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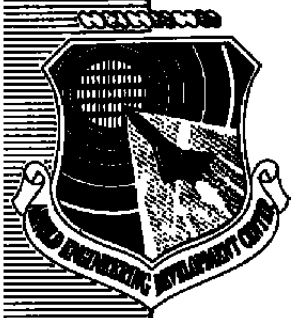

Cryosorption of Hydrogen on Anodized Aluminum at 20°K

Kenneth A. Lienemann and Ronald Dawbarn
Calspan Field Services, Inc.

February 1982

Final Report for Period February 1980 – September 1981

ARNOLD ENGINEERING DEVELOPMENT CENTER
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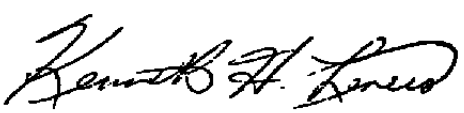

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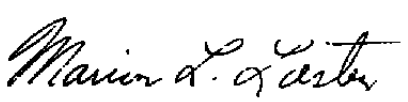

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Hydrogen was adsorbed on anodized aluminum surfaces cooled to 20°K. Experiments determined the effect of various contaminants (N_2, CO, CO_2) which might be deposited if these panels were used in a typical rocket exhaust plume. Panels were also tested after being coated with diffusion pump oil. Several cleanup techniques were evaluated, and bakeout by heat lamps proved the most effective. Work should continue in the areas of heavy anodizing

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20. ABSTRACT (Continued)

activation, structure optimization, and testing a baffle to remove rocket plume contaminants.

PREFACE

The work reported herein was sponsored by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), under Program Element 65807F. The results were obtained by Calspan Field Services, Inc., AEDC Division, operating contractor for Aerospace Flight Dynamics testing efforts at Arnold Air Force Station, Tennessee, under Calspan Project No. V32K-A8, Cryosorption Pumping of H_2. The Air Force Project Manager was Capt. K. H. Leners. The manuscript was submitted for publication on October 8, 1981.

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1.0 INTRODUCTION

The vacuum chambers at AEDC have been successfully used for simulating exoatmospheric conditions for rocket motor firings. In these tests, extensive cryopumping and cryosorption is required to trap the exhaust gases and prevent them from rebounding into the test volume. To reproduce free space conditions faithfully, all gas species must be captured as they reach the chamber walls. Of all the gas species present in both liquid and solid propellant rockets, hydrogen is the most difficult to capture.

Hydrogen may be cryopumped directly if LHe-cooled panels are available since it has a vapor pressure of about 3×10^{-7} torr at 4.2°K. The vapor pressure of H_2 is 5×10^{-5} torr at 5.2°K. This is the critical temperature of LHe and thus represents the upper limit for LHe cooling (Ref. 1). In many instances, however, LHe is not available, or is not economically feasible to use in the quantities required to pump large systems. In the past decade it has been shown (Refs. 2 through 7) that hydrogen can be successfully pumped by sorption on cryodeposited frost formed by condensing certain gases such as carbon dioxide (CO_2), water (H_2O) vapor, etc., on surfaces at temperatures between 10 and 20°K.

However, this technique has several limitations because there are difficulties in predepositing the cryofrost uniformly, it adds an additional heat load to the refrigeration equipment, and in cases where the test also includes cryogenically cooled sensors and optical surfaces the cryofrost is an unwanted contaminant. There is therefore a continuing need for a method to remove H_2 which is more economical than LHe cryopumping and less troublesome to apply than the gaseous cryodeposited sorbents.

It has been reported by Kosherov, et al. (Ref. 8) that H_2 is adsorbed on anodic oxidized aluminum cryosurfaces cooled to 77°K. Several general claims are made for the anodized aluminum cryopump, including the following:

1. Excellent thermal conductivity between substrate and sorbent.
2. The sorbent is rugged and resists abrasion or physical damage.
3. The system is reusable after a simple bakeout.
4. A five-fold increase in the thickness of the oxide film resulted in an increase in the sorption capacity by a factor of 10 to 20.

Although the amount of H_2 adsorbed at 77°K is not enough to construct a practical pumping system, the data do suggest that sufficient quantities are adsorbed to warrant further investigation of this pumping technique at colder temperatures where the capacity might increase significantly.

Experiments in 1979 developed and tested different bonds between substrate and sorbant. Results demonstrated that an effective pumping system for hydrogen could be designed using the sorption phenomenon. The gas load could be dumped without damage to the cryopanel by merely raising its temperature to 100°K.

The experiments described in the following were performed to analyze the practicality of such as sytem in an actual test environment.

2.0 APPARATUS

2.1 VACUUM CHAMBER

This work was performed in the 2- by 3-ft Research Ultrahigh Vacuum Chamber described in detail in Ref. 9 and shown in Fig. 1. After deducting the space taken by the cylindrical cryopump and the radiation shrouds, the chamber has a free volume of 300 ℓ. The radiation baffles are vented to allow free passage of gas molecules, yet they are optically tight between the outer chamber walls and the cryosorption pump. The chamber is pumped by a 6-in. diffusion pump with an LN_2 cold trap. This system can be valved off with a 6-in. gate valve.

