERIMENTAL
GAS-COOLED REACTOR (EGCR)

F. A. Anderson

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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OAK RIDGE NATIONAL LABORATORY
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ABSTRACT

Liquid and dry processes suitable for the purification of gases by the removal of CO_2 , H_2O , CO , H_2 and hydrocarbons are discussed. Recommendations follow for specific processes to be included in a "dry" (no liquid absorbents or chemicals used) purification system for the helium coolant of the EGCR. The recommended processes include (1) a catalytic converter for the oxidation of CO , H_2 and hydrocarbons to CO_2 and H_2O , (2) cooler-condensers for the removal of the bulk of the H_2O , (3) silica gel adsorbers to complete the removal of H_2O and (4) Linde Molecular Sieve adsorbers for the removal of CO_2 . No provisions are included for the planned removal of radioactive gases or particulates.

TABLE OF CONTENTS

1.0	Summary	4
2.0	Introduction	5
3.0	Review of Gas Purification Processes.	7
3.1	Removal of Water Vapor from Gases	7
3.11	Condensation Processes	7
3.12	Absorption Processes	8
3.13	Adsorption Processes	12
3.2	Removal of Carbon Dioxide from Gases	13
3.21	Condensation Processes	14
3.22	Absorption Processes	14
3.23	Adsorption Processes	16
3.3	Removal of Carbon Monoxide and Hydrogen from Gases	16
3.31	Removal of Carbon Monoxide and Hydrogen As CO and H ₂	16
3.32	Removal of Carbon Monoxide and Hydrogen as the Oxidation Products CO ₂ and H ₂ O	17
4.0	Recommended Helium Purification System	18
4.1	Description of Proposed Purification System.	19
4.11	Purification System, Option 1.	21
4.12	Purification System, Option 2.	24
4.2	Purification System Components	26
4.21	Catalytic Converter	26
4.22	Cooler-Condensers.	29
4.23	Silica Gel Adsorbers	32
4.24	Molecular Sieve Adsorbers.	35
4.25	Filters.	37
5.0	Bibliography and References	39

6.0	Appendix	41
6.1	Oxygen Requirements for Oxidation of Helium Impurities. . . .	42
6.2	Catalytic Converter Calculations.	45
6.3	Example of Water Removal Obtained by Cooling Purification Stream Helium Below Its Saturation Temperature.	46
6.4	Preliminary Cooler-Condenser Calculations	47
6.5	Silica Gel Adsorber Calculations.	51
6.6	Molecular Sieve Adsorber Calculations	54
6.7	Interpretation of Figure 3, "Water-Helium Relationships at 300 PSIA".	57
7.0	Distribution	60

Figures

1.	Simplified Flow Sheet for Option 1	22
2.	Simplified Flow Sheet for Option 2	25
3.	Water-Helium Relationships at 300 PSIA	31

1.0 Summary

In order to limit graphite burn-up and carbon mass transfer in the Experimental Gas Cooled Reactor (EGCR), the level of reactive impurities in the helium coolant must be controlled. To achieve this control, it was originally proposed that a small fraction of the high temperature coolant (about 0.03 per cent or 130 lb./hr. of helium at 1050°F) be sent through a purification system designed to remove the following impurities: H_2O , CO_2 , CO , H_2 and hydrocarbons. When the decision was made to use water-sealed blowers and compressors in the main coolant and vessel coolant circuits, the purification system was given the additional task of dehydrating an estimated 800 lb. of helium per hour (originating as buffer helium leaving the blower and compressor seals at an estimated temperature of 360°F and with an unknown water content). The purpose of this investigation was to study the EGCR helium purification problem and to recommend a system for accomplishing the desired helium purification.

A literature search revealed several processes or methods, both wet and dry, for removing the specified impurities from various gases. A study of these processes and their characteristics convinced the writer of the desirability of devising a dry (i.e., no liquid chemicals required) system for effecting the required helium purification. The dry system herein recommended is less complex than previously proposed systems, eliminates completely the storage, handling and regeneration of liquid chemicals, eliminates the dumping of liquid wastes other than water and also eliminates the presence inside the purification system of all liquids other than water. The infrequent dumping of spent adsorbents (solids), however, is required.

The proposed helium purification process consists of the following steps:

- (1) The high temperature, by-pass coolant (130 lb./hr. at 1050°F and 300 psia) passes through a filter (possibly optional), is mixed with slightly less than the stoichiometric amount of oxygen required for the complete oxidation of the CO , H_2 and hydrocarbon impurities and is then sent to a catalytic converter containing Girdler G-43 catalyst operating at approximately 1100°F.

- (2) The "oxidized" by-pass stream from (1), now at $\sim 1100^{\circ}\text{F}$ and 300 psia, joins the buffer gas (800 lb./hr. at 360°F and 305 psia) coming from the helium blower and compressor seals and then enters a cooler-condenser. Here the gas is cooled to 90°F and the bulk of its water vapor removed by condensation.
- (3) The cool, partly-dried gas from (2) next passes through a bed of silica gel adsorbent and leaves virtually free of water.
- (4) The dry gas now enters a Linde Molecular Sieve adsorber where CO_2 is removed.
- (5) The effluent gas from (4) - now dry and free of CO_2 but still containing the CO , H_2 and hydrocarbons that entered the purification system as part of the unoxidized buffer helium stream - is filtered, compressed to 318 psia and then discharged to the reactor vessel coolant system.

The proposed purification system does not include provisions for the planned removal of radioactive impurities such as krypton and xenon or for the removal of minor impurities such as nitrogen and argon. Other than this, the chief disadvantage of the proposed system lies in the necessity for introducing oxygen into the by-pass helium in order to permit the oxidation of CO , H_2 and hydrocarbons in the catalytic converter. One important system advantage is its flexibility. By-pass helium overloads as high as 50 per cent should result in no significant loss of system purification efficiency. The primary effect of overloading will be a shortening of the adsorption cycles and an increase in the frequency of adsorbent regeneration.

2.0 Introduction

The Experimental Gas-Cooled Reactor (EGCR) is an advanced concept reactor designed to operate with high temperature helium as the coolant and heat transfer medium. Although high-purity helium will be charged to the coolant system, the coolant will soon accumulate a wide variety of solid and gaseous impurities. The nature and sources of these impurities is the subject of an excellent discussion found in ORNL-2500, Part 2, "The ORNL Gas-Cooled Reactor" (18)*. As is

* A number in parentheses not otherwise identified refers to a reference in Section 5.0.

pointed out in this document, the amount of coolant impurities will vary significantly depending on particular system operating states or conditions such as graphite degassing at start-up, normal steady state operation, operation with a ruptured steam tube, etc. However, to satisfy the rigid design requirements concerning permissible graphite core burn-up and carbon mass transfer during the 20-year design life of the reactor, it will be necessary to limit the normal steady-state coolant impurities to values not to exceed those given in the following table (9):

<u>Component</u>	<u>Limit, ppm by wt.</u>
CO ₂	18000
H ₂	1000
N ₂	1000

Once graphite degassing is complete, it is expected that in-leaking water will be a major source of coolant impurities. This water will react with the hot reactor graphite to produce CO, CO₂, and H₂ as well as some CH₄ (and possibly small amounts of other hydrocarbons). Although the nature of the helium coolant impurities is not difficult to postulate, the prediction of actual impurity levels or concentrations is virtually impossible because of the complicated inter-relationships existing between the impurities themselves and between the impurities and system components, including the graphite and the metal walls. Therefore, to insure the proper control of the impurity levels, provision must be made for the steady or intermittent removal of H₂O, CO₂, CO, H₂ and hydrocarbons, the impurities which logically might be expected to be present and to build up in the coolant system. Nitrogen, for instance, is not expected to be a particular problem for this impurity should arise only from air in-leakage or accountable admittance. In a coolant system operating at 300 psia in-leakage should be nil or non-existent. Air admittance is a possibility resulting from such operations as fuel charging, but is largely controllable.

The purpose of this report, therefore, is two-fold:

- (1) To review briefly various procedures or techniques that might be used to remove H₂O, CO₂, H₂, CO and hydrocarbons from the helium coolant of the EGCR
- (2) to recommend a helium purification system for the EGCR.

3.0 Review of Gas Purification Processes and Operations

For convenience the various gas purification processes and operations that are discussed briefly in this section of the report are grouped as follows:

- (1) Removal of Water Vapor from Gases
- (2) Removal of Carbon Dioxide from Gases
- (3) Removal of Carbon Monoxide and Hydrogen from Gases.

3.1 Removal of Water Vapor from Gases

Processes used for the removal of water vapor from gases may be classified under the following headings: (1) condensation, (2) absorption and (3) adsorption. A brief discussion of each of these methods follows:

3.11 Condensation Processes

Condensation processes for the removal of water vapor from gases fall under one of three categories:

- (1) Compression. The gas containing water vapor is compressed to such a pressure that the partial pressure of the water vapor becomes greater than the saturation pressure. As a result, water condenses until the partial pressure and the saturation pressure become equal. Low gas temperatures and high pressures enhance the degree of water removal.
- (2) Cooling. The gas containing water vapor is cooled below its dew point. Water condenses until saturation conditions prevail. The degree of water removal increases as the gas temperature decreases.
- (3) Compression and Cooling. The gas is both compressed and cooled to take advantage of the combined benefits of high pressure and low temperature in effecting more complete removal of the contained water vapor.

The use of compression to remove water vapor from "non-condensable" gases is usually confined to large scale industrial operations. In general, these systems are considered to be relatively costly to operate as indicated by the following statement found in Perry's Chemical Engineers Handbook (21), "In general, compression cannot

compete on a cost basis with desiccants when the latter can effect the required degree of dryness. Equipment, power and cooling water are generally excessive; and drying by compression is not usually used, therefore, unless the gas must be compressed as part of a succeeding step in the process."

Dehumidification of a gas by cooling it below its dew point is often used in industry as well as in small-scale laboratory operations. If cooling water is available at reasonable temperatures, many industrially-used gases, such as compressed air, can often be dried to acceptable moisture contents in standard shell-and-tube exchangers. The use of refrigerated cooling water adds to the cost of the dehumidification process but decreases significantly the moisture content of the dried gas (at 60°F, for instance, the vapor pressure of water is only 0.2563 psia, or roughly 37 per cent of the vapor pressure, 0.6982 psia, at 90°F). Increasing the pressure of the gas to be dried also results in the production of a dryer gas. Brine is often used for cooling purposes when below-freezing dehumidification temperatures are desired. This not only increases the cost of the dehumidification operation but also introduces a new problem, that of ice removal from the system.

For the production of extremely dry air (i.e., air with low dew points), it is common in laboratory operations to use low boiling liquids (liquid air or nitrogen) or subliming solids (dry ice) to achieve the required low dehumidification temperatures. Although effective, these procedures are expensive on the basis of the unit weight of water removed, especially when liquid air or dry ice is used as the cooling medium. It is not uncommon, however, to produce "dry" gases having dew points of -40°F and lower by the use of these condensation processes.

