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Final Report

to

National Aeronautics and Space Administration
Langley Research Center
Langley Station
Hampton, Virginia

DEVELOPMENT OF A REGENERABLE CARBON DIOXIDE REMOVAL SYSTEM

(Contract NAS1-5277)

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15 January 1968

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DEVELOPMENT OF A REGENERABLE CARBON DIOXIDE REMOVAL SYSTEM

by F. Tepper, F. Vancheri, W. Samuel and R. Udavcak

INTRODUCTION AND SUMMARY

This report covers laboratory activities performed in the period June 1965 through January 1968. The activities that were performed could be separated into stages each lasting about five months. The first five months of the program involved a literature and laboratory search for regenerable sorbents that might remove carbon dioxide from air without excessive drying of the stream. Activated carbons and coprecipitated gels were characterized and were thought to have limited applicability.

In the second five month period efforts were directed at ion exchange resins which began to appear to have promise. One resin, IR-45, appeared to have most promise, particularly where CO_2 was to be recovered. However, methods of regeneration proved to be arduous until fluid regeneration techniques were evolved. The third five months' activities were primarily oriented toward cumulating CO_2 sorption data from which a desired laboratory model could be sized. Synthesis of experimental resins were begun, but efforts in this area were not culminated, in favor of development of a laboratory model based on IR-45. In the fourth stage, preliminary system concepts were considered. The fifth stage was directed at preliminary and final design of a steam regenerable laboratory model. The last stage involved construction and limited testing of the model.

Literature Survey

The literature was surveyed and the results of this survey are included in the following section. At the conclusion, it appeared that activated carbon, coprecipitated gels and ion exchange resins appeared worthy of laboratory investigation.

Activated Carbon

Based on gravimetric CO_2 sorption data, isotherms were constructed for a number of activated carbons and related sorbents. The capacity for CO_2 at 25°C and 4 mm CO_2 pressure was below 0.3 weight percent.

Coprecipitated Gels

Coprecipitated gels were not readily regenerable under vacuum, but heat (50°C) appeared to aid CO_2 desorption under vacuum, although prolonged periods were necessary. Higher temperatures were thought to be more effective, but at the expense of destruction of the gel structure due to hydration-dehydration cycling. Efforts in this avenue were terminated.

Preliminary Resin Screening Studies

Several resins which were either commercially available or described in prior art were screened for CO_2 activity via gram scale dynamic absorption runs. Control tests were performed using molecular sieves in dry air. Strong base resins in humid air had CO_2 capacities greater than molecular sieves in dry air, although weak base resins offered greater promise of regeneration. The effect of water content on dynamic CO_2 capacity was evaluated. The water isotherm for IR-45 was generated. Preliminary vacuum thermal regeneration studies showed that certain weak base resins are fully regenerable, although rewetting with water was necessary before reuse. Thermal stability tests showed that IR-45 was thermally stable,at least to 300°F.

Resin Formulation Studies

Studies were initiated to synthesize resins superior to IR-45. A number of resins were prepared that had dynamic CO_2 capacities superior to that of IR-45. These resins could be fully regenerated with hot water. Preliminary preparations of these superior resins resulted in too fine a particle size. Efforts in this area were curtailed to concentrate on characterizing IR-45 more fully and evolving an operating laboratory model for it.

IR-45 Characterization Studies

Dynamic CO_2 sorption parameters were studied, including temperature, flowrate, bed depth, CO_2 concentration, relative humidity and resin water content. Hot water regeneration was found to desorb CO_2 quantitatively. A steam regeneration technique was conceived where the CO_2 would be desorbed "chromatographically" allowing separation of air, CO_2 and steam. The technique permits desorption of CO_2 at ambient pressure. Laboratory scale and pound scale experiments showed the technique to offer more promise than originally anticipated. The drying and cooling cycles were evaluated, and it appeared desirable to use room air to cool the bed to the absorption temperature. Automatic cycling of IR-45 through 1000 cycles resulted in minimal affects on sorption capacity. Large bed tests showed excellent fractionation of air from CO_2, and CO_2 from steam.

Preliminary Designs

The merits of vacuum/thermal versus hot water and steam regeneration are discussed. The primary objections to the former approach are the power penalties associated with water evaporation and cooling plus rewetting requirements of the bed. The primary objections to the hot water mode are excessive drying requirements and the difficulties of separating liquid water from the gas phase and both fluid phases from the solid bed.

Laboratory Model Design Characteristics

The laboratory model fabricated for LRC is described. The system weight, for a nominal capacity of 0.4 lb CO_2/hr, is 111.4 lbs exclusive of the water boiler.

Laboratory Model Operational Characteristics

The laboratory model was operated for a total of 35 cycles over three sets of runs. The preliminary cycles showed serious water retention in the bed. This problem was counteracted by an increase in the absorption cycle, and by the use of more efficient insulation. The last 13 cycles were under steady state conditions, where the system removed between 0.37 and 0.38 lb of CO_2/hr from 77°F air containing 0.5% CO_2 at low (20-35% RH) humidity.

System Optimization

A schematic of a zero gravity resin chamber is given where the system collects and stores CO_2. Preliminary estimates are made of system fixed weight and power requirements. A flight system is projected of about 110 lbs and 470 watts of electrical power or 270 watts electrical and 300 watts waste heat using the same sorber and system functional design.

LITERATURE SURVEY

Introduction

A literature survey was undertaken on the reaction or sorption of CO_2 by solid reagents. The survey was primarily directed at those reactions which might prove to be readily reversible. Little effort was directed at the reactions of CO_2 with those metal oxides (i.e., alkali metal oxides) which form stable carbonates. The sorption of CO_2 by synthetic zeolites was not systematically surveyed.

A few of the references that are cited were not made available in sufficient time to be reviewed in detail for the purpose of this survey. Thus, conclusions with respect to applicability of some of the cited work towards regenerable CO_2 sorption could not be made.

Physical Adsorption Processes

Physical adsorption processes are ordinarily differentiated from chemisorption processes in that the bonding of the sorbed gas to the solid surface is through van der Waals forces. With such weak forces, the heat of the sorption process is ordinarily significantly less than where the sorption process occurs through chemical interaction. These van der Waals forces are significantly diminished with successive gas layers upon the primary layer such that the primary layer is ordinarily responsible for the bulk of the gas sorbed. It is therefore apparent that the adsorption capacity depends largely upon the extent of surface area per unit mass.

Table 1 shows the specific surface area of a number of adsorbents. Those sorbents with surface areas greater than 100 m^2/g are underlined.

Activated Carbon - The capacity of charcoal for sorption of gases depends both on the nature of the source used in the preparation, the character of the activating agent (usually a moderate oxidant) and the time and temperature of activation. The activation parameters affect the level of surface area and also contribute to definition of the shape of the micropores, in which ultimate adsorption occurs. The dimensions of the micropore, and the character of the adsorbate molecules affect the capacity as well as the rate of adsorption. Thus, measurable differences could exist in the capacity of different carbons for CO_2.

TABLE 1 - SPECIFIC SURFACE AREAS OF VARIOUS ADSORBENTS

Adsorbent	Specific Surface (m^2/g)
Fe_3O_4 catalyst (unreduced)	0.02
Fe catalyst 973, sample I, unpromoted	0.55
Fe catalyst 973, sample II, unpromoted	1.24
Fe catalyst 954, 10.2% Al_2O_3	11.03
Fe catalyst 424, 1.03% Al_2O_3, 0.19% ZrO_2	9.44
Fe catalyst 931, 1.3% Al_2O_3, 1.59% K_2O	4.78
Fe catalyst 958, 0.35% Al_2O_3, 0.08% K_2O	2.50
Fe catalyst 930, 1.07% K_2O	0.56
Fused Cu catalyst	0.23
Commercial Cu catalyst	0.42
Pumice	0.38
Ni on pumice, 91.8% pumice	1.27
NiO on pumice, 89.8% pumice	4.28
Cr_2O_3 gel	228
Cr_2O_3 "glowed"	28.3
KCl (finer than 200 mesh)	0.24
$CuSO_4 \cdot 5H_2O$ (40-100 mesh)	0.16
$CuSO_4$ anhydrous	6.23
Cecil soil, 9418	32.3
Cecil soil colloid, 9418	58.6
Barnes soil, 10,308	44.2
Barnes soil colloid, 10,308	101.2
Glaucosil	82
Silica gel I (nonelectrodialyzed)	584
Silica gel II (electrodialyzed)	614
Dried bacteria	0.17
Dried bacteria (pulverized)	3.41
Granular Darco B	576
Granular Darco G	2123
Activated Charcoal	775-2500
Lampblack	28
Acetylene black	64
Grade 3 rubber black	135
Carbolac 1 color black	947
Graphite	30.47
Cuprene	20.7
Paper	1.59
Cement	1.08
TiO_2	7.88
$BaSO_4$	4.30
$ZrSiO_4$	2.76
Lithopone	34.8
Lithopone, calcined	1.37
Lithopone, calcined and ground	3.43
Porous glass	125.2
Hopcalite	300
Amberlite XAD-2	300

A number of references[1-17] exist in the literature on the adsorption capacity of activated charcoal for CO_2, under varying conditions of CO_2 partial pressure and temperature. Sameshima[4] determined saturated CO_2 values at 25°C and 760 mm for charcoals prepared from a number of different sources and found them to be approximately the same. Remy[16] measured the adsorption capacity of CO_2 by moisture-containing and dry charcoal under dynamic conditions. Dietz[17] observed the rate of CO_2 adsorption of charcoal and found the rate of adsorption at 0°C to be very rapid. The general consensus with respect to the CO_2 capacity of charcoals at 75°F and approximately 4 mm is 1.5 to 3 mgms per gram of carbon.

A recent study of the use of charcoal as a regenerable CO_2 sorbent was performed by Major et al[18]. Their data verifies the low capacity of charcoal for CO_2. Dynamic sorption-desorption experiments indicated that the capacity was unaffected in a water vapor laden environment. They had also demonstrated the feasibility of desorbing CO_2 from charcoal by vacuum alone. Studies evaluating charcoal as a CO_2 sorbent were performed under an Air Force sponsored contract.[19]

<u>Metal Oxides</u> - Metal oxides make up a class of materials that can have high surface area. Benton[20] measured the CO_2 capacity of a number of oxide catalysts at 0°C and 1 atmosphere CO_2 pressure. The CO_2 capacities of these oxides tend to decrease with thermal cycling.

Lanning[21] measured the CO_2 capacity of various manganese oxides including Hopcalite while Elovich[22] measured the capacity of MnO_2 at -78, -11 and +20°C. Sokai[23] determined the capacity of MnO_2, and measured the rate of adsorption at 25°C. The CO_2 capacity of MnO_2 at low partial pressures is given by Foote[24] as approximately 4 mgms/g MnO_2. The capacity of MnO_2 is reduced by water poisoning.

Carbon dioxide sorption has been studied with NiO[25], ThO_2[26], Cr_2O_3[27], and Cr_2O_3-Al_2O_3 catalyst.[28] The CO_2 capacity of these substances appears to be too low to be of interest. NiO only absorbs CO_2 to the extent of 16% of surface coverage.[25] The CO_2 capacity of Cr_2O_3-Al_2O_3 catalysts is affected by prior adsorption of oxygen. The CO_2 adsorbability of activated magnesia was studied by Walker[29], but no isotherm data is shown in his paper.

<u>Porous Metals</u> - The CO_2 capacity of metallic catalysts was measured by Taylor[30]. Capacity values (at 25°C and 1 atmosphere CO_2) for copper, cobalt, iron, palladium, platinum sponge and platinum black are respectively 1.2, 4.0, 0.5, 0.1, 0.1 and 3.4 mgms/g catalyst. Other data[31,32] exists for nickel, iron and cobalt catalysts.

Synthetic Zeolites - The utilization of "A" Type molecular sieves for regenerable CO_2 sorption is well documented. The three dimensional chelate type structure occurring in "A" type zeolites has a greater affinity for water vapor than for CO_2. The possibility exists for altering this affinity more in favor of CO_2. Misin[33] formed CaX and AgX zeolites from the NaX form by cation exchange. At low CO_2 concentrations, the silver form has much greater CO_2 sorption capacity than the NaX form.

Gels - The capacity of silica gel for CO_2 is given[34] as 34 mgms/g. However, water vapor is preferentially adsorbed on silica gel. Nikitin[35] measured CO_2 adsorption by gels of oxides of titanium, tin, cerium and thallium.

A study of coprecipitated gels as regenerable CO_2 sorbents was performed by Clarke et al[36]. A cobalt oxide-ferric oxide gel was found to be the best of several effective and usefully reversible CO_2 sorbents. It adsorbs and desorbs reversibly (a reversible capacity of 43 mg CO_2/g gel) using a cycle of 0°C for adsorption and 25°C for desorption. It does not exhibit preferential adsorption of or poisoning by water and is regenerable with small energy consideration.

Miscellaneous Adsorbents - The CO_2 capacity of microporous glass has been found[37] to be approximately 2 mgms/g at 0.1 atm CO_2. Rutz[38] measured the CO_2 adsorption rates by porous glass.

The adsorption properties of ammonium phosphomolybdate were studied by Tourneux[39]. No inference is given as to the degree of reversibility of this sorption process.

Polymeric materials with high surface area are commercially available. One such material, Amberlite XAD-2 (Rohm and Haas Co.), has a surface area of 300 m^2/g. It is more hydrophobic than synthetic zeolites, in that organic and semi-organic species are adsorbed while the sorbent is water-wet.

Chemisorption Processes

The best single criterion for separating physical adsorption from chemisorption is the magnitude of the heat of sorption. Chemical bonds are normally stronger than physical forces of attraction; heats of chemisorption should therefore be large ($>$10 Kcal/mole) while heats of physical adsorption should be low (2-6 Kcal/mole) and in the neighborhood of heats of liquefaction. However, there are numerous sorption processes whose heats range between 5 and 10 Kcal/mole and are difficult to classify.

The higher heats of formation associated with chemisorption processes imply greater difficulty in regeneration of the sorbent. However, the capacity of sorbents for CO_2 is not particularly dependent upon surface area, such that higher capacities may be attainable with chemisorption processes.

Metal Oxides - Alkali and alkaline earth metal oxides and hydroxides are notable absorbents for carbon dioxide. The application of lithium chemicals to air regeneration was studied by Markowitz[40]. The alkali and alkaline earth metal carbonates require high temperatures for thermal regeneration of the oxide. The most thermally decomposable carbonate in this group is Mg_2CO_3, which has a CO_2 decomposition pressure of only 1 mm Hg at 800°F.[41] A solid solution of nickel oxide in lithium oxide has been examined[41] as a CO_2 sorbent. This material is likely to be non-regenerable in that the product is Li_2CO_3.

Tests[42] with silver oxide, in finely divided crystalline form, and deposited on activated alumina and other substrates (to increase the surface area), have indicated that the reaction rate, at concentrations expected in space cabin atmospheres, is too low to make this reagent practical in its present form.

There are no data available for CO_2 adsorption on cadmium oxide at room temperature. Isotherms for the sorption of CO_2 in zinc oxide are available.[43] The capacity is only 0.5 mgms/g ZnO at a partial pressure of 10 mm of CO_2.

The chemisorption of CO_2 onto solid oxide catalysts of the spinel type (i.e., $ZnCr_2O_4$) has been studied[44] at very low (10 microns) partial pressures of CO_2. No data exists at higher partial pressures.

Organic Amines - Conventionally, where CO_2 is to be reduced to very low levels, aqueous solutions of alkanolamines have been used. Ethanolamines are also used in submarine air purification systems. One of the disadvantages of ethanolamines is their appreciable volatility, when combined with their toxicity, results in a potential hazard. A secondary disadvantage is that MEA solutions would have to be supported upon some solid support in order to circumvent problems with liquid sorbents under zero gravity.

Amines with low vapor pressure have been suggested[45] for use in submarines. One compound is beta-beta[1] hydroxyamino-ethylether, a high boiling primary amine. The vapor pressure of this material in 95% solution at 70°F is about 3 microns (Hg). Another amine, which is almost completely non-volatile, is the sodium salt of methyltaurine. A German patent[46] describes the use of amino acid solutions including the salts of taurine as CO_2 absorbents. The capacity for CO_2 ranges between .55-.75 moles CO_2/mole salt. Such salts are not likely to have physiological affect and present no ingestion hazard. The use of amino acids in the industrial removal of CO_2 from natural gas has been described.[47]

High molecular weight amines, with very low volatility are available[48] in experimental quantity. Molecular weights are in the range 350-400, yet these fluids have a theoretical CO_2 capacity as high as 120 mgms/g amine.

Ion Exchange Resins - Ion exchange resins are polymeric materials that have chemical reactivity built in via the addition of active functional groups. The CO_2 capacity at high partial pressures (i.e., 1 atmosphere) is estimated to be as high as 20% by weight. No data exists on their capacity at low (i.e., 4 mm CO_2) partial pressures.

The removal of CO_2 from mixtures of CO_2 (8%) in oxygen via ion exchange resins is described by Smart[49]. Dynamic adsorption capacities about half that of a sodalime bed were obtained with one experimental resin. A feasibility study for the removal of CO_2 from submarine atmospheres by amine resins has been made[50]. One experimental resin was cycled 1000 times through the CO_2 adsorption and desorption from air and showed no decrease in adsorption efficiency on a volume basis.

Summary

The literature has been surveyed on candidate regenerable sorbents. A number of CO_2 sorbents exist that might prove to be worthwhile candidates including activated carbon, coprecipitated gels, and ion exchange resins. Both carbons and coprecipitated gels are readily regenerable but data on thermal regeneration of resins appears limited.

ACTIVATED CARBON

A screening program was pursued whereby various types of sorbents (particularly activated charcoals) were evaluated for their CO_2 sorption capacity. In performing this study an apparatus employing the Cahn microbalance was used. This device, shown in Figure 1 , permits control of the CO_2 content in the atmosphere surrounding the sample, where the weight change of the sample is continuously recorded during both the adsorption and desorption cycle.

The procedure associated with obtaining CO_2 adsorption isotherms first involved placing the sample ($\sim$0.1 gram) on the balance pan. The system was evacuated to less than 10 microns at 100°C until constant weight was obtained. The sample was cooled to test temperature (ambient or 0°C) and the sample weight was recorded. Carbon dioxide gas was admitted to the system and the sample weight and system pressure was recorded. Further increments of CO_2 were admitted to the system in order to obtain a number of isotherm points between 0 and 10 millimeters CO_2 pressure. Sample weight was continuously recorded during adsorption. The system was evacuated and desorption of the CO_2 from the sample was noted on the recorder.

Carbon dioxide adsorption isotherms for 3 activated granular carbons are shown in Figures 2, 3 and 4 . The carbon shown in Figure 2 is a coal-base activated carbon with an organic (CCl_4) capacity of approximately 70% by weight. The sorbents corresponding to Figures 3 and 4 are both coconut base granular carbons. The carbon in Figure 3 is a highly activated experimental material with a CCl_4 capacity of 140%, while that characterized by Figure 4 is a lower activity material (100% CCl_4) that is used as a starting material to make the experimental carbon seen in Figure 3. There is an apparent lack of correlation between the organic capacity of these carbons and their capacity for CO_2 gas.

Isotherms for 3 other activated carbons are seen in Figures 5-7. Type 125 granular carbon was suggested by the producers as a sorbent with possible superior CO_2 capacity. A description of their material could not be obtained, since its composition and preparative techniques are proprietary. However, as shown in Figure 5 it exhibited very poor CO_2 sorption capacity as compared to any of the other charcoals tested. A commercially available hardwood charcoal (Figure 6) was also found to be a poor CO_2 sorbent.

Type 309 charcoal was obtained from the Barnebey-Cheney Company who suggested that this material was comparable to the Type KB-1 charcoal described by Major et al[18]. This charcoal was found to be superior to the other test charcoals at both 0°C and ambient temperature.

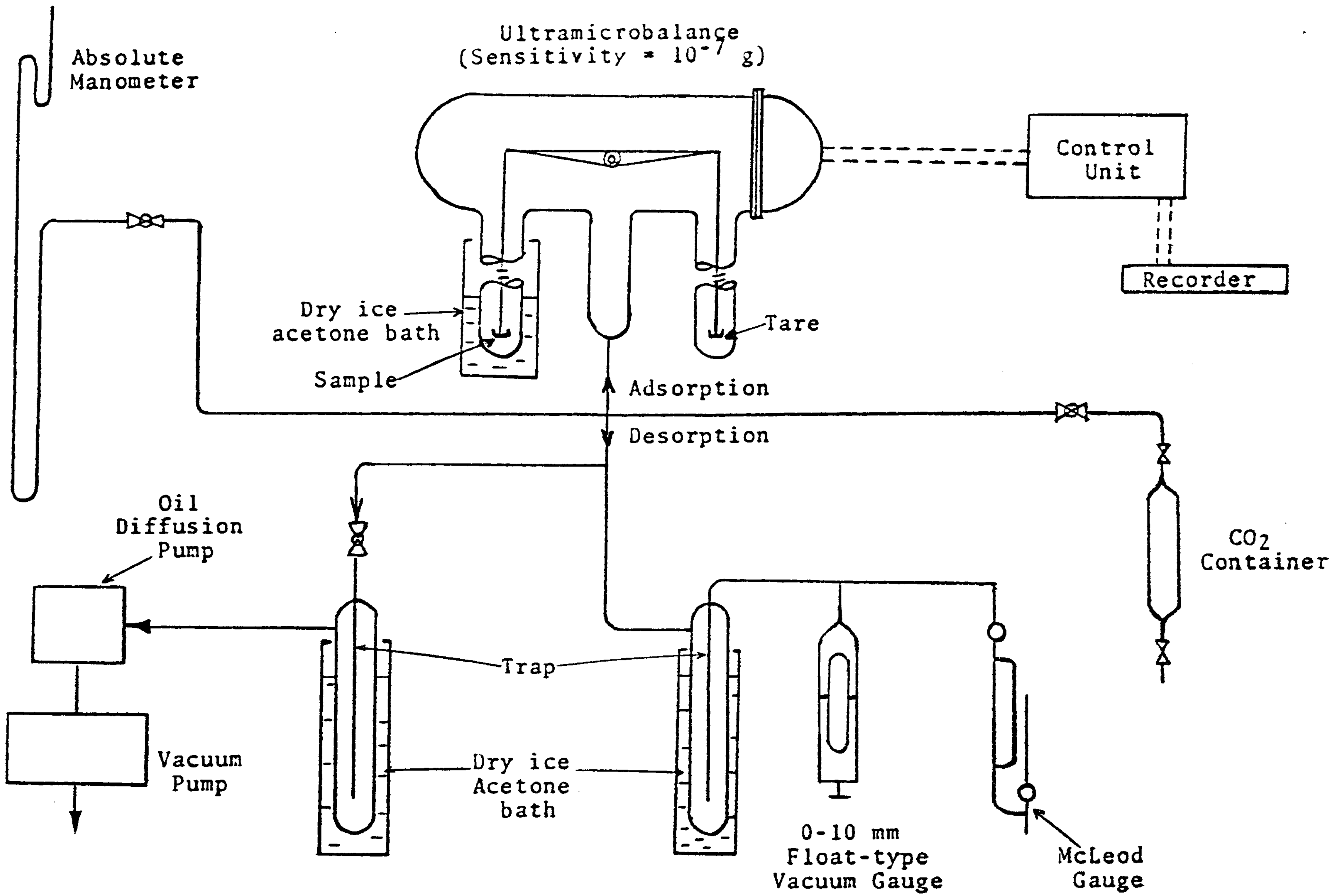


FIG. 1 - SCHEMATIC OF CO_2 ISOTHERM SYSTEM

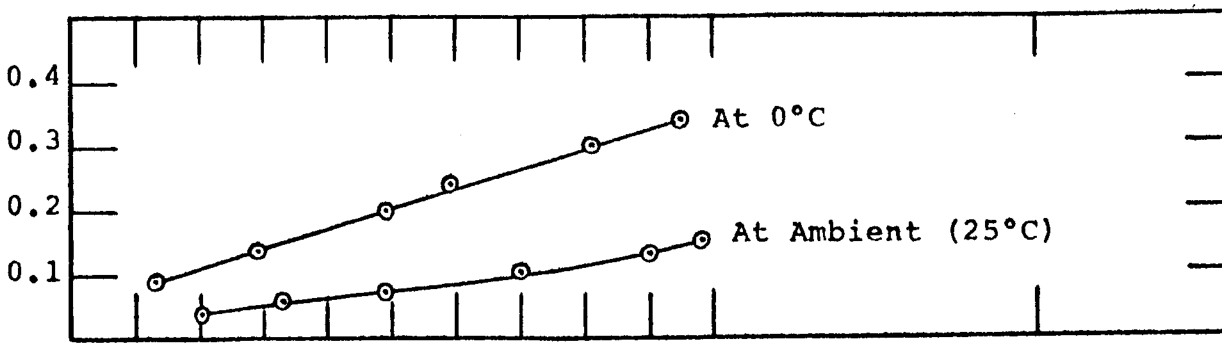


FIG. 2 - PCC ACTIVATED GRANULAR CARBON

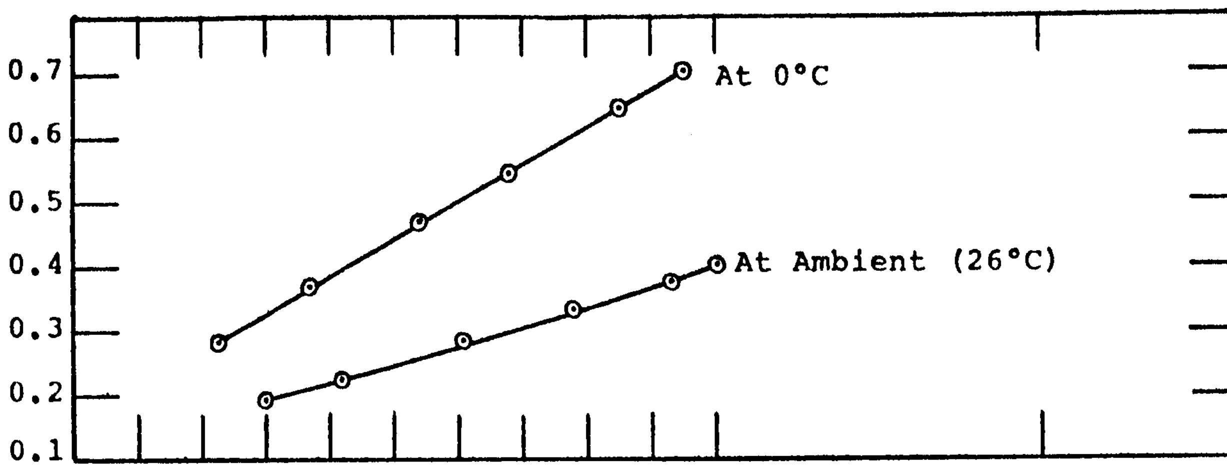


FIG. 3 - MSAR ACTIVATED GRANULAR CARBON (140%)(Type G1)

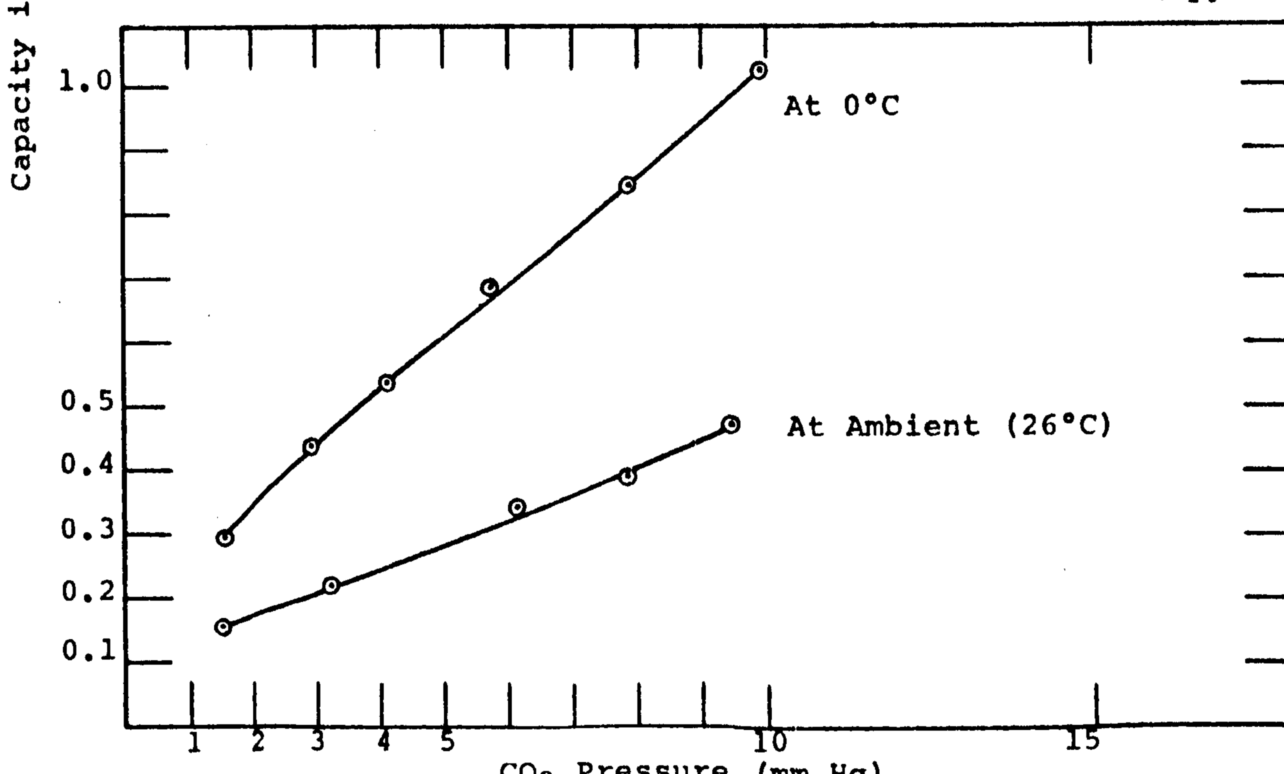


FIG. 4 - BARNEBEY-CHENEY ACTIVATED GRANULAR CARBON (100%)

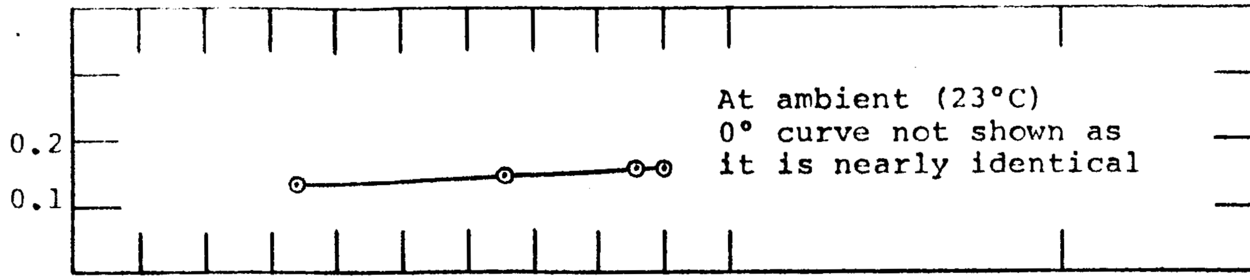


FIG. 5 - BARNEBEY-CHENEY ACTIVATED CARBON (TYPE 125)

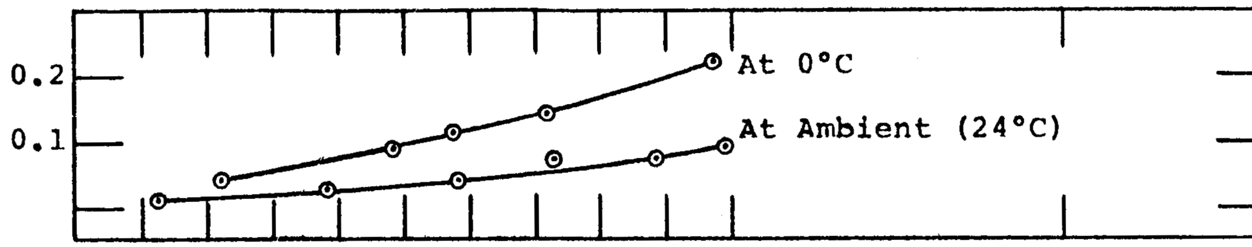


FIG. 6 - HARDWOOD CHARCOAL

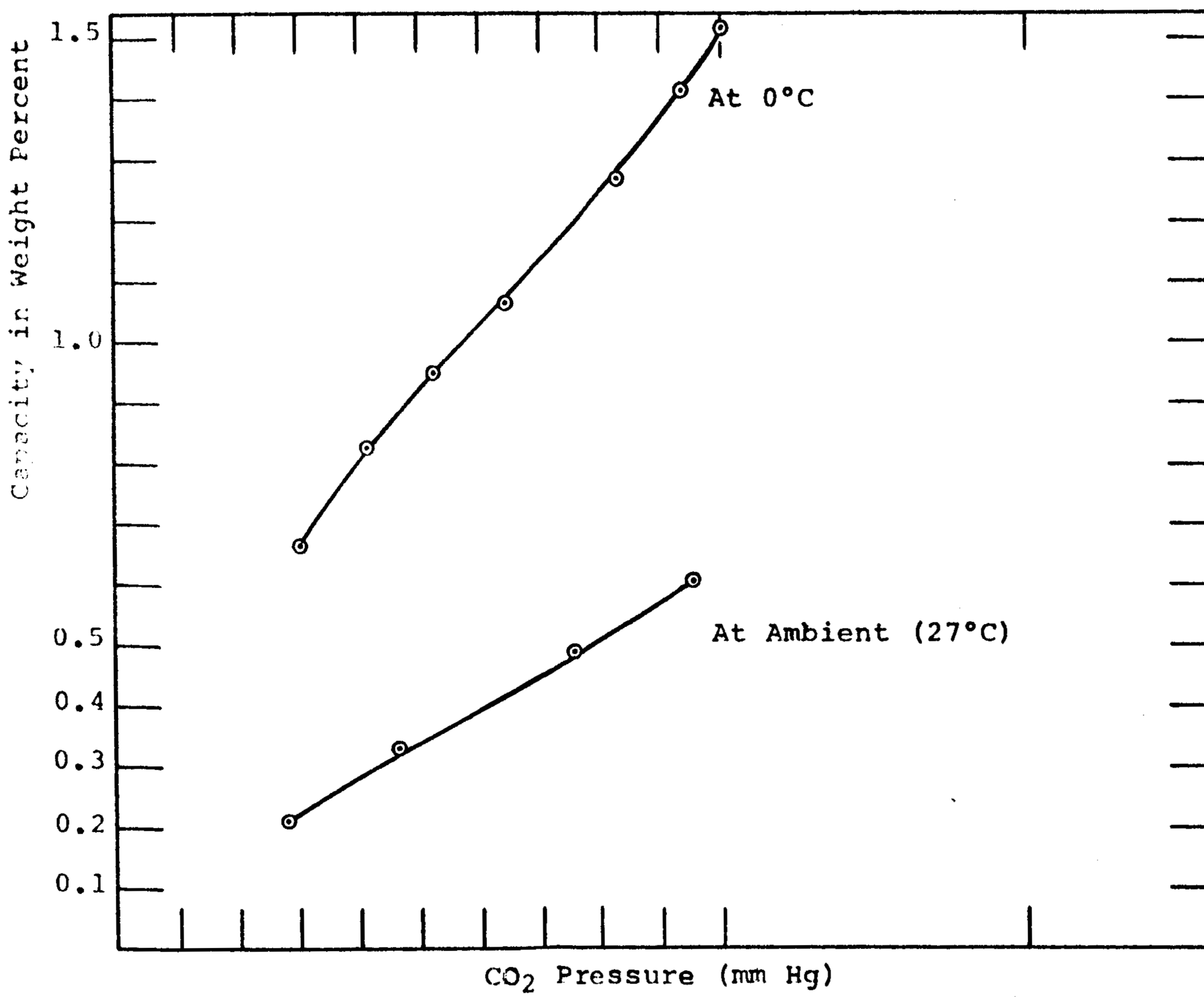


FIG. 7 - BARNEBEY-CHENEY ACTIVATED GRANULAR CARBON (TYPE 309)

Similar isotherms were obtained for a number of test samples. Table 2 shows CO_2 capacity for test samples at ambient temperature and 0°C for a CO_2 pressure of 3.8 Torr (0.5% by volume).

