SF_6 FOAMED INSULATION

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ABSTRACT

This study describes sulfur hexafluoride (SF_6) epoxy foam, a novel material which consists of a highly electronegative gas (SF_6) confined in a network of closed epoxy cells. SF_6 epoxy foam can be prepared by mixing liquid epoxy and molecular sieves that have been previously loaded with SF_6 (molecular sieves adsorb approximately 25% by weight SF_6). When the mix is heated, the molecular sieves release their adsorbed SF_6, thus foaming the epoxy. Subsequent cure traps the SF_6 in small, evenly distributed closed cells.

Some of the measured properties of SF_6 epoxy foam indicate this unique material is suitable for high voltage electrical insulation. These properties include a low dielectric constant, a high dielectric strength, the ability to regain dielectric strength when punctured (by a low power source), and a material that that does not require vacuum casting.

Since some of these properties can be directly attributed to SF_6, an analytical method was developed to determine if epoxy foams retained the SF_6 blowing agent. Neutron Activation Analysis (NAA) was the chosen method because this technique is non-destructive. Consequently, after measuring a sample's initial SF_6 concentration, the sample could be aged and reanalyzed in order to measure changes in SF_6 content due to aging.

The NAA data obtained on aged samples indicated that some materials retained SF_6 up to the point of thermal decomposition, whereas other formulations retained SF_6 provided they were not aged in excess of their glass transition temperatures. The retention of SF_6 by these foams suggests they will retain the properties attributed to SF_6 and they can therefore be used as high voltage insulation in either air or SF_6 environments.

ACKNOWLEDGMENT

Special recognition is extended to D. H. Reighter for developing the original SF_6 foam concept in 1969. I am also grateful to J. E. Cubbage for experimental work, to A. E. Stringfellow, A. W. Egli, and D. H. Reighter for helpful discussions, and to K. A. Struthers for typing this report. I would also like to thank R. E. Kennon of EPRI for his help and especially for his suggestion to perform the preliminary AC/DC evaluation. I am also grateful to L. Kovar (General Activation Analysis) for his assistance with Neutron Activation Analysis, to Professor J. E. Sturm for his contribution through Lehigh University's Materials Liaison Program, and to R. Jackson of Allied Chemical Corporation for performing the thin film diffusion studies.

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SECTION 1

INTRODUCTION

Although millions of pounds of thermoplastic foams are processed each year, most are unsuited for electrical applications due in part to their low dielectric strengths, often times attributed to the low dielectric strength of the trapped blowing agent gas (normally nitrogen, freon, or carbon dioxide). Another important shortcoming with common thermoplastics is that they do not have the temperature stability typical of thermosets.

An epoxy foam, blown with SF_6, overcomes the shortcomings of thermoplastic foams. Although SF_6 epoxy foams can not be made by conventional techniques, they can be made by mixing molecular sieves that contain about 25% by weight adsorbed SF_6 into a liquid epoxy. When heated, the sieves release their adsorbed SF_6, thus foaming (blowing) the material. Subsequent cure traps the SF_6 in the closed celled epoxy network.

SF_6 loaded molecular sieves are prepared by passing SF_6 through a column of fresh sieves. SF_6 gas is adsorbed on the internal surfaces of the molecular sieve cage structure. After mixing these loaded sieves into liquid epoxy, the SF_6 gas readily desorbs and foams the resin when heated. Other than dissolving SF_6 directly into the liquid polymer, the described technique is the only means presently available of introducing SF_6 as the blowing agent into polymers. Since molecular sieves are relatively inert, they do not degrade the electrical and physical properties of the foam.

The described method for blowing SF_6 epoxy foam differs from common plastic foams in both the foaming technique and gas used for blowing. Typical commercial blowing methods include dissolving a chemical blowing agent in a plastic. When heated, typical chemical blowing agents, such as azodicarbonamide, decompose into gaseous products at the polymer melt temperature, thus foaming the molten polymer. Epoxies can be foamed by this method, but a more common approach is to foam them with microscopically small hollow spheres of phenolic or polystyrene filled with freon or nitrogen. Epoxy foams produced by the latter method are commonly called syntactic foams.

One problem with typical blowing methods is that the common blowing agents do not have the unique properties of the highly electronegative SF_6 gas. Therefore, when plastics are foamed with solid blowing agents that breakdown and yield gases such as nitrogen or carbon dioxide, the electrical properties would be inferior compared to foams blown with SF_6. For example, CO_2 blown foams would exhibit unacceptably low corona inception levels whereas the SF_6 type foam would be corona free.

Furthermore, processing or formulation problems may occur because the solid blowing agent must be compatible with the polymer and the blowing agent must decompose into gaseous by-products at the melt temperature of the resin.

Besides retaining the excellent properties of epoxy, foaming epoxies with SF_6 results in unique properties. These properties include a low dielectric constant, high dielectric strength, the ability to regenerate dielectric strength under certain conditions, and a material that is corona free even when atmospherically poured. Also, preliminary testing indicates that the DC dielectric strength of the foam is far superior to its AC dielectric strength. These traits, along with those normally associated with epoxies, suggest that this material is a feasible electrical insulation for both DC and AC applications.

Since some properties of SF_6 epoxy foam can be attributed to the trapped SF_6 gas, it was necessary to determine whether SF_6 was retained by the epoxy foam. A major portion of the work described in this report was devoted to determining if the epoxy foam would retain SF_6. SF_6 retention studies were performed by utilizing instrumental Neutron Activation Analysis (NAA). The Fluorine (F) content of chosen samples was measured by this nondestructive technique, aged under chosen conditions, and then reanalyzed to determine if F decreased as a result of the aging.

An attempt was also made to develop a technique where 40 year life times could be extrapolated from short term data. A unique method was proposed where corona free samples were tested at elevated temperatures and high electrical stress, but unfortunately the test data was random and could not be used to obtain reliable results.

SECTION 2

EQUIPMENT

Neutron Activation Analysis (NAA) was performed by General Activation Analysis, Inc., San Diego, California, using their TRIGA Mark I Nuclear Reactor. Quantitative measurements were made by recording the gamma ray spectrum of Fluorine-20.

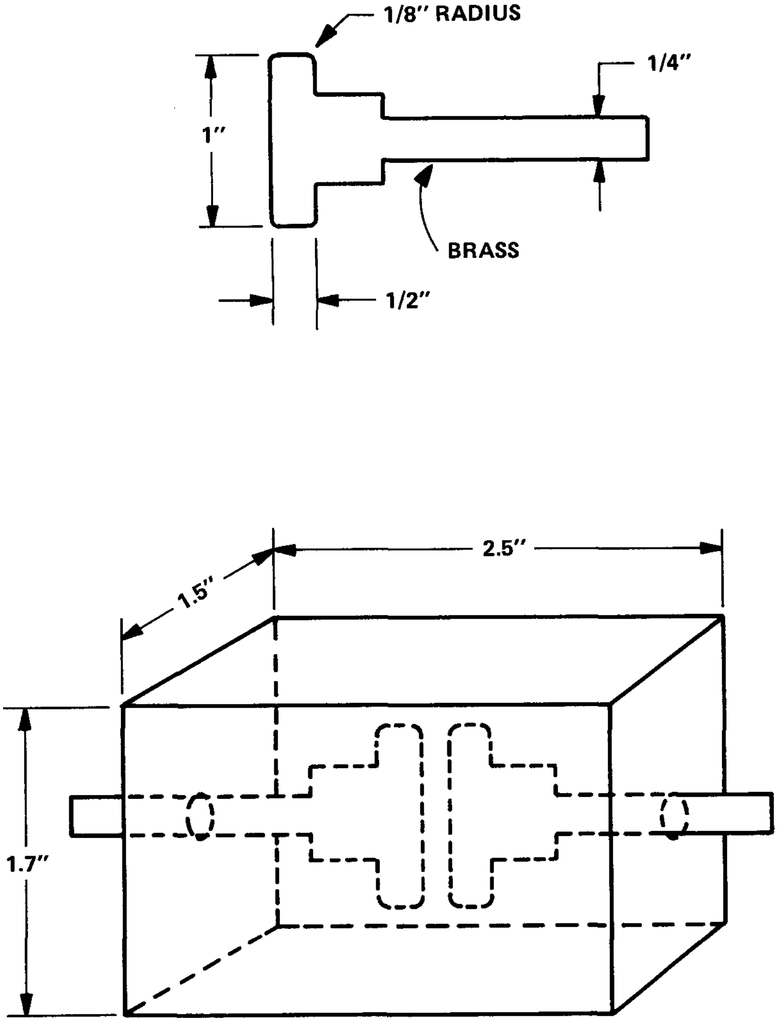
Dissipation factors and dielectric constants were measured on a Model 2821 Tettex Bridge with a type 2904 sample holder, both supplied by Tettex A. G. Zurich, Switzerland. The Tettex bridge was capable of providing a higher measuring sensitivity than a Schering Bridge due to the use of capacitors rather than resistors in the lower arms of the bridge. A resonant circuit produced a distortion-free sine wave enabling test voltages up to 2000 Volts, the maximum voltage dependent on test sample capacitance. Dissipation factors (tan δ) from 0.001% to 1000% and capacitances from 9 pF to 10000 pF could be measured.

In order to overcome the low dielectric constant of epoxy foam sheet samples, a 5-3/4" special Tettex bridge electrode was constructed as per Table 1 of ASTM D-150. Due to low capacitance, the imbedded electrode samples described in Figure 2-1 were tested in parallel. Since the gaps were equal, the value measured on the Tettex bridge was the average of both samples.

Corona measurements were made on a Biddle (Plymouth Meeting, Pennsylvania) Balanced Partial Discharge Detector with a measuring sensitivity of 1 pC.

Six Blue M ovens (Model OV510A-2, or similar), capable of 260°C, were modified with a high voltage bushing to provide a 0-20 kV, 60 Hz variable test voltage in the high temperature chamber (Figure 2-2). The material was then tested in the high voltage ovens at the desired electrical and temperature stress.

Oven temperature calibrations were made with a Fluke Model 2100A digital thermometer equipped with Copper/Constantine thermocouples capable of measurements up to 400°C.



CAST EPOXY BLOCK

Figure 2-1. Test electrode and cast epoxy sample for high voltage - high temperature life testing

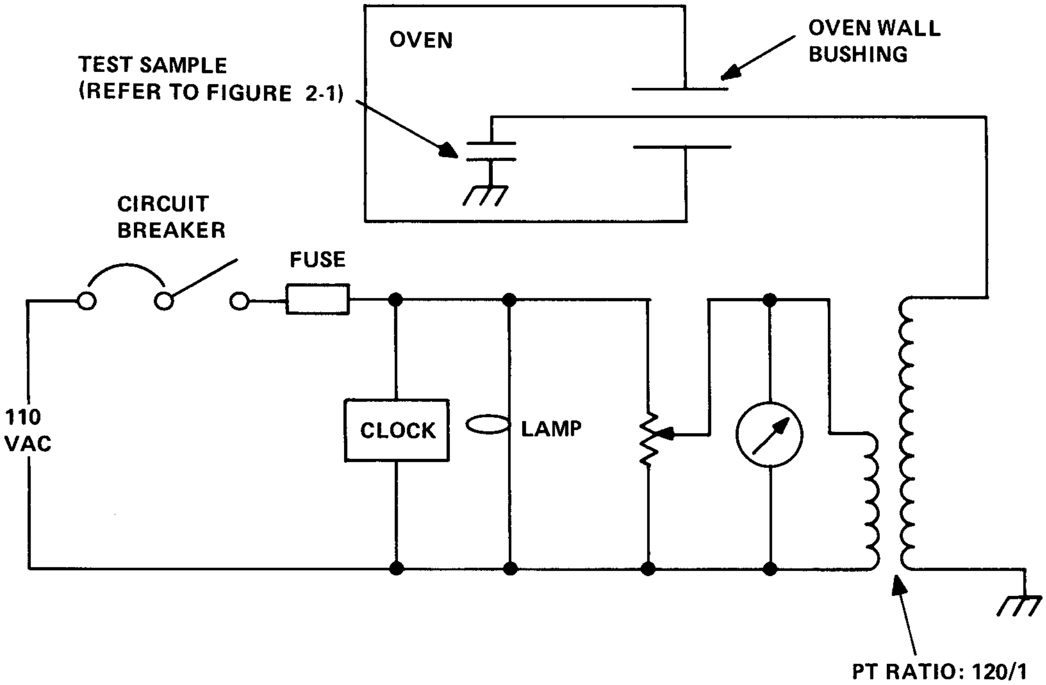


Figure 2-2. High Voltage Test Oven Schematic

SECTION 3

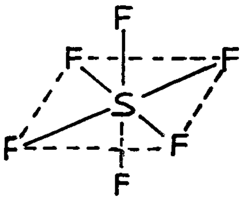
MOLECULAR SIEVES

Molecular sieves are crystalline alumina silicates commonly called zeolites. They are free flowing powders which retain their structure and crystallinity at temperatures up to about 700°C. When incorporated into epoxy resin systems or other plastics, they are unreactive and can be considered as inert fillers. Since they are crystalline, molecular sieves have a definite composition. For type X molecular sieve, the composition is $Na_{86}(AlO_2)_{86}(SiO_2)_{106}$.

The zeolite structure consists of a SiO_4 or AlO_4 tetrahydra crosslinked in three dimensional arrays. The structures are made up in such a way that there are uniform spherical cavities interconnected by common openings. They have a large internal or inner crystalline surface area which accounts for their adsorption capabilities. These surfaces inpart an extremely high affinity for water and other polar or polarizable molecules because of the sodium cations found on the walls of the internal surfaces.

Nearly all the adsorption surfaces of the material are contained in the volume of each individual cavity of the molecular sieves. Access to these interiors is controlled by the pore size of the openings. Therefore, molecules that are smaller than the openings are readily admitted into the interior where they can be adsorbed, but larger molecules are excluded. Because the openings are uniform in diameter, the selectivity of the material is sharp. Different grades of sieve material are available with openings of a few angstroms up to approximately 10 angstroms (Å) in diameter. For further information, refer to D. W. Breck's excellent review on molecular sieves (1).

Since the size of the SF_6 molecule is smaller than the pore opening of type 13X sieve, SF_6 molecules readily enter the sieve. Based on the Lennard Jones (6-12) potential, the symmetrical SF_6 molecule of the following structure



has a kinetic diameter of 5.5 Å (2). This is considerably less than the 10 Å effective pore opening for the 13X molecular sieve.

One important characteristic of the molecular sieves is their high adsorption selectivity for polar versus nonpolar molecules. This selectivity is related to the difference in heats of adsorption for the different species. Molecules such as water and ammonia have higher heats of adsorption than gases such as SF_6. Consequently, one would expect water to be preferentially adsorbed compared to SF_6.

Some important applications for molecular sieves have been to separate different hydrocarbon components and to remove moisture from certain reactions. Another area of importance for molecular sieves has been in resin and rubber systems. A catalyst is isolated from the system because it is adsorbed on the molecular sieve, and the catalyst is not released to the system until heat is applied. These preparations are commonly called chemical loaded molecular sieves (CLMS).

The application of molecular sieves in this program is similar to that for CLMS, but the material adsorbed by the sieve is used as a blowing agent rather than as a catalyst. SF_6 loaded molecular sieves are dispersed in epoxy, and with the application of heat, sulfur hexafluoride is released, thus blowing the epoxy into a foam structure.

SF_6 LOADING OF MOLECULAR SIEVES

Union Carbide's 13X molecular sieves were readily loaded by up to 25% by weight SF_6 and were found acceptable for blowing SF_6 epoxy foam. Molecular sieves were experimentally loaded with sulfur hexafluoride by passing SF_6 through a one meter by 25 mm diameter glass tube containing fresh molecular sieves (Figure 3-1). The data of Figure 3-2 indicates that maximum loading of approximately 25% by weight was achieved after two to three hours. Grace Chemical's Syloid ZN-1 material was also tested as a possible substitute for Union Carbide's 13X

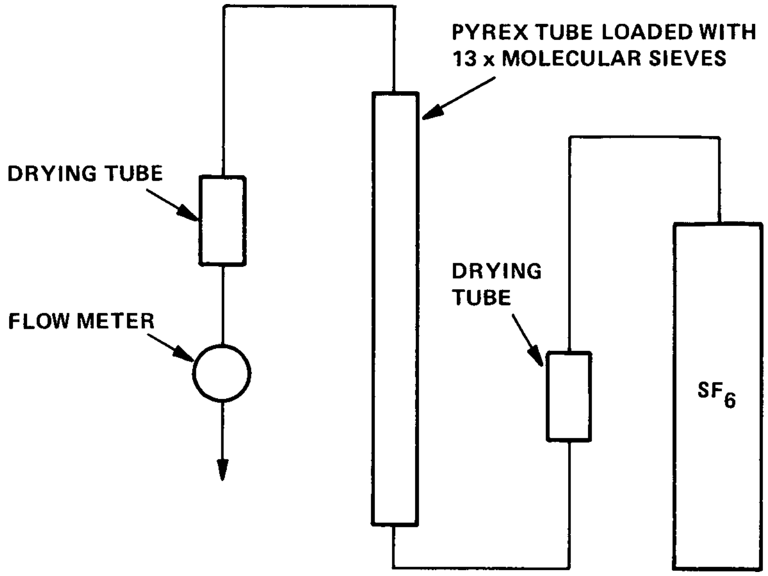


Figure 3-1. Apparatus for Loading Molecular Sieves with SF_6

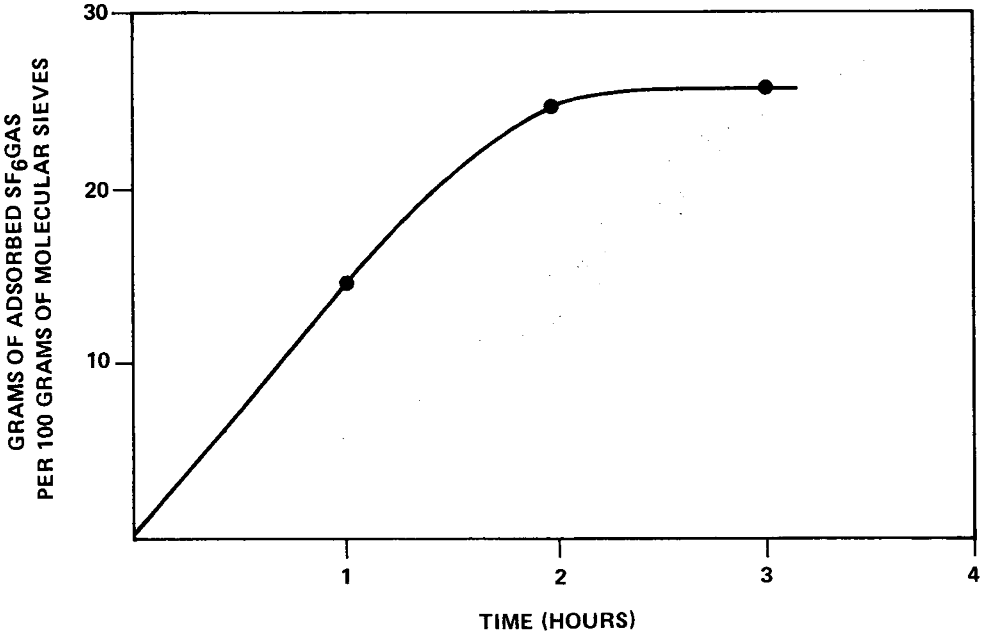


Figure 3-2. Amount of SF_6 gas adsorbed by molecular sieves versus time

Loading of SF_6 on the sieves was performed by passing SF_6 through a tube containing dry molecular sieves.

molecular sieve. Results indicated that the Union Carbide sieve material was more efficient than Grace Chemical's. The Union Carbide sieves adsorbed 23-24% by weight SF_6 versus 18-19% for the fresh Grace Chemical sieves. The Grace material took up 21.5% moisture after vacuum dryout, whereas the Carbide sieve adsorbed more than 25% by weight.

Since the Union Carbide sieve material was satisfactory, no further work was done on the Grace sieves. If it becomes desirable to develop an alternate sieve source at a later date, an evaluation should include SF_6 weight gain versus time, maximum weight uptake, the rate of SF_6 desorption, and the ability to foam an acceptable end product.

For future large scale operations, it may be necessary to either modify the present loading procedure or to purchase SF_6 loaded sieves directly from an industrial source, such as Union Carbide. In a large scale operation, it would be necessary to overcome loading exotherms, improve loading efficiencies, and promote gas flow through the bed of 13X molecular sieves. The suggested method would be to preload the sieves by passing a mixture of 1% SF_6 and 99% N_2 through the sieves. After preloading, the SF_6-N_2 ratio would be increased to 10% SF_6, and finally to pure SF_6. The nonpolar N_2 would not be adsorbed by the molecular sieves at room ambient but would effectively remove the heat from the SF_6 loading exotherm. As loading approaches the maximum, the N_2 concentration can be lowered because the loading exotherm is reduced.

Union Carbide has tentatively agreed to supply SF_6 loaded molecular sieves. Although they do not presently load molecular sieves with SF_6, they believe their present equipment is suitable for this gas. Based on SF_6 at $3 per pound, they estimate 50,000 pounds of 25% SF_6 loaded sieves can be supplied in 55 gallon steel containers at a price of $4.40 per pound.