3.12 Absorption Processes

For convenience in analysis, absorption processes may be characterized - on the basis of the initial physical state of the absorbent - as being either "liquid absorbent" or "solid absorbent".

Some type of chemical reaction probably occurs in all absorption processes although it is common to think of the processes as being more or less "physical" in nature when water is the substance absorbed.

(1) Liquid Absorbents

Liquid absorbents used to dehumidify gases may be listed under the following headings:

(a) Concentrated, hygroscopic mineral acids such as H_2SO_4 and H_3PO_4 ,

(b) Concentrated, hygroscopic, aqueous solutions of organic compounds such as glycerin and ethylene glycol,

(c) Hygroscopic, aqueous solutions of inorganic salts such as $LiCl$, $LiBr$ and $CaCl_2$.

Liquid absorbents are generally used in continuous processes with continuous regeneration of the absorbent. These liquid desiccants are good for drying large volumes of air or other gases to moderately low moisture contents ranging from 10 to 30 per cent relative humidities (at room temperature). Theoretically, of course, the anhydrous desiccants can be used to produce gases of almost any degree of dryness. However, low moisture contents are obtained only by the use of excessive amounts of the desiccant. Because anhydrous desiccants are generally difficult and expensive to regenerate, the use of these materials for drying appreciable volumes of gases to low humidities is not common practice. Anhydrous desiccants are used for laboratory gas drying problems, but in these cases no attempt is made to regenerate the spent desiccant.

Liquid absorbents are generally used in the operating temperature range of 60-130°F; however, the narrower range from 70° to 110°F is the more common. Usual solution concentrations may vary from a low of about 40 per cent (for $CaCl_2$ solutions) to highs of about 95 per cent (H_3PO_4 and diethylene glycol). Approximate costs of "dry" desiccants (concentrated

liquids or undissolved solutes) range from as little as \$0.02 per pound for sulfuric acid and calcium chloride to as much as \$1.00 per pound for lithium chloride. A brief summary of the advantages and disadvantages of using liquid desiccants to dry gases is presented in Perry's Chemical Engineers Handbook, p. 878 (21). On the same page there is also found a listing of 11 general requirements for a good liquid desiccant.

(2) Solid Absorbents

A wide variety of substances, initially solid, may be used for dehydrating gases. The moisture-removal process is probably due to a combination of mechanisms, often occurs with chemical reaction and may finally involve dissolution of the desiccant. Several solids that are or that may be used for drying gases are listed below with pertinent comments concerning their use:

(a) Calcium chloride - CaCl_2 . Low cost solid (\$0.02/pound); deliquesces in the presence of high concentrations of water vapor, eventually forming an aqueous solution.

(b) Phosphorus pentoxide - P_2O_5 . Available at \$0.15/pound; deliquesces and reacts with water to form phosphoric acid; "corrosive, toxic nature makes it impractical for an industrial drying agent" (21).

(c) Potassium Hydroxide - KOH . Costs \$0.10/pound; deliquesces; also reacts with CO_2 .

(d) Magnesium Perchlorate - $\text{Mg}(\text{ClO}_4)_2$. High cost per pound*; may be used for drying at temperatures up to about 275°F; high temperature (400-500°F) and high vacuum (not over few millimeters Hg) required for regeneration; unsafe in drying organic vapors because of explosion hazards.

(e) Calcium Oxide - CaO . Low cost per pound*; reacts with water to form $\text{Ca}(\text{OH})_2$ which holds its water up to about

*Price not listed in Chem. & Engr. Quarterly Report, June 29, 1959.

1000°F (actual decomposition temperature given as 590°C or 1076°F); also reacts with CO_2 to form CaCO_3 ; expands during hydroxide formation.

(f) Barium Oxide - BaO . Costs about \$0.14/pound; reacts both with H_2O and CO_2 , maintaining high drying activity up to 1000°F; significant expansion occurs during hydroxide formation; BaCO_3 dissociations pressure given as 0 mm. at 997°C and 5 mm at 1017°C (1826° and 1863°F, respectively) (16); Ba(OH)_2 dissociation pressure given as 0.0229 atm. (17.4 mm) at 670°C (1238°F) (16).

(g) Calcium Sulfate, Anhydrous - CaSO_4 ("Drierite"). Dew points down to -80°F can be obtained; maintains drying efficiency until nearly exhausted, even at temperatures up to 150°F; regenerated with hot air at 400 - 425°F; will withstand 200 or more regenerations; cost of technical anhydrous CaSO_4 approximately \$0.03 per pound.

One important fact should always be borne in mind with respect to the design, as well as to the use, of "solid-absorbents" and adsorbents in dehumidification systems. This concerns heat production in the desiccant bed resulting from the liberation of the latent heat of condensation of the sorbed water and the heat of wetting or the heat of chemical reaction. Unless this sensible heat is removed, the desiccant temperature will gradually rise and will cause a rise in the temperature of the effluent gas. Higher bed temperatures, thus, may result in an increase in the partial pressure of the water in the dried gas and may also result in significant decreases in the water sorption characteristics of an adsorbent-type desiccant. This, in turn, may require bed cooling, an added design consideration and an additional operating cost.

3.13 Adsorption Processes

It is not always possible to make a clear cut distinction between absorption and adsorption phenomena in dehumidification processes. Adsorption is frequently described as a surface phenomenon which, in the case of moisture removal processes, results either in the production of a monomolecular layer of water on the desiccant surface or in capillary condensation within the porous structure of the desiccant or in both of these. Regardless of the phenomenon involved, the net effect of adsorption so far as a water-containing gas is concerned is to effect condensation of the water above its saturation temperature. Since condensation results in the liberation of latent heat (about 1000 Btu per pound of water adsorbed), and the production of heat of wetting (about 400 Btu per pound of water adsorbed if silica gel is the adsorbent), adsorption obviously is a heat producing reaction. As pointed out in the preceding section of this discussion, heat production due to adsorption or condensation can cause bed temperatures to rise high enough to decrease significantly the moisture retention characteristics of the desiccant. High bed temperatures may necessitate bed cooling in order to maintain desired moisture removal capacities.

Moisture removal by adsorption is often accomplished by the use of one or more of the desiccants discussed briefly in the following paragraphs.

(1) Silica Gel (7). Lends itself to adiabatic adsorption at high rates in shallow beds; preferentially absorbs water vapor in the presence of other vapors; is capable of drying air to a dew point below -94°F (or 0.002 mm Hg); performs best at rather high relative humidities; has a heat of wetting of about 400 Btu/pound of water adsorbed; can be reactivated at bed temperatures of about $300-350^{\circ}\text{F}$; has a hardness of 5 on Moh's mineralogical scale and shows good resistance to attrition; gradually loses activity with use; credited with 4 year service lives; flow rates for industrial air-conditioning range from 0.8 -2.4 cu.ft./min./lb. for bed thicknesses between 8 and 16 inches;

maximum superficial air velocity given as 80 ft/min (13); effective bed temperatures range from 40-90°F; weight adsorption of water at break-point ranges from 10-20 per cent; has approximate cost of \$0.35 per pound.

(2) Activated Alumina. "Capable of removing substantially 100 per cent of the moisture in a non-reacting gas until it has taken up water equivalent to 12-14 per cent (at break-point) of its own weight" (21); dew points of -105°F may be reached; reactivation accomplished by passing air or gas, heated within the temperature range of 350° to 600°F, through the absorbent; in air-conditioning practice, rates of 0.16 to 0.32 cu.ft./min./lb. are used with bed thicknesses of the order of 16 to 32 in.; effective bed temperatures range between 32-80°F.

(3) Activated Carbon. Adsorbs hydrocarbon and other organic vapors in preference to water vapor but will absorb water vapor in "large amounts" (no specific values obtained); no record found concerning its commercial use for the dehumidification of air or other gases.

(4) Linde Molecular Sieves (14). Have high capacity for drying gases; capable of drying air to dew points below -100°F; unusually high capacity for drying gases that have a low relative humidity; adsorbs approximately 10 pounds water/100 pounds Sieves; Sieves do not deliquesce; also adsorbs CO₂ in amount of 10 pounds/100 pounds Sieves; bed temperature of 400-600°F recommended for regeneration; equilibrium adsorptive capacity reduced from 15-30 per cent during first 200 regenerations, little change in capacity thereafter for up to 2000 cycles; inlet gas temperature of less than 100°F recommended; superficial gas velocity should be less than 2.0 ft./sec., 1 ft./sec. usually being recommended; recommended minimum bed depth is 2.5 ft; current cost of Sieves is \$1.95 in five-pound lots (may be cheaper in larger quantities).

3.2 Removal of Carbon Dioxide from Gases

Processes used for the removal of carbon dioxide, CO₂, as an impurity in other gases will be classified and discussed under the same headings used in the preceding discussion of methods for removing water vapor from gases.

3.21 Condensation Processes

Condensation, either as a result of compression or cooling or both, is not used as a method for removing CO_2 as an impurity from other gases.

3.22 Absorption Processes

Both liquid and solid absorbents are used commercially and under laboratory conditions to remove or scrub CO_2 from other gases.

(1) Liquid Absorbents

Liquid absorbents are the most important substances used by industry for removing or recovering CO_2 from process or waste gases. Brief comments concerning the use of several common or potential absorbents are given below.

(a) Water. Applicable only for high pressure gases containing CO_2 at partial pressures over about 50 psi.

(b) Potassium Hydroxide Solution (36% KOH) or Sodium Hydroxide Solution (32% NaOH). KOH solution preferred because carbonate formed is soluble and remains in solution (Na_2CO_3 is not soluble in aqueous NaOH); CO_2 content of air reduced to 3 ppm in one commercial installation; expense of KOH and the impossibility of regenerating either absorbent by heating probably main reasons why these solutions are not widely used; NaOH solution successfully used to lower CO_2 content of gases to 10-25 ppm.

(c) Monoethanolamine (15-20%) or Diethanolamine (10-25%). Monoethanolamine generally used unless specific considerations, such as presence of carbonyl sulfide, make diethanolamine more favorable; principal drawback to use of monoethanolamine is its relatively high vapor pressure; plate efficiencies for CO_2 absorption generally below 20 per cent; partial pressures of CO_2 over alkanolamine solutions (0.5 to 8.0 normal amine) in the order of 10 mm. Hg attained at solution temperatures ranging from 32 to 165°F and at solution concentrations of about 0.5 moles CO_2 /mole of amine;

regeneration accomplished by heating CO_2 -rich amine to approximately 300°F.

(d) Hot Potassium Carbonate Solution (K_2CO_3). CO_2 solubility depends on total amount of salt in solution, ratio of bicarbonate to carbonate, temperature and partial pressure of CO_2 in the gas; regeneration effected by flashing and steam stripping; greatest economic advantage appears to be in "bulk CO_2 removal where high purity is not required or where some other process can be used for final cleanup of gas" (12). "Below this value (of about 20 psi partial pressure of CO_2) the amine process appears more economical and above it, the hot K_2CO_3 process becomes increasingly advantageous" (Ibid); removal of CO_2 below approximately 2 per cent appears to be uneconomical.

