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FREEZING OF COAL

by

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December 5, 1983
(date)

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Program Committee

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ABSTRACT

The compressive strength of frozen coal cylinders prepared with varying amounts of water were studied. The compressive strength increased with increasing water content and, at high levels of water, it was much greater than that of ice. For the bituminous coal studied in the present investigation, the key parameter affecting the compressive strength was the amount of water added to form the frozen coal samples. The initial moisture content as determined by ASTM D-2961 test did not have significant influence on the compressive strength.

The effect of ethylene glycol, ammonium acetate, urea and sugar as chemical additives on the compressive strength of the frozen coal cylinders was also studied. For the concentrations of these chemical additives studied, it has been found that ammonium acetate is the most effective in reducing the compressive strength of frozen coal cylinders, followed by ethylene glycol and then urea, whereas sugar did not have any significant effect on the compressive strength. A study of the compressive strengths of ice cylinders revealed that the addition of ethylene glycol and ammonium acetate decreased their strength, whereas sugar and urea led to an increase in the compressive strength. On the basis of these results,

it has been postulated that the decrease in the compressive strength of the frozen coal cylinders due to the addition of ethylene glycol or ammonium acetate is mainly because of the formation of the weak ice-ice bonds, whereas for urea it is due to the formation of weak ice-coal adhesive bonds.

Studies of frozen coal cylinders containing mixtures of ethylene glycol and urea showed no synergistic effect.

CHAPTER-I

INTRODUCTION

In certain parts of the world, the freezing of wet coal to form intractable masses plagues coal burning electric power plants and other coal users every winter. This is due to the fact that the coal is washed at the mine and loaded into railroad cars while it is still wet. This problem is further aggravated if the coal is exposed to rain or sleet. Therefore, for engineers at many utility and industrial power plants winter means a battle against frozen coal [Baur-1981]. Not only do the power plants, but the transportation industry, especially the railroads, suffer from frozen coal quite heavily.

The coal when delivered in winter by rail develops more severe coal handling problems. Since rail-coal is normally hauled to greater distances, it is exposed to more adverse conditions than the coal transported by conveyors or trucks. Therefore, it is more likely that rail-delivered coal will pick up moisture and experience freezing conditions during transit. As a result railroads suffer considerably from frozen coal. They waste energy hauling supposedly empty cars, and also their cars are damaged through unbalanced loading and the efforts to thaw the coal. The average amount of frozen coal that remains stuck in the bottom of cars is about 2 tons per car and is called carryback. This frozen coal burdens the railroads with hauling about 200 tons of coal on the return trip. This difficulty in handling frozen coal has led to transportation delays, inadequate coal inventories, increased labor, maintenance and demurrage costs, and production facilities curtailments [Green-1982; Hewing and Harvey-1981].

Not only is unloading often a problem in severe winter as described above but also storage causes problems. The coal often is unloaded into large piles, which are also exposed to the weather. The freezing of these piles makes it difficult to transfer the coal to the silos from which it is fed to the burners.

At the user's site, only a relatively small load reduction at a critical electric generating power plant can result in enormous additional costs. If, for example, at one of the electric power generator plants, frozen coal handling problems forced a load reduction of 300 megawatts (about 13% of full load capacity) and it was necessary to provide power by burning oil; in 1980, it would have cost $600,000 per day [Rosenburg-1980]. Another example can be given from the expreience encountered by Detroit Edison's Monroe power plant, one of the largest coal-fired power plants in the world, during the winter of 1976-1977. Typical problems were: pluggage within the cone and lower cylindrical section of the silos; pluggage at the outlet and in the corners of the surge hoppers; and buildup on the transfer chutes. The silo problem was the most severe. When coal stopped flowing here, it had an immediate effect on the pulverizers and boilers [Moaveni and Carson-1981]. Therefore, it is clear that every winter the frozen coal situation has the potential for causing very high added costs.

Problems are not confined to the users, but also to the producers of coal. The frozen coal carryback causes increased mine inventories or production curtailments. At the mine, the stored coal may freeze in the surge bins or become mixed with snow and foul the conveyor. The problem may be further aggravated by loading this coal into snow-filled cars.

Traditionally, the freezing of coal problem has been handled by heat, mechanical and chemical treatments:

- Heating of the railroad cars by methods such as steam lances, fires under the cars, and infrared heating in warming sheds have been used to unload the frozen coal. However, the capital cost associated with this type of system limits its use to large utilities. Moreover, it subjects the railroad cars to thermal stresses and this may damage the car [Parks and Nimerick-1978].

- Mechanical methods include dislodging the frozen lumps with vibration and hammering, and, in some cases, even dynamiting has been tried. Also air cannons which quickly inject a prescribed volume of air into coal stuck in a hopper have also been used. The expanding air which rushes between the hopper wall and the cohesive mass, fractures the mass and thereby dislodges the frozen or clinging coal [Chironis-1979]. These mechanical methods can shorten the cars resistance to wear and tear.
- Chemical methods are gaining wide acceptance because of their good performance and their relatively low cost. Some of the chemicals which have been used as freeze conditioning agents are described below.

(1) Some inorganic salts such as sodium chloride and calcium chloride have been used to alleviate this problem. These salts are sprayed on coal as an aqueous solution. These salts prevent the water from freezing. Their effectiveness is related to their ability to depress the freezing point of water. The freezing point lowering ΔT_f is calculated by the following expression:

$$\Delta T_f = 1000\ K_f\ g/G\ M \qquad (1.1)$$

where K_f is the molal freezing point constant, g the weight of solute, G the weight of solvent and M is the molecular weight of the solute. For a given concentration of solute, the freezing point lowering depends upon the ratio K_f/M.

One of the biggest drawback of their use is that they are highly corrosive to steel rail cars and plant equipment. Many coke plant operators refuse to use these materials because of the detrimental effect on the oven lining [Nimerick et al.-1977].

(2) Oils applied to coal provide some measure of freeze protection. Oily liquids marketed as ice crystal modifiers, e.g., Ashland Permatreat, are used for this purpose. The lubricant Niogrin, which is a mixture of cracking residue with light coker gas oil from heavy petroleum residues has been used to prevent the freezing of coal to the sides of railroad cars [Ol'kov-1979]. Light oils are as good as or better than glycols, but heavy oils are inferior to both. The oily liquids probably displace the water from the surface of the coal particles, replacing the annular rings of water with annular rings of non-freezing oil. This spreading requires that the oily liquids wet the coal surface better than the water that is displaced.

However, these oily liquids are objectionable, because of certain problems associated with them.

Certain operational problems arise when oil is used. The fumes are quite irritating to workers in confined areas such as coal loading facilities and utility tripper rooms. Also, the likelihood of an accident increases as the hopper cars and handling equipment become slippery. Furthermore, the use of oil may increase the fire hazard [Hewing and Harvey-1981].

(3) Dry, powdered water absorbent polymers such as Henkel corporation's SGP have also been considered. SGP is a tradename for a unique family of starch derivatives, which absorb and retain unusually large quantities of water as swollen gel particles. SGP polymer is water-insoluble but it is extremely water-swellable [Henkel Corporation-1979].

(4) The glycols, also known as polyhydroxy alcohols, are perhaps the most popular class of freeze conditioning agents (FCA's) in use. Various proprietary mixtures of water soluble compounds with major constituent being polyhydroxy alcohols have been marketed. Some of the typical compounds which have been mixed with polyhydroxy alcohols are fumaric acid, urea, glycolic acid, sodium acetate, ammonium salts, dimethylsiloxane, and some polymeric materials such as polyacrylamide [Beafore-1979; Glanville and Walters-1981; Montgomery-1979]. The hydrocarbon liquids which have freezing points less than -20°F

have been emulsified with 5 to 75% by weight of an aqueous solution of a polyhydroxy alcohol have also been used [Macaluso and Michalski-1974]. Normally these freeze conditioning agents are added at a rate of 2 pints per ton of coal. The mechanism by which these compounds lower the compressive strength of frozen coal is not well understood.

Since these chemical compounds have proved to be useful, some attempts to understand the mechanism which leads to a decrease in the compressive strength of frozen coal have been made. Also, Rosenburg has developed a correlation which predicts when the application of freeze conditioning agent is required [Rosenburg-1980]. It is necessary to have this information because the application of an FCA on a single unit train shipment may cost up to $10,000 [Coppola et al.-1983]. Rosenburg has defined an exposure index R_D as:

$$R_D = \Delta t \times h \qquad (1.2)$$

where Δt is equal to 32°F minus average ambient temperature during transit and h is the hours during transit. The chances of forming frozen coal slabs increases with the increase in the value of R_D. From the analysis of the actual coal delivery data of the railroad cars, the author provided rudimentary guidelines for when to apply FCA's. A value of R_D greater than 118 dictates the use of freeze conditioning agents.

Rosenburg's correlation is a simplistic one, and does not help in the selection of a freeze conditioning agent or its rate of application. Moreover, the coal freezing problem ia analogous to the material's complex physical nature. Due to heterogeneity of coal, its pyhsical properties vary significantly. Coal freezing is not governed by just a single parameter, namely, ambient temperature below the freezing point of water. But it is also a function of many other parameters, of which surface moisture, particle size, and rate of cooling are the significant ones. The main source of water for the ice crystals that bind together frozen coal particles is the surface moisture. Another significant parameter is the coal particle size. Coal fines have more surface area and fill the voids between the larger coal particles, which facilitates bridging by ice crystals. Rosenburg's exposure index does not account for these additional parameters, which also influence the mechanical strength of frozen coal.

Glanville and Haley [1982] have tried to give mechanistic explanation for the decrease in the compressive strength of frozen coal samples due to the addition of FCA's. Generally, the ice frozen from a dilute chemical solution is mechanically weaker than ice frozen from pure water. The authors used this phenomenon as the basis for the explanation of the reduction in compressive strength of a mass of frozen coal. According to them, the ice-ice bonds are weaker than ice-coal or coal-coal bonds. Therefore, during laboratory tests of breaking frozen coal, fracturing occurs along the lines within the ice structure. However, there are chemical compounds which when added to water lead to stronger ice, and it is not clear whether the addition of these compounds will lead to a decrease in the compressive strength of frozen coal.

OBJECTIVES: Following are the outlines of the studies made in this thesis:

1. The main objective of this thesis is to study the decrease in the mechanical strength of frozen coal by the addition of simple, less expensive, water soluble, pure chemical compounds.
2. Frozen coal samples with various water contents will be studied to elucidate the effect of water on the compressive strength.
3. The relative effect of internal as well as external water content on the compressive strength of a frozen

coal sample will also be studied.

4. In the literature, it has been suggested that often the mixture of two pure compounds such as ethylene glycol and urea leads to lower compressive strength than either of the pure compounds [Parks and Nimerick -1978]. One of the objectives is to study this synergistic effect.
5. The other objective is to further study if the reduction in compressive strength of frozen coal sample is solely due to weakening of ice-ice bonds. For this purpose, the compressive strength of ice prepared from water containing the same chemical compounds as used for frozen coal samples will be measured.

CHAPTER-II

EXPERIMENTAL METHODS

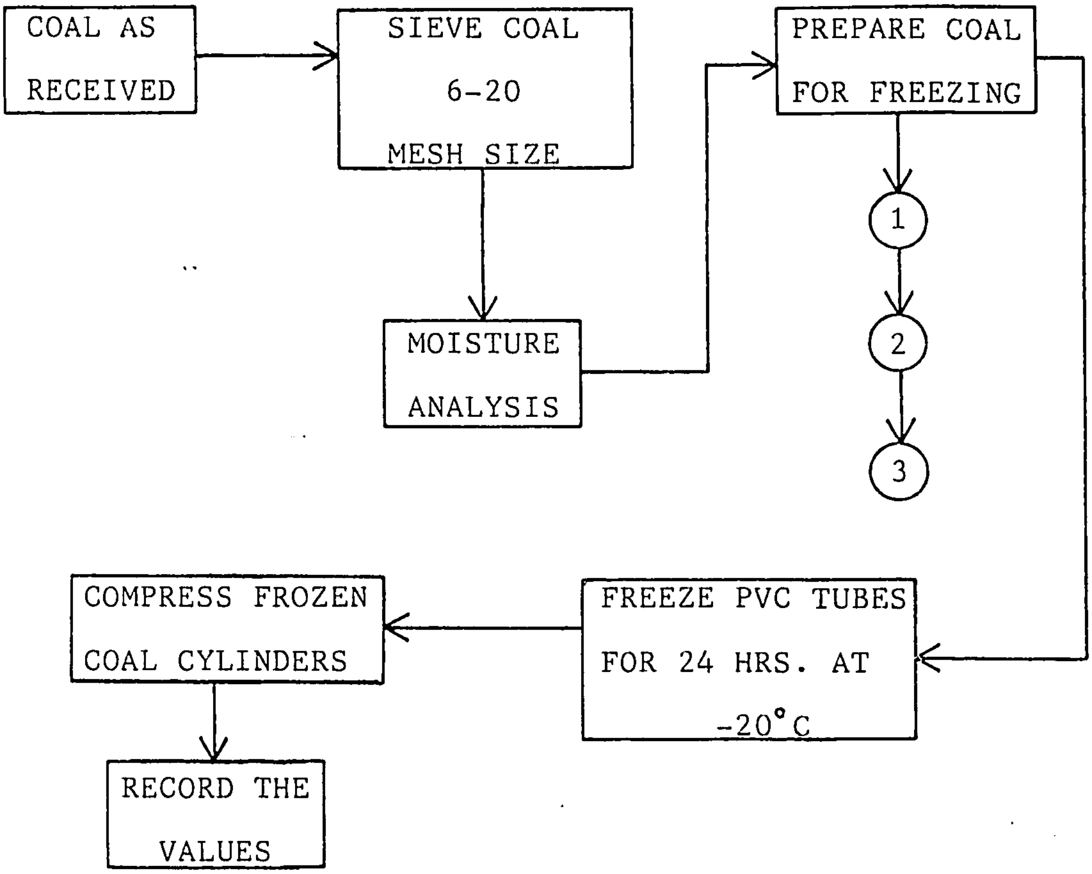
Before experimental methods are discussed, details of all the materials used in this investigation are given.

A. MATERIALS USED : The coal was ordered from Pennsylvania Power and Light Company (Greenwich coal). This coal was received in 55 gallon drums and was bituminous coal. The coal from the drum received in the first shipment was designated coal sample #1. After its supply was exhausted, the second drum was ordered, which was named coal sample #2. Similarly, subsequent shipments were designated coal sample #3 (Supplier's # U.F.S.-302) and sample #4 (Supplier's # U.F.S.-500). In this lab, previous researchers, Earhart and Ding [1983], used coal sample #1 and coal sample #2 on the freezing of coal project. Throughout this investigation, coal samples #3 and 4 have been used and were received on Nov. 17, 1982, and Feb. 16, 1983, respectively.

The chemical compounds used as freeze conditioning agents in this work were ethylene glycol, urea, sugar and ammonium acetate. High purity ethylene glycol and urea were purchased from Fisher Scientific Company, Fairlawn, New Jersy, 07410. The specific gravity of ethylene glycol at 25°C was 1.1130. The urea used was in the form of prills. Commercial, granulated pure cane sugar was uesd. It was manufactured by Amstar Corporation, New York and is sold under the brand name "Domino". High purity ammonium acetate crystals were purchased from J.T. Baker Chemical Company, Phillipsburg, N.J. 08865. The water used through out this investigation was distilled-deionized water.