Two types of Hopcalite (copper-activated manganese dioxide) were also evaluated. Neither of the two samples appeared to have CO_2 capacity as good as some of the better carbons.

Nilok is a mineral active carbon produced by halogenation of silicon carbide. This forms an activated charcoal with a structure that is significantly different from those charcoals prepared from natural sources. Its CCl_4 capacity is 40%, which is considerably lower than charcoals prepared from natural sources. Yet, even with a relatively low organic capacity, this material has CO_2 capacities somewhat greater than many of the natural base charcoals that were tested.

The CO_2 capacity of an activated carbon fiber felt, produced in experimental quantities at MSAR, is seen in Table 2. This material has an organic capacity (162% CCl_4) greater than that of any carbon obtained heretofore. Yet, the CO_2 capacity is significantly lower than the Type 309 carbon. Two other carbon samples were evaluated, a carbon activated from Saran and another from peach pits. The Saran carbon is purported to have pore sizes of the same approximate dimensions of a molecular sieve. However, it is apparent that its CO_2 capacity is rather low, along with the carbon prepared at MSAR from peach pits.

For comparative purposes, a Type 5A molecular sieve sample was tested via the static method. As expected its CO_2 adsorption capacity was higher than any of the charcoals tested. Capacity at 3, 5, 7 and 9 Torr were respectively 2.0, 3.2, 4.4 and 5.3 weight percent CO_2.

A considerable volume of adsorption rate curves were produced during the generation of isotherms. The rate curves that were generated were obtained in step-wise fashion. The rate curve in going from 0 to the first partial pressure point was first recorded. Then, a higher partial pressure of CO_2 was induced into the system and the mode by which equilibrium was obtained was recorded from the first partial pressure point to the second, rather than from zero pressure to the second partial pressure point.

The characteristics of CO_2 adsorption for each of the carbons were very similar. Figure 8 shows the adsorption rate curves for 5A molecular sieve and two of the more superior activated charcoals. It can be seen that equilibrium is nearly obtained in less than 0.2 min in the case of both charcoals.

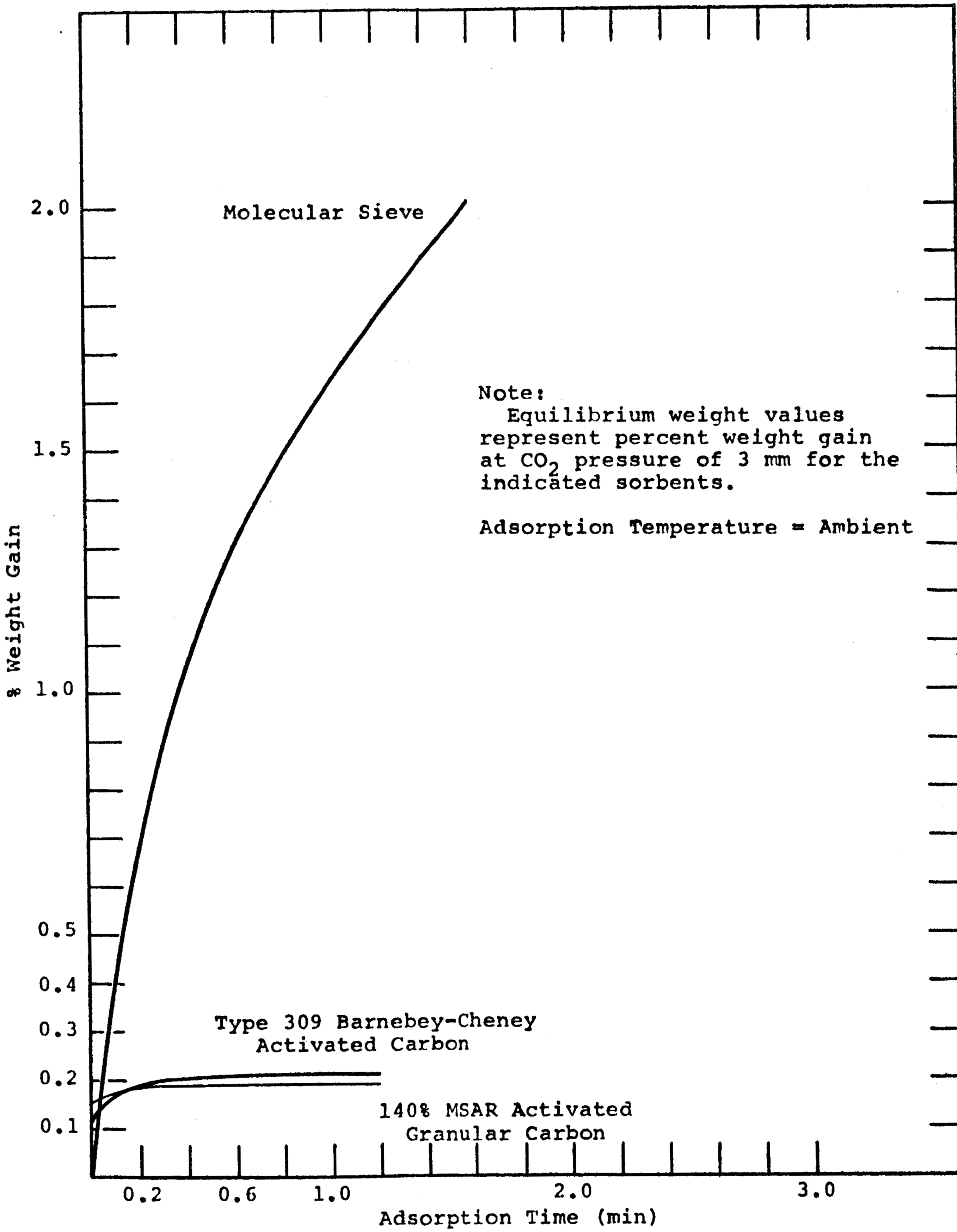


FIG 8 - CO_2 ADSORPTION RATE CURVES

Because of the uncertainty associated with manual introduction of CO_2 into the system, adsorption rates less than 0.1 min are rather tenuous. A single adsorption rate run was performed with Type 5A molecular sieves. This experiment showed that the sieve takes significantly longer to equilibrate than does the activated charcoal. However, the adsorption rate of the sieve below 0.2% weight gain is comparable to the activated carbons. The longer equilibration time for the sieve is primiarily a result of its higher capacity.

TABLE 2 - CARBON DIOXIDE CAPACITY OF TEST SAMPLES

Sorbent	Capacity in Weight % Ambient	0°C
100% Barnebey-Cheney Granular Carbon	0.25	0.51
140% MSAR Activated Granular Carbon	0.21	0.37
Type 309 Barnebey-Cheney Granular Carbon	0.29	0.78
Type 125 Barnebey-Cheney Granular Carbon	0.03	0.03
Conventional Domestic Hopcalite	0.10	0.18
German Hopcalite	0.06	0.14
Nilok Mineral Activated Carbon	0.15	0.39
Saran Activated Carbon	0.10	0.17
MSAR Activated Carbon Felt	0.12	0.22
Hardwood Charcoal	0.03	0.07
Peach Pit Charcoal	0.07	0.17
PCC Activated Granular Carbon	0.07	0.17
Type 5A Molecular Sieve	2.7	--

COPRECIPITATED GELS

The adsorption of carbon dioxide and water vapor on coprecipitated oxide gels has been reported by Clarke, Groth and Duzak[36] to be similar in magnitude with that of molecular sieves. Additionally, it was cited that these gels are less affected by water vapor.

Five oxide gels were prepared according to the procedures described by Clarke et al[36]. Preliminary static sorption studies of three of these gels showed CO_2 capacities at 4 mm CO_2 to be in the range of 1-1.5% by weight. These initial values compared unfavorably with the 5-10% CO_2 capacities claimed by the authors. These differences may be the result of over zealous degassing, in that water vapor may be necessary for the sorption of CO_2.

The cited reference suggests that these coprecipitated gels are readily regenerable at ambient temperature with vacuum. Preliminary results obtained with the first few gels evaluated suggest somewhat greater difficulty in CO_2 desorption than that described in the literature. Studies were continued in an attempt to duplicate the values of Clarke et al. These gels show no preferential adsorption of water vapor and desorption is accomplished with only small energy requirements. They found that coprecipitated gels with Fe_2O_3 base had better regenerative qualities than those with Al_2O_3 base. Thus, the majority of the investigation was directed towards the study of Fe_2O_3 based gels and their possible applications in CO_2 adsorption.

Preparation of these gels was performed according to the "improved preparation" outlined by Clarke el al using nitrates and chlorides of the salts and effecting coprecipitation with potassium carbonate. The gels prepared were: $CoO \cdot Fe_2O_3$ in both 5:95 mole percent ratio of metal ions; $NiO \cdot Fe_2O_3$ and $NiO \cdot Al_2O_3$ both at 5:95 mole percent ratio of metal ions; and $ZnO \cdot Fe_2O_3$ with a 5:95 mole percent ratio. These gels were prepared by coprecipitation of the metal chloride or nitrate together with Fe (III) or Al (III) by a K_2CO_3 solution. The composition of these gels are shown in Table 3. Also shown are the CO_2 levels present in the as-produced material. Their CO_2 content was determined by reacting the gel with 2N HCl and collecting the evolved gas (known to be nearly 100% CO_2 as analyzed by mass spectrometer).

Preliminary testing versus CO_2 in the static isotherm system described in the previous section showed CO_2 sorption capacities of $\sim$1.0-1.5% by weight. This marked difference from the 5-10% capacities claimed by Clarke was attributed to the dessicated nature of the test samples when exposed to the low CO_2 partial pressures employed in the static test method. In an attempt to verify the claimed sorption capacities in addition to determining the effects of water vapor upon CO_2 removal, a dynamic test system was fabricated.

TABLE 3 - COMPOSITION AND CO_2 CONTENT OF COPRECIPITATED SORBENT GELS

Gel	Mol. Per Cent Ratio	Weight Per Cent CO_2 1st Run	2nd Run	Average
$CoO:Fe_2O_3$	5:95	15.7	15.6	15.65
$CoO:Fe_2O_3$	33.3:66.7	8.7	8.3	8.2
$NiO:Al_2O_3$	5:95	23.6	25.8	24.7
$NiO:Fe_2O_3$	5:95	8.9	10.8	9.85
$ZnO:Fe_2O_3$	5:95	14.7	13.8	14.3

As shown in Figure 9, the system operates as follows: Three gas streams - dry air, CO_2, and water-bearing air - are mixed together via flowmeter control and passed through a humidity sensor and CO_2-level monitor. Through appropriate adjustments of the control valves, both the CO_2 and water content of the evolved gas stream were adjusted to coincide with values of interest - 0.4% CO_2 content and 50% RH. After the test gas stream was equilibrated at the selected composition it was then admitted to the microbalance system containing the sample. Extensive testing with Class S and M weights in the sample position has shown the balance mechanism to be relatively insensitive to a total test gas flow of up to 2 or 3 l/min.

A sample of gel ($CoO:Fe_2O_3$ 5:95 mol %) was placed on the microbalance and weighed after equilibration in a humid air atmosphere. The test gas stream (0.4% CO_2, 50% RH) was then passed into the balance chamber and over the sample proper, with the resulting increase in weight noted upon a recorder. After approximately 2 hours, no further weight increase was noted. This equilibrium weight corresponded to a weight increase of 1.5%. This contrasts sharply with the CO_2 content of the material as determined by the acid analysis method (Table 4). These results were verified.

After 8 hours of vacuum desorption of the second sample a weight loss of 10.2% was noted. The test gas (0.4% CO_2 in air at 50% RH) was permitted to pass over the sample overnight and the weight gain was found to be 9.9% with the major portion attributable to water vapor. Again the sample was analyzed via the acid reaction method with this time 12.2% CO_2 noted.

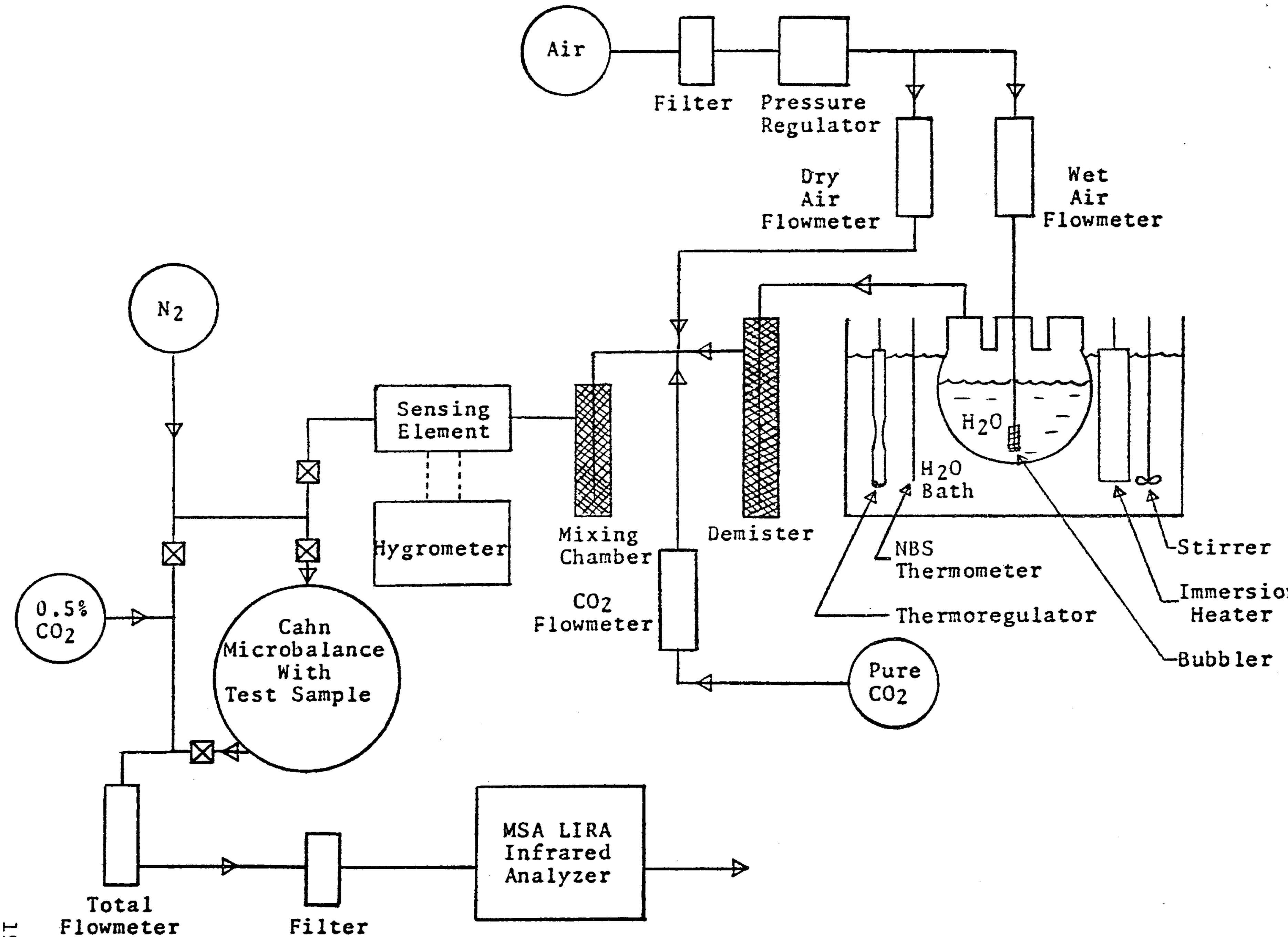


FIG. 9 - SCHEMATIC OF DYNAMIC CO_2 ISOTHERM SYSTEM

A third Co:Fe sample was placed in the test system and degassed overnight under vacuum. The sample was then equilibrated with 50% RH air and the weight gain recorded (8.7%). Carbon dioxide was then added to the gas stream until a CO_2 level of 0.4% was reached, with an increase of 0.4% due to CO_2. Acid analysis of this sample, however, showed a CO_2 content of 19.9%.

The two more promising gel forms ($CoO:Fe_2O_3$ 5:95 mol % ratio and $MgO:Al_2O_3$ 10.90 mol % ratio) were tested further. The results (Table 4) obtained with the $CoO:Fe_2O_3$ gel suggest that both treatment and form of the sample affect the CO_2 capacity. For equivalent treatment, the powdered form seems to retain more CO_2 than the coarser, granular form. All $CoO:Fe_2O_3$ samples show CO_2 contents lower than the 15.5% contained in "as prepared" material. The sample evacuated without heat shows the highest percent CO_2 content of the evacuated samples, suggesting that heat is necessary to more completely desorb CO_2.

TABLE 4 - ACID ANALYSIS OF CO_2 SORBENTS

Material	Sample Form	Vacuum Treatment	% CO_2
$CoO:Fe_2O_3$ 5:95 mol % ratio	Gran.	1 day, ambient	14.1
	Gran.	1 day @ 50°C	8.4
	Gran.	3 days "	8.2
	Powd.	1 day "	11.9
	Powd.	4 hrs "	11.9
$MgO:Al_2O_3$ 10:90 mol % ratio	Powd.	As prepared	8.8
	Powd.	1 day evacuation @ 50°C	4.0
	Powd.	" " "	4.6

It was therefore demonstrated that the considerable CO_2 content of these two metal oxide gels could be substantially reduced upon exposure to heat while in a vacuum.

The final gel tested was $MgO:Al_2O_3$ of 10:90 mol % ratio. Exposed to a test gas stream of 0.4% CO_2 in air at 50% RH, this sample was seen to gain 14.9% by weight, with an initial rate of $\sim$0.20 mg/min. Vacuum desorption at ambient temperature was then initiated and continued until equilibrium was established at a weight loss of 15.7%. The test atmosphere was then again imposed upon the sample. The weight gain experienced in this second cycle was 9.8%, nearly one-third less than the first adsorption cycle gain.

While the portion of these gains attributable to CO_2 alone was undistinguishable, these results appear to confirm observations made earlier, i.e., Mg-bearing gels may sorb the CO_2 via mechanisms of chemisorption to form surface carbonates or bicarbonates. CO_2 bound in such a manner would be very resistant to desorption via vacuum alone, a condition apparently borne-out by the significant drop in percentage weight gain.

Summary

Coprecipitated gels were not readily regenerable under vacuum, but heat appeared to aid CO_2 desorption. At mild temperatures, CO_2 desorption of the cobalt-iron form was prolonged. It was expected that more complete regeneration could be effected at higher temperatures, but at the possible destruction of the gel structure due to dehydration, particularly after extensive cycling. Efforts in this avenue were terminated.

PRELIMINARY RESIN SCREENING STUDIES

The dynamic carbon dioxide test system described in Figure 9 was modified. The Cahn microbalance was replaced by a flow-through glass tube for sample holding purposes. The tube, about 10 in. in length and 1 3/8 in. I.D., is tapered at both ends to ball-joint fittings. Approximately 3 in. from one end a glass frit of medium porosity is contained. Its purpose was to support the test sample. The effects of tube and frit upon flow rate, pressure drop, and CO_2 concentration were evaluated after being placed in the flow system, upstream from the LIRA used to determine CO_2 concentration. Tests were conducted with the following conditions:

flowrate	- 1.0 l/min
CO_2 concentration	- 0.4%
test gas moisture content	- 50% RH

After the sample tube has been mounted in the test apparatus and the foregoing conditions equilibrated, the test stream was directed through the sample bed. The effluent CO_2 concentration was monitored continuously by an MSA LIRA sensitized for the range 0 to 0.5% CO_2. The effluent CO_2 concentration was recorded until the effluent concentration reached 0.2%, or one-half the concentration of the influent stream. The time necessary for this to occur for a given sorbent has been designated the sample "half-life". The run, however, was continued until the effluent concentration reached 0.3% CO_2.

Initial Sorbent Testing

Amberlite IR-45 (Rohm & Haas) - The weak-base type of ion exchange resins were viewed as candidate CO_2 sorbents because they are reasonably heat stable and could be more amenable to regeneration than the strong-base resins, although the latter had not yet been evaluated. IR-45 was a representative resin of the weak-base classification and a material that has been examined as a CO_2 sorbent (McConnaughey[50]). In testing, a sample of this commercially-available sorbent (in the free base state) was charged into the previously mentioned sample tube. An 18.3 g charge of IR-45 (dry basis), containing 40.2% water, provided a bed depth of ~2 in. Although a quick breakthrough of CO_2 was experienced as can be seen in Figure 10, the half life of this sample, i.e., the time necessary for the effluent CO_2 concentration from the test bed to reach 0.2%, was 65 minutes.

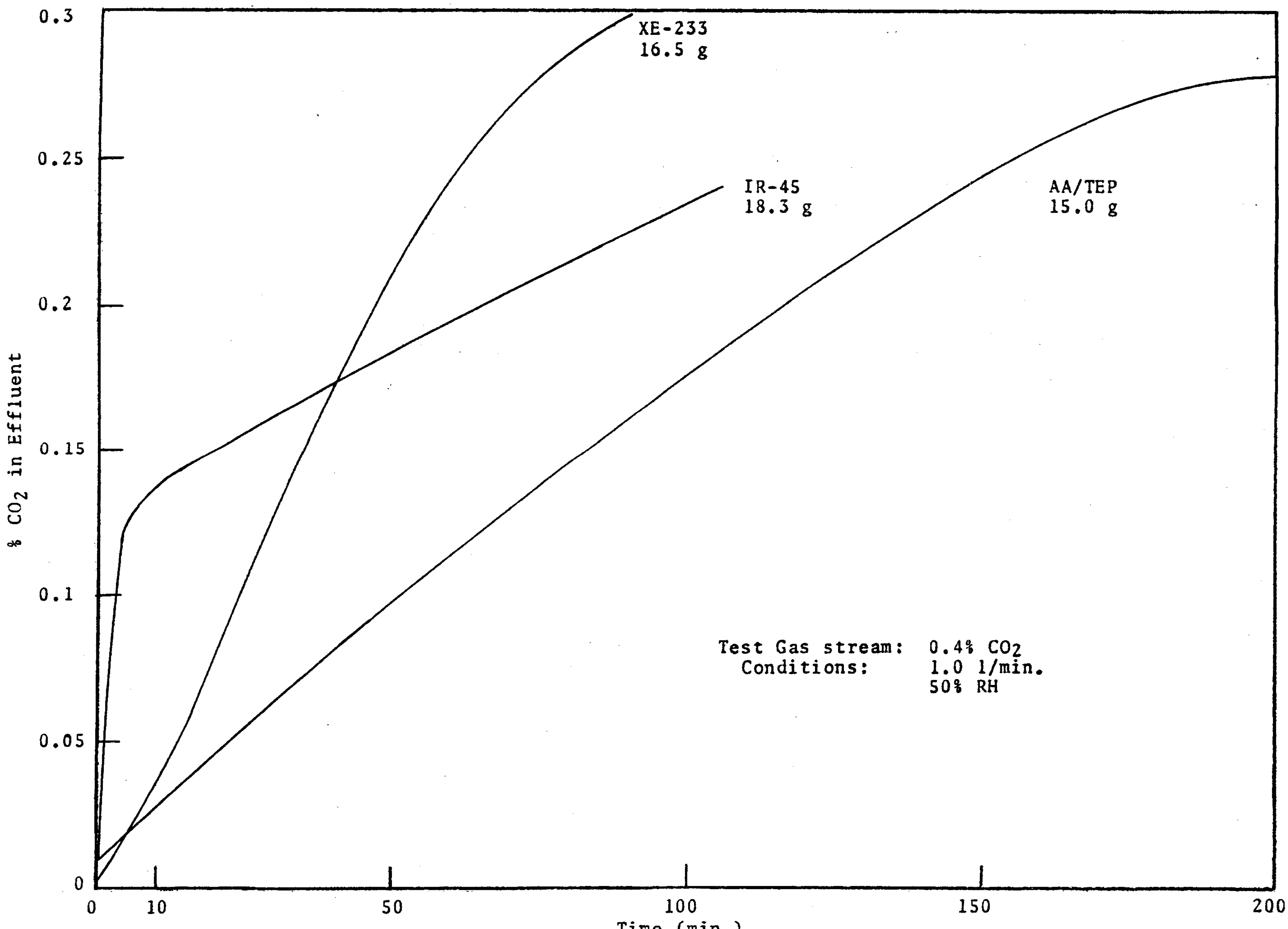


FIG 10 - CO_2 BREAKTHROUGH CURVES FOR RESINS

Amberlite XE-233 (Rohm & Haas) - This resin is chemically identical to IR-45, but it differs in physical structure. It is a macroreticular, more porous version of IR-45 and at present is not commercially available, although pilot plant quantities (500 lb) have been produced. XE-233 was selected for study because of its macroreticular characteristic, and because it may retain its CO_2 sorption capability or activity even when relatively dry. A sample of the free-base form was employed for testing. Charged into the sample tube, the 2 in. bed represented 16.5 g of the resin on a dry basis (44.2% H_2O). Shortly after the start of the run, detectable amounts of CO_2 were observed at the effluent end of the sample bed. Continued until the concentration rose to 0.3%, a plot of the test run is shown in Figure 10. The half-life value of this material was 47.5 min which was less than that observed with IR-45, though a slightly lighter charge was employed.

AA/TEP - Another weak-base resin studied was a condensation polymer composed of acrylic acid and tetraethylene pentamine, prepared according to U.S. Pat. 2,582,194.[51] Designated AA/TEP this material was formulated at 165°C, thereby offering a high degree of thermal stability not inherent in conventional resin systems. It had been suggested that this resin may be operable as a CO_2 sorbent in a relatively dry state, as compared to conventional polystyrene-based amines which require swelling for effective operation. This, however, was not the case as a bone-dry sample was essentially non-reactive. The water-swelled sample, however, which contained 65% H_2O (15.0 charged on a dry basis), exhibited comparatively good activity for CO_2. Its half-life was 115 minutes. Again, an early CO_2 breakthrough was observed and a gradual but steady increase in CO_2 occurred with increased time.

At this point, it was determined that future studies with the weak-base amines would be directed at determining if their regeneration can be effected and whether they retain their efficiency at lower moisture content. It was also observed that more efficient CO_2 sorption by resins occurs in the presence of high water content. However, to regenerate such a material, it will be necessary to remove the water along with the CO_2. Also, before such a material can be used for a second sorption cycle, the material must be re-equilibrated with water. Therefore, it was necessary to determine which resins retain their CO_2 sorption efficiency at a high CO_2 to water ratio and are regenerable.

Molecular Sieves - So that these and future experimental sorbent studies could be compared with existing CO_2 scrubbers, some of the sieve materials were examined in the experimental test apparatus. To permit their evaluation by dynamic flow, however, a 18 in. x 2 in. diameter tube containing Drierite was interposed in the gas line and the humidifier was by-passed, so that while the test gas still contained 0.4% CO_2, it was devoid of moisture. The runs were then conducted in the manner previously detailed. The breakthrough curves for three molecular sieves (Types 5A, 13X and 5AXW) are shown in Figure 11, and their half-lives detailed in Table 5.

While the sieves did not evidence the quick breakthrough characteristic of the resins, their half-life values were not superior, especially upon consideration that sieve samples weighed approximately 1/3 more than the ion exchange resin samples. It was then decided that future tests with resin samples (and other candidate CO_2 sorbents) would be made with a 23.5 g bed charge (dry basis) so as to be comparable to the molecular sieve runs.

Resin Screening

The ion exchange resins that would be applicable for CO_2 removal include that class of materials known as anion exchange resins or resins containing amine functionality capable of removing anions from aqueous solutions. The amine resins are classified into strong-base or weak-base categories. Included in the strong-base group are the quaternary ammonium salts such as derived from trimethyl or dimethyl ethanol amine:

$$R\text{-}CH_2\text{-}\overset{+}{N}(CH_3)_3 Cl^-$$

$$R\text{-}CH_2\text{-}\underset{\displaystyle CH_2\text{-}CH_2OH}{\underset{|}{\overset{+}{N}}}(CH_3)_2 Cl^-$$

The weak-base resins include the primary, secondary and tertiary amine functionality generally achieved with polyamines such as diethylenetriamine or triethylenetetramine and dimethyl amine.

$$R\text{-}CH_2\text{-}NH\text{-}C_2H_4\text{-}NH\text{-}C_2H_4\text{-}NH_2$$

$$R\text{-}CH_2\text{-}N(CH_3)_2$$

R in the above formulations represents a polymer matrix such as polystyrene/divinylbenzene copolymer, phenol formaldehyde, polyacrylic acid, polymethacrylic acid/divinylbenzene copolymer, or epoxide type polymer.