MOLECULAR SIEVE DRYNESS

Wet molecular sieves can not be directly loaded with SF_6. Due to the high polar attraction of water to the cations of the molecular sieve, SF_6 is unable to replace water. However, molecular sieves with high amounts of adsorbed moisture can be readily regenerated by placing them in a vacuum at 150°C because the adsorption isotherms of crystalline zeolites do not exhibit hysterisis (adsorption and desorption are completely reversible). As shown in Figure 3-3,

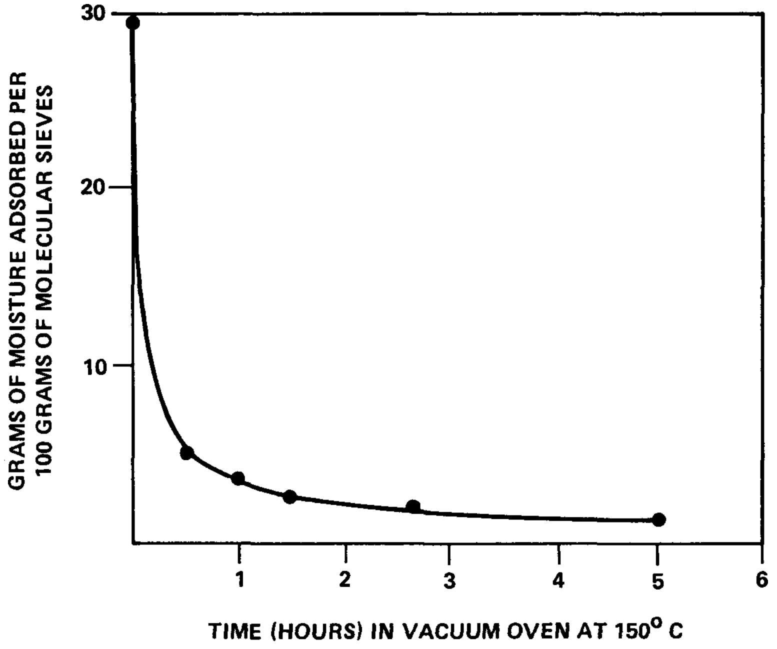


Figure 3-3. Weight loss versus time for wet molecular sieves vacuum dried at 150°C

At time zero, the sieves were fully loaded with the maximum amount possible of adsorbed water.

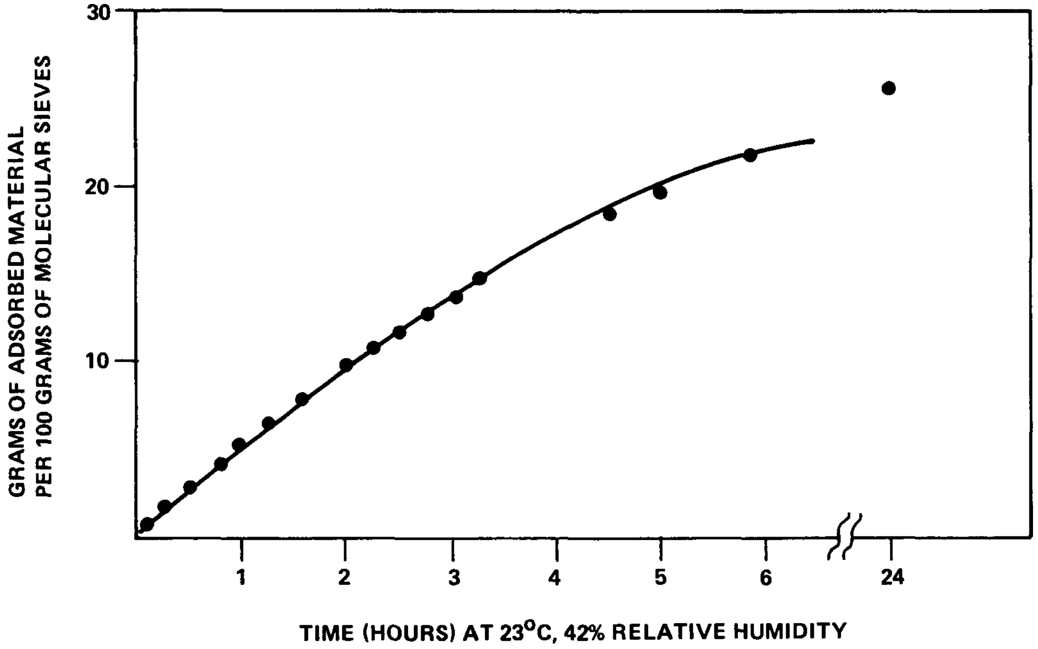


Figure 3-4. Weight uptake versus time for molecular sieves exposed to room ambient

Weight gain is due to moisture adsorption.

wet molecular sieves lost approximately 95% of their adsorbed water after three hours in vacuum at 150°C. The residual amount of adsorbed water that remained could be removed, but this would require substantially higher temperatures.

Although the loss on ignition test is the preferred method to check for dryness, fresh molecular sieves can be tested for dryness simply by placing them in high humidity. If they gain approximately 28% by weight, it can be assumed the sieves were originally dry and the weight increase was due to water adsorption. This method was used throughout this project and an average weight increase of 28% was measured when the 13X molecular sieves were exposed to 100% relative humidity overnight at 25°C.

EFFECTS OF HUMIDITY ON DRY MOLECULAR SIEVES

When placed in ambient air, molecular sieves rapidly adsorbed moisture. The data of Figure 3-4 indicates that the sieves reached their maximum loading of 28% moisture within 24 hours. For these studies, moisture uptake was measured by circulating ambient air (23°C, 42% relative humidity) over sieves that were spread in a thin layer over a large area. It should be noted that the weight uptake can not be attributed to nitrogen or oxygen. These gases are adsorbed only at cryogenic temperatures.

The rapid moisture uptake of molecular sieves plotted in Figure 3-4 indicates they must be handled carefully. Sieves must be kept in tightly closed containers to prevent adsorption of water or other highly polar molecules which could interfere with SF_6 adsorption.

EFFECT OF HUMIDITY ON SF_6 LOADED MOLECULAR SIEVES

As shown in Figure 3-5, when exposed to ambient humidity, SF_6 loaded sieves rapidly lost weight. This can be attributed to initial SF_6 desorption followed by a subsequent weight increase due to water adsorption.

This measured behavior demonstrates that SF_6 loaded molecular sieves must be handled carefully and should not be exposed to high humidity. If exposed to high humidity, SF_6 will be replaced by moisture and the resultant foam formulations will not have the desired degree of SF_6 blowing. In order to prevent loss of adsorbed SF_6, molecular sieves must therefore be stored in closed containers, preferably under a blanket of SF_6 gas.

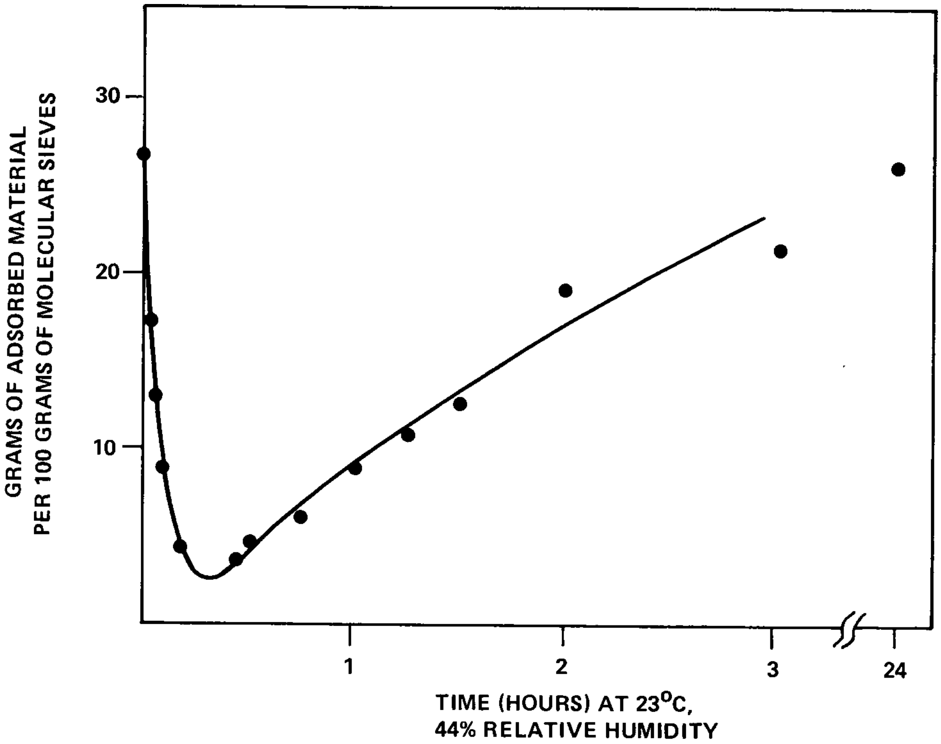


Figure 3-5. Weight change versus time for SF_6 loaded molecular sieves exposed to room ambient

Initial weight decrease is due to rapid SF_6 desorption followed by a weight increase attributed to moisture uptake. Note that moisture uptake after 24 hours approaches theoretical maximum.

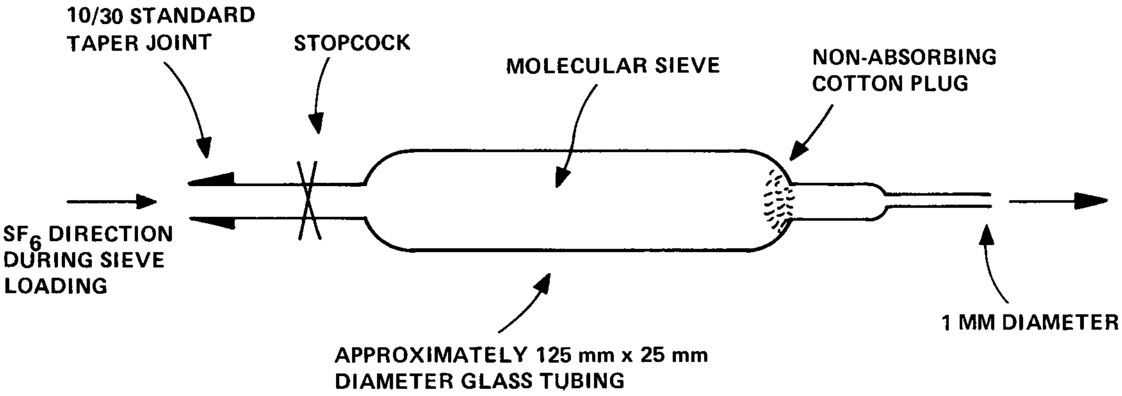


Figure 3-6. Sample holder for SF_6 loaded sieves

13X molecular sieves were loaded with SF_6 by passing gas through the tube in the direction shown by the arrow. When loading was complete, the 1 mm tube was sealed in a flame, and the stopcock was shut. The SF_6 loaded molecular sieves were then shipped for subsequent analysis.

The SF_6-H_2O exchange described above is a common adsorption phenomenon. Each adsorbed component equilibrates with respect to its partial pressure. Since the partial pressure of SF_6 at room ambient is essentially zero and that for moisture is relatively high, SF_6 rapidly desorbs whereas water is rapidly adsorbed.

ANALYSIS OF SF_6 LOADED MOLECULAR SIEVES

SF_6 loaded molecular sieve samples were prepared and stored in the apparatus depicted in Figure 3-6, and then shipped to Lehigh University for analysis. Based on the data obtained at Lehigh University (Appendix A), and the interpretation provided by Professor Sturm, the recovery of desorbed SF_6 gas from the loaded molecular sieves was consistent with the amount originally loaded on the sieves. This indicates SF_6 loaded sieves can be stored for indefinite periods provided the material is maintained in an SF_6 or other inert environment, such as dry air. Furthermore, the data of Appendix A suggests that since the SF_6 molecular sieve system obeys the Clausius-Clapeyron relationship, this relationship can be used to estimate the pressure obtained during epoxy foam cure.

SECTION 4

THE MANUFACTURE OF SF_6 EPOXY FOAM

FORMULATIONS

The formulations chosen for this investigation were developed to provide typical formulations that could be readily prepared and analyzed for SF_6 retention. All components were common and readily available (Table 4-1). No attempt was made to optimize either the properties or processability of these formulations because optimization is product dependent, and for these studies, a product was not under development.

Initial formulations (Table 4-2) were modified in an attempt to overcome the difficulties encountered in attempting to measure Fluorine concentrations via NAA. Since it was found that the aluminum nuclei of the alumina filler interfered with the gamma ray spectrum of F-20, silica was substituted for the original alumina filler.

The basic SHF-3 formulation and SHF-3 modifications (Table 4-3) extensively used in these studies primarily involved varying modifier (Empol 1022) to hardener (ZZL-0334) ratios. Smaller ratios resulted in higher heat distortion temperatures. These ratio changes were made in an attempt to determine if SF_6 retention was related to the heat distortion temperature (glass transition) of the basic resin system.

Initial attempts to determine if SF_6 retention was related to the glass transition temperature were made by preparing different base resins that had various heat distortion temperatures. This approach was terminated for two reasons. First, the different base materials would probably exhibit different diffusion characteristics when compared to each other. Secondly, it was difficult to foam some of the high temperature formulations.

Table 4-1. List of Materials

MATERIAL	DESCRIPTION	SOURCE
ERL-4221	Cycloaliphatic Epoxy Resin	Union Carbide
Empol 1022	High Molecular Weight Tribasic Acid Modifier	Emery Industries
ZZL-0334	Anhydride Hardener (methyl tetrahydrophthalic anhydride)	Archem Company
L-540	Surfactant	Union Carbide
Nuocure 28	Catalyst (Stannous 2-ethyl hexoate)	Tenneco
Molecular Sieves	Type 13X Zeolite	Union Carbide
SF_6	Gas	Union Carbide
325 Mesh Supersil	Silica (SiO_2)	G. A. Rowley Company
ERR-4090	Cycloaliphatic Epoxy Resin	Union Carbide
HHPA	Hexahydrophthalic Anhydride Hardener	Ciba Geigy Corporation
C331	Hydrated Alumina Filler	Alcoa
QZ-13	Release Agent	Ciba Geigy Corporation

Table 4-2. Typical Alumina Filled SF_6 Epoxy Foam Formulation

COMPONENT	PERCENT BY WEIGHT
ERL-4221	12.5
ERR-4090	10.2
HHPA	15.9
L540	0.09
C331 Alumina	56.8
SF_6 Loaded Molecular Sieve	4.5

Table 4-3. Epoxy foam formulations of a family of material similar in composition except for a variation in modifier (Empol 1022) to hardener (ZZL-0334) ratio

Lower ratios result in higher heat distortion temperatures.

Refer to Table 4-5 for typical mold preparation and mixing procedure.

COMPONENT	PARTS BY WEIGHT		
	SHF-3	SHF-7	SHF-8
ERL 4221	100	100	100
Empol 1022	81	30	56
ZZL-0334	11	60	36
325 Mesh Supersil (SiO_2)	93	92	93
L540	0.4	1	1
Nuocure 28	4	4	4
SF_6 Loaded Molecular Sieves	20	20	20
Measured Heat Distortion Temperature, °C	68	127	90

Note: SHF-13, 14, and 15 are similar to SHF-3, 7, and 8 respectively except the SF_6 loaded molecular sieves and filler are omitted.

Table 4-4. Typical High Temperature SF_6 Epoxy Foam Formulation SHF-235-E

Refer to Table 4-5 for processing.

COMPONENT	PARTS BY WEIGHT
ZZLA 0334	91
SiO_2	132
L540	2
Nuocure 28	4
MS with SF_6	25
Araldite 6005	15
ERL 4234	85
NP30	1

One such high temperature formulation, similar to that of Table 4-4, initially resulted in a foam with a density of 1.0 versus 1.6 for the unfoamed material. Although this low weight high temperature material may have future applications, it was not suitable for SF_6 retention analysis because of its open cell structure. NAA of the original formulation confirmed the absence of SF_6. Note, however, even though SF_6 was not retained by the plastic, the only feasible method to foam this material may be with SF_6 loaded molecular sieves.

The cell structure of the high temperature formulation described in Table 4-4 was improved by increasing surfactant concentration and reducing filler content. NAA confirmed 1.4% of SF_6 by weight was present. Although this material would be an excellent candidate for high temperature applications, this formulation was abandoned in favor of performing SF_6 diffusion studies with the SHF-3 family listed in Table 4-3.

Another major formulation change was to eliminate the relatively costly SF_6 loaded molecular sieve. Although processing may be difficult to control, elimination of the molecular sieve has the potential of cost reducing the material. Most important, however, elimination of the molecular sieve from the formulation eliminated interferences in the F-20 gamma ray spectrum due to aluminum. Therefore, precise diffusion data could be measured (Table 6-3), and accurate data of this type may be applicable in determining diffusion rates for systems both with and without filler or molecular sieves. That is, if diffusion occurs, SF_6 must diffuse through the base polymer of a closed cell system. Therefore, the resin and not the filler probably determines the SF_6 diffusion rate. If the data from an unfilled-unsieved SF_6 sample indicates the base polymer is impervious, SF_6 diffusion would probably not occur from a closed celled system of the same resin, regardless of filler or sieve content.

Many other formulation and processing changes are possible, such as variations in filler, resin, hardener, modifier, surfactant, pigment, flame retardants, UV inhibitors, mold temperature, mixing procedure, and resin temperature. Variations in any or all of these could possibly affect diffusion. Since countless variations exist, it would be impossible in this project to determine how each affects SF_6 diffusion. However, when a new material is developed for a particular application, diffusion of SF_6 from the newly developed formulation will be investigated provided SF_6 retention is essential for that particular application.

PROCESSING

Epoxy foam formulations for the Neutron Activation Analysis studies were cast in standard 8" x 8" x 1/4" aluminum sheet molds or in 1/2" diameter pyrex test tubes. The formulations (Table 4-3) and casting procedures (Table 4-5) were typical for epoxies except for the addition of the SF_6 loaded molecular sieves.

COST OF SF_6 EPOXY FOAM

As seen in Table 4-6, the cost per unit volume of SHF-3 foam is approximately 5% higher than that for the unfoamed epoxy. A unit volume of SHF-3 foam would cost $0.58 compared to $0.56 for an equivalent volume of unfoamed resin. Although the foaming dramatically reduces the density of the plastic, the added cost of the SF_6 loaded molecular sieve offsets this decrease.

Improved loading and foaming techniques could decrease the cost per unit volume. For example, if the molecular sieves were loaded in house rather than purchased from Union Carbide at $4.40/pound, the cost of SF_6 loaded sieves would be reduced to $2.40/pound (this price excludes labor and assumes SF_6 is not lost during loading). At $2.40/pound for molecular sieves, material cost would be reduced from $0.82 to $0.69/pound, or $0.49 for a volume equivalent to the volume of a pound of unfoamed material. This corresponds to 10% less than the cost of an equivalent volume of unfoamed material ($0.49 versus $0.55).

Table 4-5. Typical Mixing Procedure and Mold Preparation for SF_6 Epoxy Foam Formulations SHF-3, 7, 8, and SHF-235

Part A	Part B
Epoxy Resin	Surfactant
Hardeners	Catalyst
Filler	Molecular Sieves Loaded with SF_6

MOLD PREPARATION:

1. Clean mold.
2. Grease mold with QZ-13 release agent.
3. Preheat mold to 121°C prior to casting (for SHF-235, preheat mold to 150°C).

MIXING & POURING PROCEDURE:

1. Mix Part A in Waring blender three minutes at low speed.
2. Evacuate three to five minutes at 0.5-1.0 torr. Note: If evacuation is difficult, heat vacuum tank to 62°C to decrease viscosity and therefore promote evacuation.
3. Add Part B, one component at a time. Assure molecular sieves are completely wet by resin.
4. Mix under SF_6 atmosphere in blender for two minutes at low speed. Make sure that all air in the blender has been displaced by SF_6 prior to mixing.
5. After mixing parts A and B, pour immediately.

GEL & CURE:

1. Gel at 121°C for 15 minutes (for SHF-235, gel 3 hours at 150°C).
2. Cure at 121°C for 16 hours (for SHF-235, cure 8 hours at 205°C).

Table 4-6. Calculation of material cost for SHF-3 epoxy foam

COMPONENT	LBS.	ESTIMATED $/LB.	TOTAL $
ERL 4221	100	0.90	90
Empol 1022	81	0.65	53
ZZL-0334	11	0.84	9.3
SiO_2	93	0.03371	3.5
L540	0.4	2.75	1.1
Nuocure 28	4	2.00	8
SF_6 Loaded Molecular Sieves	20	4.40	88
TOTAL	309.4		252.9

Based on the above, 309.4 pounds of foam would cost $252.9, or $0.82 per pound. If the weight and cost of L540 and molecular sieves were subtracted, the cost of 289 pounds of unfoamed resin would be $161.80, or $0.56 per pound. However, since foaming reduces the density, the cost per unit volume is reduced accordingly. Therefore, assuming a unit volume of unfoamed material costs $0.56, an equivalent volume of foam would cost $0.82/1.4 or $0.58.

SECTION 5

EPOXY FOAM AND ITS TRAPPED SF_6

SOURCES OF SF_6 GAS IN EPOXY FOAM

Since gas can be dissolved in the liquid epoxy by the mixing procedure, all mixing was done under a blanket of SF_6 gas. As seen in Table 5-1, the amount of SF_6 introduced into the material from the mixing operation was significant for unfilled systems. However, when the filler content was increased to 30%, the added viscosity and reduced amount of agitation during mixing helped decrease the amount of SF_6 dissolved in the material. At higher filler levels, most of the foaming that occurred can be attributed to the SF_6 that unloaded from the molecular sieves.

The data of Table 5-1 indicates that in order to assure inclusion of only SF_6 in epoxy foam, all mixing should be done under SF_6, especially at low filler levels. Even though it may be possible to incorporate sufficient SF_6 into unfilled materials from the mixing operation alone, the process can not be easily controlled and the gas would tend to be released with storage time. Therefore, foaming with SF_6 loaded molecular sieves is the preferred method.

It should be noted that the percent increase in volume depicted in Table 5-1 can not be directly related to the total SF_6 concentration of the sample. Although the volume increase of the unfilled samples of Table 5-1 are similar (36.2 versus 47.2% increase), the material foamed with molecular sieve contains nearly an order of magnitude more SF_6 than the material foamed without SF_6 loaded molecular sieves.

