

PB91227819



mining research contract report

APRIL 1991

# IMPROVED METHOD FOR EXTINGUISHING COAL REFUSE FIRES

Contract J0398007  
MSA Research Corporation

BUREAU OF MINES  
UNITED STATES DEPARTMENT OF THE INTERIOR



REPRODUCED BY  
U.S. DEPARTMENT OF COMMERCE  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
SPRINGFIELD, VA 22161



REPORT DOCUMENTATION PAGE	1. REPORT NO.	2.	PB91-227819
4. Title and Subtitle Improved Method for Extinguishing Coal Refuse Fires			3. Report Date April 1991
7. Author(s) S. S. Gross			8. Performing Organization Report No. MSAR 91-14
9. Performing Organization Name and Address MSA Research Corporation Div. of Mine Safety Appliances Co. P.O. Box 429 Pittsburgh, PA 15230			10. Project/Task/Work Unit No.
			11. Contract(C) or Grant(G) No. (C) J0398007 (G)
12. Sponsoring Organization Name and Address U.S. Department of the Interior, Bureau of Mines P.O. Box 18070, Cochrans Mill Road, Bldg. 140 Pittsburgh, PA 15236-0070			13. Type of Report & Period Covered Final Report 6/89-2/91
			14.
15. Supplementary Notes			
16. Abstract (Limit 200 words)  Coal refuse fires present environmental and personnel hazards to those living in the vicinity of the fire as well as those engaged in the reclamation efforts. The fire can also increase subsidence problems as well as prevent revegetation and reclamation of the site.  Conventional efforts have been excavation and quenching; expensive, dangerous, and very often unsuccessful techniques. Water flooding has also proven unsuccessful due to the poor distribution of the water in the refuse pile.  Water quickly drains from the coal refuse pile below its injection point with little or no lateral distribution. As an alternate to excavation and/or quenching, the feasibility of using water based foams to improve the distribution of water injected into a coal refuse fire was examined. Using surfactants to foam the water and gelling agents to reduce its fluidity, tests were conducted in the lab and the field. The foam still tends to follow the larger channels/openings in the pile, although above, as well as below the injection point. While the foam does improve water distribution in the pile, additional work needs to be conducted to prevent preferential channel flow and further improve distribution.			
17. Document Analysis a. Descriptors			
b. Identifiers/Open-Ended Terms			
c. COSATI Field/Group			
18. Availability Statement		19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 107
		20. Security Class (This Page) UNCLASSIFIED	22. Price

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## FOREWORD

This report was prepared by MSA Research Corporation, a division of Mine Safety Appliances Company, Evans City, PA under USBM Contract Number J0398007. The contract was initiated under the Abandoned Mine Lands (AML) Program. It was administered under the technical direction of the U.S. Bureau of Mines with Dr. Robert F. Chaiken acting as Technical Project Officer. Mr. Larry E. Guess was the contract administrator for the Bureau of Mines. This report is a summary of the work recently completed as a part of this contract during the period June 1989 to February 1991. This report was submitted by the authors on 16 April 1991. We are currently evaluating whether the concept, process or formulations are patentable.

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

gms	grams
ft <sup>2</sup>	square foot
ft <sup>3</sup>	cubic foot
Btu	British thermal unit

## ABSTRACT

Coal refuse fires present environmental and personnel hazards to those living in the vicinity of the fire as well as those engaged in the reclamation efforts. The fire can also increase subsidence problems as well as prevent revegetation and reclamation of the site.

Conventional efforts have been excavation and quenching; expensive, dangerous, and very often unsuccessful techniques. Water flooding has also proven unsuccessful due to the poor distribution of the water in the refuse pile.

Water quickly drains from the coal refuse pile below its injection point with little or no lateral distribution. As an alternate to excavation and/or quenching, the feasibility of using water based foams to improve the distribution of water injected into a coal refuse fire was examined. Using surfactants to foam the water and gelling agents to reduce its fluidity, tests were conducted in the lab and the field. The foam still tends to follow the larger channels/openings in the pile, although above, as well as below the injection point. While the foam does improve water distribution in the pile, additional work needs to be conducted to prevent preferential channel flow and further improve distribution.

## INTRODUCTION

MSAR conducted a research program to determine if a gelling foam could control and extinguish coal refuse fires as an alternative to excavation and quenching. The foam, injected into the burning region, plugs channels and crevices, preventing water in the foam from flowing away from the fire zone. The foam could also contain a fire retardant which would be deposited in the refuse pile to prevent burnback.

It has been our observation that attempts in the past to extinguish coal refuse fires using water or foam have not met with success. A major reason for this failure appears to be that water sprayed upon or injected into the refuse pile soon channels the pile. The channels make up only a small fraction of the total cross section of the pile. As a consequence, water distribution is poor, and the fire area is not completely quenched, allowing re-ignition. Regardless of the quantity of water placed on the pile, the fire may be largely untouched.

In our method, we injected a low expansion, water-based foam into the refuse pile. The foam contained a fire extinguishing agent and a gelling agent which tends to stiffen the foam. It was theorized that the foam flow would favor the channels, but gradually close these openings, forcing the foam to adjacent areas. When the fire is extinguished, the fire retardant will remain to prevent re-ignition.

The program was divided into 6 tasks:

1. Program Plan
2. Literature Search
3. Gel Testing
4. Compatibility Testing
5. Coal Refuse Tests
6. Final Report

## TECHNICAL DISCUSSION

### Statement of the Problem

Coal refuse fires present environmental and personnel hazards to those living in the vicinity of the fire as well as those engaged in the reclamation efforts. The fire can also increase subsidence problems as well as prevent revegetation and reclamation of the site.

Conventional efforts have been excavation and quenching; expensive, dangerous, and very often unsuccessful techniques.

Coal refuse fires have also proven resistant to the use of water for extinguishment. Water would appear to be the best method of extinguishment, but applying water to the top of the refuse pile is usually ineffective. Subsurface injection is more effective, but the fire is rarely extinguished. In almost all cases, effective extinguishment can only be accomplished by excavation and quenching, an expensive and sometimes dangerous method.

The reason for the failure of water sprays and subsurface injection appears to be due to the channeling of the water as it trickles through the refuse pile (Figure 1). The channeling does not allow the water to flow through the total pile, but leaves much of the pile, and thus the fire, untouched. Applying large quantities of water does not help since it continues to flow only through the channels.

Foam has been advocated as an improved method of fire control over water alone. However, field tests done by the Bureau of Mines with MSAR's assistance,<sup>1 2</sup> indicate that the foam method has the same problem as water application; the water in the foam still flows only in channels, and large portions of the fire area may be unaffected. If a method could be developed to force the water into the areas between the channels to extinguish the fire area without excavation, a significant improvement would be made.

### Techniques for Solution

We proposed to use a method to block the channels forcing the water to wet a greater cross-section of the refuse pile. This method would inject a low expansion foam into the fire area. After several minutes the foam gels, closing off the channel areas, and forcing the foam to move to an adjacent zone. The foam also contains a fire retardant to prevent burnback.

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<sup>1</sup>RI9281, "Fire and Explosion Hazards of Oil Shale".

<sup>2</sup>One ton rubble pile tests at Bruceton with A. Furno.

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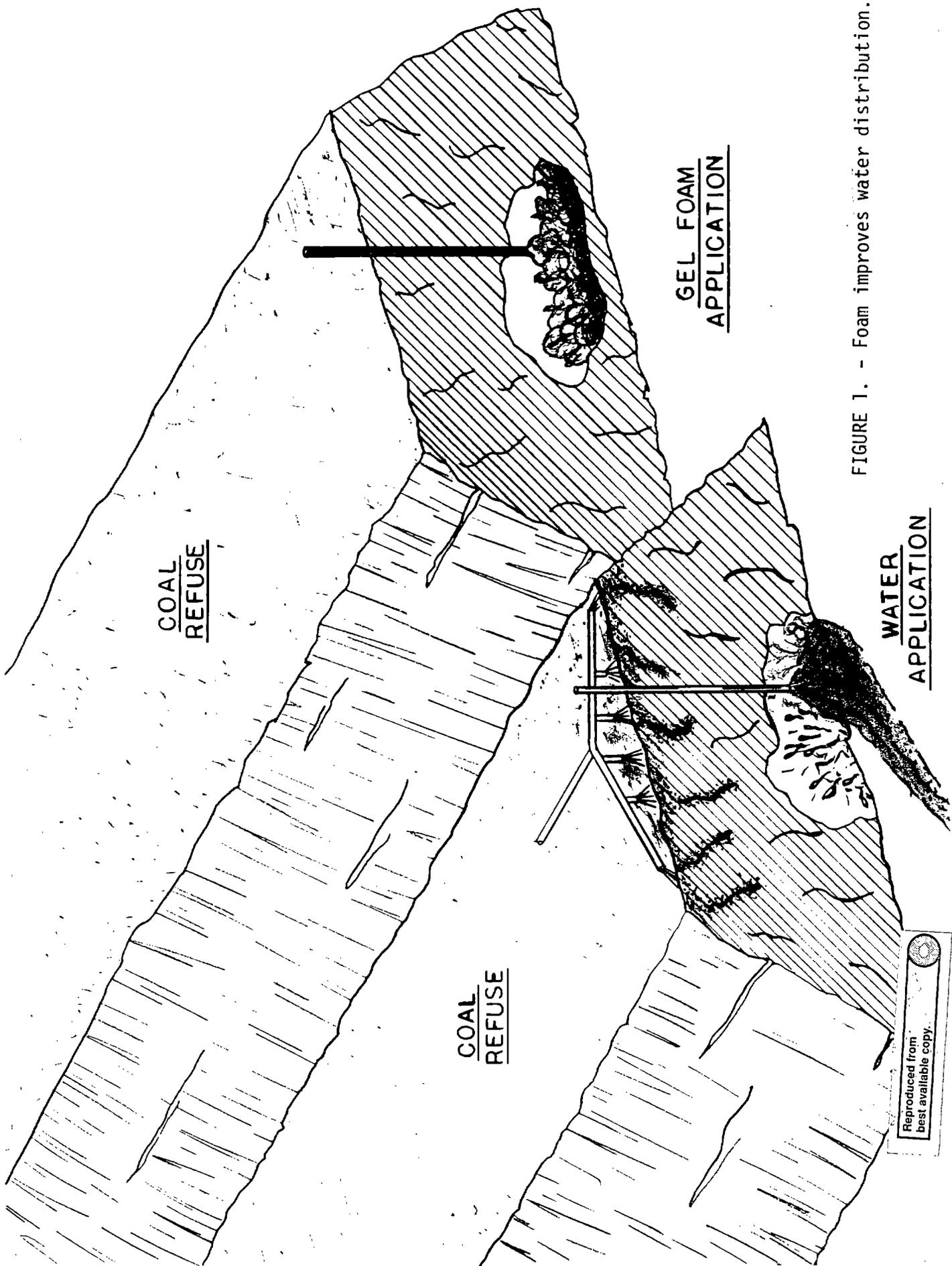


FIGURE 1. - Foam improves water distribution.

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Fire-Fighting Foams - Fire-fighting foams are presently used to blanket the fire with a continuous air-water layer which smothers the combustion. There are a variety of fire fighting foam agents available. They may be divided into five categories according to their basic starting material:

1. Protein
2. Fluoroprotein
3. Alcohol based
4. Aqueous film forming (AFFF)
5. Surfactant

The first four categories are used only as low expansion foams, with an expansion ratio of approximately 8:1. In other words, one gallon of liquid foam solution will produce eight gallons of foam. Low expansion are heavier than high expansion foams, and can be projected through air about as far as water. The last category, surfactants, can be used to produce high or low expansion foams, the surfactant-based low expansion foams are usually more fluid than protein, fluoroprotein, or alcohol-based foams.

Dry Chemicals and Flame Retardants - The biggest drawback in fighting fires with foam is the potential for burnback when foam generation is stopped. Figure 2 shows the sub-surface temperature of a wood fire in a test tunnel where high expansion foam was tested by MSAR in a program for the Bureau<sup>3</sup>. Initially, the foam quenched the burning and a large temperature decrease was noted. However, combustion continued in deep-seated areas after foam generation was stopped. Within a short period of time the fire regained its original intensity. Flame retardants were added to the foam to prevent this reignition.

A number of chemicals are available for fighting fires either as dry chemical extinguishing agents or flame retardants. Dry chemicals are divided into two classes: Class B chemicals, such as sodium bicarbonate or the salts of potassium, are recommended only for fires of flammable liquids or gases; Class A chemicals are multipurpose -- they are based on ammonium phosphates, and are recommended for combustible solids as well as flammable liquids and gases.

Flame retardant chemicals, such as zinc borates, prevent or retard combustion in solids. They are usually mixed with the solid before fabrication into final products such as plastics and textiles.

There are primary and secondary extinguishing mechanisms involved in the action of the various dry chemicals and flame retardants. (It should be noted, however, that these are not completely understood.) The primary mechanism is the interruption of the combus-

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<sup>3</sup>Contract H0308064, Incorporation of Fire Extinguishing Agents in High Expansion Foam.

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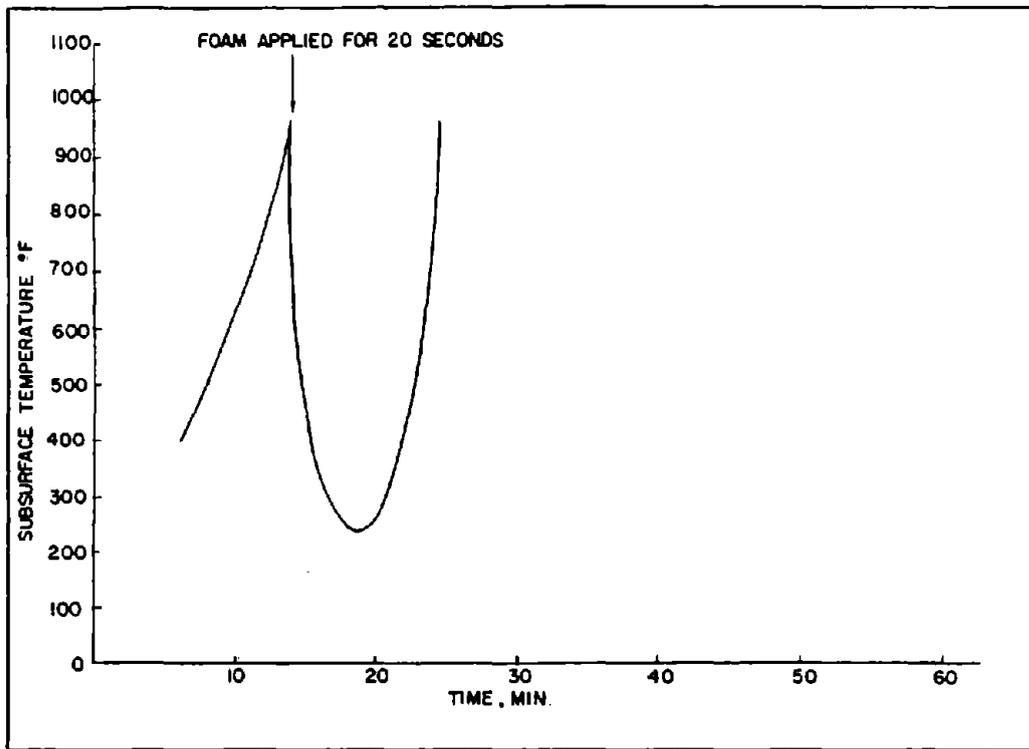


FIGURE 2. - Tunnel fire test results with foam.

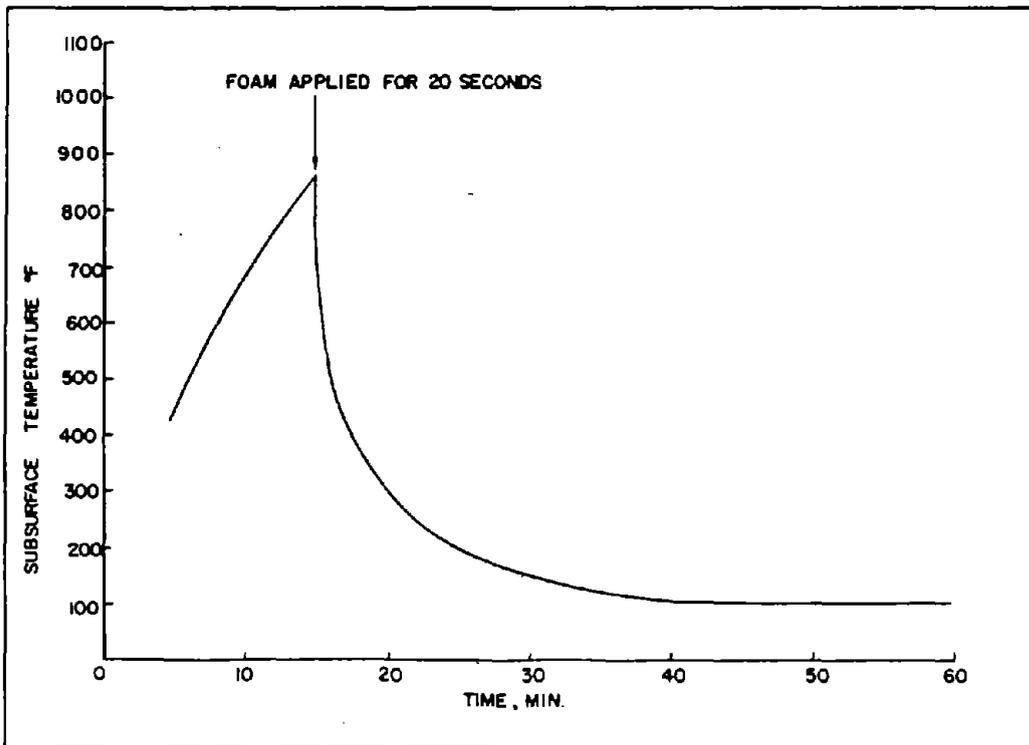


FIGURE 3. - High expansion foam + DAP (10%) tunnel fire test results.

tion chain reaction, which occurs in two ways. One, is the recombination of the radicals found during combustion on a particle surface of the agent. In this case, the effectiveness of the agent increases with a decrease in particle surface area. The smaller radical recombination on the particle surface accelerates the chain termination steps of the combustion reaction.

The second means of chain reaction interruption is accomplished through the formation of chemical species which react with the chain propagating radicals. (An example could be the formation of the  $\text{HPO}_4$  fragment from ammonium phosphate.)

The secondary extinguishing mechanisms include heat absorption and formation of oxygen-excluding coatings. The secondary mechanisms, however, are considered important factors only if large quantities of the various dry chemicals and flame retardants are used.

Phosphorous compounds appear to be very promising for incorporation into foam. Nearly all phosphorous compounds that decompose to acid fragments at low temperatures are effective flame retardants.<sup>4 5</sup> The extinguishing mechanism appears to be combustion chain reaction termination. It has been noted that the phosphorous compounds increase the char content of the burning solid and decrease the amount of flammable gases generated during combustion. This increase in effectiveness with decreased particle size is also evident.

It is also believed that phosphorous compounds form a surface barrier to oxidation by virtue of their tendency to produce a viscous or gummy material which may act as a polymeric phosphoric coating on the substrate. This physical fire extinguishant mechanism may be correct when enough of the phosphorous compound has been applied to establish a coating.

In the previous study<sup>6</sup> with ammonium phosphate we found fires were rapidly extinguished and burnback prevented even when a continuous layer of the compound could not be distinguished on the burnt surface, nor could such a small amount of phosphorous compounds exclude oxygen.

There are a number of flame retardants other than standard dry chemicals and ammonium phosphate which could be examined. These include (1) bromine and chlorine compounds, (2) phosphorous-halogen compounds, (3) phosphorous-nitrogen compounds, (4) antimony-halogen compounds, (5) aluminum hydrate, and (6) borate compounds. Those which are combinations of chemical compounds could be more effective than either compound alone due to synergism. There may be additional flame retardants used for a specific situation, which may also be considered.

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<sup>4</sup>Sharon, J., Fire Retardant Chemistry, Vol. 4, p18.

<sup>5</sup>Shafizadeh, Fire Retardant Chemistry, Vol. 2 (3, Suppl.), p195.

<sup>6</sup>USBM Contract H0308064.

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After consideration, the most likely candidates for effective fire control with foam are those compounds which retard by chemical, rather than physical means. In most cases, the chemical effects require a much smaller amount of flame retardant. For example, there is evidence that some flame retardants used in plastics have proven effective in concentrations as low as 0.001% to 2% by weight.

In most cases, the materials capable of effectively preventing burnback are those which are not rapidly consumed during the initial fire extinguishment. Persistent chemical species would then remain available to prevent reignition until the burnt surface cools. Neither are those compounds which prevent burnback necessarily the best for initial fire extinguishment. Evidence for this is seen by the decrease in the effectiveness of ammonium phosphate at temperatures in excess of 600°C.

Dry Chemicals Incorporated in Foams - Dry chemical agents dissolved in a surfactant foam solution produce a mixture which can be projected to a fire as a low-expansion foam. The water in the foam would quench the fire, while the chemical agent is deposited on the burning substrate, aiding in fire extinguishment and preventing burnback.

Combinations of AFFF or fluoroprotein low-expansion foams and dry chemicals have been used in dual applications requiring two separate delivery systems which operate simultaneously or sequentially. In fighting liquefied natural gas fires, a dry chemical is used with high expansion foam. The high expansion foam is used to knock down fire intensity and the dry chemical is used to extinguish the less intense flames. It is believed that this approach was not examined in the past due to the poor quality foams available and the incompatibility of many dry chemicals with the foam agents.

Preliminary tunnel tests<sup>7</sup> done at MSAR have shown impressive results using only 10% di- and mono-ammonium phosphates incorporated into high expansion foam. Some glowing continued after the foam had been applied to the burning wood samples, but no burnback occurred over those areas which were coated with the mixture of foam solution and ammonium phosphate. The glowing action observed is probably a solid-phase oxidation of carbon to carbon dioxide and carbon monoxide. An example of the positive results is shown in Figure 3 as compared to the negative results shown in Figure 2.

Apparently, the ammonium phosphate prevents the combustion reaction chemically, since the 10% mixture did not show any oxygen-excluding layer on the charred wood surface [by Scanning Electron Microscope (SEM) examination]. Perhaps the extinguishing mechanism in which the effectiveness increases with a decrease in particle surface area

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<sup>7</sup>USBM Contract H0308064.

(specific surface area increases) has been carried one step further. The maximum specific surface area obtained with the ammonium phosphates would be from a water solution, where the molecular surface area would be exposed to the burning substrate as the water evaporated.

During the above referenced work, other dry chemicals tested (listed in Table 1) did not delay burnback any longer than the foam solution itself. The differences observed between ammonium phosphates and for those chemicals listed in Table 1 may be due to the fact that the chemicals listed in Table 1 extinguish primarily by a physical rather than chemical mechanism, and the small amounts incorporated into the foam solution were insufficient to prevent burnback.

TABLE 1. - Extinguishants

Potassium Silicate	PS
Sodium Silicate	SS
Potassium Bicarbonate	PB
Sodium Bicarbonate	SB
Potassium Carbonate	PC
Sodium Carbonate	SC
Zinc Borate	ZB

A literature search indicated that for ammonium phosphate, the phosphorus level was responsible for the positive results, and thus the further work concentrated on increasing the phosphorus content of the solution.

Gelling Foams - Prior work by MSAR 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 for stabilizing or gelling foam masses. These included polyvinyl pyrrolidone, polyvinyl alcohol, and certain of the acid polymers, carboxylic vinyls, polyacrylics, and maleic anhydride-polyvinyl ether copolymers.

Thus, foam can be formed from a low viscosity liquid and a chemical gelling agent, which gels the foam immediately on generation, to provide a highly stable foam with liquid cell walls having a viscosity of up to 100,000 centipoise.

Polyvinyl alcohol, acrylic acid polymers and copolymers, and carboxy vinyl polymers are especially suitable for use, although other water soluble polymers forming chemically gellable solutions may be used. Suitable polymers include polyacrylic acid and polymethacrylic

acid; water soluble copolymers of acrylic acid or methacrylic acid; polymers of acrylamide, methacrylamide, N-methylolacrylamide and hydroxyethyl acrylate; carboxylated vinyl polymers such as the Carbopols. A preferred gellable foamable liquid contains fully hydrolyzed polyvinyl alcohol and boric acid.

Any surfactant foaming agent may be used that is inert to, or does not gel, the polymer solution, and selection of a particular foaming agent for a particular formulation or use is generally based on its effectiveness as a foaming agent. Neutral or acid-foaming agents are used in foam forming liquids that incorporate polymers forming acid solutions that gel when neutralized or made more basic, such as acrylic acid polymers and copolymers, Carbopols and polyvinyl alcohol-boric acid. The well known alkanesulfonates are preferred foaming agents for use with polymer solutions that are gelled with a base gelling agent. These foaming agents have the formula  $RSO_3M$ , where R is an aliphatic radical containing from about 6 to 20 carbon atoms and M is an alkali metal, alkaline earth metal or ammonium cation. Any other neutral or acid foaming agent can be generally used, such as, for example, alkylbenzenesulfonates,  $RC_6H_4SO_3M$ , and naphthalene sulfonates,  $RC_{10}H_6SO_3M$ , where R is an alkyl radical and M is an alkali metal, alkaline earth metal, ammonium, amino, or hydrogen cation, and alkoxyated and sulfonated alkylphenols.

With other gelling systems, such as those in which polyvinyl alcohol solutions are gelled with an organic gelling agent, other more basic foaming agents can be used to advantage, such as the alkyl sulfates (sulfated alcohols) and alkyl ether sulfates (alkoxyated and sulfated alcohols). Alkyl ether sulfates have the formula  $R_a(OR_b)_nOSO_3M$  where  $R_a$  is the aliphatic radical of the alcohol containing from 10 to 20 carbon atoms,  $R_b$  is methylene, ethylene or propylene, n varies from about 1 to 4, and X is an alkali metal, alkaline earth metal, ammonium or alkanolamine cation radical; generally, the cation is sodium, ammonium or triethanol amine. Alkyl sulfates have the formula  $ROSO_3M$ , where R is an aliphatic radical containing from about 6 to 20 carbon atoms, and M is an alkali metal, alkaline earth metal, ammonium or amine cation. Generally the cation is sodium, potassium, calcium, magnesium, or ammonia.

