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PROCEEDINGS OF THE THIRD WORKSHOP ON BY-PRODUCTS OF PHOSPHATE INDUSTRIES

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FLORIDA INSTITUTE OF PHOSPHATE RESEARCH

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PREFACE

Interest in finding ways to use phosphogypsum for environmentally acceptable, productive and profitable purposes has increased dramatically in the past several years. Utilization of this potentially valuable raw material - phosphogypsum - has resulted in numerous new research projects and ongoing contacts with scientists around the world who are also committed to grasping this opportunity to create not only new jobs, but perhaps even whole new industries.

One exciting aspect is the readiness of the investigators to accept the fact that phosphogypsum is not always the ideal raw material since it is possible that it could be used in a manner that would be environmentally offensive. As a result, a significant portion of their efforts is devoted to insuring that any environmental problems are resolved before an end use is recommended.

This publication reports on some of the progress made in developing agricultural, chemical and construction applications for this important state of Florida asset. The information on road building is significant since it is being used as the basis for building two county roads in Florida. Success with these first two roads will lead to increased and routine application of phosphogypsum in Florida road construction.

FLORIDA STATE STANDARDS AND PROGRAM
CONCERNING ENVIRONMENTAL RADIATION - AN UP-DATE

Presented at the Third Annual Seminar on Phosphogypsum,
December 4, 1985, Tampa, Florida

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Man is constantly exposed to radiation. In today's world this perhaps frequently comes from sources created or fashioned by human activities. The majority of exposure to the general population comes from the medical use of radiation for diagnostic and therapeutic purposes, but much smaller amounts are added to the total population dose by operation of research and power reactors, and by fallout from nuclear weapons testing. But man has been exposed to radiation since his beginning, from natural sources both cosmic and terrestrial in origin. This last source we frequently identify as "naturally occurring radioactive materials." It would be fair to say that exposure to the average American is just short of 200 millirems (mr) per year, with natural radiation accounting for about 45%, or about 90 mr; cosmic and terrestrial sources each contribute about half. There are radioactive isotopes of such common elements as potassium, sodium and carbon in our earth, but we are especially concerned with the primordial species of thorium and uranium, both U-238 and U-235. More than 99% of naturally occurring uranium is U-238, and at least in central Florida thorium is rather insignificant, so our main attention is centered on U-238. It is the first member of a chain of sequentially decaying radioactive elements that includes radium, the gas radon, radon "daughters," and eventually stable lead. The element radon is an especially troublesome member of this chain. Radon decays with the emission of a highly ionizing alpha particle, and being a gas, can be transported to the atmosphere. Its decay results in several short-lived “daughter” products, all of which are particles, and some of which are also alpha emitters. Alpha particles are highly ionizing, but unlike gamma rays, are weakly penetrating. Normally alphas do not penetrate the human skin.

We generally consider three pathways of exposure to be of major concern - inhalation, ingestion and external irradiation. From external sources, gamma radiation is the main concern. Inside the body, via either inhalation or ingestion, alpha radiation is most important. 'In terms of overall health effects, or typical dosage, internal exposure to alphas is probably an order of magnitude more significant that external gamma. Since radon is a gaseous alpha emitter that can be inhaled, its hazard potential begins to be apparent.

Uranium and its radioactive decay chain are ubiquitous on this earth, but are somewhat concentrated in selected minerals and ores. Worldwide, uranium accounts for 1 to 5 parts per million (ppm) of the earth‘s crust, but may reach 10,000 and more ppm in uranium ores. It occurs naturally in association with phosphate deposits, generally in the range of 50 to 150 ppm. In the typical undisturbed pre-mining profile, radioactivity concentrations are generally low at the surface, increase gradually with depth through the overburden and reach a local maximum in the ore or matrix and in the "leached zone" which lies just over the matrix. This naturally-occurring radioactivity is redistributed in mining, beneficiation and land reclamation and thus near-surface concentrations may be increased over those of the undisturbed stage. In addition, the phosphate matrix and associated radioactivity may occur naturally near or at the surface.

Of particular interest in the uranium decay series is the sixth member, radium-226 (1600 year half-life). In central Florida, radium-226 concentrations are on the order of 0.5 pCi/g in the undisturbed surface soil and reach values on the order of 40 pCi/g in the leached zone and matrix. After mining, radium concentrations in overburden spoils are typically an order of magnitude higher than in the original surface soil, but materials are not homogeneously mixed and the reclaimed mining tract may contain local concentrations ranging from original top soil values up to those representative of the leached zone and matrix.

Natural radiation is not unique to Florida or to deposits of phosphate. In addition to uranium deposits in the Rocky Mountain area, sources of high levels found in the northeast, the "Reading Prong,“ have elicited much recent publicity. in the northeast, levels are very variable, and frequently are much higher than the more uniform but still elevated levels found in central Florida. The U.S. Environmental Protection Agency has suggested that as many as a million homes may contain elevated levels of radiation from radon gas. A major source of indoor radon is radium in the soil and rock under and surrounding buildings. Radon moves through soil and rock and can enter a building through cracks or openings (sewer pipe and sump pump openings, cracks in concrete, wall-floor joints, hollow concrete block walls). Lower air pressure inside buildings can help to pull radon into a house. The amount of radon reaching a building depends on several factors, including the amount of radium in the surrounding soil or rock and the soil permeability.

When released outdoors, radon mixes with the outside air and is widely dispersed. Radon entering a building is confined to a relatively small space. Once inside the building, the radon will tend to remain indoors (like an odor or any other indoor pollutant) because most structures are designed to keep heated or cooled air from escaping. The accumulation of indoor radon largely depends on the rate at which indoor air is exchanged with outdoor air. To prevent radon entry into a home, one (or a combination) of five general techniques are generally advised:

(1) Build the home with a well-ventilated crawl space underneath. This means a space at least 18 inches between grade level and floor, with a vent on at least three sides of the structure. The recommended minimum vent area should be one square foot of opening for each 150 square feet of wooden flooring.

(2) Build with an improved monolithic slab, preferably with post-tensioning. This will minimize the possibility of cracking of the concrete, and intact concrete is an effective barrier to radon passage. With this method, it is important to be sure all slab penetration points are well-sealed.

(3) Cover the earth beneath the building with a tightly sealed polymeric soil/gas barrier.

(4) Place sub-slab ventilation pipes in a gravel bed in the soil beneath the home. These must be exhausted through a wall pipe to the atmosphere above the roof of the home.

(5) Excavation and removal of soil at the construction site. Replace with fill of low radioactivity.

During 1985, the state of Florida has proposed to become the first state in the nation to pass a rule regulating the exposure of its citizens to naturally occurring radioactive materials in the environment. The rule will be found in Chapter lOD-91, FAC, Part XI, and seeks to limit indoor gamma exposure and especially indoor exposure to radon decay products. The rule attempts to identify potentially hazardous lands, and then to "force" construction technology in the direction of building radon resistant housing. The Florida radiation standard incorporates certain of the above measures in recommended building techniques. The standard requires that homes built with standard construction techniques on land known to be elevated in radioactivity be tested for indoor radon decay products prior to occupancy. However, homes built with a ventilated crawl space are exempt from the test, and homes built on a monolithic slab, and also incorporating a sealed polymeric gas barrier, would have to be tested only during the first year of occupancy.

The standard states *first* that radiation exposure shall be maintained as low as reasonably achievable - the ALARA concept. Specific limits for gamma in residences of 20 microroentgens per hour, and for annual average indoor radon decay product concentration of 0.02 working levels (WL), both including background, shall be achieved. The standard is state-wide, but applicable only to homes and certain other structures built on lands *identified* as exhibiting elevated levels of natural radioactivity. That by their definition includes phosphate lands - mined, reclaimed or otherwise altered. That also includes lands mineralized with uranium, thorium, etc., to the extent that measurements demonstrate a potential hazard would likely exist in a home built thereon. Thus, the standard applies only to homes built on reclaimed phosphate lands and any other lands designated by HRS.

The intent of the standard is "technology forcing." Homes properly built with a ventilated crawl space between ground and floor are exempt from the standard, that is, the tests prescribed in the standard. A home built with a monolithic slab and effective soil gas (polymeric) barrier must be tested within one year of initial occupancy, but with the results advisory in nature to the owner/occupant. Homes built by other "non-approved" techniques, such as conventional slab-on-grade, must be tested by the department and found to meet the standard before a certificate of occupancy, or approval on final inspection, is issued. Homes failing this test must be retrofitted with passive remedial measures in order to meet the standard. The standard also provides for an educational program, to be conducted by local county health departments, to advise the public that some homes built on certain lands may have a radiation hazard, and what methods may be suitable to effect remedial action. Educational programs are viewed as especially important for owners of existing homes that might pose a risk.

The standard is scheduled to go into effect on January 1, 1986, but there are several issues that cloud its implementation - the standard has been challenged by citizens' environmental groups as "not going far enough." Both the environmentalists and the state have presented their arguments before a state hearing examiner, but as of the date of preparation of this report, no decision had been rendered. Hopefully, a decision will be announced by the time of presentation of this talk. It is quite likely, however, that a final decision will be made in court, regardless of the examiner's findings. Also, the successful implementation of this rule depends a great deal on local county building offices, for it is they that must issue building permits notifying contractors that a home site is or is not on affected land, they who must inspect to see that special construction techniques are carefully followed, and they who would issue or deny approvals after final inspections. Several details, especially the precise mapping of affected lands, remain still to be resolved. Finally, the measurement of indoor radon decay products is not an exact science. At the level of the proposed standard, 0.02 WL, the error at two standard deviations is nearly 50% of that value. There is now debate within HRS over whether to (1) declare a home "safe" if the measured value is 0.01 WL or less, or (2) to declare a home "hazardous" if the measured value is 0.03 WL or more.

At this point, the monitoring of new homes to ascertain compliance with the new rule will be performed by HRS personnel, with costs to be paid from general revenue funds. There is a part "B" of the proposed rule, however, dealing with environmental monitoring of affected lands. This also would be performed by HRS personnel, but with costs to be paid through a special assessment levied on any company either mining or reclaiming land. Costs would be based on acres involved. In this program, the state would seek to determine the radiological changes to the land caused by the processes of mining and reclamation. Prior to mining, and again after reclamation, the DHRS would measure gamma radiation at one site per acre, and measure soil radium, density, moisture and radon emanation at one site per 20 acres. Additionally, atmospheric radiation at four sites around each mine would be checked, as well as surface and groundwater in areas possibly impacted by mining operations.

This discussion cannot be closed without making reference to the issue of public notification. As currently worded, the proposed rule includes educational endeavor, but does not call for an explicit warning of a potential radiation hazard to be affixed to every deed or contract dealing with affected land, either reclaimed or identified as mineralized with radioisotopes. Such a warning has been requested by certain interests within the state, and HRS is preparing suggested wording for a regulation of this type to be considered by the 1986 Legislature. Essentially this would amount to a "class action," whereby all homes built or sold and located on reclaimed or identified “mineralized" lands would carry a statement of potential radiation hazard on all deeds and contracts for sale. This will effectively notify potential home buyers of a possible hazard, but the stigma it will place on certain homes will in all likelihood place significant economic hardships on the sellers, both builders and current owners of existing dwellings. This blanket action would seem to be not necessary in the majority of cases. In an HRS study published in 1978, "Study of Radon Daughter Concentrations in Structures in Polk and Hillsborough Counties," while 22% of homes built on reclaimed lands exceeded the proposed standard for indoor radon decay products of 0.02 WL, 78% would have been in compliance with the standard, even though the vast majority had not been built with radon resistance in mind! Yet, a blanket warning requirement would affect all such homes. Would it not be far better to promulgate a regulation somewhat similar to current termite codes? In effect, when any home is to be sold that is located on affected lands, it must be tested by the seller for indoor radon progeny. Any potential buyer must be informed of the results of the test, and could require the seller to take effective remedial action as a condition of the sale should the level be elevated.

In summary, there are areas in Florida where the levels of naturally occurring radioactive materials can present an increased health risk to persons living in homes built in those areas. The hazard, though real, is not unique to Florida; other parts of the-country have equal or greater radiation hazards. The areas in Florida that are affected include, but are not limited to, the areas where phosphatic minerals are found. The processes of mining and reclamation may, or may not, enhance natural radiation levels. Homes and other structures that are resistant to the entry of radon can be built, effectively mitigating the hazard. Given a cooperative effort by Florida's citizens, the state government, construction and realty interests and industry, the quality of life for all persons in the state can be maintained, even improved, without severe hardship on the part of anyone.

ENVIROMENTAL RADON LEVELS IN PHOSPHATE BY-PRCDUCT STRUCTURES

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ABSTRACT

Phosphogypsum, a waste product of the phosphate industry, is being tested for use as a construction material. It has a known amount of Radium with an activity of 20-25 pCi/gm (Phosphate ore mined in central Florida). A house built with phosphogypsum panels was tested for radon levels using several methods. The initial measurements were made using Terradex track etch detectors; the later measurements were made using an EDA RGA-400 Radon Gas Analyzer. The RGA was used for making short term measurements of about a week to ten days. Longer measurements lasting a month or more, were made with the track etch detectors. The study is unique in that the radioactivity of the construction material is known which is normally not the case.

INTRODUCTION

Phosphogypsum is a waste product of the Phosphate industry and this waste material has found no practical application until recently. The Phosphate Research Institute of the University of Miami, is in the process of trying to find different applications for phosphogypsum as a construction material for which it is well suited. One of the problems associated with the use of phosphogypsum as a building material is the presence of radium-226 in levels above natural background. One of the ways which phosphogypsum is used, is in the making of panels for the construction of modular structures.

The ferrocement panels were made using 50% phosphogypsum, 25% cement, and 25% sand. The dimensions of the building made from these panels are l4'x7'x8'. All six sides of the room i.e. the ceiling, the floor and four walls are made from phosphogypsum panels. The house is mounted on a trailer about 2.5 feet above ground. The release of radon into the environment as such is not a major concern. However when radon is released or diffuses into a closed place like this structure, it might create a problem. Even though the amount of radon diffusing out of the walls may be small, its accumulation over a period of time poses a problem. Measurements were made using the worst possible conditions as far as ventilation was concerned. This was done by sealing the structure and making it air tight as possible. Integrated radon measurements were made with two different measuring devices. The first device used was a track etch detector. The second method employed a RG-400 radon gas analyzer.

The room in which the readings were taken, as indicated previously, was mounted on a trailer about 2.5 feet above an asphalt surface with a clear air space between the house and the ground. This reduced the effect of radon emitted from the ground to a negligible amount. The outside of the house was painted with a water base emulsion. The inner walls of the house were left totally unpainted. This further compounded the radon levels inside the room as the escape path for the gas was facilitated in an inward direction rather than an outward one.

The panels used to construct the house were fabricated in a special way. The panels are of a ferrocement sandwich type. The center of the wall consists of a slab of polystyrene which is 2-4 inches thick. On both sides of the polystyrene is a facing of mortar (i.e. a mixture of 50% phosphogypsum, 25% cement and 25% sand) 3/8 inch thick, reinforced with a galvanized wire mesh. There are sections in the panel where the mortar is solid throughout. The joints connecting the panels also are solid mortar.

INSTRUMENTATION AND MEASUREMENT TECHNIQUES

The primary method used for the measurement of the radon concentration in the house was the track etch detector. The detector used was the type SF, marketed by the Terradex Corporation. This detector consists of a small plastic disc enclosed in a plastic cup with a filter paper at the opening to prevent radon daughters (non-gaseous) from entering the cup. Detectors were exposed for a period of 30 days and then returned to the company to be read. Alpha particles, emitted from the decaying radon, leave tracks in the plastic due to their electrostatic interactions. These tracks are made visible by rigorous controlled acid etching and are then counted (2). Radon concentration is proportional to the track density. The detectors were read in such a way that a level of radon as low as 1.0 pCi/l (picoCurie per litre) could be detected accurately. The detectors were placed at each end of the house to get an idea of the average radon concentration of the house. The house was kept closed for as long a period of time as possible. On an average, it was opened once every 7 or 8 days for a short period of time. The results obtained using this method are presented in Table 1.

The second technique used to make radon and radon daughter measurements in the house is the RGA-400 radon gas analyzer. The RGA-400 is a microprocessor controlled instrument which was developed for continuous, unattended, long-term monitoring of ambient concentration of radon gas and its daughters. The instrument consists of two independent although interconnected systems. The primary system is designed to determine radon daughters and consists of a sampling head, housing a filter, facing a Ruggedized R Series EG&G Ortec silicon surface barrier detector. The secondary system measures radon gas concentration. It consists of an electrostatic precipitator (a cylindrical tank of 3 L volume) operated from a 1500 VDC supply. A silicon surface barrier wafer detector is located at the center of the precipitator and is galvanically connected to ground potential. The outputs from the primary and secondary detectors are fed through charge sensitive preamplifiers and main amplifiers to identical spectroscopy grade multichannel analyzers. The instrument is of the active kind, i.e., uses a sampling pump to collect and carry radioactive gases and their daughter products. The pump operates at a flow rate of 1 l/min. The instrument is of the time integrating type (Ref. 1). With this instrument the levels of radon gas can be measured in pCi/l and the concentration of radon daughters RaA(Po214) and RaC'(Po214), can be measured in WL's.