B. <u>STUDIES WITH COAL SAMPLES</u> : The experimental procedure is schematically shown in Figure II-1.

B.1. <u>SIEVING</u> : As seen from schematics, the first step was sieving the coal. The size fraction of coal used was 6-20 mesh size (particles of size greater than 0.85 and up to 3.35 mm). This size range was chosen because it was representative of those used in the field. During sieving, care was taken to prevent the sieves from becoming "blinded" by particles which stick in the holes and thus prevent the smaller particles from passing through the sieve. This was achieved by the use of four U.S. Standard sieves of sizes 6, 8, 16 and 20 mesh. Coal as received was placed on sieve #6 and all four sieves were



① Add desired amount of water + FCA as determined by moisture analysis to coal sample which weighs 1500 gms in 1 gallon Nalgene containers.

② Mix it well for five minutes and let it equilibrate for 24 hours at room temperature.

③ Place this coal slurry in the PVC tubes.

Figure II-1

arranged in the proper order, and were shaken on a sieve shaker for roughly five minutes. The coal which was retained on sieve #8, 16 and 20 was collected in a bucket and was used for further experiments. The coal retained on sieve #6 and in the bottom pan was not used for the experiments. Use of more sieves gave better sieving results.

B.2. <u>DETERMINATION OF COAL MOISTURE CONTENT</u> : The moisture content of the coal was determined in accordance with the ASTM D-2961 test. According to this test, the sample used for the moisture determination must have a minimum weight of 500 gms. Therefore, about 500 gms. of sieved 6-20 mesh size coal was taken in a shallow aluminum pan. This coal sample was placed in air oven at 107 ± 3°C and was periodically weighed after 1.5 hours, and then every 0.5 hours until the weight loss was less than 0.05%. Excessive heating is reported to cause oxidation of the coal, which would increase the weight of the sample and thus introduce errors in the moisture determination [Vanderhoff et al.-1982]. The moisture content was determined on the basis of undried coal. The formula used for this purpose was:

$$\text{Moisture Content, \%} = [(A - B)/A] \times 100 \qquad (2.1)$$

where A = gms. of undried coal used.

B = gms. of coal after heating till the weight loss is less than 0.05%.

However, there is a word of caution regarding the moisture content as determined by drying methods. At temperatures of 105°C to 110°C practically all of the moisture is removed from the coal. At the same time, the surface which was previously covered by adsorbed molecules of water now becomes free of water. When the sample is cooled before being weighed, some kind of eqilibrium between the surface and the molecules of gases in the atmosphere is established. It is generally believed that the quantity of these gases adsorbed by the surface of coal particles is very small. However, it has been found out by Swietoslawski [1942] that relatively large amounts of nitrogen, oxygen and other gases are adsorbed during the cooling of the sample after it has been dried. Due to this fact, the moisture content found by the drying method may be too low. Therefore, one should weigh the dried coal sample as fast as possible to minimize this error.

ASTM D-2961 test has certain other disadvantages too. It is questionable whether it measures the total moisture content or not. During heating the coal at 107 ± 3°C, along with water, some volatiles which have lower boiling points might also evaporate with water, giving higher moisture contents. Furthermore, the quantity of water measured by this method comes from five sources: (1) decomposition of organic molecules (sometimes called combined water); (2) surface adsorbed water; (3) capillary condensed water; (4) dissolved water; (5) water of hydration of inorganic constituents of the coal. Therefore, by this method, it is difficult to discriminate the relative contribution of chemically and physically bound water to the total moisture content.

Glanville and Haley [1982] measured the moisture content of coal by drying the coal to constant weight at 95°C instead of 107 ± 3°C as suggested by ASTM D-2961 test. However, one of the drawbacks of this method could be that all of the bound water may not come out.

In the literature, it has also been mentioned that thermogravimetric analysis (TGA) could be used for the moisture determination of coal [Baur-1983]. In this method, the coal is pulverized to a size smaller than 60-mesh, and this sample is placed on a balance pan inside the thermobalance. High-purity nitrogen is introduced into the furnace. Then the sample is heated to 110°C at a constant rate. The temperature is kept constant at 110°C in a nitrogen atmosphere for approximately five minutes. TGA has certain advantages, the most important being that it speeds up the analysis. However, one of the disadvantages of this method may be that it uses a very small amount of sample and may pose sampling problems. This method was not used in the present investigation.

B.3. <u>DETERMINATION OF COAL SIZE DISTRIBUTION</u> : The size distribution of the 6-20 mesh coal fraction was determined by sieving. About 500 gms. of the sieved coal frction collected as described in Section II.B.1. was dried using the ASTM D-2961 test. This dried coal sample was placed on the top sieve of a series (numbers 6, 7, 8, 10, 12, 14, 16, 18 and 20), and was shaken for about ten minutes. Then the amount of coal retained on each sieve and the bottom pan was weighed. The particle size distribution of coal sample #3 and sample #4 was determined by this method. The results are given in the next chapter.

This sieving method introduces several possible errors: (1) some fine coal particles may be lost to the atmosphere as dust; (2) additional coal particles may be lost in the transfer from the bottom pan to other sieves; (3) some fine coal particles may stick to the larger coal particles which are retained on the smaller number sieves; (4) the sieves may become "blinded" by particles which stick in the holes and thus prevent the small particles from passing through the sieve.

To see the impact of errors on the accuracy of the above dry sieving method, Earhart and Ding measured the particle size distribution in this lab by wet sieving [Vanderhoff et al.-1982]. It was found that, generally, the values obtained by wet sieving were in reasonable agreement with the average of those obtained by dry sieving.

B.4. PREPARATION OF COAL FOR FREEZING : A bucket was filled approximately with 10 kgs. of sieved coal of fraction 6-20 mesh size. This coal content in the bucket was mixed thoroughly to achieve homogeneous size distribution. The moisture content of this coal was measured. To each one-gallon wide-mouth Nalgene polyethylene bottle, 1500 gms. of this coal was transferred. Then, to these bottles, predetermined quantities of water were added to give coal slurries of required water content. The water used was distilled-deionized water. To each bottle, water was added in two steps. First, about half of the water was added, and then the Nalgene bottle was shaken for about two minutes to allow good mixing of the coal and water. Then the remaining water was added, and the mixture was shaken vigorously for about another four minutes. Finally, this coal-water mixture was then left to equilibrate for 24 hours. Generally, six Nalgene bottles were used to allow the preparation of coal slurries containing six different total water contents. Most of the time throughout this investigation the total water content varied as 10%, 12%, 14%, 16%, 18% and 20%.

The amount of water to be added was calculated as follows:

$$W = \frac{1500(p - m)}{(100 - p)} \qquad (2.2)$$

where p is the total percent water content in the final slurry, m is the moisture content of the coal and W is the gms. of water added to Nalgene bottle containing 1500 gms. of undried coal.

When a freeze conditioning agent was used, an aqueous solution containing the desired amount of freeze conditioning agent was prepared. The coal slurries were then prepared by the method already described, using this aqueous solution instead of pure water.

The frozen coal cylinders were prepared in polyvinyl chloride (PVC) tube molds. These PVC tube molds were made by cutting 6-inch long PVC pipes of 2-inch I.D.. These tubes were slit lengthwise to form PVC tube molds. These cylindrical tube molds were held together by applying fibre-reinforced tapes around them. The bottom end of the PVC tube was closed by a Plexiglas plate of the size 3 inch X 3 inch. This Plexiglas plate was held in place by cementing it with caulking cord weather strip.

The transfer of the coal slurry to the PVC tube was done in the following way. First, all the coal slurry from Nalgene polyethylene bottle was taken out in a big shallow aluminum pan and was divided into six equal parts, and each part was transferred to one PVC tube by a stepwise addition. In the stepwise addition, two tablespoons full of wet coal was added to the PVC tube and was compacted by fifteen light poundings by the base of a graduated cylinder. This procedure was repeated with the rest of the coal, until all the required quantity of the slurry was transferred to the PVC tube. Normally, after the tube was filled, it had about an inch of empty space at the top, to allow for the possible expansion of water after freezing. To get good reproducibility in the results, it was necessary to follow the above steps strictly. One of the disadvantages of this method could be that the addition and compaction of the coal slurry was done by hand (manually) and therefore the compactness of the wet coal in the PVC tube might have varied from sample to sample. Therefore, it is more desirable to use a machine to fill and compact the wet coal in the PVC tube, but in the present investigation no such machine was used.

After a PVC tube was filled, its top end was closed by another 3 inch X 3 inch Plexiglas plate. This Plexiglas plate was held in place by a rubber band. Six PVC tubes were used for every Nalgene bottle. These tubes were then placed in the freezer at -20°C for 24 hours. Throughout this investigation, the freezing temperature used was -20°C. The freezer had a small fan which circulated the air inside, to keep the temperature same throughout the freezer.

After 24 hours, the PVC tubes were removed from the freezer, one by one; the rubber band was removed; the fiber-reinforced tape was cut; the mold was opened, and the frozen coal cylinder was placed on an aluminum pan for compression testing. The dimensions of PVC tubes were chosen so as to give frozen coal sample cylinders of diameter and height much greater than the largest coal particle size present in the sample.

B.5. MEASUREMENT OF COMPRESSIVE STRENGTH OF FROZEN COAL CYLINDERS

: The mechanical strength of frozen coal cylinders was measured in terms of the compressive force needed to fracture the sample. The compressive force was applied along the length of the cylinder (perpendicular to the two flat ends). All of the compression testing was done on a Dillon Model-LW tester machine. This machine had a 2000 lbs. maximum load capacity. It was possible to use various rates of loading. With the slower rate, the frozen coal specimens failed by relatively slow crumbling and gave higher compressive strengths, whereas, with the faster loading rate, the frozen coal specimens failed catastrophically and gave lower compressive strengths. In the present work, the loading rate of 1.0 to 1.1 inch per minute was used. Once the compressive force needed to break was measured, it was divided by the cross-sectional area of the cylinder to give the compressive strength in pounds per square inch. Since the radius of the cylinder was one inch the cross-sectional area was equal to π in^2.

It should be pointed out that other means to measure the mechanical strength of frozen coal samples have also been used in the literature. Ellman et al. [1965] have studied the degree of agglomeration of coal due to moisture by the gas pressure required to inflate a simulated ballon imbedded in the sample. In this method a rubber tube which is internally located in the center of the frozen coal sample is inflated to a pressure so as to cause the rupture of the sample. However, such a test may not simulate the real field situation. Walk [1980] and Kehoe et al. [1980] have used the drop impact shear test. In the drop impact shear test, the samples of frozen coal are dropped onto a metal grating from a predetermined height. The amount of the coal which passes through the grating is collected and weighed. The dropped coal which did not pass through the grating is also collected and then dropped from a higher height. So, the proportion of the coal breaking into pieces small enough to pass through the grating could be used as a measure of the relative ease with which the samples fracture. Glanville and Haley [1982] designed an apparatus to measure the push-down flexural strength of frozen coal sprcimens.

However, it has been pointed by some researchers [Kugel-1980] that a higher degree of reproducibility is obtained by compression testing, rather than by drop impact shear test. Probably, in principle, both the methods should be used together to measure the mechanical strength of the frozen coal. But, in the present work, only compression testing was used.

C. MEASUREMENT OF COMPRESSIVE STRENGTH OF ICE CYLINDERS :

The compressive strength of ice cylinders with and without chemical additives were also measured. The ice cylinders were prepared in the same PVC tube molds described in Section II.B.4.. Distilled-deionized water was used to make the ice cylinders.

Water when frozen in a PVC tube develops strong adhesive bonds with the PVC surface. Furthermore, at times there are leak problems from the joints of the PVC molds. To overcome these problems, water was filled in a polyethylene bag, which was placed in a PVC tube. The size of polyethylene bag was 6½ inches long and the width was chosen such that the water filled polyethylene bag would have approximately the same diameter as that of the PVC tube. Since the circumference of the PVC tube was about 6.3 inches and therefore the approximate width of the polyethylene bag chosen was about 3.1 inches. The PVC tube and its bottom end were secured as described in Section II.B.4. The polyethylene bag was then placed in the PVC tube and about 250 ml. of water was added. The top end of the PVC tube was then closed and it was kept in the freezer at -20°C for 24 hours.

When a chemical additive was used, an aqueous solution containing the desired amount of the chemical was prepared. The polyethylene bag was filled with this aqueous solution instead of pure water.

After twenty four hours, the PVC tubes were taken out of the freezer, one at a time. The PVC tube and the polyethylene bag were removed from the ice cylinder and its compression testing was done immediately as described for frozen coal cylinders in Section II.B.5.

CHAPTER-III

RESULTS AND DISCUSSION

The evaluation of freeze conditioning agents requires the measurement of physical properties of ice containing these agents as well as those of coal-ice composites. In the literature, it has been speculated that, since ice-ice bonds are weaker than coal-coal, the compressive strength of frozen coal samples is determined by the strength of ice [Glanville and Haley-1982]. Therefore, it has been suggested that a chemical compound which lowers the compressive strength of ice, would also be effective as a freeze conditioning agent for frozen coal samples. To check this hypothesis, and to gain some more insight, the compressive strength of ice along with the frozen coal samples have also been studied.

A. STUDIES WITH ICE : The compressive strength results of pure ice are first discussed and are then followed by ice containing chemical compounds.

A.1. PURE ICE : The compressive strength of ice cylinders was determined by the method described in Chapter II. Table III-1 gives the compressive strengths of pure

TABLE III-1

Compressive Strength of Pure Ice Cylinders

Tube	Compressive Strength, psi							
Number	Test: 1				2	3	4	5
1	134	239	255	146	271	242	156	251
2	111	404	115	207	213	124	290	185
3	280	277	271		331	201	137	226
4	166	296	258		178	204	290	201
5	143	105	306		194	194	226	191
6	92	127	258		178	213		210
$\overline{X}$	210				228	196	220	211
	86				61	39	72	25

Overall: $\overline{X}$ = 212 psi

σ = 67 psi

n = 43

ice of five series of experiments. Series 1 had twenty samples, series 4 had five samples, whereas the other series had six samples each. All the series were done on different dates. The overall average ($\bar{X}$) of all 43 samples was 212 psi with a standard deviation (σ) of 67 psi. The averages for these five series range from 196 to 228 psi and the standard deviations from 25 to 86 psi. Therefore, the statistical analysis was applied to determine whether the values measured in each series were actually measures of the same quantity or whether differences between each series were statistically significant. The F-test was applied [Herdan-1960]. The calculated F-value was 0.17 as compared with the critical value at 95% probability level of 2.63 (i.e., this value will be exceeded only 5 out of every 100 times if the values are measures of the same quantity). Thus it is reasonable to assume that all the values are measures of the same quantity and that the overall average (212 psi) and standard deviation (67 psi) can be taken as representative of the compressive strength of pure ice measured in this way.