Other suitable foaming agents include sulfated fatty acids and esters, such as the disodium salt of oleic acid, or sulfated esters of oleic or ricinoleic acid with low molecular weight alcohols.

Any base material can be used as the gelling agent for solutions of polymers that are dissolved in their acid form in water but gel upon neutralization. Ammonia is a preferred gaseous gelling agent and gaseous amines, such as monomethylamine, dimethylamine and trimethylamine, can also be conveniently used. A great variety of liquid bases can be used by spraying as a fog in the foam-generating air stream; suitably liquid amines, for example, diethylamine, triethylamine, triamylamine, di-n-butylamine and pyridine; alkanolamines, for example, triethanolamine; and solutions, preferably aqueous, of inorganic bases,

for example, alkali metal hydroxides and ammonium hydroxide. Other types of gelling agents may be used in a similar manner if desired. For example, polyvinyl alcohol is gelled by a variety of organic reagents, such as sodium dibutylphenoldisulfonate, Congo red acid, p-(methyl-amino)phenol sulfate, resorcinol and catechol, which may be dispersed in solution in the air stream.

Foam Concrete - Another method of sealing the channels is the use of foam concrete.

Foamed, or cellular concrete, is formed by blending cement slurry with a fine bubble water foam. The density (up to 80% air) and thus strength can be varied to meet requirements by varying the quantity of foam added. It requires only the transfer of cement in bulk to the work area, the logistics of which have already been worked out for rock-dust, a similar material. It is readily prepared in available, permissible equipment, and can be pumped to the immediate work site and cast in place. Forming can be simple and lightweight.

Foam Cooling Capacity - If we assume a coal refuse density of 80 pounds/ft.<sup>3</sup> (we measured 80 pounds/ft.<sup>3</sup> of dry refuse from a site in Homer City, PA), the void space is 30%. On a coal/rock mixture the specific heat is approximately 0.3 Btu/pound/°F. The heat removed is:

$$(80 \text{ \#/ft.}^3)(T-200^\circ\text{F})(0.3 \text{ Btu/\#/}^\circ\text{F})$$

where T is the initial temperature of the hot refuse. The amount of heat removed at various initial temperatures is:

<u>2000°F</u>	<u>1000°F</u>	<u>600°F</u>	<u>300°F</u>
43,200 Btu/ft. <sup>3</sup>	19,200 Btu/ft. <sup>3</sup>	9,600 Btu/ft. <sup>3</sup>	2,400 Btu/ft. <sup>3</sup>

If one cubic foot of refuse has a 30% void space, 0.3 ft.<sup>3</sup> of space is available for water. The weight of water is (0.3 ft.<sup>3</sup>)(62.43 #/ft.<sup>3</sup>) = 18.73 pounds. If the heat of vaporization is 970 Btu/#, then 18,168 Btu's are available for cooling, assuming no makeup. As the liquid is foamed, the water content decreases. The Btu's available at the following expansion ratios are:

Expansion ratios:	5:1	10:1	20:1	50:1	100:1
Btu's:	3634	1817	908	363	182

Comparing the heat content of a refuse pile with the cooling available from foam, shows that as the expansion increases the cooling capacity is greatly reduced. We have limited our expansion to less than 20:1. On a particularly "hot" spot, it may even be desirable to use a lower expansion of 5:1.

## PROGRAM PLAN

The program was divided into six tasks:

1. Program Plan
2. Literature/Information Search
3. Gel Testing
4. Capability Test
5. Coal Refuse Pile Tests
6. Final Report.

Task 1 involved the preparation of a program plan to be approved by the Bureau before the start of work. This plan detailed the tasks, costs, reporting, materials and personnel for the program.

Task 2 was a literature search for improved gelling compounds for foam. We have much of the background data but we needed to update the information.

Task 3 involved the development of bench scale tests to determine the effectiveness of the gelled foam to improve the water distribution in a coal refuse pile. This test was conducted with limestone aggregate and coal refuse.

Task 4 involved compatibility testing to determine if a flame retardant could be incorporated into the foam solution, yet not interfere with the gelling. This involved conducting tests using the gel foam with and without the flame retardant.

Task 5 involved coal refuse pile tests using the foam from Task 4. The tests were conducted in an expanded metal box which was 5 feet by 5 feet by 5 feet equipped with thermocouples. A fire was started by using charcoal/charcoal starter. Tests were conducted using water, then the gel foam/flame retardant formulations.

Task 6 involved the submittal of the Final Report.

### TASK 1 - PROGRAM PLAN

Task 1, Program Plan, was submitted during the first 30 days of the program.

### TASK 2 - LITERATURE SEARCH

A literature search was conducted which included water based foams which gel or are thixotropic. In addition the literature search included data on foam flow in porous media. The following data base

files were used in the search:

NTIS  
COMPENDEX PLUS  
INSPEC-77-89/ISS 15  
INSPEC-1969 thru 1976  
Kirk-Othmer Encyc. of Chem. Technology  
Chemical Engineering Abstract 1971-89/Jul  
Ceramic Abstracts, (Issue 3) 06/89  
CA Search 1967-1989  
GEOARCHIVE  
GEOREF  
PASCAL  
GEOBASE

A number of articles pertaining to foam and gelled foam used in porous media have been found. Most of these articles are related to secondary and tertiary oil recovery. The media is also sandstone or other oil bearing rock which has a porosity much less than a refuse pile. However, the articles do discuss possible gelled foam as well as horizontal flow in the porous media. Titles and abstracts of the articles are included.

The references are primarily for surfactant injection in oil fields to improve recovery of oil. While the characteristics and flow of surfactant foams are significantly different in an oil formation (tight sandstone) than a coal refuse pile, we have found useful information in several areas. These are primarily gelled foams and surfactants which can produce foams at higher temperatures (up to 175°C). In addition many of these surfactants can tolerate high salt loading.

In addition to the surfactants of interest, the equipment used to inject foam in oil field applications may also be applicable to coal refuse piles.

Several articles obtained during the initial survey of pertinent literature have served to guide the secondary inquiries. Investigation concerning secondary or tertiary oil recovery were, themselves, based upon previous work with specific surfactants and gelling foam technology.

The overview by Marsden (1986) and reviews by Handy (1989) and Freeman et al. (1986) broadened the base for developing our own background in this area. Their reports, and the results of screening tests, have stimulated further inquiries into a secondary series of references pertaining to more specific aspects of applying foams in wells and bore holes. These and the American Petroleum Institute "Standard Procedures for Evaluation of Hydraulic Fluids" were used to assess further modifications.

We have received the publication of "Standard Procedures for Evaluation of Hydraulic Fluids" from the American Petroleum Institute.

These methods and apparatus are more directly related to sandstone and the less permeable media in which oil reservoirs are found rather than coal refuse. The basic ideas and approach are applicable, however, if more quantitative descriptions of the coal refuse and/or the interactions of foams and refuse are found to be required.

The paper by Harris and Reidenbach describing their "High-Temperature Rheological Study of Foam Fracturing Fluids" has also been analyzed in terms of its applicability towards coal refuse fires. Again, this work and the general background and development are associated with specific aspects of oil recovery. Their general conclusions, especially that, "high-temperature, dynamic stability depends upon surfactant type and concentration.....", confirm our approach towards treating coal refuse. They also found that high-expansion foams were better able to maintain their viscosity at high temperatures than fluids containing the standard viscosity modifiers, such as hydroxypropyl guar.

We feel that the surfactants used in our fire-fighting foams should be satisfactory in both aspects.

Our own experience in this area, and those published concerning other investigations into the gelling process, agree that the types of reactions which would work well in these situations (i.e. those having short gelling times), are not presently available.

#### TASKS 3 AND 4 - GEL AND COMPATIBILITY TESTING

Tasks 3 and 4 were combined since they were to be conducted simultaneously.

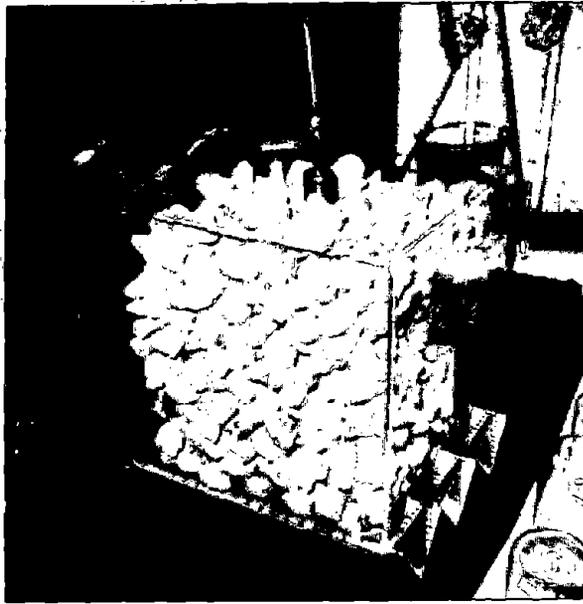
Screening lab tests on foam flow were conducted. Using No. 3 slag to simulate mine refuse, the test was conducted in a 12 in. x 12 in. x 12 in. clear plastic box. We ran low expansion foam (2:1) with little or no improvement in horizontal flow over water. Medium expansion foam (approximately 100:1) using a 1 inch generator show much better horizontal flow. The 1 inch foam generator was placed in the top middle of the box approximately 2 inches below the surface of the slag (Figure 4). Tests were then run on water, standard foam and a foam with a thickener "Rheothik" (20 gms/liter of surfactant solution). Rheothik is a polysulfonic acid used as a thickener. The following results were:

Water - no horizontal movement from the 1 inch foam generator.

Standard foam - approximately 2 inches of horizontal flow from center of foam generator.

Rheothik solution - over 6 inches of horizontal flow from center of the foam generator.



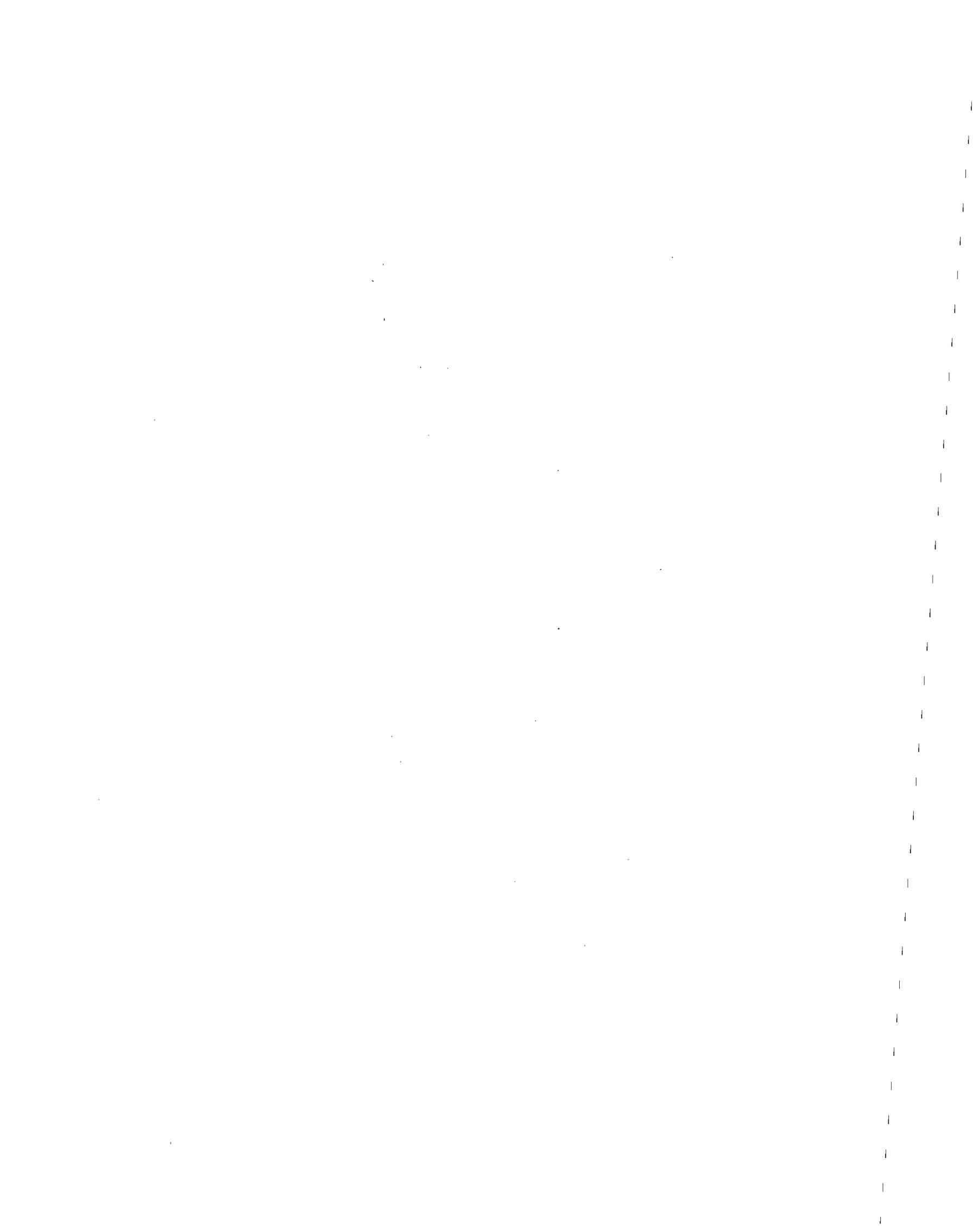


A



B

FIGURE 4. - Foam injection.



Figures 4A and 4B show the foamaker in the top and standard foam coming out the bottom. Figures 5 and 6 show the test using Rheothik. In Figure 6, foam can be seen against the sides of the clear box.

The next series of tests were conducted with gelled foams and other thickeners such as:

- Polysaccharides
- Acrylic polymers
- Polyvinyl alcohol
- Cellulose ethers

The initial results with "thickened" foam showed the concept of better distribution with foam has promise. We tried a series of tests with polyvinyl alcohol (PVA). These tests are grouped into two areas, the production of a medium expansion foam and gelling. It was found that the amount of PVA in solution must be approximately 3% in order to successfully produce medium expansion foam. The reaction rate of gelling agents such as boric acid is so rapid that we cannot pre-mix the solution, then produce foam. We must mix the boric acid with the PVA solution just before making foam. A mixing head was made to accomplish this.

Additional polymer samples and information were requested from suppliers. These polymers have been selected based upon our desire to have a low viscosity solution (at high shear rates) which can thicken or gel after making the medium expansion foam. The specific polymers requested were:

- Elvanol 90-50 (PVA) - duPont
- Acrysol ICS-1 (Acrylic) - Rohm-Haas
- Galactasol 245 (Polysaccharide) - Henkel
- Galactasol 640
- Galactasol 510

Additional information on these polymers was requested:

- Amatex Gums (Galactomannano) - Henkel
- Gengel (modified Galactomannano) - Henkel
- Culminol (Cellulose Ether) - Henkel

The tests with Acrysol, Galactasol and Elvanol 90-50 did not produce a delayed gelled foam. The polymer still gels so rapidly that we cannot inject it into the simulated coal refuse pile.

We achieved minor success in delaying the kinetics of gelling reaction. These slight changes have, however, been sufficient to permit foaming the mixtures. This preliminary success has permitted the pursuit of secondary goals including greater stability in the foam; higher expansion ratios; and/or the preparation of pumpable gelled foams.



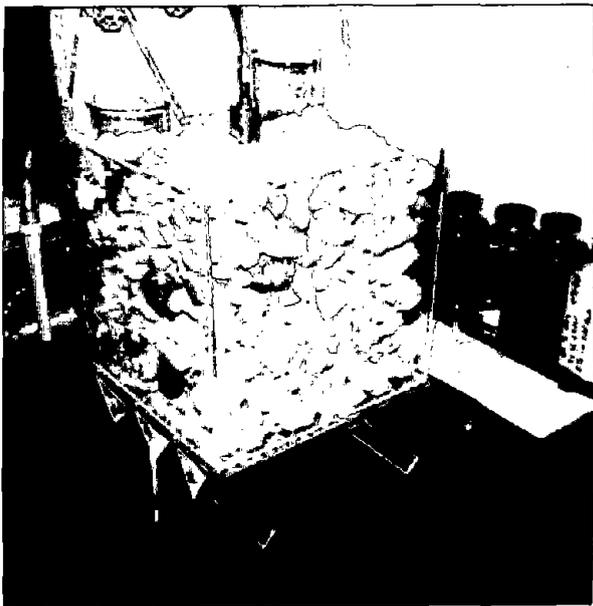
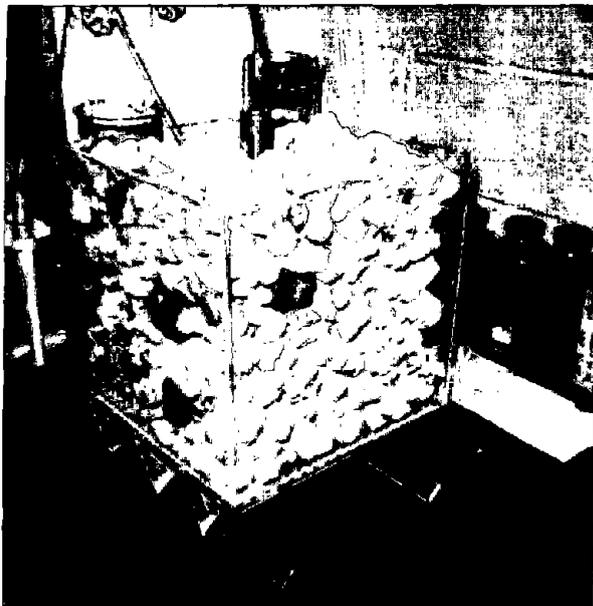
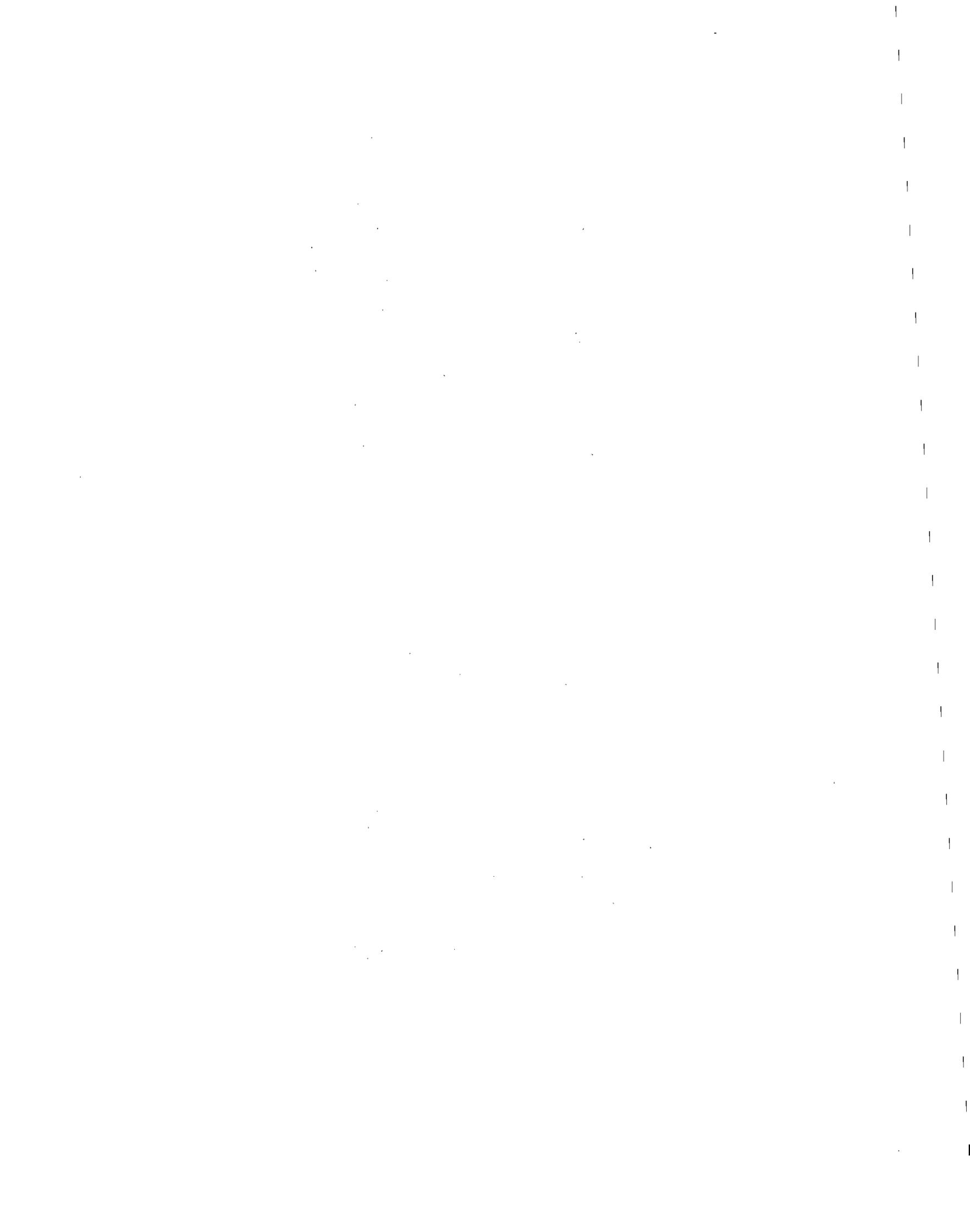


FIGURE 5. - Foam injection using Rheothik formulation.



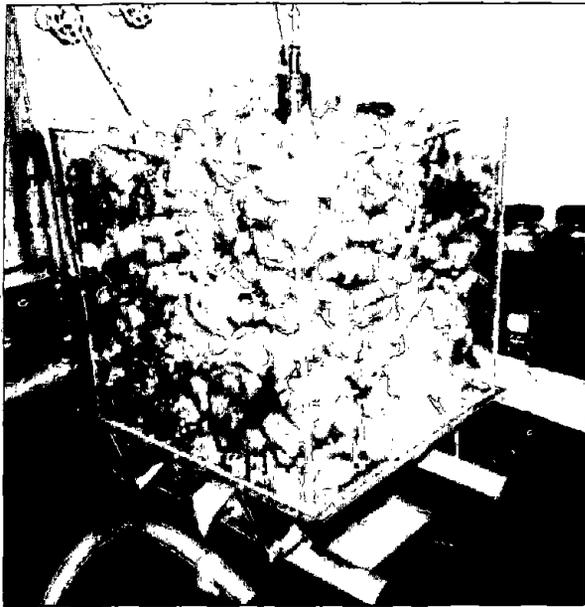
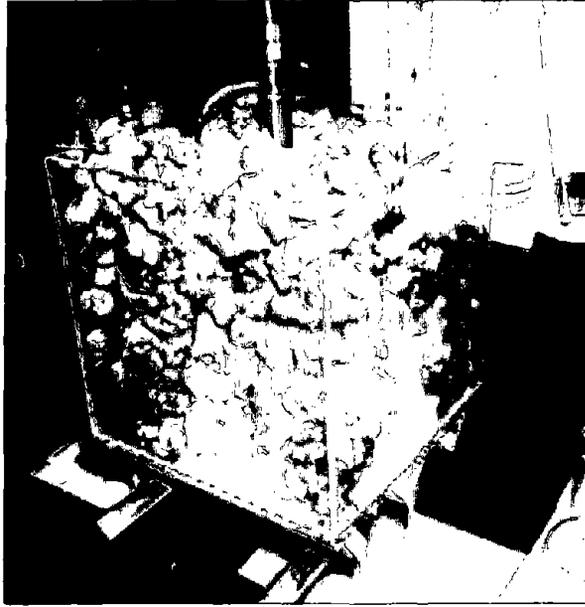


FIGURE 6. - Foam injection using Rheothik formulation.



These foams have been prepared with two-component formulations, which are mixed immediately before foaming. The two components contain polyvinyl alcohol and polyacrylate in one solution and a silicate/carbonate solution as the second component.

Screening tests with this formulation have shown that it will form a foam, with the expansion ratios considered acceptable for placing in a bore hole (10-100/1). Screening tests continued, to determine the flow in No. 3 slag and samples of mine refuse. The results of these preliminary tests were used to direct further modification and development of the formulation.

Additional screening studies continued for an alternative foam formulation. Tentative results indicated that combinations of carbonates, silicates and/or urea with boric acid may slow the gelation of polyvinyl alcohol enough to permit foaming.

The primary objective of this task was to develop aqueous formulations which will produce foams having desirable characteristics for treating coal refuse piles. The following set of five characteristics was used to direct this work.

- 1) good coal refuse wetting ability
- 2) slow drainage
- 3) low pumping viscosity of the liquid(s)
- 4) slow chemical gelling reaction
- 5) compatibility with the acidic conditions of coal refuse

Several standard viscosity modifiers have been used as components in preparing experimental formulations. Those presented in Table 2 comprise the most promising of the candidates investigated.

TABLE 2. - Standard viscosity modifiers investigated as means to develop a gelling-foam formulation

<u>Example</u>	<u>Source</u>	<u>Type</u>
Galaxy Type 1083	Aqualon Company	guar product
Galactasol 510	Aqualon Company	guar product
Galactasol 245	Aqualon Company	guar product
Polyox 301	Union Carbide Corporation	polyethylene oxide
Polyox 303	Union Carbide Corporation	polyethylene oxide
Rheothik	Henkel Corporation	polysulfonic acid
Cellosize QP-09-L	Union Carbide Corporation	modified cellulose
Cellosize QP-09-H	Union Carbide Corporation	modified cellulose
Cellosize QP-4400-H	Union Carbide Corporation	modified cellulose

Each of these examples has some unique attribute to influence the characteristics of the foam; but as a group their negative influence on the pumping, flow and generation of foam must be weighed against these attributes.

