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PREPARATION AND CHARACTERIZATION OF SLUSH HYDROGEN AND NITROGEN GELS

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PREPARATION AND CHARACTERIZATION OF SLUSH HYDROGEN AND NITROGEN GELS*

A. S. Rapial and D. E. Daney

An experimental apparatus has been developed for the gelation of slush hydrogen, and slush hydrogen was gelled for the first time. Measurements of the weight-bearing capacity of the gel as a function of mass percent gelant were made for liquid and slush nitrogen and hydrogen. These measurements verify the simple models discussed here for gelled liquid and slush within the experimental accuracy; the models predict a reduction in gelant concentration from 38 mass percent to 25 mass percent in going from Normal Boiling Point liquid hydrogen to slush hydrogen of 0.40 solid fraction for the silica gelant used in this work. Reduction in the mass percent gelant for other gelants should be similar.

Key Words: Gels, liquid hydrogen gels, liquid nitrogen gels, liquid-solid hydrogen mixtures, rocket propellants, slush hydrogen, slush hydrogen gels, slush nitrogen gels.

1. Introduction

Because of the high specific impulse achieved with liquid hydrogen in combination with various oxidizers (liquid oxygen and liquid fluorine, for example), it has become an important rocket fuel in spite of the problems associated with its use. Some of these problems or disadvantages are: a) low density, b) temperature stratification, c) short holding time due to the low latent heat of hydrogen, d) hazards associated with the high vent rates, and e) unstable flight conditions caused by sloshing of the liquid in the fuel tank.

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*This work was carried out at the National Bureau of Standards under the sponsorship of the NASA-George C. Marshall Space Flight Center with added support from the International Atomic Energy Agency and the University of Colorado. A more detailed report is given in an M. S. Thesis by Rapial [1969].

Recently, two independent techniques have been developed which can completely eliminate some of these undesirable features and partially eliminate others. One is the production of liquid-solid hydrogen mixtures, "slush hydrogen," by further refrigeration of the liquid. The other is the gelation of liquid hydrogen by the addition of a fine particle gelling substance. A third method, the subject of this Technical Note, combines the slushing and gelling techniques to produce a unique product, gelled slush hydrogen, which combines most of the advantages of both gelled and slush hydrogen.

The use of slush hydrogen offers a number of advantages. The increased density of slush hydrogen compared to Normal Boiling Point (NBP) liquid hydrogen (15 percent greater density for a 50 percent solid fraction) reduces fuel tank capacity requirements or, conversely, increases existing fuel tank mass capacities. Thermal stratification should be eliminated in the region where solids are present and the lower enthalpy of slush hydrogen compared to NBP liquid (165 J/mol* lower enthalpy for 50 percent solid fraction slush) results in longer holding times and/or reduced insulation requirements. Venting is reduced or eliminated thus reducing a potential hazard. However, it should be noted that slush must be made at a reduced pressure, 7.1 kN/m^2 (1 psia), so that precautions must be taken against air contamination of the mixture.

Gelled liquid hydrogen, which flows as a liquid under moderate applied force yet retains a semisolid structure at low stresses in storage, offers other advantages. Sloshing of liquid, which has a considerable

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*The SI (Systéme International d' Unités) system of units [ASTM, 1967] has been used throughout this text. Equivalent British units have been given in parentheses when applicable, but alternative metric units and other units have not been given in the text. As an aid to those not familiar with SI units, some conversion factors are given in the Appendix.

effect on the vehicle stability, can be minimized. Liquid in gelled form has been reported to evaporate at about one-half the rate of pure liquid [Kartluke, et al., 1964], and gelled liquids can be retained by screens. In a punctured pipe the flow may stop if the pressure on the gel is relieved. However, there are also some problems or disadvantages associated with the use of gelled hydrogen. These include: a) difficulty in handling gels in pumps and nozzles, b) restart problems due to residual, nonvolatile gelant left in the pumps, valves, etc., and c) degradation of the propellant by the addition of a less energetic gelling agent (i. e., a gelling agent which reduces the specific impulse of the propellant).

Efforts are underway to minimize these disadvantages by reducing the amount of gelling agent, by choosing more energetic gelling agents, and by using a gelling agent, such as solid methane, which will evaporate on heating.

One method for reducing the amount of gelling agent is found in the gelation of slush hydrogen, since only the liquid portion of the slush requires a gelling agent. Gelled slush also combines most of the desirable features of both gel and slush. The resulting semisolid substance has a high density and low enthalpy. As with slush, holding times would be increased and/or insulation requirements decreased. Whereas the structure of liquid gels is strengthened by heat input and the resulting evaporation of the gelled liquid, heat transfer to gelled slush melts the solids, dilutes the gel, and weakens it.

In the experiments described here, a commercial pyrogenic silica (Cab-O-Sil®) was chosen as the gelling agent. Although it has no

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®Cabot Corporation trademark. Precise specifications in this paper of the pyrogenic silica employed has been necessary to make the results of the work sufficiently meaningful. Identification of the pyrogenic silica or its manufacturer by the National Bureau of Standards in no way implies a recommendation or endorsement by the Bureau. Furthermore, use of other trade names in this Note is for the sake of clarity and does not in any way imply a recommendation or endorsement by the Bureau.

fuel value, and thus would not be suitable for use in a gelled hydrogen rocket propellant, it does have a small particle size (7 nm), is commercially available, and has been used by previous investigators [Kartluke, et al., 1964, and McKinney and Tarpley, 1966]. On the basis of the simple theory of gelled slush presented here, the results of these studies using pyrogenic silica probably can be extended to other liquid hydrogen-gelling agent combinations.

Although gelling of liquids is not new, gelation of rocket fuels and oxidizers has been practiced for only a decade. Extensive investigations have been made on gelation of liquid hydrogen by Kartluke, et al. [1964]. Their study covered gelation of liquid hydrogen with several gelants. McKinney and Tarpley [1966] described gelation of liquid hydrogen in a larger capacity dewar and found that the gel in the larger batch behaved no differently than in a smaller batch. Significant efforts are presently being made to study gelation of space storable propellants. Workers at Aerojet-General [1967a] have been successful in gelling liquid OF_2 in situ with solid ClF_3 produced by bubbling a dilute mixture of He-ClF_3 into liquid OF_2. Earlier, Aerojet-General presented a feasibility study which showed that gelled propellants may be used in rocket engines with little difficulty [1967b]. Work in this field is still actively being pursued by Aerojet-General [1968].

2. Gel Models

2.1 Gelled Liquid

The gelation of liquid hydrogen presents considerable difficulties because of its abnormal properties in comparison with other liquids. A few of the properties for various liquids are shown in Table I.

Table I

Selected Properties of Some Liquids

Liquid	Melting Point, K	Boiling Point, K	Heat of Vaporization, J/mol	Density at NBP kg/m^3	Trouton Constant	Dielectric Constant
H_2O	273.16	373.16	40,758	958	28.3	80.37
H_2	13.80	20.27	898	70	10.5	1.25
N_2	63.15	77.36	5,535	810	17.1	1.48
CH_4	90.68	111.67	8,143	424	17.1	1.68

From Table I, it is seen that LH_2 is rather unique in its properties as related to water and other substances. The familiar gelling of water with gelatine powder leads one to think that a gelant should possess two properties: (1) long chain molecules with lyophilic substituted groups, and (2) partial solubility. Liquid hydrogen is characteristically a nonsolvent; only helium and neon can be dissolved in it to a significant extent. The nonsolvent property of LH_2 can also be deduced from other physical properties. For instance, a low value of Trouton's constant (Table I) indicates negligible associative property. Low association of molecules of a substance is a measure of its low solvent action. On the other hand, the low value of the dielectric constant shows that LH_2 exists in essentially an un-ionized state. Such a state does not promote affinity for macromolecules.

These properties thus rule out any possibility of finding a gelling substance whose action depends upon its partial solubility in LH_2 and its macromolecular structure. Gelation of LH_2 requires a substance capable of surface interaction with LH_2 molecules and capable of being produced with large specific surface area. This means that almost any substance can be used, provided one can produce from it very fine particles of large specific area. We shall not deal here with the methods for high surface area production but only allude to the basic need for a search for these methods. This need arises from the end use of gelled LH_2 or gelled slush in rockets as a fuel.

Addition of a substance to LH_2 may impair its effectiveness as a fuel, i. e., the specific impulse generated by burning the gel with a given oxidizer may be smaller. Both the quantity and the fuel value of the added substance are important. There is no dearth of substances having good specific fuel value. Substances like solid methane, lithium, etc., are available. However, one must be able to produce these substances in desirable particle size and quantities. It should be remembered here that the most desirable substances to consider for the gelant should also be capable of easy evaporation on heating. Most low order aliphatic hydrocarbons such as methane are good in this respect.

Kartluke, et al. [1964] give a semiempirical relationship between particle density and diameter, liquid density, and gelling agent concentration which is shown in figure 1. These curves are based on the following assumptions:

a) The particle-liquid surface forces are the same for all liquid-gelling agent combinations, i. e., the number of particles per unit volume is a constant.

b) There is no excess volume of mixing, i. e., the volume of the gel is equal to the volume of the liquid plus the volume of the gelling agent.