2.2 ANODIZED CRYOPUMP

The anodized cryopump consists of a 30-cm by 42-cm by 0.32-cm aluminum plate. On one side is welded a 1/2-in.-inside-diam tube which carries the cold GHe from the refrigerators. A 5-cm-thick layer of expanded foam aluminum was bonded to the other side. The complete panel is shown in Fig. 2.

Cryopanels were first constructed by anodizing the foam and then cementing it to the panel with a low-temperature epoxy (Furane Epibond®). Although this method produced a bond that would withstand repeated heat shocks, it was felt that soldering would yield better thermal transfer.

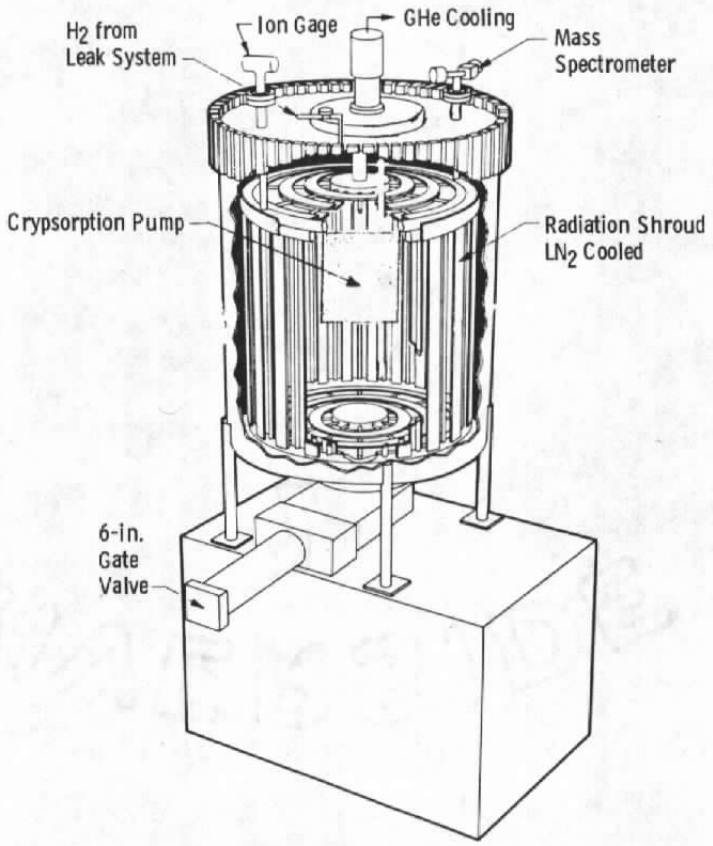
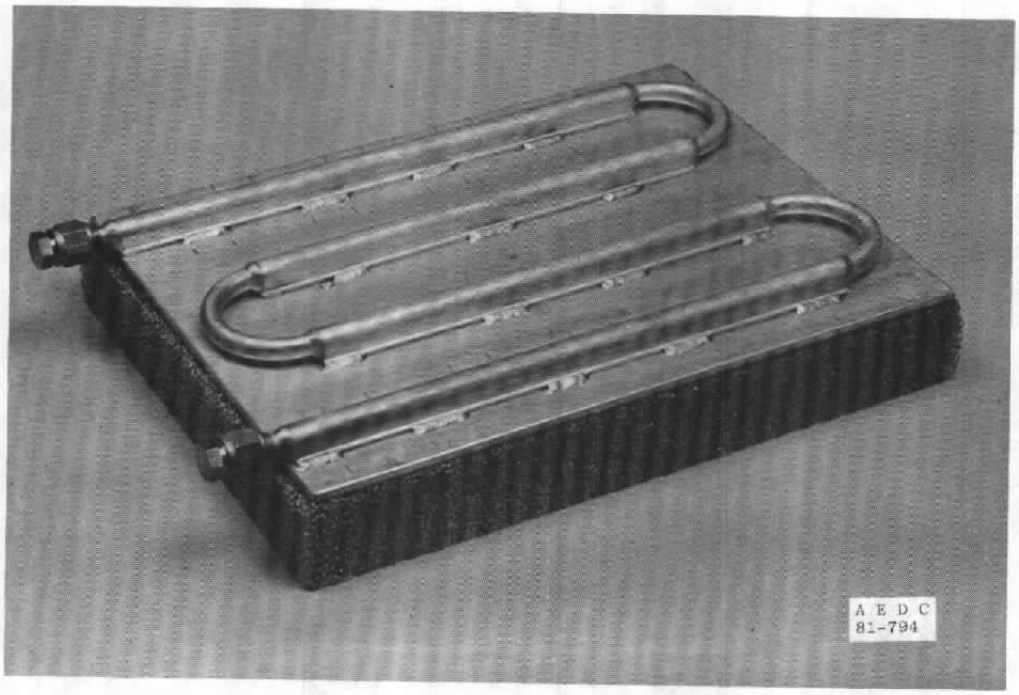


