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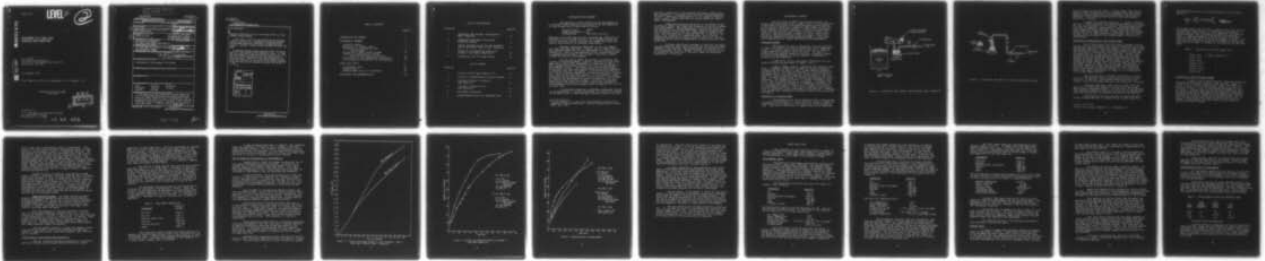
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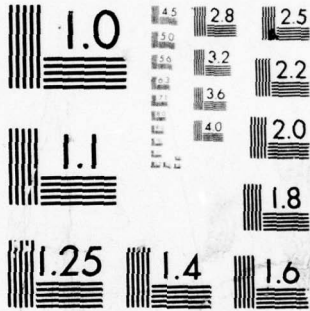
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**DEVELOPMENT OF A STABLE HIGH
EXPANSION WATER-BASED FOAM**

J. V. Friel
MSA Research Corporation
Division of Mine Safety Appliances Co.
Evans City, PA 16033

27 November 1978

Final Report for Period 23 September 1977-1 December 1978

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The objective of this program was the development of a long life water based surfactant foam capable of being generated at a 1000/1 expansion using a 5% concentrate. Half of the generated foam was to last for 24 hours at which time the foamed mass should be capable of conforming to the surface of an intruded object. In addition, foamed masses were to be (continued)		

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capable of being built to a 10 foot height within a 30 foot diameter spread distance.

In this study a long life foam formulation was developed largely on the basis of a comprehensive screening program. The developed formulation consisted of polyethyleneimine, glycerin, sorbitol, lithium chloride and MSA salt water foam agent.

The developed recipe yielded foams which meet the design goals for life, expansion and concentration usage. As foams aged they dried to a closed cell but delicate structure. This loss of fluidity prevented the foam from conforming to an intruding object. Large scale field tests showed that aged foams were vulnerable to wind gusts and that spread distances of over 50 feet would be required to achieve foam heights of 10 feet.

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INTRODUCTION AND SUMMARY

The objective of this program was the development of a surfactant foam formulation which would allow the generation of foam to meet the following specifications:

Expansion Ratio	- 1000/1
Usage Concentration	- 5%
Collapse Rate	- 50% within 24 hours

Additional specified foam qualities included the capability of building to a 10 ft height within a 30 ft diameter spread and a 24 hr intrusion quality such that the foamed mass would conform to the surface of an inserted large object.

Numerous laboratory reportings of long life bubble and foams have been published. However, few of these efforts have provided guidelines for the development of a long life foam formulation. Thus, at the beginning of this program there were no predetermined avenues to be followed in evolving a system to meet the specific requirements.

Earlier work by MSAR¹ has evolved a formulation consisting of polyethyleneimine, glycerin and MSA salt water foam agent which could yield foam masses at expansions of 200 to 300:1 possessing collapse rates of 0.1 in./hr in the absence of environmental effects. This early study had evaluated other formulations but none could approach this particular combination in yielding long life foam masses. In this work foam life was the critical property; expansion, concentrate additions, fluidity, etc., were not a significant concern. In the absence of other guidelines and the short duration of the program, it was decided to continue the development of earlier formulations in lieu of searching for new candidate systems. This would include the noted formulation above, plus other formulations abandoned in the referenced study which showed promise of meeting a 2-4 in./hr collapse rate.

An extensive screening of candidate systems was carried out investigating all possible mechanisms of controlling collapse of the foam as well as the drainage rate which controls fluidity.

¹"The Development of a Long Lived High Expansion Foam for Entrapping Air Bearing Noble Gas." Douglas United Nuclear Project #7221, Feb. 1971.

The basic variability in the formulas were water soluble polymeric materials. It became quite clear that polyethyleneimine-glycerin combinations were superior to all others in terms of foam collapse. Other additives did provide additional incremental improvements.

Formulations were evolved which in the absence of environmental effects would meet the expansion, usage and collapse rate requirements. The maintenance of fluidity over 24 hours was not met nor was the height-diameter relation achieved. When the influences of sun, wind, etc., were added it became quite clear that survivability of the foam mass was in reality a few hours. The influence of evaporative water loss to the atmosphere was shown to be a major factor in foam life, one not heretofore given serious consideration in the evolution of foam technology.

Although significant increases in foam life and drainage were made over those obtainable with the currently available commercial high expansion foam concentrates, the objectives of the program were not met. Neither fluidity nor stability could be maintained for more than a few hours under the conditions experienced in field use.

EXPERIMENTAL PROGRAM

The prior work by MSAR¹ had evolved an anionic surfactant foam concentrate which yielded a long life foam employing as the stabilizing agent a polyethyleneimine-glycerin mixture. In the course of that work a number of other water soluble polymeric materials had shown potential of stabilizing foam masses. These included polyvinyl pyrrolidone, polyvinyl alcohol, and certain of the acid polymers, carboxylic vinyls, polyacrylics, and maleic anhydride-polyvinyl ether copolymers. The initial effort was directed at reviewing these systems to select base line formulations for further modification and development.

Screening Studies

The major difficulty in developing long life qualities in foam is the absence of chemical guidelines. What compounds, alone or in concert, impart significant stability to foams has largely been the outcome of trial and error. The lack of a predictive type approach therefore requires a screening program in which the performance of various chemical ingredients or groupings can be identified.

Screening of various foam agent formulations was conducted using the systems shown in Figure 1 and 2.