(e) Aqueous Ammonia (NH_3). Relatively new method for removing CO_2 ; useful for purifying gas streams containing up to about 30 per cent CO_2 ; some indications that process is most economical for treating gases of relatively low CO_2 content (about 2 per cent); can reduce CO_2 content to 150 ppm; 2-5 per cent aqueous ammonia used in one installation; carbonated NH_3 solution regenerated by heating with direct steam.

(2) Solid Absorbents

No record was found in the literature concerning the commercial use of solid absorbents for the removal of CO_2 from gas streams. Solid absorbents find use in the laboratory but are used in relatively small amounts and are discarded when "saturated".

(a) Sodium or Potassium Hydroxide (NaOH or KOH); releases one mole of H_2O per mole CO_2 reacting, thus causing hydroxide to deliquesce; should be capable of removing CO_2 to few ppm; absorbent not capable of regeneration.

(b) Soda-Lime (Mixture of CaO and NaOH); used for removing CO_2 and H_2O from gases, no record of performance found but considered to be effective; cannot be regenerated.

(c) Ascarite (Sodium Hydroxide on Asbestos); no performance data found but generally considered to be good; cannot be regenerated.

3.23 Adsorption Processes

The industrial use of adsorption processes for removing CO_2 from gases either is not widespread or is poorly publicized.

- (1) Activated Charcoal. No industrial performance data located.
- (2) Linde Molecular Sieves.

A relatively new material (14) that will adsorb about 10 pounds of CO_2 /100 pounds of Sieves at 10 mm. Hg partial pressure or about 4 pounds of CO_2 /100 pounds Sieves at 1 mm. Hg partial pressure (with adsorbent at 25°C); performance increases significantly as adsorbent temperature decreases; adsorbent regenerated by heating and purging at $400\text{--}600^\circ\text{F}$; (see discussion under dehydration processes for additional information).

3.3 Removal of Carbon Monoxide and Hydrogen from Gases

Methods used for the removal of carbon monoxide (CO) and hydrogen (H_2) from gas streams are considered jointly in this section of the report. Two distinct approaches to this purification problem come to mind immediately:

(1) Removal of the aforementioned impurities as CO and H_2 and (2) oxidation of the CO and H_2 , followed by the removal of the oxidation products CO_2 and H_2O . Both of these approaches are discussed briefly in the following paragraphs.

3.31 Removal of Carbon Monoxide and Hydrogen as CO and H_2

(1) Carbon Monoxide Removal. Probably the best known and most widely used process for removing CO from gases is that which utilizes the complexing action of an ammoniacal cuprous salt. The CO -containing gas, preferably at an elevated pressure, is absorbed in an aqueous solution of a copper-ammonium salt in a countercurrent contactor. Preferred compounds for this use are copper-ammonium formate, carbonate and acetate. Regeneration of the absorbent is accomplished by the application of heat which destroys the complex and liberates most of the CO .

Carbon monoxide may also be separated from other gases by fractional condensation and distillation at low temperatures. So far as is known to the writer, this method has only been used for the recovery of the pure compound and not for the removal of small amounts of CO present as a gas stream impurity. Another low temperature CO removal process utilizes CO solubility in liquid N_2 as a means of effecting gas purification. A similar process uses low temperature methanol as an absorbent for CO. Although this procedure has some interesting aspects (low heat and energy requirements, for instance), there are two serious disadvantages - a complex flow scheme and relatively high methanol vaporization losses.

(2) Hydrogen Removal. The removal of small amounts of H_2 from other gases without first oxidizing the hydrogen to water appears to be an unpracticed art. Conceivably, H_2 might be selectively removed from some gases by occlusion in finely-divided palladium or by diffusion through a suitable membrane. H_2 is adsorbed by Linde Molecular Sieves (14) but only in appreciable amounts at extremely low temperatures (-300 to -350°F). This adsorption is not preferential so would probably be useful only for certain gas compositions.

3.32 Removal of Carbon Monoxide and Hydrogen as the Oxidation Products CO_2 and H_2O

(1) By hot, black copper oxide (CuO). If CO and H_2 are passed over cupric oxide at a temperature of about 525°F, oxidation readily occurs, CO_2 and H_2O being formed in stoichiometric amounts. Regeneration of the resulting copper can be effected by passing oxygen or air through the oxidizer bed at bed temperatures variously reported as being between 580° to 925°F. Bed temperatures, according to one report (4), should not be allowed to rise above 1022°F in order to prevent evolution of oxygen (i.e. reduction of CuO to Cu_2O). The same report states "Reduction to the commercial-formed CuO at 450-555°C (842-1031°F) by a gas containing hydrogen and oxygen for at least four hours at the same temperature gave an oxygen content of about 40 per cent of the theoretical." This and other statements

appearing in the literature lead the writer to believe that possibly as little as 40 per cent of the oxidizer capacity of a CuO bed can be utilized in the oxidation of CO and H₂ to CO₂ and H₂O. No information was located concerning the ability of CuO to resist attrition. Commercial black copper oxide is currently quoted at \$0.46 per pound.

(2) By Oxidizer Catalysts. Catalysts are available, such as Girdler G-43, which promote the reaction of oxygen with hydrogen, carbon monoxide and hydrocarbons (11). These catalysts require that oxygen be present in the gas to support the oxidation process, i.e. no oxygen for the reaction is provided by the oxidizing catalyst. If oxygen is not normally present in the gas, it must be added in sufficient amount to permit the desired oxidation reactions to take place. Girdler Catalyst G-43 operates between 400° - 1500°F, does not require regeneration, may be left on stream indefinitely without loss of activity, has been exposed to temperatures as high as 2500°F without losing activity or suffering physical disintegration, resists physical deterioration and has an estimated service life in excess of two years. Hydrocarbon oxidation requires catalyst temperatures of 1000°F or higher. Catalyst G-43 weighs approximately 55 pounds per cu. ft. and is currently quoted at \$3.45 per pound.

4.0 Recommended Helium Purification System

As pointed out in Section 2.0, Introduction, the level of impurities in the EGCR helium coolant must be controlled in order to limit graphite burn-up and carbon mass transfer during the 20-year design life of the reactor. Since impurity concentrations will normally be low, adequate control of the helium coolant impurity level can be achieved by continuously removing a small percentage of the impure helium (variously given as 0.03-0.05 per cent of the coolant flow of 4.27×10^5 lbs/hr), purifying it and then returning it to the coolant system. Although the actual weight of helium passing through the purification system on this basis would be small, ranging from 130 to 200 pounds/hr, the total daily flow of purified helium would amount to between 2.3 to 3.5 times the weight of helium in the coolant system. The amount of helium to be by-passed to the purification system was originally determined by calculation on the basis of "The time required to reduce the CO₂ level in the coolant from 10 to 1.8 per cent in one day of operation" (6).

The EGCR helium purification problem was modified somewhat when it was revealed that water-sealed blowers would be used to circulate the helium in the coolant system. According to Kaiser Engineers' Drawing No. 5917-EGCR-P11, the helium which is to be purified will enter the gas purification system via two routes: (1) as by-pass helium withdrawn at the rate of 130 lb./hr. from one, or both, of the two main coolant streams (at 1050°F and 305 psia) just before they enter the steam generators, and (2) as buffer helium (at 360°F and 300 psia) leaving the water seal catch basins of the two coolant blowers and the two vessel coolant compressors.

As is evident from Section 3.0, Review of Gas Purification Processes and Operations, a variety of methods are potentially available for use in effecting the desired purification of the EGCR helium coolant. In selecting the particular operations or processing steps and equipment to be specified for a proposed purification system, the following criteria or stipulations were used as guides:

- (1) The system should operate at or near 300 psia, the pressure at which the impure helium is available for purification.
- (2) Each step, or combination of steps, should be economically attractive in comparison with alternative procedures.
- (3) Each operation should be based on known and proved principles and technology, if possible.
- (4) Each step should be simple, safe and as fool-and failure-proof as possible and should require a minimum of attention.
- (5) The entire purification system should retain a high degree of effectiveness over a relatively wide range of operating conditions.

The remainder of this section of the report is devoted to a general description of the proposed helium purification system and to discussions which highlight the reasons for selecting each step, or item of equipment, for the system.

4.1 Description of Proposed Purification System

As previously indicated in the introductory remarks of this section of the report, the helium to be purified will come from two sources: Directly from the hot main coolant streams (identified as by-pass helium) and from the seals of the main coolant blowers and the vessel coolant compressors (identified as buffer helium). The amount of by-pass helium

is readily controllable and has been specified as being 130 lb/hr. The amount of buffer helium has also been specified - as 800 pounds per hour - but this specification is subject to possible, if not probable, modification as the design of the coolant blowers and compressors is developed and as test data are accumulated. Simple, approximate calculations show that the total flow of buffer helium might be as low as 50 lb./hr. Because of this uncertainty, three options for handling the purification streams present themselves: (1) combine both streams and send the combined flow through the given purification system, or (2) keep each stream separate and carry out the desired purification in separate systems, or (3) carry out some combination of options (1) and (2). Essentially, these options arise for two reasons: (1) the by-pass helium is available at 1050°F whereas the buffer helium will probably be available at or near 360°F and (2) the two streams will probably differ markedly in their concentrations of water vapor. Because the buffer helium will be in more-or-less intimate contact with the blower and compressor sealing water, this helium stream will probably have a much greater water vapor content than the by-pass helium.

If the by-pass helium stream (1050°F) is at the design value of 130 lb./hr. and if the rate of flow of buffer helium (360°F) is about 50 lb./hr. or less, the two streams might be combined for their trip through the proposed purification system as shown in Fig. 1. Combining the streams (hereinafter referred to as Option 1) results in an approximate helium temperature of 859°F, a temperature high enough for efficient operation of the catalytic oxidizer. At buffer helium flow rates much higher than 50 lb./hr., the temperature of the feed stream to the oxidizer will be too low for rapid oxidation of methane and other hydrocarbons (1000°F or higher is recommended). This difficulty could be overcome, of course, by providing a pre-heater for the buffer helium. However, this is an added complication to the purification system and is not considered necessary or desirable. Combining the helium purification streams before they enter the oxidizer offers the advantage that a larger flow rate of gas will be available for the complete purification cycle.

If the flow of buffer helium exceeds the approximate value of 50 lb./hr., the flow scheme shown in Fig. 2 (and hereinafter referred to as Option 2) appears to be the most desirable. This scheme has the disadvantage that the CO and H₂ in the buffer helium are not oxidized and removed during passage through the system. However, if the 130 lb./hr. flow of by-pass helium provides adequate coolant clean-up, this disadvantage is not particularly meaningful.

Since there appear to be no significant or compelling reasons to consider alternate options for the EGCR purification system, the discussion in the following portions of this section of the report will be limited to Options 1 and 2.