Laboratory tests in the one-cubic-foot plexiglass box simulated the conditions for foam flowing through No. 3 limestone slag and coal refuse piles. The first series of tests attempted to drive a high-expansion, gelled foam into No. 3 slag. The results of this test are documented in the series of seven photographs compiled in Figures 7 & 8. These photographs were taken at regular intervals as the apparatus was prepared (A); just starting the generator (B); as the foam filled the top layers of slag (C); foam backed up through the standpipe delivery tube and onto the surface (D); as the foam expansion decreased during flow through the slag (E); and after foam generation stopped (F).

No foam was observed to flow through the slag and out the bottom of the box. Although not evident in these photographs, radial flow of the foam was equal in all directions.

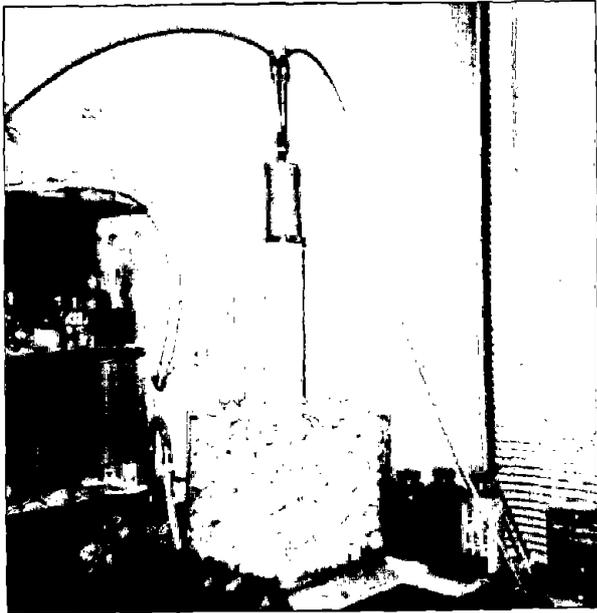
The flow resulting from a similar test, with a poorer gelling foam, is shown in the seventh photograph (G), for comparison. The flow of foam out the bottom is quite evident.

Efforts to push foams through coal refuse were less successful. When the high-expansion, gelled foam was directed into coal refuse (Figure 9, H), the foam flowed back along the sides of the delivery tube to the surface. Similar results were obtained with several delivery systems and injection points (I & J). Foams flowed radially about 3 inches from the delivery tube and then backed up the outer walls of the tube, to the surface.

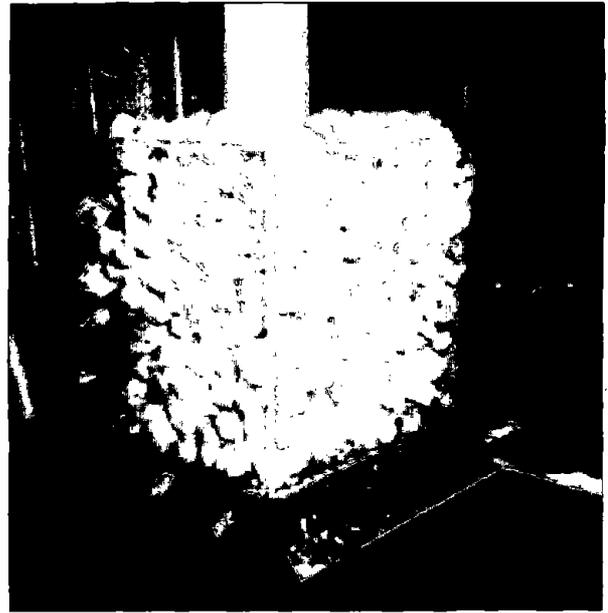
Several tests were done in which the foam was delivered to the coal refuse/plexiglass interface. This procedure offered a means for observing the flow, although it is not a good simulation.

Delivery of low-expansion, gelled foam in this manner showed significant differences in the radial flow. As shown in Figure 10, photographs K, L, M, & N, this foam extended only 2 or 3 inches from the delivery tube when flowing at about 5 ml/min and 5 psig delivery pressure (K, L). As the pressure increased to 20 psig, and flow increased to 200 ml/min (M, N), radial flow extended out almost 4 or 5 inches and the foam penetrated the refuse more than one inch below the delivery tube. Foam generation continued until the column broke the surface in every test. A typical time sequence is shown in Figure 11, photographs O, P, & Q, where foam dispersal is shown at 5 minute intervals for a test flow of about 50 ml/min.

A similar test, using a non-gelling foam, was done for comparison. In this test, the flowrate was about 250 ml/min, and the duration commensurately shorter. The results, however, shown in Figure 12,



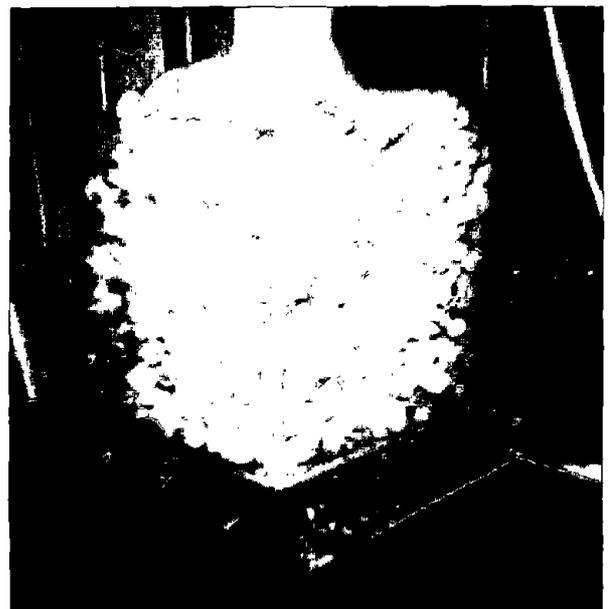
A



B



C



D

FIGURE 7. - Surface foam application.





E



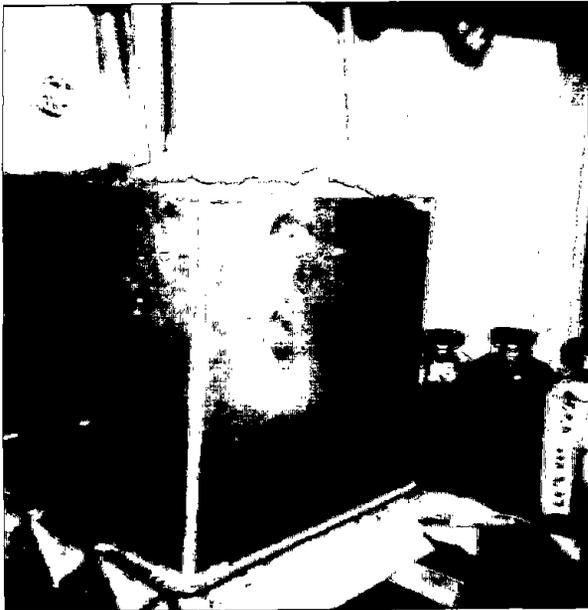
F



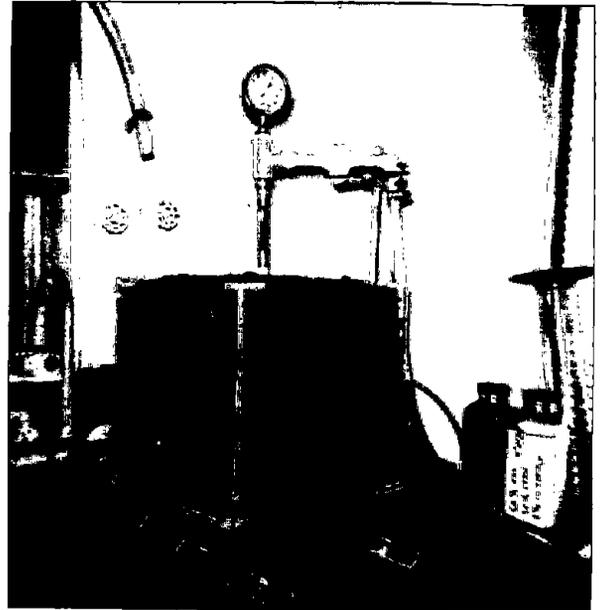
G

FIGURE 8. - Surface foam application.





H



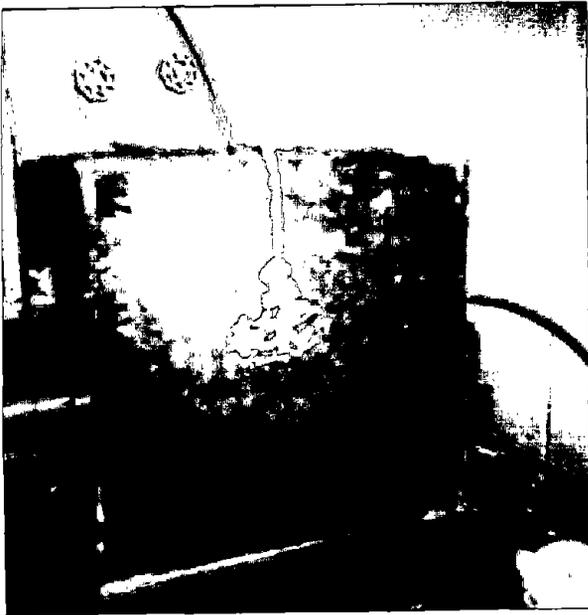
I



J

FIGURE 9. - Gelled foam application.





K



L

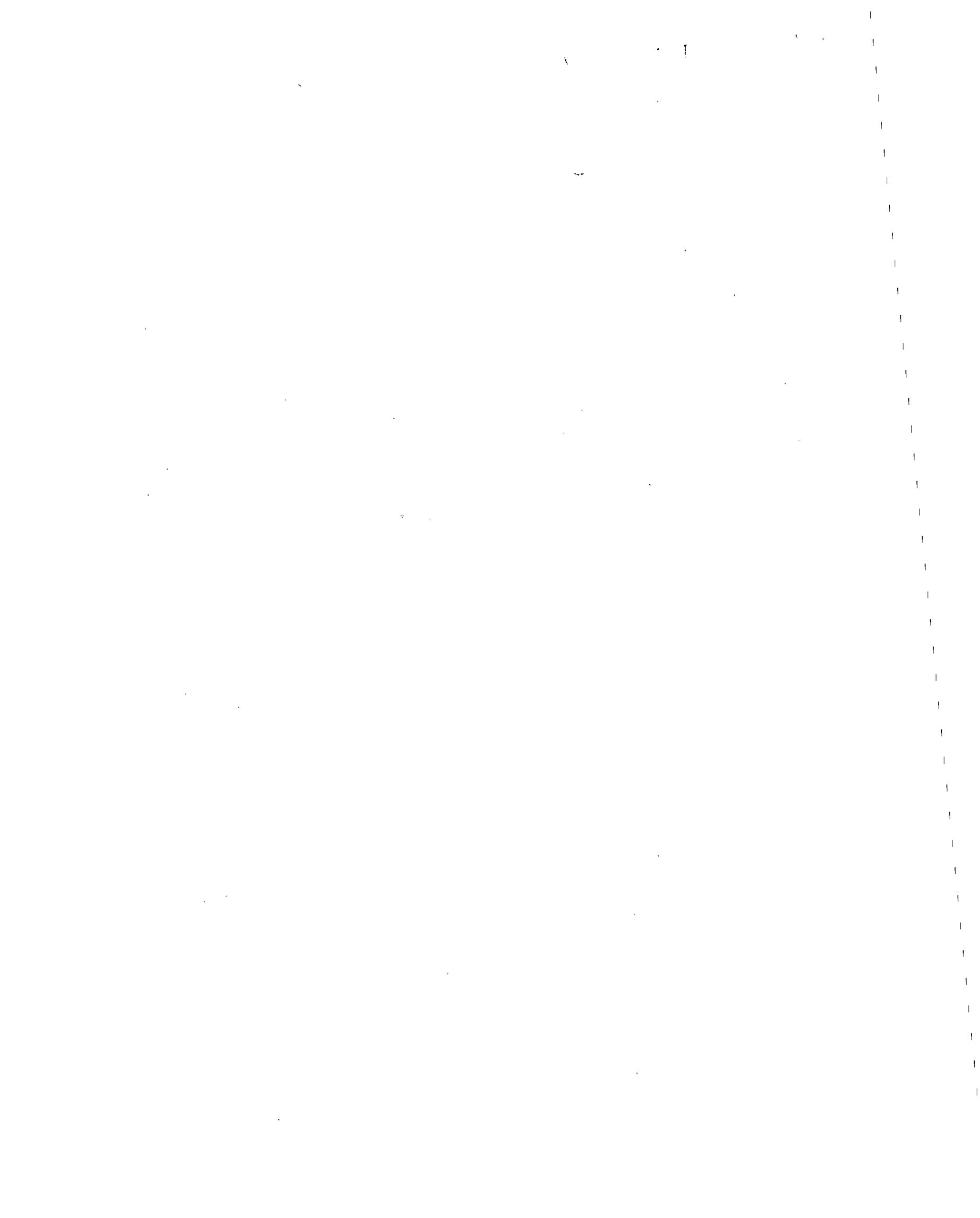


M



N

FIGURE 10. - Gelled foam flow tests.





O



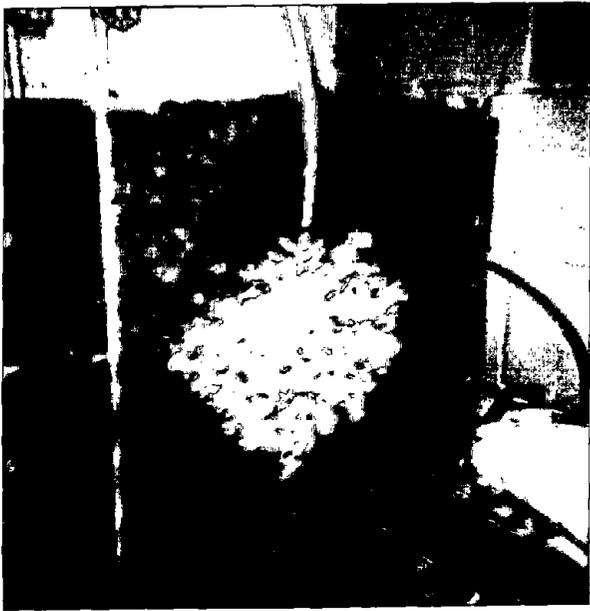
P



Q

FIGURE 11. - Time sequence.

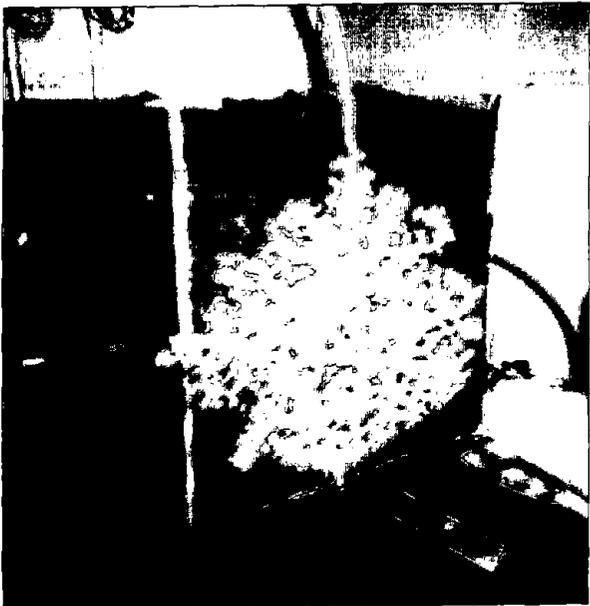




R



S



T



U

FIGURE 12. - Non-gelling foam test.



photographs R, S, T, & U, show that dispersal through the void volume of coal refuse is inversely proportional to the viscosity of the foam.

Generation and/or delivery of gelled foam at greater pressures is the best way to overcome the difficulty of flowing. This approach is limited for small scale tests, however, when the line of least resistance is usually back along the walls of the delivery tube.

Several aqueous foams were formulated which exhibit the characteristics desired for treating coal refuse piles. The "best" of the gelling formulations has two component solutions, which are mixed just prior to foaming. The first component is a solution containing a polyacrylate/polyvinyl alcohol mixture, which provides good wetting ability with controlled gelation. The second component is a solution of sodium carbonate, sodium silicate and surfactants, which aid and control the gelation reaction and foam ability of the mixture.

Some non-gelling formulations, based on Mine Safety Appliances Co.'s fire-fighting foams, have also been investigated as alternatives. These have been used in conjunction with viscosity modifiers, especially those which impart thixotropy.

Apparatus for generating and/or delivering the gelling foams in a coal refuse pile are limited by the kinetics of the gelation reaction and the final viscosities of the gels produced. A Waukesha pump has been used as the primary means for preparing and delivering the gelling foams formulated during this investigation. Although these mixtures have been used to prepare high-expansion foams, the viscosity increases with time and temperature, making it difficult to incorporate a reservoir or secondary pressurizing stage.

The non-gelling foams may be used in any typical foam generator. Those which are most stable (slowest drainage) have also been placed in a reservoir and delivered into the test apparatus under regulated pressures.

### Laboratory Scale-up Tests

A larger apparatus has been constructed to continue and expand upon the results obtained with the one-cubic-foot container. This apparatus, shown in Figures 13 and 14, was constructed from steel plate, to provide the strength necessary to hold about 1/4 ton charges (about 8 ft.<sup>3</sup> capacity).

The apparatus is hinged on one side (see Fig. 13), to permit opening the unit to see the way these foams are dispersed through the test media. Several holes were placed along the sides which also provide a means for following the dispersal of foam through the apparatus. The bottom was covered with a 4-mesh screen, to show when the foam penetrated the media.

The two segments of the apparatus are closed with a wire mesh screen, to hold the media in place as the bed is opened, while permitting the foam to flow throughout (see Fig. 14). This turned out to



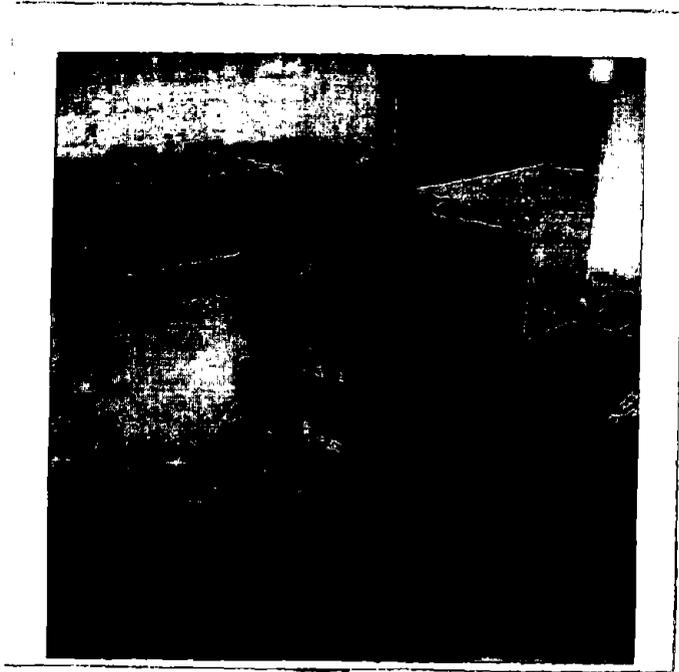
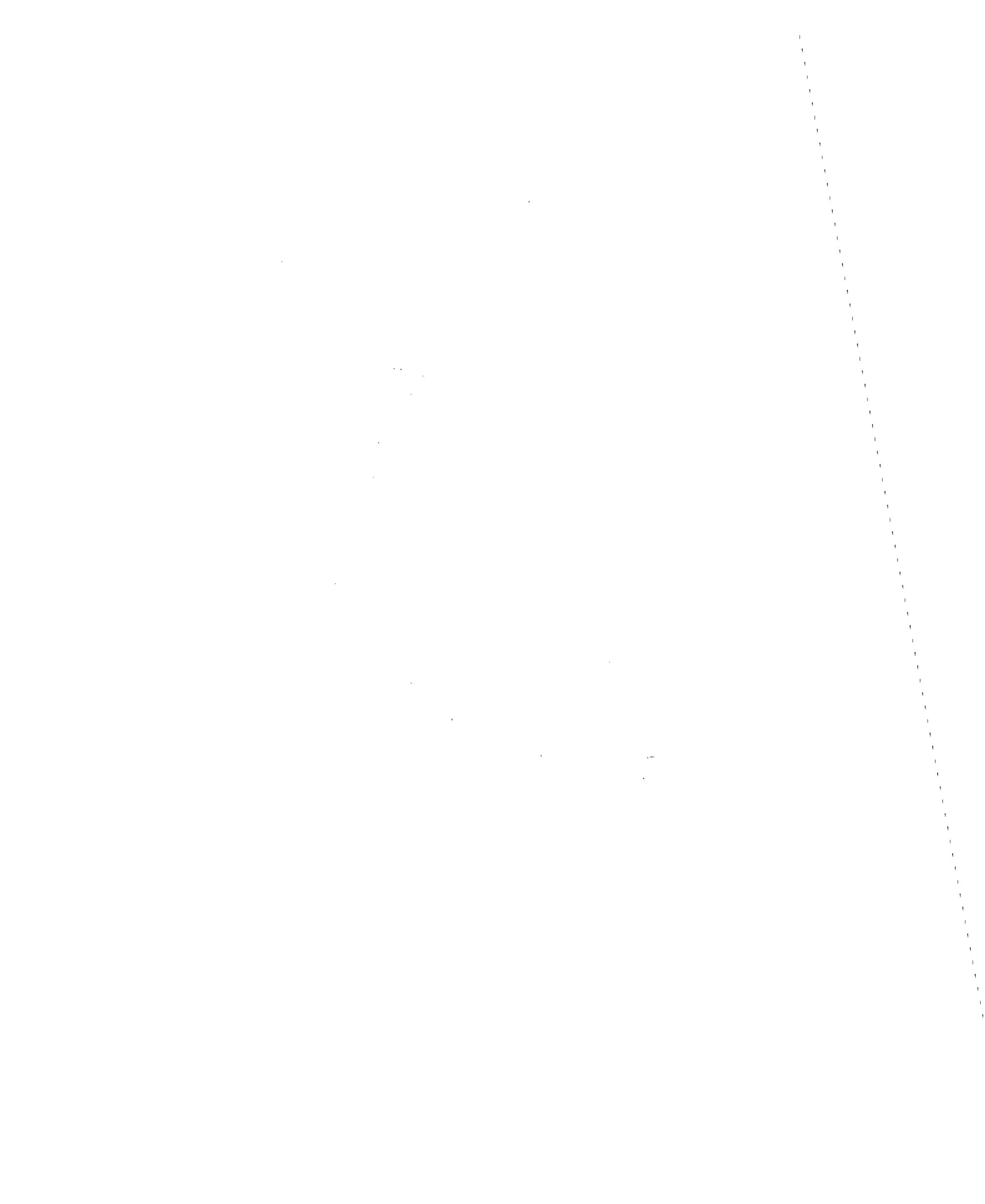


FIGURE 13. - Larger-scale, experimental unit showing hinged, compartmental construction. Total volume of coal refuse about 8 cubic feet.



FIGURE 14. - Opened test container showing separator screens and foam delivery tube.



be a necessary evil, since, even with conscientious packing of the test media, the space around these screens proved to be the line of least resistance for the foam to flow. This was partially mitigated in subsequent tests when portions of these screens were removed to place the 25-pound charge of coal and minimize channelling near the foam delivery tube.

The flow of foam up the outside surfaces of the delivery tube to the surface of the coal refuse samples was a problem encountered in tests with the 1 ft.<sup>3</sup> apparatus. The initial tests with the larger apparatus were designed to investigate this problem and determine some means to solve it.

Injecting the foam at a point 20 inches beneath the surface was tried first. The foam did not flow much laterally, but preferentially through the remaining portion (~4 inches) and out the bottom. This is shown in Figure 15, where most of the flow appears to have been between the separator screens.

Raising the injection point to about 18 inches beneath the surface and attaching baffles to the delivery tube created a better dispersion, as shown in Figure 16; but much of the foam flowed out the bottom.

