Carbon Dioxide Management in Spacecraft Atmospheres

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ONE OF THE methods currently being investigated for the regenerable removal of carbon dioxide from space vehicle atmospheres involves its adsorption on synthetic zeolites. These materials, known commercially as "molecular sieves" (Linde Company) or "microtraps" (Davison Chemical Company) are crystalline alumino silicates of alkali and alkaline earth metals. Synthetic zeolites being crystalline are characterized by a large number of channels of regular diameter in the crystal lattice. The diameter of these channels can be varied by changing the nature of the alkali ion associated with the alumino-silicate groupings. In this manner, synthetic zeolites can be prepared to adsorb molecules of specific size, although it must be remembered that molecular forces, in addition to molecular size, influence adsorption. Thus, synthetic zeolites can be prepared which show an appreciable adsorption capacity for carbon dioxide.

Synthetic zeolites are classified according to structure type and pore diameter. Materials which have been found to have good adsorption capacity for carbon dioxide are listed in Table I.

TABLE I. ADSORPTION PROPERTIES OF SYNTHETIC ZEOLITES

Pore Diameter, A°	Linde Designation	Davison Designation
4	4A	510-517
5	5A	520-526
10	13X	530-

Because of its excellent performance, the experiments reported here were performed with a Linde Type 5A molecular sieve. Equilibrium isotherms for the adsorption of carbon dioxide on Type 5A are shown in Figure 1. Examination of these isotherms indicates that the adsorptive capacity of Type 5A increases as temperature is lowered.

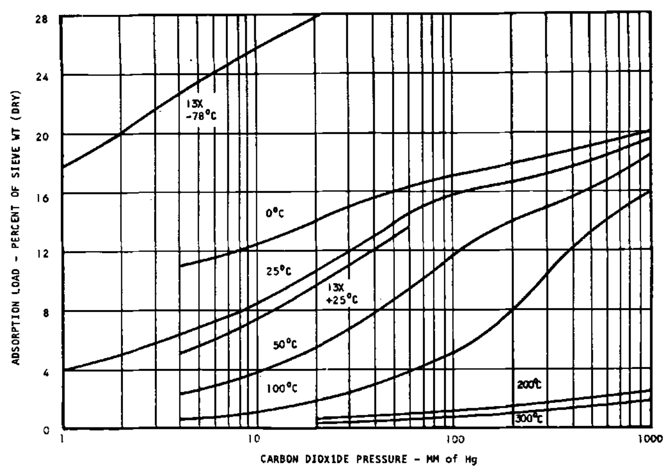

Fig. 1. Carbon dioxide capacity, Type 5A sieve (Linde Data) (Type 13X also plotted for comparison).

The purpose of this present investigation was to evaluate the use of sub-atmospheric temperatures to enhance the adsorption of carbon dioxide by synthetic zeolites and thus increase the efficiency of the carbon dioxide removal process. In a number of space vehicles, cryogenic fluids will be carried aboard to supply atmospheric gases for breathing and leakage makeup and for chemical power supplies. It is possible that these fluids can be employed simultaneously to lower the temperature of the process air entering the synthetic zeolite adsorption bed. In addition, special systems for carbon dioxide removal are being considered wherein a radiator and coolant loop are used to reduce the temperature of the process air as low as –60°F to freeze out the moisture in the air prior to entry into the synthetic zeolite bed.

Dynamic test data were obtained in the test apparatus and according to the procedures discussed in the following section of this report. After this section, the test results and their correlation will be discussed in detail.

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APPARATUS AND PROCEDURE

The synthetic zeolite to be tested was contained in a cylindrical aluminum canister, 3.55 inches in diameter and 18 inches long. The adsorbent bed length was 6 inches. The synthetic zeolite was contained within the canister by a fine mesh screen and a perforated metal plate located at each end. The holes in the baffle plate (0.25 inch in diameter) were omitted near the center to ensure more uniform flow. Inlet and outlet connections to the canister were 1.5-inch O.D. tubes. During test, the canister was covered with a 1-inch blanket of insulation to minimize heat transfer from the atmosphere.