Inspection of Table III-1 reveals some scatter in the values of the compressive strength of pure ice. The possible reasons for the scatter could be the foolowing: (1) Though distilled-deionized water was used for preparing ice cylinders, presence of trace quantities of impurities such as dust particles cannot be ruled out. These particles could act as nucleus of crystal growth and might lead to polycrystalline ice. It is known that the two samples of polycrystalline material, while having the same structure at the unit cell level, can differ in the number and orientation of their microcrystals. Also, the dust particles can accumulate at the grain boundaries between the ice crystals [Pounder-1965]. All these factors can have a very great effect on the compressive strength of ice cylinders and might have contributed to the scatter in the data.

(2) Possible entrapment of the small air bubbles could also contribute to the scatter in the measured compressive strengths.

(3) In most cases, the ice cylinders showed little cracks on their surface and this might have been one of the causes for the scatter (however, later on, when the experiments were done with the chemical additives, the surface of the ice cylinders were fairly smooth and no cracks were visible).

Therefore, large number of tests were done, so that a reasonable confidence level could be achieved in the final average value of the compressive strength of the ice cylinders.

A.2. ICE CONTAINING PURE COMPOUNDS : The binary solutions of water with ethylene glycol (EG), sugar (SUG), urea (UR) and ammonium acetate (A Ac) were prepared. These solutions were then frozen at -20°C for 24 hours. The compressive strength of the ice cylinders formed were measured to see the effect of these additives on the mechanical strength of ice.

Table III-2 gives the results of the compressive strength of ice containing various chemical additives. The concentrations in this table are in weight precent of the solution. Figure III-1 shows the variation of compressive strength with percent additives for these compounds. As can be seen from this figure, at high concentrations, both ethylene glycol and ammonium acetate decreased the compressive strength of ice cylinders, whereas urea increased the compressive strength drastically. Sugar also increased the compressive strength of ice cylinders but to a lesser extent.

These results were analyzed statistically using the t-test, which assesses the probability that two sets of data are measures of the same quantity. The t-value is calculated from the difference between the averages of the two data sets and the scatter of the individual data points, and the number of data points (the degree of freedom (DF) is the total number of measurements minus

TABLE III-2

Compressive Strength of Ice Containing Pure Compounds

ETHYLENE GLYCOL

Percent	Compressive Strength, psi							
EG	Tube: 1	2	3	4	5	6	ave.	sigma
0.00	178*	194*	178*	271	213	331	228	61
0.25	213	417	175	274	188	293	260	90
0.50	315	191	296	242	251	232	255	45
1.00	166	207	210	159	175	137	176	28
2.00	111	105	127	111	140	92	115	17
3.00	86	38	70	73	73	95	73	19

* specimens failed; values taken from two other series, nine of which failed.

UREA

Percent	Compressive Strength, psi							
UR	Tube: 1	2	3	4	5	6	ave.	sigma
0.00	242	124	201	204	194	213	196	39
0.25	372	427	471	398	462	398	421	39
0.50	417	449	433	576	357	592	471	93
1.00	414	411	560	379	458	630	475	99
2.00	519	500	369	538	484	478	481	59
3.00	541	427	477	598	589	468	517	70

SUGAR

Percent	Compressive Strength, psi							
SUG	Tube: 1	2	3	4	5	6	ave.	sigma
0.00	156	290	137	290	---	226	220	72
0.25	404	226	296	274	156	302	276	83
0.50	277	286	325	449	---	290	325	71
1.00	226	490	309	404	299	286	336	95
2.00	465	321	325	474	242	369	366	90
3.00	344	---	293	---	226	267	283	49

Continued on next page ------

TABLE III-2 (Continued from earlier page)

Compressive Strength of Ice Containing Pure Compounds

AMMONIUM ACETATE

Percent	Compressive Strength, psi							
A Ac Tube:	1	2	3	4	5	6	ave.	sigma
0.00	251	185	226	200	191	210	211	25
0.25	207	245	309	194	258	280	249	43
0.50	210	251	321	207	350	286	271	59
1.00	331	255	162	200	283	172	234	67
2.00	67	124	255	194	67	118	137	74
3.00	89	67	70	70	76	57	72	11

LEGEND:
EG : Ethylene glycol
UR : Urea
SUG : Sugar
A Ac : Ammonium acetate
ave. : average
sigma : standard deviation

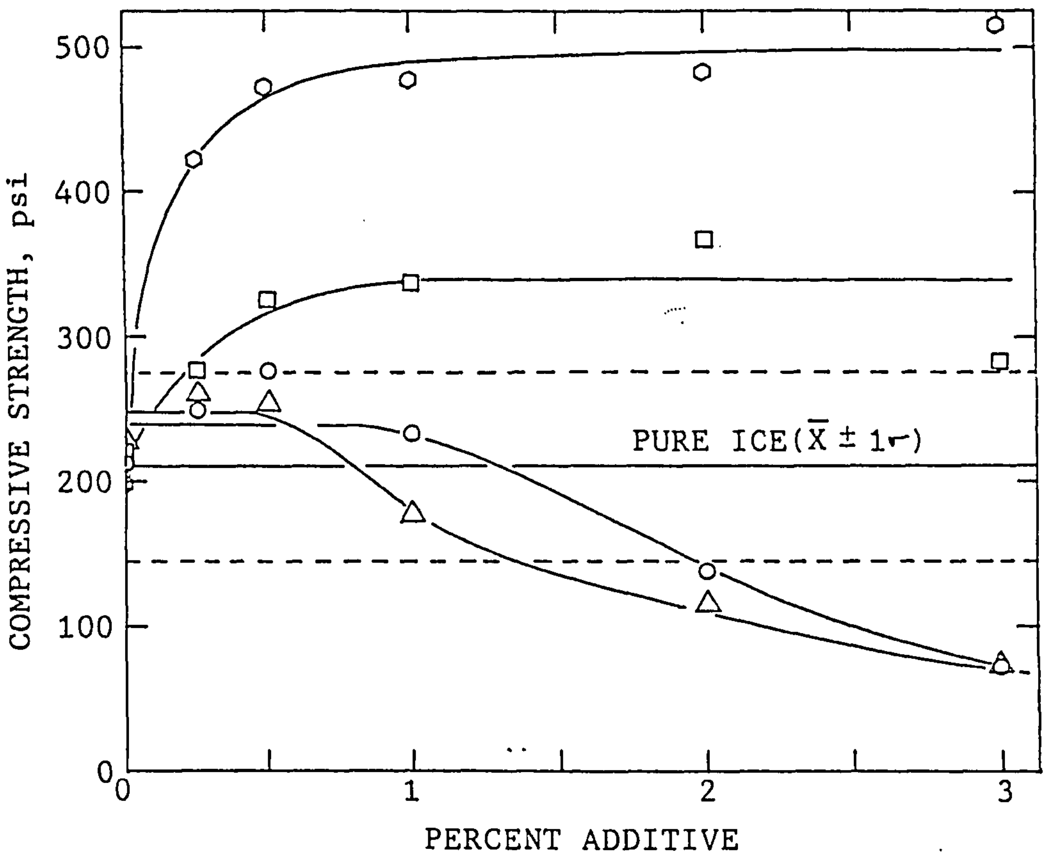


Fig. III-1: Variation of compressive strength with percent additive for ice cylinders.

<u>LEGEND</u>:

○	Ammonium acetate
△	Ethylene glycol
□	Sugar
○	Urea

two). This calculated t-value is compared with theoretical values for different probabilities. In this work, the critical t-value used is that for 95% probability, i.e., the critical t-value that will be exceeded only 5 times out of 100 if the two data sets are measures of the same quantity. Table III-3 gives the calculated t-values and the critical t-values for 95% probability for the compressive strengths of ice cylinders containing ethylene glycol, sugar, urea and ammonium acetate.

For the ethylene glycol, the compressive strengths were about the same over the 0.00-0.50% concentration range, and then decreased gradually to 73 psi at 3.00% ethylene glycol concentration. The t-values for 0.00-0.25% and 0.25-0.50% pairs were much smaller than the critical values for 95% probability, indicating that these values may be measures of the same quantity. This was confirmed by the F-test, which gave F = 0.39 as compared with the critical value of 3.68 for 95% probability; the overall average compressive strength over this 0.00-0.50% concentration range was 248 psi and the standard deviation was 64 psi. Above 0.50% concentration, the compressive strength decreased progressively with increasing ethylene glycol concentration. The t-values for the 0.50-1.00%, 1.00-2.00% and 2.00-3.00% pairs were greater than the critical values for 95% probability of

TABLE III-3

Statistical Comparison of Samples of Various Concentrations

Ice Cylinders Containing Ethylene Glycol

Percent EG	$\bar{X}$	calcd. t	crit. t(95%)
0.00-0.25	228-260	0.72	2.23
0.25-0.50	260-255	0.12	2.23
0.50-1.00	255-176	3.65	2.23
1.00-2.00	176-115	4.56	2.23
2.00-3.00	115-73	4.04	2.23

Ice Cylinders Containing Sugar

Percent SUG	$\bar{X}$	calcd. t	crit. t(95%)
0.00-0.25	220-276	1.18	2.26
0.25-0.50	276-325	1.04	2.26
0.50-1.00	325-336	0.21	2.26
1.00-2.00	336-366	0.56	2.23
2.00-3.00	366-283	1.67	2.31

Ice Cylinders Containing Urea

Percent UR	$\bar{X}$	calcd. t	crit. t(95%)
0.00-0.25	196-421	9.99	2.23
0.25-0.50	421-471	1.21	2.23
0.50-1.00	471-475	0.07	2.23
1.00-2.00	475-481	0.13	2.23
2.00-3.00	481-517	0.96	2.23

Ice Cylinders Containing Ammonium Acetate

Percent A Ac	$\bar{X}$	calcd. t	crit. t(95%)
0.00-0.25	211-249	1.87	2.23
0.25-0.50	249-271	0.74	2.23
0.50-1.00	271-234	1.02	2.23
1.00-2.00	234-137	2.38	2.23
2.00-3.00	137-72	2.13	2.23

$\bar{X}$ is the average compressive strength in psi

2.23, indicating that these values may not be measures of the same quantity.

For sugar, the compressive strength increased to an apparent plateau at 0.50-3.00% (Fig.III-1). Table III-3 gives the calculated t-values along with the critical t-values for 95% probability. All of the calculated t-values were below the critical t-values for 95% probability, indicating that all of them may be measures of the same quantity. This was confirmed by F-test which gave a value of F = 2.26 for all samples averaged together as compared with a critical value of 2.59 for 95% probability; this corresponded to an overall average of 304 psi and a standard deviation of 88 psi. The samples in the 0.50-3.00% concentration range gave a value of F = 0.85 as compared with the critical value for 95% probability of 3.20; this corresponded to an average compressive strength of 332 psi and a standard deviation of 75 psi. Thus sugar in 0.50-3.00% concentration gives a compressive strength higher than that of the control (pure ice).

For the urea, the compressive strength increased strongly with increasing urea concentration to a plateau value significantly greater than that for the control. Table III-3 gives the calculated t-values along with the critical t-values for 95% probability. The calculated t-value for the 0.00-0.25% pair was much greater than the critical value for 95% probability. All other t-values were smaller than the critical value. Thus the compressive strengths of the samples in the 0.25-3.00% concentration range may be measures of the same quantity. This was confirmed by the F-test, which gave a value of F = 1.23 for the 473 psi overall average (sigma = 77 psi) compared with the critical value of 2.76 for 95% probability. Similarly, the samples in the 0.50-3.00% concentration range gave a value of F = 0.39 for the 486 psi overall average (sigma = 79 psi) compared with the critical value of 3.10 for 95% probability. Thus the addition of urea to water makes strong ice, with a compressive strength ca. 225% of that of the control.

For ammonium acetate, the compressive strengths were about the same over the 0.00-1.00% concentration range and then decreased gradually to 72 psi at 3.00% ammonium acetate concentration. The t-values for the 0.00-0.25%, 0.25-0.50% and 0.50-1.00% pairs were smaller than the critical t-value for 95% probability, indicating that these values may be measures of the same quantity. This was confirmed by the F-test, which gave F = 1.47 as compared with the critical value of 3.10 for 95% probability; the overall average compressive strength over this 0.00-1.00% concentration range was 241 psi and the standard deviation was 48 psi. Above 1.00% concentration, the compressive strength decreased progressively with increasing ammonium acetate concentration.

For the foregoing tests, the compressive strengths of the controls (pure ice) were similar: 228 psi for ethylene glycol; 220 psi for sugar; 196 psi for urea; and 211 psi for ammonium acetate. The F-test, used to determine whether the controls of each series were measures of the same quantity, gave a value of F = 0.42 as compared with the critical value (95% probability) of 3.10; this corresponded to an overall average of 213 psi and a standard deviation of 48 psi. This value of control was in excellent agreement with overall average value of 212 psi with a standard deviation of 67 psi for pure ice.

An inspection of Figure III-1 reveals that ethylene glycol and ammonium acetate give similar decreases in the compressive strengths. To check this observation, a statistical comparison was done between them. Table III-4 gives the calculated t-values along with the critical t-values for 95% probability. It is seen from the t-test that, within the experimental error, the compressive strength of ice cylinders containing ethylene glycol were essentially the same as those of ice cylinders containing ammonium acetate. A similar comparison between urea and sugar has also been made and their results are

TABLE III-4

Statistical Comparison of Ice Cylinders

Ethylene Glycol With Ammonium Acetate

	Compressive Strength, psi					
Percent	Ethylene Glycol		Ammonium Acetate		Calcd.	Crit.
Additive	ave.	sigma	ave.	sigma	t	t(95%)
0.00	228	61	211	25	0.63	2.23
0.25	260	90	249	43	0.27	2.23
0.50	255	45	271	59	0.53	2.23
1.00	176	28	234	67	1.96	2.23
2.00	114	17	137	74	0.74	2.23
3.00	73	19	72	11	0.11	2.23

Urea With Sugar

	Compressive Strength, psi					
Percent	Urea		Sugar		Calcd.	Crit.
Additive	ave.	sigma	ave.	sigma	t	t(95%)
0.00	196	39	220	72	0.71	2.26
0.25	421	39	276	83	3.87	2.23
0.50	471	93	325	72	2.86	2.26
1.00	475	99	336	95	2.48	2.23
2.00	481	59	366	90	2.62	2.23
3.00	517	70	283	49	5.76	2.31

also listed in Table III-4. It is seen that compressive srengths of urea were significantly different from those of sugar, except for the control, which was the same within experimental error. The compressive strengths of ice cylinders containing urea were higher than those of ice cylinders containing sugar.