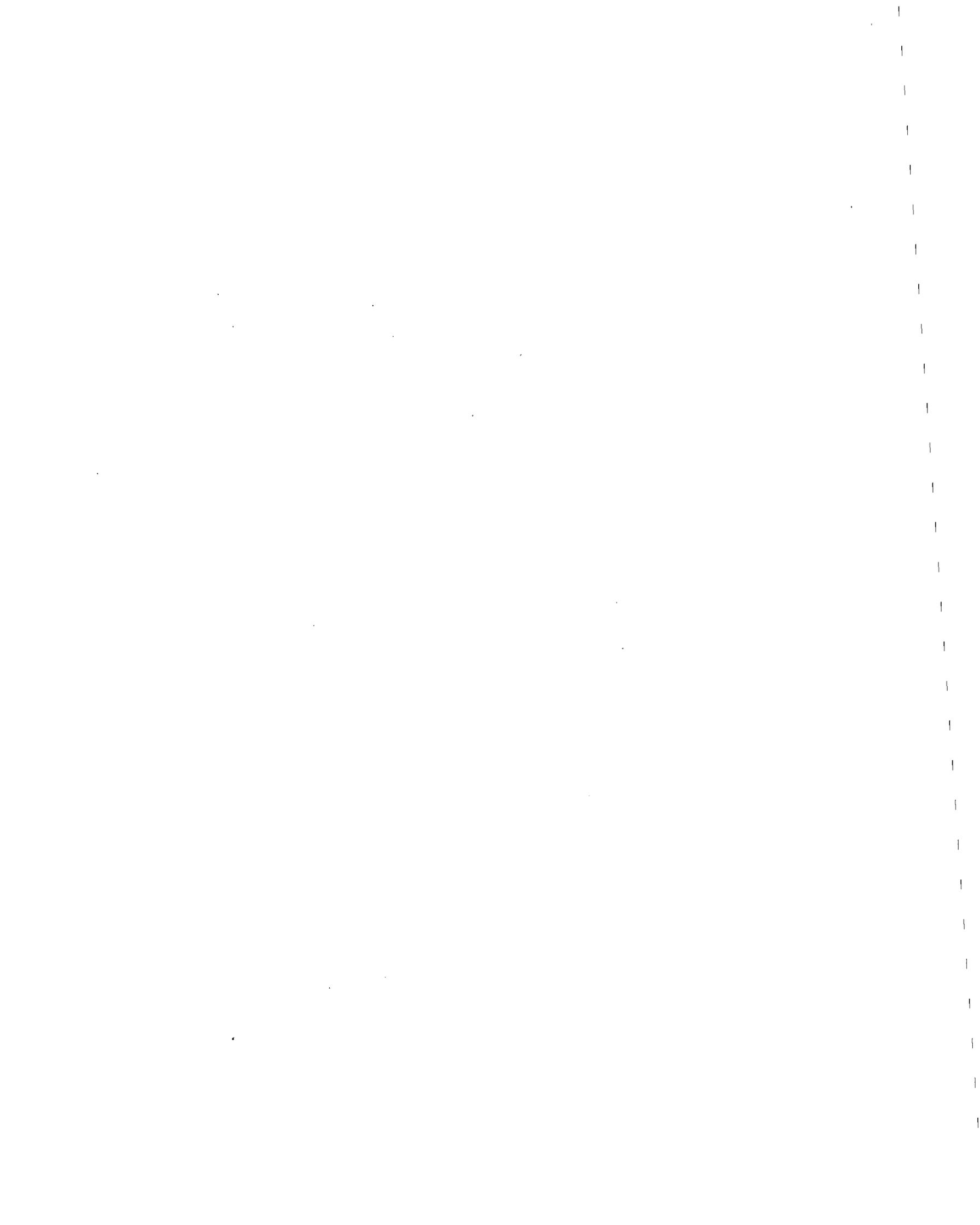
Raising the injection point to 10 in. beneath the surface and using baffles and extra weight to hold the tube in place significantly helped the lateral flow of the foam. Foam flowed from the thermocouple well, located across from the injection point, before it erupted through the surface (Figure 17). Penetration was not as good as anticipated, however, and the flow appeared to follow the separator screens, as shown in Figure 18.

Foam dispersal through coal refuse could only be obtained when the injection point was 10 inches or more beneath the surface and various means were used to hold the tube and keep the surface from heaving. These problems would be corrected, however, as the depth of injection and the size of the coal refuse sample increase. The coal refuse sample we have been using has a void volume of about 33%, which impaired the flow of foam in both of the experimental apparatus.

### Test with Coal Fire

Extinguishing fires within the coal refuse is the primary objective of this investigation. The difficulties in dispersing the candidate foams through coal refuse, however, steered the fire tests towards the more open media, No. 3 limestone slag.

Several foams were dispersed easily and rapidly through slag samples in the 1 ft.<sup>3</sup> apparatus. This material has a void volume of about 40%, compared to about 33% for the coal refuse. It was chosen to permit a more rapid evaluation of fire fighting capability of these foams.



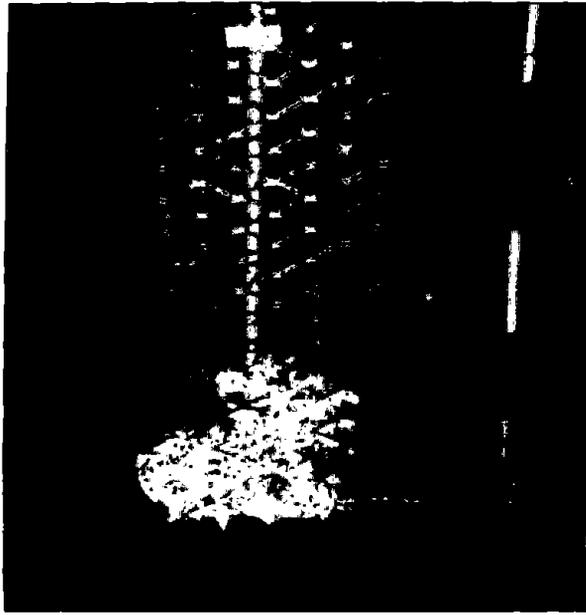


FIGURE 15. - Test with gelling foam delivered to a point 20 inches beneath the surface of coal refuse.

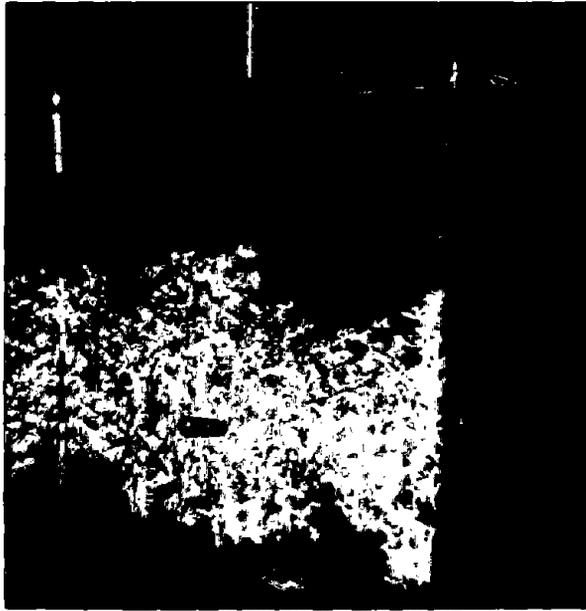


FIGURE 16. - Foam delivered through tube with baffles to the point where red marker indicates (approx. 18 in. beneath surface).





FIGURE 17. - Test with gelling foam delivered through a tube with baffles. First flow of foam occurred through the thermocouple well, located directly horizontal to the delivery point.

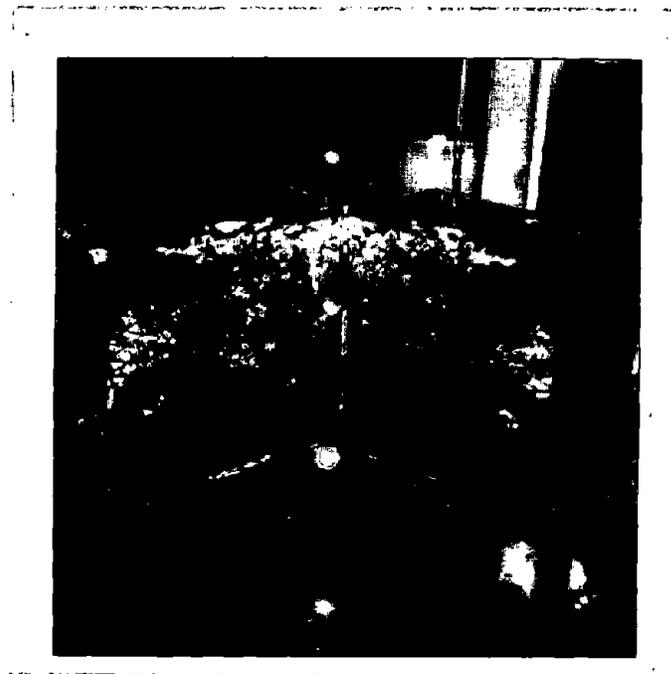


FIGURE 18. - Foam delivered through tube with baffles to the point where red marker indicates (approx. 10 in. beneath the surface).



The 8 ft.<sup>3</sup> apparatus was prepared for fire tests by removing the center section from the separator screens. This provides a guide for repetitive positioning of a 25-pound charge of coal, which was used as the fuel. Although air could infiltrate the bed through many paths, the ignition and time to attain a representative fire were significantly reduced by placing an oxygen lance into the center of the sphere of coal.

Temperatures were monitored with three Type K thermocouples, at the top of the coal, across from the foam inlet, and about 4 inches away from the coal in the slag media. These thermocouples, and the general layout of the test apparatus are visible in the photograph, taken just prior to starting the test, shown in Figure 19.

The coal, located in the center of the limestone slag, was ignited with a gas torch. A pre-burn of approximately 20 minutes was used to establish the fire and temperature equilibrium throughout the apparatus. During this time, oxygen was added through a lance, located in the center of the coal. The equilibrated temperatures were: 1850°F in the fire zone, and 1450°F at the edge of the coal. The temperature of the slag increased from 40°F to 88°F during the pre-burn.

The test proceeded well, in that the flame was extinguished and replaced with steam during the first minute, as shown on Figure 20. The foam appeared to disperse throughout the box and erupted through several openings along the sides within, as shown in Figure 21.

When opened, however, the fire was rekindled even though the foam had flowed almost completely around it (Figures 22 & 23). The foam had neither penetrated the fire zone nor flowed directly beneath the sphere of coal.

The results of tests done with the larger apparatus have provided some indications of scale-up problems. The problem of sealing the delivery tube to the surface may be corrected by increasing the depth of injection; but this leads to penetration of the bed in this apparatus. The fire-fighting capabilities of the gelling foam appear good; but the rush of air over the coal occurring when the unit is opened increases the possibility for reignition. Opening the bed is the best way to determine the nature and extent of foam dispersal, however.

Temperatures in this test unit may be greater than experienced in actual coal refuse pile fires, due to the greater exposure to air. We feel that the system should be designed for the worst case, however, and that the merits of this larger apparatus outweigh its shortcomings.

An identical logic can be used to explain the fact that the foam appeared to circumvent the coal fire area. The implications are, that if the system was more tightly sealed, the foam would be forced through under greater pressure into the fire zone.





FIGURE 19 - Fire test utilizing 25 lb of coal in the center of No. 3 limestone slag media (pre-test).





FIGURE 20. - Fire test approximately 1/2 minute after starting foam generator.

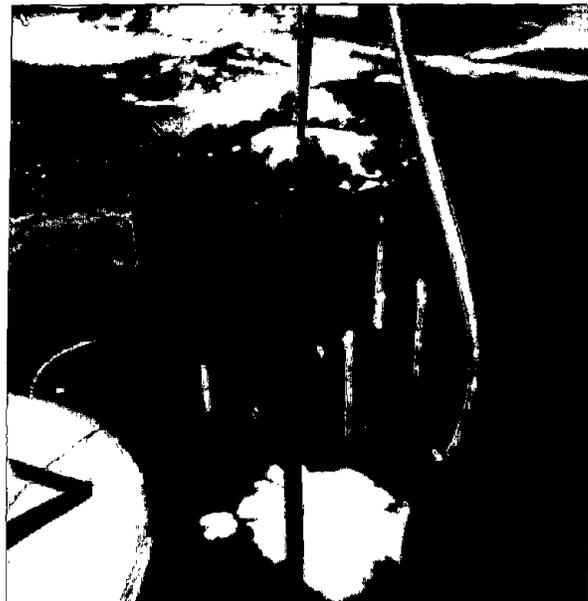


FIGURE 21. - Fire test after about 2 minutes and nearly 10 gallons of foam added.

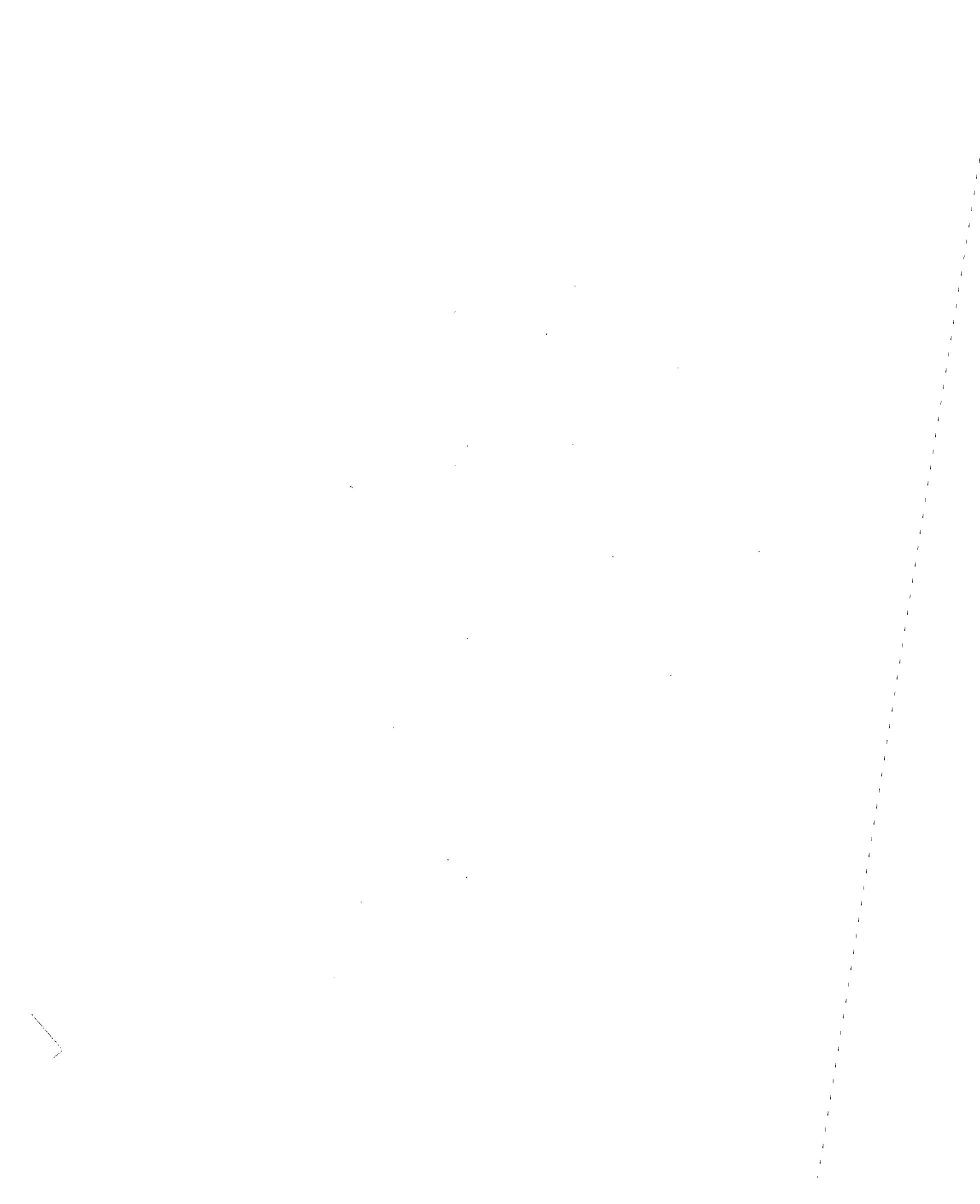




FIGURE 22. - Fire test when opened for examination and analysis of results.

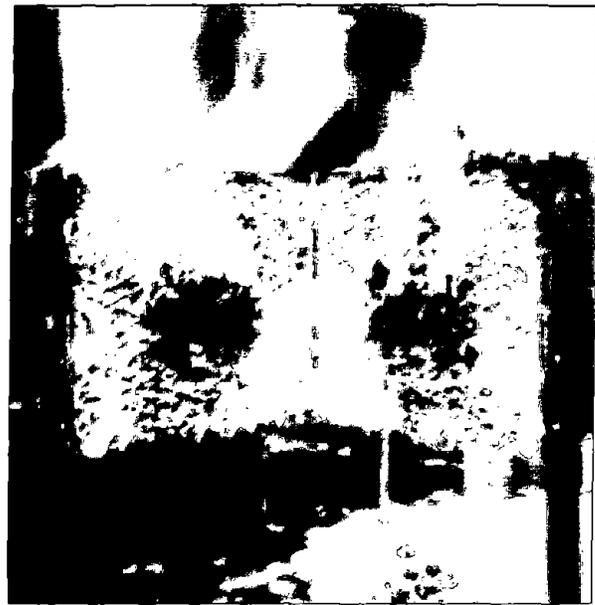


FIGURE 23. - Fire test after sitting open for approximately 10 minutes.



## Laboratory Scale-up Tests

The larger, steel apparatus for simulating coal refuse piles has been used in a series of tests designed to examine the dispersion of foams as they are delivered underground, and their fire-fighting capabilities. The apparatus was described in Monthly Report No. 8, but is presented in Figures 24 & 25, for reference.

This apparatus is a cube measuring 2 feet on each side (8 ft<sup>3</sup> volume), hinged at the center to permit visual evaluation of the dispersion of foams. The two halves are enclosed with screens, having 1 1/2-by 2-inch, diamond-shaped mesh.

These tests were controlled by keeping the total volume of coal refuse or slag (weight of coal), the location of the foam-delivery-tube outlet, and the rate of foam delivery constant. Temperatures, linear penetrations, and total volume of foam dispersed through the coal or slag media were measured for each test.

A small Waukesha pump was used to generate the foams in all tests. This unit, visible in many of the test photographs, generates approximately 5 gal/min of gelled foam (18 gal/min with zero back pressure) and standard fire-fighting foam, with an expansion ratio of about 16 volumes of foam for each liquid volume used.

Foam Dispersal - All of these tests were done using a 3/4-inch, stainless steel tube to deliver the foam into the test vessel. This tubing was directed across the surface and into the center of the bed, to a depth of 6 to 7 inches. This method was found to be the best means to alleviate the problem of foam flowing back along the delivery tube.

The generating pressure and momentum of the foam were the major factors influencing the initial dispersion of the foam as it entered the test apparatus. Factors such as void volume, buoyancy, and crevices or packing became more influential as the foam dispersed from the delivery tube.

This series of tests continued and expanded our investigation of methods to stop the back-flow of foam along the delivery tube. These methods included packing and covering the surface, heaping the coal or slag to achieve delivery depths of more than 1 foot, and anchoring the delivery tube to the separator screens to minimize any movement.

The initial force developed as the foam entered the apparatus opened a cavity, which started the path of least resistance for subsequent flow. These foams also appeared to be dispersed into the separator screens, where the difficulties for uniform filling and unequal wetting characteristics made penetration somewhat easier. A typical flow pattern is shown in Figure 26. The foam moved horizontally through the coal and slag, but vertical movement between the screens was easier. Tests with gelling-foams resulted in penetrating either the top or bottom of the apparatus, whereas several tests with non-gelling foams showed





FIGURE 24. - Experimental unit.

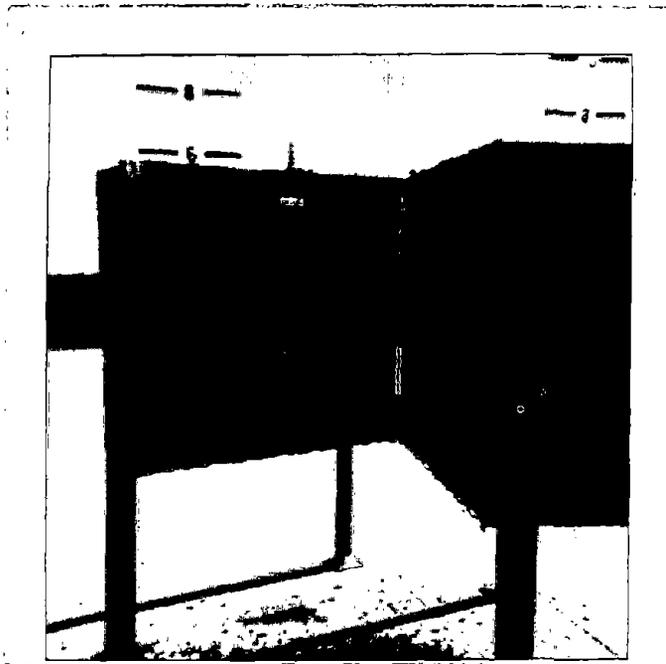


FIGURE 25. - Experimental unit split open.





FIGURE 26. - Typical dispersion of gelling foam through No. 3 limestone slag.



more horizontal movement. The total volume of coal refuse or slag affected was similar in both cases, however.

Our observations during these tests resulted in three general conclusions concerning tests with coal refuse:

- 1) The initial forces developed as foam entered the apparatus opened cavities in the piles.
- 2) This initial force also moved the delivery tube in many tests, breaking or weakening any seal with the surrounding material.
- 3) The dimensions and construction of this experimental apparatus are insufficient to achieve an adequate seal and fulfill the other objectives of the investigation.

Both the flowrate and extent of dispersion of foam were greater through No. 3 limestone slag than through coal refuse. This performance reflects the difference in particle size and void volumes. The void volumes of coal refuse samples were between 30 and 33%; while about 10 to 20% of the material consisted of particles less than 1/4 in. diameter. No. 3 limestone slag samples had a void volume between 40 and 42%; with no particulates smaller than about 1 inch in diameter. The 5-gallon/minute output from the Waukesha pump could be directed through the No. 3 slag with much less tendency towards back-flow.

Fire-Fighting Tests - A series of 9 tests has been completed in the larger, experimental apparatus, to determine the fire-fighting capabilities of these foams. Since the primary objective was to observe and measure fire-fighting capabilities, these tests were prepared and done under conditions which were controlled to be as nearly identical as possible with fire tests.

The procedures and conditions used to define these tests were as follows:

- 1) Twenty-five pounds of cannel coal was packed in a sphere at the center of the experimental chamber.
- 2) The apparatus was filled with No. 3 slag (or coal refuse) to position and surround the charge of coal.
- 3) An oxygen lance was placed in the center of the cannel coal, to expedite the pre-burn.
- 4) Three Type K thermocouples were placed in stainless steel wells to monitor the temperature. One was placed in the center of the coal. The second at the top of the coal, and the third in the slag or refuse. The temperature data was manually recorded on a digital output using a 3-way switch.

- 5) The oxygen-enhanced pre-burn was done for 20-30 minutes to establish the fire and obtain a temperature equilibrium.
- 6) The oxygen lance was removed and temperatures re-equilibrated prior to adding foam.
- 7) The apparatus was opened for inspection immediately after the test was finished.

A typical test required filling the apparatus with slag or coal refuse, while positioning the charge of cannel coal in the center; positioning the stainless steel tubes for the thermocouples and oxygen lance; igniting the coal with a gas torch; and monitoring the system during the 20-30 minute pre-burn before starting the foam generator.

The thermocouple in the coal often measured temperatures exceeding 2000°F during the pre-burn periods. Flames and steam usually erupted through the surface as seen in Figures 27 & 28.

This temperature decreased when the oxygen lance was removed, reflecting the influences of air inflow through the particulates and the ambient temperature. The temperature of the cannel coal re-equilibrated in the range of 1600 to 1900°F before the test with a candidate foam agent began. Temperatures at the edge of the cannel coal were less easily controlled and ranged from 600 to 1700°F. The temperature of the slag or coal refuse containing media did not change much throughout a test; usually 75 to 80°F during pre-burn and the prevailing ambient temperature at all other times.

The void volume of the apparatus, when using slag, was about 26 gal. This represented about 5 minutes operation for the Waukesha pump. When coal refuse was used to fill the apparatus, the void volume was about 18 gallons; representing only slightly more than 3 minutes operation. Foam was driven out through the holes in the side of the apparatus within 1 to 3 minutes, as shown in Figures 29, 30 and 31.

The temperature within the cannel coal charge decreased rapidly from the equilibrated fire temperature range of 1600 to 1900°F. The thermocouple in the coal measured temperatures of 1200 to 1600°F within the first minute that the foam flowed into the apparatus. A slower decrease occurred after the initial passage of foam and continued until the apparatus was opened for inspection; with the exception of one test using gelling foam and coal refuse. Foam penetration was minimal in this test, as it flowed back out the surface preferentially, and the coal ignited when opened while the temperature was about 1600°F (Figure 32). The foam dispersed only in top 6-8 inches of the coal refuse, indicating only about 2 inch penetration.

These foams dispersed through the apparatus to fill everything but the coal and the material directly beneath the coal (i.e. see Figures 33 & 34 for non-gelling foams and Figures 35, 36 & 37 for gelling foams).



FIGURE 27. - Pre-burn during fire test with No. 3 limestone slag surrounding the 25-pound charge of cannel coal.



FIGURE 28. - Pre-burn during fire test with coal refuse surrounding the 25-pound charge of cannel coal.