The test apparatus is shown schematically in Figure 2. Laboratory air, cleaned and dehumidified to a 0°F

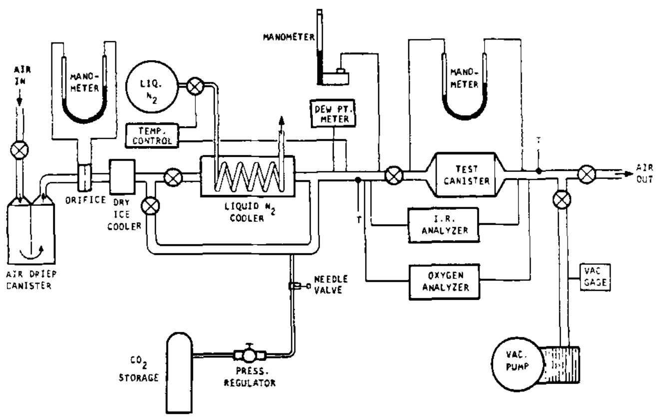

Fig. 2. Test apparatus, low temperature adsorption test.

dewpoint, was admitted through a pressure regulator into the test unit. The first step consisted of drying the air to a −80°F dewpoint by using a large canister containing a silica gel bed followed by a bed of Linde Type 13X molecular sieve. These beds were regenerated as required to maintain a constant low humidity in the exit air. After leaving the drying section, the air flow rate was measured by a calibrated orifice meter accurate to ± 2.5 per cent. From here the air temperature was brought to the desired test value by either a dry ice or liquid nitrogen bath. Electric heaters or a warm air bypass were used to adjust the temperature of the exit air from the bath to the desired value. Carbon dioxide gas was admitted to the warm air bypass stream in order to avoid carbon dioxide freeze-out at the lower temperatures and to ensure proper mixing with the air.

Downstream from the temperature control equipment, final measurements were made on the airstream to determine the following properties:

Temperature
Pressure
Dewpoint
Carbon dioxide concentration
Oxygen partial pressure

Oxygen partial pressure was measured to determine if adsorption of either oxygen or nitrogen was appreciable at the lower temperatures. These parameters, except for the dewpoint and pressure, were also measured at the canister outlet.

Tests on vacuum desorption of the canister were performed by means of a Kinney KMB 1200/KDH-130 vacuum pump rated at 1000 cfm in the pressure range 0.5 mm. Hg to 0.01 mm. Hg and 750 cfm at 0.001 mm. Hg. A three-inch diameter copper pipe was used between the pump and the test canister. High vacuum valves were employed and all connections silver-soldered.

Test Instrumentation:—A Beckman 15A Infrared Analyzer with a dual range cell for carbon dioxide detection (0-5 per cent and 0-100 per cent) was used to measure the carbon dioxide concentration at the canister inlet and outlet. The analyzer measurement was continuously recorded on an Esterline-Angus Strip Chart Recorder, Model AW (50 microamperes). The accuracy of the analyzer and recorder combinations was estimated as ± 5 per cent (i.e., 1 mole per cent concentration 1.0 ± .05 per cent). The I-R analyzer was calibrated using Beckman calibration gas and was also checked at intermediate concentrations by an Orsat Gas Analyzer.

Dewpoint measurements were performed with an instrument designed and fabricated by AiResearch. In this device which is capable of measuring dewpoints to − 100°F at 14.7 psia, the air sample is allowed to traverse a liquid nitrogen-cooled mirror in a cell maintained at controlled temperatures. Deposition of a moisture film on the mirror is observed visually by means of a lens, when the dewpoint temperature is obtained.

A Beckman Oxygen Analyzer, Type F3, dual range (0-200 mm. Hg and 0-800 mm. Hg oxygen partial pressure), was used to indicate whether there was any oxygen or nitrogen adsorption during the low temperature tests. Accuracy was ± 1 per cent of full scale.

The vacuum in the vacuum line was measured using a Televac, Model 2AMI-5, Vacuum Gage. A McLeod gage was used to double-check the vacuum readings periodically.