4.11 Purification System, Option 1

As shown in Fig. 1, the by-pass helium stream (130 lb./hr., 1050°F, 305 psia) is mixed with the buffer helium (50 lb./hr., 360°F, 300 psia) and the resulting mixture (180 lb./hr., 859°F, 300 psia) sent through a filter or strainer (possibly using Demister packing or microporous stainless steel for the removal of particulate matter such as graphite particles and metal or metal oxides which have broken loose from the system walls). Further consideration might show (1) that the filter is not needed or (2) that two filters should be used in parallel. If there is a likelihood that the catalyst in the catalytic converter will pick up particulate activity which will liberate enough heat to cause an undesirable or intolerable temperature rise in the catalyst bed, filtration or some other means for removing activity might prove to be a necessity.

The stoichiometric amount (or slightly less) of oxygen required for the oxidation of the CO, H₂ and hydrocarbon impurities in the helium is next added to the gas stream flowing to the platinum-base catalytic oxidizer (Girdler G-43 Catalyst) which operates efficiently at temperatures of about 1000°F. Lower temperatures are satisfactory for CO and H₂ oxidation, but temperatures of 1000°F or higher are required for the oxidation of methane and other hydrocarbons. Although the temperature of the inlet helium is only 859°F, the heats of reaction

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Figure 1

SIMPLIFIED FLOW SHEET FOR OPTION 1

[Combined flow of by-pass Helium (130 lb./hr.) and buffer Helium (50 lb./hr.)
passing through entire purification system]

are exothermic and will raise the catalyst operating temperature to 1000°F or more. For each per cent of CO reacted with oxygen, the rise in temperature of the catalyst bed will be approximately 169°F. For the reaction of H_2 and O_2 , the catalyst temperature rise will be approximately 148°F for each per cent H_2 (Private communication, James M. Moe, Girdler Catalysts, July 29, 1959). Although Catalyst G-43 has been used at temperatures as high as 2500°F, it is recommended that the maximum temperature in the catalyst bed be kept under 1500°F.

The oxidized helium stream - still at approximately 300 psia but now substantially free of CO and H_2 and at an approximate temperature of 900° to 1100°F (depending on the original concentration of CO and H_2 and the degree of oxidation achieved) - now passes to a cooler-condenser which is designed to drop the gas temperature to 90°F (or less) using 80°F (or less) cooling water. Since the water vapor content of saturated helium at 90°F and 300 psia is 0.01 pound/pound He, the condenser is expected to remove from 75 to 99 per cent of the water in the inlet gas. The removal of the condensed water will be enhanced by the use of a cyclone separator attached directly to the gas outlet side of the condenser. Such separators are manufactured by the R. P. Adams Company (5) for use in compressed air cooling and drying systems.

The saturated gas leaving the cyclone separator enters the silica gel adsorber where substantially all of the remaining water is removed. Adsorption can be carried out (1) isothermally, by providing means for cooling the silica gel bed to remove the latent heat of condensation of the water adsorbed (approximately 1000 Btu/lb) and the heat of wetting (about 400 Btu/lb), or (2) adiabatically. Adiabatic bed operation is simpler but results in a loss of adsorptive capacity since silica gel, like all adsorbents, gradually loses its ability to retain moisture as its temperature rises.

The dry gas effluent from the silica gel adsorber next passes through a bed of Linde Molecular Sieves which have the unique ability of adsorbing about 10 per cent of their weight of carbon dioxide. Water is preferentially adsorbed but since the incoming gas is virtually dry the adsorptive capacity of the Sieves should be available almost exclusively for CO₂ adsorption.

The purified helium, now free for all intents and purposes of H₂, CO, CO₂, H₂O and hydrocarbons, may contain small amounts of particulate matter which should be removed before the gas is admitted to the reactor vessel coolant system. The particulate material may include solids which entered the purification system and escaped removal and/or solids arising from adsorber bed breakdown due to attrition. Filtration of the cool, purified helium through CWS (Chemical Warfare Service), microporous stainless steel or Demister filters should provide a clean gas, substantially free of particulates and suitable for compression to 319 psia and discharge to the reactor vessel coolant system.

4.12 Purification System, Option 2

The flow diagram for this system is shown simply in the block diagram, Fig. 2. A comparison of this figure with Fig. 1 shows that the only flow difference for the two options lies in the handling of the buffer helium. In Option 1, the buffer helium joins the by-pass stream and passes through the entire purification system. In Option 2, the buffer helium joins the by-pass helium after the latter stream has passed through the catalytic converter. For buffer flows appreciably greater than 50 lb./hr., the cooling effect of the 360°F buffer helium on the approximately 1100°F "oxidized" by-pass helium will result in the gas stream entering the cooler-condenser at a temperature substantially lower than is the case in Option 1. Cooler-condenser design considerations involving thermal stresses may be such that the higher inlet gas temperatures inherent in Option 1 will prove to be impractical and will thus eliminate Option 1 from

Figure 2

SIMPLIFIED FLOW SHEET FOR OPTION 2

[Buffer Helium ($> 50 \text{ lb./hr.}$) joins by-pass Helium (130 lb./hr.)
after the catalytic converter]

further consideration. (The possible use of a venturi scrubber for gas cooling and water vapor condensation instead of a heat exchanger is discussed in Section 4.22.)

One disadvantage of Option 2 is that the only purification actually achieved on the buffer helium component passing through the purification system is water removal. Since the buffer stream does not pass through the catalytic converter, the CO and H₂ content is unaffected and is present in the stream of "purified" helium discharged to the reactor vessel coolant system.

4.2 Purification System Components

In section 4.0 the general scheme for performing the desired purification of the EGCR helium coolant was outlined. The purpose of this section of the report is to discuss the selection of the processes or devices recommended for use in the purification system and to give preliminary design data that will permit a visualization of system component sizes and an estimation of component capabilities.

4.21 Catalytic Converter

Original plans for the EGCR helium purification system envisaged the use of black cupric oxide as the oxidant for the CO, H₂ and hydrocarbon impurities in the helium coolant. These same plans contemplated a converter operating temperature of approximately 1000°F and the use of a hot air system for periodic regeneration of the oxidant. A review of the literature uncovered conflicting reports concerning cupric oxide reduction and regeneration. Oxide reduction temperatures ranging from 87 to 205°C (189° to 401°F) were reported for hydrogen; values from 60 to 265°C (140 to 509°F) were reported for CO (16). The CO and H₂ oxidation reactions were reported to be "quite slow", however, unless the CuO was kept "well above 275°C" (527°F) (17). Another interesting report stated that "the reaction (i.e. the reduction of CuO by hydrogen) is retarded by the presence of water vapor". Although a statement (16) was found to the effect that "hydrocarbons can be completely oxidized by hot cupric oxide", the required or recommended temperature for rapid reaction was not stated.

The regeneration or oxidation of copper was reported in the literature as occurring at temperatures above 300° to 350°C (572° to 662°F). Another report (4) stated that "Higher temperatures (i.e. above 450-550°C (842° to 1022°F)) do not facilitate oxidation, as CuO begins to evolve oxygen at temperatures above 550°C." In Mellor's Treatise (16) the statement is made that "if copper is not finely divided--about 40 per cent conversion (to the oxide) after 12 hours heating in muffle--." Another report (4) stated that "Reduction of the commercial wire-formed CuO at 450°-555°C by a gas containing hydrogen and oxidation for at least four hours at the same temperature gave an oxygen content of about 40 per cent of theoretical."

On the basis of the foregoing remarks, it was concluded by the writer (1) that black cupric oxide can not be assumed to be more than 40 per cent efficient as a source of oxygen for oxidizing CO, H₂ and hydrocarbons, (2) that the reduction reaction should be carried out at 600-700°F and (3) that regeneration should be performed at 800-900°F. Thus, if the original plan were carried out to use a CuO converter in the gas purification system, conclusion (2) above would indicate the need for installing a helium pre-cooler before the converter. On this basis, the converter portion of the purification system would include, in addition to the converter, the helium pre-cooler, a heater for heating the required regeneration air, and the associated piping and valves for switching back and forth between the reduction and oxidation parts of the cycle and for conveying the waste regeneration gas to the EGCR gas vent system.

In an effort to simplify the converter portion of the purification system, the writer investigated the possibility of using a catalytic converter in place of the contemplated CuO unit. For the reasons given below, it was subsequently decided to recommend that a catalytic oxidizer or converter using Girdler G-43 catalyst be used instead of a black cupric oxide unit:

(1) A catalytic oxidation unit using Girdler G-43 platinum catalyst will operate dependably and efficiently at the normal helium

coolant temperature of 1050°F to oxidize CO, H₂ and hydrocarbons. Catalyst temperatures as low as 800°F will still permit initiation of the CO reaction while temperatures down to 400°F will keep the hydrogen reaction going. The high operating temperature of Catalyst G-43 (up to 1500°F) means that the helium pre-cooler needed if the CuO converter is used can be eliminated.

(2) Girdler G-43 catalyst resists physical deterioration, is estimated to have a life in excess of two years, and does not require regeneration. This latter property means that the air regeneration system (heater, piping, valves) required for the CuO converter can be eliminated as a part of the purification system accoutrements. Unfortunately, this desirable simplification is not all milk and honey. Since the helium purification stream does not contain the oxygen required for the oxidation of the CO, H₂ and hydrocarbons and since this oxygen is not provided by the catalyst, oxygen must be added to the helium stream before it enters the catalyst chamber. For complete oxidation, stoichiometric amounts of oxygen obviously are required. However, to avoid the possibility of having excess, unreacted oxygen in the converter effluent, it is recommended that slightly less than the stoichiometric amount of oxygen be used. The actual amount of oxygen required for oxidation will depend, of course, on the level of oxidizable impurities in the helium. Appendix 6.1 shows this amount for two assumed helium coolant compositions.

(3) The space velocity recommended for Girdler G-43 catalyst is 20,000 cubic feet of gas per hour, measured at STP, per cubic foot of catalyst. If only the by-pass helium (130 lb./hr.) passes through the converter, less than 0.6 cu. ft. of catalyst (about 35 pounds) is required, an amount that could be contained in a 2-ft. length of 8-in. pipe. (See Appendix 6.2 for calculations.) The catalytic converter, therefore, can be a small compact unit. In contrast, the black CuO converter would be considerably larger if it were properly designed to contain the 1000 pounds of oxide once

specified, or suggested, as being required (basis of calculation unknown to writer) in the unit.

Because catalyst operation is so dependable and because the estimated life of G-43 Catalyst is reasonably long (about two years), the writer questions the necessity for having more than one catalytic converter in the purification system. For this reason the second units shown in Figs. 1 and 2 are indicated by dashed lines. Unless subsequent system reliability considerations necessitate the second unit or unless the estimated time required to replace a damaged or exhausted unit is unduly long, one catalytic converter should be ample for the purification system.

In summary, the use of the proposed catalytic converter has the disadvantage of requiring the addition of oxygen to the helium by-pass purification stream but has the advantage (1) of being more compact than a CuO converter, (2) of eliminating the need for a helium pre-cooler, and (3) of eliminating the need for an air heater and all the associated regeneration system piping.