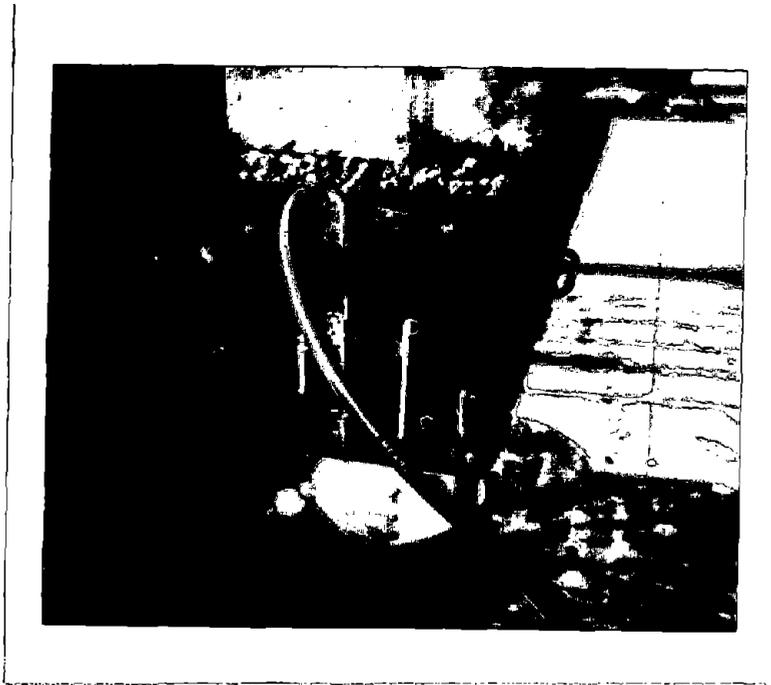
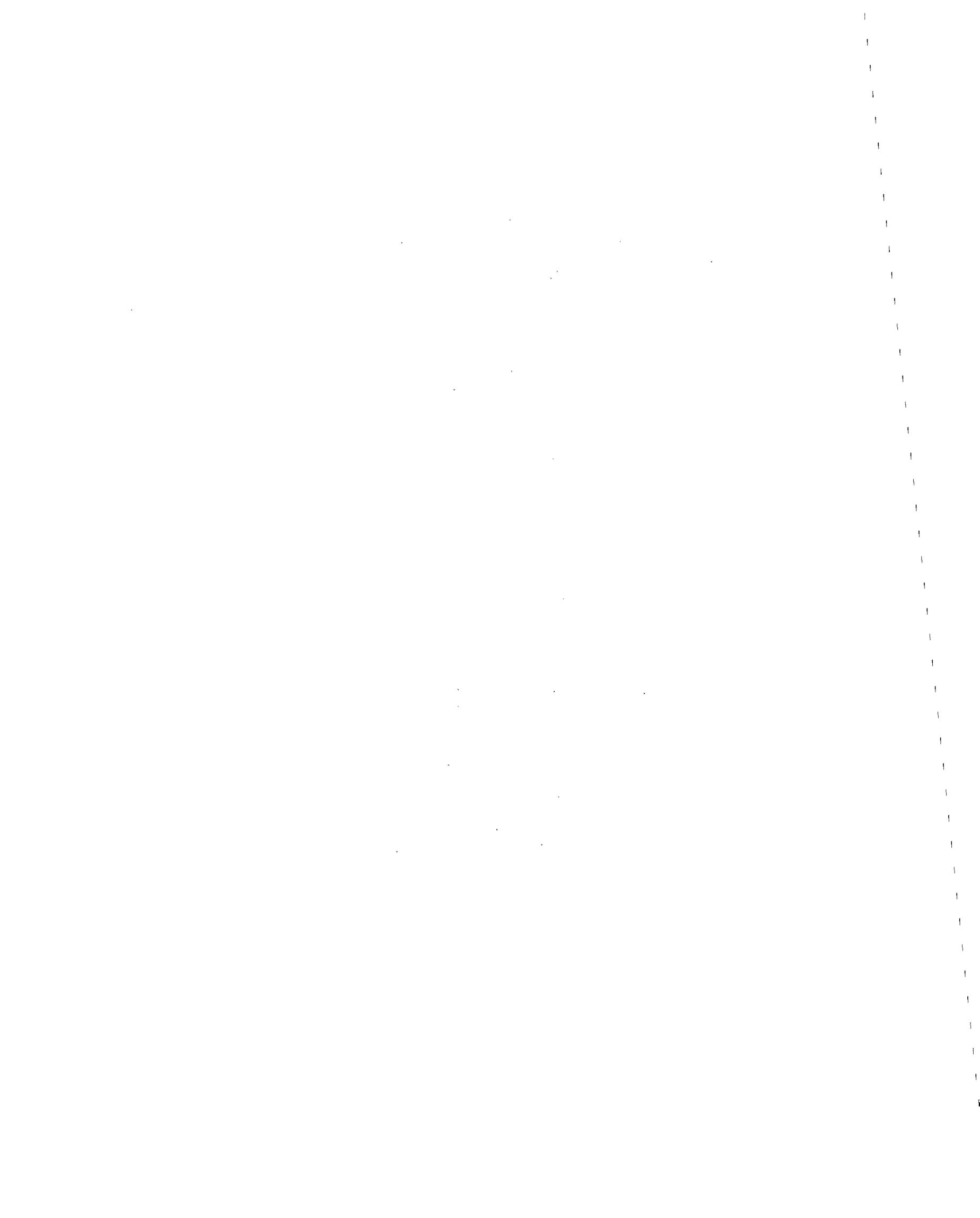


FIGURE 29. - Dispersed foam flowing out the sides of the apparatus 2 minutes after starting the flow with gelling foam.



FIGURE 30. - Dispersed foam flowing from test using coal refuse with the gelling foam, 1 minute after starting the flow.



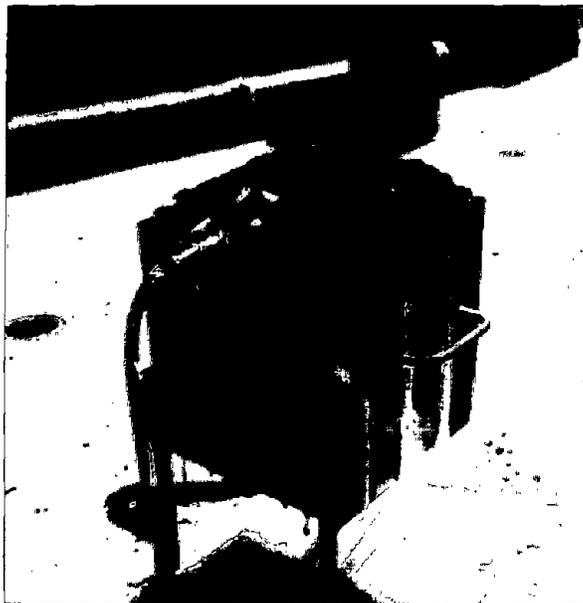


FIGURE 31. - Same test as #7 (different side), 3 minutes after starting the flow of foam.



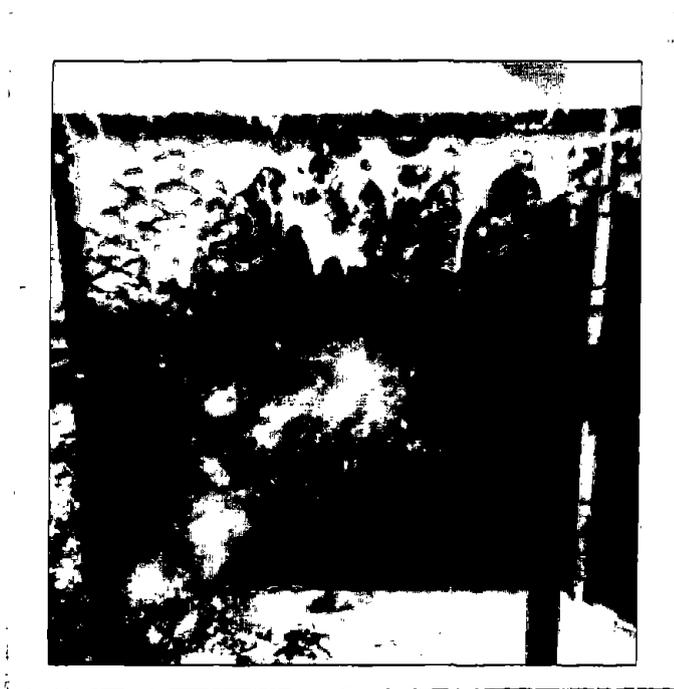


FIGURE 32. - Re-ignition of cannel coal fire after opening the apparatus. Penetration and dispersal of the gelling foam was limited to the top 6-8 inches of the coal refuse used.

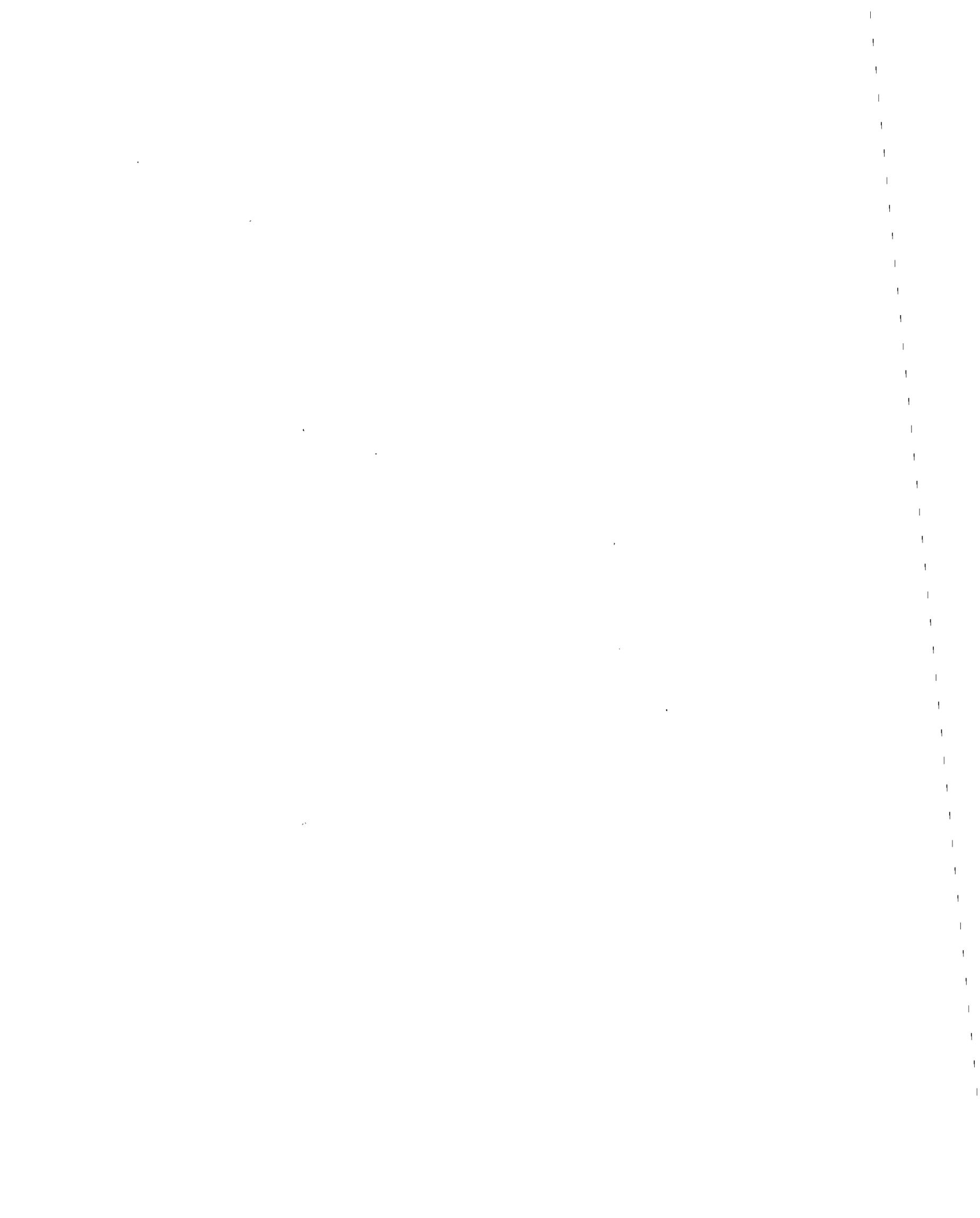




FIGURE 33. - Penetration and dispersion of a thickened foam added to the cannel coal fire, surrounded by No. 3 limestone slag.

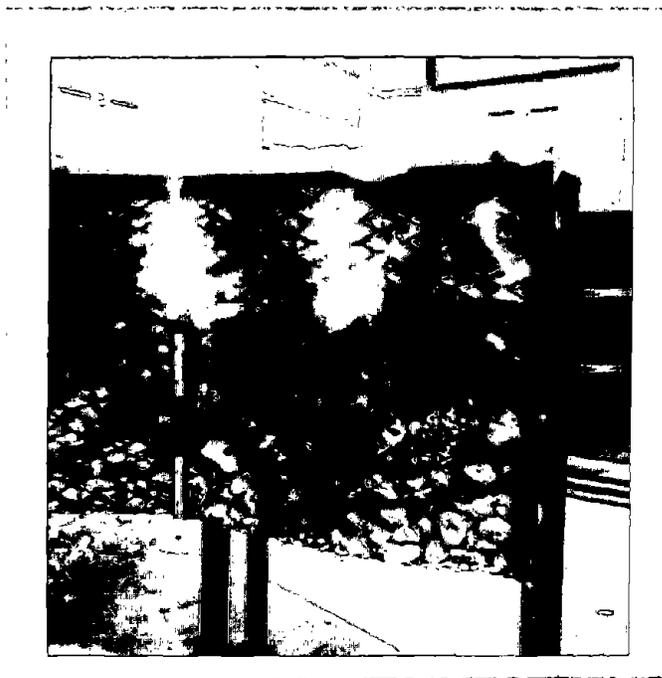
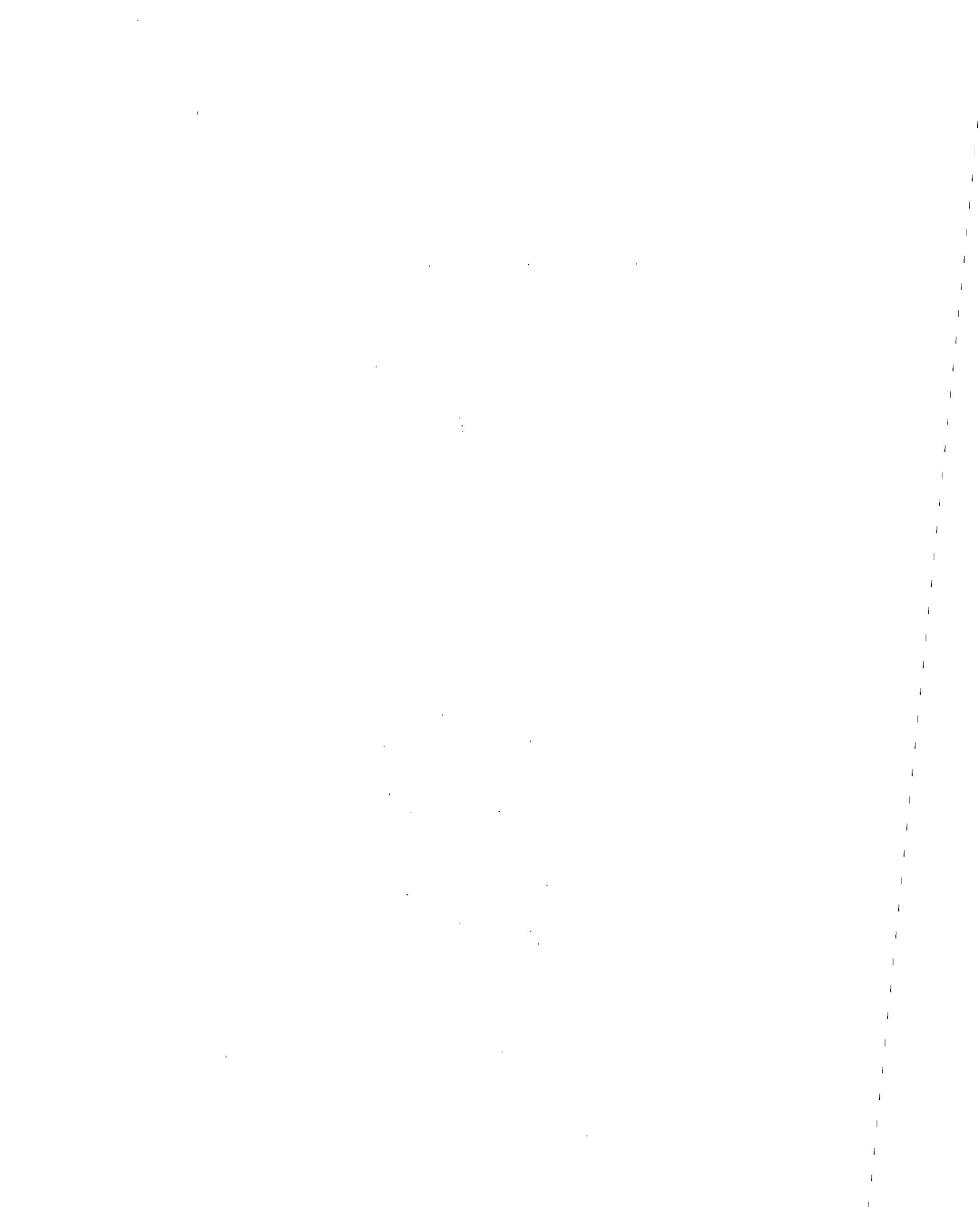


FIGURE 34. - Penetration and dispersion of a standard foam added to the cannel coal fire, surrounded by No. 3 limestone slag.



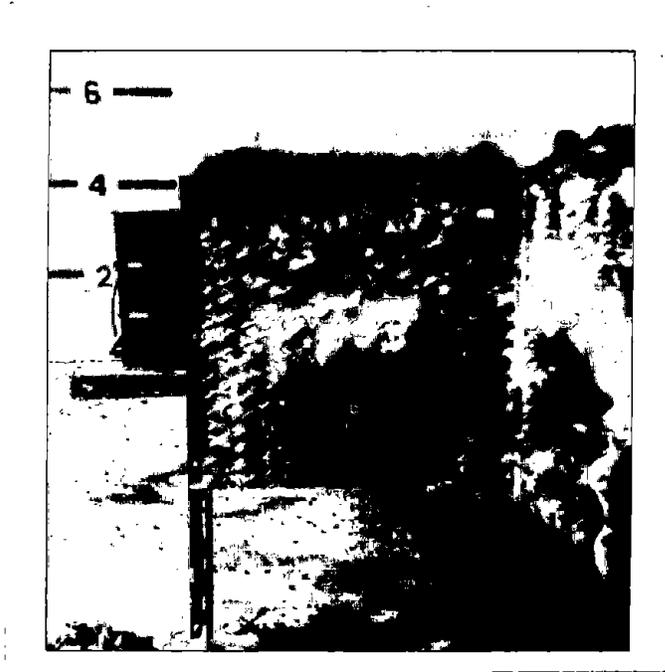


FIGURE 35. - Penetration and dispersion of a gelling foam added to the cannel coal fire, surrounded by No. 3 limestone slag.

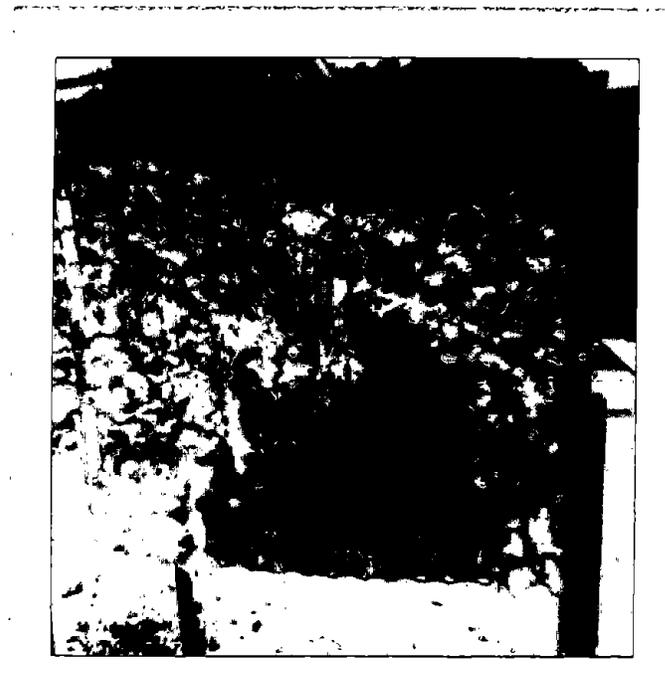
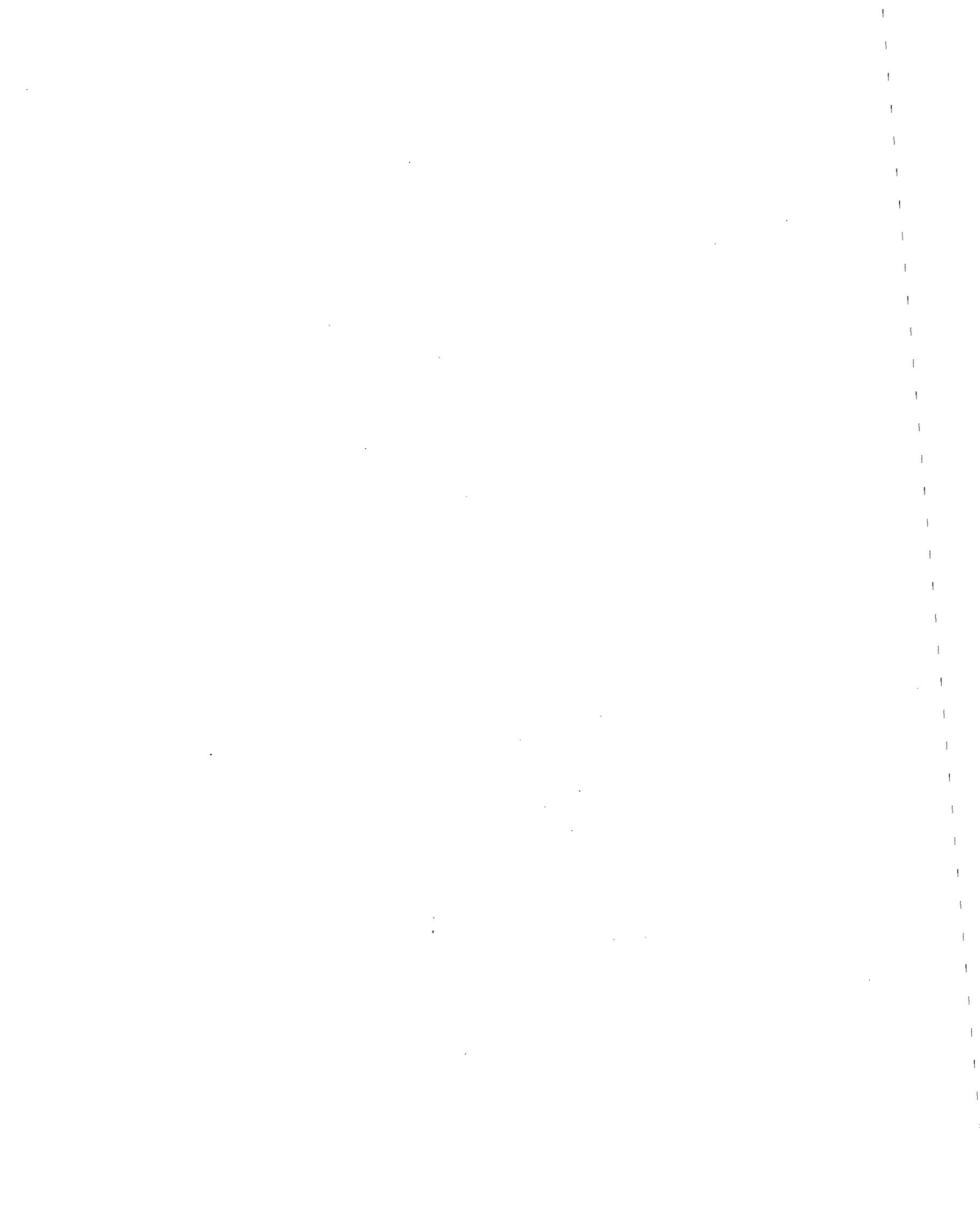


FIGURE 36. - The differences apparent between gelling foam exposed to the fire and that flowing around the fire in cooler zones.



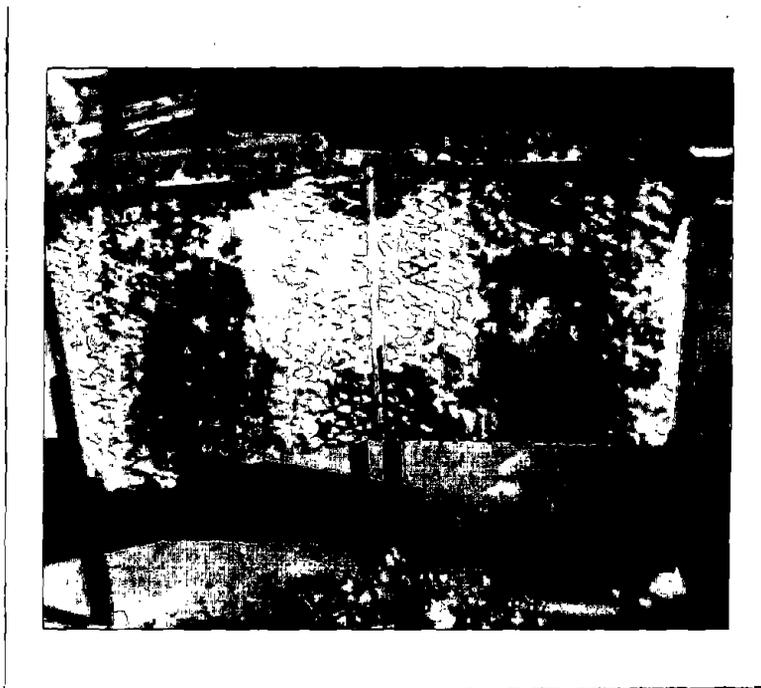


FIGURE 37. - Typical example of the penetration and dispersion of a gelling foam where no back-flow occurred to the surface.



Standard foams containing the "Rheothik" thickening agent filled the chamber, except under the fire, as shown in Figure 33. These foams are stable and have a longer life, as seen in this photograph. Without these thickeners, the standard foams experienced nearly total collapse, as seen in Figure 34.

Gelling-foam formulations showed similar penetration and dispersion through the apparatus. They produced a compact mass of slag or coal refuse, held together by gelling liquid in those areas exposed to the fire, or by gelled foam, in the cooler regions. Typical results are shown in Figures 35, 36, & 37.

These foams appear to have the capability to extinguish fires in a simulated underground environment. The full extent of their capabilities may be lost in the design of the experimental apparatus, which was prepared for visual observation. The Waukesha generator, although capable of producing foams at 50 psig, did not operate at more than 10 psig in short spurts, and usually in the range of 5-7 psig. It is possible that the foams would be forced to encapsulate the fire if there was a greater generating pressure and fewer avenues of escape.

Some characteristics of the flow of foams through coal refuse have been examined using new experimental apparatus. These apparatus have been adapted from the methods described in the API publication, Recommended Practices for Standard Procedures for Evaluation of Hydraulic Fracturing Fluids (Section 5). We have used them to study the dispersion of both standard and gelling foams through coal refuse, when they are generated with a Waukesha pump.

Two apparatus were fabricated during the course of this investigation: the first, based on an hemispherical head, welded to 8-inch-diameter pipe, with a flanged nipple at the end. The second, a similar construction, having an overall length of about 73 inches. These two apparatus are presented, schematically, in Figure 38.