MEASURED FLUORINE CONCENTRATION VERSUS THEORETICAL CONCENTRATION

When the concentration of SF_6 was measured in unaged samples, only 50% of the theoretical amount was detected. These low measurements were initially thought to be related to both the composition and content of filler in the resin. It was believed that SF_6 may have diffused from the epoxy during gel, possibly by diffusing out along the epoxy-filler interface.

Table 5-1. Amount of Foaming Caused by SF_6 during Mixing Compared to the Amount of Foaming Caused by SF_6 Released from Loaded Molecular Sieves as a Function of Filler Content.

	Percent Volume Increase Due to Foaming		
Silica Content Percent by Weight	Evacuated Resin and Filler Only	Evacuated Resin and Filler Mixed under SF_6. No molecular sieves.	Resin, Filler and SF_6 Loaded Sieves Mixed under SF_6. (1)
0	0	36.2	47.2
20	0	15.2	42.7
30	0	11.1	41.7

(1) Material was evacuated and then mixed in a Waring type industrial blender under a blanket of SF_6 gas. Some SF_6 was dissolved in the material during the mixing operation.

Table 5-2. Concentration of SF_6 detected by NAA versus maximum theoretical amount present

Formulation	Calculated Maximum Percent of SF_6 in the Formulation	Actual Percent of SF_6 Detected by NAA	Percent of Theoretical Actually Measured
SHF-9	2.1	0.94	45
SHF-10	1.86	0.81	44
SHF-11	1.72	0.95	55
SHF-12	1.66	0.67	41

As seen in Figure 5-1, a plot of the percent of detectible fluorine versus filler content did not exhibit any appreciable differences. Since the data appeared to drop off at higher loadings, an attempt was made to extend these studies up to 60% filler loadings, but due to the difficulty in blowing samples with high filler loadings, the experiments were stopped. In any case, each sample had approximately 50% of the theoretical amount of SF_6 (Table 5-2), and this indicated the apparent loss could not be attributed to filler loadings.

In a further attempt to determine the cause for losing 50% of the SF_6, an uncured liquid epoxy sample and a cured foam sample of the same material were compared. The NAA results suggested there was slight loss from the liquid to the gel or cure state (Table 5-3), but not enough to account for the suspected 50% loss.

Since it is well known that molecular sieves rapidly desorb SF_6 (Figure 3-5), it is possible that SF_6 was lost when the sieves were exposed to air during the mixing operation. Even though a 50% SF_6 loss may occur, this loss may not be significant because there is sufficient gas pressure to cause foaming (refer to next topic in this section). Also, the material does exhibit the unique properties attributed to the SF_6 blowing agent. However, if future processing becomes a problem, the SF_6 loss should be further investigated as a means of improving blowing efficiencies.

SF_6 PRESSURE IN EPOXY FOAM

In order to calculate the average SF_6 pressure in epoxy foam, the following assumptions can be made:

1. From Table 5-2, approximately 0.9% of the total material weight is SF_6.
2. The molecular sieves completely unload.
3. As per Table 5-1, foaming increases material volume by approximately 42%. That is, 1.37 grams of unfoamed material, which originally occupied 1 cm^3, occupies 1.42 cm^3 after foaming resulting in a new density of 0.97 gm/cm^3 ($1.37\ gm/1.42\ cm^3 = 0.97\ gm/cm^3$).

Based on these assumptions, the number of moles of SF_6 per cm^3 of unfoamed material

Table 5-3. Comparison of F detected in liquid and gelled epoxy

	Amount of F detected by NAA-ppm	
SAMPLE NUMBER	Liquid epoxy (not gelled) SHF-7 formulation	Cured epoxy foam SHF-7 formulation
1	8010	7550
2	7390	5810
3	7910	6370
4	7290	6260
AVERAGE	7650	6500

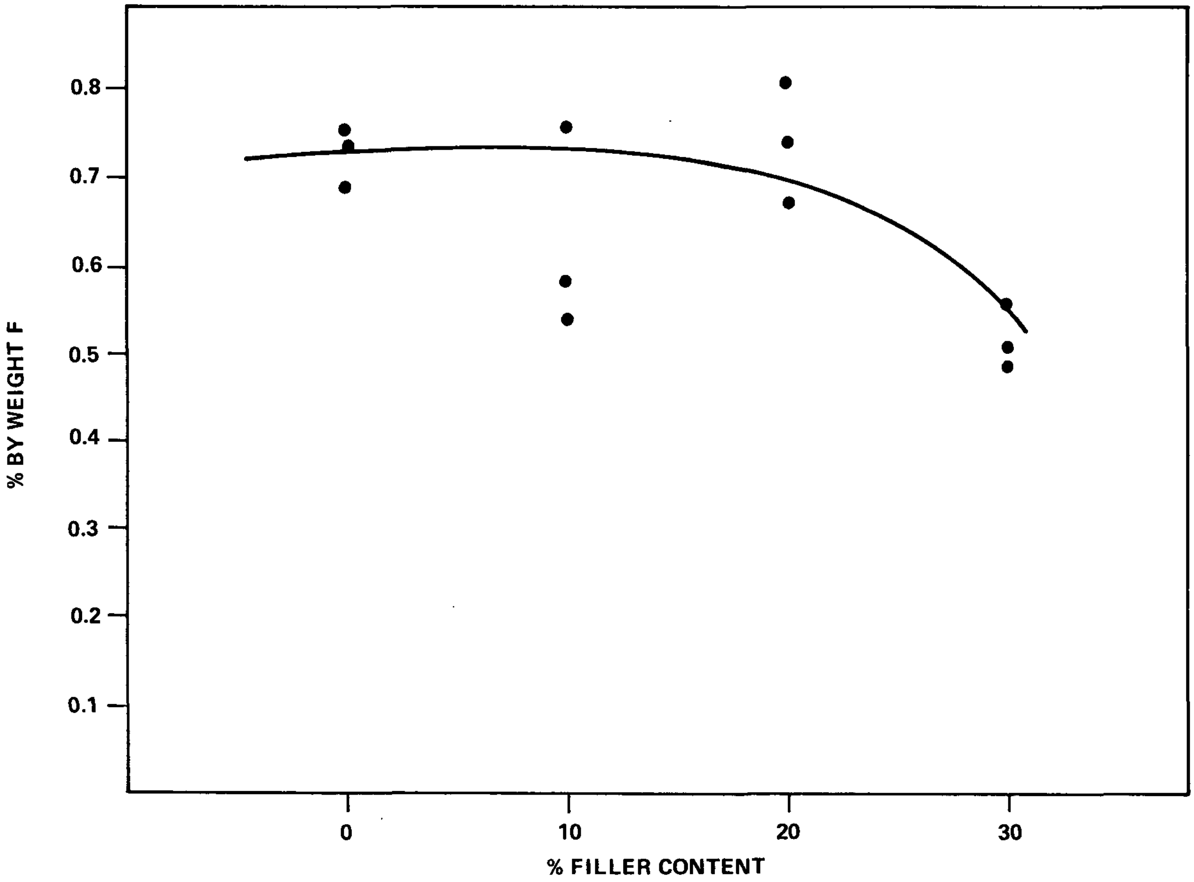


Figure 5-1. Fluorine concentration as a function of filler content

Fluorine was measured via Neutron Activation Analysis in triplicate 2" x 1/2" x 1/4" samples cut from sheets with 0, 10, 20, and 30% by weight filler loadings (Formulations SHF-9, 10, 11, and 12 respectively).

$$= \frac{(0.97\ \text{gm/cm})\ (0.9\%\ \text{by weight}\ SF_6\ \text{for foam})}{146\ \text{gm}\ SF_6/\text{Mole}}$$

$$= 0.000060\ \text{moles}$$

Since $P = nRT/V$

$$P = (0.6 \times 10^{-4}\ \text{moles})(0.082\ \frac{\text{L-Atm}}{°\text{K-Mole}})\ (300°\text{K})/(0.00042\ \text{L})$$

$$= 3.5\ \text{Atm}$$

The above calculation indicates that sufficient SF_6 gas is present to cause foaming.

SECTION 6

STUDIES ON THE RETENTION OF SULFUR HEXAFLUORIDE BY EPOXY FOAM

Since preliminary test data indicated that some of the properties of SF_6 foam could be attributed to trapped SF_6, the major goal of this research was to confirm the presence of SF_6 in epoxy foam. If SF_6 were detected, the goal would then be to determine if SF_6 were retained by the epoxy.

Various techniques have been tried by others in order to analyze gases trapped in foam materials. For example, the material can be destroyed in a vacuum with sulfuric acid and the released gases can be analyzed by a mass spectrometer (3). Another technique includes crushing the sample in argon followed by mass spectrometric analysis (4). Also, a method has been developed where a needle is inserted into the foam while under vacuum, and the gas is then analyzed by a gas chromatograph (5). Although these methods could possibly be used for our studies with SF_6 foam, they all suffer from the fact that samples are destroyed during analysis.

Since a non-destructive test was required for these studies, instrumental Neutron Activation Analysis was chosen. This non-destructive analytical technique is suitable because it can be used repeatedly on the same sample. Therefore, after measuring the initial SF_6 concentration in an SF_6 foam sample, the sample can be artificially aged and then reanalyzed to measure any changes in SF_6 concentration. This is the first time that Neutron Activation Analysis has been used for these types of studies.

Fluorine determinations are performed routinely by instrumental activation analysis. Instrumental Neutron Activation Analysis is rapid, sensitive (down to 0.4 micrograms of F) and precise (±5% of the value). Since neutrons activate the nucleus of an atom, the method determines total fluorine content regardless of oxidation state or chemical form. Since all fluorine is attributed to SF_6, the measured fluorine concentration can be directly converted to SF_6 concentration.

NEUTRON ACTIVATION ANALYSIS (NAA) EXPERIMENTAL

Test samples were irradiated along with comparitor samples for thirty seconds in General Activation Analysis, Inc.'s TRIGA Mark I Nuclear Reactor at a flux of 4.3×10^{12} n/cm^{2}sec. (Molecular sieves can withstand 6.2×10^{17} neutrons/cm^2 before damage is detected.) The stable Fluorine-19 produced Fluorine-20 with a half life of 10.7 seconds. After a decay time of 20 seconds, the gamma ray decay spectra of both the known and unknown were measured in a Ge(Li) detector coupled to a multichannel gamma ray spectrometer.

To assure that the QZ-13 fluorocarbon release agent did not interfere with F analysis, standard epoxy samples were tested. The F concentration of these unfoamed samples was less than 80 ppm (0.008%), far below the value of 0.8% in typical SF_6 foamed samples.

Unfortunately, large concentrations of aluminum nuclei from the high alumina filler concentration (Table 4-2) interfered with the initial attempts to measure fluorine. In an attempt to overcome interference from the aluminum nuclei of the filler, the samples were covered with cadmium foil and tested three different times after irradiation with different reactor power levels. Since Fluorine-19 also produces Oxygen-19 with a half life of 29 seconds, it was hoped that Fluorine could be detected from the decay spectrum of Oxygen-19. Unfortunately, this method was also unsuccessful. As a result, the foam formulation was changed by substituting silica for an alumina filler.

Although substitution of silica for alumina filler allowed F to be detected via NAA, the low precision NAA data made it difficult to accurately determine the diffusion of SF_6 from the epoxy. As seen in the first two columns of Table 6-1, the noise was considerable. For example, the detected F concentration of two identical samples, each aged at 85°C, was 5250 and 6910 PPM. Since these similar samples were aged under identical conditions, the results should have been within a few percent.

In an attempt to improve the precision of the data, larger samples were prepared (2" x 0.5" diameter tubes versus the original 2" x 1/2" x 1/4" samples cut from sheets). Although the F weight percent remained constant, it was thought the larger absolute F concentration would improve the counting statistics. The results appeared slightly improved, but the error and lack of precision remained large (Table 6-1).

Table 6-1. Comparison of F concentration measurements made on aged SHF-8 tube and sheet samples

2" x 1/2" x 1/4" sheet samples were aged 7 days and the 2" x 1/2" diameter tubes were aged 10 days at the indicated temperatures. Samples 1 and 2 were each prepared, aged, and tested under similar conditions.

Aging Temp. °C	F concentration measured by NAA-ppm					
	2" x ½" x ¼" sample cut from sheet		2" x 0.5" cast tube Initial irradiation 20 seconds		2" x 0.5" cast tube Measurement repeated after 30 second irradiation	
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
25	6630	5560	8690	6190	7450	7120
60	6530	6890	7980	7260	8660	7370
75	5940	4420	7840	5960	6850	7410
85	5250	6910	6530	8190	6250	8050
105	5180	3670	--	--	--	--
110	--	--	7700	6230	7520	5270
125	4580	5360	--	--	--	--

Table 6-2. Comparison of repeated F concentration measurments on aged SHF-7 epoxy

Two identical tube samples were aged one week at each temperature indicated. NAA was repeated on each set of samples after F-20 completely decayed.

AGING TEMP. °C	F concentration measured by instrumental NAA-ppm						
	Initial Measurement 20 Second Irradiation		Second Measurement 20 Second Irradiation		Third Measurement 30 Second Irradiation		
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Average
25	5330	6180	6850	6810	7690	4300	6190
85	9850	7420	7570	6970	6730	7880	7740
125	8030	4690	5870	5160	5860	7600	6200
140	5230	4960	6090	6950	7490	6330	6180

The low precision was then thought due to inaccurate sample transport times during the NAA process. Since irradiation was short (20-30 seconds) compared to the half life of F-20 (10.7 seconds), small timing errors could lead to significant measurement inaccuracies. Unfortunately, carefully controlled irradiations and subsequent gamma ray detections still resulted in noisy data (Table 6-2 and Figure 6-1) even after the instrument was thoroughly calibrated and checked by repeating the analysis on the SF_6 samples. Measurements were also repeated on samples submitted by other sources; the accuracy of their data confirmed the instrument was properly calibrated.

When the measurements were repeated as described above, an attempt was also made to improve results by reducing irradiation times. Reducing sample irradiation times often reduces the number of counts from interfering species. Decreasing the irradiation from 30 seconds to 20 seconds did not improve the F measuring accuracy (Tables 6-1 and 6-2, Figures 6-1 and 6-2).

It was also thought that if the initial unaged samples differed in their original SF_6 content, aging would lead to random results. For example, a sample with an initially high concentration of SF_6 could lose SF_6 through moderate diffusion if aged at a relatively high temperature. If the final concentration of the aged sample were then compared to an unaged sample initially low in SF_6 concentration, the unaged sample would appear to have less SF_6 than the aged one.

In an attempt to determine if this were possible, a 8" x 8" x 1/4" sheet was prepared and sampled as shown in Figure 6-3. As seen in this figure, there were no significant or measurable SF_6 concentration differences. All differences appeared related to the inaccuracies of the measurement technique and not from actual differences in SF_6 concentration.

The above experiment was also performed by sequentially pouring 20 tube samples and then analyzing these samples for changes in SF_6 concentration as a function of the tube pouring sequence. All samples appeared to have the same initial concentration. Noticeable changes could not be detected (Figure 6-4).

Since the reported measuring difficulties could not be attributed to either the instrument of sample preparation, two other possible approaches to improve the data were considered. First, since gamma ray detection is based on counting statistics, it was thought that data averaging would improve statistical

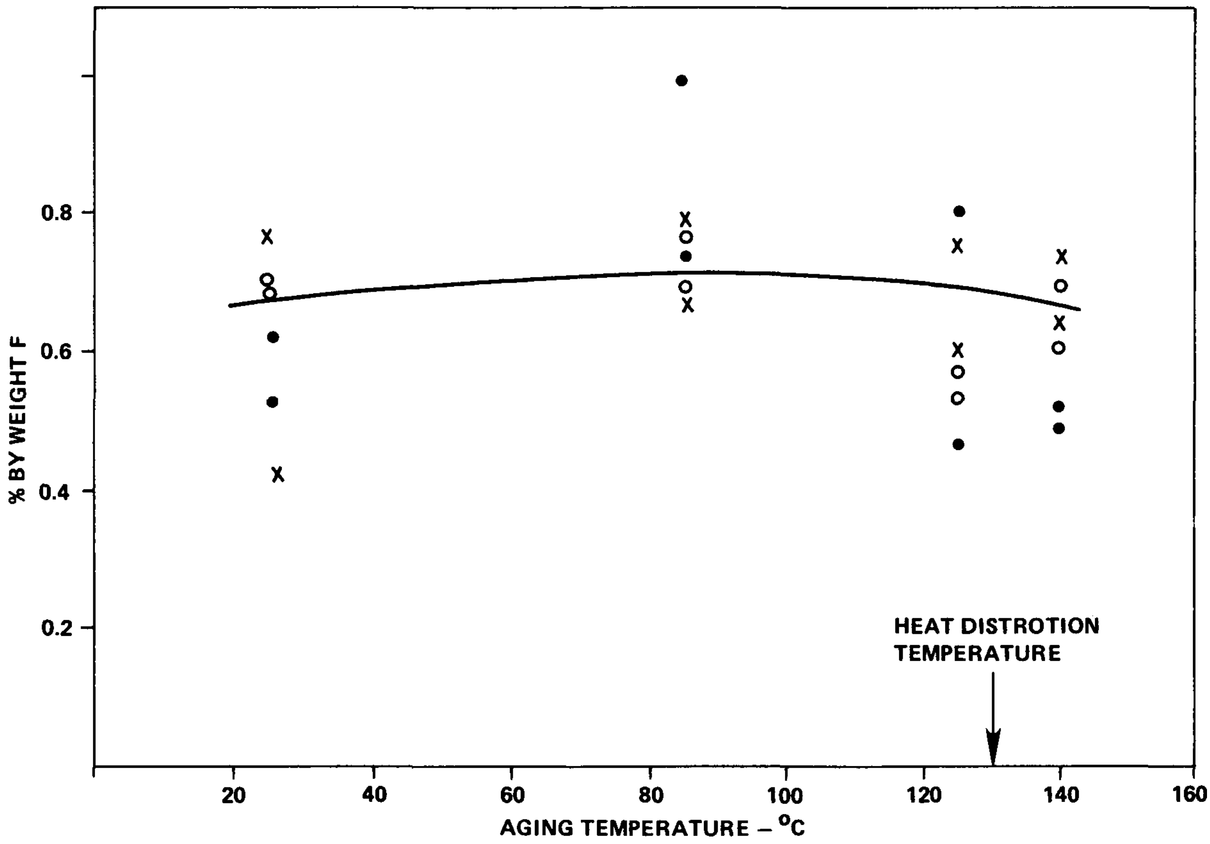


Figure 6-1. Random results obtained for F determination via NAA in aged samples of SHF-7

Duplicate 2" x 1/2" diameter samples of SHF-7 were aged one week at the indicated temperature. F-20 was allowed to completely decay prior to subsequent irradiations.

● - initial results with 20 second irradiation
o - analysis repeated with 20 second irradiation
x - final F determination - 30 second irradiation

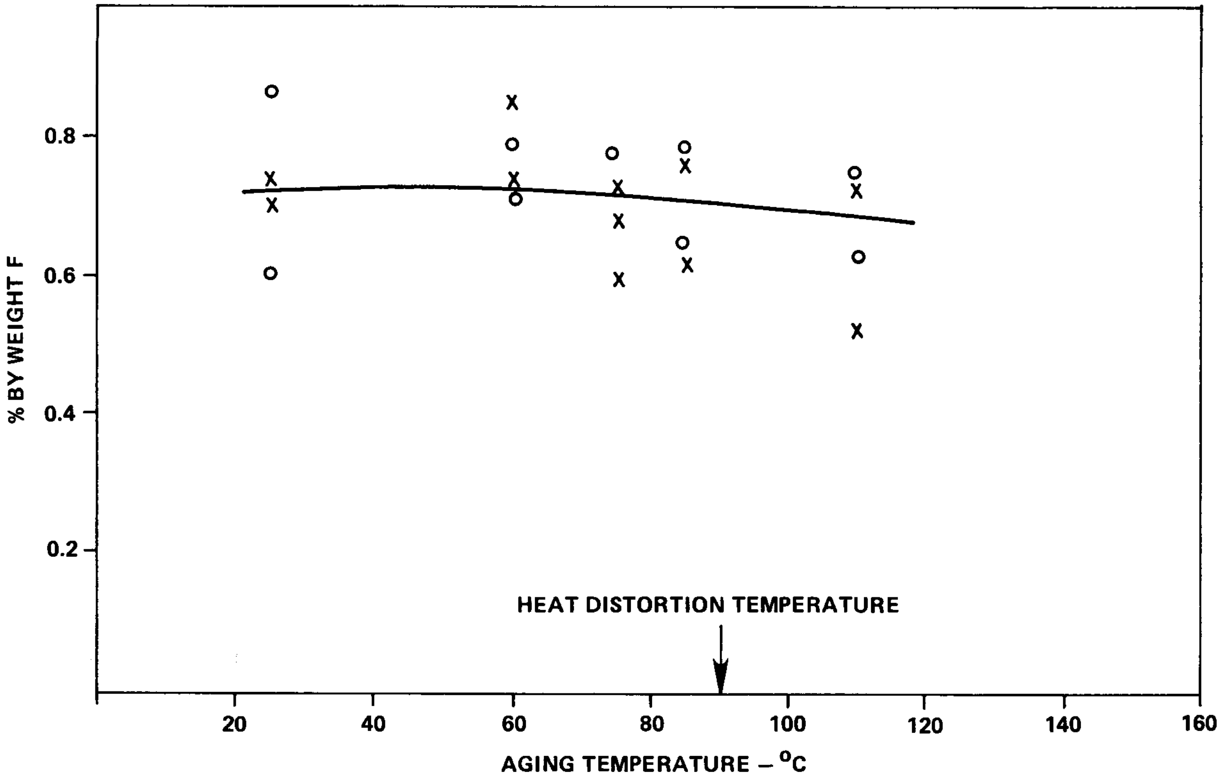


Figure 6-2. Effect of different irradiation times on the analysis of Fluorine by NAA in heat aged SF_6 epoxy foam

Duplicate 2" x 1/2" diameter SHF-8 tube samples were aged at the indicated temperatures for ten days. All samples were first irradiated for twenty seconds. The analysis was repeated with a 30 second irradiation on the same samples 18 days later. Since the half life of F-20 is 10.7 seconds, all residual F-20 decayed before the second irradiation.

o - 20 second irradiation
x - 30 second irradiation

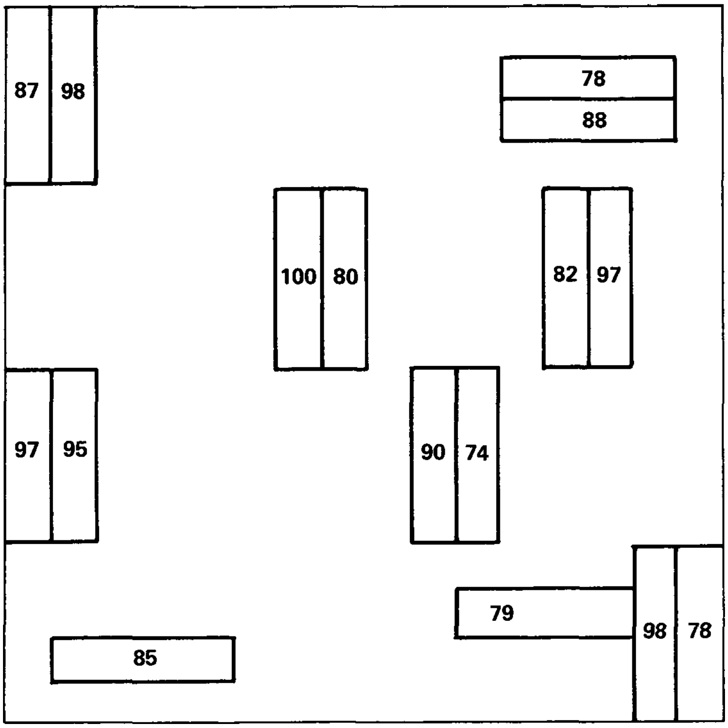


Figure 6-3. Relative F concentration determined at various locations in an 8" x 8" x 1/4" SHF-12 sheet casting

Normalized value of 100 corresponds to 0.65% F (0.83% SF_6) as measured by Neutron Activation Analysis in 1/2" x 2" x 1/4" thick samples located as shown.

