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Preliminary Survey of Polymer-Impregnated Rock

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By Lester J. Crow, Dennis J. Kelsh, Meyer Steinberg,
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PRELIMINARY SURVEY OF POLYMER-IMPREGNATED ROCK

by

Lester J. Crow,[1] Dennis J. Kelsh,[2] Meyer Steinberg,[3] and Peter Colombo[4]

ABSTRACT

A preliminary survey was performed to investigate the impregnation of relatively weak, porous volcanic tuff and a relatively strong, dense sandstone with five different monomers. Increases in compressive strengths by factors of 2 to 5, and elastic moduli by factors of 2 to 3.5, are reported for natural rocks (tuff, sandstone, dacite), which were impregnated with five monomers (methyl methacrylate; chlorostyrene; 40 percent TMPTMA-60 percent styrene; 40 percent TMPTMA-60 percent chlorostyrene; 60 percent polyester-40 percent styrene); polymerization took place after monomers were forced into the rock. Impregnation was performed (1) by pressurizing rock specimens from one end, or (2) by a vacuum-soak operation. Polymerization was accomplished by either radiation or chemical initiation techniques.

Strength improvement is dependent on (1) the type of monomer used, (2) the amount of polymer incorporated into the rock, and (3) the degree of water saturation of the rock. Water saturation strongly reduced the effectiveness of the method for the polymer systems tested. The more viscous monomers (for example, 60 percent polyester-40 percent styrene) were more effective in displacing the water from the rock, and compressive strengths of wet rock were doubled with these systems. Water saturations ranging from 25 to 100 percent of maximum saturation gave essentially identical results.

Further tests on other types of mine rock, including shale and coal, are planned. Water-compatible polymer systems should be developed, or present systems should be suitably modified. For application to tunnel stabilization, design studies evaluating the improvement in rock strength and its influence on the support system are also recommended.

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INTRODUCTION

Strengthening of soils by injection of grout has been an engineering practice for some time. Most commonly used are dilute suspensions of finely granulated solids (for example, cement), which work very well in loosely compacted, porous material or for sealing rather large cracks or rock fissures. The suspended material will penetrate rock pores approximately twice the diameter of the suspended particles, but smaller pores will not be filled. Consequently, only materials which are true solutions will completely fill all voids in a porous body. Such materials are commonly called chemical grouts.

The Bureau of Mines has recognized the need for new, efficient ground support in underground workings, particularly in view of the inadequacy of older practices such as timbers, concrete beams, rock bolts, etc. Hence, the potential application of chemical grouting as the primary method of control motivated this study at the Spokane Mining Research Laboratory (SMRL) in July 1968. An extensive survey of chemical grouts currently utilized revealed that most of them, although providing good soil penetration and adequate sealing against water flow, do not impart appreciably greater strength to soil or broken rock.

However, utilization of epoxy and polyester resins to achieve ground control by injection through drill holes considerably improved competence and strength of fractured mine rock. Studies by the Bureau of Mines have indicated how such systems can be used to cement coal-mine roof strata (5),[5] as well as to stabilize bolted, fractured wall rock along passageways in a western gold mine (6). In the latter instance, the resin was used to anchor steel reinforcing bars placed in boreholes in the fractured rock. The resin was pumped under pressure into the holes and intersecting fractures until the wall rock was thoroughly impregnated. These reports suggested that resin or resin-rebar support could be exploited advantageously and economically in mining practice, but neither method has received wide acceptance.

The survey then turned to new materials not in present-day use, which could, under moderate pressure, thoroughly penetrate natural mine rock in a reasonably short time, and combine with the rock to form a composite material of high strength. If the proper material could be discovered and a method of rapid application developed, safety for the miner could be achieved in addition to improved mining efficiency. Elimination of internal supports such as timbers (in favor of support created within the rock itself) would allow usage of smaller entries and passageways and also markedly reduce the materials-handling problem.

In December 1968, scientists at Brookhaven National Laboratory (BNL) and the U.S. Bureau of Reclamation (USBR) reported dramatic increases in tensile and compressive strengths of concrete as a result of impregnation with polymer-forming materials, followed by in-situ polymerization (1). Loading of concrete to the point of saturation (up to 6.7 percent by weight) with

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[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

polymethylmethacrylate resulted in increases in compressive and tensile strengths of approximately 400 percent (from 5,000 to 20,000 psi compressive strength, and from 400 to 1,600 psi tensile strength).

In recognition of the possibility of enhancing the strength of natural rock by similar techniques, and thereby creating a totally new method of structural support for underground-mine openings, a cooperative project was begun in July 1969 by the Bureau of Mines and Brookhaven National Laboratory. The program was primarily aimed at developing monomer systems for underground usage. This is a preliminary report of the results of that study.

Brief Review of Concrete-Polymer Work

Since early 1967, the Brookhaven National Laboratory and the Bureau of Reclamation, in a joint program supported by the U.S. Atomic Energy Commission (AEC) and the Department of the Interior, have been developing polymer-impregnated concrete composites as improved construction materials. These composites, or concrete-polymer materials, are prepared by impregnating cured precast concrete mixes with a liquid monomer, which is polymerized in situ by radiation or chemical initiation. This treatment of concrete yields very significant improvements in strength and durability. For example, (1) the compressive and tensile strength increases by a factor of 4, (2) the modulus of elasticity almost doubles, (3) the modulus of rupture increases by a factor of 3.5, (4) the hardness is nearly doubled, (5) water permeability and water absorption decrease to a negligible value, and (6) resistance to chemical attack by distilled water, sulfate brines, and acid is markedly improved. Two complete reports describing the tests performed on this material have been published (1-2).

A number of applications of concrete-polymer have been suggested: concrete sewage and pressure pipe, building materials for housing and for underwater structures, and improved materials for highway construction; for example, in bridge decking. A special application being studied for the Office of Saline Water is in the construction of multistage, flash-distillation units in desalination plants. For this application, resistance to chemical attack by hot brine is important, in addition to improvement in strength properties.

Application to Underground-Support Program

A desire to develop a rapid, effective, and economically competitive method of mine support through polymer impregnation prompted some exploratory studies at SMRL and BNL early in 1969. A porous rock, "dacite," was impregnated with methyl methacrylate, and the polymerized specimens were tested for compressive strength and Young's modulus. Based on the improved strength of these specimens, a more detailed program was organized. Its purpose was to perform a series of preliminary survey tests--involving several different monomers--to determine the effects of moisture and impregnation (from one surface only) on the strength properties of two types of polymer-impregnated rock specimens. These factors would be important in applying the impregnation process to the wall structure of a mine.

The monomer survey work, methods of impregnation, and results of strength tests are the subject of this report; the work was performed from July 1969 through June 1970. To assist the reader, a matrix of the test program is shown in figure 1.

ACKNOWLEDGMENTS

The authors wish to acknowledge the helpful aid in program planning of W. R. Wayment of the Spokane Mining Research Laboratory, B. Manowitz of Brookhaven National Laboratory, E. R. Podnieks of Twin Cities Mining Research Center, and W. E. Mott and G. J. Rotariu of the U.S. Atomic Energy Commission. P. Chamberlain of Twin Cities Mining Research Center supervised the determination of porosity and permeability of rocks, impregnation of rocks with predetermined amounts of water, and structural testing of rock cores. J. Fraley of Spokane Mining Research Laboratory evaluated monomer systems and tested polymer-impregnated rock slabs. J. Fontana, L. Jefferson, and G. Farber of Brookhaven National Laboratory performed impregnation of the rock cores.

BACKGROUND: POLYMERIZATION

Monomer Survey

Properties of Monomers

Polymerization is basically a process of creating very large molecules (polymers) from hundreds or thousands of small molecules (monomers). To form polymers, the monomers must be capable of reacting with two or more other molecules to form a link in the chain; that is, the monomers must be at least difunctional. Consequently, only certain types of chemical compounds can participate in polymer formation.

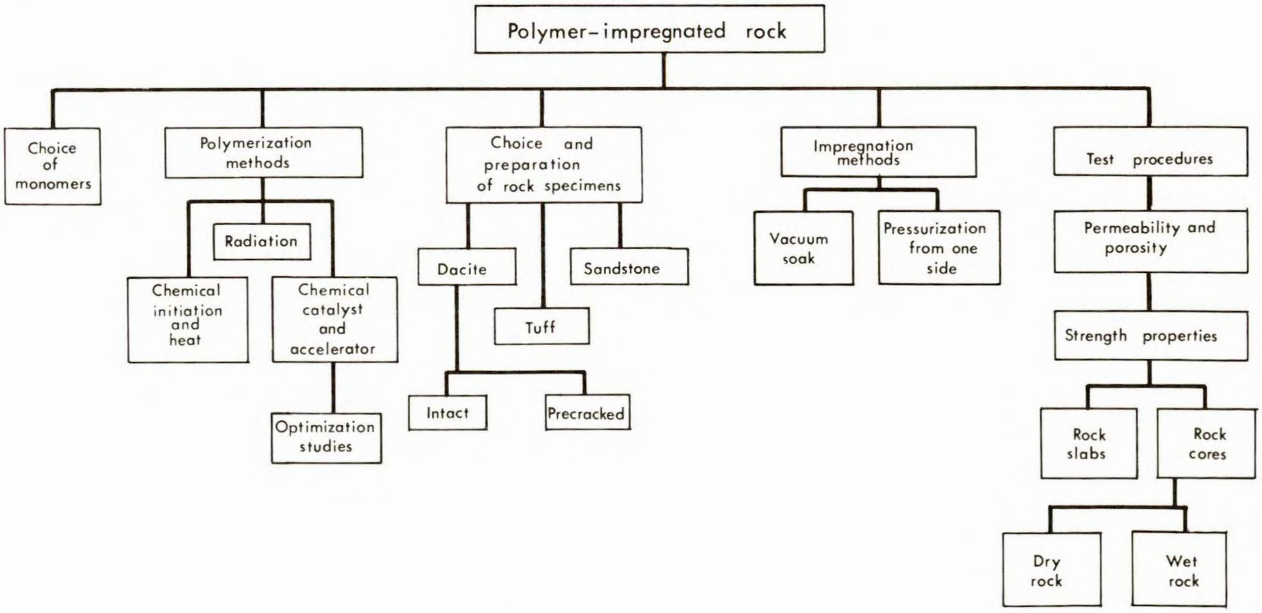

FIGURE 1. - Test Program Matrix.

Historically, polymers have been divided into two broad classes: condensation polymers, in which the molecular formula of the structural unit lacks certain atoms present in the monomer from which it is formed; and addition polymers, in which the molecular formula of the structural unit is identical with that of the monomer from which the polymer was derived. With respect to their potential as strength-enhancing agents in natural rock, this classification is perhaps a very useful one. Two characteristics of condensation polymerization seem to work against this process for in situ strengthening of mine rock: the necessity of having high purity and exact stoichiometric amounts of reactants in order to achieve a high molecular weight polymer; and the formation of rather large quantities of water or other byproducts of the condensation process, which are not incorporated into the polymer structure and therefore do not impart strength to the rock. Consequently, this study has concerned itself only with addition polymerizations, which are not subject to these limitations.