Figure 1 shows a typical laboratory high expansion foam setup. A prepared formulation diluted with water is placed in a pressurized pot and fed to a small blower operated generator. The blown foam is collected and retained in a 50 gallon drum for subsequent study. This apparatus was found to be too time consuming for the preliminary screening studies needed in this program. A simpler system shown in Figure 2 was selected for initial screening. The system consisted of a standard Erlenmeyer flask with a fine tip pipette serving as a downpipe. A standard flow of air (250 cc/min) was metered to the downpipe and portions of the generated foam were collected on flat fishes and stored in a fully exposed condition. This latter system was found acceptable for discerning large differences in foam behavior. Promising foam systems were subsequently evaluated further using the system of Figure 1.

Selection of a Foaming Agent

High expansion foam can be generated from a wide variety of surface active chemicals. There are now a number of commercial formulations on the market for the production of high expansion foam. They offer a wide range of capabilities mostly associated

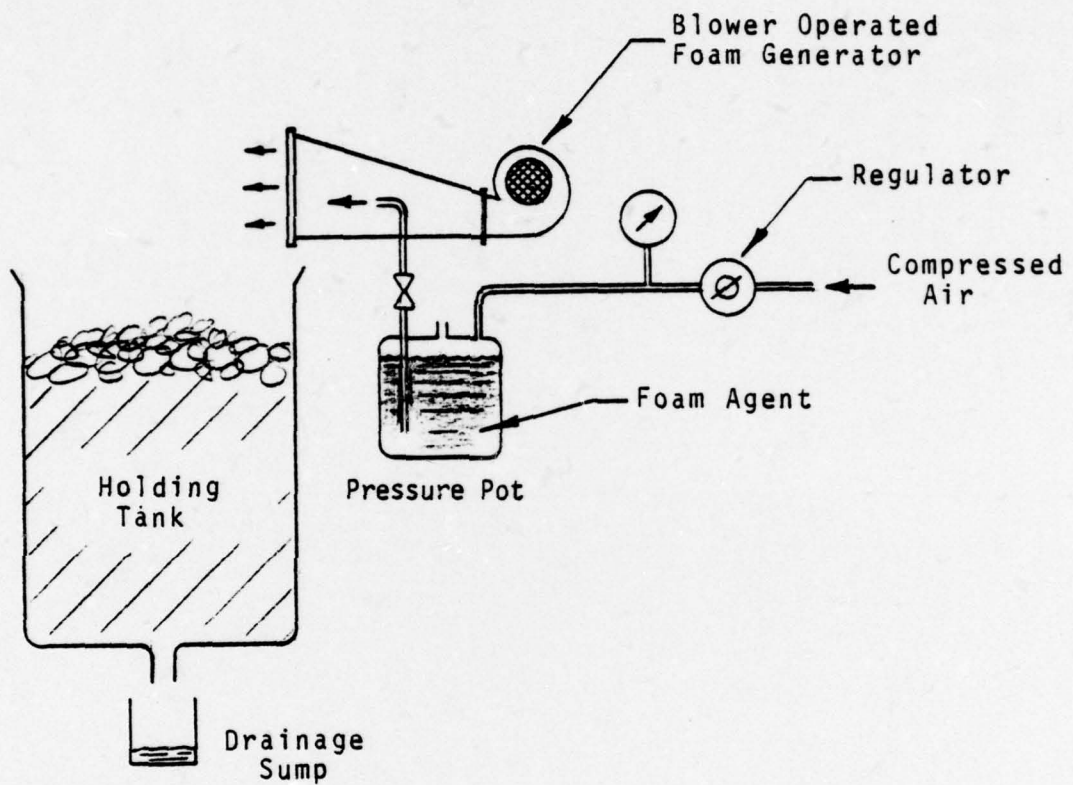


Figure 1. Laboratory Test System, Foam Generator 500/1 Expansion

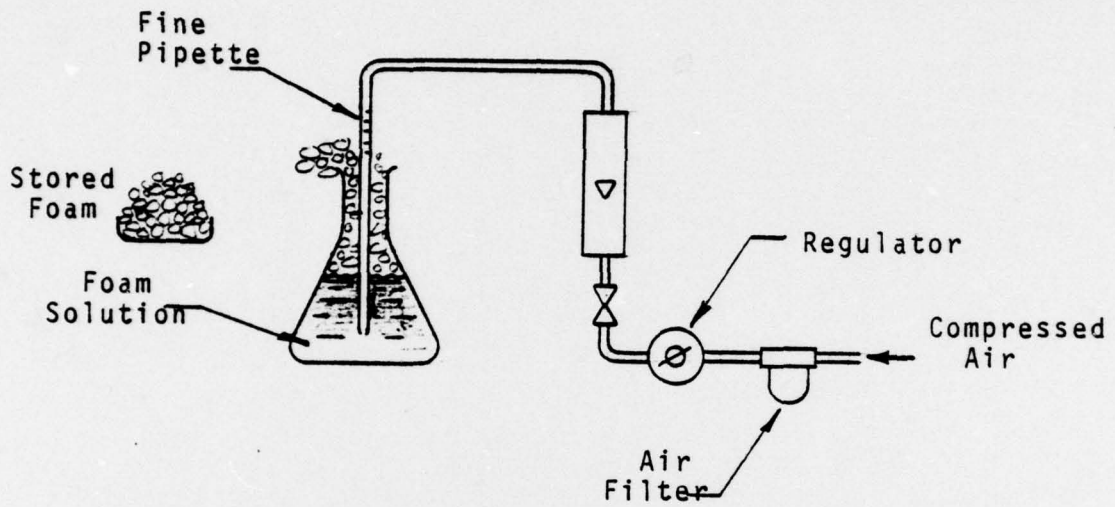


Figure 2. Laboratory Foam Maker for Routine Screening Studies

with collapse and drainage rates. Although these items are important in this program it was also necessary that the foaming agent selected be compatible with the potential additives and modifiers. Past work had shown that PEI posed the greatest difficulty in foaming.

A number of surfactant materials -- anionic, cationic, nonionic -- were compatible with the proposed additives including PEI, but none had good life or drainage. These advantages were available in commercial preparations. Tests showed that salt water compatible agents marketed by MSA, Kidde and Laurentian Concentrates were compatible and provided good life and drainage per se. Since all were essentially equivalent, MSA salt water concentrate was selected as the foaming agent on the basis of availability.