Mathematically, these assumptions can be expressed as

$$\frac{N_p}{V} = c_1 , \tag{1}$$

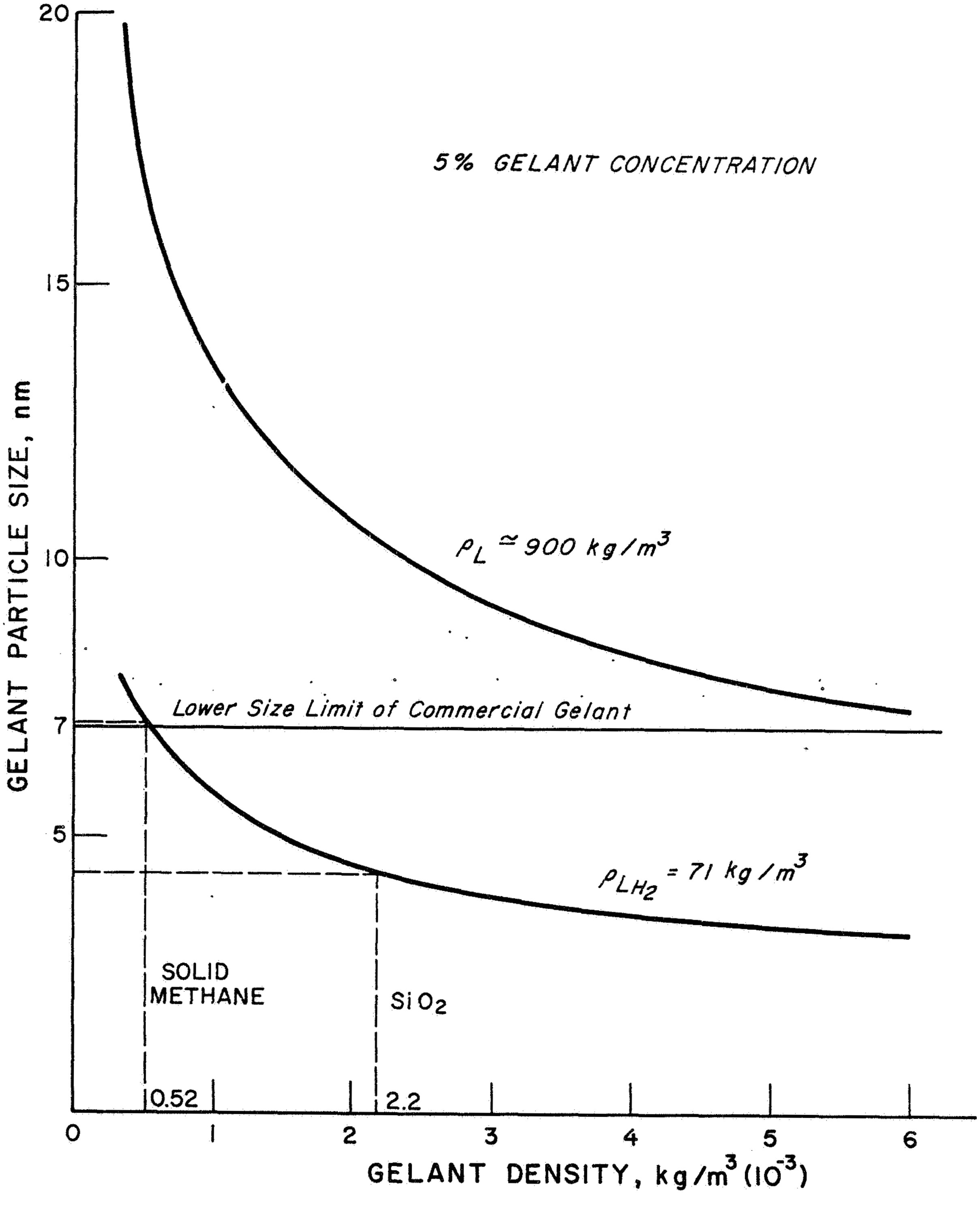


Figure 1. The Effect of Gelant Particle Size and Density on Gel Composition.

and

$$V = V_\ell + V_g = \frac{m_\ell}{\rho_\ell} + V_g \,. \tag{2}$$

With the definition of the mass percent gelling agent,

$$Y = 100 \frac{m_g}{m_g + m_\ell} \,,$$

and the assumption that the gelling agent particles are spheres,

$$V_p = \frac{\pi}{6} d^3 \,,$$

the following expression for the gelling agent concentration may be derived:

$$Y = \frac{100}{1 + \frac{\rho_\ell}{\rho_g}\left(\frac{6}{\pi c_1 d^3} - 1\right)} \,. \tag{3}$$

The number of particles per unit volume, c_1, is evaluated empirically. The curves of Kartluke, et al. (fig. 1) may be reproduced by selecting a value of $3.86(10)^{22}$ particles/meter^3 for c_1. The interparticle distance for a cubic matrix with this value of c_1 is 30 nm, or about 100 molecular diameters for hydrogen. Equation (3) describes the dependence of Y only at the initiation of gelling, i.e., for a gel of zero yield strength. For fixed ρ_g, ρ_ℓ, and d, Y increases with yield strength. This relationship is treated empirically in this study.

For small gelant particle diameters (less than 10 nm), and for values of c_1 having the same order of magnitude as given above, (3) reduces to

$$Y = \frac{600}{\pi c_1} (\rho_g / \rho_\ell) \, d^3 \, . \tag{4}$$

This simplified form of the gel model shows the dependence of Y on ρ_g and d more clearly. Because of the cubic dependence of Y on the particle radius, efforts to reduce this parameter should yield the most significant improvement in reducing Y. Since only one size and kind of gelant was used in the work described here, only the dependence of Y on the liquid density could be tested.

2.2 Gelled Slush

A simple model for slush hydrogen gelation assumes that the solid hydrogen particles do not interact with the gelling agent particles, i.e., that the relatively large slush particles, 0.1 mm to 10 mm [Mann, et al., 1966], will not influence the gelation of the liquid portion of the slush. The resulting gel is then a mixture of gelled liquid with solid particles of hydrogen either dispersed in the gelled liquid or settled in the lower portion of the mixture. Thus, one would expect that with an increase of the solid fraction (hydrogen) in the slush, the amount of gelling agent required for gelation will decrease and will be proportional to the liquid fraction. As before, it is assumed that the number of gelant particles per unit volume in the liquid is a constant at the initiation of gelling.

The model for gelled slush may be expressed mathematically as follows: The mass percent gelling agent in a liquid gel, Y_ℓ, can be converted to a volume percent by

$$Y_\ell^* = Y_\ell \rho_\ell / (100 - Y_\ell)\, \rho_g \,, \tag{5}$$

where ρ_ℓ is the density of the liquid forming a liquid gel of weight fraction Y_ℓ and weight-bearing capacity W, ρ_g is the density of the gelant, and Y_ℓ^* is the volume percent of the gelant/unit volume of the liquid. If X is the mass fraction of the solid cryogen in the slush, then the volume of the liquid in the slush is given by

$$(1 - X)/\rho_{\ell t} \,, \tag{6}$$

where $\rho_{\ell t}$ is the density of the liquid at the triple point. Expression (6) has the dimensions:

volume of liquid/unit mass of the slush.

By multiplying (5) and (6) together we can obtain the volume of gelant present in a unit mass of the slush, $Y_{S\ell}^*$, or,

$$Y_{S\ell}^* = Y_\ell \rho_\ell (1 - X)/(100 - Y_\ell)\, \rho_g \rho_{\ell t} \,. \tag{7}$$

To represent the results in mass we have

$$Y_{S\ell} = \frac{Y_{S\ell}^* \rho_g}{100 + Y_{S\ell}^* \rho_g} \,, \tag{8}$$

where $Y_{S\ell}$ is the mass percent of the gelling agent in the gelled slush. Equation (8) may be rewritten in terms of the known quantities Y_ℓ and X as

$$Y_{S\ell} = \frac{Y_\ell(1 - X)}{\frac{\rho_{\ell t}}{\rho_\ell}(100 - Y_\ell) + Y_\ell(1 - X)} . \qquad (9)$$

Since existing data on yield stress and gelant concentration were insufficient to describe the proposed model mathematically, it was necessary to acquire additional experimental data to relate the weight-bearing capacity of the gelled liquids with various Cab-O-Sil concentrations.

Another aspect of gelled slush noted previously is the effect of heat leak on the melting of solid hydrogen. Kartluke, et al. [1964] report that gelation of LH_2 reduces the evaporation rate of LH_2 by a factor of 2 over that for pure hydrogen. Assuming analogous behavior with gelled slush, one would expect a comparative slower rate of melting for solid hydrogen; however, accurate predictions of the enhancement of the storage time for gelled slush cannot be made at this time because of the lack of data.

3. Apparatus

Some problems encountered in the design of the apparatus were: (a) precooling and weighing of the gelant and its introduction to the system; (b) production, measurement, and transfer of slush hydrogen; (c) stirring both for slush hydrogen production and for blending the gelant and slush hydrogen; and (d) measurement of the gel yield strength.

In a small laboratory setup, the gelling agent used in this work (Cab-O-Sil) was studied for its fluidized flow properties. These studies revealed that the silica develops a static charge while being handled and that, even with a widemouthed conical flask of 0.003 m^3 capacity, the silica would not flow smoothly when the 2/3-full flask was inverted. Bridging of the material occurred, but not necessarily at the narrowest point. Although the fluidized flow system showed that the transfer of silica was smooth at high velocities, any effort to regulate the flow resulted in choking of the 13-mm (1/2-inch) diameter tube, and dismantling of the test apparatus was often required. No satisfactory transfer or weighing method was found.