Foams were generated at approximately 50 psig with a Waukesha pump, and delivered to the capped-end of the pipe. The pipe was filled with coal refuse, held in position by heavy wire mesh at both ends. Eleven penetrations were placed at 6 in. intervals, diametrically opposed, along the length of the pipe. These penetrations included a 1-inch annulus and 1/2-inch tubing nipple, fitted so as to indicate the flow of foam along the pipe wall or through the coal refuse matrix (as shown in Figure 38).

The smaller of these apparatus was about 16 inches long and presented no challenge to the generating capabilities of the Waukesha pump. The total volume of coal refuse was about 3 1/3 gallons (approx. 1 gallon void volume), which represents less than 1 minute's flow from this generator. The foam traversed the entire apparatus in about 10 seconds, and the flowrate was equal to that measured during completely free flow from the generator.

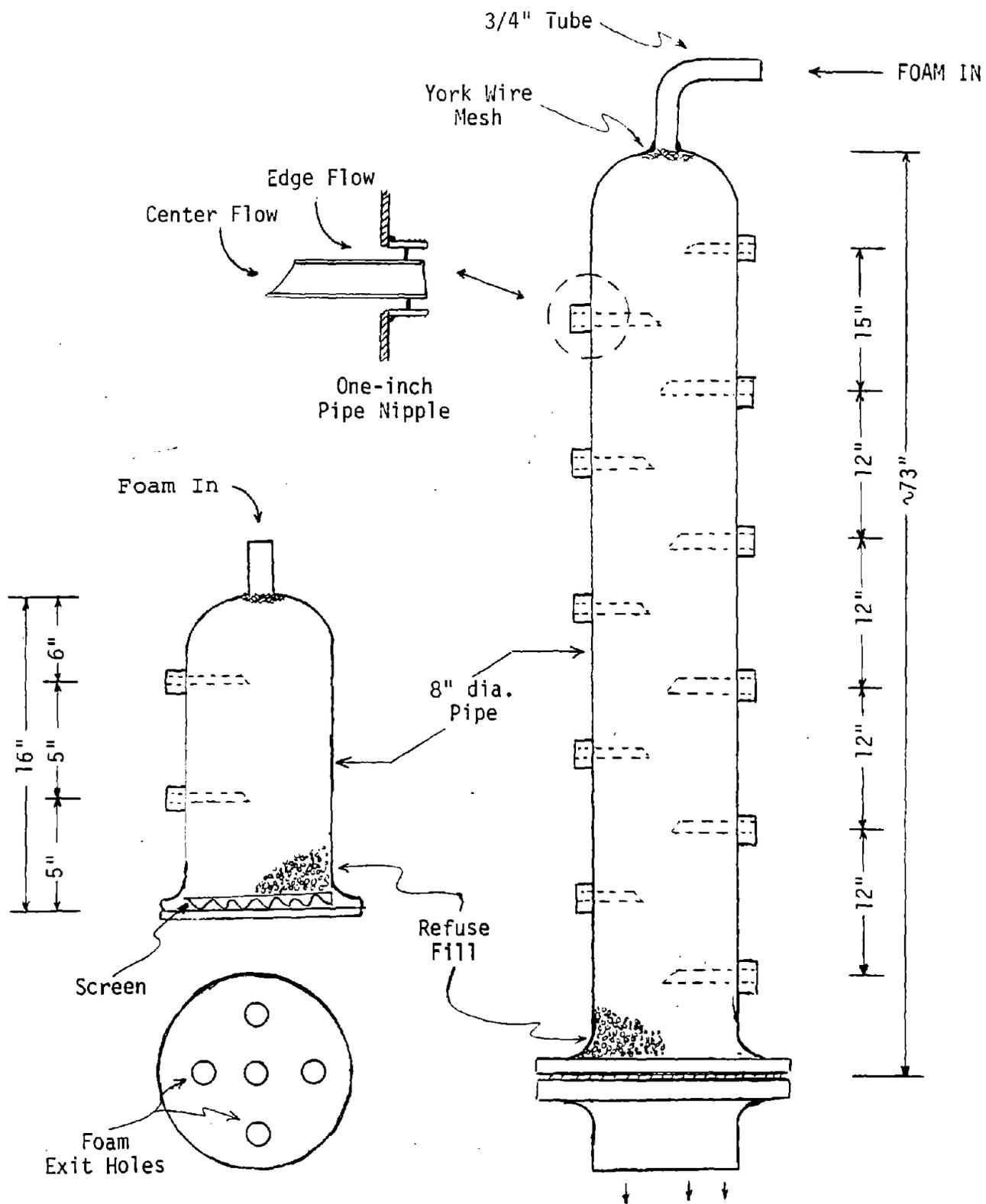


FIGURE 38. - Apparatus for examining and measuring the flow of foams through coal refuse.

These tests used standard foam formulations and proved that the entire cross-sections of the coal refuse was permeated by the foam. There was no evidence that the foam collapsed, or that the flow was impaired, as it moved through this apparatus.

The larger apparatus, shown in Figure 39, did provide a greater challenge for the Waukesha pump and a better means for evaluating the dispersion and flow of foams through the coal refuse. The flow of foam was monitored at each of the penetrations along the 8-inch pipe, where the flow along the walls appeared first, and differentiation increased with distance from the delivery tube.

The 50 psig operating pressure of the Waukesha pump was insufficient to push the standard (non-gelling) foam through the entire column of coal refuse. This foam permeated the pipe for about 57 inches, but the penetration at 57 inches showed flow only along the wall. Although the foam generation continued for another 3 minutes, neither interior flow nor further advance along the walls could be observed.

The final state of the apparatus during this test is shown in Figure 40. The photograph does not provide an adequate means to distinguish between the flow through the coal refuse and that along the wall, but does show the extent of penetration through the pipe.

The time required to traverse the pipe is plotted against the distance from the delivery tube in Figure 41. This graph shows a significant decrease in the rate of penetration after 1 minute. The slow rate of dispersion noted between 3 and 7 minutes, as well as the poor performance observed at the Waukesha generator and observations during the final clean-out, verify the conclusion that this was the maximum foam dispersion attainable under the test conditions.

The difference in the rates of dispersion of standard and gelling foams through coal refuse are also evident in Figure 41. The initial surge of foam into the test bed showed only minor differences. As the foams penetrated more than 2 feet, however, there was a greater divergence in the rates of dispersion. The incremental changes; due to fluid characteristics, foam collapse, pressure drop, or other factors; were not as great for the gelling foam as for the standard. Total dispersion of the gelling foam equalled that of the standard foam after about 6 minutes generating time, and continued on to penetrate the entire apparatus. The gelling foam continued to flow out the open end, although there was some blow-back through the generator and the flowrate was only 0.8 gallon/min, vs 5 gallon/min under free flow.

The rate of dispersion of the gelling foam appeared linear through most of the measuring points. The decrease noted as the foam exits the apparatus may be real, or may also reflect the changes occurring as the foam exits the coal refuse and encounters only ambient pressure and normal gravity settling into the collector. The first foam to exit the apparatus appeared along the wall (Figure 42). The entire





FIGURE 39. - Large apparatus, as prepared for laboratory test, to study the dispersal of foams through coal refuse under pressure.



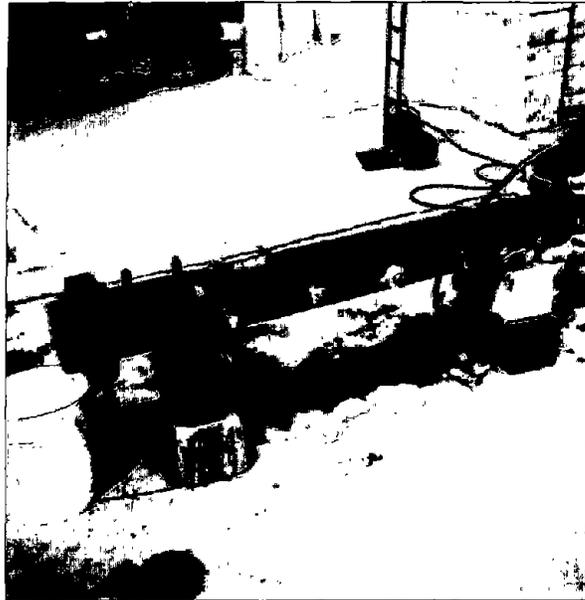
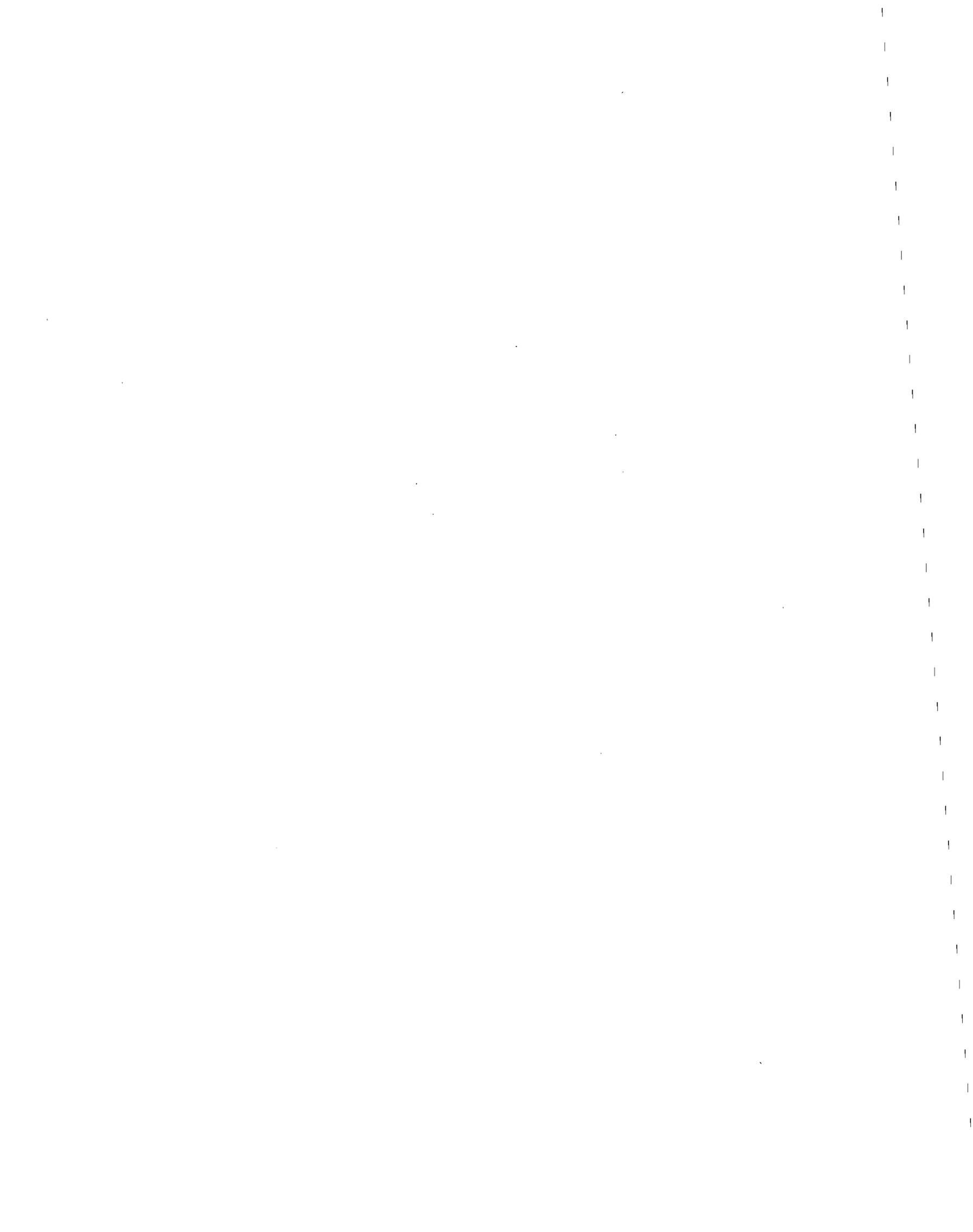


FIGURE 40. - Apparatus in test with non-gelling foam (this foam flowed through 57 in. length of the pipe, and then only at the wall).



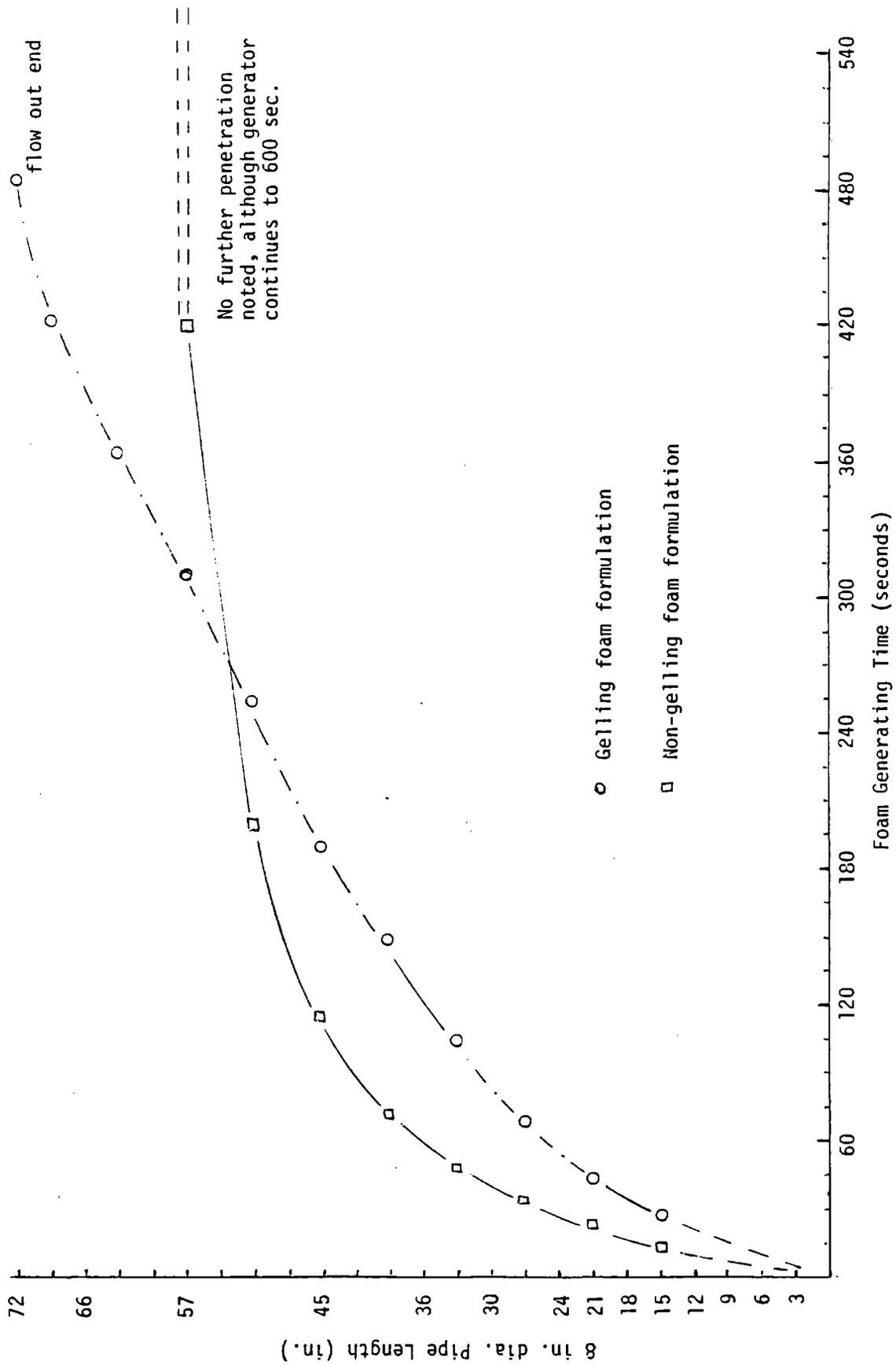


FIGURE 41. - Dispersion of test foams through coal refuse.



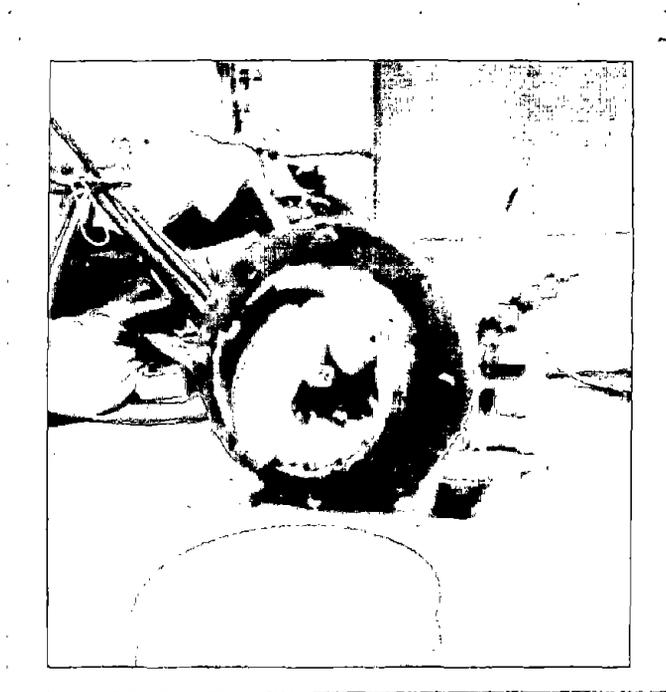


FIGURE 42. - Apparatus in test with gelling foam (foam permeated the apparatus, with the initial outflow only along the walls; full diameter flow required about 30 seconds).



surface of the screen at the end of the pipe was filled by the foam flowing through the coal refuse after about 30 seconds.

### Test Conclusions

The following conclusions have been derived from the experimental tests completed until this time:

- 1) The gelling foam appears more capable for applications requiring generation and delivery underground at elevated pressures.
- 2) The Waukesha pump generator is sufficient for preparing foams at 50 psig; and will treat a volume of roughly 6 feet radius around the injection point.
- 3) A larger scale test will significantly increase our knowledge of the capabilities of these foams.
- 4) The criteria used to evaluate the performance of foams should include both the dispersibility and heat absorbing capabilities.

The following formulation was used in subsequent fire tests.

#### A. Components

15 liters of PVA solution (5% Elvanol 90-50 in water)  
1.4 liters of ICS-1 Acrysol (Rohm & Haas)

#### B. Components

12 liters of 10%  $\text{Na}_2\text{CO}_3$   
2.75 liters of sodium silicate solution  
1.65 liters of surfactant pre-mix

Mixed 50:50.

### TASK 5 - REFUSE PILE FIRE TESTS

Before fire tests were conducted, the characteristics of the foam pump were determined. The variation of pressure with expansion ratio and pump suction is shown in Figures 43 and 44. It was expected that by varying the pump parameter the injection technique could accommodate variations in pile density and porosity. In order to reduce the cost of the portable generator, we converted the foam pump from 3 $\phi$  220V motor to a 1 $\phi$  220V motor. This enabled us to use a smaller portable generator. The cost of conversion was made-up by elimination of the cost of rental of a 3 $\phi$  220V generator. Table 3 is a summary of the test.

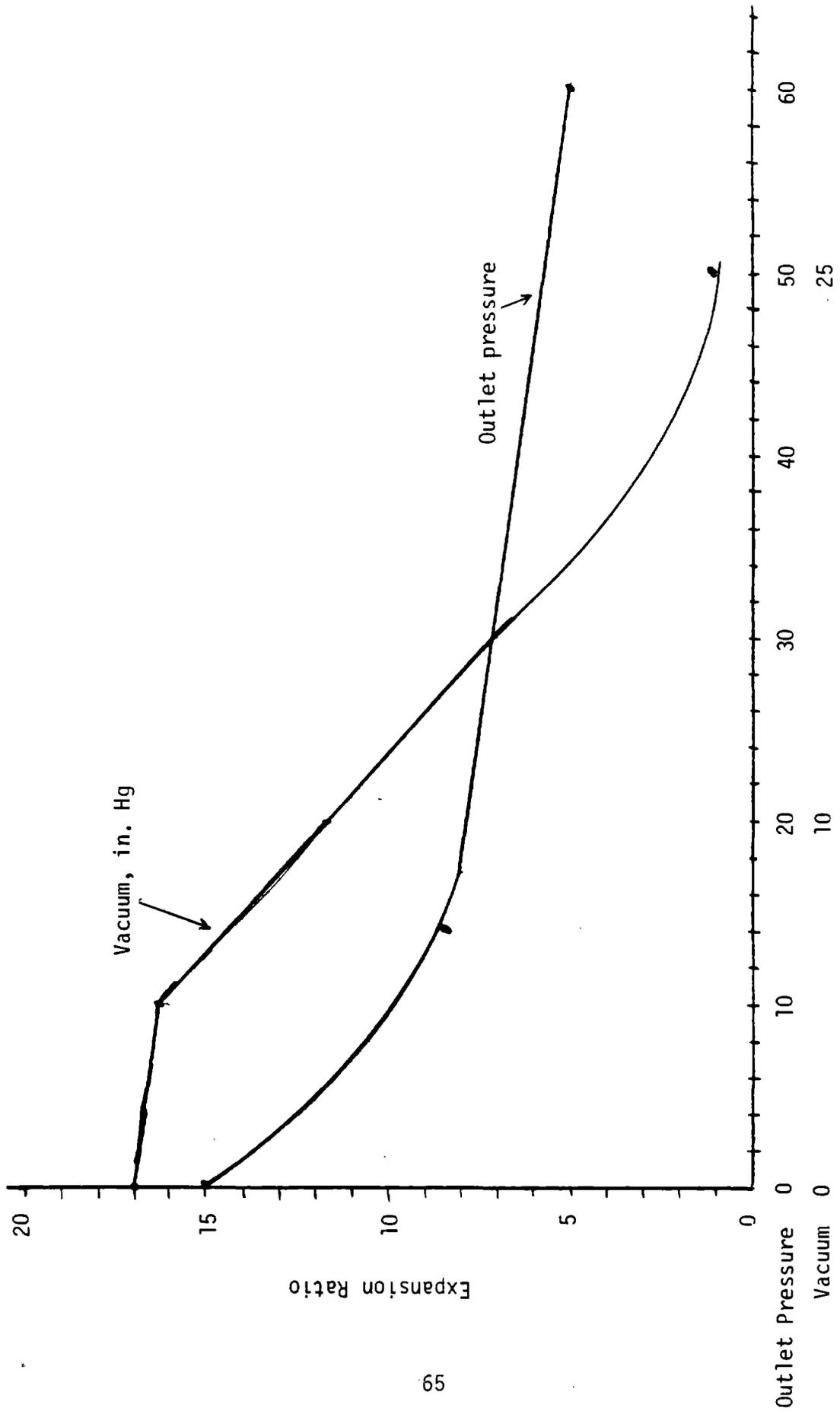


FIGURE 43. - Outlet pressure vs expansion ratio, suction vacuum vs expansion ratio.

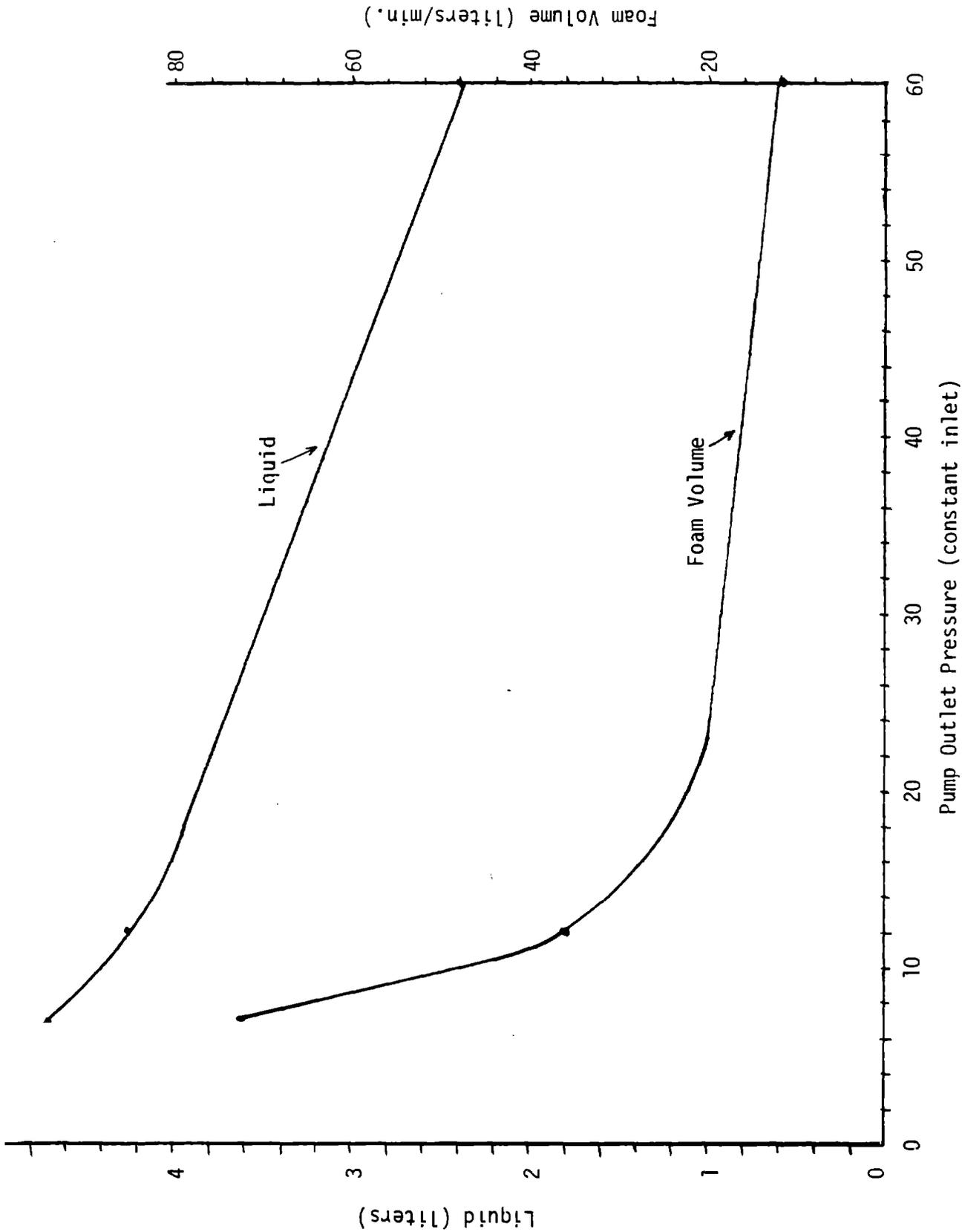


FIGURE 44. - Liquid flow vs pump outlet pressure, foam volume flow vs pump outlet pressure.