Procedure:—As stated in the introduction, the primary purpose of the test program was to determine the effect of low temperatures on the adsorption of carbon dioxide by synthetic zeolites. By varying the superficial velocity and canister length, other data useful in system design were also obtained.

Carbon dioxide adsorption data were obtained at temperatures of 530°R, 500°R, 450°R, 400°R, 350°R, and 300°R. Most of the tests were performed with a Linde Type 5A molecular sieve because of its high adsorptivity for carbon dioxide and long history in such applications. The greater experience with, and data on, Type 5A material was considered to afford a greater opportunity for understanding the dynamic adsorption process. The molecular sieves are supplied as broken extrudate of varying length but with uniform diameter. In these tests, ⅛-inch diameter material was selected from pressure drop considerations.

A carbon dioxide concentration of 1 mole per cent was used for the majority of the tests, since this concentration has been of most interest and has been specified as a suitable level for long term exposure during space vehicle missions. Several tests were also conducted at 0.5 mole per cent for comparative purposes.

Canisters were loaded prior to test with 650 grams of synthetic zeolite for the 6-inch bed length, 1300 grams for the 12-inch length and 1950 grams for the 18-inch length. Slight variations occurred in the actual weight loads. However, this variation was so slight that it could not be detected in plotting the data. Loading of the canisters was performed in a manner to prevent contamination of the material with water from the atmosphere. During each test the following data was recorded at the canister inlet and outlet:

Process air temperature
Carbon dioxide concentration
Oxygen partial pressure

Process air-inlet dewpoint and canister-pressure drop were also recorded.

Carbon dioxide concentration was measured continuously and controlled within ± 0.05 mole per cent. For most of the tests processed, air dewpoint was maintained below −80°F. The highest dewpoint of any test was −75°F. Temperature control of ± 1°R was achieved except for the extreme low temperature tests where the variation was ± 2°R.

In the initial tests, periodic weighing was employed to check the weight of carbon dioxide adsorbed during the progress of the test. Graphical integration of the carbon dioxide outlet concentration curve proved to be an accurate method for determining the amount of carbon dioxide adsorbed. Since this method simplified the procedure by making it unnecessary to remove the canister from the test line, and also led to greater temperature uniformity, it was employed for the majority of the tests. All canisters were weighed before and after the tests as a double check of adsorption capacity.

DISCUSSION

To facilitate the discussion of the test results, several terms have been employed. These terms are defined as follows:

1. Adsorption load—refers to the quantity of carbon dioxide adsorbed on the synthetic zeolite at any given time. It is expressed as per cent of the dry adsorbent weight.
2. Dynamic adsorption capacity—is defined as the quantity of carbon dioxide adsorbed when the synthetic zeolite is saturated. It is determined in a test by measurement of the adsorption load when the concentration of carbon dioxide in the outlet gas from the canister equals that of the inlet gas.

The effect of temperature on the dynamic adsorption capacity is summarized by Figure 3. Values plotted for 1 mole per cent and 0.5 mole per cent represent the average from a total of about 70 tests and include tests performed at various flow values. The expected increase in adsorption capacity as temperature is lowered was realized.

In the design of a synthetic zeolite system for carbon dioxide management in space vehicles it is important to know the rate at which carbon dioxide is adsorbed in a dynamic system.

The rate of adsorption of carbon dioxide in the test setup of this investigation was approached by determining the effect of superficial velocity on the adsorption of carbon dioxide by synthetic zeolites at various temperatures. These tests were performed with the 6-inch canisters (3.55 inches in diameter) containing 650 grams of Linde Type 5A molecular sieve. Process air flow rates were selected to have the following values:

0.154 lb. per min.	30 fpm at 530°R
0.308 lb. per min.	60 fpm at 530°R
0.463 lb. per min.	90 fpm at 530°R
0.616 lb. per min.	120 fpm at 530°R
0.72 lb. per min.	140 fpm at 530°R

These tests were repeated at temperatures of 500°R, 450°R, 400°R, 350°R, and 300°R. Adsorption load as a function of elapsed test time was determined and converted into the parameter: lb. carbon dioxide adsorbed per lb. synthetic zeolite per hour.