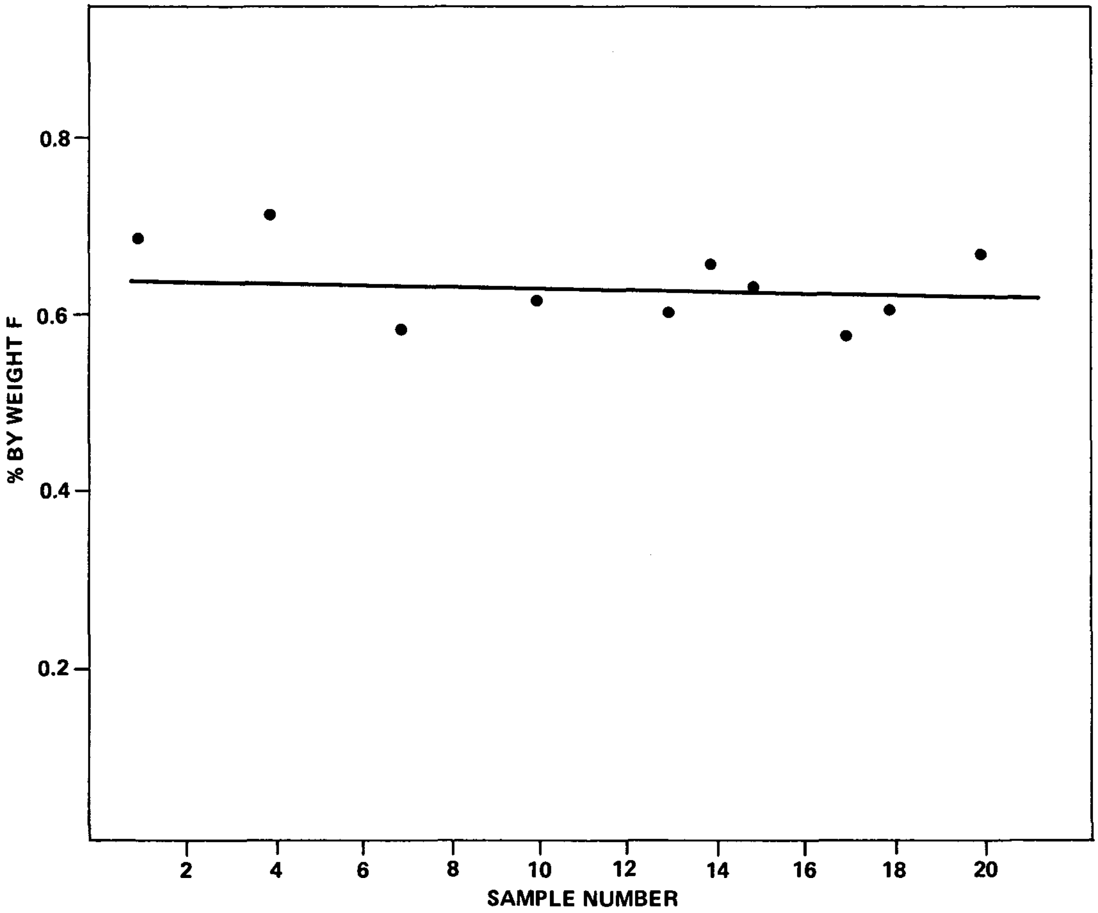


Figure 6-4. Average F concentration measured in unaged tube samples of SHF-3

Twenty tubes were cast consecutively from the same batch of mix. Only the indicated samples were then selected for F analysis via Neutron Activation Analysis.

reliability. As seen in Figures 6-8 and 6-11, averaging the data for both the sheet and tube samples dramatically improved results.

Secondly, if all sources of aluminum could be removed, the F gamma ray spectrum could be accurately measured. As shown in Table -3 and depicted in Figures 6-7, 6-10, and 6-15, F analysis results were dramatically improved by omitting all sources of F (the molecular sieve was deleted from the formulation). The accurate diffusion results of Figures 6-7, 10, and 15 indicate that the previously reported random results were entirely due to the interference of Al-28 with the F-20 gamma ray spectrum.

In summary, in order to improve the reliability of the SF_6 diffusion results, data must be averaged or all sources of aluminum must be omitted from the foam. However, it should be emphasized that even though unaveraged data appears random, this raw data confirms the presence of SF_6 and confirms that some aged samples retain SF_6.

DIFFUSION VERSUS GLASS TRANSITION TEMPERATURE

The formulations studied in this program were similar except resin to modifier ratios were varied to obtain different glass transition temperatures (Table 4-3). These formulations were easy to produce and resulted in relatively consistent castings. Although the rate of SF_6 loss from the epoxy is probably a complicated function of sample thickness, skin integrity, cell size, cell wall thickness, filler composition, as well as many others, these variables were kept constant.

The measured data suggests that SF_6 epoxy foam retains SF_6 at high temperatures provided the material has a high heat distortion temperature (the heat distortion temperature approximates the glass transition temperature, Tg). For some high temperature formulations, SF_6 losses did not occur unless the aging temperature was high enough to cause material decomposition. Formulations with low heat distortion temperatures lost SF_6 at elevated temperatures.

The epoxy foams retained the SF_6 blowing agent because the crosslink density of the polymer was relatively high. But in some cases when the tightly knit, highly crosslinked system was raised above its glass transition temperature, SF_6 diffusion could occur because of the breakage of the attractive bonds between chains which originally hindered diffusion. At low temperatures, highly flexible epoxy foams lose SF_6 because of their loosely knit structure.

Low Temperature Formulation

Initial neutron activation analysis results on the low temperature SHF-3 formulation were noisy. After averaging three runs from the same sample, the results were acceptable (Figure 6-5). Figure 6-5 represents the Fluorine concentration after a total of one, two, and six weeks of aging. As indicated in this figure, a considerable amount of sulfur hexafluoride was lost when the material was aged for only one week above its heat distortion temperature. At 125°C, complete loss of SF_6 occurred after two weeks of aging. An additional four weeks of aging indicates the material may also have lost SF_6 at room ambient and 60°C. However, due to the noise present in the analysis, these samples should be remeasured.

When the diffusion data for SHF-3 is compared to the tan δ versus temperature for the same formulation (Figure 6-6), it is noted that the rapid increase in tan δ corresponds to the same temperature at which the formulation loses SF_6 after one week of aging. These corresponding changes, both of which occur at similar temperatures, can be attributed to the glass transition temperature of the resin. This supports the contention that molecular changes occur at the glass transition of the resin, and these changes affect the dissipation factor and diffusion of SF_6 from the material.

Diffusion studies were also performed on the SHF-3 low temperature base resin foamed without molecular sieves (SHF-13). As seen in Figure 6-7, the unfilled-unsieved system also lost SF_6 after one week of aging, and the rate of loss compares favorably with that for the filled system (Figure 6-5). This supports the contention that the base polymer controls diffusion in a closed celled system. This would suggest that if an unfilled polymer does not lose SF_6 at a given temperature, a closed celled filled system of the same base resin will also retain SF_6 at the chosen temperature, regardless of filler (assuming, of course, that the filler is inert, as most are).

The measured SF_6 content of the unfilled SHF-13 samples remained constant even after an additional two weeks of aging (Figure 6-7). Although slight losses may have occurred, it appears as though the SF_6 concentration reached an equilibrium value.

The data of Figure 6-7 could also suggest that the extreme aging temperatures deteriorated the surfaces of the samples, thus allowing SF_6 to escape from

Table 6-3. F content measured by NAA in unaged SF_6 epoxy foamed without molecular sieves.

	F-ppm		
SAMPLE NUMBER	SHF-13	SHF-14	SHF-15
1	1360 ± 40	641 ± 30	1630 ± 60
2	1300 ± 40	663 ± 30	1700 ± 50
3	1330 ± 40	586 ± 29	1660 ± 50
4	1330 ± 40	563 ± 29	1540 ± 60
5	1280 ± 40	591 ± 29	1630 ± 50

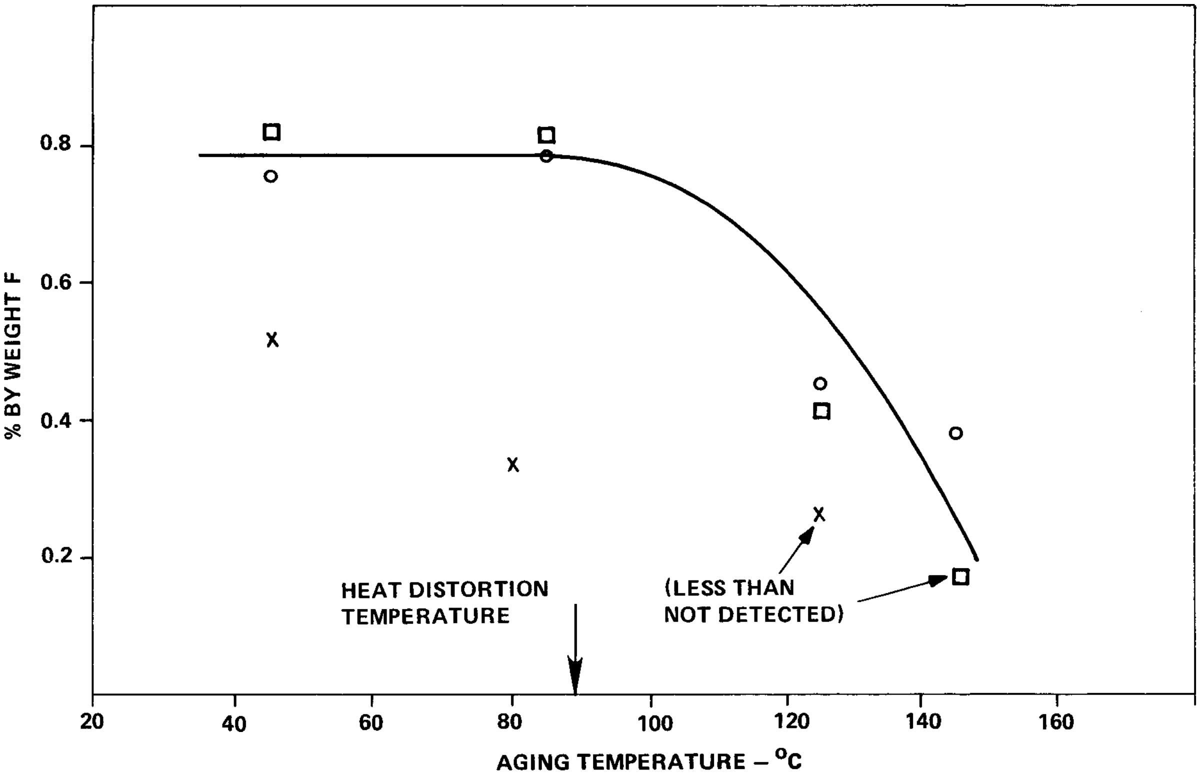


Figure 6-5. Effect of heat aging on F content of SHF-3

The 2" x 1/2" x 1/4" samples were cut from the same 8" x 8" x 1/4" sheet casting and aged as follows at the indicated temperatures:

o - aged one week
□ - same as o, but aged an additional week
x - same as □, but aged an additional 4 weeks for a total of 6 weeks

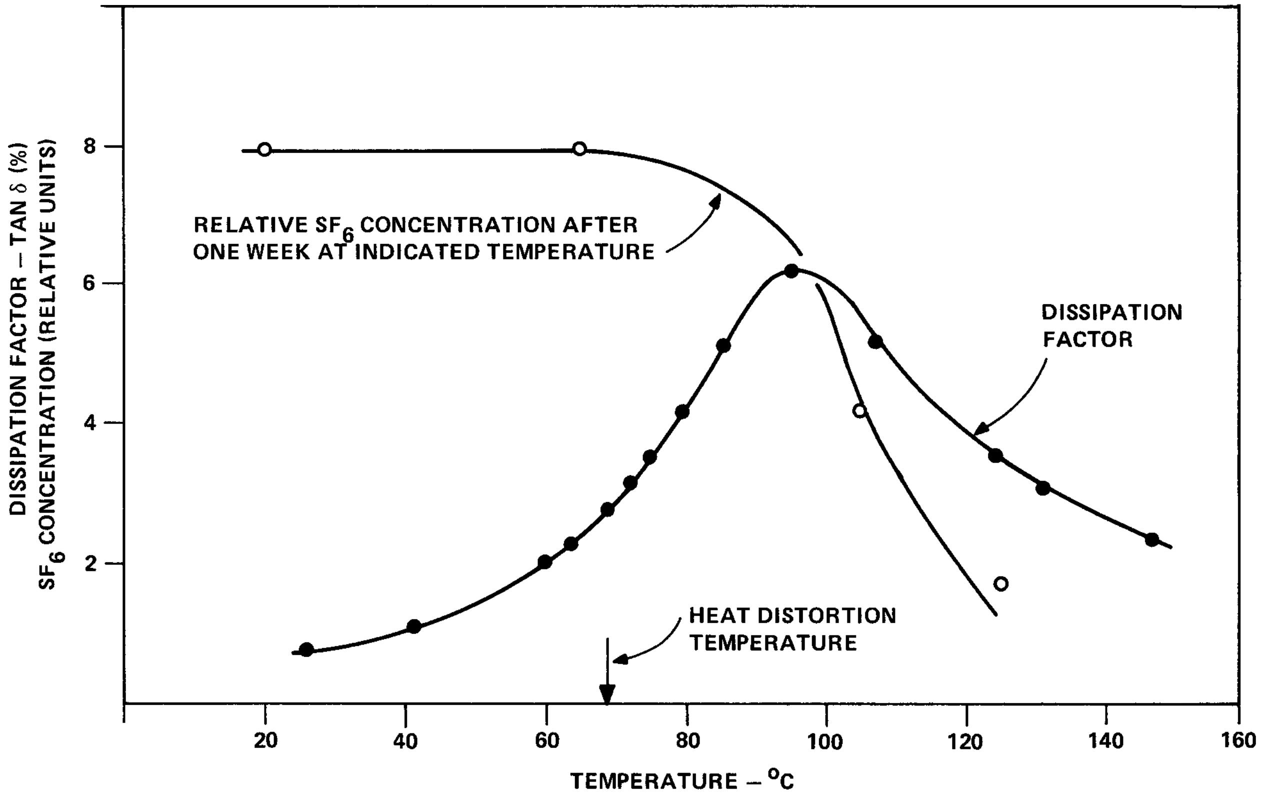


Figure 6-6 Comparison of tan δ versus temperature with the effects of aging temperature on the loss of SF_6 from SHF-3 epoxy foam

● - dissipation factor - Measured at 1500V, 60HZ on unfoamed SHF-3 resin

o - relative SF_6 concentration after one week of aging at indicated temperature (Refer to Figure 6-5)

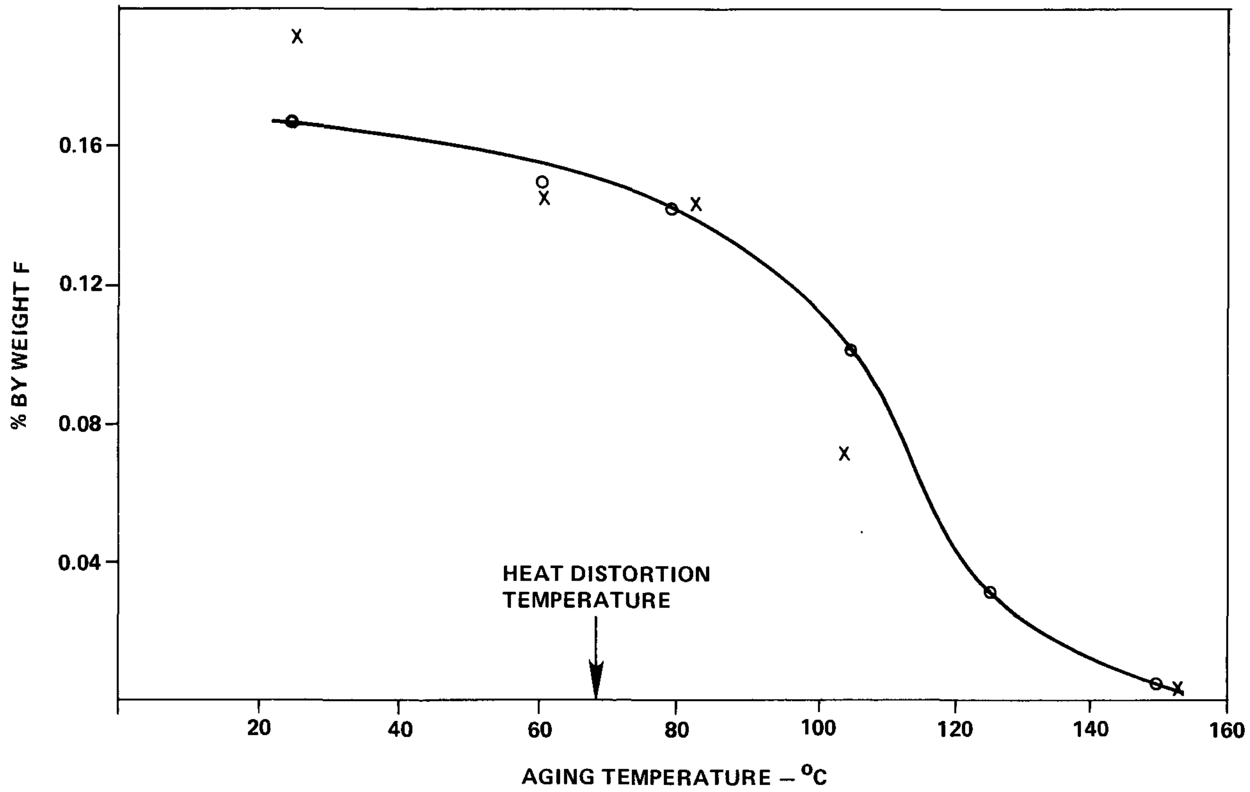


Figure 6-7. Effect of heat aging on F content of SHF-13

Each 1/2" x 2" x 1/4" sample was cut from the same 8" x 8" x 1/4" sheet casting, and then aged as follows:

o - one week at the indicated temperature
x - same as o except aged an additional two weeks

the surface cells. Subsequent heat aging would not appreciably reduce the measured SF_6 concentration because further surface degradation would not occur until the test temperature were raised above the initial aging temperature.

Moderate Temperature Formulation

A moderate temperature formulation (SHF-8) with a heat distortion temperature of 90°C was also studied. The averaged data (Figures 6-8 and 6-9) from the filled standard system was consistent with that measured for SHF-3 and 7. As expected, the formulation retained SF_6 at higher temperatures than SHF-3, and appears to exhibit slight SF_6 loss at lower temperatures than SHF-7. An additional four weeks aging on the tube samples did not appear to result in further SF_6 loss. However, as expected, the sample aged at 150°C exhibited a major depletion of SF_6 (Figure 6-9).

The data of Figure 6-10 for the moderate temperature unsieved-unfilled samples is consistent with the diffusion data of Figure 6-9. As expected, the moderate temperature formulation retained SF_6 at higher temperatures than the lower temperature formulation. Furthermore, as seen with the lower temperature resin, comparison of Figure 6-10 with either 6-8 or 6-9 indicates that the rate of SF_6 diffusion from the unfilled system is consistent with the rate of loss measured in the filled material.