EXPOSURE FROM	PERIOD TO	RADON LEVELS PCI/L	% STD. DEV
14-JUN 85	19-AUG 85	3.03	28.3
19-AUG 85	25-SEP 85	4.8	22.1
17-OCT 85	21-NOV 85	3.4	27.5
06-DEC 85	22-JAN 86	4.8	19.7

RADON LEVELS MEASURED WITH TRACK ETCH DETECTORS

TABLE 1.

DATE	TIME	RANGE		MEAN		INT.
		pCi/l	WL	pCi/L	WL	WL
09/12-09/18	23:30-19:30	1.2-10.9	.0012-.043	2.74	.012	.010
10/24-10/31	24:00-12:00	2.5-15.9	.0028-.045	7.02	.012	.019
08/30-09/05	23:00-19:00	1.1-10.0	.0038-.047	6.50	.017	.020
10/11-10/17	05:00-13:00	3.7-13.0	.0048-.048	6.53	.020	.022
10/17-10/24	01:00-11:00	2.1-12.9	.0066-.032	5.16	.008	.012
08/20-08/27	05:00-11:00	1.1-07.1	----------	3.52	----	---
09/07-09/12	02:59-09/12	1.1-12.1	.0040-.048	4.41	.018	.020

Sampling period one week

RADON LEVELS MEASURED USING RADON GAS ANALYSER RGA-400

TABLE 2.

The sample interval over which the WL is calculated can also be varied anywhere from one minute to 999 minutes. The procedure for using the RGA-400 is as follows. The gas analyzer is placed about 3 feet above the floor. The house is closed and after 8-10 hours, needed for the radon to reach equilibrium, the analyzer is automatically turned on. The sample interval used for monitoring the house is 120 minutes. This sample interval is the time over which the differentiated and the corresponding integrated working levels are calculated. Air sampling was done in blocks, each block being eight days during which time the house was kept shut with little or no air exchange allowed. The average differential WL and the integrated WL values obtained are shown in Table 2.

RESULTS AND DISCUSSION

The results obtained using the track etch detectors are shown in Table 1. The radon levels obtained range from 3.03-4.8 pCi/l. The mean value measured by this technique is 3.8 pCi/l. Using a working level ratio (the working level ratio is defined as the ratio of radon daughters to radon gas) of 0.5 this would result in an average WL of .02. This corresponds to the maximum radon level in houses built on reclaimed land allowed by the State of Florida and is also considered acceptable by the Environmental Protection Agency.

The radon and radon daughter concentrations measured with the radon gas analyzer are in Table 2. The radon levels measured in pCi/l range from 1.1-15.9 pCi/l. with the mean being 5.1 pCi/l. These are the numbers obtained when the sample interval was 120 minutes and the period

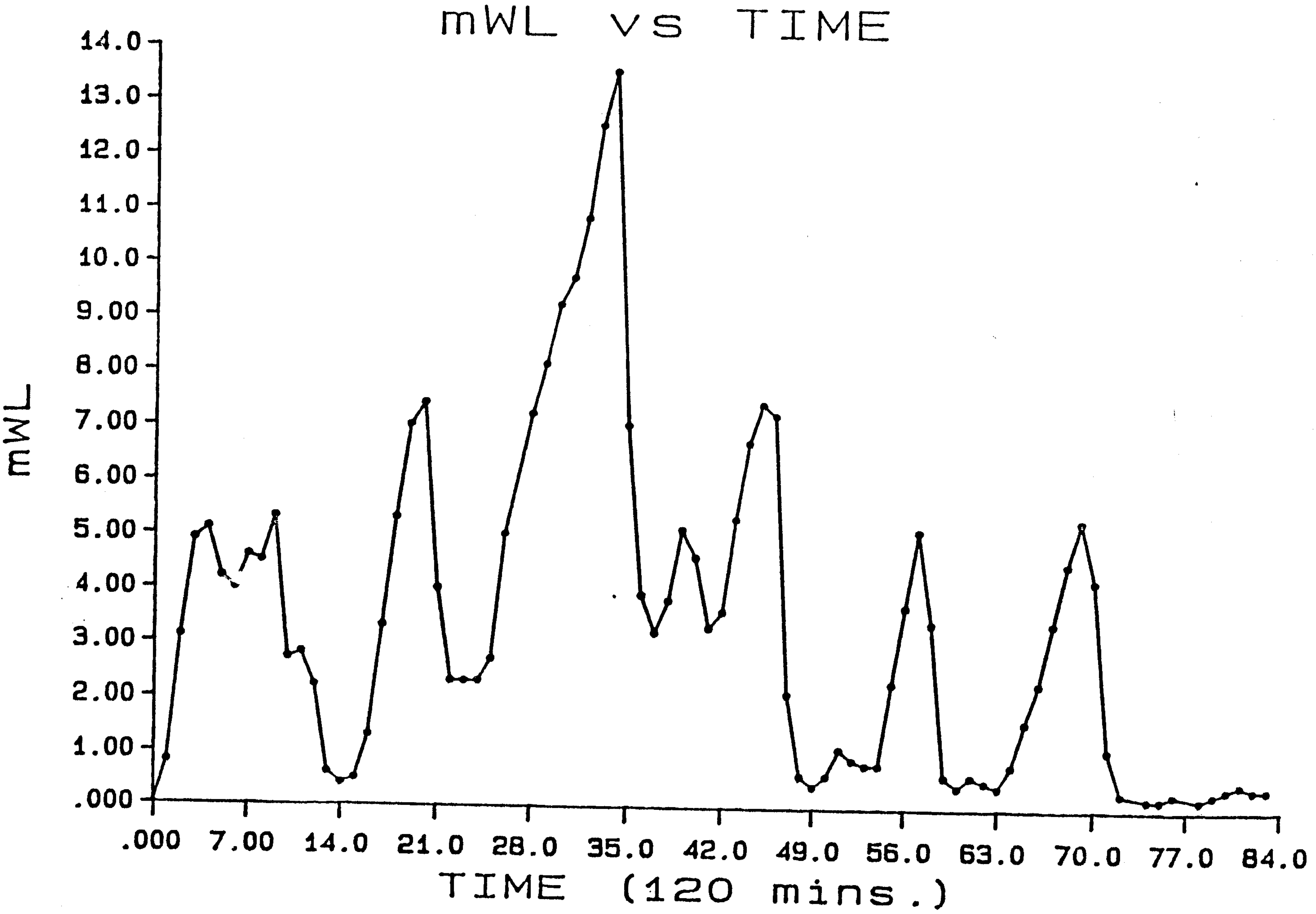

Figure 1. Differential Working Levels Vs. Time.

of sampling was one week. The WL's that were obtained with the same measurement conditions indicated above range from .0012-.048 with a mean of .01 WL's. The integrated WL's in this case range from .01-.022. The immediate conclusion that can be drawn from these numbers is that they fall just within the levels of radon daughters considered acceptable by the State of Florida and the EPA. The working levels shown are the average differential WL and the final integrated WL. The differential WL is the WL measured during a particular sample interval, while the integrated WL is the working level averaged over time since the first sample is counted.

Figure 1, shows a graph of differential WL versus time: each division on the time axis is 120 minutes. From the graph one can clearly see the phenomenon of diurnal variation of the radon levels in the house. One peak is observed for every 24 hours of sampling. The reason for this occurrence may be the change in the temperature. The maximum radon levels occur when the house and hence the walls are at their lowest temperature. The diurnal variation, though well documented in the literature, is not a very well understood phenomenon and needs further investigation. The other aspect of importance that will be investigated next is the effect of different meteorological parameters on the radon levels in the house.

Future research will involve the investigation of different ways in which the radon levels can be mitigated. One of the methods being considered is painting the inner walls with a paint which would reduce the level of radon diffusing into the room. The second method being considered is the reduction of the phosphogypsum content in the wall panels. This is an important consideration as, from the engineering standpoint, lower levels of phosphogypsum in the mortar seem to be better suited for this type of construction. The final parameter that could be looked at to reduce the radon levels is the ventilation rate.

ACKNOWLEDGEMENT

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CORRELATION BETWEEN ATMOSPHERIC CONDITIONS AND RADON LEVELS IN A PHOSPHOGYPSUM-BASED STRUCTURE

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ABSTRACT

It is well known that materials containing elevated levels of Radium-226 emit the radioactive, inert gas radon (R-222) into the atmosphere. There exists in the literature, however, a significant controversy concerning the effect of atmospheric parameters upon the rate of radon emanation.

A recent publication by Wolfs et al. (7), contends that there is no correlation between radon concentration and atmospheric pressure. The work of Jonassen (4), shows a negative correlation between atmospheric pressure and radon concentration whereas that of Hernandez et al. (3), shows a correlation between radon concentration and rate of pressure change but none with pressure itself. Our measurements of radon concentration in a sealed environment show significant oscillations with time and we have installed sensors to measure the pressure, temperature and relative humidity in this structure. This paper discusses the correlation between the measured radon concentrations and these atmospheric parameters.

INTRODUCTION

In conjunction with the Phosphate Research Institute of the University of Miami, we have been conducting a study to monitor the emission of radon into a single-roomed structure constructed in part from a mixture of cement and phosphogypsum (5). One series of measurements involved evaluating the integrated radon concentration (over 30 minute periods) of air samples drawn into a RGA-400 radon gas analyzer. The results of these measurements for a typical one week period are shown in Figure 1.

The most obvious feature in Figure 1 is the extreme diurnal variation of the radon levels in the structure. It is clear that once each day the radon level exhibits a distinct peak from which it drops too rapidly to reach a minimum value between 9 and 12 hours later. Since one of our aims in this study is to investigate means of controlling the radon emanation from building materials, it was of interest to ascertain the reasons for this extreme variation.

Several authors have measured the effect of various atmospheric parameters upon radon emanation rates and radon levels in other structures. Cohen (1) has presented a survey of work done in this area previous to 1978. He reports two studies that show diurnal variations in radon emanation from soil while at least two others reported no differences between day and night. He reports that wet soil emanates at about 1/3 the rate of dry soil while a recent work by Ghan et al.(2) shows that relative humidity increases are associated with significant increases in emanation of radon both from soil and a laboratory source, Stranden et al. (6), have

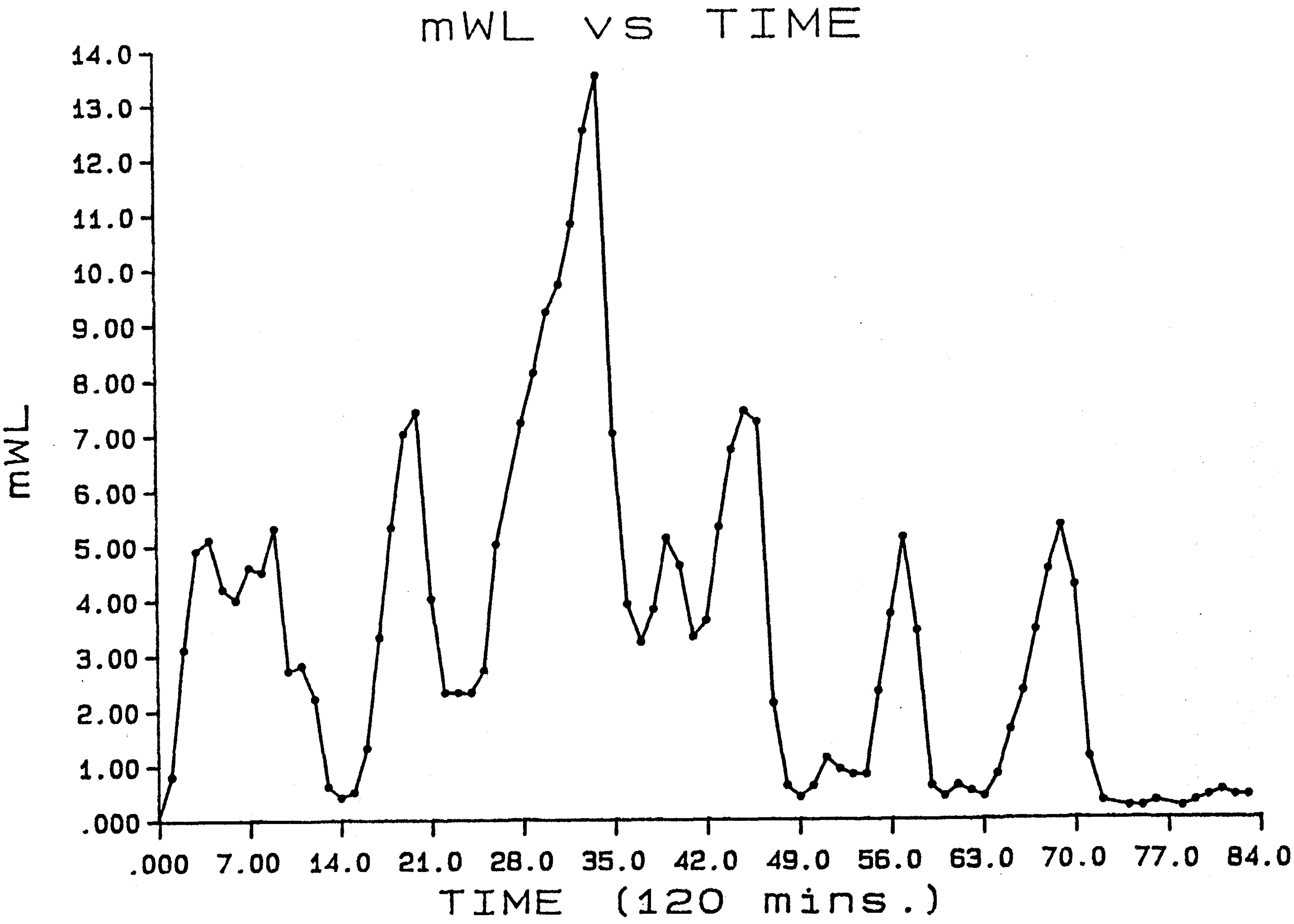

Figure 1: Plot of Radon Concentration (Milli-Working Level) Versus Time

reported results that indicate an increase in emanation from both soil and concrete over relative humidity ranges which in the region below 20% and a decrease as the humidity is further increased. Cohen reports that although cold or frozen soil emits radon less than when it is warm, temperature changes of a few degrees have little effects while Ghan et al. show significant increases in emanation when the temperature is raised. Stranden et al., also report small increases in emanation with temperature. Concerning the effect of atmospheric pressure, Wolfs et al., claim Jonassen shows a decrease in radon when pressure increases and Hernandez et al., measured a correlation between radon emanation and pressure change but none with pressure itself.

In order to understand what was occurring in our structure, we set up equipment to measure radon concentration, temperature, relative humidity and atmospheric pressure simultaneously.

MATERIALS AND METHODS

Measurements of radon gas concentration, temperature, relative humidity and atmospheric pressure were made over a period of several weeks in a single room structure. The structure (5) was constructed partially of phosphogypsum -a material known to have an elevated concentration of Ra-226 (20-25 pCi/gm). The room was mounted on a trailer approximately 2-l/2 feet above the ground to minimize diffusion of radon from the soil.

The RGA-400 radon gas analyzer can be used to make measurements of both the radon gas concentration and the activity of radon daughters. For this work, only measurements of radon gas are considered. The instrument is an active one in that it draws gas from the environment into the instrument using a pump. After passing through a filter to remove radon daughters, the gas is fed into a 3 litre electrostatic precipitation chamber. The radioactive decay of radon in the gas is measured using a silicon barrier detector and analyzed by a multichannel analyzer. The temperature and relative humidity in the chamber are continuously monitored so that the detector sensitivity can be calibrated. The output consists of both a complete decay spectrum and the radon concentration in the chamber integrated over the sampling period. The RGA-400 was placed on a table about 3 feet from the floor of the room and the room closed for at least 8 hours before measurements were taken. Subsequently, samples were read every thirty minutes for a period of one day (or every 120 minutes for a one week period) before the room was opened to retrieve the data.