The reason for the decrease in compressive srength of ice cylinders which contained ethylene glycol and ammonium acetate may be due to the fact that the ice becomes polycrystalline. There is no homogeneous nucleation, but rather a heterogeneous nucleation [Fletcher-1970, Gilpin-1978]. The water freezes with multiple centers of nucleation and the individual crystals grow together. According to Pounder [1958,1965], if an aqueous salt solution is frozen extremely slowly, the foreign ions remain in the solution and perfectly pure ice is formed. This is due to the fact that the growing ice lattice rejects impurities and these impurities are concentrated at grain boundaries or in the liquid phase between growing ice crystals. In order to completely freeze the solution, one must decrease the temperature below a certain value called the "Eutectic Temperature". Above the eutectic temperature there is always some liquid phase between the ice crystals. Therefore, if the freezing temperature is above the eutectic temperature, then, depending upon the ultimate temperature and the amount of the solute present, there will be some liquid in the grain boundary regions of the ice crystals. The reduction in strength of ice results from the presence of liquid layers separating the crystals and permitting them to slide fairly readily with respect to each other. These intercrystalline layers can be of microscopic thickness, in which the solution contains too high a concentration of additives to freeze. It may be that for both ethylene glycol and ammonium acetate the eutectic temperature is below -20°C and therefore might have led to a decrease in compressive strengths. For ethylene glycol, it is known in the literature that a solution of 54 wt% has a freezing point of -45°C [Perry and Chilton-1973]. Therefore, it supports the view that, in ice cylinders containing ethylene glycol, some liquid phase very high in ethylene glycol concentration may exist between the ice crystals.

In the literature, it has also been suggested that freezing of the solution below eutectic temperature may lead to an increase in the mechanical strength of ice. This has been attributed to the reinforcement of the mechanical strength of the ice by the deposit of solid additives in it [Pounder-1965]. The eutectic temperature for either urea or sugar were not available, but, if they were higher than -20°C, then this could be one of the possible explanations for the increase in the compressive srength of ice.

An alternative explanation for the decrease in compressive strength by the compounds such as ethylene glycol and ammonium acetate has been provided by Copeland [1980]. It has been argued that, in the presence of these compounds, the completely frozen ice is structurally weak. The glycol and other compounds that are water soluble are not soluble in ice. The additives therefore separate from the ice as it freezes, which prevents the ice crystals from fusing together. Therefore, the ice formed is structurally weak and any solid material it binds together is weakly consolidated.

B. STUDIES WITH COAL : Having talked about the compressive strength of ice and ice containing various additives, the compressive strength of frozen coal samples are now discussed.

B.1. MOISTURE CONTENT : The moisture content of the coal sample #3 was determined using the ASTM D-2961 test. Table III-5 gives the results for two determinations of the coal collected from the top part of the drum on Jan. 8, 1983. For both runs, the weight loss during the 3.0-

TABLE III-5

Moisture Analysis of Coal Sample #3 (6-20 mesh)

Heating	Run #1 (107°C)		Run #2 (107°C)	
Time, hrs.	Wt.(gm)	% Water	Wt.(gm)	% Water
0.0	526.3	----	519.7	----
1.5	494.8	5.99	488.7	5.96
2.0	493.5	6.23	487.4	6.22
2.5	493.1	6.31	486.9	6.31
3.0	492.7	6.38	486.7	6.35
3.5	492.6	6.40	486.6	6.37

3.5 hour heating period was less than 0.05%, so the average of the 3.5 hour samoles, 6.38%, was taken as representative of this coal sample. However, the moisture contents of samples taken at later dates were different. Table III-6 gives the moisture contents of samples taken over a four-month period. The moisture content varied according to the date of sampling the coal sample and the part of the sample taken.

It is seen from Table III-6 that, with the lapse of time, the moisture content of the coal sample #3 decreased and finally stabilized to an approximate value of 4.50%. One of the possible reasons could be that, in winter, the air in the lab is relatively dry. The drum could not be closed seal tight and therefore the coal might have lost its moisture with the passage of time. The other reason could be that the coal in the top portion of the drum probably had higher moisture content than the one at the bottom.

After the supply of coal sample #3 was exhausted, the remaining experiments were done with coal sample #4. The moisture contents of the coal sample #4 were also measured and are summarized in Table III-7. It is observed from this table that, for the duration of its use, the moisture content was relatively constant.

TABLE III-6

Moisture Contents of Coal Sample #3 (6-20 mesh)

Date of Measurement	Moisture Content, %
1/08/83	6.38
1/22/83	5.34
2/11/83	4.80
3/22/83	4.95
5/13/83	4.52
5/25/83	4.50

TABLE III-7

Moisture Contents of Coal Sample #4 (6-20 mesh)

Date of Measurement	Moisture Content, %
6/21/83	4.17
7/21/83	4.06
8/8/83	4.06

B.2. PARTICLE SIZE DISTRIBUTION OF THE COAL SAMPLES : Table III-8 gives the particle size disribution for both coal samples #3 and 4. These results are also plotted in Figure III-2. The distribution curves are similar (unimodal); however the fourth coal sample had slightly less small coal particles than the third coal sample.

B.3. COMPRESSIVE STRENGTH OF FROZEN COAL CYLINDERS WITHOUT ANY CHEMICAL ADDITIVES : The compressive strengths of frozen coal cylinders were determined as described in Sections II.B.4 and II.B.5. In this work, the frozen coal cylinders without any chemical additives are referred to as "CONTROL". For coal sample #3, the compressive strengths as a function of percent water are listed in Table III-9. The percent water includes the added water plus the initial moisture present in the coal.

For the first set of experiments in Table III-9, the moisture content was 6.38%. Later, a second set of experiments were also done, and this time the moisture content was 4.95%. These results are also plotted in Figure III-3. It is observed that the compressive strength of coal frozen with different water contents increased with increasing water content, linearly from 10% to 16% water and more rapidly thereafter, reaching a

TABLE III-8

Size Distributions of Coal Samples #3 and #4
By Sieving of Dried Coal

		Coal Retained on Sieve			
Sieve	Sieve	Coal Sample #3		Coal Sample #4	
Number	Opening(mm)	Wt.(g)	Wt.(%)	Wt.(g)	Wt.(%)
6	3.35	1.6	0.32	2.0	0.40
7	2.80	39.3	7.89	41.9	8.40
8	2.36	34.8	6.99	42.3	8.48
10	2.00	41.9	8.41	49.4	9.90
12	1.70	47.5	9.54	52.6	10.54
14	1.40	37.0	7.43	51.2	10.26
16	1.18	36.9	7.41	35.9	7.20
18	1.00	34.8	6.99	48.7	9.76
20	0.85	44.7	8.97	62.5	12.53
20	0.85	179.6	36.06	112.4	22.53
Total		498.1	100.00	498.9	100.00

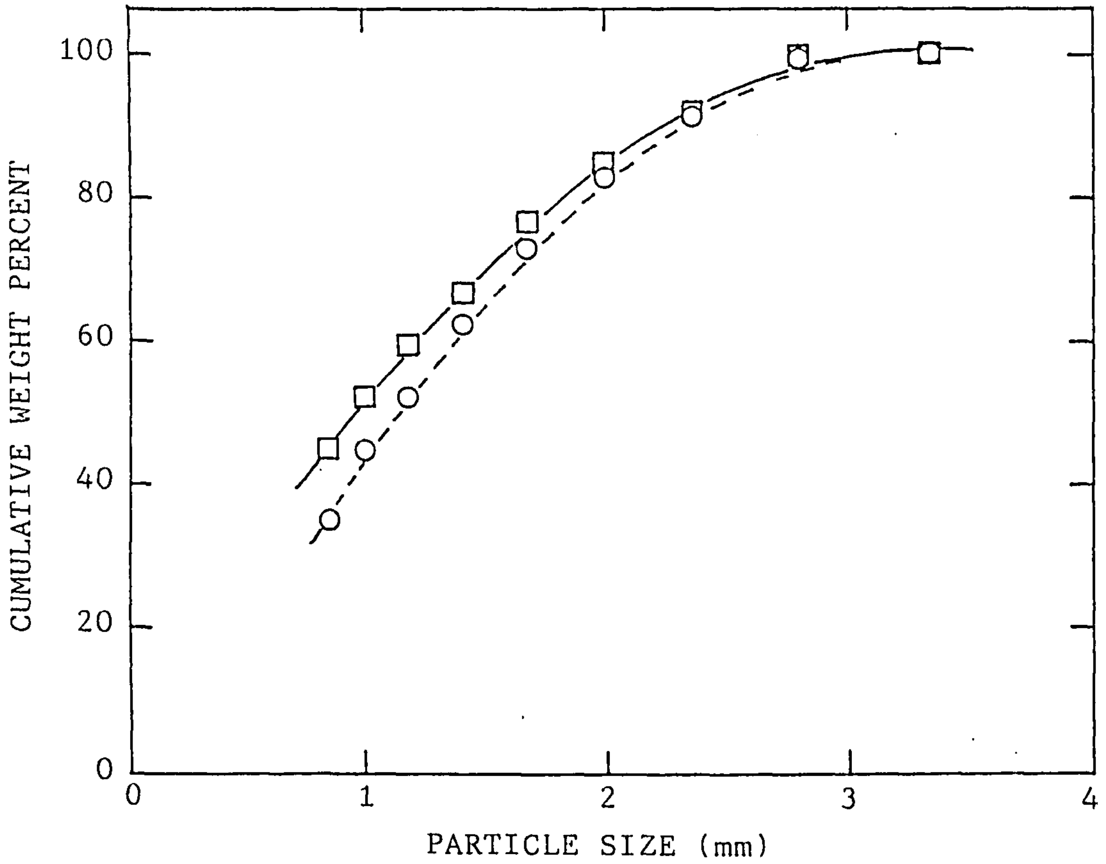


Fig. III-2: Cumulative weight percent as a function of particle size for coal samples #3 and #4.
<u>LEGEND</u>:

- ☐ Coal sample #3
- ○ Coal sample #4

TABLE III-9

Compressive Strength of Frozen Coal Cylinders Prepared From Coal Sample #3 Sampled at Different Times

(Controls)

Moisture Content = 6.38%

Percent Water	Compressive Strength, psi Tube: 1	2	3	4	5	6	ave.	sigma
10	35	32	35	32	35	35	34	2
12	64	54	80	54	67	54	62	10
14	64	76	86	89	102	99	86	14
16	134	124	156	95	121	131	127	20
18	207	239	197	213	166	181	201	26
20	420	255	264	372	452	341	351	80

Moisture Content = 4.95%

Percent Water	Compressive Strength, psi Tube: 1	2	3	4	5	6	ave.	sigma
10	54	51	51	60	45	54	53	5
12	89	86	95	95	102	80	91	8
14	111	102	105	102	105	80	101	11
16	162	131	185	156	137	178	158	22
18	258	251	216	226	236	248	239	16
20	353	395	474	344	299	398	377	60

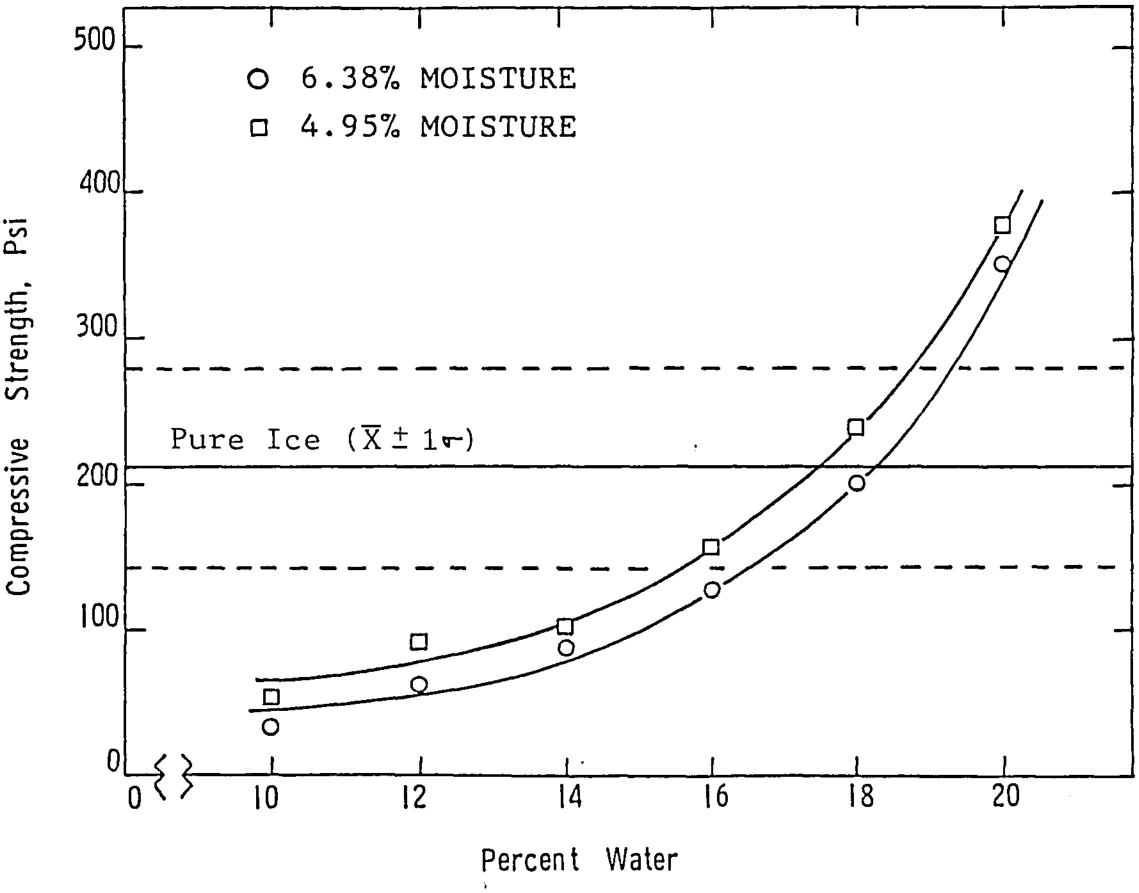


Fig. III-3: Variation of compressive strength of frozen coal cylinders with percent water for two different samples of coal sample#3.

value at 20% water which is greater than the value of ice alone. The initial linear increase may be attributed to the increasing size of the annular ice rings arond the points of contact between the particles, and the more rapid increase to the filling of the interstices between the packed particles. Another accompanying phenomenon may be that, at very low water content, all the ice contacts may not have been made between the coal particles and therefore some of the initial linear increase might be due to the formation of more of these ice contacts.

It is seen from Figure III-3 that, for the same totat percent water, the coal sample containing 6.38% water gave slightly lower compressive strengths than that containing 4.95% water. Moreover, Table III-10 shows that the differences were statistically significant except possibly for the samples containing 14% and 20% water. The differences between the two curves of Figure III-3 along the percent water abscissa (average 1.2%) were approximately equal to, or slightly smaller than, 1.43% difference in moisture content. Thus these results suggest that the initial water content has less influence on the compressive strength of the frozen coal cylinder than the amount of water added to the sample to make up the total water content to the desired value.

TABLE III-10

Statistical Comparison Between Frozen Coal Cylinders Prepared From Coal Sample #3 Sampled at Different Times

(Controls)

Moisture Content	= 6.38%		4.95%			
	Compressive Strength, psi					
Percent	Control		Control		Calcd.	Crit.
Water	ave.	sigma	ave.	sigma	t	t(95%)
10	34	2	53	5	8.64	2.23
12	62	10	91	8	5.55	2.23
14	86	14	101	11	2.06	2.23
16	127	20	158	22	2.55	2.23
18	201	26	239	16	3.05	2.23
20	351	80	377	60	0.64	2.23

B.3.1. <u>EFFECT OF WATER CONTENT</u> : To test the foregoing hypothesis, the data in Table III-9 were replotted in Figure III-4 as a fuction of the amount of water added per 100 gm of "as is" coal. It is observed that all the points fell on the same continuous curve. The coincidence of these points may be due to two possible reasons: (i) the moisture initially present in the coal does not contribute significantly to the compressive strength of the frozen coal cylinders; (ii) most of the added water remains as external water and only a negligible amount fills the pores of the coal particles. Therefore, the added water forms annular rings around the contact points between the coal particles which, when frozen, contribute to the compressive strength of the frozen coal cylinders.