TABLE 3. - Test summary

Size of Container:	5 x 5 x 5 feet
Sides:	Expanded metal/angle bracing
Thermocouples: (Type K)	1 foot centers from sides - 64 total
Data Collection:	2 Molytek recorders - 32 t/c each
Refuse:	Approx. 10 tons from a local reclaim operation
Fire Locations:	One foot in from the top & each side at two opposing corners. The adjacent corners had fires at one foot from the bottom of the test bed (bag of cannel coal + O <sub>2</sub> for starting).
Injection Point:	Geometric center of box
Injection Equipment:	Waukesha pump - horizontal injection
Locations:	U.S. Bureau of Mines, Lake Lynn facility

Field tests were conducted at the Bureau of Mines Lake Lynn facility. A box which was 5 ft x 5 ft x 5 ft was constructed (Figure 45A). The sides of the box were made of expanded metal.

Mine refuse was collected from a waste bank reclaim operation nearby. Laboratory percolation tests indicate a rate of 0.42 liters/min/ft<sup>2</sup>. The foam pump (Figure 45B) was modified to operate on 1ø 220V (2 HP). Foam pump performance data is shown in Table 4. The injection tube was located in the geometric center of the box.

The test set-up was next to the explosives testing area (Figure 45C). Four charcoal inserts in the pile were used for the initial fires. The charcoal was ignited using charcoal starter fluid and air oxygen. Thermocouples were placed on 1 foot centers (64) throughout the bed with the outputs to two Molytek recorders.

Fires were started but could not be kept lit unless oxygen was continuously supplied. In addition, only localized high temperatures in the coal were found. No temperature increase was seen in the refuse. We had hoped that igniting the coal and returning the next morning would provide high temperatures throughout the bed. However, the fires were out and the bed was cold.

Temperature data was not recorded due to the problem of heating the bed and poor foam distribution. It was felt that until good foam distribution was obtained, the effort to record a large number of thermocouples would not be worthwhile.

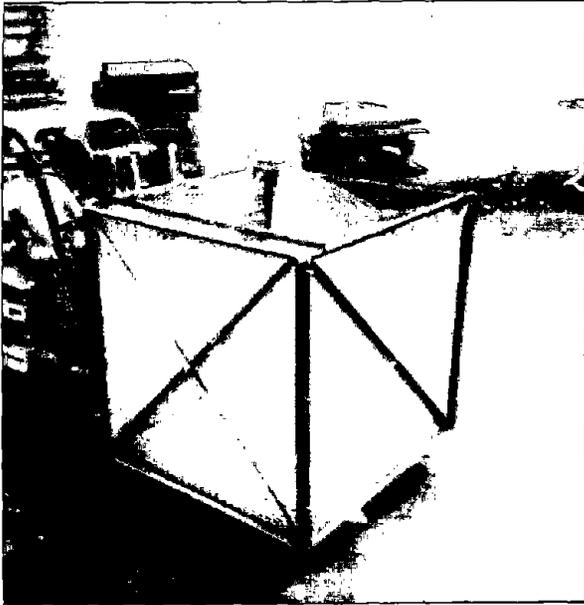
Every time foam was injected it flowed out of the pile on the outside of the injection tube. After opening the box, foam was found to have flowed through the larger channels in all directions, but not in the more densely packed areas (Figure 45D).

It appears the problem is one of flow, not fire extinguishment. Therefore, a second series of tests were planned where the injection tube had a baffle plate and a balloon section. It was expected that these steps would prevent flow over the outside of the injection tube. The foam formulation was also modified to increase its viscosity and produce a thixotropic foam which should block the larger channels and force the foam to flow into the denser areas of the refuse pile.

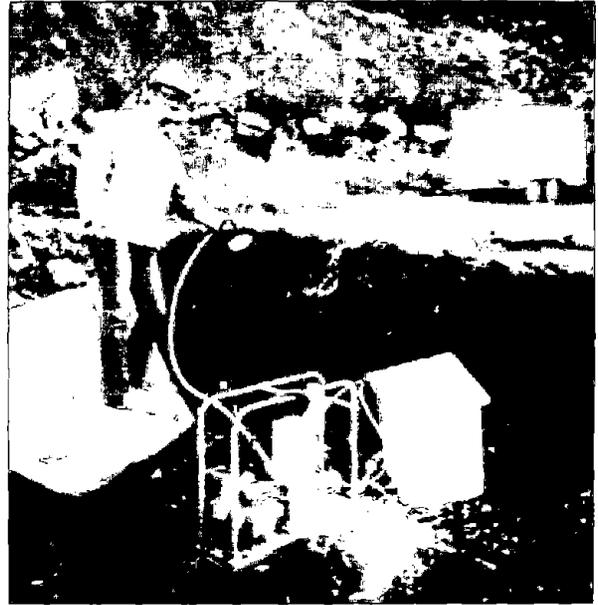
During the second series of tests a number of approaches were taken. These were:

1. Use of Type P - a lower viscosity single component foam solution.
2. Gelling foam with a thickener (Xanthan gum) with an initial injection, followed by subsequent injections the next morning.
3. Lowering the expansion of the initial injection.

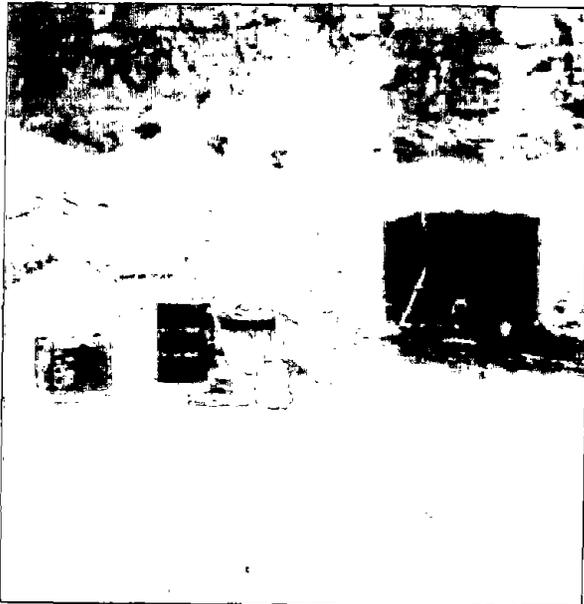




A



B



C



D

FIGURE 45. - Field tests at Lake Lynn.

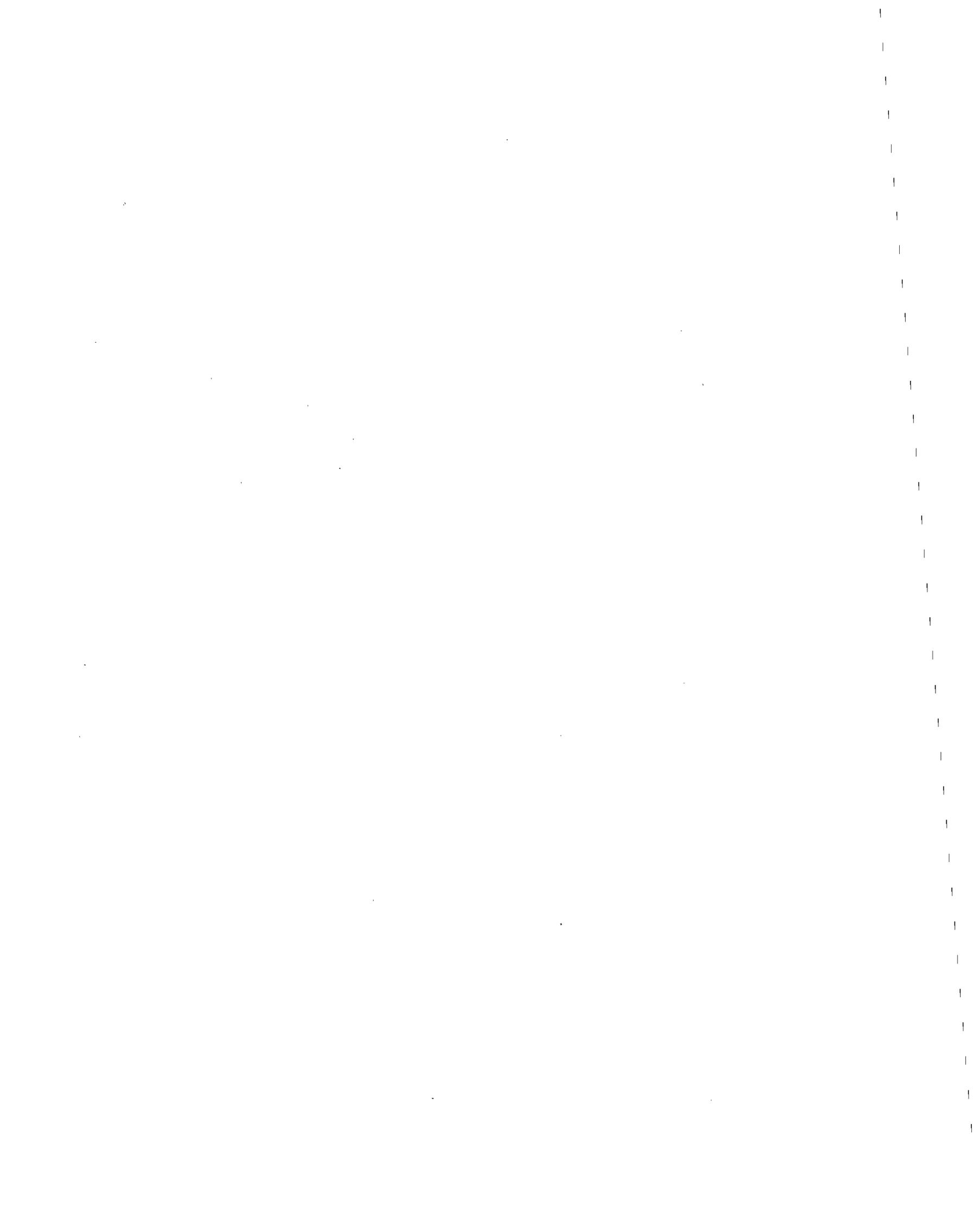


TABLE 4. - Foam pump performance data

<u>Elapsed Time</u>	<u>Pump Pressure (neg.) In</u>	<u>Pump Pressure (pos.) Out</u>	<u>Foam Agent (liters)</u>	<u>Foam Generated (liters)</u>	<u>Expansion Rate</u>
25.5	0.0	7.0	2.0	31.0	15.00:1
28.0	0.0	12.0	2.0	17.0	8.50:1
50.0	0.0	60.0	2.0	10.0	5.00:1
17.5	25.0	0.0	2.0	2.0	1.00:1
28.0	0.0	7.0	2.0	34.0	17.00:1
26.0	5.0	--	2.0	32.5	16.25:1
22.0	10.0	5.0	2.0	21.0	11.50:1
28.0	0.0	5.0	2.0	30.0	15.00:1
30.0	6.0	35.0	2.0	14.0	7.00:1

4. Placing the injection tube on the side of the pile.

In all these cases, flow up the outside of the injection tube was present, but preferential flow (always up) out the larger channels occurred. A picture of the foam on the top of the pile is shown in Figure 46.

Economics

Discussions were held with a contractor at a site located near the Lake Lynn facility. Costs of a burning coal seam were examined to provide a preliminary cost calculation. The cost to excavate and quench an estimated 95,000 yd.<sup>3</sup> of overburden and coal was \$167,000. However the coal zone where the fire was burning was estimated to be 56,000 square feet by 10 feet in depth. The fire was approximately 50 feet below the surface. Therefore a significant volume of overburden must be removed before the fire zone is reached. The cost of the gelled foam liquid is approximately \$2.80 per gallon on a small quantity (5 gal.) basis. The cost for a large volume (greater than 1000 gallons) is estimated at approximately \$2.00 per gallon.

The total volume in the affected zone is 560,000 ft.<sup>3</sup>. With a 30% void space (assumed), 168,000 ft.<sup>3</sup> (1,260,000 gal.) is available for liquid/foam flow. At the following expansion ratios the amount of liquid (no makeup) needed would be:

		Cost @ \$2/gal.
1:1	1,260,000 gal.	2,520,000
5:1	252,000 gal.	504,000
10:1	126,000 gal.	252,000
20:1	63,000 gal.	126,000

These costs do not include the cost for drill holes, pump, labor, etc.

It became apparent that material costs are significantly reduced as the expansion ratio increases. However, this must be weighed against the decrease in heat capacity.



FIGURE 46. - Foam escape from top of the pile.



## CONCLUSIONS

- Gelling foams did not provide enough resistance to block flow through major channels. The channels must be blocked to provide more uniform distribution, by forcing the foam into the denser areas of the coal refuse pile.

- Low expansion foams (20:1 max.) provided the best injection and extinguishing properties because of its smaller bubble size and higher water content.

- Preliminary cost calculations indicate that the foam injection methods are competitive with excavation.

## RECOMMENDATIONS

- This is the initial research effort in this area. While we have shown that foam improves water distribution, further improvements are needed to provide better assurance of fire extinguishment. The foam flow is primarily in the larger channels.

- Initial injection of a porous plug material (i.e. foam concrete) strong enough to block larger channels and force the foam to flow into the denser areas should be explored. Subsequent injections could be with the standard foams.

- Injection pressure is a function of bubble size, porosity, injection rate and pressure. A better understanding of these parameters is needed.

- Bench scale tests need to be developed to simulate refuse piles. The tests in the 5 ft x 5 ft x 5 ft bed at Lake Lynn appear to simulate actual field conditions. However our bench scale tests indicated that foam flow would be much more uniform than was the case with the Lake Lynn tests.

- Foam flow in porous media such as coal refuse piles needs to be studied further in order to design or select equipment for injection.

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Handy, L.L., "Chemical Additives for Improving Steamflood Performance", Report DE89-000722, Contract No. AT03-84SF11999, January, 1989.

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APPENDIX. -- ABSTRACTS

Laboratory Studies for the Design and Analysis of Hydraulic Fracture Stimulations in Tight Gas Reservoirs

Sattler, A. R. ; Hudson, P. J. ; Raible, C. J. ; Gall, B. L. ; Maloney, D. R.

Sandia National Labs., Albuquerque, NM.

Corp. Source Codes: 068123000; 9511100

Sponsor: Dowell Schlumberger.; National Inst. for Petroleum and Energy Research, Bartlesville, OK.; Department of Energy, Washington, DC.

Report No.: SAND-85-2507C; CONF-860567-3

1986 15p

Languages: English Document Type: Conference proceeding

Journal Announcement: GRAI8616; NSA1100

SPE unconventional gas technology symposium, Louisville, KY, USA, 18 May 1986.

Portions of this document are illegible in microfiche products.

NTIS Prices: PC A02/MF A01

Country of Publication: United States

Contract No.: AC04-76DP00789

Laboratory studies were used as an aid in designing stimulation treatments and to assist in the analysis of production results. These analyses were done in conjunction with coastal zone stimulation operations at the Department of Energy's Multiwell Experiment near Rifle, Colorado. A multitreatment stimulation plan was designed for the coastal zone because of apparent damage to the paludal zone formations in prior stimulation operations. The stimulation plan was made to minimize the use of water-based, gelled fluids. Two small stimulations were performed in the same coastal interval: an unpropped nitrogen gas frac and a propped, nitrogen foam frac. Gas production decreased from that of the gas frac after the nitrogen foam stimulation and formation damage was apparent. The laboratory program was used to (1) aid stimulation design; (2) help eliminate several possible causes of damage such as permeability degradation in the matrix rock, a gel block in the sand pack, proppant effects, or imbibition of brine from workover operations; and (3) examine the more probable causes, damage that may be centered around fluid effects in the natural fracture system. A unique explanation is not possible because there are some aspects of these damage mechanisms that cannot be verified in the laboratory. However, comparable damage mechanisms that have been seen in cracked core are described. Also, other postulated forms of fluid damage are discussed, largely in terms of natural fractures in core in combination with other measured core properties. 37 refs., 1 fig., 8 tabs. (ERA citation 11:025359)

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1/7/2

02295434 Monthly No: EI8708082388

DYNAMIC FLUID-LOSS CHARACTERISTICS OF CO//2-FOAM FRACTURING FLUIDS.

Harris, Phillip C.

Halliburton Services

Source: SPE Prod Eng v 2 n 2 May 1987 SPE 13180, p 89-94

Publication Year: 1987

CODEN: SPENES

Language: ENGLISH

Document Type: JA; (Journal Article) Treatment: X; (Experimental)

Journal Announcement: 8708

High-quality CO//2-foam fracturing has recently become a very popular stimulation tool. Dynamic fluid-loss measurements were performed on a broad range of core samples to measure the effect of several parameters on CO//2-foam fluid-loss coefficients. The parameters tested were core permeability, foam quality, gelling-agent concentration in the aqueous phase, and core temperature. Measurements were performed in a recirculating fluid-flow test loop. A variation of one order of magnitude in C//I//I//I for two-orders-of-magnitude change in permeability was observed from 0.02 to 10 md. For permeability below 1 md, foam quality had no effect. Fluid-loss control improved as gelling agent concentration in the liquid phase increased. Passage of CO//2 foams through porous media caused a significant modification in quality from the input to the effluent fluid. (Edited author abstract) 11 refs.

1/7/3

02255116 Monthly No: EIMS706-040931

RHEOLOGICAL PROPERTIES OF FOAM FRACTURING FLUIDS UNDER DOWNHOLE CONDITIONS.

Cawiezel, K. E.; Niles, T. D.

Dowell Schlumberger

Conference Title: Proceedings - Production Operations Symposium.

Conference Location: Oklahoma City, OK, USA Conference Date: 1987 Mar 8-10

Sponsor: Soc of Petroleum Engineers of AIME, Richardson, TX, USA

E.I. Conference No.: 09570

Source: Society of Petroleum Engineers of AIME, (Paper) SPE Publ by Soc of Petroleum Engineers of AIME, Richardson, TX, USA SPE 16131, p 53-63

Publication Year: 1987

CODEN: SEAPAZ

Language: English

Document Type: PA; (Conference Paper)

Journal Announcement: 8706

Foams are complex mixtures of gas and liquid whose rheological properties are largely influenced by foam quality, temperature, pressure and shear rates. A comprehensive study of the effects of these variables on the rheological properties of foams was conducted as a first step to understanding, defining and predicting the rheological properties of foam fracturing fluids. Rheological properties of nitrogen/water/surfactant foams and gelled foam fluids were evaluated using a recently developed foam rheology simulator. Results indicate that the rheological behavior of foam fluid is primarily that of a yield-pseudoplastic fluid and can best be described by a Herschel-Bulkley model. The complexity of foam systems and their sensitivity to external conditions require that foam system properties be closely controlled and monitored in field use to optimize the frictional pressure required to utilize foam fracturing fluids. (Edited author abstract) 9 refs.

02243886 Monthly No: EIMS704-028024

SUCCESSFUL FIELD APPLICATIONS OF CO//2 FOAM FRACTURING FLUIDS IN THE ARK-LA-TEX REGION.

Warnock, W. E. Jr.; Harris, P. C.; King, D. S.

Crystal Oil Co

Conference Title: Proceedings of the Thirty-First Annual Southwestern Petroleum Short Course.

Conference Location: Lubbock, TX, USA Conference Date: 1984 Apr 25-26.

Sponsor: Southwestern Petroleum Short Course Assoc, USA; Petroleum Industry of West Texas, USA; Texas Tech Univ, Dep of Petroleum Engineering, Lubbock, TX, USA

E.I. Conference No.: 09420

Source: Proceedings of the Annual Southwestern Petroleum Short Course 31st. Publ by Southwestern Petroleum Short Course Assoc Inc, USA: p 135-150.

Publication Year: 1984

CODEN: PSPCD3 ISSN: 0361-5987

Language: English

Document Type: PA; (Conference Paper)

Journal Announcement: 8704

The CO//2 foam fracturing fluid provides a gas drive to assist removal of the treating (load) fluids after the proppant has been placed in the formation, establishes permeability to gas within the formation volume that has been saturated by load fluids, and minimizes the actual water volume that is required to place a given volume of proppant in the formation. Due to the high density of the liquid CO//2 mixture, the CO//2 foam can be utilized on deep, high pressure formations without experiencing prohibitive wellhead treating pressures. The CO//2 also reacts with the water in the foam to form carbonic acid, so that the overall pH of the system is reduced (thus reducing the damaging effect of the fluids), and it lowers the surface tension of the load fluids so that they can be recovered more rapidly and efficiently. (Edited author abstract) 6 refs.

1/7/5

02113532 Monthly No: EIM8608-056144

EFFECTIVE WELL STIMULATIONS WITH GELLED METHANOL/CARBON DIOXIDE FRACTURING FLUIDS.

Fairless, C. M.; Joseph, W.

Service Fracturing Co

Conference Title: Proceedings - New Reserves Through Technology Symposium, 1986 East Texas Regional Meeting.

Conference Location: Tyler, TX, USA Conference Date: 1986 Apr 21-22

Sponsor: Soc of Petroleum Engineers, East Texas Section, USA; East Texas Geological Society, USA; Gas Research Inst, Chicago, IL, USA

E.I. Conference No.: 07957

Source: Society of Petroleum Engineers of AIME, (Paper) SPE Publ by Soc of Petroleum Engineers, Richardson, TX, USA SPE 14656, p 63-66

Publication Year: 1986

CODEN: SEAPAZ

Language: English

Document Type: PA; (Conference Paper)

Journal Announcement: 8608

CO<sub>2</sub> foam fracturing fluids with gelled methanol as the external phase have been developed. These CO<sub>2</sub> foams are generated on the surface by a patented CO<sub>2</sub> heating process. Field applications of these fluids demonstrate that they are effective well stimulation fluids for hydrocarbon bearing formations that exhibit low permeability, low reservoir pressure or water sensitivity. With this system water can be completely eliminated from the treatment fluid while the CO<sub>2</sub> provides a gas drive to assist in returning load fluid to the wellbore. Since the density of these fluids is near that of water, they can be utilized to fracture stimulate deep formations without experiencing excessive wellhead pressures. (Edited author abstract) 8 refs.

PT 1/7/6-10

1/7/6

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1/7/5

02113532 Monthly No: EIM8608-056144

EFFECTIVE WELL STIMULATIONS WITH GELLED METHANOL/CARBON DIOXIDE  
FRACTURING FLUIDS.

Fairless, C. M.; Joseph, W.

Service Fracturing Co

Conference Title: Proceedings - New Reserves Through Technology  
Symposium, 1986 East Texas Regional Meeting.

Conference Location: Tyler, TX, USA Conference Date: 1986 Apr 21-22

Sponsor: Soc of Petroleum Engineers, East Texas Section, USA; East Texas  
Geological Society, USA; Gas Research Inst, Chicago, IL, USA

E.I. Conference No.: 07957

Source: Society of Petroleum Engineers of AIME, (Paper) SPE Publ by Soc  
of Petroleum Engineers, Richardson, TX, USA SPE 14656, p 63-66

Publication Year: 1986

CODEN: SEAPAZ

Language: English

Document Type: PA; (Conference Paper)

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CO<sub>2</sub> foam fracturing fluids with gelled methanol as the external phase  
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bearing formations that exhibit low permeability, low reservoir pressure or  
water sensitivity. With this system water can be completely eliminated from  
the treatment fluid while the CO<sub>2</sub> provides a gas drive to assist in  
returning load fluid to the wellbore. Since the density of these fluids is  
near that of water, they can be utilized to fracture stimulate deep  
formations without experiencing excessive wellhead pressures. (Edited  
author abstract) 8 refs.

PT 1/7/6-10

1/776

02111078 Monthly No: EIM8608-053668

DELAYED CROSSLINKED GELS: THEIR ROLE IN AQUEOUS FOAM FRACTURING.

Freeman, E. R.; Bilden, D. M.; Hossaini, M.

BJ-Titan Services Co

Conference Title: Proceedings 14993-15090, 56th Annual California Regional Meeting, Society of Petroleum Engineers.

Conference Location: Oakland, CA, USA Conference Date: 1986 Apr 2-4

Sponsor: Soc of Petroleum Engineers, Golden Gate Sect, CA, USA

E.I. Conference No.: 07906

Source: Society of Petroleum Engineers of AIME, (Paper) SPE v 1. Publ by Soc of Petroleum Engineers, Richardson, TX, USA SPE 15070, p 235-248

Publication Year: 1986

CODEN: SEAPAZ

Language: English

Document Type: PA; (Conference Paper)

Journal Announcement: 8608

Laboratory results indicate that the foaming of a delayed crosslinking gel increases apparent viscosity, improves proppant transport capabilities, and extends fluid loss properties beyond those of foamed linear gels. More than 200 treatments have been completed in various formations in California, Texas, and Oklahoma. A review of local formation characteristics and treatment conditions are discussed regarding the application and successful use of a crosslinked versus conventional linear gel foam. Noteworthy is that crosslinking the gelled phase of a foam system requires limited modification of current foam fracturing procedures or equipment. (Edited author abstract) 21 refs.

1/7/7

02018640 Monthly No: EI8609064546 E.I. Yearly No: EI86054234  
Alkaline Silicates as Raw Materials for Insulating Mineral Foams:  
Bibliographic Study.  
LES SILICATES ALCALINS, MATIERE DE BASE DES MOUSSES MINERALES ISOLANTES:  
ETUDE BIBLIOGRAPHIQUE.

Lesage, J.; Mergier, N.