In the initial screening program representative materials from each class were examined for CO_2 absorption efficiency and the results of this study are in Table 5. It is readily seen that strong-base resins, IRA-400, 910, have the greatest capacity for CO_2. Of the weak-base amines, the secondary amine resins were considerably more promising than the tertiary amine functionality. Two macroreticular resins, IRA-93 and XE-233, were not

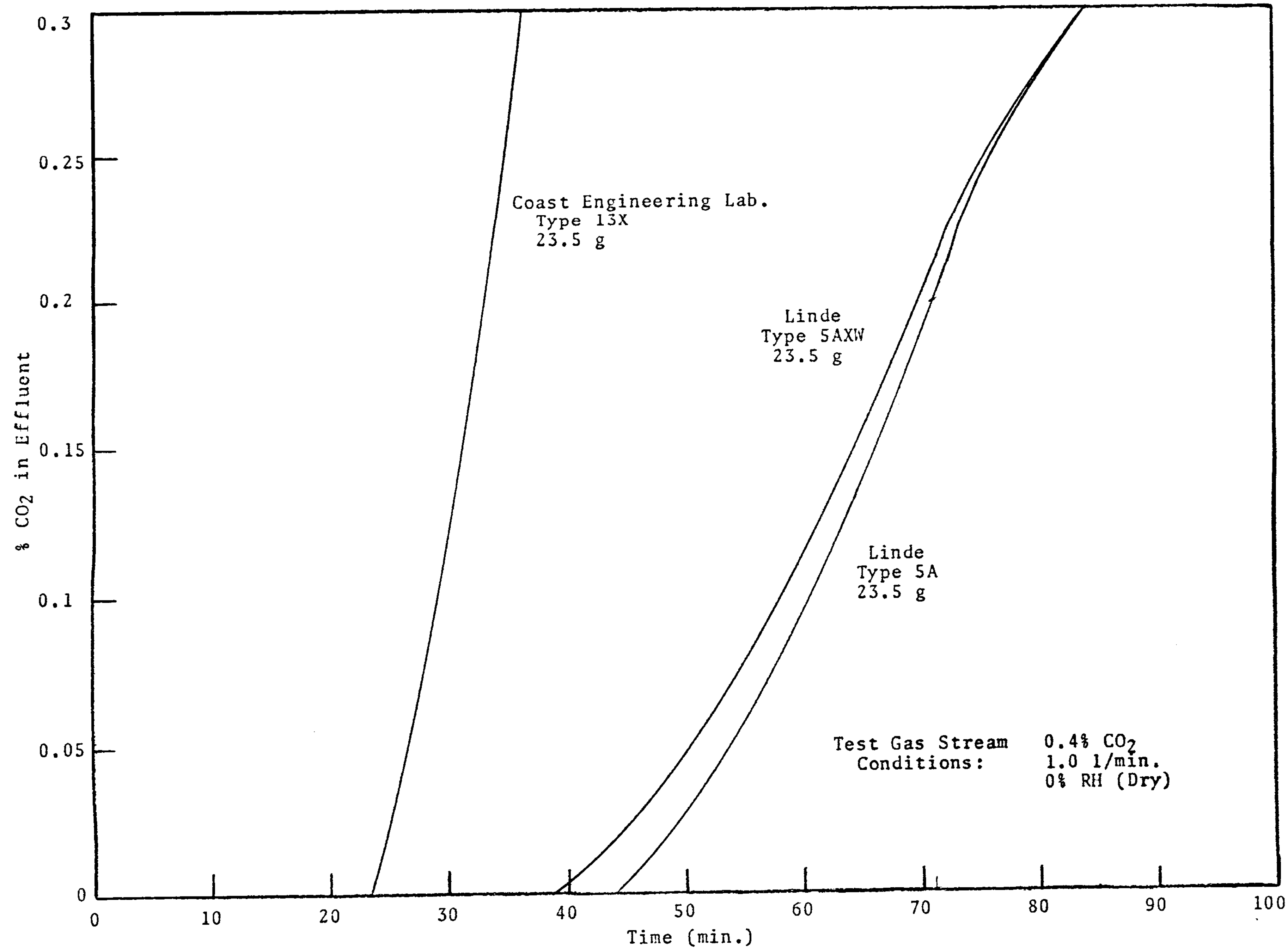


FIG 11 - CO_2 BREAKTHROUGH CURVES FOR MOLECULAR SIEVES

TABLE 5 - HALF-LIVES OF CO_2 TEST SORBENTS

Sample	Description: Polymer Matrix	Description: Functionality	H_2O Content (%)	Dry Wt. (g)	Bed Depth (mm)	Half-life[1] (min)
IRA-93	polystyrene/divinylbenzene	$-N(CH_3)_2$	56	23.5	112	26
IRA-68	polymethylmethacrylate/ divinylbenzene	$-N(CH_3)_2$	60	23.5	95	1
XE-236	"	$-NH-C_2H_4NH-C_2H_4NH_2$	56	23.5	87	11
XE-233	polystyrene/divinylbenzene	"	50	23.5	82	67
IR-45	"	"	40	23.5	60	112
Epon 812/ DET	epoxide	"	48	23.5	127	188
AA/TEP	polyacrylic acid	$-HN(C_2H_4NH)_4H$	65	15.0	110	116
IRA-400	polystyrene/divinylbenzene	$-N(CH_3)_3OH^-$	47	23.5	108	260
IRA-910	"	$-\overset{+}{N}(CH_3)_2OH^-$ CH_2CH_2OH	65	23.5	127	346
Type 5A	Linde Molecular Sieve (20 x 40 mesh)		0	23.5	51	71
Type 5AXW	" "		0	23.5	39	70
Type 13X	Coast Eng. Lab Sieve (42 x 60 mesh)		0	23.5	58	33

(1) Time required for effluent CO_2 concentration from the sample bed to reach 0.2%

particularly efficient and in one case, the XE-233 was not as efficient as its conventional gel-type counterpart, IR-45.

All resins were compared on a constant 23.5 g dry weight basis. However, depending upon the material and the moisture content, various densities were obtained and consequently various bed depths ranging from 50 mm to 130 mm resulted. In two runs with acrylic acid/tetraethylenepentamine polymer, at 65 and 50% H_2O, the material swelled to such an extent that it was not possible to charge 23.5 g (dry basis) into the tube and for these tests a slightly lower charge weight was employed.

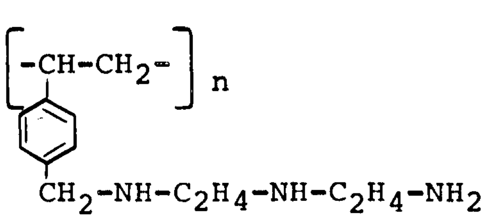
Although the strong-base materials have high capacity, the CO_2 bond with these materials is considerably stronger than for the weak base resins and consequently regeneration is not readily achieved by thermal vacuum/techniques. This factor limits the utility of the strong-base resins. The regeneration studies for these materials will be discussed later.

The activity exhibited by the several weak-base amines warranted further study of these systems. The initial studies were directed at establishing the effect of resin water content on its efficiency and also on the regenerability of these materials by thermal/vacuum techniques.

Selected Weak-Base Amine Resins

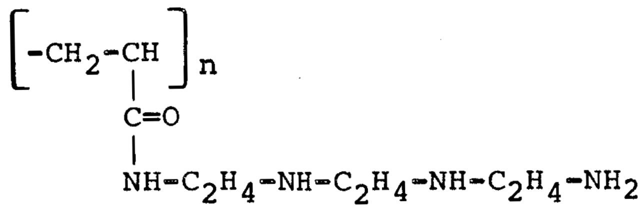
Those weak-base amine resins which showed high initial activity in the CO_2 sorption test and which were subjected to further study are described below. All are weak-base polymers containing primary, secondary and/or tertiary amine-functionality derived from condensation with a poly-amine. However, each material represents a different type of polymer matrix.

IR-45 - Commercially available chlormethylated polystyrene-divinylbenzene copolymer aminated with diethylenetriamine. The polymer is obtained and also evaluated as 20 x 50 mesh beads.

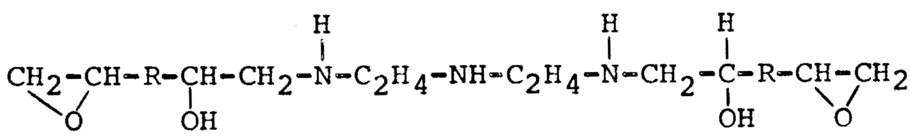


XE-233 - Polystyrene/divinylbenzene polymer chemically identical to IR-45, however, prepared as a macroreticular polymer having higher surface area than IR-45.

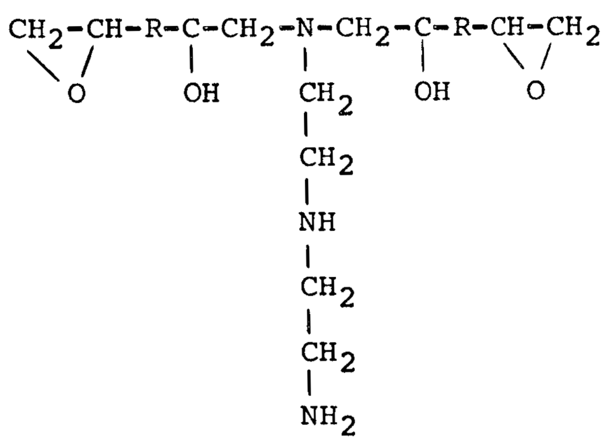
AA/TEP - Polyacrylic acid polymer aminated with tetraethylene-pentamine. Synthesized according to procedure in USP 2,582,194 and obtained as flake-like brittle product which was screened to 20 x 50 mesh for CO_2 evaluation.



Epon 812/DET - Polymer prepared by adding a polyamine to a commercial epoxide resin (Epon 812, Shell Chemical Company). This polymer was prepared in xylene according to a procedure described in an NRL report (McConnaughey, 1957). Evaporation of the xylene purportedly induces porosity in the structure. The product was recovered as a yellow amorphous material which softened somewhat in heating at 100°C. The polymer was pulverized in a Waring blender and screened to 20 x 50 mesh. The reported structures for the Epon 812/DET are



or



where $R = -CH_2[-O-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2]_n-O-CH_2$

The Effect of Water Content in Resin on CO_2 Sorption Efficiency

Conventional ion exchange resins are considered to be essentially homogeneous crosslinked polyelectrolyte gel structures with ion exchange sites distributed statistically throughout the entire particle. The porosity of the gel structure is solely dependent on the swelling characteristics of the gel structure. The greater the amount of crosslinking, the less the degree of swelling. Reaction rates which are controlled by diffusion to the reactive sites are in effect controlled by the swelling properties of the resins, particularly since these materials have little or no surface area. (In recent years, macroreticular resins with well-defined surface areas have been introduced and have in particular cases afforded improved reactivity as well as improved stability.)

The swelling in conventional gel-type resins is generally achieved by water and these materials are marketed in the wet state containing 40-60% water. In most ion exchange procedures, the resins are employed in aqueous processes with maximum swelling.

In the current study, however, it was conceivable and even very probable that the high initial water content is not only undesirable but may be prohibitive. A study was therefore undertaken to determine the CO_2 removal efficiency of the several effective resins at various water levels. The results of this study are summarized in Table 6 and discussed below.

IR-45 - This material was examined over the range 0-40% water. The half-life efficiency, or time required for the CO_2 effluent to reach 0.2%, increased from 17 minutes at 0% water to ~110 minutes at 40% water.

The plots of CO_2 effluent concentration vs time are shown in Figure 12. Although the half-life (0.2% CO_2) increased with increased water content, an unusual phenomenon occurred with the resin containing 40% H_2O. In this run, the initial breakthrough was early, but steady state sorption was established after 20 minutes and although the concentration was at 0.18% CO_2 at this time, 0.2% CO_2 was not reached until 105 minutes. Because of the unusual reaction of this sample, the run was repeated and duplication was achieved. It appears that excess water has hindered the diffusion of CO_2 to the resin. With the "dry" resins this water barrier was not present and an immediate penetration into the resin matrix is attained. In view of this unusual occurance with the polystyrene/divinylbenzene polymer, it was decided to reevaluate some of the other weak-base amines of this type reported in Table 5 at the lower water content.

TABLE 6 - EFFECT OF WATER CONTENT IN RESIN ON CO_2 SORPTION EFFICIENCY

Sample	Water Content (%)	Dry Weight (g)	Bed Depth (mm)	$\Delta P^{(1)}$ (mm Hg)	Half-Life[2] (min)
IR-45	40	23.5	80	1.2	112
	20	23.5	65	0.8	83
	15	23.5	63	0.6	75
	10	23.5	60	---	45
	0	23.5	50	0.8	18
AA/TEP	65	15.0	110	2.9	116
	50	15.4	107	---	120
	25	23.5	128	---	105
	0	23.5	90	0.6	<0.5
Epon 812/DET	48	23.5	127	---	188
	25	23.5	113	0.6	109
	15	23.5	120	---	14
	0	23.5	52	2.2	<0.5
XE-233	50	23.5	82	---	67
	29	23.5	75	---	70

(1) Pressure drop across packed sample column

(2) Time required for effluent to reach 0.2% CO_2

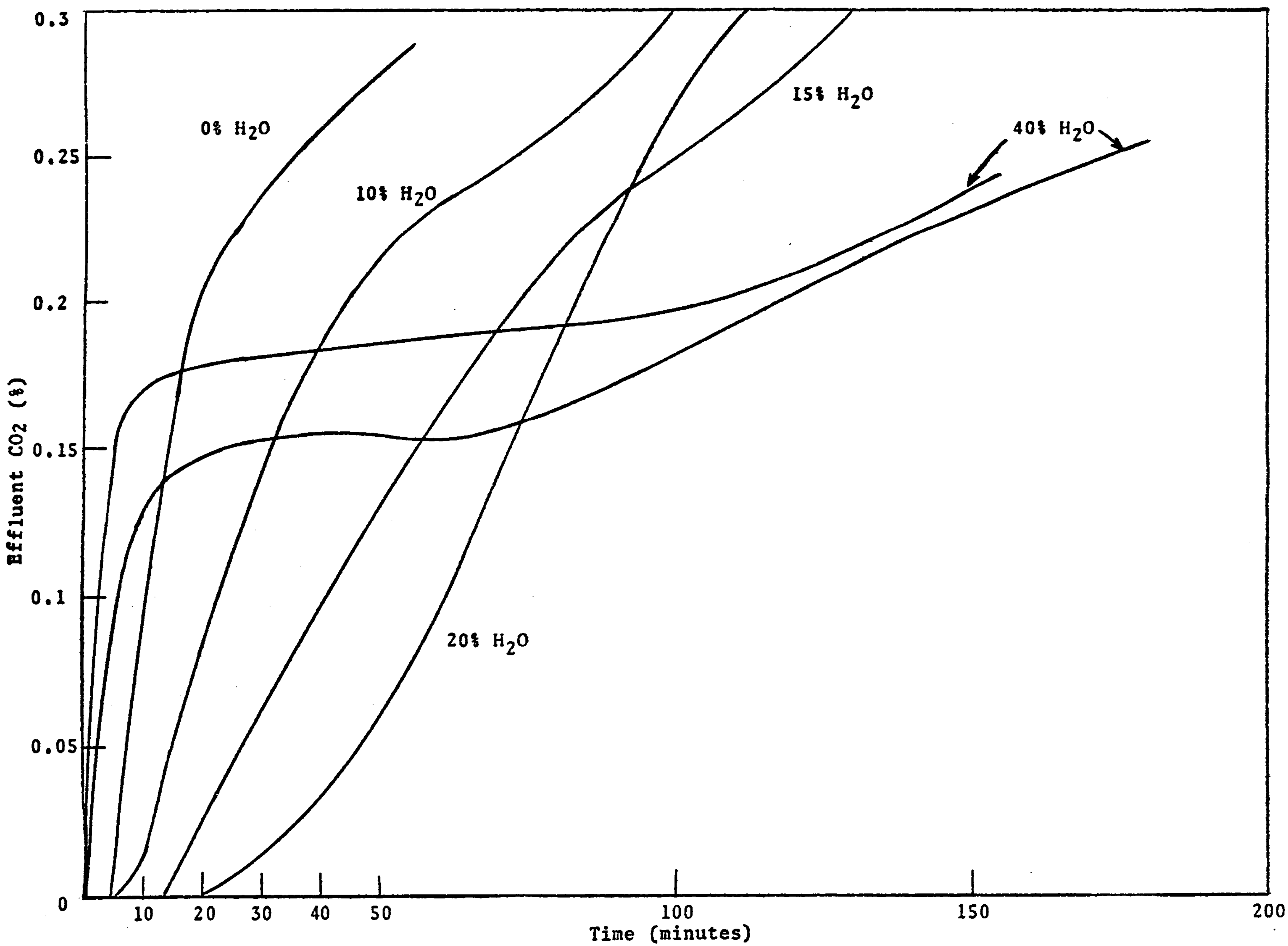


FIG. 12 - EFFECT OF RESIN WATER CONTENT ON CO_2 ABSORPTION EFFICIENCY OF AMBERLITE IR-45

It was interesting to note that in the dry state IR-45 retains sufficient porosity so that some initial CO_2 sorption is attained. This is attributed to the unique highly crosslinked character of the resin which not only limits the degree of swelling but also prohibits gross shrinkage. Resins with little cross-linking, such as Epon 812/DET, undergo significant swelling and shrinkage and in the bone-dry state shrinkage is such that no activity can be measured.

XE-233 - In two runs with 50 and 20% water, the activity of this resin remained unchanged and further tests at lower water content were required to establish the minimum effective operating condition. The resin at 50% water did not follow the same reaction kinetics as observed with IR-45 at 40% H_2O and this could be attributed in part to the macroreticular structure of the polymer. In later tests, XE-233 was seen to have a similar sorption life at 15% H_2O content, but was not as effective when its water content was dropped to 0%.

AA/TEP - The acrylic acid tetraethylenepentramine polymer was equilibrated at 25, 50 and 65% water content, and the half-life remained essentially unchanged, i.e., 105-116 minutes. This resin is less dense than the others and swells even further at 50 and 65% water content. The volume was such that only a 15 g (dry basis) charge could be employed, as compared to 23.5 g for the 25% water sample. A run at 0% H_2O in the resin indicated essentially no activity, with a half-life of <0.5 minutes. Similarly, a run at 15% H_2O yielded only a 1.5 min half-life.

The fact that, unlike the IR-45, the AA/TEP was highly active at 50 and 65% water in the early stages of the run suggests that the phenomena observed with IR-45 at 40% water is specific and is due to the intrinsic nature of the polymer itself. The diffusion of CO_2 into the polyacrylic acid or epoxide type materials is not restricted by the presence of excessive water.

Epon 812/DET - Samples of this polymer were equilibrated at 48, 25 and 15% H_2O and the half-life in the CO_2 test was 188, 109 and 14 minutes respectively,indicating that the activity of this material is very dependent on water content. When wet at 15-48% water content, the material is a spongy-like substance. In the dry state, however, which was essentially non-reactive, it was an amorphous crystalline material. Since significant activity was observed at 25% water, regeneration studies were made at this condition.

IRA-93 - This resin which contains a tertiary amine functionality was previously evaluated at 50% water content and a half-life of 26 min was reported. A run was made with a 20% water content; however, half-life was essentially unchanged. No further studies were made with this resin.

IRA-68 - This material, a tertiary amine resin which was not reactive at 60% water content, was also found to be unreactive at 20% water content.

Regeneration Studies

One of the requirements for an operable CO_2 sorbent system is that it must be fully regenerable. Although it is known that ion exchange resins are readily regenerable with alkaline solutions, the regeneration efficiency with thermal/vacuum was not known. McConnaughey,[51] in evaluating various weak-base ion exchange materials as CO_2 sorbents, showed that some are regenerable by steam treatment. He indicated that an epoxide-amine derivative (Epon 516/DET, equivalent to MSAR Epon 812/DET) was completely regenerable and that IR-45 was only partially regenerable by this technique.

Studies were undertaken to establish the regenerability of the various active systems by the thermal/vacuum technique. Regeneration procedures were the same for all systems in that the sample (after CO_2 exposure) was left in the tube and placed horizontally in an oven and vacuum dried a prescribed time at a particular temperature. A weight before and after was recorded and the material considered regenerated when the initial dry weight was recovered. The sample was then removed from the tube, soaked in H_2O (usually several hours or longer), filtered and transferred to a dish and equilibrated in the vacuum oven at 55°C to the desired moisture level. The material was then transferred into the tube and the CO_2 exposure repeated. Regeneration data are summarized in Table 7.

IR-45 - Unlike the steam regeneration studies reported by McConnaughey, it was found that the IR-45 was almost completely regenerable at least for the initial five cycles. Regeneration studies which were made with resins containing both 15 and 20% water indicated effective regeneration particularly with the latter. In all cases, 55°C regeneration temperature was employed and a laboratory model National Appliance Company vacuum oven was used. The pump was a standard laboratory forepump which was pumping through a restricted needle valve on the oven and regeneration times are therefore conservative. Although 11 and 16 hour treatments were employed, it was found that the minimum regeneration time in this system was 3 hours. Minimum effective regeneration temperatures were not established.

Although studies with 15% water content were discontinued, five additional cycles were made with the 20% water sample. The samples, which were soaked in water after regeneration, were equilibrated to the desired moisture content directly in the absorption tube. Regeneration in vacuo to 0.15-0.2 Torr for 3 hr at 55°C indicated that no apparent deterioration had occurred in the ten cycles. The half-life for the 10 cycles ranged from 74.5 to 93 min and the average half-life was 82 min.

TABLE 7 - REGENERATION EFFICIENCY OF WEAK-BASE RESINS

Sample	Cycle No.	Dry Weight (g)	Bed Depth (mm)	ΔP (mm Hg)	Half-Life (min)	Regeneration Conditions
IR-45 ($20\%\ H_2O$)	1	23.5	65	---	83	Vacuum 11 hours @ 55°C
	2	23.6	67	---	86	" 16 " "
	3	23.6	63	---	91	" 3 1/2 "
	4	23.4	62	---	79	" 16 " "
	5	23.1	61	0.8	70	
IR-45 ($15\%\ H_2O$)	1	23.5	63	---	75	Vacuum 3 1/2 hours @ 55°C
	2	23.5	65	---	58	" " "
	3	23.5	58	0.6	55	" 4 " "
	4	23.2	53	0.9	48	" 3 " "
	5	23.2	55	0.6	56	
AA/TEP ($65\%\ H_2O$)	1	15.0	---	---	116	Vacuum 16 hours @ 70°C
	2	15.3	---	---	43	" " 105°C
	3	14.3	102	---	108	" " "
	4	13.4	95	---	85	" " "
	5	13.0	100	2.9	106	
AA/TEP ($50\%\ H_2O$)	1	15.4	---	---	120	Vacuum 16 hours @ 105°C
	2	15.3	107	---	115	
AA/TEP ($25\%\ H_2O$)	1	23.5	128	---	105	Vacuum 7 hours @ 105°C
	2	23.5	127	9.6	97	
Epon 812/DET ($48\%\ H_2O$)	1	23.5	127	---	188	Vacuum 7 hours @ 70°C
	2	18.7	111	---	134	
Epon 812/DET ($25\%\ H_2O$)	1	23.5	113	0.6	109	Vacuum 6 hours @ 55°C
	2	23.2	127	0.8	71	" 16 " "
	3	24.9	120	1.2	13	
XE-233 ($50\%\ H_2O$)	1	23.5	82	---	67	Vacuum 3 hours @ 80°C
	2	23.5	82	---	2.5	5% NaOH
	3	23.5	82	---	40	
XE-233 ($29\%\ H_2O$)	1	23.5	75	---	70	Vacuum 6 hours @ 55°C
	2	23.5	75	---	14	" 12 " "
	3	23.5	75	---	27	5% NaOH
	4	23.5	75	---	31	
IR-910 ($65\%\ H_2O$)	1	23.5	127	---	346	Vacuum 16 hours @ 70°C
	2	21.0	---	---	1	5% NaOH
	3	22.2	---	---	350	

Also included in Figure 13 are the quarter-life (0.1% CO_2 in effluent) and 3/4-life (0.3% CO_2 in effluent) values for the ten cycles. The average for these values was 62 and 109 min respectively. These values have been shown because, at that time, the optimum bed-break time was not established and parametric studies might eventually prove that a break-time other than half-life might prove desirable. Indeed, the reasonable CO_2 capacity of the bed between half-life and 3/4-life suggested that the bed might be used to higher CO_2 capacities while still performing efficiently.

AA/TEP - Regeneration cycles with this material indicated effective regeneration with vacuum at 105°C. Five cycles at 65% H_2O and two cycles each at 50% and 25% water levels were effected. A single regeneration cycle at 70°C indicated that this was not acceptable, despite a 16 hour treatment at this temperature (Table 7). Although a 6-hour treatment at 105°C indicated complete regeneration for the 25% water sample, the subsequent run was made with a relatively high ΔP (9.6 mm Hg) and this could have favorably influenced the half-life.

Drastic reduction of sorption capability for the 15% water content sample was seen in the third cycle - the CO_2 life was only 29 min. Prior to the third cycle, the resin was regenerated 24 hr in the vacuum oven at 105°C. No further regeneration cycles were made, but it appears that at the condition of regeneration, this resin is not as regenerable as IR-45. The reason for loss in activity was not established and further studies would be required to determine whether or not deterioration and loss of NH_3 has occurred.

Epon 812/DET - This resin was effectively regenerated with steam in the NRL work and a total of 1008 cycles was reported. However, limited thermal/vacuum regeneration studies with this resin indicated that a marked decrease in activity was observed at both 48% and 25% H_2O content (Table 7). Significant activity losses occurred at both 70 and 55°C regeneration temperatures. Further work would be required to establish whether or not these losses can be avoided by employing less stringent conditions. The reason for the losses are not readily apparent; however, it is noted that with each run some weight loss occurs and since mechanical loss due to handling is minimal, this could be due to partial decomposition.

XE-233 - Regeneration studies with XE-233 indicated that this material behaved quite differently from the IR-45 product. We were not able to effect a regeneration by thermal/vacuum means and further regeneration with NaOH did not effect complete regeneration (Table 7). The reasons for this were not immediately apparent, since the XE-233 and IR-45 are chemically identical.

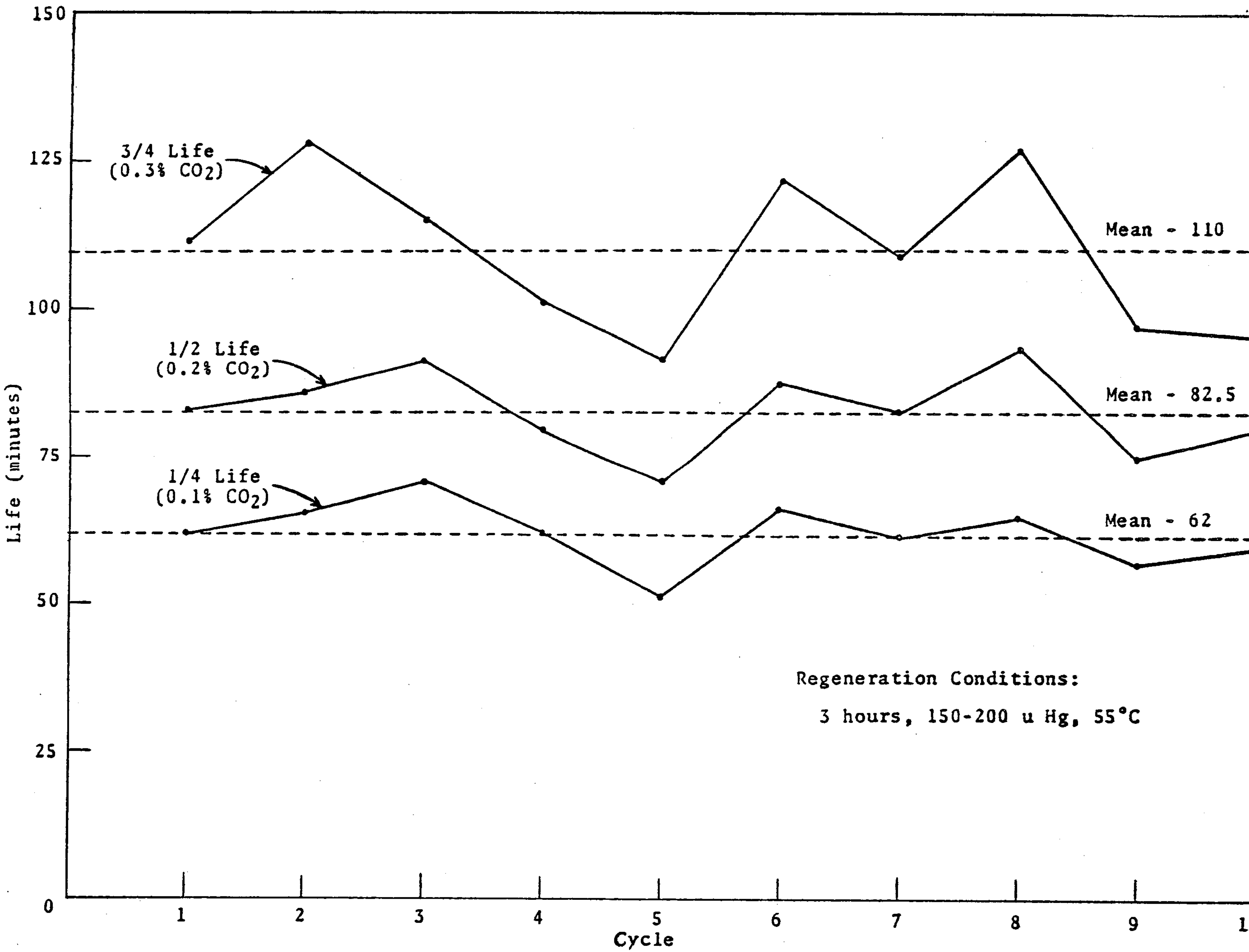


FIG. 13 - REGENERATION EFFICIENCY OF IR-45 - TEN CYCLES

The unexpected behavior exhibited by XE-233 must be attributed to its macroreticular structure which may have been irreversibly altered in the thermal/vacuum treatment.

A final test was conducted, wherein a resin sample containing 15% water gave an initial life of 72 min. However, vacuum regeneration for 11 hr at 55°C was not successful as the half-life in the second cycle was only 33 min. It should be noted that the 11 hr at 55°C did not return the resin to its initial weight, which suggests that the CO_2 was not completely desorbed at these conditions.

In summary, vacuum regeneration at 55 and 80°C, as well as regeneration with NaOH solutions, have not completely regenerated XE-233. The reason for this was not known but must be attributed to the macroreticular structure of this resin. One possibility that was yet to be examined is a higher regeneration temperature (i.e. 100°C) for XE-233. In view of the regeneration difficulties encountered with this material,it is not likely that this resin will be preferred over IR-45, particularly since the initial activities are approximately equal.

Strong-Base Resins - In addition to the weak-base regeneration work, some limited studies were made with strong-base resins. As the data in Table 7 shows, the run with IRA-910 indicated that thermal/vacuum regeneration was not effective, at least at the conditions employed, i.e., 16 hours at 70°C with vacuum. Although more stringent conditions might be effective, the strong-base resins are not as heat stable and therefore temperatures above 70°C could be harmful and effect resin deterioration. It was demonstrated, however, that regeneration could readily be achieved by treatment with 5% solution of NaOH.

Room Temperature Regeneration Studies

In addition to the 55°C regeneration runs discussed in the preceding sections, attempts were made to effect vacuum regeneration at room temperature (~25°C). An IR-45 resin bed was used and showed regeneration efficiencies of 105, 90, 68, 68 and 25% respectively for vacuum exposures of 40, 20, 10, 5 and 1 hours. In all cases, the low rate of regeneration, i.e., the lengthy evacuation times, render this mode of regeneration prohibitive.

Water Equilibration Procedures

After regeneration, the resin is in a dry state, i.e., 5% H_2O and equilibration with H_2O must be effected to return the resin to its operative H_2O content. In prior studies, the sample was soaked in water, filtered and evacuated to the desired water content. This method of water equilibration is not desirable from a space-system viewpoint.

Vapor Phase Equilibration - Vapor phase equilibration was evaluated as a means of returning the resin to its optimum water content. Calculations as well as experimental tests showed that at 75°F, even fully saturated air did not have sufficient water capacity to deliver sufficient water to the resin within a reasonable time.

Attempts were made to use the Cahn Electrobalance mentioned earlier to rapidly derive water equilibration values with accompanying kinetic data. Air at ambient temperature and 50% RH was passed through the balance chamber. An equilibration weight of 7.9% water was attained in 6.5 hours, while at 80% RH the equilibration weight was 16.8% and was attained in 10.5 hours. It was observed that equilibration water weights were approximately the same as measured in the adsorption tubes with larger (23.5 g) samples. The only difference was that a shorter time was required to reach equilibrium and this must be attributed to the higher contact area presented.

