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A. J. Beardell and R. Gere

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FINAL REPORT

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ABSTRACT

A freeze dry method was developed for the preparation of ultrafine particle size lithium fluoride. The ultrafine material, in the form of rods having approximately a length of 0.4μ and a width of 0.04μ, will thicken OF_2 but not liquid F_2. The liquid OF_2-LiF gel is both thermally stable and shock insensitive but is not stable under flow conditions.

Liquid OF_2-Cab-O-Sil gels were prepared in quantities of up to 1 lb. The gels were examined rheologically and mechanical stability tests, slosh tests and boiloff rates were measured. Pressure drops of 1 to 12 psi were produced across a capillary tube and apparent viscosities of 0.21 to 7.16 poise were measured. The OF_2-Cab-O-Sil gel behaved satisfactorily in slosh tests but boiloff rates and inverted tube tests gave inconclusive results.

FOREWORD

This report was prepared by Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, under Contract NAS 3-6286. The work was administered under the technical direction of the Liquid Rocket Technology Branch, NASA Lewis Research Center.

The research effort reported here was conducted during the period 5 May 1965 to 4 September 1966 on RMD Project 5070. Dr. S. Tannenbaum was program manager. The bulk of the OF_2 and F_2 gel formulation and testing studies were performed under the direction of Mr. A. Lum with assistance from Mr. E. Avrutik, Mr. P. Minetti, and Mr. R. Walker. The new gellant investigation was conducted by Dr. A. Young, Mr. R. Gere supervised the scaled up OF_2 gel studies with the assistance of Mr. D. Sinclair. Dr. A. J. Beardell acted as program consultant and was program supervisor during the terminal phases of the program.

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GELLING OF CRYOGENIC OXIDIZERS

by

A. J. Beardell and R. Gere

Thiokol Chemical Corporation
Reaction Motors Division

I. SUMMARY

Oxygen difluoride when gelled with Cab-O-Sil (a pyrogenic silica) appears to be shock sensitive when tested in the Trauzl Block test. However, it will not propagate a detonation when initiated with 100 g of tetryl in a detonation velocity test. The OF_2-Cab-O-Sil gel cannot be characterized rheologically because of liquid exudation and apparent dilatency under dynamic flow conditions. Both a laboratory type capillary viscometer and a Brookfield viscometer were used in the attempt to produce rheological data.

OF_2-Cab-O-Sil gels were prepared in up to 1 lb quantities and pressure drop, slosh, boiloff and mechanical stability information were obtained. At pressure drops of 1 to 12 psi, apparent viscosities ranging from 0.21 to 7.16 poise were obtained for a system containing 2.3 percent gellant. A gelled OF_2 (2.7 percent Cab-O-Sil) showed no discernible motion in slosh tests and boiloff rate tests were inconclusive.

Several explosions occurred with OF_2 gels but all occurred in high friction areas where Teflon was present and therefore could be attributed to the instability of Teflon in the presence of OF_2 under dynamic flow conditions.

A freeze drying method was developed for preparing lithium fluoride in ultrafine particle size. The resulting material will thicken OF_2 but the gel characteristic of this system appears to be less satisfactory than the Cab-O-Sil system. The OF_2-LiF gels (at approximately 3.0 percent gellant concentration) are thermally stable and shock insensitive as determined by the Trauzl Block test. It was not possible to obtain rheological data on the gel because it appeared to be unstable under flow conditions.

Lithium fluoride in ultrafine particle size did not give a satisfactory gel with liquid fluorine.

II. INTRODUCTION

Gelled propellants can improve spacecraft system performance in several ways. (1) gel rigidity limits or eliminates sloshing and unpredictable movement of the propellant center of gravity; (2) improved expulsion and propellant utilization may result from a gel's tendency to cohere to itself; (3) decreased free convection transfer from gels should help to minimize propellant boiloff with cryogenic or space storable propellants; (4) high energy solids can be dispersed in gels and this can result in improved specific impulse.

With these possible advantages in mind, Thiokol-RMD undertook a program under NASA sponsorship to investigate the possibility of gelling liquid oxygen difluoride, which is a prime candidate oxidizer. In a previous program (Ref 1), inorganic oxides and fluorides were screened as possible OF_2 gellants and Cab-O-Sil, a pyrogenic silica, appeared to form a suitable gel. Alon C (Al_2O_3) and TiO_2 also gave satisfactory gels, although these did not appear to be of comparable quality. The OF_2-Cab-O-Sil gel was evaluated for thermal stability and mechanical stability, and boiloff rates were determined but the shock sensitivity of the mixture was not satisfactorily evaluated. Also, quantitative rheological data were not obtained and the gel was prepared only in limited batch sizes (2 to 4 g).

The current program is concerned with the preparation and characterization of scaled up quantities of gelled OF_2. In addition, new gellants for OF_2 were investigated, and a limited effort was devoted to the gelation of fluorine.

The program has been conveniently divided into three tasks which are:

Task I - Liquid OF_2 Gels Made with SiO_2

This work involved the investigation of the shock sensitivity of the OF_2-SiO_2 gels, the measurement of its flow characteristics, the preparation and characterization of scaled up quantities of the gel, and if necessary, the testing of alternate oxide systems.

Task II - New Gelling Agents

This study involved the preparation and evaluation of fluoride type OF_2 gellants which are compatible with OF_2.

Task III - Gelling of Liquid Fluorine

The objective of this study was the preparation and characterization of gelled liquid fluorine.

III. LABORATORY STUDIES

A. Apparatus and Procedure

1. OF_2 and F_2 Handling

Conventional vacuum line procedures were used in handling both OF_2 and F_2. For laboratory usage, the oxidizer was transferred from commercial tanks to 1 liter stainless steel vessels, which were then attached to the vacuum line.

A system was also constructed so that relatively large quantities of OF_2 could be handled remotely. The system was designed so that the OF_2 could be transferred to a mixing vessel and after mixing, transferred by means of the dip tube to an apparatus in which gel sensitivity could be tested. A typical operation where this procedure was used consisted of the following. The mixing vessel was charged with the required amount of gellant after which it was degassed. The required amount of OF_2 was then transferred to the vessel at liquid nitrogen temperature and mixed with the gellant using a magnetically actuated stirrer. The vessel was then pressurized with He to transfer the OF_2 gel through the dip tube into the testing vessel. Unfortunately, repeated attempts to make the transfer failed because of coring or gel separation and the technique was abandoned.

2. Shock Sensitivity Tests

a. Trauzl Block Tests

The RMD modified Trauzl Block test consists of attempting to initiate 1 to 2 grams of a test sample in a lead cylinder 2.5 in. high, 2 inches in diameter, with an internal diameter bored to one inch. The sample, contained in a glass ampoule, is inserted into the lead block cavity and is subjected to a shock generated from a No. 8 blasting cap. In the case of OF_2, the samples were tested at liquid nitrogen temperature. This is accomplished by sealing the sample in the glass ampoule at liquid nitrogen temperature, placing it in the Trauzl block immediately and firing.

The rating in the Trauzl Block test depends on the expansion of the cavity due to the sample. Blanks are run so that the expansion due to the blasting cap, plus inert mass, can be subtracted from the total expansion. When cryogenic materials are tested, blank values are obtained from tests using liquid nitrogen as the inert mass. Liquid nitrogen is used to simulate the cryogenic properties of OF_2.

b. Detonation Velocity Tests

The detonation velocity tests were performed using a constant current resistance wire method. The method provides complete and accurate history of any detonation that passes through a container of any size or shape. The functioning of the resistance wire method depends on the high degree of ionization existing in the reaction zone of a detonation. The advancing detonation completes the circuit between a central resistance wire and the metal test container maintained at ground potential. A constant current is maintained through the circuit during the test and the progress of the detonation wave is followed by monitoring the potential across the wire as a function of time. Under constant current conditions, the potential is related to the resistance which is directly proportional to the length of the resistance wire in the circuit. The data are obtained in terms of a voltage-time trace on an oscilloscope and a Polaroid camera is used to record the event.

Several experiments employing the resistance wire method were aborted due to a compatibility problem between the OF_2 and the feed-thru connector in the sample container. Therefore, another method of sensing a detonation wave was employed which depends on the high pressure present in the reaction zone. The sensing probe used in these experiments consisted of a carbon transducer placed on the exterior wall of the sample container. It operates under the principle that the resistance of the element depends on the degree of compression of the carbon. Therefore as the shock front passes, it compresses the carbon element. By employing a constant current source (identical to that used in the resistance wire method) voltage is varied and is monitored on an oscilloscope. By placing the transducer at a fixed point on the sample container, detonation velocities can be obtained by noting the time before the transducer is activated.

The detonation velocity tests were performed in stainless steel tubes one inch in diameter and eight inches long. Initiation was attempted with 100 g of Tetryl which was ignited with a No. 9, "Engineers Special" blasting cap. The bottoms of the tubes were sealed with 0.015 inch steel diaphragms welded in place. The tops of the tubes were sealed with 1/2 inch thick 5 in. x 5 in. steel plate centrally welded to the stainless steel tube. The steel plate is tapped to provide for a 3/8 in. AN fitting employed to fill the sample container. An insulated feed-thru connector is also fitted into the plate to provide an external connection for the resistance wire.

The plate welded at the top of the sample tube also serves as a witness plate. If a detonation takes place, a hole is cleanly punched through the plate and of course, when no detonations occur, no damage to the plate is observed.

The tests were conducted at liquid nitrogen temperatures and under these conditions the plate fragments slightly, due to the brittleness of the metal at the low temperatures.

3. Rheological Measurements

A capillary flow viscometer was investigated as a means of measuring the flow properties of OF_2 gels. A sketch of the apparatus is given in Figure 1. The apparatus consists of a glass tube in which a reciprocal stirrer and a capillary tube are inserted. They are attached to the tube through the use of Teflon seals which can be easily loosened. In a given run a weighed quantity of the gellant is placed in the tube and the OF_2 is condensed over the gellant through a side arm which is attached to a vacuum section.

The quantity of OF_2 used is determined from PV relations. The mixture is then stirred with the capillary tube positioned above the gel. The stirrer is then lowered to the bottom of the tube and the capillary tube is set in place. By means of helium gas pressure, the OF_2 gel is forced to flow through the capillary and past two reference points. By obtaining the flow time as a function of pressure and applying the appropriate flow equations, shear stress and shear rate relationships for the OF_2 gel can be obtained.

In addition, a Brookfield Synchro-Electric viscometer, Model No. HBF, was used with a helipath stand. The cup used to contain the gel was the tube section of the capillary apparatus. The capillary tube was replaced by a bar type spindle of the Brookfield instrument. The data obtained from the standard bar type spindle could be converted to absolute viscosity by means of a conversion table supplied by the manufacturer. A flat rectangular spindle was also used in the investigation in attempts to measure flow data on the gels.

4. Thermal Stability Studies

In order to determine the long term storage characteristics of OF_2-LiF gel at -196° C, stability studies were performed. Weighed samples of LiF, vacuum dried at 160° C, were placed in both Kel-F tubes and Pyrex glass breakseal ampoules and known amounts of OF_2, as determined from PVT relationships, condensed on top of the LiF.