Selection of Monomers

The selection of monomers for impregnating rock depends primarily on the properties of the monomer and the corresponding polymer. The most practical type of monomer for mine-wall application is one that remains liquid over the range of temperature normally encountered in mines. In addition, the viscosity of the liquid monomer at ambient mine temperature should be low enough to allow diffusion through a required thickness of rock under reasonable pressure conditions. The ability of a monomer of a given viscosity to diffuse through a rock specimen is governed mainly by the density of the rock, its pore sizes, and its internal structure. Another important property is the vapor pressure of the monomer. Since all organic monomers are volatile to some degree, the two major conditions that must be considered are safety hazards (that is, toxicity and combustibility) and loss of monomer from impregnated mine walls by vaporization prior to polymerization. Selecting monomers with relatively low vapor pressures can minimize both conditions. Finally, the polymer properties resulting from polymerization of the selected monomers should be such that both the physical and chemical properties of the impregnated rock are appreciably enhanced.

Table 1 shows the basic monomer systems selected for initial screening tests. It also gives some values for the monomer properties described earlier. The monomer selections were based on a cross section of the various properties: (1) high- and low-vapor-pressure monomers, (2) cross-linking monomers, (3) low- and high-viscosity monomers, and (4) flame-resistant monomers. The selection of monomers was also founded, in part, on the experience obtained in the concrete-polymer program. They can also be mixed in varying proportions to improve the chemical and physical properties of the monomer or polymer.

TABLE 1. - Properties of selected monomer system

Monomer	Vapor pressure, mm Hg at 20° C	Density, g/cu cm at 25° C	Viscosity, centipoises at 25° C	Polymer density at 25° C
Chlorostyrene...........	0.7	1.01	1.04	1.25
Methyl methacrylate......	35.0	.94	.57	1.24
Styrene..................	5.0	.91	.71	1.05
Trimethylolpropane trimethacrylate (TMPTMA)	<.5	1.06	50.0	-
Polyester-styrene........	≤5.0	1.13	700.0	1.2

Polymerization Methods

Radiation Polymerization

Ionizing radiation as a method of initiating addition polymerizations is well known (3). Radiation-induced polymerization reactions are unique in several important respects. Probably the most significant is that the initiation step is independent of temperature, which allows polymerizations to take place at ambient or lower temperatures. Resultantly, the vapor pressure of the monomer is lower, and this minimizes its vaporization from the impregnated walls.

Since, in effect, the gamma rays act as the catalyst for the reaction, chemical initiators need not be added to the monomer prior to the impregnation step. This fact prolongs the shelf-life of the monomer and eliminates the hazards involved in handling and storage of monomer-catalyst mixed systems. When necessary, the polymerization rates obtained with Co^{60} gamma radiation at ambient temperature can be increased by raising the reaction temperature or by adding to the monomer a chemical initiator such as benzoyl peroxide.

Chemical Initiation and Heat

The most universal commercial technique for conducting free-radical initiated polymerization reactions is that of using a chemical initiator (catalyst) and heating the solution to an elevated temperature. This process involves mixing a chemical initiator with the monomer and subjecting the mixture to a temperature sufficiently high to decompose the initiator. The decomposed initiator then reacts with the monomer, and polymerization begins. The temperature required to sustain the reaction depends on the initiator-monomer system. For application of this technique to mine-wall impregnation, it would probably be necessary to heat the wall area in depth for the time required to complete the reaction.

Chemical Catalyst and Accelerator

Another polymerization technique that does not require elevating the temperature above ambient is the chemical catalyst-accelerator system.

An accelerator is a chemical material that induces the decomposition of the catalyst. The polymerization rates or cure times can be controlled to some extent by varying the catalyst or accelerator concentrations, or by varying the temperature. Normally, as the temperature is increased, the polymerization rate increases. An accelerator, where applicable, eliminates the need for a radiation source or for high-temperature heaters. This reaction takes place readily at room temperature. However, the mix proportion of catalyst and accelerator must be carefully controlled, so that polymerization does not occur prematurely. For mine-wall impregnation, the accelerator could be safely mixed and stored with the monomer. Immediately prior to impregnation, the catalyst can be added to the monomer to allow the greatest possible time for the monomer to diffuse through the mine wall before polymerization takes place.

Optimization of the Monomer-Polymer System

Although each of the polymerization methods discussed above has its attractive features as well as unique problems, the method which presently appears to have the greatest potential for underground utilization is the chemical catalyst and accelerator. Deterring the use of high-energy radiation are (1) the relative slowness of curing (approximately 6 hours under constant irradiation of 3.5×10^5 rad/hour); (2) the radiation-shielding requirements which may necessitate curing by remote control, with no miners permitted in the near vicinity; and (3) the relatively high cost, both of radiation itself and the expenses resulting from the time and shielding requirements mentioned previously.

The difficulties associated with the application of heat to mine walls argue strongly against unpromoted chemical initiation of polymerization. Consequently, considerable effort was devoted to the understanding and optimization of promoted catalytic polymerization. The system chosen for study was felt to be a likely prospect for eventual underground use.

To achieve a superior polymeric product in the shortest polymerization time, various monomer mixtures were prepared and allowed to polymerize in bulk at room temperature. GR-941 polyester resin was diluted either with styrene (S) or monochlorostyrene (MCS), after which various amounts of the cross-linking agent trimethylolpropane trimethacrylate (TMPTMA) were added. Polymerizations were initiated with benzoyl peroxide (BPO) promoted by N, N-dimethylaniline (DMA). Results are tabulated in table 2. The listed amounts of chemicals were added to 400-ml pyrex beakers, with BPO dissolved in S or MCS. A thermocouple was placed under the beaker to measure temperature, and thereby provide an estimate of the heat generated during polymerization.

TABLE 2. - Optimization of monomer-polymer system

Weight of materials, grams					Time, minutes		Maximum temper-ature, ° F	Time of maximum temperature, minutes	Later temper-ature, ° F	Later time, minutes	Condition of polymer
GR-941	Diluent	TMPTMA	BPO	DMA	Gelation	Curing					
32.3	64.9 S	58.3	1.9	0.5	46	55.5	-	-	-	-	Excessive cracking
32.3	64.9 S	58.3	1.9	1.0	32	40.7	-	-	-	-	Do.
26.0	32.5 S	29.2	1.0	.5	28	34.5	-	-	-	-	Do.
51.9	64.9 S	58.3	1.9	1.0	28	35.7	-	-	-	-	Do.
36.0	32.5 S	29.2	1.0	.5	26	32.2	-	-	-	-	Do.
16.2	32.5 S	4.9	1.0	.5	13	23	-	-	-	-	Rubbery
16.2	32.5 S	7.3	1.0	.5	14	24	198	32	149	51	Hard; several cracks
16.2	32.5 S	9.9	1.0	.5	14	22.5	215	31	148	51	Hard; many cracks
16.2	32.5 S	2.5	1.0	.5	10	19	179	28	127	45	Few cracks
16.2	32.5 S	12.3	1.0	.5	15	24.5	212	31	145	51	Hard; many cracks
16.2	32.5 S	14.8	1.0	.5	16	24.5	214	32	148	51	Do.
16.2	32.5 MCS	9.9	1.0	.5	13	19	200	25	140	39	Hard; no cracks--Best
26.0	32.5 MCS	9.9	1.0	.5	14	18	200	26	132	51	Hard; many cracks

The following generalized observations can be made concerning these tests:

1. MCS solutions are more reactive than S solutions.

2. Shorter polymerization times are achieved with solutions having high concentrations of GR-941, but more dilute solutions have lower viscosity.

3. When limited amounts of TMPTMA were added to the reaction system, superior physical properties of polymer were obtained. With no TMPTMA, the polymer was rubberlike; but employing TMPTMA, a hard, tough plastic was formed. Too much TMPTMA caused excessive cracking of the polymer, increased solution viscosity, and increased gel and curing times.

4. To achieve fastest reaction and a superior product, DMA molar concentration should approximately equal BPO concentration.

In conclusion, the optimum mixture of those tested contains the following weight-percentages: GR-941, 27.0 percent; MCS, 54.0 percent; TMPTMA, 16.5 percent; BPO, 1.7 percent; DMA, 0.8 percent. These proportions, however, would vary with the total amount of material polymerized, as the heat generated in large systems would not be dissipated. Consequently, the peak temperature achieved would be raised, and this in turn might cause excessive cracking. In rock, all concentrations will be small; therefore, less thermal energy will be evolved, which results in longer polymerization times. In summary, optimization studies should recognize that total size of impregnated rock, as well as rock porosity, will be critical factors in determining the final choice of material.

TEST PROCEDURES

Preparation and Testing of Rock Specimens

Selection of Specimens

Two very different types of rocks--tuff and an arkose sandstone--were chosen for the initial evaluation of polymerization within the rock as a strength-inducing technique. It was felt that these rocks, which bracket a wide range of porosities and permeabilities, should provide valuable information regarding the effects of concentration of monomer on polymerization rates, rate of monomer penetration, and dependence of strength enhancement on rock porosity.

Tuff was obtained directly from a quarry near Madras, Oreg.; the feldspathic sandstone from Indiana was purchased from a local company dealing in natural building stone. Tuff samples 7 inches square and up to 30 inches in length were sources of the cylindrical cores needed for rock testing; blocks, 10 by 12 by 3 inches, were used for pressure-impregnation tests. The irregularly shaped pieces of arkose sandstone were also cut to the above dimensions. Specimens selected for testing were uniform in texture as determined visually; samples with obvious faults, cracks, etc., were rejected.

Specimen Preparation

Rock specimens were prepared in two ways. In order to test the feasibility of impregnating large-area slabs with monomer, tuff blocks, 3 by 10 by 12 inches, were cut and shipped to Spokane for impregnation. After polymer impregnation and curing, cylindrical cores (1-1/4-inch diameter by 2-1/2-inch length) were prepared from the slabs. Cores were drilled along the diagonal of the slab to observe variations in polymer loading and strength.

Tests performed at BNL were conducted on the standard, cylindrical cores (1-1/4 by 2-1/2 inches), which had been prepared from the natural rocks at SMRL and Twin Cities Mining Research Center (TCMRC). Prior to use, all samples were checked dimensionally. Tolerance limits were 0.25 degree off from perpendicularity between the vertical axis and the ends of the sample, and 0.005-inch-variation in longitudinal dimension.

Permeability and Porosity

Porosity and permeability tests were performed at TCMRC on nonimpregnated cores of tuff and sandstone. Porosity was determined by helium-gas absorption; permeability was ascertained by forcing distilled water through the specimens. Before being tested, all specimens were ultrasonically cleaned and dried.

Porosity results were quite uniform, whereas permeability data exhibited wide variance, particularly for the arkose sandstone. Average results for 10 samples of each type of rock are summarized below (uncertainties reported are standard deviations):

Rock type	Porosity (percent)	Permeability (10^{-3} darcys)	Density (g/cm^3)
Tuff..........	44.36±0.95	22.2 ±11.9	1.564±0.023
Sandstone.....	16.42± .86	.41± .44	2.340± .030

Permeability measurements indicate the rate at which a liquid passes through the rock, whereas porosity specifies the void space in a rock, which also is the upper limit of polymer loading. The large variance in permeability, particularly with sandstone, was reflected in the times required to fully impregnate these samples with monomer.

Strength Properties--Uniaxial Compression Testing

Preliminary evaluations of strength enhancement were based on results of uniaxial compression testing of standard cylindrical cores. Determined were Young's modulus and compressive strength. Compressive loads were applied so as to maintain a constant strain rate of 1×10^{-5} cm/cm/sec.

Methods of Impregnation

Vacuum-Soak Technique

The vacuum-soak method of impregnating rock specimens is similar to that now being used at BNL for impregnating precast concrete (1-2). Although this procedure is not directly applicable to mine-wall treatment, the maximum monomer loadings obtained provide reference data for comparison with other impregnation techniques. The vacuum-soak technique involves the following methodology:

1. Prior to evacuation, all rock specimens are dried to constant weight in a heated oven. They are then cooled to room temperature in a desiccator.