Analog instruments for the recording of temperature, relative humidity and atmospheric pressure were placed on the table near the radon gas analyzer. These instruments were: 1. a Cole-Parmer barograph for the measurement of atmospheric pressure and 2. a Cole-Parmer hygrothermograph for measurement of temperature and relative humidity. The manufacturer's specifications for these instruments indicate pressure accuracy to within 1 millibar, temperature to within 1 degree Celsius and relative humidity to within 3 percent. For the purposes of this investigation, relative values of these parameters are of greater interest than absolute accuracy and it is reasonable to expect that the instruments respond to changes more accurately than to absolute values. All measurements were read from the analog graphs and recorded manually.

RESULTS AND DISCUSSION

Figure 1 shows a typical variation of radon concentration in the structure over a period of one week. Figure 2 shows the simultaneous variations over a single day of the radon concentration and the three atmospheric parameters. From these data, the dependence of the radon concentration upon the individual parameters was extracted simply by choosing a median range of two parameters - for example temperature between 80 and 81 degrees Fahrenheit and relative humidity between 83% and 84% - and plotting all the values radon concentration (versus atmospheric pressure) that were found over several days when temperature and humidity fell within the chosen range. A typical plot of radon concentration versus pressure is shown in Figure 3, while Figures 4 and 5 show plots of radon versus temperature and relative humidity respectively.

Figures 3 through 5 have, superimposed upon the experimental data, a straight line fit to that data. The fit was obtained by a linear regression analysis. The correlation coefficient for the fits were -0.796 for the temperature data, 0.448 for relative humidity and 0.338 for atmospheric pressure. The implication of these numbers is that the best correlation between the radon gas concentration in the structure and any of the

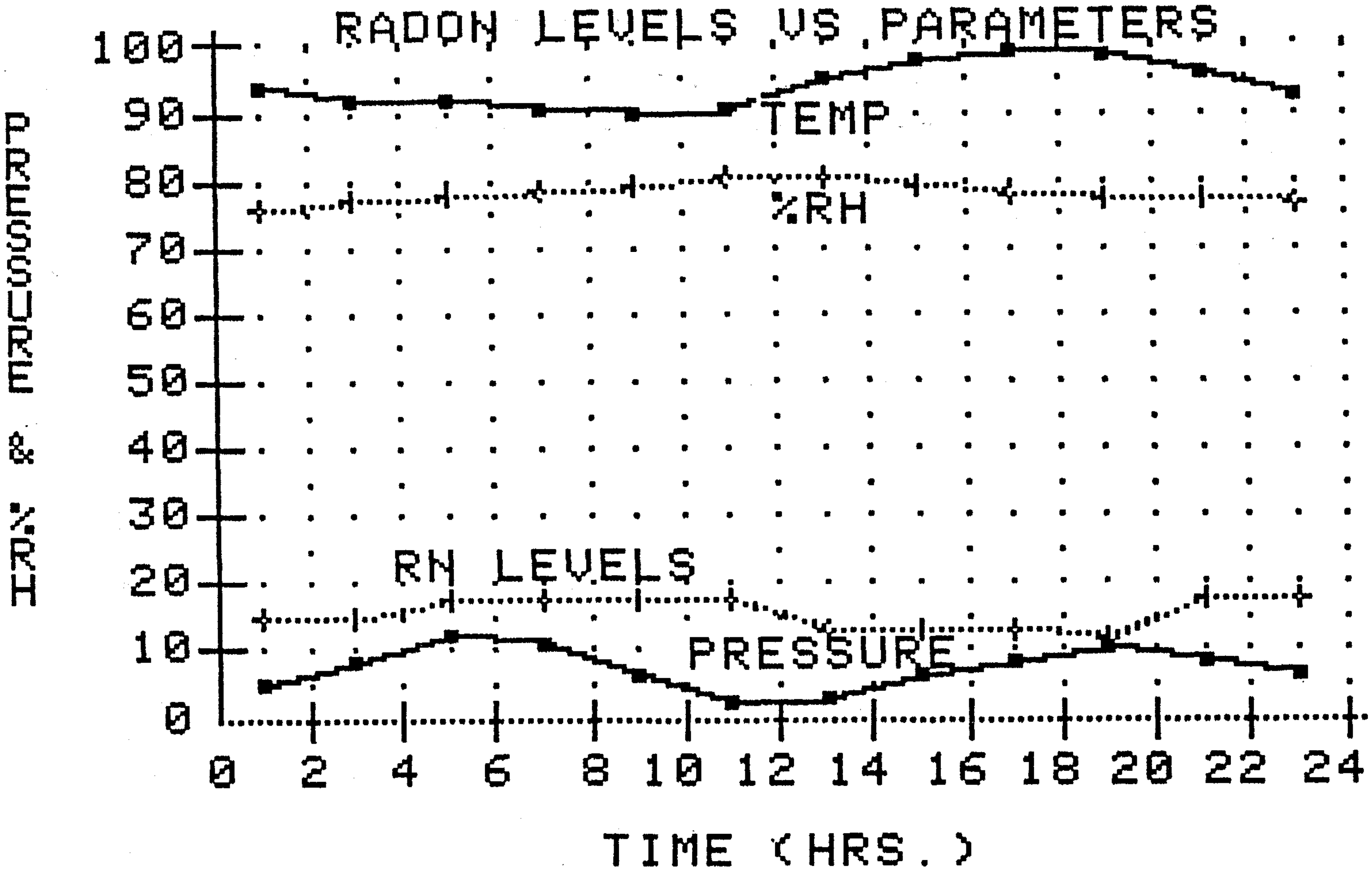

Figure 2: Plot of Radon Concentration, % Relative Humidity, and Atmospheric Pressure (all relative units) versus Time (HRS.) Over A Period of 24 hours.

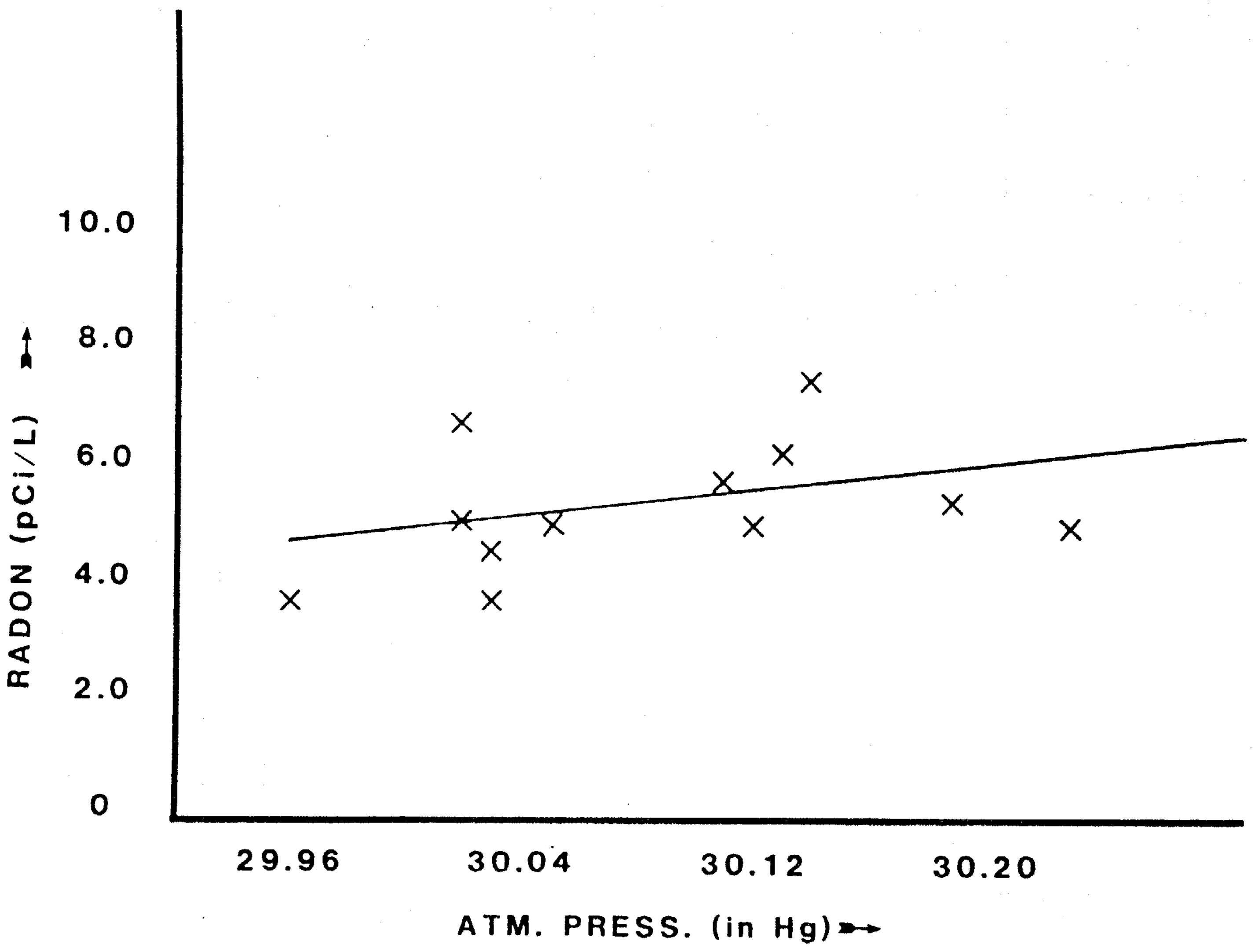

Figure 3: Plot of Radon Concentration (pCi/L) Versus Atmospheric Pressure (in Hg).

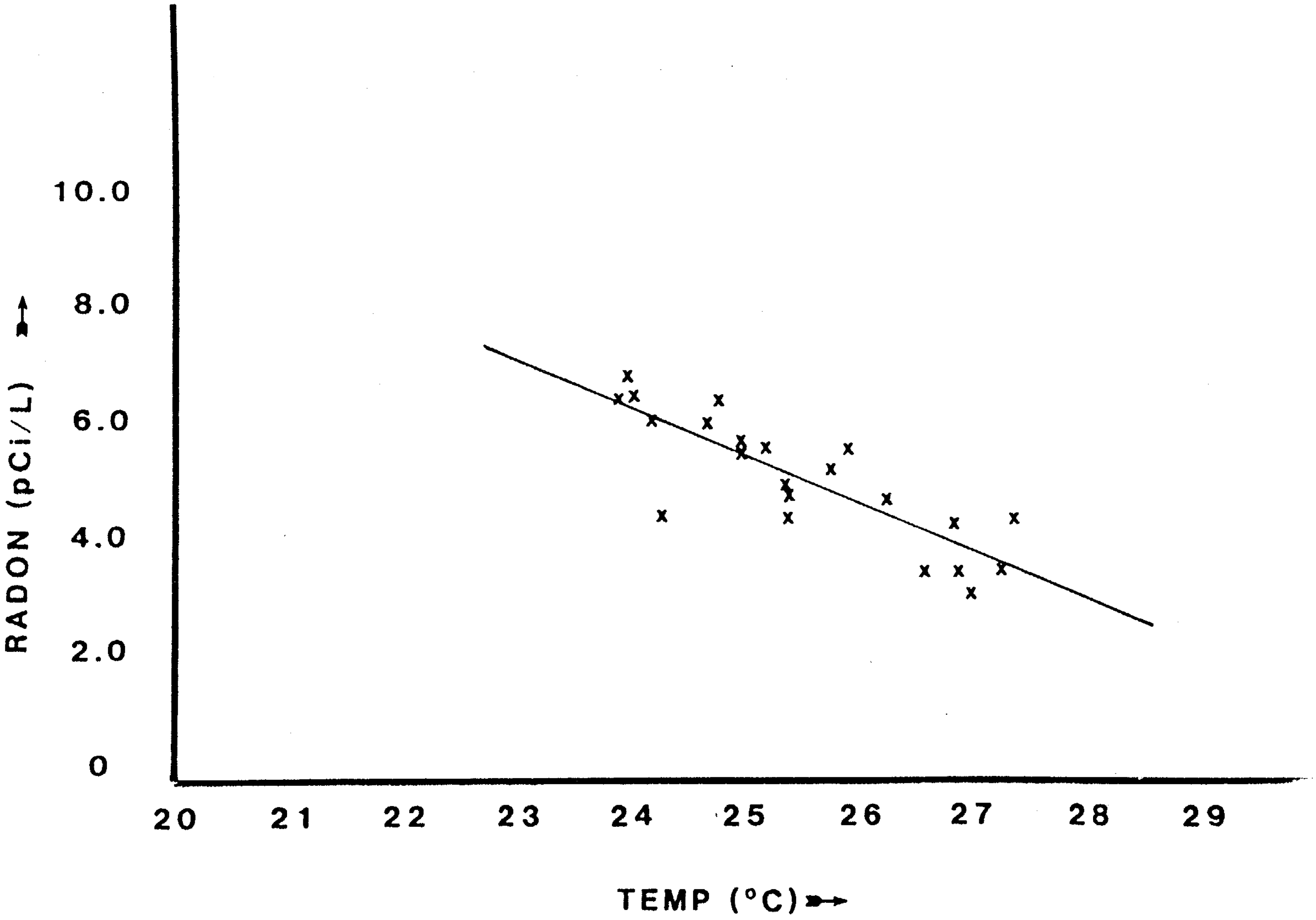

Figure 4: Plot of Radon Concentration (pCi/L) Versus Temperature (Degrees Celsius).

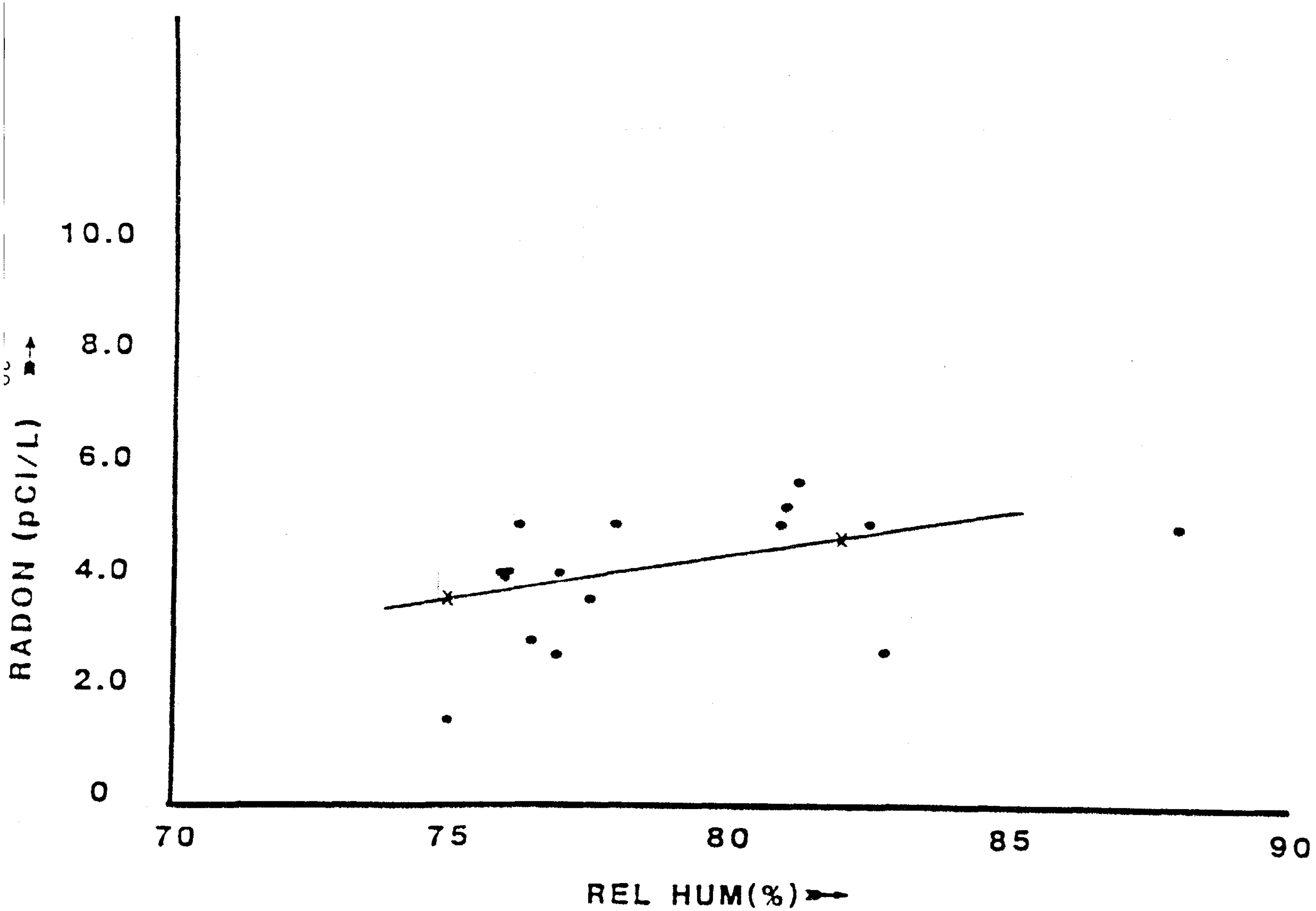

Figure 5: Plot of Radon Concentration (pCi/L) Versus Relative Humidity (Percent).

measured atmospheric parameters was obtained with room temperature. The correlation is good that radon concentration varies inversely with temperature. Since these data were obtained in late Summer in Miami, it is expected that relative humidity and temperature will vary inversely to each other on a daily basis. This indeed does lead to a positive correlation between radon concentration and humidity. Since this correlation is not as strong as that between temperature and humidity, it is tempting to conclude that the primary correlation is with temperature and that the correlation with humidity is secondary i.e., a result of the correlation between humidity and temperature.