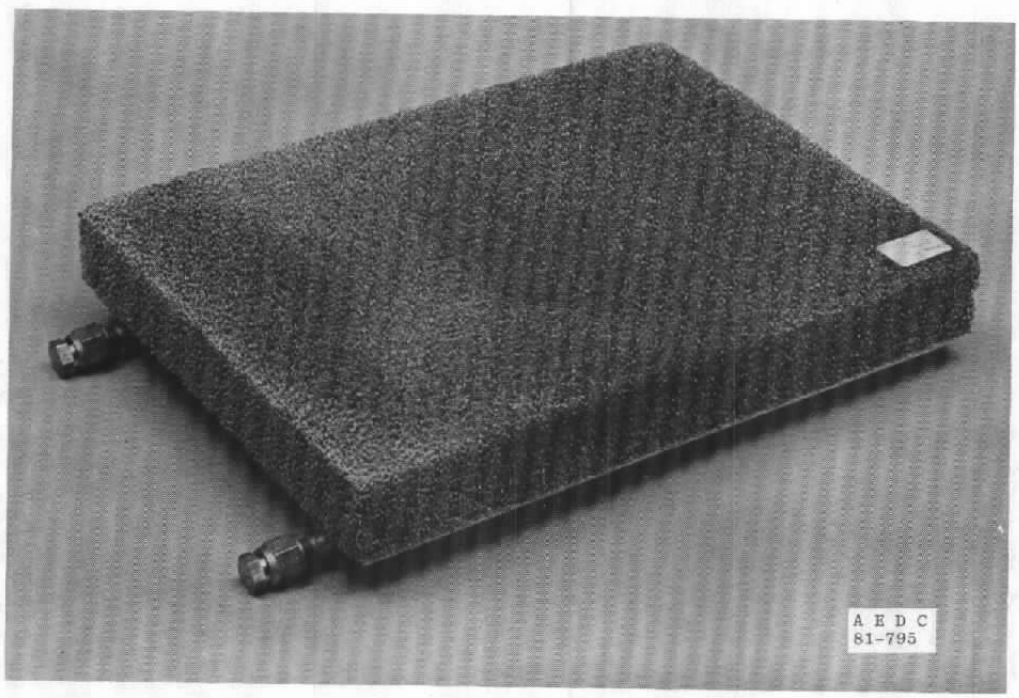
Figure 1. Schematic of pumping research chamber.

Samples of the foam were bonded to the substrate using Alutin 51-9 solder. During the anodizing process, however, the solder interface became brittle and subsequently fractured when it was cooled to LN_2 temperatures.

A sample of the foam was anodized and bonded to a plate with aluminum-filled epoxy. The epoxy was oven cured and survived repeated cooldowns to cryogenic temperatures. Poor thermal conductivity of the bond led to relatively high foam temperature, however. This in turn caused very poor pumping performance. It was concluded that the Furane Epibond® method was the most effective, and future efforts would concentrate in this direction.



a. Back with "D" tubes showing
Figure 2. Anodized cryopanel assembly (foam).



b. Front
Figure 2. Concluded.

The panel specifications are presented in Table 1.

Table 1. Sorption Pump Specifications

Material: Duocel Foam Aluminum® 6101 aluminum, 6-percent density

Size: 42 cm x 30 cm x 5 cm

Processing: Anodized - no seal - no dye
60 min at 250 amps
80°F, 15-percent H_2SO_4 solution

Bonding: Furane Epibond® 123 with 9615-10 hardener (2:1)
Air cure

Ratio of area/vol. of foam: 1.8 cm^2/cm^3

Effective surface area for sorption: 7.4×10^4 cm^2

Area of pump envelope: 1.98×10^3 cm^2

2.3 GAS ADDITION SYSTEMS

Associated with the chamber is the gas addition system shown in Fig. 3. This system uses a set of sintered steel leaks which have been calibrated in situ, through which gases may be metered into the chamber at various rates. Gas added thus has to diffuse through the open shroud before reaching the pump surface.

2.4 INSTRUMENTATION

Pressures in the vacuum chamber were monitored by an ionization gage connected to a tube which penetrated the shroud and thus sampled a gas flux similar to that "seen" by the pump surface. Temperatures of the gaseous He-cooled panel were monitored with copper-constantan thermocouples. Inlet and outlet temperatures of the gaseous helium refrigerator were monitored with H_2 vapor pressure thermometers.

