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**Advanced Technology Section Semiannual
Progress Report for the Period
September 1, 1976, to March 31, 1977
Volume 2: Engineering Science Programs**

OAK RIDGE NATIONAL LABORATORY
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CHEMICAL TECHNOLOGY DIVISION

ADVANCED TECHNOLOGY SECTION SEMIANNUAL PROGRESS REPORT

FOR THE PERIOD SEPTEMBER 1, 1976, TO MARCH 31, 1977

VOLUME 2: ENGINEERING SCIENCE PROGRAMS

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SUMMARY

Chemical Engineering Research

Several important changes have been made to improve the performance of the continuous annular chromatograph. The feed system was modified to reduce the concentration variation in the radial direction, to reduce the angular dispersion near the feed position, to provide more uniform elution flow rates, and to permit the use of various eluent solutions in different regions of the chromatograph (gradient elution). These modifications permitted: (1) meaningful evaluations of the effects of several variables on band dispersion and HETS, and (2) demonstration of continuous chromatography with gradient elution.

Studies of gas-liquid-solid fluidized beds have resulted in the determination of minimum gas and liquid velocities necessary for fluidization in 7.62- and 15.2-cm-ID columns. The minimum fluidization velocities depended upon the size and density of the particles but were independent of the initial bed height or column diameter over the conditions tested. Values for both local and overall holdup of all three phases were determined using several solids and a variety of flow conditions. Residence-time distribution measurements have been initiated to determine the degree of axial dispersion in the liquid phase.

Evaluations of hydroclones for removing solids from viscous liquids involved measurements of hydroclone efficiency, pressure drop, and the ratio of underflow rate to overflow rate in a 10-mm Dorr-Oliver Dowie Type A hydroclone. Three solid materials screened to <400 mesh (37 μ m) were tested using fluids with viscosities from 1 to 85 cP. Another way to enhance removal of solids from viscous liquids such as those produced

by coal conversion processes involves agglomeration of the particles so filtration or even settling can be more effective. Addition of solvents such as decane to some coal-derived liquids is known to cause agglomeration. Efforts to understand these processes involve two approaches. First, the surface properties of the solids are being studied, and an electrophoretic mass-transport apparatus is being tested for measuring zeta potentials in these solid-liquid systems. Second, the coal liquids are being separated into components, and the role of each component in the agglomeration process is being investigated. An interesting result is the observation that asphaltenes play a crucial role in agglomeration. The solids are not agglomerated by decane unless asphaltenes are present.

A study of deuterium (or tritium) oxidation as it permeates metal walls has been completed. This study has been important in evaluations of tritium containment problems in fusion and fission reactor systems. Deuterium oxidation efficiencies increased with increasing metal surface temperature but were unaffected by oxygen partial pressures between 0.005 and 0.2 torr. With palladium at 25°C, the conversion efficiency was approximately 90%, increasing to 97% at 60°C. With a nickel surface, the efficiency increased from 88% at 200°C to 94% at 500°C. A 304-L stainless steel surface gave an efficiency of 57% at 300°C, increasing to 91% at 600°C.

Magnetic Fusion Energy

Cryosorption vacuum pumping studies have demonstrated that a single panel of a 5A molecular sieve cannot pump mixtures of deuterium (or tritium) and helium under fusion reactor conditions. When a 95% deuterium--5% helium mixture was fed to the Excalibur CVR 1106 pump

while both chevrons were at 77K, the pumping speed quickly dropped to zero, and a cryogenic runaway (loss of coolant) occurred. This apparently resulted because deuterium freezing on the sieve panel prevented sorption of helium. This condition can be avoided by condensing or sorbing deuterium on a chevron or panel in front of the 4.2K molecular sieve panel. The feasibility of this approach was demonstrated by cooling the inner chevron of the Excalibur pump to a temperature where deuterium condensed. Although cooling of the chevron was marginal, steady pumping was observed with the deuterium-helium mixture.

A special cooling system was designed and constructed to permit operation of the Excalibur pump with sieve panel temperatures well above 4.2K (usually between 10 and 20K). Certain advantages are noted in operating hydrogen, deuterium, or tritium panels at these higher temperatures, particularly in refrigeration requirements. At these temperatures, no simple relationships exist between speed and pressure. Speeds vary with feed rate, loading, and thermal treatment between runs; and cyclic behavior is often observed. Resistance to diffusion into the sieve microstructure appears to play an important role in this behavior. A more open sieve structure, which can be achieved with other molecular sieve types (13X or Na-Y), is expected to improve pump performance. A new test pump has been designed which will allow the sieve panel to be replaced (with different sieve materials), and improved temperature control and instrumentation is planned in the new pump.

Recent experiments on tritium sorption from liquid lithium by solid yttrium have given most favorable results. At 300°C, a yttrium sample reduced the concentration in a small test chamber by a factor of 2 in

24 min. Furthermore, the lithium phase seems to contribute significantly to the mass transfer resistance, and there is reason to expect higher rates with forced convection. These rates are much higher than those reported previously for sorption from liquid potassium, and sorption by metal getters now appears to be an attractive process for the recovery of tritium from lithium blankets.

Studies of tritium removal from solid lithium-aluminum (Li-Al) alloys and sintered aluminum product (SAP) continued. High- and well-behaved removal rates were observed from SAP samples at temperatures between 400 and 500°C. The removal rate is controlled by diffusion within the solid alloy, and the diffusion coefficient, D , was found to be the following:

$$D = 2.64 \times 10^{-2} \exp \left(- \frac{24,890}{RT} \right) .$$

A mathematical model for predicting sorption pumping rates in a deep bed of sorbents was completed, and the results were compared with experimental data on CO_2 sorption by deep beds of type 5A molecular sieve. The agreement between the calculated and measured results was good; the only significant differences occurred during the first few seconds of pumping. This fluctuation is believed to result from resistance to diffusion through the sieve macropores which is most important during the initial period when the pumping speeds are extremely high. The model ignores this resistance, but a good fit to the data can be obtained by adjusting to an effective starting time.

A small effort is being devoted to the design of tritium and process systems for The Next (Tokamak) Step (TNS). Detailed design is being done at Westinghouse; direction and assistance in the work are being provided at ORNL.

1. INTRODUCTION

The Engineering Science Program in the Advanced Technology Section consists of two parts: (1) Chemical Engineering Research studies and (2) Magnetic Fusion Energy studies. The Chemical Engineering Research studies are all supported by the DOE/Basic Energy Sciences, and the Magnetic Fusion Energy studies are supported in part by the DOE Division of Magnetic Fusion Energy and in part by the DOE/Basic Energy Sciences.

2. CHEMICAL ENGINEERING RESEARCH

The Chemical Engineering Research Program includes several fundamental studies of chemical engineering problems of importance to energy development. These studies are funded by the U.S. Department of Energy/Basic Energy Sciences. Current studies are concerned with the new separation processes (both chemical and physical), the performance of three-phase fluidized beds that are potential choices for coal conversion reactors, and the oxidation of hydrogen isotopes (especially tritium) that permeate metal surfaces.

2.1 Continuous Chromatography

R. M. Canon and W. G. Sisson

2.1.1 Single eluent studies

Separation studies of the cobalt-nickel system which have been described previously¹ continued during this report period. The feed system was modified to reduce concentration variations in the radial direction (i.e., the variation of bandwidth with position across the annulus). Problems in reproducibility had been encountered with a single feed nozzle in the center of the annulus. Moving the nozzle to the outside wall reduced the capacity of the chromatograph and did not improve the data. A two-nozzle feed system has been introduced to improve feed distribution. The nozzles are located approximately 1/4 in. apart and 1/8 in. from each annulus wall and are aligned along a radius. Additional problems were encountered because of the cone-shaped feed in the region of the nozzles. The initial bandwidth could not be defined under those

circumstances; interaction with the resin began immediately and occurred simultaneously with hydrodynamic band spreading caused by the feed velocity adjusting to the eluent velocity. This problem has been overcome by the placing of two layers of inert glass beads above the resin. Initially, beads with a diameter of 0.18 mm were tested on the 0.060-mm ion exchange resin, and the feed nozzles extended only into the glass beads. This situation proved to be unsatisfactory because of the plowing effect of the feed nozzles moving through the small glass beads. The glass particles would pile up, and the top surface of the bed became uneven. However, no intermixing of beads with resin was observed. A second layer of larger 0.45-mm-diam beads was added, and the plowing effect did not occur. The larger diameter beads are more mobile and flow back into place as the nozzles pass. With two layers of beads (each about 3/4 in. deep), little degradation of the surface is observed. The glass beads allow time for the feed band to spread until its velocity matches the eluent velocity. At this point hydrodynamic spreading ceases, and an initial bandwidth is developed which can be discussed without introducing complications from hydrodynamics. These changes in the feed system result in more consistent data and allow operation at much higher feed rates than were possible previously.

Visual examination of the chromatographic bands revealed a change in slope at the point of the nickel-cobalt split. The change always occurs, but the degree varies with run conditions. This phenomenon is responsible for the inconsistency in some of the previous data. Since the data are usually taken from a point below the position where nickel separates from cobalt, it has not been meaningful to extrapolate back

through the discontinuity to the feed point. In order to avoid this problem, several runs were made with a single species in the feed. These experiments resulted in straight bands on the chromatograph. Results of some of these experiments are given in Table 2.1. The distribution coefficients are calculated by regression analysis. The height equivalent of a theoretical plate (HETP) has been calculated from bandwidth and elution position data. Refinement of the optical band detecting device during this report period improved bandwidth data considerably. The device has been tuned to the appropriate wavelength based on absorption curves for nickel and Co-1. This refinement alone increased the signal-to-noise ratio by more than an order of magnitude. A new, multiple-detector system is presently being fabricated and is expected to further improve bandwidth analysis.

Preliminary investigations have been made to determine the bed capacity. The effects of the feed rate (f) and the superficial eluent velocity (U) on the initial bandwidth have been studied. The data for nickel are shown in Fig. 2.1. As anticipated, the initial bandwidth increases approximately linearly with the feed-to-eluent ratio. When the initial resin loading (W_f^0) is considered, the results for nickel, as shown in Fig. 2.2, are as expected. The increased flow rates result in increased initial loading but little change in HETP. The data for Co-1 in Fig. 2.3, however, show an increase in HETP with increased resin loading. This is more noticeable with Co-1 because of its higher distribution coefficient. In Fig. 2.4, HETP is shown as a function of the feed rate for Co-1. No allowance is made for changes in initial feeding area. In this case, one might expect that a change in the feed

Table 2.1. Results from regression analysis of nickel and Co-1 on the continuous chromatograph; 95% confidence limits are given

Run	pH	Feed rate (cc/min)	Eluent velocity (cm/min)	Distribution coefficient		Height equivalent to theoretical plate (HETP) (cm)
				Ni	Co-1	
A1	8.07	2.00	1.33	3.43		0.168 $\pm$ 0.031
A2	8.07	2.00	2.67	3.17		0.224 $\pm$ 0.022
A3	7.94	2.00	0.65	2.81		0.208 $\pm$ 0.022
A4	7.97	2.00	2.00	3.29		0.300 $\pm$ 0.087
B1	8.02	2.00	0.71		6.38	0.037 $\pm$ 0.007
B2	7.86	2.00	1.34		5.45	0.098 $\pm$ 0.028
B3	8.05	2.00	1.95		5.25	0.151 $\pm$ 0.077
B4	7.94	2.00	2.49		4.66	0.164 $\pm$ 0.075

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Fig. 2.1. Initial bandwidth as a function of the ratio of feed volume to eluent velocity for nickel in $(\text{NH}_4)_2\text{CO}_3$.

Fig. 2.2. HETP as a function of initial loading for 3.80 g of nickel per liter. Eluent, $(\text{NH}_4)_2\text{CO}_3$.

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Fig. 2.3. Effect of initial loading on HETP for 3.80 g of Co-1 per liter. Eluent, $(\text{NH}_4)_2\text{CO}_3$.

Fig. 2.4. HETP as a function of feed rate for Co-1 with an $(\text{NH}_4)_2\text{CO}_3$ eluent of pH 8.0 and eluent velocity of 2.63 cm/min.

concentration (C_f) would have a different effect than a change in feed volume (f), but no difference is apparent at this point.

Elution position is only a function of reciprocal eluent velocity for constant rotation and a given system. These relations are shown for nickel and Co-1 in Fig. 2.5. A linear relation should also exist between HETP and the eluent velocity (i.e., higher velocities resulting in a smaller number of stages in the device). This relationship is presented in Fig. 2.6, based on Co-1 elution.

Investigations with the nickel-cobalt amine system are continuing. The new detector system should markedly improve data reproducibility. The new system contains a bank of six optical devices rigidly mounted in a vertical configuration. The detectors are 3 in. apart and will allow determination of bandwidth in the same flow line at all locations. This method is expected to reduce errors introduced by circumferential variations in the resin bed. A new take-off system is presently being fabricated. The continuous chromatograph has always experienced problems with mixing with the old exit system. The resin bed support and drip systems both contributed to this trouble. The new system is expected to reduce the difficulties from mixing but will involve a complete redesign of the bottom of the chromatograph.

Uncertainty in rotation rate measurements has been eliminated with the installation of a new drive system. Previously, rotation rates were determined by direct observation of the rotating chromatograph. Since rotation rates were commonly on the order of 50°/hr, this method was very time-consuming. The new drive system utilizes a feed-back-controlled digitally set drive motor with digital readout of the motor rotation rate.

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Fig. 2.5. Elution position of nickel and Co-1 with $(\text{NH}_4)_2\text{CO}_3$ as a function of reciprocal eluent velocity. Rotation rate = $50^\circ/\text{hr}$; pH = 8.0.

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Fig. 2.6. Effect of superficial eluent velocity on HETP for Co-1 with 1 M $(\text{NH}_4)_2\text{CO}_3$ at pH 8.0 as eluent. Volumetric feed rate = $2.00 \text{ cm}^3/\text{min}$; feed concentration = 3.80 g of Co-1 per liter.

This results in a stable, easily selected rotation rate with an accuracy of $\sim 0.5\%$. It has contributed considerably to data improvement.

2.1.2 Gradient elution studies

The continuous chromatograph can now be operated in the gradient elution mode. Major changes (from single eluent mode) include use of a manifold header system and indirect control of the eluent velocity. The header system was described in the previous semiannual.² The control system consists of an optical meniscus detector and associated electronics to control a valve in the exit-gas stream from the chromatograph head space. A side glass has been built into the outer wall of the chromatograph with the bottom of the well adjacent to the layer of the glass beads. An optical detector observes the meniscus in the side glass and initiates proper action to maintain the liquid (eluent) level within the glass bead layer to within $\pm 1/16$ in. of a set point. The eluents are pumped through the header system at constant rates. The air overpressure is supplied by regulated air, and the controller acts to seek the proper pressure to maintain the liquid level constant; hence, very small variations in air pressure ($\sim \pm 1\%$) are required to maintain a constant liquid level. This method of control has a strong advantage over liquid rate control systems because increasing the number of eluents does not cause control problems. It can handle six eluents (or more) as easily as a single eluent. Operation with this system has been very encouraging. It has operated successfully for periods of several hours with no operator attention. The optical detector does suffer somewhat from extraneous light variations. A second-generation continuous chromatograph is likely to utilize a mechanical liquid level detector.

While the cobalt-nickel amine system does not require gradient elution for separation, its vivid colors make an impressive demonstration and show graphically the effectiveness of the continuous annular chromatograph in this mode of operation. This operation is shown in Fig. 2.7. One molar ammonium carbonate was introduced into all quadrants, but the pH varied in the different quadrants. The pH was 9.68 in quadrants one and four and 8.01 in quadrants two and three. The rotation rate was $35^\circ/\text{hr}$, and the eluent velocity was 1.37 cm/min in all quadrants. The feed consisted of 4 g per liter of nickel, 1 g per liter of Co-1, and 1 g per liter of Co-2 in 1 M $(\text{NH}_4)_2\text{CO}_3$ at 3 cm³/min. The distribution coefficient for nickel is a strong function of pH for this system, but the cobalt curves show little change. Nickel has the highest distribution coefficient at pH 9.68 and is therefore highest on the chromatograph in quadrant one (shown at the left of the picture). A drastic change in slope of the nickel band occurs at the interface between quadrants one and two. Nickel has the lowest distribution coefficient at pH 8.0 and therefore exhibits a steeper slope in quadrant two. The sharpness of the slope change demonstrates that little mixing of eluents is occurring at the quadrant interfaces. The power of this method can be seen by noting that proper adjustment of the pH in quadrants two and three will result in any band separation desired. For instance, nickel and Co-1 can be eluted 180° apart. Since the operation is continuous, separation time is not a factor for preparative work. Visual observation of the point at which the nickel band changes did not detect any fluctuation of position with time--another indication of the system stability.

Fig. 2.7. Continuous separation of the nickel-cobalt amine system utilizing pH gradient elution with $1\text{ M }(\text{NH}_4)_2\text{CO}_3$.

Studies in gradient elution continuous chromatography are continuing. Efforts are now centered on the design of a second-generation chromatograph for higher pressure operation and on a search for separations for which the continuous chromatograph is particularly well suited. Areas presently under preliminary study include lanthanide separations, the americium separation for waste partitioning, and separations related to the resource recovery program (particularly fly-ash utilization). Flow sheets involving ion exchange separations of metals in the acid leach process for fly-ash separation are being examined.

2.2 Three-Phase Fluidized-Bed Reacting Systems

J. M. Begovich

The study of gas-liquid-solid fluidized beds continued during this period using various packings in 7.62- and 15.2-cm-ID columns. The minimum gas and liquid velocities necessary to fluidize a bed were determined as a function of the particle size and density, while no effect was found as the initial bed height or column diameter was varied. Operating the columns with nondistinct bed heights has shown the variation of the phase holdups with axial position in the bed and the effects of gas and liquid velocities upon those variations. Residence-time-distribution (RTD) experiments have been initiated in the 7.62-cm-ID column to determine the degree of axial dispersion present in the liquid phase of a three-phase fluidized bed.

2.2.1 Experimental

A schematic of the experimental apparatus is shown in Fig. 2.8. Air and water pass together through a fluid distributor into the bottom

Fig. 2.8. Schematic of three-phase fluidization apparatus.

of either the 7.62-cm or 15.2-cm-ID column and flow cocurrently upward through the bed. The details of the electroconductivity probes, meter, and digital readout have been presented previously.²

To permit RTD experiments, the 7.62-cm-ID column was altered as follows: (1) five pressure taps were added along the column wall for a total of 16 taps located at 8-cm intervals and starting 1 cm above the fluid distributor; (2) two platinum electrodes were located 180° apart and fixed to the column wall at 7 cm above the fluid distributor. These fixed electrodes were connected to a second conductivity meter, and the output of both meters was recorded on a dual-pen recorder. Saturated KCl solution was injected into the bed 1 cm above the fluid distributor and perpendicular to the direction of flow through six 1-mm-diam holes drilled into a length of 3.2-mm-OD stainless steel tubing. An electrical timer, in addition to activating the solenoid for the injection of the KCl tracer by either air or water pressure, simultaneously activated the event markers on the dual pen recorder. The resulting concentration-time curves were then analyzed in two ways: (1) by the standard analysis of moments,³ and (2) by the utilization of the Laplace transform method.^{4,5} The second method was designed to reduce the influence of tailing of the tracer pulses on the calculated values of the axial dispersion coefficient.

2.2.2 Results

Minimum fluidization. The minimum fluid flow rates required to achieve fluidization are determined by a plot of the pressure drop across the bed vs the superficial liquid velocity at a constant gas flow rate. As shown previously,⁶ the flow rates at which a break in the curve occurs correspond to the minimum fluidization velocities.

(Effect of column diameter and static bed height). The effect of column diameter and static bed height (or bed mass) on the minimum fluidization velocities for the air--water--glass beads and the air--water--plexiglass beads systems is shown in Fig. 2.9 and 2.10 respectively. For both systems, the minimum liquid velocity required to fluidize the bed with no gas phase present is indicated by the arrow on the ordinate of the plot as calculated from the two-phase correlation of Wen and Yu.⁷ Excellent agreement between the calculated and experimental point for each system can be observed.

Neither the column diameter nor the mass of solids present in the column appeared to have any significant effect upon the minimum fluidization velocities. A slight dependence on column diameter might be indicated for the air--water--plexiglass beads system; however, the small density difference between the water and solid phases made the breakpoint in the pressure-drop-vs-liquid-velocity curve very difficult to determine and subject to error. Since fluidization of a bed is achieved when the upward drag force exerted on the particles by the fluids equals the bouyant weight of the bed, an effect of static bed height on the minimum fluidization velocities would only be expected if end effects⁶ were present in the bed. One would not expect the minimum fluidization velocities to be a function of column diameter unless the size of the gas bubbles approached that of the column diameter or unless channeling occurred.

(Effect of particle size and density). Minimum fluidization velocities are shown in Fig. 2.11 for the air--water--alumino-silicate beads system and in Fig. 2.12 for each of the four systems studied to

Fig. 2.9. Minimum fluidization velocities for the air--water--
glass beads system.

Fig. 2.10. Minimum fluidization velocities for the air--water--plexiglass beads system.

ORNL DWG 77-248

Fig. 2.11. Minimum fluidization velocities for the air--water--alumino-silicate beads system.

Fig. 2.12. Effect of particle size and density on the minimum fluidization velocities.

date. Note that the smooth curves of Figs. 2.9-2.11 correspond to those shown in Fig. 2.12.

As the gas velocity is increased, the minimum liquid velocity required to achieve fluidization in each of the four systems decreases. The magnitude of this decrease is considerably different for the plexiglass beads with their small solid/liquid density difference as compared to the other three systems which have a larger solid/liquid density difference.

Wen and Yu,⁷ in their two-phase correlation, noted that the minimum fluidization velocity was proportional to the particle diameter and solid/liquid density difference, but inversely proportional to the fluid viscosity. The plexiglass beads, which have the same diameter as the alumina beads, also have a much smaller solid/liquid density difference and thus fluidize at lower velocities. The alumina and alumino-silicate beads have approximately the same density, but the smaller diameter of the latter particles causes them to fluidize at lower velocities. It is of interest to note that the larger diameter of the alumina beads overrides the influence of the higher density of the glass beads requiring a larger minimum liquid fluidization velocity at low gas velocities for the alumina beads. At higher gas velocities (>7 cm/sec), the minimum fluidization curves for the glass and alumina beads essentially merge into one.