Liquid Water Injection - A second method employed was to apply liquid water to the top of the bed with a syringe. The exact amount of water (5.24 g) was obtained by weighing the tube before and after water addition. The water initially wets approximately 20 mm of the dry 50 mm bed height. Several procedures for distributing the water through the bed were examined. In one test, the unmixed bed was exposed directly to CO_2 in the dynamic adsorption cycle and, during the run, the water was partially dissipated through the bed by the air stream. The half-life in this run was 71 minutes, suggesting that this method of water addition is effective. It was noted that, throughout the duration of the run, the wetted portion of the bed was cooled, due to water evaporation, while the lower portion of the bed warmed slightly due to the heat of water absorption.

In another test, after application of the water, the stoppered tube was placed in an oven at 55°C to aid in the dissipation of the water. However, the water did not appear to spread through the bed, even after a 16-hour heating time. The half-life exposure to CO_2 was 66 minutes, which was similar to the above run made without heating.

The most effective means of wetting the bed was achieved by applying the exact amount of water and then gently mixing a few minutes (by shaking the tube) until a uniform, free-flowing resin bed was achieved. Two runs made in this manner gave half-lives of 75 and 81 minutes, which was also equivalent to prior runs in which the resin was equilibrated by soaking in water.

The rapid equilibration achieved by simple addition of liquid water suggested the possibility that a final system could also be equilibrated by the addition of liquid water. In a column operation, water injection at various bed levels could provide the uniform wetting that is desired. No mixing or agitation would be required prior to the CO_2 exposure.

Static Water Sorption Studies

Another attempt was made with the Cahn microbalance to generate water vapor equilibrium data for IR-45, using a static method. In the static test method, a glass tube containing distilled water was attached to the balance sorption system. Separated from the system by a vacuum stopcock, this tube extended into a constant, sub-ambient temperature bath, which was regulated to $\pm$ 0.1°C. The portion of the microbalance system containing the resin sample is also regulated via a water bath. With the sample at ambient and the water tube pre-set to a selected sub-ambient temperature, the water vapor partial pressure (P/P_o) was controlled to approximate that of a desired level of relative humidity. After the sample has been evacuated at 45°C to $<10\ \mu$ pressure and when both water and sample temperature are equilibrated, the separating stopcock was opened and the sample weight gain due to water vapor is again monitored with a recorder. The desired water pressure was verified with a manometer as the run proceeds and in 30-60 minutes equilibrium was reached.

The water isotherm values for IR-45 was constructed from six pressure values. The resultant isotherm (Figure 14) shows a 21.5% by weight capacity at 90% RH, dropping off to 0.4% at 23% RH. The equilibrium weight at 50% RH is indicated to be 5.5% H_2O.

At this point, the water temperature was lowered $\sim$5°C and, while a small sample weight loss was observed, it was not large in magnitude, even after several hours of equilibration. The RH was then lowered further (water container cooled another 5°C) and the effect was again almost negligible. The system P/P_o did not decrease at all, suggesting hysteresis, an effect not as apparent in a sorbent such as activated carbon, which responds rapidly to changes in RH.

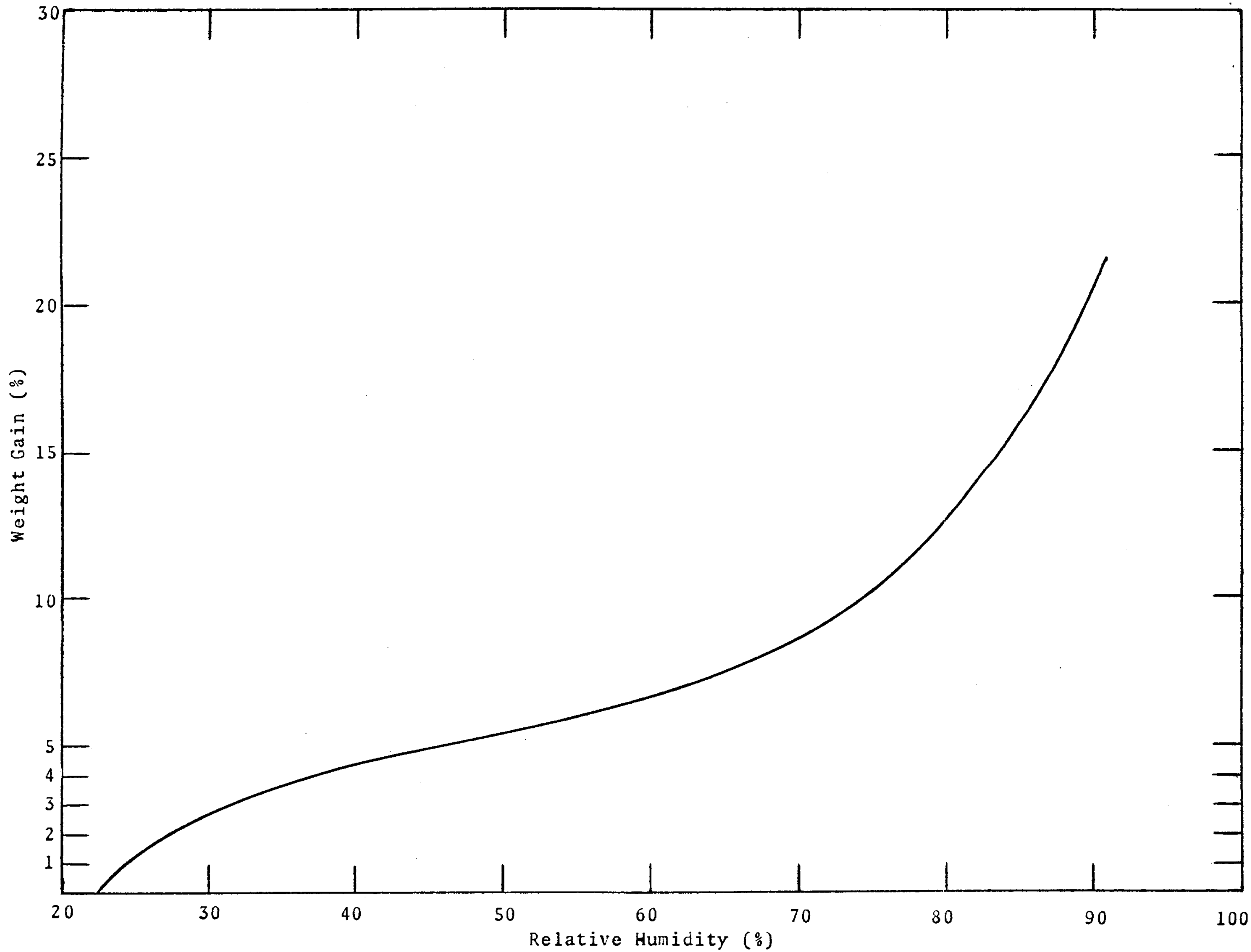


FIG 14 - WATER ISOTHERM FOR IR-45 AT ROOM TEMPERATURE

Thermal Stability Tests

Initial tests conducted at 110 and 150 °C (302°F) in vacuo indicate an unusually high stability even at 150°C. Little to no sign of degradation of sorption capability has been observed after two 5-hour intervals at 150°C. After the initial 5-hour test, the half-life in the CO_2 absorption tests was 85 minutes. This material was then treated an additional 5 hours at 150°C to determine the effect of additional cycling and also to effect regeneration at the same time. The CO_2 absorption half-life after the second exposure was 86 minutes. The sample treated 5 hours at 110°C yielded a slightly higher half-life of 90 minutes in the CO_2 absorption test.

The unusual stability of IR-45 at 150°C was somewhat surprising. It was stated earlier that most commercial ion exchange resins are not stable at temperatures above 100°C, and in general, temperatures below this are recommended by the manufacturer. IR-45 is one of the few materials whose recommended use temperature is as high as 100°C. It has in fact been found that temperatures of 150°C were detrimental and resulted in degradation of the resin (MSA Final Report, 29 October 1964, Contract No. DA-19-129-AMC-210(N), U.S. Army Natick Labs). These data were obtained in an air circulating oven and the degradation was attributed to thermal decomposition. The present stability data in the absence of air indicates that the deteriorations observed before were probably due to oxidation rather than thermal decomposition.

Additional tests were then initiated to establish the upper limits of stability and also to determine whether or not degradation will occur with prolonged heating at elevated temperatures.

IR-45, 175°C Regeneration - A sample of IR-45 that had been exposed to CO_2 was regenerated in vacuum for five hours at 175°C. A conventional life-test was then performed. Five additional cycles were performed at the same conditions and the half-lives varied from 63-97 minutes, with the average of the 6 runs 77 minutes. A 67 minute half-life was obtained in the sixth cycle and, in addition, a relatively high initial breakthrough was observed. This suggested that continued treatment at 175°C (347°F) may be detrimental.

In addition to the sorption data, it was observed that the resin color darkened somewhat on continued treatments, changing from a light yellow initially to a darker, yellow-brown. This occurred despite the fact that only minor weight losses (<1%) were observed during the six cycles (Table 8). It was also observed that the resin bed did not wet as readily as the untreated resin. The addition of sufficient water to restore the condition of 20% water did not result in a free flowing bed; i.e., wet aggregates resulted and the excess water was stripped off during the early part of the CO_2 sorption run. The reason for this could be attributed to destruction of the internal pore structure during heating at 175°C.

TABLE 8 - EFFECT OF HEAT ON IR-45 ACTIVITY

Regeneration Conditions: 175°C vacuum, 5 hours
CO_2 Sorption Conditions: 0.4% CO_2, 1 l/min, 50% RH, 20% H_2O in resin bed

Cycle No.	Initial Wt (g)	Half-Life (min)	Regen. Wt. Loss/Cycle (g)
---	24.45	---	- 0.12
1	23.33	83	- .04
2	23.29	80	- .01
3	23.28	97	- .15
4	23.13	63	+ .07
5	23.20	73	- .07
6	23.13	67	---

IR-45, 150°C Regeneration - The effects of prolonged heating at 150°C was also examined. Resin activity was monitored by running CO_2 life-tests after heating at 5, 10, 75, 100, 150 and 200 hours. The data for these runs are shown in Table 9.

The half-life at 75, 100 and 150 hours was approximately 70 minutes, which was lower than the initial 85 minute life. After 100 and 150 hour heating initial CO_2 breakthough occurred almost immediately. After 200 hours at 150°C, a half-life of 95 minutes was measured. However, in this case the initial breakthrough was even more pronounded, indicating lower over-all capacity.

It is to be noted that prolonged heating at 150°C yielded a yellow-brown resin coloration (darker than that observed after six 5-hour treatments at 175°C). Weight losses, however, were again low (<1%). In addition, upon rewetting, the resin bed reacted the same as did the resin which was treated at 175°C; i.e., it did not readily absorb 20% water, presumably due to pore structure alteration.

TABLE 9 - EFFECT OF PROLONGED VACUUM HEATING AT 150°C ON IR-45 ACTIVITY

Initial Wt (g)	Heating Time (hrs)	Wt. Loss (g)	Half-Life (min)
23.50	5	0.05	85
23.45	10	0.00	86
23.45	75	0.06	69
23.39	100	0.00	70
23.39	150	0.03	70
23.36	200	0.02	95

XE-233, 175°C Regeneration - In view of the indicated stability in vacuum of IR-45, additional regeneration tests were made on XE-233, the macroreticular version of IR-45. Regeneration temperature was increased to 175°C. The CO_2-exposed sample was placed in the vacuum oven at this temperature for two hours. Two cycles were made and, in each case, despite the fact that the original dry weight was recovered, the initial activity was not attained. The half-lives for the two cycles were 25 and 22 minutes, which are similar to the half-lives obtained in previous regeneration studies with this resin at 55°C (33 minutes). Since the initial weight of the resin was recovered at 175°C, it appears that the internal pore structure of the resin has been altered so that the initial activity cannot be recovered.

IR-410, 150°C Regeneration - An attempt was made to establish whether or not the strong-base resin could be regenerated at 150°C in vacuum. This was unsuccessful, however, as some apparent decomposition occurred after four hours at this temperature. The sample darkened considerably, while the sample underwent irreversible shrinkage, and did not swell upon the addition of water. The crosslinked resin matrix was apparently destroyed in the process. A CO_2 absorption run on the material in this condition indicated CO_2 half-life of <1 min.

Physical Stability

In addition to the thermal stability exhibited by IR-45 it has been observed that this material also has a significant structural stability. The resin is obtained as 20 x 50 mesh beads and in repeated tests, including 10 regeneration cycles at 55°C as well as the 110 and 150°C studies, no sign of physical degradation has been observed. Although no measurements have been taken, visual observation indicates little to no signs of breakdown. This is despite the fact that the resin has been repeatedly dried and re-wet.

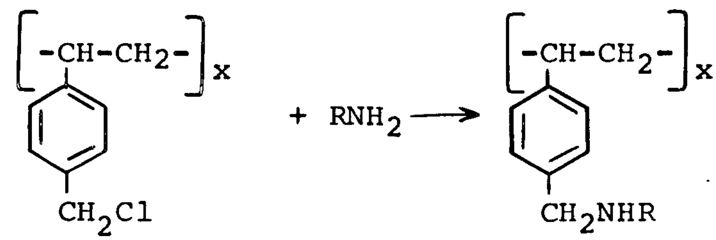
In some cases, resins will not stand repeated drying and wetting cycles. It was observed that the acrylic acid tetraethylene pentamine polymer, which was flake-like initially, underwent some powdering after only limited regeneration cycles. Similarly, the Epon-812/diethylenetriamine polymer was also observed to powder somewhat on repeated cycling. Other commercial ion exchange bead polymers are known to crack and eventually powder upon drying-wetting cycles. The physical integrity exhibited by the IR-45 is a very desirable feature and will not only aid in minimizing operating difficulties but will also aid in providing more consistant and more reliable performance.

<u>Summary</u>

Several resins which were either commercially available or described in prior art were screened for CO_2 activity via gram scale dynamic absorption runs. Control tests were performed using molecular sieves in dry air. Strong base resins in humid air had CO_2 capacities greater than molecular sieves in dry air, although weak base resins offered greater promise of regeneration. The effect of water content on dynamic CO_2 capacity was evaluated. The water isotherm for IR-45 was generated. Preliminary vacuum thermal regeneration studies showed that certain weak base resins are fully regenerable, although rewetting with water was necessary before reuse. Thermal stability tests showed that IR-45 was thermally stable, at least to 150°C.

RESIN FORMULATION STUDIES

Studies directed toward formulation of superior ion exchange resins were initiated. Anion exchange polymers are in general formed by incorporating the amines: trimethylamine, dimethylethanol amine, diethylenetriamine, triethylenetetramine and tetraethylenepentamine. Initial preparations with diethylenetriamine and monoethanol amine were made. The amine resins are prepared by reacting with chloromethylated styrene-divinylbenzene polymer



The chloromethylated intermediate used for the initial preparations was a Dow Chemical Company product containing 4% divinylbenzene and was 50 x 100 mesh. The generalized procedure employed in MSAR labs for the amination reaction is as follows:

> Suspend 37.5 g (0.25 moles) of chloromethylated beads in 200 ml of toluene. Add 0.50 moles of the amine. Reflux with stirring for four hours. Cool to room temperature. Transfer the slurry to a beaker, add 200 ml of water and allow the beads to stand for one hour. Filter through a Buchner funnel and wash the beads twice with water. Resuspend the beads in 500 ml of 10% by volume HCl overnight. Wash the chloride-form beads in a Buchner funnel until the effluent is neutral to methyl orange.

In addition to the above procedure with toluene as a solvent, samples were also prepared according to USP 2,591,574 in which benzene was employed. Except for the different solvent, both procedures are essentially the same.

The reaction as described above employs an equimolar (or an excess) of amine so that the reaction favors condensation of one chloromethyl group with one amino group according to the following:

$$-CH_2Cl + NH_2CH_2CH_2NHCH_2CH_2NH_2 \longrightarrow -CH_2-NH-CH_2-CH_2NHCH_2CH_2NH_2$$

Preparations, however, have also been made in which one-half the amount of amine is present so that the following condensation will be favored.

$$-CH_2-Cl + 1/2(NH_2CH_2CH_2NHCH_2CH_2NH_2) \rightarrow -CH_2-NH-CH_2-NH-CH_2-NH-CH_2-$$

The latter provides additional crosslinking in the polymer and also provides predominately secondary amine functionality. Previous work in our laboratories had indicated that the IR-45 structure favored the latter. The final resin samples were analyzed to determine their solids content and anion exchange capacity.

Effect of Amine

The initial ion exchange resins were prepared in the manner described above and were examined for CO_2 sorption capacity. CO_2 half-life tests on resins prepared with different amines indicated that tetraethylenepentamine (TEPA) was slightly more effective than diethylenetriamine (DETA) or triethylenetetramine (TETA) (Table 10). The resins were all prepared with Dow Chemical chloromethylated beads containing 4% divinylbenzene. The ion exchange capacity of the resin with TEPA (8.55 meq/g) was also slightly higher than that obtained with DETA or TEPA.

TABLE 10 - ION EXCHANGE RESINS FROM STYRENE-4% DIVINYLBENZENE COPOLYMER (DOW CHEMICAL COMPANY)

Sample	Solvent	Amine[1]	Amine/ $-CH_2Cl$	Ion Exchange Capacity meq/g	Moisture Content (%)	CO_2 Sorption Half-Life (minutes)
FV-1	Toluene	DETA	0.5/1	4.38	24.2	10
FV-2	"	"	1/1	6.38	32.4	49
FV-3	Benzene	"	4/1	8.26	39.8	150
FV-4	"	"	0.5/1	4.70	29.5	2
FV-5	"	MEA	4/1	4.09	30.5	50
FV-12	"	TETA	"	8.00	38.8	150
FV-13	"	TEPA	"	8.55	34.4	198

[1] DETA = diethylenetriamine
MEA = monoethanolamine
TETA = triethylenetetramine
TEPA = tetraethylenepentamine

Effect of Crosslinking

The ion exchange resin properties are to a great extent controlled by the amount of crosslinking incorporated into the structure. This affects swelling, porosity and moisture-holding capacity. A study was undertaken to determine the optimum crosslinking for CO_2 sorption.

Copolymers containing from 1-40% divinyl benzene were prepared according to a procedure described in USP 2,591,574. These were prepared by a pearl polymerization technique employing styrene, divinylbenzene, water, benzoyl peroxide and gelatin. The copolymer was then reacted with chloromethyl ether (at either 16 hours at 30°C or 5 hours at 60°C) and finally aminated with diethylenetriamine in benzene. A description of the polymer and the CO_2 sorption efficiency is shown in Table 11. Also shown in Table 11 are the chloromethylation conditions and the chlorine content of the intermediates. Several of the materials had initial CO_2 capacities greater than that found with IR-45. A very effective polymer was one prepared with 3% divinylbenzene (FV-32). Polymers with 10-40% divinylbenzene were not as reactive. The highly cross-linked structures prevented complete chloromethylation; and consequently low ion exchange capacity, as well as low CO_2 capacity resulted.

Two preparations (FV-35, FV-36) were made in which toluene was present in the initial polymerization. This is purported to provide a more porous substrate. The toluene is occluded in the bead polymer and is removed by heating to yield particles which are more porous than those prepared without toluene. Sample FV-35 prepared in this manner with 5% divinylbenzene cross-linking showed a marked improvement in activity (453 minute half-life) over the same preparation without toluene (FV-30, 275 minute half-life). Some minor improvement in activity was also achieved by preparing the sample with 20% divinylbenzene in the presence of toluene. In this case, however, the CO_2 capacity was still relatively poor.

Particle Size

Attempts to prepare resins with larger particle size, which would provide lower pressure drop in columnar reactions, were unsuccessful. The three separate reaction steps were examined; and, although it is possible to prepare and maintain a larger particle during the polymerization and chloromethylation step, in all cases the particle is fractured in the final amination step. The use of the more porous polymer substrates and little to no mechanical agitation during reaction did not enhance the bead strength. Particle size deteriorated from approximately 10x20 mesh to 40x60 mesh.

Regeneration Studies

The regenerative capability of the synthetic preparations was also examined. Seventeen of the new resin forms were exposed to hot water regeneration treatment (95-98°C in water and then centrifugation for 5 min @ 500 rpm to remove excess water). They were then retested with CO_2 and only five showed regenerative promise (FV-3, FV-17, FV-30, FV-32 and FV-35). As shown in Table 12, these resins were cycled repeatedly and the half-lives noted. With the exception of FV-30, all maintain high CO_2 sorption capability.

TABLE 11- EFFECT OF DIVINYLBENZENE CROSSLINKING ON ION-EXCHANGE CAPACITIES

Sample No.	Divinylbenzene Crosslinking (%)	Chloromethylation Temperature (°C)	Chloromethylation % Cl	Moisture Content (%)	Ion-Exchange Capacity (meq/g)	CO_2 Half-Life (minutes)
FV-24	1	30	19.30	49.0	6.64	260
FV-32	3	30	17.65	49.2	8.10	368
FV-17	5	30	15.80	41.3	8.02	>200
FV-30	5	30	14.15	43.7	6.06	275
FV-25	5	0	6.70	28.2	2.45	56
FV-35(1)	5	30	15.00	45.0	7.40	453
FV-22	10	30	10.80	29.4	5.12	57
FV-20	20	60	5.46	21.8	0.69	<5
FV-36(1)	20	30	10.70	29.6	3.94	10
FV-21	40	60	0.84	10.7	0.38	8

(1) Porous type

TABLE 12 - CO_2 SORPTION TESTS OF ANION EXCHANGE RESIN

	CO_2 Half-Lives (min.)								
Resin	2nd Cycle	3rd	4th	5th	6th	7th	8th	9th	10th
FV-3	270	366	>350	>200	~440				
FV-17	98	98	138	94	>155				
FV-30	116	54	40						
FV-32	146	150	75	110	150	189	141	~100	~150
FV-35	295	151	119	350	143	>180	129	114	

Between Cycle Regeneration Treatment: Heated to ~98°C in water until no more gas was evolved. Resin then centrifuged for 5 min. @ 500 rpm. Replaced in tube for next cycle.

Effect of Bed Depth

Another batch of resin FV-3 was formulated in order to verify the earlier findings. Designated FV-37, the resin was tested after preparation and found to have an exchange capacity of 9.14 meq/g, which was comparable to the 8.26 meq/g of the original FV-3. As in all tests, a sample equivalent to 23.5 g on a dry basis was placed in the tube for CO_2 sorption testing. When only a 53 min half-life resulted, the material was hot water regenerated in the usual manner and retested. Again, the half-life was low (36 min). It was then noted that the bed depth of these FV-37 samples was ~60 mm, while FV-3 beds of the same weight were ~90 mm.

To determine whether this difference in bulk densities could be responsible for its ineffective CO_2 sorption, more FV-37 was added to the tube increasing bed depth to ~90 mm. The subsequent life test yielded a value of 370 min, which is comparable to the earlier FV-3 runs. It is believed that this higher bulk density for FV-37 is due to irreversible shrinkage of its internal pore structure during preparation, which occurred upon drying, after reaction with the diethylenetriamine.

To further view this suggested effect of bed depth on CO_2 sorption efficiency, the original batch, FV-3, was restudied. Beds were made up of 22.5, 45 and 90 mm depths, which corresponds to 1/4, 1/2 and full beds respectively. Upon testing, their respective CO_2 half-lives were 8, 24 and 191 minutes. While each of the beds contain increasing amounts of FV-3, the increase in half-life is larger than the proportionate gain in bed weight, suggestive of the presence of a "critical bed depth" - a minimum bed thickness necessary for first adsorption. A large critical bed is suggested by the large increase in CO_2 sorption capacity of resin FV-37 when there is a 50% gain in bed depth. It appears that the 60 mm bed is a substantial part of this "critical bed depth."

Effect of Water Content

To determine whether resin FV-3 could still operate as an effective CO_2 sorbent at a lower water content, a regenerated sample (50% H_2O content) was evacuated to a water content of ~20% and tested. The half-life was 30 min. The sample was then regenerated and run at its usual 50% water level and the half-life was 157 min, indicating that a water content higher than 20 weight percent is apparently necessary.

Final Studies

Attempts to obtain the chloromethylated form of styrene-divinylbenzene copolymer from Dow Chemical Company were not successful. This material had been used to formulate the promising resin, FV-3. In lieu of this, Dow supplied us with 20 x 50 mesh copolymer that had not been chloromethylated. Chloromethylation and subsequent treatment, as outlined previously, yielded a material (FV-39) with an ion exchange capacity of 8.50 meq/g. It was noted that laboratory chloromethylation resulted in a product with smaller particle size than that resulting from Dow's production scale chloromethylation procedure.

Initial tests on FV-39 made at 2 l/min flow have indicated good activity at 42% moisture content (80 minute half-life). Additional adsorption data at lower water content, however, again indicated that this activity falls off rapidly as the water content is lowered. After hot water regeneration, a second cycle yielded a 60 min half-life.

The resin again was obtained as a relatively fine particle. The initial 20 x 50 mesh particle was apparently weakened during the chloromethylation step and then completely fractured during amination, resulting in a particle size distribution of 40% 60 x 100 mesh and 60% -100 mesh. This has resulted in tighter packing and consequently greater pressure drop in the adsorption tube. The pressure drop was observed to increase as the water content was lowered. At 2 l/min flow, the pressure drop increased from 100 mm H_2O at 42% water to 270 mm H_2O at 20% water and to 390 mm H_2O at 10% water content.

It was concluded that in order to produce resins of uniform, large-bead size, some development would have to be pursued. Further synthesis attempts were terminated to concentrate on IR-45, which was relatively inexpensive, easily available, and of adequate promise as a CO_2 sorbent. IR-45 also presented a particle of uniform, large size, with negligible physical and chemical degradation under the defined use conditions.

IR-45 CHARACTERIZATION STUDIES

In addition to the preliminary screening studies of commercially-available sorbents, attempts were also made to synthesize ion exchange resins with superior CO_2 sorption capabilities. While these latter studies proceeded, however, it was recognized that more complete evaluation of other operation parameters was yet to be done. Although primarily concerned with establishment of a regeneration method, it was also necessary to further elucidate the effects of input CO_2 concentration, bed depth, gas velocity, relative humidity, and so forth upon sorbent performance. IR-45 was selected as the sorbent upon which the studies would be performed. It was selected because of availability, low cost and good sorption performance. Although it was recognized that it (IR-45) might be supplanted as the system sorbent of choice, it was expected that the data evolved in the characterization studies could be largely translated (or at least be relatable) to any other sorbent system.

Study of Absorption Parameters

The factors or conditions that affect dynamic CO_2 capacity include bed depth and temperature, the velocity and concentration of the input CO_2 gas stream and relative humidity.

Bed Temperature - It was considered that adsorption at lower temperature could be advantageous from two standpoints: (1) eliminate water desorption during the adsorption cycle and (2) possible improvement in dynamic adsorption rate. To determine whether either or both would occur, a jacketed column was fabricated and IR-45 was tested at 41°F by continuously pumping a refrigerant through the jacket during the run. The process air was also cooled to 41°F (~80% RH). Samples of IR-45 containing zero and 20% water were examined at 1 l/min flow. The half-lives of 32 and 108 minutes respectively are slightly higher than the 19 and 87 minute half-lives obtained at 75°F, indicating marginal improvement in adsorption efficiency. Reductions in efficiency are probable at increased temperatures.

Bed Depth and Input Flow Rate - IR-45 beds of 23.5, 47.0, 70.5 and 127.5 g were prepared for testing in the conventional glass sample tubes. They yielded bed depths of 2 5/8, 5 1/2, 8 1/2 and 14 1/2 in. respectively and were tested versus the standard gas stream of 0.4% CO_2 at 50% RH. Compared against test streams at 5, 10 and 15 l/min velocities, the CO_2 sorption capacity of the beds was seen to increase with bed depth and be inversely related to input flow rate.

The CO_2 capacity of these beds was then calculated as % CO_2 loading for the detectable breakthrough concentration of 0.2% CO_2. These values were then plotted versus air flow rate, as shown in Figure 15. Some data scattering is shown; however, a trend is evident. A capacity of the order of

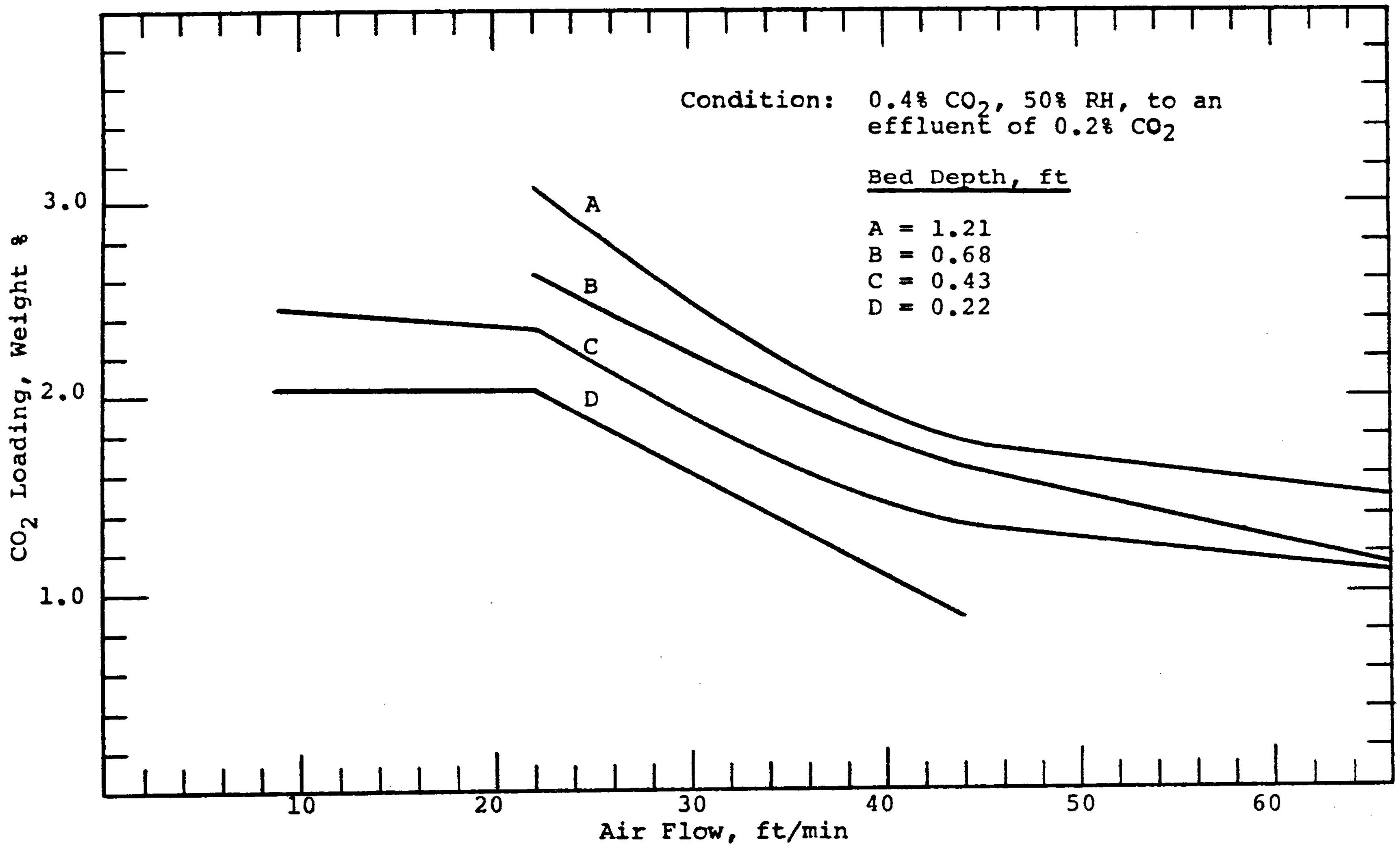


FIG 15 - DYNAMIC CO_2 CAPACITY AS A FUNCTION OF VELOCITY AND BED DEPTH

2.4% can be achieved by operation at 16 ft/min flow in a 0.43 ft bed, or at about 28 ft/min flow in a 1.21 ft bed. As expected, the capacity drops off rapidly as the flow rate is increased.

CO_2 Input Concentration - Several runs were made to determine the effect of higher CO_2 input concentration on the adsorption capacity of IR-45. A run at 0.9% CO_2 (Fig. 16) revealed that the time to initial breakthrough is almost identical to that obtained at 0.4% CO_2 concentrations. After initial breakthrough the adsorption curve effluent to reach one-half the input was shorter than for the 0.4% CO_2 run. A comparison also was made with 0.5% CO_2. Again the initial break is identical with 0.4% and a steeper slope occurs with a shorter half-life indicated. In subsequent work all runs were made at 0.5% which more closely approximates the design specifications.