3.0 CALIBRATION

3.1 LEAKS

Each leak in the gas addition system was calibrated for hydrogen, nitrogen, carbon dioxide, and carbon monoxide. The method consisted of monitoring the rate of pressure drop in the reservoir of known volume as the gas flowed from this volume, through the leak, and into the vacuum chamber. Pressures in the reservoir were in the 5- to 800-mm range and were recorded by instruments calibrated against mercury manometer standards. Full details of this procedure and analysis of the method are included in Ref. 5.

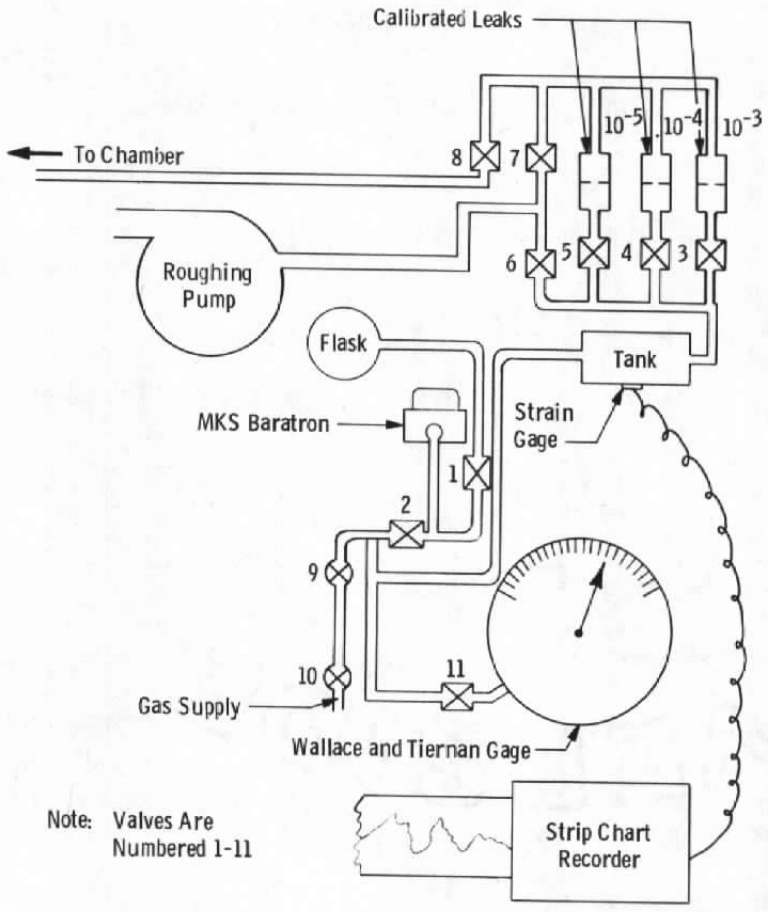


Figure 3. Gas addition system.

3.2 GAGE CALIBRATION

The ion gage was calibrated in situ for each of the gases mentioned earlier. The method used was to bleed a gas into the chamber at various known rates through the calibrated leak system and to record both the rate of rise with the diffusion pump valved off and the equilibrium pressure with the gate valve open. This method is outlined in detail in Ref. 5. The data produced can be used to determine both the calibration constant for the ion gage and the pumping speed of the diffusion pump. A thermal transpiration factor was used to correct the ion gage calibration constant when the liner was cooled to 77°K.

4.0 PROCEDURE

4.1 GAS ADDITION

The chamber was pumped to its base pressure of 8×10^{-7} torr and the ion gage was calibrated for H_2. The cryogenic systems were then turned on; the shroud was cooled to 77°K with LN_2, and the aluminum cryopump was cooled by the gaseous helium refrigerator. With all systems cold the base pressure dropped to low 10^{-8} torr. At this point the diffusion pump was valved off.

Hydrogen was admitted via the calibrated leak system and resulting pressure rise on the ion gage was noted. When the chamber pressure had risen to mid-10^{-5} torr, all H_2 addition was stopped and the gate valve to the diffusion pump was opened. The refrigeration to the aluminum cryopump was bypassed, and the panel was allowed to warm up to 100°K. After the H_2 had been removed by the diffusion pump, the gate valve was closed, and the procedure was repeated with the panel recooled. Different gas addition rates were used to determine the effect on pumping capacity.

4.2 CONTAMINATION AND CLEANUP

Since a likely use of hydrogen cryosorption would be in simulating exoatmospheric rocket firings, its performance in the presence of contaminants both from the rocket and from the test chamber was studied. The candidates selected were nitrogen, carbon dioxide, carbon monoxide, and DC-10® diffusion pump oil. In separate series of test runs, a deposit of each contaminant was applied to the aluminum cryopump. The gases were added through the calibrated leak system. To simulate backstreaming from a diffusion pump attributable to chamber overpressure, the chamber was opened and an oil mist was sprayed on the aluminum foam until all surfaces were coated. Then, following the procedure above, hydrogen pumping runs were made and performance data were recorded.