Evaluation of PEI/Glycerin, MSA Foaming Agent

Due to the success with PEI-glycerin systems in prior studies work was initiated on this type of formulation while more preliminary screening studies were going on with the other candidate polymer additives. The first studies looked at reduction of the PEI-glycerin concentration below the 20-30% by volume used to achieve the 0.1 in. per hour collapse rate. Shortly after beginning this work we were notified that the long chain PEI polymer (molecular weight 500,000 to 1,000,000) that had been used was no longer available. Substitution of a shorter chain polymer (molecular weight 30,000 to 50,000) caused a decrease in the effect of PEI on foam life. As will be seen, however, it was still superior to other polymer systems. Studies using PEI-P145*, glycerin and MSA salt water foam agent showed the proper ratio of PEI to glycerin was about a 1:1 volume ratio with a foam agent concentration of about 1.5 to 2.0% measured in the final water solution.

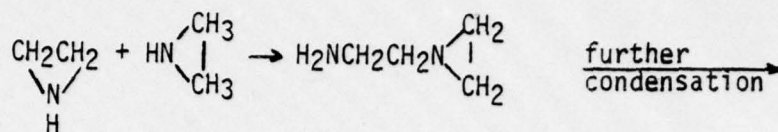
The collapse rate of the best formulation was about 3 to 4 inches per hour versus a design goal of about 2 inches per hour. In addition, the prepared foamed mass dried out rapidly leaving an extremely delicate but closed cell structure.

Drainage rates were found to be no better than commercially available foam agents and intrusion of the foamed mass caused accelerated collapse. At this point it was apparent that the basic formulation was falling short of the design goals given the restrictions on expansion and percent foam addition.

Modifications would be required to achieve the goals either through additives or changes in the polymer chemistry.

* Corcat 145, Cardova Chemical Co., Sacramento, CA

The manufacture of PEI can be approximated by the following equation:



The polymer which forms contains a number of available primary and secondary amine groups. An investigation was made of changing the polymer by adding acidic compounds into these reactive groupings. The acid types examined are presented in Table 1. They were added to a 25% PEI solution in concentrations sufficient to raise the pH to between 7.5 to 8.0. This effort was not successful since the acid additions either precipitated the polymer or rendered it incompatible with the foam agent.

TABLE 1. LISTING OF ACID TYPES ADDED TO PEI

Citric acid	-	Fisher Scientific Co.
Tannic acid	-	"
Lauryl acid	..	"
Succinic acid	-	"
Stearic acid	-	"
Sulfuric acid	-	"
Oleic acid	-	"

Evaluation of Other Polymer Systems

In parallel with the PEI studies, screening evaluations were made of other water soluble polymer systems. These included acrylics, maleic anhydride-vinyl ether copolymers, carboxylic vinyls, polyvinyl pyrrolidone, methyl cellulose and polyvinyl alcohol. A list of the polymer tradenames is given in Table 2. Although some such as the maleic anhydrides and the pyrrolidones gave improvements over commercial foam agents, none even up to 10% by volume in the concentrate were able to approach the life being exhibited by the PEI system. As a result, the continuing investigation concentrated on the PEI system. These polymers and other materials were tested as additives to the PEI system.

TABLE 2. LISTING OF SCREENED WATER SOLUBLE POLYMERS

Acrysol A-1	Rohm and Haas
Rhoplex A-34	Rohm and Haas
Hycar 1471	B. F. Goodrich
Cyanomer P26	American Cyanamid Co.
Acryloid A101	Rohm and Haas
Methyl Cellulose	Fisher Scientific Co.
Airco 126-L (PVA)	Airco
Gantrez AN3953	General Aniline & Film (gaf)
Gantrez AN3152	General Aniline & Film (gaf)
Polyem 550	Spencer Chemical Co.
Acrysol ASE 60	Rohm and Haas
VVP-K90	General Aniline & Film (gaf)

Screening of Additives to the PEI-Glycerin-Foam Agent Concentrate

The initial evaluation of basic modifiers to a commercial high expansion foam concentrate clearly showed that maximum improvement in foam life was effected by the incorporation of polyethyleneimine with glycerin as a plasticizer. Optimum conditions were achieved at an equal volume mixture of PEI, glycerin and MSA salt water foam agent given the restriction of less than 6% by volume of the concentrate in water for foam generation.

This formulation approached the desired collapse rate of 2 in. per hour but was not satisfactory for the retained fluidity necessary to accommodate intrusion. Starting with the basic composition a variety of materials were analyzed in an effort to meet the total system requirements. In some cases the additive selections were based on known chemical properties, in others the selection was based upon usage in other, usually low expansion, foam systems.

Alcohol/Polyols - A number of alcohol type materials were examined predominately with a view toward improving life and/or the intrusion quality of the aged foam. These compounds are often used as so-called moisturizers in low expansion foams. Those listed in Table 3 were added to the 1/3 PEI-P145, 1/3 glycerin and 1/3 MSA salt water foam agent concentrate to achieve a 2% concentration in the final foaming solution. The results showed that sorbitol had some effect in improving life. The remaining materials were found ineffective. Although there was

evidence that sorbitol did increase foam life, the major benefit derived from sorbitol was that it could be added as a substitute for portions of PEI and glycerin.

TABLE 3. LISTING OF ALCOHOL OR HYDROXYL TYPE MATERIALS

Ethylene glycol	Fisher Scientific Co.
Ethanolamine	"
Diethanolamine	"
Polyalcohol (Airco 125-1)	"
Methyl cellulose	"
Mannitol	"
Sorbitol	"
Triethylene glycol	"
Sucrose	"
Super Slurp	U.S. Dept. of Agriculture
Alcohol RA-800	---

Overall, the polyol screening studies failed to uncover a promising candidate. The findings with sorbitol were only a minor step forward. There was a disadvantage in that most additives of this type caused an increase in viscosity which was already high due to the glycerin and PEI.