4.22 Cooler Condensers

The recommendation to use cooler-condensers to remove the bulk of the water present in the combined by-pass and buffer helium streams is in accord with the plans of Kaiser Engineers as shown in their drawing, No. 5917-EGCR-P11. This method of water removal, by cooling the helium below its saturation temperature, is straight-forward, reliable and economic and should serve to remove the bulk of the water present in the incoming helium stream. The illustrative calculation shown in Appendix 6.3 (based on a helium by-pass flow of 130 lb./hr. and a buffer flow of 800 lb./hr. containing 0.3 lb. H_2O vapor/lb. He) indicates, for instance, that for the assumed conditions over 96 per cent of the vapor entering the condenser will be condensed.

An approximate idea of the size of cooler-condenser required to handle a 130 lb./hr. by-pass flow and an 800 lb./hr. buffer helium flow may be obtained from the preliminary cooler-condenser calculations shown in Appendix 6.4. These calculations, admittedly incorrect

because of several simplifying assumptions, yield a heat transfer area of 879 sq. ft. For lower weight-rates of helium flow - especially lower buffer helium flow rates - and for lower initial moisture contents of the buffer helium, smaller heat transfer areas would be required. Since the buffer helium flow rate and moisture content are currently the controlling factors in the design of the purification system cooler-condensers, every possible consideration should be given in the helium blower and compressor designs (1) to decrease the amount of buffer helium required and (2) to control the amount of sealant water so as to permit the design of smaller, more compact heat exchangers. A study of Fig. 3 will show the various possible relationships that may exist between the rates of flow of sealing water and buffer helium and the temperatures and moisture contents of the helium leaving the compressor and blower seals. For sealing water flow rates below about 0.3 lb. H_2O /lb. He, for instance, complete vaporization of the water can be expected. At flow rates of 5.0 lb. H_2O /lb. He or greater, the cooling effect of the sealing water (assuming intimate mixing of sealant and gas) becomes so great that exit helium temperatures are low (below 200°F) and moisture contents are as little as one-third of the value assumed for the illustrative calculation shown in Appendix 6-4. Strictly from the point of view of purification system cooler-condenser considerations, it would thus appear desirable to keep blower and compressor sealing water flow rates below 0.10 lb. H_2O /lb. He or above 10 lb. H_2O /lb. He, with the higher rate the more attractive.

The use of cooler-condensers to remove water from the helium purification system envisages the simultaneous use of a cyclone separator, immediately after the exchanger, to minimize the carry over of mist or entrained water to the silica gel adsorbers. Such separators are designed and built by the R. P. Adams Company (5) for use with their pipe line aftercoolers for cooling and dehumidifying compressed air.

An alternate method of removing the bulk of the water vapor from the helium purification stream is mentioned here briefly as an interesting possibility. This method involves the use of a venturi scrubber to effect simultaneously the desired cooling and dehumidification operations. The water required for the scrubber operation could be recirculated indefinitely but would have to be cooled in an auxiliary water-to-water exchanger. Since the volume of water in the recirculation system would gradually increase because of the condensation of the water introduced by the helium, periodic withdrawal or dumping of water would be required. The use of a venturi scrubber would complicate the purification system somewhat but would permit the use of a standard water-to-water exchanger in place of the presently proposed helium-to-water cooler-condensers. Additional study would be required to determine the overall feasibility of this suggestion.

4.23 Silica Gel Adsorbers

If the cooled and dehumidified helium leaving the cooler-condensers is dry and saturated at 90°F and 300 psia, it will contain approximately 0.01 pounds H_2O /pound He (See calculation in Appendix 6.3). On the basis of pure He, this amounts to about 1 per cent by weight or 0.23 per cent by volume of water vapor. As this concentration is above the steady-state water content limit of 0.2 per cent (volume) specified for the helium coolant, the removal of some, if not all, of this water is mandatory. The use of silica gel is recommended for this job for the following reasons:

(1) Silica gel (7) is a solid, "dry", non-corrosive adsorbent that can be regenerated countless times (service lives up to four years reported) and which requires only hot air (300-350°F at adsorber inlet) for regeneration. The use of a dry adsorbent instead of a liquid absorbent eliminates the probable need of a recirculation pump for the liquid system, eliminates the need for absorption liquid

storage tanks, eliminates the probable need for an after-scrubber to remove entrainment in a liquid system and also eliminates the possibility of liquid leaks that seem to plague most industrial absorption systems.

The fact that silica gel remains dry, i.e., does not deliquesce, is an important factor in comparing silica gel with "chemical type" solid adsorbents such as CaCl_2 or KOH . Obviously, the dry silica gel bed will not settle due to dissolution and will not form liquids that ultimately have to be removed and dumped.

(2) Silica gel is a cheaper dry adsorbent than Linde Molecular Sieves (\$0.35 per pound vs. \$1.95 per pound - no price data obtained from activated alumina) and appears to be a decidedly better water adsorber than either Molecular Sieves or activated alumina at water vapor pressures of 10 mm Hg and greater (based on manufacturers' literature and assuming that water adsorption from helium will follow the same general patterns as adsorption from air). Indications are that a silica gel bed might be expected to produce substantially dry helium up to bed capacities of 20 per cent (water content of bed as a percentage of the activated weight) at bed temperatures as high as 120°F.

(3) The use of silica gel adsorbers before the second-stage Molecular Sieve adsorbers will help to reserve the more expensive Sieves for the particular task of CO_2 removal.

According to the silica gel adsorber calculations shown in Appendix 6.5 (assuming a total flow of 930 lb./hr. of helium leaving the cooler-condensers with 0.01 pound H_2O /lb. He), a dehumidification unit 2.0 ft. in diameter and 4.0 ft. high will provide sufficient adsorbent capacity to dry the design flow rate of helium on a 12-hr. adsorbing cycle. The estimated rise in temperature of the dehydrated gas is approximately 7°F, a value low enough to indicate that adsorbent bed cooling will not be

required. A final decision on bed cooling, however, will have to wait until it can be predicted how much activity the adsorbent might be expected to pick up and how much heat will be released as a result of radioactive decay.

The final design of a silica gel adsorber for the helium purification system should incorporate the use of a layer of special buffer silica gel which resists deterioration and break-up in the presence of liquid water. The usual grade of adsorbent silica gel will break up if drops of liquid water come in contact with it when it is highly active (immediately after regeneration).

At the end of each adsorption period (assumed to be 12 hours in Appendix 6.5 calculations), the silica gel bed must be reactivated, i.e., the adsorbed water must be removed. This operation requires heat which is usually supplied in one of two ways: (1) by steam or electric coils imbedded in the desiccant or (2) by heated gas which is blown through the bed. Regeneration usually is carried out at bed temperatures about 350°F; higher temperatures may be used in order to obtain better activation, but in all cases bed temperatures should be held below 600°F. If steam or electric coils are used to supply regeneration heat, a small flow of gas (preferably flowing counter current to normal gas flow) should be used to help sweep out the desorbed water. If heated gas is to be used, consideration must be given to the choice of gas. Although He would be preferable, and could be used without significant loss by the design of an auxiliary condenser to remove the desorbed water, air will be suitable if the desiccant is purged of air before it is put back into use. Activation might thus be accomplished by blowing hot air (~400-450°F) through the silica gel until the bed reaches a pre-determined temperature and then letting cool air flow through the system until the bed temperature has dropped to, say, 200°F. At this point the air supply is shut off and vacuum applied until substantially all the air has been removed from the adsorber system. Helium is now supplied to bring the adsorber

up to system pressure so that it will be ready for the next adsorption cycle. Heat loss to the surroundings during the interim period between the end of the regeneration step and the beginning of the new adsorption cycle is expected to drop the desiccant bed temperature to 90°F, the temperature of the helium entering the adsorber system.

4.24 Molecular Sieve Adsorbers

The helium stream leaving the silica gel adsorbers and entering the Molecular Sieve adsorbers is substantially dry but contains CO₂ (and some H₂, CO and hydrocarbons that entered the purification system with the buffer stream but which did not pass through the catalytic converter) which must be removed before the purification process is complete. CO₂ removal is the primary function of the Molecular Sieves, an adsorbent which has the unique ability of adsorbing about 10 pounds of CO₂ per 100 lb. of adsorbent at normal temperatures and at low CO₂ pressures. As silica gel is a poor CO₂ adsorber, it is not suitable for use in this part of the purification system. Activated carbon is only about one-fifth as effective as Molecular Sieves for CO₂ removal so it, too, is eliminated from further consideration. Liquid absorbents (such as ethanolamine, hot potassium carbonate solution or caustic solution) are widely used by industry for CO₂ absorption and could be used in the EGCR purification system. In spite of the various possible alternates, Linde Molecular Sieves are recommended for the CO₂ removal operation for the following reasons:

(1) The use of dry, non-deliquescent Sieves will eliminate the need for the absorbent interceptor specified for the liquid absorption system in Kaiser Engineers Drawing 5917-EGCR-P11. It will also eliminate the water scrubber (not shown in Dwg. 5917-EGCR-P11) which would be required, in all probability, in a liquid absorption system. Also eliminated will be the absorption liquid storage tank and associated liquid transfer piping.

(2) Elimination of a liquid absorbent will completely remove the possibility of a liquid other than water being present in the entire purification system.

(3) Elimination of a liquid absorbent will eliminate the possibility of liquid leakage from the absorption system to the surroundings, a problem that appears to be common to most industrial liquid absorption systems.

(4) Molecular Sieves have been regenerated over 2000 times with a total loss in CO_2 -retaining capacity of only about 15 per cent. If an alkaline absorbent such as KOH or NaOH is used, CO_2 removal will be excellent, but regeneration will be impossible.

(5) Should extremely complete CO_2 removal be required, Molecular Sieves appear to be capable of producing a cleaner (less CO_2) effluent than can be produced by the practical use of a regeneratable liquid absorbent. CO_2 concentrations of a few parts per million may be achieved in the gases leaving a Molecular Sieve adsorber.

According to the calculations shown in Appendix 6.6, if 930 lb./hr. of He (dry, CO_2 -free basis) containing 1.8% of CO_2 pass through the Molecular Sieve adsorbers, a total of 202 pounds of CO_2 is available for removal during the assumed 12-hour adsorption period. This amount of CO_2 requires the use of an adsorption tower containing 44.9 cu. ft. or 2020 lb. of Sieves. A tower 3.0 ft. in diameter would have to have a height of 6.35 ft. to hold the required amount of adsorbent. If the quoted price of the Sieves, \$1.95 per pound in five-pound lots, is also assumed to be the bulk price, the cost of one charge of adsorbent (having an estimated life of 5.5 years) will be \$3940. Shortening the length of the adsorption cycle will reduce this initial cost proportionately but will increase the frequency of regeneration and thus raise operating costs.