The correlation between atmospheric pressure and radon concentration is extremely tenuous (coefficient 0.388). Due to the very minor changes in pressure over the data collection periods, it was not possible to analyze any correlations with change in pressure. It is expected that larger pressure variations in the winter months will allow this analysis to be made.

CONCLUSIONS

Our measurements of radon concentration in a closed structure constructed, in part, of phosphogypsum have shown large diurnal variations in concentration. We have shown that these variations correlate, well with temperature variations within the structure. Correlations with relative humidity and atmospheric pressure are less conclusive. However these data are incomplete since the range of variation in these parameters is relatively small at the time of year the experiment was in progress. The experiments are being continued during the winter months. Further analysis, including correlations between radon concentrations and changes in the atmospheric parameters and time lags between the various parameters, will be carried out so that our understanding of the conditions that promote radon emanation will be increased.

ACKNOWLEDGEMENT

The research is funded by a grant from the Florida Institute of Phosphate Research, Bartow, Florida.

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A METHODOLOGY FOR ASSESSING THE IMPACT OF A PHOSPHOGYPSUM ROADWAY ON LOCAL GROUNDWATER QUALITY

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ABSTRACT

A potentially useful application of phosphogypsum is as a constituent of the base material in a secondary roadway. A comprehensive analysis of the impact of such a roadway on the local groundwater quality is a vital component of an overall program designed to assess the feasibility of using phosphogypsum in road construction. This paper describes the procedures used to measure changes in groundwater quality. Methodology used in determining the location and design of monitoring wells, measurement parameters, sampling methodology, laboratory analyses, quality control considerations, and data analyses are discussed.

INTRODUCTION

A new application of phosphogypsum has been its use as a component of the base course in a roadway. Major criteria that are used to evaluate benefits of such use are: (a) the effects of the phosphogypsum on local groundwater quality, (b) the effects on air quality, (c) the effects on the structural characteristics of the roadway, and (d) the economics of the road construction. A project to evaluate (a) through (c) was conceived and developed at the Phosphate Research Institute at the University of Miami. Comments on the proposed study were solicited from Federal, State, and Local agencies who have jurisdiction over areas covered in the study. At the Federal level: Environmental Protection Agency (EPS), at the State Level: Department of Environmental Regulation (DER), Department of Transportation (DOT), Department of Health and Rehabilitative Services (HRS), and Florida Institute of Phosphate Research (FIPR), at the Local level: the county representatives of Polk County, where the proposed road is to be constructed. Comments from these agencies were incorporated into a formal proposal for which funding was requested. The project was funded by the Florida Institute of Phosphate Research. The entire review and funding process is shown in Figure 1. The objective of this paper is to describe the important elements of the methodology to be used in assessing the impact of the roadway on local groundwater quality.

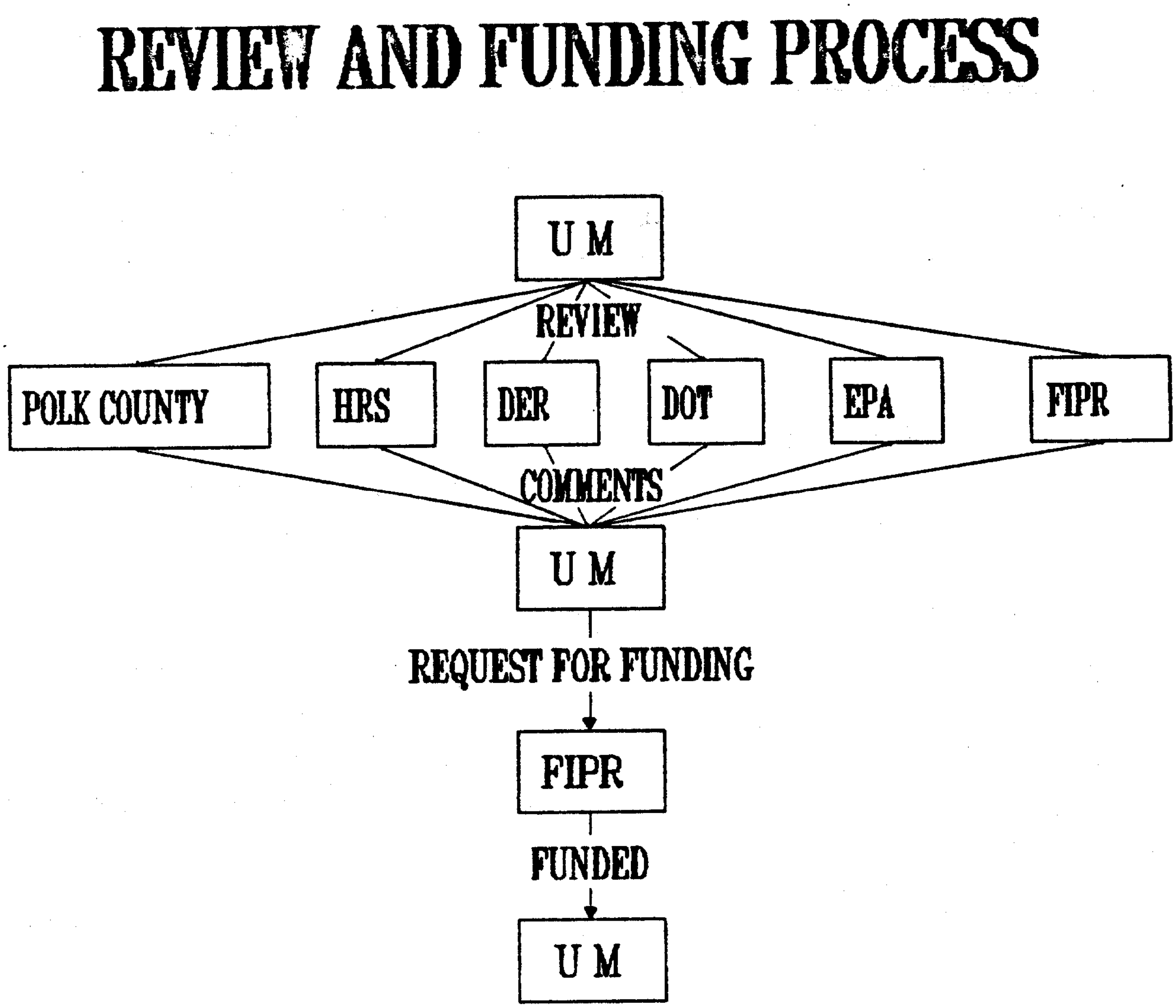


Figure 1. Review and Funding Process

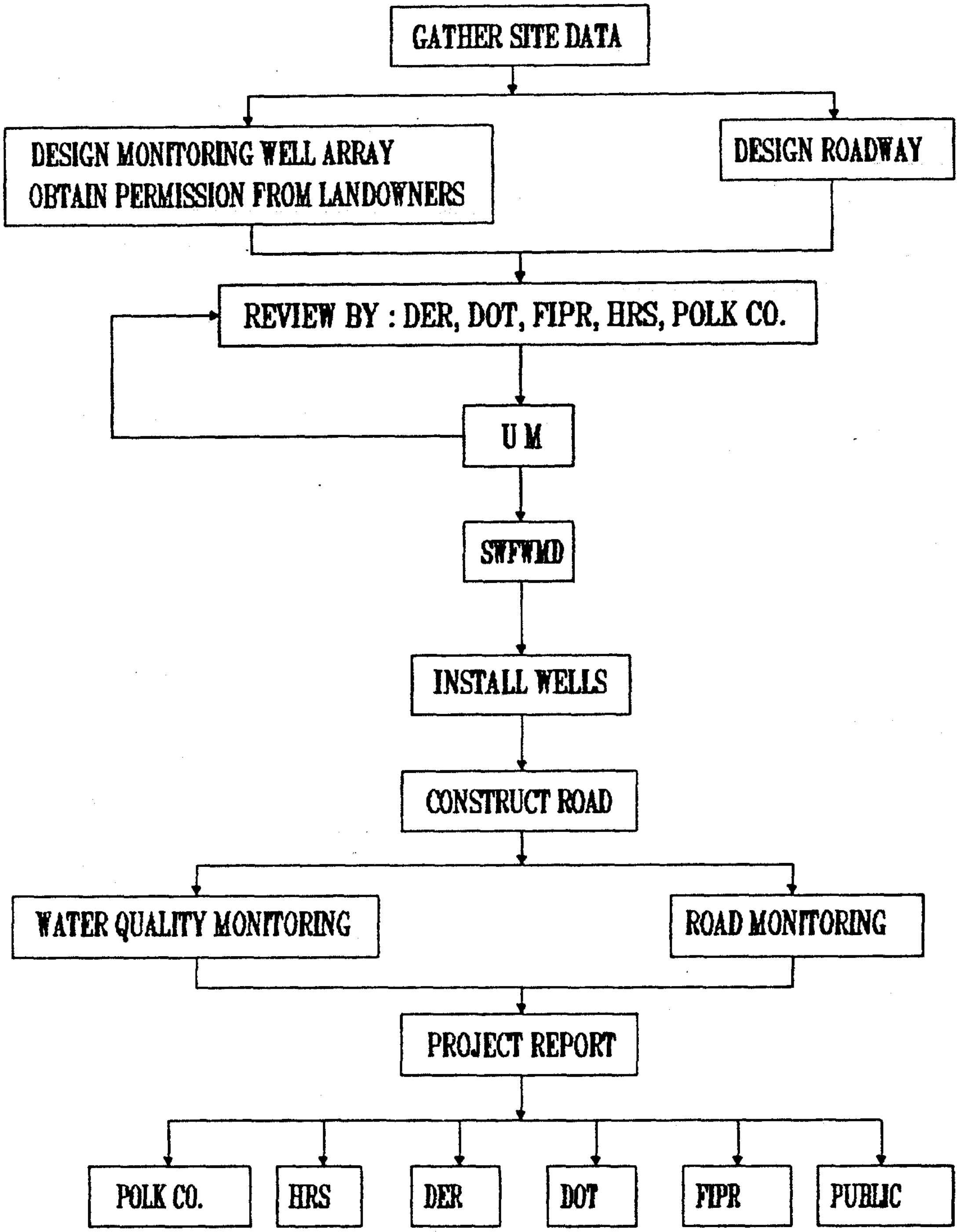
PROJECT ACTIVITIES

The project activities are shown in Figure 2. The initial step was to gather topographic and hydrogeologic data at the site of the road. A site survey was carried out to obtain the topographic data. Groundwater elevations were obtained by measuring the levels of several lakes adjacent to the proposed roadway. Soil samples were collected from the upper layers of the site. Geological data was obtained from the Southwest Florida Water Management District and area residents were interviewed about observed fluctuations in local lake levels.

After all the site data had been gathered, the monitoring wells were designed and locations assigned. At this stage the structural elements of the roadway were also designed. Plans indicating the well design and locations, as well as the roadway design, were then circulated for comment to DER, DOT, FIPR, HRS and Polk County. Comments from these agencies were evaluated by the project staff and, where necessary, revisions were implemented, All agencies who forwarded comments were either sent revised designs or informed as to why their suggested modification was not adopted. After all agencies were satisfied, the project proceeded.

Installation of wells was the next step and was carried out by a private contractor. A permit for well installation was obtained from the Southwest Florida Water Management District (SWFWMD). At the present time (February, 1986) the wells have just been installed. Monitoring of the groundwater quality at the well locations has begun.

PROJECT ACTIVITIES



The next steps are to construct the roadway, continue water quality monitoring, and monitor the structural performance of the road. Data measurements will continue for about two and one half years. At the end of that period, the results of the study will be compiled into a project report which will be forwarded to the sponsoring agency as well as the interested Federal, State and Local Agencies.

Subsequent sections of this paper describe in detail various components of the groundwater monitoring program.

LOCATION OF MONITORING WELLS

An elevation and plan view of the existing roadway is shown in Figure 3. The first 2000 ft. is bordered on both sides by open land and relatively flat terrain. From 2000 ft. to 4000 ft. there is rugged terrain on one side of the road and flat open land on the other side. From 4000 ft. until the end, houses and mobile homes are located on both sides of the roadway. Surveys of lake levels on both sides of the road indicated that the levels were approximately equal and hence there was no discernible groundwater flow direction.

Based on the above information, it was decided to place the wells symmetrically about the roadway, which would only be possible within the first 2000 ft. of the roadway. Populated areas were ruled out as well locations, because of concerns of potential contamination from septic tanks. The monitoring well locations are shown in Figure 4. Six wells were placed at 30 ft. from the centerline of the roadway and four wells at 80 ft.