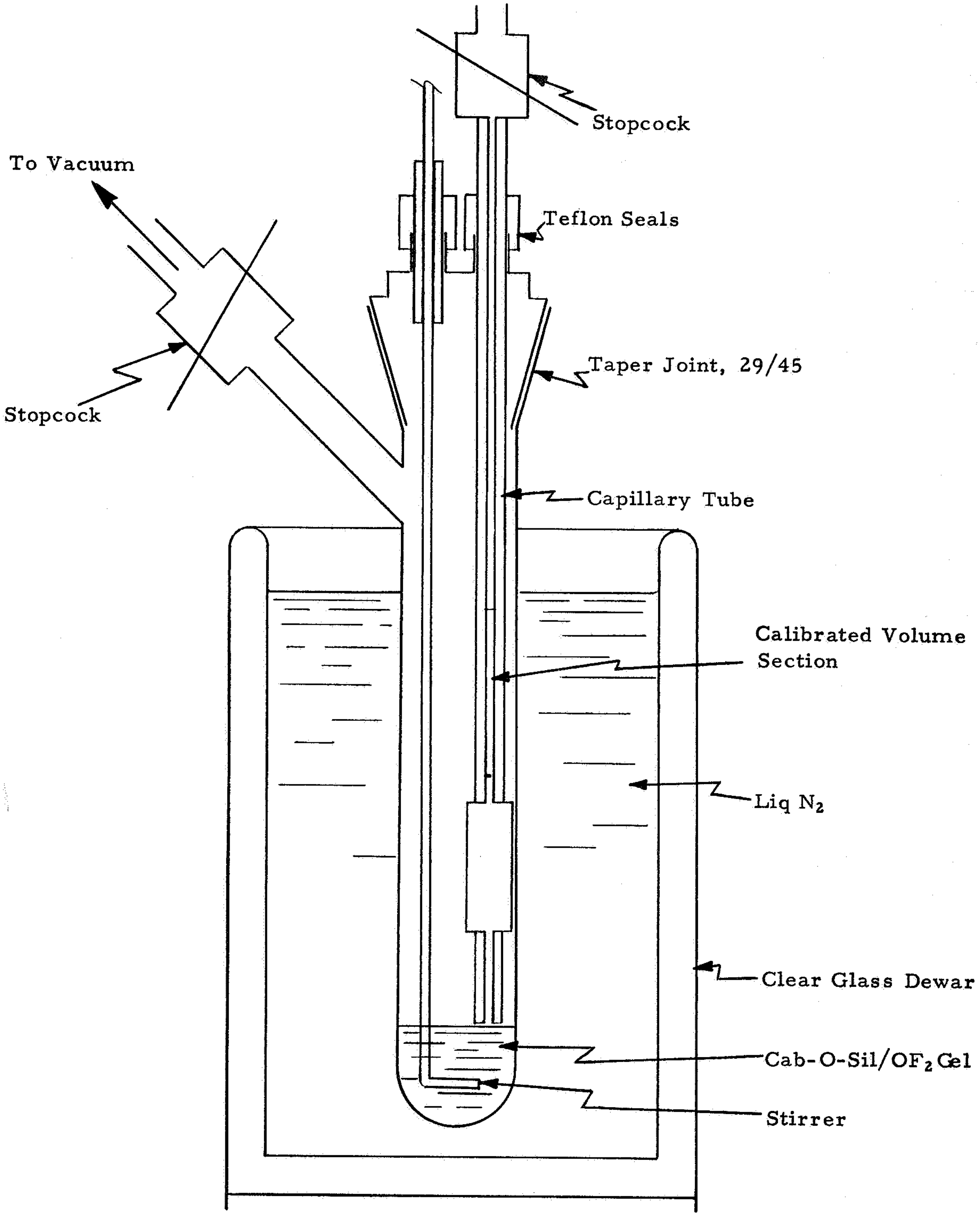


Figure 1. Cryogenic Viscometer

5. Inverted Tube Test

In conjunction with the long term stability studies, inverted tube tests on LiF-OF_2 gels were initiated to determine if OF_2 exudation would occur. In this test, samples of OF_2-LiF gels in the range of 3 to 4.2 wt percent were sealed off under vacuum and carefully inverted so that the gel remains at the top of the tube. Visual observation to determine the bleeding characteristics, if any, of the system were then made.

B. Materials

1. Oxygen Difluoride and Fluorine

The OF_2 and F_2 were obtained from Allied Chemical Corporation. The purity of the OF_2 as received was 97 percent, and was purified in the laboratory by vacuum pumping at -196°C. Mass spectral analysis shows 99 percent + OF_2 with a trace quantity of CO_2 as the only impurity present. The fluorine was used as received.

2. Cab-O-Sil

The Cab-O-Sil was received from Cabot Laboratories. The various grades used and their distinguishing features are shown below:

Grade	Particle Size (microns)	Surface Area (m^2/g)	Density (lbs/cu ft)
M-5	0.012	200	2.3
M-7	0.012	200	4.0
MS-7	0.012	200	4.0-5.0
HS-5	0.007	325	2.3
EH-5	0.007	390	2.3

3. Inorganic Fluorides

The LiF and NaF are reagent grade from Fisher Scientific Company. The fine particle size fluorides were prepared by the freeze-drying technique. The method requires a means of rapidly freezing a solution with subsequent vacuum evaporation for the removal of the solvent.

In initial studies to prepare ultrafine particle size fluorides, standard laboratory equipment was used. The initial freeze drying apparatus consisted simply of a 1 liter round bottom flask, a 2 liter filter flask, and a vacuum pump. A 200 ml aliquot of a filtered saturated solution of LiF in water was poured into the 1 liter round bottom flask. The solution was rapidly frozen to give a thin uniform layer on the walls of the flask by rotating the flask in a Dewar containing a dry ice-acetone slush bath. The flask containing the frozen solution was attached to the 2 liter flask by means of a short length of heavy walled rubber tubing and evacuated. The filter flask was immersed in a dry ice-acetone bath, thus serving as a trap for the water which began to sublime from the frozen solution at pressures of 0.1 mm or less. When a proper balance between sublimation rate and the heat input to the flask was maintained the solution remained frozen until all the water was removed, even though the flask was in an ambient environment. The residual LiF was in the form of a solid foam which assumed the shape of the container. The foam was easily broken up to yield feathery, electrostatically charged agglomerates. If on the other hand, the pressure rose above 0.1 mm during the sublimation for reasons such as air leakage, or plugging of the condensation trap, then the residual LiF was obtained in the form of macro particles.

The production of submicron LiF by this procedure was therefore limited by the surface area and capacity of the condensation trap and by the rate of evaporation of dry ice from the slush bath. (The latter factor was a serious problem on overnight or week end runs.) By using a manifold arrangement we were able to process three 200 ml aliquots or approixmately 0.4 gm LiF every 20 hours (excluding week ends) in our crude laboratory apparatus. A great improvement in our ability to remove the submicron LiF to a storage jar with minimal loss was made by substituting commercial freeze drying flasks for the ordinary laboratory round bottom flasks used in the initial runs.

The commercial freeze dryer is a Thermovac Model FD-6. The unit is a mechanically refrigerated mobile freeze dryer providing temperatures on the condenser to -60° F and with a condenser capacity of 6 liters. There are 20 drying ports which are provided with special vacuum valves which allows for easy connecting and disconnecting of flasks while the unit is under vacuum. Since each flask can provide enough LiF solution to produce about 2 g of LiF, the apparatus is capable of a maximum production capacity of 40 g per run although this amount was not achieved in practice. A photograph of the unit is shown in Figure 2.

Figure 2. Commercial Freeze-Dry Unit

C. Results and Discussion

1. Preparation of New Gellants

A recent paper by Landsberg and Campbell (Ref 2) describes the use of a freeze-drying technique for the production of metal particles of size in the 20-50 Å range. Since particle size is a primary factor controlling the utilization of particulate matter as gelling agents, this technique was investigated as an approach to obtaining submicron particles of inorganic fluorides.

Briefly, freeze-drying involves two steps, namely; (a) a solution of the fluoride is frozen at such a rapid rate that precipitation of solute does not occur; and, (b) the solvent is removed by sublimation in vacuo, leaving the solute in approximately the state of subdivision in which it existed in the original solution.

Water is an ideal solvent for the preparation of the inorganic fluorides by use of the freeze-drying technique. It has a freezing point near ambient, a significant vapor pressure below its freezing point, and a high heat of sublimation. The latter property is important because the bulk of the solvent can be maintained below its freezing point by the cooling effect of sublimation. If melting occurs during the removal of the solvent, the solute may redissolve and undergo particle growth and precipitation as the solvent evaporates.

a. NaF-Glacial Acetic Acid

A solution of NaF in glacial acetic acid was used in an initial examination of the freeze-drying technique as a means of producing OF_2 gellants. Acetic acid has excellent physical properties to recommend it as a solvent for freeze-drying and the solubility of NaF in the acid is low (1-2 percent). Its freezing point is 16.7°C and it has a significant vapor pressure at 17°C. Upon freeze-drying a dilute NaF solution in acetic acid, a residue was obtained that obviously consisted of submicron size particles. Unfortunately, however, the NaF had undergone partial solvolysis ($NaF + CH_3COOH \rightleftarrows HF + CH_3COONa$) and the residue contained a large proportion of sodium acetate.

b. LiF-Water

Experiments were performed on aqueous solutions of LiF, which has a low solubility in water (0.125 g/100 ml at 27°C). After several unsuccessful runs caused by a poor vacuum (which reduces the rate of sublimation), 0.1 g samples of LiF were obtained which appeared to be in the particle size range typical of the Cab-O-Sil gellants currently being used for OF_2. Subsequent experiments were performed in which 0.5 gram of LiF was obtained in six hours.

Three semiquantitative indications of the particle size range of the freeze-dried LiF were obtained: (a) its sedimentation volume in toluene is over 100-fold greater than that of LiF as received from the vendor, which has a sedimentation volume of 6 ml/g in toluene; (b) small quantities of the freeze-dried LiF dispersed in toluene displays the Tyndall effect, and (c) particles of freeze-dried LiF could not be resolved by a microscope having a resolution of $\sim$0.25 microns.

A sample of LiF, freeze-dried from 200 ml of a saturated aqueous solution (0.125 g/100 ml) was also examined by electron microscopy. The micrographs (Figure 3) show that the freeze-dried LiF exists in the form of rods which are approximately 0.4 μ long and 0.04 μ thick.

c. Gelation Studies

In order to test the effectiveness of freeze-dried LiF as a gellant for liquid OF_2, 1 gram of liquid OF_2 was condensed onto 0.03 gm LiF at -196°C in an evacuated glass apparatus. Gel formation was observed upon stirring the mixture at -196°C.

2. OF_2 Gel Characterization

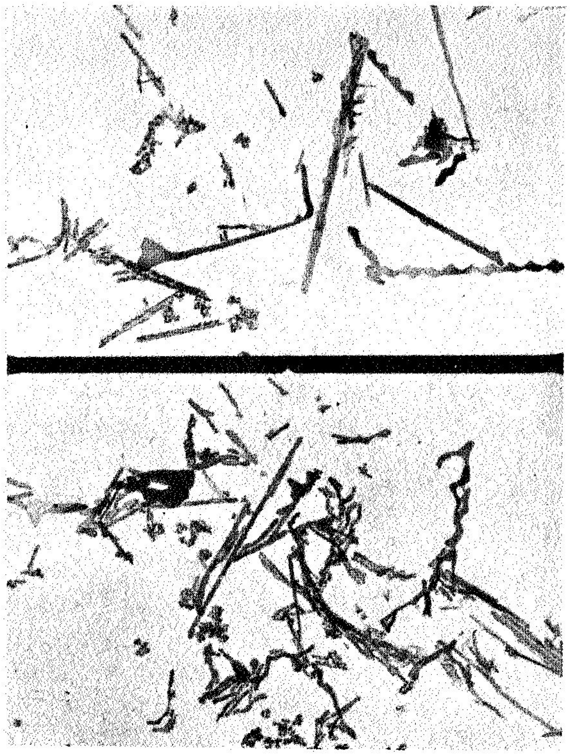
a. OF_2-Silica Gel

(1) Shock Sensitivity Tests

During the previous program only limited safety testing was performed on the Cab-O-Sil/OF_2 system and these data indicated that the Cab-O-Sil/OF_2 system was safe to handle. However, this system is capable, thermodynamically, of a considerable energy release. It was, therefore, considered necessary to evaluate and assess its safety in a more thorough manner. The Trauzl Block test was used in the major portion of the testing. The effect of gellant concentration, of silica gel type and heat treatment were investigated. In addition to Trauzl tests, detonation velocity tests were also performed in which larger samples were used.

(a) Trauzl Block Tests

The first series of Trauzl Block experiments were performed on neat OF_2 in glass and in Kel-F containers. Two sample loadings (1.45 g and



Magnification: 5000X

Figure 3. Electron Micrograph on Ultrafine Lithium Fluoride

2.9 g) were employed and the data are presented in Table I. From these data it appears that OF_2/Kel-F is explosive but with glass, the results are not as definitive. When 1.45 g is used, essentially no expansion over and above that of the liquid nitrogen blank was experienced. When 2.9 g of OF_2 was used, expansion values of 8 cc/g were obtained indicating a mild explosion, which is probably a result of the reaction of the OF_2 with fuel decomposition gases of the blasting cap.

Table I

Results of Trauzl Block Tests on Neat OF_2 at -196°C

Weight of OF_2 (g)	Container Material	Expansion+ (cc/g)
1.45	Kel-F	10.0
1.45	Kel-F	10.7
1.45	Glass	1.7
1.45	Glass	1
2.90	Glass	8.0
2.87	Glass	7.1

+Corrected for a blank containing liquid nitrogen.

A series of Trauzl block tests were also performed on OF_2/Cab-O-Sil gel system. These tests were performed with various grades of Cab-O-Sil and two OF_2 weights of 1.45 and 2.9 g and with Cab-O-Sil concentrations ranging from 3.3 to 9.3 percent. In addition, one series of runs was performed in which the silica gel was dried at 500°F for 72 hours. Evaluation of the Trauzl Block data was based on the use of liquid nitrogen as a blank, which allowed for corrections due to rapid vaporization of the cryogenic liquid at the moment of initiation.