In general, the reactivation of the molecular sieves at the end of an adsorption cycle will follow the same pattern described for the

reactivation of the silica gel adsorbent (see Section 5.3). Reactivation should be carried out at a bed temperature of 500°F, and purge gas should be used. If hot air is used for bed heating and purging, all traces of air should be removed from the adsorber at the end of the regeneration cycle. This might be accomplished by drawing a vacuum on the adsorption column or by passing a small amount of helium purge gas through the column. For this purpose, the producers of Linde Molecular Sieves state (14) that "only one cubic foot per hour of helium purge is necessary per pound of adsorbent." How much helium this actually amounts to is not presently known for the purging time is not specified. Should purging require an hour, the weight of purge helium would amount to over 20 pounds, a loss of helium that cannot be tolerated. Air removal by vacuum purging, or drawing, thus appears to be indicated unless an auxiliary chemical system for purifying purge helium is shown to be feasible.

4.25 Filters

Both Options 1 and 2 of the proposed purification system envisage the possible use of filters for the removal of particulate matter originating either in the main EGCR coolant system or in the purification system. Particulates generated in the coolant system may include graphite and iron oxide particles but neither the amount of this solid matter nor the absolute necessity for removing the particles is known at this writing. In Section 6.6 of ORNL Report 2500, "The ORNL Gas-Cooled Reactor", (19) the following statements appear, "The use of cyclone separators and/or particulate filters to remove carbon dust and iron oxide particles from the circulating gas stream was considered.---Since the operation of the Calder Hall plant has demonstrated that separators and filters are not necessary, they are not provided in the design of GCR-2."

In the purification system, particulates may result from attrition of the catalyst, the silica gel adsorbent and the Linde Molecular Sieves. Although proper design of the catalyst and adsorbent

containment vessels will keep bed movement at a minimum, it must be assumed that some particle break-down will occur even though the particles are relatively hard and resistant to crushing and grinding. Unless it is shown subsequently that there is a compelling reason for removing coolant system particulates from the gas in the purification system before the gas enters the catalyst converter or the adsorption beds, it appears that one set of filters immediately preceding the receiver compressors (items J-14-1, J-14-2, Kaiser Drawing 5917-EGCR-P11) will suffice to handle the filtration problem for the entire purification system. The primary function of the filters will be to protect the receiver compressors and to prevent particulates from leaving the purification system and entering the coolant systems.

It is expected, of course, that some removal of particulate matter will occur naturally in the purification system as a result of the following effects:

- (1) Settling of particulates on system walls.
- (2) Settling of particles in catalyst and adsorption beds.
- (3) Scrubbing out of particles by the moisture condensing in the cooler-condensers.

No attempt has been made by the writer to predict the magnitude of these effects.

When the probable size distribution of the particulate impurities in the EGCR helium coolant has been established or estimated and when a decision has been reached concerning the size limits of the solid impurities which must be removed from the gas, one of the following filters should prove to be suitable for use in the purification system:

- (1) A filter containing compacted stainless steel Demister packing.
- (2) A microporous stainless steel filter.
- (3) A Chemical Warfare Service (CWS) filter.

5.0 Bibliography and References

1. Allowable Contamination of Helium Coolant Operating Specification for the Prototype Enriched Gas-Cooled Power Reactor, ACF-GCPR Study No. 3-215 (Feb. 17, 1959)
2. American Metal Products Company Inert Gas Purification System, American Metal Products Co. (P. O. Box 465, Ann Arbor, Michigan)
3. Anonymous, Cell Wrings Helium from Natural Gas, Chemical Engineering, Vol. 65, No. 13, p. 60 (June 30, 1958)
4. H. Bruckner and R. Schick, The Use of Activated Copper Oxide in the Fractional Combustion of Hydrogen and Methane, Gas-u. Wasserfach 82, 189-93 (1939)
5. Compressed Air and Gases, Bulletin 714, R. P. Adams Company, Inc. (Buffalo 17, New York)
6. Contamination and Purification of Helium During Reactor Operations, ACF Job Report No. 3-215-1.0 (Nov. 10, 1958)
7. Dehydration of Air and Gas with Davison Silica Gel, Bulletin 202, Davison Chemical Company (Baltimore 3, Maryland)
8. The Deoxo Gas Purifiers (and other technical literature), Engelhard Industries, Inc. (760 Market Street, San Francisco, California)
9. Experimental Gas-Cooled Reactor Preliminary Hazards Summary Report, ORO-196 p. 4-14 (May 1959)
10. Gas Cooled Power Reactor, IDO-24027 (Kaiser Engineers Report No. 59-3-RE, March 1959)
11. Girdler Catalyst Catalog, Girdler Catalysts (P. O. Box 337, Louisville 1, Kentucky)
12. A. L. Kohl and F. C. Riesenfeld, Today's Processes for Gas Purification, Chemical Engineering, Vol. 66, No. 12 (June 15, 1959)
13. E. Ledoux, Vapor Adsorption, Chemical Publishing Co., Brooklyn, N. Y. (1945)
14. Linde Molecular Sieves, Linde Company (Pleasant Valley Road and Route 38, Moorestown, N. J.)

15. Means of Limiting Impurities in the Gas System of the Prototype Gas-Cooled Power Reactor, ACF Job Report No. 3-215-5.0 (Feb. 19, 1959)
16. J. W. Mellor, A Comprehensive Treatise of Inorganic and Theoretical Chemistry, Vol. III, Longmans, Green and Co., London (1925)
17. P. W. Mullen, Modern Gas Analysis, Interscience Publishers, New York (1955)
18. The ORNL Gas-Cooled Reactor--Part 2, ORNL-2500 (April 1, 1958)
19. The ORNL Gas-Cooled Reactor--Part 3, ORNL-2500 (April 1, 1958)
20. The ORNL Gas-Cooled Reactor--Part 4, ORNL-2500 (April 1, 1958)
21. J. H. Perry, et al., Chemical Engineers Handbook, 3rd Ed., p. 884, McGraw-Hill, New York (1950)
22. Techniques of Diffusion Separation, Bell Telephone Laboratories (Murray Hill, New Jersey)

6.0 Appendix

- 6.1 Oxygen Requirements for Oxidation of Helium Impurities
- 6.2 Catalytic Converter Calculations
- 6.3 Example of Water Removal Obtained by Cooling Purification Stream Helium Below Its Saturation Temperature
- 6.4 Preliminary Cooler-Condenser Calculations
- 6.5 Silica Gel Adsorber Calculations
- 6.6 Molecular Sieve Adsorber Calculations
- 6.7 Interpretation of Fig. 3, "Water-Helium Relationships at 300 PSIA"

APPENDIX 6.1

Oxygen Requirements for Oxidation of Helium Impurities (Reference: Section 4.21, Item (2))

Possible Reactions:

Oxygen requirement for complete oxidation:

Reaction 1 - 8.0 pounds O_2 /pound H_2

Reaction 2 - 16.0 pounds O_2 /28 pounds CO, or
0.5714 pounds O_2 /pound CO

Reaction 3 - 64.0 pounds O_2 /16 pounds CH_4 , or
4.0 pounds O_2 /pound CH_4

Example 1

Assume 130 lb./hr. of impure helium of the following composition is passing through the catalytic converter:

He	99.6% (Vol.)
H_2O	0.1
H_2	0.1
CO_2	0.2
	<hr/> 100.0%

How much pure oxygen should be fed to the helium stream to provide the stoichiometric amount of gas required for complete oxidation?

Solution:

(1) Assume 100 pound-moles of impure helium

<u>Component and Molecular Weight</u>	<u>Volume and Mole Percent Composition</u>	<u>Weight of Component, Pounds</u>
He - 4	99.6	$99.6 \times 4 = 398.4$
H ₂ O - 18	0.1	$0.1 \times 18 = 1.8$
H ₂ - 2	0.1	$0.1 \times 2 = 0.2$
CO ₂ - 44	0.2	$0.2 \times 44 = 8.8$
		409.2

$$\text{Ave. molecular weight of gas} = \frac{409.2 \text{ pounds}}{100 \text{ pound-moles}} = 4.092$$

$$\begin{aligned} (2) \text{ Pounds H}_2 \text{ present} &= \frac{130 \text{ lb. gas/hr.}}{4.092 \text{ lb./lb.-mole}} \times 0.001 \times \frac{2 \text{ lb. H}_2}{\text{pound-mole}} \\ &= 0.0635 \text{ pounds H}_2/\text{hr.} \end{aligned}$$

$$\begin{aligned} (3) \text{ Oxygen required} &= \frac{0.0635 \text{ lb. H}_2}{\text{hr.}} \times \frac{8.0 \text{ lb. O}_2}{\text{lb. H}_2} \\ &= 0.508 \text{ lb./hr.} \end{aligned}$$

Example 2

Assume 130 lb./hr. of impure helium of the given composition is passing through the catalytic converter. What weight of pure oxygen is required for complete oxidation of the helium impurities?

He	99.4 % (Vol.)
H ₂ O	0.08
CO ₂	0.10
CO	0.11
H ₂	<u>0.31</u>
	100.00%

Solution:

(1) Find average molecular weight of gas (using method shown in example 1) = 4.071

$$(2) \text{ Pounds CO present} = \frac{130 \text{ lb. gas/hr.}}{4.07 \text{ lb./lb.-mole}} \times 0.0011 \times \frac{28 \text{ lb. CO}}{\text{lb.-mole}}$$

$$= 0.983 \text{ lb./hr.}$$

Pounds O₂ required for CO oxidation

$$= \frac{0.983 \text{ lb. CO}}{\text{hr.}} \times \frac{0.5714 \text{ lb. O}_2}{\text{lb. CO}} = \frac{0.56 \text{ lb. O}_2}{\text{hr.}}$$

$$(3) \text{ Pounds H}_2 \text{ present} = \frac{130 \text{ lb. gas/hr.}}{4.07 \text{ lb./lb.-mole}} \times 0.0031 \times \frac{2 \text{ lb. H}_2}{\text{lb.-mole}}$$

$$= 0.198 \text{ lb./hr.}$$

Pounds O₂ required for H₂ oxidation

$$= \frac{0.198 \text{ lb. H}_2}{\text{hr.}} \times \frac{8 \text{ lb. O}_2}{\text{lb. H}_2} = 1.58 \text{ lb. O}_2/\text{hr.}$$

$$(4) \text{ Total weight oxygen required/hr.} = 0.56 + 1.58 = \underline{\underline{2.14}}$$

APPENDIX 6.2

Catalytic Converter Calculations (Reference: Section 4.21, Item (3))

Assume 130 lb./hr. of impure helium (design rate of flow of by-pass helium) plus the required oxygen entering a Girdler G-43 catalytic converter. To simplify the calculations, neglect the presence of all impurities and oxygen.