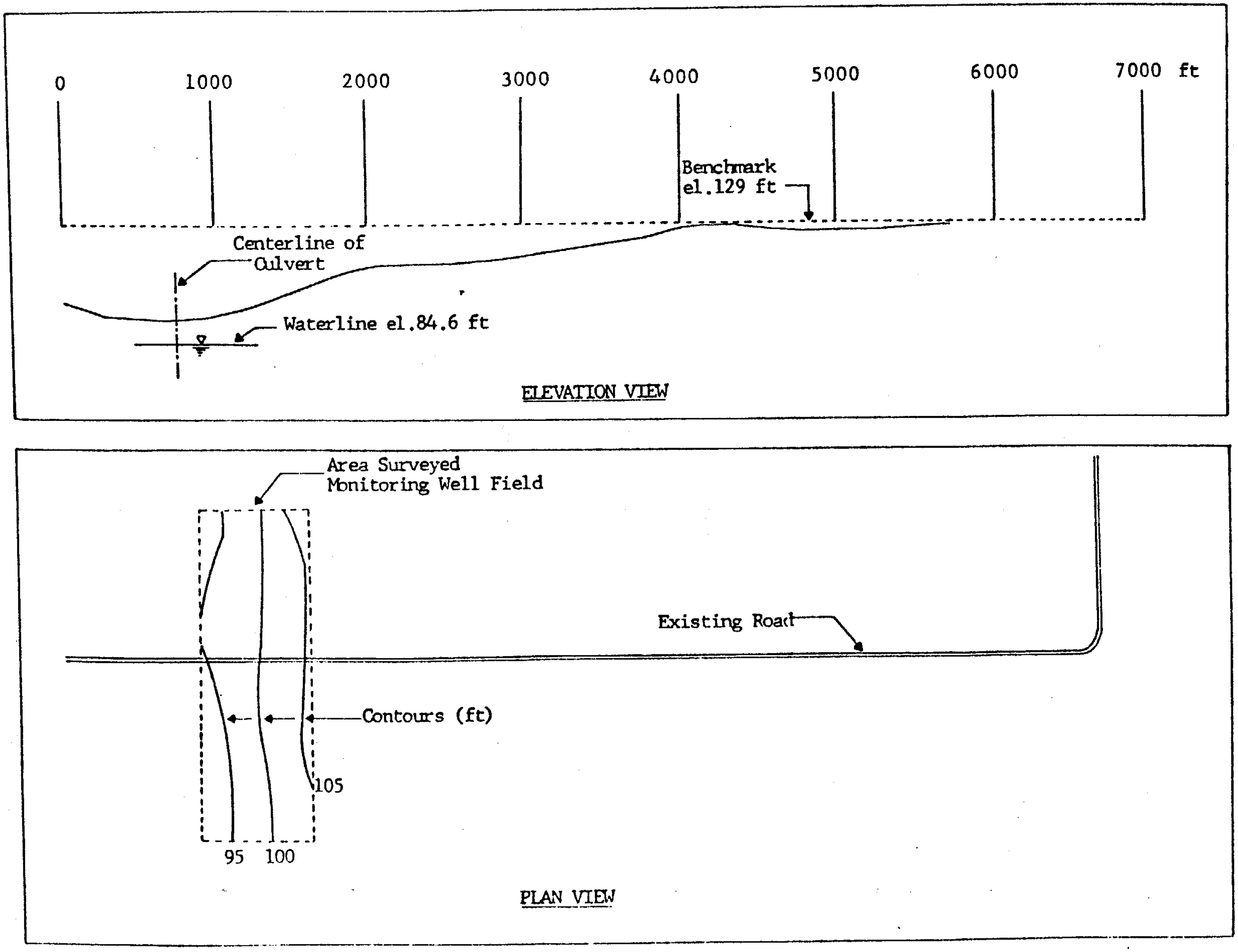


Figure 3. Elevation and Plan View of the
Existing Roadway

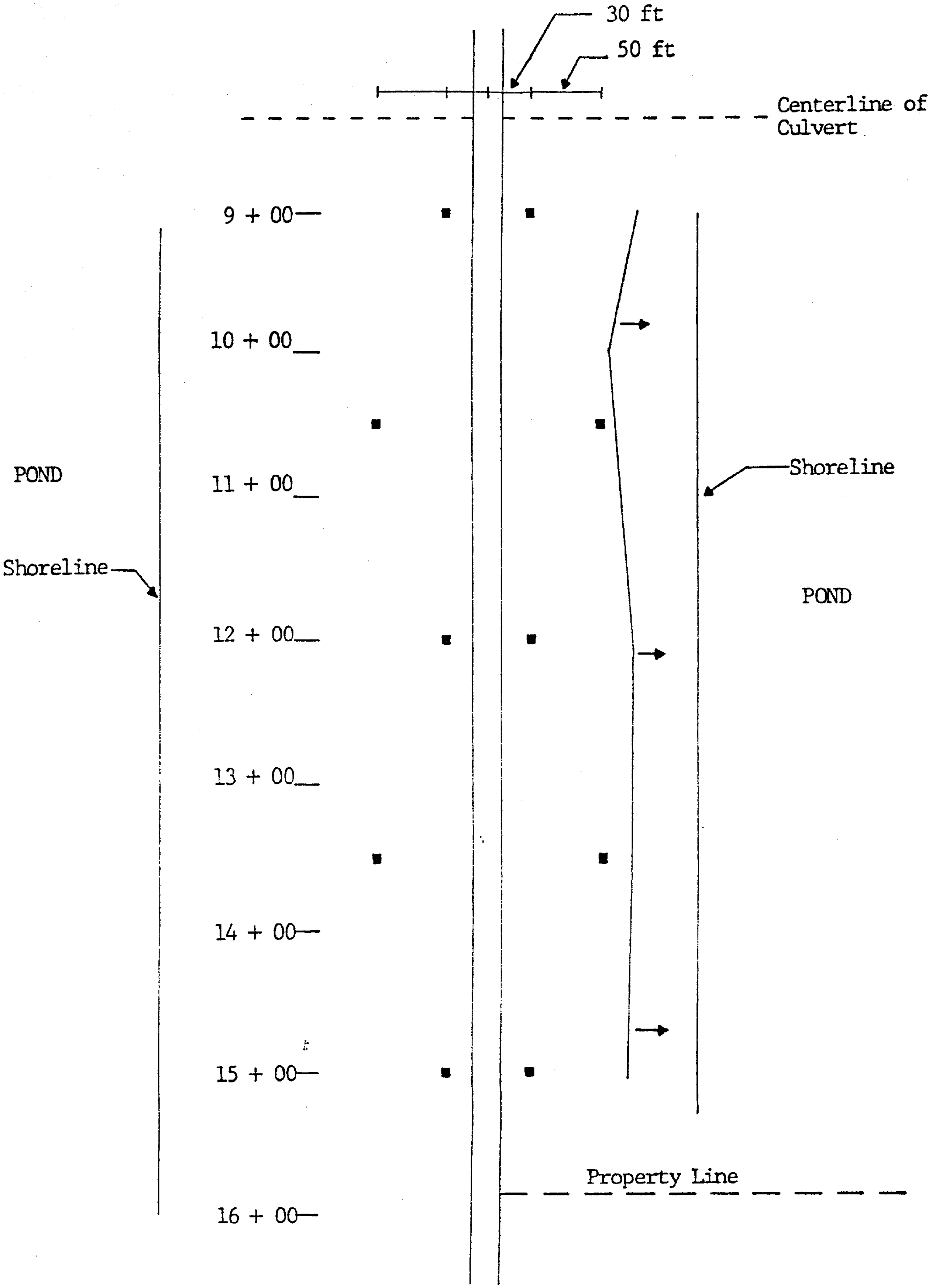


Figure 4. Monitoring Well Locations

from the centerline. The criteria for selecting the distances of the wells from the roadway were: (a) the closest wells should be at about a location where leachate from the roadway would intersect the groundwater table, (b) the further wells should be sufficiently close to the first line of wells to be able to measure any attenuation characteristics of leachate within the time constraints of the project, (c) there should be sufficient wells at a given distance so that local geologic anomalies will not unduly influence the results, (d) there should be sufficient wells such that lateral spreading characteristics may be identified, and (e) economic constraints of the project must be considered.

DESIGN OF MONITORING WELLS

Design of monitoring wells generally involve: (a) selection of well depth, (b) selection of screen length, (c) selection of well diameter, (d) selection of gravel pack, if any, and (d) selection of screen in lot size.

Selection of Well Depth and Screen Length

Required well depths were determined from the results of the topographic survey and measured groundwater elevations. Since the field survey was done at the end of the wet season, the top of the screen was specified to be at the same level as the measured groundwater. Interviewing local residents indicated that local lake levels fell about 5 ft. during the dry season. A minimum length of screen within the groundwater of 5 ft. was desired, therefore it was necessary to use 10 ft. screen extending downward from the wet season water level. The total well depths were then specified to be. from the ground surface to 10 ft. below measured water levels.

Selection of Well Diameter

Well diameters of 2” were adequate for the monitoring wells. Standard pvc pipe was used.

Selection of Gravel Pack

The gravel pack was selected based on criteria developed by the U. S. Bureau of Reclamation (3). A sieve analysis of the aquifer material is shown in Figure 5. This material has a uniformity coefficient of .25. Following the USBR recommendations the following steps were taken: (a) Multiply the 30% passing size of the aquifer by 6 and 9 and locate the points on the grain-size distribution graph on the same horizontal line, (b) Through these points draw two parallel lines representing materials with uniformity coefficient less than or equal to 2.5, and (c) Select a gravel pack material that falls between the two lines. Combining this procedure with a survey of commercially available products, it was decided to use a silica sand with 100% retained between sieves 6 and 20. The gravel pack envelope was 2 in. thick.

Selection of Screen Slot Size

The screen slot size was selected based on the following criteria: (a) The slot size should be less than or equal to the 10 percent passing size of the gravel pack, (b) Should be commercially available in 2 in

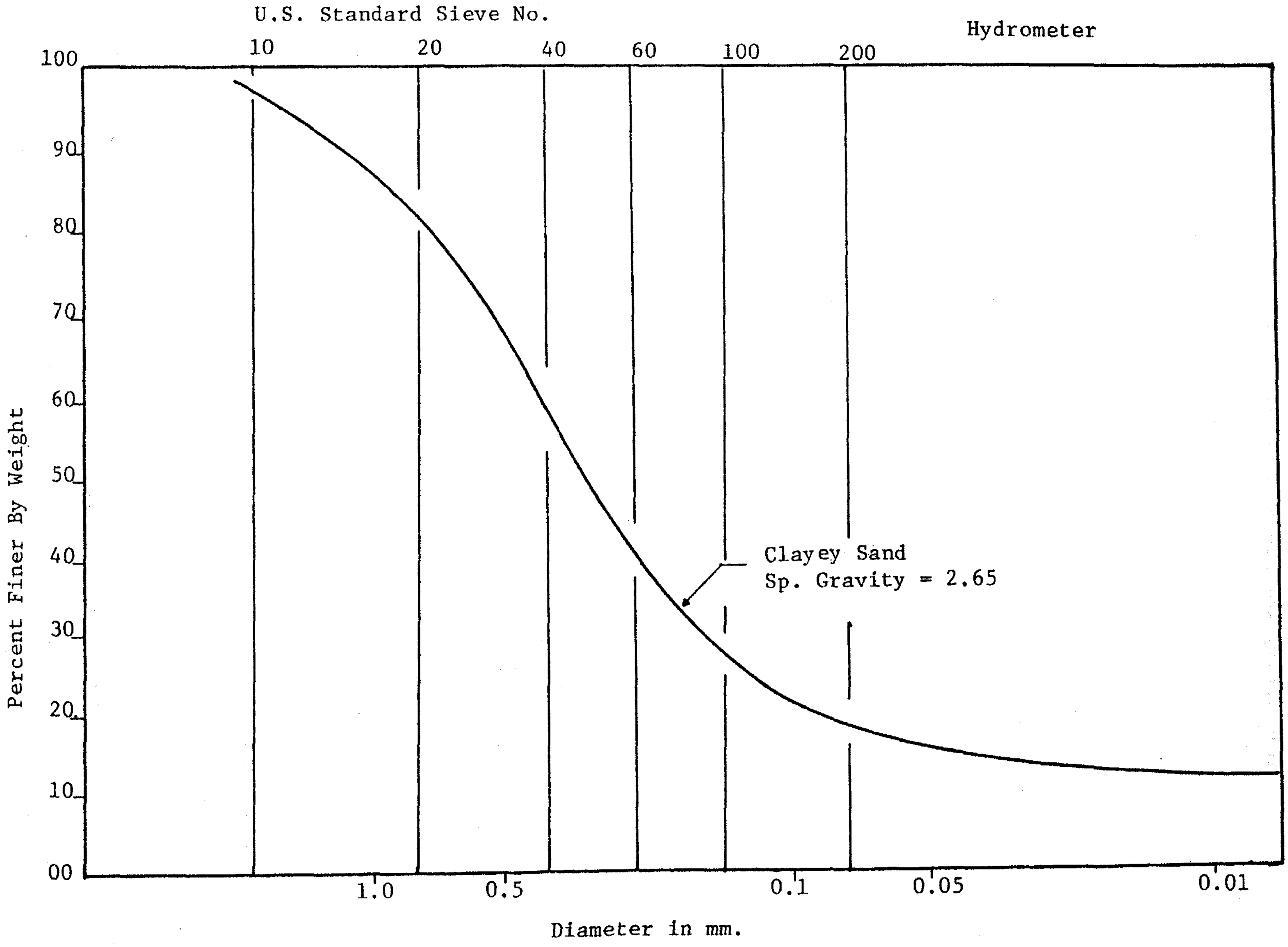


Figure 5. Grain Size Distribution of Aquifer Material

diameter pvc, and (c) The velocity through the slots should be less than 0.2 feet per second when the well is being pumped. The sampling rate is about 1.5 gpm. A slot size of .01 in. was selected based on these criteria.

Well Construction

Details of the well are shown in Figure 6. The main features to be noted are: (a) the centralizer, which ensures that the well is centered in the hole and is installed vertically, (b) the bentonite seal, which prevents water from seeping vertically into the gravel pack, and (c) the concrete seal and steel casing which ensures stability and security of the well.

PARAMETERS TO BE MEASURED

Water samples are to be analyzed for substances that may have originated from the roadway as well as major cat ions and anions. The parameters to be measured at each monitoring well are:

1. Major Cations: Ca^{++} , Mg^{++}, Na^+, K, $^+NH_4^+$
2. Major Anions: CO_3^{--}, HCO_3^-, SO_4^{--}, Cl^-, NO_3^-, F^-, PO_4^{--}
3. pH
4. Phosphorous
5. Conductivity
6. Total Dissolved Solids
7. Trace Metals: Cd, Cr, Cu, Fe, Mn, Pb
8. Ra-226

Two forms of combined phosphorous are measured, PO_4^{-3} (important in the anion-cation balance) and total phosphorous (important in determining whether any phosphorous has been leached).

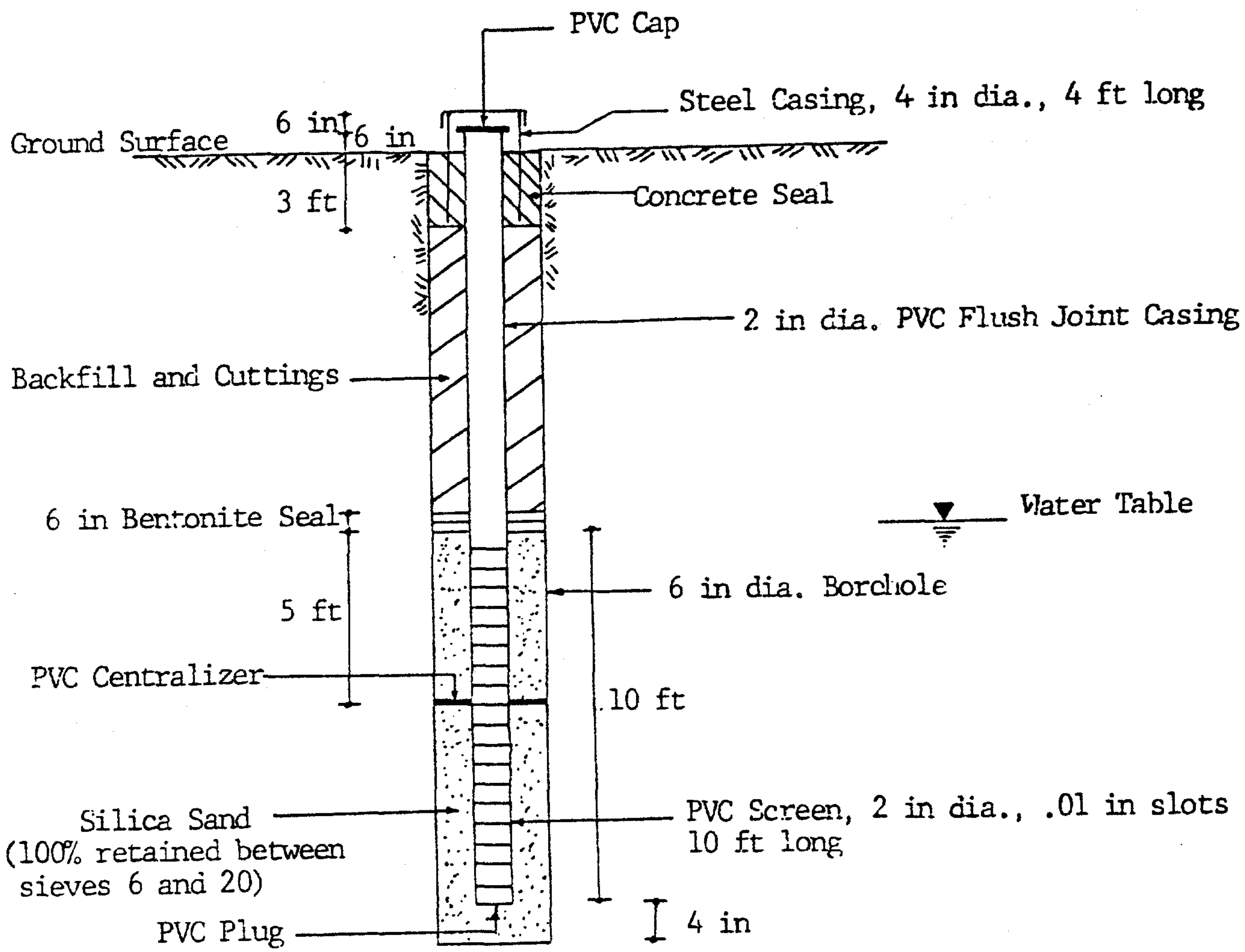


Figure 6. Monitoring Well Detail

SAMPLING METHOD

During the dry season it is expected that the groundwater level in the deepest well will be at least 22 ft. below the ground surface and, accounting for a 1 ft. projection of the well above the ground surface, the required suction lift of the pump may approach its limit of 27 ft. Because of uncertainties regarding groundwater level fluctuations, it was decided to use a submersible pump. The ISCO Model 2600 pump was selected. This pump is about 1.75 in. in diameter, easily fits inside the 2 in. diameter monitoring well, and delivers about 1.5 gallons per minute at a head of 25 ft. This pump is powered by a portable compressor operated at the surface.

The procedure for collecting a sample consists of first pumping the water into a container in which the conductivity is measured by a portable conductivity meter. When the conductivity has stabilized, the pH of the water is measured and recorded. Since there are five different preservation methods to be used (Figure 7), five sampling bottles are filled and each preserved accordingly. Well and sample numbers are recorded on the bottle labels and in a field log, shown in Figures 8 and 9.

LABORATORY ANALYSES

Most analyses are being conducted in the Environmental Engineering Laboratory at the University of Miami. Samples will be delivered to the laboratory manager who will forward samples to the appropriate workstation to be analyzed, Figure 7. Samples will be analyzed within the maximum storage period recommended by Standard Methods, Table I. The methods used in the analyses are those recommended by Standard Methods (1). Ra-226 analyses will be conducted at the HRS Laboratory in Orlando, Florida.