After each run, the aluminum foam was cycled to room temperature to determine whether this would remove the contaminant-hydrogen mixture. Performance degradation on a subsequent run would indicate incomplete removal. Two different methods were used to remove the diffusion pump oil. For the first, heat lamps were installed in the test chamber. After oil application and hydrogen pumping, the lamps were turned on and the gate valve was opened. This allowed the pump to remove the oil as it evaporated from the foam. The second method involved opening the chamber and washing the aluminum cryosorption panel with freon. Finally, both were tried in conjunction: the freon wash

followed by the bakeout. Each cleanup was succeeded by an uncontaminated hydrogen pumping run. This procedure yielded data on the relative effectiveness of cleanup methods.

4.3 PANEL CONFIGURATION

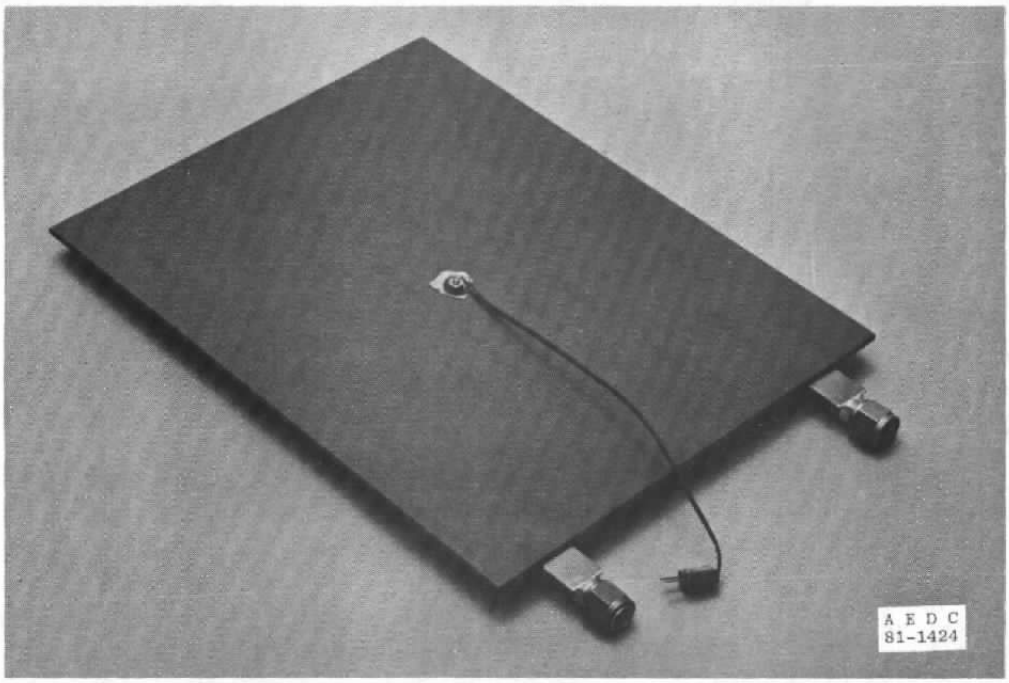
The last variable to be considered was panel structure and coating. The original foam panel was cut to half its thickness and retested. A flat plate with a special heavy anodizing was also tested (Fig. 4). The same special coating was applied to a panel with a high-V surface, but insufficient funds were available to test this final configuration.

5.0 RESULTS

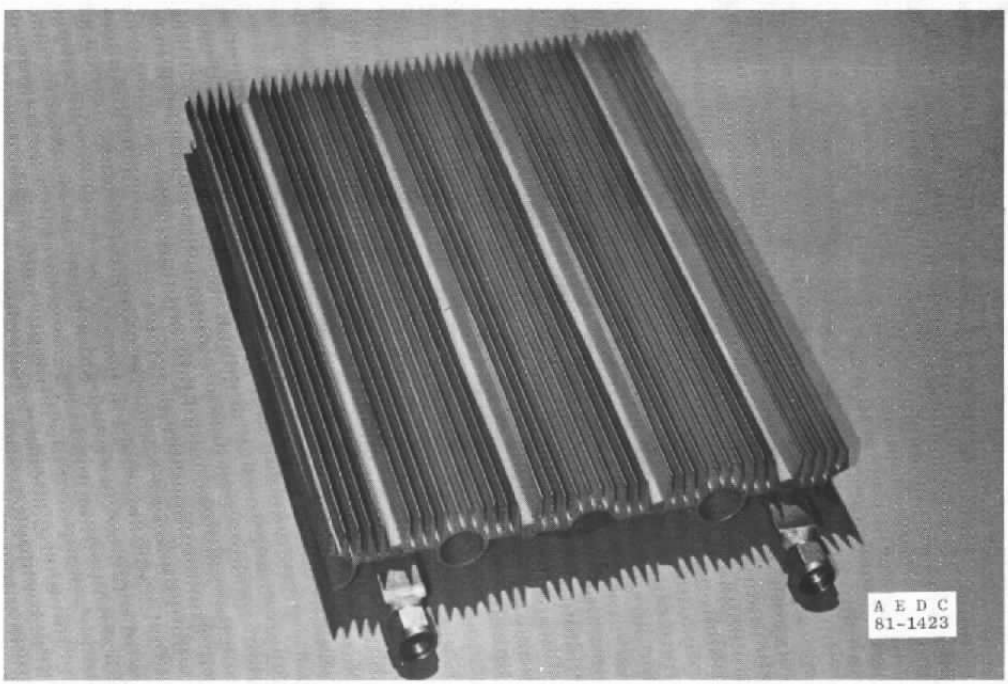
Previous work had obtained a pumping speed of 4.2×10^4 ℓ/sec which compared with a theoretical speed of 4.5×10^4 ℓ/sec. This year's results were slightly higher, 4.4×10^4 ℓ/sec. Pumping capacity of the foam had decreased from 198 torr-ℓ to 191 torr-ℓ (about 4 percent). When continous gas addition and addition at higher rates were tried, there was surprisingly little change in pumping speed. A deterioration had been expected, since earlier tests suggested a pumping speed limited by the slow migration of hydrogen molecules deeper into the foam. A reduction in pumping speed may yet be observed at still higher gas addition rates; however, this experiment could not be performed because of the limited refrigeration capacity in the research facility.