2. As needed, the dried specimens are removed from the desiccator, and evacuated for several hours in a sealed vessel.

3. While under vacuum, monomer is introduced into the vessel to a level above that of the rock specimens. The totally submerged specimens are then allowed to soak, for several hours, under an air-pressure blanket.

4. After soaking, the specimens are removed from the vessel and placed in a curing medium.

Figure 2 shows the apparatus used for preparing specimens by the vacuum-soak technique.

Pressurization From One Side--Rock Slabs

Closely simulating a mine-wall application is impregnation by pressure loading the monomer from one end of a rock specimen. A model device for impregnation of rock slabs with monomer was designed, built, and tested at SMRL, and a patent application submitted.[6] The unit (figs. 3-4) consists of a steel headplate with a flexible flange of vulcanized rubber, which is forced against the rock surface by hydraulic pressure. Monomer is fed through a series of small holes in the back of the headplate, and forced into the rock by air (or nitrogen) pressure. In order to maintain a seal between the head and the rock surface, the total pressure in the head of the machine must be less than the backup hydraulic pressure on the head. If polymerization is initiated thermocatalytically, the catalyst may be premixed with the monomer before entering the machine; or mixing can be accomplished in an extra chamber in the machine head just before application to the rock surface.

With this device, rock slabs (10 by 12 by 3 inches) of tuff and sandstone were successfully impregnated. Complete impregnation of tuff slabs with monochlorostyrene containing 1 percent BPO was performed in 20 to 30 minutes (using 25-psi air pressure), whereas the less permeable sandstone required

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[6] Surface-pressure grouting machine and method of application for underground support, by L. J. Crow and E. W. Parsons. Invention Report MIN-1635, submitted Dec. 4, 1969.

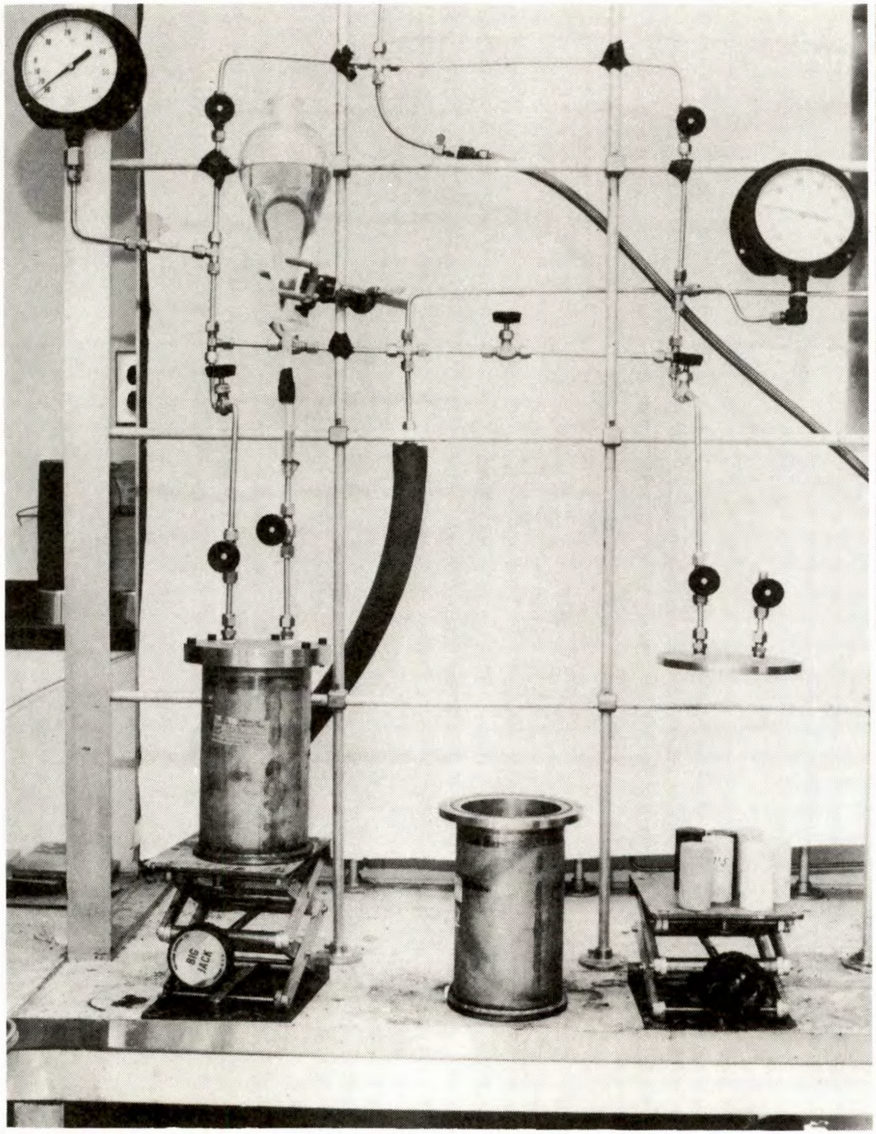

FIGURE 2. - Apparatus for Impregnating Rock Specimens by the Vacuum-Soak Technique.

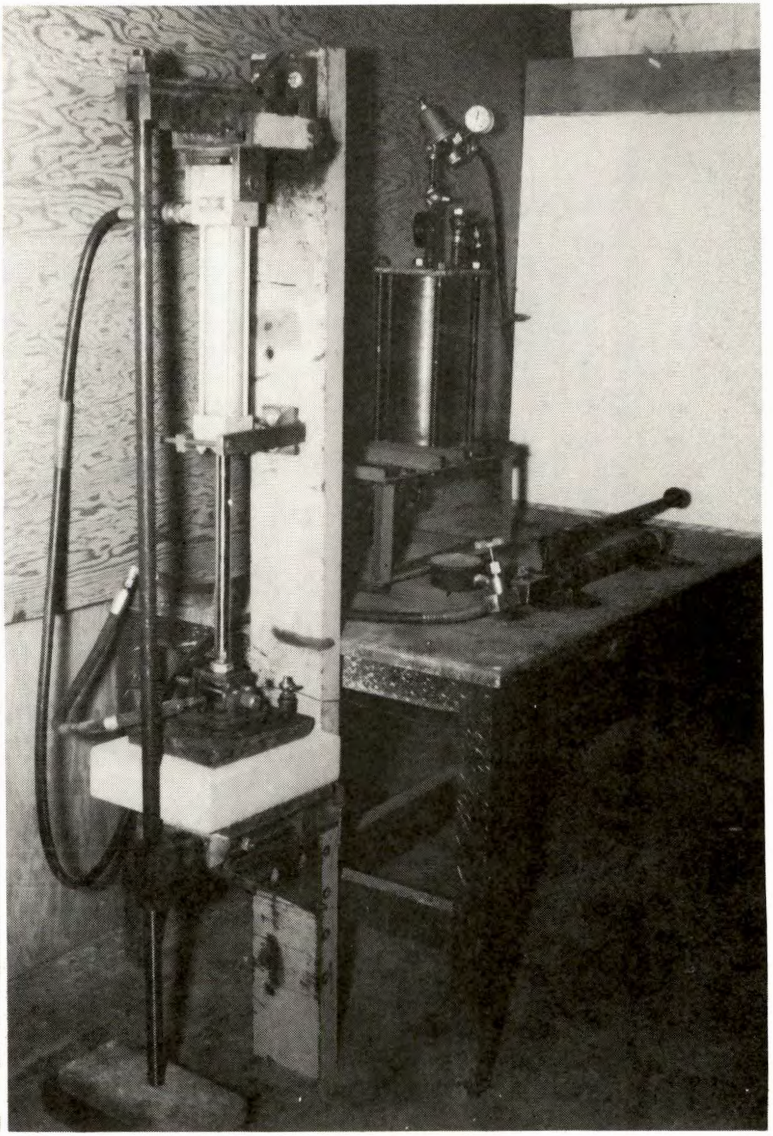

FIGURE 3. - Apparatus for Impregnating Rock Slabs by Pressure Loading From One Side.

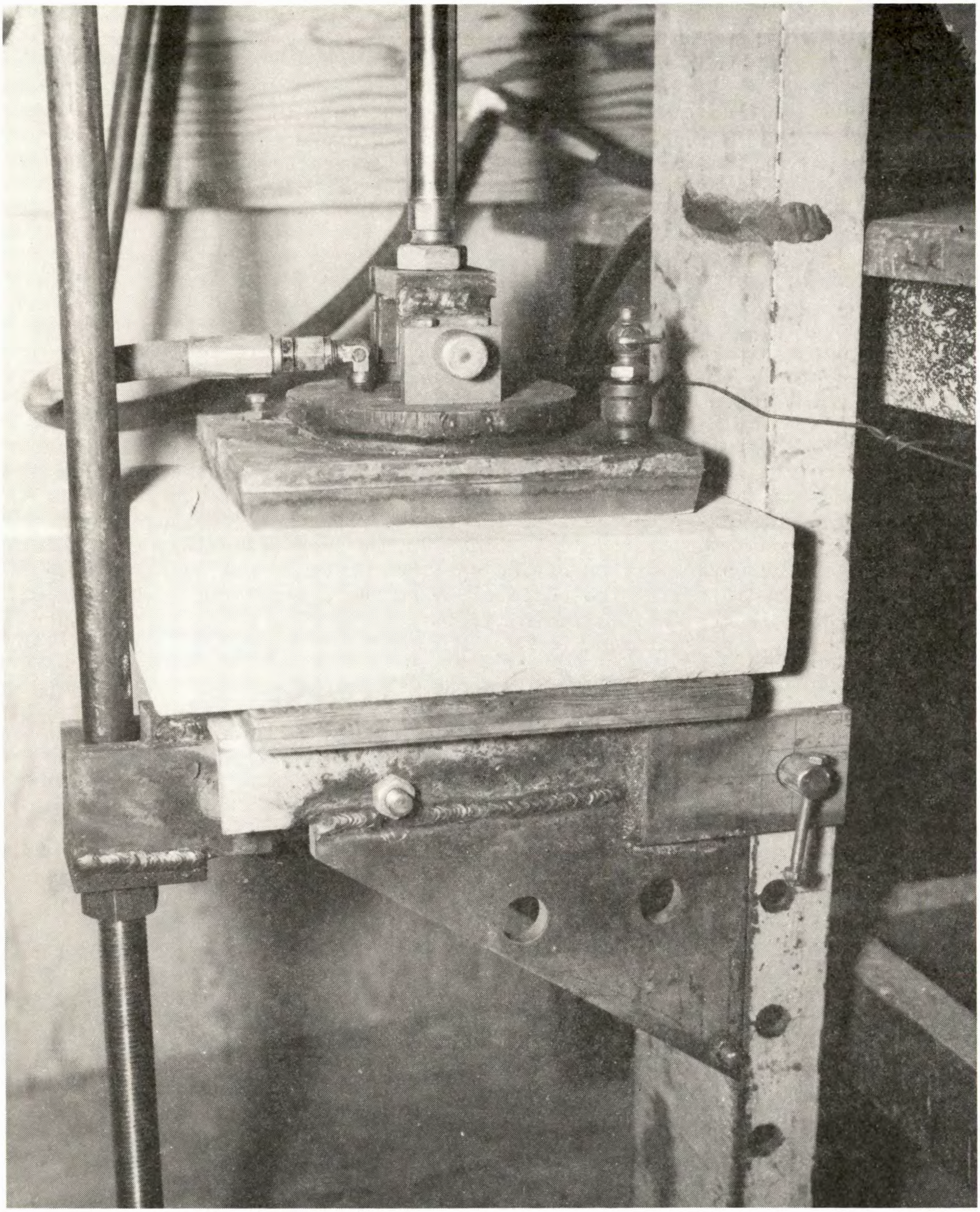

FIGURE 4. - Closeup View of Surface-Pressure Grouting Machine Head With Rock Mounted for Impregnation.

several hours at 90 psi to achieve saturation. More viscous materials (for example, polyester resins) necessitated proportionally greater times and pressure.