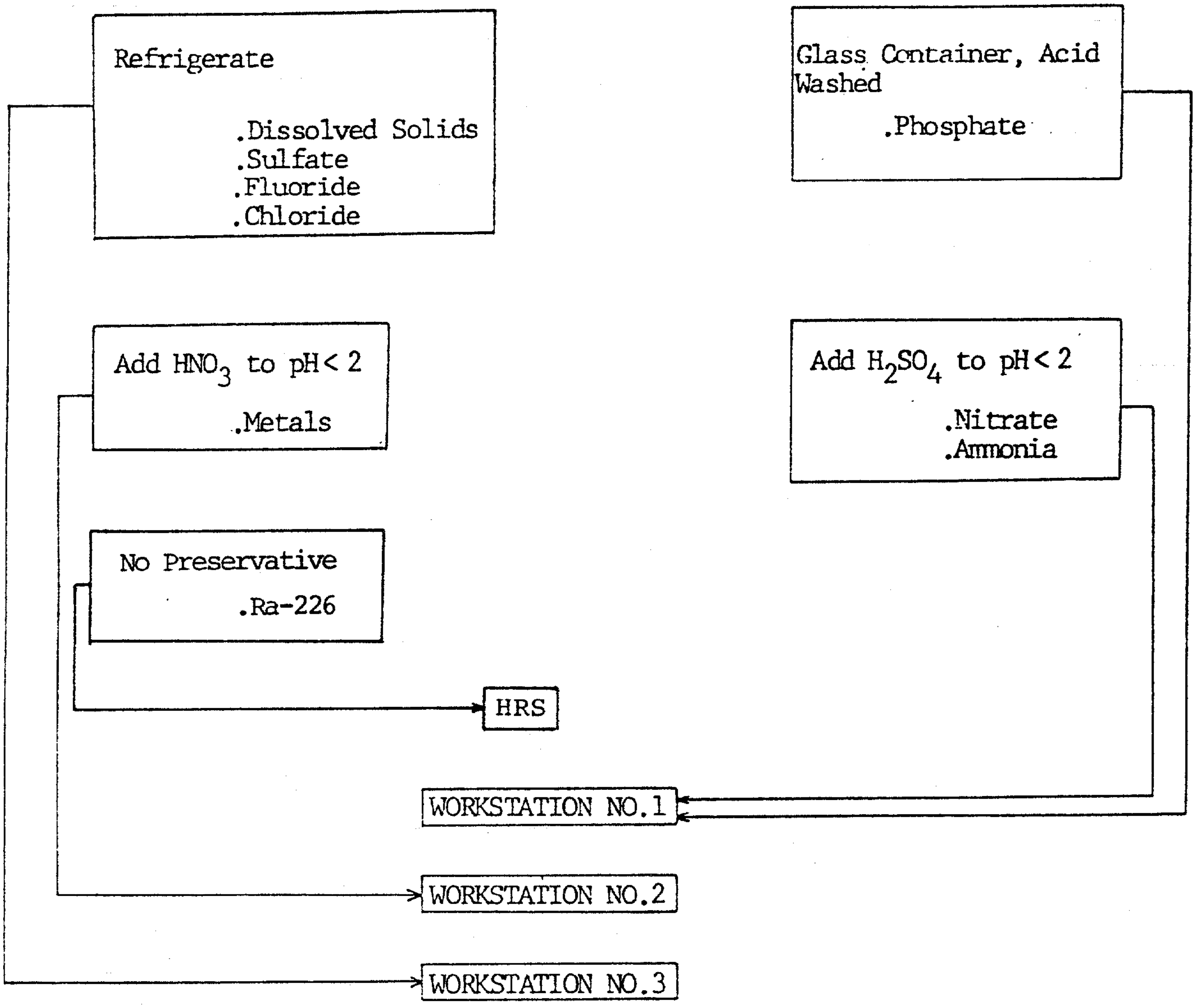


Figure 7. Destinations of Samples in Laboratory

FIELD TRACKING REPORT: Parrish Road, Polk County, Florida

Field Sample Code	Brief Description	Date	Time	Sampler	Notes

Figure 9. Field Tracking Report Form

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Sample Description: ____________________
____
Date: __________ Time: __________ Location: ______
Preservative: __________ Sampled by: __________
Field Sample Code: ____________________
Notes: ____________________
____

Figure 8. Sample Labels

QUALITY CONTROL

A detail description of quality control procedures was submitted to the Department of Environmental Regulations (DER) for their approval. Internal quality control generally consisted of the use of quality control samples, after every tenth field sample, and replicate analysis, also after every tenth field sample. Control charts were used to analyze control sample measurements. External quality control consisted of analyzing samples sent directly from DER for measurement.

DATA ANALYSIS

The objective in analyzing the variations in parameter concentrations are to determine whether the roadway produces any significant change in groundwater quality. Samples collected before road construction will indicate the pre-construction variations. It will be determined from statistical goodness-of-fit tests whether variations in parameter concentrations before and after road construction follow the same probability distribution. If the parameter concentrations change significantly, it will be determined whether these changes have an adverse effect on ambient water quality. If significant leaching of phosphogypsum constituents occurs, a pollutant transport model (2) will be applied to the observed data and dispersion and decay coefficients estimated.

CONCLUSION

This paper describes a methodology which is being used to assess the impact of a phosphogypsum roadway on local groundwater quality. Procedures used to determine monitoring well location and design are described in detail. A description of the sampling method and laboratory handling procedures has also been included. Although this paper describes a particular project, many of the techniques used are fairly general and may be applied to a wide variety of monitoring studies.

ACKNOWLEDGEMENTS

The authors are indebted to the Florida Institute of Phosphate Research for sponsoring this project. The cooperation of Dr. Wen F. Chang, Project Manager, has also been invaluable.

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CONVERSION OF PHOSPHOGYPSUM TO SULFUR

PART 1. - REDUCTION OF CALCIUM SULFATE TO CALCIUM SULFIDE

By Annie G. Smelley, Margaret M. Ragin, D. R. Brooks,
and B. J. Scheiner

For publication in the Proceedings of the Third
Seminar on Phosphogypsum

Research at the Tuscaloosa Research Center is carried out under a memorandum of agreement between the U.S. Department of the Interior, Bureau of Mines, and the University of Alabama

CONVERSION OF PHOSPHOGYPSUM TO SULFUR

PART 1. - REDUCTION OF CALCIUM SULFATE TO CALCIUM SULFIDE

By Annie G. Smelley[1], Margaret M. Ragin[2]
D. R. Brooks[3], and B. J. Scheiner[4]

ABSTRACT

In a cooperative effort between the U.S. Bureau of Mines and the Florida Institute of Phosphate Research (FIPR), with input from the phosphate industry, the conversion of phosphogypsum to sulfur is being investigated. The first step in the conversion scheme involves the reduction of phosphogypsum to calcium sulfide. In baseline experiments it was determined that phosphogypsum could be reduced to calcium sulfide at 850° to 1,000° C using either coal or carbon monoxide as the reductant. The required temperature was lowered to 750" C using Fe_2O_3 or Fe_3O_4 as a catalyst for the reduction reaction. The effects of temperature, catalyst, reaction time, and type of reductant (carbon monoxide and coal) *are* discussed.

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[1] Supervisory research chemist.
[2] Physical scientist.
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[4] Research supervisor.

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INTRODUCTION

The phosphate industry in Florida is a vital segment of the Nation's economy. Phosphate fertilizer manufacturers produce wet-process phosphoric acid, which is a major ingredient for fertilizers. The phosphoric acid is made by the reaction of phosphate rock with sulfuric acid, with phosphogypsum being the byproduct.

Estimates indicate that over 500 million tons of phosphogypsum have accumulated in Florida stockpiles. In 1980, phosphogypsum was being generated at a rate of about 33 million tons a year. The projected accumulation by the year 2000 would be over 1 billion tons (1)[5].

Numerous investigations of the environmental aspects and possible uses of phosphogypsum have been conducted by the U.S. Bureau of Mines, the U.S. Environmental Protection Agency, the U.S. Geological Survey, the Florida Institute of Phosphate Research, the phosphate industry, and many universities (1-5). In general, these investigations have characterized the phosphogypyusm, established its environmental impact on air and water, and proposed several high-volume potential end uses. Some research has focused on conversion of phosphogypsum directly to sulfuric acid (6)., Only a minimum amount of effort has focused on the technology of converting the material to sulfur.

The consensus of the Florida phosphate fertilizer manufacturers is that the conversion of phosphogypsum to elemental sulfur would be very advantageous. The future need for additional phosphogypsum waste piles would be eliminated, and the sulfur could be recycled back into fertilizer production through existing sulfur-burning sulfuric acid plants. This conceivably could eliminate the need to purchase additional sulfur.

Processes have been developed to produce sulfuric acid from gypsum, and commercial plants have been built in Germany, England, France, Austria, South Africa, and Poland (4). The processes involve the reductive roasting of gypsum using coal, natural gas, carbon monoxide, or hydrogen to produce sulfur dioxide, which is converted to sulfuric acid. The Bureau has investigated the reductive roasting of gypsum (7), the conversion of calcium sulfide to elemental sulfur (8), and sulfur dioxide emission control (9). The latter process involved the reaction of sulfur dioxide and hydrogen sulfide to produce elemental sulfur (Claus Process). In a cooperative effort with FIPR, the Bureau of Mines is investigating the conversion of phosphogypsum to elemental sulfur. Part 1 of this investigation discusses the reduction of phosphogypsum to calcium sulfide. Part 2 will discuss the conversion of calcium sulfide to sulfur. Studies are underway to determine if the addition of catalysts in the reductive roasting of phosphogypsum can be used to reduce the disassociation temperatures, thereby producing calcium sulfide more economically for use in direct conversion to elemental sulfur. This paper describes the results of the first year's efforts.

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

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance and advice of Dr. David P. Borris, Executive Director of FIPR, and Mr. Mike Lloyd, Research Director of FIPR. The voluntary cooperation of the following Florida phosphate companies in offering valuable advice and suggestions on the research efforts is also gratefully acknowledged: Gardinier, Inc., Agrico Chemical Co., Farmland Industries, Royster Co., W. R. Grace, Occidental Chemical Co., Conserve, International Minerals and Chemical Corp., and CF Industries.

MATERIALS

The experiments *were* conducted with reagent-grade calcium sulfate (anhydrite) and an air-dried phosphogypsum waste from central Florida. The chemical composition of the phosphogypsum waste is given in table 1, and a screen analysis is shown in table 2. Commercial-grade carbon monoxide and coal were used *as* reductants. The coal was used as a reductant in nitrogen and helium atmospheres. The analyses of the different coals used in these studies are shown in table 3. Reagent-grade ferric oxide (Fe_2O_3) and a 0.05-µm magnetite (Fe_3O_4) *served* as catalysts. The "fused salt" catalysts were prepared with reagent-grade chemicals. The salts used were the chlorides and carbonates of lithium, sodium, and potassium; the fluorides of lithium and sodium; and the iodide and iodate of potassium.

TABLE 1. - Chemical analysis of air-dried phosphogypsum waste, pct

$CaSO_4$................	70.4
H_2O..................	19.0
SiO_2.................	6.3
CaO..................	1.1
Other................	3.2
Total..............	100.0

TABLE 2. - Screen analysis of air-dried phosphogypsum waste

Mesh size	Pct
Plus 28............	1.4
Minus 28 plus 65....	6.1
Minus 65 plus 100...	17.2
Minus 100 plus 200..	51.5
Minus 200...........	23.8
Composite.........	100.0

TABLE 3. - Analysis of coals used in study

	Analysis, pct				
	Moisture	Ash	Volatiles	Fixed carbon	Btu/lb
Sample 1:					
as received	6.04	13.03	7.81	73.12	11,819
dried at 105° C	NAp	13.87	8.31	77.82	12,579
Sample 2:					
as received	2.76	4.32	18.54	74.38	14,605
dried at 105° C	NAp	4.44	19.07	76.49	15,020
Sample 3:					
as received	1.78	4.69	19.31	74.22	14,730
dried at 105° C	NAp	4.77	19.66	75.57	14,997
Sample 4:					
as received	1.31	7.90	20.35	70.44	14,220
dried at 105° C	NAp	8.00	20.62	71.38	14,409
Sample 5:					
as received	13.73	8.42	20.32	57.53	12,076
dried at 105° C	NAp	9.76	23.55	66.69	13,998
Sample 6:					
as received	1.98	7.07	23.53	67.42	14,191
dried at 105° C		7.21	24.01	68.78	14,478
Sample 7:					
as received	2.71	3.05	33.21	61.03	14,212
dried at 105° C	NAP	3.14	34.13	62.73	14,608

EQUIPMENT AND PROCEDURES

All thermogravimetric analysis (TGA) tests *were* made using a Dupont 1090 thermal analysis-data system[6]. The apparatus consists of a microbalance and tube furnace unit interfaced with a data analyzer which evaluates the weight changes. The experimental variables studied were reaction temperature from 680° to 1,000° C; reaction time from 25 to 60 min; catalyst concentration from 2 to 20 pct; and carbon-to-sulfur mole ratio from 2 to 3.7. A heating rate of 50°/min was used. Carbon monoxide of 100-pct concentration was used at a flow rate of 162 mL/min and provided an excess of CO for the reduction. During the pre-isothermal phase of the test, helium was used as purge gas.

Sample preparation consisted of weighing the appropriate amounts of each constituent and combining them in plastic vials which were placed in a shaker mixer for 5 min. The "fused salts" were prepared by mixing each salt in a 1:1 molar ratio with calcium carbonate and heating the mixture at 1,000" C for 1 h. The solidified melt was ground to minus 100 mesh and intimately mixed with reagent-grade calcium sulfate prior to TGA tests.

In the test procedure, approximately 50 mg of sample *or* mixture *was* weighed into the Pt crucible of the TGA apparatus. The reaction chamber

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[6] Reference to specific brand *or* trade names does not imply endorsement by the Bureau of Mines.

was closed, and the system was purged with helium until the isothermal temperature was reached. At this time the appropriate gas for the experiment was continued or introduced and the reaction was monitored.

Tube furnace studies also were conducted as part of this work. The tube used was 1 in diam and 30 in long. One- to seven-gram samples were prepared for testing by weighing the necessary components into plastic bottles and shaking them until they were thoroughly mixed. The raw materials were then transferred to ceramic boats and heated in the tube furnace. The furnace atmosphere was controlled by flowing measured amounts of the desired gases through the furnace during heating. When nitrogen was used, a fixed quantity was allowed to flow over the samples during initial heating, reduction, and cooling. When carbon monoxide was used as the reductant, the initial heating was done under nitrogen and the gas flow was changed to carbon monoxide when the sample was at the desired temperature. Carbon monoxide was varied between 1 and 2 times the stoichiometric amount. At the end of the reduction time the gas flow was changed back to nitrogen while the samples cooled. All samples were allowed to cool to 100° C or below in the furnace.

Periodically during heating, samples of the effluent gas stream from the tube furnace were removed through a septum and injected into a gas chromatograph to evaluate the gaseous reaction products. Weight loss was used to calculate the yield of calcium sulfide for the TGA experiments. For the tube furnace experiments, both weight loss and chemical analysis were used to calculate the yield of calcium sulfide. The predominant sulfur compound in the effluent gases appears to be carbonyl sulfide. Only trace amounts of sulfur compounds are being lost in the gas stream.

EXPERIMENTATION WITH TGA APPARATUS

An initial series of experiments was conducted in the TGA apparatus to determine the effect of temperature on the reduction of phosphogypsum to calcium sulfide using carbon monoxide as the reductant at temperatures ranging from 750° to 900° C. The feed material was phosphogypsum as received from Florida. The results of these experiments are summarized in table 4.

TABLE 4. - Reduction of phosphogypsum to calcium sulfide with carbon monoxide in TGA apparatus

Temperature, ° C	Conversion[1], pct	Reduction time, min
750...........	8	40.0
800...........	60	24.5
850...........	100	15.5
900...........	100	12.0

[1] Based on weight loss.

The results indicate that a temperature of at least 850° C was required to obtain complete reduction of phosphogypsum to calcium sulfide. As expected, the data also showed that as the temperature was increased, the reaction rate increased.