Results of the contamination test are shown in Figs. 5 and 6. Figure 5 indicates the amount of hydrogen held by the foam with various amounts of nitrogen. With a monolayer of N_2 (190 torr-ℓ), capacity drops about 10 percent. Capacity continues to decrease as more nitrogen is applied, but even with a layer ten molecules thick, the panel holds about 15 percent of the original volume of hydrogen. This result would suggest that in a test situation where N_2 comprised a significant percentage of the exhaust gases, some kind of 20°K baffle would have to be installed in front of the aluminum foam pump. This would trap the N_2 and yet allow the H_2 to pass through to the foam pump. It should also be noted, however, that this baffle would reduce the effective pumping speed of the foam pump.

Figure 6 gives comparative results with a monolayer of each of the other contaminants. Since CO_2 frost can be used to absorb hydrogen, it is not surprising that it improves panel performance. There is only a slight degradation with CO. Oil seriously damages performance but capacity remains at about 50 percent. After a bakeout, the panel was completely rejuvenated. When the foam was re-covered with oil and washed with freon, results were very poor (less than 10 percent capacity), but a subsequent bakeout again restored pumping capacity.



a. Flat plate
Figure 4. Alternate cryopanel configurations.



b. High-V
Figure 4. Concluded.

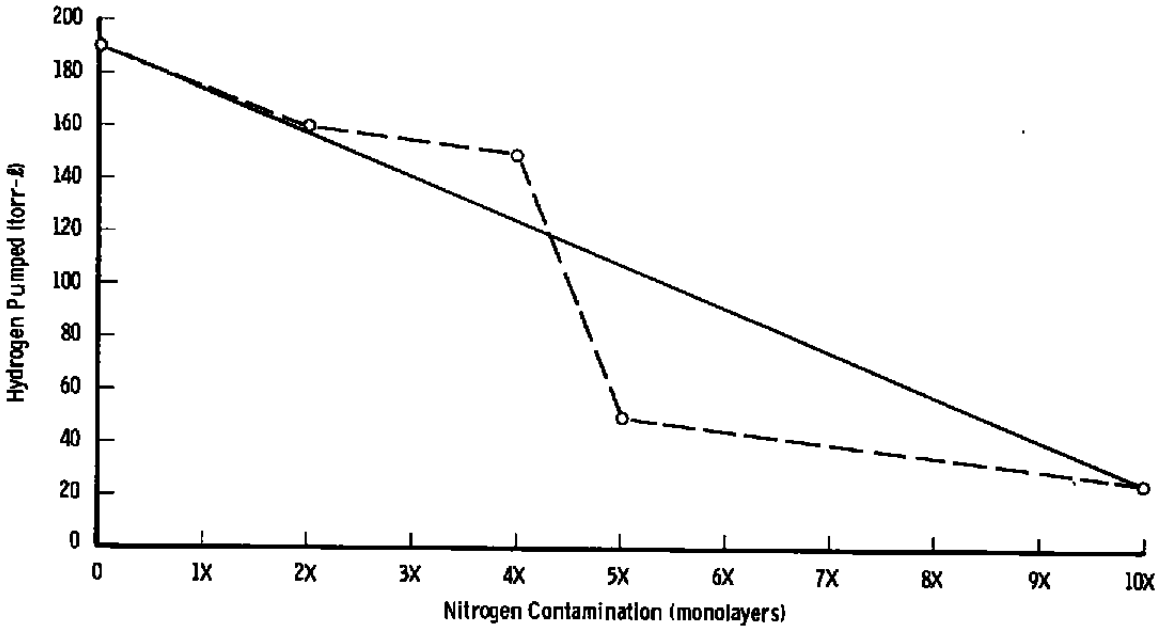


Figure 5. Cryopanel capacity with nitrogen contamination.