This latter explanation is supported by the adsorption on the coal particles of nitrogen at liquid nitrogen temperature and water vapor at 25°C. Nitrogen adsorption showed that the specific surface area of the coal was 2.2 m^2/gm, a relatively small surface area. The water vapor adsorption studies showed that 0.0179 gm water/gm coal was adsorbed on a sample which had been evacuated at 25°C for 24 hours at 10^{-6} torr. Since the surface area and pore volume of the coal particles are small relative to the amount of water added to prepare

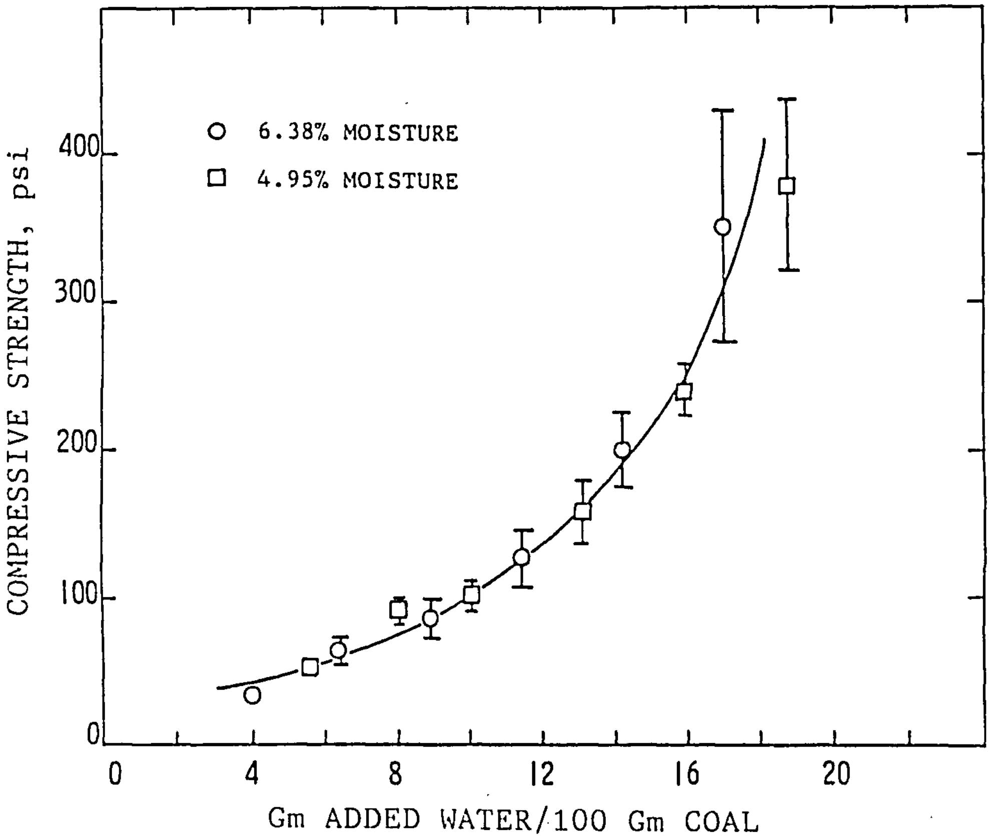


Fig. III-4: Variation of compressive strength ($\overline{X} \pm 1\sigma$) of frozen coal samples with gm added water/100 gm coal for two different samples of coal sample#3. The compressive strengths of the same coal samples are also plotted in fig. III-3.

the frozen coal cylinders, only a negligible amount of the added water goes into the coal particles and the major part remains on the surface as external water.

This conclusion was confirmed by another experiment in which the coal paticles retained on sieve #6 (opening 3.35 mm) were blown with air to remove any loose carbon particles clinging to their surface, weighed, and placed in a beaker with an excess of deionized water for 24-48 hours. The coal particles were then removed from the beaker, dried by rolling them on blotting paper, and reweighed. The amount of water absorbed was negligible (zero within experimental error). In another experiment, coal particles of the same size were dried at 107 C for 3 hours (ASTM D-2961), weighed, then immersed in water and dried using blotting paper as described above. The amount of water absorbed was 1.92%, in good agreement with the 1.79% found by adsorption of water vapor. These experiments confirm that the water added to the coal remains as external water and forms annular rings at the contact points between adjacent coal particles which, when frozen, increases the compressive strength.

The compressive strengths of frozen coal cylinders prepared from coal sample #4 were also determined and are given in Table III-11. The moisture content of this coal

TABLE III-11

Compressive Strength of Frozen Coal Cylinders (Control)

(Coal Sample #4)

Moisture Content = 4.17%

Percent		Compressive Strength, psi							
Water	Tube:	1	2	3	4	5	6	ave.	sigma
10		76	92	70	76	83	83	80	8
12		86	86	86	86	76	102	87	8
14		111	105	115	105	108	118	110	5
16		134	162	115	124	185	169	148	28
18		201	194	169	216	201	220	200	18
20		201	251	255	236	201	185	221	30

sample was 4.17%.

Encouraged by the observations for the coal sample #3 in Figure III-4, the compressive strengths of all the controls from various coal samples were plotted as a function of the amount of water added per 100 gm coal in Figure III-5. This figure also contains the results for the coal sample #2 collected by the earlier investigators in this lab [Earhart and Ding-1983]. Within experimental error, the results for all the coal samples #2, #3 (three different samples), and #4 fell on the same curve, confirming that the factors determining the compressive strength of frozen coal cylinders are essentially the same for different coal samples from the same source but with different moisture contents.

Regression analysis was used to fit the data of Figure III-5 to the following equation,

$$Y = be^{ax} - b \qquad (3.1)$$

where Y is the compressive strength in psi, x is the gm water added per 100 gm coal, and a and b are constants with values of 0.0690 and 118, respectively. The curve of Figure III-5 calculated from equation 3.1 fits the experimental points well. The average error was -2.42% and the mean absolute error was 16.45%. These errors are

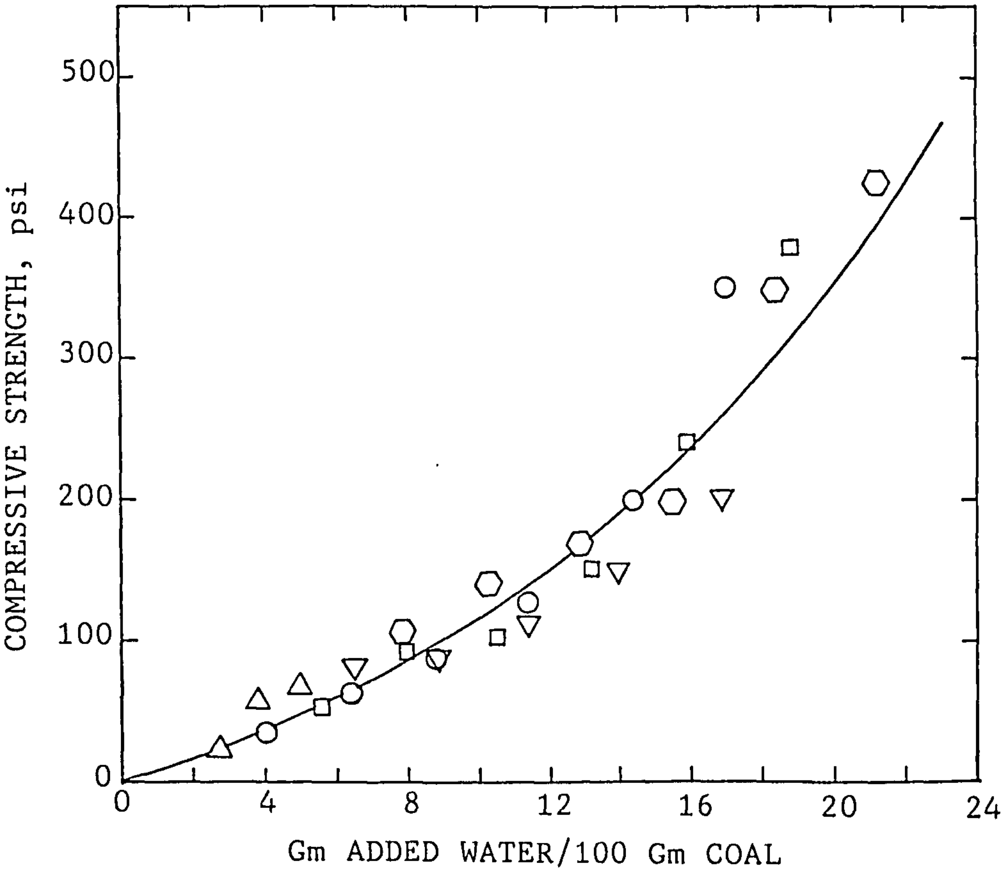


Fig. III-5: Variation of compressive strength of frozen coal cylinders (6-20 mesh) with gm water added/100 gm coal for various coal samples #2, #3 and #4 of different moisture contents.
LEGEND:

⬡ 2.95% water (#2)
○ 6.38% water (#3)
□ 4.95% water (#3)
△ 4.50% water (#3)
▽ 4.17% water (#4)

defined as follows,

$$\% \text{ error} = [100(\text{calcd} - \text{exptl})/\text{calcd}], \qquad (3.2)$$

$$\text{average error} = \Sigma\, \% \text{ error}/n, \qquad (3.3)$$

$$\text{mean absolute error} = (\,\Sigma\, |\% \text{ error}|\,)/n, \qquad (3.4)$$

where n is the number of data points. Equation 3.1 was chosen such that when the amount of water added is zero, the calculated compressive strength would be zero. The other feature of this equation is that for low amounts of added water it provides an approximate linear relation with the compressive atrength ($Y \cong bax$). Furthermore, for high values of x, it provides an exponential growth of the compressive strength. This equation may be used to predict the compressive strength of frozen coal cylinders containing up to 22 gm added water/100 gm coal.

A word of caution about the effect of moisture content on the compressive strength of frozen coal cylinders is in order. In the present investigation, the coal used had very low surface area and pore volume. However, in the literature, coals with high surface areas and pore volumes of the order of 10-23 ml/100 gm of coal have been reported [Fuller-1981, Mahajan and Walker-

1978]. For these coals with high surface areas and high pore volumes, the influence of initial water content (moisture content) on the compressive strength of the frozen coal cylinders is uncertain, whereas, in the present investigation, it has already been seen that the influence of moisture content on the compressive strength is negligible.

Experiments were also conducted with coal sample #3 to find the amount of water added for which the frozen coal cylinders, when taken out of PVC tube, would crumble. For this purpose, compressive strengths of frozen coal cylinders with 4.95, 3.8, 2.7 and 1.6 gm of water/ 100 gm of coal were measured. The moisture content for this coal was 4.50%. The coal cylinder with 1.6 gm water/100 gm coal crumbled, whereas the others with 4.95, 3.8 and 2.7 gm water/100 gm coal gave compressive strengths of 68 ± 7, 57 ± 4 and 21 ± 3 psi respectively. These results were also plotted in Figure III-5.

B.3.2. COMPARISON OF COAL SAMPLE #3 AND 4 : The compressive strengths of frozen coal cylinders prepared from coal sample #4 (4.17% moisture content) are compared with that of coal sample #3 (4.95% moisture content) in Table III-12. The coal sample #4 gave higher compressive strength at 10% water. This may be because coal sample

TAB1E III-12

Statistical Comparison Between Frozen Coal Cylinders Prepared From Coal Sample #3 And #4

(Controls)

Moisture Content = 4.95% 4.17%

Percent Water	Compressive Strength, psi				Calcd. t	Crit. t(95%)
	Coal Sample #3		Coal Sample #4			
	ave.	sigma	ave.	sigma		
10	53	5	80	8	7.01	2.23
12	91	8	87	8	0.87	2.23
14	101	11	110	5	1.82	2.23
16	158	22	148	28	0.69	2.23
18	239	16	200	18	3.97	2.23
20	377	60	221	30	5.70	2.23

#4 had more larger-size coal paricles than coal sample #3. As a result, for the same mass of coal, sample #4 had less total external surface area than coal sample #3. Therefore, it may be that, at 10% water level, sufficient water was not available to form all the ice contacts for the sample #3 and gave compressive strength lower than sample #4. When the percent water was increased above 10%, it is observed that the compressive strengths were roughly the same within experimental error. However, for 18% and 20% water contents, the compressive strength of coal sample #3 was higher than that of coal sample #4. This may be explained on the basis that, for coal sample #4, there were more larger-size particles and therefore, overall, there were fewer ice contacts, even though they may be thicker than those of coal sample #3. It may be that, owing to more ice contacts, coal sample #3 gave higher compressive strength at 18% and 20% water. Similar conclusions have been drawn by Lebedev et al. [1976].

B.3.3. <u>EFFECT OF RATE OF LOADING</u> : As described in Section II.B.5., all of the compression testing was done at the loading rate of 1.0 to 1.1 inch per minute. For coal sample #4 with 20% water content, the compression testing was done at loading rates of 1.07 inch per minute and 2.34 inch per minute. The moisture content was 4.06%. For a loading rate of 1.07 inch/min, the compressive strength was 221 ± 20 psi, and for a loading rate of 2.43 inch/min, it was 166 ± 19 psi. Therefore, an increase in loading rate by a factor of 2.2 resulted in a decrease in compressive strength by 25%. It was observed that, with the slower rate, the frozen coal specimens failed by relatively slow crumbling rather than by massive fracture. With the faster loading rate, the frozen coal samples failed catastrophically.

B.4. COMPRESSIVE STRENGTH OF FROZEN COAL CYLINDERS WITH CHEMICAL COMPOUNDS AS ADDITIVES : The chemical compounds which have been used as an additives are ethylene glycol, urea, sugar and ammonium acetate.