High Temperature Formulation

The high temperature SHF-7 foam retained SF_6 even when aged one week at temperatures above 150°C (Figure 6-11), which far exceeds the material's 129°C heat distortion temperature. This can be attributed to the fact that this formulation is highly crosslinked. This phenomenon is supported by a plot of the tan δ versus temperature. As seen in Figures 6-11 and 6-12, there is no rapid increase in tan δ as the temperature of the system is increased. This suggests that the polymer does not exhibit the dramatic low temperature molecular transitions reported in Figure 6-6 for SHF-3. As shown in Figure 6-12, the loss of SF_6 after 5 weeks of aging corresponds fairly well to the moderate increase in the tan δ curve.

Samples of SHF-7 were thermally re-aged for an additional four and eight week intervals. As seen in Figures 6-12 and 6-13, SF_6 loss at 150°C appeared considerable. Note, however, that the 150°C thermal aging temperature is well

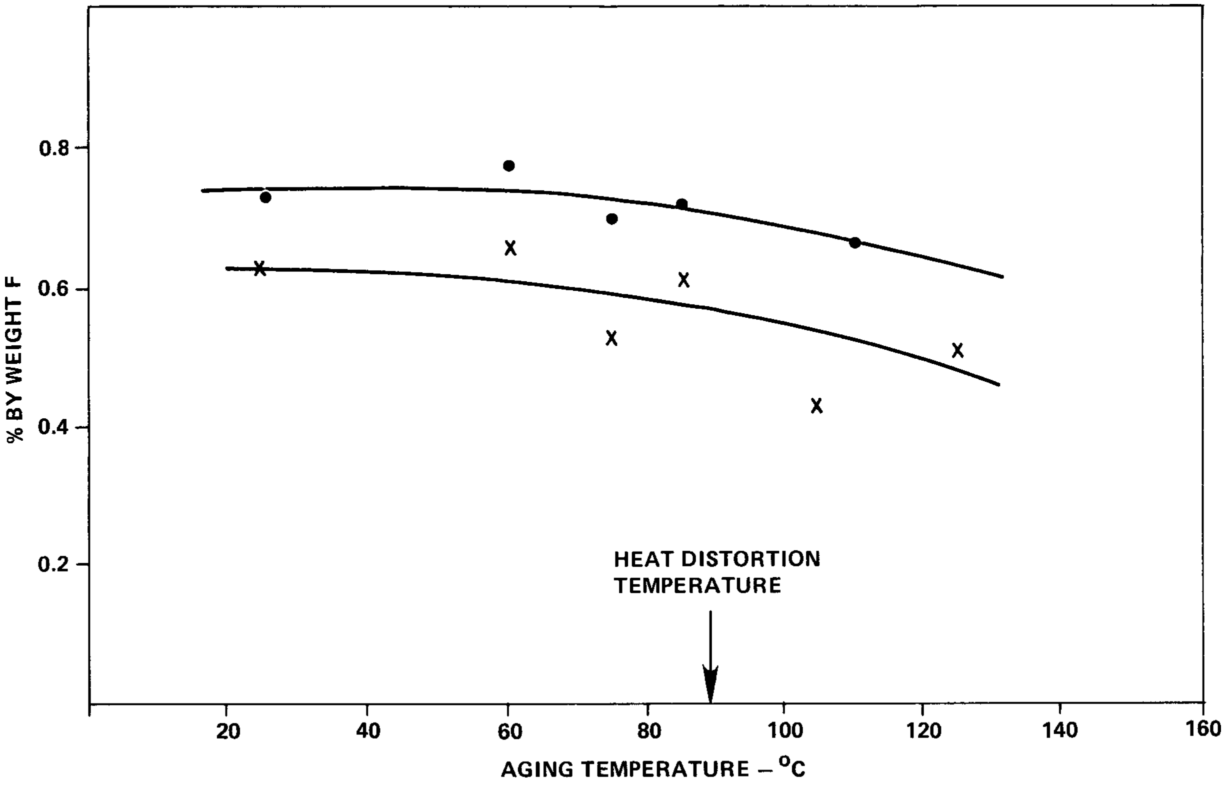


Figure 6-8. Effect of heat aging on F concentration of SHF-8

x - average of two 2″ x 1/2″ x 1/4″ sheet samples aged one week at each temperature

● - value obtained by averaging duplicate measurements made on two 2″ x 1/2″ diameter tube samples aged 10 days at each temperature shown

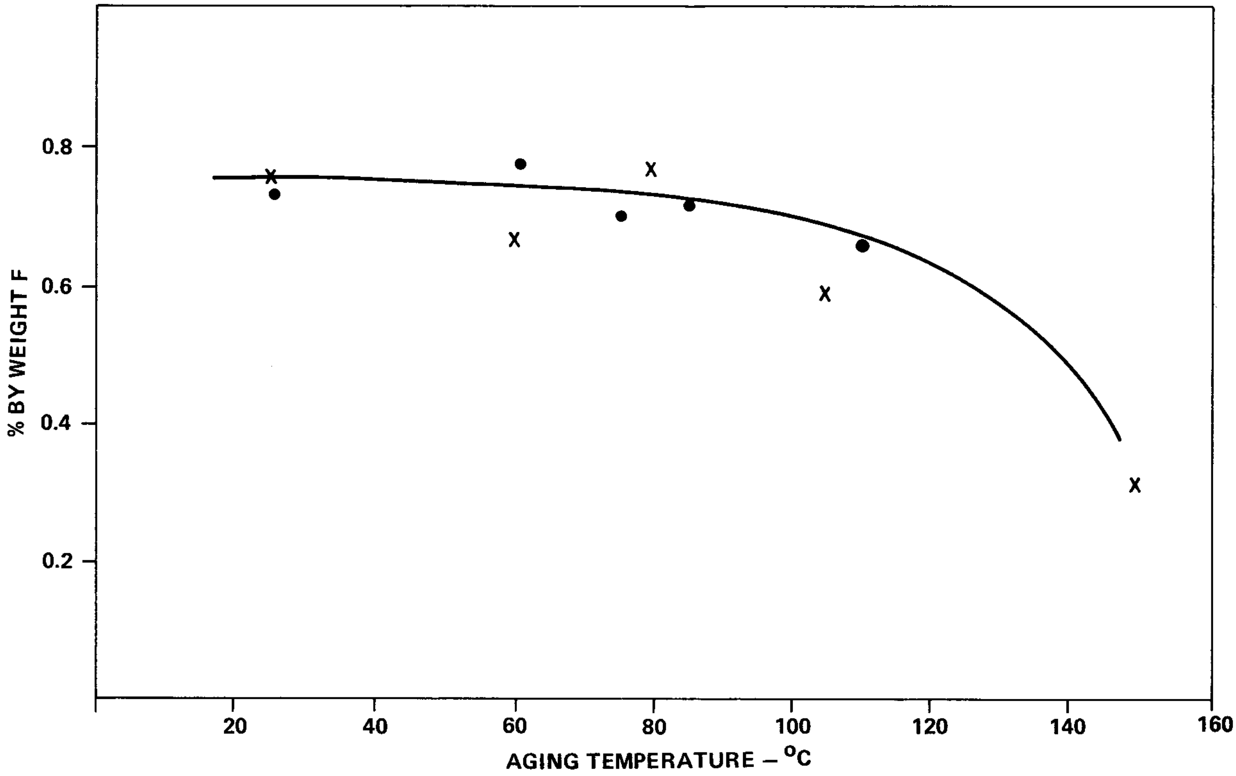


Figure 6-9. Effect of heat aging on F concentration of SHF-8 tube samples

● - aged ten days at indicated temperature
x - above samples aged an additional 4 weeks

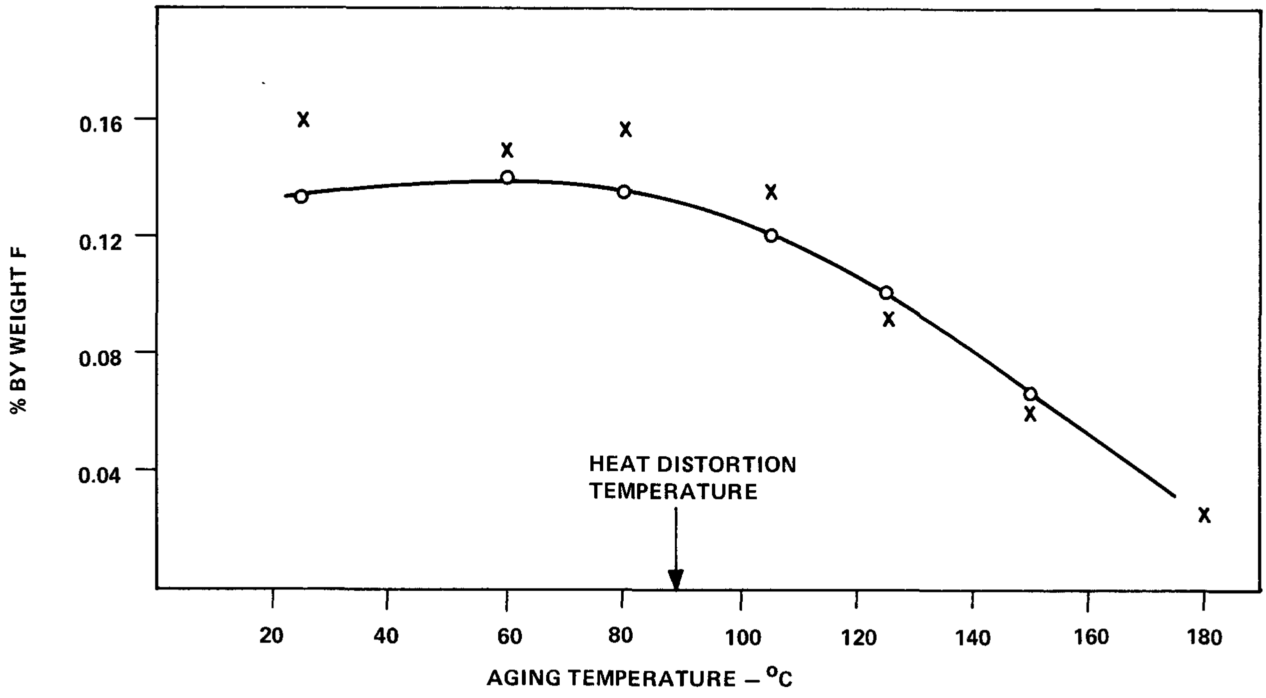


Figure 6-10. Effect of heat aging on F content of SHF-15

Each 1/2" x 2" x 1/4" sample was cut from the same 8" x 8" x 1/4" sheet casting

o - aged one week at the indicated temperature
x - samples from above aged an additional two weeks

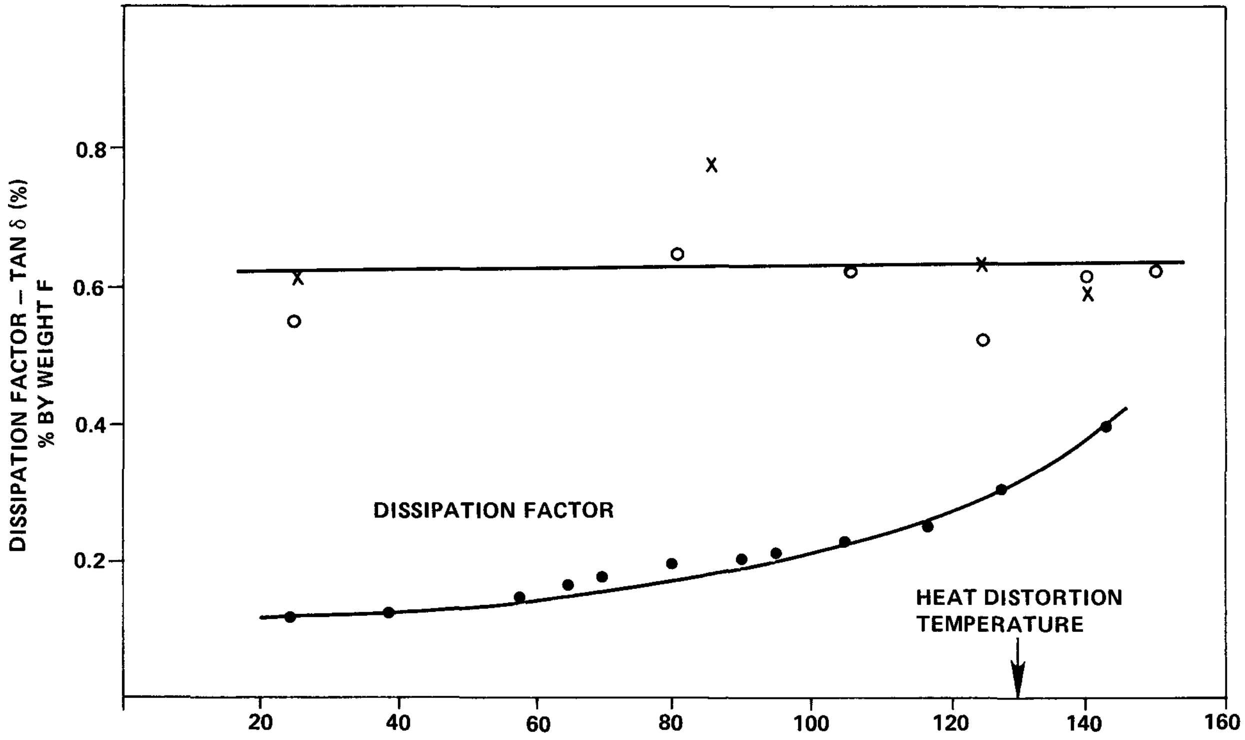


Figure 6-11. Effect of heat aging on F concentration of SHF-7 Samples were aged one week at the indicated temperatures.

x - tube samples - average values from Table 6-2
o - sheet samples - average of two samples

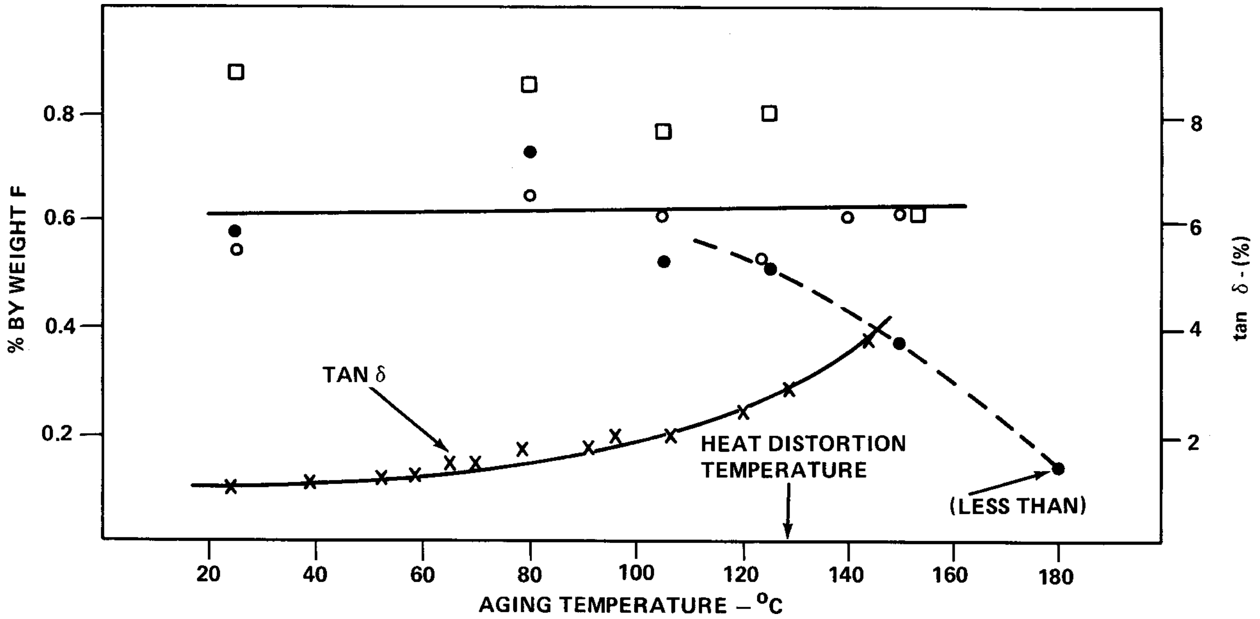


Figure 6-12. Tan δ compared to effect of heat aging on F concentration of SHF-7 sheet samples

○	-	samples aged one week at the indicated temperatures
●	-	same samples as above except aged an additional four weeks
□	-	same as ● above except aged an additional eight weeks for a total of thirteen weeks

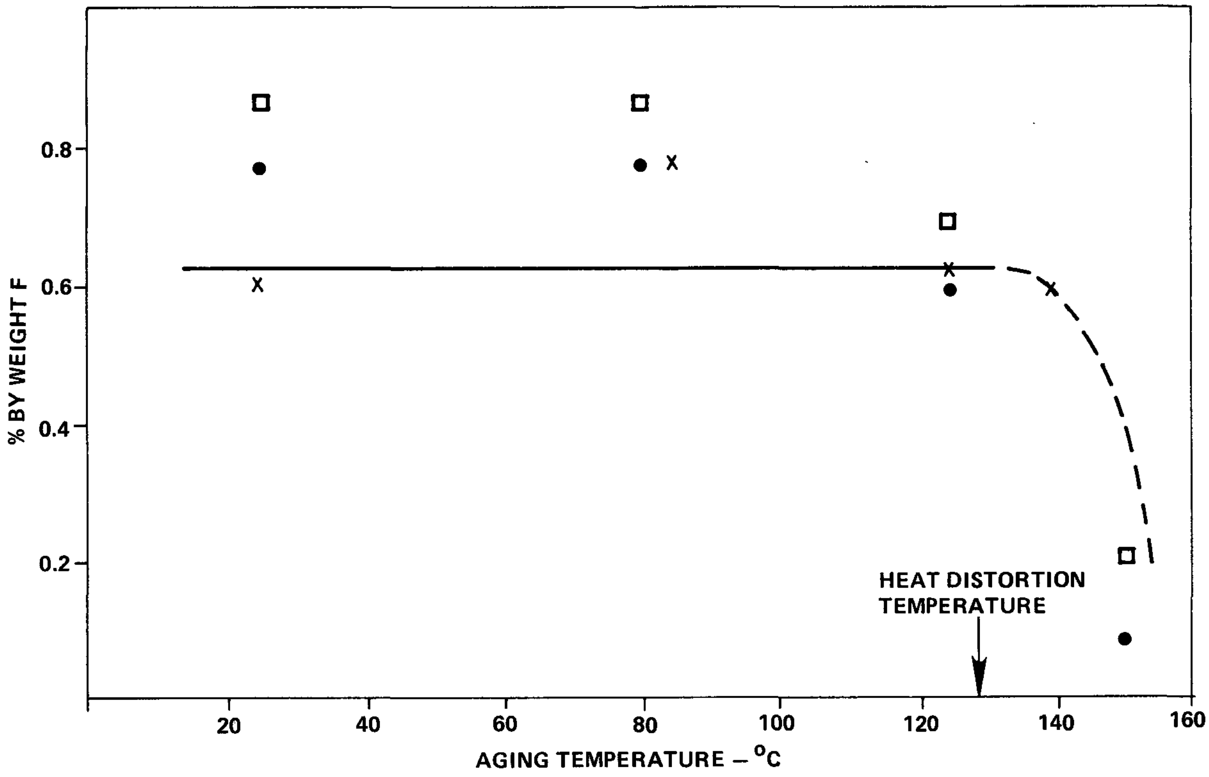


Figure 6-13. Effect of heat aging on F concentration of SHF-7 tube samples

x - samples aged one week at the indicated temperature

● - same aged samples as above except aged an additional four weeks

□ - above samples (●) aged an additional seven weeks for a total of twelve weeks in excess of the mechanical limits of material (approximately 127°C, or the heat distortion temperature). Furthermore, the aging samples of Figure 6-12 represented the worse possible case, namely, thin 2" x 1/2" x 1/4" samples with at least four cut sides, all of which would favor diffusion.

The results on unfilled-unsieved samples of SHF-7 (Formulation SHF-14) confirmed that the resin with the highest heat distortion temperature had the greatest tendency to retain SF_6 at high temperatures (refer to Figure 6-14 for a comparison of resins with different heat distortion temperatures). As seen in Figure 6-15, the base polymer (SHF-14) retained SF_6 even after aging a total of eleven weeks at 150°C, whereas moderate losses occurred at higher temperatures. Again, as seen for the other formulations, the unfilled resin exhibited SF_6 diffusion characteristics that closely matched those of the filled resin.

The F content of unfilled SHF-14 (foamed without molecular sieves) was also measured as a function of thermal aging time at various temperatures. As shown in Figure 6-15, each temperature appeared to exhibit a rapid initial SF_6 loss followed by a nearly equilibrium concentration. This could suggest that the measured SF_6 depletion was a result of thermal decomposition of the surface of each sample. As the temperature was increased, such as from 180°C to 200°C, polymer decomposition increased, thus permitting more SF_6 loss. When the darkened and charred samples were cut open, it was found that material decomposition, as measured by material charring, was more extensive in the samples aged longest or at the highest temperatures.

The results plotted in Figure 6-16 suggest that the tested resin is nonpermeable to SF_6 even at temperatures well in excess of its heat distortion temperature. This data therefore indicates that SF_6 is retained by the foam regardless of aging temperature unless the aging temperature is severe enough to cause material degradation. When material degradation occurs, SF_6 can rapidly escape from the destroyed cells.