In addition to the weighing requirement, it was also necessary to cool the silica before it was added to the slush hydrogen to minimize loss of slush by melting. Unfortunately, any cooling device designed for efficient transfer of heat from the gelling agent not only tended to hinder the flow of the silica, but also presented difficulties in weighing. The ideal solution would have been a scheme whereby the gelling agent could be cooled and weighed independently before being added to the slush hydrogen. Since no such solution was found for these problems, other methods were investigated. Most of the problems were finally solved by preweighing a quantity of the gelant and placing the gelant in a dewar directly below a vessel in which the slush hydrogen was produced; the latter was then transferred to the gelant-containing dewar below.

Figure 2 shows this experimental arrangement. The gel dewar and the slush generator, positioned above the gel dewar, are enclosed in a 152-mm (6-inch) I. D. strip silvered Pyrex shielding dewar. During the liquid and slush hydrogen gelation experiments, this 152-mm shielding dewar was in turn immersed in a 254-mm (10-inch) I. D. strip silvered liquid nitrogen shielding dewar. The gel dewar is a 102-mm (4-inch) I. D. by 178-mm (7-inch) deep unsilvered double-walled Pyrex vessel with a 0.0013 m^3 capacity in the double-walled portion. The 102-mm diameter stainless steel-to-glass joint forming the neck of the dewar makes it possible to solder the gel dewar to the double-ended cap which separates the gel and slush containers. The slush generator is a 102-mm (4-inch) diameter, 203-mm (8-inch) long single-walled Pyrex

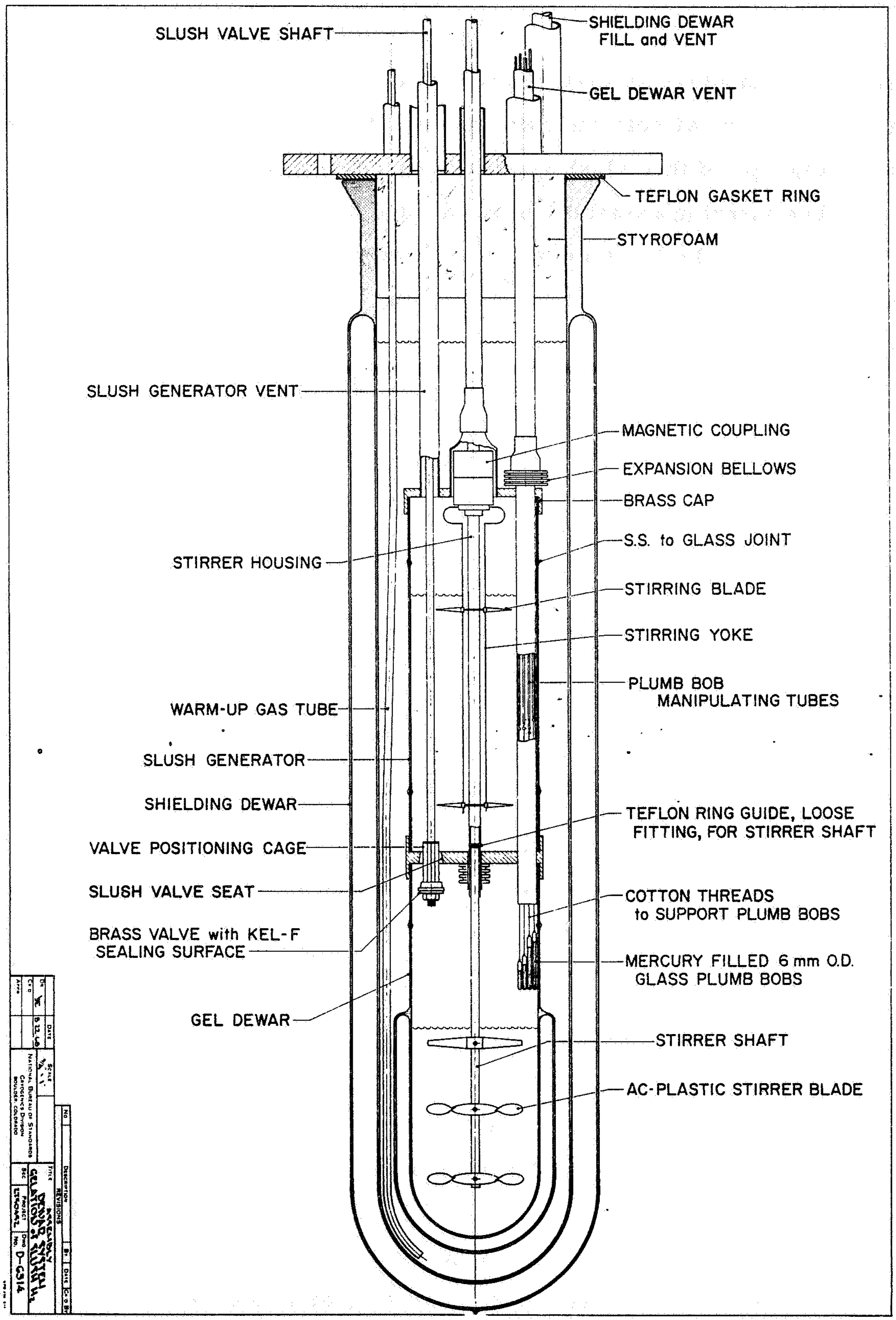


Figure 2. Dewar Arrangement.

vessel with stainless steel-to-Pyrex joints at either end. It is soldered to the brass caps at both ends and has a 0.0014 m^3 capacity. Figure 3 is a photograph of this slush generator-gel dewar assembly.

The stirring assembly seals the gel and slush vessels from each other, from the shielding dewar, and from the environment. The 6.4-mm (1/4-inch) diameter main stirring shaft extends from the air motor through the dewar arrangement to the gel vessel. Above the gel vessel this shaft is sheathed by a 9.5-mm (3/8-inch) diameter tube which extends up to the magnetic coupling and from there to an external packing gland. Above the magnetic coupling this assembly is housed in a 12.7-mm (1/2-inch) O. D. stainless steel tube which seals it from the shielding dewar. The magnetic coupling, composed of concentric, radially magnetized magnets, transmits the rotation of the inner drive shaft to the slush generator stirrer housing while providing a hermetic seal between the inner drive shaft and the slush generator. Figure 4 shows the details of this unique coupling.

In order to permit transfer of slush or liquid from the slush generator to the gel dewar, a valve was provided in the double-ended cap separating the two containers. The valve consists essentially of a 3.2-mm (1/8-inch) thick Teflon ring, with a 0.16 rad (9°) taper, sandwiched between two brass pieces (fig. 2). A matching seat is machined in the double-ended brass cap. A pneumatic actuator opens the valve up to 13 mm (1/2 inch).

In order to define the gel structure, the yield strength or weight-bearing capacity must be measured. Because of their simplicity, plumb bobs were used. These plumb bobs are 6-mm (0.236-inch) O. D. glass tubes with hemispherical ends and are filled with mercury through a capillary arm to give each plumb bob the desired weight. In this study four plumb bobs with masses of 2.3, 5, 7.5, and 10 g were used.