(Effect of liquid viscosity). The effect of liquid viscosity on the minimum fluidization velocities has been reported previously.^{1,8} Using a computer analysis, it was found that for a given gas velocity, the minimum liquid fluidization velocity decreased as the liquid viscosity

increased. However, during this report period, a comparison of the computer analysis with an analysis made by hand revealed that the minimum liquid fluidization velocities obtained by the computer method were too high. The corrected results are shown in Fig. 2.13. The smooth curve is the same as in Fig. 2.9 for the same glass beads in the 7.62- and 15.2-cm-ID columns. The points shown for zero gas velocity are calculated values and are shown only to indicate the expected influence of liquid viscosity.

The conclusions reported previously¹ have not been altered; for a given gas velocity, the minimum liquid fluidization velocity decreases as the liquid viscosity increases. However, the influence of the liquid viscosity appeared to decrease for the higher viscosities. Also, as noted previously, the gas velocity did not appreciably affect the minimum liquid fluidization velocity for the more viscous aqueous glycerol solutions studied.

Overall phase holdups comparison. As described in a previous report,² an overall holdup can be calculated for each phase in two ways: (1) by placing the electrode in the middle of the bed and measuring the conductivity of the bed at that point, and (2) by using the measured pressure gradient over the column. Both of these methods assume that the phase holdups are constant over the entire bed.

A comparison of the overall gas holdup determined by each of the above methods is shown in Fig. 2.14 for air-water flow only (i.e., no solids present, in both columns.) A least-squares fit of the data yields a line with nearly unity slope and zero intercept.

Fig. 2.13. Effect of liquid viscosity on the minimum fluidization velocities.

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Fig. 2.14. Comparison of overall gas holdup by two different methods in columns with air-water flow.

The glass and plexiglass beads were used in both columns without any difficulty, but the conductivity readings obtained using the porous alumina beads, the likely catalyst support for a coal liquefaction reactor, had to be corrected by a factor approximately proportional to the volume of liquid residing in the internal pores of the solids to account for the effective conductivity of the solids. Plots of the overall solid holdup measured using the conductivity method vs those measured using the pressure gradient method are shown in Fig. 2.15 for water fluidization only, and similar comparisons are made for air-water fluidization of each of the systems studied (see Figs. 2.16-2.20). Least-squares fits of these data also result in lines of approximately unity slope and zero intercept as indicated in Table 2.2.

Table 2.2. Comparison of overall solid holdups by two different methods

$$\epsilon_{S, \text{ conductivity}} = a + b \epsilon_{S, \text{ pressure gradient}}$$

Solid	Column diameter (cm)	a	b	Correlation coefficient	Number of points
Glass	7.62	-0.052	1.067	0.985	96
Glass	15.2	-0.016	1.005	0.985	56
Plexiglass	7.62	0.005	0.862	0.914	48
Plexiglass	15.2	-0.028	0.841	0.875	84
Alumina	7.62	-0.023	1.054	0.985	98

ORNL DWG. 77-136

Fig. 2.15. Comparison of overall solid holdup by two different methods in water-solids fluidization.

Fig. 2.16. Comparison of overall solid holdup in the 7.62-cm-ID column by two different methods for the air--water--glass beads system.

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Fig. 2.17. Comparison of overall solid holdup in the 15.2-cm-ID column by two different methods for the air--water--glass beads system.

Fig. 2.18. Comparison of overall solid holdup in the 7.62-cm-ID column by two different methods for the air--water--plexiglass beads system.

Fig. 2.19. Comparison of overall solid holdup in the 15.2-cm-ID column by two different methods for the air--water--plexiglass beads system.

Fig. 2.20. Comparison of overall solid holdup by two different methods for the air--water--alumina beads system.

Deviations from complete agreement between the two methods occur chiefly for low values of solid holdups — that is, where the fluid flow rates are high and the bed height is not distinct. At such conditions, the pressure-gradient method yields a solid holdup based on a uniform bed. The conductivity method, however, yields a solid holdup based on the middle of the bed. Since the bed, in reality, goes from a fairly uniform lower section through a transition region of slowly decreasing solid holdup to a gas-liquid-only region, the solid holdup obtained by conductivity at the middle of the bed is lower than that obtained from the pressure-gradient method.

Axial variation in holdups. As discussed above and in a previous report,² the solid holdup in a three-phase fluidized reactor is fairly uniform in the lower section of the bed, then goes through a transition region of slowly decreasing solids concentration to a two-phase gas-liquid region above the bed. The liquid holdup remains fairly constant in lower portions of the bed and then increases to a constant value in the gas-liquid region. Although the data have not been completely analyzed, some preliminary observations can be made.

(Effect of column diameter). The effects of column diameter upon the axial variation of the liquid and solid holdups can be seen in Figs. 2.21 and 2.22. These results, typical of most of the data, were obtained in the 7.62- and 15.2-cm-ID columns under identical conditions (i.e., identical gas velocities, liquid velocities, particle type, and static bed height).

Neither figure indicates a dependence of the holdups on column diameter in the lower portion of the beds. However, for the lower liquid

Fig. 2.21. Effect of column diameter upon the axial variation in holdups.

Fig. 2.22. Effect of column diameter upon the axial variation in holdups.

velocity used in Fig. 2.21, the transition region from three phases to two phases appeared to be broader in the smaller column. This effect is not evident in Fig. 2.22 where the same relationship between the holdups and height was obtained in both columns.

(Effect of liquid velocity). Under conditions of constant gas velocity in the 7.62-cm-ID column, the effect of liquid velocity on the axial variation in solid holdup is shown in Fig. 2.23. As the liquid velocity was increased, the bed expanded, and thus the solid holdup decreased. The calculated bed height, as found from the intersection of the measured pressure gradients in and above the bed, is indicated on the curves for each flow rate. This bed height corresponds to the height the same bed would have if the solids concentration in the column was uniformly distributed. The highest position where solids were detected was higher than this calculated bed height, since the bed contains a rather wide transition region where flow changes from a three-phase to a two-phase column. The width of this transition region appeared to remain approximately constant with changing liquid velocity — that is, the solid holdup decreased from the approximately constant value in the bed to zero over about 20 cm of bed height.

(Effect of gas velocity). When the liquid velocity was held constant and the gas velocity was increased, the width of the transition region increased substantially (see Fig. 2.24). The solid holdup in the lower portion of the bed was decreased slightly by the fairly large increase in gas velocity; however, the transition region increased from ~20 to ~35 cm in width. As expected, the calculated bed height for the

Fig. 2.23. Effect of liquid velocity upon the axial variation in the solid holdup.

Fig. 2.24. Effect of gas velocity upon the axial variation in the solid holdup.

high gas velocity indicated a much lower bed height (highest position with solids) than one observed visually. This can be explained by Fig. 2.24.

Residence-time-distribution experiments. RTD experiments have been initiated in the 7.62-cm-ID column to determine the degree of axial dispersion present in the liquid phase of a three-phase fluidized bed. Some preliminary results using the 4.6-mm-diam glass beads indicate that dispersion increases as the gas velocity is increased.⁹ Further work will be done with the 4.6-mm-diam glass beads, with glass beads having diameters of 3.2 and 6.2 mm, and the 6.3-mm-diam plexiglass spheres. These studies will determine the effects of gas and liquid velocity and the physical characteristics of the solids upon the liquid-phase axial dispersion coefficient. When dispersion has been characterized, it will be possible to conduct gas-liquid mass transfer experiments and calculate meaningful liquid-film mass transfer coefficients over a wide range of conditions.

2.3 Hydraulic Cyclone Studies

J. B. Talbot

Hydraulic cyclones (hydroclones) are potentially useful devices for removing solids from coal liquids, but their ability to separate particles from relatively viscous liquids has not been adequately evaluated. Therefore, experiments using a 10-mm diam hydroclone were continued to study particle separation as a function of feed rate, density of particles, and density and viscosity of the liquid medium. Performance criteria are usually defined by cyclone efficiency, pressure drop, and the ratio of the underflow rate to the overflow rate.

2.3.1 Background

The selective separation of solid particles from a liquid in a hydroclone results from the viscous drag and centrifugal force on each particle. Its separational power develops through the use of fluid pressure energy, relating the inlet-to-overflow pressure drop to the tangential feed rate. For a given hydroclone design and particle density, the pressure differential is related to the inlet flow rate as follows:

$$\Delta P = A Q^2 ,$$

where

ΔP = feed-to-overflow pressure drop, psi,

Q = feed rate, gal/min,

A = constant.

Hydroclone efficiency is defined in several different ways in the literature.¹⁰ Gross efficiency, G , is the ratio of the solids discharged at the underflow-to-solids feed rate. The efficiency most often used is the centrifugal efficiency, E , which is defined as follows:

$$E = \left(\frac{G - R_f}{1 - R_f} \right) ,$$

where

R_f = ratio of underflow rate to feed flow rate.

For example, if all solids entering the hydroclone leave at the underflow, $G = 1$. If all the liquid leaves at the underflow, $R_f = 0$, and the centrifugal efficiency equals 100%. Since all of the solids in the

feed material may not be the same size, efficiency must be referenced to a size distribution. Therefore, point efficiency expresses the centrifugal efficiency at a given size particle or the fraction of particles of a given size from the feed stream which are removed through the underflow. Typical results are given in Fig. 2.25 which relate point efficiency to particle diameter for a particular hydroclone and flow rate. The particle diameter that gives a point efficiency of 50%, d_{50} , is often used to describe the efficiency of a particular hydroclone. Performance variables, such as cyclone diameter, liquid viscosity, feed rate, particle density, and liquid density, are usually correlated with the d_{50} value, as shown in a previous report.²

2.3.2 Experimental

The apparatus and procedure to study hydroclones has been described previously.¹ Slurry from stirred tank is recirculated by a Reeves Moyno pump through a 10-mm Dorr-Oliver Doxie Type A hydroclone (Fig. 2.26). The inlet, overflow, and underflow streams are sampled for each pressure drop, and particle size distributions are determined using a ZB Coulter Counter with a Model H4 Channelyzer. Samples of the overflow and underflow are dried and weighed to determine solids concentrations.

Experiments have been conducted¹¹ using slurries containing approximately 5 wt % solids in water-glycerin solutions with viscosities from 1 to 85 cp. The particles used included aluminum oxide (sp gr, 3.72 g/cm³), a commercially available test dust "Air Cleaner Test Dust", sp gr, 2.64 g/cm³, and fly ash (sp gr, 2.28 g/cm³). The powders were screened to <400 mesh (37 μ m in diameter).

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Fig. 2.25. Typical point efficiency curve.

Fig. 2.26. A schematic diagram of the 10-mm Dorr-Oliver Doxie Type A hydroclone.

2.3.3 Results

Experiments were conducted to determine the effect of flow rate and viscosity on both pressure drop and hydroclone efficiency.¹¹ Information concerning the specifications of the 10-mm diam Dorr Clone was obtained from Dorr-Oliver. Their separation data are based on a solid (a quartz and sand mixture) with a 2.7 sp gr and at a feed concentration < 25 wt % in water.¹² Figure 2.27 compares our data for the feed-to-overflow pressure drop versus the feed rate at 1 cP with data supplied by Dorr-Oliver. The experimental results and the Dorr-Oliver correlation agree well with a relationship in the literature¹⁰ which states that the pressure drop is proportional to the square of the feed rate. Density of the solid does not seem to affect this relationship, but the experimental results do not show the same capacity for a given pressure drop as the Dorr-Oliver correlation.

The viscosity of the fluid had a pronounced effect on the pressure-drop--flow-rate correlation. As observed in Fig. 2.28, the slope of the curves decreases as the viscosity increases. At low viscosities, the pressure drop is proportional to the square of the flow rate. This indicates that centrifugal acceleration, proportional to the velocity squared, has a more predominate effect than viscous drag on pressure drop. As viscosity increases, the viscous force becomes more important, and the pressure drop is proportional to the velocity (as for laminar Newtonian flow in a pipe).

Hydroclone efficiency was also affected by an increase in viscosity. Figure 2.29 shows that the rate at which solids and liquid are discharged to the underflow decreases at higher viscosities. At viscosities greater

Fig. 2.27. Pressure-drop-vs-feed-capacity correlation at 1 cP viscosity.

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Fig. 2.28. Effect of viscosity on the pressure drop-flow rate relationship for AC Test Dust.

Fig. 2.29. Effect of viscosity on gross efficiency and underflow-to-feed-rate ratio.

than 30 cP, the fraction of solids and the fraction of liquid that go to the underflow are essentially equal. An overall centrifugal efficiency was calculated for various flow rates for AC Test Dust, as shown in Fig. 2.30. Efficiency increases with increasing flow rate, as expected, but again viscosity has a pronounced effect above about 30 cP. At high viscosities, the centrifugal efficiency is essentially zero.

Point efficiencies were not determined due to problems encountered with the Coulter Counter system. Improvements have been made to minimize background noise detected by the particle counter, and a better understanding of the channelizer system has been attained. The data processor has been programed by Coulter Electronics so that the maximum computed particle volume must not exceed $10,000 \mu\text{m}^3$, a particle diameter of $27.6 \mu\text{m}$. Thus future work will be done using particle sizes under this limit; kaolin (sp gr, 2.40 g/cm^3) and Fe_2O_3 (sp gr, 5.36 g/cm^3) powders are available. Also, other powders will be sieved to $<20 \mu\text{m}$. Viscosities up to 30 cP will be studied further, and particle size distributions will be determined to evaluate the hydroclone point efficiency.

2.4 Fundamental Agglomeration Studies in Heavy Organic Media

B. R. Rodgers and J. D. Hewitt

2.4.1 Introduction

The tendency for particles to agglomerate and precipitate, or to disperse and stabilize, is characterized by a number of physical parameters. The most obvious parameters are size and density relative to the suspending matrix. Generally, colloidal solutions are characterized by dispersed particles having diameters of $<1 \mu\text{m}$, an artificial limit

Fig. 2.30. Relation between centrifugal efficiency and flow rate for AC Test Dust.

corresponding roughly to the maximum size particle that will stay in suspension for a reasonable time. In heavy organic systems, such as coal liquefaction products, unconverted coal and mineral matter may be present both as a suspension (particles $>1\ \mu\text{m}$) and as a colloidal dispersion (particles $<1\ \mu\text{m}$). The former particles are not difficult to remove by conventional techniques, but the remaining dispersed particles often constitute up to 50% by volume of the total mass of particles. The smaller particles must be removed to meet stringent EPA specifications.

The properties of these colloidal dispersions may be altered in two ways: (1) by effecting a change in particle size distribution, and hence the superficial interfacial area, and (2) by changing the nature of the interfacial forces by adding electrolytes or surface-active agents. Even though the agglomerated condition represents the lowest thermodynamic energy state, an energy barrier exists which prevents particle adhesion on contact. Thus the rate of agglomeration depends on the collision frequency of colloidal particles and the surface energy relative to the energy barrier. Because colloidal particles undergo Brownian motion, the collision frequency can be increased by raising the solution temperature. However, the energy barrier which prevents the close approach of particles must be lowered, or little agglomeration will occur. Verwey and Overbeek¹³ have shown that energy barriers can be caused by overlapping double layers which interact to increase the free energy of the system, thus leading to a potential energy of repulsion. The stability of an electrolyte suspension is determined by the balance between these repulsive forces and the attractive Van de Waals dispersion

forces. The zeta potential is a measure of the repulsive strength of the outer electrical double layer and thus can be related to the agglomerating tendency of the dispersion. This type of agglomeration is usually referred to as coagulation. Kitahara,^{14,15} among others, has extended the above theory to nonaqueous (low-electrolyte) systems.

Determination of zeta potential traditionally has required dilute solutions (<2% solids). However, there are many heavy organic-solids systems of much higher concentrations; the Solvent-Refined-Coal Liquefaction reactor product contains ~10 wt % solids. For these solutions, special techniques must be employed. One of the more promising techniques is electrophoretic mass transport. Since the ultimate goal of this project is to measure agglomerating tendencies in heavy organic systems of varying solids concentration, this technique was utilized in the experiments described below.

Another method of agglomerating particles in dispersions is by flocculation. This is usually accomplished by adding long organic chains which "wrap around" particles and around each other to form a floc which settles rapidly. Both paraffinic and aromatic solvents have been shown to produce flocculation in coal-derived solutions.^{16,17} It has been speculated that some component in the coal liquids is precipitated by these "antisolvents," and this component acts as a collecting agent for the floc. Thus the second of our approaches has centered around separating coal liquids into component classes and reconstituting them in steps (with solvent addition) to determine which components affect the agglomeration.

2.4.2 Description of methods

Coagulation. An Electrophoretic Mass Transport Analyzer (EMTA) is commercially available from Micromeritics Corp., Norcross, Georgia, and its operation is described by Akers.¹⁸ Briefly, the method consists of assembling a reservoir and sample cell (each containing an electrode and the sample solution), imposing a voltage between the electrodes, and measuring mass transport into the sample cell over a prescribed period of time. The mass transport is determined by measuring the weight difference of the sample cell plus contents. This weight difference, along with accurate measurement of sample physical properties, is used to calculate the electrophoretic mobility, which is needed to calculate the zeta potential.

$$v_e = \frac{(\Delta w)k}{Rti \phi(1-\phi)(\rho_p - \rho_l)}, \quad (1)$$

where

v_e = electrophoretic mobility, $\frac{\text{cm/sec}}{\text{volt/cm}}$,

Δw = weight difference, g,

k = conductivity cell constant, cm,

R = sample resistance, ohms,

t = time, sec,

i = current, amps,

ρ_p = density of solids, g/cc,

ρ_l = density of liquid, g/cc,

ϕ = volume fraction of solids, unitless.

and

$$\zeta = \frac{4 \pi V \lambda A \eta}{D i}, \quad (2)$$

where

ζ = zeta potential, v (e.s.u.),

V = particle electrophoretic velocity, cm/sec,

λ = specific conductance, ohm⁻¹ cm⁻¹,

A = cross-sectional area of sample cell entrance passageway, cm²,

D = specific dielectric constant (relative to air), dimensionless,

η = specific viscosity (relative to water), dimensionless.

Combining Eqs. (1) and (2) and converting e.s.u. volts to standard volts yields the following equation:

$$\zeta = \frac{(36 \times 10^4) \pi v_{\epsilon} \eta}{D}$$

Flocculation. In order to identify the component responsible for flocculation of particles in coal liquids upon addition of solvent, it was necessary to first separate the coal liquid into the following components:

<u>Component</u>	<u>Method</u>
Solids	Precoat filtration at 530°F
Carbenes and carboids	Soxlett extraction with benzene (insoluble portion)
Asphaltenes	Soxlett extraction of recovered extract from procedure (2) with pentane (insoluble portion)
Oils and resins	Recovered portion (solvent free) from procedure (3)

Decane, a proven flocculation solvent for coal-derived oils containing solids, was sequentially added to the following:

1. oils and resins;
2. oils, resins, and asphaltenes;
3. oils, resins, asphaltenes, and solids; and
4. original unfiltered oil

These mixtures were examined with an American Optical Microstar binocular microscope using both regular and oil-immersion techniques.

2.4.3 Results

Coagulation. The Micromeritics EMTA was operated initially on kaolin-water mixtures to obtain operating experience and to check the instrument calibration. Five runs with 20 wt % kaolin-water mixtures gave, $\zeta = -0.095$ v with a standard deviation (σ) of ± 0.032 v. This may be compared to values reported by Micromeritics for this system, $\zeta = -0.059$ v. Eight runs using 5% carbon black in benzene gave $\bar{\zeta} = -0.274$ v, $\sigma = 0.167$ v. In a benzene-carbon black system where both components were meticulously purified, Kitahara et al.¹⁵ found that $\zeta = 0$. Since our components were used as received, this demonstrates the importance of small concentrations of impurities in these sensitive measurements. Additional experiments with nonaqueous-solid systems are planned.

Flocculation. Asphaltenes were successfully produced using the techniques described by Mima et al.¹⁹ They had a light brown, grainy, amorphous appearance. The materials were stored under a nitrogen blanket because of a tendency to oxidize. The oils and resins obtained by these procedures can best be described as clear, medium-yellow liquids

(observed as a thin film at 450X). Addition of 30% wt n-decane to the oils and resins only produced a lighter yellow solution. Addition of asphaltenes changed the solution to an orange color; no solids could be observed at 1000X, indicating complete solubility in the oils and resins. When 30% n-decane was added to this solution, a stringy precipitate (presumably asphaltenes) could be observed. Although many existed as separate units, some of these stringy particles attached themselves to a second phase of spherical droplets (see Fig. 2.31). Since decane is completely miscible with the oil and resin phase, the origin of the second liquid phase is unknown. However, it is of interest that the second phase disappeared with time, and yellow crystalline spheres were found surrounded by asphaltene chains (see Fig. 2.32).

When 8% filtered solids were suspended in oils and resins and 30% n-decane was added, the solids remained dispersed, as seen in Fig. 2.33. However, when asphaltenes were present in n-decane, the solid phase agglomerated (see Figs. 2.34 and 2.35), proving that asphaltenes are a necessary component for agglomeration in these systems. When decane was added to pure asphaltenes, the grainy amorphous, near-spherical material remained. Upon more thorough mixing, some of the amorphous materials were broken and a clear, very viscous orange material was seen (see Fig. 2.36). Further study on pure asphaltenes showed that this orange material is present in asphaltenes even when decane is absent. The orange semi-solid material appeared to hold the amorphous material together from the inside, whether exposed to air or decane. The asphaltenes themselves appear to stick the solids together, and the role of n-decane is to precipitate these asphaltene components from the

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0 100 200
SCALE-MICRONS

Fig. 2.31. Stringy asphaltene units attaching to the surface of a second liquid phase in a solution of oils, resins, and 30% n-decane. Magnification 100X.

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SCALE - MICRONS

0 20 40

Fig. 2.32. An asphaltene unit in oils, resins, and 30% n-decane, which shows spherical crystals. Magnification 450X.

ORNL DWG 77-277

SCALE - MICRONS

Fig. 2.33. Dispersed coal-derived solids (from SRC unfiltered oil) in oils, resins, and 30% n-decane. Magnification 100X.

ORNL DWG 77-306

SCALE - MICRONS

Fig. 2.34. Agglomeration when asphaltenes are added to the component mixture of oils, resins, coal-derived solids, and 30% n-decane.

ORNL-DWG 77-305

0 100 200
SCALE MICRONS

Fig. 2.35. Agglomeration of unfiltered coal-derived oil (SRC) containing asphaltenes upon addition of 30% n-decane.