The data are presented in Table II. The runs were performed in duplicate except for the OF_2 mixed with the M-7 Cab-O-Sil. In most cases the expansion for a given set of runs agreed to within 2-3 cc/g. The following statements summarize the results.

(a) The OF_2-Cab-O-Sil mixtures gave expansions ranging from 3 cc/g to rupture of the lead block.

(b) There were no indications of a relation between the expansion of the lead block and the particle size of the Cab-O-Sil. In fact, the EH-5 Cab-O-Sil gave the lowest expansions even though it has the largest surface area.

(c) The Cab-O-Sil after drying at 500°C for 72 hours showed no difference in the magnitude of the expansion except in one test in which the lead block ruptured.

(d) In general, the extent of the reaction in the Trauzl test is independent of concentration of gellant, and size of the sample used.

Table II

Trauzl Data on OF_2-Cab-O-Sil Gels

Number of Runs	Cab-O-Sil Grade	OF_2 (g)	Cab-O-Sil (percent bw)	Expansion (cc/g)
5	M-7	1.45	3.3	6 ± 5
1			3.7	23
2			7.0	17 ± 2
2			9.3	17 ± 1
2		2.9	3.5	15 ± 0
2			6.5	9 ± 1
2			9.8	8 ± 1
2	HS-5	1.45	3.3	14 ± 0
2			6.5	12 ± 2
2			9.3	16 ± 0
2		2.9	3.3	13 ± 2
2			6.5	11 ± 1
			9.3	12 ± 1
2	M-5	1.45	3.3	12 ± 3
			6.5	13 ± 1
			9.3	13 ± 1
2		2.90	3.5	12 ± 4
2			6.5	9 ± 4
2			9.3	12 ± 6

Table II (Continued)

Number of Runs	Cab-O-Sil Grade	OF_2 (g)	Cab-O-Sil (percent bw)	Expansion (cc/g)
2	MS-7	1.45	3.3	11 ± 2
2			6.5	19 ± 2
2			9.4	12 ± 1
2		2.90	3.3	15 ± 1
2			6.5	14 ± 4
2			9.4	3 ± 0
2	EH-5	1.45	3.3	8 ± 1
2			6.5	10 ± 2
2			9.4	9 ± 0
2		2.9	3.3	8 ± 0
2			6.5	4 ± 0
2			9.3	8 ± 1
2	M-7 Dried (500°C for 72 hours)	1.45	3.3	8 ± 0
2			6.5	10 ± 1
2			9.5	16 ± 0
2		2.90	3.5	9 ± 1
2			6.5	9 ± 1
1			9.3	18
1			9.3	Rupture

Tests were also performed using a silica gellant obtained from Midwest Research Institute, and Aerosil, a silica gellant having properties comparable to Cab-O-Sil. These results are shown in Table III and the data are similar to those obtained with Cab-O-Sil.

The data undoubtedly indicate that a reaction is taking place between the OF_2 and the silica gellant. This does not seem unreasonable since thermodynamically, the interreaction is possible. This test, however, may be too severe for this system since it imparts conditions on the sample which may never exist in practical use. In the Trauzl test, a No. 8 blasting cap is ignited which produces a detonation wave which travels through a relatively small mass of material. The wave front contains ionized particles and excited species which could initiate a reaction, and this, coupled with the shock front (which is a compression wave), provides an ideal condition for adiabatic heating. This could elevate temperatures considerably and serve to initiate a reaction between the OF_2 and Cab-O-Sil. Since relatively small samples are used there is insufficient material in the environment to act as a heat sink.

Table III

Trauzl Data on OF_2-SiO_2 Gels

Number of Runs	Silica Gellant	OF_2 (g)	Gellant (percent bw)	Expansion (cc/g)
2	Midwest	1.45	3.3	2 ± 1
2	Research		6.5	10 ± 1
2	Institute		9.5	13 ± 1
		2.9	3.3	2 ± 1
			6.5	19 ± 3
			9.5	3 ± 1
2	Aerosil	1.45	3.3	8
1			6.5	15
1			6.5	Rupture

(b) Detonation Velocity Tests

Because of the inconclusive nature of the Trauzl test data, the OF_2/Cab-O-Sil gels were subjected to large scale shock tests. Three tests on 2 percent Cab-O-Sil gels were performed using the modified detonation apparatus. The probes were fixed 2-1/2 inches above the donor charge and no detonations were observed as exhibited by both photographic and physical evidence after each test. The physical damage on the sample tube was identical to that obtained for liquid nitrogen. Had the material detonated, the sample tube would have been completely disintegrated. With the theory that perhaps the run fixture and sample size (75 g) of the initial experiments were not sufficient to allow a detonation to develop, an 8 in. long x 1 in. sample tube filled with 160 g of the 2 percent Cab-O-Sil gel was tested. The probe was positioned seven inches from the donor charge and again, no evidence of a detonation was observed. Approximately 3 in. of the sample tube was recovered which is identical to that recovered for liquid nitrogen. No pressure change was observed on the oscilloscope monitoring the pressure probe.

A similar test was performed using a 3.7 percent Cab-O-Sil gel. In this experiment the fixture was sealed with a 0.015 inch steel diaphragm rather than the 0.025 inch diaphragm used previously. This was done in order to decrease the attenuation of the shock pressure as it passes through the diaphragm. The 0.025 inch diaphragm is equivalent to 5 cards of attenuation when these data are compared to card gap values. With the use of the 0.015 inch diaphragm, a greater shock pressure would be experienced by the sample. Again, this experiment gave no indication of a detonation occurring in the sample.

The detonation velocity tests indicate that the system is safe to handle. However, this does not agree with the data obtained from the Trauzl block tests where there were clear indications that a reaction is occurring between the OF_2 and Cab-O-Sil. Perhaps, in the case of the large scale tests, the mass of the sample is playing a role in preventing propagation of the reaction.

(2) Rheological Studies

A major effort was directed toward the development of a suitable apparatus for the determination of the rheological characteristics of OF_2 gels. Previous attempts to secure flow data on the OF_2-SiO_2 system (Ref 1) using rotational type viscometers (Epprecht Rheomat Model RM15 or a Brookfield Model HBF) proved unsuccessful due to coring by the rotating bob. In addition, a capillary viscometer was tested without success.

The capillary viscometer was redesigned to avoid some of the undesirable elements previously encountered. The major modification involved the position of the capillary. In the previous study, the capillary was attached horizontally to the bottom of the tube. In the current design, the capillary section is positioned vertically inside the tube and is immersed in the gelled medium.

The flow equations that are required for a glass capillary viscometer with an applied external pressure are as follows.

The rate of shear is given by

$$-\frac{dv}{dr} = 4V/\pi R^3 t \qquad (1)$$

where $\frac{dv}{dr}$ is the shear rate in sec^{-1}

V is the volume of the reservoir in cc's

R is the radius of the capillary in cm's

t is the time in seconds

The shear stress is given by

$$S = (4V/\pi R^3)(ap + bH - c/t^3) \tag{2}$$

where S is the shear stress in dynes/cm^2

H is the applied pressure head in dynes/cm^2

p is the density of the mixture in g/cc

a, b, and c are constants

The constants can be determined by the use of three different standard oils.

Before attempting to run viscosities on the OF_2 gels, the apparatus was tested to determine its utility and pressure-flow rate data were obtained on select systems which could be used as calibration fluids. Also an OF_2-SiO_2 gel was prepared, and an attempt was made to measure its flow characteristics, using the capillary viscometer.

(a) Capillary Viscometer Feasibility and Calibration

As previously indicated, it is necessary to have flow data on three standard fluids for calibration purposes. The approach taken was to use gels of known flow characteristics instead of standard oils. Thus, the calibrating fluids would have non-Newtonian characteristics similar to the OF_2 gels; the study also provides information on the feasibility of the apparatus as a rheological instrument.

One of the gels initially chosen for investigation was a liquid O_2-SiO_2 (Cab-O-Sil) system. A 3.85 percent bw mixture was made using 0.4 g SiO_2 and 10 g of liquid O_2. Mixing at -196°C was accomplished by use of a reciprocating stirrer through a Teflon seal. However, as soon as the mixing ceased, the SiO_2 settled out and no gel could be formed. Following this, a dodecane-SiO_2 gel was prepared and tested. However, repeated tests on this system failed to show reproducibility of the flow rate of the material at a given pressure (5 to 50 mm Hg). It appears that the gel shear thins after pressurization or on standing.

The decision was then made to test a water-Carbopol gel. This gel has been tested by a number of laboratories under the supervision of the Interagency Chemical Rocket Propulsion Group (ICRPG) in an attempt to supply a standardized gelled fluid to the propellant industry.

The Carbopol 940-H_2O gel was run at ambient temperature and the results for this gel system are shown in Table IV.

Table IV

Calibration Tests of Capillary Viscometer With 0.5 Percent Carbopol 940-Water Gel

	He Pressure (mm Hg)	Time to Fill Calibrated Vol (sec)
Run No. 1	46	282.0
	52	132.1
	61	73.7
	66	80.0
	75	38.6
	86	35.6
Run No. 2	44	401.0
	50	202.4
	59	103.6
	66	64.5
	70	53.5
	73	44.2
	90	19.3

These results show good reproducibility and appear to justify the feasibility of the apparatus.

A second gel tested was the water-SiO_2 system. A gel of approximately 10 percent Cab-O-Sil (M-7) and 90 percent water was prepared. This mixture was creamy white in appearance and did not show signs of shear thinning when tested in a syringe. A portion of the gel was placed in the viscometer and tests were run as before. The results are shown in Table V.

Table V

Capillary Viscometer Tests on SiO_2-Water System

He Pressure (mm Hg)	Time (sec)
25	126
25	155
25	137 let gel stand 30 minutes
25	159 let gel stand 15 minutes
25	179 let gel stand 15 minutes
25	159
Ave	152

From the above data it appears that a suitable degree of reproducibility could be obtained with a Cab-O-Sil-H_2O gel; however, it was observed that the rate of initial pressurization was an important factor in flow measurements.

(b) OF_2 Gel Studies

Before proceeding further with the calibration it was decided to run OF_2 and an OF_2 gel in the apparatus. If pressure-flow rate data could be obtained, then further efforts would be made to complete the calibration runs.

As a prelude to studies on the OF_2-SiO_2 system, initial tests were made using OF_2 alone at -196°C. Approximately 8.7 g of OF_2 was condensed from a calibrated vacuum system into the viscosity apparatus. Since the capillary tube being used was larger in diameter than required for extremely fluid materials, such as OF_2, no significant readings were obtained; however, the mechanical feasibility of the apparatus was found to be satisfactory.

Since the above data have shown that a capillary type viscometer could be used for SiO_2-H_2O gels, OF_2-SiO_2 gels (3-3.5 percent SiO_2) were prepared and attempts were made to secure viscosity data. The results are shown in Table VI.

Table VI

Viscosity Measurements for OF_2-SiO_2 Systems

Number of Runs	Gellant Concentration (percent bw)	He Pressure (mm Hg)	Time to Fill Calibrated Volume (sec)	Remarks
1	3	5	---	Gel separated under pressure. Let stand 30 min after remixing for 5 min.
1	3	14	34	Appeared satisfactory. Mixed 5 min more and let stand for 30 min.
1	3	10	---	Gel separated under pressure.
2	3.5	20	---	Gel separated under pressure.

It appears that the OF_2-SiO_2 gel, when exposed to an external stress, separates much in the manner that water can be squeezed from a sponge. This was also noted with SiO_2-dodecane gels, and indicates that the gel may thicken under stress (dilatancy) and therefore will resist flow.

Further attempts to characterize the gel produced the following information.

(a) The gel, after separation in the capillary viscometer, was remixed for 30 minutes, but separation again occurred when attempts were made to measure flow properties.

(b) A 3.5 percent SiO_2 gel of OF_2 was vented allowing all of the OF_2 to evaporate. After approximately 24 hours, the OF_2 was again condensed over the SiO_2 and mixed but no gel formed.

Since it was found that Cab-O-Sil-OF_2 gels sheared thick under slight pressures, gelation of OF_2 with ultrafine particles of LiF (prepared by the freeze-dry method) was then attempted, to ascertain if this system exhibited like properties. Initially, a 3.3 wt percent LiF-OF_2 gel was prepared. However, this gel was too thick, necessitating dilution by addition of more OF_2. The resulting system had a gellant content of 3.1 percent and after remixing was about equal in consistency to a 3.5 percent Cab-O-Sil gel; it appeared by visual observation to be stable for at least three hours.