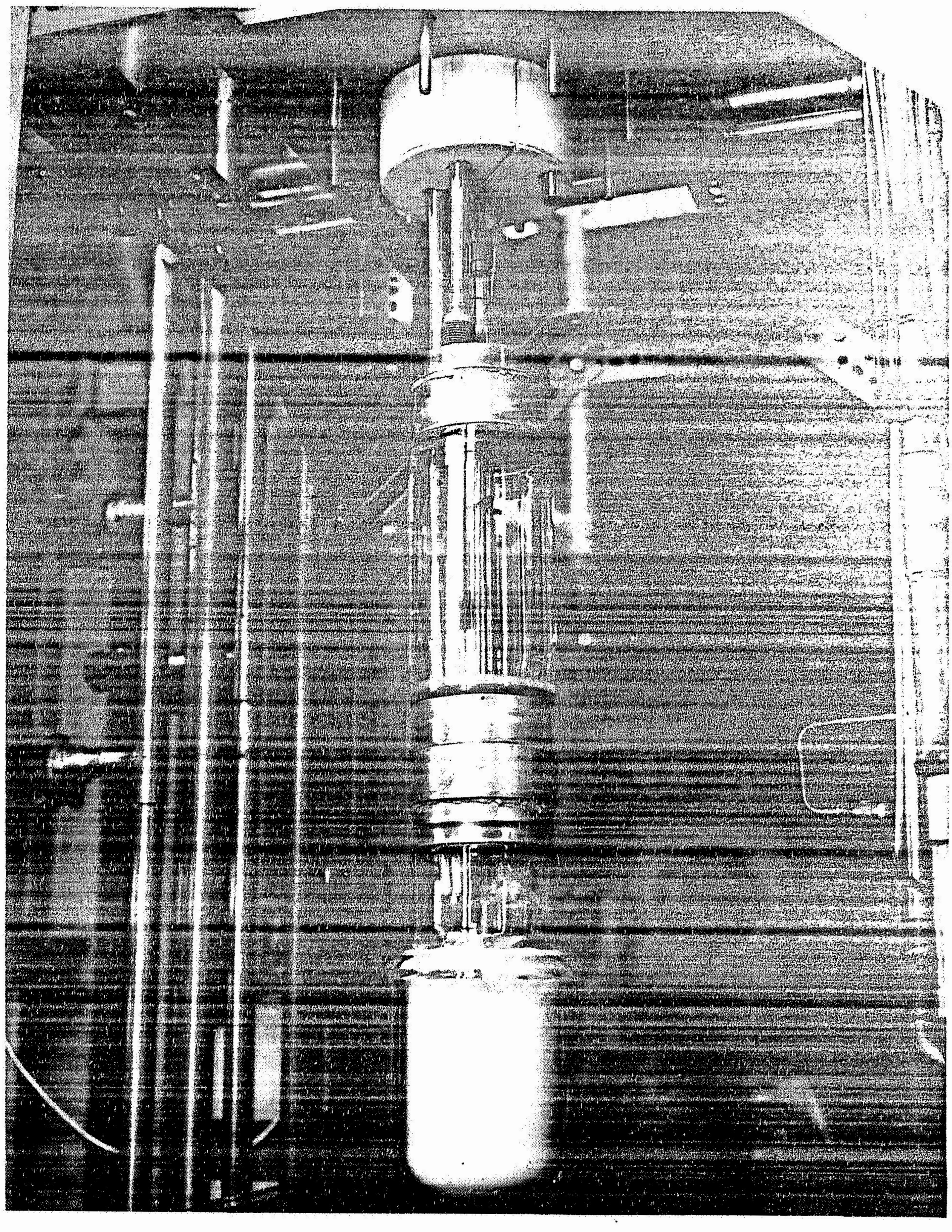
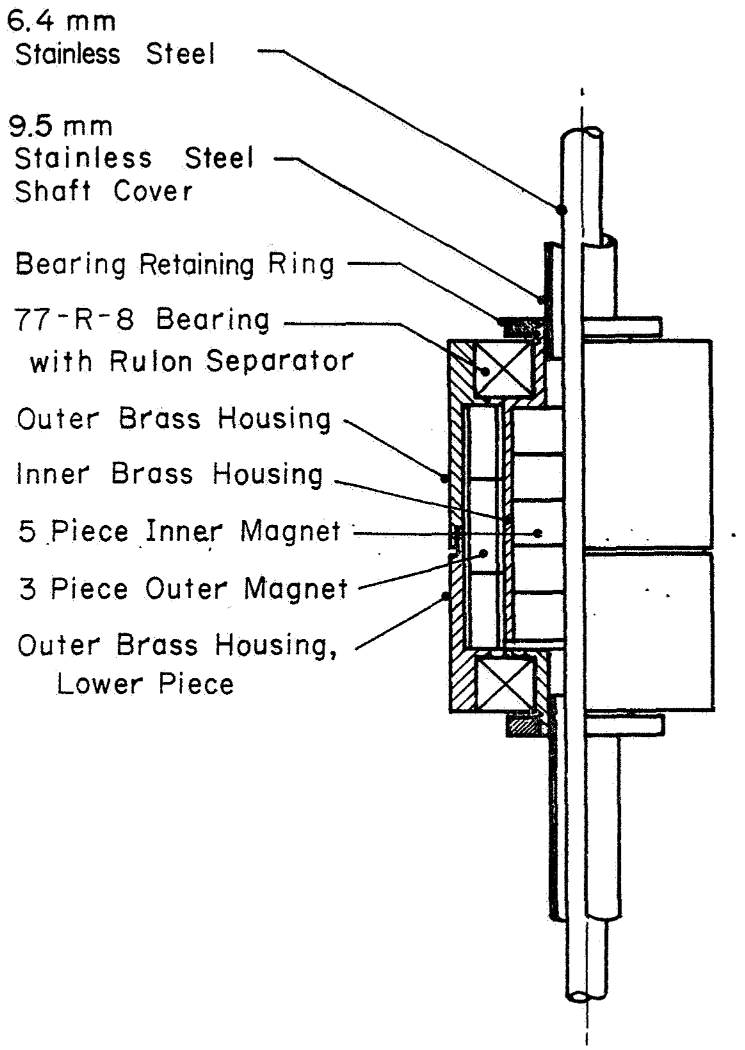


Figure 3. Photograph of the System without Shielding Dewar.



Notes:

1. Stainless Steel Bearings are Non-lubricated
2. Retainining Ring is Soldered with Woods' Metal.
3. 5 Piece Inner Magnet is Joined onto the Shaft with Epoxy.
4. 3 Piece Outer Magnet is Held in Lower Housing with Epoxy.
5. Outer Housing Dimensions (36 mm O.D. x 51 mm Long)

Figure 4. Magnetic Coupling.

Although in this work the directly measured weight-bearing capacity is used to characterize the gel, McKinney's [1968] relationship between the plumb bob weight and the yield stress as determined by a viscometer also is given for completeness.

Yield Strength as a Function of Plumb Bob Weight

Plumb bob weight supported by gel cN	Plumb bob weight not supported by gel cN	Has yield strength of N/m^2
--	2.3	<20.0
2.3	4.9	20.0 - 34.5
4.9	7.4	34.5 - 47.8
7.4	9.8	47.8 - 61.1
9.8	--	>61.1

The plumb bobs are raised and lowered through a 178-mm (7-inch) travel by 3.2-mm (1/8-inch) diameter stainless steel rods which are attached to the plumb bobs via black threads (for good visibility). These rods pass through packing glands and are manually manipulated.

Each vessel (the gel dewar, the slush generator, and the shielding dewar) can be evacuated, vented, and filled with hydrogen or nitrogen gas. Figure 5 is a schematic of the system. Valves 1, 2, 3, and 21 permit evacuation. Venting is accomplished directly through valves 11, 12, and 13, or through the 20 cfh wet test meter via valves 8, 9, and 10. Valves 5, 6, and 7 control the supply of hydrogen or nitrogen gas to each vessel. Over-pressuring of the vessels is prevented by relief valves S1, S2, and S3. Gas pumped from the vessels can be measured by the 150 cfh wet test meter. Pressures are measured by absolute manometers and compound pressure gauges.

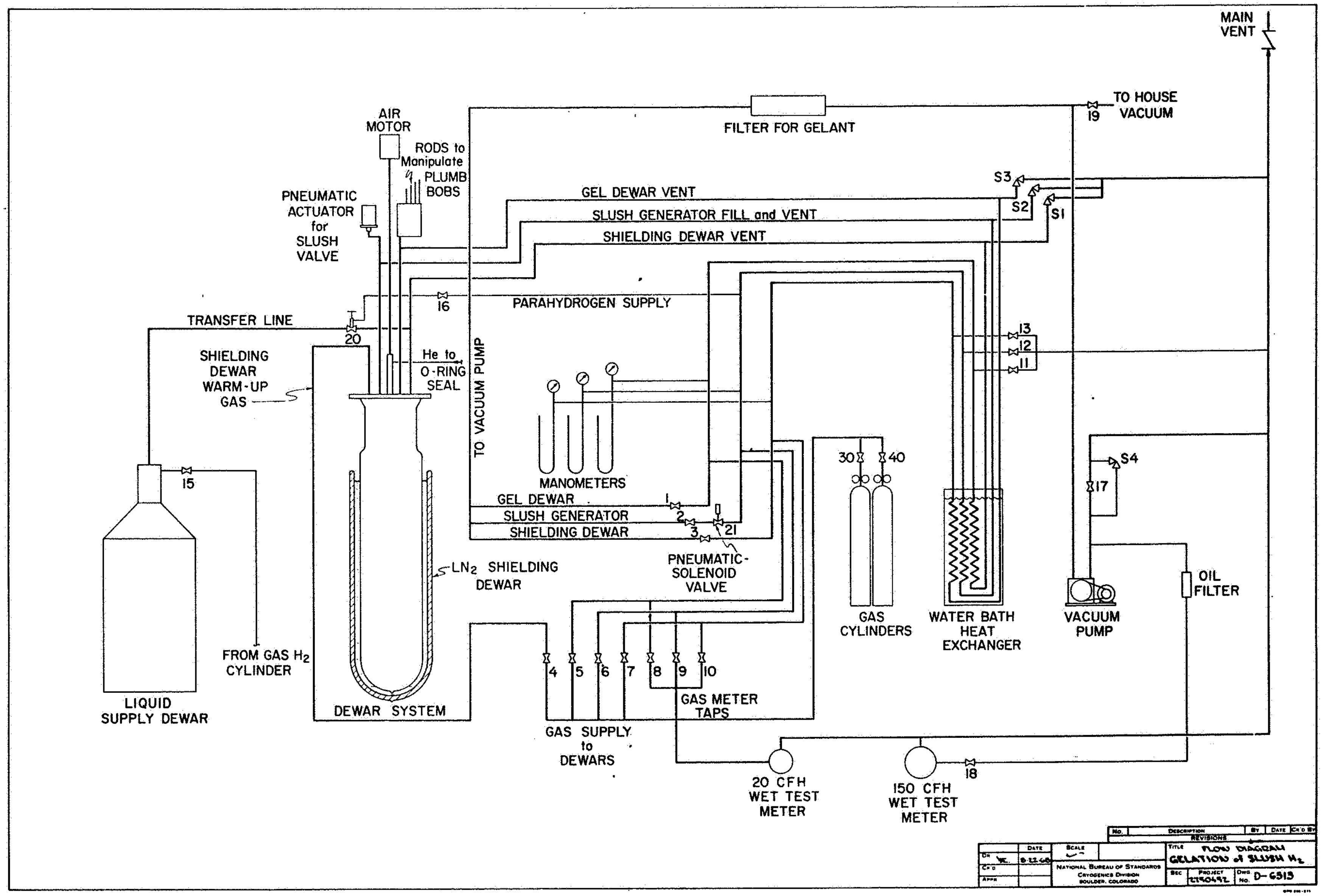


Figure 5. Schematic of the Apparatus.