B.4.1. STUDIES WITH ETHYLENE GLYCOL : The compressive strength of frozen coal cylinders containing 2 pints ethylene glycol/ton coal were measured; since the density of ethylene glycol is 1.113 gm/cm^3, this concentration amounts to 2.32 lbs/ton coal. These results are listed in Table III-13, and have been compared with control in Table III-14. These results were compared with control of moisture content 4.95% rather than 6.38% because 4.95% was closer to 5.34%. It is seen from the Table III-14

TABLE III-13

Compressive Strength of Frozen Coal Cylinders Containing 2 pints Ethylene Glycol/ton Coal

(Coal Sample #3)

Moisture Content = 5.34%

Percent	Compressive Strength, psi							
Water	Tube: 1	2	3	4	5	6	ave.	sigma
10	13	13	16	13	13	19	14	3
12	51	57	48	38	45	54	49	7
14	118	121	99	108	76	115	106	17
16	159	159	191	229	140	178	176	35
18	255	229	216	277	213	264	242	27
20	427	407	433	436	455	506	444	34

TABLE III-14

Statistical Comparison of Frozen Coal Cylinders Containing Ethylene Glycol With Control

(Coal Sample #3)

Moisture Content	=	5.34%		4.95%			
	Compressive Strength, psi						
Percent	Ethylene Glycol*		Control			Calcd.	Crit.
Water	ave.	sigma	ave.	sigma		t	t(95%)
10	14	3	53	5		16.38	2.23
12	49	7	91	8		9.68	2.23
14	106	17	101	11		0.60	2.23
16	176	35	158	22		1.07	2.23
18	242	27	239	16		0.23	2.23
20	444	34	377	60		2.38	2.23

* Ethylene glycol is used in concentration equivalent to 2 pints/ton of coal.

that the compressive strength of the frozen coal cylinders were smaller for the ethylene glycol-containing samples at 10-12% water and roughly the same at 14-18% water and greater at 20% water. Thus the addition of ethylene glycol in 2 pints/ton coal concentration at 10% water gave a compressive strength only 26% of that of the control; the same concentration at 12% water gave a compressive strength 54% of that of the control. Further dilution with increasing water contents gave compressive strengths statistically similar to those of control at 14-18% water and about 18% greater at 20% water.

To verify the increase in compressive strength of coal samples containing ethylene glycol over those of control at higher percent water, the data are plotted as a fuction of amount of water added/100 gm coal in Figure III-6. The continuous curve shown in Figure III-6 is same as drawn in Figure III-4. Thus it is seen from this figure that, while, at low water contents, the decrease in compressive strength due to ethylene glycol is real, at higher water contents, within the experimental error, there is no difference between the control samples and those containing ethylene glycol. These results are not unexpected because the ice cylinders containing ethylene glycol gave compressive strengths which decreased with increasing ethylene glycol concentration or,

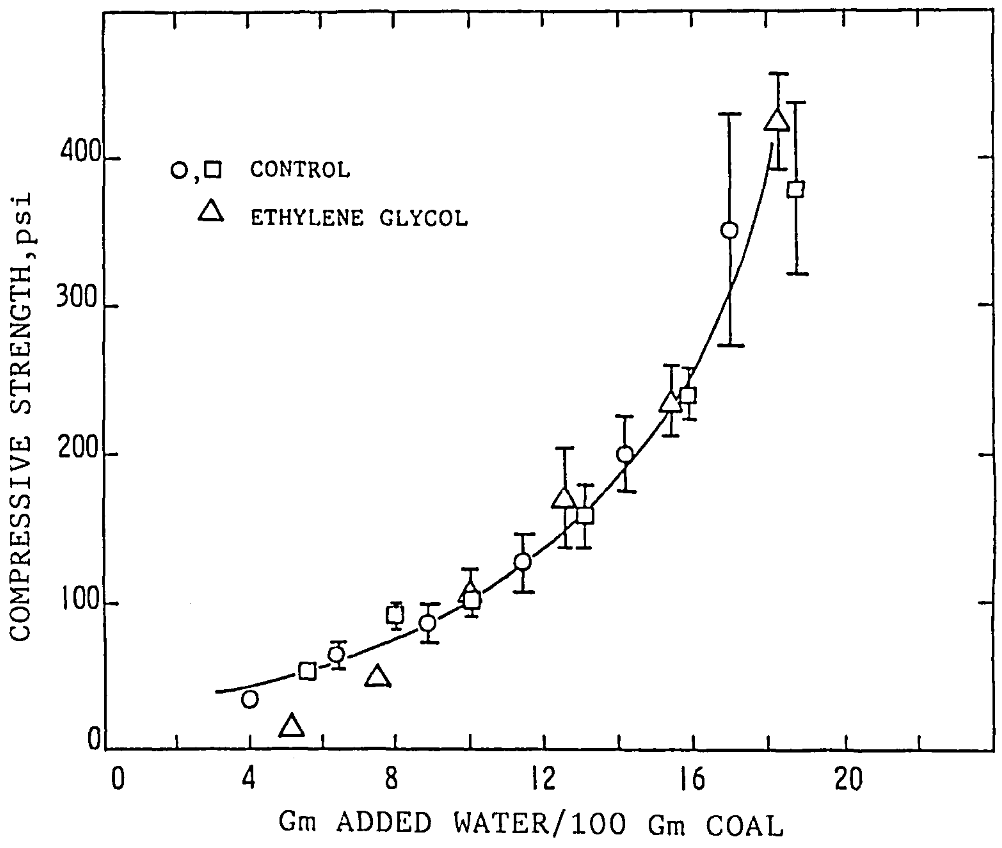


Fig. III-6: Variation of compressive strength ($\overline{X} \pm 1\sigma$) of frozen coal cylinders with gm water added/100 gm coal for the two control samples and the sample containing 2 pints ethylene glycol/ton of coal.

in other words, with increase of water content, the compressive strength increased.

The decrease in the effectiveness of ethylene glycol with increasing water content is expected because the amount of ethylene glycol was held constant while the water content was increased, so that the ethylene glycol was effectively diluted. For example, the concentration of ethylene glycol in the solution used to prepare frozen coal cylinders with 10% water was 2.04 wt%, whereas this concentration dropped to 1.05 wt% for frozen coal cylinders with 14% water. Furthermore, it is seen from figure III-1 that ethylene glycol is effective in reducing the compressive strength of ice cylinders only when added in concentrations greater than 1.5 wt%. Thus it is not a great surprise that, for water contents greater than 14%, the use of ethylene glycol in concentration of 2 pints/ton of coal is ineffective in reducing the compressive strength.

Therefore, another series of experiments were done in which the concentration of ethylene glycol was maintained at a constant 2 wt% based on added water solution, while the water content in the frozen coal samples was increased from 10% to 20%. Table III-15 gives the compressive strengths of frozen coal cylinders. Figure III-7 shows the variation of compressive strength of

TABLE III-15

Compressive Strength of Frozen Coal Cylinders Containing 2 wt% Ethylene Glycol Based on the Water Solution Added

(Coal Sample #3)

Moisture Content = 5.34%

Percent	Compressive Strength, psi							
Water	Tube: 1	2	3	4	5	6	ave.	sigma
10	22	16	25	25	25	---	23	4
12	38	45	38	48	---	25	39	9
14	86	---	70	70	57	64	69	11
16	131	115	99	115	131	140	118	13
18	181	175	162	191	223	156	187	23
20	258	296	353	328	255	239	298	43

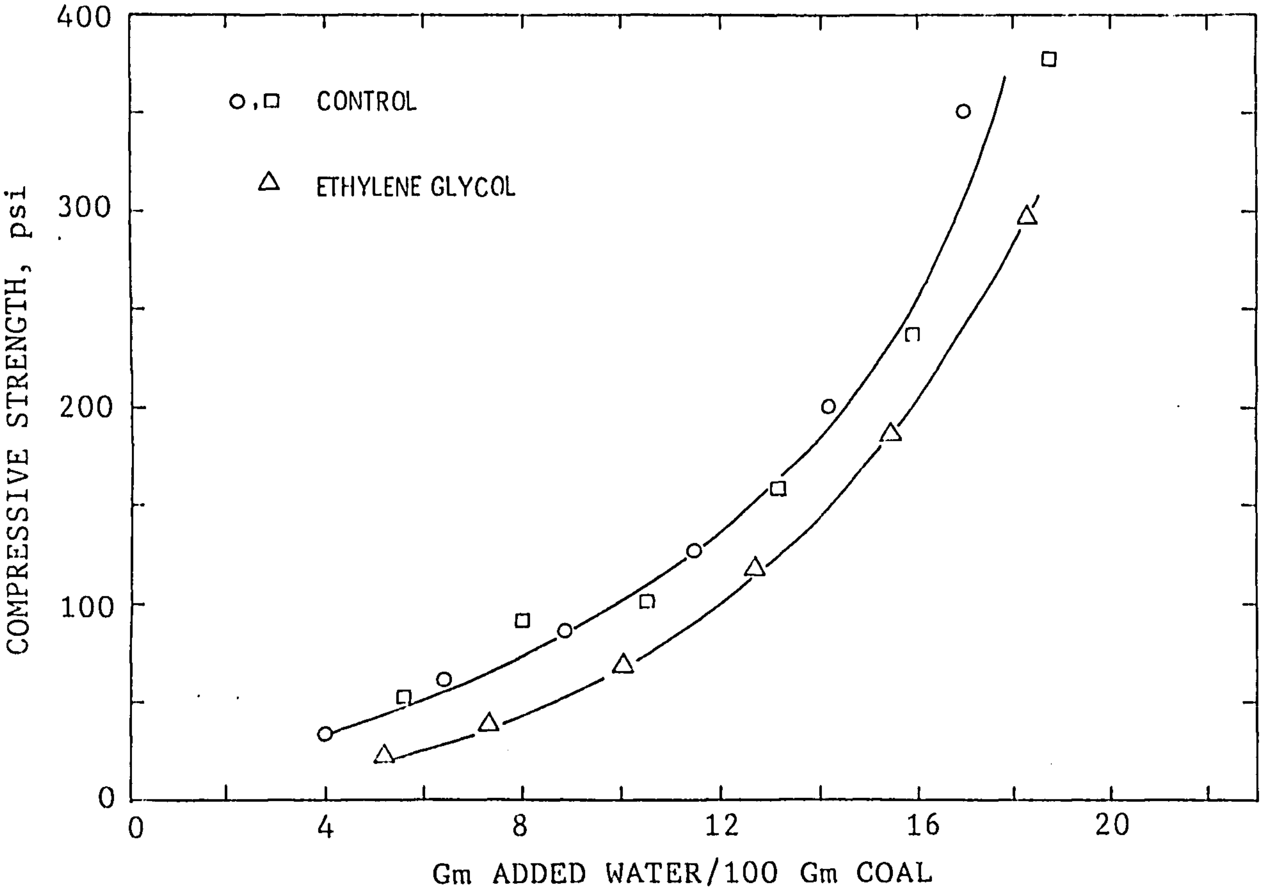


Fig. III-7: Variation of compressive strength of frozen coal cylinders with gm added water/100 gm coal for two control samples and the sample containing 2 wt% ethylene glycol based on water solution.

frozen coal samples with gm added water/100 gm coal for two different control samples and the sample containing ethylene glycol. A statistical comparison of these results along with the percent reduction in compressive strength due to ethylene glycol is given in Table III-16. It is concluded that the compressive strengths of the ethylene glycol-containing samples were all smaller than those of the controls; 2 wt% ethylene glycol based on added water gave smaller compressive strengths than the control at all water contents upto 20%.

In all composites, the ultimate physical strength depends upon the cohesion of the adhesive and its adhesion to the filler or substrate. When a composite fails, it is not always obvious whether the mechanism of failure is cohesive or adhesive. In the present case, the coal is the filler and the ice is the adhesive. The cohesion of the ice is represented by its compressive strength. Yancey and Geer [1968] have reported compressive strengths of coal-coal bonds which are much higher than the compressive strength of frozen coal composites observed in these experiments. Therefore, the compressive strength of frozen coal composites is represented by the combination of cohesion of ice and its adhesion to coal.

The addition of ethylene glycol to water makes

TABLE III-16

Statistical Comparison of Frozen Coal Cylinders Containing Ethylene Glycol With Control

(Coal Sample #3)

Moisture Content = 5.34% 4.95%

Percent Water	Compressive Strength, psi				Calcd. t	Crit. t(95%)	% Reduction in Strength
	Ethylene Glycol*		Control				
	ave.	sigma	ave.	sigma			
10	23	4	53	5	10.81	2.26	56
12	39	9	91	8	10.15	2.26	57
14	69	11	101	11	4.80	2.26	31
16	118	13	158	22	3.83	2.23	26
18	187	23	239	16	4.55	2.23	22
20	298	43	377	60	2.62	2.23	21

* The concentration of Ethylene glycol in solution is 2 wt%.

weaker ice and hence weaker frozen coal composites. Therefore, the mechanism of failure can be cohesive, i.e., the presence of the ethylene glycol during freezing makes weaker ice, which will fail even if the ice-coal adhesive bond is strong. However, it is not clear whether the addition of ethylene glycol would also lower the adhesive strength of ice-coal bonds and contribute to the decrease in compressive strength of frozen coal composites.

It may be concluded that ethylene glycol can be a possible choice as a good freeze conditioning agent.

B.4.2. STUDIES WITH UREA : In order to study the compressive strength of frozen coal cylinders containing urea equivalent to 2 pints/ton of coal, the amount of urea used was 2.32 lbs/ton of coal. The urea was used in the form of prills. Since the calculation of the amount of urea needed to be equivalent to 2 pints/ton of coal requires the density of urea, and it was not clear whether to use the true density or the packing density of the urea prills; therefore, the amount used was same as for ethylene glycol, i.e., 2.32 lbs/ton of coal. This was done to provide a good comparison on the weight basis between the results of ethylene glycol and urea. The results for urea are given in Table III-17.

TABLE III-17

Compressive Strength of Frozen Coal Cylinders Containing Urea Equivalent to 2.32 lbs/ton coal

(Coal Sample #3)

Moisture Content = 6.38%

Percent		Compressive Strength, psi							
Water	Tube:	1	2	3	4	5	6	ave.	sigma
10		6	---	10	6	13	---	9	3
12		41	48	38	38	45	48	42	4
14		105	95	70	73	70	102	86	17
16		169	159	194	137	137	162	160	22
18		245	299	197	306	321	309	280	48
20		462	420	414	433	446	516	448	37

Table III-18 gives the statistical comparison of the frozen coal cylinders containing urea with those of the control cylinders. Figure III-8 shows the variation of compressive strength with the amount of water added/ 100 gm of coal. The addition of urea in a concentration equivalent to 2 pints/ton coal gave compressive strengths only 26% and 68% of those for the control at 10% and 12% water, respectively, the same value as the control at 14% water, and 26%, 39%, and 28% greater values at 16%, 18% and 20% water, respectively. The actual increase in compressive strengths were 33, 79 and 97 psi at 16%, 18% and 20% water, respectively. Thus the compressive strengths were unexpectedly low for 10% and 12% water, considering that the addition of urea to water gave much stronger ice than the control (pure ice).

As seen from Table III-18, for the overall water contents greater than 12%, urea was ineffective in lowering the compressive strength. This was probably due to dilution effect as described for ethylene glycol, i.e., the concentration of urea was kept constant based on the coal and not on the amount of added water. Therefore, with the increase of overall percent water, the concentration of urea decreased and was probably ineffective in lowering the compressive strength. As a result, another set of experiments similar to those of ethylene glycol

TABLE III-18

Statistical Comparison of Frozen Coal Cylinders Containing Urea With Control

(Coal Sample #3)

Moisture Content = 6.38% 6.38%

	Compressive Strength, psi					
Percent	Urea*		Control		Calcd.	Crit.
Water	ave.	sigma	ave.	sigma	t	t(95%)
10	9	3	34	2	15.98	2.31
12	42	4	62	10	4.55	2.23
14	86	17	86	14	0.00	2.23
16	160	22	127	20	2.72	2.23
18	280	48	201	26	3.54	2.23
20	448	37	351	80	2.70	2.23

* Urea is used in concentration equivalent to 2.32 lbs/ton of coal.