Values of this carbon dioxide removal rate were calculated at various percentage sieve saturations and temperatures and plotted as a function of mass flow rate. Curves for 70 per cent saturation are presented in Figure 4 and for 100 per cent saturation in Figure 5.

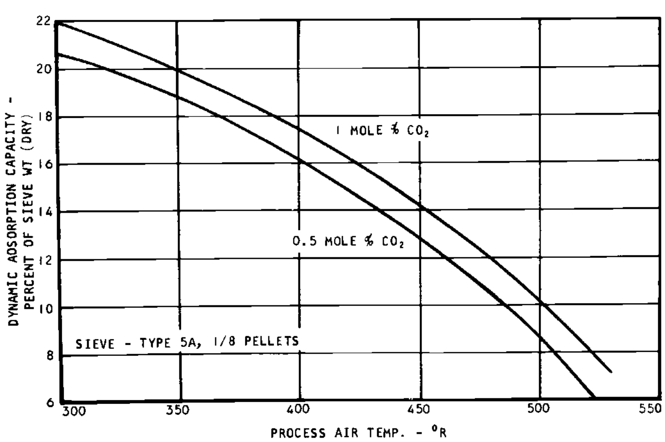

Fig. 3. Temperature effect on the dynamic adsorption capacity.

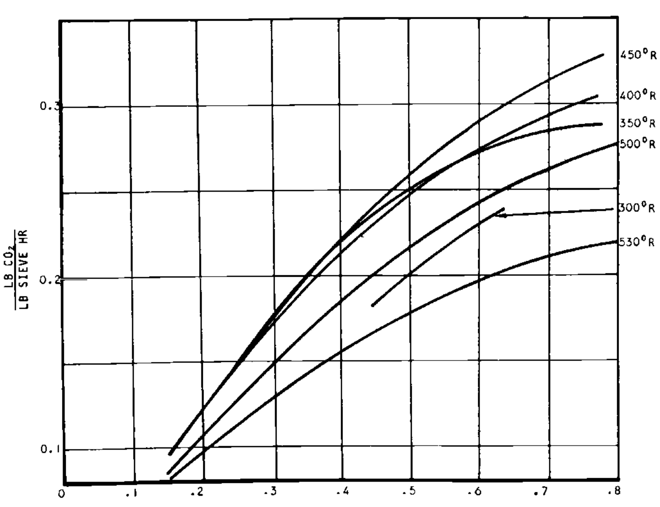

Fig. 4. Rate of adsorption at 70 per cent saturation.

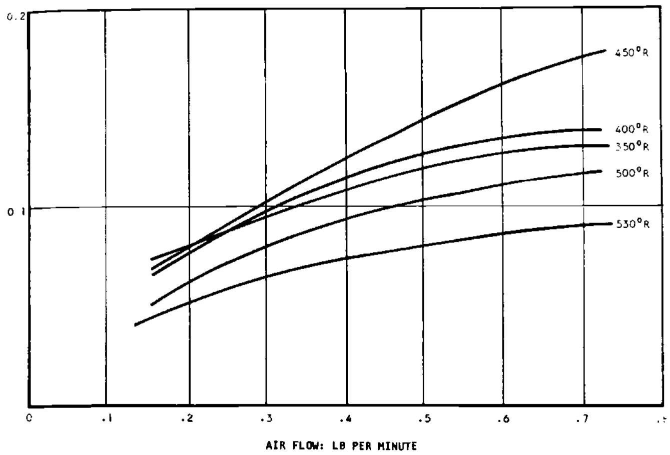

Fig. 5. Rate of adsorption at saturation.