Inorganic Additives - A number of inorganic or ionic type additives were next examined (Table 4). These materials

TABLE 4. LISTING OF INORGANIC/IONIC TYPE ADDITIVES

Ammonium chloride	Fisher Scientific Co.
Sodium stearate	"
Ammonium sulfamate	"
Barium chloride	"
Lithium chloride	"
Lithium bromide	"
Copper sulfate	"
Ammonium citrate	"
Sodium carbonate	"
Lithium hydroxide	"

fall in the class of hygroscopic salts or hermetants. Their action is to hold water and resist evaporative losses, an item which will be discussed in detail in subsequent sections. The performance of the additives was evaluated using 2 gms of the additive to 1000 cc of foam solution containing 1% PEI-Pl45, 1% glycerin, 2% MSA salt water foam agent and 1% sorbitol. The results showed that lithium chloride exerted a significant effect on prolonging foam life. Ammonium salts showed a somewhat similar effect but their use resulted in some salting out of the foam agent. Other additives either caused exaggerated foam collapse or the formation of a precipitate. This latter effect was especially prominent with the use of copper (complex formation) and with the barium salt.

Studies of the LiCl additive using the test system shown in Figure 1 confirmed the earlier findings that it effected significant increase in life. In some cases, the half life of these foams was well in excess of 35 hours and it was frequently possible to preserve small masses of foam for several days. On the negative side, the prepared foams dried to a very delicate structure which collapsed upon contact. Although significant improvement in foam life, expansion and concentrate usage was achieved with the LiCl addition, there was no improvement in fluidity and the aged foams lacked the ability to wet or outline the surface of an intruded object.

Water Soluble Polymer - The water soluble polymeric materials previously examined as the prime additive were re-examined to determine if the gelling or film forming properties of these materials could improve the intrusion quality of the developed foam agent. Additions up to 10% by volume of the polymers in Table 2 were added to the basic foam agent formulation to evaluate their influence.

With the exception of the polyvinylpyrrolidone (PVP-K90) all the polymers adversely affected foam life. The distinguishing feature of PVP-K90 is that its use invariably resulted in the production of a heavier or wetter foam. In general, foams blown with PVP-K90 were invariably of lower expansion. For example, in an isolated study in which methods of generation were identical, foam made with PVP-K90 were three times heavier than foams prepared without the material.

The foam bubbles dried to a glazed and somewhat opaque film versus the crystal clear finish observed with the base formula. Evaporative water losses were somewhat lower with the use of PVP-K90.

Finalization of the Concentrate Formulation

When the screening studies had exhausted all potential additives, studies were directed toward defining the proper

composition of the formulation. The five ingredients of interest were: PEI, glycerin, MSA salt water foam agent, sorbitol and lithium chloride. The study was hindered somewhat by the fact that in most cases a time of 5 to 8 hours was required in order to observe significant effects in generated foam. In that time period some changes in temperature and/or humidity could occur in the laboratory. These were uncontrollable factors which could have an effect on foam behavior. It is doubtful, however, that these influences would be major.

The results of these studies show that PEI and glycerin were best used in a 1:1 volume ratio. The amount of MSA salt water foam agent was set by the need for a 2% by volume mixture in the final water solution to achieve satisfactory foam generation. The optimum amounts of lithium chloride and sorbitol were never defined with any degree of exactness. Both ingredients could be varied considerably with little or no change in foam behavior. The upper limits to the amount of sorbitol was limited by the capacity of the concentrate to dissolve this material.

The developed formulation based on the preparation of 5 gallons of concentrate is presented in Table 5. Both the sorbitol and the water can be considered as contributing least to the ultimate properties of the foam. The solid sorbitol is a less expensive substitute for PEI-glycerin. It thickens the concentrate. The water is used as a solvent and a viscosity modifier.

TABLE 5. FOAM AGENT FORMULATION

<u>Ingredient</u>	<u>Quantity/ 5 gal.</u>
PEI-P147	2150 cc
Glycerin	2150 cc
MSA salt water foam	9000 cc
Sorbitol	8000 gms
Lithium chloride	900 gms
Water	4500 cc

The formulation overall showed excellent potential for meeting the required specifications for life, expansion ratio and concentrate usage. Although some advances were achieved in terms of drainage rate, significant improvements in the retention of fluidity (water content) were not achieved.

It must be appreciated that, in general, the laboratory study was conducted on relatively small volumes of foam with highly exposed surfaces. This condition favored water loss by evaporation as well as drainage. It was hoped that evaporative losses would not be as severe a factor in large scale tests where the ratio of surface to volume would be much reduced.

The Influence of Evaporation on Foam Behavior

Conventionally, foams are assumed to decay by loss of bulk water through gravitational drainage. The majority of current uses of foams require foam persistence of only short duration measured in minutes rather than hours. Over these time spans evaporation is not a significant factor and thus its influence on foam behavior has not received much attention.

In prior MSA work, the high concentration of PEI and glycerin in the foam solution resulted in a residual polymer film as the bubble wall. In addition, the application did not require fluidity to be retained by the foam mass nor for it to be subjected to environmental exposure. It was not until this program was initiated that the effects of evaporation became important.

Bulk drainage is the principal method of water loss from surfactant foams. Loss of 50 to 70% of the water by drainage occurs in the first 30 minutes or so after generation. The quantity varies as a function of formulation. In this program all attempts to slow the drainage beyond that already possible with the premium commercial agents were unsuccessful.

Beyond the first 30 minutes drainage slows down to a slow rate and further water loss seems to parallel the linear collapse rate. A typical drainage curve of a premium agent is given in Figure 3. Admittedly, however, drainage measurements are rarely extended beyond 60 minutes and values are normally reported only through 30 minutes. Upon examining the behavior of foams over several hours it was obvious that another water loss mechanism was involved. This mechanism is logically evaporation.

With evaporation established as an important mechanism affecting foam behavior over the long term, it became necessary to measure evaporative losses and investigate means of controlling it. A laboratory procedure was set up to measure evaporation. Foam masses were collected on tared petri dishes. The foam and dish were placed on a balance and loss of weight followed with time.