Investigations to determine if the addition of a catalyst could be used to lower the temperature and increase the rate of reduction also were conducted. Several fused salt materials were investigated using anhydrite as the feed material. Anhydrite was used instead of phosphogypsum to eliminate the possible side effects caused by impurities in the phosphogypsum. The fused salts tested consisted of halide and carbonate salts of lithium, sodium, and potassium mixed and fused with calcium carbonate. TGA in a carbon monoxide atmosphere indicated no catalytic activity for these salts. In other experiments Fe_2O_3 was determined to be an effective catalyst for the reduction of anhydrite to calcium sulfide in a carbon monoxide atmosphere at 680° C. The TGA curve in figure 1 shows that initially there was some weight loss, due to removal of moisture, prior to the point at which the isothermal temperature was reached. This loss was equivalent to the weight loss obtained when the anhydrite was dried in an oven at 220° C for 1 h. The region beyond the onset of the isothermal conditions showed a marked decrease in weight. The largest amount of loss occurred in the initial minutes of the reaction. This reflected the reduction of calcium sulfate to calcium sulfide and indicated that the reaction is fast (10). X-ray analysis of the residue indicated that the major constituent was calcium sulfide. The presence of iron carbide was also identified in the residue and is consistent with data reported in the literature for the reduction of iron oxide in a carbon monoxide atmosphere with excess carbon monoxide present in the system (11).

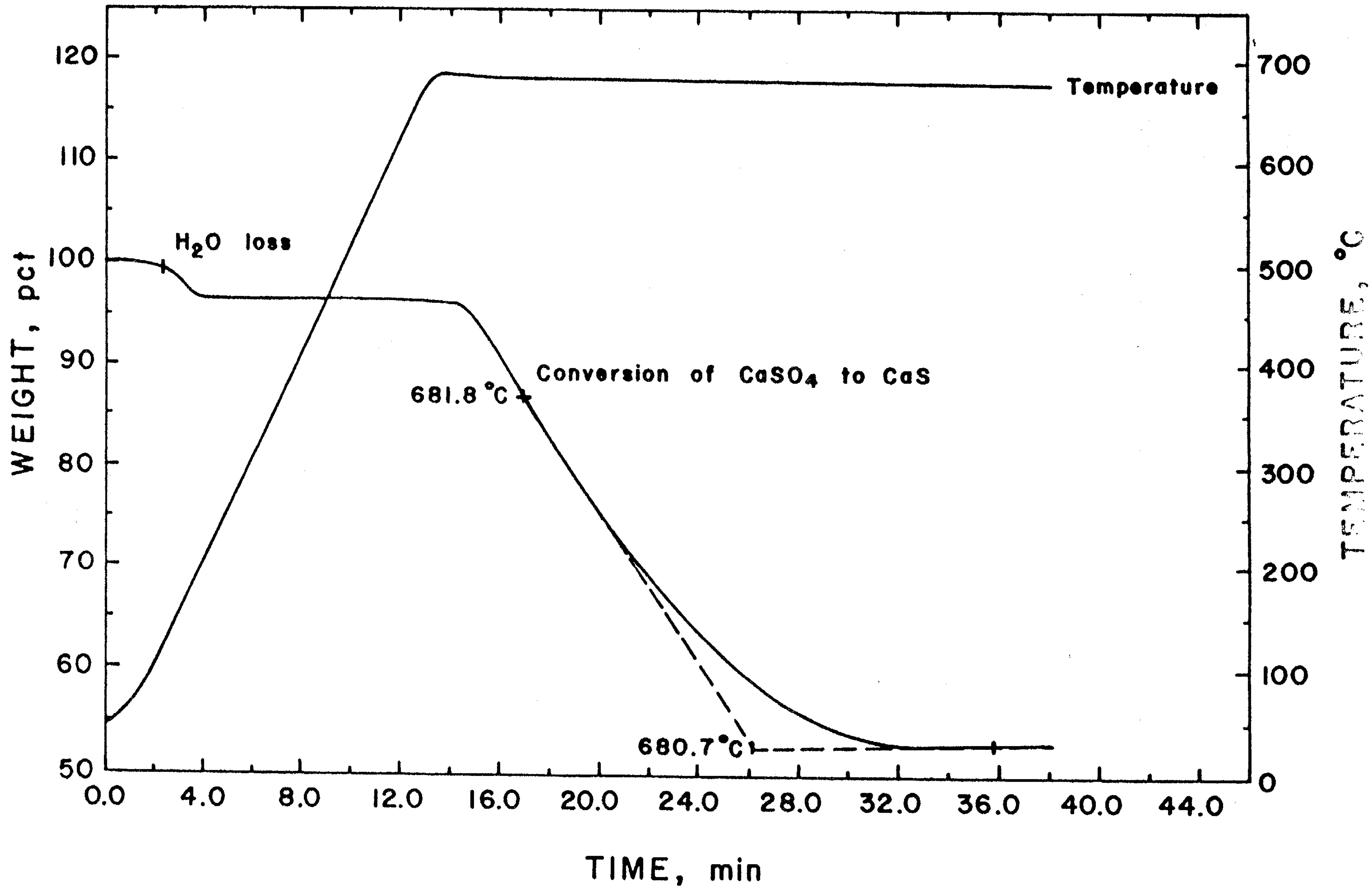
In other TGA experiments, magnetite was also shown to have the same catalytic effect as Fe_2O_3 on the reduction of anhydrite to calcium sulfide with complete reduction occurring at 680° C. In the absence of ferric oxide or magnetite, as previously shown, a temperature of 850° C was required to achieve complete conversion of anhydrite to calcium sulfide.

To determine the optimum amount of catalyst required, a *series* of experiments *was* conducted at 680° C using carbon monoxide as the reductant while varying the amount of magnetite. The results are shown in table 5.

TABLE 5. - Conversion of calcium sulfate to calcium sulfide using carbon monoxide as a reductant at 680° C

Fe_3O_4, pct	Conversion, pct
2.0.....	63.2
5.0.....	93.8
8.3.....	96.5
9.0.....	97.2
12.0.....	96.5
20.0.....	96.0

For the reaction conditions used, 8.3 to 12 pct magnetite is required to achieve 97-pct reduction, essentially the same as results reported by Zadick and others (12).


120
110
100
90
80
70
60
50
WEIGHT, pct
700
600
500
400
300
200
100
0
TEMPERATURE, °C
Temperature
H₂O loss
Conversion of CaSO₄ to CaS
681.8 °C
680.7 °C
0.0
4.0
8.0
12.0
16.0
20.0
24.0
28.0
32.0
36.0
40.0
44.0
TIME, min

Results from the tests conducted using anhydrite were the basis for a series using phosphogypsum as the feed material with ferric oxide and magnetite as the catalyst. The results of this series are given in table 6.

TABLE 6. - Conversion of phosphogypsum[1] to calcium sulfide using carbon monoxide as a reductant

Temperature, ° C	Catalyst concentration, pct	Conversion, pct	
		Fe_3O_4	Fe_2O_3
680........	8.3	45	-
745........	8.3	98	-
750........	8.3	98	99
745........	5.0	94	-
750........	5.0	97	97
775........	5.0	98	-

[1] Based on weight loss.

The results show that for phosphogypsum the temperature required for reduction is about 750° C. This is an increase of 70° when compared to anhydrite. This increase in temperature was probably caused by the impurities contained in the phosphogypsum.

TUBE FURNACE EXPERIMENTS

Based upon the results from TGA experiments, the reduction reaction of calcium sulfate to calcium sulfide was evaluated in a tube furnace. Initial experiments were conducted using anhydrite. A series of experiments varying the temperature and using 100 pct carbon monoxide as the reducing gas showed that a temperature of 850° C resulted in 99.9-pct conversion to calcium sulfide. At lower temperatures the conversion was less; for example, at 800° C only 85.4-pct reduction was observed. In previous experiments in the TGA apparatus, the reduction time was 15.5 min, whereas for the tube furnace, the reduction time increased to greater than 30 min, as shown in table 7.

TABLE 7. - Effect of time on the reduction of calcium sulfate with 100 pct carbon monoxide at 850° C

Reduction time, h	Conversion, pct[1]
1/2.........	89
1...........	100
2...........	100

[1] Based on weight loss.

The experiments previously described were conducted using 100 pct carbon monoxide as the reductant. Since such a concentration would be difficult to obtain by heating *coal* or carbon, which is desirable from an economical standpoint, a series of experiments using a mixture of 5 pct carbon monoxide and 95 pct nitrogen was conducted; the results are shown in table 8.

TABLE 8. - Effect of temperature on the reduction of calcium sulfate with 5 pct carbon monoxide

Temperature, ° C	Reduction time, h	Conversion, pct
800.........	2	61
850.........	1	84
850.........	2	99
900.........	2	100

As expected, the decrease in carbon monoxide concentration from 100 pct to 5 pct increased the time required to obtain complete conversion.

In another series of experiments, phosphogypsum as received was air-dried and treated in the tube furnace for 2 h using 10 pct carbon monoxide and 90 pct nitrogen as the reducing gas, and the results indicated that a temperature of 900° C was required to obtain 99-pct conversion. This was an increase of 50° C when compared to the reduction of anhydrite. This temperature was lowered to 750° C by adding 8.3 pct ferric oxide *or* magnetite to the phosphogypsum prior to reduction. The required reduction time to obtain greater than 90-pct conversion was *2* h.

These test results from the tube furnace parallel the results obtained in the TGA apparatus. The major difference is in time required to do the reduction. The reason for this increase in time is probably due to the difference in configuration of the sample in the TGA and the tube furnace. In the tube furnace, the sample was packed into a boat with the gas flow over the boat. Since the reaction between the carbon monoxide and the calcium sulfate is a diffusion-controlled reaction, this configuration and the fact that a larger sample is being used would decrease the reaction rate.

REDUCTION OF PHOSPHOGYPSUM USING COAL AS THE REDUCTANT

In experiments previously described, carbon monoxide had been used as the reductant for calcium sulfate. In actual practice, carbon is combined with oxygen to produce carbon dioxide in a powerful exothermic reaction:

$$C + O_2 = CO_2 \qquad (1)$$

In an oxygen-deficient atmosphere, the carbon dioxide produced in reaction 1 can react with carbon to produce carbon monoxide:

$$C + CO_2 = 2CO \qquad (2)$$

Reaction 2, is favored by high temperatures. The combination of reactions 1 and 2 is shown in equation 3 (13):

$$2C + O_2 = 2CO \qquad (3)$$

The reduction of calcium sulfate by carbon can yield calcium sulfide and sulfur dioxide. Preferential reduction can be achieved to yield essentially either calcium sulfide or sulfur dioxide by control of the amount of carbon added, relative to the amount of the sulfate. The reactions for the conversion are shown in equations 4 and 5:

$$CaSO_4 + 2C \rightarrow CaS + 2CO_2 \quad (4)$$

$$2CaSO_4 + C \rightarrow 2CaO + 2SO_2 + CO_2 \quad (5)$$

To produce calcium sulfide the molar C:S ratio in the charge should be slightly above the stoichiometric value 2:1 (14).

Experiments were conducted in the tube furnace to determine if results obtained with carbon monoxide as the reductant could be reproduced using phosphogypsum as the feed and coal as the reductant. In preliminary experiments it was determined that to obtain 90-pct conversion of calcium sulfate to calcium sulfide required a temperature of 1,000° C with carbon-to-sulfur ratios greater than 2.0. The addition of magnetite did not lower the reduction temperature as expected. To better define the effect of magnetite on the reduction reaction, a series of experiments using coal, sample 5, at carbon-to-sulfur ratios of 2.8 to 3.7 was conducted, and the results are summarized in table 9. The results show that the conversion of phosphogypsum to calcium sulfide was increased when magnatite was used. For example, for a ratio of carbon to sulfur of 2.8, the addition of 9 pct magnetite increased the yield from 87 to 94 pct. The results also indicate that all the carbon added did not react with 28 to 31 pct of the carbon remaining after the reduction, even though the reaction time was 2 h.

TABLE 9. - The effect of magnetite on the reduction of phosphogypsum with coal #5 at 1,000° C with a reaction time of 2 h

Carbon to sulfur ratio, pct	Fe_3O_4 addition, pct	Conversion to CaS, pct	Carbon unreacted, pct
2.8	0	87	--
2.8	9	94	31
3.2	0	84	28
3.2	9	96	29
3.7	9	96	28

From previous experiments in the TGA apparatus using carbon monoxide as the reductant, it was determined that 12 min were required to complete the reduction. To determine how the reduction time is affected when coal is used as the reductant, a series of experiments was conducted at 1,000° C, using a carbon-to-sulfur ratio of 3.7. It was determined that the time required to achieve complete reduction was only 4 min. These results indicate that phosphogypsum could be reduced rapidly to calcium sulfide in high yields. This is in contrast to the tube furnace, where long reaction times are required. Also, these results strongly suggest that the use of a tube furnace, where phosphogypsum and coal are packed in a boat, is inadequate for optimizing the reduction.

To further determine the reaction between coal and phosphogypsum, a series of experiments was conducted to evaluate the different coals where there is a wide variation in ash, fixed carbon, BTU value, and volatile content (see table 3). The results are summarized in table 10. The results indicate that the maximum conversion was obtained with the coal containing the highest content of volatiles. The results also indicate that ash, fixed carbon, and BTU values follow no set pattern and appear not to be important in the range of compositions tested. The exact role of the volatiles is unknown since it is expected that the volatiles would be removed at temperatures lower than the 1,000° C where the reduction is accomplished.

TABLE 10. - Reduction of phosphogypsum with various coals with a carbon-to-calcium-sulfate ratio of 2.0 at 1,000° C

Coal	Volatiles, pct	Yield of CaS, pct	Unreacted C, pct
1...	8.31	75	11
2...	19.07	75	19
3...	19.66	74	16
4...	20.62	78	15
5...	23.55	83	11
6...	24.01	85	13
7...	34.13	93	11

Based upon the results obtained to date, it appears that the use of a static tube furnace and packed boats will not allow optimization and complete utilization of the coal. To overcome these problems, the reduction reaction will be studied in a sealed rotary tube furnace where better utilization of the reductant can be accomplished.

CONCLUSIONS

The conversion of the calcium sulfate in the phosphogypsum to calcium sulfide was accomplished using carbon monoxide as reductant, at temperatures of 850° C in a TGA apparatus and of 900° C in a tube furnace. The temperature was lowered to 750° C using ferric oxide or magnetite as catalyst in both TGA and tube furnace experiments. A temperature of 1,000° C is required when coal is used as reductant in an inert atmosphere.

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CONVERSION OF PHOSPHOGYPSUM TO SULFUR

PART 2. - OXIDATION OF CALCIUM SULFIDE TO SULFUR

By Alexander May and John W. Sweeney

For publication in the Proceedings of the Third
Seminar on Phosphogypsum

This report is based upon work done under an agreement between the University of Alabama and the Bureau of Mines.

CONVERSION OF PHOSPHOGYPSUM TO SULFUR

PART 2, - OXIDATION OF CALCIUM SULFIDE TO SULFUR

By Alexander May[1] and John W. Sweeney[2]

ABSTRACT

As part of a cooperative effort between the U.S. Bureau of Mines and the Florida Institute of Phosphate Research (FIPR), with input from the phosphate industry, the conversion of phosphogypsum to sulfur is being investigated. The research described herein is focused on converting calcium sulfide to ammonium bisulfide by reaction of an aqueous slurry with ammonia and carbon dioxide. Calcium carbonate is removed by filtration, and the ammonium bisulfide is oxidized to sulfur using *air in* the presence of a carbon catalyst. This paper discusses the reaction parameters and their effect upon sulfur yield.

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INTRODUCTION

This work was cofunded by the Bureau and FIPR, since its purpose addresses the missions of both agencies. The mission of FIPR is to encourage research related to problems of the phosphate industry in Florida, while that of the Bureau is to ensure that the Nation has an adequate supply of minerals. The objective of this work was to develop a process to convert phosphogypsum to elemental sulfur. The project being conducted by the Bureau of Mines is divided into two parts: (1) investigation of thermal reduction of phosphogypsum to calcium sulfide, the subject of Part 1 (1)[3] of this paper; and (2) investigation of a hydrometallurgical process to convert calcium sulfide to elemental sulfur, the subject of Part 2 of this paper.

Forecasts of sulfur supply between 1990 and 2000 predict a depletion in primary sulfur sources and an increase in sulfur demands and prices on a worldwide scale (2). The fertilizer industry in the United States consumes about 65pct of the Nation's sulfur (3). This sulfur is used to make sulfuric acid, which is mixed with phosphyte rock to make phosphoric acid, the major ingredient used to make phosphate fertilizers. The byproduct of the phosphoric acid production is calcium sulfate dihydrate, phosphogypsum. The sulfur, although consumed, is not lost, but is converted to phosphogypsum, from which it is potentially available. By the year 2000 the estimated quantity of stockpiled phosphogypsum will be about 1 billion tons (4). Its available sulfur would help meet the increased demand for sulfur in the United States.

Calcium sulfide was produced by the catalytic reduction of phosphogypsum because it is thermodynamically and kinetically favored over other products, such as sulfur dioxide. Details of this reduction are given in Part 1 (1) of this paper.