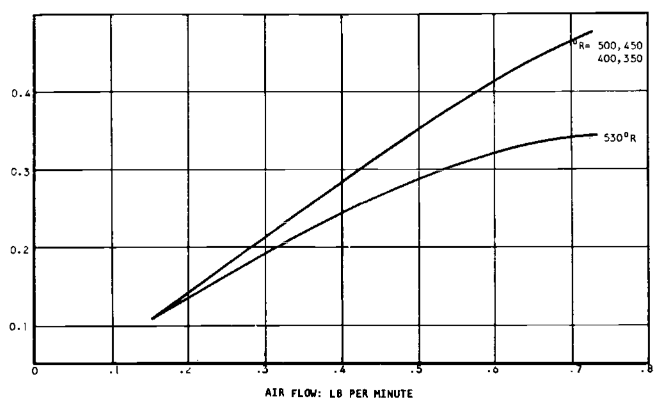

Fig. 6. Rate of adsorption at 9 per cent saturation.

Curves for 0 per cent saturation, obtained by extrapolation, are presented in Figure 6. In all cases the rate of adsorption or carbon dioxide removal from the airstream increases as the mass flow rate is increased. At zero per cent saturation the rate appears to be independent of temperature except for runs made at 530°R, in which case the rate of adsorption is lower. At the higher per cent saturation values, it is observed that the rate of adsorption reaches a maximum at a temperature of approximately 450°R and as temperature is lowered further the rate decreases. This is possibly due to the lower mobility of adsorbed carbon dioxide at the lower temperatures, making it more difficult for incoming carbon dioxide molecules to penetrate the channels and locate an adsorption site.

To determine the actual rate of adsorption, independent of the rate at which carbon dioxide is supplied to the synthetic zeolite, the rate values were extrapolated to the point at which the curves become horizontal. A plot of these rates versus temperature is shown in Figure 7, for the condition of 70 per cent saturation. These rate values again indicate that a maximum rate of adsorption occurs at an intermediate temperature for the higher saturation values.

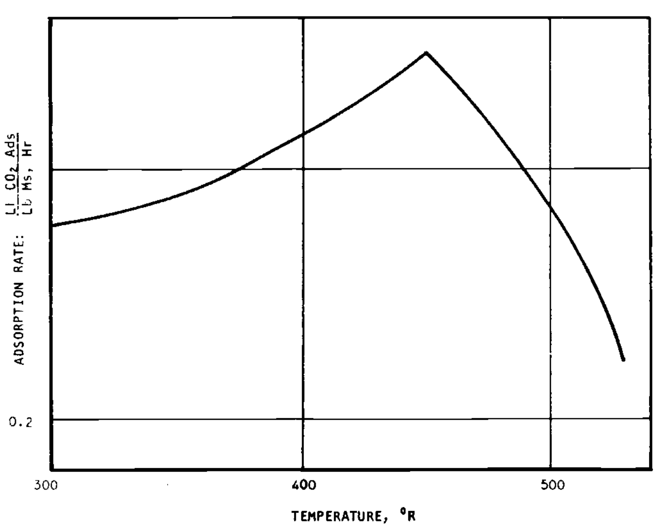

Fig. 7. Maximum rate of carbon dioxide adsorption as a function of temperature (70 per cent saturation).

Correlation of the rate data was attempted by means of the laminar layer concept. By employing the mass transfer factor of Colburn and Chilton as outlined in Reference 1, values were obtained for the height of the gas film mass transfer unit as given in Equation (1).

$$H = \frac{I}{aj}\left(\frac{\mu}{\rho D_f}\right)^{2/3} \qquad (1)$$

The mass transfer factor, j, was obtained by the correlation with Reynolds number according to the method of Gamson, Thodos and Hougen[1] as in expression (2).

$$j = 1.82\left(\frac{dG}{\mu}\right)^{-0.51} \qquad (2)$$

In these expressions,

- a = interfacial area of the synthetic zeolite per unit volume
- μ = viscosity of the gas
- ρ = density of the gas
- D_f = diffusion coefficient
- d = effective diameter

The diffusion coefficient for carbon dioxide in air was calculated by the empirical equation of Gilliland.[2]

$$D = 0.0167\frac{T^{3/2}}{\pi(v_{CO2} + v_{air})^2}\left(\frac{1}{M_{CO2}} + \frac{1}{M_{air}}\right)^{1/2} \qquad (3)$$

where v = molecular volume
M = molecular weight
T = temperature, °K
π = total pressure

Values of H obtained were used in the equation for rate of adsorption to calculate the value of y^*, the concentration of adsorbate in the gas phase in equilibrium that adsorbed on the synthetic zeolite. The rate equation employed is given in Equation (4)

$$r = \frac{G}{H}(y - y^*) \qquad (4)$$

where y is the adsorbate concentration in the fluid stream. In the present case, y = 0.0153 lb. carbon dioxide per lb. of air.