Figure 5 displays (A) a 3-inch-thick slab of tuff in its natural state; (B) a similar slab impregnated with monomer and wrapped in a polyethylene sheet to be polymerized in an oven at elevated temperatures (typically 150° F); and (C) a slab of tuff after polymerization has taken place. Figure 6 pictures the slab of figure 5 after core samples (1.25-inch diameter) have been taken.

Pressurization From One End--Rock Cores

The success achieved with the model device for impregnating rock slabs suggested that a similar method could effectively impregnate rock cores. Using the apparatus (figs. 7-8) which was fabricated for this purpose, impregnation is accomplished as follows:

1. The specimen to be impregnated is inserted in a preformed silicone rubber sleeve (fig. 7). The sleeve, which is not affected by the monomer, forms a tight seal between the rock and the wall of the metal rig. A shelf with a central opening at the base of the cylinder prevents the specimen from being pushed through the cylindrical holder during pressurization. The metal insert ring on the upper portion of the specimen prevents the rubber sleeve from collapsing and blocking the surface. When the upper portion of the apparatus is screwed into place, a fitting allows the monomer to be introduced into the system and pressurized.

2. Monomer is then fed into the top of the assembly. The amount introduced is in excess of the calculated requirements for maximum monomer loading

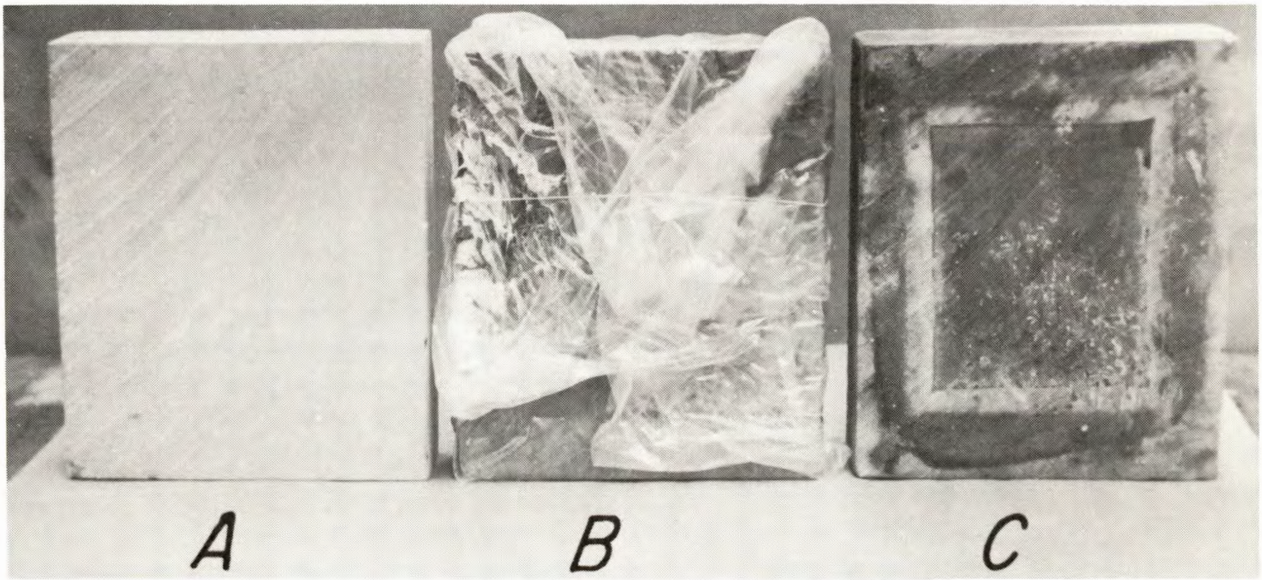

FIGURE 5. - Tuff Slabs: *A*, Before Impregnation; *B*, Impregnated and Wrapped for Oven Curing; and *C*, After Impregnation and Curing.

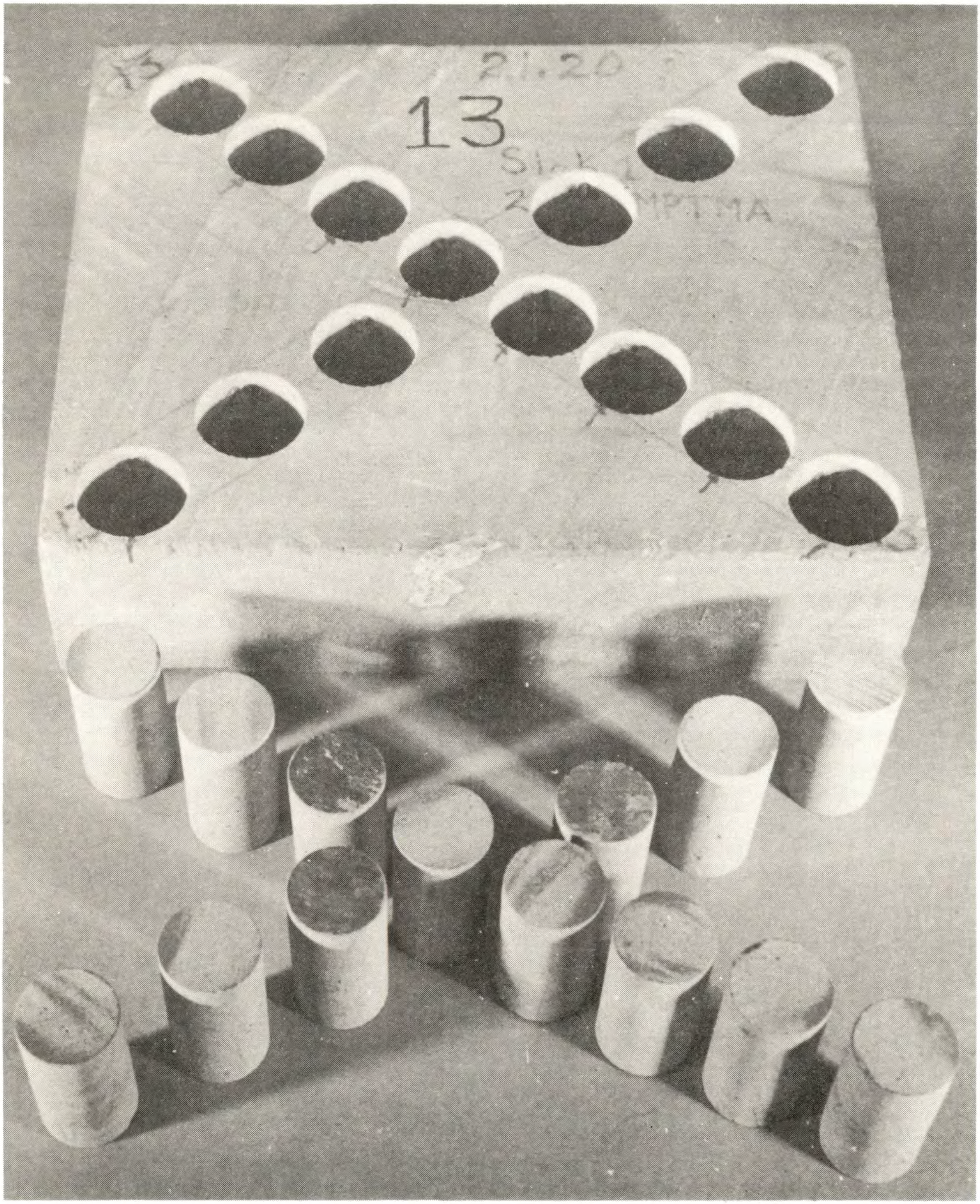

FIGURE 6. - Impregnated Slab After Coring.

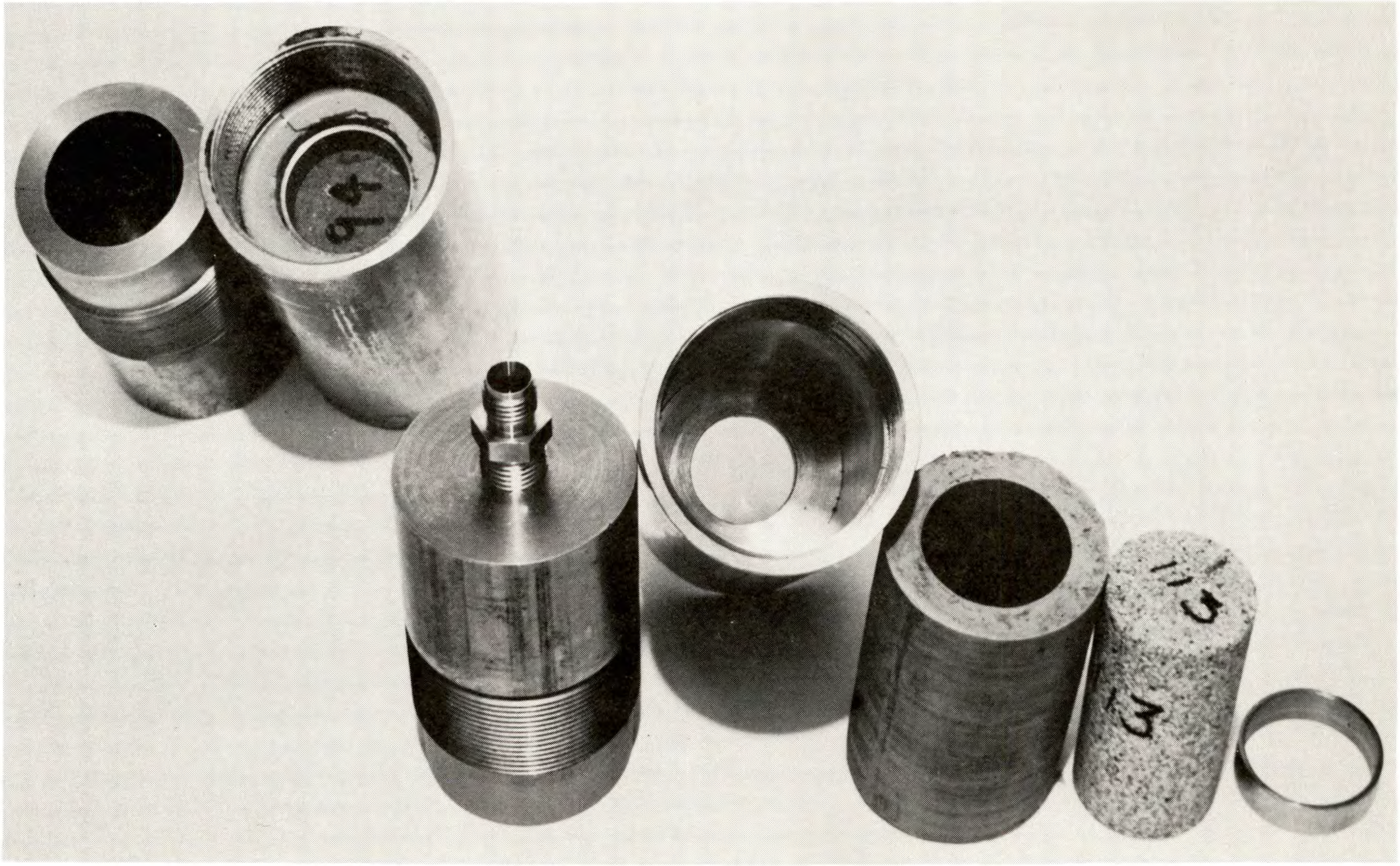

FIGURE 7. - Assemblies for Impregnation of Rock Specimens by Pressurization From One End.