4. Experimental Technique

Before the gelling agent is placed in the gel dewar it is prepared and weighed. About 60 g of pyrogenic silica is placed in a desiccator (previously cleaned and dried) and dried at 105° C under a vacuum of about 0.1 kN/m^2 for several hours. The vacuum is broken with dry nitrogen, and about 50 g of silica is placed in the gel dewar. The gelling agent is weighed in the gel dewar which is placed directly on a balancing scale. The weighing accuracy is ± 0.2 g. The gel dewar is then soldered in place on the apparatus, and the silica is evacuated in situ with occasional stirring for 12 hours or more to remove any moisture adsorbed during the approximately 30-minute weighing and assembly procedure. Several times during the room temperature evacuation period, dry nitrogen gas is admitted to the gel dewar and the pressure is raised to 0.12 MN/m^2 before resuming evacuation. This procedure helps break up any agglomerates which may be formed during the weighing or evacuation steps. Because the silica bed expands rather rapidly under evacuation, care must be taken not to pump powder into the lines. Thus, it is essential that the pressure over the silica bed be carefully controlled at all times. The bed is allowed to rise about 38 mm (1-1/2 inch) before the evacuation valve is closed. The degassing is clearly visible from the "boiling" bed surface. The bed sinks slowly as the degassing progresses. Stirring is carried on throughout the evacuation process. When the bed returns to its original position, further evacuation may be resumed--cautiously. The cycle is repeated until further opening of the valve does not swell the gelant bed. This procedure is also carried out after each experimental run is completed, and after the bed has undergone evacuation for several hours.

The slush generator is filled by condensing hydrogen gas (or nitrogen gas during the nitrogen tests) in the generator at the expense of the liquid hydrogen in the 152-mm (6-inch) shielding dewar. Because the heat generation caused by the spontaneous conversion from normal hydrogen to parahydrogen would be undesirable, parahydrogen gas is condensed from the liquid transfer line via valve 16. Maintenance of a pressure difference between the generator and the shielding dewar provides the temperature difference for condensation.

The gelant is also cooled by the shielding bath. Hydrogen gas (or nitrogen gas for the N_2 tests) is bled into the gel dewar where it acts as a transfer gas, cooling the gelling agent by natural convection heat transfer between the silica and the single-walled portion of the vessel. Occasional stirring of the gelant is carried out to accomplish uniform cooling of the gelling agent. To further insure cooldown of the silica, the shielding dewar is kept at the triple point, and sufficient time (up to 1 h) is allowed for the gel dewar pressure to reach a steady state value. The gel cooldown is tested by bleeding a small amount of hydrogen gas into the gel dewar. If the pressure in the vessel falls back to the triple-point pressure within a few seconds, it is assumed that the gel dewar and its contents are cooled to the triple-point temperature.

After the liquid in the slush generator has been cooled by natural convection to the triple point, slush production by the "freeze-thaw" method [Mann, et al., 1966] is begun. In practice, the freeze-thaw slush production is accomplished by opening valve 2, and then alternately opening and closing valve 21. When 21 is open, vapor is pumped from the slush generator, and solid hydrogen is formed on the liquid surface. When valve 21 is closed, this newly formed solid sinks below the surface and is stirred into the slush mixture. By this cyclic procedure, slush with a solid fraction up to approximately 0.40 can be generated. The irregular geometry of the particles hinders closer packing of the freshly generated solid particles. Because some solids are left behind during the transfer of slush to the gel dewar, the maximum solid fraction obtainable in the gel dewar was about 0.30.

Upon completion of the slush generating process, the slush valve separating the slush and gel vessels is opened; the slush is transferred to the gel dewar; and the gel is formed with vigorous stirring. Work with liquid nitrogen showed that it is advisable to transfer the entire quantity of liquid or slush at once, rather than meter it in steps. When step-wise liquid nitrogen transfer was tried, the first portion of LN_2 introduced produced a hard gel at the top of the gelant bed. This would often stall the motor used to drive the stirrer. Also, the downward progress of gelation was extremely slow. In fact, one would visually observe the slow progress of wetting the silica from top to bottom. Although this was of no consequence while gelling with a liquid, excessive time lapse could seriously affect the slush experiment. The heat ingress would not only partially melt the slush already transferred to the gel dewar, but the quality of the slush in the generator would also deteriorate.

Due to heat ingress and heat of stirring, the solid hydrogen melts, thus producing more liquid. An accurate record is kept of the time intervals that stirring is carried out and the time when measurements are taken. The amount of solid at any particular time is estimated from the heat ingress rate. Gel strength is measured until the 2.3-g plumb bob sinks or until the solid has melted. Once the solid has melted, the gel is allowed to heat up. The heating process is aided by stirring the gel and by evaporating the shielding dewar liquid with warm gas. As the liquid evaporates, the gel structure hardens and can bear more and more weight. An experiment is terminated when the gel hardens to such an extent that it can bear the 10-g plumb bob. Thus two sets of measurements, one of gelled slush and one of gelled liquid, are made in succession. The hydrogen from the gel dewar is metered until no further reading is observed on the gas meter. In this manner the mass of hydrogen contained in the gel dewar during each stage of the experiment is determined.

5. Experimental Results

Although the principal objective of the tests was to characterize gelled slush hydrogen, liquid hydrogen as well as liquid and slush nitrogen was also gelled. The measurements on the gelled liquids served as a basis of comparison for the gelled slush data. In addition, the gelled liquid data are valuable in their own right since the previously existing data on gelled liquid hydrogen and nitrogen are limited. Comparison of these liquid data with the data of others yields an estimate of the systematic error. Because nitrogen is a relatively hazardless material requiring much less stringent safety requirements than hydrogen, preliminary tests necessary for developing the experimental equipment and techniques were made with nitrogen. These nitrogen tests also provide a useful experimental check of the validity of the models for gelled liquid and slush, equations (3) and (9).

5.1 Gelled Liquid Nitrogen

Table II summarizes the measurements of weight-bearing capacity versus mass percent Cab-O-Sil in the gel for gelled liquid nitrogen.

Table II

Liquid Nitrogen Gel Data

Weight-bearing capacity as a function of Cab-O-Sil concentration

	Plumb Bob Weight			
	2.3 cN	4.9 cN	7.4 cN	9.8 cN
	Cab-O-Sil Concentration in Gel (mass percent)			
Expt 1	5.4	6.4	7.1	7.7
Expt 2	---	6.4	7.1	7.8
Expt 3	4.9	5.6	6.5	6.9
Expt 4	5.1	5.7	6.5	7.0
Average	5.13	6.02	6.79	7.35

The silica in experiments 1 and 2 had been used in previous attempts at LN_2 gelation. Fresh silica was used for experiment 3 and was reused in experiment 4. A consistent difference between the fresh and used silica data is apparent, but since the data for the four runs are within the measurement accuracy, the average values are assumed to be representative. Figure 6 presents these average values for the mass percent of Cab-O-Sil in the liquid nitrogen gel versus the weight-bearing capacity of the gel. The shape of the broken curve drawn through the points is suggestive of a slight nonlinearity. However, at this stage no importance can be ascribed to it since the data can be represented equally well with a straight line. Tacitly, a linear relationship is assumed which may be expressed as

$$Y_{LN_2} = 4.57 + 28\ W\ . \tag{10}$$

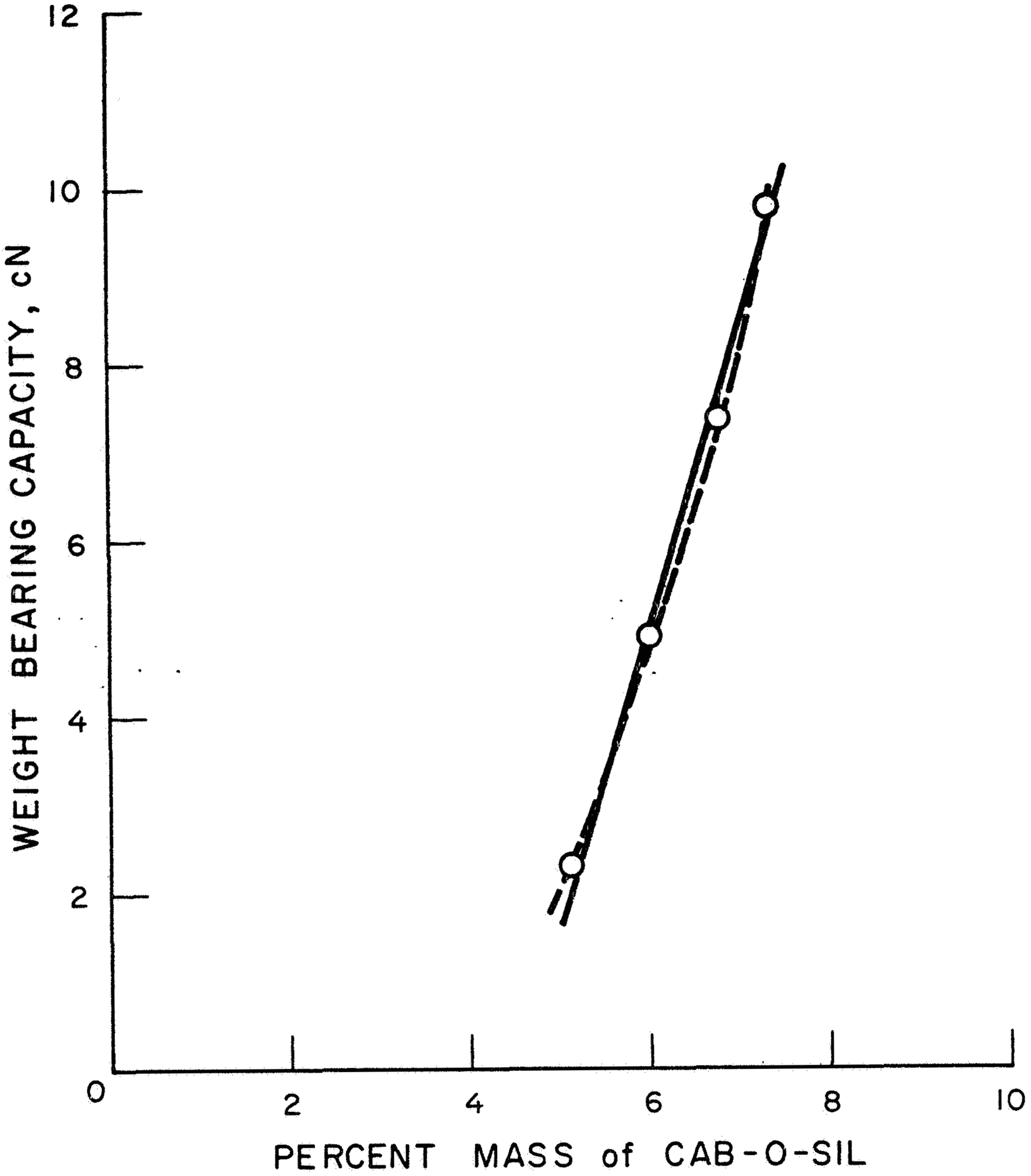


Figure 6. Liquid Nitrogen Gel Characterization.