DIFFUSION THROUGH THIN FILLED SAMPLES

Diffusion studies were performed on films that were 5 to 10 thousandths of an inch thick. These films were both filled and unfilled, similar to SHF-3 (Table 4-3). The SF_6 diffusion data obtained by Allied Chemical indicated SF_6 did not diffuse through either the filled or unfilled sample. If diffusion did occur, it was at the lower detection limit of their equipment. The samples

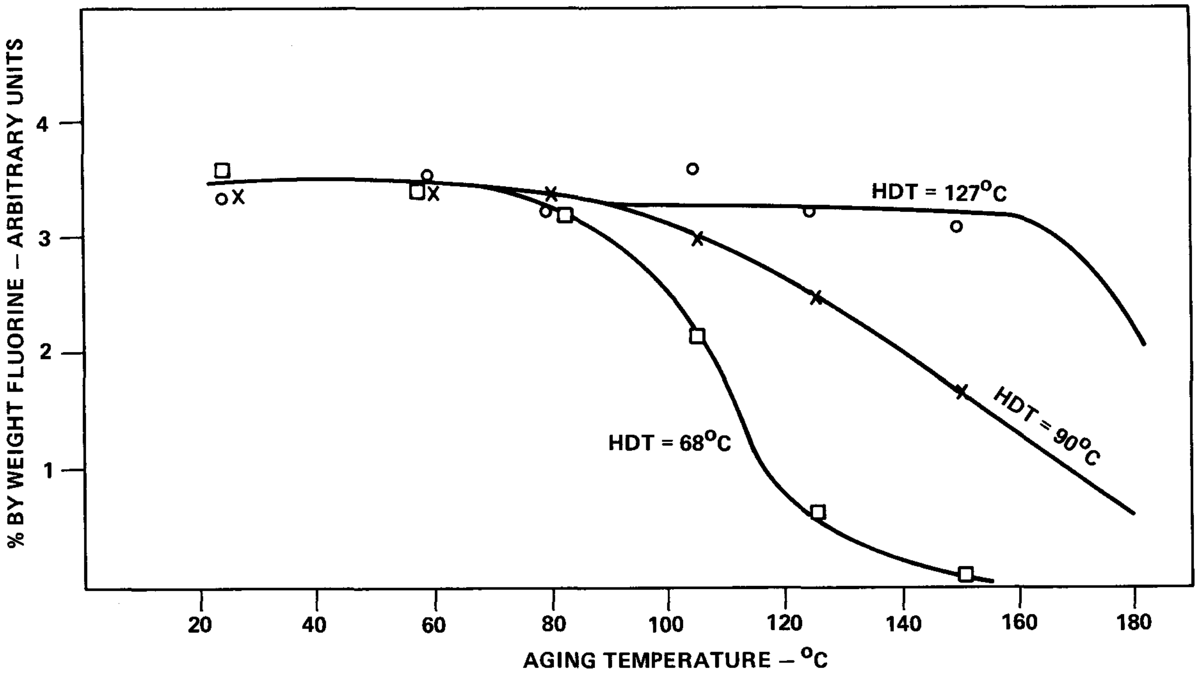


Figure 6-14. Comparison of the effect of one week heat aging on the F content of unfilled resins with different heat distortion temperatures (HDT)

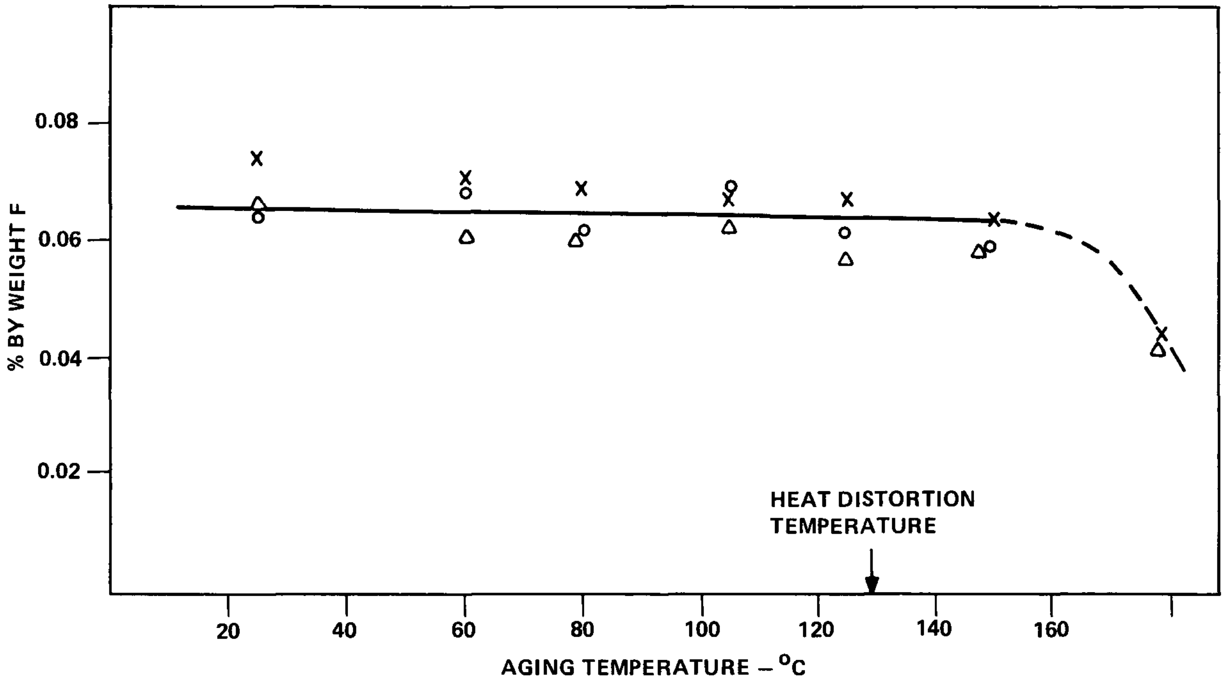


Figure 6-15. Effect of heat aging on F content of SHF-14

Each 1/2" x 2" x 1/4" sample was cut from the same sheet casting

o - aged one week at the indicated temperature
x - samples from above aged an additional two weeks
Δ - same as x except each sample aged an additional eight weeks for a total of 11 weeks

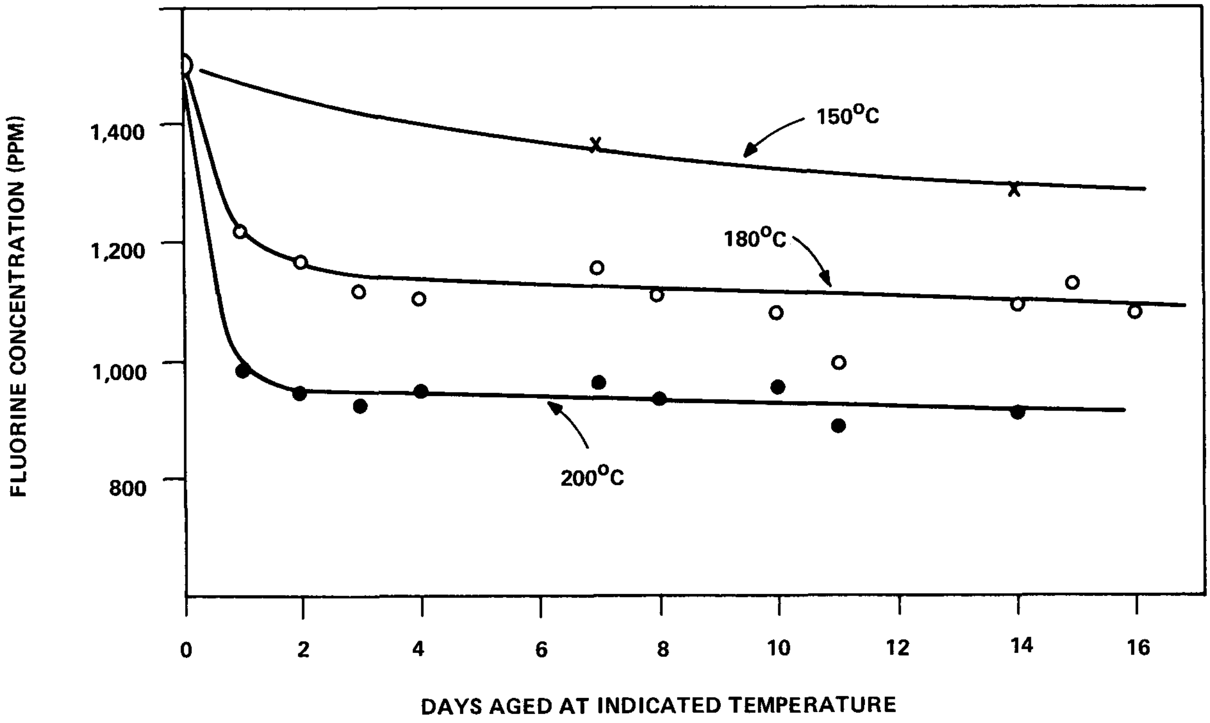


Figure 6-16. Amount of Fluorine lost in SHF-14 epoxy foam as a function of time aged at various temperatures

were also tested with N_2. Although N_2 appeared to diffuse through the thin filled sample, its rate also approached the lower detection limits of the instrumention. Allied's experimental technique is described in reference 6.

The above results suggest that diffusion of gas from a closed cell system is resin dependent. That is, if the base resin is nonpermeable, a closed celled filled system will not exhibit diffusion. This supports the contention that diffusion results obtained from unfilled thin films may be extended to filled foams, and the diffusion results obtained from unfilled samples foamed without molecular sieves may be extended to filled samples of the same base resin. As previously mentioned, this contention is further supported by comparing Figures 6-5 with 6-7, 6-8 with 6-10, and 6-11 with 6-15. As seen from each of these comparisons, the loss of SF_6 from the base resin compared favorably with diffusion from filled systems of the same base resin.

Unfortunately, the data on thin films in itself is not conclusive. For example, the rate of diffusion for the filled sample may be more rapid than the rate of the unfilled film, but since the filled sample was thicker than the unfilled, the added thickness may have decreased the amount of detectible diffusion. Furthermore, the fact that SF_6 diffusion was not detected does not mean it did not occur.

EFFECT OF MOLDED SKIN ON RETENTION OF SF_6

Samples of SHF-13 were aged at 150°C in an attempt to determine the effect of molded skin on SF_6 retention. As seen in Figure 6-17, the 1/2" diameter tube samples with molded skin exhibited a slightly lower rate of SF_6 loss than the samples that had the molded skin sanded off. However, the sheet samples both with and without skin lost SF_6 at about the same rate.

The results indicate that the molded skin can reduce the rate of SF_6 diffusion, but if the resin is permeable, SF_6 diffusion will occur regardless of the presence of a molded skin. Removing the molded skin is analgous to simply decreasing the thickness of the resin that SF_6 must diffuse through. As a result, if a closed celled polymer system is not capable of retaining SF_6, molding this polymer with a smooth and well defined skin will only slow diffusion, not stop it. The only way to prevent diffusion would be to either cast the foam with a nonpermeable resin or reformulate.

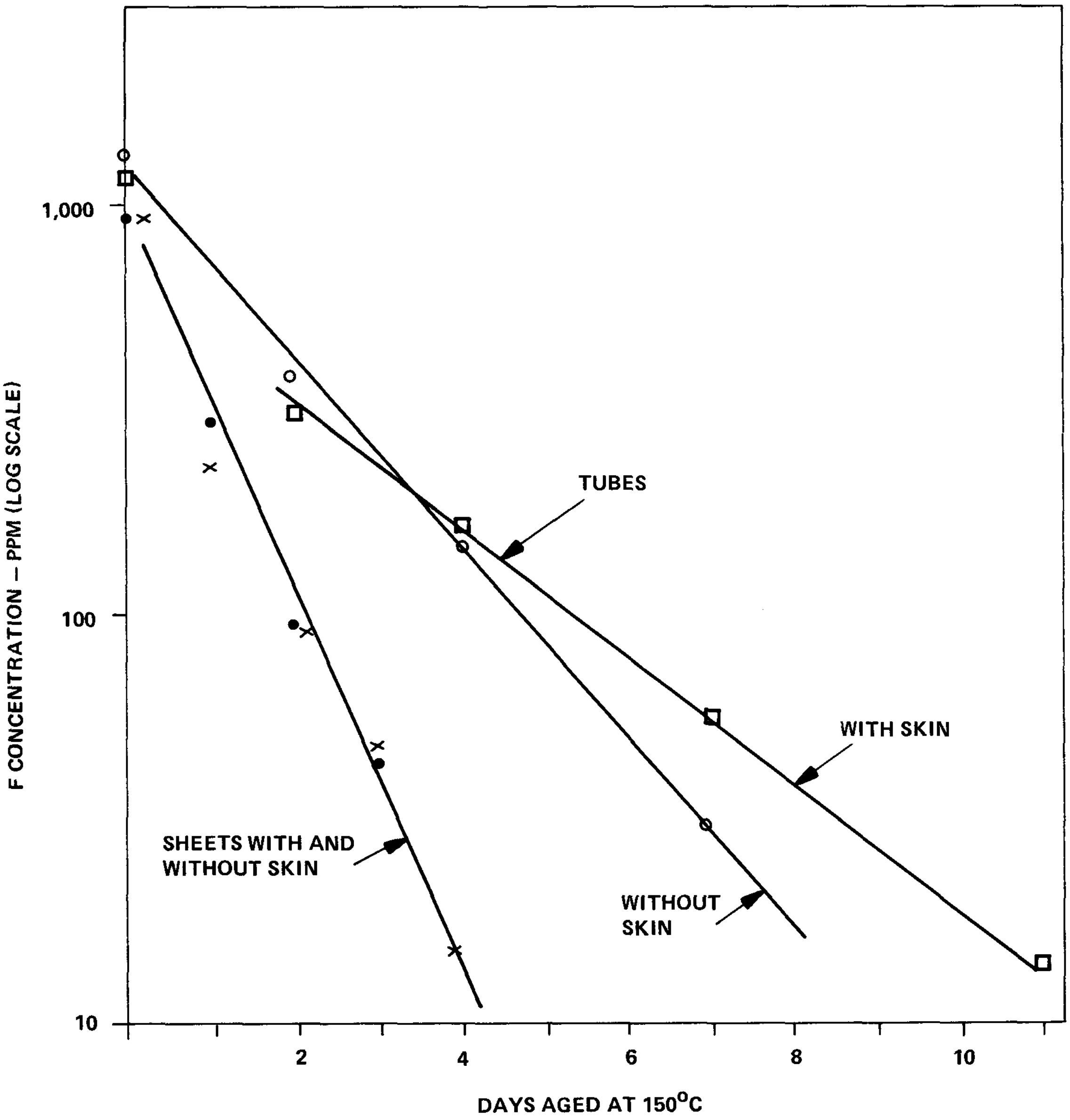


Figure 6-17. Effect of molded skin on the retention of Fluorine in SHF-13 epoxy foam as a function of time aged at 150°C

The results of Figure 6-17 also suggest that larger samples reduce the rate of SF_6 diffusion. As seen in this figure, the more massive 1/2" diameter tube samples lost SF_6 at a slower rate than the sheet samples (1/2" x 1/4" cross section). This is due simply to the fact that SF_6 gas has more polymer to diffuse through in the tube sample.

EFFECT OF VOLTAGE ON THE RETENTION OF SF_6 BY EPOXY FOAM

Samples of standard SHF-13 and SHF-19 (same as SHF-13 except for 2.5 times as much surfactant) were prepared and aged in an attempt to measure the effects of voltage stress and surfactant concentration on the retention of SF_6. The 1/4" thick samples were silver painted to prevent external corona discharges, and then aged at 105°C both with and without an applied voltage of 50 VPM.

The results of Table 6-4 indicated that voltage did not measurably add to SF_6 diffusion. The measured SF_6 losses were consistent with those previously obtained for SHF-13 at 105°C (Figure 6-7) and all losses could be attributed to thermal aging.

The retention of SF_6 by the formulation with the increased amount of surfactant (SHF-19) also appeared to be independent of applied voltage. Even though the initial concentration of SF_6 was much higher in SHF-19, the rate of loss of SF_6 was comparable to that for the standard SHF-3 material. Therefore, it appears as though the surfactant can affect the amount of SF_6 that can be incorporated into the foam, but it does not appreciably affect the rate of SF_6 diffusion.

Table 6-4. Effect of voltage on the diffusion of SF_6 from epoxy foam

SAMPLE CONDITIONING	FLUORINE CONCENTRATION DETECTED BY NAA - PPM [1]	
	SHF-13	SHF-19 [2]
Unaged. Maintained at room ambient.	902	1887
Aged one week at 105°C	566	967
Aged one week at 105°C, silver painted	451	1018
Aged one week at 105°C, silver painted and stressed at 50 VPM	500	918

[1] All values were obtained by averaging the results of eight 2" x 1/2" x 1/4" samples cut from similar sheets

[2] Similar to SHF-13 of Table 4-3 except the surfactant concentration was increased by a factor of 2.5

SECTION 7

ELECTRICAL & MECHANICAL PROPERTIES

In order to ascertain the affect of foaming epoxy, typical electrical and mechanical properties were measured (Table 7-1). In general, the foam's mechanical properties were slightly lower than those for unfoamed material. However, the electrical properties of the foam appeared superior to those of the unfoamed resin of the same composition.

CORONA

Both foamed and unfoamed samples of SHF-9 and 12 were prepared with 3/32" gaps as depicted by Figure 2-1. Even though the foam samples were cast in air, they were corona free up to 25-30kV. Puncture occurred at 30 kV (280 VPM). The unfoamed samples were initially cracked between the electrodes and these samples immediately punctured when the high voltage was energized.

The above indicates that foaming reduces the tendency of the material to crack, especially when imbedments are present. Most important, however, corona free foam samples can be readily cast in air whereas nonfoamed samples are totally unacceptable (cracked). The data also suggests that high temperature materials will not crack even if cast with imbedments.

DIELECTRIC STRENGTH

The dielectric strength data of Table 7-2 indicates that the dielectric strength of SF_6 foam is equivalent to unfoamed epoxy whereas the dielectric strength of CO_2 foam is somewhat lower. This was confirmed for two formulations. Furthermore, the dielectric strength of the material appeared related to filler content. When the filler content of the SHF-3 formulation was reduced to 10%, the dielectric strength decreased for all samples. The most significant change was for the CO_2 foam.

Table 7-1. Physical and electrical properties of some foamed and unfoamed epoxy formulations

PROPERTY MEASURED	SHF-3		SHF-7		SHF-235	
	FOAMED	UNFOAMED	FOAMED	UNFOAMED	FOAMED	UNFOAMED
Arc Resistance - sec.	123	119	63	85	135	140
Dielectric Strength - VPM	300	300	--	--	--	--
Dissipation Factor - tan δ (%) at 25°C (fresh sample)	1.83	1.01	1.25	0.66	2.02	1.41
Dielectric Constant (fresh sample)	2.65	3.40	2.76	3.62	3.23	4.21
Heat Distortion Temperature - °C	55	56	128	137	161	194
Track Resistance - min.	51	151	77	80	--	--
Specific Gravity	0.99	1.37	1.02	1.40	1.25	1.55
Ratio: S.G./Dielectric Constant	0.37	0.40	0.37	0.39	0.39	0.37

Table 7-2. Dielectric strength of SF_6 foam, CO_2 foam, and unfoamed epoxy with different filler loads

	DIELECTRIC STRENGTH - volts per mil	
MATERIAL	10% FILLER [1]	30% FILLER [1]
unfoamed SHF-3	265	300
SHF-3 SF_6 foam	270	300
SHF-3 CO_2 foam	215	280

[1] The standard SHF-3 formulation has 30% by weight silica filler

Based on the above data for highly filled systems, dielectric strength appears nearly independent of the blowing agent (SF_6 or CO_2). However, for unfilled or systems with low filler content, the blowing agent has a dramatic effect on the dielectric strength. SF_6 gas enables the foam to retain the dielectric strength of the unfoamed resin, whereas CO_2 foam has a lower dielectric strength. Further work, not included in this phase of the study, would be needed to confirm this suspected behavior.

REGENERATION OF DIELECTRIC STRENGTH

One unique property of SF_6 epoxy foam is its ability to regenerate its dielectric strength after puncture under certain conditions. The mechanism for regeneration can be attributed to the ability of SF_6 in the cells of the material to ionize and conduct current at high voltages. After the test circuit is cleared, it is well known that SF_6 can reestablish itself, thus restoring the cells to their original nonconducting, high dielectric strength condition. However, each time a fault occurs, carbon paths are formed between cells in order for current to be conducted through the sample. Continual arcing will finally carbonize the cell walls, thus overcoming the current shunt action of the SF_6.

This observation has been confirmed by preparing block samples of SHF-8 with imbedded electrodes (Figure 2-1). These were tested by grounding one electrode and subjecting the other to high voltage. (If failure occurs, a circuit breaker on the primary of the high voltage transformer clears the circuit.) For samples with a 1/4" electrode gap, after an initial puncture at 55 kV, the samples were retested 15 seconds later and withstood 33 kV before the second failure. A second sample withstood 38 kV after waiting 15 seconds from the initial failure at 50 kV. The dielectric strength was not reestablished for those samples with the smaller 3/32" electrode gaps.

This data suggests that when tested as described, thick samples (1/4") are capable of at least one regeneration after 15 seconds, but 3/32" samples are not. Although the gas cells in the 3/32" samples are well defined, the initial puncture probably causes enough permanent damage to prevent reestablishment of the dielectric strength.

DIELECTRIC CONSTANT

As predicted, the dielectric constant of epoxy foam decreased with density. As a first approximation, the ratio of specific gravity to dielectric constant remained constant at about 0.39 in all cases (Table 7-1). If the specific gravity of any of these formulations were reduced by additional foaming, this would result in still lower dielectric constants.

DISSIPATION FACTOR

The dissipation factors of the foamed materials reported in Table 7-1 are nearly a factor of two greater than the unfoamed material of similar composition. Although moisture could account for the high tan δ in the foam sample of Table 7-1, further investigation would be necessary in order to obtain a satisfactory explanation.