Vol. of gas at standard conditions

$$= \frac{130 \text{ lb./hr.}}{4 \text{ lb. He/mole}} \times \frac{359 \text{ cu. ft. gas}}{\text{lb.-mole}} = 11,670 \text{ cu. ft.}$$

Recommended space velocity for catalyst

$$= 20,000 \text{ cu. ft. gas (standard conditions)/(hr.) (cu. ft. catalyst)}$$

$$\therefore \text{Volume of catalyst} = \frac{11,670}{20,000} = 0.583 \text{ cu. ft.}$$

$$\frac{\text{Catalyst Bed Length}}{\text{Bed Diameter}} > 1.0 \text{ recommended}$$

Assume 8.0 in. I.D. pipe is used for catalyst chamber.

$$\therefore \text{Bed length} = \frac{0.583 \text{ cu. ft.}}{\frac{\pi(8.0)^2}{4 \times 144} \text{ sq. ft.}} = 1.67 \text{ ft. (minimum)}$$

$$\text{Minimum weight of catalyst} = 0.583 \text{ cu. ft.} \times 60 \text{ lbs/cu. ft.} = \underline{\underline{35 \text{ pounds}}}$$

$$\text{Approximate cost of catalyst/charge} = \$3.45/\text{lb.} \times 35 \text{ lb.} = \underline{\underline{\$120.50}}$$

APPENDIX 6.3

EXAMPLE OF WATER REMOVAL OBTAINED BY COOLING PURIFICATION STREAM HELIUM BELOW ITS SATURATION TEMPERATURE (Reference: Section 4.22)

Assumptions:

- (1) By-pass helium (130 lb./hr.) contains a negligible amount of water (so far as this illustrative calculation is concerned)
- (2) Buffer helium contains 0.3 lb. H_2O /lb. He and is available at the rate of 800 pounds per hour (dry)
- (3) Helium leaves the cooler-condenser saturated and at 90°F and 300 psia.

Solution:

- (1) Weight of water entering cooler-condenser

$$= 0.3 \text{ lb. } H_2O/\text{lb. He} \times 800 \text{ lb. He} = 240 \text{ lb./hr.}$$

- (2) Vapor pressure of H_2O at 90°F = 0.6982 psi

Pounds of water at saturation per pound of dry helium

$$= \frac{0.6982}{300 - 0.6982} \frac{\text{moles } H_2O}{\text{mole dry He}} \times \frac{18 \text{ lb. } H_2O}{\text{mole } H_2O} \times \frac{1}{4 \text{ lb. He/mole He}}$$

$$= 0.01049 \text{ or } 0.01$$

- (3) Weight of water vapor in helium leaving cooler-condenser

$$= 0.01 \text{ lb. } H_2O/\text{lb. He} \times (800 + 130) \text{ lb. He/hr.} = 9.30 \text{ lb. } H_2O/\text{hr.}$$

- (4) Percentage of incoming water removed by condensation

$$= \frac{240 - 9.3}{240} \times 100 = \underline{\underline{96.2\%}}$$

APPENDIX 6.4

PRELIMINARY COOLER-CONDENSER CALCULATIONS
(Reference: Section 4.22)

The following calculations are presented for the sole purpose of providing a preliminary evaluation of the cooler-condenser requirements for the EGCR helium purification system. Since specific information regarding buffer helium flow rates and water vapor contents is unknown at this time, the calculations shown are based on a number of simplifying assumptions and should not be used for design purposes.

Assumptions:

- (1) By-pass helium leaving catalytic converter is at 1100°F and 300 psia, contains a negligible amount of water vapor and flows at the rate of 130 lb./hr.
- (2) Buffer helium is at 360°F, 300 psia, contains 0.3 pounds water vapor per pound of He, and amounts to 800 lb. dry He/hr.
- (3) Cooling water is available at 70°F and will leave the condensing section of exchanger at 80°F.
- (4) Temperature of water-saturated helium leaving condenser is 90°F.
- (5) Condenser tubes are 1", 12 gauge, steel (O.D. = 1.000; I.D. = 0.782; wall thickness = 0.109 in.).
- (6) Helium velocity entering condenser tubes = 10 ft./sec.
- (7) Specific heat of helium = 1.24 Btu/(lb.) (°F)

Solution:

- (1) Total weight of dry helium entering exchanger

$$= 130 + 800 = 930 \text{ lb./hr.}$$

Approximate weight of water vapor present in helium

$$= \frac{800 \text{ lb. He}}{\text{hr.}} \times \frac{0.3 \text{ lb. H}_2\text{O}}{\text{lb. He}} = 240 \text{ lb./hr.}$$

$$\begin{aligned} (2) \text{ Exchanger cooling duty} &= \left[\frac{130 \text{ lb. He}}{\text{hr.}} \times \frac{1.24 \text{ Btu}}{(\text{lb.})(^\circ\text{F})} \times (1100 - 90)^\circ\text{F} \right] \\ &+ \left[\frac{800 \text{ lb. He}}{\text{hr.}} \times \frac{1.24 \text{ Btu}}{(\text{lb.})(^\circ\text{F})} \times (360 - 90)^\circ\text{F} \right] + \left[\frac{240 \text{ lb. H}_2\text{O vapor}}{\text{hr.}} \right. \\ &\left. \times \frac{0.45 \text{ Btu}}{(\text{lb.})(^\circ\text{F})} \times (360 - 90)^\circ\text{F} \right] \\ &= 162,900 + 268,000 + 29,200 = 460,100 \text{ Btu/lb.} \end{aligned}$$

Exchanger condensing duty (assuming for simplicity that condensation takes place at 90°F) = $\frac{240 \text{ lb. H}_2\text{O vapor}}{\text{hr.}} \times 1042.9 \text{ Btu/lb.}$

$$= 250,200 \text{ Btu/hr.}$$

- (3) Approximate temperature T of impure He entering exchanger may be estimated from heat balance:

$$\begin{aligned} 130 \text{ lb. He} \times \frac{1.24 \text{ Btu}}{(\text{lb.})(^\circ\text{F})} \times (1100 - T) &= \left[800 \text{ lb. He} \times \frac{1.24 \text{ Btu}}{(\text{lb.})(^\circ\text{F})} \times (T - 360)^\circ\text{F} \right] \\ &+ \left[240 \text{ lb. H}_2\text{O vapor} \times \frac{0.45 \text{ Btu}}{(\text{lb.})(^\circ\text{F})} \times (T - 360)^\circ\text{F} \right] \end{aligned}$$

$$T = 455^\circ\text{F}$$

Assume (incorrectly, but for the sake of simplicity since this is not a design calculation) that the heat exchanger consists of a cooling and a

condensing section, that water vapor condensation takes place at 90°F and that cooling water enters the condensing section at 70°F and leaves at 80°F.

$$\therefore \text{Condensing section log mean } \Delta T = \frac{(90-70) - (90-80)}{\ln \frac{90-70}{90-80}} = 14.4^\circ$$

Weight of water required for condensing station

$$= \frac{250,200 \text{ Btu/hr.}}{\frac{1.0 \text{ Btu}}{(\text{lb.})(^\circ\text{F})} \times (80-70)^\circ\text{F}} = 25,020 \text{ lb./hr.}$$

Let t_o = temperature of water leaving exchanger

$$\frac{25,020 \text{ lb. H}_2\text{O}}{\text{hr.}} \times \frac{1.0 \text{ Btu}}{(\text{lb.})(^\circ\text{F})} \times (t_o - 80)^\circ\text{F} = 460,100 \text{ Btu/hr.}$$

$$t_o = 98.4^\circ\text{F or } 99^\circ\text{F}$$

$$\therefore \text{Cooling section log mean } \Delta T = \frac{(455-99) - (90-80)}{\ln \frac{455-99}{90-80}} = 99.3^\circ$$

(4) Assume helium film coefficient of heat transfer can be predicted by the Dittus-Boelter equation:

$$h = \frac{0.0025 k}{D} \left(\frac{Du\rho}{\mu} \right)^{0.8} \left(\frac{C_p \mu}{k} \right)^{0.4}$$

$$\text{Average temperature of He in cooling section} = \frac{455 + 90}{2} = 273^\circ\text{F}$$

Properties of helium at 273°F and 300 psia:

$$\text{Thermal conductivity} = 0.107 \text{ Btu/(hr.)(sq.ft.)(}^\circ\text{F/ft.)} = k$$

$$\text{Density} = 0.148 \text{ lb./cu. ft.} = \rho$$

$$\text{Viscosity} = 0.062 \text{ lb./(ft.)(hr.)}$$

$$\text{Prandtl Number } \left(\frac{C_p \mu}{k} \right) = 0.716$$

$$\therefore h = \frac{0.0225 \times 0.107}{0.782/12} \left(\frac{0.782 \times 10 \times 3600 \times 0.148}{12 \times 0.062} \right)^{0.8} (0.716)^{0.4}$$

$$= 0.0359 \times 997 \times 0.874 = 31.3$$

Since the helium coefficient will be controlling, assume an overall coefficient of heat transfer U equal to 25.

$$Q = UA_1 \Delta T, \text{ or } A_1 \text{ (area for cooling)} = \frac{Q}{U \Delta T}$$

$$= \frac{460,100}{25 \times 99.3} = 185 \text{ sq. ft.}$$

- (5) One disadvantage in trying to simplify the cooler-condenser calculations - by assuming that gas cooling occurs in one distinct section of the exchanger and that water vapor condensation occurs in another - lies in the predication of a condensing coefficient or an overall coefficient of heat transfer for the condensing section. Although a procedure is available for a time-consuming calculation of an average overall coefficient, the reliability of the calculated result is unknown. Therefore, for the purposes of this report, it will be assumed that the desired coefficient will be the same as that for the cooling section of the exchanger, or that $U_{\text{cond.}} = 25 \text{ Btu/(hr.)(sq.ft.)(}^\circ\text{F)}$.

$$A_2 \text{ (area for condensing)} = \frac{Q}{U \Delta T} = \frac{250,200}{25 \times 14.4}$$

$$= 694 \text{ sq. ft.}$$

- (6) Estimated total area of heat transfer = $185 + 694 = 879 \text{ sq. ft.}$

APPENDIX 6.5

SILICA GEL ADSORBER CALCULATIONS (Reference: Section 4.23)

Assumptions:

- (1) Weight of dry He entering adsorber = 930 lb./hr.
- (2) He contains 0.01 lb. H_2O /lb. He and is at 90°F and 300 psia.
- (3) He will leave adsorber substantially free of water.
- (4) Silica gel will hold 20 per cent of water based on its activated weight, i.e., 20 lb. H_2O is adsorbed per 100 lb. dry gel.
- (5) Gas velocity through adsorbent bed should not exceed 40 ft./min.
- (6) Heat of wetting of activated silica gel is 400 Btu/lb. H_2O adsorbed.
- (7) Bulk density of silica gel is 45 lb./cu. ft.; specific heat is 0.22 Btu/(lb.)(°F).
- (8) Silica gel bed should be at least 12, and preferably 24 in. deep.
Height-to-diameter ratios ranging from 4:1 to 6:1 should not be exceeded.

Solution:

Base calculations on adsorption cycle of 12 hours.