Due to the limited quantity of LiF available for testing, it was not possible to prepare enough OF_2-LiF gel for viscosity measurements in the capillary viscometer.

b. OF_2-LiF Gels

As previously stated, OF_2 was gelled with approximately 3 percent LiF. The mixture had a putty-like consistency and remained in place when the tube was inverted. The low concentration of LiF required to form a gel and these visual observations led us to believe that a true gel may have been formed. It was therefore desirable to attempt a further characterization of this system.

(1) Rheological Studies

Since the capillary viscometer did not appear to be applicable for OF_2-LiF gels, it was next decided to attempt to secure viscosity measurements by utilizing the Brookfield Synchro-Electric Model HBF viscometer in conjunction with the helipath stand. The use of the helipath stand permits the rotating spindle to be continuously lowered into the test material, thus eliminating the "channeling" effect which occurs when the spindle is allowed to rotate in the cavity created by its rotation.

Initially, a 3.6 wt percent LiF-OF_2 gel was prepared, and an attempt was made to secure rheological data using the smallest bar type spindle available. Repeated efforts to secure readings on the Brookfield were unsuccessful. It appeared that the gels did not offer enough resistance to rotation even at the extremely slow rotational speed of 1 rpm to give a scale reading. In order to determine if a thicker gel would offer enough resistance to give a scale reading, a 4.5 wt percent LiF-OF_2 mixture was prepared and mixed until it appeared to be homogeneous. A number of runs were made, in which the rotational speed was varied over the available range, and the gel was remixed between runs. Initially, a slight difference in scale readings was observed (from 5.5 at the fastest speed to 1.5 on the slowest speed) however, these readings could not be reproduced. Repeated runs on the same batch gave the same reading, 1.5, at all speeds. A gel containing 5.2 percent bw LiF was prepared and attempts were made to secure rheological data by means of the Brookfield viscometer and helipath. As in the previous run, no meaningful, or reproducible numbers were obtained at any of the four speeds. The spindle appeared to core as it cut a path through the gel. Difficulties were encountered using a wire type spindle. It therefore appears that, with the equipment available, no suitable method for securing reliable and/or meaningful rheological data for OF_2 gels is possible.

(2) Safety Tests of LiF-OF_2 Gels

Trauzl block tests were performed on the OF_2-LiF gel system. The expansion values group in the range of 4 to 8 cc/g which is practically identical to the range obtained for neat OF_2. These data are presented in Table VII.

Table VII

Trauzl Data on the OF_2-LiF Gels

Wt of OF_2 (g)	LiF (percent bw)	Expansion (cc/g)
1.45	6.5	4.0
1.45	6.5	6.0
1.45	9.4	5.6
1.45	9.4	4.4
2.90	3.3	8.1
2.90	3.3	7.0

(3) Thermal Stability Studies

Since ultrafine LiF thickens OF_2 to a gel-like mass, long term thermal stability studies of this system at -196°C were initiated. A fresh sample of OF_2 was secured and purified by pumping at -196°C. Mass spectral analysis of the purified OF_2 showed only a trace of CO_2 present. The LiF was vacuum dried at 170°C for 24 hours, and IR analysis showed only trace amounts of water. Weighed amounts of the dried LiF were placed in Kel-F tubes attached to Hoke needle valves, and known quantities of OF_2 were condensed into the tube from a calibrated vacuum system. Four samples were immersed in a Dewar of liquid N_2 for storage. The data for these samples are shown in Table VIII.

Table VIII

Thermal Stability of OF_2-LiF Gels at -196°C

Sample No.	LiF (g)	Initial OF_2 Charged (mm Hg at -196 °C)	OF_2 After Storage (mm Hg)	Days
1	0.0200	104	102	8
2	0.0290	99	97	23
3	0.0210	106	103	34
4	0.0247	106	104	37

In all cases, no non-condensable gases were found and mass spectrometric analysis of the recovered OF_2 showed it to be essentially that of the starting material. IR analysis of the LiF after storage showed it to be essentially that of the starting material. IR analysis of the LiF after storage showed no significant change from that of the starting material. It appears that OF_2-LiF gels are thermally stable at -196°C for at least 37 days.

(4) Inverted Tube Tests

In addition to the thermal stability studies, inverted tube tests on four samples of LiF-OF_2 gels in the range of 3 to 4.2 percent LiF were performed. In these tests, the gel samples were sealed off in Pyrex glass tubes which were then inverted and placed in a large Dewar at -196°C. Visual observation of any bleeding of OF_2 from the gel was made at stated intervals.

After one week's storage, no sign of liquid exudation was observed in any of the four samples. After one month's storage, three of the four samples showed a small amount of liquid exudation. It is believed that the observed bleeding occurred because the gel was not adequately mixed since homogeneous mixing of laboratory samples of OF_2-LiF is not possible due to the limitations of the equipment involved.

3. Fluorine Gelling Studies

a. Screening of Gellants

A study was initiated to determine if it is possible to gel liquid F_2 using particulate gellants. In view of the finding that inorganic oxide-OF_2 mixtures may be shock sensitive, the gellant chosen for study was LiF.

In initial studies, the liquid F_2 was condensed at -196°C over the LiF in a Kel-F tube fitted with a valve and observed visually. The mixture appeared to be solidified in the manner of a gel and when inverted did not exude liquid.

A 3.2 percent LiF gel in liquid F_2 was then stored at -196°C for six hours in the same tube; the tube was then transferred from the storage bath to a laboratory Dewar filled with liquid N_2. A few minutes after the transfer, the mixture exploded. The Kel-F tube was recovered with the bottom blown out which was broken at the point where it was attached to the valve. This leads us to believe that it was a high pressure release rather than a detonation.

Shock sensitivity tests were then conducted on the liquid F_2 gel in both glass and Kel-F tubes in an attempt to determine the cause of the explosion. The results are shown in Table IX.

Table IX

Trauzl Test Data on Liquid F_2 and Gelled F_2

Fluorine (g)	Gellant Concentration (percent bw)	Trauzl Expansion Container	(cc/g)$^+$
0.50	0	Glass	8
0.52	0	Kel-F	11
0.50	5	Kel-F	19

$^+$Corrected for cryogenic blank (12 cc/g)

It appears from the data that a Kel-F-F_2 reaction contributes to the expansion of the Trauzl block. Since only one test was run, the fact that the LiF-F_2 mixture gave the largest expansion is inconclusive and indicates the necessity for further investigation.

In a subsequent test, the gel studies were performed using heavy walled glass tubes which were immersed in clear Dewar flasks so that the mixture could be visually observed. A 5 wt percent gel of LiF-F_2 (0.27 g LiF, 5.27 g F_2) was prepared by condensing a known quantity of fluorine from a calibrated vacuum system onto a weighed amount of dry LiF. Visual observation of the mixture showed no gel formation, and two definite layers (LiF and F_2) were present. The LiF did not appear to adsorb any F_2 as compared to SiO_2 and no reaction occurred as indicated by no rise in vapor pressure after 3 hours at -196°C.

In order to determine if mixing would cause a gel to form, a new glass apparatus was constructed which contained a small glass covered magnetic bar to which was attached a glass mixing rod. By raising and lowering this magnetic bar with a magnet, remove mixing could be safely accomplished. Initially a 9.5 wt percent mixture was prepared by condensing 1.92 g F_2 on top of 0.2 g LiF, at -196°C. This mixture appeared to be too thick and no mixing could be accomplished. An additional 2.0 g of F_2 was then condensed into the above mixture to determine if 5 percent (wt) LiF-F_2 would gel (3.92 g F_2, 0.2 g LiF). The components were easily mixed at this concentration; however, when mixing ceased, the LiF rapidly settled out. Repeated attempts were made to form a gel and in all cases separation occurred, indicating that no gel was or could be formed under these conditions.

IV. ENGINEERING STUDIES

Preliminary laboratory studies, as discussed previously showed the feasibility of preparing OF_2 gels and generated certain physical, rheological and safety data. However, in order to complete the characterization of this gel system and to establish the beginning of a block of engineering design data, it was necessary to perform a series of tests directed at showing the feasibility of the system by preparing relatively large quantities of the gel and performing preliminary engineering studies. Work was directed, therefore, at studying mixing procedures in gel batches up to one pound and performing flow tests (Δ P vs flow rate), establishing slosh characteristics, boiloff rates, inverted tube tests to indicate Bond numbers, and capillary rise tests to see if surface tension effects would separate the gel. Subsequent sections will describe the efforts devoted to these various areas.

A. General Apparatus Description

A facility for scaled-up mixing and characterization of OF_2 gels was designed and fabricated. An overall view of the facility is shown in Figure 4. The nominal capacity of this system is 0.4 to 1.0 lb of gel with potential capacity up to 2 lbs. The setup was housed in a barricade, with OF_2 supply and disposal tanks and auxiliary He and liquid N_2 systems located outside of the barricade. A double-decked steel table formed the base of the unit with a jack, mounted in slides, on the lower deck. The jack could be raised or lowered using a reversible electric motor mounted under the deck; the jack carried an unsilvered 1800 ml Dewar and a frame which suspended a glass or stainless mix vessel in the Dewar. The jack handle also permitted manual raising or lowering of the jack. The mix vessel was an 8 inch long section of 2 inch ID Pyrex pipe closed at one end and fitted with a pressurization inlet which consisted of a glass side arm attached to a stainless flexible hose. A stainless vessel was also used which is identical in dimensions and internal configuration to the glass version. In the top deck were two copper inserts carrying Teflon gaskets, visible in Figure 5. These formed a sealed top for the mix vessel when it is raised into position by the jack. Guides below the top deck ensure proper alignment. The mixer employed was a Premier "Dispersator." This unit is a high shear type and has proved effective for making particulate gels.

The mixer could readily have been exchanged for a different type, although no changes were necessary. The mixer shaft passed through one of the copper inserts with sufficiently large clearance to prevent metal to metal contact. A flat Teflon seal pressed on the shaft rides against the top surface of the copper on a film of Kel-F grease and provides a vacuum seal and a vapor barrier at ambient pressure. A vacuum connection is also made through the copper. The second copper insert, located about 12 inches from the first insert, carries a dip tube for extracting the gel and a vent-disposal port for OF_2 gas.

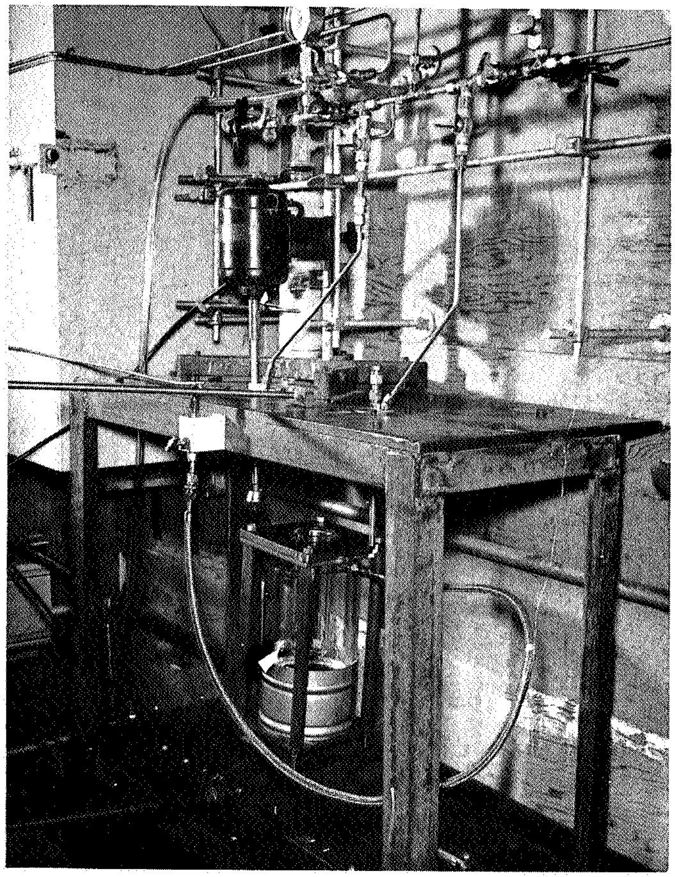


Figure 4. OF_2 Gel Scaled Up Mix Facility, Overall View

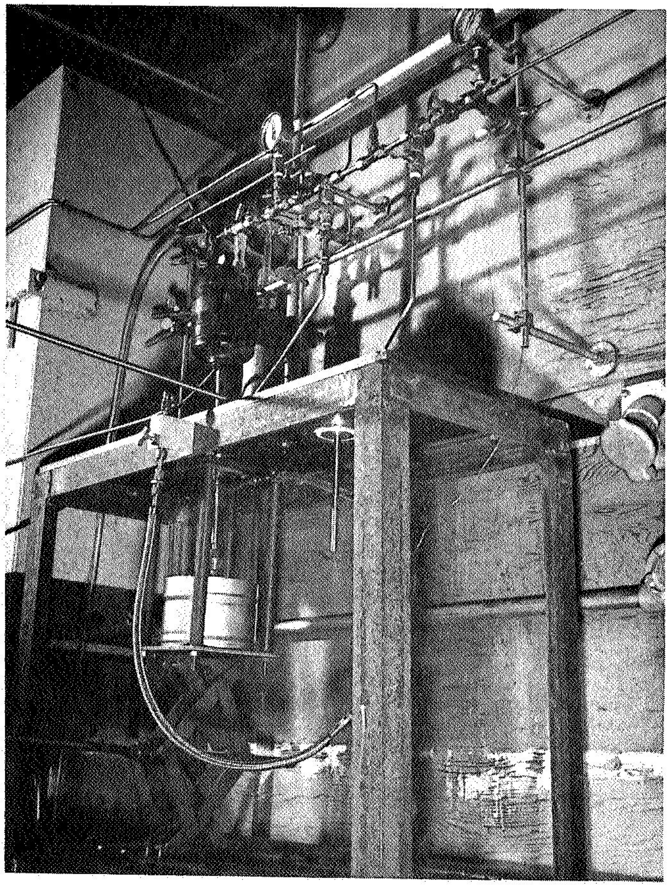


Figure 5. OF_2 Gel Scaled Up Mix Facility
(Shows Vessel Seated in Mix Position and also shows Dip Tube)