EFFECTS OF MOISTURE ON DISSIPATION FACTOR & DIELECTRIC CONSTANT

The diffusion of water and other gases into foam is essentially independent of the SF_6 pressure in the epoxy cells. Even if it is shown that SF_6 is retained by the foam, it is possible that moisture can affect the samples by diffusing into the material, thus degrading properties such as dielectric constant and tan δ.

Samples of both foamed and unfoamed material were exposed to high humidity. As seen in Figure 7-1, the tan δ of foamed sheet material increased rapidly to 5%, but the unfoamed sheet and foamed block samples remained relatively constant.

As seen in Figure 7-2, the behavior of the dielectric constant (ε_r) was similar to that of the dissipation factor. When exposed to humidity, the ε_r of the sheet samples rapidly increased from 2.5 and then leveled off at approximately 7-10 after 30 days. After dryout at 105°C for 24 hours, the dielectric constant of the foam decreased; but even an additional 72 hour 105°C dryout was not sufficient to reduce the dielectric constant to its original value. One explanation is that some moisture may have been adsorbed by the sample's molecular sieves.

Since the 1/4" thick sheets described above have a large surface to volume ratio, one would expect thicker samples to show improved behavior when exposed to high humidity. To verify this, tan δ and dielectric constant measurements were made on samples prepared as per Figure 2-1. As depicted in Figures 7-3 and 7-4, the dielectric constant and tan δ of the block samples were unaffected by prolonged humidity exposure. Moisture was unable to diffuse through the blocks and reside

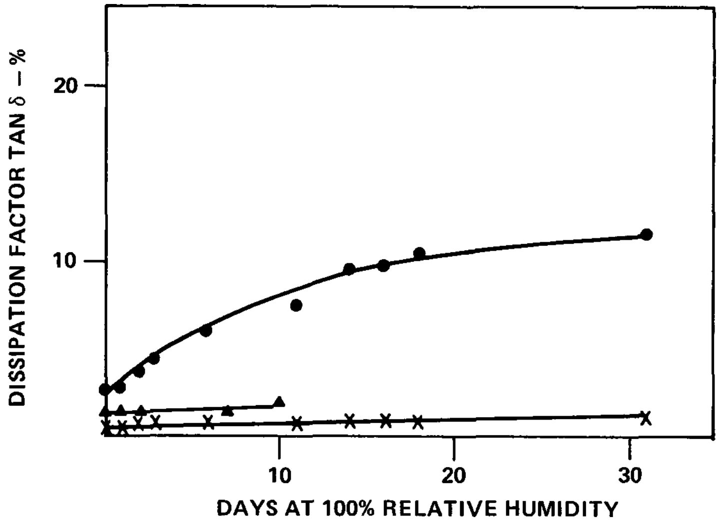


Figure 7-1. Effect of exposure to 100% relative humidity on tan δ of foamed and unfoamed epoxy

- ● SHF-7 epoxy foam 1/4" thick sheet
- ▲ SHF-12 epoxy foam. Imbedded electrode samples as per Figure 2-1
- X SHF-7 epoxy, unfoamed

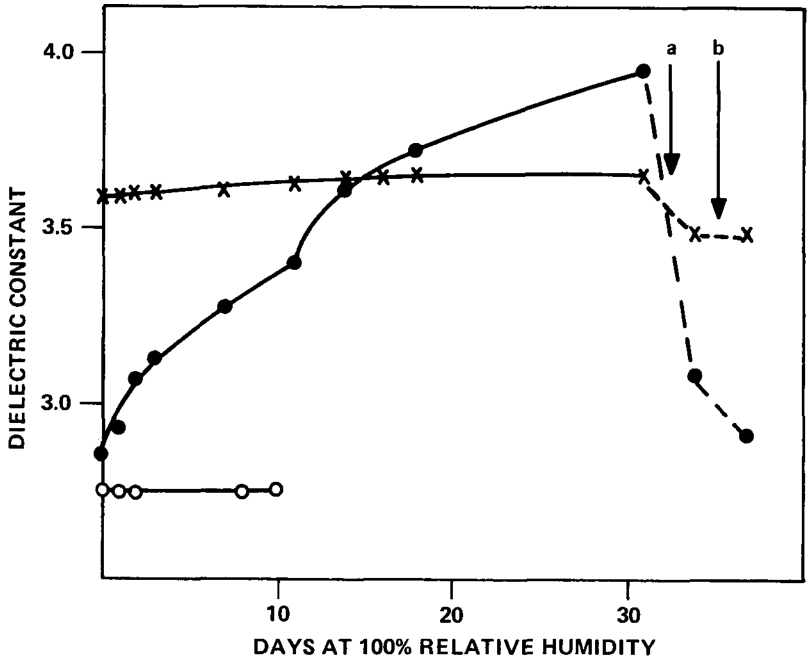


Figure 7-2. Effect of exposure to 100% relative humidity on the dielectric constant of foamed and unfoamed epoxy sheets and blocks

- X - unfoamed SHF-7 - 1/4" sheet
- ● - foamed SHF-7 - 1/4" sheet
- o - foamed SHF-12. Cast block as per Figure 2-1

Point a: samples dried for 24 hours at 105°C
Point b: samples dried an additional 72 hours at 105°C

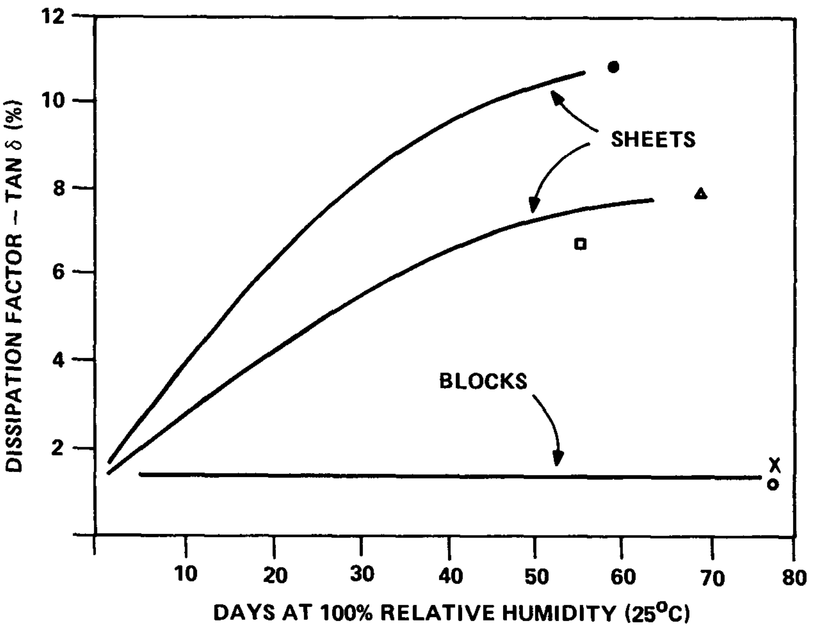


Figure 7-3. Effect of exposure to 100% relative humidity at 25°C on the dissipation factor of sheets and blocks of SF_6 epoxy foam

●, △, and □ - SHF-7 sheet samples

x and o - SHF-9 and SHF-12 block samples

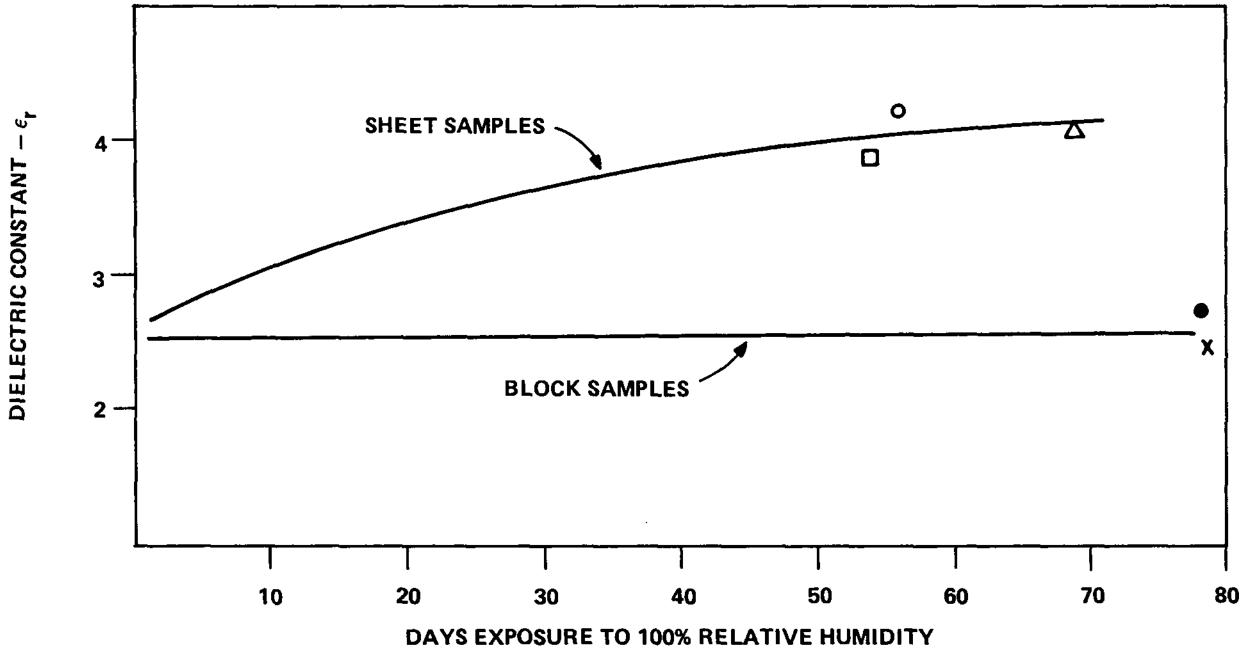


Figure 7-4. Effect of exposure to 100% relative humidity at 25°C on the dielectric constant of SF_6 foamed sheet and block samples

o, □ and △ - final values obtained for SHF-7 sheet samples

x and ● - final values obtained for SHF-9 and SHF-12 block samples between the imbedded electrodes during the time span allowed.

The data of Figures 7-1 and 7-2 suggest that moisture is absorbed by the foam. The measured increases in tan δ and dielectric constant are probably due to moisture absorption rather than a surface effect. If the measured increases were due to a surface phenomenon, the dielectric constant and tan δ values of the sheet samples would reach equilibrium rapidly rather than continually increase. Also, a short dryout period would return the material to its initial condition if this were a surface phenomenon.

Since the surface of the foam is resin rich and would behave similar to the unfoamed material, it is possible that well defined molded skins could reduce moisture uptake. However, if the base resin is water permeable, the molded skin can not stop water absorption but can reduce the rate of uptake.

If a sheet product were required for use in high humidity, and if the asymptotic values of tan δ and ε_r of Figures 7-1 and 7-2 were unacceptable, the tested foam material would be unacceptable. However, insulation is not normally exposed to high humidity, and it must also be understood that the tan δ for typical epoxies also exhibit large tan δ increase when exposed to high humidities for extended periods.

Humidity effects would not exist in a large product provided surface characteristics are not important (such as in the imbedded electrode sample). Furthermore, it may be possible to overcome humidity effects on sheet samples or other configurations by improving the molded skin. This would require improving processing control or by foaming with a base resin that is relatively impervious to moisture.

Since the acceptability of the measured humidity effects are product dependent, they may not be significant for certain products. For example, if the insulation is handled properly prior to installation and is intended for use in a dry SF_6 environment, humidity effects can be neglected.

COMPARISON OF DC & AC ELECTRICAL STRESS ON SF_6 EPOXY FOAM

In an attempt to obtain preliminary data to evaluate the DC capability of SF_6 epoxy foam, samples were cast as per Figure 7-5. Both plane and pointed electrodes (Figure 7-6) were used. Prior to testing for breakdown strength, each sample was corona tested. As expected, the corona levels were far higher

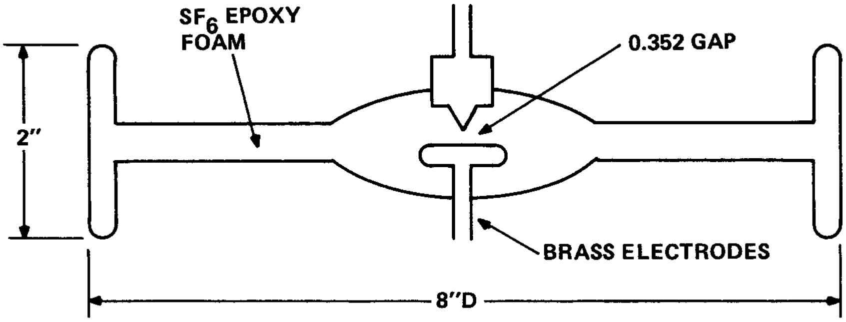


Figure 7-5. Sample configuration for AC/DC electrical testing

Refer to Figure 7-6 for electrode dimensions.

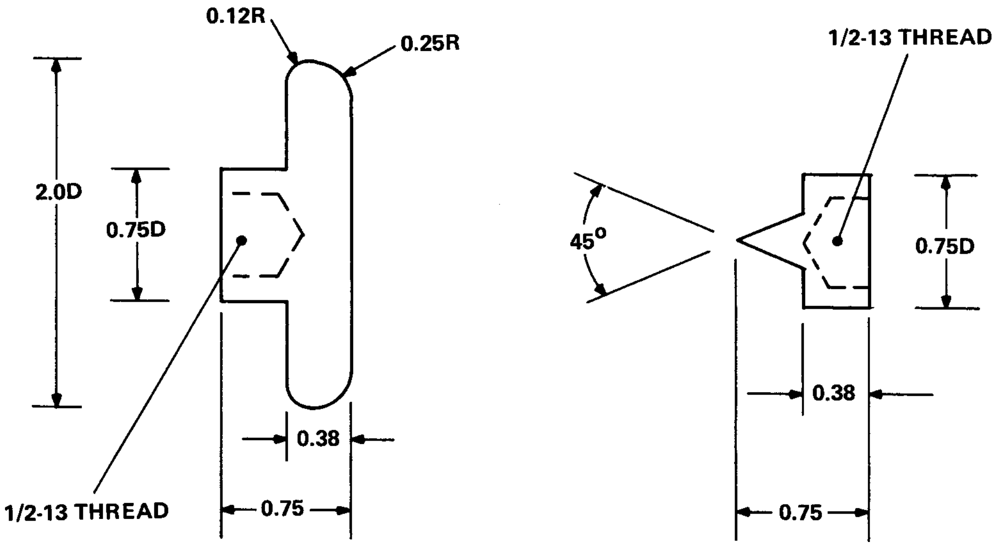


Figure 7-6. Electrode configuration used in AC/DC electrical testing

Electrodes were imbedded in an SF_6 epoxy foam disc as depicted in Figure 7-5.

(superior) to those typical for unfoamed epoxy. Also, as expected, the corona inception voltage (CIV) and corona extinction voltage (CEV) values for the plane to plane samples (67/57 kV) far exceeded the point to plane values (19/12 kV).

AC Voltage Evaluation

In a uniform field (plane to plane electrode configuration), an average voltage breakdown strength of 304 V/mil crest was achieved (Table 7-3). In a non-uniform field (point to plane configuration), the breakdown strength was reduced by approximately 50% to an average of 145 V/mil crest. Corona values (CIV/CEV) for the uniform field were approximately 67/57 kV r.m.s. and 19/12 kV r.m.s. for the nonuniform field.

DC Voltage Evaluation

In a uniform field an average voltage breakdown strength of approximately 438 V/mil was achieved. In a point to plane configuration (point at positive, plane at negative polarity) the breakdown strength was approximately 409 V/mil nearly equivalent to the uniform field values. However, with the plane at positive and the point at negative polarity, the breakdown strength was nearly halved to 241 V/mil.

AC/DC Comparison

The lowest values were obtained under AC conditions in a nonuniform field. When compared to values for breakdown strength, the DC values were approximately 66% higher than the nonuniform field conditions and approximately 44% higher for uniform field conditions.

Conclusion DC Versus AC

The data indicates that the DC dielectric strength of SF_6 epoxy foam far exceeds its AC dielectric strength. As a future experiment, it would be interesting for one to compare these results with samples of identical design but using nonfoamed epoxy material. Note, however, that previous data indicates that nonfoamed samples may crack and would therefore fail at low test voltages.

Table 7-3. Results of DC/AC Testing of SF_6 Foamed Epoxy

No. of Samples Tested	Electrode Configuration	V Type	Dielectric Breakdown kV Crest Min.	Dielectric Breakdown kV Crest Max.	Dielectric Breakdown kV Crest Avg.	Dielectric Breakdown Average Stress Across 0.352 Gap V/mil Crest	Average Corona Threshold CIV/CEV kV r.m.s.
3	plane to plane	AC	102	109	107	304	67/57
5	point to plane	AC	40	62	51	145	19/12
6	plane to plane	DC	140	*>162	*>154	>438	58/52
5	+ point to - plane	DC	114	**>162	**>144	>409	17/9
5	+ plane to - point	DC	54	117	85	241	20/15

* 3 samples did not puncture, flashovers occurred in air

** 1 sample did not puncture, flashover occurred in air

SECTION 8

ACCELERATED AGING STUDIES

An attempt was made to determine the feasibility of obtaining accelerated aging data on SF_6 epoxy foam by a unique method. The proposed method was unique because the time-to-failure (dielectric puncture) was monitored while the material was maintained at both high electrical and temperature stresses.

This technique is different from the common procedure described in IEEE 101. In the IEEE procedure, materials are artifically aged at various elevated temperatures. Samples are periodically removed from the aging oven, and after the material has cooled to room ambient, the property of interest, such as flexural strength, is measured. When this measured property reaches 50% of the initial value for an unaged sample, the sample is considered failed. Finally, the log of time-to-failure versus aging temperature is plotted. These plots are then used to extrapolate forty year life times.

Theoretically, extrapolations can be readily made because it is well known that the relationship between insulation life and temperature can be approximated by the Arrhenius equation:

$$L = Ae^{B/T}$$

where L = time (life of insulation)
A = constant (similar to frequency factor in chemical kinetics)
e = natural log base
B = constant (analgous to activation energy)
T = absolute temperature (°K)

Taking the log of equation (1):

$$\log L = \frac{B}{T} \log e + \log A$$

Therefore, for systems that follow the Arrhenius relationship, a straight line is obtained when log L versus 1/T is plotted. Consequently, linear extrapolations similar to that shown in Figure 8-1 are easily obtained. In a study of this type, it is desirable to obtain a data point corresponding to a few hours (point a, Figure 8-1) and another data point in a few days (point c, Figure 8-1). When these short term data points are used along with those obtained after longer periods, such as 1/2 year (point b, Figure 8-1), forty year life expectancies can be readily extrapolated.

If the short term data points were omitted, extrapolation would become difficult. As seen in Figure 8-1, the line segment upon which extrapolation is based would be reduced by a factor of two, thus significantly reducing the reliability of the extrapolation. Therefore, provided they can be obtained, the short term data points are extremely significant.

Since the expected failures are a function of both electrical and temperature stresses, data similar to that plotted in Figure 8-1 can be obtained at various electrical stress levels. Each set of data can then be extrapolated to forty years, and the extrapolated temperatures then plotted as a function of the electrical stress level to obtain a relationship similar to Figure 8-2. Note that data point (S_E, T_E) of Figure 8-2 was obtained from Figure 8-1.

Area A in Figure 8-2 represents all temperature-electrical stress combinations for which the hypothetical insulation is predicted to survive for forty years or more. For example, insulation at Temperature T_2 and electrical stress S_2 will survive a minimum of forty years. However, failure would occur in less than forty years if the temperature were increased from T_2 to T_3 since these coordinates are in Area B. Also, if a material were electrically stressed at a known value S_1, in order for the material to last forty years or more, Figure 8-2 indicates the maximum continuous operating temperature should not exceed temperature T_3.

Since the proposed method is unique and has never been attempted, there is no assurance that the technique will work. Therefore, the intention of this study was to determine the feasibility of the method. Some data exists which suggests the proposed method may be feasible. Based on data obtained for a flexible epoxy system (Figure 8-3), a plot of log of time-to-failure versus reciprocal temperature was linear.

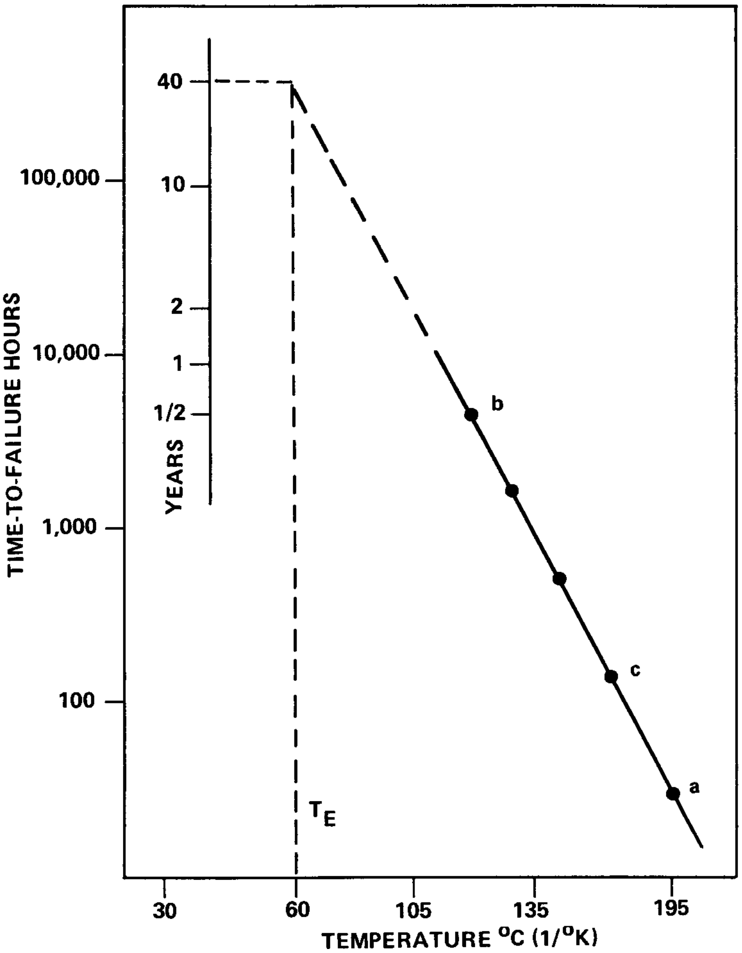


Figure 8-1. Log of Time-to-Failure Versus Reciprocal Temperature for hypothetical insulation with electrical stress S_E

Temperature T_E is obtained by extrapolating experimental line ab to 40 years.