Representative evaporation rates obtained with various modifications of the developed formulations are shown in Figures 4 and 5. The data shows variation in loss of water for changes

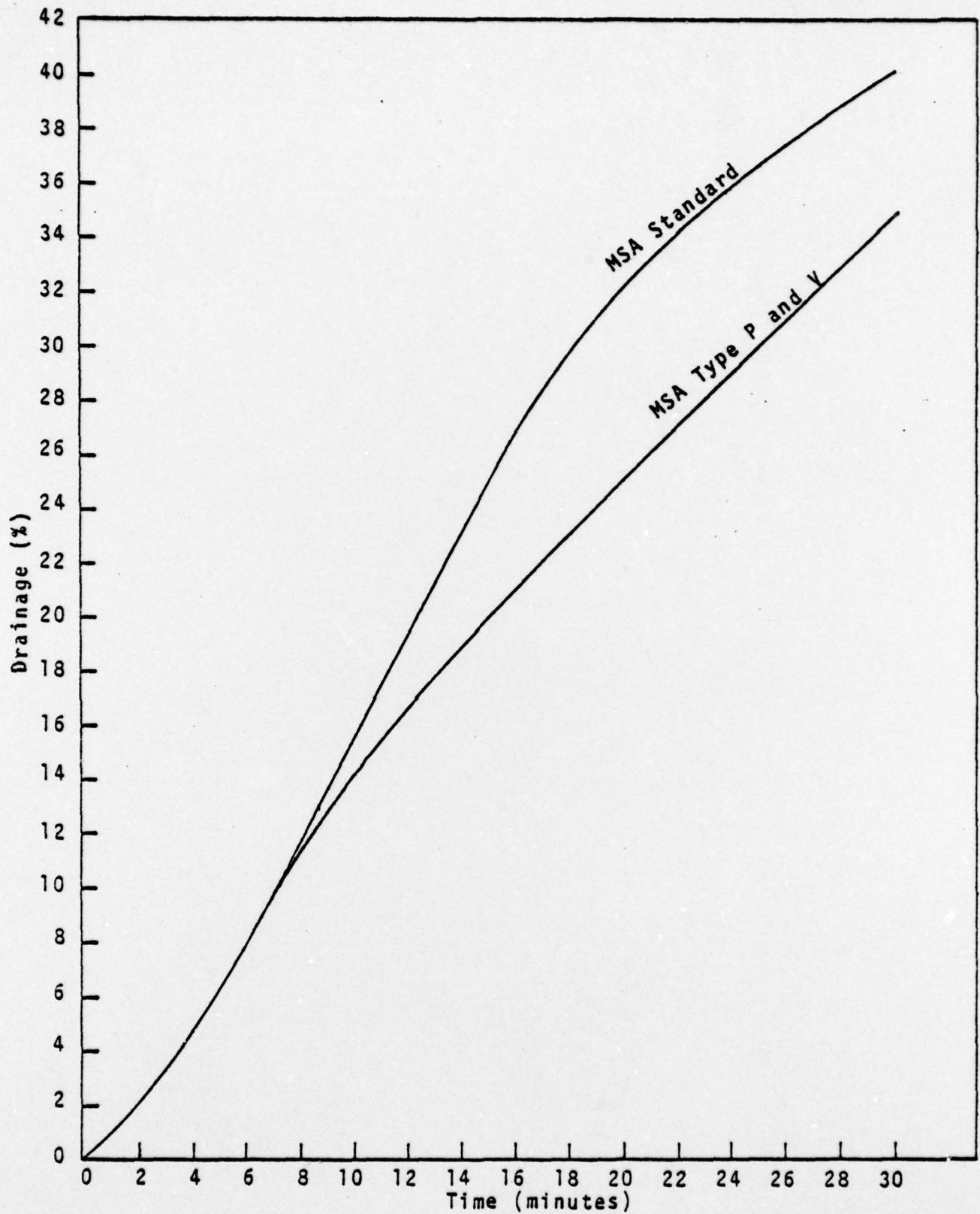


Figure 3. Typical Drainage Curves for MSA Standard, Type P and Type V Foam at 500:1 Expansion