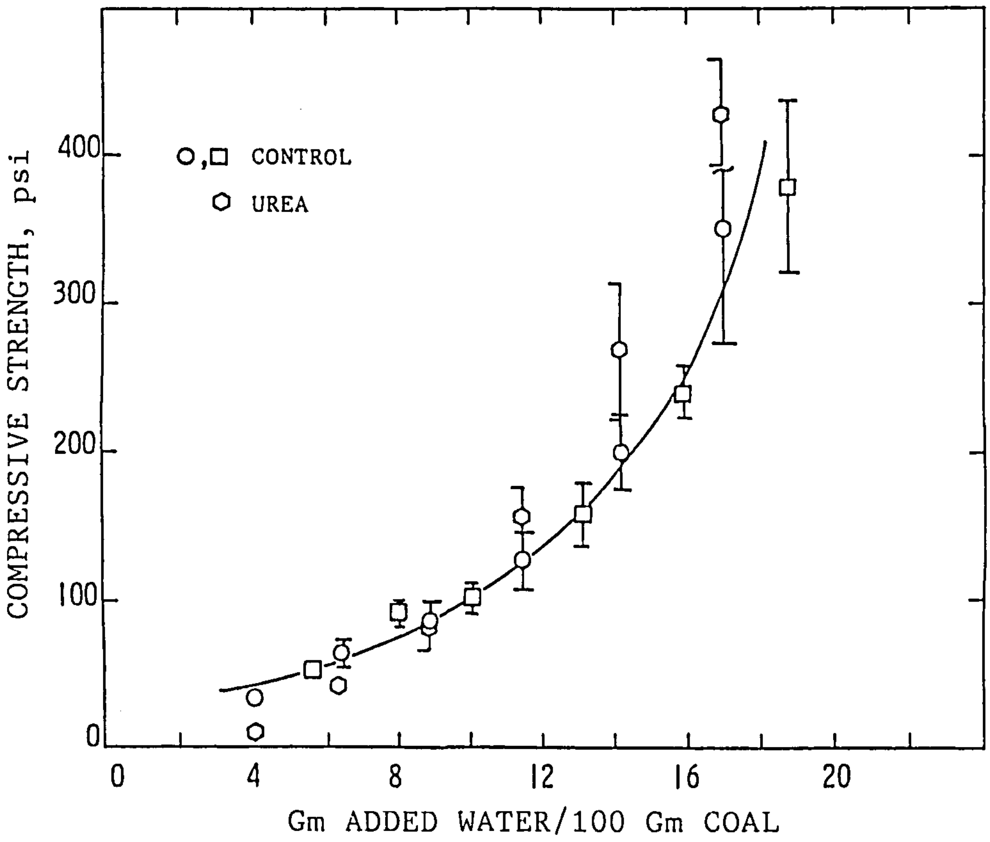


Fig. III-8: Variation of compressive strength ($\overline{X} \pm 1\sigma$) of frozen coal cylinders with gm added water/100 gm coal for two control samples and the sample containing equivalent of 2 pints/ton of coal.

were done with urea. The concentration used this time was a constant 2 wt% based on the water solution added and not on coal. Table III-19 gives the compressive strengths of frozen coal cylinders containing 2 wt% urea. The moisture content of the coal used was 4.80%.

The results of Table III-19 are compared with the control for which the moisture content was 4.95% in Table III-20. From the t-tests, it is seen that up to 12% water content the reduction in compressive strength was quite significant, but from 14% water content and higher, the difference in compressive strength was statistically insignificant. Probably for urea, a higher concentration would be more effective in reducing the compressive strength.

Figure III-9 shows the variation of compressive strength with percent water of frozen coal cylinders containing 2 wt% urea based on the added water solution and the controls containing 4.95% and 6.38% moisture. The points for the urea containing samples virtually coincided with those of the control containing 4.95% water while those for the control containing 6.38% water were lower. Figure III-10 shows the same data plotted against the amount of added water/100 gm coal, as well as those for 2 wt% ethylene glycol based on water solution. The curves for both controls virtually coincided, whereas

TABLE III-19

Compressive Strength of Frozen Coal Cylinders Containing 2 wt% Urea Based on the Water Solution Added

(Coal Sample #3)

Moisture Content = 4.80%

Percent	Compressive Strength, psi							
Water	Tube: 1	2	3	4	5	6	ave.	sigma
10	35	29	25	29	35	35	31	4
12	54	76	67	83	80	80	73	11
14	86	102	108	115	80	---	98	15
16	156	108	143	153	159	194	152	28
18	226	255	299	245	277	267	262	26
20	420	350	414	363	232	328	351	69

TABLE III-20

Statistical Comparison of Frozen Coal Cylinders Containing Urea With Control

(Coal Sample #3)

Moisture Content	=	4.80%		4.95%			
	Compressive Strength, psi						
Percent	Urea*		Control		Calcd.	Crit.	
Water	ave.	sigma	ave.	sigma	t	t(95%)	
10	31	4	53	5	8.42	2.23	
12	73	11	91	8	3.24	2.23	
14	98	15	101	11	0.38	2.26	
16	152	28	158	22	0.41	2.23	
18	262	26	239	16	1.85	2.23	
20	351	69	377	60	0.70	2.23	

* The concentration of Urea in solution is 2 wt%.

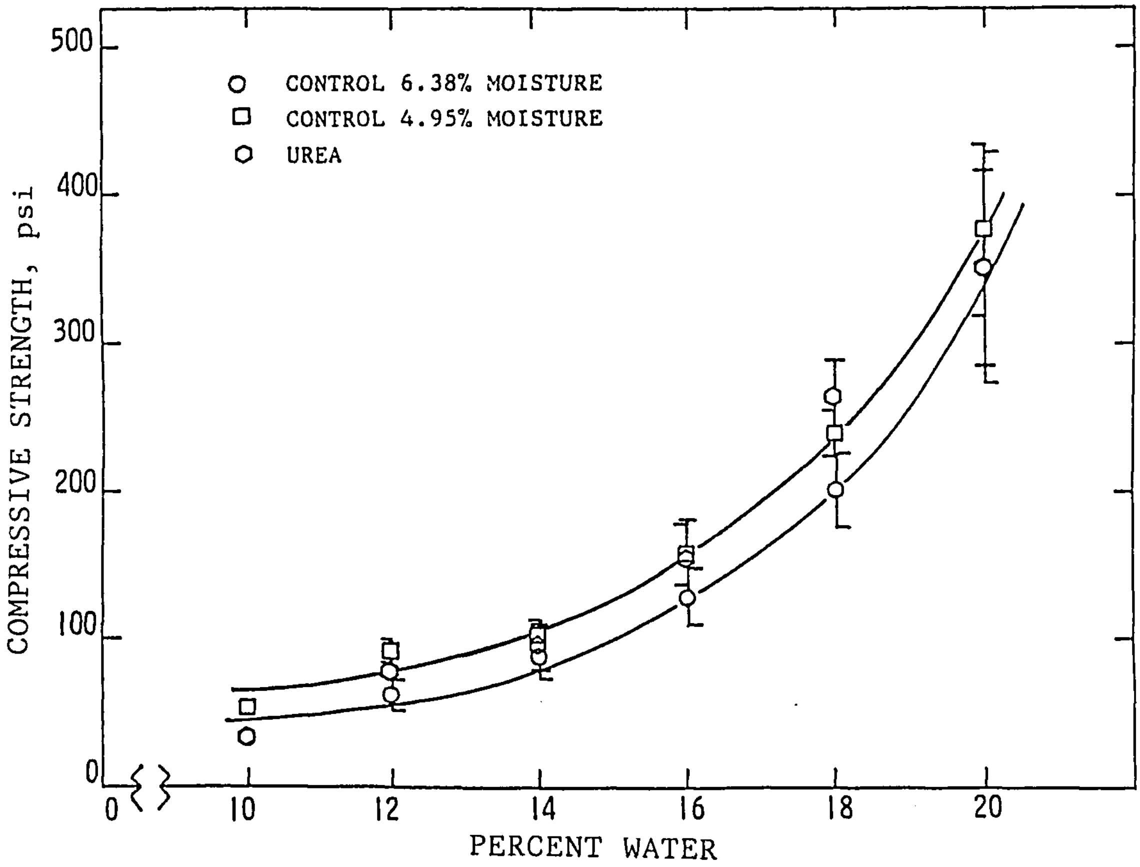


Fig. III-9: Variation of compressive strength ($\overline{X} \pm 1\sigma$) of frozen coal cylinders with percent water for samples containing 2wt% urea based on water solution compared with two control samples.

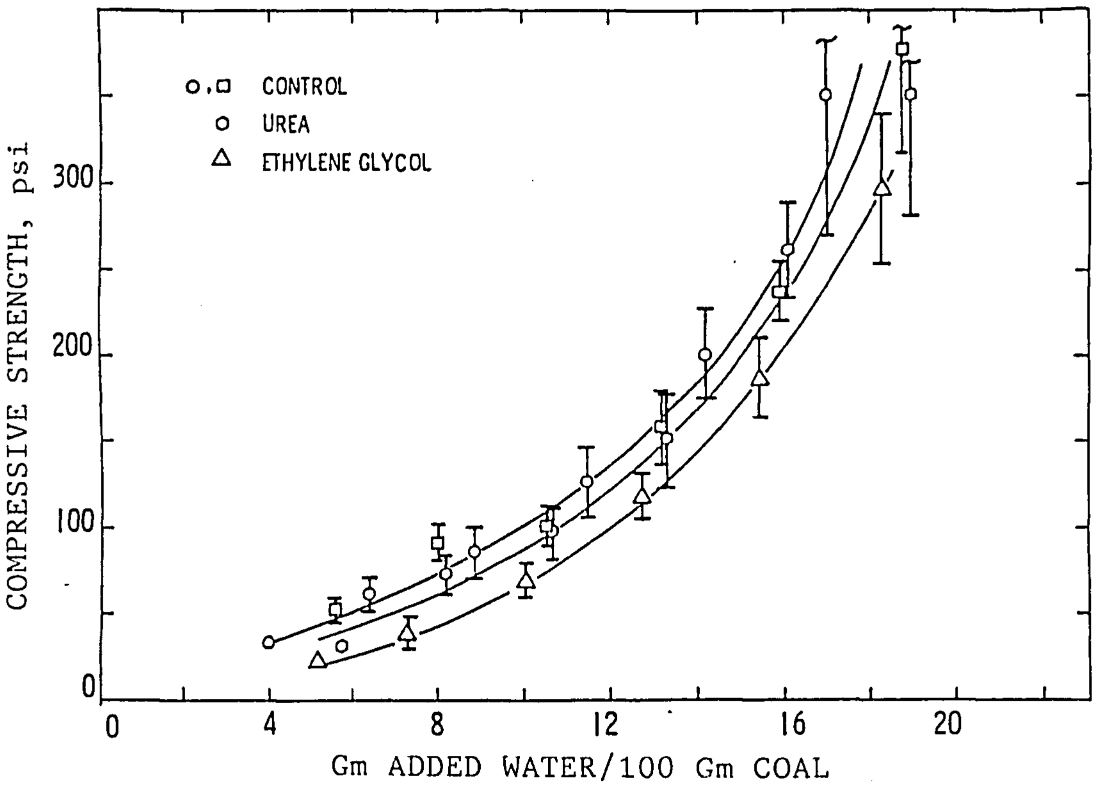


Fig. III-10: Variation of compressive strength ($\overline{X} \pm 1\sigma$) of frozen coal cylinders with gm water added per 100 gm coal for the two control samples, the sample containing 2wt% urea based on water solution also shown in fig. III-9 and the sample containing 2wt% ethylene glycol based on water solution.

the curve for urea fell below that for the controls, and that for ethylene glycol fell below the curve for urea, thus confirming that the compressive strength is determined by the amount of water added rather than the total water content.

As discussed earlier, the compressive strength of frozen coal composites is determined by the combination of the cohesion of ice and its adhesion to coal. Urea forms strong ice, but weak frozen coal composites. Therefore the mechanism of failure of frozen coal compostes must be adhesive, i.e., the presence of urea during freezing process gives a weak ice-coal adhesive bond.

As discussed in Chapter I, Glanville and Haley [1982] attributed the decrease in compressive strength of frozen coal samples due to the addition of FCA's solely to the weakening of cohesive strength of ice. While their reasoning does explain the decrease in the compressive strength of frozen coal composites due to the addition of ethylene glycol, it fails to explain the decrease due to the addition of urea. In the present investigation, it has been demonstrated that, while the addition of a chemical compound may increase the strength of ice-ice bonds, it can also simultaneously decrease the strength of ice-coal adhesive bonds, leading to an overall decrease in the compressive strength of frozen coal composites.

B.4.3. STUDIES WITH ETHYLENE GLYCOL AND UREA MIXTURES : Both ethylene glycol and urea lower the compressive strength of frozen coal cylinders. Ethylene glycol forms weak ice; urea forms strong ice but weak ice-coal adhesive bonds. The possibility of a synergistic interaction between the two compounds was investigated by measuring the compressive strengths of frozen coal cylinders (coal sample #3). Several solutions in water were prepared such that the total amount of ethylene glycol and urea in solution was 2 wt%. The relative amounts of urea and ethylene glycol were different for each solution. The frozen coal samples were prepared with these solutions such that the final water content was 16%. The results are summarized in Table III-21 and are also plotted in Figure III-11. It is seen from the figure that there is no synergistic effect observed. The variation of compressive strength with composition was linear from 127 psi for ethylene glycol to 171 psi for urea. The compressive strength can be easily described by a best-fit straight line. The data were fitted by the regression equation,

$$\text{compressive strength} = c_1 w + c_2 (1 - w) \qquad (3.5)$$

TABLE III-21

Compressive Strength of Frozen Coal Cylinders Containing 2 wt% Ethylene Glycol-Urea Mixture at 16% Water Content

(Coal Sample #3)

Moisture Content = 4.52%

Relative Amount of UR (%)	Relative Amount of EG (%)	Compressive Strength, psi							
		Tube: 1	2	3	4	5	6	ave.	sigma
100	0	172	143	159	166	204	181	171	21
75	25	166	169	162	150	137	166	158	12
50	50	127	178	137	140	150	153	147	18
25	75	140	131	111	140	140	124	131	12
0	100	105	131	131	137	134	124	127	11
Pure Water		216	232	213	213	245	220	223	13