Various CO_2 concentrations up to 2.0% were examined to determine the effect of higher CO_2 partial pressure on the adsorption efficiency. This was studied with the 29.4 g resin bed containing 20% water, 90% RH, 2 l/min flow (8.6 ft/min), 1.22 inch diameter tube. The capacity data at various effluent concentrations is summarized in Table 13. The overall capacity can be increased by operating at the higher CO_2 partial pressure. At 2% CO_2 partial pressure, the CO_2 weight percent pickup was 3.98% at an effluent concentration of 1.5%. However, at the comparable effluent concentration of 0.1% and 0.2%, the capacity was greatest with the lower CO_2 partial pressure of 0.5%. Also, the capacity of 2.12% CO_2 pickup at 0.2% effluent for the lower concentration would be increased substantially if the effluent were taken to 75-80% of the input as was done with the higher concentration runs.

Relative Humidity - Until this point in the program all runs were made at 50% RH. It has been observed that, at this condition, some drying of the bed occurs during the run when the initial water content of the bed is at 20%. The effect of 90% RH on the resin water content and on its adsorption capacity was also studied. It was found that no measurable water loss occurs in the run. Since the influent side of the resin does not dry out at 90% RH, a capacity increase occurs, particularly as regards the initial CO_2 breakpoint.

Tests were performed with 50 and 90% RH test streams at 1, 5 and 10 l/min versus IR-45 beds. The slopes of the breakthrough curves were about the same for the different RH conditions; however, in several cases, the time for initial CO_2 penetration was increased considerably at 90% RH. With relatively deep beds 127.5 g (1.208 ft), the time to breakthrough for 5 l/min flow increased almost one-third at 90% RH. It was also noted that the CO_2 free air capacities of the beds were larger at 90% RH as the beds became thicker. For beds less than a foot thick, there was not appreciable difference at the two humidity levels.

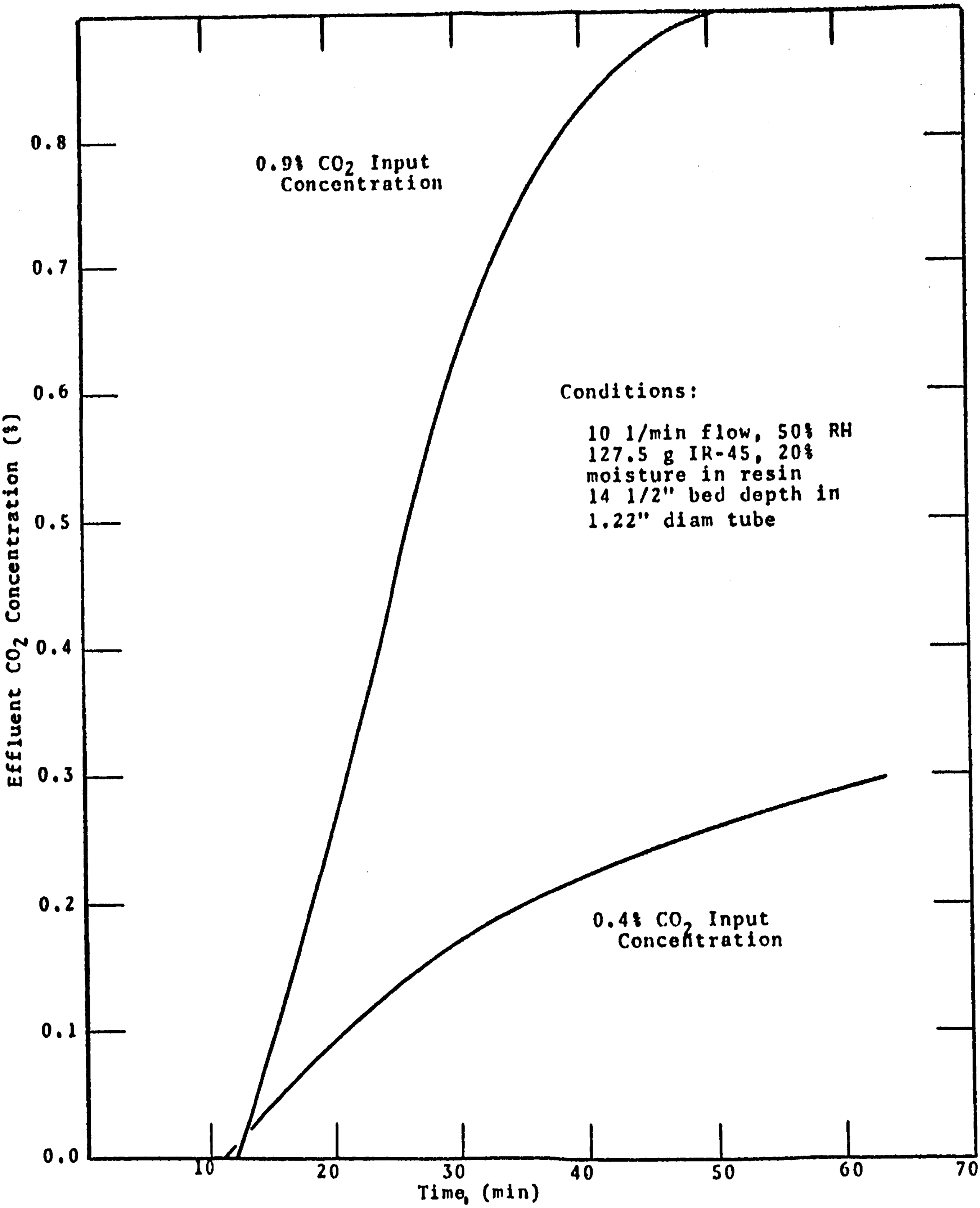


FIG 16 - EFFECT OF INPUT CO_2 CONCENTRATION ON ABSORPTION RATE WITH IR-45

TABLE 13 - THE EFFECT OF CO_2 PARTIAL PRESSURE ON IR-45 CAPACITY

Conditions: 29.4 g IR-45, 2 l/min flow, 90% RH, 20% H_2O content in IR-45, 1.22 in. dia tube.

Run No.	Input CO_2 Conc.	WT % CO_2 Pick-up at Various Effluent CO_2 Concentrations							
		Initial Break	0.1% CO_2	0.2% CO_2	0.5% CO_2	0.7% CO_2	1.0% CO_2	1.2% CO_2	1.5% CO_2
1199-14	0.5	0.66	1.69	2.12	--	--	--	--	--
1197-16	1.0	0.71	1.30	1.59	2.22	2.66	--	--	--
1197-17	1.5	0.86	1.42	1.82	2.37	--	3.50	3.90	--
1197-19	2.0	0.71	1.53	1.65	2.21	--	3.02	--	3.98

Two additional runs were made to further demonstrate these effects. These runs were made in the 1.22 inch diameter tube with a 1.2 ft bed (159.5 g IR-45 containing 20% water), and a flow of 15 l/min or 66 ft/min flow through the bed. The capacity data showed a slight increase in adsorption efficiency achieved by operating at 90% RH. At 0.27% effluent, the wt% pickup is increased from 1.75% at 50% RH to 1.85% at 90% RH. At 66 ft/min, the ΔP increased to 920 mm H_2O.

Effect of Resin Water Content - An earlier study of the effect of resin water content on IR-45 sorption efficiency was made with 23.5 g resin at 50% RH, 0.4% CO_2 concentration and 1 l/min flows. Additional tests were made at the following conditions: 47.0 g IR-45, 5 l/min flow, 90% RH and 0.5% CO_2. The range of 10-35% water content was examined and, as in the earlier study, it appears that the best initial adsorption is obtained at 20% water content, although the time to reach 0.2% effluent was slightly greater at 30% water. Adsorption efficiency was poor at 10 and also at 35% water.

Effect of Water on Swelling - Resin swelling varies with the water content. An approximation of the swelling in IR-45 was made. The range of 5-42% water content was studied and the data are plotted in Figure 17. Swelling increased from 6% at 5% water content to 41% at 42% water content. The amount of swelling was measured by first drying out the resin then adding the desired amount of liquid water and shaking to equilibrate. Bed depth changes were measured in the 1.2 inch diameter adsorption tube.

Thermal/Vacuum Regeneration

One of the requirements for operable CO_2 sorption systems for space application is that the system be fully regenerable without resorting to chemical regeneration. To this end studies were undertaken to establish the regenerability of the resins by various means, i.e., thermal/vacuum, hot water and steam. Vacuum regeneration was described in a previous section. While this method of regeneration was seen to be effective, two major difficulties tended to preclude its use. The first involved separation of the CO_2 from the water vapor and the second was concerned with the high heat input necessary to elevate the resin bed temperature. A related difficulty was the high temperature gradients experienced in the relatively dry beds upon heating and evacuation.

Hot Water Regeneration

An advantage of hot water regeneration over thermal/vacuum means is the more efficient mode of heating. The initial attempts at hot water regeneration involved an 80°C water wash. This was followed by centrifugation of the sample @ 500 rpm for five minutes to remove the excess "free" water contained in the resin bed. The sorbent was then replaced in the sample tube and

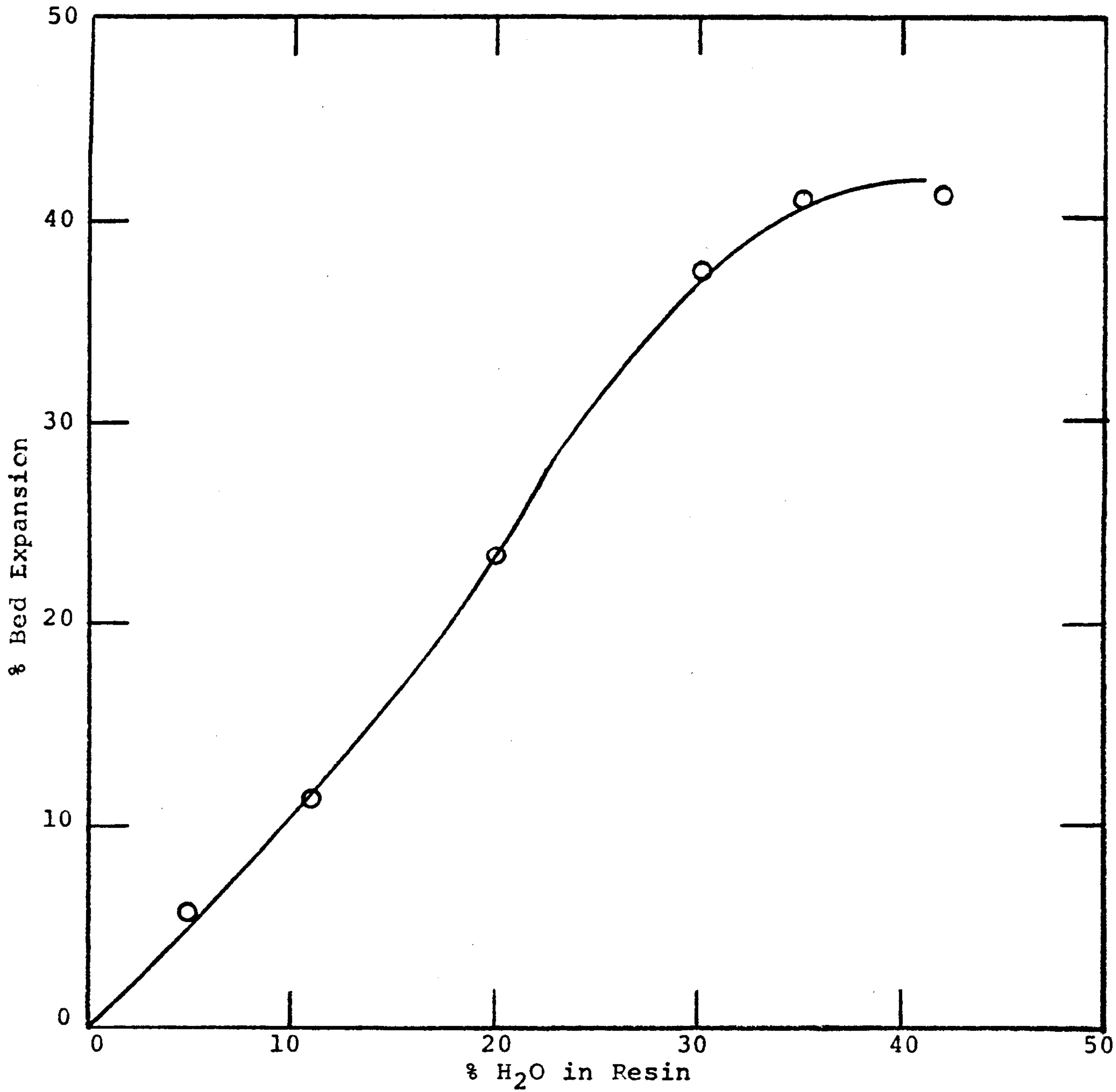


FIG 17 - THE EFFECT OF WATER CONTENT ON RESIN SWELLING - IR-45 retested versus the CO_2 gas stream. Negligible half-lives resulted and it appeared that residual CO_2, left on the resin after regeneration, had the effect of poisoning the sorbent for subsequent CO_2 sorption cycling.

In an attempt to correct this condition, the water temperature of the regeneration step was increased to 95-98°C. The exposure of the resin to the hot water was stopped when no further gas evolution occurred. The resin was then centrifuged as before (5 min @ 500 rpm) and reloaded into the sample tube for sorption testing. Some improvement in half-lives was noticed as they ranged from 10-25 min for IR-45 regenerated in this manner. While these were shorter than the half-life of fresh unused material, they were considerably better than the ~1 min values secured after the 80°C regeneration method. At this point, the relative humidity of the test gas stream was changed from 50% to 90% and increase in CO_2 capacity for IR-45 was observed.

Preliminary testing had indicated poor CO_2 recovery but suggested that CO_2 desorption is complete using water in excess of 190°F. The apparatus shown in Figure 18 was used for hot water regeneration studies. Regeneration water is collected in a flask of boiling water (the CO_2 solubility at this temperature is essentially nil). The CO_2 is measured by displacing water in calibrated cylinders. Initially oil was used in the gas collection apparatus; however, it was found that the rate of solution of 100% CO_2 collected over water was very slow (~1 cc/hr) and this would not cause significant error. An attempt was made to eliminate the gas burette and measure the CO_2 on a LIRA analyzer. The CO_2 was diluted with a known amount of air to 1-2% CO_2 concentration and the streams were passed through the analyzer. This was not effective as the CO_2 was not evolved as a steady stream but slugging occurred and this resulted in considerable fluctuations in the LIRA meter. The meter readings were recorded continuously, but the fluctuations gave a poor graph and, although an indication of the rate could be observed, only an approximation of the total amount could be obtained.

During these studies we also encountered runs in which more gas was evolved than was adsorbed as CO_2. This was traced to dissolved gas in the water and was corrected by either using air-saturated water and then subtracting the air input from the total gas evolved, or by the more preferred method of using water that was pre-boiled immediately prior to use in the regeneration.

In six preliminary regeneration experiments, it was found that the rate of regeneration appears dependent on how fast the bed temperature can be elevated to 180-200°F. In our system with a 23.5 g bed, a 20 cc/min water flow yielded 90% regeneration in about 20 minutes and at a 60 cc/min flow, 90% regeneration was achieved in 10-15 minutes. At this point, no deterioation of resin sorption capability or particle strength was observed.

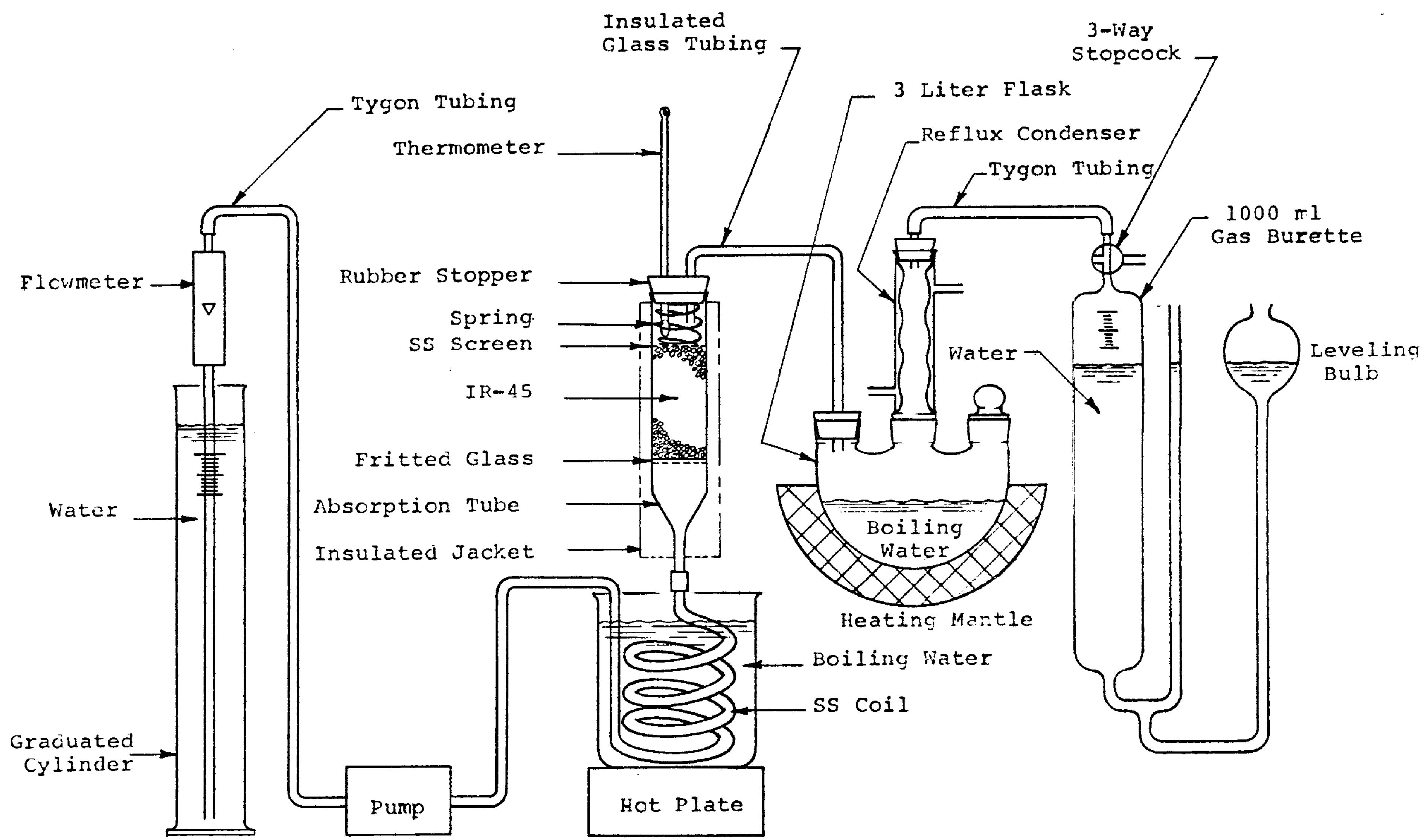


FIG 18 - LABORATORY HOT WATER REGENERATION APPARATUS

The study was continued and several regeneration runs were made to determine the effect on adsorption after stopping the regeneration at 10 minutes. Three consecutive 10 minute regeneration cycles were made after three 12 minute adsorption runs. A buildup of residual CO_2 occurred as 95, 69 and 63% of the total CO_2 was removed in the three regeneration cycles. The residual CO_2, however, had an insignificant effect on the subsequent adsorption cycles, at least as far as the initial 12 minutes was concerned. After the three 10 minute regeneration cycles, a 50 minute regeneration (14th cycle) was made and all the CO_2, including residual, was removed. The results of this series is shown in Table 14.

In addition to adsorption runs to initial (0.02-0.04% effluent CO_2) break, runs which were taken to 0.2% CO_2 effluent were also regenerated. Two cycles (15 and 16) were made at this latter condition and 80-90% of the CO_2 was recovered after 15-20 minutes at a water flow of 60 cc/min. Complete regeneration required 45-50 minutes. After 16 adsorption/hot water regeneration cycles the resin appeared unchanged in activity and in particle strength. However, the problems associated with reduction of the bed water content to 20% were considerable, and another regeneration approach was sought.

Steam Regeneration

McConnaughey[50] had found that resins could be regenerated by passing steam through the spent bed. Such a regeneration cycle would prove undesirable in a space application because of considerable heating and cooling requirements, as well as the difficulty of separating water from CO_2 in space.

A steam regeneration technique was conceived where CO_2 is evolved chromatographically. Consider a spent ion exchange resin column as shown schematically in Figure 19. Water is boiled and steam is condensed on the resin in much the same fashion as during the startup of a distillation column. In this case, however, the condensed fluid is absorbed on the packing and the latent heat of the vapor is transferred to the solid. As steam is generated, the condensing "ring" moves up the column displacing air and carbon dioxide ahead of it. Because of the increase in partial pressure of CO_2 ahead of the condensing ring, CO_2 is reabsorbed such that the air originally in the bed is eluted more rapidly than the CO_2. If we assume that CO_2 desorption is complete whenever a resin particle attains 212°F, then we can assume the desorption of CO_2 from the bed should be complete when the temperature of the effluent gas reaches 212°F. Another feature of this regeneration mode is the self-correcting character of steam flow through the packed bed, thus minimizing channeling. Wherever there are sites in the bed which are cold, these sites act as condensation points with the water serving to increase the pressure drop. This forces steam to be condensed elsewhere such that the bed has a very uniform temperature in any cross-sectional plane.

TABLE 14—HOT WATER REGENERATION OF IR-45

Run No.	Cycle No.	Ads. Cycle (min)	Maximum Effluent CO_2 Conc (%)	CO_2 Input mg	Residual CO_2 mg	Regeneration H_2O Input cc/min	Regeneration Time (min)	Regeneration Max. Effluent Temp.	CO_2 Rec. (mg)	% CO_2 Input Rec.	% Total CO_2 Rec.
1197-1	11	12	0.016	202	0	60	10	207	193	95.5	95.5
1197-2	12	12	0.038	198	9	60	10	208	143	72.5	69.1
1197-3	13	12	0.028	202	64	60	10	208	169	83.9	63.5
1197-4	14	12	0.044	196	97	60	50	209	293	100.0	100.0
1197-5	15	32	0.200	490	0	60	45	208	306	103.0	--
1197-6	16	33	0.205	485	0	60	50	208	552	113.8	--

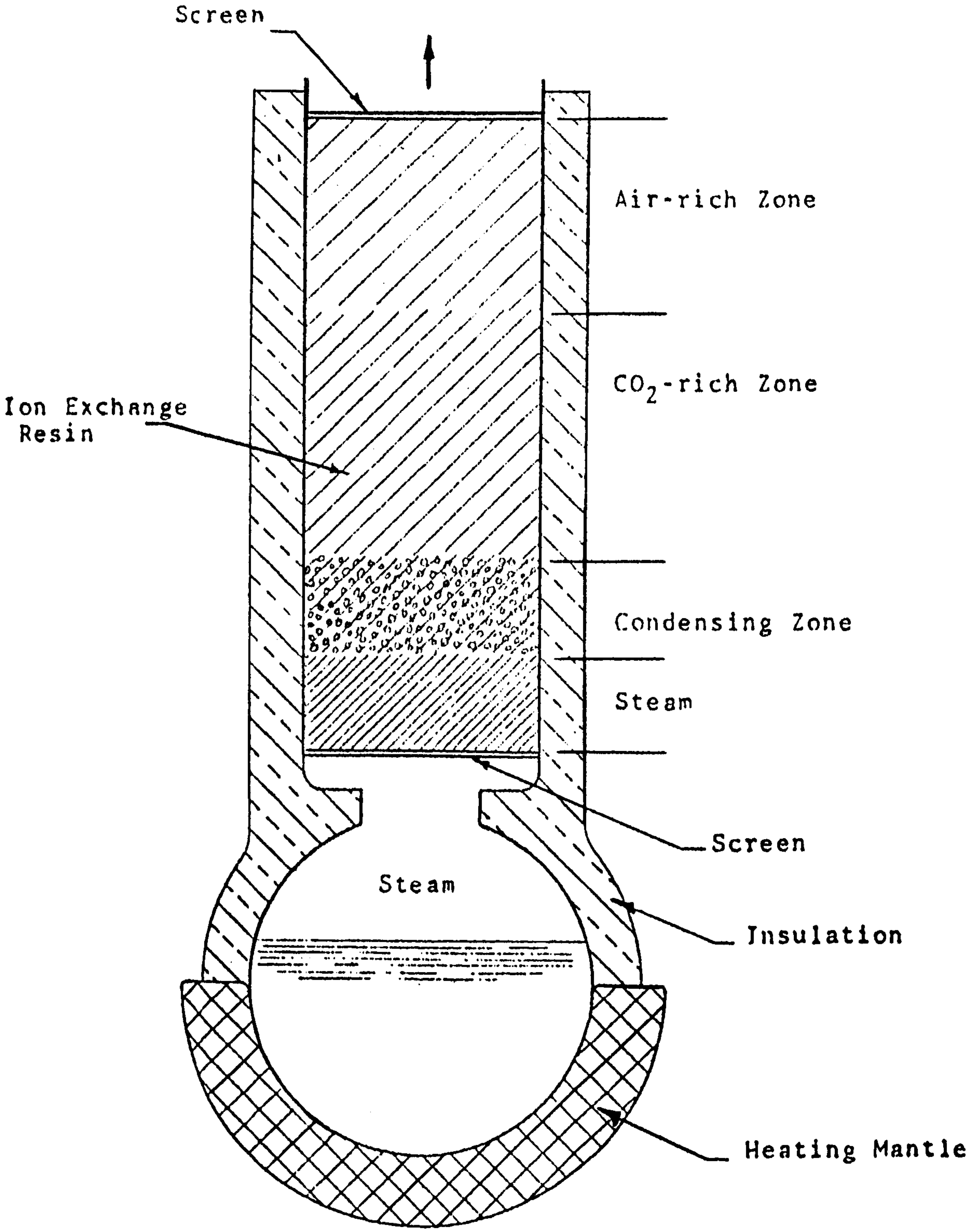


FIG 19 - CHROMATOGRAPHIC STEAM REGENERATION OF SPENT ION EXCHANGE RESIN

An attractive feature of the steam elution technique is that the amount of steam that is necessary to regenerate the bed is quite predictable, if we assume a perfectly insulated column. That is, the amount of steam necessary to supply the process is a function of:

1. Heat capacity of dry resin between room and regeneration temperatures.

2. Heat capacity of absorbed water between room and regeneration temperatures.

3. Dissociation energy to form CO_2.

4. Sensible heat of displaced air.

5. Sensible heat of desorbed CO_2.

6. Heat capacity of the canister.

In the first steam regeneration test steam was generated from boiling water contained in a 250 ml flask placed immediately beneath the adsorption tube. The latter was placed in an insulated jacket but no external heat was applied. Steam was distilled into the column until the head temperature above the IR-45 bed reached 200°F, at which point the regeneration was assumed completed. The CO_2 was collected and measured in a gas burette over water as in the hot water regeneration runs. The apparatus is shown in Figure 20.

Initial laboratory sorption tests showed the chromatographic steam regeneration to be feasible. A total of 10 cycles were made in the 1.22 in. diameter tube with 23.5 g of IR-45 (2.625 bed depth), a flow rate of 2 l/min (8.6 ft/min) and the CO_2 concentration at 0.5% and 90% RH. Six runs were stopped after a 12-minute adsorption cycle or just past initial break and four runs were taken to 0.25% CO_2 effluent concentration. The average CO_2 pickup to initial break was 0.67% for the 10 cycles. The average wt % pickup for the final 4 cycles to 0.1% and 0.22% effluent concentration was 1.64 and 2.3% respectively. The average time to reach 0.22% CO_2 effluent concentration was 34.9 minutes.

Regeneration was effected by passing a slow stream of steam through the insulated column until the effluent temperature reached 205-210°F. No external heat was applied to the column. The regeneration rate was dependent on the steam generation rate and regeneration times of 6 minutes (2.2 ml H_2O/min) to 80 minutes (0.2 ml H_2O/min) were equally effective. In all cases, the regeneration is essentially complete when the steam reached the top of the column, regardless of the amount of CO_2 present or the time required to reach 205-210°F. The bed was finally dried back to 20% water content by passing air through the bed at 2 l/min flow and the bed was mixed before the next adsorption run.

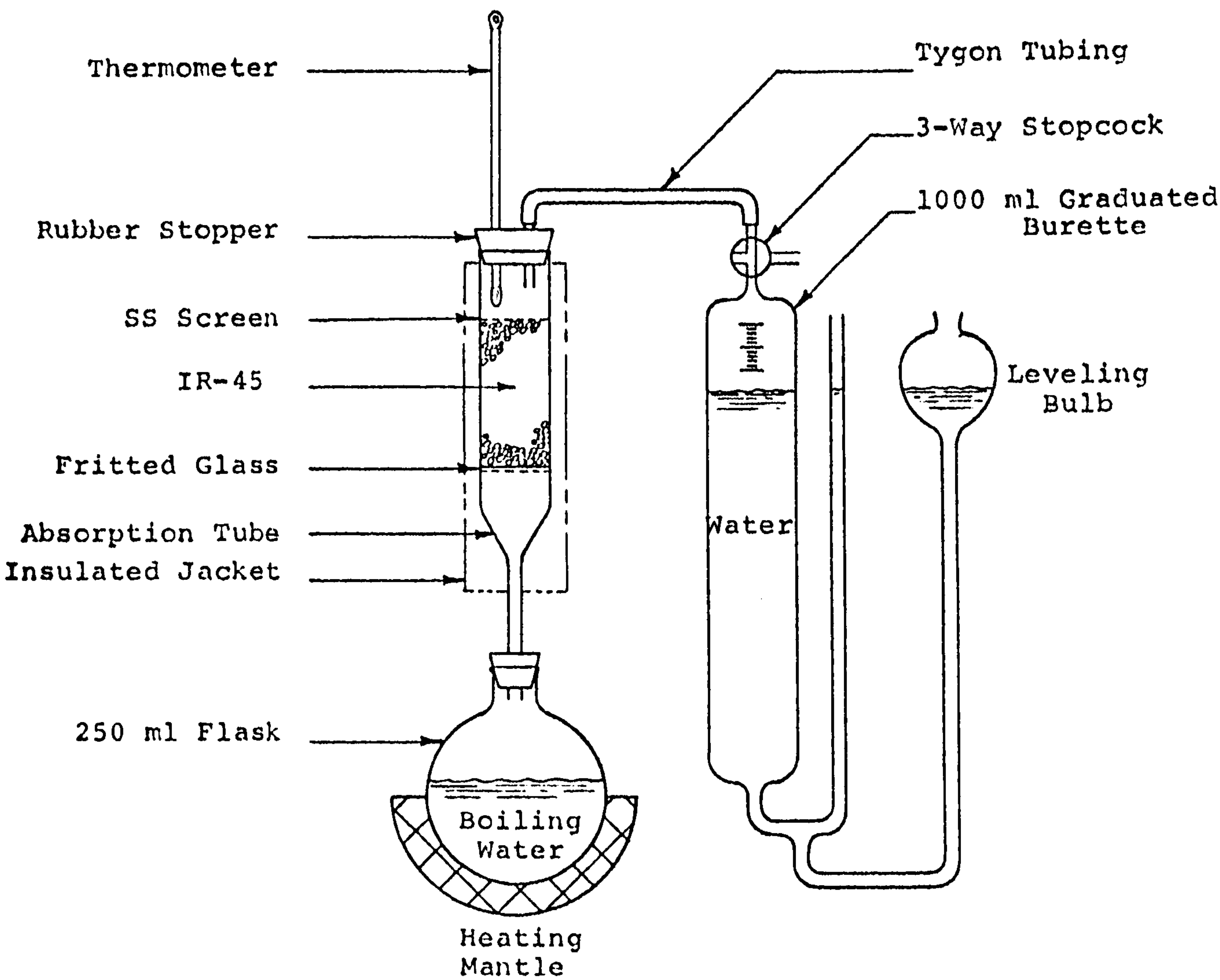


FIG 20 - LABORATORY STEAM REGENERATION APPARATUS

Despite the fact that effective regeneration was attained as determined by the succeeding adsorption cycle, the CO_2 recovery, measured by collecting CO_2 in a gas burette, was poor. Two cycles yielded 99.5% recovery, 6 cycles 81-86% and 1 cycle 108.5% recovery. The poor material balances were attributed to the low CO_2 quantities involved and when larger beds were examined, more consistent and considerably better balances were obtained.