ORNL DWG 77-279

SCALE - MICRONS

0 100 200

Fig. 2.36. The effect of n-decane on asphaltenes.

oil and resin solution. Further efforts are underway to separate the viscous orange material from the brown amorphous material and identify each.

2.5 Hydrogen Permeation Oxidation Studies

S. D. Clinton and J. S. Watson

2.5.1 Introduction

Due to the large permeation rates of tritium through containment barriers at even moderate temperatures (300 to 500°C), the handling of tritium in fusion reactors can create a hazardous situation. The oxidation of tritium to a nonpermeating and recoverable form should make secondary containment practical, and, in addition, the technique could be used for recovering tritium produced in some blanket designs.²⁰ Low concentrations of oxygen will be present in either a helium coolant or system containment atmosphere, and higher concentrations of oxygen could be added. Atomic tritium, permeating a metal barrier, should react with oxygen sorbed on the metal surface to form the oxide. An experimental study has been completed to determine the oxidation efficiency of deuterium permeating a metal wall at conditions expected within fusion power reactor systems. Data were obtained with deuterium permeating through palladium, nickel, and 304-L stainless steel tubes.

The deuterium oxidation efficiency at the metal surfaces increased with increasing temperature, but it was unaffected by oxygen partial pressure variations in the range of 0.005 to 0.2 torr. The conversion of permeating deuterium to heavy water was ~90% with a palladium tube at 25°C, and increasing the palladium temperature to 60°C increased the

deuterium oxidation efficiency to 97%.¹ With a nickel surface, the deuterium oxidation efficiency increased from 88% at 200°C to 94% at 500°C.² With a 304-L stainless steel surface, the conversion efficiency increased from 57% at 300°C to 91% at 600°C.

2.5.2 Experimental equipment

An equipment diagram and photograph of the hydrogen isotope permeation-oxidation experiment has been published.⁶ The system basically consists of a permeation tube surrounded by a 1 1/2-in.-diam tubular vacuum chamber and furnace, a variable leak valve for oxygen addition, and a noble-ion pump operating at 20 liters/sec. Two nude ion gauges measure the system pressure, and the gas composition within the vacuum chamber was monitored by a mass spectrometer. Since the operating pressure of the UTI Model 100C gas analyzer is limited, the vacuum chamber contains a 2-mil-diam orifice to permit higher oxygen partial pressures at the permeation tube surface. The spectrometer emission current becomes unstable at pressures greater than 10^{-5} torr.

2.5.3 Results and discussion

Additional permeation-oxidation data were obtained with deuterium and a 304-L stainless steel tube at 550 and 600°C. The stainless steel tube measured 0.250 in. OD by 2.0 in. long with a 15-mil wall. To maintain a stable spectrometer emission current, the deuterium driving-force pressure ranged between 200 and 500 mm. Oxygen partial pressures at the steel surface were varied from 0.005 to 0.2 torr with no significant change in the heavy water-to-deuterium ratio. As the temperature of the stainless steel was increased from 550 to 600°C, the deuterium

oxidation efficiency increased from approximately 90 to 91%. These data, along with oxidation efficiencies at 300 to 500°C from the previous report period,² are shown graphically in Fig. 2.37. Each data point represents a steady-state condition. With temperatures up to 600°C and oxygen partial pressures up to 0.2 torr, it can be concluded that the catalytic effectiveness of the stainless steel surface is insufficient to achieve deuterium oxidation efficiencies significantly > 90%.

2.5.4 Program status

Hydrogen permeation-oxidation studies at conditions expected for fusion power reactor systems have been concluded. No further permeation-oxidation testing has been planned for the immediate future.

Fig. 2.37. Oxidation efficiency of deuterium permeating a 304-L stainless steel surface as a function of temperature.

2.6 References for Section 2

1. C. D. Scott et al., Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs), Sept. 1, 1975, to Feb. 29, 1976, ORNL/TM-5533 (July 1977).
2. J. S. Watson and S. D. Clinton (compilers), Experimental Engineering Sect. Semiannu. Prog. Rep. Mar. 1 to Aug. 31, 1976: Volume 3: Engineering Science Programs, ORNL/TM-5865/V3 (June 1978).
3. O. Levenspiel, Chemical Reaction Engineering, 2nd ed., Chapt. 9, Wiley, New York, 1972.
4. K. Ostergaard and M. L. Michelsen, "On the Use of the Imperfect Tracer Pulse Method for Determination of Hold-Up and Axial Mixing," Can. J. of Chem. Eng. 47, 107 (1969).
5. M. L. Michelsen and K. Ostergaard, "The Use of Residence Time Distribution Data for Estimation of Parameters in the Axial Dispersion Model," Chem. Eng. Sci. 25, 583 (1970).
6. C. D. Scott et al., Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs), Mar. 1, 1975, to Aug. 31, 1975, ORNL/TM-5291 (September 1976).
7. C. Y. Wen and Y. H. Yu, "Mechanics of Fluidization," CEP Sym. Ser. 62, 62, 100 (1966).
8. S. R. Bloxom et al., Determination and Correlation of Hydrodynamic Variables in a Three-Phase Fluidized Bed, Part IV, ORNL/MIT-219 (1975).
9. D. R. Christman et al., Dispersion in a Three-Phase Fluidized Bed, ORNL/MIT-251 (1977).
10. D. Bradley, The Hydroclone, pp. 63-88, Pergamon, New York, 1965.
11. T. Trinh, J. J. Monge, and W. A. Chrusciel, Efficiency of Particle Removal from Viscous Liquids with a Hydroclone, ORNL/MIT-237 (October 1976).
12. The DorrClone, Dorr-Oliver, Inc., Stamford, Conn. (1976).
13. E. J. W. Verwey and J. T. G. Overbeek, "Theory of the Stability of Lyophobic Colloids," Elsevier, New York, 1948.
14. Ayao Kitahara, "Zeta Potential in Nonaqueous Media and Its Effect on Dispersion Stability," Prog. Org. Coat. 2, 81-98 (1973/74).

15. Ayao Kitahara, Fujii Todishi, and Seiji Katano, "Dependence of Zeta Potential Upon Particle Size and Capillary Radius and Streaming Potential Study in Nonaqueous Media," Bull. Chem. Soc. Jpn., 44, 3242-45 (1971).
16. B. R. Rodgers and S. Katz, Supporting Research and Development on Separations Technology, Phase II Report: Scouting Experiments, ORNL/TM-4968 (October 1975).
17. B. R. Rodgers and S. Katz, Supporting Research and Development on Separations Technology: Final Report, ORNL/TM-5843 (To be published).
18. R. J. Akers, "Zeta Potential and the Use of the Electrophoretic Mass Transport Analyzer," Am. Lab., pp. 41-53 (June, 1972).
19. M. J. Mima, H. Schultz, and W. E. McKinstry, Method for the Determination of Benzene Insolubles, Asphaltenes, and Oils in Coal-Derived Liquids, PERC/R1-76/6 (September 1976).
20. J. S. Watson, A Summary of Tritium Handling Problems in Fusion Reactors, ORNL/TM-4022 (November 1972).

3. MAGNETIC FUSION ENERGY

The efforts of the Chemical Technology Division in the area of fusion energy include fuel handling, processing, and containment. These studies are closely coordinated with the ORNL Fusion Energy Division. Current experimental studies are concerned with the development of vacuum pumps for fusion reactors, the evaluation and development of techniques for recovering tritium (fuel) from either solid or liquid lithium containing blankets, and the use of deep beds of sorbents as roughing pumps and/or transfer operations. In addition, a small effort is devoted to the support of the ORNL design of The Next Step (TNS) in tokamak reactor development. The more applied studies--vacuum pump development and TNS design--are funded by the DOE/Magnetic Fusion Energy, and the more fundamental studies--blanket recovery and sorption in deep beds--are funded by the DOE/Basic Energy Sciences.

3.1 Cryosorption Vacuum Pumping

P. W. Fisher

Cryosorption vacuum pumps are of significant interest for plasma recovery systems for use in fusion reactors because they hold promise for pumping all plasma constituents (deuterium, tritium, and helium) with a single pump. Our work has centered around a commercial (Excalibur Model CVR 1106) cryosorption pump. This pump is designed to operate with a liquid helium cooled (4.2 K) molecular sieve Type 5A (MS-5A) adsorbent. Results obtained for pure deuterium, hydrogen, and helium have been presented in previous reports¹⁻³ and will not be discussed here except when they pertain to the present study.

Work during this period has been performed in several areas which relate to fusion reactor needs. First, the problem of cryosorption pumping of plasma composition mixtures was addressed experimentally. It was found that the Excalibur pump would accommodate mixtures of 95% deuterium--5% helium at all normal pressures, but this could only be accomplished at high pressures ($>10^{-4}$ torr) when some or all of the deuterium was collected on the inner chevron. High-pressure operation is not possible if this condensation on the chevron is prevented. It is concluded from this work that if no improvement is made in the choice of adsorbent, compound pumps (separate pump panels for helium and hydrogen isotopes) will be required for plasma recovery systems.

The second area examined was the pumping of deuterium and hydrogen at elevated (above 4.2 K) temperatures. Because the Excalibur pump is not designed to be operated at these temperatures, a special cooling system was assembled to achieve these temperatures. Results of this

work indicate that no simple relationship of speed and pressure exists for MS-5A at higher temperatures. Speeds were found to vary with feed rate, loading prior to the run, loading during the run, and thermal treatment between runs. It was also found that deuterium pumping at these temperatures produces cyclic variation in the pumping speed similar to variations observed for helium at 4.2 K. Hydrogen appears to exhibit two separate and distinct behaviors which are postulated to be associated with the state of the MS-5A surface. Possible explanations for observed behavior are presented. It is concluded that cryosorption pumping of hydrogen isotopes at elevated temperatures will require considerable development before it can be selected to replace cryocondensation pumps for the neutral beam injector.

The final phase of the work during this period was concerned with extending the program to effect an orderly development of cryosorption pumps. A new pump has been designed and constructed with close cooperation between the Chemical Technology Division and the Fusion Energy Division. The new pump is demountable so that various adsorbents, substrates, and baffles can be tested with accurate control of all temperatures over the entire range of interest. The pump has been incorporated into our test stand; details of its construction are presented.

3.1.1 Cryosorption pumping of 95% deuterium--5% helium

Recovery of plasma between fusion reactor burns is necessary to remove the fusion reaction ash (helium) and other impurities from the reactor vacuum chamber in preparation for refueling for the next burn. Helium concentrations in the range of 1 to 15% can be expected in these

mixtures; the remaining portion consists of 50% deuterium and 50% tritium. Reactors producing <1% helium would be uneconomical, and the reaction is quenched when the concentration exceeds 15%. When the requirements (e.g., good helium pumping capability, low base pressure, tritium containment and recoverability, ability to prevent the introduction of impurities into the plasma system, and sound economics) are judged against the types of vacuum pumps which are available, only cryosorption pumps are found to meet all of the criteria. These pumps, however, have never been tested for their ability to pump these mixtures at fusion reactor conditions.

Some concern has arisen because previous experimental results indicate behavior which will preclude the achievement of all of the goals. Deuterium data has shown that the principal mechanism for pumping at high feed rates was condensation, not adsorption. This effect is highly undesirable because the accumulation of a condensed film of hydrogen isotopes on the adsorbent surface could block the sieve surface and thereby prevent helium pumping. Results for hydrogen pumping show that this condensation effect does not occur below $\sim 4 \times 10^{-3}$ torr-liter/sec (3×10^{-6} torr). Therefore, at low pressures, blockage should not affect performance, but a normal fusion reactor operating pressures near 10^{-4} torr condensation would inhibit adsorption.

Experimental results for pure helium pumping also show behavior which is unacceptable in fusion reactors: cyclic variation of pumping speed at high feed rates is accompanied by high-pressure excursions in the test chamber at the end of each cycle. It is expected that this behavior will occur with mixtures as well as with pure helium. Since

the onset of this behavior (which occurs between 2 and 3×10^{-3} torr-liter/sec on the Excalibur pump) is clearly defined, its effect can therefore be avoided by making the cryosorption surface large enough to stay below this critical feed-rate-per-unit area.

The following alternatives could eliminate or reduce deleterious cyclic pump behavior: (1) the use of an adsorbent which is not blocked by condensation, (2) the employment of a tandem or compound pump in which the constituents are pumped on separate panels, or (3) the trapping of helium in a layer of frozen hydrogen (isotopes). Only the latter two alternatives can be tested in the Excalibur pump. The possibility of utilizing alternate adsorbents will be studied in the future on the new demountable pump.

Experimental. The experimental apparatus consists of an Excalibur CVR 1106 cryosorption pump, a feed-gas system with an adjustable feed rate, and a vacuum test chamber for the measurement of pumping speed. The pump has an MS-5A adsorption panel that is cooled with liquid helium. Boil-off gas from the liquid helium reservoir is routed through both the inner chevron and the radiation shield during normal operation. When the pump is operated at high pressures (in excess of 10^{-4} torr), the helium boils rapidly and cools the inner chevron to a temperature near 4.2 K (Fig. 3.1). When this occurs, the inner chevron can become a pump for hydrogen isotopes. If all incoming hydrogen condenses on the chevron, this leaves the adsorption panel unobstructed to collect helium. Thus the pump could become a compound pump.

The pump can be forced to act as a single cryosorption pump at high pressures by backflushing the inner radiation shield and chevron with

Fig. 3.1. Schematic of Excalibur CVR 1106 pump with normal cooling circuit and modified cooling circuit.

77 K helium (see Fig. 3.1). This precludes any separation of components on different pump surfaces. To pump mixtures in this configuration at high pressures, the helium must either be adsorbed through the layer of frozen deuterium or it must be trapped by frozen deuterium.

A mixture of 95% deuterium and 5% helium was prepared by alternate additions of the two constituents to be the 6-liter feed-gas reservoir. The reservoir was allowed to equilibrate for a day before the runs were made. Gas samples which were taken before the first run and after the last run were 4.7 and 4.8% of helium respectively. Details of the experimental apparatus and procedure are given in previous reports.^{1,2}

Results and discussion. Table 3.1 gives a summary of the fourteen experimental runs that fall into two groups: (1) runs made with the inner chevron cooled by helium boil-off vapor, and (2) runs made with the inner chevron cooled by 77 K helium. Three distinct types of behavior were observed: (1) the speed decreases monotonically, (2) the speeds decrease sharply and recover to intermediate values, and (3) the speeds decrease sharply and remain at zero. At low feed rates (below 4×10^{-2} torr-liter/sec), speeds decrease monotonically with loading regardless of the inner chevron temperature, as shown in Fig. 3.2. Speeds for high feed rates are shown in Fig. 3.3. Here the response of the pump was dependent on the inner chevron temperature. All three runs began with an initial sharp decline in pumping speed. When the inner chevron was cooled by boil-off vapor, partial recovery in speed was observed. However, when the chevron temperature was fixed at 77 K, the pump ceased to operate, and the run was terminated because of cryogenic runaway.

Table 3.1. Summary of 95% deuterium--5% helium pumping runs

Run no.	Q (torr-liter/sec)	Q _{He} (torr-liter/sec)	Chevron cooled by
1	2.0 E-4	1.0 E-5	Boil-off
2	1.5 E-3	7.4 E-5	Boil-off
3	6.9 E-3	3.5 E-4	Boil-off
4	2.0 E-2	1.0 E-3	Boil-off
5	4.3 E-2	2.1 E-3	Boil-off
TL 6	2.8 E-1	1.4 E-2	Boil-off
TL 7	1.3 - 0.58	6.5 E-2 - 2.9 E-2	Boil-off
8	1.7 E-4	8.3 E-6	77 K helium
9	1.3 E-3	6.4 E-5	77 K helium
10	4.8 E-3	2.4 E-4	77 K helium
11	1.1 E-2	5.7 E-4	77 K helium
12	2.3 E-2	1.2 E-3	77 K helium
13	2.2 E-2	1.1 E-3	77 K helium
14	1.3 E-1	6.5 E-3	77 K helium

Fig. 3.2. Speed of the Excalibur C/R 1106 pump as a function of total accumulation of 95% deuterium--5% helium, low-pressure operation.

Fig. 3.3. Speed of the Excalibur CVR 1106 pump as a function of total accumulation 95% deuterium--5% helium, high-pressure operation.

At low feed rates, speeds decline not only within each run but also from run to run. Overall, the speed declines 50% for a total loading of about 30% of the adsorption saturation capacity. Raising the temperature of the inner chevron from 20 K in the first five runs to 77 K in runs 8 to 13 may contribute to the lower observed speeds, but the present data are not definitive on this point. At very low loadings ($<0.2\%$), speeds are about 200 liters/sec higher than those measured for pure deuterium. At higher loadings, they approach initial speeds observed for pure helium, ~ 650 liters/sec.

High feed rates (Fig. 3.3) begin with a rapid decrease in speed resulting from helium accumulation in the test chamber which is apparently caused by frozen deuterium blocking the adsorbent surface. As the system pressure increases, the heat load on the liquid-helium reservoir increases and causes a corresponding increase in coolant flow through the inner chevron. When the chevron temperature drops, it becomes a condensation pump for deuterium. Maintenance of this phenomena allows the speed to increase to and remain in the approximate range of 500 to 600 liters/sec. The fact that speeds do not reach the rate of 1000 liters/sec observed for deuterium can be a result of either physical phenomena or incomplete data. Sticking coefficients for hydrogen isotopes may be reduced by both the presence of trapped helium and by the inadequate cooling of the chevron. Since partial pressures cannot be determined from the data, they had to be inferred from the feed composition; underestimation of the partial pressure of helium would lead to low estimates of the deuterium pumping speed. The exact nature of the controlling phenomena cannot be determined from these data.

Figure 3.4 shows the system pressure as a function of time after run 6. The structure of the curve is similar to those presented previously for systems recovering from hydrogen pumping.² The first spike in the curve corresponds to the unloading of deuterium from the chevron to the cryosorption panel. This occurs when pumping is terminated because the liquid-helium reservoir no longer has an excessive heat load. Therefore, rapid boiling ceases, and adequate coolant is no longer supplied to the inner chevron. The slow rise in pressure following the spike may be caused by the warming of the condensed deuterium film (possibly dissolved or trapped helium) which has resulted from the increased radiation heating from the warming inner chevron. The sharp decline in pressure which follows can be due either to the renewal of the coolant flow to the inner chevron (resulting from increased radiation and conduction heat load from the warming inner chevron) or to the readsorption on the condensed surface film and the return to very low equilibrium adsorption pressures.

The last curve in Fig. 3.3 (run 14) also represents an attempt to test the ability of deuterium to cryotrap helium. This run had a 77 K inner chevron to prevent deuterium condensation on the chevron. Thus all constituents had to either (1) condense or be trapped on the 4.2 K sieve surface, or (2) accumulate in and pressurize the system. Adsorption could not occur because of the high feed rate. The scale has been expanded for clarity, but the curve is essentially identical to the initial decline in speed in runs 6 and 7. While runs 6 and 7 show improvement in speeds after this point, run 14 terminates with cryogenic runaway. System pressurization causes increased heat load which elevates

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Fig. 3.4. Recovery pressure of system after 95% deuterium--5% helium
run 6.

the panel temperature (perhaps to 5 K). At this time, rapid boiling begins and again cools the panel. However, the system pressure continued to decline, boiling became very intense, and the run was terminated due to a loss of coolant. Nearly 6 liters of liquid helium were consumed in this 1-min run. Failure of the pump during this run demonstrates that helium cannot be sorbed on MS-5A or trapped by deuterium at the 5% helium level.

When the pump was operating in the compound mode (run 6 and 7), helium should have been the principal constituent accumulated on the adsorbent. These high feed rates were above the point where cyclic variations in speed had been observed for pumping of helium alone. Therefore, if the pump is operated long enough, it should go through a rapid transition. Only run 7 approaches the accumulation of a full cycle of helium. For this run, the transition should occur at 1500 torr-liters (on this scale). Declining speed over the latter portion of the curve could be attributed to the declining helium speed and the approach of the end of a cycle.

Figure 3.5 summarizes the average pumping speeds for runs 1 to 13. Superimposed on the data is the pumping speed for pure deuterium at 4.2 K. The promising upturn observed for deuterium at high pressures is not observed for the 95% deuterium--5% helium mixtures; mixture speeds decline over the experimental range. Possible explanations for this have been previously discussed. Also plotted here is the demarcation line between the low- and high-pressure helium pumping regimes.

Conclusion. Results presented here have direct bearing on the design of plasma recovery systems for fusion reactors. Relatively

Fig. 3.5. Average speeds as a function of pressure for 95% deuterium--
 5% helium mixtures.

stable pumping can be achieved for pumps similar to the CVR 1106 if pumping systems are operated to the left of the helium transition line shown in Fig. 3.5. Speeds on the order of 650 liters/sec can be expected for a 5% helium mixture, but operating pressures of the pump must be kept below 5×10^{-5} torr. If high reactor pressures are to be accommodated, improvements must be made in the cryosorption pumps, or separate pumps must be used for hydrogen isotopes and helium. Design of compound cryogenic pumps for mixtures is not straightforward. The present results have shown that helium may reduce hydrogen condensation pumping speeds. This effect has not yet been quantified but, if true, may increase the required size of condensation pumps for hydrogen isotopes. Alternatively, hydrogen isotopes could be collected on a higher temperature cryosorption pump. However, results presented by Southerlan⁴ show that even a small amount of preadsorbed helium drastically reduces hydrogen pumping speeds at 13.6 K. Beyond this, the effect of either spontaneous or accidental pressure excursions could block the helium pump. In any case, it appears that, at present, compound pumps are the best choice for plasma recovery systems; however, if the proper adsorbent can be found, a single pump may eliminate several potential problems.

3.1.2 Cryosorption pumping of deuterium and hydrogen at elevated temperatures

Several fusion reactor vacuum systems will be required to recover only hydrogen isotopes (no helium). These systems include neutral beam injection systems, pellet fueling systems, and some embodiments of blanket recovery systems. Requirements of these systems can be fulfilled by either cryocondensation or cryosorption pumps. Neutral-beam injection

systems are presently being operated with cryocondensation pumps. However, cryosorption pumps have the following possible advantages which would make them attractive for future systems: (1) the ability to operate at higher temperatures; (2) the ability to operate in more hostile environments where heat fluxes would preclude the use of liquid helium as a coolant; (3) more operating flexibility because equilibrium adsorption is less sensitive to temperature fluctuations than equilibrium vapor pressure; and (4) easier control of pump regeneration.