Values of y^* obtained in this manner are presented in Table II.

Examination of these results verifies the expected increase in y^* with increase in the carbon dioxide load-

TABLE II. CALCULATED VALUES OF y*

T°R	Per Cent Saturation of Molecular Sieve 0	70	100
530	0.00965	0.0112	0.0136
500	0.00956	0.0104	0.0128
450	0.00956	0.0094	0.0120
400	0.0093	0.00965	0.0127
350	0.00916	0.00972	0.0126

ing of the synthetic zeolite. A slight decrease in y* as temperature is lowered from 530°R appears to be evident.

TRADE-OFF STUDIES

Pressure drop measurements were made on the packed canisters during the adsorption tests. Some variation was observed in this data, due apparently to slight nonuniformity in packing the canisters with the molecular sieve pellets. For this reason the data has been plotted in the form of a band, as shown in Figure 8, where pressure drop is shown as a function of mass velocity.

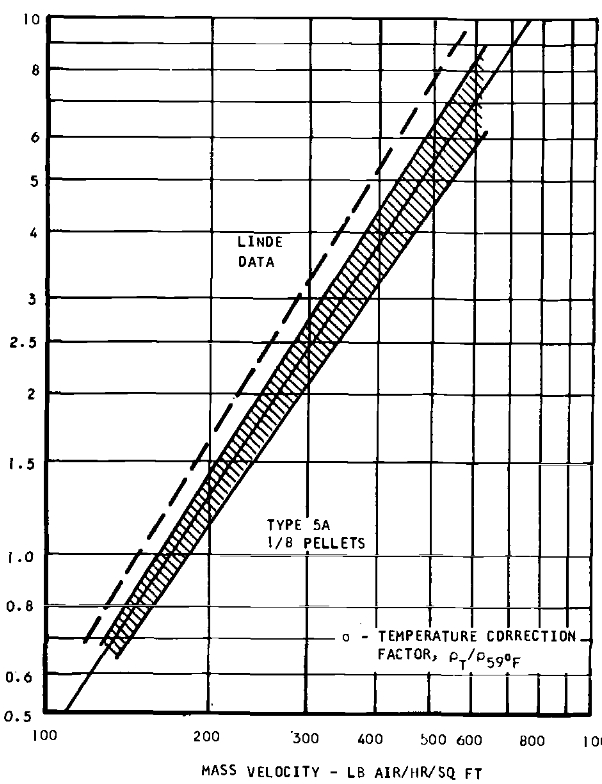

Fig. 8. Pressure drop (59F).

At the higher mass flow rates the pressure drop through the canister increases as expected. The rate of carbon dioxide removal also increases so that less synthetic zeolite is required. A comparison was made to determine the minimum system weight as a function of mass flow rate. In this study, power penalties of 0.8 lb. and 0.5 lb. per kilowatt were assumed. The efficiency of the circulation fan was assumed to be 45 per cent. Canister weight was calculated by the equation

$$W_c = 5.76\,A + 2.552\,L\sqrt{A} \quad (5)$$

where W_C = canister weight, lb.
A = area of bed face, ft.^{2}
L = bed length, ft.