Experiments have been performed to show that an ion exchange resin can be regenerated exactly as hypothesized. In a typical experiment, done in simple fashion as shown graphically in Figure 19, IR-45 was completely generated by steam. This was performed on a bed 1.22 in. diameter and 3 in. long. Figure 21 shows the volume of gas evolved as a function of time. The temperature was measured at the effluent end of the bed and temperature readings are superimposed on the time axis. Relatively little gas is displaced from the bed until the temperature of the effluent gas is 82°F, at which point gas evolution is considerable. Analysis of the gas delivered below 82°F showed the CO_2 composition of the air to be approximately 1%, while that fraction displaced between 82°F and 206°F was 92% CO_2, with the balance air and water vapor. The bed was retested in an adsorption cycle and its life was equivalent to that prior to desorption. Such cycles have been repeated at least 15 times on one sample.

In order to minimize heat losses, and also to gain an insight into the capacity in a bigger bed, the adsorption tube was scaled up from 1.2 in. to 3.187 in. diameter. The bed depth was kept at 2.625 in. and the flow was increased accordingly to 13.5 l/min, maintaining the linear flow of 8.6 ft/min.

Adsorption was again run at 90% RH and 0.5% CO_2 concentration. All runs were taken to 0.3% CO_2 effluent concentration and the data are summarized in Table 15.

It is to be noted that cycles 8 and 9 indicated poor adsorption characteristics and were attributed to an exhausted Baralyme column used in removing CO_2 from air. The drying air contained CO_2 and the resin bed was partly consumed during this operation. Consequently, a poor capacity in the adsorption cycle was indicated and an excessive amount of CO_2 was recovered on regeneration. Recovery is noted in cycles 10 and 11 after the Baralyme was replaced.

Regeneration of the larger bed was effected in the same manner as with the small tube studies. Steam was generated from water contained in a 1 liter flask placed immediately beneath the adsorption tube. The evolved gas was measured with a wet test meter. No attempts were made to separate or isolate the air or CO_2 fractions. Again, as in the prior studies, the regeneration rate was dependent on the steam generation rate. Regeneration times of 11 minutes (3.1 ml H_2O/min) to 26 minutes (1.5 ml H_2O/min) were employed. The regeneration data is summarized in Table 16. Using the larger resin bed and the higher CO_2 inputs, good CO_2 material balances were obtained. In 7 of the 11 cycles, 95-101% of the adsorbed CO_2 was recovered.

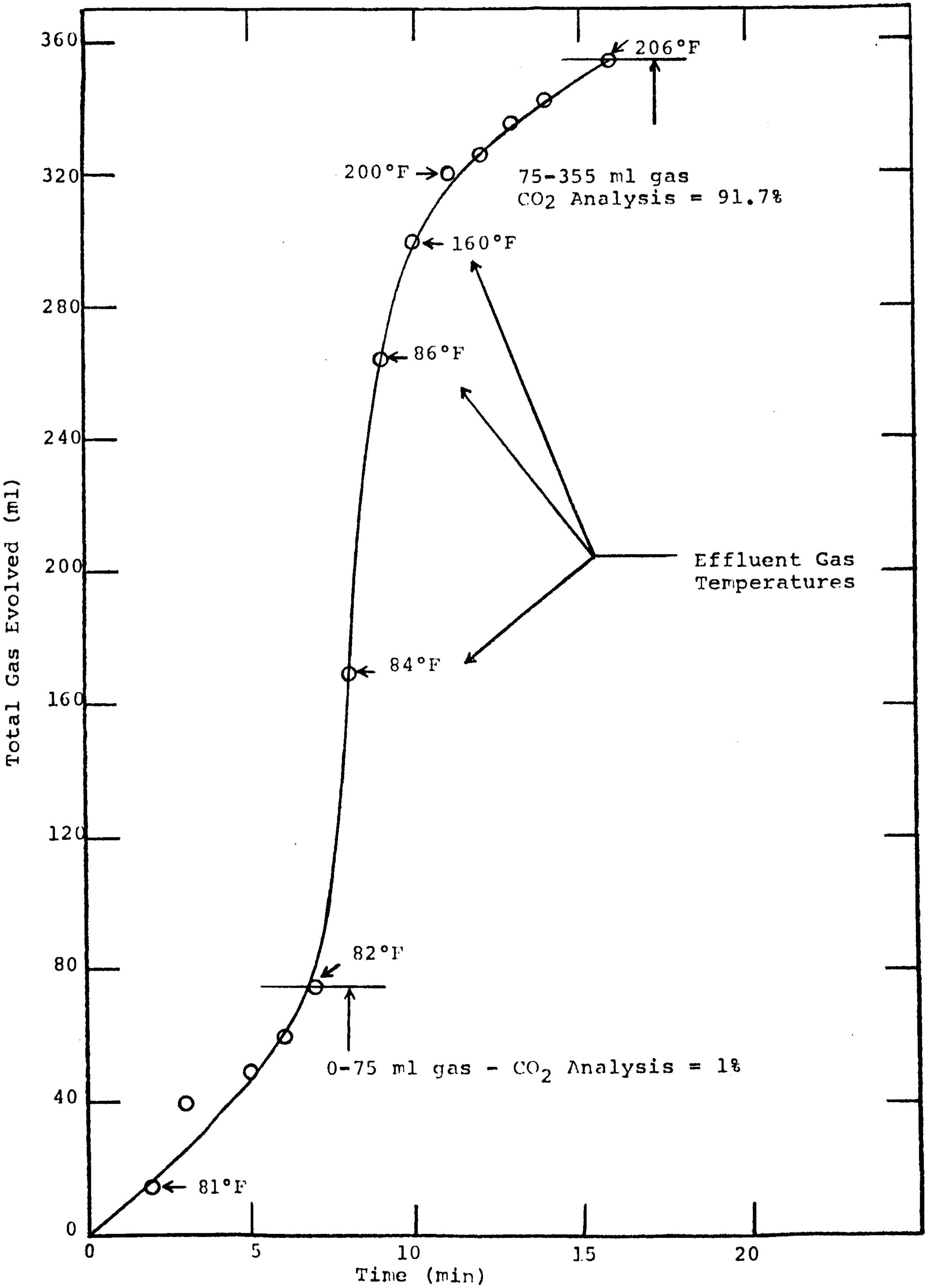


FIG 21 - GAS EVOLUTION DURING STEAM REGENERATION OF IR-45

TABLE 15 - ADSORPTION CYCLES - 3.187" DIA TUBE

Conditions: 195 g IR-45 containing 20% H_2O, 2.625" bed depth, 90% RH, 0.5% CO_2 conc., 13.5 l/min, 8.6 ft/min flow.

Run No.	Cycle No.	ΔP mm H_2O	Time to Different Effluent CO_2 Conc. (min): Initial Break	0.1% CO_2	0.2% CO_2	0.25% CO_2	0.3% CO_2	Wt % Pick-up at Different Effluent CO_2 Conc.: Initial Break	0.1% CO_2	0.2% CO_2	0.25% CO_2	0.3% CO_2
1197-31	1	17	6.0	11.0	17.0	46.0	59.0	0.38	0.65	0.88	2.24	2.36
1197-34	2	18	4.5	18.3	27.0	32.0	37.0	0.33	1.25	1.69	1.89	2.12
1197-36	3	18	5.0	18.3	27.7	32.4	39.0	0.37	1.26	1.73	1.93	2.16
1197-38	4	18	3.5	20.0	30.0	35.0	41.0	0.26	1.37	1.88	2.08	2.28
1197-41	5	18	2.5	17.0	27.2	32.2	37.5	0.18	1.14	1.66	1.86	2.04
1197-43	6	20	1.5	13.5	27.2	34.0	42.5	0.11	0.89	1.60	1.87	2.14
1197-45	7	26	1.0	14.8	26.0	31.5	38.0	0.07	1.00	1.57	1.81	2.01
1197-47(1)	8	19	0.0	11.0	21.9	27.2	34.0	0.0	0.74	1.30	1.52	1.74
1197-49(1)	9	18	0.0	10.2	18.2	22.3	27.5	0.0	0.68	0.91	1.12	1.29
1197-51	10	18	0.5	13.8	26.0	33.2	42.0	0.04	0.92	1.55	1.83	2.11
1197-53	11	19	2.0	15.7	28.2	36.0	44.0	0.15	1.07	1.69	2.00	2.28

(1) CO_2 inadvertently ddsorbed during drying cycle indicating low capacity and high CO_2 recovery (see Table 4).

TABLE 16 - STEAM REGENERATION CYCLES - 3.187" DIA TUBE

Run No.	Cycle No.	Adsorption Run Time (min)	CO_2 Adsorbed (ml)	Regeneration Time (min)	Steam Rate (ml H_2O/min)	Drying Time (min)(2)	IR-45 (1) Water Content After Steam Treatment (%)	CO_2 Recovered (ml)	CO_2 Recovered (% of Adsorbed)
1197-31	1	59.0	2180	15	3.5	180	34.0	2176	99.8
1197-34	2	37.0	1970	18	2.9	245	33.0	1968	100.0
1197-36	3	39.0	1980	17	3.2	180	34.5	2018	101.6
1197-38	4	41.0	2095	16	3.4	210	34.0	2119	101.0
1197-41	5	37.5	1890	11	3.1	90	29.8	2027	107.2
1197-43	6	42.5	1980	12	3.0	95	29.1	2006	101.0
1197-45	7	38.0	1840	26	1.5	60	29.7	1962	106.7
1197-47(1)	8	34.0	1585	25	1.5	95	29.8	1816	114.5
1197-49(1)	9	27.5	1190	23	1.6	150	29.7	1951	164.0
1197-51	10	42.0	1950	22	1.6	130	29.8	1893	97.0
1197-53	11	44.0	2100	17	2.2	225(3)	30.9	2009	95.5

(1) CO_2 picked up during drying cycle.

(2) 13.5 l/min air at 20% RH. Air passed into bed at 200°F. Bed mixed before next adsorption cycle.

(3) Air passed into bed at 75°F.

In addition to the 11 cycle series, a run was made in a 13 inch long tube. In this run 750 g IR-45 containing 20% water was used. The flow rate was increased to 15 l/min providing a linear flow of 9.55 ft/min through the 10 in. bed depth. The contact time, however, was 5.24 seconds as compared to 1.53 seconds in the 2.625 in. bed. The increased contact time provided larger CO_2 capacities. The weight % CO_2 pickup was 1.04% at the initial break point and 2.20, 2.38, 2.56 and 2.66 at 0.1, 0.2, 0.25 and 0.3% effluent CO_2 concentration. The pressure drop in the 10 inch bed, however, was increased accordingly to 97 mm H_2O as compared to 25 mm H_2O in the 2.625 inch bed. A faint organic odor was detected in the steam regeneration cycle, particularly in this run. The odor appeared similar to toluene and may have been organic solvents used in resin manufacture that were steam-distilled out.

Regeneration at Reduced Pressure - Several tests were run at a total pressure of 380 mm to evaluate the degree of regeneration obtained with 180°F steam. We found that desorption was incomplete at that temperature, and the resin gradually lost its capacity. It was fully restored, however, by 212° steam. Although some intermediate temperature would most likely be satisfactory, the normal boiling point was selected as the design value for the laboratory model (which will be operated at 1 atmosphere). These tests also showed that the desorption rate could be increased appreciably by supplying the steam more rapidly.

Bed Conditioning

Experiments were performed to determine the optimum direction for air-drying the bed and cooling it prior to the absorption cycle. It was found that the drying air cycle, when countercurrent to the absorption air cycle, left the influent side of the bed with a higher water content. A higher CO_2 capacity was observed then when drying air and the process air were moved in the same direction. Later the advantages of cooling the bed with room (CO_2-containing) air were realized, obviating the countercurrent drying cycle.

In air drying, it was observed that the bulk of the water vapor was evolved in the first few minutes of air drying. Attempts to precool the bed by external cooling prior to air cooling resulted in a prolonged drying cycle.

The effect of moisture content on sorption capacity was again evaluated, but with the larger bed. The earlier results were duplicated in that a cooler content between 20 and 28% was found to be most effective.

The ΔP in the 2.625 in. bed at 13.5 l/min flow is about 20 mm H_2O. However, after steam regeneration, condensed water exists in the bed and the average moisture content of the bed has increased from 28 to 37%. When drying air is passed through the bed, there is an initial increase in ΔP. This has been measured for 2 cycles and found to be of the order of 200 mm H_2O or a 10-fold increase. This rapidly decreased as the free water is blown from the bed and the ΔP is at 20-30 mm in a few minutes.

Stability

All experiments with the larger bed had employed a single charge and all studies have been made with the same bed. A total of 38 cycles has been recorded with no indication of degradation in activity or in particle size. The faint organic odor detected in the first 29 cycles was hardly detected even at the 210°F steam regeneration temperature after cycle 29.

Extensive Cycling Studies

An MSAR-sponsored study was performed on cyclic absorption regeneration of IR-45. It is included here to complement LRC-sponsored information. The initial purpose of this project was to build an apparatus for testing the cyclic life of an amine resin and to operate this automatic system through one thousand absorption and regeneration cycles (2000 hours). Periodic absorption rate measurements were made during the operation. The project included the following:

1. Correlate the effects of steam temperature on moisture content of an IR-45 resin bed.

2. Construct an automatic cycling system using an unheated bed and modified to include reverse-flow air drying.

3. Mass balance studies.

4. The 1000 cycle life test.

A schematic of the apparatus used for this study is shown in Figure 22.

The typical resin bed had a diameter of 1 3/8 in. and its height, when filled with a 42 gram sample of IR-45, was approximately 3 in. The resin sample was 80% by weight dry resin with the remainder approximately 20% water. The humidity range was fixed by the aforementioned water bubbler and the absorption gas composition was fixed by metering in 1.5% (by volume) CO_2.

During the absorption, 1.5% CO_2 in the air at 2 liters/min was passed through the bed for 30 minutes (approximately 210 cm/min). Regeneration was accomplished with 220-240°F steam at 2 cc (condensate)/min for 4.0 min (0.2 cm/min). The drying step was effected by passing CO_2-free air at 6.5 liters/min through the bed for 24 min (680 cm/min).

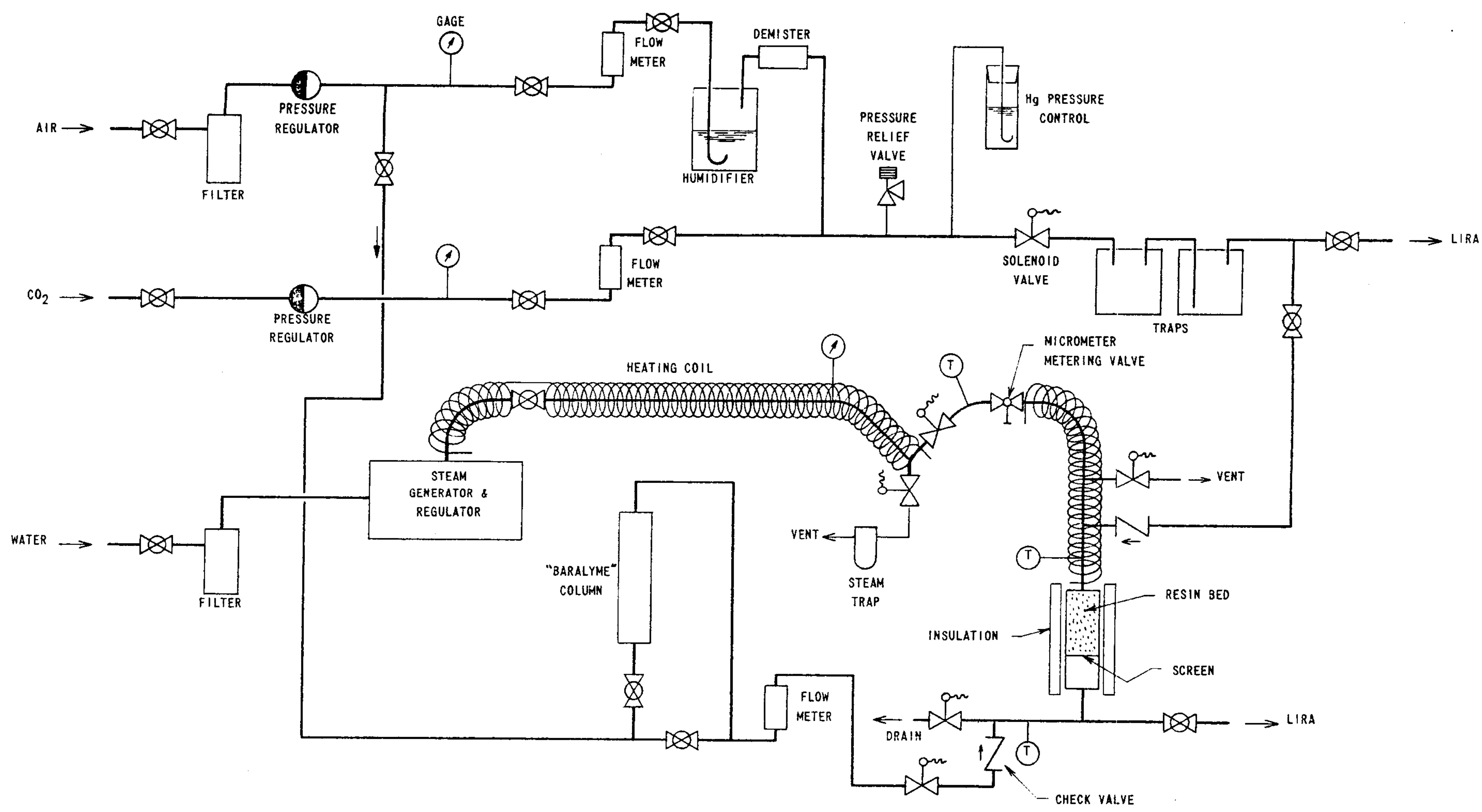


FIG 22 - STEAM REGENERATION APPARATUS

The mass balance studies that were conducted demonstrated the feasibility of maintaining an IR-45 resin bed at a constant moisture level corresponding to approximately 20-25% Wt% of the bed. Absorption rate analysis showed that the resin was significantly regenerable, even though it was exposed to up to 240°F steam for a total of 70 hours during the 1029 cycles. Although there was an estimated 5% reduction in the resin CO_2 sorption capacity toward the end of the cycling regimen there is evidence that this effect could be markedly reduced, or eliminated completely. This can be done by (1) increasing the steam regeneration time and (2) reducing the steam temperature.

Large Bed Studies

Another MSAR-sponsored study was conducted. In this investigation, approximately 1/4 cu ft of IR-45 (8.1 lb) was used as the sorbent. It was contained in a 6 in. diameter canister and had a bed depth of approximately 18 in. Carbon dioxide at 0.5% was passed through the bed with an air flow of approximately 4 1/4 cu ft/min and a velocity of 22 ft/min. The bed life, or time necessary for the effluent CO_2 concentration of the bed to reach 0.2%, approximated two hours. The bed was successfully regenerated with hot steam in the manner of other steam regeneration studies. While only a few cycles have been run to date, there is no evidence of bed deterioration. In fact, the bed life (defined above) on the fourth cycle was found to be 153 min versus 123 min for the first sorption cycle.

The latter, large-bed system, was also used to verify another important advantage of resin CO_2 sorbents - no auxiliary cooling of the bed is necessary after regeneration, the next absorption cycle can be started immediately. Briefly, the moisture level of the resin bed is increased markedly with condensed steam. The bed is also hot, via the latent heat of condensation of the steam which is left as sensible heat. The absorption cycle is started and the air stream lowers the temperature of the leading edge of the bed by evaporative cooling. This cooling front now advances through the bed, preceding the sorption front. As shown in Figure 23, the CO_2 capacity of the bed is restored. Successive cycles do not degrade bed performance. Mass spectrographic analysis of the effluent gas stream during regeneration yielded CO_2 containing less than 0.4% total $O_2 + N_2$.

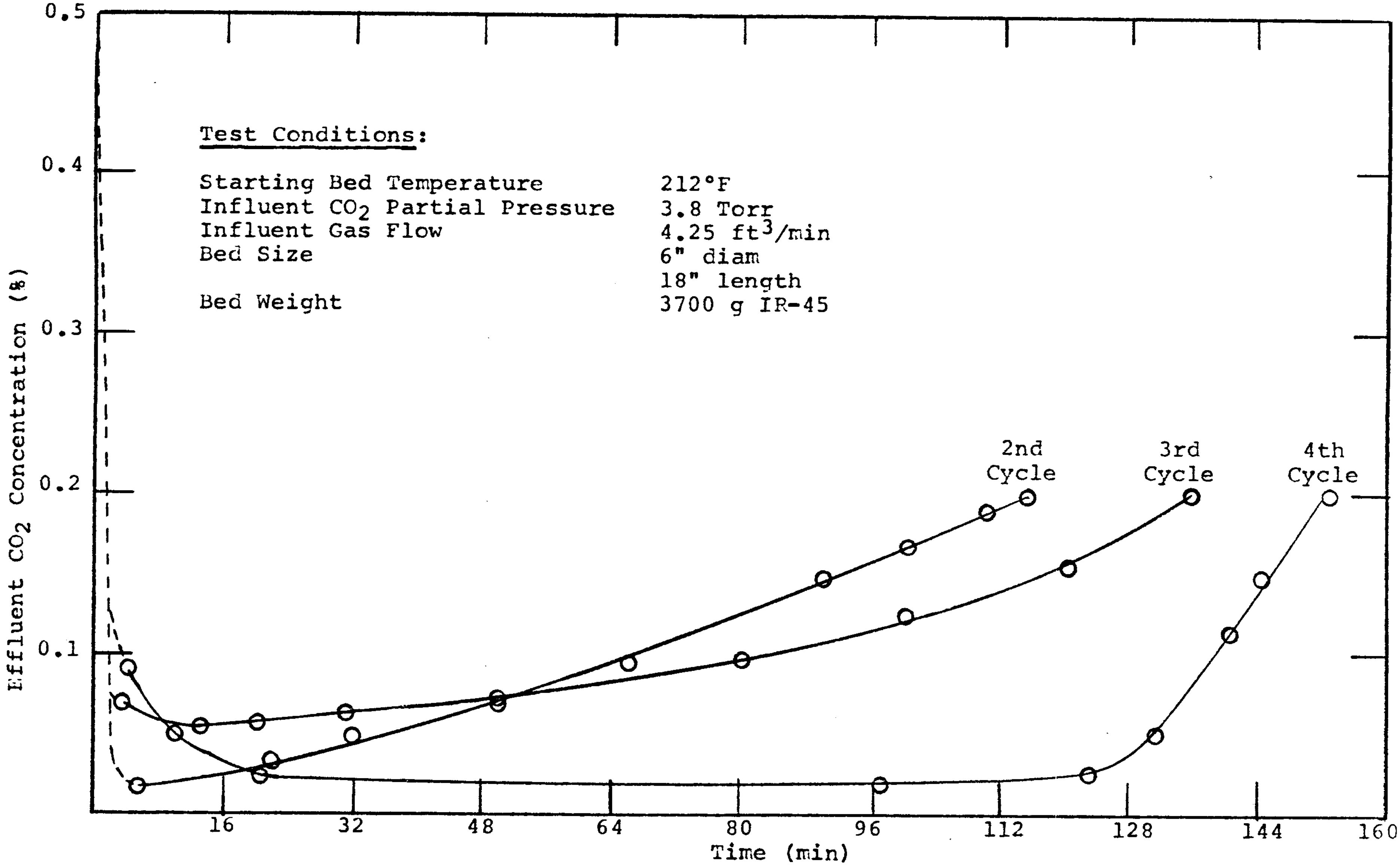


FIG 23 - CO_2 SORPTION PERFORMANCE OF A HOT, WET IR-45 RESIN BED

PRELIMINARY DESIGNS

Introduction

Three types of systems were considered in the development of a laboratory model system. In each of the systems, the desorption cycle is different - specifically vacuum, hot water or steam regeneration techniques.

The purpose of this section is to detail the disadvantages and merits of the first two approaches and to summarize preliminary design efforts that were performed during the program. The following sections describe in detail the laboratory model that is being submitted to LRC and gives some operation characteristics. In this and in subsequent sections, only one resin, IR-45, is considered from a system point of view. This resin appears to offer the greatest possibility of those that are commercially available. Resins synthesized in the laboratory were not evaluated in sufficient detail to allow these others to be considered for application at this writing. However, it is quite reasonable to assume that resin development could lead to the systems that offer distinct advantages over that based upon IR-45.

Vacuum Regeneration

The optimum conditions for CO_2 absorption by all of the resins studied, is one where the resin is in equilibrium with air saturated with water vapor. While most of the work performed was done at 75°F, there is reason to believe that the equilibrium capacity for CO_2 at a given RH would increase with a decrease in temperature. However, this increase in CO_2 capacity might be gained at the expense of the sorption kinetics for CO_2. Thus, optimum sorption temperatures probably lie someplace in the region of about 55-75°F.

Reconsidering Figure 14 , if it is assumed that the only function of the resin system was to remove CO_2, then it is preferable that the system operate at high relative humidity. However, such operation poses a number of operational difficulties and power-weight penalties. For instance, if 20% absorbed water is chosen as a design point to start the CO_2 absorption cycle, then a CO_2 capacity of approximately 2-2.5% by weight is attained, depending upon influent concentration and maximum allowable CO_2 effluent concentration. Laboratory studies described earlier show that water lost from the resin precedes the desorption of

CO_2. Therefore, in vacuum desorption it would be necessary to evaporate as much as 10 weights of water for every weight of CO_2, or approximately 25 moles of H_2O/mole CO_2. After vacuum regeneration, it would then be necessary to replace the water in some fashion prior to the absorption process. This replacement can be achieved through either liquid water injection or by water absorption from the air.

Another operational difficulty involves the requirement for a homogeneous means of heating of the bed to affect desorption. Heat transfer measurements were performed with both molecular sieves and IR-45 to measure and compare heat transfer during external heating of a packed bed. The molecular sieve experiment served as a method check. The bed container was an aluminum cylinder 5 inches in diameter and 5 inches high and an external nichrome resistance element provided heating. Temperatures were measured with mercury thermometers inserted into the bed at various distances from the heater. Initial tests were conducted in air, and it was apparent that most of the heat conduction was being accomplished by the mechanism of convection of air and water vapor, since both the sieve (Linde 13X) and IR-45 experienced similar heating rates and had similar temperature gradients.

In a vacuum environment, after being completely dried, the ion exchange resin appeared to have a slightly higher heat conduction. Approximately 50 minutes was required to attain an axial temperature of 130°F, with a temperature gradient of 63°F. The sieve required approximately 70 minutes to attain the same axial temperature, only the temperature gradient was 81°F. Tests were performed where ion exchange resin containing 20 wt % water was externally heated in the 5 inch bed while vacuum was simultaneously applied to the canister. Even though thermometers located at the periphery of the canister registered 212°F, the temperature within the 5 inch diameter bed decreased to less than 50°F, and in one experiment, ice was noted during attempts to regenerate the resin. Based upon these preliminary experiments, it was assumed therefore that a considerable quantity of heat transfer surface, homogeneously distributed throughout the resin bed, would be necessary to effect rapid desorption, particularly in view of the fact that the amount of water to be evaporated was significantly greater than the CO_2 contained upon the resin.

The dependence of high CO_2 capacity on water content, the necessity for rewetting the bed prior to absorption and the poor heat transfer characteristics in a vacuum regenerable mode resulted in deemphasis of this mode for the laboratory model. However, the possibility does exist that vacuum desorption could become of interest if the resin were to be considered as a means of concentration of both carbon dioxide and water vapor. If we refer back to Figure 12 it is evident that IR-45 has a detectable

CO_2 capacity even when it starts out completely anhydrous. Under these conditions, the resin is a very effective drying agent. It is probable that a bed can be designed so as to have near-quantitative removal of water and CO_2. Regeneration using space vacuum would result in discarding of both CO_2 and water, such that this approach could only be used in those missions where water is in excess and can be discarded.

Hot Water Regeneration

Toward the latter part of the first year of the program, emphasis was directed toward an attempt to evolve a system whereby CO_2 might be recovered for eventual dissociation into useable oxygen. This departure suggested that thermal regeneration could be effected through the use of some heat transfer fluid, and preferably one that could be added directly to the resin bed. The obvious fluid is water, which is necessary for effective CO_2 sorption. Yet, laboratory data suggested that water contents in excess of about 30% interfered with the CO_2 sorption reaction, probably due to the fact that water in excess of that that can be absorbed by resin appears as a second phase and acts as a barrier through which the CO_2 must diffuse. Therefore, methods were considered whereby hot water would be injected into the resin, and after CO_2 regeneration, the regeneration fluid and the CO_2 would be separable from the bed and from each other.

Figure 24 is a schematic utilizing the concept of hot water regeneration. The resin is fixed between screens in a rotating canister during the absorption cycle and CO_2-laden air at 50% RH is forced through the bed while it is immobile. Regeneration is effected by closing electrically operated valves on air entry and air effluent sides of the bed. Hot water (preferably 200-212°F) is injected from a reservoir into the bed as the canister begins to rotate. Addition is through one lead of the rotary union capable of two way flow. The hot water causes CO_2 desorption and excess water is centrifugally separated from the CO_2 and is collected in a channel that is connected to a second two way rotary union for return of the hot water to the reservoir. The CO_2 which forms is vented through a relief valve to the CO_2 collection system. Hot water is recycled until CO_2 desorption is complete. The water pump is shut down and rotation is continued to move excess water from the bed.

Experiments were performed with IR-45 that was fully soaked in water and was then centrifuged to determine the degree of difficulty associated with the separation of excess of liquid water from the resin. It was apparent that even at speeds greater than 1000 rpm the total water content of the resin could not be reduced below about 40 wt %. However, laboratory studies had shown that beyond about 30 wt % water, there is an unfavorable

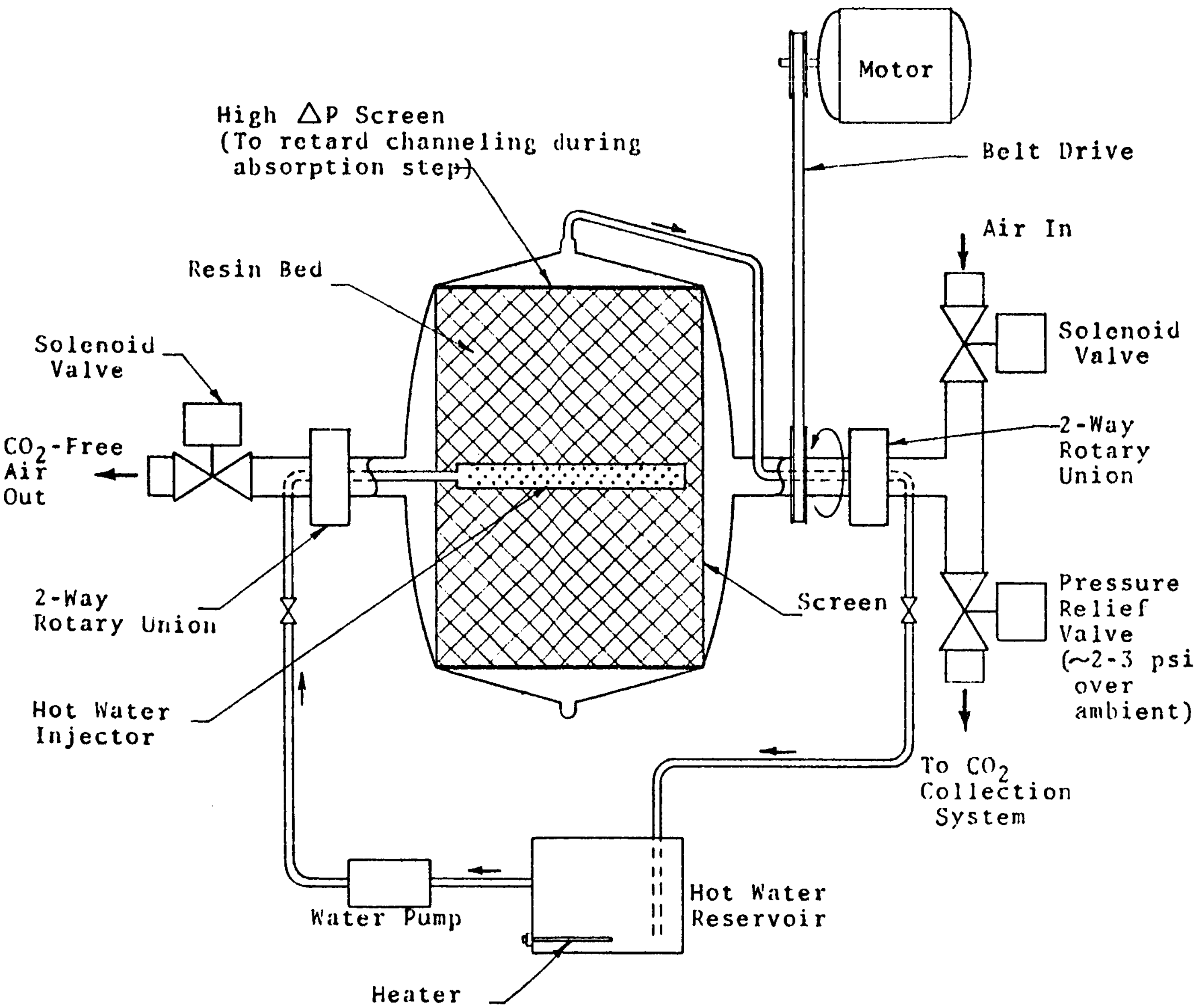


FIG 24- SCHEMATIC OF HOT WATER REGENERABLE RESIN CO_2 REMOVAL SYSTEM reduction in CO_2 sorption kinetics. Therefore, in any system employing centrifugal separation, it is probable that at least one part water must be removed from ten parts of hot water regenerated resin prior to the adsorption step. The power penalty associated with the evaporation and condensation of water and the difficulties associated with the operation of rotating machinery in space suggested that this route would not compete with other CO_2 removal schemes.