Inst Francais du Petrole, Rueil-Malmaison, Fr

Source: Revue de l'Institut Francais du Petrole v 39 n 3 May-Jun 1984 p  
309-335

Publication Year: 1984

CODEN: RFPTBH ISSN: 0373-532X

Language: FRENCH

Document Type: JA; (Journal Article) Treatment: L; (Literature  
Review/Bibliography)

Journal Announcement: 8609

This article gives a bibliographic survey of methods for obtaining alkaline silicates as well as their properties and the properties of their polymers. A method is recommended for obtaining foams from aqueous silicate solutions. The influence of different additives such as surfactants, foaming gelling and hardening agents on the properties of these foams is discussed. This study shows that soluble polysilicate foams may be obtained from silicate solutions with a low  $SiO_2/Na_2O/20$  molar ratio. (Edited author abstract) Refs. In french.

1/7/8

02015921 Monthly No: EI8609088496 E.I. Yearly No: EI86095847

COLLOIDAL STABILIZERS - PART I.

Athey, Robert D. Jr.

Athey Technologies, El Cerrito, CA, USA

Source: Metal Finishing v 84 n 7 Jul 1986 p 61-62

Publication Year: 1986

CODEN: MEFIA7 ISSN: 0026-0576

Language: ENGLISH

Document Type: JA; (Journal Article) Treatment: G; (General Review)

Journal Announcement: 3609

The waterborne coating is composed of colloidal materials. There may also be pigment particles that are likely to be colloidal in size (if the grind is correct). Problems of foam, substrate wetting, gelling, viscosity rise and/or coagulation crop up now and again during the application of the coating. The article looks at such colloidal systems and the chemicals that are added to coatings to stabilize the colloids. The discussion covers surfactants, wetting agents (hydrotropes) and dispersants.

1/7/9

02004486 Monthly No: E18608071581 E.I. Yearly No: E185046245  
RHEOLOGICAL STUDY OF FOAM FRACTURING FLUIDS USING NITROGEN AND CARBON  
DIOXIDE.

Reidenbach, U. G.; Harris, P. C.; Lee, Y. N.; Lord, D. L.  
Halliburton Services

Source: SPE Prod Eng v 1 n 1 Jan 1986 SPE 12026, p 31-41

Publication Year: 1986

CODEN: SPENES

Language: ENGLISH

Document Type: JA; (Journal Article) Treatment: A; (Applications); T;  
(Theoretical); X; (Experimental)

Journal Announcement: 8608

A practical mathematical model based on experimental data is presented for calculation of rheological properties of N<sub>2</sub> and CO<sub>2</sub> foam stimulation fluids. The laminar flow model is a yield pseudoplastic type, with viscosity dependent on foam quality, yield point, base liquid consistency index ( $K'$ ), and flow behavior index ( $n'$ ). ( $n'$ ). foam flow data were analyzed with API RP39 procedures but were modified to include variable density effects of foam fluids. Water-based foam apparent viscosities compare closely to Mitchell's Bingham plastic model at high shear rates. The yield pseudoplastic model also includes viscous effects of gelling agents and measurement at much lower shear rates. Comparison of predicted pipe friction was made to actual field wellhead pressures with good agreement. (Edited author abstract) 36 refs.

1/7/11

01852864 Monthly No: EIM8502-007407

DYNAMIC FLUID-LOSS CHARACTERISTICS OF CO//2 FOAM FRACTURING FLUIDS.

Harris, Phillip C.

Halliburton Services

Conference Title: 59th Annual Technical Conference and Exhibition  
(Society of Petroleum Engineers of AIME).

Conference Location: Houston, TX, USA Conference Date: 1984 Sep 16-19

Sponsor: Soc of Petroleum Engineers of AIME, Richardson, TX, USA

E.I. Conference No.: 05224

Source: Society of Petroleum Engineers of AIME, (Paper) SPE Publ by Soc  
of Petroleum Engineers of AIME, Richardson, TX, USA SPE 13180, 7p

Publication Year: 1984

CODEN: SEAPAZ

Language: English

Document Type: PA; (Conference Paper)

Journal Announcement: 8502

High quality carbon dioxide foam fracturing has become a very popular new stimulation tool in the past two years. Dynamic fluid loss measurements were performed on a broad range of core samples to measure the effect of several parameters on CO//2 foam fluid loss coefficients. The parameters tested were core permeability, foam quality, gelling agent concentration in the aqueous phase, and core temperature. Measurements were performed in a recirculating fluid flow test loop. A variation of one order of magnitude in  $C_w$  for two orders of magnitude change in permeability was observed from 0.02 to 10 md. 8 refs.

1/7/12  
01852861 Monthly No: EIM8502-007404  
HIGH-TEMPERATURE RHEOLOGICAL STUDY OF FOAM FRACTURING FLUIDS.  
Harris, Phillip C.; Reidenbach, Vincent G.  
Halliburton Services  
Conference Title: 59th Annual Technical Conference and Exhibition  
(Society of Petroleum Engineers of AIME).  
Conference Location: Houston, TX, USA Conference Date: 1984 Sep 16-19  
Sponsor: Soc of Petroleum Engineers of AIME, Richardson, TX, USA  
E.I. Conference No.: 05224  
Source: Society of Petroleum Engineers of AIME, (Paper) SPE Publ by Soc  
of Petroleum Engineers of AIME, Richardson, TX, USA SPE 13177, 8p  
Publication Year: 1984  
CODEN: SEAPAZ  
Language: English  
Document Type: PA; (Conference Paper)  
Journal Announcement: 8502  
Nitrogen foam properties were measured up to 300 DEGREE F in a high  
temperature and pressure recirculating loop viscometer. Foam fluids did not  
thin as rapidly as gel fluids under similar conditions. Therefore, foams  
offer inherent advantages for high temperature stimulation work. Higher  
gelling agent concentrations do not improve dynamic foam stability. Rather,  
high temperature dynamic stability is dependent upon surfactant type and  
concentration. Mathematical equations have been developed to describe foam  
rheological behavior from 75 to 300 DEGREE F, 0 to 80 quality, containing 0  
to 80 lb HPG/Mgal in the aqueous phase. 9 refs.

1/7/15

00872618 Monthly No: EI7910080371 E.I. Yearly No: EI79058324

NIOBRARA SHALLOW CHALK COMPLETION AND DEVELOPMENT.

Rohret, Matthew T.

Kans-Nebr Nat Gas Co

Source: Sel Pap of the Heart of Am Drilling and Prod Inst, Liberal, Kans,  
Feb 6-7 1979 Sponsored by Univ of Kans West Regents Cent, Garden City, 1979

8 p.

Publication Year: 1979

Language: ENGLISH

Journal Announcement: 7910

Several types of stimulation treatments have been tried in the tight Niobrara formation of eastern Colorado. High quality foam fracs have proven very successful at keeping water requirements to an absolute minimum, while at the same time providing enough sand for adequate propping of the created fracture. Other techniques that show great promise are alcohol foam fracs, CO<sub>2</sub>-gelled water fracs, and combination frac treatments. 8 refs.

1/7/17

00085140 Monthly No: EI70X029718

Rheological properties of foam in a porous medium.

EVGEN'EV, A. E.; TURNIER, V. N.

I.M.Gubkin Inst of the Petrochemical and Gas Industry, Moscow

Source: Int Chem Eng v 9 n 2 Apr 1969 p 261-3

Publication Year: 1969

Language: ENGLISH

Journal Announcement: 70X0

Foam properties play an important role, especially where it is necessary to isolate low-permeability streaks (intercalations) in the bottomhole zones of wells in underground gas storage facilities. The first field-scale experiment using a foam-forming surfactant, carried out on the Shchelkovsk underground gas storage facility, made it possible to bring into production two wells which were previously shut in because they were producing water and sand. Experiments allow the following conclusions to be drawn: the initiation of foam movement and flow occurs at a definite initial pressure gradient; the threshold pressure gradient depends on the length of time the foam is at rest; consequently, the foam has thixotropic properties; cessation of foam flow takes place at a pressure gradient which is not dependent on the threshold pressure gradient. 7 refs. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Neft i Gaz "13" n 12(1967).

5/7/1

1382234 DE89000715/XAB

Development of Novel EOR (Enhanced Oil Recovery) Methods: Foams for Mobility Control in Surfactant Flooding

Llave, F. M. ; Sturm, J. M. ; Olsen, D. K.

National Inst. for Petroleum and Energy Research, Bartlesville, OK.

Corp. Source Codes: 079684000; 9516859

Sponsor: Department of Energy, Washington, DC.

Report No.: NIPER-369

Jan 89 44p

Languages: English

Journal Announcement: GRAI8912; NSA1400

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NTIS Prices: PC A03/MF A01

Country of Publication: United States

Contract No.: FC22-83FE60149

The use of foam as a novel method for mobility control in surfactant flooding was investigated. This report presents an initial evaluation of the potential application of foam as a mobility control agent behind a low concentration surfactant flood. This enhanced oil recovery (EOR) process involves the injection of alternate slugs of gas and surfactant solution as drive fluids behind the active surfactant slug front as an alternative to the use of polymers in order to eliminate unfavorable surfactant-polymer interactions. Experiments were performed to determine in situ foam generation and propagation using varying concentrations of surfactants in a Berea sandstone core. An apparatus was designed and built to accurately measure differential pressures along sections of the core. Bottle or shake tests using the various concentrations of surfactants and experiments to determine the effect of foam flow on reducing mobility and involved steady-state measurement of differential pressures in the presence of foam were performed. Coreflood displacement experiments in the presence of oil were performed using varying concentrations of surfactants to compare various injection modes and oil recovery efficiency. 15 refs., 18 figs., 5 tabs. (ERA citation 14:012580)

5/7/2  
1379087 DE89000722/XAB  
Chemical Additives for Improving Steamflood Performance: Final Report,  
January 1, 1984-May 31, 1987  
Handy, L. L.  
University of Southern California, Los Angeles. Dept. of Petroleum  
Engineering.  
Corp. Source Codes: 016356111; 9507194  
Sponsor: Department of Energy, Washington, DC.  
Report No.: DOE/SF/11999-2  
Jan 89 115p  
Languages: English  
Journal Announcement: GRAI8911; NSA1400  
Portions of this document are illegible in microfiche products.  
NTIS Prices: PC A06/MF A01  
Country of Publication: United States  
Contract No.: AS03-84SF11999

Relative oil and water permeabilities have been measured experimentally as functions of both temperature and interfacial tension. The effect of temperature appears to shift the curves in the direction of more water wet systems. Reducing interfacial tension or increasing the capillary number above about 10 (sup -3) moves the curves in the direction towards a direct proportionality between the relative permeability of the specific phase and its corresponding saturation, which might be predicted for totally miscible fluids. Correlations have been developed which permit the application of these data in the simulator model. Questions are discussed with respect to the use of the capillary number and the residual wetting phase saturation in the correlations for the wetting phase. Studies have continued on the mechanism of foam flow. Of particular interest are open tap pressure measurements in the presence of foam which suggest that the gas in the foam is semi-continuous with a pressure greater than the liquid by an amount about equal to the capillary entry pressure. This suggests, but does not prove, that the bubble concept of flow for foams is not the correct one. (ERA citation 14:012574)

5/7/3

1332600 DE88005268/XAB

Influence of Surfactants on the Flow of Long Bubbles Through Cylindrical Capillaries

Ginley, G. M. ; Radke, C. J.

Lawrence Berkeley Lab., CA.

Corp. Source Codes: 086929000; 9513034

Sponsor: Department of Energy, Washington, DC.

Report No.: LBL-24370; CONF-880659-1

Dec 87 14p

Languages: English Document Type: Conference proceeding

Journal Announcement: GRAI8819; NSA1300

Symposium on advances in oil field chemistry, Toronto, Canada, 5 Jun 1988.

NTIS Prices: PC A03/MF A01

Country of Publication: United States

Contract No.: AC03-76SF00098

Foam is a promising fluid for increasing mobility control in underground enhanced oil recovery. An understanding of the fundamentals of foam flow in porous media may be gained by studying the flow of surfactant-stabilized bubble trains in capillary tubes. Thus, by scaling arguments similar to those used for non-Newtonian polymer solutions (3), it appears possible to predict foam-flow behavior in porous media using measurements of a theory for bubble flow in tubes. This work considers the behavior of a single gas bubble in a capillary with the continuous liquid phase containing surfactant whose concentration is near or above the critical micelle concentration. We extend Bretherton's analysis for a clean gas bubble to include the effects of a kinetically hindered, soluble surfactant in the liquid phase on the shape of the bubble, and on the resulting pressure drop across the bubble. 6 refs., 3 figs. (ERA citation 13:031486)

5/7/4  
1235506 DE86000300/XAB  
Enhanced Oil Recovery by CO<sub>2</sub> (2) Foam Flooding. Final Report, October 1,  
1981-December 31, 1985  
Patton, J. T.  
New Mexico State Univ., Las Cruces. Engineering Research Center.  
Corp. Source Codes: 012643001; 9521000  
Sponsor: Department of Energy, Washington, DC.  
Report No.: DOE/MC/16551-19  
Sep 86 202p  
Languages: English  
Journal Announcement: GRAI8709; NSA1100  
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copy available until stock is exhausted.  
NTIS Prices: PC A10/MF A01  
Country of Publication: United States  
Contract No.: AC21-81MC16551

The objective is to identify commercially available additives which are effective in reducing the mobility of carbon dioxide, CO<sub>2</sub>, thereby improving its efficiency in the recovery of tertiary oil, and which are low enough in cost to be economically attractive. During the course of the project significant progress has been made in developing a commercial method of reducing the mobility of carbon dioxide in enhanced oil recovery processes. Experiments on gas mobility control, conducted in linear sand-pack models, show only a general correlation with the static foam test. The static test, which utilizes a blender to generate foam from an aqueous surfactant solution, is useful mainly for studying the effects of pH, temperature, salinity and crude oil on the relative foamability of any given surfactant. Surfactants that produce reasonable quantities of foam in the blender test also impart some degree of mobility control to gas during two-phase flow. The best mobility control additives however, are only modest foam volume producers. In addition, the best additives spontaneously produce a viscous foam under flow conditions and rates typical of petroleum reservoirs. Three basic chemical structures listed below appear to show most promise for gas mobility control: (1) ethoxylated adducts of C<sub>8</sub> to C<sub>14</sub> linear alcohols; (2) sulfate esters of ethoxylated C<sub>9</sub> to C<sub>16</sub> linear alcohols; (3) low molecular weight co-polymers of ethylene oxide and propylene oxide. For an immiscible CO<sub>2</sub> flood, reducing CO<sub>2</sub> mobility by a factor of 10 increased overall recovery by 20 percent. More importantly, incremental oil production was more than doubled during the early phase when only CO<sub>2</sub> was injected. Attempts to simulate the mobility controlled miscible CO<sub>2</sub> process were not successful. More work is planned. 98 refs., 73 figs., 23 tabs. (ERA citation 11:049772)

5/7/5

204881 DES6000290/XAB

Foams in Porous Media

Marsden, S. S.

Stanford Univ., CA. Petroleum Research Inst.

Corp. Source Codes: 009225154; 9504372

Sponsor: Department of Energy, Washington, DC.

Report No.: DOE/SF/11564-15; SUPRI-TR-49

Jul 86 27p

Languages: English

Journal Announcement: GRAI8620; NSA1100

NTIS Prices: PC A03/MF A01

Country of Publication: United States

Contract No.: AC03-81SF11564

In 1978 a literature search on selective blocking of fluid flow in porous media was done by Professor S.S. Marsden and two of his graduate students, Tom Elson and Kern Huppy. This was presented as SUPRI Report No. TR-3 entitled "Literature Preview of the Selected Blockage of Fluids in Thermal Recovery Projects." Since then a lot of research on foam in porous media has been done on the SUPRI project and a great deal of new information has appeared in the literature. Therefore we believed that a new, up-to-date search should be done on foam alone, one which would be helpful to our students and perhaps of interest to others. This is a chronological survey showing the development of foam flow, blockage and use in porous media, starting with laboratory studies and eventually getting into field tests and demonstrations. It is arbitrarily divided into five-year time periods. 31 refs. (ERA citation 11:033675)

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5/7/6

175148 DE86000260/XAB

Apparent Viscosity Measurements of Surfactant Foam in Porous Media  
Treinen, R. J. ; Brigham, W. E. ; Castanier, L. M.

Stanford Univ., CA. Petroleum Research Inst,

Corp. Source Codes: 009225154; 9504372

Sponsor: Department of Energy, Washington, DC.

Report No.: DOE/SF/11564-13

Dec 85 37p

Languages: English

Journal Announcement: GRAI8608; NSA1100

Report No. SUPRI TR-48.

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NTIS Prices: PC A03/MF A01

Country of Publication: United States

Contract No.: AC03-81SF11564

The apparent viscosity of surfactant foam in a sand pack model was measured at reservoir flow velocities. The effects of foam quality, surfactant concentration, and flow rate were investigated. Ottawa sand, 120 to 140-mesh, was packed into a 1 by 24 inch tube. Porosity was 38%, and permeability ranged from 5 to 8 darcies. Foam of a known quality and flow rate was continuously injected into the sand pack until a steady state condition was reached. Pressure drop was measured across three different segments of the sand pack. A system back pressure of 50 psig was applied to minimize changing foam quality caused by gas expansion. The surfactant used in this study was Suntech IV. All measurements were made at room temperature. Results show that the apparent viscosity of surfactant foam ranges from 50 to 70 centipoise at reservoir flow velocities. Increasing the foam quality corresponded to small increase in the apparent viscosity of foam. Changes in surfactant concentration from 0.005 to 0.05 wt % caused a rapid increase in apparent viscosity. Changes in concentration above 0.05 wt % had little effect on apparent viscosity. Increasing the flow rate resulted in a reduction of the apparent viscosity of foam. This pseudo-plastic flow behavior has been widely reported in the literature. The apparent viscosity of foam in porous media was significantly effected by flow rate history. 21 refs., 15 figs., 2 tabs. (ERA citation 11:008294)

5/7/7

1072912 DE84012410

Flow of Foam Through Porous Media

Owete, O. S. ; Brigham, W. E.

Stanford Univ., CA. Petroleum Research Inst.

Corp. Source Codes: 009225154; 9504372

Sponsor: Department of Energy, Washington, DC.

Report No.: DOE/SF/11564-6; SUPRI-TR-37

Jun 84 124p

Languages: English

Journal Announcement: GRA18420; NSA0900

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NTIS Prices: PC A06/MF A01

Country of Publication: United States

Contract No.: AC03-81SF11564

This study focuses on the pore level behavior of foam in porous media. Air was injected into porous micromodels which had previously been filled with an aqueous solution of surfactant. The micromodels consist of an etched silicon wafer anodically bonded to a glass plate. The model simulates a monolayer of porous matrix. Three homogenous models of different pore dimensions and one heterogeneous model were used. Visual observations were made to determine the flow characteristics of foam under varying air injection rates, pore dimensions and surfactant concentration. Foam flow mechanisms, as observed in the micromodels, were recorded on video tapes. These tapes are available at the Stanford University Petroleum Research Institute, Stanford, California. The observed mechanisms can be broadly classified into two: membrane and foam bubble propagation. Propagation of membranes, air-liquid interfaces, occurred in the homogeneous porous media at both low and high surfactant concentrations, and in the heterogeneous model at low surfactant concentration. Foam bubble propagation occurred only in the heterogeneous model at high surfactant concentrations. In the homogeneous micromodels, the wetting phase (surfactant solution) formed a continuous liquid network around the matrix. The air was found to propagate as tubular bubbles moving and extending over several pores. The flow mechanism was only slightly affected when different air injection rates, pore dimensions and surfactant concentrations were used. Foam was found to be generated in the heterogeneous model. Air and liquid were propagated by a combination of channel flow (with liquid confined to small pores) and a bubble break and reform process. The break and reform process was caused by snap-off actions at pore constrictions. A considerable reduction of effective mobility was observed in the presence of foam, compared to air-water systems without surfactant. 44 references, 43 figures, 5 tables. (ERA citation 09:025299)

5/7/8

1010426 DE83013818

Enhanced Oil Recovery by CO<sub>2</sub> Foam Flooding. First Annual Report (Ethoxylated Adducts of C<sub>8</sub>-C<sub>14</sub> Linear Alcohols; Sulfate Esters of Ethoxylated C<sub>9</sub>-C<sub>16</sub> Linear Alcohols; Low Molecular Weight CO-Polymers of Ethylene Oxide and Propylene Oxide)

Patton, J. T.

New Mexico State Univ., Las Cruces. Dept. of Chemical Engineering.

Corp. Source Codes: 012643025; 9504341

Sponsor: Department of Energy, Washington, DC.

Report No.: DOE/MC/16551-6

Jun 83 87p

Languages: English

Journal Announcement: GRAI8325; NSA0800

NTIS Prices: PC A05/MF A01

Country of Publication: United States

Contract No.: AC21-81MC16551

The objective is to identify commercially available additives which are effective in reducing the mobility of carbon dioxide, CO<sub>2</sub>, thereby improving its efficiency in the recovery of tertiary oil, and which are low enough in cost to be economically attractive. During the past year significant progress has been made in developing a commercial method of reducing the mobility of carbon dioxide in enhanced oil recovery processes. Interest in the industry is high and several companies have agreed to underwrite a portion of funding necessary to continue the research over the next two years. Experiments on gas mobility control, conducted in linear sand-pack models, show only a general correlation with the static foam test. In general, all surfactants that produce reasonable quantities of foam in the blender test also impart some degree of mobility control to gas during two-phase flow. The best mobility control additives however, are only modest foam volume producers. In addition, the best additives spontaneously produce a viscous foam under flow conditions present in a petroleum reservoir. Three basic chemical structures listed below appear to show most promise for gas mobility control: (1) ethoxylated adducts of C<sub>8</sub>-C<sub>14</sub> linear alcohols, (2) sulfate esters of ethoxylated C<sub>9</sub>-C<sub>16</sub> linear alcohols, (3) low molecular weight co-polymers of ethylene oxide and propylene oxide. (ERA citation 08:038444)

5/7/9

953233 DE82906120

Enhanced Oil Recovery by CO sub 2 Foam Flooding. Final Report  
Patton, J. T.

New Mexico Energy Research and Development Inst., Albuquerque.

Corp. Source Codes: 075399000; 9514573

Sponsor: New Mexico State Univ., Las Cruces. Dept. of Chemical  
Engineering.

Report No.: NP-2906120

Jul 82 152p

Languages: English

Journal Announcement: GRAI8307; NSA0700

Portions of document are illegible.

NTIS Prices: PC A08/MF A01

Country of Publication: United States

The objective of this project is to identify commercially available additives which are effective in reducing the mobility of carbon dioxide, CO sub 2, thereby improving its efficiency in the recovery of tertiary oil, and which are low enough in cost to be economically attractive. Experiments on gas mobility control, conducted in linear sand-pack models, show only a general correlation with the static foam test. The static test, which utilizes a blender to generate foam from an aqueous surfactant solution, is useful mainly for studying the effects of pH, temperature, salinity and crude oil on the relative foamability of any given surfactant. In general, all surfactants which produce reasonable quantities of foam in the blender test also impart some degree of mobility control to gas during two-phase flow. The best mobility control additives; however, are only modest foam volume producers. They all spontaneously produce a viscous foam under flow conditions present in a petroleum reservoir. Three basic chemical structures appear to show most promise for gas mobility control: (1.) Ethoxylated adducts of C sub 8 - C sub 14 linear alcohols; (2.) Sulfate ethers of ethoxylated C sub 9 - C sub 16 linear alcohols; and (3.) Low molecular weight co-polymers of ethylene oxide and propylene oxide. A significant portion of the research effort centered on the rheology of foams. These studies were conducted in small capillaries of varying length and diameter. Mobility control increased recovery by 40% over a CO sub 2 enhanced waterflood and 93% over a conventional waterflood plus primary production. No adverse effects, such as emulsion formation, due to mobility control additives were noted. Mass transfer of CO sub 2 from the foam to the oil did not appear to be impeded. (ERA citation 07:052662)

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5/7/11

338434 DOE/MC/03259-10

Enhanced Oil Recovery by CO sub 2 Foam Flooding. Second Annual Report  
New Mexico State Univ., Las Cruces. Dept. of Chemical Engineering.

Corp. Source Codes: 012643025; 9504341

Sponsor: Department of Energy, Bartlesville, OK. Bartlesville Energy  
Technology Center.; Department of Energy, Washington, DC.

Nov 80 36p

Languages: English

Journal Announcement: GRAI8115; NSA0600

NTIS Prices: PC A05/MF A01

Country of Publication: United States

Contract No.: AC21-78MC03259

The objective is to identify commercially available additives which are effective in reducing the mobility of carbon dioxide, CO sub 2, thereby improving its efficiency in the recovery of tertiary oil, and which are low enough in cost to be economically attractive. During 1980 significant progress has been accomplished on each major contract objective. The apparatus, design and construction phase of this project is essentially complete. Correlation work on dynamic foam stability, in two-phase flow experiments in a linear sandpack, has shown that the most active foaming agents, as identified in static tests, may not necessarily be the best choices for mobility control in the field. The Alipal CD128-Monamid 150AD system, the leading foam generator in the static test, is slightly inferior to an ethoxylated alcohol, Neodol 23-6.5, that produces only a modest amount of foam in the static test. In the dynamic test, Neodol 23-6.5 lowered gas mobility by about a factor of 2 greater than the Alipal system. Both systems are outstanding in their performance, and further comparative tests are scheduled. A third structure which looks promising based on the interpretation of the above test is a Pluronic surfactant whose hydrophobe consists of polypropylene oxide rather than a linear alcohol as used in the Neodol surfactants. Additional tests on the hydrolysis rate of Alipal-type surfactants indicate that molecular breakdown may not be as rapid as at first suspected. Under neutral conditions the half-life of ethoxylated alcohol sulfates appears to be two to three years at a reservoir temperature of 120 exp 0 F. The Neodol and Pluronic structures should be even more stable. (ERA citation 06:010242)