Response of the CVR 1106 pump to deuterium and hydrogen at 4.2 K has been reported previously.² This work gave some indication of what can be expected at higher temperatures. For instance, both hydrogen and deuterium will condense on MS-5A at 4.2 K and block the surface for cryosorption at pressures above 10^{-5} torr. This effect could manifest itself any time the cryosorption surface is operated below this critical point of the isotope. Additionally, diffusion limitations could block the inner regions of the adsorbent at temperatures even above the critical point.

Several studies of hydrogen cryosorption on MS-5A in the range of 10 to 20 K have been reported. Southerlan⁴ reported initial pumping speeds (for no previously accumulated hydrogen) which are equivalent to between 1300 and 1400 liters/sec (near 10^{-7} torr and 17 to 20 K) on the CVR 1106 pump. (Corrections were made for a 300 K pressure measurement, the conductance of 1600 liters/sec between the gauge and the cryopanel, and a 50-in.² cryosorption surface area.) Measured unbaffled pumping speeds were inversely proportional to the feed rate; the data fit this pattern even when the feed rate was not increased monotonically from

run to run. This indicates that total loading is less important than the feed rate in determining pumping speed. Tests of different activation procedures showed that an activation of 200°C after exposure to the atmosphere restored initial speeds to high values; however, activation to the same temperature under high vacuum conditions without atmospheric exposure produced low initial speeds which were comparable to the last speed measured before activation. Stern, Hemstreet, and Ruttenbur⁵ reported pumping speeds for three runs in the range of 10^{-8} to 10^{-7} torr at 20 K to 0.2% of the saturation capacity. The speeds are all approximately equal and equivalent to 950 liters/sec on the CVR 1106. The authors also showed that the pumping speed decreases significantly with loading at a constant feed rate. Gareis and Pitlor⁶ measured speeds in the 5×10^{-8} torr range with 20 K panels. Initial speeds were equivalent to 600 liters/sec with a 77 K chevron and 1000 liters/sec with a 20 K chevron on the CVR 1106. Measured speeds actually increase with increasing feed rate and pressure when the effect of background pressure is removed from reported speeds. Reactivation, even with atmospheric exposure, causes degradation in pumping speed.

Two distinct types of behavior have been reported: (1) high initial speeds that decrease with increasing feed rate and loading, and (2) low initial speeds that increase with feed rate and pressure. Extrapolating these results to the 10^{-4} torr range, in which fusion reactor systems will operate, indicates that this type of pump will either operate adequately or not operate at all. The present work is necessary to extend experimental measurements for hydrogen cryosorption at elevated

(4.2 K) temperatures into the pressure range of interest in fusion reactor applications and to initiate measurements for deuterium.

Experimental apparatus. The Excalibur CVR 1106 cryosorption pump is not well-suited for elevated temperature operation. In its normal operational mode it is cooled by pool boiling of liquid helium. Controlling the vapor pressure of the liquid helium could be used to collect data up to 5.2 K, but this is not a significant extrapolation from existing data. Liquid hydrogen is the only cryogenic fluid whose normal boiling point (20 K) falls in the range of interest, but, for safety reasons, this alternative was not selected. To obtain the data in the desired temperature range, the pump reservoir was fed with a gas at a controlled temperature.

Figure 3.6 shows a schematic diagram of the apparatus. The system used liquid helium boil-off vapor as the coolant for the pump. The system has two basic components: (1) a liquid-helium dewar fitted with a heater to supply 4.2 K gas, and (2) a feed-gas heater which controlled the temperature of the gas as it entered the pump reservoir. Liquid helium was supplied in a standard Linde (model LSHe-100) dewar. A nicrome resistance heater was inserted into the liquid, and a vacuum insulated transfer line was installed between the dewar and the feed-gas heater. The nicrome heater was controlled with a power supply that was normally set to deliver about 6 W to the heater. The feed-gas heater was vacuum insulated and liquid-nitrogen shielded. The temperature of the exit gas was measured with a germanium resistance thermometer and controlled with a Scientific Instruments Model 3610 controller driving a 35-ohm nicrome heater. The heater was mounted on a vertical tube.

Fig. 3.6. Experimental apparatus for elevated temperature runs.

Gas was routed down through the center of the heated tube then up around the outside of the tube. Cold gas was delivered through a distributor tube to the pump by a vacuum insulated line that was an integral part of the feed-gas heater. The distributor tube discharged the gas through a series of graduated holes to give balanced cooling across the back of the cryosorption panel. A calibrated germanium resistance thermometer was mounted in a nipple located at the bottom of the reservoir. Two such nipples were mounted by the manufacturer to provide structural support during shipping. Temperatures reported here were read directly from this thermometer. Only the temperature of the feed gas was controlled; the panel temperature fluctuated with heavy load. Most experimental runs were made with the inner chevron cooled to 77 K by backflushing with liquid-nitrogen-cooled helium gas. Gas flow through the chevron was set at about 1 liter/min, and gas flow through the reservoir was on the order of 25 liters/min at room temperature. One run was made with helium vent gas cooling the chevron.

3.1.3 Deuterium pumping at elevated temperatures.

Table 3.2 shows a summary of deuterium runs made at temperatures between 6 and 20 K. There were a total of 4 pump activations and runs including 28 separate feed rates. Figure 3.7 shows a composite of pumping speed data for all runs with a 77 K inner chevron. The pumping speed is shown as a function of total loading after activation. Initial speeds for the first run after activation ranged from 400 to 900 liters/sec, no speeds below 400 liters/sec were measured until about 100 torr-liters of deuterium was accumulated on the panel. This is equivalent to about 2% of equilibrium saturation capacity. Speeds anywhere from 0 to 100

Table 3.2. Summary of deuterium runs

Activation	Run	Quantity pumped (torr-liters)		Feed rate (torr-liter/sec)	Average during run			Comments
		Prior to run	During run		Pressure (torr)	Speed (liter/sec)	Temperature (K)	
A	1	0	350.0	2.3 E-1	1.4 E-3	280	9.6	LHe vapor cooled chevron cycles
B	1	0	924.6	2.3 E-1	5.1 E-3	105	19.6	Chevrans at 77 K for all succeeding runs
	2	924.6	0.9	1.6 E-3	5.7 E-6	284	9.4	
	3	925.5	0.4	1.2 E-3	4.4 E-6	277	9.5	
	4	925.9	8.4	1.6 E-2	1.5 E-3	113	9.7	
C	1	0	5.4	1.6 E-2	2.6 E-4	621	7.2	Panel heated to 77 K between runs 4 and 5
	2	5.4	6.4	1.4 E-2	3.1 E-5	453	7.8	
	3	11.8	70.8	1.0 E-1	1.8 E-4	582	7.5	
	4	82.6	61.6	8.7 E-2	2.9 E-7	297	7.7	
	5	144.2	55.7	8.0 E-2	1.6 E-3	546	7.7	
	6	199.8	109.0	7.7 E-2	5.8 E-4	328	8.3	
D	1	0	0.9	5.1 E-3	1.3 E-5	379	15.5	Cyclic behavior
	2	0.9	2.2	1.0 E-2	2.2 E-5	513	15.1	
	3	3.1	5.0	2.8 E-2	2.8 E-5	1003	15.5	
	4	8.1	60.7	9.2 E-2	1.6 E-4	654	15.8	
	5	68.8	88.9	7.8 E-2	5.5 E-3	420	16.6	
	6	157.8	0.8	3.3 E-3	9.0 E-6	365	15.0	
	7	158.5	2.0	1.1 E-2	2.7 E-5	414	15.4	
	8	160.5	4.3	2.4 E-2	6.7 E-5	359	15.7	
	9	164.8	10.6	6.3 E-2	7.6 E-5	829	16.0	
	10	175.4	274.6	5.2 E-1	8.6 E-3	98	23.8	
	11	450.0	0.6	3.5 E-3	1.2 E-5	294	15.2	
	12	450.6	2.0	1.1 E-2	3.2 E-5	339	15.4	
	13	452.6	5.2	3.1 E-2	9.9 E-5	314	15.6	
	14	457.8	0.6	3.8 E-3	2.5 E-5	153	20.4	
	15	458.4	1.2	1.1 E-2	4.5 E-5	245	20.1	
	16	459.6	4.3	3.0 E-2	1.0 E-4	301	19.8	
	17	464.0	154.4	5.5 E-2	4.1 E-4	326	20.0	
Panel to 43 K between 13 and 14

Fig. 3.7. Speed as a function of total deuterium accumulation.

liters/sec were obtained with panel loading from 100 to 1000 torr-liters, (the specific nature of individual runs will be described later.) It was possible to obtain speeds near 400 liters/sec (the lowest observed initial speed) with approximately 1000 torr-liters, which is about 20% of the saturation capacity. The initial pumping speed appears to decrease with the log of the total panel loading. The line in Fig. 3.7 is drawn to intercept the ordinate at the equilibrium saturation capacity based on 30 g of MS-5A on the panel. This intercept is in good agreement with the data.

Figure 3.8 shows the effect of loading during each individual run. Initial speeds on the order of 400 liters/sec were observed for loadings of <1 torr-liter. A dramatic increase in initial speed to ~ 1000 liters/sec occurred at a loading of ~ 1 torr-liter. This is quite similar to the behavior observed for helium at 4.2 K in that a marked increase in the sticking coefficient occurred after ~ 1 torr-liter was accumulated at high feed rates ($>3 \times 10^{-3}$ torr-liter/sec). Figures 3.9 and 3.10 show the pumping speed as a function of pressure and feed rate respectively. Initial speeds go through a maximum at $\sim 10^{-4}$ torr and 10^{-1} torr-liter/sec. Below a pressure of about 10^{-5} torr, it appears that the initial speed is always 400 liters/sec.

Figure 3.11 shows pumping speed pressure and temperature as a function of total loading for a feed rate of 0.23 torr-liter/sec. During this particular run, the inner chevron was cooled by reservoir coolant gas which was vented through the chevron and radiation shield. The instabilities observed were initially attributed to coupling of the two coolant circuits in series; therefore, a run was made at the same

Fig. 3.8. Speed as a function of loading during each individual run for deuterium.

Fig. 3.9. Speed as a function of pressure for deuterium at elevated temperatures.

Fig. 3.10. Speed as a function of feed rate for deuterium at elevated temperatures.

Fig. 3.11. Speed, pressure, and temperature as a function of loading for deuterium run A-1: inner chevron cooled by LHe vapor, feed rate equals 0.23 torr-liter/sec.

feed rate with the inner chevron cooled by 77 K helium gas (see Fig. 3.12). This eliminated the oscillations, but cooling was not sufficient to maintain steady panel temperature. The temperature rose from 10 to 20 K during the run. Speeds for the 77 K chevron are always less than those for the cooler chevron and could result (at least in part) from the rising panel temperature. Because the 77 K chevron was able to eliminate oscillations, it was adopted for all succeeding runs.

An explanation for oscillations could be the surface clearing effect proposed for helium pumping periodicity. In short, this postulate states that material accumulates in surface pores until they become saturated, then pumping speed decreases, and the chamber pressure rises. This causes additional heat loads on the panel. The warm panel exhibits higher diffusion rates which allows the surface material to transfer to the bulk of the adsorbent. It was not convenient to test this effect with the pump cooled by liquid helium. However, during the studies of the deuterium and hydrogen pumping under conditions of elevated temperatures, the temperature could be regulated; hence the testing of this effect was feasible.

Figure 3.13 shows a series of three consecutive runs--all with feed rates near 0.1 torr-liters/sec. Run C3 shows speed decreasing monotonically with loading as expected. Runs C3 and C4 are separated by an 8-min interruption in flow during which time the panel was maintained at about 7 K. The initial speed for run C4 was nearly equal to the final speed in run C3. This indicates that no material diffused from the surface micropores to the bulk adsorbent. Between runs C4 and C5, the cryopanel was put through an artificial temperature excursion induced

Fig. 3.12. Speed, pressure, and temperature as a function of loading for deuterium run B-1: inner chevron at 77 K, feed rate equals 0.23 torr-liter/sec.

Fig. 3.13. CVR 1106 response to four consecutive deuterium runs with various temperature treatments between runs.

by cutting the coolant gas flow to the reservoir. The panel was then re-cooled to about 7 K, and run C5 was initiated. An initial speed of 1000 liter/sec was observed with a subsequent decrease in speed with loading (comparable to run C3). This recovery indicates that the surface had been cleared during this interruption. A 37-min interruption in flow, during which the surface temperature was maintained at ~ 7 K, was made between runs C5 and C6 to determine if the time interval by itself had any effect on pumping speed. Results indicate that it did not. The speed in run C6 started where run C5 ended. Run C6 went through two spontaneous recoveries before it was terminated. In each case, a pressure rose to about 10^{-2} torr causing the panel temperature to rise to about 12 K (the actual surface temperature may have been much higher). The temperature excursions were followed by recovery to high pumping speeds. The characteristics of these cycles were the same as those observed for helium pumping at 4.2 K. The rapid spontaneous oscillation observed in Fig. 3.11 can be attributed to the inability of the surface to clear itself completely during an excursion. The panel temperature in this case is limited by the lower temperature of the inner chevron.

Figure 3.14 shows two consecutive runs made near 15 K. The decrease in speed observed in the first run was quite similar to that shown in Fig. 3.13. After the 21-min interruption in flow (during which time the temperature was maintained at 15 K), a much higher initial pumping speed was observed indicating that the surface had partially cleared at this higher temperature. The speed, however, fell very rapidly causing a pressure spike. The peak pressure was not high enough to cause a corresponding increase in the panel temperature, and no recovery in

Fig. 3.14. CVR 1106 response to two consecutive deuterium runs (D-4 and D-5) with run temperature maintained during leak interruption.

speed was observed. Subsequently, a second, more intense pressure peak (near 10^{-2} torr) occurred at approximately 100 torr-liters. This caused the panel temperature to reach approximately 24 K; the temperature peak was closely followed by a recovery in pumping speed.

Discussion of results. Qualitative explanations for observed results have been given, but it is desirable to quantify these results in terms of physical models. To begin this modeling process, it is necessary to determine what effect changes in surface condition will have on the measured speed after the speeds are damped by the (significant) flow restrictions which exist between the panel and the inlet pressure measuring point (~ 10 in. in front of the outer chevron). If F is the conductance between the gauge and the cryopanel, S_o is the maximum speed of the panel if all incident molecules stick, and α is the sticking coefficient, then the measured speed, S , is given by the equation:

$$\frac{1}{S} = \frac{1}{F} + \frac{1}{\alpha S_o} \quad (1)$$

The maximum speed, S_o (in liters/sec), is given by

$$S_o = 3.64 A \left(\frac{T}{M} \right)^{1/2}, \quad (2)$$

where

A = area of panel, cm^2 ;

T = temperature, K;

M = molecular weight of gas.

The conductance of any component, i , in the system is similarly calculated in the following manner:

$$F_i = 3.64 A K_i \left(\frac{T}{M} \right)^{1/2}, \quad (3)$$

where K_i is the Clausing factor for the element. F for the entire system is then given by

$$\frac{1}{F} = \sum \frac{1}{F_i} \quad (4)$$

Figure 3.15 shows the various restrictions that exist in the experimental apparatus. Flow is assumed to be directed into the tube between the gauge and the outer chevron because it is preceded by another section of the tube. It is also assumed that this effect can be taken into account by subtracting out the effect of a series orifice placed in front of the tube. A similar assumption is made for the outer chevron. Corrections are not made for the inner chevron and cryopanel because molecules leaving the chevron surface should leave in random directions. Equation (4) applied to this system would become the following:

$$\frac{1}{F} = \frac{1}{F_T} - \frac{1}{F_O} + \frac{1}{F_{C1}} - \frac{1}{F_O} + \frac{1}{F_{C2}} \quad (5)$$

The Clausing factors listed in Fig. 3.15 lead to a conductance for deuterium of $F_{D_2} = 1140$ liters/sec at 300 K. A similar calculation for hydrogen would lead to $F_{H_2} = 1610$ liters/sec. The value of S_O is 10,100 liters/sec for deuterium and 14,300 liters/sec for hydrogen. Substituting these values into Eq. (1), assuming $\alpha = 1$, yields $S_{D_2} = 1020$ liters/sec and $S_{H_2} = 1450$ liters/sec. These values are equal to low-pressure values for pumping speeds with a 4.2 K panel.² Figure 3.15 shows the pumping speed as a function of the sticking coefficient calculated from Eq. (1), with values supplied from Eqs. (2) and (5).

A plausible mechanism for cryosorption pumping is to assume that molecules impinging on the cryosorption surface stick only if they hit

ACTUAL SYSTEM MOLECULAR FLOW MODEL

Fig. 3.15. Diagram of conduction restrictions between pressure gauge and cryopanel.

a window to an adsorption cavity. The sticking coefficient would then be simply the ratio of the area of the windows to the total surface area. The effective diameter, D , of an MS-5A window is about $5 \text{ \AA}$. Molecular sieve-5A has cavities arranged in a cubic array with a window between each cavity face and a lattice parameter, a , of $12.3 \text{ \AA}$. If the cross-milled metal panel is assumed, the sieve occupies 75% of the cryopanel surface; therefore

$$\alpha = .75 \frac{\pi D^2}{4a^2} = .10 . \quad (6)$$

Thus from Fig. 3.16, the maximum speed expected for cryosorption on the Excalibur CVR 1106 would be about 500 liters/sec. This compares favorably with observed initial speeds at low pressures of 400 liters/sec.

Disregarding instantaneous spikes, the maximum speeds observed in Figs. 3.11 to 3.14 are about 800 liters/sec. This corresponds to a sticking coefficient of about 0.26 from Fig. 3.16. Solving Eq. (6) for D given α and a yields an estimate for the effective D of $8 \text{ \AA}$. It is reasonable to postulate that a deuterium molecule adsorbed in a surface window creates an adsorption site for another atom which is actually larger than the window. Such a model would be qualitatively similar to assumptions made in the BET isotherm. This is a simplified model which ignores such factors as the partial covering of normally exposed stainless steel surfaces, the decrease in sieve "window" diameter at low temperatures, and the increased probability for adsorption of molecules which fell between sieve crystallites. The model is intended to be only a possible explanation for the abrupt increase of pumping speed with increased loading. Much more information would be required to verify this or any other model.

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Fig. 3.16. Speed for hydrogen and deuterium on CVR 1106 pump as a function of sticking coefficient.

It is possible to estimate the amount of material which must be accumulated to place one molecule in every surface cavity. Crystallites of MS-5A are about 2μ in diameter. The volume occupied by each crystallite is $8 \times 10^{-12} \text{ cm}^3$ (assuming cubic packing). The volume of adsorbent in the $50\text{-in.}^2 \times 1/16\text{-in.}$ deep cross-milled (75% surface coverage) cryosorption panel is $\sim 38 \text{ cm}^3$. The number of crystallites in the surface is $38 \text{ cm}^3 / (8 \times 10^{-12} \text{ cm}^3/\text{crystallite})$ or 4.8×10^{12} crystallites. The number of surface cavities is given by the surface area of the crystallite divided by the area of one face of a cubic unit cell, which for MS-5A has a lattice parameter of $12.3\text{\AA}$. With these assumptions, the number of surface cavities per crystallite is 8.3×10^6 ; and the number of surface cavities in the entire cryosorption panel is then 4.0×10^{19} . The amount of material adsorbed at a rate of one molecule per surface cavity is then 1.2 torr-liters. Since about thirteen molecules are adsorbed per cavity at saturation, it follows that the surface saturation capacity is 16 torr-liters. (Note how these loadings correspond to observed changes in pump behavior.) Figure 3.8 shows that approximately 1 torr-liter must be adsorbed at high feed rates before speed enhancement begins. This is equivalent to the loading of one molecule per surface cavity. Beyond this, note that ~ 80 to ~ 100 torr-liters are accumulated per cycle. This corresponds to from 3 to 6 surface layers of cavities being filled per cycle.

In summary, deuterium pumping at higher temperatures exhibits many qualitative aspects of helium pumping at 4.2 K. This would be expected because they have equal molecular weights providing they have similar adsorption properties. However, they do have some markedly different

properties (such as the quadrupole amount of deuterium) that should affect adsorption processes. Therefore, similarities between the two systems is somewhat surprising. Some possible explanations for these similarities will be given when hydrogen results are presented in the next section.

3.1.4 Cryosorption pumping of hydrogen at elevated temperatures

Table 3.3 contains a summary of all the hydrogen runs. A total of 7 activations were made, and 52 separate feed rates were employed. Figure 3.17 shows a composite of all data on hydrogen pumping speed as a function of total loading. Initial speeds for freshly activated surfaces are in the range of 400 to 1500 liters/sec. The low initial speed was equivalent to that observed for deuterium and the high speed was higher than initial values measured for cryosorption pumping at 4.2 K. The pumping speed curves show approximately the same decline with total loading that was observed with deuterium. However, the line crosses the abscissa ~1500 torr-liters earlier than the corresponding line for deuterium (see Fig. 3.7). This suggests that hydrogen pumping speeds are more strongly affected by loading than deuterium.

Figure 3.18 shows the pumping speed of each individual run as a function of loading during the run. High speeds were observed earlier than for deuterium (shown in Fig. 3.8), and some very low speeds were recorded at low loading. Hydrogen pumping speeds do not appear to have as simple a dependence on loading as did deuterium speeds.