Steam Desorption

Experiments suggested that steam would be an effective means of thermally desorbing CO_2 from the resin. A novel means of regenerating spent resin via a chromatographic approach was conceived. Laboratory experiments, detailed in an earlier section, described the effectiveness of this route on a laboratory basis. Detailed discussion of this approach is given in the next three sections.

LABORATORY MODEL DESIGN CHARACTERISTICS

A schematic of the laboratory model supplied to LRC is shown in Figure 25. The single-bed system is designed for a one-hour cycle - 40 minutes absorption, 20 minutes regeneration-desorption. The maximum temperature, at the boiler, is about 220°F.

During the first 40 minutes, the blower forces air through the resin chamber and the condenser. The CO_2 is absorbed as water is simultaneously stripped from the resin. Most of the moisture is condensed. No attempts have been made in this preliminary system to conserve condensate.

The bed is regenerated by steam from the boiler. For the first few minutes, the bed is vented to the cabin, recovering virtually all of the residual air with only minimal CO_2. Then, as the bed temperature rises, the evolved CO_2 is vented through a separate line.

The system is designed to operate automatically and has a nominal CO_2 removal capacity of 0.4 lb of CO_2 per hour. The system is insulated where necessary to minimize heat loss to the room. The boiler and condensate separator is only suitable for 1-G.

Subsystem Details

Resin Chamber - The heart of this CO_2 removal system is a disk-shaped bed of ion exchange resin (Rohm & Haas IR-45). Figure 26 gives dimensions of the resin bed. The moisture content of the resin may vary within certain limits, and such variation is accompanied by changes in volume. These changes are compensated for by encasing the bed with a proportionately thick layer of open-pore polyurethane foam, sufficiently compressed to permit further compression or relaxation within predetermined limits. Lateral surfaces of the foam are blinded to prevent air from by-passing the bed. This maintains a stable geometry, and permits the bed to operate in any attitude. The foam also serves as a bed support or retainer for the resin. It is reinforced with a suitable mechanical structure.

The size of the bed is based on tests in which air with PCO_2 of 3.8 Torr was passed through a 5 1/2 inch thick bed at a velocity of 22 feet per minute. After 38 minutes, the bed had absorbed CO_2 to the extent of 2.34% of its own weight (dry basis). The bed size is:

$$W = \frac{C}{c}\theta \tag{1}$$

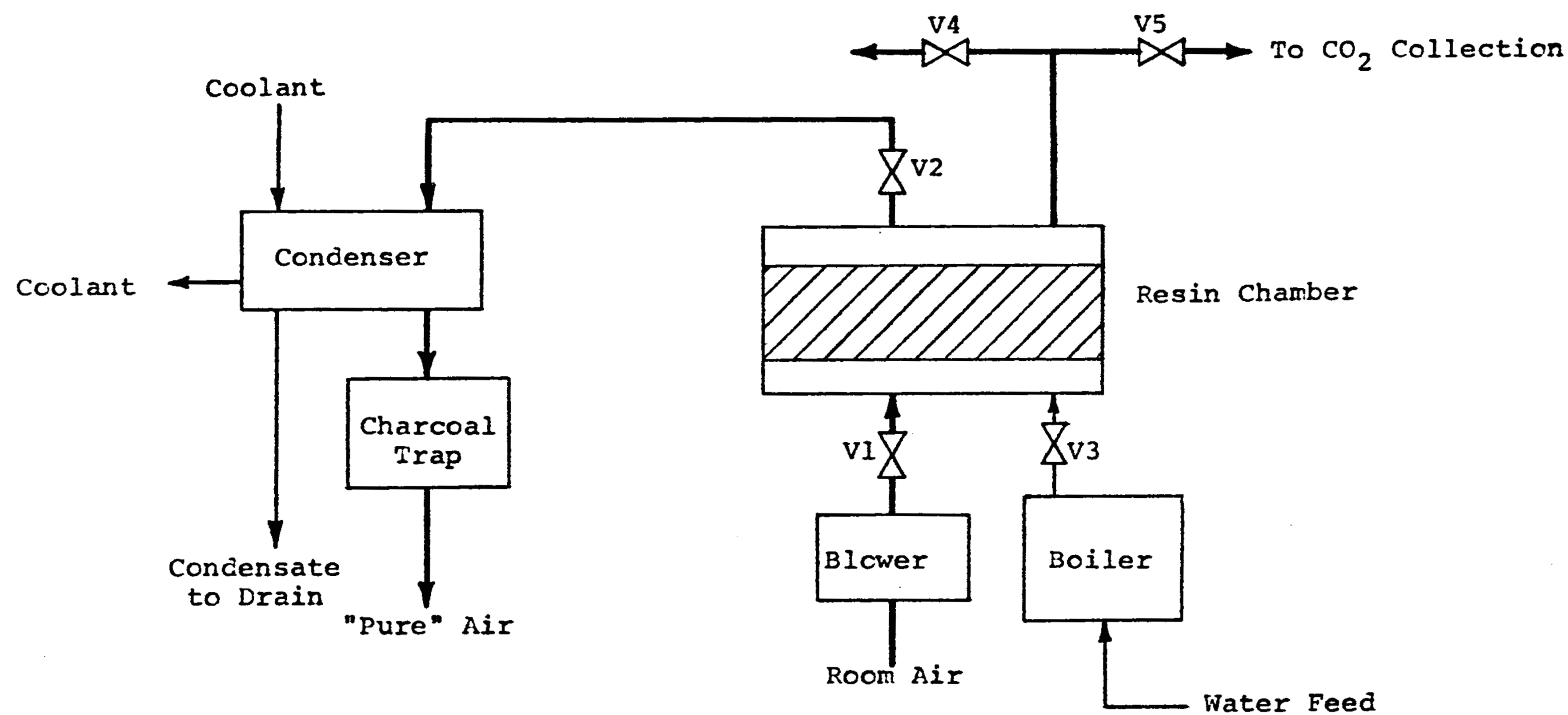


FIG 25 - SCHEMATIC OF LABORATORY MODEL CO_2 REMOVAL SYSTEM

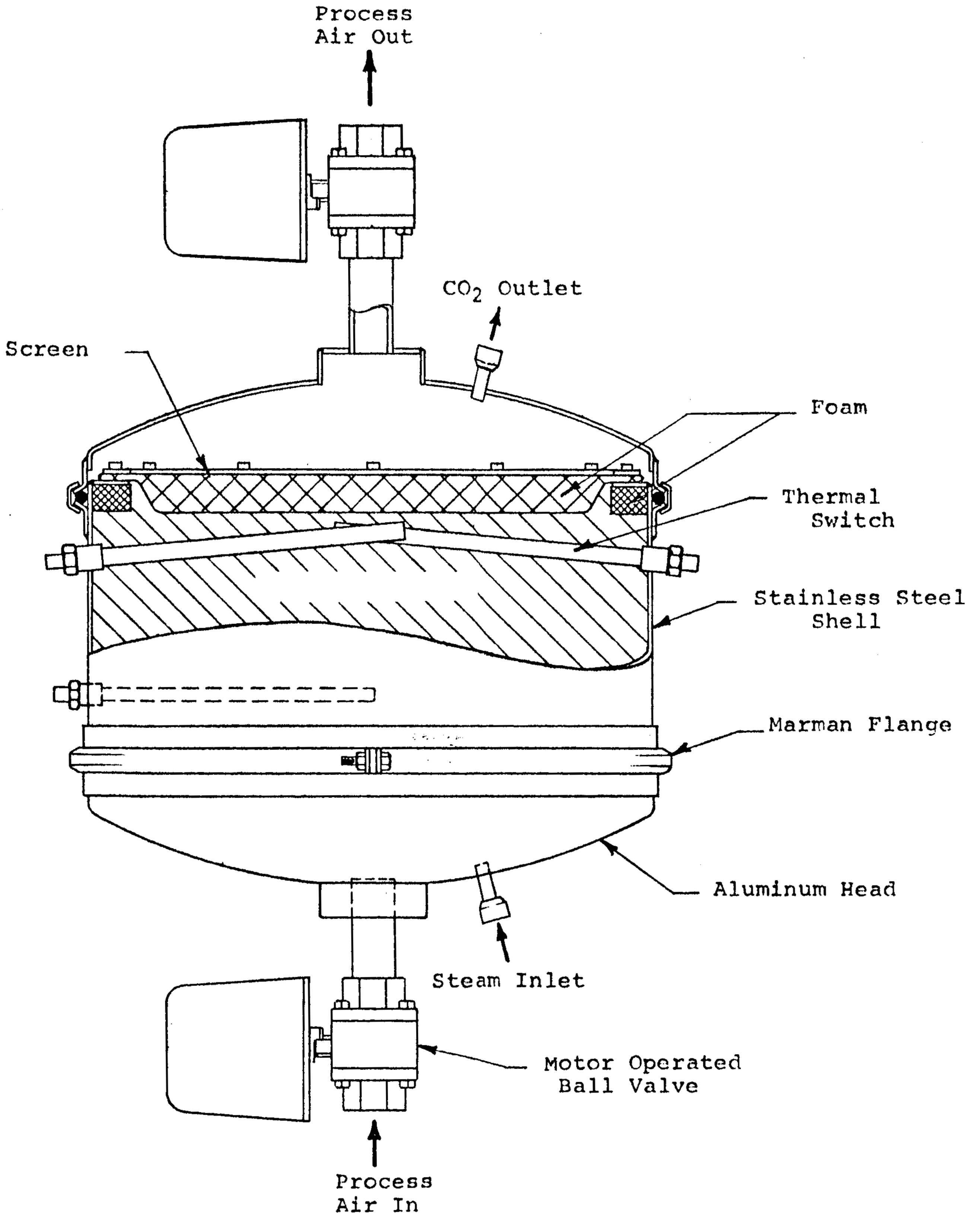


FIG 26 - SCHEMATIC OF LABORATORY MODEL RESIN BED where W is the amount of dry resin needed to absorb C pounds of CO_2 for a total cycle time of θ hours if the bed capacity is c. For a one hour cycle,

$$W = \frac{0.4}{0.0234} \times 1 = 17.1 \text{ pounds of dry resin.}$$

For resin with a nominal moisture content of 20%, we would need

$$\frac{17.1}{0.8} = 21.4 \text{ pounds.}$$

At 20% moisture content, the resin weighs 36 pounds per cubic foot, so our bed must contain at least 0.6 cubic feet. We have added a safety factor and selected 26 lbs (0.72 ft^3) of resin (containing 20 wt % water).

At the downstream side of the resin bed, two thermal switches (Fenwal or equivalent) are installed - one set to open at about 90°F, the other at about 210°F. Their purpose will be stated later when the complete cycle is described.

The chamber shell is fabricated of stainless steel, with at least both ends fully removable to provide complete access to the interior. The heads are fabricated of aluminum, which had been anodized after fabrication. Marman ring seals are used as closures. The inlet and outlet ports are provided with 1 in. pipe size valves (Worcester #A433-5-SE) with aluminum bodies. Other connections to the chamber include the steam supply (at the air inlet side) and the CO_2-vent line (at the downstream side).

Regeneration Desorption - The combined regeneration desorption step consists of heating the bed to approximately 212°F with steam. When the steam first enters the relatively cold chamber, the first condensation heats the metal walls. Insulation is used to minimize heat transmission to the enclosure, since any losses hinder the drying operation which follows later. The steam requirements are described in Figure 27. The point to be emphasized is that the regeneration operation is largely adiabatic - heat being lost only as the sensible heat plus heat of desorption of the evolved gases, which is small compared to the heat of condensation of the steam. Most of the heat, therefore, serves to raise the bed temperature with the result that water condenses on the sorbent. The weight of water condensed is also shown in Figure 27.

Heat required to raise bed temperature from 77°F to 212°F ($\Delta T = 135°F$)

$$(C_p)_{H_2O} = 1.0$$

$$\frac{Q_s}{W} = 35.1 + 100\ m_n \qquad (C_p)_{resin} = 0.26$$

$$\frac{\text{lb of steam req'd}}{\text{lb of resin}} = \frac{Q_s}{\lambda W} = 1.03 \times 10^{-3}\ \frac{Q_s}{W}$$

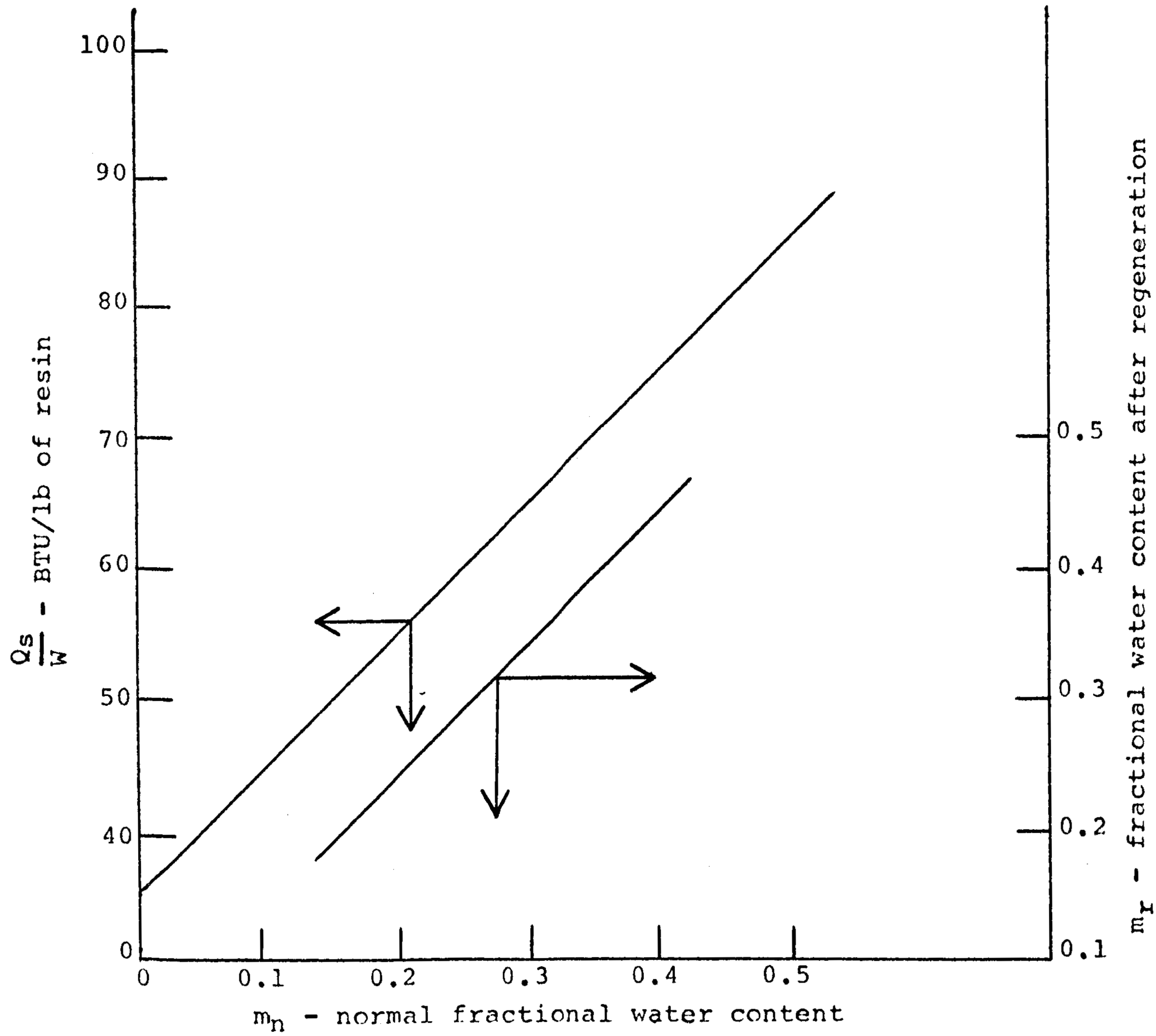
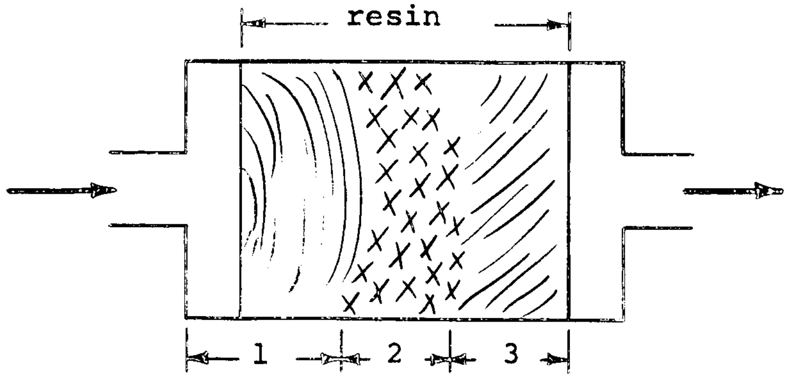


FIG 27 -RESIN HEATING REQUIREMENTS

As described earlier, when steam enters, it will condense on, and heat up, all cooler surfaces, simultaneously displacing air. Meanwhile, the pressure drops in the condensation zone. Then pressure pushes more steam past the hot, wet surface into contact with more cool material. The mixture proceeding through the bed is steam + CO_2 (desorbed) + air. The steam condenses (zone 1).



The hot CO_2-air mixture passes onward and is cooled by the bed. The CO_2 partial pressure is quite high in this region (zone 2) and it tends to be reabsorbed (up to the theoretical capacity of the resin). Meanwhile, the air is pushed through the rest of the bed (zone 3), and is recovered separately via V-4. The cool portion of the bed, then, serves to reabsorb, and thus to separate, the CO_2 from the air.

The theoretical exchange capacity for IR-45 at 20% H_2O content is 4 meq/g. If applicable for CO_2, this would be a capacity of $\sim$ 8 1/2% if the equivalent weight of CO_2 is 22, which we might expect at low CO_2 partial pressures. At high partial pressures, however, equivalent weight might approach 44 (bicarbonate analog), providing a theoretical capacity on the order of 17%. Our dynamic capacity at 4 mm CO_2 is only about 2.3%. This suggests that, if the steam heating is carried out slowly enough to permit maximum reabsorption, almost 7/8 of the residual air in the chamber can be recovered with virtually no CO_2 content. Experiments have verified this air recovery will be better if the bed is less heavily loaded and if some CO_2 is recycled to the cabin. The over-sized bed should limit air loss to almost zero. By merely returning about 1/8 cubic foot of CO_2 to the cabin each cycle, all of the air could be displaced.

If the steam is admitted to the bed far too fast, it may channel or interfere with CO_2 reabsorption. We have found, however, that the process is self-correcting over a wide range of steam rates. As the steam condenses, it locally increases the pressure drop, diverting the flow toward cooler surfaces.

Our tests with resin beds of the required thickness (5 1/2 inches) show that desorption can easily be completed in about 15 minutes. Tests with the laboratory prototype show 13-15 minutes. Our system is conservative; we allow 20 minutes.

For normal operation, the heat requirement at the 20% moisture content is 55 BTU-lb. Again:

$$W_{20} = \frac{17.1}{0.8} = 21.4 \text{ pounds of wet resin}$$

$$(21.4)(55) = 1177 \text{ BTU}$$

$$\text{Less superheat} \cong \underline{250 \text{ BTU}}$$

$$\text{Net heat} \quad 927 \text{ BTU in 20 minutes}$$

The hourly rating of 2780 BTU requires 927 watts, which is well within the ability of the 3 KW boiler.

The heat requirements go up slightly if the initial bed temperature is lower. The values in Figure 27 are based on a temperature rise of 135°F. For other temperatures -

$$\left(\frac{Q_s}{W}\right)_{t_2} = \left(\frac{Q_s}{W}\right)_{135} \times \left(\frac{t_2}{135}\right)$$

For example, the heat needed to raise the temperature of 1 pound of resin of 20% moisture content from 55°F to 212°F would be

$$\left(\frac{Q_s}{W}\right)_{157} = 55 \times \frac{157}{135} = 64 \text{ BTU/lb}$$

<u>Boiler</u> - A small commercial boiler (Reimer's Electra Steam, Type AR-4), designed to meet ASME requirements and registered with the National Board of Boiler and Pressure Vessel Inspectors, serves to heat the bed. The 3 KW, 240V, 3 phase boiler is rated for steam pressure to 50 psig. Tests show that the boiler supplies sufficient steam to regenerate in less than 15 minutes.

<u>Absorption and Drying</u> - These steps have already been well discussed elsewhere. The throughput air simultaneously cools and dries the freshly regenerated bed. CO_2 is then absorbed by the cooled portion of the bed. This part of the cycle lasts about forty minutes.

Condenser - The water that was condensed on the resin bed and later removed during the absorption-drying step must be largely recovered. Prior studies have shown that most of the water is removed in the first 5 or so minutes of the drying, while the effluent is quite hot.

The spined heat exchange tube (Heatron's "Thermek") provides 2.64 square feet per lineal foot. We have installed 10.5 lineal feet. The tubes are arranged to fit inside a 6.25 inch aluminum tubing.

The condenser is mounted in a horizontal position so that approximately 6 lbs of water are retained at the end of the absorption cycle. This water serves to reduce the effluent temperature of the first surge at the beginning of the next absorption cycle.

Blower - The blower (Rotron MRPU Type A5-701) is a 208V, 60 cps, 3 phase, 60 W unit which can deliver 27 cfm at a pressure drop of 7 in. of water.

Valves - The system consists of five valves, two of them motor operated (V1 and V2) and the other three (V3, V4 and V5) solenoid operated. The motor operaters for the two main valves are Worcester Model #35A and draw about 1 amp maximum. The closure time of the 1 in. pipe aluminum ball valves is about six seconds. The two solenoid valves for cold gases are ASCO #G-8263A23, while the steam cycle solenoid valve is an ASCO #G-8262A94. All solenoids operate off of 110V, 60 cps.

Attempts were made in the initial configuration to use as valves V1 and V2, 3 inch diameter discs operated by Bellofram rolling diaphragm actuators. It had been hoped that such devices could be driven by the pressure head of the blower, forcing them open when the blower was in operation. With the blower off, return springs would reseat the discs. Such devices would lower system weight and power. Unfortunately, difficulty was encountered in opening both valves simultaneously, and in seating such the large diameter disc to prevent steam loss during regeneration.

Operational Sequence - Table 17 shows the events in a full cycle operation.

Charcoal Bed - Odors, particularly prevalent at the beginning of use of a particular batch of resin have emenated from the bed during the desorption cycle. These barely perceptable odors have not been identified but are thought to be residual organic solvents. A charcoal bed was used initially to ensure their removal. Later, the charcoal bed was removed.

TABLE 17- EVENTS IN A FULL CYCLE OPERATION

Elapsed Time min - sec	Events
0	Timer stops blower, causing V-1 and V-2 to close.
0 - 1	Timer energizes V-4 and V-3, a lockout relay to V-5, and the leads to V-5.
0 - 2 on to as much as 5 - 0	Air is expelled from V-4. If temperature at 90 degree thermoswitch reaches that point prior to 5 min., it will open the switch. Then V-4 will close, and the lockout relay will be de-energized, allowing V-5 to be energized. If the thermoswitch is not activated after 5 minutes, the timer will open a relay to cause the same sequence of actions. Meanwhile, the steam (water) has flashed from the boiler, and steam is being generated.
5 - 1 to as much as 20 - 0	CO_2 is being evolved at increasing rates and the bed temperature is rising. If the temperature gets high enough to activate the 210 degree thermoswitch, it will open the circuits to V-5 and V-3, causing those valves to close. It will also release a relay that will open V-4 for 5 seconds to equalize the pressure. If the thermoswitch is not activated, then the timer will operate a relay at 20 minutes, causing the same sequence.
20 - 1 to 60	Blower is turned on, activating V-1 and V-2. The first surge of very moist heated air will enter the precooled condenser. All of its sensible heat will help condense the moisture. Absorption starts and continues until the timer ends the cycle.

System Weight and Power - Table 18 shows the weight of components of the laboratory model. System weight total exclusive of the 1-G boiler is 111.4 lbs, and the total weight is 213.4 lbs. Peak power requirements are:

Boiler - 3 KW, 240V, 3-phase (peak power for 15 min, standby for 45 min)

2 Air System Valves - 120V, 2 amps max (during six second closure time)

Blower - 208V, 60W, 3-phase (operable 2/3 of cycle)

3 Solenoids - 110V, ~20W each

TABLE 18 - WEIGHT OF CO_2 SYSTEM COMPONENTS

Component	Weight (lbs)
Blower	14.3
Aluminum ball valves (2)	2.8
Valve operators (2)	9.4
Control cabinet	8.0
Control components (timer, relays, temperature indicator)	13.1
Solenoid valves (3)	3.0
Condenser	7.4
Resin chamber	
Stainless steel shell	13.2
Aluminum heads (2)	5.8
Marman flanges (2)	2.0
Retaining screens and nuts	3.0
Resin	25.8
Foam	0.7
Assorted pipe, tubing and fittings	1.0
Plastic hose and couplings	1.9
	111.4
Boiler (empty)	102
	213.4

LABORATORY MODEL OPERATIONAL CHARACTERISTICS

The resin bed shown in Figure 26 was tested to determine its operating characteristics under conditions characteristic of a normal space cabin environment.

Figure 28 is a modification of Figure 25, but with a number of features added to permit characterization of the operating system. Room air at a temperature of approximately 77°F (RH between 20-35%) was drawn into the blower along with sufficient carbon dioxide to result in a concentration of 0.4-0.5% CO_2. A Model 300 LIRA Analyzer (0-0.5 and 0-2.0% full scale) was used to monitor inlet and outlet CO_2 concentration. The room humidity was measured using a Serdex B humidity sensor. Thermocouple temperature measurements were taken of the bed temperature and thermometer temperature measurements were taken of air exiting from the cooler. Gas evolved during the steam regeneration step was measured by using a wet test meter.

Preliminary runs suggested that the condenser was somewhat undersize in that copious quantities of water vapor issued from the condenser for at least five minutes at the beginning of the absorption-drying cycle. However, by placing the cooler in a horizontal position approximately 6 lbs of water would be retained at the end of each absorption-drying cycle, and this water significantly aided in cooling the warm air surge issuing from the cooler at the beginning of the absorption cycle. The quantity of water necessary to regenerate was not monitored, although condensate overflow from the cooler was measured at the end of each cycle.

Four series of runs were made. In the first series, where there was no insulation on the canister, nine consecutive runs showed progressive deterioration of the CO_2 capacity of the bed. This deterioration was accompanied by the following observations:

1. A longer time to effect desorption - after the first absorption cycle, desorption was complete (as determined by a 210+°F temperature near the upper plenum) in only 15 minutes. With each cycle, there was an increase in the time necessary to effect desorption until it became necessary to allow 29 minutes for desorption at the end of Cycle No. 9.

2. The amount of condensate recovered increased from about 1000 ml during Cycle 2 to 1800 ml at tne end of Cycle No. 9.

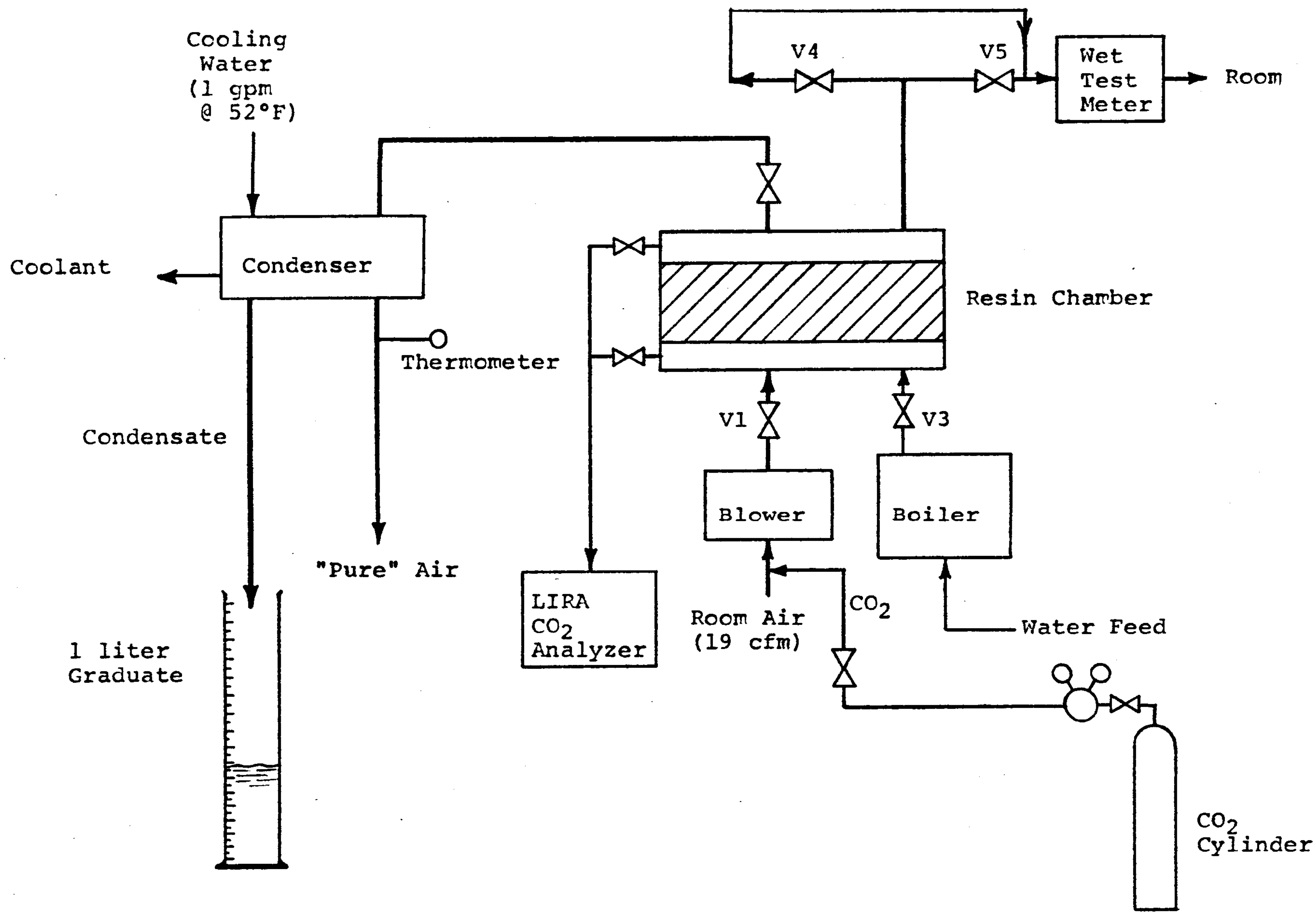


FIG 28 - SCHEMATIC OF LABORATORY MODEL CO_2 REMOVAL SYSTEM

3. Cooling of the bed during the absorption cycle became more prolonged with each cycle.

It became apparent from these observations that an incremental addition of water existed at the end of each cycle, which significantly increased the heat capacity of the bed, resulting in greater and greater steam necessary for regeneration. The cause of this progressive deterioration was thought to be ineffective insulation, which resulted in a significant heat leak, such that the 40 min absorption-drying cycle was not sufficient to allow drying the bed down to its original water content. The bed was dried down to about 10 weight percent by blowing air through the bed overnight.

The second series of runs were performed with but a minimal quantity of insulation. This second series totalled 19 separate cycles and deterioration was again noted, with the exception that it was considerably less evident on a per cycle basis. In fact, deterioration did not become significantly evident until about the fourteenth cycle. The deterioration was again noted by the same factors listed above with the exception that in each of the factors the increment per cycle was significantly less. After cycle No. 14, it became obvious that a greater absorption time was necessary to effect drying of the bed to attempt to counteract an excessive water condition. Even with an increase in sorption time from 40 to 50 min, it was not possible to return the bed to its initial water condition, which was estimated to be about 10 wt %.