Vacuum and vent systems were carried on a wall rack. The OF_2 fill system consisted of a 2100 in.^{3} low pressure tank supplied from an OF_2 shipping cylinder and connected with the vacuum system and the mix vessel. The tank was used to measure the OF_2 by a pressure-volume relationship. OF_2 disposal is accomplished by releasing the gas into a storage cylinder. All operations are carried out remotely from an adjacent control room which has a direct view of the system. Pressures were measured using Bourdon gauges and, in the case of tests, recorded by Polaroid camera.

Materials of construction were stainless steel, copper and glass. Teflon was used for seals where there was no contact with the gel or liquid (copper was used for wet seals). Finally, brass gauges with soldered tubes were used successfully in the gel after thorough cleaning.

B. Mixing Studies

The general preparation technique was as follows (refer to schematic Figure 6). The desired weight of gellant is placed in the mix vessel and the vessel jacked up against its seat under the mixer. The vessel is then evacuated and the Dewar filled with liquid N_2. The temperature of the low pressure OF_2 tank is taken with a mercury thermometer and the pressure of the desired weight of OF_2 is picked off a series of pressure vs temperature curves plotted for the volume of the tank (2100 in.^{3}). The curves were derived using the formula

$$PV = \frac{MRT}{\overline{M}}$$

where

P = pressure in atmospheres

M = mass in lb (varies with batch size)

V = volume in cubic feet (1.215)

R = gas constant (0.73)

T = temperature in °R

$\overline{M}$ = molecular wt of OF_2

OF_2 gas from the storage cylinder is admitted to the load tank after which valve (1) is closed. The tank is then opened to the vacuum system through valve (2) and the gas flows to the evacuated mix vessel where it is condensed over the gellant. The mix vessel valve (3) is closed and the

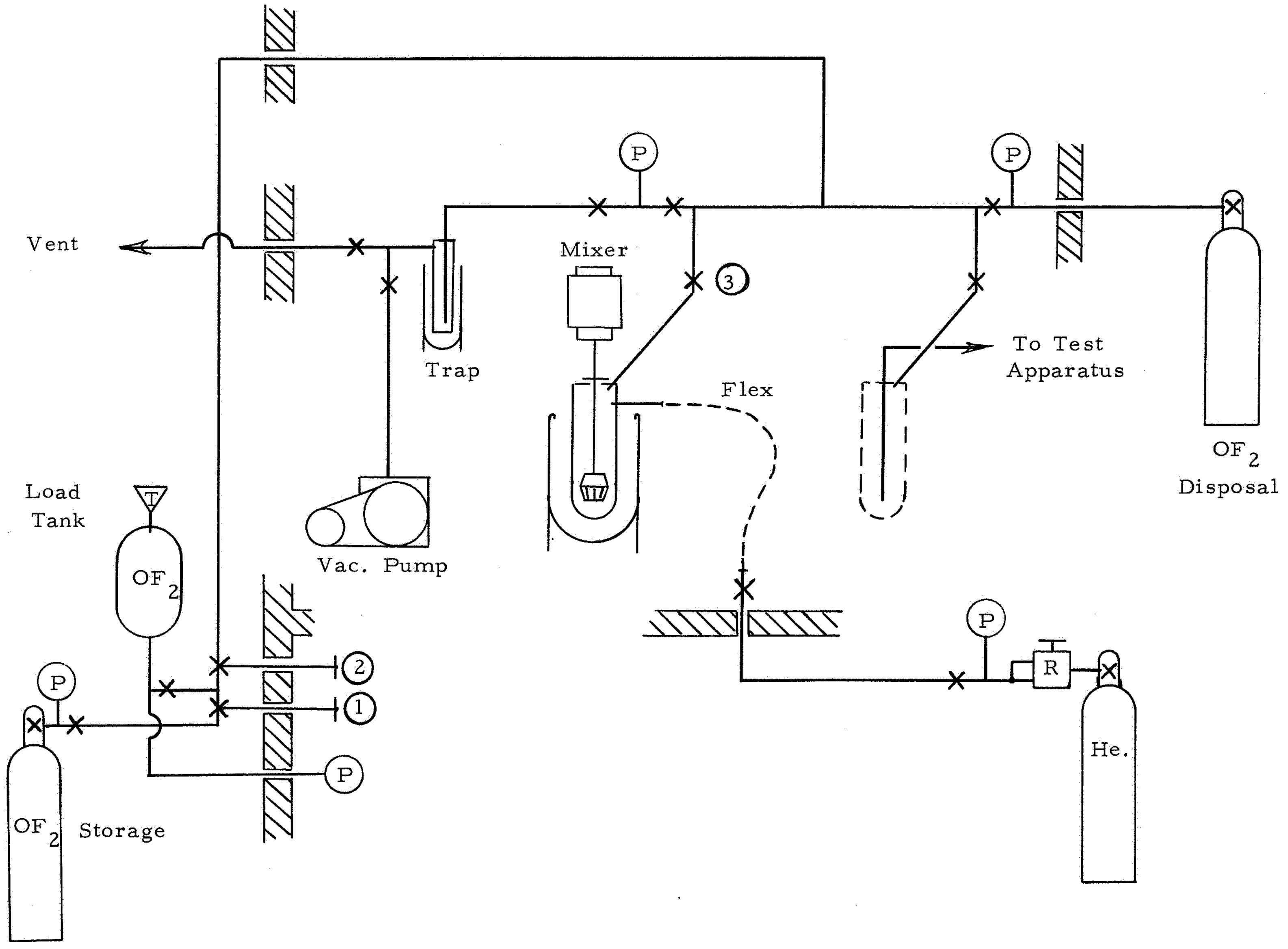


Figure 6. Mix Facility Piping Schematic

mix vessel brought up to ambient pressure with helium through the side arm connection on the vessel. The mixer is then operated as desired to form the gel. During these operations, liquid N_2 is added to the Dewar as required by pressurizing and venting the storage flask. When the gel is formed, a helium bleed is put on the vessel and the jack lowered and traversed to the test side of the table where the jack is stopped at alignment marks on the slide and raised until the mix vessel seats in the test position (alignment is aided by guide fingers under the table top). For disposal, the vent line valve is opened to the disposal cylinder. The liquid N_2 is allowed to boil off and the OF_2 permitted to gas off into the disposal tank. When the gellant remaining is dry, the disposal container is closed and the system pumped down through the liquid N_2 cooled vacuum pump trap. The trap is then vented to atmosphere and the small amount of condensed gas allowed to escape.

No difficulties were encountered with the high shear mix system. The mixer gave best action for 0.45 lb mixes at about half speed which was quite adequate for making these gels. About 30 seconds were required to initially stiffen the material. Mix times varied from 2 to 15 minutes, depending on the quantity mixed; however, in most the minimum mix time was five minutes.

During a one lb mix operation, when the mixer could be run at full speed without cavitation, and after it had been doing so for about 30 seconds, a distinct glow appeared in the gel in the vicinity of the mixer head. The mixer was stopped and the glow disappeared. There were no further effects. It is assumed that local heating promoted a local reaction and in view of this, prolonged high speed mixing was discontinued.

A total of 32 batches of gel were made with this facility for various purposes, ranging in weight from 0.2 lb to 1.0 lb although the usual weight was about 0.45 lb. The first six of these were gelled with lithium fluoride and all but one of the remainder with HS-5 Cab-O-Sil. The exception was an attempt with potassium titanium fluoride (KTF) which had been prepared by freeze drying. No gel formed in this case, even with 4.5 percent bw of KTF.

During overnight disposal of the OF_2 from the KTF, an overpressure occurred which shattered the glass mix vessel and Dewar flask. There was no sign of detonation. The expected pressure rise during disposal was 20 psi and since the glassware will stand at least 150 psi, it is assumed that a reaction took place between the OF_2 and the gellant.

Five LiF gels were made with concentrations of 3.18 to 7.41 percent bw LiF. The 3.18 percent gel was too loose and had separated after 30 minutes. What appeared to be good gels were formed at 3.5 percent, 4.88 percent and 5.42 percent bw LiF, while 7.41 percent was too stiff. Not one was seen to separate. To check the possibility of reusing the LiF gellant, the 4.88 percent gel was allowed to boil off overnight in the usual manner, and the dry gellant residue was used to gel another batch by condensing more OF_2 over it and mixing. The resulting 4.1 percent gel separated after 15 minutes verifying the laboratory finding that LiF can be used only once. No attempt was made to obtain physical or rheological data on any of these gels.

Cab-O-Sil gels were used for test purposes during the remainder of the program, as excessive time was required to prepare useful amounts of freeze-dried LiF. By trial, 2.7 percent Cab-O-Sil-OF_2 gel was arrived at as the equivalent of a 4.5-4.8 percent LiF gel, and it is this percentage which was used during subsequent testing. This gel showed no separation after three hours and demonstrates a substantially reduced gellant requirement with Cab-O-Sil. An initial 3.1 percent gel was too stiff. All comparisons of gels and gellant used in this facility were necessarily on a strictly qualitative basis.

A fair comparison of the character of the gels was obtained by noting the speed at which steady mixing was interrupted by "skips" and the speed at which definite cavitation occurred. This was supplemented by observing the movement of material in the vessel while mixing, the surface settlement at rest, sticking (on the vessel walls) and separation.

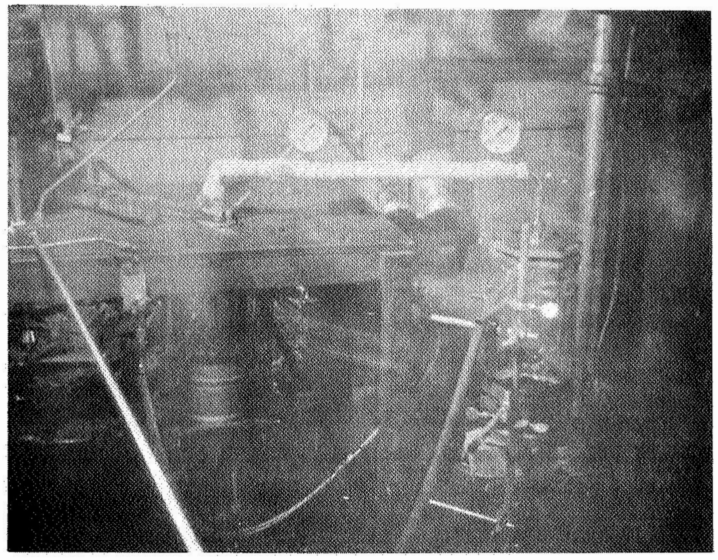
C. Flow Studies

Approximately half the gels made were used in an effort to obtain pressure drop data and calculated viscosities. The work was hampered by difficulties encountered in moving the gel out of the mix vessel and through the test system.