Figure 3.19 shows pumping speeds as a function of pressure. A distinct maximum, as was observed for deuterium (see Fig. 3.9), is not evident for hydrogen. Instead, a broad plateau of initial high pumping

Table 3.3. Summary of hydrogen runs

Activation	Run	Quantity pumped (torr-liters)		Feed rate (torr-liter/sec)	Average during run		
		Prior to run	During run		Pressure (torr)	Speed (liter/sec)	Temperature (K)
A	1	0	0.5	1.3 E-3	2.1 E-6	619	8.3
	2	0.5	1.5	4.8 E-3	7.5 E-6	631	8.2
	3	2.0	3.9	1.2 E-2	2.0 E-5	601	8.2
	4	5.9	5.0	2.6 E-2	4.1 E-5	630	8.2
	5	10.9	9.7	5.4 E-2	1.0 E-4	519	8.2
	6	20.6	810.0	5.0 E-1	3.9 E-3	176	11.0
B	1	0	0.8	1.9 E-3	1.4 E-6	1328	14.5
	2	0.8	1.6	5.9 E-3	5.7 E-6	1244	14.5
	3	2.5	5.8	2.1 E-2	2.4 E-5	889	14.5
C	1	0	0.2	1.5 E-4	3.3 E-7	486	15.3
	2	0.2	0.7	1.3 E-3	2.1 E-6	614	15.3
	3	0.9	1.5	5.1 E-3	9.0 E-6	570	15.4
	4	2.5	5.4	1.5 E-2	2.1 E-5	637	15.8
	5	7.9	8.7	3.3 E-2	7.2 E-5	529	16.0
	6	16.5	49.7	6.9 E-2	1.3 E-4	558	16.1
	7	66.2	240.0	1.0 E-0	5.7 E-2	190	21.0
	8	306.2	0.2	1.3 E-4	1.6 E-5	82	15.3
	9	306.4	0.2	1.1 E-4	1.5 E-5	74	15.3
	10	306.5	0.5	1.2 E-3	1.7 E-5	73	15.3
	11	307.1	2.0	5.6 E-3	7.2 E-5	78	15.3
	12	309.1	12.8	1.7 E-2	1.2 E-4	156	15.4
	13	321.9	16.0	4.6 E-2	3.7 E-4	124	15.7
	14	338.0	663.0	1.7 E-1	2.6 E-3	79	17.3
D	1	0	3.6	2.3 E-3	6.4 E-6	358	20.1
	2	3.6	8.0	8.5 E-3	1.3 E-5	672	20.0
	3	11.5	24.0	2.5 E-2	3.7 E-5	692	20.1
	4	35.5	66.7	5.5 E-2	1.7 E-4	372	20.6
	5	102.2	3.1	2.3 E-3	4.1 E-5	56	20.1
	6	105.3	8.5	8.4 E-3	4.7 E-5	180	20.1
	7	113.7	63.5	2.3 E-2	9.8 E-5	244	20.5
	8	177.2	86.4	5.0 E-2	4.4 E-4	126	21.4
	9	263.6	34.8	2.4 E-2	1.2 E-4	202	20.3

Table 3.3 (continued)

Activation	Run	Quantity pumped (torr-liters)		Feed rate (torr-liter/sec)	Average during run		
		Prior to run	During run		Pressure (torr)	Speed (liter/sec)	Temperature (K)
E	1	0	2.1	2.3 E-3	1.5 E-6	1500	15.1
	2	2.1	5.7	9.1 E-3	6.4 E-6	1430	15.2
	3	7.8	24.3	2.6 E-2	2.0 E-5	1313	15.0
	4	32.2	46.0	5.4 E-2	8.1 E-5	705	15.2
	5	78.2	2.1	2.2 E-3	1.5 E-6	1489	14.9
	6	80.3	9.6	8.4 E-3	6.1 E-6	1382	14.9
	7	89.9	13.0	2.3 E-2	2.0 E-5	1158	15.0
	8	102.8	40.1	5.3 E-2	6.7 E-5	822	15.0
	9	142.9	1054.2	3.5 E-1	4.4 E-3	96	18.9
	10	1197.1	454.0	3.9 E-1	7.7 E-3	59	14.6
F	1	0	5.2	8.5 E-3	7.0 E-6	1226	14.7
	2	5.2	14.7	5.1 E-2	5.3 E-5	981	14.8
	3	19.9	76.4	7.0 E-2	2.6 E-4	332	15.6
	4	96.3	251.7	6.3 E-2	1.2 E-3	176	17.0
	5	348.1	2.9	7.8 E-3	2.0 E-5	394	14.2
	6	351.0	299.5	2.6 E-1	5.4 E-3	51	24.0
	7	650.5	2.3	8.2 E-3	3.0 E-5	296	14.2
	8	652.8	77.3	1.4 E-1	1.7 E-3	88	17.8
	9	730.0	89.8	1.1 E-1	1.9 E-3	90	18.2
	10	819.8	43.1	6.2 E-2	8.5 E-4	76	15.8

Fig. 3.17. Speed as a function of total loading for hydrogen at elevated temperatures.

Fig. 3.18. Speed as a function of loading during individual runs for hydrogen at elevated temperatures.

speeds was observed from 10^{-6} to 10^{-4} torr. Plotted on the same figure are representative data from Southerlan⁴ showing steady-state speeds for individual runs in a single activation. Also shown is one of the highest sets of speeds reported by Gareis and Pitlor.⁶ As mentioned previously, these two sets of data show contradictory behavior. The data presented here appear to contain both types of behavior. After some activations, the initial speeds were low; the speeds increased in succeeding runs. After other activations, initial speeds were high, and the speeds decreased in succeeding runs. This behavior can be followed in early stages of runs shown in Fig. 3.17. Note that curves following the former behavior appear to show a broad maxima in speed near 10 torr-liters total loading.

Figure 3.20 shows a series of four successive runs that exhibit low initial speeds and go through a maxima in the next three runs with increasing feed rate and loading. Figure 3.21 shows eight successive runs taken on two consecutive days. Both sets show almost identical behavior with high initial speeds, decreasing with loading and feed rate. These curves also indicate that pumping speed is a stronger function of loading than feed rate. However, the general shape of the curves in Fig. 3.20 must result from both feed rate and loading.

With deuterium pumping, it was possible to increase the pumping speed by heating the panel to allow the material from the surface to diffuse into the bulk of the adsorbent. Figure 3.21 shows the only run in which this was achieved for hydrogen. Other consecutive runs were made with warming between them which showed no significant recovery in pumping speed. Another effect observed frequently with deuterium was

Fig. 3.20. Speed, pressure, and temperature as a function of loading for four consecutive hydrogen runs.

Fig. 3.21. Speed, pressure, and temperature as a function of loading for eight consecutive hydrogen runs on two consecutive days.

spontaneous recovery in speed during a run via rapid transitions similar to those observed for helium. Such behavior was observed in only one run with hydrogen, this run is shown in Fig. 3.22 along with the three runs which preceded it. The first three runs showed the high initial speed with declining speeds thereafter. This behavior is almost identical to that shown in Fig. 3.21. The fourth run, however, contained two instabilities--neither of which restored the speed to its original value.

Discussion. Hydrogen pumping at elevated temperatures is markedly different from deuterium pumping and shows inconsistencies from activation to activation and author to author which have no obvious correlation. Hydrogen pumping appears to show two separate and distinct types of behavior. Two behaviors could occur because hydrogen molecules have two distinct forms, ortho and para hydrogen. Stern et al.,⁷ in the course of measuring equilibrium adsorption isotherms of hydrogen on MS-13X at 20.2 K, found that the pressure first decreased, then increased, and then decreased again to the equilibrium pressure. It was also observed that the equilibrium pressure did not increase monotonically with loading. The authors suggested that ortho-para hydrogen transition could have caused this effect. However, tests with normal hydrogen and p-hydrogen indicated that both materials behaved identically, and anomalous behavior cannot be associated with such transitions. Specific interactions between a hydrogen molecule and the surface are very similar in MS-13X and MS-5A, therefore, since ortho-para transition does not effect adsorption on MS-13X, it would be expected to have no effect on the MS-5A as well.

Fig. 3.22. Speed, pressure, and temperature as a function of loading for four consecutive hydrogen runs.

Molecular sieving action has been observed to be a strong function of temperature for several materials.⁸ Nitrogen for instance undergoes equilibrium adsorption in MS-4A cavities down to a temperature of about -100°C; at this point, the size of the cavity windows becomes comparable to the size of the nitrogen molecule. Adsorption inside the cavities is precluded from occurring at lower temperatures because the nitrogen molecules cannot pass through the windows into the cavities. Such effects have also been observed for hydrogen in MS-3A which will adsorb hydrogen at normal temperatures but will not adsorb it at 77 K. This effect could cause significant reductions in pumping speed and adsorption capacity at low temperatures. By itself, however, this does not seem likely to account for the sieve having two apparently different states at a given temperature as has been observed for hydrogen.

In previous discussions concerning deuterium, it was shown that many aspects of deuterium pumping are qualitatively similar to helium pumping. Specifically, one observation of importance is the fact that for both materials the sticking coefficient increases after one molecule has been adsorbed in each surface cavity. One generic set of hydrogen data appears to follow the same type of behavior. It seems paradoxical that such an effect should be noted for both helium (a nonpolar molecule) and hydrogen (a molecule with a permanent quadrupole), since they adsorb preferentially at different sites in the MS-5A cavity. Because helium normally occupies sites near cavity windows, one could expect the presence of an adsorbed atom inside the cavity window to enhance the probability of another atom sticking outside the window at the corresponding site on the surface of the adsorbent. Hydrogen, on the other hand, would be

adsorbed preferentially near cations which are not near cavity windows. It is difficult to reconcile enhancement in sticking coefficient if preadsorbed molecules are not located near the cavity window. The fact that these similarities exist between helium and hydrogen isotopes could indicate that the cavity loses its electric field at low temperatures.

Equilibrium adsorption isotherms for hydrogen at 90, 77, and 20 K are shown in Fig. 3.23. Information about the nature of specific molecule-surface interactions can be discerned from evaluation of equilibrium adsorption in the Henry's Law region of the isotherm (coverage proportional to pressure). Unfortunately, the 20 K data do not extend into this region. In order to extrapolate equilibrium adsorption into this region, it is necessary to fit the data to an isotherm which considers the microscopic interactions present in the cavity. The Fowler-Guggenheim model, which assumes that molecules are adsorbed on specific sites and assumes nearest-neighbor interactions, fits all data well. The values of the first configuration integrals which were calculated from the Henry's Law constants from the Fowler-Guggenheim isotherms are plotted in Fig. 3.24. The solid lines correspond to three model predictions of the first configuration integral for hydrogen in an MS-5A cavity: (1) the line labeled "S & S Ca⁺² Model" employs the Seff and Shoemaker atomic coordinates for MS-5A and assigns a charge of +2 to calcium ions; (2) the line labeled "B & S Ca⁺¹ Model" employs the Brussard and Shoemaker atomic coordinates for MS-5A and assumes atoms have a +1 charge; and (3) the line designated "No Electric Field" assumes calcium and sodium atoms have no ionic charge. Calculation for the ionic cavities assume that the hydrogen quadrupole is always in its most

Fig. 3.23. Equilibrium adsorption isotherms for hydrogen on MS-5A.

Fig. 3.24. First configuration integrals for adsorption of hydrogen on MS-5A.

favorable orientation with respect to the cations. Figure 3.24 shows that the two polar models bracket the 90 and 77 K data, but they overshoot the 20 K data by a large margin. The model with no specific electric field comes much closer to the 20 K data. This suggests that the cavity does lose its ionic character somewhere below 77 K. This would explain similarities noted between hydrogen, deuterium, and helium pumping.

Loss of ionic interactions in the cavity with decreasing temperature implies motion of the cations with temperature and offers a possible explanation of the two different behaviors noted for hydrogen. Cations are normally located in the center of the hexagonal oxygen rings inside the cavity in what is normally referred as site II. Site II is slightly out of the oxygen plane towards the center of the adsorption cavity. This is the normal high-temperature position. If the normal low-temperature position of the cations would be inside the sodalite units (possibly into Site II), it might be possible to trap the cations near the high-temperature equilibrium position by closing the oxygen ring before the ion could pass through. Such an effect could lead to the two observed hydrogen behaviors. If the cation is removed from the hexagonal ring, the ring may be large enough to admit hydrogen molecules to the inside of the sodalite units. This would lead to enhanced initial speeds after activation because the surface has a large number of these rings (each cavity window is surrounded by four). If, on the other hand, the cations were trapped in the hexagonal ring (thus blocking the passage to the sodalite unit), then only the normal windows would be available for sorption.

For deuterium one can postulate that its higher molecular weight prevents it from gaining enough vibrational energy to pass through the energy barrier at the hexagonal window. For helium it is possible that the atom can enter the sodalite unit in both cases. Initial speeds for helium at 4.2 K are generally about 600 liters/sec (at all feed rates) as opposed to about 400 liters/sec for deuterium at low feed rates. This suggests that more surface is available for helium adsorption than for deuterium adsorption. Therefore, this model seems to be consistent with other observed data.

The impact of these observations is the realization that one must understand why speed enhancement occurs so that it can be utilized to obtain higher pumping speeds. If the postulates proposed here are correct, controlling the cool-down rate from 77 K to the operating temperature may be an important factor. Fast cooling rates should trap cations near high-temperature sites and slow cooling rates should allow time for them to pass into the sodalite units.

3.1.5 Roughing system after hydrogen adsorption

Control of pump pressurization during regeneration becomes a very important consideration if the cryosorption pumps are being roughed by mechanical pumps, such as turbomolecular pumps, which cannot tolerate pressure excursions. Cryosorption pump pressure should be readily predictable from equilibrium adsorption isotherms.

The experimental apparatus consists of the CVR 1106 pump, test chamber, and two roughing pumps as described in ref. 1. The roughing pumps are of the adsorption type (Varian Vac-Sorb), each containing about 2 lb of MS-5A. Prior to exposure to the system, the roughing

pumps were baked under vacuum from a liquid-nitrogen (LN_2)-trapped mechanical pump. Before opening to the system, the pumps are cooled with liquid nitrogen. All runs reported here were made in conjunction with speed measurements. Several runs are reported in which the CVR 1106 pump was simply being cooled or warmed prior to or after obtaining speed measurements. Two warming runs were made with the system opened to the roughing pumps.

Figure 3.25 shows the pump pressure as a function of temperature for four different thermal swings of the closed system. The total amount adsorbed is different in each case. However, the characteristic of all curves are quite similar; all exhibit a plateau at $\sim 10^{-4}$ torr.

Figure 3.26 shows the pressure for both cooling and roughing the pump loaded with 860 torr-liters of adsorbed hydrogen. For comparison, the equilibrium pressure predicted from the Fowler-Guggenheim equation are given for both cooling and roughing. The following pressures have been corrected for thermal transportation below 10^{-2} torr:

$$P_{300} = P_T \sqrt{300/T}, \quad P_T < 10^{-4} \text{ torr}$$

$$P_{300} = P_T \{1 - .217 (\sqrt{300/T} - 1) [4.60 + \ln(P_T)]\}, \quad 10^{-4} < P_T < 10^{-2} \text{ torr}$$

$$P_{300} = P_T, \quad P_T > 10^{-2} \text{ torr}.$$

The cooling curve follows the equilibrium curve to about 30 K where it enters a plateau, and no significant reduction in pressure is observed until the temperature reaches 17 K. Apparently, diffusion becomes the controlling factor below 30 K. At 17 K, for instance, the pump pressure is on the order of 10^{-4} torr, and the equilibrium pressure is near

Fig. 3.25. System pressure as a function of temperature for fixed loadings. Arrows indicate progress in time.

Fig. 3.26. System pressure as a function of temperature when cooling the pump after accumulation of 860 torr-liters hydrogen and when warming the pump and roughing the system.

10^{-9} torr. Material trapped in surface micropores at 30 K remains there and controls the system pressure to 17 K. At this point, the temperature becomes low enough that adsorption on the external surface reduces the system pressure. Given enough time at these lower pressures, equilibrium should be reached.

Following the roughing curve in Fig. 3.26 one sees that, although the first Vac-Sorb pump was opened at about 30 K, no significant system pressurization occurred until 40 K. Because of diffusion limitations, some hysteresis in the dynamic system response is expected. The system pressure rises above equilibrium pressure when the second Vac-Sorb pump is open as a result of the conductance restriction between the roughing pump and the systems.

Figure 3.27 shows the dynamic response of the systems to roughing with one and two Vac-Sorb pumps and different heating rates. The heating rate and the number of Vac-Sorb pumps have no significant effect in this time and loading frame. The significant pressure rise is noted to begin in both cases between 40 and 50 K and peak pressures reached are in the mid- 10^{-2} -torr range.

Although it appears that adequate pressure control can be achieved during roughing by controlling the temperature of the sieve surface, quantitative models for MS-5A must include diffusion within the sieve at low temperatures and conductance to the roughing pump at high pressures. Beyond this, these results indicate once again that only the external surface of the adsorbent is accounting for all the cryosorption pumping action.

Fig. 3.27. System pressure and temperature as a function of time for two similar loadings during roughing at significantly different warming rate.

3.1.6 Preparation of a new, more versatile cryosorption pump

A new pump has been designed, constructed, and added to the test stand. This pump will facilitate optimization of the following important variables for cryosorption pumping: (1) type of adsorbent, (2) operating temperature, (3) adsorbent support design, and (4) baffle design. Figure 3.28 shows a schematic cross section of the pump. The cryogenic envelope is an Andonian Model 024/7M-15L variable-temperature cryostat that has the capability of continuous temperature control from 4.2 to 300 K. Temperature control is achieved by metering the flow of the liquid helium to the back of the cryosorption panel which is heated and controlled at the desired temperature. Several temperature sensors are attached to both the front and back of the panel to determine the magnitude of temperature gradients which may develop during pumping. A combination germanium resistance thermometers and gold doped with 0.07% iron versus chromel thermocouples are employed for this purpose. The temperatures of the chevron and radiation shield are also measured. The guard vacuum inside the cryostat is separate from the pump vacuum space so that high pump operating pressures can be employed without suffering cryogenic runaway. A 77 K copper radiation shield is attached to the Andonian LN₂ reservoir and extends down over the outside of the cryosorption panel. A thermocouple is mounted at the lower edge of this shield. The cryosorption panel is supported on a thin-wall stainless steel tube from the same 77 K plate. Cryosorption panels are attached to the cryostat through a 4.7-in.-OD lead "O"-ring joint. Any cryosorption panel with a compatible flange can be tested. Panels may also be accommodated on the 1.7-in.-OD lead "O"-ring flange located at the center of the stem.

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Fig. 3.28. Cross section of the demountable cryosorption pump.

The chevron assembly is a separate unit which may be modified or exchanged for other units if necessary. This unit is all stainless steel. Chevrons have 90° included angles and are just optically dense with a spacing of $1/2$ in. The three chevron surfaces that are not exposed to the cryosorption panel are painted black to reduce transmitted radiation while maintaining low emissivity on the surface facing the cryosorption panel. A thermocouple is mounted at the center of the middle chevron.

Figure 3.29 shows a cryosorption panel which was prepared by Excalibur Corporation. The panel has MS-5A adsorbent mounted on a stainless steel substrate with $1/16$ in. cross-milled grooves; studs and holes in the panel are for mounting resistance thermometers and thermocouples. The diameter of the cryosorption surface is 4 in. Panels have been prepared with MS-5A, MS-13X, and Na-Y molecular sieve on cross-milled and screen substrates. Other panels will be prepared as needed.

Figure 3.30 shows a schematic of the experimental test stands. The two cryosorption pumps are mounted and operated independently, each with its own vacuum test chamber. The pumps share the mass spectrometer and automatic liquid-nitrogen supply. Figure 3.31 shows the test stands and associated instrumentation. The Excalibur pump is in the background on the left, and the new pump is next to the instrumentation. Vacuum test chambers are insulated for bake-out. Changing cryosorption panels can be accomplished by lifting the cryostat vertically out of the test stand.

Program status. Preliminary elevated temperatures runs on the Excalibur CVR-1106 pump are now complete, and the controlled-temperature helium system has been removed from the pump. The Excalibur pump will

Fig. 3.25. Photograph of the cryosorption panel.

Fig. 3.30. Schematic of the test stand.

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Fig. 3.31. Photograph of test stand.

continue to be used in the pool boiling mode. To get a better estimate of the actual amount of adsorbent panel, equilibrium measurements will be made at 77 K. A series of pulse tests will follow. These tests are important because, even though cryosorption of hydrogen on MS-5A is severely limited by diffusion, it may be adequate on a short pulse-long downtime pumping schedule (which is expected for near-term fusion devices).

A new pump has been assembled and added to the test stand; this system has been leak-checked. Bake-out and test of the temperature control system will be complete in the immediate future. The first test will be with a MS-5A panel to obtain data for comparison with results from the CVR 1106.

3.2 Tritium Sorption from Liquid Metals

S. D. Clinton and J. S. Watson

3.2.1 Introduction

A molten lithium blanket appears to be the most promising means for achieving tritium breeding for tokamak fusion reactors. Three recovery techniques are currently being considered for the removal of tritium from liquid lithium: (1) extraction with a molten salt, (2) permeation through a niobium window, and (3) sorption on a hydrogen-gettering metal. Tritium sorption from molten lithium is being studied in a batch contactor using metal sorbent samples of yttrium and zirconium. At 300°C, a yttrium sample reduced the concentration of tritium in lithium by a factor of two in 24 min. The controlling mass transfer resistance appears to be in the liquid lithium phase, and, consequently, the mass

transfer rate could be increased perhaps by an order of magnitude with forced convection. Although not conclusive, the results demonstrate the feasibility of such a blanket-recovery process system.

3.2.2 Experimental equipment

A schematic diagram and photograph of the equipment to contact tritiated lithium with selected metal sorbents has been published.¹ Basically, the equipment consists of a tritiated-lithium reservoir, two sampling valves, two isolated contacting chambers, a vacuum source, and an argon supply. The tritiated lithium can be drawn into the two contacting chambers at a temperature between 200 and 400°C. One chamber contains the metal sorbent, and the second chamber serves as a control. To terminate an experiment, the two lithium samples are removed from the contactor chambers and analyzed for tritium by liquid scintillation counting.^{3,9} To reduce the problems of oxygen contamination, the entire process is enclosed in a glove box with a once-through, dry argon atmosphere. The glove box also serves as a secondary tritium containment, operating at a slightly negative pressure and exhausting to a hot off-gas system.

3.2.3 Results and discussion

Twenty-one sorption runs were made at 300°C with the same yttrium metal sample obtained from Research Chemicals (Division of NUCOR Corporation). The metal sample dimensions were 0.30 cm x 1.35 cm x 3.72 cm (geometric surface area of 13.1 cm²); the weight was 3.45 g. The contacting time for each run ranged from 5 min to 90 hr. A lithium control sample was removed with each sorption run to confirm the initial

concentration of tritium in the lithium. From the 21 control analyses, the average tritium concentration in the lithium feed reservoir was 833 ± 54 ppb.

The results of the 21 sorption runs are shown in Fig. 3.32 in which the tritium concentration remaining in the lithium divided by the initial concentration is plotted as a function of the contact time. Except for runs 1, 15, 18, and 19, the tritium concentration in the lithium decreased with contact time as two distinct first-order reactions. The reaction half-time decreased from 24 min for the first half-hour of contact time to 20 hr for contact times >2 hr. The apparent mass transfer resistance in run 1 could be explained by an activation of the yttrium surface. A similar phenomenon occurred with a previously reported tritium-sorption experiment using potassium and yttrium.¹ The apparent rate decrease in runs 15, 18, and 19 can be explained by a reduced driving force due to the accumulation of tritium in the yttrium sample. Comparing runs 2 and 15, the bulk tritium concentration in the yttrium sorber increased from 2 to 20 ppm.