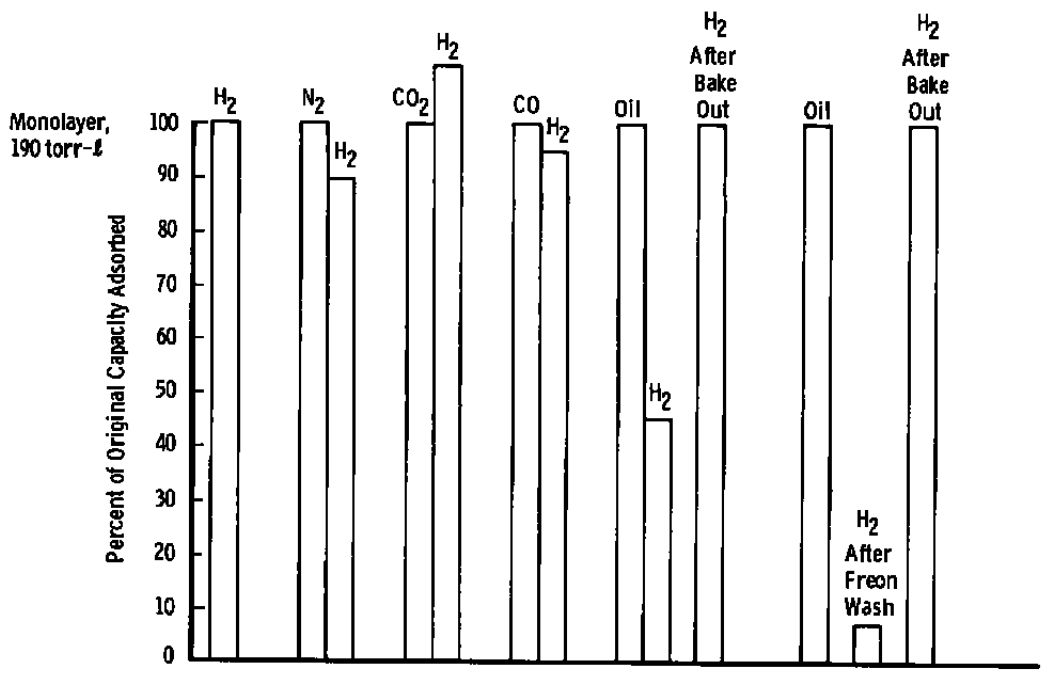


Figure 6. Effect of contaminants on panel performance.

The capacity of the panel was reduced to 120 torr-ℓ (63 percent) when its thickness was halved. Since pumping capacity should be a direct function of aluminum foam volume, this indicates that the original thickness was not fully utilized. Confirming this, a "full" panel gains additional pumping capacity after a rest period. Hydrogen molecules trapped on the surface migrate deeper into the foam, leaving available area on the outer surfaces.

The aluminum foam provides a complex surface area which cannot be accurately measured or computed. The flat plate tested did not have this disadvantage. Its dimensions were 30 cm by 42 cm by 0.32 cm., similar to the plate backing the aluminum foam panel. It had a surface area of 2,600 cm^2.

This plate also provided an opportunity to examine the characteristics of a special deep anodize coating (Sanford Hardcoat, Sanford Process Corporation, 65 North Ave., Natick, MA 01760). An ordinary coating was one mil thick and displayed extensive crevicing. The deep coating was less pitted and 8-10 mils thick. Reference 12 details the anodizing process.

The hydrogen capacity of the flat plate was 81 torr-ℓ. Adjusting for reduced surface area, this was 12.5 times greater than the amount pumped by the foam; i.e.,

$$\text{Foam } C_\chi = \frac{191 \text{ torr}-\ell}{6.300 \text{ cm}^3 \quad \frac{11.8 \text{ cm}^2}{\text{cm}^3}} = 2.50 \times 10^{-3} \text{ torr}-\ell/\text{cm}^2$$

$$\text{Flat Plate } C_\chi = \frac{81 \text{ torr} \cdot \ell}{2,600 \text{ cm}^2} = 3.12 \times 10^{-2} \text{ torr}-\ell/\text{cm}^2$$

The pumping speed of the flat plate was 2.8×10^4 ℓ/sec. A theoretical maximum pumping speed can be calculated by considering the strike rate of the H_2 gas and the area of the outer surface (envelope).

$$S_{theor} = 3.65 \, A\sqrt{T/M} \; (\ell/\text{sec}) \tag{1}$$

where

A = envelope surface area = 2,600 cm^2

T = temperature of gas = 77°

M = molecular weight of gas = 2

Since $S_{theor} = 4.88 \times 10^4$ ℓ/sec, the plate is operating at 57 percent efficiency.