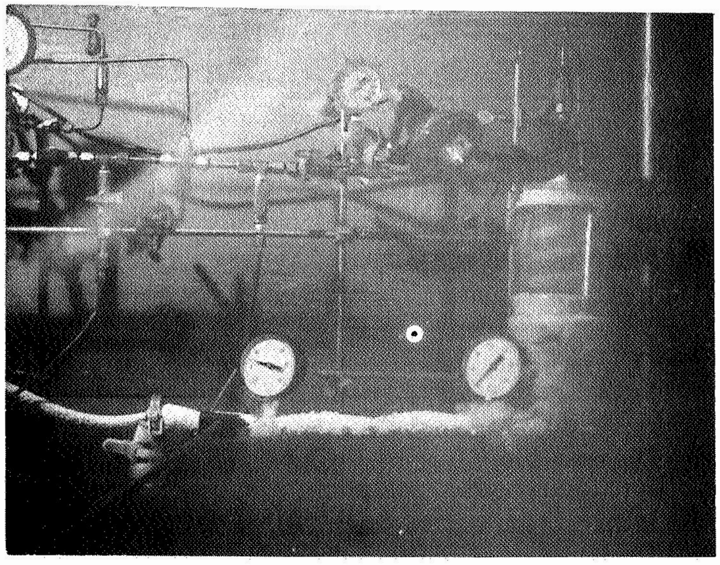
The test system consisted of a 1/4 inch OD, 0.180 in. ID, stainless steel tube test section 13 inches long with pressure gauges mounted on it 12 inches apart. The tube was connected to the 3/8 in. dip tube in the mix vessel by a 1/4 in. ball valve and ended in a glass receiver calibrated for volume in cc (see Figure 7). The whole system was jacketed and cooled with liquid N_2. The system and all equipment installed in it was passivated with OF_2 gas at 5-10 psi for a minimum of two hours. Piston assemblies used for expelling gels were passivated as parts and assembled afterward.

Flow was controlled manually with the ball valve and timed with an electric timer. Gauge readings were taken either visually or with a Polaroid camera, or both, and flow volume was read from the receiver calibrations. These readings gave ΔP and weight flow rates from which apparent viscosities could be calculated.

The original receiver was a large unvented volume in which the gel entered from the top, but volume readings were uncertain due to the small amount of gel flowed. Also,



Large Closed Receiver Installed
The Test Section is Inside the LN_2
Jacket Between the Gages



Coiled Tube Receiver Installed
The Reach Rod is on the Ball Valve

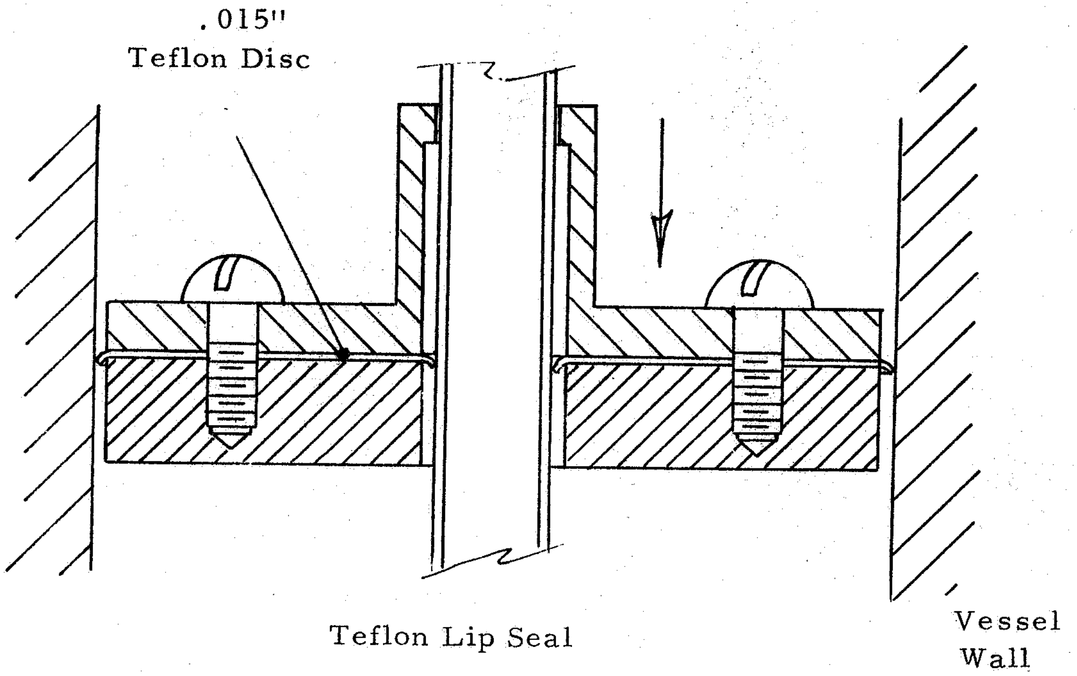
Figure 7. The Flow Test System
(Pressurized Expulsion)

in some cases, spatter occurred. The receiver was changed to a coiled 1/2 in. glass tube vented to the disposal system, in which the gel entered from below. This design worked well and was retained.

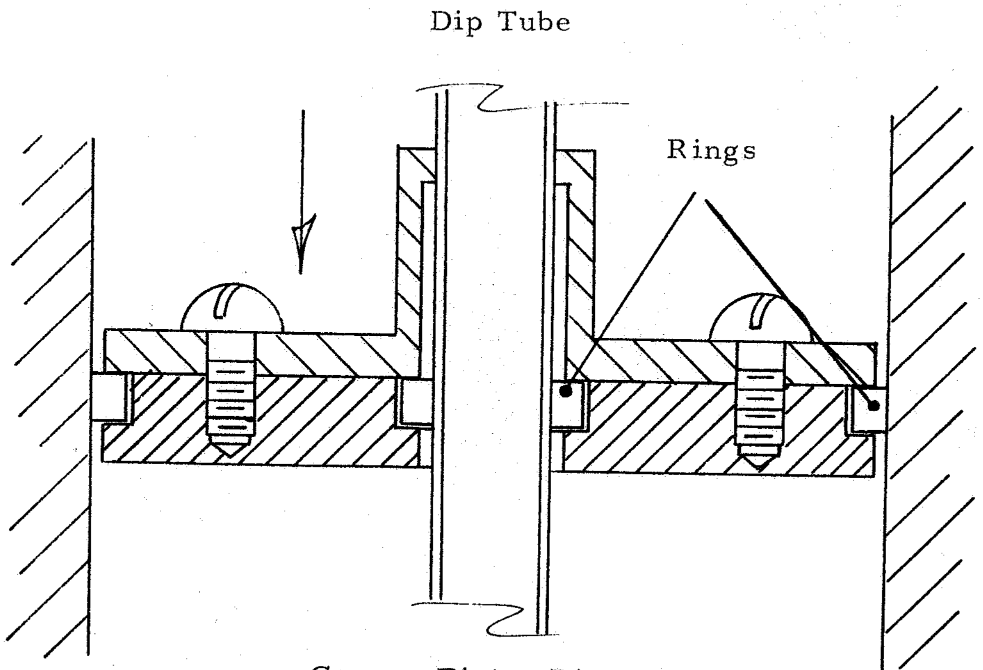
The major difficulty with the system was moving the gel. Helium pressurization resulted in blowing a hole through the gel to the dip tube. Raising the gel level helped, but did not cure the problem. A copper piston with a Teflon lip seal (Figure 8) was designed to separate the gel from the gas but was not successful due to leakage of helium past the lip seal. A steel mix vessel having smoother walls than the glass one was of little help. The 0.015 in. thick Teflon was not compliant enough at low temperatures to seal gas properly, although it retained some spring tension. The piston, also, had a tendency to stick.

Finally, a pneumatic cylinder was set up to move the piston via a yoke extending down into the vessel (Figure 9). This worked, but overpressurizations were experienced on the first and third of three attempts to use the system. In both cases the cause was traced to the lip seal. The mechanically driven piston had a leading lip seal designed to spread under the pressure of the gel below it. The resulting high contact pressure with the walls probably generated enough friction to cause the OF_2 to react with the Teflon. An explosion traceable to a Teflon ball seat, was also experienced in the ball valve. The replacement valve was fitted with copper seats. A second blow occurred two mixes later in a blind Teflon O-ring behind the copper seat. In no instance did a detonation propagate in the gel. The lip seal piston design was discarded and a new copper piston was built with copper piston rings (Figure 8). This design gave no trouble but tended to stick if the mix vessel was not well aligned with the dip tube. Metal-to-metal friction did not cause problems with this gel. A small detonation, occurring when the rotating mixer head struck the side of the steel mix vessel, was tentatively traced to contamination in the female threads of a hub screw, but the possibility of gel reacting at the point of contact was not discarded.

The data obtained from this system shows considerable scatter, as indicated in Table X. A rheological curve drawn from calculations based on this data is shown in Figure 10.