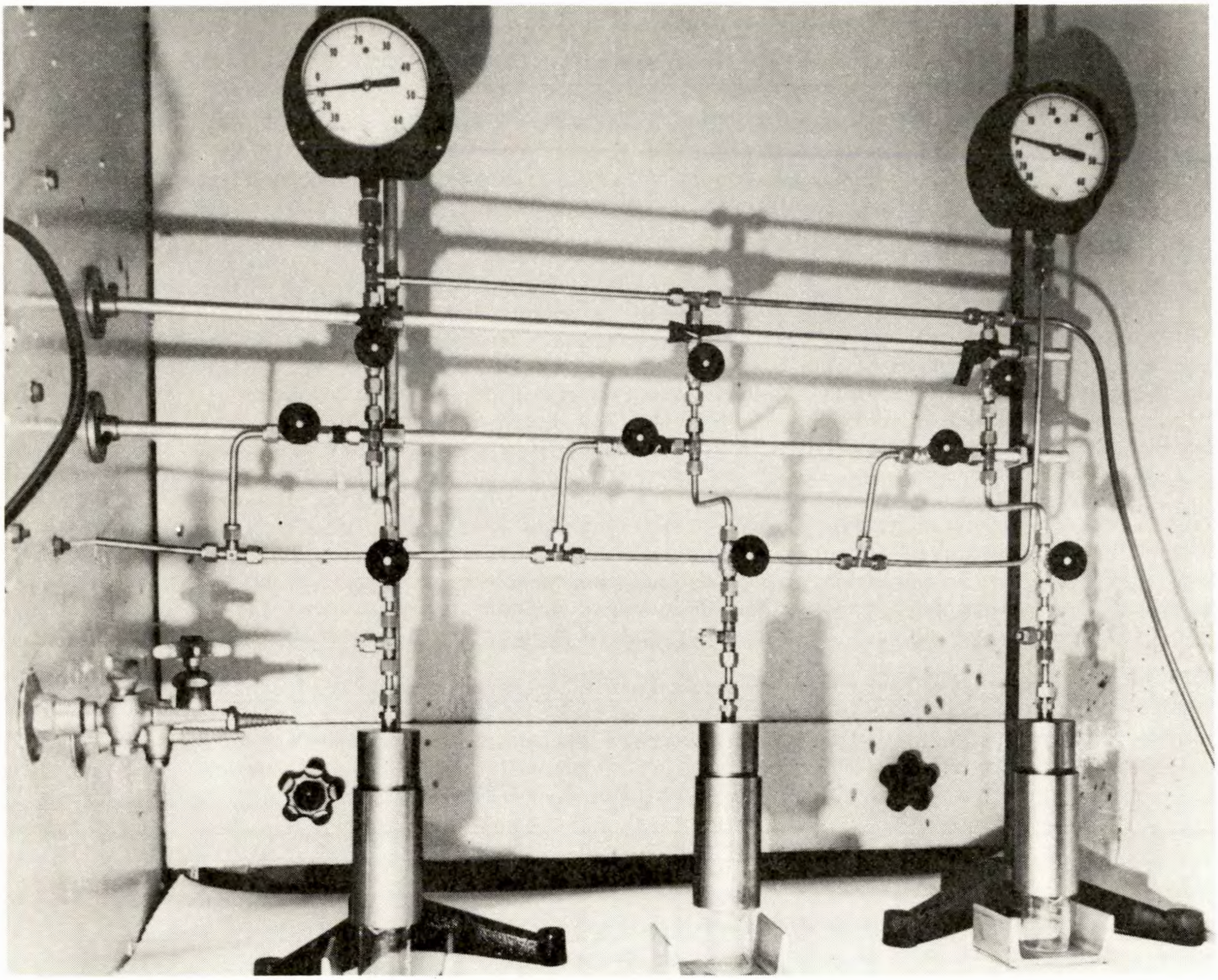

FIGURE 8. - Apparatus for Impregnation of Rock Specimens by Pressurization From One End.

in the rock, based on the reported porosity and the results obtained from the vacuum-soak technique. To reduce the time required for the monomer to diffuse through a given length of rock, air pressure is applied over the monomer.

3. To measure the amount of monomer flowing through the specimen, a collecting vessel is placed under the bottom of the apparatus. When monomer equivalent to two times the void volume of the specimen has been collected, the procedure is terminated. Experiments have determined that the specimen is at an equilibrium monomer loading after a few cubic centimeters of monomer have been discharged through the bottom.

4. Immediately following monomer loading, the specimen is removed from the apparatus, and either wrapped in aluminum foil or placed in a close-fitting glass container to minimize evaporation during the polymerization step. For the more volatile monomers, this precaution is especially important. For initiation of polymerization, the specimens are then placed either in a Co^{60} radiation cell, or in an oven.

RESULTS OF TESTS

Preliminary Tests With Dacite

Initial tests were made with dacite, a relatively weak, porous rock from a site near Bend, Oreg. Dacite specimens were selected from a suite of simulated lunar material (4) by the Twin Cities Mining Research Center (TCMRC). Physical properties of particular importance in this study is as follows: porosity, 17-30 volume-percent; density, 1.75-1.98 g/cm^3; compressive strength, 5-9 × 10^3 psi; and Young's modulus, 1.7-2.5 × 10^6 psi.

Except for variations in porosity, the dacite appeared relatively homogeneous and free of fractures. Because of the preferred orientation of ellipsoidal vesicles, the dacite was anisotropic. Therefore, all cylindrical test specimens were cored with their axes parallel to the mean short dimension of the ellipsoidal vesicles. Finished cores (of 1-inch diameter and 2-inch length) were randomly sorted into two groups: one for impregnation, one for a control. Each group was again divided; one portion comprised those specimens containing natural vesicles only; whereas the other was composed of specimens with induced fractures. Since no fractures existed in the original rock block, fractures were introduced into the selected test specimens by carefully loading them to their compressive strengths and then rapidly releasing the load before complete fragmentation could occur. Four unfractured cores and four cores with induced fractures were impregnated (at BNL) by the vacuum-soak technique; the compressive tests were made at TCMRC. Prior to physical-property tests, the cores were dried and experienced little loss of water (1.1 weight-percent). Results on physical properties are summarized in table 3.

TABLE 3. - Summary of compressive test results of impregnated dacite cores[1]

Impregnation: Methyl methacrylate monomer--vacuum-soak
Minimum Co^{60} gamma radiation intensity--5 × 10^5 rads/hr
Minimum total radiation dose--24 × 10^6 rads

	PMMA wt[2] loading, pct	Compressive strength, 10^3 psi				Young's modulus, 10^6 psi			
		Original	After fracture	Change, pct	Increase, pct	Original	After fracture	Change, pct	Increase, pct
Unfractured:									
Nonimpregnated	0.0	5.759	-	-	105	1.892	-	-	45
Impregnated...	10.2	11.82				2.744			
Fractured:									
Nonimpregnated	.0	[3]6.255	5.624	-10	73	[3]1.859	1.814	-2	35
Impregnated...	11.4	[3]5.221	8.510	+63		[3]1.727	2.294	+33	
Nonimpregnated unfractured....	.0	-	5.759	-	48	-	1.892	-	17
Impregnated fractured......	11.4	-	8.510			-	2.294		

[1] Values given are averages of four specimens.

[2] Polymer loading--weight-percent of unimpregnated dry cores.

[3] Determined during induction of fractures.

Preliminary Tests With Tuff Slabs

Three core samples, taken along the diagonal of each impregnated tuff slab, were tested for uniaxial compressive strength. Results are reported in table 4. The ends of the cores were cut with a diamond saw, and the cores were ground so that their length was exactly twice the diameter. The weight of each core was recorded in order to determine polymer loadings by comparison with weights of equal-sized, air-dried control cores; however, the density of the rock varies sufficiently so that such data cannot be used to accurately calculate polymer loading. Table 5 presents results of uniaxial compression testing of air-dried, nonimpregnated cores; it indicates the range of weights and compressive strengths observed for samples of nearly identical size. As expected, a heavier core gives a greater compressive strength. A linear regression was computed, using compression as the dependent variable, and weight as the independent variable. The slope of the line was deemed statistically significant, the correlation coefficient being 0.65 (which is significant at the 0.01 level). Because of the variation in rock density in a given slab, larger impregnated core weights do not necessarily imply greater polymer loading. Fully impregnated cores were typically 20 to 25 percent heavier than the nonimpregnated control cores.

TABLE 4. - Impregnated tuff cores from slabs

Slab number-core number	Weight of impregnated core, g	Total load,[1] lb_f	Compressive[1] strength, psi	Type of failure
5-2	NA[2]	17,500	14,158	Conical
5-4	NA	15,900	12,947	Diag.-conical
5-6	NA	16,500	13,436	Conical
6-13	NA	11,000	8,972	Diagonal
6-15	NA	11,400	9,298	Do.
6-17	NA	12,000	9,771	Diag.-conical
8-33	95.03	20,500	16,532	Conical
8-35	95.19	19,400	15,670	Do.
8-37	95.30	18,200	14,701	Do.
9-42	91.35	9,000	[3]7,258	Do.
9-44	94.19	19,500	15,751	Do.
9-46	95.07	13,400	10,806	Diag.-vertical
10-52	94.70	19,000	15,322	Vertical
10-54	95.73	17,600	14,193	Conical
10-56	95.47	16,500	13,327	Do.
11-62	90.51	16,500	[3]5,267	Diag.-vertical
11-64	96.50	16,500	13,306	Diagonal
11-66	98.19	17,500	14,112	Conical
12-72	93.43	17,200	13,915	Do.
12-74	96.49	20,500	16,558	Do.
12-76	97.19	21,000	16,935	Do.
13-83	93.92	17,200	13,870	Diag.-conical
13-84	94.66	19,700	15,887	Conical
13-86	94.02	18,400	14,838	Do.

[1] Compression values accurate to ±500 lb_f load.

[2] Impregnated weights were not taken.

[3] Incomplete impregnation (core taken from corner of slab).

TABLE 5. - Tuff cores from slabs (air-dried, nonimpregnated)

Sample number	Weight of air-dried, nonimpregnated core, g	Total load, lb_f	Compressive strength, psi
1c	85.76	3,500	2,836
3c	85.61	5,425	4,396
5c	86.87	4,250	3,444
7c	85.62	3,525	2,861
9c	86.30	4,700	3,814
12c	83.57	3,250	2,633
13c	85.82	3,300	2,674
14c	83.92	2,675	2,167
15c	86.06	4,900	3,977
16c	84.62	3,250	2,642
17c	84.92	4,875	3,950
18c	89.55	6,425	5,198
19c	86.02	4,050	3,282
22c	83.41	4,450	3,606
23c	85.12	4,500	3,646
26c	89.50	6,875	5,571
27c	85.51	3,325	2,690
28c	82.68	2,525	2,052
72c	80.22	4,425	3,609
76c	78.60	2,550	2,079

Table 6 describes the properties of the monomer systems used to impregnate the slabs. All slabs were cured by being heated overnight at 150° F. All except slab 6 were tightly wrapped with polyethylene sheet after impregnation and until cured. Slab 6 was coated with a plastic cellulose acetate butyrate (Maskcoat No. 2 from Western Coating Co.).[7] This plastic lost its adhesiveness and reacted with the monomer. Figure 9 shows the plastic coating after the slab had cured overnight in the oven.