If this material were electrically stressed at value S_E and maintained at constant temperature T_E, it would have an expected life time of 40 years.

Refer to Figure 8-2 where T_E is plotted versus S_E.

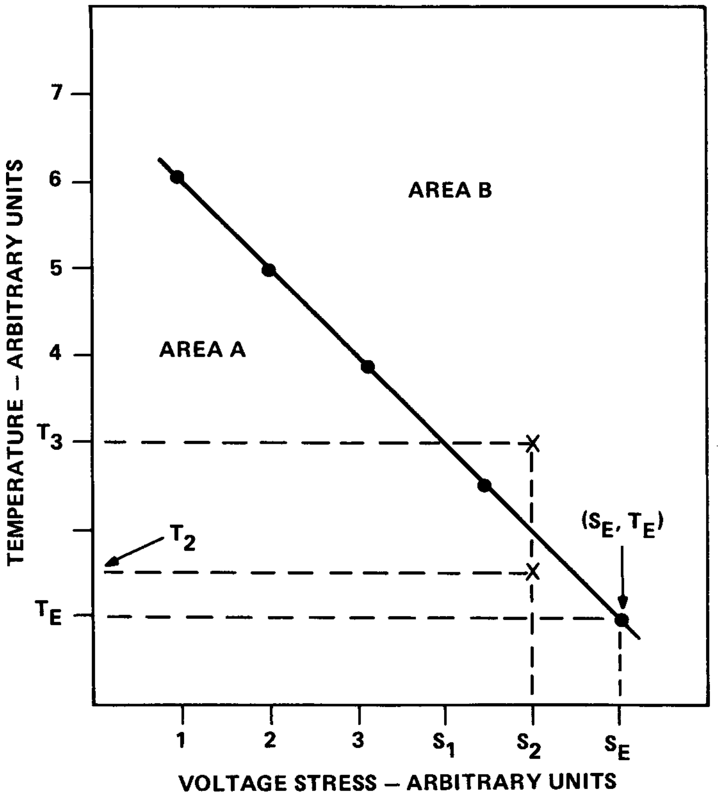


Figure 8-2. Theoretical Curve of temperature versus electrical stress for extrapolated 40 year life times

Temperature-electrical stress combinations represented by area A will survive for 40 years or more; those in area B will fail.

Refer to Figure 8-1 for extrapolation that resulted in data point (S_E, T_E).

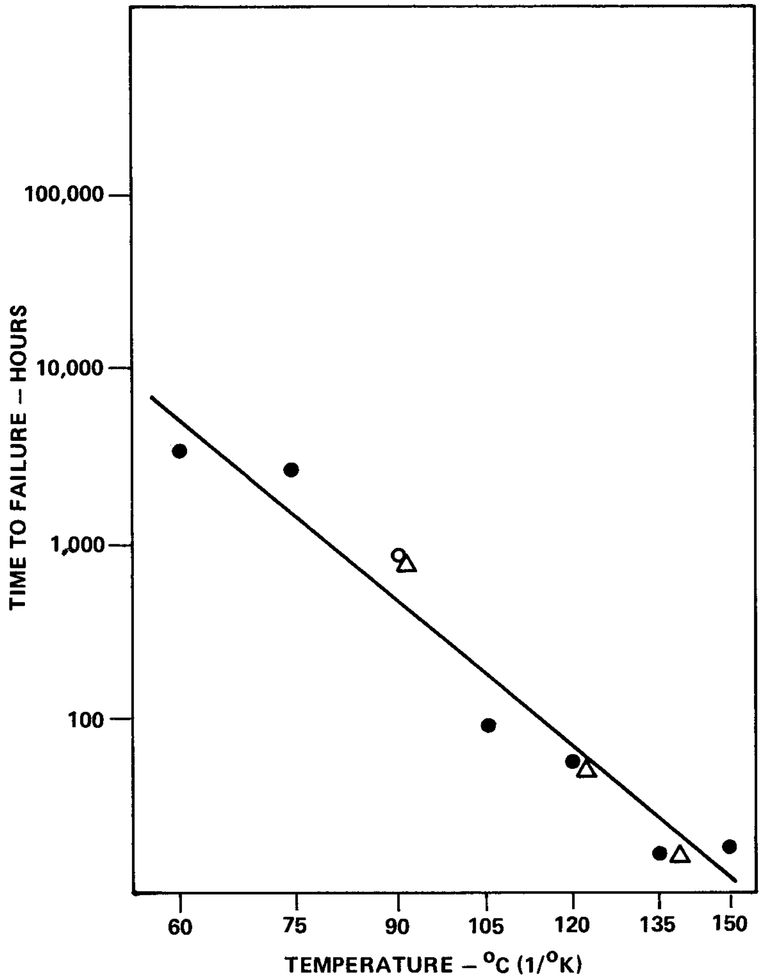


Figure 8-3. Time to Failure Versus Reciprocal Temperature for a flexible epoxy formulation

- ● Test condition A. Refer to I-T-E TD-6216C, available on request.
- △ Corona free test condition. Refer to I-T-E TD-6216C.

The success of the proposed short term aging study presupposes short term reproducible failures. Non-reproducible failures would result in uncertain extrapolations. The absence of reproducible failures is a major reason why there is no commonly accepted aging technique today. Furthermore, another difficulty to contend with is that even if the data were reproducible, it is possible that competing mechanisms could lead to a non-linear relationship between the log of time-to-failure and the reciprocal temperature.

EXPERIMENTAL RESULTS

Samples were cast as per Figure 2-1 and tested in the modified ovens (Figure 2-2). Since corona is a major source of random failures, all samples were checked for corona at 23 kV, slightly above the maximum oven test voltage of 20 kV. All samples were corona free (<1 pC).

Although the measured data was random, some of the data points have been plotted in Figure 8-4 in order to demonstrate the randomness and to add perspective to the type of data needed for extrapolation. A typical example of the random measured failures occurred at 151°C, 200 VPM. The initial sample ran 238 hours prior to failure whereas when an additional sample was tested under the same conditions, the sample failed as soon as it reached temperature.

It should be noted that the chosen parameters, such as 200 VPM at 151°C, were far in excess of typical operating conditions for electrical insulation. These excessive conditions were chosen so that short term failures could be obtained. If the material were tested at or slightly above typical operating parameters (50 VPM, 105°C), the data suggests the material would survive for long periods. Therefore, short term failures would not occur and the purpose of the proposed technique would be defeated.

It must be emphasized that the failures recorded in this program occurred at extreme stresses far in excess of normal operating conditions. The measured failures in no way necessarily imply that the test material is unsatisfactory. Furthermore, the inability to obtain reproducible failures does not imply the method is unsatisfactory. Due to the many competing failure mechanisms which are not fully understood for most insulations, slight variations in parameters such as voltage, impurities, electrode configurations, and the like can all lead to random time-to-failures.

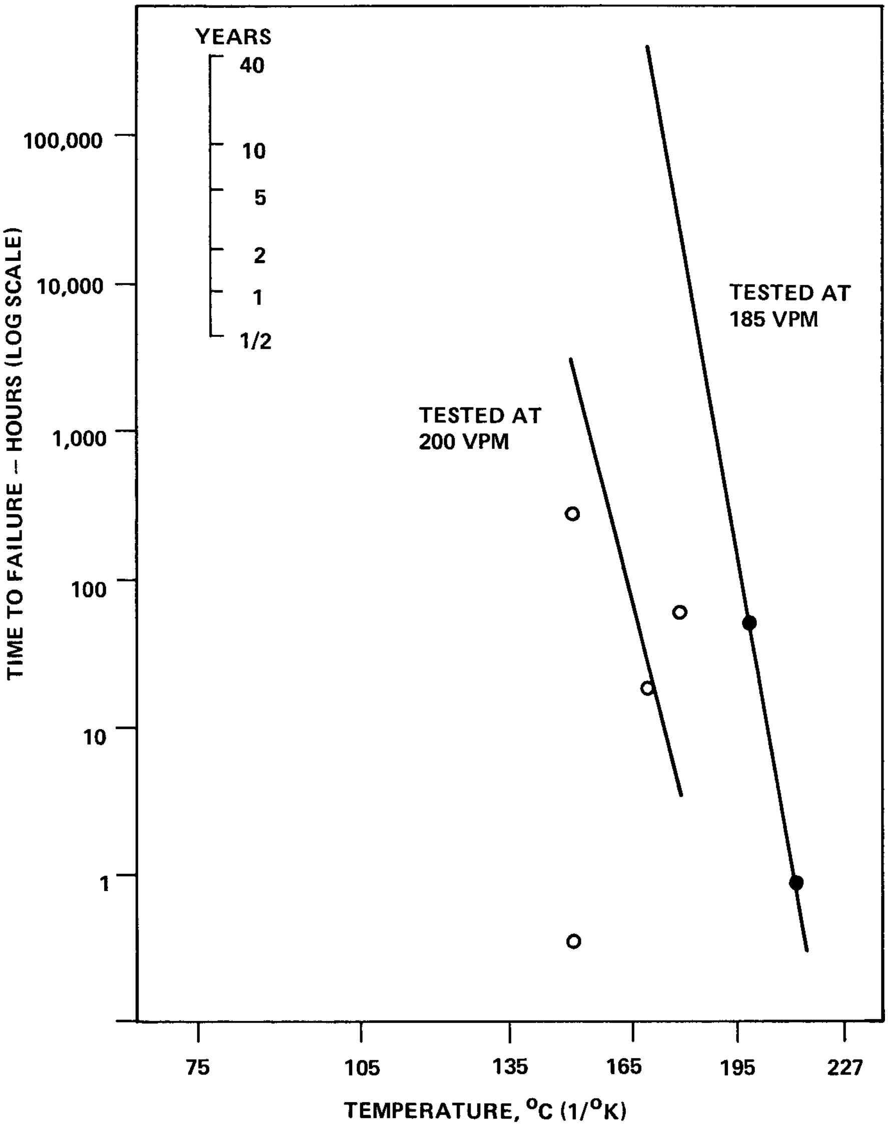


Figure 8-4. Sample random data for log of time-to-failure as a function of aging temperature and electrical stress

For clarity, non-reproducible, random data points were omitted. Closed circles (●) were tested at 185 VPM; open circles (o) tested at 200 VPM. Refer to Figure 2-1 for sample configuration and Figure 2-2 for high temperature voltage set up.

In summary, the proposed method of predicting long term insulation life from short term data does not appear feasible. Perhaps improvements in electrode configuration, elimination of impurities, or the like, would improve results. However, even if precise, non-random short term failure data were obtained, there is no assurance that the complex failure mechanisms would obey the Arrhenius projection. Furthermore, there is no guarantee that the failure mechanisms which operate at high temperatures also hold at the lower, nominal operating temperatures of the insulation.

SECTION 9

APPLICATION FOR SF_6 FOAM

Many possible uses exist for SF_6 epoxy foam. The low weight and low dielectric constant suggest that it could be used to mold either the conical or disc insulators used in SF_6 bus runs. SF_6 foam would result in a considerable cost savings due to a weight reduction and a reduction in mold cycle time. Another possible use where the low dielectric constant and weight could be important would be in switchgear barriers.

A preliminary attempt was made to cast a 7.5kV standoff out of SF_6 epoxy foam. The weight of the 12 cm by 11.5 cm diameter insulator was reduced from 2,550 grams (porcelain) to 950 grams. The foam insulator was corona free (<1 pC) at 25kV. The test was stopped at 25kV because of interference from external corona (flashover) between the high voltage test lead and ground. The foam insulator far surpassed that required for a 7.5kV standoff insulator and far exceeded the 12kV inception level of the porcelain.

Preliminary work with this standoff insulator and other simpler shapes indicated a considerable amount of development work would be needed in order to obtain acceptable castings. The sheet and tube castings extensively used for this study were acceptable, but bubbles appeared at the undercut surfaces of more complicated shapes.

Since this processing problem is somewhat product dependent, and since the prime objective of this project was not to develop a product, only preliminary work has been done to solve this processing difficulty. Many variables, such as mold temperature, material temperature, type and amount of filler, and many others, can all affect the surface of the product. Each must be further examined with respect to the product or shape in question.

SECTION 10

SUMMARY

The following statements briefly summarize the major developments accomplished and documented in this report:

- described and measured some of the unique properties of SF_6 epoxy foam, a new and novel material
- described the unique method used to make this material
- presented the molecular sieve loading and handling techniques essential in the manufacture of the foam
- have shown that Neutron Activation Analysis can be used to non-destructively measure Fluorine (SF_6) in epoxy foam
- demonstrated that some formulations retain SF_6 even up to the thermal decomposition temperature of the material

SECTION 11

CONCLUSION

Due to its excellent electrical properties, some of which are unique, SF_6 epoxy foam is an excellent candidate for high voltage electrical insulation. Since some foam formulations retain SF_6, they will retain the properties attributed to the trapped SF_6 even if maintained at high temperatures in an air environment.

APPENDIX A. Excerpts from a report on SF_6 loaded molecular sieves prepared July 16, 1976 by Professor J. E. Sturm, Lehigh University. Condensed August 30, 1976 by B. G. Giessner.

The SF_6 loaded molecular sieve sample holder (Figure 3-6) was attached as illustrated in Figure A-1 and treated as follows:

1. Zeolite sample was cooled in an ice bath (0°C). Vacuum system pumped clean.
2. With stopcock #4 to pump closed, stopcocks 1, 2. 3, V_B, and V_S were opened. Gas pressure was read as a function of time:

t(s)	3	10	40	100	300	1800 (i.e., 30 min.)
P(torr)	30.5	32.5	38.5	40.5	42.4	46.8

3. Stopcock #1 was closed to isolate the drawn-off gas from the zeolite.
4. By means of a cold finger, the contents of V_B were frozen in liquid N_2. Residual pressure: 1.5 torr.
5. The contents of V_B were thawed and a gas sample was taken for later analysis. Remaining gas in V_B was pumped away.
6. Zeolite sample was warmed to room temperature (25°C). P = 115 torr (in about 5 min.). This is probably not equilibrium pressure.
7. Zeolite sample was cooled to 0°C again. P = 52 torr.
8. Longer equilibration at room T. P = 150 torr.
9. Manifold evacuated, reexposed to zeolite at room T. P = 145 torr, consistent with previous measurement.
10. Attempt to remove all adsorbed gas. Hot water (80°C) was put around zeolite sample and contents were frozen in cold finger of V_B. Residual pressure = 3 torr. Thereafter, stopcock #2 was closed and the cold finger was warmed to room T. P = 106 torr.
11. Another gas sample was taken of contents of V_B for analysis.

One can use the measurements above to obtain an independent estimate of the amount of adsorbed gas. In step #2, the 30 torr of gas initially given off represents supernatant gas rather than gas adsorbed on the zeolite. The remaining amount, corresponding to 47 - 30 = 16 torr, represents gas desorbed as the pressure dropped below its phase equilibrium value.

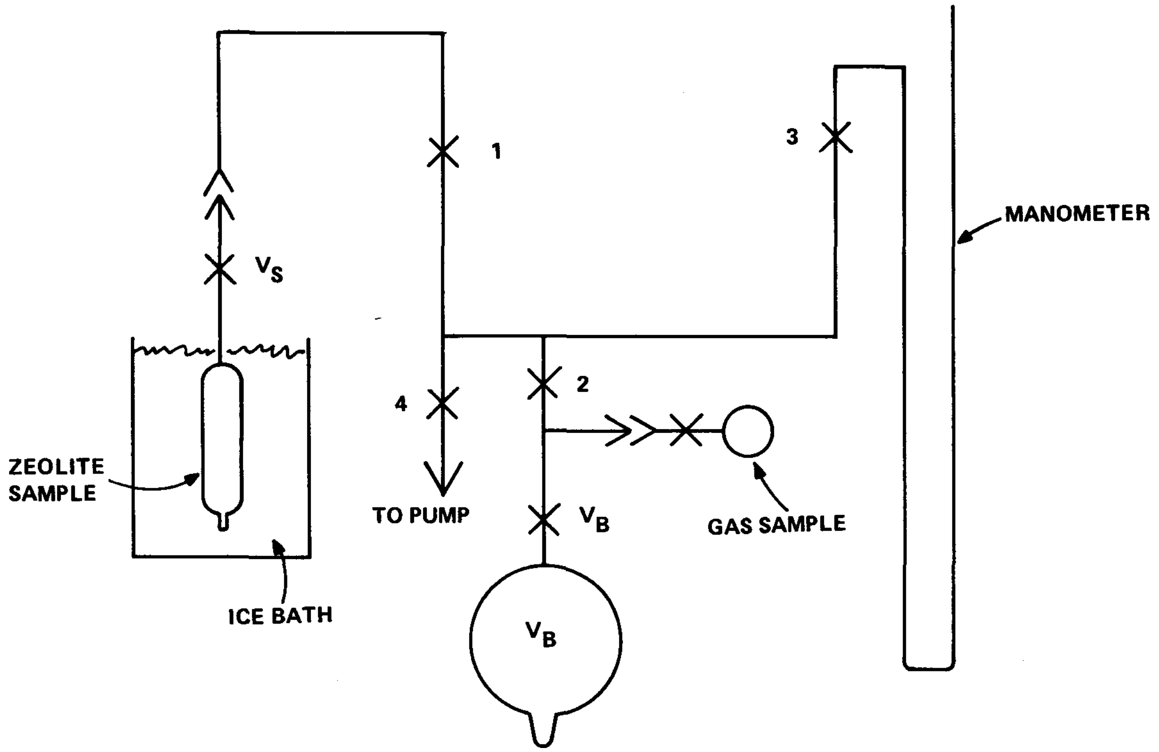


Figure A-1. Gas Handling System for SF_6 Molecular Sieve Analysis

The total desorbed gas amounts to:

$$(PV)_{tot} = (16.3 + 106)(2.2 \times 10^3) = 2.7 \times 10^5 \text{ cm}^3\text{torr}$$

We can compare this amount with that corresponding to the mass adsorbed. If we assume that 2.4 g adsorbed by the test apparatus (Figure 3-6) was SF_6:

$$(PV)_{calc'd} = \frac{(2.4)}{146}(82.03)(760)(298) = 3.05 \times 10^5 \text{ cm}^3\text{torr}$$

CONCLUSIONS:

A. Steps 2-7 show that the zeolite-gas equilibrium is reversible. The Clausius-Clapeyron relation (Figure A-2), although based upon only two points, permits estimation of the pressure built up during the epoxy curing process.

B. Recovery of gas desorbed from the zeolite was consistent with that predicted from the mass adsorbed.

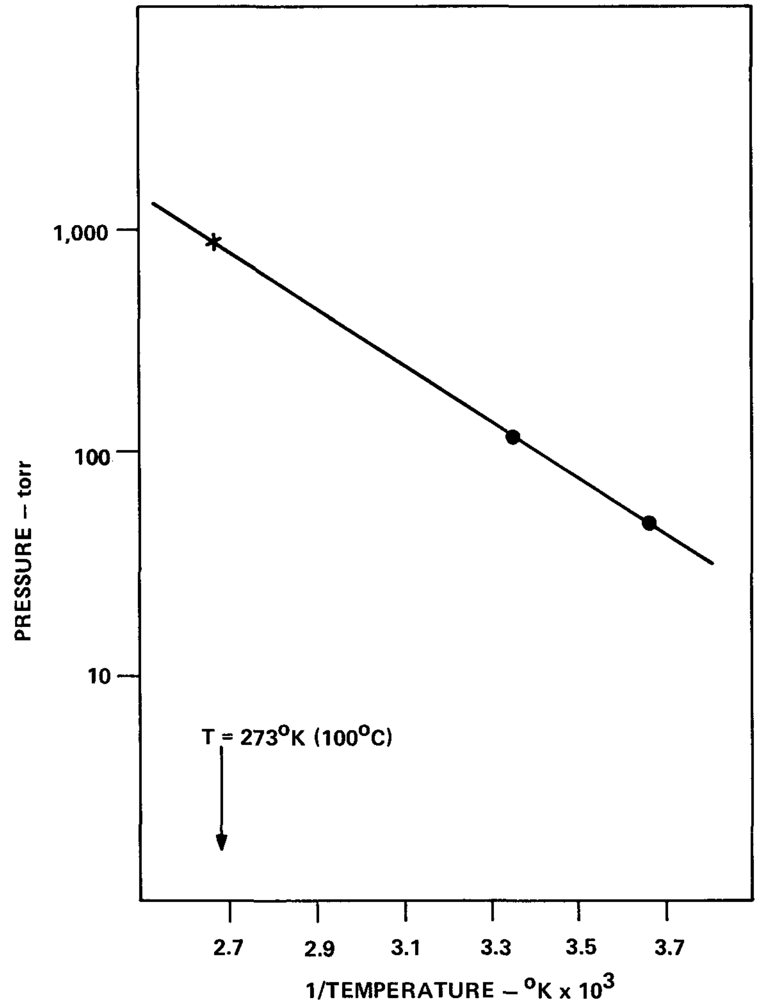


Figure A-2. Clausius-Clapeyron plot of SF6 pressure versus 1/T

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