Runs 9, 11, 13, and 16 (respective contact times of 30, 15, 10, and 5 min) were used to obtain an average mass transfer coefficient of $(6.1 \pm 1.1) \times 10^{-4}$ cm per sec. The surface film driving force was assumed to be the tritium concentration in the lithium, and the ratio of the yttrium surface area to the lithium volume for the four runs was 0.82 ± 0.02 cm⁻¹. The magnitude of the mass transfer coefficient and the variation of sorption rate with time suggest that the controlling mass transfer resistance is in the liquid-lithium phase. Consequently,

Fig. 3.32. Normalized tritium concentration in lithium as a function of contact time for yttrium sorber experiments.

the mass transfer rate could be increased perhaps by an order of magnitude with forced convection.

The results of runs 20 and 21 exhibit strong evidence that the controlling mass transfer resistance is in the liquid phase. During the first 20 runs, a minimum time period of 24 hr was maintained between runs to flatten any existing tritium concentration gradient in the yttrium sample. Only 18 min separated the termination and start of runs 20 and 21. After 2-hr contact times, the normalized tritium concentrations in the lithium for runs 20 and 21 were respectively 0.38 and 0.30. These results would also suggest that the subsequent mass transfer rate (contact times greater than 2 hr) is controlled by bulk-diffusion of tritium in the liquid lithium rather than in the yttrium.

After a sorber-contact time of 66 hr, the tritium concentration in the lithium (7.32 g) for run 19 was 86 ppb. Based on subsequent dissolution of the sorber sample (3.45 g), the tritium concentration in the yttrium was determined to be 25 ppm. F. J. Smith has measured the solubility of tritium in lithium as a function of temperature (700 to 1000°C) and pressure (0.1 to 760 torr).¹⁰ The temperature dependence of the solubility, $\ln$, is given by the following equation when the LIT mole fraction is <0.1:

$$\ln K_s = 9.226 - 5085/T, \quad (1)$$

K_s = Sieverts' law constant, $\text{torr}^{1/2}$ / atom fraction,

T = temperature, K.

Extrapolating Eq. (1) to 300°C, the value of K_s becomes 1.4 $\text{torr}^{1/2}$ /atom fraction. Using this value for Sieverts' constant and a tritium in lithium concentration of 80 ppb, the equilibrium tritium gas pressure

is calculated to be 6.8×10^{-14} torr. With this tritium pressure and a tritium-in-yttrium concentration of 25 ppm, the calculated Sieverts' constant for YT at 300°C is 3.5×10^{-4} torr^{1/2}/atom fraction. The reciprocal of the calculated Sieverts' constant for yttrium on a weight basis is 9.6×10^7 ppm/torr^{1/2} at 300°C compared to 3.1×10^5 ppm/torr^{1/2} for lithium. These values can be compared directly with the hydrogen-gettering potentials of selected metals compiled by R. C. Forrester.¹¹ Extrapolating the data of Yannopoulos,¹² Forrester estimated the hydrogen-gettering potential of yttrium to range between 10^3 and 10^8 ppm/torr^{1/2} at 300°C. The calculated yttrium value from run 19 substantiates the higher estimate by Forrester.

At the end of run 21, the yttrium metal sample was analyzed for tritium content by dissolving the metal in dilute hydrochloric acid and counting the resulting solutions in a liquid scintillation spectrometer. On removal from the contactor chamber, the yttrium sample appeared to be unchanged by the extended contact time with lithium at 300°C. A water rinse of the yttrium sample prior to dissolution revealed that 0.3 g of lithium had adhered to the yttrium surface. From the lithium control and sorber samples, the estimated accumulation of tritium in the yttrium during the 21 sorption experiments was 0.78 Ci (~23 ppm). The tritium recovered from dissolution of the yttrium was 0.90 Ci (115% of the estimated amount) indicating a tritium concentration in the sorber sample of 27 ppm. The error in any tritium concentration determination is ±5 to 10%. Sampling losses of lithium between runs (0.3 to 0.6 g) could cause the estimated tritium accumulation in the yttrium to be low by 5 to

10%. The amount of tritium recovered in the water rinse prior to yttrium dissolution was <0.1% (0.0008 Ci).

Four sorption runs were made with tritiated lithium and a zirconium sorber sample. The zirconium sample dimensions were 0.07 cm x 1.25 x 3.82 cm (geometric surface area of 10.3 cm^2); the weight was 2.11 g. The results of the zirconium - tritium sorption experiments in liquid lithium are shown in Table 3.4.

Table 3.4. Results of the tritiated lithium-zirconium sorption experiments

Run no.	Temperature (°C)	Contact time (hr)	Tritium concentration in lithium		
			Sorber, C (ppb)	Control, C ₀ (ppb)	Ratio of C to C ₀
1	300	25	770	792	0.97
2	300	140	746	783	0.95
3	300	72	766	780	0.98
4	400	72	788	775	1.02

The first three runs were conducted at 300°C, and the fourth run was made at 400°C. Contact times for each run ranged from 25 to 140 hr. From the four control analyses, the average initial tritium concentration in the lithium was 782 ± 7 ppb. After 140 hr of contact time with zirconium at 300°C (run 2), the normalized tritium concentration remaining in the lithium was only 0.95. For run 4, the temperature was increased to 400°C; after 72 hr, the normalized tritium concentration in the lithium

indicated a 2% increase when compared with the run 4 control sample. Although the tritium concentration determinations are subject to errors greater than $\pm 5\%$, the results show that zirconium does not compare favorably with yttrium as a metal sorbent material for recovering tritium from molten lithium. Any zirconium oxide surface film acting as a barrier to mass transfer should be reduced by the lithium at 300°C .

After completing run 4, the zirconium metal sorber was analyzed for tritium content by dissolution of the sample in dilute hydrofluoric acid. From the lithium control and sorber samples, the tritium accumulation in the zirconium was estimated to be 0.0034 Ci corresponding to a concentration of 170 ppb . The total amount of tritium recovered from the zirconium dissolution was 0.0015 Ci (44% recovery of the estimated amount) indicating a final tritium concentration in the sorber sample of 75 ppb . Due to both the small amount of tritium transferred in each run and the uncertainties in the tritium concentration determinations, the estimated accumulation of tritium in the zirconium could easily be high by a factor of 2 to 3.

Extrapolating the equilibrium data of Smith¹⁰ and Kearns,¹³ the tritium sorption results with liquid lithium and zirconium would not be unexpected. With a tritium-in-lithium concentration of 782 ppb , the Sieverts relationships predict a tritium concentration in zirconium of 130 ppb at 300°C and 100 ppb at 400°C . The zirconium equilibrium concentration at 300°C can be achieved by reducing the tritium concentration in a single 6-g lithium sample from 782 to 736 ppb . Assuming the tritium-zirconium system was close to equilibrium at the end of run 3, then tritium would be released from the zirconium at 400°C as shown in run 4.

Program status. Sorption experiments are continuing with tritiated lithium and yttrium at 400°C in the batch contactor system and should be completed by July. Other hydrogen-gettering metals such as cerium may be tested with the remaining available tritiated lithium during the months of August and September. A preliminary design on a forced convection tritium sorption system will be completed during the next report period.

3.3 Tritium Recovery from Solid Lithium-Aluminum and SAP Blanket Materials

J. B. Talbot

The study of tritium release rates from irradiated aluminum and sintered aluminum product (SAP) was continued during this reporting period. Solid lithium-aluminum alloy has been suggested as a potential tritium breeding material for fusion reactors, and SAP has been suggested as a blanket or structural material.¹⁴ This investigation differs from current studies¹⁵ of solid aluminum alloy blanket material at other laboratories because of the low (ppm) lithium content, the incorporation of oxygen (18 wt % of Al_2O_3) within some of the samples (SAP), and the use of large (~1-in.-long wafers) samples with known dimensions rather than powders.

3.3.1 Experimental

The apparatus and experimental procedure used to examine tritium release rates from the aluminum alloy samples has been described previously.¹ Basically, a sample is heated to a desired temperature, and the released tritium is swept to a tritium monitor. Then, the tritium-bearing argon is routed to a trapping system composed of a CuO bed (600°C),

two water bubblers, a molecular sieve trap, and a second tritium monitor to detect the tritium released to the ORNL "hot" off-gas stack via the hot-cell's ventilation system.

The fraction of tritium released was determined from the integral of the signal from the tritium monitor and the remaining tritium in the sample, determined by dissolution and conventional liquid scintillation methods.¹⁶ To determine the amount of tritium in a liquid sample, an aliquot was mixed with 10 ml of scintillation counting solution. The amount of the tritiated aliquot varied from 10 λ (0.01 ml) to 1 ml, depending upon the volume needed to obtain sufficient tritium for accurate counting in the range of 100,000 to 500,000 counts per minute. The tritium content in each solution was measured with a Packard Model 574 Tri-carb scintillation spectrometer that had a counting efficiency of 20%. Previously, the counter efficiency (or disintegrations per counts) had been determined with a standard solution from the National Bureau of Standards. Series of experiments were conducted to determine the effect of sample dilution on the counter efficiency. Aliquots of a 10-ml sample containing 4.45×10^6 dpm per ml of tritium were diluted with water to alter the total sample volumes from .01 to 1 ml. Figure 3.33 shows the count rate for each sample volume counted. A precipitate formed with 0.3- and 0.4-ml sample volumes and increased the count rate measured. Counter efficiencies were determined for each sample volume counted, as shown in Fig. 3.34. The figure also includes data collected by S. D. Clinton. The counter efficiency ranges from 24 to 18% for sample volumes of .01 to 1 ml, respectively. Therefore, it was concluded that in subsequent runs, the samples would be diluted to decrease the count

Fig. 3.33. Effect of sample dilution on scintillation counting of tritium.

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Fig. 3.34. Scintillation spectrometer counting efficiency as a function of sample volume.

rate to the acceptable range, and then a 0.5-ml aliquot of the sample would be counted so the counter efficiency would be a constant 20%. Data gathered prior to this experiment were corrected using the efficiency dictated by the sample volume used.

Due to the relatively long length of each run, some tritium diffused from the apparatus. Subsequently, material balances of the tritium trapped in the water bubblers and molecular sieve bed did not compare well with the monitored tritium release rate. To improve the capture of tritium, the size of the CuO bed was increased by an order of magnitude (to ~250 g). As shown in Table 3.5, for most of the runs only about half of the tritium released from a sample was captured in the bubblers. The increased capacity of the CuO bed did not improve the trapping system. Apparently the trapping efficiency is limited by HTO sorption in the bubblers rather than by oxidation in the CuO beds. Some of the loss may result from evaporation from the bubblers.

3.3.2 Results

A series of six runs were made to measure the release rate of tritium from irradiated SAP samples. The data are tabulated in Table 3.5. The objective of the first run was to determine the temperature at which a significant tritium release was observed; this took place at about 250°C. The temperature of the sample (sample No. 7) was steadily increased to 450°C over a 32-hr period. The next two runs (sample Nos. 1 and 3) were made at a sample temperature of 400°C. Difficulties were encountered in controlling the temperature of sample No. 1; the temperature decreased to 340°C after 10 hr, then increased to 420°C after 15 hr. The temperature controller was adjusted, and the 400°C experiment was repeated with

Table 3.5. Tritium release from SAP samples and amount captured in the trapping system

	Sample number					
	7	1	2	3	5	6
Temperature of sample, °C	26-450	400	450	400	450	500
Weight of sample, g	0.3425	0.4870	0.1312	0.1690	0.2550	0.1928
Sample thickness, cm	0.0813	0.1143	0.0508	0.0609	0.0609	0.0533
Sample surface area, cm ²	3.8971	4.3273	2.7106	3.0012	3.7100	3.3520
Length of run, hr	32	30	30	26.5	121	47
Tritium released from sample, m Ci	4.581	3.042	4.704	0.626	2.193	17.875
% tritium from:						
a) First water bubbler	11.7	11.9	4.3	12.2	0.9	1.1
b) Second water bubbler	4.0	32.8	76.5	52.2	53.3	23.6
c) Molecular sieve bed	3.1	8.6	?	?	8.4	3.3
d) Exhaust monitor	25.8	10.3	0.3	1.7	13.1	28.3
% tritium trapped	18.8	53.3	80.8	64.4	62.6	28.0
Tritium from sample dissolution, m Ci	39.13	35.24	11.425	3.358	5.639	10.938
% tritium released	10.5	7.95	29.2	15.7	28.0	62.0
CuO weight, g, and type	25 Harshaw pellets	29.2 Harshaw pellets	15.4 Engelhard pellets	12.4 Engelhard pellets	15 Engelhard pellets	272.2 Engelhard pellets
Total amount of tritium in sample, wppm	12.8	7.86	12.29	2.36	3.07	14.95

sample No. 3. Sample Nos. 2 and 6 were heated to 450 and 500°C, respectively. Also, sample No. 5 was heated to 450°C for a 100-hr run. The percent of tritium released from the sample and the total tritium concentration (wppm) determined for each sample is shown in Table 3.5. The concentration of tritium ranged from about 2 to 15 wppm.

Helium analysis, measured by Atomics International (AI) with a mass spectrometric method, indicated the amount of tritium originally in the sample. The procedure for the determination of the helium concentration was as follows.¹⁷ The samples were examined under the microscope for adhesions or blemishes and then cut with wire cutters to a size suitable for mass spectrometric analysis. Determinations of the helium content of the aluminum alloy specimens were made by vaporizing each specimen under vacuum using a resistance-heated tungsten wire basket. After melting, the temperature of the tungsten was increased until the sample was observed to vaporize; finally, the tungsten itself disintegrated. After sample vaporization, a known small fraction (0.1%) of the gas sample was taken for isotopic analysis. By doing this, the concentration of ^3He relative to the more abundant ^4He was first obtained before a precisely known number of ^3He atoms was added to the vacuum enclosure. After mixing of the isotopes, the gas passed over the getters directly into the mass spectrometer volume. A measurement of the $^4\text{He}/^3\text{He}$ ratio and a knowledge of the weight of the material then produced the ^4He concentrations. Table 3.6 shows the results of these analyses. Using the ^4He analyses, the amount of tritium originally in the samples was calculated to be 20.91 ± 0.59 wppm and 33.04 ± 0.04 wppm for the SAP and AL samples, respectively. The SAP sample analyzed for ^4He corresponds to

Table 3.6. Concentrations of ^3He and ^4He in irradiated Al-Al₂O₃ alloys containing ^6Li

Sample number	Concentration Al ₂ O ₃ in Al alloy	Sample mass (mg)	Analysis date (1976)	Number of atoms released		Helium concentration (appm) ^a		
				^3He	^4He	^3He	^4He measured value	^4He weighted average
SAP 7A	18 wt %	1.7535	9/13	5.920×10^{14}	7.162×10^{15}	12.3	172.9	176.5 ± 5.0
B		1.5050	9/29	1.219×10^{15}	8.102×10^{15}	27.1	180.0	
6-9 Al 11A	0 wt %	1.3350	9/13	2.381×10^{14}	8.102×10^{15}	7.94	295.3	295.6 ± 0.4
B		1.3730	9/29	2.414×10^{14}	9.066×10^{15}	7.88	295.8	

^aHelium concentrations are calculated with respect to the total number of atoms of aluminum and oxygen present.

sample No. 7 in Table 3.5. These values are higher than anticipated and higher than the results shown in Table 3.5 from the tritium release rates.

However, there is an inconsistency between the ^3He and ^4He analyses reported by AI. The ^4He concentration corresponds to the tritium originally in the sample since equal amounts of tritium and ^4He are formed by irradiation.

The ^3He concentration is produced from tritium decay, as shown in the following equation:

Considering the tritium decay factor, the ^3He concentration (appm) should be about 7% of the ^4He concentration (appm). Only the value for sample SAP 7A agrees with this calculation. The other ^3He analyses show results both higher and lower than the percentage expected. Also, the variation of tritium contents for the samples in Table 3.5 suggests a lack of uniformity in the tritium content of the samples. Since just one sample of SAP was analyzed for ^4He and discrepancies are evident, the tritium content determined from the ^4He should not be compared to the tritium concentration in the other samples.

From analysis of the data, the release rates follow the pattern expected for bulk diffusion in the solid. Solid diffusion is indicated by the slope of one-half of the curves at a constant temperature interval in Fig. 3.35. From a model of diffusion in solid slabs¹⁸ and slope of the curves in Fig. 3.36, which shows the fraction of tritium released as

Fig. 3.35. Tritium release from solid Li-SAP alloys.

Fig. 3.36. Tritium release from solid Li-SAP alloy as a function of sample thickness and time.

a function of time and sample thickness, the diffusion coefficients at 400, 450, and 500°C were determined to be 2.12×10^{-10} cm²/sec, 8.36×10^{-10} cm²/sec, and 2.35×10^{-9} cm²/sec, respectively. From an Arrhenius relationship in Fig. 3.37, the dependence of the diffusion coefficient on temperature was found to be:

$$D = 2.64 \times 10^{-2} \exp \left(- \frac{24,890}{RT} \right),$$

where

D = diffusion coefficient, cm²/sec,

R = gas constant, 1.987 cal · K⁻¹ g-mole⁻¹,

T = sample temperature, K.

The release rates observed by Wiswall and Wirsing¹⁹ for lithium-aluminum powder form did not follow a one-half slope, as seen in Fig. 3.38, and attempts to interpret their results were not successful. Figure 3.39 compares the tritium release rates for SAP and LiAlO₂, which do follow a one-half slope. However, in their experiments, the sizes of the lithium-aluminum and LiAlO₂ particles were not known accurately (materials were crushed and screened) and diffusion coefficients could not be determined.

The experiments with SAP samples indicate that reasonably rapid tritium removal rates are possible. The rates follow simple relationships corresponding to diffusion through a bulk solid. Three additional runs will be made at other temperatures in the range of interest.

Fig. 3.37. Diffusion coefficients for solid Li-SAP alloy.

Fig. 3.33. A comparison of the tritium release from solid Li-SAP and Li-Al alloys.

Fig. 3.39. A comparison of the tritium release from solid Li-SAP and LiAlO_2 alloys.

3.4 Sorptive Pumping of Gases by Deep Beds of Sorbents

C. P. Tung

3.4.1 Introduction

Sorptive pumping is the utilization of a sorbent which takes up gases at lower temperatures and releases them at higher temperatures to pump or move gases, usually from vacuum chambers. The advantages of sorptive pumps are: (1) their cleanliness (no hydrocarbons or other lubricants), (2) the absence of moving parts, (3) the recoverability of the pumped gases, (4) the applicability over the entire range of roughing to ultra-high vacuum conditions, and (5) the production of very high pumping speeds at relatively low cost when compared to conventional pumping systems.²⁰⁻²²

This study was conceived by consideration of the tritium-handling problem in future deuterium-tritium (D-T) fusion reactor plants, but the results can be applied to other vacuum sorption pumping processes.

Sorptive pumping in deep beds of sorbents is probably most applicable to "rough pumps" and "transfer pumps." Since high-vacuum pumps require that the sorbent be refrigerated to temperatures in the neighborhood of 4.2 to 20 K, the sorbents need to bond to a thin metal plate for adequate heat transfer.^{5,23} It is evident that a sorptive pump is only capable of exhausting (adsorbing) a limited quantity of gases and would eventually become saturated. At this point, the sorptive pump must be reactivated by heating or must be allowed to warm to higher temperatures, where the pumped gases are released. The degree of bed saturation achieved during a cycle depends on the sorbent properties (isotherm and mass transfer properties), bed depth, desired vacuum, and required pumping rates. After

recycling, the pump is ready to be returned to service. For continuous operation, dual (parallel) pumping beds must be provided so that one can be in service while the other is being regenerated. For roughing operations, the size of the required sorption system is strongly dependent on the ultimate vacuum which must be achieved and the volume of vacuum chamber. Thus it is necessary to specify the operating pressures, the pumpdown times, and the ultimate vacuum between cycles as accurately as possible.

In this study, a model has been suggested to describe the transport phenomena in sorption beds. This model differs from the other models in that it includes the pressure variation along the depth of the sorbent beds. A computer code has been developed to simulate the importance of parameters in the proposed model, and it can be used to design deep beds for pumping operations.

3.4.2 Theory

In its most general form, the physical situation for a gas stream passing through a fixed bed of granular sorbent solids can be quite complicated. A major objective in this model is to include the effect of adsorption rate on sorbent and the variation of pressure down the bed, but some simplifications are needed. The following assumptions are used: (1) constant physical properties of sorbent solid (spherical shape is assumed); (2) negligible thermal effects (temperature is assumed to be constant in the sorption bed); and (3) one-dimensional plug flow down the bed (negligible diffusion in the direction of flow). Then the concentration of solute gas in the external void space in the fixed bed can be described²⁴ by the following equation:

$$\left(\frac{\partial C_g}{\partial t} \right)_z + \left(\frac{\partial U_z C_g}{\partial z} \right)_t = - \frac{1}{\epsilon} \left(\frac{\partial n}{\partial t} \right)_z, \quad (1)$$

where

C_g = gas-phase concentration, g-mole/cm³,

U_z = interstitial fluid velocity, cm/sec,

z = distance from bed entrance, cm,

t = time, sec,

n = sorption loading in bed, g-mole/cm³ bed,

ϵ = void fraction of bed, dimensionless.

The gas-phase equation of state is the following (assuming ideal gas law behavior):

$$P = C_g RT, \quad (2)$$

where

P = gas-phase pressure, atm,

R = gas constant, $82.057 \text{ atm} \cdot \text{cm}^3 \text{ K}^{-1} \text{ g-mole}^{-1}$,

T = gas-phase temperature, K.

The flow rate of the gas passing through the sorbent bed can be described by Darcy's Law:²⁵

$$u_z = \epsilon U_z = \frac{-k}{\mu} \frac{dP}{dz}, \quad (3)$$

$$U_z = -A \frac{dP}{dz}, \quad (3')$$

where

u_z = superficial velocity of gas, cm/sec,

k = specific permeability, cm^2 ,

μ = viscosity of gas, $\text{g cm}^{-1} \text{ sec}^{-1}$,

A = proportional constant, $\text{cm}^2 \text{ atm}^{-1} \text{ sec}^{-1}$.