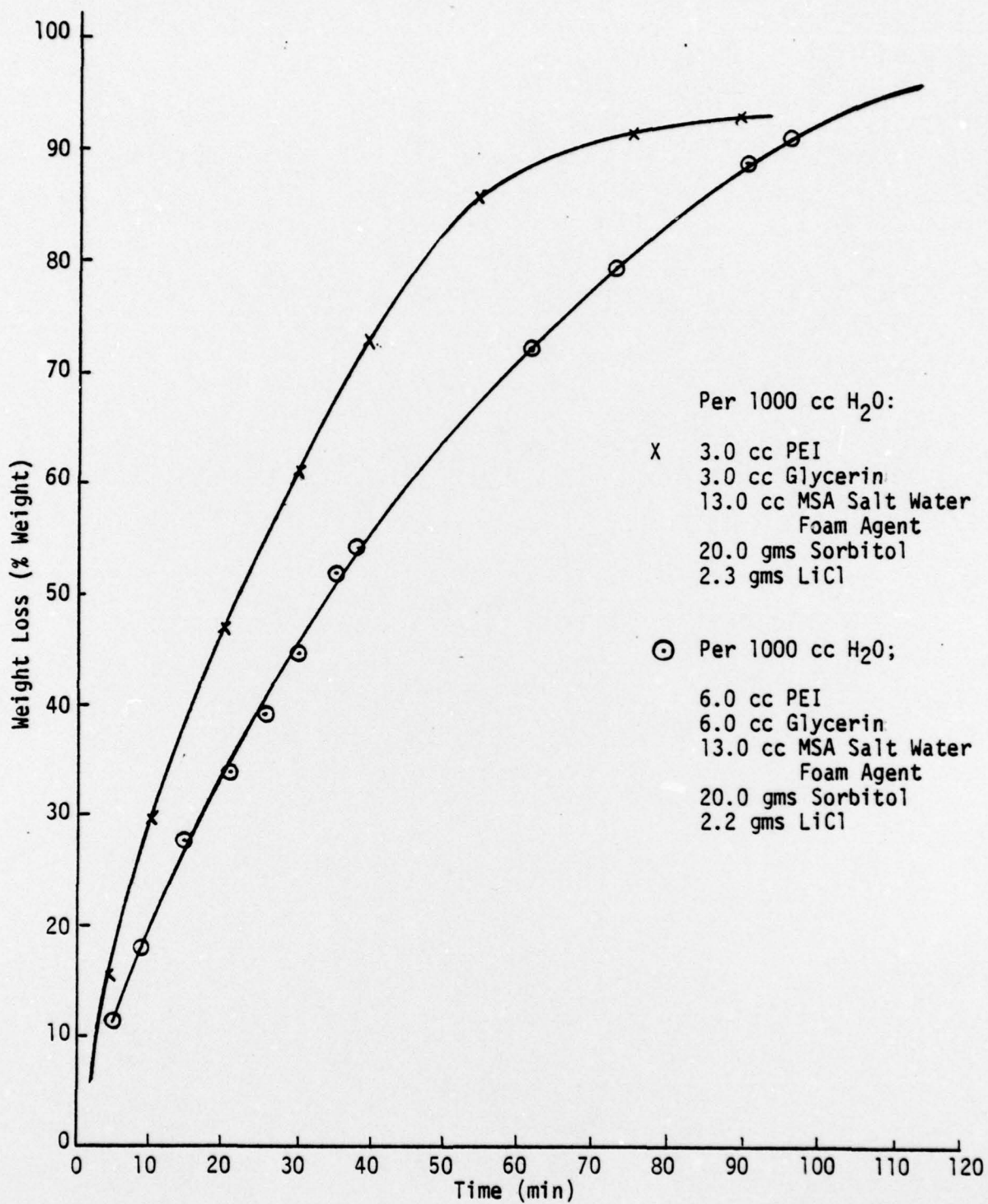


Figure 4. Variation of Evaporation Rates with Changes in Foam Agent Composition

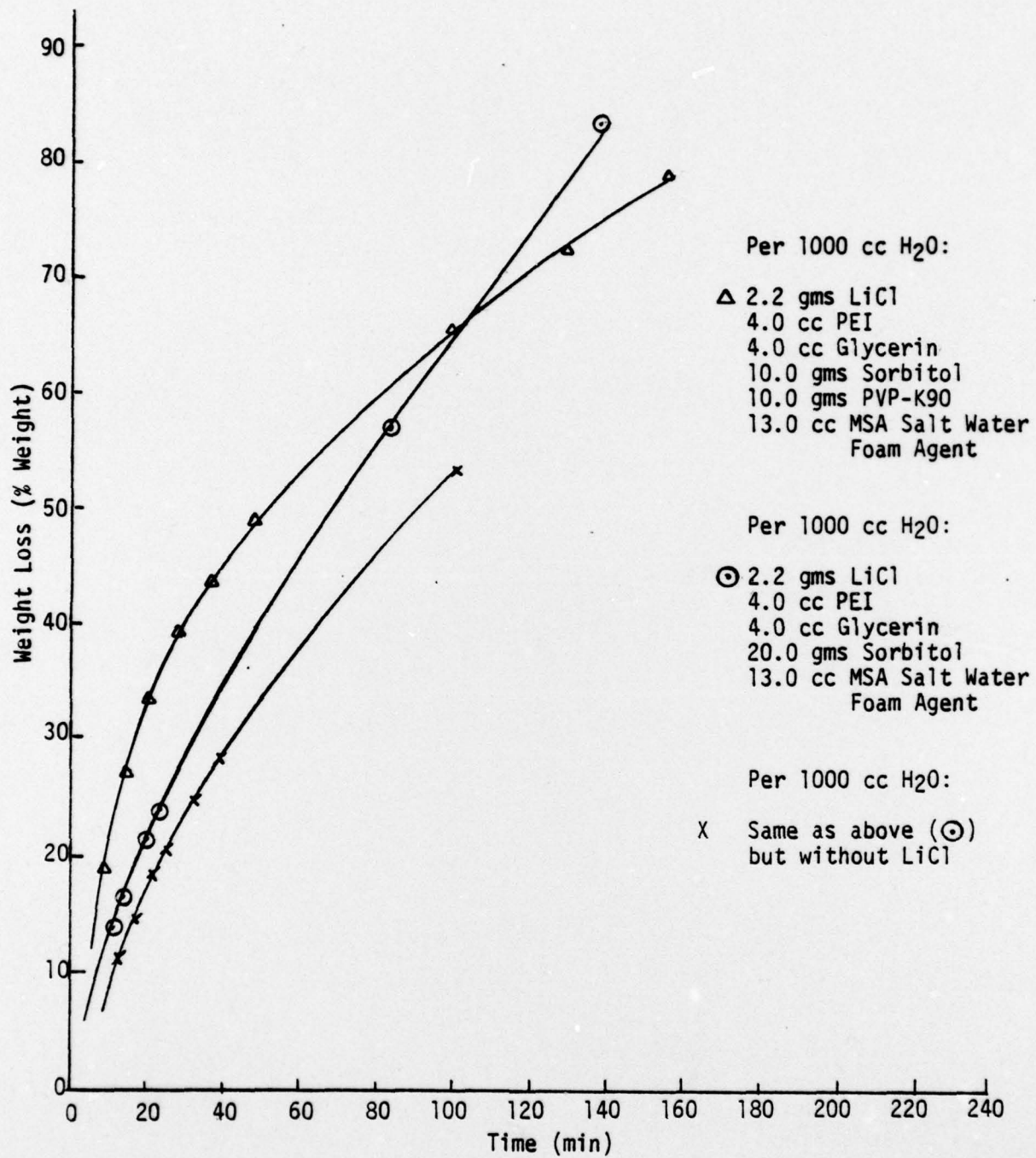


Figure 5. Evaporative Loss of Foamed Masses

in composition. The most significant finding is the extent of the drying out process. As can be observed, approximately 90% or more of the foamed mass is lost to evaporation within the first several hours. In the tests which are reported, the original structure of the foamed mass remained virtually intact even though the residual structure consisted of less than 0.1% of its original mass. Analogously, the aged foam is equivalent to a freshly generated foam blown at an expansion ratio of over 5000/1. Obviously, the high rate of evaporation and the extent of the evaporative loss provide a ready answer as to why the aged foam possesses such poor intrusion quality.

A closer examination of the evaporation rate curves show a slight break occurring approximately 30 minutes after generation. This time frame correlates with the drainage behavior and with obvious surface changes that take place in the bubble. Prior to 30 minutes, the foam bubbles are sensitive to contact especially by dry or nonwetted objects. Contact within this period causes the bubble to shatter and fragment. After this period the bubble develops a plastic like consistency in which rupturing occurs by a tearing open followed by a rolling back of the wall. The evaporative rate curves show that, in spite of the development of this highly viscous surface, the evaporation process proceeds only slightly interrupted.