Teflon Lip Seal



Copper Piston Rings

Figure 8. Expulsion Pistons

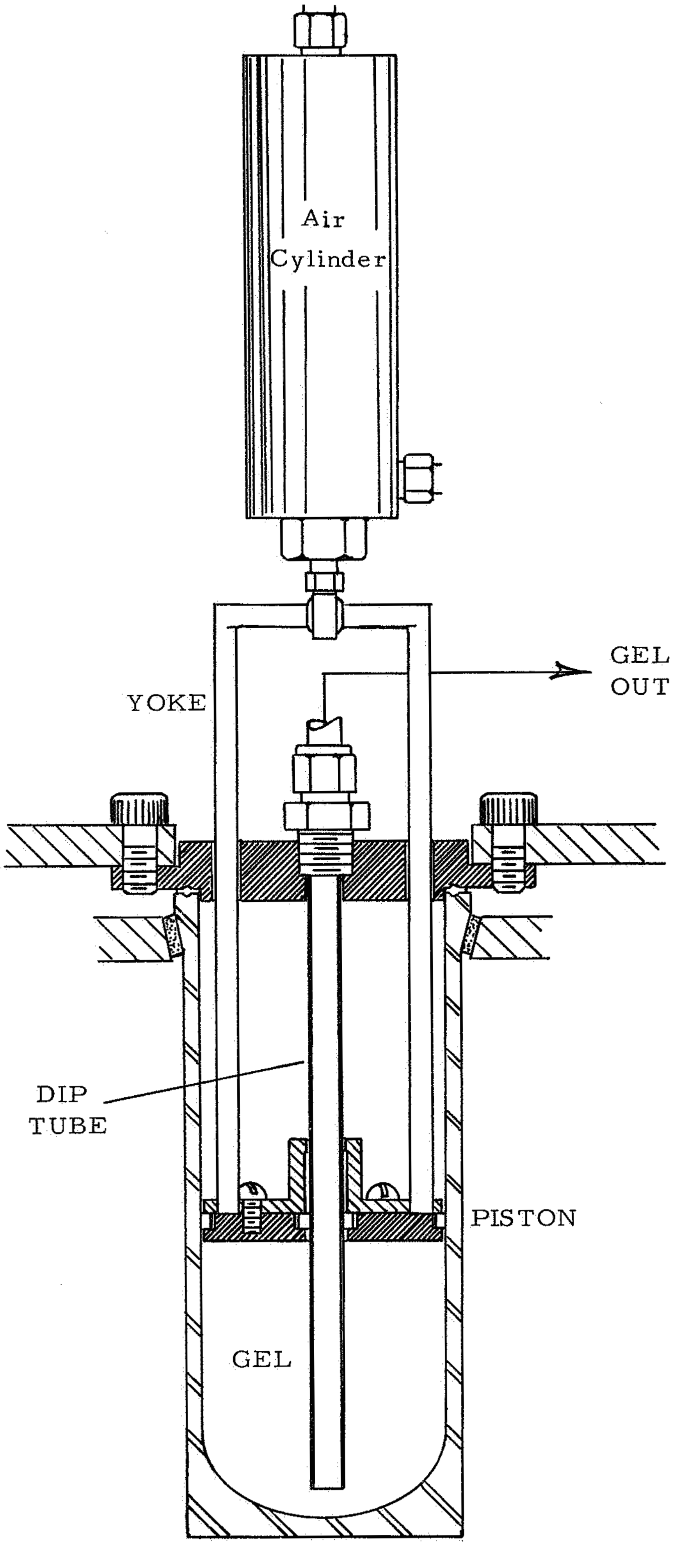


Figure 9. Yoke and Piston Assembly

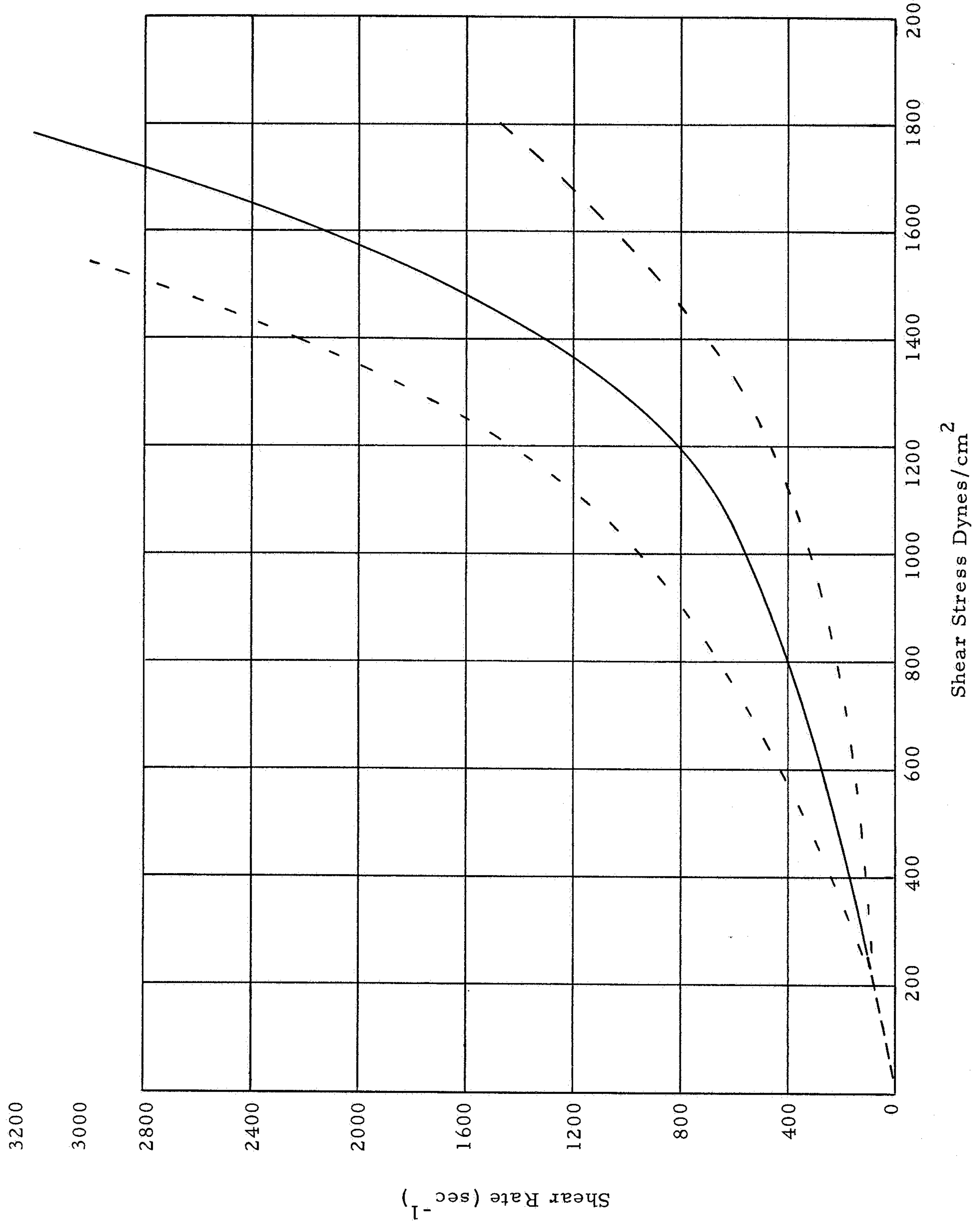


Figure 10. Composite Rheogram for 2.7 Percent Cab-O-Sil-OF_2 Gel

Table X

Results of Flow Tests with 2.7 percent Cab-O-Sil-OF_2 Gel In a 12 Inch Test Section of 0.180 Inch ID Listed in Increasing Order of $\dot{w}$

$\dot{w}$ (lb/sec)	ΔP (psi)	Apparent Viscosity (Poise)	Shear Rate (sec^{-1})	Shear Stress ($Dynes/cm^2$)
.0032	1	2.48	105	259
.0042	1	1.95	133	259
.0044	2	3.71	139	517
.0046	4	7.12	145	1033
.007	2	2.42	213	516
.011+	8	5.98	346	2070
.011	2	1.51	342	516
.019	4	1.67	618	1033
.034	4	0.96	1075	1033
.046	7	1.23	1450	1790
.064	3.5	0.45	2020	904
.071+	12	1.38	2240	3100
.074++	2	0.22	2335	517
.094	6	0.52	2975	1550
.103	7	0.55	3250	1790

+Volume readings in doubt.

++2.3 percent gellant.

In calculating points for the curve the shear rate, in reciprocal seconds, was arrived at with the formula $32\ Q/\pi\ D^3$ where Q is the volumetric flow in in.^{3}/sec and D is the test section diameter in inches. Shear stress in lb/in.^{2} was found using $\Delta PD/L4$ in which ΔP is the pressure drop between the gauges in psi, L is the distance between gauges in inches and D is again the ID of the test section. Multiplying the stress in lb/in.^{2} by 68,948 gives the result in dynes/cm^2 for the plot.

Apparent viscosity μ (in poise) was calculated using the formula

$$14.88 \times \frac{\Delta P\ g\ D^2}{32\ LV}$$

where ΔP = the pressure drop in lb/ft^2

L = length of test section in ft

D = diameter of test section in ft

and V = gel velocity in ft/sec $\left(\text{from } \frac{\dot{w}}{\rho A}\right)$

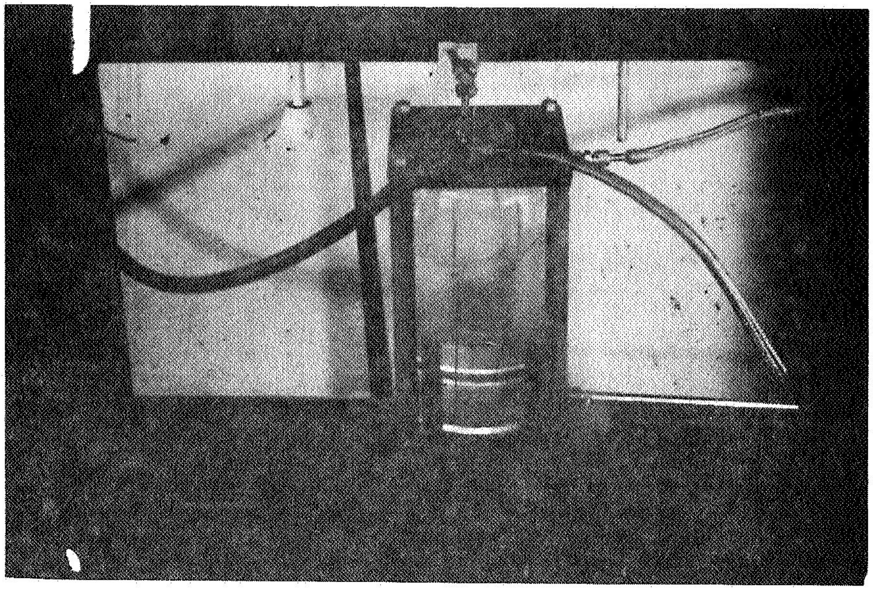
The curve is incomplete because no yield values were obtained, but extrapolation indicates an extremely low yield point in any case. Attempts were made to flow a 2.7 percent gel through chamfered orifices of 0.033 in. dia and 0.0465 in. dia (twice the area of the 0.033 in.) installed in the end of the 1/4 in. tube. The gel would not pass through in either case because of blockage at pressures up to 25 psi. This precluded doing falling strand tests for yield values, the test being based on extruding the gel through a small diameter tube.

D. Slosh Characteristics

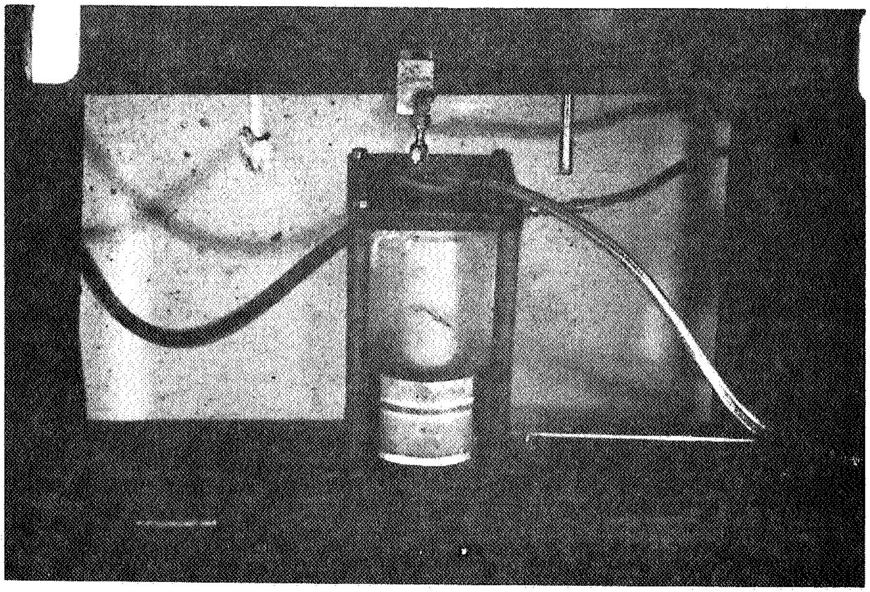
A comparison of the slosh characteristics of neat and gelled OF_2 was made by shaking samples of each in the glass mix vessel and recording the action at one half normal speed on motion picture film. The material was agitated in the mix vessel by lowering the jack, moving it to the center of the ways, and attaching a push rod. The push rod was driven by an electric motor through a variable speed drive. A helium blanket was maintained over the gel at all times. Movies were taken of the 0.44 lb samples at rest and being agitated at two different speeds. The gelled OF_2 (2.7 percent Cab-O-Sil bw) showed no motion during testing while the liquid OF_2, as expected, sloshed violently under the same conditions. Good motion pictures were obtained (Figure 11). The gel showed no signs of separation following the demonstration.

E. Boiloff Characteristics

A comparison was made of the evaporation (boiloff) rates of neat OF_2 and 2.7 percent Cab-O-Sil-OF_2 gel. A 1/2 in. dia stainless steel tubular electric heater of 48 watts was made up and installed in place of the dip tube in the test side. About



Liquid OF_2. The Dark Area in the Center of the Container is Sloshing Liquid



OF_2 Gelled with 2.7% Cab-O-Sil. The Gel Surface is the Horizontal Dark Area Near the Center of the Mix Vessel. There is a Residual Coating of Gel on the Walls Above the Surface.

Figure 11. Slosh Tests

1-3/4 in. of the heater was immersed in test samples of 0.44 lb. A 1 liter Hoke bottle was hooked into the disposal system as a gas receiver (the usual cylinder being too large) and liquid losses in the test samples were read as gas pressure in the system. The system was filled with one atmosphere of the helium before heating. The gel was mixed in the glass mix vessel and moved into position in the usual manner. To perform the test the heater and electric timer were started simultaneously and the pressure generated by vaporizing OF_2 was read from a 50 psig compound visual gauge.

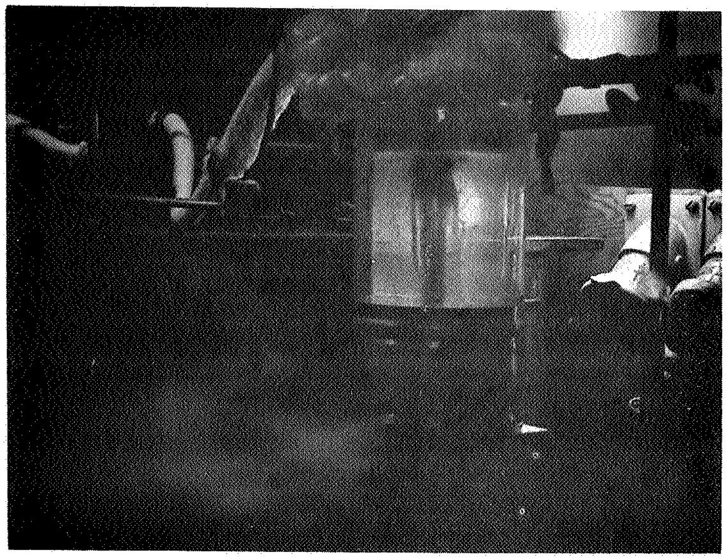
In the test with neat OF_2 there was a delay of 60 seconds, after which the pressure rose slowly and steadily (accompanied by formation of white vapor in the pot) to 48 psig. The total time was 218.5 seconds. During the latter part of this test there was vigorous boiling at the surface of the heater.

When the test was repeated with 2.7 percent Cab-O-Sil gel the pressure rise started almost immediately and rose quickly and smoothly to 48 psig in 126.4 seconds. A previous test on the gel (with somewhat less accurate timing) also gave a pressure rise within a few seconds and at 13 psi the gauge needle began oscillating up and down the scale as if there were sharp pressure peaks (one to 60 psig). A pressure of 48 psig was reached in approximately 100 seconds.