The average compressive strength of cores from slab 5 was 13,500 psi, whereas that from slab 6 was 9,300 psi. All of these cores were completely impregnated by virtue of their close proximity to the center of the slabs. The apparent significant difference in average compressive strengths of cores from these two slabs may be due to differences in rock densities, or could be attributable to the cellulose acetate butyrate coating on slab 6, which may have inhibited complete curing of the monomer.

Because of the very high viscosity of the 60 percent polyester-40 percent styrene monomer system, slab 7 was impregnated to a depth of only 1/4 inch after 5 hours at a pressure of 25 psig. The high percentage of impregnated monomer lost during curing is not surprising, since evaporation is most rapid near the rock surface. No testing was performed on the cores.

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[7] Reference to specific trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

TABLE 6. - Properties of monomer systems

Slab No.	Monomer system	Monomer viscosity, centipoise at 25° C	Impregnation time	Polymer loading of slab, wt pct of air-dried slab	Monomer loss during cure, wt pct
5	Monochlorostyrene (CX-3873 from Dow Chemical Co.).	1	25 at 25 psig	15.4	7
6	Monochlorostyrene (CX-3873 from Dow Chemical Co.).	1	36 at 25 psig	15.2	11.6
7	60 pct polyester-40 pct styrene (GR-941 from W. R. Grace Chemical Co.).	600	300 at 25 psig	.9	35
8	40 pct GR-941-60 pct styrene	35	275 at 40 psig	14.8	4.9
9	50 pct GR-941-50 pct styrene	143	300 at 40 psig (Incomplete penetration).	8.1	5.2
10	50 pct MCS-50 pct TMPTMA....	4.2	26 at 30 psig	14.3	5.3
11	60 pct MCS-40 pct TMPTMA....	4.1	30 at 30 psig	12.4	6.1
12	70 pct MCS-30 pct TMPTMA....	3.8	22 at 30 psig	16.3	4.8
13	80 pct MCS-20 pct TMPTMA....	3.4	12 at 30 psig	16.0	5.9

FIGURE 9. - Cellulose Acetate Butyrate Plastic Coating on Rock Slab.

In summary, sample cores from impregnated slabs exhibited average compressive strengths of 11,000 psi to nearly 16,000 psi, as compared with 3,300 psi for the average strength of 20 cores from nonimpregnated slabs. Best results of those reported (slab 12) were achieved with a mixture consisting of 70 percent monochlorostyrene and 30 percent trimethylolpropane trimethacrylate, where complete impregnation was achieved in 22 minutes at 30 psig, and a compressive strength of 15,800 psi was attained.

Preliminary Tests With Tuff and Sandstone Cores

Prior to extensive tests on the volcanic tuff and sandstone, several trial tests were made on single samples, using several monomers and different polymerization techniques. The specimens were undried and were used as received. Impregnation was by pressurization from one end. Table 7 reveals the following determination:

1. Because of its greater porosity, the tuff gave polymer loadings ranging from 11.3 to 14.6 percent, much higher than the sandstone loadings of 1.9 to 2.4 percent.

2. Strength improvement compared with that of unimpregnated control cores was much higher for the tuff than for the sandstone. The relative improvement in Young's modulus was also higher for the tuff.

3. Initiation by heat and catalyst gave results essentially identical to those achieved with radiation. Increases in strength of approximately 250 percent were obtained for each method, when tuff was impregnated with polyester-styrene.

TABLE 7. - Trial test results on impregnated tuff and sandstone cores 1-1/4-inch-diameter X 2-1/2-inch-long specimen

	Type of rock	Monomer	Method of polymerization	Weight loading, pct[1]	Compressive strength, 10^3 psi	Young's modulus 10^6 psi
Av control	Tuff.....	-	-	-	5.436	1.185
1	...do....	80 pct GR-941-20 pct styrene[2]	Rad.[3]	14.6	18.986	2.260
2	...do....	Methyl methacrylate..........	C & Ht.[4]	11.3	14.301	2.167
3	...do....	65 pct GR-941-35 pct styrene[2]	C & Ht.[4]	14.2	18.416	2.046
Av control	Sandstone	-	-	-	9.697	1.673
1	...do....	Methyl methacrylate..........	R.T.[5]	1.9	10.553	1.884
2	...do....	90 pct chlorostyrene-10 pct TMPTMA.	C & Ht.[4]	2.4	9.778	1.746
3	...do....	Methyl methacrylate[6].........	Rad.[3]	1.7 est.	8.841	2.009

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[1] Specimens were all impregnated by pressurization from one side.

[2] Polyester-styrene diluted with styrene to reduce viscosity.

[3] Co^{60} gamma radiation polymerization--intensity 3.5×10^5 rads/hr. Total dose 2×10^6 rads.

[4] Initiation of polymerization by catalyst and heat -2.3-percent benzoyl peroxide and heated to 75° C.

[5] Room temperature polymerization with 2-percent benzoyl peroxide catalyst plus 0.5-percent dimethyl aniline promoter.

[6] Sample saturated with water prior to penetration with methyl methacrylate.

Based on these trial experiments, more definitive data on the effect of monomer type, method of polymerization, and presence of water were then obtained from an extensive series of tests as described in the following section.

Test Series

Survey Series

For this series, the procedure was to select one rock and perform impregnations with a number of monomers--first on a group of fully dried specimens and then on a series of water-saturated rocks. Determination of the effect of monomer type and loading on the compressive strength of the rock was the objective of this series.

A series of dried tuff specimens, of 1-1/4-inch diameter by 2-1/2-inch length, were impregnated with five different monomer systems, as shown in table 8. Selected were those monomer systems listed in table 1, except that in several cases combinations of two monomers were used. Measured amounts of low-viscosity styrene monomer were added to TMPTMA, and to the polyester system, in order to reduce the viscosity of these monomers sufficiently to allow them to diffuse through tuff. To further reduce the viscosity, chlorostyrene was also added to TMPTMA. Also recorded in table 8 is the measured viscosity of each monomer system. Thirty specimens were prepared. Three of dried tuff were impregnated with each of the five monomer systems (table 8); and three specimens of water-saturated tuff were impregnated with each of the monomer systems (table 9).

TABLE 8. - Polymer impregnation of dried tuff

Monomer	Viscosity, cps	Impregnation time at 25 psi, min	Monomer loading		Young's modulus of elasticity		Compressive strength	
			Wt pct	Average	10^6 psi	10^6 psi average	Psi	Average
Control (6 specimens)	-	-	-	-	-	0.515	-	3,328
Methyl methacrylate..	0.5	10-15	12.8	14.2	1.350	1.232	8,590	10,660
			12.7		1.349		12,880	
			17.2		.996		10,500	
Chlorostyrene........	1.0	10-15	15.1	13.9	2.069	1.566	13,160	11,120
			12.3		1.268		10,090	
			14.2		1.362		10,100	
40 pct TMPTMA-60 pct styrene.	2.5	45-60	17.5	15.1	-	1.867	-	12,980
			14.5		1.798		12,150	
			13.6		1.935		13,810	
40 pct TMPTMA-60 pct chlorostyrene.	5.0	120	16.6	17.3	1.900	1.603	15,100	13,020
			18.9		1.188		10,660	
			16.3		1.721		13,320	
60 pct polyester-40 pct styrene.	29.0	300	14.2	16.1	1.987	1.783	19,350	16,680
			-		-		-	
			18.1		1.678		14,010	

TABLE 9. - Polymer impregnation of water-saturated tuff

Monomer	Viscosity, cps	Monomer loading		Young's modulus of elasticity		Compressive strength	
		Wt pct	Average	10^6 psi	10^6 psi average	Psi	Average
Control (dry) (6 specimens)........	-	-	-	-	0.515	-	3,328
Methyl methacrylate...	0.5	7.2 4.2 4.2	5.2	1.116 .592 -	.854	5,100 2,470 -	3,785
Chlorostyrene.........	1.0	- 5.2 6.7	6.0	- .718 .924	.821	- 4,310 5,500	4,900
40 pct TMPTMA-60 pct styrene.	2.5	10.9 6.0 9.8	8.9	.805 .775 -	.790	4,990 4,770 -	4,880
40 pct TMPTMA-60 pct chlorostyrene.	5.0	7.9 7.4 5.5	6.9	1.228 .869 .954	1.017	9,500 5,200 4,190	6,297
60 pct polyester-40 pct styrene.	29.0	9.7 11.0 17.2	12.6	.662 1.041 1.003	.902	4,210 8,290 7,560	6,686

The 30 specimens were initially dried to constant weight at a temperature of 150° C. Following drying, 15 weighed specimens were saturated with water. These were impregnated by pressurization from one end; the monomer pressure was 25 psi. Impregnation time (table 8) was measured from the time pressure was applied to the top end of the cylinder, to the time monomer appeared at the bottom of the sample. For the water-saturated samples, impregnation time was increased to allow 30 cu cm of liquid to pass through the samples. Following impregnation, the specimens were cured in Co^{60} gamma radiation at room temperature.

Further, tables 8 and 9 record the polymer-weight increases obtained and the compressive strengths for the impregnated specimens, as compared with those for the nonimpregnated control specimens.

Several general observations derive from these survey experiments.

1. For dried-tuff specimens, the monomer loadings (percent weight increase) generally increase as the viscosity increases. The lower loadings obtained with lower-viscosity monomers may be due to diffusion of monomer out of the rock, or evaporation of monomer during curing. A similar effect has been observed with concrete.

2. The compressive-strength value for impregnated dry tuff increased from 220 to 400 percent over that for the nonimpregnated specimens. Young's modulus increased to a lesser extent--from 140 to 260 percent. The increases in compressive strength and modulus appear to be a function of the viscosity and monomer loading.

3. The compressive strength for impregnated water-saturated tuff specimens exhibits a much smaller improvement than for the dried specimens. The polymer loadings for the water-saturated rock are 40 to 80 percent of the loadings for the dried tuff, indicating that only part of the water in the specimen was displaced by monomer during impregnation. In general, however, the same trends with respect to viscosity and loading can be observed. The polymer loadings--and subsequently the strength values--increase with increasing viscosity.

To determine the actual polymer loadings, the water-saturated specimens were dried (after curing) to equilibrium weight. It is possible, however, that some of the residual water was trapped by polymer. The weight-loading values (table 9) should therefore be considered only as maximum values.

Monomer loadings (table 9) were not so high as would be expected on the basis of porosity measurements made for tuff. Measurements with helium gas gave an average porosity value of 44.4 percent. The maximum-weight loadings for stone can be calculated from the porosity values as follows:

$$\text{Max wt loading} = \frac{\text{density of polymer}}{\text{density of rock}} \times \text{porosity.}$$

The maximum amount of polychlorostyrene, for example, that can be loaded into tuff, based on the porosity value mentioned above, is thus:

$$\text{Max wt polychlorostyrene} = \frac{1.248 \text{ g/cu cm}}{1.564 \text{ g/cu cm}} \times 44.36 \text{ pct} = 35.3 \text{ pct.}$$

The average polymer loading obtained for polychlorostyrene (table 4) is 13.9 weight-percent; therefore, the polymer-filled volume $= \frac{13.9}{35.3} \times 100 =$ 39 percent.

Several factors that can influence the monomer loadings are as follows:

(a) Channeling

Low-viscosity monomers such as chlorostyrene tend to take the path of least resistance when forced through a structure such as rock. This tendency results in bypassed areas and voids that have not been completely filled with monomer.