UR : Urea, EG : Ethylene Glycol

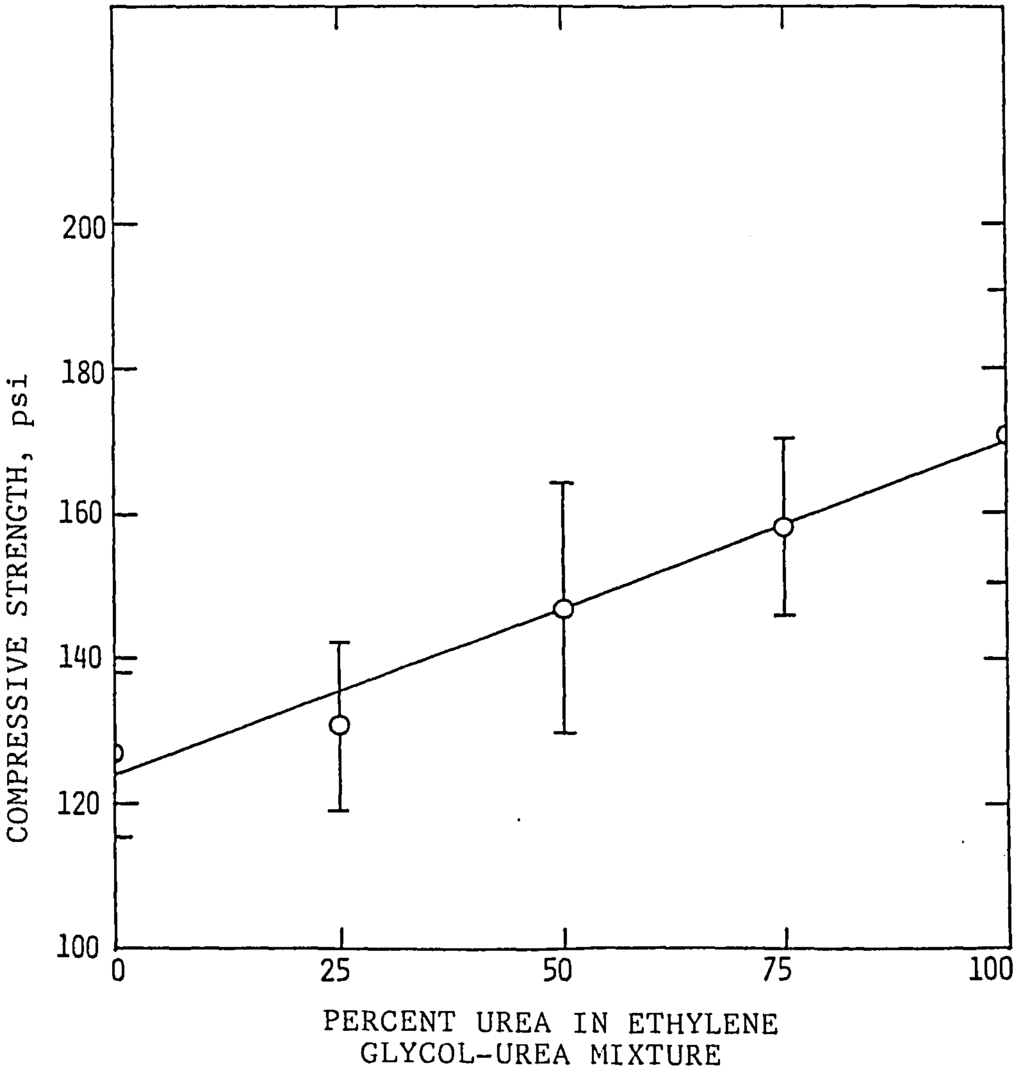


Fig. III-11: The effect of relative amount of urea and ethylene glycol on the compressive strength ($\overline{X} \pm 1\sigma$) of frozen coal samples containing 16% overall water content. Total concentration of ethylene glycol + urea in solution is 2wt%.

where w is the weight fraction of urea in the ethylene glycol-urea mixture; c_1 and c_2 are constants with values of 170 and 124 psi, respectively.

B.4.4. <u>STUDIES WITH SUGAR</u> : The compressive strengths of frozen coal cylinders containing a constant 2 wt% sugar based on the water solution added were also measured. The results are given in Table III-22. The moisture content of coal used was 4.06%. The results of this experiment were compared with the control for which the moisture content was 4.17% and are given in Table III-23. Both these experiments were done coal sample #4. These results are plotted in Figure III-12. Also in this figure, the coal samples containing ammonium acetate are plotted, which are discussed in the next Section (B.4.5.).

The compressive strengths of the frozen coal cylinders containing sugar were generally about the same as those of the control. The average values at 10%, 16%, and 20% water were the same within experimental error; the values at 12% and 14% water may or may not be measures of the same quantity; those at 18% water were smaller than those of the control. The differences in compressive strengths for 12% and 14% water were only 11 and 13 psi, respectively, with the values for the sugar-

TABLE III-22

Compressive Strength of Frozen Coal Cylinders Containing 2 wt% Sugar Based on the Water Solution Added

(Coal Sample #4)

Moisture Content = 4.06%

Precent		Compressive Strength, psi							
Water	Tube:	1	2	3	4	5	6	ave.	sigma
10		64	67	99	80	60	---	74	16
12		95	102	86	111	99	95	98	8
14		118	118	115	140	134	111	123	12
16		172	137	134	134	191	156	154	24
18		143	194	153	140	175	166	162	21
20		216	143	166	220	185	232	194	35

TABLE III-23

Statistical Comparison of Frozen Coal Cylinders Containing Sugar With Control

(Coal Sample #4)

Moisture Content	=	4.06%		4.17%			
	Compressive Strength, psi						
Percent	Sugar*		Control		Calcd.	Crit.	
Water	ave.	sigma	ave.	sigma	t	t(95%)	
10	74	16	80	8	0.81	2.26	
12	98	8	87	8	2.38	2.23	
14	123	12	110	5	2.45	2.23	
16	154	24	148	28	0.40	2.23	
18	162	21	200	18	3.37	2.23	
20	194	35	221	30	1.43	2.23	

* The concentration of sugar in solution is 2 wt%.

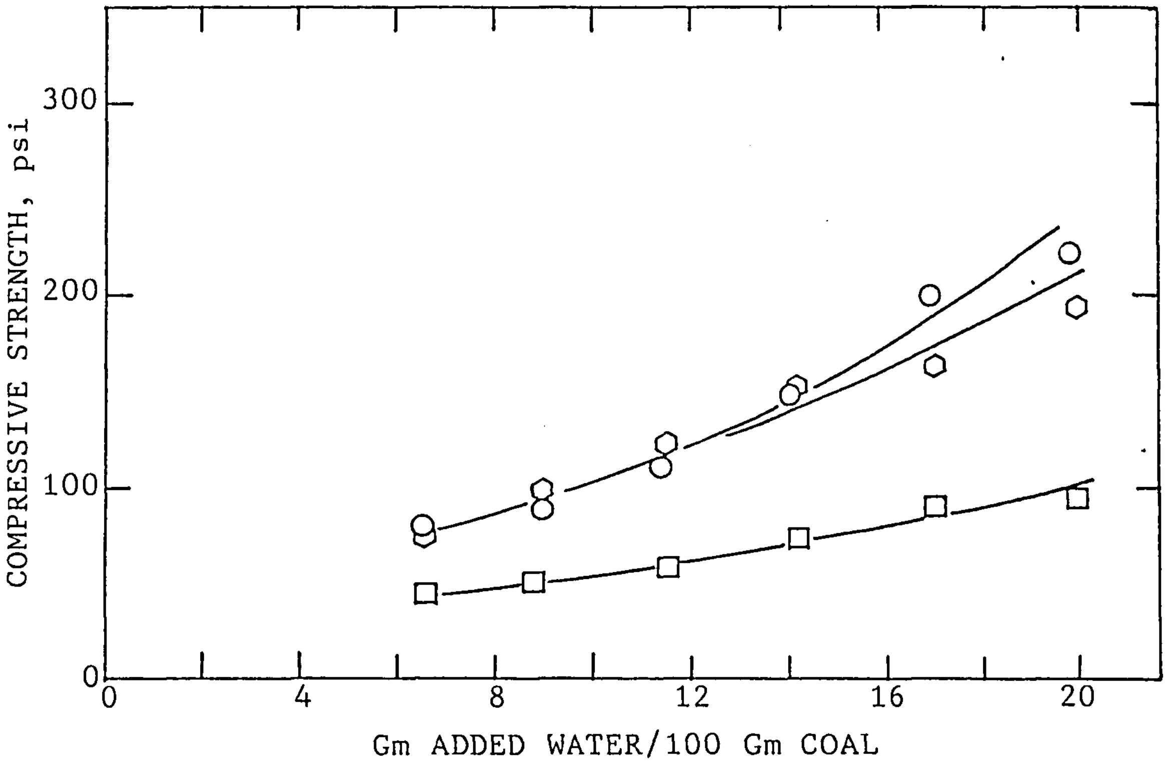


Fig. III-12: Variation of compressive strength of frozen coal cylinders with gm added water/100 gm coal for control, sugar and ammonium acetate. Sugar and ammonium acetate have been applied in constant 2 wt% based on the water solution added. All this data is from coal sample #4.

LEGEND:

- □ Ammonium acetate
- ○ Control
- ⬡ Sugar

containing samples being the higher in both cases. Thus the addition of sugar to the water did not decrease the compressive strength of the frozen coal cylinders.

Similar to urea, sugar forms stronger ice-ice bonds, but is probably unable to weaken the ice-coal adhesive bonds to give an overall decrease in the compressive strength of the frozen coal composites. Therefore, sugar is not a good choice as a freeze conditioning agent.

B.4.5. STUDIES WITH AMMONIUM ACETATE : Table III-24 gives the compressive strength of frozen coal cylinders containing a constant 2 wt% ammonium acetate based on the water solution added. The moisture content of coal used was 4.06%. In Table III-25, the results of this experiment have been compared with the control for which the moisture content was 4.17%. Both these experiments were done with coal sample #4. It is seen from Table III-25 that, for all levels of water contents tested, the constant 2 wt% ammonium acetate solution reduced the compressive strength of frozen coal samples considerably. The percent reduction in compressive strength for various level of water is also given in this table. Figure III-12 shows the variation of compressive strength with the amount of water added/100 gm coal. As seen from this

TABLE III-24

Compressive Strength of Frozen Coal Cylinders Containing 2 wt% Ammonium Acetate Based on the Water Solution Added

(Coal Sample #4)

Moisture Content = 4.06%

Percent	Compressive Strength, psi							
Water Tube:	1	2	3	4	5	6	ave.	sigma
10	35	41	51	51	35	48	44	7
12	54	54	45	48	48	48	49	4
14	51	70	51	54	48	70	57	10
16	70	54	80	76	67	89	73	12
18	99	95	95	80	86	83	90	8
20	92	86	99	86	99	102	94	7

TABLE III-25

Statistical Comparison of Frozen Coal Cylinders Containing Ammonium Acetate With Control

(Coal Sample #4)

Moisture Content = 4.06% 4.17%

	Compressive Strength, psi						
Percent	Ammonium Acetate*		Control		Calcd.	Crit.	% Reduction
Water	ave.	sigma	ave.	sigma	t	t(95%)	in Strength
10	44	7	80	8	8.30	2.23	45
12	49	4	87	8	10.41	2.23	44
14	57	10	110	5	11.61	2.23	48
16	73	12	148	28	6.03	2.23	51
18	90	8	200	18	13.68	2.23	55
20	94	7	221	30	10.10	2.23	58

* The concentration of ammonium acetate in solution is 2 wt%.

figure, ammonium acetate is very effective in reducing the compressive strength of frozen coal cylinders.

Ammonium acetate behaves like ethlene glycol in reducing the compressive strength of ice, as well as frozen coal cylinders. Therefore, the mechanism for lowering the compressive strength seems to be the same for both of these chemical compounds. A comparison of Table III-16 with Table III-25 reveals that, at higher percent water levels, ammonium acetate is more effective than ethylene glycol in reducing the compressive strength of frozen coal cylinders. Therefore, ammonium actate is a good choice for use as a freeze conditioning agent.

CHAPTER-IV

CONCLUSIONS

1. The coal used in the present investigation had a very small surface area and pore volume. As a result, most of the added water remained as external water. The moisture content of the coal sample varied from one part of the sample to another; the water determined by ASTM D-2961 is internal water, which does not affect the compressive strength. Therefore, the compressive strengths of frozen coal cylinders depended upon the added water and not the overall water content.
2. Frozen coal cylinders prepared from undried coal are strong. Depending on the water added, their compressive strengths can be 75% greater than those of ice.
3. The compressive srengths of frozen coal cylinders of coal samples #2, #3 and #4 of varying water content followed the same smooth curve when plotted against the added water content. An analytical equation was fitted to this curve by regression analysis.
4. An increase in loading rate by a factor of 2.2 over the usual rate of one inch per minute resulted in a decrease in compressive strength of frozen coal

cylinders by 25%. At the slower rate, the frozen coal specimens failed by relatively slow crumbling as against by massive fracture at the faster loading rate.

5. For coal samlpe #3, it was found that, when the amount of water added was 1.6 gms/100 gms of coal, the frozen coal cylinders crumbled as they were taken out of the PVC tubes.
6. The compressive strengths of frozen coal cylinders of sample #4 were smaller than those of coal sample #3 at 18% and 20% overall water content, greater at 10% and within the experimental error same at 12%, 14% and 16%. The differences were attributed to the fact that coal sample #4 had less smaller-size particles as compared to coal sample #3.
7. The compressive strengths of ice cylinders containing ethylene glycol or ammonium acetate were lower than those of the control, but those containing sugar or urea were greater; ethylene glycol and ammonium acetate form weaker ice, but sugar and urea form stronger ice.
8. It is found that ethylene glycol was only effective in reducing the compressive strength of frozen coal cylinders when its concentration is greater than 1.5 wt% in the water solution added. Thus, when

ethylene glycol was used in concentration of 2 pints per ton of coal, it was effective only for 10-12% water; and at higher amounts of water, the compressive strengths of frozen coal cylinders were roughly same as those of control. When experiments were done with 2 wt% ethylene glycol, as expected, the compressive strengths were lower at all the water contents studied. Ethylene glycol forms weaker ice and ice-coal adhesive bonds of indeterminate strength. Therefore, the possible mechanism of failure seems to be weak ice-ice bonds.

9. At 2 wt% concentrations, ammonium acetate was highly effective in reducing the compressive strength of frozen coal cylinders. At higher levels of water, it was even more effective than ethylene glycol. Since ammonium acetate also formed weaker ice, the mechanism of failure seems to be the same as that of ethylene glycol.

10. The compressive strengths of frozen coal cylinders containing the equivalent of 2 pints urea/ton coal were lower than those of the control at 10%-12% water and slightly greater at higher amonunts of water. Urea was more effective when used at concentrations of 2 wt% based on the water solution. However, it was less effective than either ethylene glycol or

ammonium acetate at the same concentration level of 2 wt%. Urea forms stronger ice. Therefore, it seems that the decrease in the compressive strength of frozen coal cylinders is due to formation of weak ice-coal adhesive bonds.

11. The variation of compressive strength of frozen coal cylinders containing 2 wt% of varying ethylene glycol-urea mixtures based on water solution were also studied at 16% water level. No synergistic effect was observed. The compressive strength-composition variation was linear from 127 psi for ethylene glycol to 171 psi for urea.
12. The compressive strengths of frozen coal cylinders containing sugar were equal to, or greater than, those of control. It seems that sugar forms stronger ice without weakening the ice-coal adhesive bonds substantially to give an overall lower compressive strength.
13. The effectiveness of urea as a freeze conditioning agent demonstrates the complex relationship that the compressive strength of ice containing chemical additives is not a good measure of their effectiveness, and indeed, may give misleading results.
14. Ethylene glycol, ammonium acetate and urea are promising candidates for use as freeze conditioning

agents.

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