The bed was reinsulated with a single layer of 1/2 in. thick Johns-Manville microquartz felt. The timer was adjusted to permit an increase of the sorption time from about 40 to 60 min. Thirteen full cycles were run under these conditions and it was noted that there was hardly any significant difference between Cycles 2 and 13.

The fourth series of runs were performed at a CO_2 concentration of 1.05%, while other conditions were kept constant. Figure 29 shows CO_2 effluent concentration as a function of time, where the influent concentration is 1.05 and 0.48% CO_2. In each case, room air containing the indicated CO_2 concentration is added at the indicated flow rate to the bed with the bed starting out at approximately 215°F. The instantaneous CO_2 capacity is poor but because of evaporative cooling at the influent side of the bed the effectiveness of the sorbent increases until after about 6 minutes, the effluent concentration is but a small fraction of the influent concentration.

Table 19 summarizes the CO_2 capacity of the system for the 2 runs shown in Figure 29. Estimates are given for different absorption times. With increasing effluent concentration there is an increase in the CO_2 capacity of the system per unit time, until the effluent concentration is approximately 40-50% of the

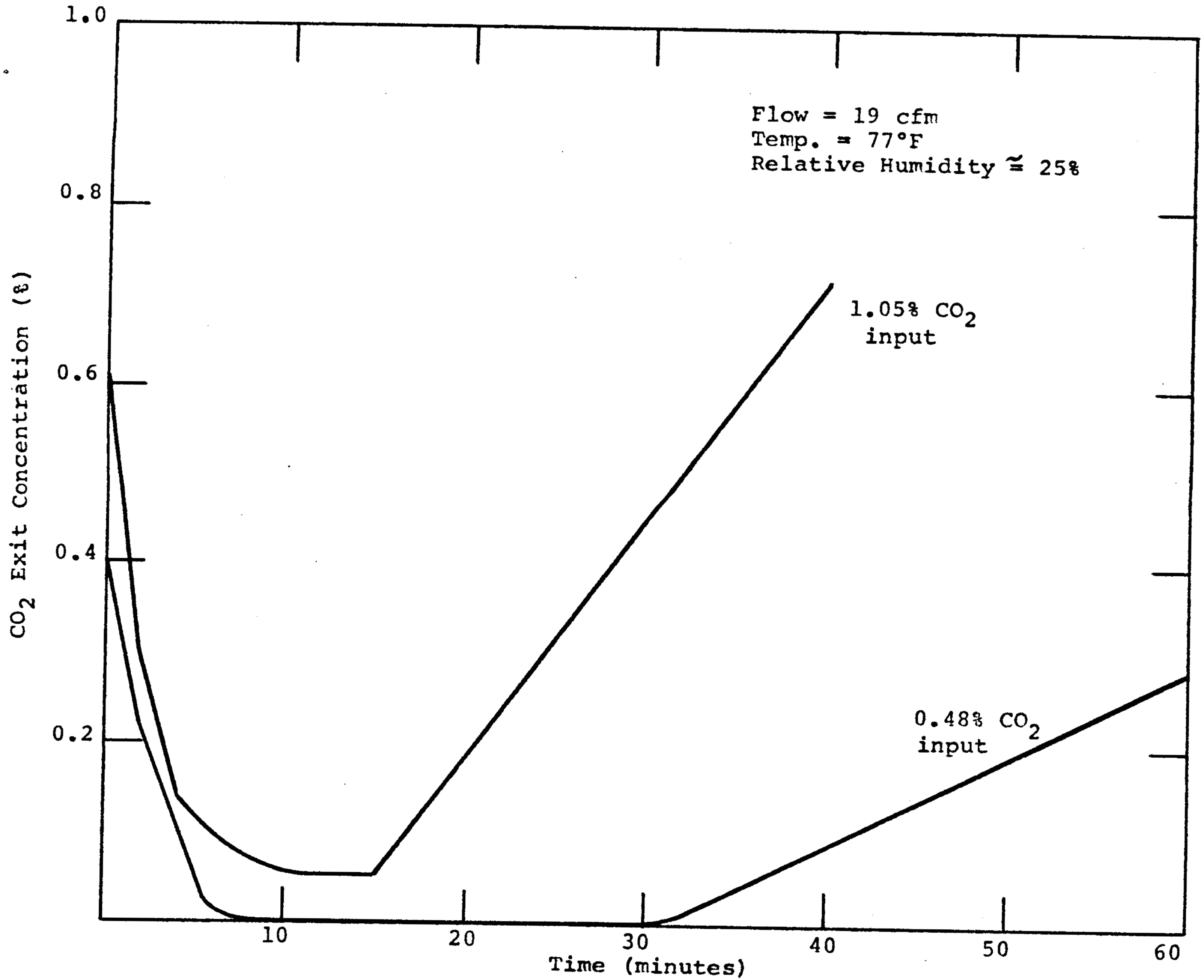


FIG 29 - CO_2 EFFLUENT CONCENTRATION FROM THE LABORATORY MODEL

TABLE 19 - SUMMARY OF TYPICAL SYSTEM CO_2 CAPACITY AS A FUNCTION OF ABSORPTION CYCLE TIME

CO_2 Concentration (%)	Adsorption Cycle Duration (min)	Sorption Efficiency[1] (%)	CO_2 Sorbed (scf)	CO_2 Sorbed (#)	Sorption Capacity[2] (#/hr)
0.48	30	92.5	2.30	0.283	0.340
0.48	40	92.2	3.06	0.377	0.377
0.48	50	87.1	3.61	0.433	0.380
0.48	60	81.7	4.06	0.497	0.372
1.05	20	85.9	3.11	0.382	0.572
1.05	30	80.0	4.36	0.535	0.642
1.05	40	71.0	5.15	0.633	0.633

1 Estimated by determining area under curve, and calculating from CO_2 sorbed/CO_2 entering x 100.

2 Capacity is determined from:
\# sorbed/total cycle time,

where total cycle time = adsorption time plus 20 minutes for desorption.

influent concentration. Since the energy necessary for desorption is essentially independent of the CO_2 loading on the bed, it follows that there might be even greater advantage to operating the system to high CO_2 effluent concentrations, when power and weight are considered in an optimized system.

Through the use of a wet test meter the volume of gas displaced from the bed through the desorption cycle was measured. Figure 30 is a curve showing the volume of gas desorbed at 1 atm during a typical 13 min desorption run. The gas displaced at the very beginning of the cycle (region A) corresponds to the displacement of air by steam in the entry plenum. This displacement occurs quite rapidly, and then the rate of gas displaced from the system is reduced. It is during this period (region B) that the air within the bed itself is displaced. The total of volumes of A + B is a fairly close approximation of the calculated volumes of the entry plenum and the void volume of the packed bed. After about 8 minutes, the gas evolution rate increases significantly and reaches a rather steady value of about 0.63 cfm. It is in this region the bulk of the CO_2 is eliminated from the canister. The one apparent objection to the design is the rather large and undesirable volume of the exit plenum. In order to effect complete CO_2 and displacement into the CO_2 delivery system, it is necessary to displace the CO_2 in the exit plenum with steam. An exit plenum of minimum volume while increasing the pressure drop of the system during the absorption cycle, would significantly increase the efficiency of CO_2 removal into the collection system.

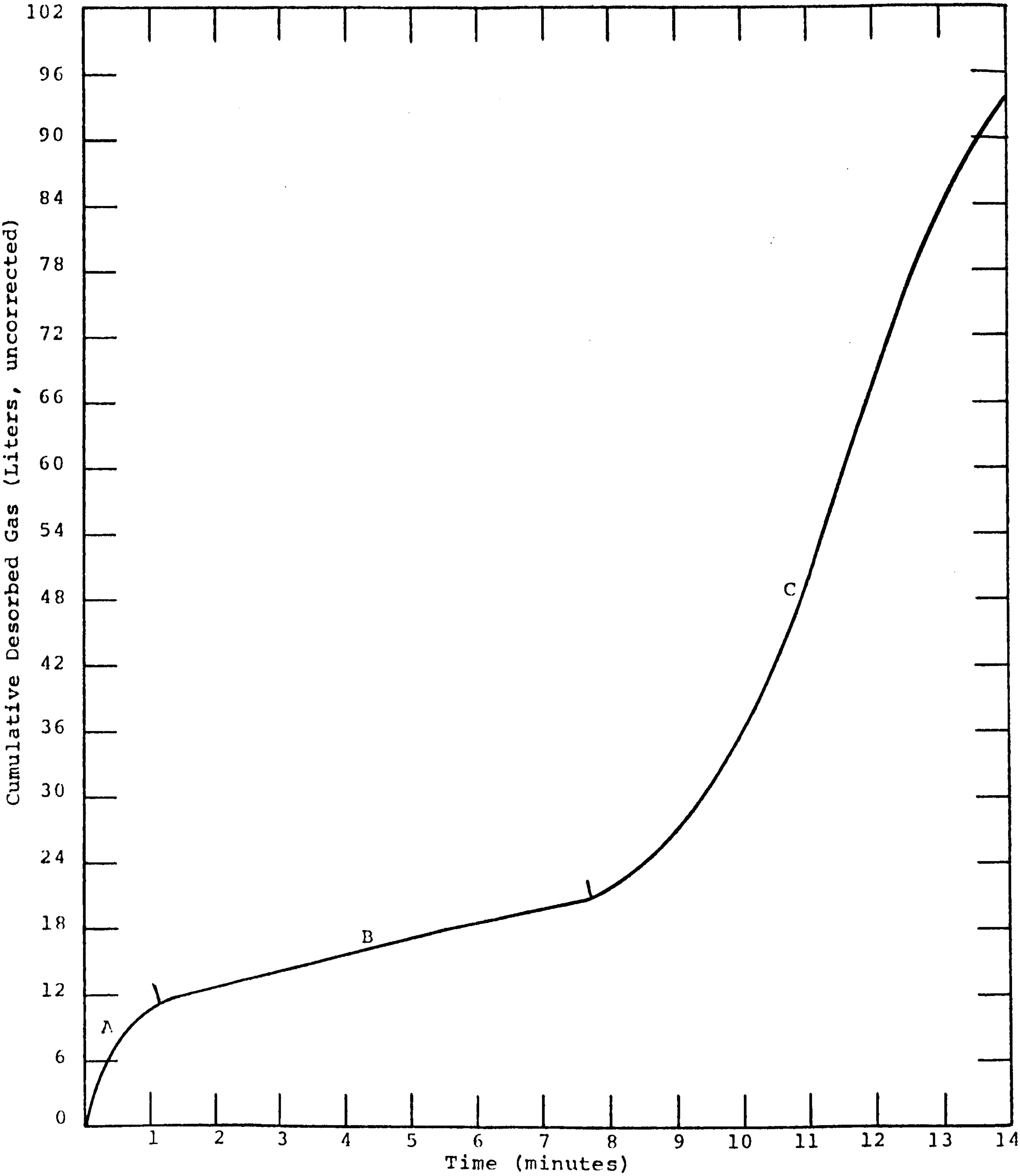


FIG 30 - GAS EVOLUTION DURING DESORPTION

SYSTEM OPTIMIZATION

The evolution of a fully operational zero-G CO_2 removal system with minimum weight and power requirements requires significant departures from the laboratory model described earlier. For the purposes of this discussion it is assumed that CO_2 is to be recovered for the purposes of producing oxygen, and that the resin system operates essentially independently of the dehumidification systems. That is, the resin system would not be operated under conditions where it would sorb CO_2 and H_2O simultaneously.

A schematic of the major components of a fully operational model is shown in Figure 31. This system is more sophisticated than the laboratory model in that water condensate is conserved and CO_2 is compressed from ambient pressure and stored.

During the absorption cycle room air is forced through Valve A into the central plenum of the resin chamber, and out through Valve B into an air cooler. The cooler would be designed to remove the bulk of the water prior to directing the air stream through the dehumidification subsystem.

During regeneration, steam generated from the condensate is directed into the entry plenum, and during the first part of the cycle, air is displaced from the bed through Valve C. Valve C is closed, causing a pressure increase, forcing CO_2 at one atmosphere pressure through check valve D. The CO_2 compressor raises the CO_2 pressure to at least 20 psia, and the gas is stored in the accumulator. Water vapor that is removed as a result of CO_2 compression is returned as water, along with water from the air cooler.

Resin Bed

The studies performed to date have been primarily with one resin, IR-45. The dynamic capacity at a CO_2 pressure of 3.8 Torr is limited to about 2.5% weight percent. It is likely that resins could be evolved that have superior characteristics. These characteristics could be:

a. higher CO_2 equilibrium capacity at $P_{CO_2} = 3.8$ mm

b. higher CO_2 sorption rate (both a and b contribute to dynamic sorption capacity)

c. resins that retain their CO_2 capacity when anhydrous - this factor reduces dependence on high RH in air stream and reduces the C_p of the resin. At a lower C_p, less steam is necessary to heat the resin to desorption temperature resulting in less condensate.

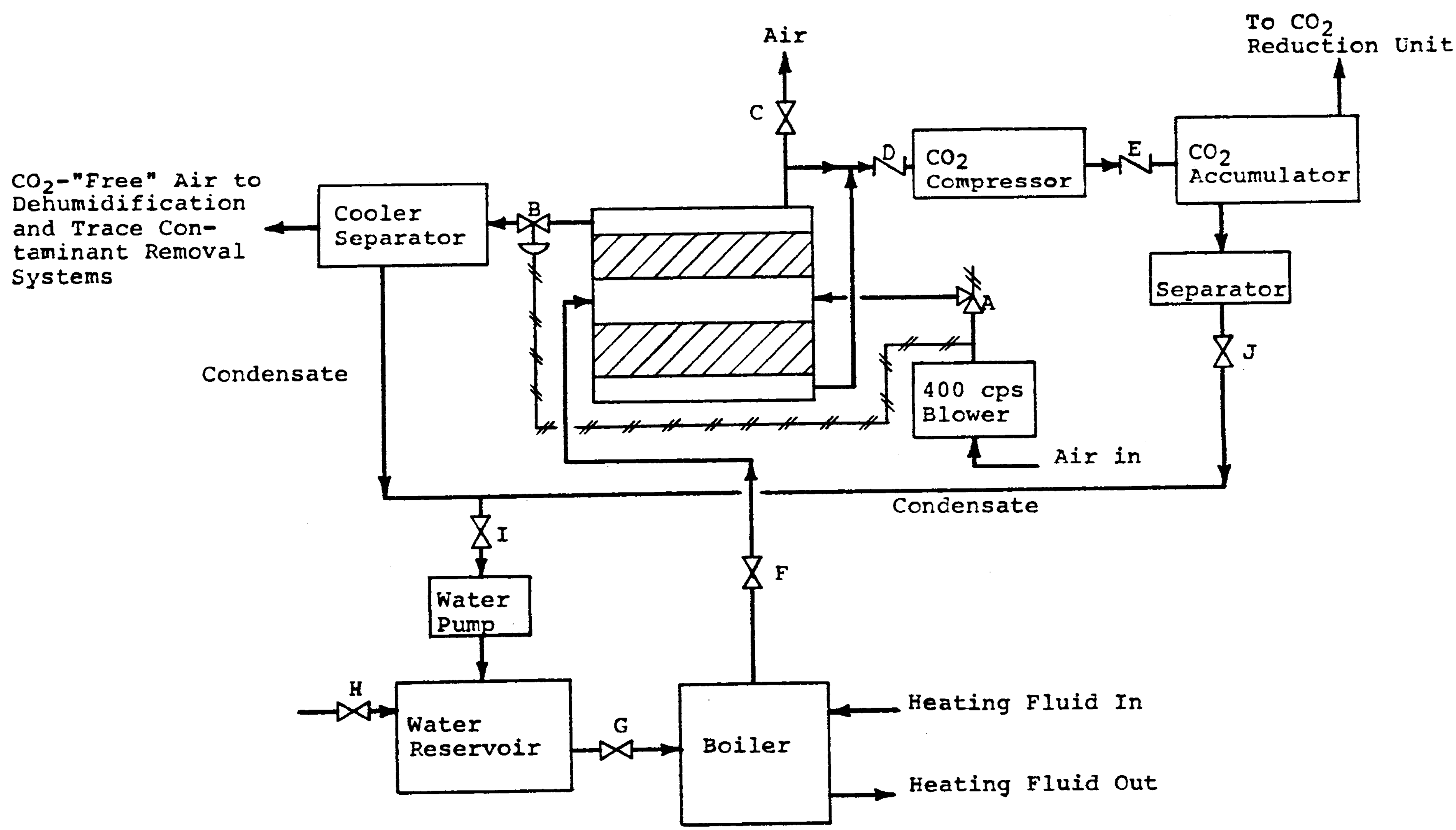


FIG 31 - SCHEMATIC OF A FULLY-OPERATIVE ZERO-G CO_2 REMOVAL SYSTEM

In addition to improvement in specific capacity by changing resin, systematic evaluation of optimum sorbent configuration and weight could result in weight reductions. In this respect, the cycle time and other factors must be considered to arrive at optimum weight-power reliability for the total system.

A single bed resin system is shown. The ability to desorb CO_2 from the bed in a short time (5-15 minutes, depending upon steam delivery rate) allows consideration of a single bed, with a resultant gain in simplicity and reliability.

The resin bed configuration shown in Figure 31 is a cylindrical arrangement, where the entry plenum is the axial compartment and the exit plenum on the periphery of the cylinder. This configuration could result in significant energy savings as compared to the laboratory model.

Where the external pressure is one atmsophere the wall and heads of the resin bed chamber need only serve as a structural skin, rather than a pressure vessel or vacuum chamber. This is because all functions of the cycle are performed at or near 1 atmosphere pressure. Regeneration can be effected down to about 190°F, where the steam pressure is about 9.3 psia. If ambient pressures are below this minimum value, the resin chamber must serve as a pressure vessel for the ΔP resulting during the desorption cycle. The cylindrical bed arrangement minimizes container weight when there are pressure differences across the container wall.

Blower

By suitable arrangement of the resin bed, bed thicknesses of the order of 2 1/2 in. may be attained. At the necessary volumetric throughput, the pressure drop would be 0.7 in. Blowers are commercially available that would handle 40 cfm at 0.82 in. under high altitude conditions. They weigh about 0.9 lbs and draw 35 watts of 400 cps power. For a total system pressure drop of 2.0 in. the electrical power requirements would double but with no increase in blower weight. A longer bed may provide a sharper separation of CO_2 and H_2O/air, but would result in a larger pressure drop and increased blower power. At present, bed pressure drop is assumed to be a factor that should be reduced.

Boiler

The use of waste heat to boil water provides power economy. It is assumed that there is sufficient waste heat available to boil all of the water necessary for regeneration. The boiler weight is dependent upon the heating fluid temperatures, and temperatures in excess of 300°F, and temperatures of 400°F are preferable.

Estimates have been made for the weight of a once-through porous plug boiler necessary to regenerate the resin in a 4-man system. The assumptions are that at least 68 lb/hr of organic fluid at 400°F could be delivered to a stainless steel tube-in-tube heat exchanger. The heat exchanger would be about 1 in. OD x 115 in. long, and would be filled with thermal conductive packing to an estimated porosity of 25%. Estimated tube exchanger weight is 14-18 lbs. The exchanger could be helically coiled to be compact.

Valves

As shown in Figure 31, there are at least nine valves. The air cycle valves through which the total process air flows may be a positive pressure type check valve similar to the valve used in pressure demand breathing equipment (estimated weight = 0.7 lb each). Valve B would be made to open by pressure produced from the head of the blower, through a pressure connection. The third air cycle valve is a normally-closed solenoid which opens to allow displaced air to vent into the space cabin. When this valve is allowed to close, CO_2 pressure causes flow through check valve at D. A second CO_2 cycle check valve is located between the compressor and CO_2 accumulator. Solenoid valves are located at F, G, H, I and J.

CO_2 Delivery System

The CO_2 delivery system would receive CO_2 (at 10-14 psia) during a portion of each desorption cycle. A compressor would delivery CO_2 at 20 psia to an accumulator for use in a CO_2 reduction subsystem. For 20 psia delivery, it is possible that steam regeneration at 228°F would eliminate the need for a compressor, but at the possible expense of limiting resin life.

System Weight

Table 20 lists the estimated weight of components for an optimized system. The fixed weight is estimated at 110 lbs, or approximately 27.5 lb/min.

Energy Requirements

The electrical power requirements might be about 70 watts for a blower and about 20 watts DC for solenoid operated valves, if they are not operated simultaneously. The only other electrical power requirement envisioned at this writing is for some of the instrumentation package that would be necessary for system operation. No power penalty is taken for indicating instruments since, other than the timing device, the system may be operable on a planned program basis. Should indicating instruments be desired for the end package, these instruments are likely to be no greater in power and weight penalty than if used in a silica gel-molecular sieve CO_2 removal system.

TABLE 20 - ESTIMATED WEIGHT OF COMPONENTS IN AN OPTIMIZED SYSTEM
NOMINAL CAPACITY = 0.4 lb CO_2/hr

Component	Fixed Weight (lb)	Avg. Power Requirements (watts)
Ion exchange resin	20.0	
Resin bed and screens	8.0	
Compressor, accumulator and water separator	12.0	50
Blower	3.0	35
Air cooler	13.0	
Boiler and superheater	18.0	350
Air cycle valves (3) (one solenoid)	2.4	5
CO_2 cycle check valves (2)	1.3	
Water cycle valves (4 solenoids)	2.4	15
Steam valve	0.7	
Water pump	2.0	10
Insulation	3.0	
Timer	1.0	5
Thermoswitches (2)	0.5	
Relays and switches	0.5	
Miscellaneous tubing, pipe	4.0	
Structural supports	18.0	
	109.8	470

The thermal energy requirements for such a system are considered to heat about 20 lbs of resin per hour to the boiling point of water and cool it back down to operating temperature. If we assume that there is no heat leak during steam regeneration and that the heat capacity of the column is nil, then the heat necessary for desorption is the sum of:

1. The heat capacity of the resin (containing absorbed water).

2. The heat capacity of screens and sorbent bed separators.

3. The sensible heat of the eluted air and CO_2.

4. The dissociation energy for decomposition of the amine-carbonate salt.

We have measured the heat capacity of IR-45 containing 20 wt % water and find it to be approximately 0.40 Btu/lb/°F of a thermal requirement of about 1096 Btu/hr at a rate of 3288 Btu/hr. In addition to this requirement, sufficient heat must be supplied to replace the sensible heat of the gas that is displaced. From a previous experiment we found that 90% of the gas is displaced at approximately room temperature and that only a small fraction of it has any measurable heat. We have also estimated the thermal requirements for the dissociation of the resin carbonate salt. If we assume a value of 5 K/cal per mole of CO_2 (a reasonable value in the light of weak regenerable absorption reactions) we only require about 71 Btu for a total of about 1170 Btu.

The average power requirements for components in the optimized system are also shown in Table 20. The four man system requires 470 watts or 117.5 watts/man.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

A number of sorbents were evaluated for their ability to sorb CO_2 from humid air and to be regenerated by thermal or vacuum means. Activated carbon was found to have a low capacity at the CO_2 pressure of 4 mm. Coprecipitated gels could be partially regenerated but this avenue did not prove to be promising.

Screening studies had demonstrated that basic amine organic polymers had high equilibrium CO_2 capacities, and that the sorption rates were also favorable. Such polymers would sorb CO_2 out of a humid environment with a dynamic CO_2 capacity greater than 2.5%. (Their static equilibrium capacity at 4 mm CO_2 ranged between 5 and 10%.) They are in fact dependent upon water vapor for effective CO_2 sorption, and will ordinarily equilibrate at about 5-10 weight percent water at 75°F and 50% RH. In excess of 30 weight percent, the water is unabsorbed, and hinders CO_2 sorption. Vacuum thermal regeneration results in complete dehydration of the resin with the result that more water is evolved than CO_2. Vacuum regeneration has therefore excess power requirements, and requires replacement of the water.

Weak base ion exchange resins and particularly IR-45, were studied in detail. However, only the weak base resins appeared to be thermally regenerable. Vacuum/thermal, hot water and steam regeneration methods were evaluated, and a steam regeneration "chromatographic" technique was most promising because of lower power requirements, and its ability to separate CO_2 from air relatively easily.

Cyclic life tests were performed on IR-45 and the material was shown to have a life of at least 1000 cycles. Laboratory adsorption and desorption data were collected and were used to design a laboratory model. This model had a nominal CO_2 capacity of 0.4 lb/hr in humid air containing 4 mm CO_2. The system, exclusive of a 102 lb boiler, weighs 111.4 lb, and consumes 790 kw of electrical power.

The model was operated with laboratory air (~77°F) containing 0.4 to 0.5% CO_2. It was found to have a capacity between 0.34 and 0.38 lb CO_2/hr. When improperly insulated, an increasing incremental addition of water resulted, which eventually deteriorated the sorption effectiveness of the device.

The fixed weight and power penalties for an optimized resin type CO_2 removal system was considered. The fixed weight for a 0.4 lb CO_2/hr system is estimated at 110 lb. Electrical power requirements are 470 W, or 270 and 300 W waste heat.

The apparent primary advantages of an ion exchange resin system (steam-chromatographic regeneration) as compared to a molecular sieve-silica gel system are:

1. Air predrying is not necessary (nor desirable).

2. The adsorption and desorption is performed essentially at ambient pressure. This reduces the fixed weight of the canister, eliminates the need for vacuum pumps and complicated vacuum valving.

3. The CO_2 gas is recoverable at ambient pressure, reducing compressor requirements.

4. The CO_2 may be recovered with little air loss, and is rather pure ($<$1% total O_2 and N_2).

5. Fluid heating of the resin is more rapid than heating of dry molecular sieve granules in vacuo, so that desorption time can be a small fraction of the total cycle.

6. The adsorption and cooling steps can be performed simultaneously with only small penalties in system performance.

The apparent disadvantages are:

1. Considerably less is known about possible long term deterioration effects.

2. The capacity of the sorbent is affected by temperature and humidity of the air stream. These effects result in changes in the drying capabilities of the process air, which could result in eventual "flooding" of the bed if the sorption cycle is not sufficiently prolonged.

3. A zero-G boiler must be designed, and zero-G condensation requirements may be greater than those presently being considered for dehumidification.

Recommendations

Rather limited operational data has been generated using the laboratory model, such that the operational character and deficiencies of the resin approach are not yet known. While the limited full scale system appears to behave as expected from laboratory information, the following studies with the full scale model are recommended:

1. Determine the effect of varying temperature and higher humidities on the existing bed.

2. Determine the operating characteristics of the bed at different air velocities, with varying bed length to diameter ratio.

3. Determine the purity of delivered CO_2 as a function of steam desorption rate.

Once the inter-relation of the above factors are known, it would be possible to determine the primary faults of the systems and attempt to redesign the model accordingly. In addition, the evolution of sorbents with properties superior to IR-45 should be pursued, once the real deficiencies of IR-45 are known. An obvious improvement would be the increase of dynamic CO_2 capacity, with the resulting reduction of heating and cooling requirements per unit weight of CO_2.

LIST OF REFERENCES

1. Magnus, A. and Cahn, L., Z. anorg. allgem. Chem. 155, p 205 (1926).

2. Magnus, A. and Kratz, H., Z. anorg. Chem. 184, p 241 (1929).

3. Rowe, H., Phil. Mag (7) 1, p. 659 (1926).

4. Sameshima, J., Bull. Chem. Soc. Japan 2 p. 1 (1926).

5. Shiels, D. O., J. Phys. Chem. 33, p. 1386 (1929).

6. Allmand, A. J. Burrage, L.J., and Chaplin, R., Trans. Faraday Soc. 28, p. 218 (1932).

7. Burrage, L. J., J. Phys. Chem. 36, p. 2272 (1932).

8. Coolidge, A. S., and Fornwalt, H. J., J. Amer. Chem. Soc. 56, p. 561 (1934).

9. Wicke, E., Kolloid Z. 93, p. 129 (1940).

10. Munemori, M., Science Reports, Tohoku Univ. 35, p. 165 (1951).

11. Magnus, A. and Giebenhain, H., Z. Physik Chem. A164, p 209 (1933).

12. Szepezy, L. and Illes, V., Acta Chim, Akad Sci. Hungary 35, p. 37 (1953) (In English).

13. Bobleter, O. and Gruben, H., Kolloid-Z, 151, p. 116 (1957).

14. Turnizumi, A., Nippon Kagaku Zasshi 80, p. 221 (1959).

15. Ray, G. C. and Box, E. O., Jr., Ind. Eng. Chem. 42 p. 1315 (1950).

16. Remy, H. and Heine, W., Kolloid Z. 62, p. 154 (1933).

17. Dietz, V. R., Carpenter, F. G., and Arnold, R. G., Carbon 1, p. 245 (1964).

18. Major, C. J., Sollami, B. J., and Kammermeyer, K., I & EC, Process Design and Development 4, #3, p. 327 (1965).

19. A. F. Contract AF 33(615)-2443 to Pioneer Central Div., Bendix Corp., Development of a Laboratory Type Regenerative CO_2 Removal System Using Charcoal.

20. Benton, A. F., Jour. Amer. Chem. Soc. 45, p. 887 (1923).

21. Lanning, C. E., Jour. Amer. Chem. Soc. 52, p. 2411 (1930).

22. Elovich, S. Yu and Margolis, L. Ya., Izvest. Akad Nauk SSSR, Ser. Fiz. 21, p. 206 (1957).

23. Sokai, W., et al., J. Soc. Chem. Ind. Japan 45, p. 25 (1942).

24. Foote, H.W. and Dixon, J. K., Jour. Amer. Chem. Soc. 53, p. 55 (1931).

25. Teichner, S. J., et al., Advances in Catalysis 9, p. 458 (1957).

26. Pitt, C. H., Sci. Dissertation Abstr. 20, p. 981 (1959).

27. Tarama, K., et al, Nippon Kazaku Zasshi 81, p. 1665 (1960).

28. Holland, C. D. and Murdock, P. G., A.I.Ch.E. Jour. 3, p. 386 (1957).

29. Walker, W.C. and Zottlemeyer, A.C., Jour. Phys. Chem. 57, p. 182 (1953).

30. Taylor, H. S. and Burns, R. M., Jour. Amer. Chem. Soc. 43, p. 1273 (1921).

31. Kwan, T. and Fujita, Y., Bull. Chem. Soc. Japan 24, p. 46 (1951).

32. Kozo, H., et al., Bull.Chem. Soc. Japan 34, p. 1213 (1961).

33. Misin, M.S., et al., Sintetich. Tseolity, Poluchenie, Issled, i Primenenie, Akad Nauk SSSR, Otd. Khim Nauk p. 135-151 (1962).

34. Burtt, B. P. and Jurbatov, J.D., Journ. Amer. Chem. Soc. 70 p. 2278 (1948).

35. Nikitin, N. I. and Yur'ev, V.I., Jour. Russ. Phys. Chem. Soc. 61, p. 1029 (1929).

36. Clarke, R. G., Groth, R. H. and Duzak, E. J., Jour. Chem. and Engr. Data 7, p. 120 (1962).

37. Rutz, L.O., Graham, J.B. and Kammermeyer, J., Jour. Chem. Eng. Data 4, p. 307 (1959).

38. Rutz, L. O., Jour. Chem. Eng. Data 8, p. 519 (1963).

39. Tourneux, C. and Devin, C., Comptes Rendus 232, p. 2430 (1951).

40. Markowitz, M. M. and Dezmelyk, E.W., Report AMRL-TDR-64-1 on AF Contr. 33 (657)-9124 (Feb. 1964).

41. Keiar, N. P., Izv. Akad, Nauk, SSSR, Ot. Khim, Nauk, p. 797 (1959).

42. Rousseau, J., Report ASD-TDR-62-527, Part II on Contr. AF 33(657)-8953 (1964).

43. Sartori, G.,Gazz.Chim. Ital. 67 p. 69 (1937).

44. Kwan, T. and Fujita, Y., Nature 171, p. 705 (1953).

45. Oliver, R. C. and Riesenfeld, F. C., in Closed Circuit Respiratory Systems Symposium, WADD Tech. Rept. 60-574,p.95.

46. Walfram, A., German Patent #1,071,674, Dec. 1959.

47. Leuhddemann, R., Oil and Gas Journal 57, p. 100 (1959).

48. Rohm and Haas Co., Bulletin IE-41-58, Aug. 1958.

49. Smart, R. C. and Derrick, W. S., Anesthesiology 18, p. 216 (1957).

50. McConnaughey, W. E., et al., NRL Rept. 5022, Nov. 1957.