No visible action was noted during the gel tests. The unexpected fast starting and high rate of boiloff for the gel may be due to lack of convective cooling from the outer walls of the vessel. The possibility exists that as the area around the heater is depleted of OF_2, the dry gellant would become an insulator and the rate of loss would decrease. To check this, the test was repeated in the steel mix vessel to a pressure of 250 psi. Apparently, however, a cavity remained in the gel where the mixer head had been (in spite of shaking down after mixing) and the heater hung in this cavity without contact with the gel. Boiloff was extremely slow and no signs of cooked gellant remained on the heater surface afterward. One psig was reached in 30 seconds and 200 psig in 3550 seconds. The boiloff rate accelerated slowly during the whole test. Lack of time precluded further investigation in this area.

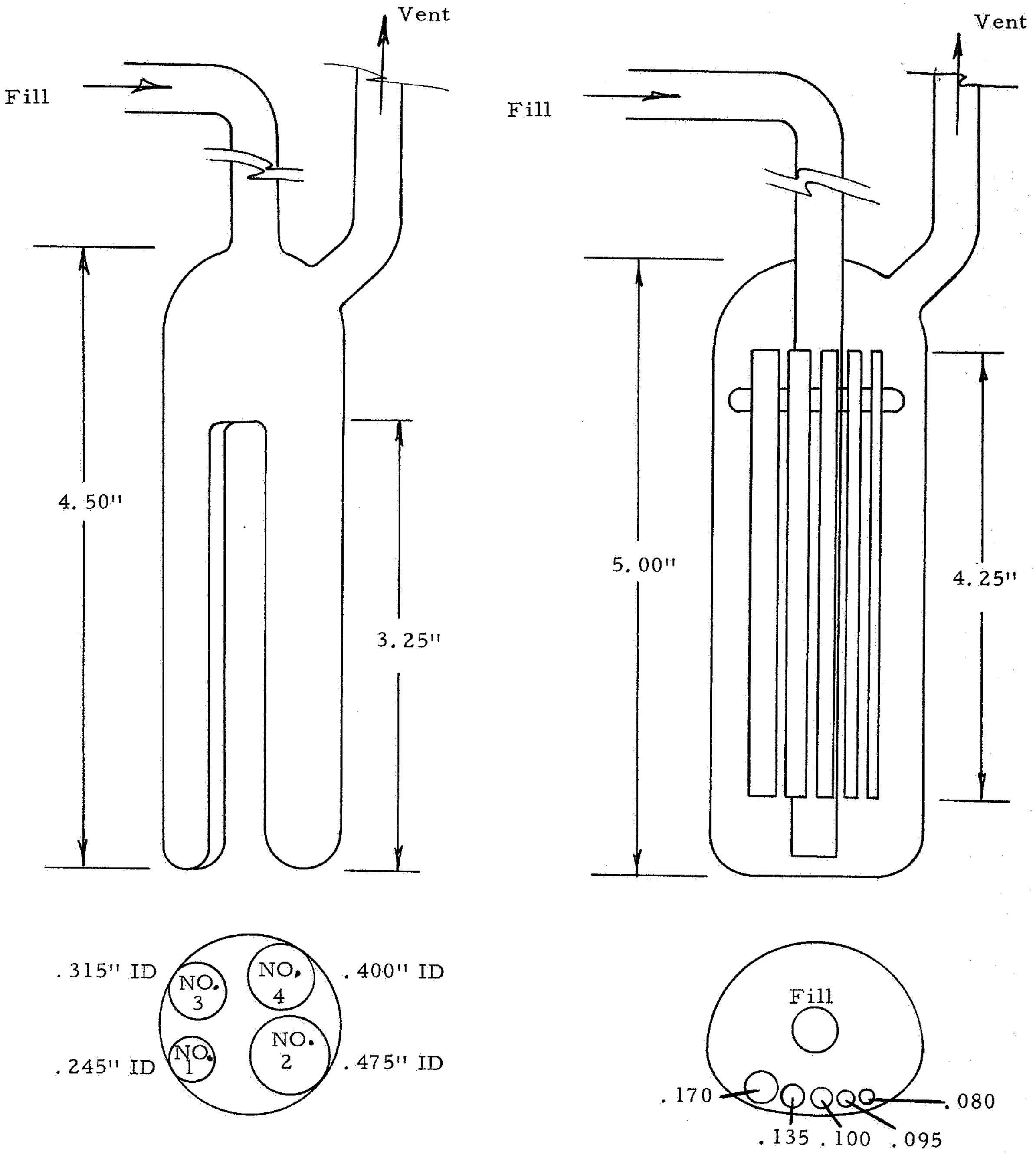
F. Inverted Tube and Capillary Rise Tests

The apparatus for the inverted tube test, as shown in Figures 12 and 13A, consisted of a group of four vertical glass tubes of different diameters originating at a common chamber and closed at their lower ends. The chamber was connected to a 3/8 in. stainless extension of the dip tube in the mix vessel and also vented to the disposal system. No valve was included as the available ball valves were considered liable to detonation due to Teflon seals, and other types would have produced unwanted shear. The whole system was cooled with liquid N_2. Transfer was effected by raising the gel



The cluster of tubes is submerged in liquid N_2. The dark area immediately above them is the common chamber filled with gel. The picture was taken just before termination of the test. Note the largest tube two thirds full of separated gel and the others at varying levels of neat OF_2. The tube bottoms are even with the bottom of the glass.

Figure 12. Inverted Tube Test



A, Inverted Tube

B, Capillary Rise

Figure 13. Glass Test Apparatus

vessel around a copper disc fixed to the bottom of the dip tube (in effect, a piston). The gel was forced into the common chamber of the apparatus until it was filled and the gel squeezed into the tops of the tubes. The pressure on the fill line was relieved to prevent possible extrusion of gel further down into the tubes. The apparatus was left undisturbed and visual observations made of the gel behavior, primarily the liquid leakage out of the gel matrix.

The first test was with 2.7 percent Cab-O-Sil gel. The gel appeared to be breaking down even as it entered the chamber of the apparatus. The tubes filled with loose gel and liquid OF_2 during transfer and the test was terminated.

The second test was done with a 4 percent Cab-O-Sil gel. This transferred satisfactorily and the test proceeded as planned. This gel extruded as a rod from the vertical loading line and broke off in nearly even pieces 3/4 in. long. Sufficient gel was pushed into the chamber to squeeze it into a reasonably homogeneous mass. Liquid OF_2 appeared in the vent leg after loading, apparently from the fill line. It did not appear to drain down into the tubes.

At the end of 15 minutes all the tubes showed 3/16 in. of liquid OF_2. After 18 minutes some gel broke away, fell into the largest tube and separated quickly. The tubes continued to show increasing liquid levels roughly in proportion to their diameters until 50 minutes after the start of the test. No increase was noted after 75 minutes and the test was terminated. Observations made during the test are summarized in Table XI.

For the capillary rise tests the facility was left in the same configuration as for inverted tube testing except that a set of five glass capillary tubes in a vented glass envelope (Figure 13B) was substituted for the inverted tube apparatus. The transfer of gel was also accomplished in the same manner. Enough gel was transferred to submerge the lower ends of the tubes to a depth of 1.0 inch. The gel did not enter the capillary tubes. The gel came across in slugs and the vertical leg of the loading tube was left empty when loading was complete; almost immediately after loading, liquid OF_2 began to appear in the tubes, and built up to a depth of 3 inches above the surface of the gel. This liquid either drained out of the horizontal run of transfer line or evaporated out of the fill line (however, the liquid N_2 was left on) and condensed in the vertical leg. Thirty-three minutes after starting the test, the liquid had dropped to two inches above the gel and liquid appeared around the capillary tubes. The main body of gel appeared satisfactory so the liquid was probably that which had drained or condensed out of the fill tube.

After 48 minutes the center tube had not drained appreciably more, but a 1/8 inch layer of liquid had formed across the top of the gel indicating that it was separating. There was also liquid in the capillaries but not gel. At this point the test was terminated since the gel had shown no tendency to rise in the capillaries at any time before the liquid appeared.

Inasmuch as even 4 percent Cab-O-Sil gels proved to be fairly unstable after transfer, the acceleration and vibration testing was cancelled. Both types of testing would have required transferring the gel to smaller containers with valves. This alone would have caused instability and the test results therefore, would have been meaningless.

Table XI

Inverted Tube Test Data

(Run No. 2)

Time (min)	Remarks			
Tube[+] Number →	1	2	3	4
1	---	Gel fragment dropped into tube.	---	---
10	---	Fragment formed liquid layer.	---	---
15	---	Gel fragment dropped into tube.	1/8" liquid layer developed.	---
20	---	Large mass of gel dropped into tube.	---	---
25	1/4" liquid layer.	Gel separated.	1/2" liquid layer.	1/4" liquid layer.
35	3/4" liquid layer.	2 1/2" liquid layer.	1 1/2" liquid layer.	1" liquid layer.
50	1 1/4" liquid	Same	2" liquid	1 3/4" liquid layer.
75	Same	Same	Same	Same

[+] See Figure 13A for tube size.

V. CONCLUSIONS

As far as could be determined from the work accomplished, gels were formed with OF_2, using both lithium fluoride prepared by freeze drying, and HS-5 grade Cab-O-Sil (SiO_2). In both cases, high shear mixing is very effective and some hazard appears to exist with either gellant in OF_2 during mixing operations. The SiO_2 system showed non-violent local reaction under the influence of extreme mixer speeds ($\sim$11,000 rpm) but the reaction did not sustain when the mixer was stopped. At lower speeds, or when vortexing or cavitation was present, the reaction was not noted with either system. Detonations in, or at the surface of, the SiO_2 gel failed to propagate.

While OF_2 thickened with SiO_2 is thermally stable at low temperatures, the mechanical stability is only fair. When left undisturbed in its mix vessel and kept at liquid N_2 temperature, the material retains its gelled characteristics (a 2.7 percent Cab-O-Sil gel was observed to be intact after three hours), but when disturbed in a manner which induces shear, the material becomes mechanically unstable and phase separation occurs.

Although LiF gel was not subjected to flow conditions, it is assumed to have about the same mechanical characteristics as SiO_2 gel. Rotational viscometer data could not be obtained on either gel due to shear thinning in the immediate vicinity of the rotating parts.

Under local heating conditions the rate of OF_2 loss from the gel is about 1.7 times that from an equal volume of liquid OF_2 under the same conditions. Lack of convective cooling of the warm area in the gel probably accounts for this. The chance that continued heating would form an insulating area of dry gellant and slow the rate of OF_2 loss seems small, as the extended boiloff test indicated a continuing increase in the loss rate. As the conditions of the extended test were not comparable to the short tests, the problem is not really resolved.

The detonations which occurred during the test series were all in high friction areas where Teflon was present. The involvement of the Teflon seems the most likely cause, as no trouble was experienced in the same situations with metal-to-metal friction. On the strength of the evidence Teflon cannot be recommended for dynamic wet seals with OF_2 gels.

Liquid OF_2 can be safely thickened with LiF or SiO_2, and appears to remain stable if left undisturbed. Both gels can be handled safely in properly constructed systems, but once subjected to shear they became mechanically unstable.

The inability encountered on this program to characterize the cryogenic oxidizers rheologically can be attributed to a very weak gel structure. Generally, the most stable and rigid gels are those in which extensive association such as bonding or polymeric tangling can occur. The oxidizing power of both OF_2 and F_2 preclude the possibility of using gellants in which these mechanisms may be used to advantage. Both oxidizers are extremely reactive with hydrogen containing molecules and polymeric materials are susceptible to oxidative attack whether or not they are organic in nature.

Ultrafine lithium fluoride does not appear to gel liquid fluorine. Mixtures are translucent and have a grain appearance; in one case the solid powder settled out. This observation is in sharp contrast to mixtures of LiF in chlorine trifluoride. In that case a transparent gel-like mixture was formed with approximately 3 percent LiF. The difference may be due to the larger electric moment of ClF_3 which makes possible the formation of weak forces of attraction between the oxidizer and LiF.

In addition, the available gellants which are compatible with the oxidizers must be used at cryogenic temperatures. The low temperature weakens the forces that contribute to the gel structure which is formed when silica or LiF are used as gellants.

As a result of the experience in producing gelled cryogenic oxidizers that has been gained on this program, it is our belief that the particulate gellants do not produce satisfactory gels. If there is further interest in the concept, extensive studies must be performed to produce new gellants which have a high molecular weight, a fine particle size and are partially soluble in the oxidizer.

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