When the speeds of the flat plate and the foam are compared on the basis of envelope area, the plate shows a decrease in pumping speed.

$$\text{Foam } S_x = \frac{4.4 \times 10^4 \ \ell/\text{sec}}{1{,}980 \ \text{cm}^2} = 22.22 \ \ell/\text{sec/cm}^2$$

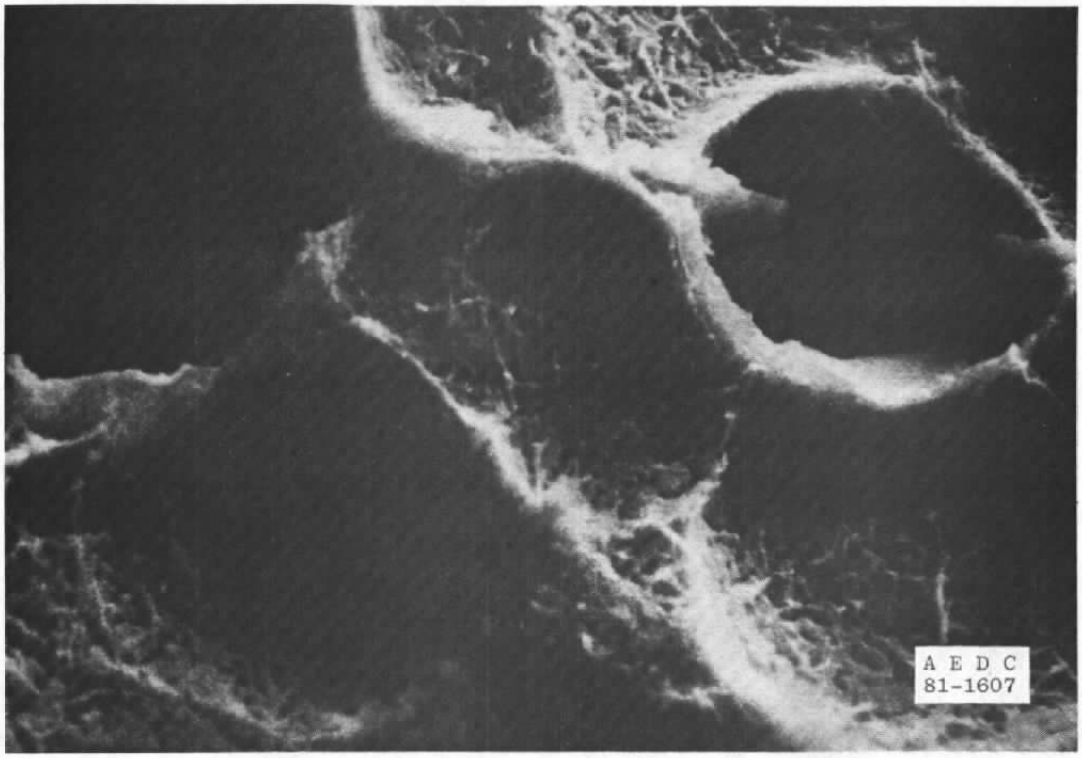
$$\text{Flat Plate } S_x = \frac{2.8 \times 10^4 \ \ell/\text{sec}}{2{,}600 \ \text{cm}^2} = 10.7 \ \ell/\text{sec/cm}^2$$

Corresponding to this, difficulty was experienced in "dumping" the hydrogen when the plate was warmed to 100°K. At this temperature it took several days for the plate to recover. This time was shortened by increasing the temperature to 365°K with the heat lamps.

Evidence indicates that while deep anodizing increases the sorption capacity, hydrogen molecules have a more difficult time migrating into and out of the Al_2O_3 layer. Figure 7 shows the difference in surface structure as seen under the scanning electron microscope. Note that the pitting on the deep anodized sample is on a much smaller scale. At even higher magnifications, this surface appears as smooth dimples, while the standard anodizing continues to display smaller and smaller crevices.

a. Standard anodizing (900x)

Figure 7. Surface comparison of anodic coatings.



b. Deep anodizing (900x)
Figure 7. Concluded.

6.0 CONCLUSIONS

The results of this work are supportive of a full-scale hydrogen sorption system. Contamination results were particularly encouraging; the aluminum cryopanel performed well in the presence of all contaminants tested, and cleanup appears feasible. Enhanced hydrogen sorption with deep anodizing could eliminate the need for extended surface area if a method can be found to shorten the desorption cycle time and to open up the structure of the anodic coating.

The high-V panel with deep anodizing remains to be tested. Preliminary work should begin on a 20°K baffle for N_2 to determine its effect on pumping speed. An optimum configuration (depth of anodizing, surface formation, panel thickness) for a cryosorption panel has yet to be determined. Further effort on these areas is recommended.

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NOMENCLATURE

A	Area, cm^2
C	Capacity, torr-ℓ
M	Molecular weight
S	Pumping speed, ℓ/sec
T	Temperature, °K

SUBSCRIPTS

x	Specific, quantity per cm^2