The net effect, of the manner in which the foam matrix decays, is that underlying foam bubbles accumulate a thickened skin formed by material supplied by collapsed neighbors. The reason for the high evaporative loss can possibly be traced to the loose alignment of surfactant(s) which control the surface. For the most part, the materials which retard water evaporation best are generally insoluble in water and/or are nonfoamers.

The only additive which helped evaporative losses was PVP. As indicated in Figure 5, that effect was limited to the latter stages of foam life. The net effect over the long term was not significant. As has been noted, PVP has an adverse effect on expansion and, as will be reported, also an effect on fluidity which for this application is negative.

LARGE SCALE TESTS

Upon completion of the laboratory efforts a number of large scale tests were performed using commercial sized high expansion generators. These tests were conducted intermittently during midwinter to early summer as the weather allowed.

Cold Weather Tests

The severity of the winter precluded any outside tests during that time. Tests were conducted in an unheated steel building using a MSA Model 3000 Foamaker. The generator under normal conditions provides a nominal 3000 cfm at about a 1000/1 expansion. Foam was generated at a topside location and foam cascaded into a metal walled holding chamber. This is a standard method of determining expansion and generator output for compliance with regulations for foam use in firefighting. This type of test gives dynamic values which due to inherent errors are lower than actual values.

The concentrate formulation for the first tests consisted of the following:

<u>Ingredient</u>	<u>Quantity</u>
PEI	570 cc
Glycerin	570 cc
MSA Salt Water Foam Agent	1140 cc
Sorbitol	870 gms
LiCl	140 gms
Water	100 cc
n-Propyl Alcohol	300 cc

The concentrate injection rate was measured at 6.0%. The concentrate was injected directly into the water at the generator. The following is a list of test conditions:

Air Temperature	37°F
Water Temperature	37°F
Water Flow Rate	28 gpm
Concentrate Volume	0.80 gal (lab), 1.1 gal (diluted)
Volume of Foam	500 ft ³
% Concentrate	6.0% (lab mix)

Due to the small volume of foam being collected in a tank of measured volume versus the amount of foam being generated, no accurate determination of expansion was possible. The height of the generated foam was measured at about 4.5 feet and remained unchanged throughout the day. The following morning the top of the foam mass had broken down somewhat irregularly.

A crevasse had formed through the foam adjacent to an opening in the building wall, obviously due to rain driven in through the opening during the night. Overall, the bulk of the foam mass remained intact and, with the exception of the fissure, had collapsed less than 1 foot in 20 hours. Intrusion quality was measured by dropping objects into the mass. Initially the foam followed around them. Several hours after generation, however, intruding objects left permanent holes in the foam mass.

In the second test, polyvinylpyrrolidone (PVP-K90) was substituted for some of the sorbitol. The concentrate was injected at a location 20 feet upstream from the generator since it was suspected that due to the concentrate viscosity a longer mixing time was needed. As described earlier, PVP-K90 was added to form a crustlike surface to minimize evaporation and to improve the intrusion quality. The formulation for the second test consisted of:

<u>Ingredient</u>	<u>Quantity</u>
PEI	855 cc
Glycerin	855 cc
MSA Salt Water Foam Agent	1740 cc
Sorbitol	906 gms
PVP-K90	210 gms
LiCl	180 gms
Water	1240 cc
n-Propyl Alcohol	150 cc

Test data are summarized below:

Air Temperature	12°F
Water Temperature	37°F
Water Flow Rate	27 gpm
Concentrate Volume	1.3 gal (lab), 1.6 gal (diluted)
Volume of Foam	575 ft ³
% Concentrate	3.3% (lab), 4.1% (diluted)
Storage Temperature	4°F-12°F (overnight range)

The concentrate injection rate was considerably lower than was planned. Again, no accurate measure of expansion was made but the time of fill was longer than in the first tests indicating that expansion was lower. This was an expected occurrence since the laboratory tests had shown PVP to give a heavier, wetter foam. The intrusion quality was not significantly improved and any advantage of this formulation could easily be traced to the lower expansion. The collapse rate of the foam was about 1 to 1.5 inches per hour over an initial 4 hour period. After 20 hours the foam had collapsed about 3.5 feet to yield an average collapse rate of about 2 inches per hour.

The final indoor tests were conducted during mild ambient weather (70-75°F). In these tests a MSA Model 6000 electric generator was used. It gives a nominal 6000 cfm at 900/1 expansion. The prepared foam agent was fed to the generator via a pressurized pot similar to that shown in Figure 1. The composition of the foam agent was:

<u>Ingredient</u>	<u>Quantity</u>
PEI-P145	2100 cc
Glycerin	2100 cc
MSA Salt Water Foam Agent	8500 cc
Sorbitol	7800 gms
LiCl	875 gms
Water	4500 cc

The foam was again cascaded from overhead but into a much larger volume of 3880 ft to allow determination of the expansion ratio. The data for these particular tests is summarized below:

Ambient Temperature	70-75°F
Water Flow Rate	67 gpm
Time of Test	40 sec
Volume of Foam	3800-4100 ft ³
Foam Agent Used	2.5 gal
Concentrate Usage	6.0%
Calculated Expansion	~700/1

The use of the pressurized pot to inject the foam agent was a decisive improvement over the use of the pump. The expansion ratio of 700/1 was lower than expected but not unexpected given the viscosity increase of the fluid provided by the concentrate injection.

The stored foam collapsed at a rate of about 2 in./hr when averaged over 24 hours. The foam collapsed uniformly, except in the vicinity of cracks or holes in the wall and in the area directly below the generator where water drained from the generator when foam generation was terminated.

The intrusion quality of the foam was equivalent to that observed in the earlier tests.

Outdoor Tests

A series of tests were conducted outdoors at temperatures in the range of 70-80°F. Three types of tests were run using equipment and foam concentrate of the final indoor test. In one case the foam was generated against the side of a building, in a second against a chain link fence and last in free fall by inverting the generator and pointing it downward from a position

10 feet above ground level. The latter two types of tests and also the indoors foam test were conducted as a demonstration for the Technical Project Officer.

The outdoor tests all followed a similar pattern of foam degradation, one which differs from those conducted indoors mainly by virtue of wind effects. In all outdoor tests the height of the foam varied between 5 and 6 feet at its deepest point. Equally in all tests foam life was of the order of 3 to 5 hours rather than 24 hours as could be extrapolated from the indoor results.