(b) Monomer molecule size

Because of side chains, most organic monomers are large and bulky. Consequently, the ability of monomer molecules to pass through micro passages is restricted by their size and shape. Surface-tension effects such as wettability can also affect monomer loading. Monomer can be expected to fill only a fraction of the void volume that can be filled with helium.

(c) Shrinkage

Density changes cause all monomers to exhibit a certain amount of volume shrinkage after polymerization. For example, chlorostyrene has a density of 1.010 g/cu cm at 25° C; polychlorostyrene, 1.248 g/cu cm at 25° C--representing a 19-percent volume change. For 60 percent polyester-40 percent styrene, shrinkage is the least (estimated to be about 10 percent), since part of the mix is already in the form of a polymer.

Dry Reference Series

This series of experiments was conducted to provide reference data by using dried specimens and the impregnation technique known to give the highest monomer loadings. Specimens of tuff and sandstone were impregnated by the vacuum-soak technique. For each rock, two monomer systems and two methods of polymerization were employed.

The monomer systems selected were based on the results obtained in the first survey series. Chlorostyrene was chosen primarily because of its low vapor pressure and the flame-extinguishing properties of chlorine. The polyester-styrene system was selected because it showed the highest strength in the survey series and because it can polymerize rapidly.

Polymerization was initiated by Co^{60} gamma radiation and by chemical catalyst-accelerator. The two methods were selected so that the reactions could take place at room temperature. Prior to impregnation, all specimens were dried to equilibrium at 150° C. Impregnated specimens of chlorostyrene and polyester-styrene monomers required a radiation dose of 8 and 2 megarads, respectively, to complete the polymerization. The data obtained for this series of experiments are shown in tables 10 and 11.

Some difficulties were encountered with the chemical catalyst-accelerator method. Once the components are mixed together, the polymerization reaction starts almost immediately. As a result, the specimen must be impregnated before the monomer solution becomes too viscous to diffuse through the rock during the soak cycle, for this condition can cause a lower weight loading. Indications of this occurrence can be found in tables 10 and 11. Lower average loadings were obtained with the catalyst-accelerator method than when the same monomers were polymerized by radiation. This effect appears more pronounced in the more dense sandstone.

The improvement in loading efficiency afforded by the vacuum-soak technique can be readily observed in table 10. When chlorostyrene is again chosen as an example (and based on a rock density of 1.564 g/cu cm and a helium porosity of 44.33 percent), the polymer-filled volume for tuff is 70 percent. This figure is almost two times the loading fraction obtained by the pressurization method in the first survey-series experiments.

TABLE 10. - Polymer-impregnated tuff

Monomer	Method of polymerization	Mean weight[1] loading, pct	Mean[1] Young's modulus, 10^6 psi	Mean[1] compressive strength, psi
Control.............	-	0.0	1.089	4,390
Chlorostyrene........	Radiation at room temp..	24.6	2.724	12,710
Polyester-styrene (GR-941 diluted with 40 pct styrene).	Radiation at room temp..	23.4	2.749	19,740
Chlorostyrene........	Chemical initiation 0.5 pct Co naphthenate 1.0 pct t-butyl perbenzoate at room temp.	24.1	2.796	18,690
Polyester-styrene (CX-37 diluted with 40 pct styrene).	Chemical initiation 0.5 pct methyl ethyl ketone peroxide at room temp.	19.6	2.361	14,840

[1] Mean value for 6 specimens.

TABLE 11. - Polymer-impregnated sandstone

Monomer	Method of polymerization	Mean weight[1] loading, pct	Mean[1] Young's modulus, 10^6 psi	Mean[1] compressive strength, psi
Control.............	-	0.0	2.840	13,980
Chlorostyrene........	Radiation at room temp..	3.8	5.625	28,780
Polyester-styrene (GR-941 diluted with 40 pct styrene).	Radiation at room temp..	4.5	6.632	27,850
Chlorostyrene........	Chemical initiation 0.5 pct Co naphthenate 1.0 pct t-butyl perbenzoate at room temp.	2.5	4.110	17,080
Polyester-styrene (CX-37 diluted with 40 pct styrene).	Chemical initiation 0.5 pct methyl ethyl ketone peroxide at room temp.	3.6	5.383	23,530

[1] Mean value for 6 specimens.

The highest mean compressive strength value for tuff was 19,740 psi, an improvement of 350 percent. This figure was obtained with a polyester-styrene mixture polymerized by radiation. Young's modulus values for impregnated specimens increased by 150 percent. It should be noted that the mean compressive strength of tuff for this dry reference series was 4,390 psi. In the previous survey series, the mean strength of the tuff controls was 3,328 psi, reflecting the statistical differences obtained with a natural product like rock. If we apply the conventional statistical test (t-test with unequal variances), the test statistic is 5.34 compared with the "critical t-value" of 3.15; thus, the two control groups are quite different. Polymer loading with the vacuum-soak technique was approximately 45 to 75 percent higher than in the survey series, in which pressurization from one end was used. This latitude indicates that significantly greater loadings can be obtained by the vacuum-soak technique, resulting in a greater rock strength.

Because of the greater density and lower porosity of sandstone, the maximum weight loading obtained by using chlorostyrene was limited to 4.5 percent. Given a helium porosity of 16.42 percent and a rock density of 2.34 g/cu cm, only 51 percent of the helium porosity was filled with polymer. Evidently, the high density of the rock, having a more pronounced effect on monomer permeation, limited the void fraction filled by monomer. The maximum mean compressive strength of impregnated sandstone was approximately twice that of the control value. This result is rather remarkable, considering the relatively low-weight loading of polymer. The mean Young's modulus increased by as much as 130 percent, a somewhat unexpected phenomenon, since the modulus usually advances to a lesser degree than does the compressive strength.

For tables 8-11, a 1-way analysis of variance was utilized to determine if the various impregnated rocks and control groups could be considered alike or not. Further, another run was made that eliminated the control group, thus testing to see if the rocks impregnated with different polymers differed from one another. In most cases the controls differ from the impregnated rocks, but often the polymers were alike in their ability to strengthen rock. The results are shown in table 12.

Effect of Water Content in Rock

Standard cylindrical specimens were prepared to determine the effect of varying degrees of water content in rock on the polymer impregnation and the properties of impregnated rock. Test conditions were as follows:

a. Two types of rock: tuff and sandstone.

b. Two monomers: chlorostyrene and mixtures of polyester-styrene.

c. Two polymerization techniques: Co^{60} gamma radiation and catalyst plus accelerator.

d. Five degrees of water saturation: 100 percent, 75 percent, 50 percent, 25 percent, and 0 percent.

TABLE 12. - Statistical summary of tables 8-11

Table title	Controls and impregnated rocks[1]	Impregnated rocks only
8. Dried tuff: Compressive strength...	F_{data} = 24.20; $F_{0.01}$(5,13) = 4.86 ....critical difference.......	F_{data} = 2.53; $F_{0.01}$(4,8) = 7.01 ....not different..........
Young's modulus........	F_{data} = 15.32; $F_{0.01}$(5,13) = 4.86 ....critical difference.......	F_{data} = 1.64; $F_{0.01}$(4,8) = 7.01 ....not different..........
9. Water-saturated tuff: Compressive strength...	F_{data} = 2.44; $F_{0.01}$(5,12) = 5.06 ....not different..........	F_{data} = 0.80; $F_{0.01}$(4,8) = 7.01 ....not different..........
Young's modulus........	F_{data} = 3.62; $F_{0.01}$(5,12) = 5.06 ....not different..........	F_{data} = 0.45; $F_{0.01}$(4,8) = 7.01 ....not different..........
10. Tuff: Compressive strength...	F_{data} = 78.53; $F_{0.01}$(4,24) = 4.22 ....critical difference.......	F_{data} = 23.59; $F_{0.01}$(3,20) = 4.94 ....critical difference.......
Young's modulus........	F_{data} = 96.79; $F_{0.01}$(4,24) = 4.22 ....critical difference.......	F_{data} = 7.93; $F_{0.01}$(3,20) = 4.94 ....critical difference.......
11. Sandstone: Compressive strength...	F_{data} = 91.98; $F_{0.01}$(4,24) = 4.22 ....critical difference.......	F_{data} = 65.76; $F_{0.01}$(3,20) = 4.94 ....critical difference.......
Young's modulus........	F_{data} = 15.93; $F_{0.01}$(4,24) = 4.22 ....critical difference.......	F_{data} = 7.35; $F_{0.01}$(3,20) = 4.94 ....critical difference.......

[1] F_A(a,b) distinguishes between groups that are alike and those that are different. A = level of significance, (a,b) are determined by the number of groups and number of replicates used.
If F_{data} is greater than $F_{0.01}$, then a critical difference exists.
If F_{data} is less than $F_{0.01}$, there is no critical difference.

The following methods were used for preparing the specimens and determining the data:

1. Dried weight. All specimens were placed in a vacuum oven and dried to equilibrium weight at 150° F.

2. Water saturation. Immediately after drying, the specimens were placed in a vacuum vessel and evacuated for several hours. Water was then introduced into the vessel until the specimens were completely submerged. Samples were left in the water for 5 days. These conditions insured complete saturation of rock specimens.

3. Water content. The fully saturated specimens were weighed and placed in a room at approximately 65° F, which allowed slow evaporation until the desired degree of water content for each specimen was obtained. Permissible evaporation was based on the initially saturated water content. When the desired weight or degree of saturation was obtained, the specimens were placed in close-fitting (small free-volume) glass jars and sealed with screw caps. Here they remained (at 65° F) for several days to allow the remaining water to distribute itself uniformly throughout the specimens.

4. Total loading. Those specimens containing known amounts of water were removed from the glass jars as needed, and impregnated with monomer. During this process, the water displaced by the monomer was collected and measured. Monomer was allowed to pass through the length of the specimen until approximately 5 cu cm was collected. After impregnation, a total weight loading, consisting of monomer plus residual water, was obtained for each specimen.

5. It should be noted that, by increasing the pressure, the time for impregnation by pressurization from one end was reduced.

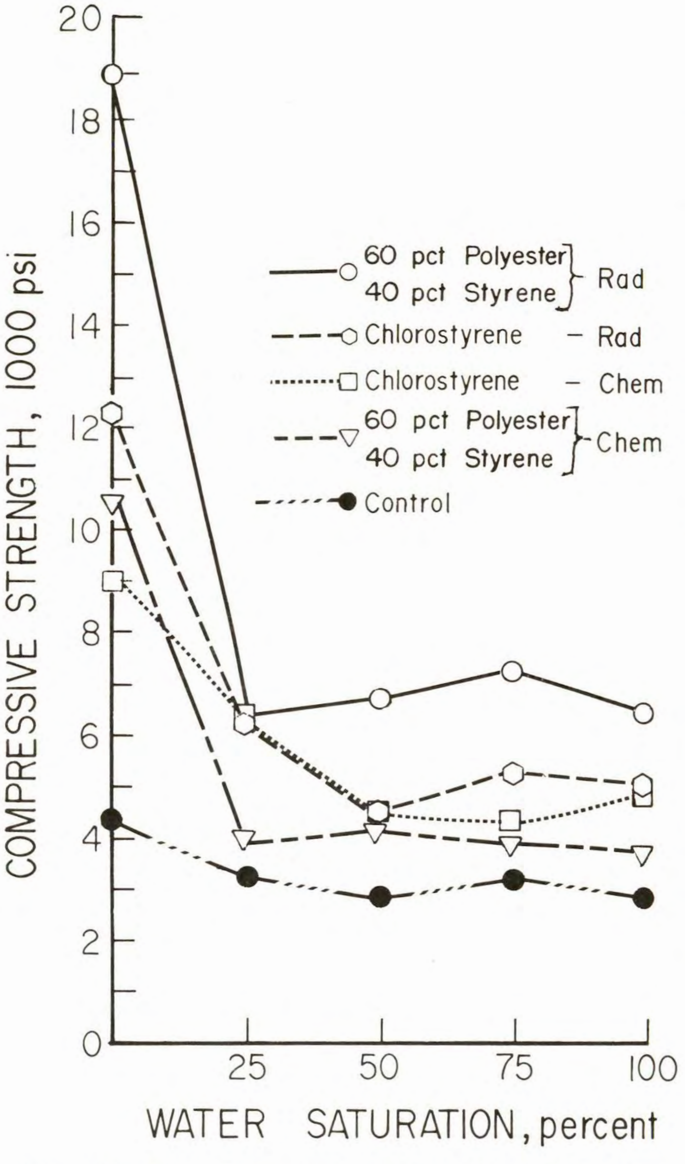

FIGURE 10. - Compressive Strength of Polymer-Impregnated Rock as a Function of Water Content—Tuff.