This expression for Y can now be substituted for Y_ℓ in (9) and the theoretical gel structure for gelled slush nitrogen can be calculated.

5.2 Gelled Slush Nitrogen

The results of the gelation of slush nitrogen are given in Table III. The estimate of solid nitrogen in the gel is made from the heat leak data. Equations (9) and (10) are used to calculate the theoretical amount of Cab-O-Sil that is required in the gelation of the slush. The cryogen solid fraction, required to satisfy (9), is taken from column 2 of Table III, for various values of the weight-bearing capacity.

Table III

Slush Nitrogen Gel Data

A comparison between the theoretical and actual amounts of Cab-O-Sil in gelled slush for various estimated solid nitrogen fractions and weight-bearing capacity

Weight-bearing capacity, cN	Estimated solid fraction of N_2 slush	Mass % Cab-O-Sil Actual	Theoretical
2.3	0.19	4.20	4.05
2.3	0.08	5.17	4.61
4.9	0.19	5.17	4.71
7.4	0.29	5.17	4.63
9.8	0.33	5.17	4.94

Table III shows that the theoretical and actual Cab-O-Sil weight percentages required for producing gelled slush nitrogen mixtures of comparable yield strength are in substantial agreement. These data are also plotted in figure 7. The curves represent the theoretical gel structure defined by (9) using the results of the gelled liquid tests, (10), as a base.

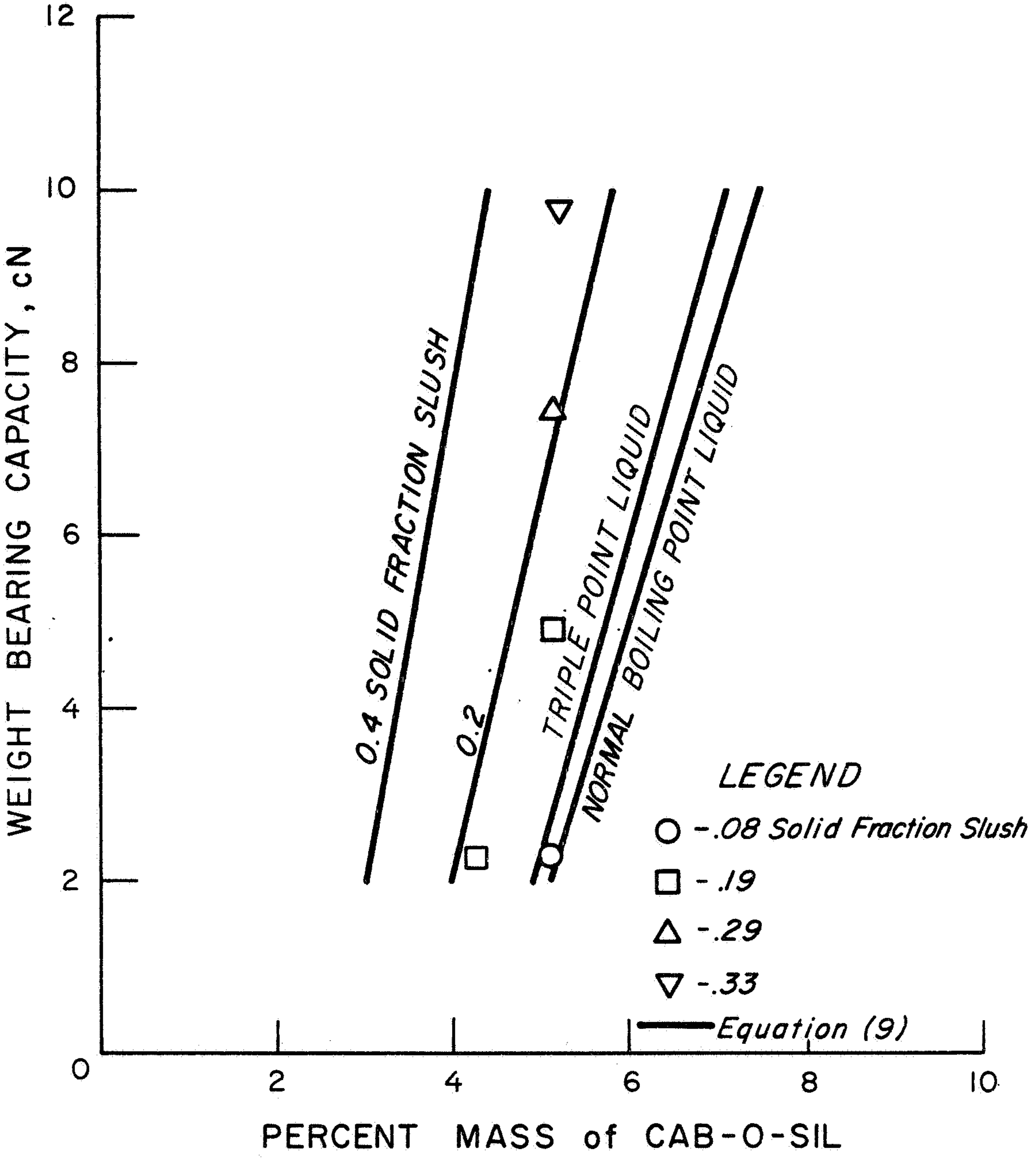


Figure 7. Slush Nitrogen Gel Characterization.

5.3 Gelled Liquid Hydrogen

The results of the gelled liquid hydrogen tests are summarized in Table IV which presents the mass percent of Cab-O-Sil required to support the various plumb bobs.

Table IV

Liquid Hydrogen Gel Data

Weight-bearing capacity as a function of Cab-O-Sil concentration

Expt. No.	Cab-O-Sil Condition	Plumb Bob Weight 2.3 cN	4.9 cN	7.4 cN	9.8 cN
		Cab-O-Sil Concentration in Gel (mass percent)			
5	Fresh	34.8	35.3	37.3	39.1
6	Fresh	35.4	37.0	38.6	40.6
7	Used*	35.2	----	----	41.2
Average		35.1	36.2	38.0	40.3

*The Cab-O-Sil used in experiment No. 6 was reused in experiment No. 7. The Cab-O-Sil was not purged with nitrogen at the end of experiment No. 6. Instead it was kept under vacuum until experiment No. 7 was begun.

Figure 8 presents the average values for the weight percent Cab-O-Sil in the liquid hydrogen gel. The straight line drawn through the points is given by

$$Y_{LH_2} = 33.3 + 65\ W . \tag{11}$$

An apparent increase in the data scatter in figure 8 compared with figure 6 is a result of the expanded scale in figure 8. Equations (9) and (11) may be combined to give a semiempirical model for gelled slush hydrogen.