Strictly speaking, Darcy's Law is not applicable over all velocity ranges; however, at low flow rate, which is characteristic of viscous flow, the above relation will be applicable.²⁶ At very low pressure, the molecular mean free paths of the flowing gas become comparable with, or larger than, the distances of the walls confining the fluid; the originally viscous flow of gas undergoes a transition to slip flow. Darcy's Law no longer becomes valid for gas in slip flow.²⁷ Several modifications of Darcy's Law for the slip flow have been reported.^{28,29,30,31} Applications of Klinkenberg's modification gave results similar to those obtained for Darcy's Law applied in the deep-bed model.

Substitution of Eqs. (2) and (3') into Eq. (1) yields:

$$\frac{\partial P}{\partial t} - \frac{A}{2} \frac{\partial^2 P^2}{\partial z^2} = - \frac{RT}{\epsilon} \left(\frac{\partial n}{\partial t} \right)_z . \quad (4)$$

The equation for continuity of mass in the solid phase is:

$$\frac{\partial C_s}{\partial t} = D_e \left(\frac{\partial^2 C_s}{\partial r^2} + \frac{2}{r} \frac{\partial C_s}{\partial r} \right) , \quad (5)$$

where

C_s = concentration in solid sorbent, g-mole/cm³,

D_e = effective diffusivity of gas in sorbent phase, cm²/sec,

r = radial position in sorbent particle, cm.

The specific surface area for commercial sorbents is usually in the range of 300 (silica gel) to 1300 m²/g (activated carbon). Diffusion in porous sorbents is a complicated process and depends on the pore-size distribution, but the detailed structure in solid sorbent will not be investigated in this study. The solid phase has been idealized in the model.

The solid-gas interface equilibrium relation is, in general,

$$C_s = f(P, T) , \quad (6)$$

where C_s is the amount of gas adsorbed by a unit volume of sorbent, and f is an algebraic function of pressure, P , and temperature, T .

The rate of sorbent loading per unit bed volume is:

$$\left(\frac{\partial n}{\partial t} \right)_z = 4\pi z_n \left\{ \frac{\partial}{\partial t} \int_0^{R_1} r^2 C_s dr \right\} , \quad (7)$$

where

Z_n = number of spherical sorbent particles per unit bed volume, cm^{-3} ,

R_I = radius of spherical sorbent particle, cm.

In this study, the sorbate gases are stored in a tank with fixed volume. Since pressure changes at constant volume are followed easily, a wide range of experimental conditions can be achieved using a simple apparatus. The system is shown in Fig. 3.40. The initial and boundary conditions are as follows:

The initial conditions at $t = 0$ are:

in the gas storage tank, $P_V = P_{VI}$, (8)

in the sorption bed, $P = P_{SI}$ for all z , (9)

in the sorbent particle, $C_{SI} = f(P_{SI}, T)$ for all z and r . (10)

The boundary conditions at the closed end of the sorption bed, where $z = L$ and $t > 0$, are the following:

$$\left(\frac{\partial P}{\partial z}\right) = 0. \quad (11)$$

Since the amount of sorbate gas in the system is fixed, the quantities of sorbate gas removed from the gas storage chamber must be equal to the quantities accumulated in the sorption bed and adsorbed by the sorbent. Thus the boundary condition for the open end of the sorption bed is expressed by the following:

$$\begin{aligned} \frac{V_g}{RT} \frac{dP_v}{dt} &= \frac{P_v A_c A \epsilon}{RT} \left(\frac{\partial P}{\partial z}\right)_{z=0} \\ &= \int_0^L A_c \left[\frac{\epsilon}{RT} \left(\frac{\partial P}{\partial t}\right)_z + \left(\frac{\partial n}{\partial t}\right)_z \right] dz, \end{aligned} \quad (12)$$

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Fig. 3.40. Schematic of sorption pumping by deep beds of sorbent.

where

A_c = cross-sectional area of sorption bed, cm^2 ,

P_V = pressure in gas storage chamber, atm,

V_g = volume of storage chamber, cm^3 ,

L = depth of sorption bed, cm.

Symmetry is present at the center of the sorbent particle, and equilibrium is assumed to exist at the surface of the sorbent particle. Hence the boundary conditions are the following:

where

$$r=0, \quad \left(\frac{\partial C_s}{\partial r} \right) = 0; \quad (13)$$

where

$$r=R_I, \quad C_S = f(P(z,t) T). \quad (14)$$

Equations (4), (5), and (7), are the basis for the solution of the mathematical model of the system. To generalize the variables so that simple design correlations are possible, these equations were put in the dimensionless form, using the following variables:

$$P = \frac{P}{P_V(0)} = \frac{P}{P_{VI}}, \quad (15)$$

$$Z = \frac{z}{L}, \quad (16)$$

$$\tau = \frac{D_e t}{R_I^2}, \quad (17)$$

$$\xi = \frac{r}{R_I}, \quad (18)$$

$$\bar{C}_S = \frac{C_S}{f(P_{VI}, T)} = \frac{C_S}{C_{SR}}, \quad (19)$$

$$\kappa = \frac{AP_{VI}R_I^2}{2L^2D_e}, \quad (20)$$

$$\eta = \frac{\frac{1}{3} \pi R_I^3 Z_n C_{SR}}{\frac{P_{VI}}{RT} \epsilon}, \quad (21)$$

$$\nu = \frac{A_c L \epsilon}{V_g}, \quad (22)$$

$$\theta = \kappa \tau, \quad (23)$$

where

C_{SR} = the concentration of sorbent particles that would be in equilibrium with the initial gas pressure (P_{VI}) in the gas storage chamber. Also, ν , η , and κ are dimensionless constants; ν is a parameter related to the volume ratio of the sorbent and the gas storage chamber; κ is the time constant ratio of sorption bed and sorbent particle; and η is a parameter relating the ratio of the g-moles of gases which can be adsorbed by sorbents in a unit volume of sorbent to the g-moles of gases contained in a unit volume at the initial pressure of the gas storage chamber. The dimensionless specific sorption rate in unit bed volume is expressed by the following equation:

$$J_Z = \frac{RT}{\epsilon A P_{VI}^2} \frac{2L^2}{\left(\frac{\partial n}{\partial t}\right)_Z} = \eta \left\{ \frac{\partial}{\partial \theta} \int_0^1 3\xi^2 \bar{C}_S d\xi \right\}. \quad (24)$$

The dimensionless equation for the continuity of mass in the sorbent is expressed in the following manner:

$$\frac{\partial \bar{C}_S}{\partial \tau} = \frac{\partial^2 \bar{C}_S}{\partial \xi^2} + \frac{2}{\xi} \frac{\partial \bar{C}_S}{\partial \xi}; \quad (25)$$

and the dimensionless equation for sorption within the bed is expressed by the equation:

$$\frac{\partial \bar{P}}{\partial \theta} - \frac{\partial^2 \bar{P}^2}{\partial Z^2} = - J_z. \quad (26)$$

The dimensionless initial and boundary conditions are the following:

$$\text{at } \theta=0, \quad 0 \leq Z \leq 1 \quad \bar{P} = \frac{P_{SI}}{P_{VI}}, \quad (27)$$

$$0 \leq \xi \leq 1 \quad \bar{C}_s = \frac{C_{SI}}{C_{SR}}, \quad (28)$$

$$P_v = \frac{P_{VI}}{P_{VI}} = 1; \quad (29)$$

$$\text{at } \theta > 0, \quad \left(\frac{\partial C_s}{\partial \xi} \right)_{\xi=0} = 0, \quad (30)$$

$$\left(\frac{\partial C_s}{\partial \xi} \right)_{\xi=1} = \frac{f(P(Z, \theta), T)}{C_{SR}}, \quad (31)$$

$$\left(\frac{\partial \bar{P}}{\partial Z} \right)_{Z=1} = 0, \quad (32)$$

$$\frac{\partial \bar{P}_v}{\partial \theta} = v \int_0^1 \left[\left(\frac{\partial \bar{P}}{\partial \theta} \right) + J_z \right] dZ. \quad (33)$$

From the foregoing mathematical description of the proposed kinetic model, one finds that there are two dependent variables: sorption rate $J(Z, \theta)$, and pressure $P(Z, \theta)$ in the sorption bed--both are functions of time and position along the sorption bed. For given initial conditions and known isotherms of sorbent, the solution of the proposed model will be determined by dimensionless parameters v , η , and κ .

When the pressure of the sorption bed is uniform from top to bottom, the model can be simplified. The concentration at a distance, r , from the center of a sorbent sphere is defined by Eq. (5):

$$\frac{\partial C_S}{\partial t} = D_e \left(\frac{\partial^2 C_S}{\partial r^2} + \frac{2}{r} \frac{\partial C_S}{\partial r} \right) . \quad (5)$$

The pressure changes in the system are:

$$\frac{V_g}{RT} \frac{dP}{dt} = -V_s N A_I D_e \left(\frac{\partial C_S}{\partial r} \right)_{r=R_I} , \quad (34)$$

where

N = number of crystal particles per unit volume sorbent, cm^{-3} ,

A_I = surface area of sorbent particle, cm^2 ,

V_s = total volume of sorbents, cm^3 .

Assuming that a linear equilibrium relationship exists between the sorbent surface and gaseous phase,

$$C_s = K_p P = K_g C_g \quad \text{for } r = R_I , \quad (35)$$

where K_g and K_p are equilibrium constants.

The initial and boundary conditions are the following:

$$\begin{aligned} P_V &= P_{VI} & t &= 0 \\ P &= P_{SI} & t &= 0 \end{aligned} \quad (36)$$

$$\left(\frac{\partial C_s}{\partial r} \right) = 0 \quad t > 0 \quad r = 0 .$$

For these conditions, the solution of Eq. (5) is given by Carslaw:³²

$$F = \frac{P - P_{SI}}{P_{VI} - P_{SI}} = \frac{1}{1 + \omega} + 2 \sum_{n=1}^{\infty} \frac{\exp(-\tau S_n^2)}{3(\omega+1) + S_n^2/3\omega} , \quad (37)$$

where S_n is the n th positive non-zero root of

$$S_n \cot S_n = 1 + S_n^2/3\omega \quad (38)$$

$$\omega = K_g V_s/V_g \quad (39)$$

The n th root, S_n , of Eq. (38) can be seen from a graph of the function $\tan S$ and $S/(1+S^2/3\omega)$ to lie between $n\pi$ and $(n+1/2)\pi^2$. The roots of Eq. (38) are given by Crank¹⁸ for several values of ω .

Where $\tau < 0.1$, a close approximation is given by Paterson:³³

$$F = \frac{1}{\omega_1 - \omega_2} \left\{ \omega_1 e^{\omega_1^2 \tau} (1 + \operatorname{erf} \omega_1 \sqrt{\tau}) - \omega_2 e^{\omega_2^2 \tau} (1 + \operatorname{erf} \omega_2 \sqrt{\tau}) \right\}, \quad (40)$$

where

$$\omega_1 = \frac{1}{2} (-3\omega + \sqrt{9\omega^2 + 12\omega}) \quad (41)$$

$$\omega_2 = \frac{1}{2} (-3\omega - \sqrt{9\omega^2 + 12\omega}) \quad (42)$$

The solution for this simple model is determined by a single parameter, ω , and will be compared with those from the proposed deep-bed model.

3.4.3 Numerical solution of deep-bed model

Numerical solutions to the model can be obtained by finite-difference methods. The three independent variables are the following: Z , θ , and ξ . Subdivide the space of Z , θ , and ξ into sets of equal rectangles of sides $\delta Z = h$, $\delta \theta = \ell$, $\delta \xi = m$, as shown in Fig. 3.41, and let the coordinates of the representative mesh point $S(Z, \theta, \xi)$ be:

$$Z = ih, \quad \theta = j\ell, \quad \text{and } \xi = km.$$

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Fig. 3.41. Numerical grid representation of the bed.

The pressure, sorption rate, and sorbent phase concentration are expressed as:

$$\begin{aligned}\bar{P}_{i,j} &= \bar{P}(ih, j\ell) = \bar{P}(Z, \theta) \\ J_{i,j} &= J(ih, j\ell) = J(Z, \theta) \\ C_{s\ i,j,k} &= C_s(ih, j\ell, km) = C_s(Z, \theta, \xi).\end{aligned}$$

Calculation of pressure profile in sorption bed. A general finite-difference method for solving Eq. (26) was derived by Taylor's expansion theorem, and the terms of higher powers of ΔZ and $\Delta \theta$ were neglected as follows:

$$\begin{aligned}\frac{\bar{P}_{i,j+1} - \bar{P}_{i,j}}{\Delta \theta} &= \beta \left\{ \frac{\bar{P}_{i+1,j+1}^2 - 2\bar{P}_{i,j+1}^2 + \bar{P}_{i-1,j+1}^2}{\Delta Z^2} - J_{i,j+1} \right\} \\ &+ (1+\beta) \left\{ \frac{\bar{P}_{i+1,j}^2 - 2\bar{P}_{i,j}^2 + \bar{P}_{i-1,j}^2}{\Delta Z^2} - J_{i,j} \right\}, \quad (43)\end{aligned}$$

where, in practice, $0 \leq \beta \leq 1$. For $\beta = 0$, the solution is explicit; for $\beta = 1/2$, the solution is the implicit Crank-Nicolson; and for $\beta = 1$, the solution is the fully implicit backward time-difference method.

The boundary condition for the closed (usually the bottom) end of the sorption bed can be written as follows:

$$\bar{P}_{n-1,j+1} = \bar{P}_{n+1,j+1}, \quad (44)$$

where n is the number of subdivisions in the bed.

The boundary condition for the open end (usually the top) of the sorption bed can be written as follows:

$$\frac{\bar{P}_{1,j+1} - \bar{P}_{1,j}}{\Delta \theta} = \nu \int_0^1 \left[\frac{\bar{P}_{i,j+1} - \bar{P}_{i,j}}{\Delta \theta} + J_{i,j} \right] dz. \quad (45)$$

The integral in the above equation was solved by Simpson's method.³⁴ The $n+1$ unknowns, $\bar{P}_{i,j+1}$, can be obtained by solving Eqs. (44) and (45), and $n-1$ from Eq. (43). Since the nonlinear terms existing in Eq. (43) make the equations difficult to solve by the algebraic method, the trial-and-error method was adopted in this study. Let $\bar{P}_{i,j+1}^*$ be an assumed value of $\bar{P}_{i,j+1}$. The nonlinear terms in Eq. (43) are all present as difference squares, which may be factored in three different ways:

$$\bar{P}_{i,j+1}^2 - \bar{P}_{i-1,j+1}^2 = \bar{P}_{i,j+1}^* \bar{P}_{i,j+1} - \bar{P}_{i-1,j+1}^* \bar{P}_{i-1,j+1} \quad (46a)$$

$$\bar{P}_{i,j+1}^2 - \bar{P}_{i-1,j+1}^2 = (\bar{P}_{i,j+1}^* + \bar{P}_{i-1,j+1}^*) (\bar{P}_{i,j+1} - \bar{P}_{i-1,j+1}) \quad (46b)$$

$$\bar{P}_{i,j+1}^2 - \bar{P}_{i-1,j+1}^2 = (\bar{P}_{i,j+1}^* - \bar{P}_{i-1,j+1}^*) (\bar{P}_{i,j+1} + \bar{P}_{i-1,j+1}) \quad (46c)$$

The second method of factoring, Eq. (46b), is used with Eq. (43).

Then Eq. (43) can be written in the following form:

$$A_{i+1} \bar{P}_{i+1,j+1} + B_i \bar{P}_{i,j+1} + C_{i-1} \bar{P}_{i-1,j+1} = D_i, \quad (47)$$

where

$$A_{i+1} = - \frac{\Delta\theta\beta}{\Delta Z^2} (\bar{P}_{i+1,j+1}^* + \bar{P}_{i,j+1}^*) \quad (48)$$

$$B_i = 1 + \frac{\Delta\theta\beta}{\Delta Z^2} \left[(\bar{P}_{i+1,j+1}^* + \bar{P}_{i,j+1}^*) + (\bar{P}_{i,j+1}^* + \bar{P}_{i-1,j+1}^*) \right] \quad (49)$$

$$C_{i-1} = - \frac{\Delta\theta\beta}{\Delta Z^2} (\bar{P}_{i,j+1}^* + \bar{P}_{i-1,j+1}^*) \quad (50)$$

$$D_i = \bar{P}_{i,j} + \frac{(1-\beta)\Delta\theta}{\Delta Z^2} (\bar{P}_{i+1,j}^2 - 2\bar{P}_{i,j}^2 + \bar{P}_{i-1,j}^2) \\ \Delta\theta \left[\rho J_{i,j+1}^* + (1-\beta) J_{i,j} \right], \quad (51)$$

and $J_{i,j+1}^*$ is calculated by using the assumed value, $\bar{P}_{i,j+1}^*$.

Equations (44) and (45), and n-1 Eq. (47) can be solved by direct elimination. The n+1 unknowns, $\bar{P}_{i,j+1}$, obtained from the solutions are compared with the n+1 assumed values, $\bar{P}_{i,j+1}^*$. If they are not equal, new values of $\bar{P}_{i,j+1}^*$ are assumed, and the calculations are repeated. The real solution of $\bar{P}_{i,j+1}$ is obtained when every value of $\bar{P}_{i,j+1}$ is equal to its corresponding values of $\bar{P}_{i,j+1}^*$.

Calculation of sorbent sorption rate. If we let $U = \bar{C}_s \xi$, Eq. (25) can be written as:

$$\frac{\partial U}{\partial \tau} = \frac{\partial^2 U}{\partial \xi^2} \quad (52)$$

The boundary conditions then become:

$$U_{1,j+1} = \bar{C}_s \quad \xi = 0 \quad \text{as } \xi \rightarrow 0, \quad (53)$$

$$U_{m,j+1} = \bar{C}_{Si,j+1} \xi = \bar{C}_{Si,j+1} \quad \text{as } \xi \rightarrow 1. \quad (54)$$

A general finite-difference approximation for Eq. (52) can be written as:

$$\begin{aligned} \frac{U_{k,j+1} - U_{k,j}}{\Delta \tau} = & \beta \left(\frac{U_{k+1,j+1} - 2U_{k,j+1} + U_{k-1,j+1}}{\Delta \xi^2} \right) \\ & + (1-\beta) \left(\frac{U_{k+1,j} - 2U_{k,j} + U_{k-1,j}}{\Delta \xi^2} \right), \end{aligned} \quad (55)$$

where

$$k = 2, 3, 4, \dots, m-1.$$

Equation (55) is m-2 simultaneous equations with m unknowns, $U_{k,j+1}$. Then with the boundary Eqs. (53) and (54), there are m unknowns in m equations. With a known profile of $U_{k,j}$, the profile $U_{k,j+1}$ can be solved.

The computer code for solutions of the above equations is reported elsewhere.³⁵ The sorption rate is expressed as follows:

$$J_{i,j+1} = \frac{\eta}{\Delta\theta} \int_0^1 3 \left(\xi U_{k,j+1} - \xi U_{k,j} \right) d\xi. \quad (56)$$

Computing algorithm. The pressure, $\bar{P}_{i,j+1}$, at the internal mesh point along the time row $j+1$ can be calculated from the previous time row j .

The computing algorithm contains the following steps:

- (1) assume a set of values for $\bar{P} = \bar{P}(Z)$ at the end of the current time step $j+1$ (call it $\bar{P}_{i,j+1}^*$);
- (2) compute the sorbent surface concentration from Eq. (6);
- (3) solve Eq. (55) for $U_{k,j+1} = U(\xi)$ for each Z at the end of the current time step $j+1$;
- (4) compute the sorption rate for each Z from Eq. (56). Note that steps 2 and 3 are calculated by subroutine JP;
- (5) compute new values of $\bar{P} = \bar{P}(Z)$, called $\bar{P}_{i,j+1}$, from Eq. (47);
- (6) compare these new values ($\bar{P}_{i,j+1}$) with assumed values ($\bar{P}_{i,j+1}^*$); if they are not equal, assume a new set of values for $\bar{P} = \bar{P}(Z)$ and repeat the procedure from step 2 to convergence.

Figure 3.42 presents the flowsheet for the calculation procedure of the above algorithm. Figure 3.43 shows the flowsheet for the entire deep-bed system.

3.4.4 Results and discussion

Effects of the initial condition in sorption bed. Figure 3.44 shows $F, (P - P_{SI}) / (P_{VI} - P_{SI})$, as a function of dimensionless time, τ , with P_{SI} as a parameter at specific values of κ , η , and ν . Large differences

Fig. 3.42. Flowchart of subroutine NUM.

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Fig. 3.43. Flowchart of deep-bed model.

Fig. 3.44. Effects of P_{SI} on pump-down curve.

appear in the curves for different initial conditions in the sorption bed. Since Eq. (4), which describes the pressure relations in the sorption bed, is not linear, $\bar{P} = P/P_{VI}$ has been used for the dimensionless pressure parameter in Eq. (26) instead of F . When $P_{SI} = 0$, no difference exists between F and $\bar{P}$.

Effects of parameter κ . The ratio of the time constant of the sorption bed to the time constant of the sorbent particle is denoted by κ . This parameter can be used to evaluate the importance of pressure gradients along the sorption bed. Figure 3.45 shows F as a function of dimensionless time, τ , with κ as a parameter at specific values of η and ν . For large values of κ , the curve approaches that which would be obtained for no pressure gradients in bed. The curve for $A = \infty$ corresponds to a thin bed with no pressure gradient. A large value of κ means higher gaseous flow rates in the bed, and the pumping rate is controlled by the sorption rate of sorbent particle. On the other hand, small values of κ mean lower gaseous flow rates, and the pumping rate is controlled by gaseous flow resistances in the bed. Figure 3.46 shows the pressure profile within the sorption bed at dimensionless time, τ . Figure 3.46 also shows that, for small values of κ , large pressure gradients occur in the bed. For large values of κ , the pressure profile is nearly a horizontal line and is approaching the line corresponding to no gradient in the bed.

Effects of parameter ν . The ratio of sorbent volume to the gas storage chamber is denoted by ν . Figure 3.47 shows F as a function of dimensionless time, τ , at specific values of κ , η , and ν . It is evident that the pressure gradients in the sorption beds have large effects for

Fig. 3.45. Effects of κ on pump-down curve.

Fig. 3.46. Pressure profile in scorpion bed for $\tau = 0.001$.