As specified in table 13 the impregnation time was reduced to 1 hour by increasing the pressure to 50 psi. For the sandstone, the polyester-styrene was diluted to 10 percent polyester, and pressures up to 80 psi were used to achieve impregnation in 1 hour.

TABLE 13. - Effect of water on polymer-impregnated tuff[1]

Impregnation time for 60 pct polyester-40 pct styrene: 1 hr at 50 psig;
for chlorostyrene: 1 hr at 30 psig

Series	Monomer	Polymerization method	Water saturation, wt pct	Water loading, wt pct	Monomer loading, wt pct	Modulus of elasticity, 10^6 psi	Compressive strength, 10^3 psi
Controls	-	-	0	0	0	1.07	4.39
			25	5.3	0	.86	3.23
			50	12.2	0	.80	2.88
			75	17.9	0	.83	3.14
			100	23.4	0	.80	2.88
A	60 pct polyester-40 pct styrene.	Radiation	0	.0	22.3	2.75	18.88
			25	4.5	14.5	1.16	6.28
			50	7.4	13.7	1.21	6.75
			75	8.4	14.0	1.12	7.24
			100	9.2	15.0	1.08	6.40
B	Chlorostyrene....	Radiation	0	.0	24.0	2.52	12.28
			25	6.4	12.8	1.23	6.40
			50	8.9	11.6	1.01	4.51
			75	10.0	11.5	1.15	5.28
			100	11.4	14.5	1.10	5.07
E	60 pct polyester-40 pct styrene.	Chemical.	0	.0	21.2	2.08	10.54
			25	6.0	12.7	.97	4.02
			50	7.4	10.7	.97	4.16
			75	8.1	12.3	.92	3.81
			100	8.8	15.6	.91	3.69
F	Chlorostyrene....	Chemical.	0	.0	19.4	2.28	9.03
			25	6.0	12.6	1.17	6.40
			50	9.4	13.6	1.02	4.48
			75	10.0	11.8	1.01	4.33
			100	10.6	14.1	1.04	4.83

[1] All data shown are averages for three samples.

Tables 13 and 14 summarize the results of strength tests for tuff and sandstone. In this series, 121 specimens were prepared and tested. In figures 10 and 11, the compressive strengths of the two sets of rocks are plotted as a function of their initial water content. Summarized as follows are the main conclusions of these tests.

TABLE 14. - Effect of water on polymer-impregnated sandstone[1]

Impregnation time for 10 pct polyester-90 pct styrene: 1 hr at 80 psig;
for chlorostyrene: 1 hr at 60 psig

Series	Monomer	Polymerization method	Water saturation, wt pct	Water loading, wt pct	Monomer loading, wt pct	Modulus of elasticity, 10^6 psi	Compressive strength, 10^3 psi
Controls	-	-	0	0.0	0	2.84	13.98
			25	1.3	0	1.55	6.34
			50	2.2	0	1.59	6.68
			75	3.7	0	1.54	6.29
			100	4.4	0	1.63	6.01
D	Chlorostyrene....	Radiation	0	0	3.1	3.73	14.99
			25	1.2	2.1	2.20	8.52
			50	.6	2.3	1.56	6.07
			75	2.1	2.6	1.53	6.36
			100	2.1	2.1	1.37	7.00
G	10 pct polyester-90 pct styrene.	Radiation	0	.0	3.6	4.96	16.56
			25	1.3	2.3	1.38	7.46
			50	1.7	1.8	1.81	7.75
			75	2.1	2.1	1.09	5.94
			100	2.1	2.3	2.05	8.71
H	10 pct polyester-90 pct styrene.	Chemical.	0	.0	2.8	3.66	16.45
			25	.8	2.5	1.47	6.70
			50	1.7	1.8	1.33	5.67
			75	2.1	2.2	1.23	5.31
			100	2.1	2.4	1.12	5.78
I	Chlorostyrene....	Chemical.	0	.0	4.0	5.29	17.58
			25	1.0	2.7	1.53	7.22
			50	1.7	2.3	1.51	6.11
			75	1.7	2.4	1.32	5.65
			100	2.1	2.5	1.43	6.26

[1] All data shown are averages for three samples.

1. In contrast to the dry specimens, the presence of water in the unimpregnated (control) rocks decreased the strength and modulus of elasticity. For the more porous tuff, the average decrease in compressive strength for 25- to 100-percent water saturation is about 30 percent below the dry value. In the less porous, denser sandstone, the average decrease in strength is 55 percent (for water contents ranging from 25- to 100-percent saturation) below the dry sandstone. These data indicate that the presence of water affects, in varying degrees, the strength of different types of rock.

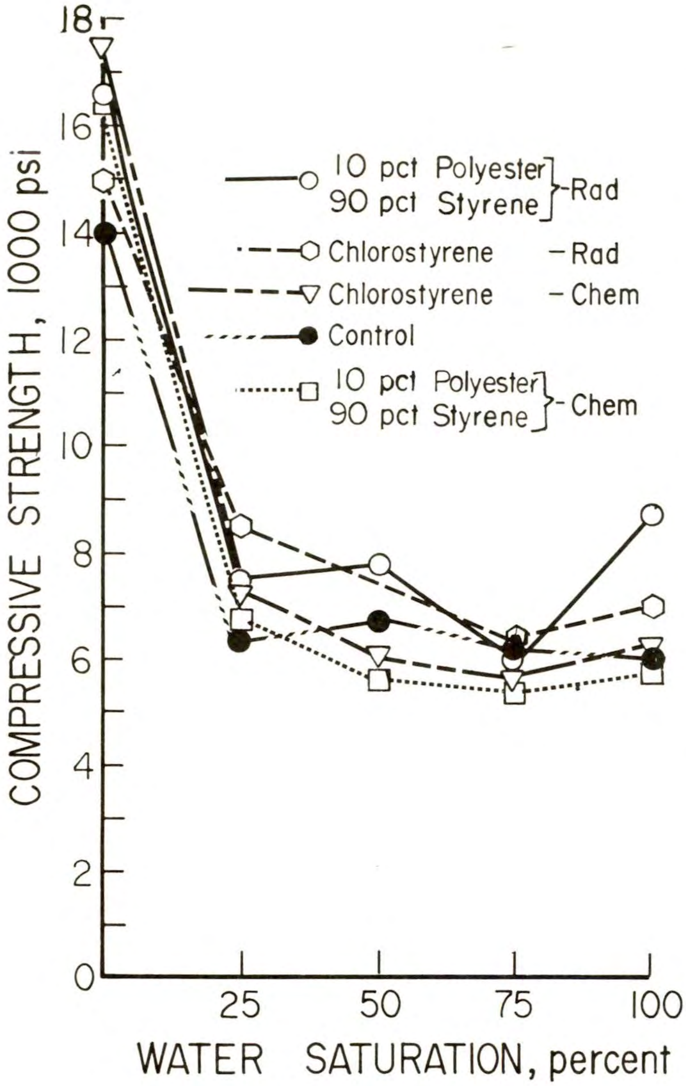

FIGURE 11. - Compressive Strength of Polymer-Impregnated Rock as a Function of Water Content—Sandstone.

2. The polymer-impregnated dried tuff, impregnated by pressurization from one end, showed strength increases in general agreement with those experiments in which impregnation was effected by the vacuum-soak technique. Based on the weight of the unimpregnated specimens, the polymer-weight loadings extended from 19 to 24 percent. The radiation-treated samples gave strength results generally slightly higher than those for the chemically initiated systems. For dry sandstone, strength increases due to polymer impregnation were much less, varying from 7 to 26 percent. This range is in contrast to the results obtained for similar specimens in the Dry Reference Series, in which improvements in strength were 22 to 106 percent higher than the values for the unimpregnated controls. Possibly the control-rock samples in the two series were of different quality. For statistical verification it would be desirable to carry out further tests to clarify this point.

3. Water content of 25-percent saturation markedly decreases the strength of polymer-impregnated rock. For both tuff and sandstone at 25-percent water saturation, the strength is approximately half that of fully impregnated dry rock samples. Beyond 25-percent saturation, the strength of the impregnated specimens remains approximately the same.

4. The strength improvement due to polymer impregnation of wet tuff sample ranged from 25 to 100 percent; wet sandstone generally exhibited no significant change in strength or elastic modulus.

5. Interestingly, whenever water was present in the rock, not all of it was displaced by the monomer. The remaining water prevented full polymer loading of the pore volume of the rock. This reduction in loading probably explains the marked decrease in strength compared with that of dry rock specimens. A similar effect is observed in the impregnation of undried concrete specimens (1). Noted also is that beyond 25-percent water saturation, the

water content after impregnation of rock with a given monomer system remains approximately constant. The porosity of the rocks is such that once water enters certain passageways, it cannot be displaced by the monomer. However, the extent of water displacement is dependent on the monomer used, and the controlling property is monomer viscosity. The 60 percent polyester-40 percent styrene has a higher viscosity than the chlorostyrene; the residual water content was 9.2 percent for the former system, compared with 11.4 percent for the latter. Polymer-weight loadings with polyester-styrene were also higher than with chlorostyrene. This distinction might well explain the greater improvement in strength shown by water-saturated specimens impregnated with polyester-styrene.

CONCLUSIONS

The preliminary survey has shown that rock of varying degrees of porosity can be impregnated with a liquid monomer followed by polymerization initiated by either radiation or chemical techniques. Significant improvement in strength properties of the rock results.

As applied to ground-support systems in mines, these results are significant:

1. For dry mine walls, marked improvement in strength and the modulus of elasticity can be expected by polymer impregnation.

2. For water-saturated mine walls, a much smaller improvement in strength can be expected, and then only under a certain combination of conditions.

It should be pointed out that the water content in tuff and sandstone at atmospheric conditions of 100-percent relative humidity was found to be less than the water content at 25-percent water saturation. Thus, an inference is that in many mines the water content in the walls may be less than 25 percent of the saturation value, so that water effects may not be so deleterious as indicated. Additional polymer-impregnation tests should be performed with water contents between 0- and 25-percent saturation in order to determine the trend in strength improvement for specimens containing smaller amounts of water.

3. The compressive strength of dacite, a relatively porous rock, can be increased by 70 percent even after fracturing. Thus, impregnation apparently has a healing effect.

4. The possibility of drying the surface of the mine walls prior to impregnation should be investigated, or the use of water-compatible monomers. Moreover, further tests should include other types of rock encountered in mines, such as shale and coal. A design effort should be undertaken to determine the value of the application of the above information to underground-support systems.

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