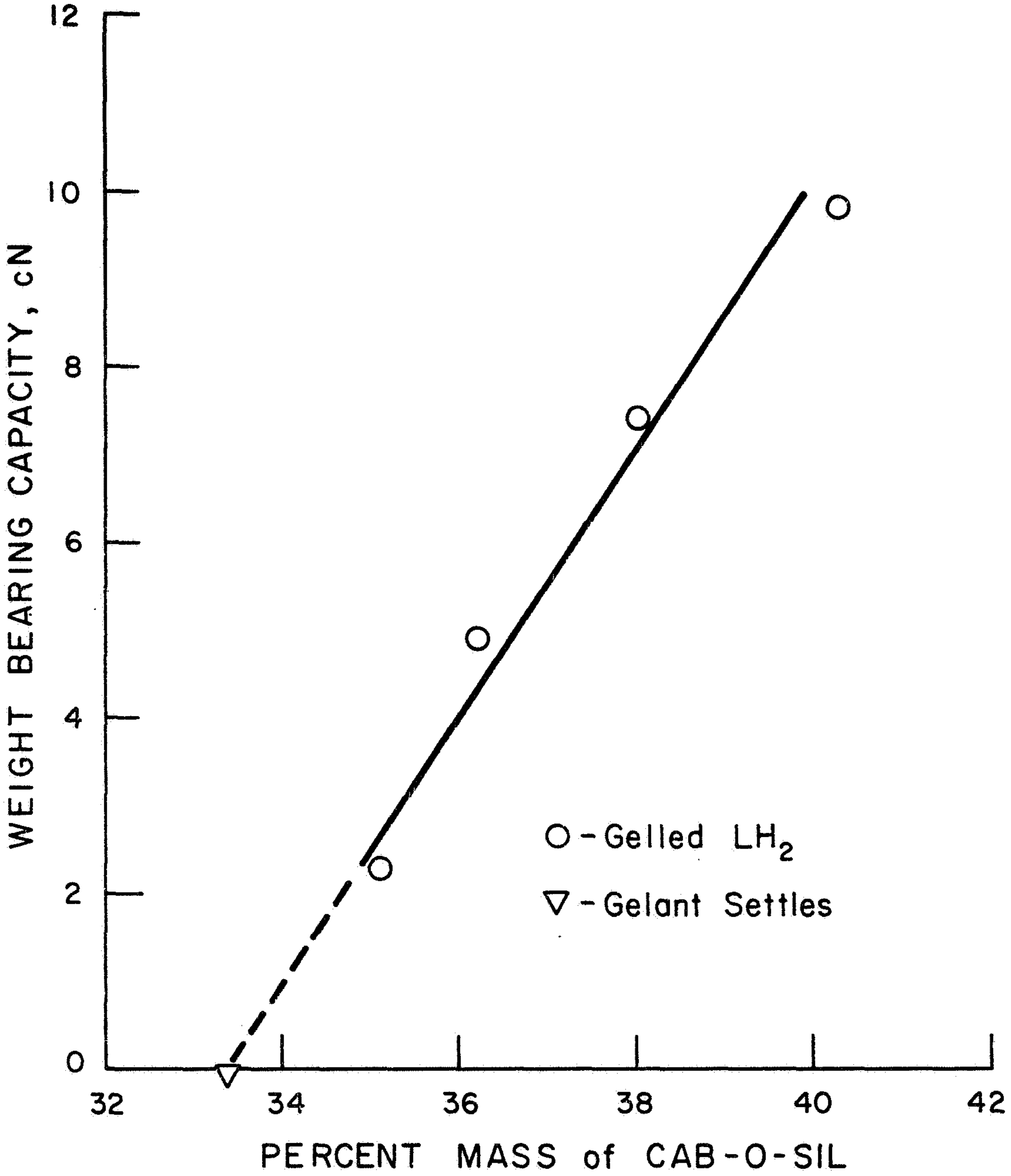


Figure 8. Liquid Hydrogen Gel Characterization.

5.4 Gelled Slush Hydrogen

The results of the gelation of slush hydrogen are summarized in Table V.

Table V

Slush Hydrogen Gel Data

Expt. No.	Weight-bearing capacity, cN	Estimated solid fraction of H_2 slush	Mass % Cab-O-Sil Actual	Mass % Cab-O-Sil Theoretical
5	2.3	Gelled mass at boiling point	34.8	34.8
	4.9	0.01	34.8	34.7
	7.4	0.11	34.8	34.1
6	4.9	0.01	34.7	34.6
	7.4	0.10	34.7	34.2
	9.8	0.21	34.7	32.8
7	2.3	Gelled mass at boiling point	35.2	35.2
	4.9	Gelled mass at saturated liquid at 0.4 atm.	35.2	35.9
	7.4	0.09	35.2	34.3
	9.8	0.16	35.2	34.2

The theoretical mass percent Cab-O-Sil is calculated from (9) and (11), using the solid cryogen contents listed in column 3. Figure 9 is a plot of these data. The slush solid fractions have been rounded off to the nearest 0.05 increment. As before, the curves represent the theoretical gel structure defined by (9) using the results of the gelled liquid hydrogen tests, (11), as a base.

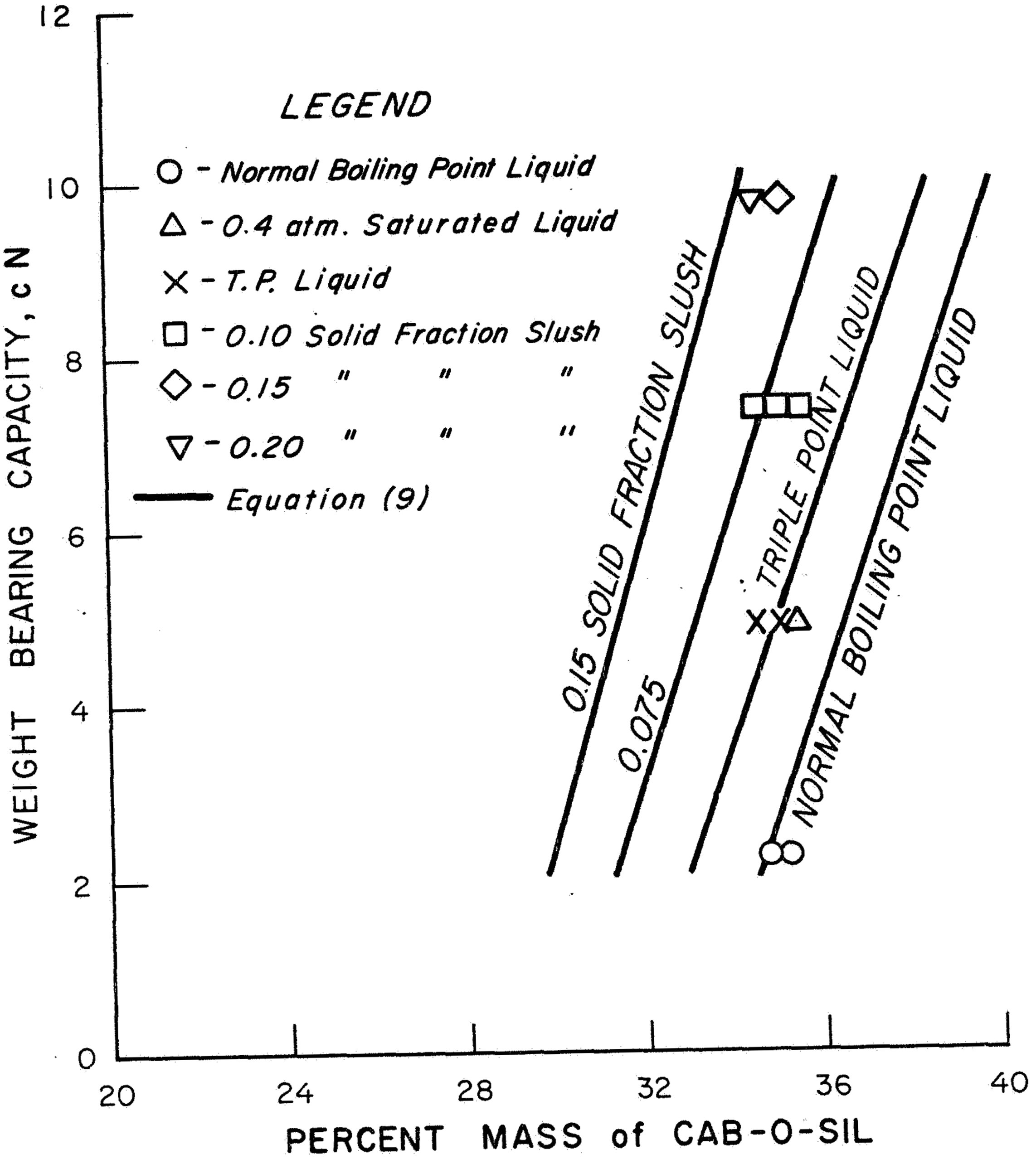


Figure 9. Slush Hydrogen Gel Characterization.

6. Discussion of Results

6.1 Discussion of Errors

Four basic parameters are measured in the experiments: mass percent of gelling agent in the gel, consistency or weight-bearing capacity of the gel, solid fraction of the slush, and density of the liquid.

The mass percent gelant in the gel is determined by weighing the gelant in the gel dewar to an estimated precision of 0.5 g or 1 percent of the gel mass. The systematic error is also estimated to be about 1 percent of the gel weight. The weight or mass of the liquid or slush in the gel is determined by measuring the gas evaporated from the gel by a 20 cfh wet test meter. Since only moderate care was taken, this measurement is estimated to be accurate within 2 percent. The random error is also estimated to be about 2 percent of the liquid mass. The limits of random and systematic error of the mass percent gelling agent are 2 percent and 3 percent, respectively. A typical value of Y and its systematic error limits for the hydrogen experiments would be 34 ±1 percent.

The gel consistency or yield strength is determined using plumb bobs. The plumb bob weights were reported directly here, so the accuracy of McKinney's [1968] relation between yield strength and plumb bob weight is not considered. The random error or the repeatability of these measurements in a gel of fixed composition is the dominant error here, since the weight and diameter of the plumb bobs are known to much greater accuracy. This random error in the weight of plumb bob required to penetrate a gel of given composition was estimated from the liquid hydrogen and liquid nitrogen gel data (Tables II and IV). The standard deviation of the plumb bob weights about the straight line curve fits provided by equations (10) and (11) is 1.3 cN. Thus, 95 percent of the measurements of weight-bearing capacity have an error less than 2.6 cN, the 2 sigma limits.

The solid hydrogen content of the slush was determined from the length of time required to melt the solids together with heat leak data. Thus, an account is kept of the heat introduced into the gel from the time it is formed until all the solid cryogen is melted. A rise in the vapor pressure above the triple-point value indicates that all the solid is melted.