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Fig. 3.47. Effects of ν on pump-down curve.

small ν . The average concentration of gases adsorbed in the solid increases with decreasing ν . The pressure gradient in the sorption bed decreases the sorption rates in the deeper parts of the bed. For increasing values of ν , the average concentration of gases adsorbed in the sorbents decreases. If ν is larger than is required, the sorption bed is overdesigned, and the decreasing sorption rates in the deeper parts of the bed do not contribute significantly to pumping. These effects will be discussed later.

Effects of parameter η . The ratio of g-moles of sorbate gas which can be adsorbed in a unit volume of sorbent to the g-moles of sorbate gas contained in a unit volume is denoted by η . Figure 3.48 shows F as a function of dimensionless time, τ , with η as a parameter and for specific values of κ and ν . The curves resemble those in Fig. 3.47. Since the product of η and ν is ω , ω is the ratio of the amount of sorbate gas in the gas chamber to the amount of sorbate gas which could be adsorbed by the sorbent at that pressure. The parameter, ω , is not an important factor in determining pumping rates which are controlled by sorption rates in the sorbent or by gaseous flow rates in the sorption bed. It is, however, the important factor in determining the cycle time and the final vacuum which can be achieved.

3.4.5 Experimental work and discussion

The purpose of the experimental work was to test the proposed deep-bed model so that it could then be used to describe the transport phenomena in deep beds of sorbents. The apparatus has been described previously. In the experiments, F could be measured as a function of time and compared with the theoretical curve calculated by the proposed

Fig. 3.48. Effects of η on pump-down curve.

model. Good agreement would mean that the model could represent the physical problem and could be used to design deep-bed sorption pumps. To compute F from the proposed model, it is necessary to have values for the parameters ϵ , P_{VI} , L , A_c , V_g , D_e , and A as well as for the equilibrium isotherm between the gas and the sorbent. The values of ϵ , P_{VI} , L , A_c , and V_g are set by the experimental conditions, while the values of D_e and equilibrium isotherms have been reported in the literature.³⁶⁻⁴⁰ These values (especially these for D_e) are badly scattered. Use of those data would introduce large errors or uncertainties in the model; therefore, independent measurements of these parameters were made.

Determination of isotherm. The isotherm data used in this study were measured using very shallow sorption beds. In each test, a known quantity of gas was injected into the gas storage chamber, and then the solenoid valve was opened. When the pressure in the gas storage chamber became steady, equilibrium conditions were assumed to exist. Some of the results are plotted in Fig. 3.49. Since the pressure is low, the equilibrium isotherms follow Henry's Law. The Henry's Law constants (slope) calculated by the least-squares method are given in Table 3.7. The lines in Fig. 3.49 do not pass through the origin. This means that the gases adsorbed by the sorbent are relative values rather than absolute values. The experimental procedure was reversed for desorption tests in the following manner. A known quantity of gases was evacuated from the gas storage chamber, and then the solenoid valve was opened. The pressure in the gas storage chamber would then increase to a new equilibrium state. The desorption points, indicated in Fig. 3.49 by a

Fig. 3.49. Isotherms of CO₂ on Linde molecular sieve type 5A.

Table 3.7. Equilibrium constant^a and diffusivity of carbon dioxide in Linde Molecular Sieve Type 5A

T (C)	K_p (10^{-7} g-mole/micron cm^3)	K_s (10^4)	D_e (10^{-12} cm^2 /sec)
25	9.1082	-1.6915	1.900
35	4.9536	0.9508	2.723
45	3.2689	0.6478	3.995
55	2.1079	0.4309	5.725

$$^a C_s = K_p P - K_s C_g$$

solid point, are in good agreement with the sorption points, indicating that the isotherms are reversible. The van't Hoff plot, showing the temperature dependence of the Henry's Law constants, is presented in Fig. 3.50. The values of q and K were calculated from the curve according to the following equation:

$$K = K_0 \exp(q_0/RT). \quad (57)$$

The value of q_0 was found to be 9.475 kcal/g-mole, and K_0 was 1.02×10^{-13} g-mole/ μ cm³. The equilibrium loading of molecular sieve measured in this study was compared with Fukungua's value³⁷ at 25°C. The result was about 25% lower for a pressure of 0.2 mm Hg. Compared with Glessner's⁴¹ (20) at 35°C, the result was about 33% lower for a pressure of 0.33 mm Hg. The reason for these differences may be the incomplete bake-out of the molecular sieve samples. Because of the limitation of the liquid nitrogen-chilled roughing pump, samples of molecular sieve for this study were baked out at a temperature of 320°C and a pressure of $\sim 10\mu$. Water contained at these conditions is 0.002 g per gram of molecular sieve.⁴² In their study of molecular sieve samples, Glessner and Fukungua used a bake-out at the temperature of 320°C and a pressure of 1×10^{-5} mm Hg (0.01 μ).

Determination of diffusivities. When the sorption bed in these experiments is very short, one can neglect pressure gradients in the sorption bed. The diffusivities can be calculated from the pressure history curves by the following procedure. First, w can be calculated by Eq. (39). Once w is established in a given experiment, a master plot of $F, (P - P_{SI})/(P_{VI} - P_{SI})$, against τ can be constructed which follows Eqs. (37) and (40), and this is shown in Fig. 3.51. Then, from

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Fig. 3.50. The van't Hoff plot of CO₂-Linde molecular sieve type 5A.

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Fig. 3.51. The value of F vs τ for different values of ω .

experimental values of F , corresponding values of τ are read off. A plot of τ against t should give a straight line passing through the origin, and D_e can be calculated from the gradient by using the following equation:

$$D_e = \text{gradient} \times R_I^2. \quad (58)$$

Figures 3.52-3.55 show results from experiments. Note that D_e was calculated from the slope of a straight line which does not intersect the origin. Possible reasons for this are the following: (1) resistance to gas transfer in the macropore of the molecular sieve pellet, (2) variation of D_e in the range of the experiment, (3) thermal effects such as failure to remove heat of adsorption (i.e., temperature gradients), particularly at the beginning of a run when sorption rates are high, (4) nonspherical shape and nonuniform size of the molecular sieve crystals, and (5) finite thickness (2 cm) of the sorption bed. The first reason is suspected of being the most important. There could be significant resistance to gas transfer even in this sorption bed. The first four effects are less marked in the latter part of experiments, and the data from that portion of the experiments were used in evaluating D_e . The net result is an apparent error in time zero. The best values of D_e are obtained using the higher values of time. The values for temperature of 25, 35, 45, and 55°C are shown in Table 3.7. The value of D_e can also be calculated from the desorption data as shown in Fig. 3.49. Results from desorption data are indicated by solid points in Fig. 3.54. The desorption results are in good agreement with the sorption data, but the apparent error in the time zero is smaller in the desorption cases. This is because the pressure range for the desorption type of operation is smaller than for sorption. One can conclude that the same values of D_e can be used in sorption and desorption.

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Fig. 3.52. The value of τ vs time at 25°C.

Fig. 3.53. The value of τ vs time at 35°C.

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Fig. 3.54. The value of τ vs time at 45°C.

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Fig. 3.55. The value of τ vs time at 55°C.

The diffusivities obtained by Barrer and Brook⁴³ range from 5×10^{-12} cm^2/sec for the sorption of argon in lithium-mordenite to 5×10^{-15} cm^2/sec for the sorption of nitrogen in calcium-mordenite. An exact comparison of results for such different systems is not possible; however, considering the relative effective size of gas molecules and zeolite windows, the comparison with the present data is not unreasonable. Figure 3.56 is a plot of the variation of diffusivities with temperature; the results follow the Arrhenius equation, and they can be expressed in the following manner:

$$\frac{D}{R_I} = 53.33 \exp\left(-\frac{7456}{RT}\right) \quad (59)$$

The activation energy is 7.456 kcal/g-mole.

Determination of constant A. The parameter A was evaluated from plots of F against time when the sorption bed was very long. In those curves, the pumping rates for the sorption bed were controlled by gaseous sorbate flow through the bed. The pump-down curve (F vs t) for a 33-cm-deep bed is shown in Fig. 3.57. Calculated curves from the proposed deep-bed model with different values of A are given in Fig. 3.58. As discussed in the previous section, some differences will be noted between the experimental data and the theoretical curves calculated by the deep-bed model at the beginning of a run. The line in Fig. 3.52 intersects the x-axis at 23 sec. This means that the experimental data gives a better fit to the calculated curve if one assumes a 23-sec delay between the response calculated by the simple model (uniform pressure in sorption bed). As mentioned earlier, the delay was caused by simplifications of the model. Therefore, in evaluating the values for A, the

Fig. 3.56. Variation of diffusivities with temperature.

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Fig. 3.57. Pump-down curve for 33-cm-deep bed at 25°C.

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Fig. 3.58. Theoretical pump-down curve for 33-cm-deep bed at 25°C.

experimental curve was plotted on translucent paper and moved along the time axis in the calculated curves (Fig. 3.58). When moved 10.5 sec, the experimental curve coincided with a calculated curve. The delay is less than the delay for D_e testing in Fig. 3.52. Because the theoretical curve calculated by the deep-bed model included the effects of pressure variation in the deep bed, it is a better fit than the simpler model. A value of $5 \times 10^6 \text{ cm}^2/\text{atm sec}$ for A has been evaluated for 33-cm-deep bed at 25°C , and the same value of A was used to predict the bed performances having depths of 15.3 and 4 cm. Sample data and theoretical curves are plotted in Figs. 3.59 and 3.60. The agreement between calculated and experimental curves is good; thus the value of A measured by this method is accurate, and the application of the proposed deep-bed model has been demonstrated. The same 33-cm-deep bed has been tested at 35, 45, and 55°C . The values of A have been corrected to account for changes in viscosity at the different temperatures. The experimental and theoretical curves (see Figs. 3.61-3.63) are in good agreement. Thus A is believed to depend on the structure of the sorbent and on the viscosity of the gas.

Determination of the effects of bed depth. Sorption beds of three different depths have been tested at slightly different initial conditions, and the experimental pump-down curves are shown in Fig. 3.64. A series of pressure profiles were calculated by the proposed model at different sorption times, as shown in Fig. 3.65. Fig. 3.65 shows that at $Z = 0.22$, the pressure increase in a 33-cm-deep bed is $<1\%$ of $(P_{VI} - P_{SI})$ when 95% of the gases in the storage chamber have been adsorbed. This means that most of the gases are adsorbed by the sorbents from the top of the bed to a depth of 7.2 cm ($Z = 0.22$). Thus a

Fig. 3.59. Pump-down curve for 15.3-cm-deep bed at 25°C.

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Fig. 3.60. Pump-down curve for 4-cm-deep bed at 25°C.

Fig. 3.61. Pump-down curve for 33-cm-deep bed at 35°C.

Fig. 3.62. Pump-down curve for 33-cm-deep bed at 45°C.

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Fig. 3.63. Pump-down curve for 33-cm-deep bed at 55°C.

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Fig. 3.64. Pump-down curve for three different bed depths.

Fig. 3.65. Pressure profile of bed for different depths.

7.2-cm-deep bed should provide approximately the same pumping rates as a 33-cm-deep bed under these conditions. The depth where the pressure increase is $<1\%$ of $(P_{VI} - P_{SI})$ when 95% of the sorbate gases have been adsorbed can be defined as a theoretically "useful depth" of the sorption bed; in the particular example just given, this was 7.2 cm. This is not a unique definition, since it is a function of the bed depth (in this case, 33 cm) chosen to make the determination. To be useful, the defined "useful depth" can not be a strong function of the larger depth related for the determination. Using the definition, the theoretically useful depth determined from operating at the same experimental conditions except with a 15.3-cm-deep bed was 6.9 cm. Since the experimental conditions for a 33-cm-deep bed and a 15.3-cm-deep bed are only slightly different, the pump-down curves for both should be only slightly different. This is shown in Figs. 3.64 and 3.65. However, with a 4-cm-deep bed, the theoretical useful bed is now greater than the real depth, and the pumping speed are strongly affected by bed depth. Thus the rate at which gases accumulate in the sorption bed and the time required to achieve the same vacuum are significantly different for the 4-cm-deep bed and the 15.3-cm-deep or the 33-cm-deep bed. This definition of "useful depth" is used here only to show how the model can be used to select a bed depth. Note that, in many systems, one must take into account the costs involved. Since these considerations are specific to each application, no attempt was made in this study to optimize the bed depth in an economic sense.

3.5 TNS Support Studies

J. S. Watson

At the beginning of FY 1977, ORNL initiated design studies for a tokamak reactor experiment to be built after the Tokamak Fusion Test Reactor (TFTR) currently under construction at Princeton. The device has been temporarily named The Next Step (TNS) since a major goal of the design study is to evaluate what can be done to most effectively advance fusion power after TFTR. ORNL is the prime contractor for the study, but much of the work is subcontracted to Westinghouse. Although all of the detailed engineering design is to be done by Westinghouse, ORNL has the responsibility for supervising and guiding the Westinghouse work. A similar and competitive design study is being made under the guidance of General Atomics (GA) with Argonne National Laboratory (ANL) as the subcontractor.

The TNS is an outgrowth of the Experimental Power Reactor (EPR) design studies conducted at ORNL, GA, and ANL during FY 1976. One of the important conclusions of the EPR study was that the criteria set for EPR resulted in a device which was too large a step beyond TFTR. TNS will be smaller in size than EPR, but recent developments in plasma physics are likely to hold the power to comparable levels. Currently, comparisons are being made of several magnetic field options, but TNS is likely to be an ignition device with superconducting magnets at least for the TF coils.

Chemical Technology involvement in TNS is in two areas: (1) fuel cycle and (2) tritium containment. Our role is to follow and direct the Westinghouse design, not to do detailed design. We have reviewed

their work, requested changes in the vacuum pumping and fuel processing systems, and assisted in developing a list of R&D needs for TNS.

However, current activities in fuel-handling design are limited until Westinghouse completes "trade studies" which compare different TF coil designs.

Efforts are also being made to obtain better estimates of particle and energy confinement times for reactors with and without magnetic diverters. The question of the need for a diverter and the performance of a plasma-diverter system has been identified as the most crucial item affecting fuel-handling needs. A diverter can decrease the particle confinement (residence) time in the plasma by one to several orders of magnitude, and this directly affects the throughput of the fuel processing system. Diverter designs have been proposed for TNS which could not physically be pumped by vacuum pumps mounted outside the TF coils. The only feasible pumping system would involve D-T trapping material such as liquid lithium as the diverter target. Although such a system has been proposed, it would introduce the following serious problems: (1) lithium contamination throughout the reactor, (2) complicated tritium recovery from the lithium, (3) lithium damage to the externally placed helium vacuum pumps, and (4) lithium flow across the magnetic field lines in the diverter target. These problems appear to be so difficult that renewed interest has appeared in determining the need for a diverter in TNS. It currently appears likely that TNS can operate successfully and meet its goal without using a diverter.

At the present time, various options in the TNS design are being compared, and no reference design has been developed. Such a design will be prepared during the second half of FY 1977.

3.6 References for Section 3

1. C. D. Scott et al., Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs), Mar. 1, 1975, to Aug. 31, 1975, ORNL/TM-5291 (September 1976).
2. C. D. Scott et al., Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs), Sept. 1, 1975, to Feb. 29, 1976, ORNL/TM-5533 (July 1977).
3. J. S. Watson and S. D. Clinton (compilers), Experimental Engineering Sect. Semiannu. Prog. Rep. Mar. 1 to Aug. 31, 1976: Volume 3: Engineering Science Programs, ORNL/TM-5865/V3 (June 1978).
4. R. E. Southerlan, Developmental Evaluation of Near 17°K Molecular Sieve 5A for Hydrogen Cryosorption, Report AEDC-TR-65-48, Arnold Engineering Development Center (1965).
5. S. A. Stern et al., "Cryosorption Pumping of Hydrogen at 20°K-II. Development and Performance of Cryosorption Panels," J. Vac. Sci. Technol. 3, 99 (1966).
6. P. J. Gareis and J. R. Pitlor, "Development and Application of Cryosorption Pumping of Hydrogen at 20°K by Molecular Sieve Adsorbent Panels," Report ADEC-TR-65-18, Arnold Engineering Development Center (1965).
7. S. A. Stern et al., "Cryosorption Pumping of Hydrogen and Helium at 20°K," J. Vac. Sci. Technol. 2, 165 (1965).
8. D. W. Breck, Zeolite Molecular Sieves, p. 635, Wiley, New York, 1974.
9. R. C. Forrester, III, and J. S. Watson, "A Procedure for Determination of Tritium in Potassium," Anal. Lett. 8, 63-70 (1975).
10. F. J. Smith, A. M. La Gamma de Batistoni, G. M. Begun, and J. F. Land, "The Solubility of Hydrogen Isotopes in Lithium," Proceedings of the 9th Symposium on Fusion Technology, Pergamon, Oxford and New York, 1976.
11. C. D. Scott et al., Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs), Sept. 1, 1973, to Feb. 28, 1974, ORNL/TM-4602 (December 1974).
12. L. N. Yannopoulos, R. K. Edwards, and P. G. Wahlbeck, "The Thermodynamics of the Yttrium-Hydrogen System," J. Phys. Chem. 69, 2510-15 (1965).
13. J. J. Kearns, "Terminal Solubility and Partitioning of Hydrogen in the Alpha Phase of Zirconium, Zircaloy-2, and Zircaloy-4," J. Nucl. Mat. 22, 292-303 (1967).

14. J. R. Powell et al., Studies of Fusion Reactor Blankets with Minimum Inventory and with Tritium Breeding in Solid Lithium Compounds: A Preliminary Report, BNL-18230 (June 1973).
15. R. H. Wiswall and E. Wirsing, "Removal of Tritium from Solid CTR Blanket Material," presented at the American Nuclear Society Winter Meeting, Washington, D.C., October 1974.
16. C. D. Scott et al., Experimental Engineering Sect. Semiannu. Prog. Rep. (Excluding Reactor Programs), Sept. 1, 1974, to Feb. 28, 1975, ORNL/TM-4961 (January 1976).
17. H. Farrar IV, Atomics International, Canoga Park, Calif., correspondence to F. W. Wiffen, Metals and Ceramics Division, ORNL, Nov. 8, 1976.
18. J. Crank, The Mathematics of Diffusion, p. 218, Clarendon, Oxford, 1956.
19. R. H. Wiswall and E. Wirsing, "Tritium Recovery from Fusion Blankets Using Solid Lithium Compounds-II: Experiments on Tritium Removal and Absorption," Radiation Effects and Tritium Technology for Fusion Reactors, CONF-750989, Vol. III, pp. 232-42 (March 1976).
20. D. J. Garies and Gr. F. Hagenbach, "Cryosorption," Ind. Eng. Chem. 57(5), 27 (1965).
21. J. P. Hobson, "Cryopumping," J. Vac. Sci. Technol. 10(1), 73 (1973).
22. S. A. Stern and F. S. Dipaolo, "Cryosorption Pumping of Air on Molecular Sieve at 77°K - The Ultimate Achievable Vacuum," J. Vac. Sci. Technol. 6(6), 941 (1969).
23. G. E. Grenier and S. A. Stern, "Cryosorption Pumping of He at 4.2 K," J. Vac. Sci. Technol. 3(6), 334 (1966).
24. I. M. Klotz, "The Adsorption Curve," Chem. Rev. 39, 211 (1946).
25. A. E. Scheidegger, The Physics of Flow Through Porous Media, 3rd ed., Univ. of Toronto Press, Toronto, Canada, 1974.
26. S. Ergun, "Fluid Flow Through Packed Columns," Chem. Eng. Prog. 48(2), 89 (1952).
27. T. Seitz, R. Woods, M. Wallis, and R. L. Henkel, "The Safe Handling of Large Quantities of Tritium Gas at the Los Alamos Tandem Accelerator Facility," Nucl. Instrum. Methods 93, 125 (1971).
28. H. Adzmi, "On the Flow of Gases Through a Porous Wall," Bull. Chem. Soc. Jpn. 12, 304 (1937).

29. J. C. Arnell, "Surface Area Measurements Using a Modified Kozeny Equation," *Canad. J. Res.* A24, 103 (1946).
30. P. C. Carman, "Diffusion and Flow of Gases and Vapour Through Micropore, I. Slip Flow and Molecular Streaming," *Proc. Roy. Soc. of London, Ser. A203*, 55 (1950).
31. P. J. Rigden, "The Specific Surface of Powders, A Modification of the Air-Permeability Method for Rapid Routine Testing," *J. Soc. Chem. Ind., London* 62, 1 (1942).
32. H. S. Carslaw and J. C. Jaeger, Condition of Heat in Solids, p.240, Oxford Univ. Press, London, 1959.
33. S. Paterson, "The Heating or Cooling of Solid Spheres in a Well-Stirred Fluid," *Proc. Phy. Soc.* 59, 50 (1947).
34. B. Carnahan, H. A. Luther, and J. O. Wilks, Applied Numerical Methods, p. 73, Wiley, New York, 1969.
35. C. P. Tung, "Sorpitive Pumping of Gases by Deep Beds of Sorbents," Ph.D. Dissertation, University of Tennessee, Knoxville, August 1977.
36. L. Dell'Osso and J. Winnick, "Mixed-Gas Adsorption and Vacuum Desorption of Carbon Dioxide on Molecular Sieve," *Ind. Eng. Chem., Process Des. Dev.* 8(4), 469 (1969).
37. P. Fukunaga, K. C. Hwang, S. H. Davis, and J. Winnick, "Mixed-Gas Adsorption and Vacuum Desorption of CO₂," *Ind. Eng. Chem., Process Des. Dev.* 17(2), 269 (1968).
38. Linde Division, Union Carbide Corporation, "Molecular Sieves Non-Hydrocarbon Materials Data Sheets, Isotherm Data Sheet No. 22," 1959.
39. C. N. Satterfield, Mass Transfer in Heterogenous Catalysis, MIT Press, Cambridge, Mass., 1970.
40. C. D. Scott, "Removal of Water and Carbon Dioxide from Helium Coolant by Molecular Sieve," *Nucl. Sci. Eng.* 34, 214 (1968).
41. A. J. Glessner and A. L. Myers, "The Sorption of Gas Mixtures in M.S.," *AIChE Symp. Ser.* 65 (96), 73 (1968).
42. Linde Division, Union Carbide Corporation, "Linde Molecular Sieves Water and Air Data, Sheets F-3035," 1959.
43. R. M. Barrer and D. W. Brook, "Molecular Diffusion in Chabazite, Mordenite and Levynite," *Trans. Faraday Soc.* 49, 1049 (1953).

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