The effects of wind followed a distinct pattern. For the first 15 to 20 minutes following generation the wind gusts produced ripple effects on the foam surface. For free standing foam masses, after about 30 minutes wind velocities above 5 mph began to skim off the top layer beginning at the upwind location and either carried it away or rolled it backward across the top of the mass. After about 60 minutes the entire foamed mass would be displaced downwind to distances of 30 to 40 feet and only about 70 to 80% of the original foam mass could be accounted for. Within 2 to 3 hours the original foam mass would be reduced to isolated clusters trapped by downwind physical obstacles.

Where some protection was provided such as by a building wall, a fence or a ditch or ground depression, the wind effects were reduced but not eliminated. Such protection prevented displacement of the foam but not the skimming effect of the surface.

This behavior can be correlated with the water loss mechanism which has been proposed. Bulk drainage accounts for the loss of some 50% of the contained water over the first 30 minutes of foam life. In the top layers the retained water is probably in the range of 30% of the initial value assuming that the leveling off of the drainage curve is indicative of pseudo stable condition within the bubble wall. At this point in time, evaporative water loss may be the predominant factor in water loss from the top layers of foam.

Over the first 30 minutes the foam shows essentially ripple effects on the surface due to wind, although some bubble collapse is occurring. Where protection is afforded so that the total mass cannot be moved, the next wind effect noted is the skimming of a layer from the surface. This layer will be several inches thick. Once this layer is lost, the foam returns to essentially a stable condition. This lasts for 15 to 30 minutes depending on wind speed, temperature and possible relative humidity.

Following a stable period, there will be another skimming of a layer. The process repeats itself until the mass is completely degraded.

During the first hour the foam changes from a wet fluid mass to a nonfluid sticky bubble mass, but the resistance to wind effects does not appear to improve significantly. There is a change in response to an intruding object. In its fluid state the foam does tend to conform to the object and to reflow behind it. In the nonfluid state it does not reflow. The foam does adhere to intruding objects and coats the front and sides as they penetrate.

Large objects, vehicles, are coated but tend to push the foam in front of them with a plow effect. There is some tendency for the foam to roll back across the top if the foam is higher than the intruding vehicle.

Height/Spread Factor of Foam Masses

For the outdoor tests involving free fall of the foam, markers were installed to measure the rate of spread and the height of the foam at various diameters. This was to determine how closely the goal of a 10 ft height within a 30 ft diameter could be approximated.

These tests involved the Model 6000 MSA Foamaker hung inverted such that the discharge end was 10 ft above ground level. The foam agent was the developed material and was injected into the water line 50 ft from the generator. The total injection time was 1.1 minutes yielding a 6.3% concentration. Table 6 shows the height which the foam reached versus the spread diameter.

TABLE 6. HEIGHT/SPREAD FACTOR FOR GENERATED FOAM

<u>Time (min)</u>	<u>Foam Height (center)*</u>	<u>Foam Spread (dia)</u>	<u>Foam Front</u>
0.20	3'	30'	18"
0.80	6'	37-40'	18"
1.00	7.5'	45'	18-24"

*Directly under the generator

A similar series of tests were run using a formulation containing PVP. Under the same conditions a foam height of 6 ft required a foam spread of 100 ft (200 ft diameter). At 30 feet the height of the PVP formulation was only 3.5 ft at the highest point of the mass. This is due partially to a lower expansion which occurs with PVP but basically to an initially much more fluid foam.

CONCLUSIONS AND RECOMMENDATIONS

A long life foam formulation was developed which consisted of the following ingredients: polyethyleneimine (P145, Cordova Chemical Company), glycerin, MSA salt water foam agent, sorbitol and lithium chloride.

Overall, the formulation yielded foams which reasonably met the design goals for expansion, life and concentrate usage. The blown foams failed to meet the specification to conform to the surface of an intruding object and fell short of exhibiting a buildup rate of 10 ft height per 30 ft diameter spread.

It is inferred that the poor intrusion quality of the stored foam is loss of water through initial drainage followed by extensive evaporation. Small scale laboratory studies clearly showed how extensive the evaporative loss can be. The quality of long life is attributed to the formation of a plastic-like consistency on the surface of the prepared foam. The formation of this highly viscous surface and the accompanying fixation or gelling of the available water or fluids undoubtedly also contributes somewhat to the loss of the fluidized properties of the aged foam.

Large scale field tests showed that wind exhibited a distinct influence on foam life, exaggerating the collapse rate an order of magnitude over that observed in a protected environment.

The question arises as to whether any foam mass blown initially at 800/l to 1000/l could be made resistant to moderate winds. From observations made in the field it is apparent that freshly blown foam as it exits from the generator is extremely resistant to wind effects. Wind gusts have little net effect other than the formation of small nondestructive ripples. In addition, the intrusion quality of the foam during this stage would appear to be excellent as evidenced by the manner in which the spreading foam wets and flows through and around major obstacles. The time frame in which the foam possesses these desirable features is relatively short, less than 30 minutes following generation. Beyond this time frame, wind effects become noticeable and the resulting adverse effects increase as the foam ages. It is in this period where loss of mass in the foam through evaporation reaches significant levels. It is estimated that the surface layers of foamed masses aged for 30 minutes are equivalent in density to a foam blown with an expansion ratio in excess of 2000/l. This delicate structure has little if any wind resistance.

A conclusion that can be drawn from this analysis is that the design goals were established with some justification. The failure to meet some of the major specifications is attributed to the complexity of a multicomponent surfactant system coupled with the absence of established guidelines. It is suggested, however, that foam blown to a 1000/1 expansion could be made wind resistant provided the initial ingredients could be preserved and utilized in an optimum manner. It would be necessary to analyze the residual components in the aged bubble wall to optimize the concentrate. This would aid in overcoming the influence of wind, but the retention of fluidity lies in controlling drainage and evaporation. No improvement was made in these two effects beyond that already possible with premium commercial high expansion foam agents. It would appear that a radically new approach is required. Evaporation might be controlled by gelling the surface of the foam mass. Technology for gelling foam does exist. At present there is no sound basis for new approaches to the control of bulk drainage.