The heat leak into the gel dewar, as determined from liquid boil-off measurements at one atmosphere is as follows:

Gel Dewar Heat Leak

Fluid	Stirrer Speed	Heat Leak
Nitrogen	no stirring	2.5 watts
"	200 rad/s	12.0 watts
Hydrogen	no stirring	0.6 watts
	200 rad/s	3.0 watts

The lower nonstirring heat leak for hydrogen resulted because a nitrogen shielding dewar was used in these experiments. The variability of the heat leak values is estimated to be about 15 percent. During a typical slush hydrogen experiment, 1410 s elapsed from the first measurement of the gel consistency until all the solid hydrogen was melted. Out of this time 990 s were without stirring and 420 s with stirring. The random error of the slush solid fraction is estimated to be less than 20 percent, the systematic error less than 10 percent. A typical solid fraction and its limits of random error would be 0.20 ±0.04.

The density of the liquid in the gelled liquid experiments was determined by measuring the vapor pressure with a mercury manometer. The random and systematic errors are each estimated to be about 0.2 percent in density.

6.2 Liquid Data

The gelled liquid data (figs. 6 and 8) indicate that LN_2 and LH_2 gels exhibit approximately linearly varying weight-bearing characteristics with Cab-O-Sil concentration in the range of 0- to 10-cN weight-bearing capacity. The extrapolation of the gelled LH_2 curve (fig. 8) to zero weight-bearing capacity matches the observed value of Cab-O-Sil concentration at which the gelling agent separates from LH_2.

The dependence of Y on the density of the liquid expressed in (3) may be checked by comparing the experimental values of Y for liquid nitrogen and hydrogen. Based on the experimentally determined value of 4.57 for Y_{LN_2} at zero weight-bearing capacity [from (10)], (3) predicts a Y value of 35.3 for hydrogen compared to the experimental value of 33.3 [from (11)] at zero weight-bearing capacity. This 6 percent difference between Y predicted and Y experimental is within the random error limits of the experiment so that the density dependence expressed by (3) may be considered to hold with moderate accuracy.

Differences in the gelling agent preparation techniques and variations in particle size from sample to sample result in corresponding variations in the mass percent Cab-O-Sil required to produce gels of the same consistency. An estimate of a combination of these variations in Y and the systematic errors in this and other studies is obtained by comparing the results of this study with the results of others. A summary of this comparison is as follows.

Gel	Mass Percent Cab-O-Sil Other Studies	 This Study	Plumb Bob Weight or Yield Strength
	Kartluke, et al. [1964]		
LN_2	4.6	5.1	2.3 cN (20 N/m^2)
LH_2	35.1	35.1	2.3 cN (20 N/m^2)
	McKinney & Tarpley [1966]		
LH_2	36.1	38.0	7.9 cN (48 N/m^2)

Kartluke, et al., out-gassed the Cab-O-Sil at 250° C and 70 mN/m^2 pressure and afterwards kept the samples in a helium atmosphere. They later reduced the baking temperature to 100° C with no significant change in the results. The work of McKinney and Tarpley represents a continuation of this work. In this study the Cab-O-Sil was baked at 100° C, but it was exposed to air during the weighing and assembly processes.

As noted in the liquid nitrogen experiments, Cab-O-Sil may tend to deteriorate on reuse in a succeeding experiment. This was observed also in the preliminary runs with LH_2 when silica from the previous experimental runs with liquid and slush nitrogen was reused. Partly because of this deterioration, experimental run No. 7 was not purged with nitrogen as noted earlier. However, no significant difference is evident with the hydrogen experimental runs in which fresh silica was reused.

6.3 Slush Data

Comparison of the slush data points in figures 7 and 9 with the semiempirical curves based on (9) indicates a fair agreement between the experiments and the model for gelled slush. An apparent tendency to underestimate the slush solid fraction is evident in figure 9, but this discrepancy is within the experimental error. Thus, the assumption that gelant concentration is proportional to the volume fraction of the liquid in slush is confirmed within the limited accuracy of the experiments. Although the data on slush hydrogen gelation only cover solid cryogen fractions up to 0.20, the model for gelled slush hydrogen should hold at higher concentrations as well. To illustrate this reduction in the gelling agent requirement, comparative values of Cab-O-Sil concentration are given below in Table VI for various liquid conditions and slush solid fractions. A gel of 6-cN weight-bearing capacity (equivalent to 40 N/m^2 yield stress) is chosen.

Table VI

Comparison Between Slush and Liquid Hydrogen Gels
6-cN weight-bearing capacity

Gels	Liquid Hydrogen		Slush Hydrogen Solid Fraction		
	At NBP	At Triple Point	0.10	0.20	0.40
Mass percent Cab-O-Sil	37.7	35.5	33.1	30.5	24.8

6.4 Observations

It is pertinent to point out some observations made during the course of the experiments. When an excess amount of LH_2 is present in the gel, the silica will settle, leaving a supernatant liquid at the top. However, once a gel is formed that can support any weight of plumb bob, no such settling occurs. The gel generally behaves like a semisolid homogeneous mass. There is some difficulty in stirring the gel when its weight-bearing capacity is large. In such cases, the stirrer would carve a hole in the center and compact gel on the gel dewar wall. Compaction of the mass presented a problem with weight-bearing capacity measurements close to the 10-cN weight range. This was overcome by increasing the silica mass in the gel dewar from 47 g to 51 g. The compaction occurs at higher than 10-cN weight-bearing capacity and continues until the gel becomes dry.

Prolonged stirring at high speed does not affect the gel structure. During the course of a slow evaporation for the measurement of the weight-bearing capacity, LH_2 gel showed no degeneration over a 2- to 3-hour period. If the silica is not kept well stirred and fluffed-up before the addition of liquid or slush, compaction of the dry gelant hinders thorough mixing of the mass to a homogeneous mixture. This could be serious with slush where prolonged stirring may melt away the solid fraction, thus rendering a slush run useless. The well-fluffed-up gelant does not produce agglomerates.

7. Conclusions

An experimental apparatus has been developed for the gelation of slush hydrogen, and gelation of liquid and slush nitrogen and hydrogen has been accomplished. This gelation of slush hydrogen is the first known attempt. The measurements of weight-bearing capacity of the gel versus weight percent gelling agent verify the gelled liquid and slush models discussed within the accuracy of the experiments. These models state that the number of gelling agent particles in the liquid is a constant, and that the mass percent gelling agent is proportional to the volume fraction of liquid in the slush. Only the effect of liquid density on the gelled liquid was verified. The effect of gelant particle diameter was untested. As an example of the reduction in the gelant requirement resulting from the use of slush, the mass percent Cab-O-Sil is reduced from 37.7 percent to 24.8 percent in going from NBP liquid hydrogen to slush hydrogen of 0.40 solid fraction.

In general, gelled liquid and gelled slush behave similarly. One important exception should be noted, however. The yield strength or weight-bearing capacity of gelled liquid nitrogen or hydrogen increases with the addition of heat because of liquid evaporation. The yield strength of gelled slush is reduced by the addition of heat because the melting solids dilute the gel.

The underlying objective in this work is to reduce Y, the mass percent gelant, in order to reduce degradation of the specific impulse of the fuel-oxidizer combination for rockets. Inspection of the models for gelled liquid and slush [equations (3) and (9)] point the way for future work on gelled hydrogen. Because Y is approximately proportional to the density of the gelling agent, less dense materials which also have a fuel value such as methane are desirable. The mass percent gelling agent should also be approximately proportional to the cube of the particle diameter. Thus, not only should particle size reductions yield significant improvement, but care must be taken in the preparation of low density gelants so that the gains due to reduced density are not counteracted by increased particle diameter. Finally, as demonstrated by this work, significant reductions in Y can be accomplished through the use of slush hydrogen.

8. Acknowledgments

The authors are indebted to D. B. Chelton and K. D. Timmerhaus for much valuable comment and discussion. We also wish to thank a number of the Cryogenics Division Staff who aided in the successful completion of this work.

9. Nomenclature

d	diameter of a gelling agent particle in meters
m	mass in kilograms
N_p	number of gelling agent particles in a gel
V	volume of the gel in m^3
V_ℓ	volume of liquid in the gel, m^3
V_g	volume of gelling agent in the gel, m^3
V_p	volume of gelling agent particle, m^3
W	plumb bob weight, newtons
X	solid cryogen fraction by mass
Y	mass percent of gelling agent in the gel

Y^*_ℓ	percent volume of gelling agent per unit volume of the liquid
$Y^*_{S\ell}$	100 × volume of gelling agent per unit mass of slush
ρ	density in kg/m^3

Subscripts

g	gelling agent
ℓ	liquid
ℓt	triple-point liquid
LH_2	liquid hydrogen
LN_2	liquid nitrogen
$S\ell$	slush
$S\ell H_2$	slush hydrogen
$S\ell N_2$	slush nitrogen

10. References

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11. Appendix

Approximate Conversion Factors

To convert from	to	multiply by
Length		
millimeter (mm)	inches	$3.937\ (10)^{-2}$
Pressure or Stress		
Newton/meter^2 (N/m^2)	psi	$1.450\ (10)^{-4}$
Newton/meter^2 (N/m^2)	mmHg (O C)	$7.501\ (10)^{-3}$
Newton/meter^2 (N/m^2)	dynes/cm^2	$1.000\ (10)$
Rotational Speed		
Radian/second (rad/s)	rpm	9.549
Volume		
meters^3 (m^3)	liter	$1.000\ (10)^3$
Weight or Force		
newton (N)	gram weight	$1.020\ (10)^2$
centinewton (cN)	gram weight	1.020

Prefixes

Prefix	SI Symbol	Multiplication factor
mega	M	10^6
kilo	k	10^3
centi	c	10^{-2}
milli	m	10^{-3}
nano	n	10^{-9}

GPO 850-889