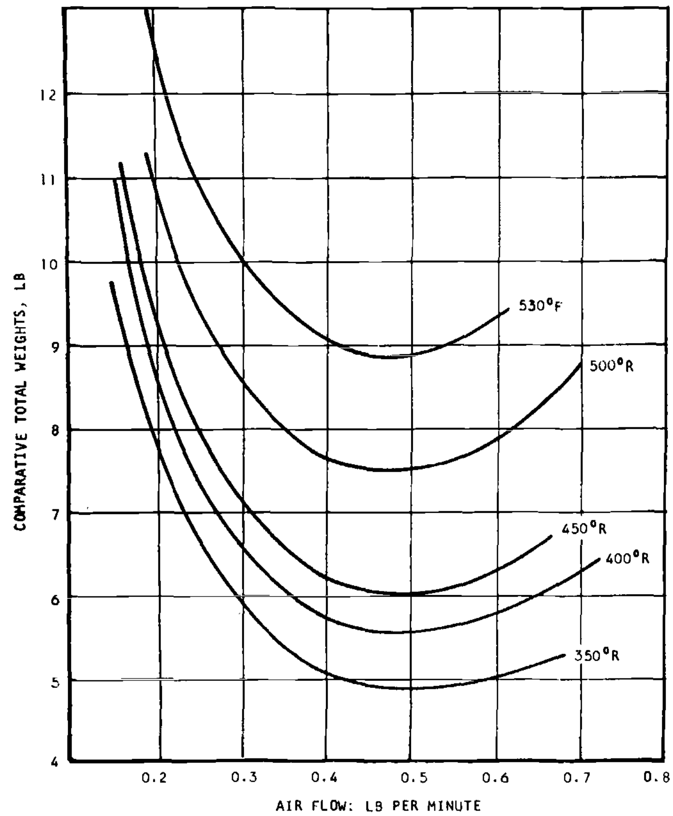

Fig. 9. Trade-off study—power penalty 0.5 lb. per watt.

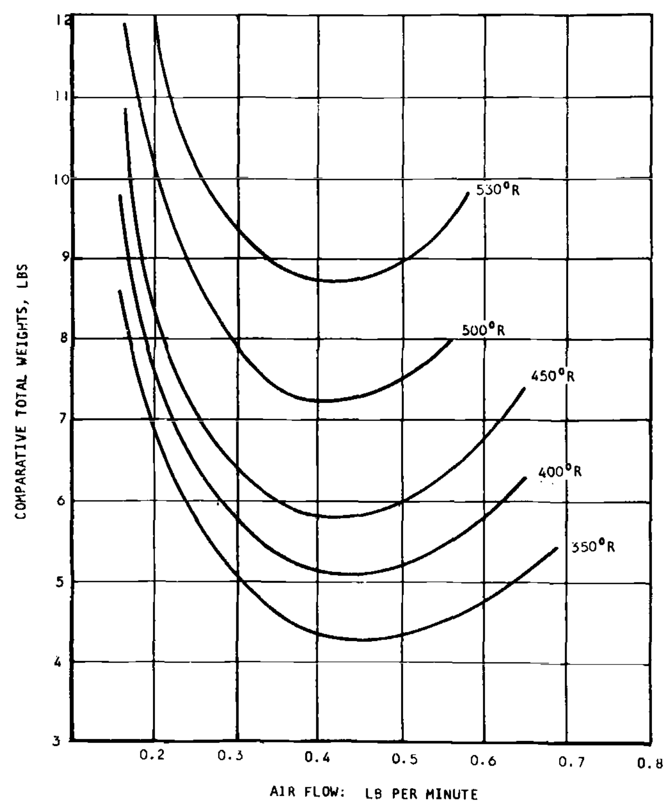

Fig. 10. Trade-off study—power penalty 0.8 lb. per watt.

The total system weight was calculated by the equation

$$W_T = W_S + W_C + 0.45\,\pi\,\frac{(\Delta PG)}{\rho} \qquad (6)$$

where W_S = weight of synthetic zeolite
G = mass flow rate
π = weight penalty for power
ΔP = pressure drop
ρ = density of air

The adsorption rate was taken as an average of the rates at 30 per cent saturation and 70 per cent saturation since these were considered to be typical of an adsorbent cycling procedure.

Results of this study are presented in the curves of Figure 9 for the case of 0.5 lb. per watt power penalty and in Figure 10 for 0.8 lb. per watt power penalty. Examination of these curves shows a minimum total weight at 3.9 lb. air per minute at 350°R (0.5 lb. per watt power penalty) and 4.3 lb. air per minute at 0.8 lb. per watt power penalty, also 350°R.

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