- (1) Weight water to be adsorbed

$$= \frac{930 \text{ lb. He}}{\text{hr.}} \times \frac{0.01 \text{ lb. } H_2O}{\text{lb. He}} \times 12 \text{ hr.} = 111.5 \text{ lb.}$$

- (2) Weight silica gel required = $\frac{11.5 \text{ lb. } H_2O}{20 \text{ lb. } H_2O/100 \text{ lb. Gel}} = 558 \text{ lb.}$

$$\text{Volume silica gel} = \frac{558 \text{ lb.}}{45 \text{ lb./cu. ft.}} = 12.4 \text{ cu. ft.}$$

- (3) Assume bed diameter of 2.0 ft.

$$\therefore \text{Required bed height} = \frac{12.4 \text{ cu. ft.}}{\frac{\pi (2.0)^2}{4} \text{ sq. ft.}} = 3.94 \text{ or } \underline{\underline{4 \text{ ft.}}}$$

$$\text{Height to diameter ratio} = \frac{4}{2} = 2$$

- (4) Volume entering gas

$$\begin{aligned} &= \frac{930 \text{ lb. He}}{\text{hr.}} \times \frac{1}{\frac{4 \text{ lb. He}}{\text{lb.-mole}}} \times \frac{359 \text{ cu. ft.}}{\text{lb.-mole}} \times \frac{460 + 90}{460 + 32} \times \frac{14.7}{300} \\ &+ \frac{9.3 \text{ lb. H}_2\text{O}}{\text{hr.}} \times \frac{1}{\frac{18 \text{ lb. H}_2\text{O}}{\text{lb.-mole}}} \times \frac{359 \text{ cu. ft.}}{\text{lb.-mole}} \times \frac{460 + 90}{460 + 32} \times \frac{14.7}{300} \end{aligned}$$

$$= 4565 + 10.15 = 4575 \text{ cu. ft./hr.}$$

$$\text{Superficial velocity} = \frac{4575 \text{ cu. ft.}}{\text{hr.}} \times \frac{1}{\frac{\pi (2.0)^2}{4} \text{ sq. ft.}} \times \frac{1}{\frac{60 \text{ min.}}{\text{hr.}}}$$

$$= 24.2 \text{ ft./min. (Acceptable since it is lower than 40 ft/min limit specified)}$$

- (5) The approximate temperature rise of the dehydrated gas can be estimated, according to the information supplied by a manufacturer of silica gel, by the following relationship:

$$\begin{aligned} \Delta T &= 10^\circ\text{F} \times \frac{\text{Grains H}_2\text{O adsorbed}}{\text{cu. ft.}} \times \frac{1}{P_{\text{atmos}}} \\ \Delta T &= 10^\circ\text{F} \times \frac{9.3 \text{ lbs. H}_2\text{O}}{4575 \text{ cu. ft.}} \times \frac{7000 \text{ grains}}{\text{lb.}} \times \frac{1}{\frac{300 \text{ psia}}{14.7 \text{ psi/atmos}}} \\ &= 7^\circ\text{F} \end{aligned}$$

- (6) Estimated cost of silica gel per charge

$$= 558 \text{ lb.} \times \$0.35/\text{lb.} = \$195.50$$

- (7) Reactivation heat may be assumed to amount to 300 Btu/lb. of water desorbed.

Estimated heat for reactivation or regeneration

$$= 111.5 \text{ lb. H}_2\text{O} \times 3000 \text{ Btu/lb.} = 334,500 \text{ Btu}$$

- (8) Estimated pressure drop through bed = 0.5 in. H₂O/in. silica gel*

$$= \frac{0.5 \text{ in. H}_2\text{O}}{\text{in. silica gel}} \times \frac{(4 \times 12) \text{ in. gel}}{12 \text{ in./ft.}} \times \frac{14.7 \text{ psi}}{34 \text{ ft. H}_2\text{O}} = 0.865 \text{ psi}$$

(*Estimated from technical literature)

APPENDIX 6.6

MOLECULAR SIEVE ADSORBER CALCULATIONS (Reference: Section 4.24)

Assumptions:

- (1) Weight of dry He entering adsorber = 930 lb./hr.
- (2) Helium is at 97°F and 300 psia.
- (3) Helium will leave adsorber substantially free of CO₂.
- (4) Molecular Sieves will retain 10 lb. CO₂/100 lb. Sieves.
- (5) Recommended superficial gas velocity is 60 ft./min.
- (6) Recommended minimum bed depth is 2.5 ft.
- (7) Bulk density of Sieves is 45 lb./cu. ft.

Solution:

Base calculations on an adsorption cycle of 12 hours.

Since the concentration of CO₂ in the helium is unknown, assume a weight concentration of 1.8%, the specified value below which the concentration in the coolant must be maintained according to the information presented in Section 2.0, Introduction.

- (1) Neglect all impurities other than the 1.8% CO₂;

$$\text{Therefore, pounds CO}_2 / \text{lb. He} = \frac{1.8}{98.2} = 0.01815$$

Weight CO₂ to be adsorbed/12 hr.

$$= \frac{930 \text{ lb. He}}{\text{hr.}} \times \frac{0.01815 \text{ lb. CO}_2}{\text{lb. He}} \times 12 \text{ hr.} = 202 \text{ lb.}$$

$$(2) \text{ Weight Molecular Sieves required} = \frac{202 \text{ lb. CO}_2}{10 \text{ lb. CO}_2 / 100 \text{ lb. Sieves}} = 2020 \text{ lb.}$$

$$\text{Volume of Sieves} = \frac{2020 \text{ lb.}}{45 \text{ lb./cu.ft.}} = 44.9 \text{ cu. ft.}$$

$$(3) \text{ Assumed bed diameter of 3.0 ft.}$$

$$\text{Required bed height} = \frac{44.9 \text{ cu. ft.}}{\frac{\pi (3.0)^2}{4} \text{ sq. ft.}} = 6.35 \text{ ft.}$$

$$(4) \text{ Volume of entering gas}$$

$$= \left[\frac{930 \text{ lb. He}}{\text{hr.}} \times \frac{1}{\frac{4 \text{ lb. He}}{\text{lb.-mole}}} \times \frac{359 \text{ cu. ft.}}{\text{lb.-mole}} \times \frac{460 + 97}{460 + 32} \times \frac{14.7}{300} \right] \\ + \left[\frac{930 \text{ lb. He}}{\text{hr.}} \times \frac{0.01815 \text{ lb. CO}_2}{\text{lb. He}} \times \frac{1}{\frac{44 \text{ lb. CO}_2}{\text{lb.-mole}}} \times \frac{359 \text{ cu.ft.}}{\text{lb.-mole}} \right. \\ \left. \times \frac{460 + 97}{460 + 32} \times \frac{14.7}{300} \right]$$

$$= 4630 + 7.63 = 4637 \text{ cu. ft./hr.}$$

$$\text{Superficial velocity} = \frac{4637 \text{ cu. ft.}}{\text{hr.}} \times \frac{1}{\frac{\pi (3.0)^2}{4} \text{ sq. ft.}} \times \frac{1}{60 \frac{\text{min.}}{\text{hr.}}}$$

$$= 10.9 \text{ ft./min. (This is much lower than the}$$

permissible value of 60 ft./min. and suggests that bed dimensions should be reevaluated. From the point of view of a sharper advancing CO₂ front in the adsorber, a narrower unit appears to be attractive. However, a narrower unit will mean a greater superficial velocity and a greater pressure drop. A narrower column, on the other hand,

will have the added advantage of permitting better removal to the surroundings of the heats of condensation and reaction, thus permitting column operation to be maintained at a lower, and more desirable, temperature.)

- (5) Since the latent heat of condensation of CO_2 at 97°F is only approximately 21.2 Btu/lb., about 1/50 the value for water, it is not anticipated that the rise in temperature of the Molecular Sieves will be sufficient to require the use of bed cooling in order to permit the attainment of the expected bed capacity.
- (6) Estimated cost of Molecular Sieves per charge
- $$= 2020 \text{ lbs.} \times \$1.95/\text{lb.} = \$3940$$
- (7) With an assumed life of a minimum of 2000 regenerations and assuming one regeneration per bed per day, anticipated life of Sieves
- $$= \frac{2000 \text{ regenerations}}{365 \text{ regenerations/yr.}} = 5.5 \text{ years}$$

APPENDIX 6.7

INTERPRETATION OF FIG. 3, "WATER-HELIUM RELATIONSHIPS AT 300 PSIA" (Reference: Section 4.22)

Figure 3, "Water-Helium Relationships at 300 PSIA", was constructed to permit the rapid visualization of the liquid-gas relationships which could exist between the components of the effluent streams leaving the seal water catch basins of the EGCR helium coolant blowers. The following assumptions were used as the basis for making the calculations required for the construction of the chart.

- (1) Sealing water enters the catch basins at 150°F (initial water temperature) and 300 psia.
- (2) Buffer helium enters the catch basins at 510°F (initial helium temperature) and 300 psia.
- (3) Sealing water and buffer helium are in intimate contact in the catch basins.
- (4) No heat transfer occurs in the sealing basins except between the water and the helium.

Meaning of various curves in Figure 3:

300 PSIA Saturation Curve. This curve (solid line) shows the relationship at 300 psia between the temperature (°F) and the water-vapor content (pounds water vapor per pound of dry helium) of saturated helium. The dashed curves which parallel the saturation curve and which are labeled 10, 30, 50 and 80 per cent saturation permit the reader to determine the moisture content of partially saturated helium at various temperatures.

100% Vaporization Curve. This curve (solid line) shows the temperature-gas composition relationships which will exist if all of the sealing water entering the catch basins vaporizes. Thus, for the particular assumptions previously stated, it is seen that if 0.335 pounds or less of sealing water is used per pound of buffer helium it is possible for all of the water to vaporize in establishing equilibrium with the helium. The dashed curves which "parallel" the 100% vaporization curve indicate temperature and composition data for cases in which water vaporization is not complete.

An inspection of Figure 3 shows, for example, that if 0.10 lb. sealing water is used per pound of buffer helium the equilibrium temperature will be about 418°F and the gas composition will be 0.10 lb. H₂O/lb. He. If the rate of sealing water is increased to about 13 lb. H₂O/lb. He, the equilibrium temperature will drop to about 174°F but the gas composition will still be 0.10 lb. H₂O/lb. He. In the first case, vaporization of the water is complete but not enough water is present to saturate the helium or cool it markedly. In the latter case, less than 2 per cent of the sealing water vaporizes but the helium is saturated. This, of course, is due to the fact that the large amount of water present is able to drop the equilibrium temperature of the water-gas mixture to such a low value that only a small amount of water must be vaporized to saturate the gas.

Figure 3 also shows that the use of less than 0.335 lb. sealing water per pound of buffer helium may result in a "dry" catch basin, i.e., water vaporization will be complete and only gaseous matter will leave the basin. The use of

larger amounts of sealing water means that a mixture of liquid water and helium will leave the catch basin. If the first condition prevails, then obviously no water-gas separator will be required in the effluent line leaving the catch basin and leading to the purification system cooler-condensers. However, should the latter condition prevail, it might be necessary or desirable to include a separator in order to decrease the liquid load on the cooler-condensers.

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