Thermodynamic evaluation of literature data on the dry Ca-O-S system showed that at equilibrium, oxidation of CaS would produce some $CaSO_4$ under all reasonable conditions at which elemental sulfur was stable. Kinetics of the oxidation of dry CaS (5) also showed the formation of $CaSO_4$ and, at high temperatures, the formation of CaO and SO_2. However, laboratory experience and numerous literature references indicated that CaS can be oxidized to elemental sulfur in aqueous systems. Lefers, Koetsier, and Van Swaaij (6) and Chen and Morris (7) dealt with the kinetics of this oxidation: while Rosenwald, Hamblin, Urban, and Zimmerman (8) proposed a process to make elemental sulfur. Therefore, a hydrometallurgical process was indicated.

The major objective of this investigation was to produce elemental sulfur. Side reactions, intermediate products, and optimum conditions were investigated only to the extent that they added to the process being developed.

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

ACKNOWLEDGMENTS

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MATERIALS USED

Reagent-grade chemicals and demineralized water were used in this investigation.

ANALYTICAL METHODS

In aqueous O-S systems, a pH-dependent equilibrium exists between many sulfur species, These are shown in table 1. Elemental sulfur was determined by CS_2 extraction. The $S^=$, $S_2O_3^=$, $SO_3^=$, and H_2S species were determined by 12 titration methods (9). Sulfate *was* determined by precipitation as $BaSO_4$ and total sulfur by oxidation with Na_2O_2 followed by sulfate determination, However, the NH_4SH solutions reacted explosively with Na_2O_2. The sulfides in these solutions were converted to insoluble ZnS (10), which was not filtered off but, along with any other sulfur species in solutions, was oxidized by Na_2O_2. Bisulfide was determined as S= and the pH of the system (11). The polysulfides and polythionates were not quantitatively determined.

TABLE 1. - Sulfur species that may exist in an aqueous sulfur-oxygen system

S^0	Elemental sulfur
$S^=$	Sulfide
$S_2O_3^=$	Thiosulfate
$SO_3^=$	Sulfite
$SO_4^=$	Sulfate
$S_xS^=$	Polysulfides or sulfanes
$S_x(SO_3)^=$	Polythionates or polydisulfonates
H_2S	Hydrogen sulfide
SH^-	Bisulfide

Ammonia was determined by titration with standard acid.

INITIAL TESTS

Tests *were* performed on direct oxidation of pure CaS by air or oxygen. Bubblers, vortex mixing, a shearing-blade reaction chamber, and a modified fluidized-bed reactor were used with air, oxygen, and carbon as a catalyst. Sulfur recoveries were low using these techniques as shown in table 2.

TABLE 2. - Sulfur recovery by direct oxidation of aqueous CaS slurries with air or O_2

	Sulfur recovery, pct
Bubblers, shearing-blade reaction chamber, fluidized-bed reactor......................	trace
Vortex mixing................................	3 to 7
Vortex mixing plus carbon....................	4 to 10

Rosenwald, Hamblin, Urban, and Zimmerman (8) claimed that NH_4SH could be converted to elemental sulfur with yields of 90 to 100 pct. Since these results were much better than our first experiments, where only 10-pct sulfur yields were achieved using CaS, the investigation was redirected to convert CaS to NH_4SH.

Nearly complete conversion of CaS to NH_4SH was achieved using three different aqueous systems illustrated by equations 1 through 3:

$$CaS + (NH_4)_2CO_3 + H_2O \rightarrow CaCO_3 + NH_4SH + NH_4OH \quad (1)$$

$$CaS + NH_3 + CO_2 + H_2O \rightarrow CaCO_3 + NH_4SH \quad (2)$$

$$CaS + NH_4HCO_3 \rightarrow CaCO_3 + NH_4SH \quad (3)$$

Sulfur species in NH_4SH solutions made from CaS are shown in table 3.

TABLE 3. - Sulfur species in NH_4SH solutions produced from CaS

Species	Percent in NH_4SH Solution
SH^-.......	92 to 94
$S_2O_3^=$.....	4 to 6
$SO_3^=$......	0 to 2
$SO_4^=$......	0 to 0.4

NH_4SH solution: 11 pct = 16 pct CaS

The solubility of CaS in water is only 0.2 pct, while that of NH_4SH is 56 pct -- equivalent to 79 pct CaS. Solutions containing as much as 11 pct NH_4SH -- equivalent to 16 pct CaS -- were made. These solutions readily evolved H_2S and formed polysulfides. These higher concentrations of NH_4SH are *very* significant because they showed that slurries of CaS could be converted to NH_4SH and then to elemental sulfur with a minimum amount of water.

Numerous tests were performed--on the oxidation of NH_4SH to elemental sulfur. By restricting the amount of air in the tests, the O/S ratios were maintained near 1. It was determined that the oxidation of NH_4SH proceeded through the formation of polysulfides. The polysulfides were decomposed by distillation to give elemental sulfur. These results were greatly improved over those obtained with CaS. Some of the factors that increased sulfur yields were (1) increase in percent carbon, (2) increase in time of reaction, and (3) use of NH_4HCO_3 *or* $NH_3 + CO_2 + H_2O$. Twenty-four tests had sulfur yields ranging from 14 to 41 pct, averaging 27 pct, and five other tests had sulfur yields ranging from 42 to 45 pct, averaging 44 pct.

PROCESS DEVELOPMENT

Based on the oxidation tests of NH_4SH, a new process for the conversion of calcium sulfide to elemental sulfur was devised that involved:

(1) Reaction of CaS with aqueous solutions of NH_4HCO_3 or NH_3 plus CO_2, to produce $CaCO_3$ plus NH_4SH. The $CaCO_3$ was removed by filtering.

(2) Oxidization of the NH_4SH by air, using a carbon catalyst, to produce NH_4OH and NH_4S_4SH (an ammonium polysulfide).

(3) Distillation, which removes NH_3, H_2S, and some H_2O, and precipitates elemental sulfur.

(4) Reaction of the NH_3 and H_2O with CO_2 to produce NH_4HCO_3, which is recycled to the first step.

The H_2S removed in step (3) by distillation amounts to about 20 pct of the total sulfur. However, the H_2S reacts with NH_4OH in the distillate to form NH_4SH plus H_2O, which is also recycled.

All steps in the process were experimentally tested by bench-scale batch tests. Steps (1) and (4) *were* quantitative. The yield of elemental sulfur from steps (2) and (3) *reached 45* pct of the amount initially present in the CaS. The H_2S from the distillation, step (3), was not converted into elemental sulfur and is not included in the 45-pct sulfur yield. Because the objective of this phase of the work *was* not restricted to demonstrating that the proposed reactions actually occurred, complete materials balances *were* not determined.

This hydrometallurgical process perfectly matches with the thermal catalytic reduction of phosphogypsum since the latter produces the calcium sulfide plus a twofold excess of CO_2 needed in the process. The reactions involved are shown by equations 4 through 9:

$$4CaSO_4 \cdot 2H_2O + 8C \rightarrow 8H_2O + 8CO_2 + 4CaS \quad (4)$$

$$4CaS + 4NH_4HCO_3 \rightarrow 4NH_4SH + 4CaCO_3\downarrow \quad (5)$$

$$5NH_4SH + 2O_2 \text{ (air)} \xrightarrow{\text{carbon}} 4NH_4OH + NH_4S_4SH \quad (6)$$

$$NH_4S_4SH \xrightarrow{\text{distill}} NH_3 + H_2S + 4S^\circ \quad (7)$$

$$NH_3 + H_2S \rightarrow NH_4SH \quad (8)$$

$$4NH_4OH + 4CO_2 \rightarrow 4NH_4HCO_3 \quad (9)$$

Equation 4 shows the reduction of phosphogypsum, $CaSO_4 \cdot 2H_2O$, and produces the CaS needed in equation 5 and the CO_2 needed in equation 9. The NH_4OH produced in equation 6 is sufficient to produce the NH_4HCO_3, equation 9, which is recycled to the reaction, equation 5. The NH_4SH, equation 8, is recycled to equation 6, along with the NH_4SH from equation 5.

A simplified flow sheet of the process is shown in figure 1. The CaS, CO_2, and air are raw materials; the $CaCO_3$ and sulfur are products; and NH_3, H_2S, and C are recycled in the process.

The bench-scale batch tests of the process *were* typically as follows. A weighed amount of CaS was placed in a reaction chamber with stoichiometric quantities of NH_4HCO_3. Water was put *into* the chamber to completely fill it to exclude air. After stirring 1 h, the $CaCO_3$, equation 5, was filtered off; the NH_4SH solution, the filtrate, was collected in another reactor which contained air and the desired quantity of carbon catalyst. The second reactor was sealed and its contents stirred vigorously for 1 to 18 h.

The quantity of CaS and volume of NH_4SH solution were initially adjusted so that the amount of air in the second reactor gave an O/S ratio of 1. This restricted the tests to dilute NH_4SH solutions, of about 1 pct.

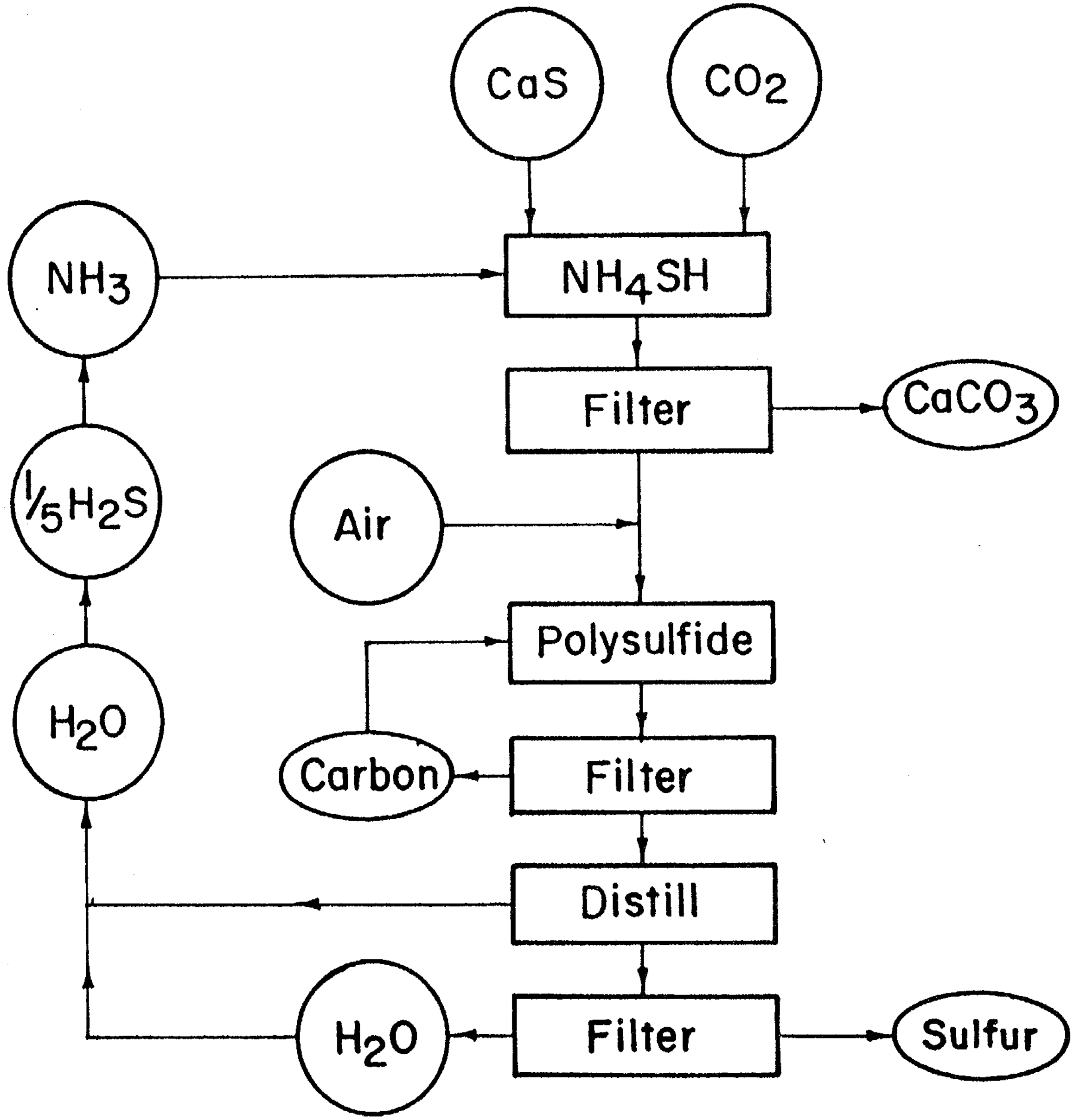
The reaction between air and the NH_4SH solutions produced a bright yellow polysulfide solution, equation 6. These solutions were filtered to remove the carbon. The carbon was dried at 105° C, and elemental sulfur was extracted from the carbon with CS_2 and weighed.

The polysulfide solutions were distilled until tests for NH_3 and H_2S, equation 7, *were* negative. About 20 pct distillate was required. Elemental sulfur precipitated in the distilling flask. This was filtered off, dried, extracted with CS_2, and weighed.

The distillate was analyzed for $S^=$ and NH_4^+. These analyses verified that close to 20 pct of the sulfur was evolved as H_2S, as indicated by equation 7. The distillates were treated with CO_2 until the pH reached 8.1, equation 9, forming an NH_4HCO_3 solution containing NH_4SH, equation 8, which was recycled to the process, equation 5.

Variations of this typical procedure were tested to identify factors involved in the process.

FLOW SHEET-DISTILLATION



As stated previously, all steps in the process illustrated by equations 4 through 9 were tested on a laboratory scale. However, for commercial application the process had several undesirable features:

(1) Large volumes of solutions would be needed for dilute NH_4SH solutions.

(2) Distillation - Only about 20 pct of the solution need be distilled to achieve the liberation of sulfur, equation 7, but on a large scale this would be expensive.

(3) The time for the reaction, up to 18 h, is too long.

(4) Yields of sulfur *were* low. The yields given were on a batch basis. Twenty percent of the sulfur would be recycled in the system. Thus, *a* 46-pct yield would actually be a 57-pct yield on a continuous basis, which is still considered too low.

(5) Three filtering steps are needed; that of the $CaCO_3$, that of the carbon to be returned to the system, and that of the sulfur precipitated in the distilling flask.

PROCESS IMPROVEMENT

Further investigations of the hydrometallurgical process resulted in significant improvements.

Instead of using a fixed-volume reaction chamber to oxidize NH_4SH solutions, sequential recycling systems were used. Also, NH_4SH solutions and air were simultaneously pumped through columns of carbon-coated mullite beads. This allowed use of more concentrated solutions of NH_4SH.

These new techniques also led to a major improvement. The distillation step was eliminated. The carbon both acted as *a* catalyst and absorbed elemental sulfur. The reactions, equations 6 and 7, both occurred on the carbon. H_2S evolution was about 6 pct compared to 20 pct for distillation. Details of the system are still being investigated.

The time for the oxidation of NH_4SH solutions was reduced from 18 to 7 h, and the yields of sulfur increased from 45 pct to 65 pct.

These improvements also eliminated two filtering steps, that of the carbon and that of the sulfur. After absorbing the sulfur on the carbon column, the sulfur can be removed by extraction, melting, or vaporizing. These aspects are being investigated.

These new improvements versus the initial undesirable features of the sulfur process are summarized in table 4.

TABLE 4. - Improvements in the sulfur from CaS process

Objection to initial process	Improvements
Volumes of solutions needed were too large	Concentrated solutions of NH_4SH resulted in smaller volume requirements
Distillation required	Distillation eliminated
Time for reaction too long, 18 h	Time decreased to 7 h
Yields of sulfur too low, 45 pct	Yields increased to 65 pct
Three filtering steps required	Decreased to one filtering, that of $CaCO_3$

The final hydrometallurgical sulfur process can be represented by equations 10 through 12:

$$CaS + NH_4HCO_3 \dashrightarrow NH_4SH + CaCO_3\downarrow \qquad (10)$$

$$NH_4SH + 1/2O_2\ (air) \xrightarrow{carbon} NH_4OH + S^0 \qquad (11)$$

$$NH_4OH + CO_2 \dashrightarrow NH_4HCO_3 \qquad (12)$$

These reactions occur at ambient temperature and pressure.

CONCLUSIONS

1. It has been demonstrated that CaS can be converted to NH_4SH.

2. It has been demonstrated that NH_4SH can be oxidized to elemental sulfur.

3. A process has been developed to convert CaS, via NH_4SH, to elemental sulfur.

4. The improved process, shown in figure 2, has the potential to become an economically feasible industrial process. However, research is still in progress to better define some of the process variables and increase sulfur yields.

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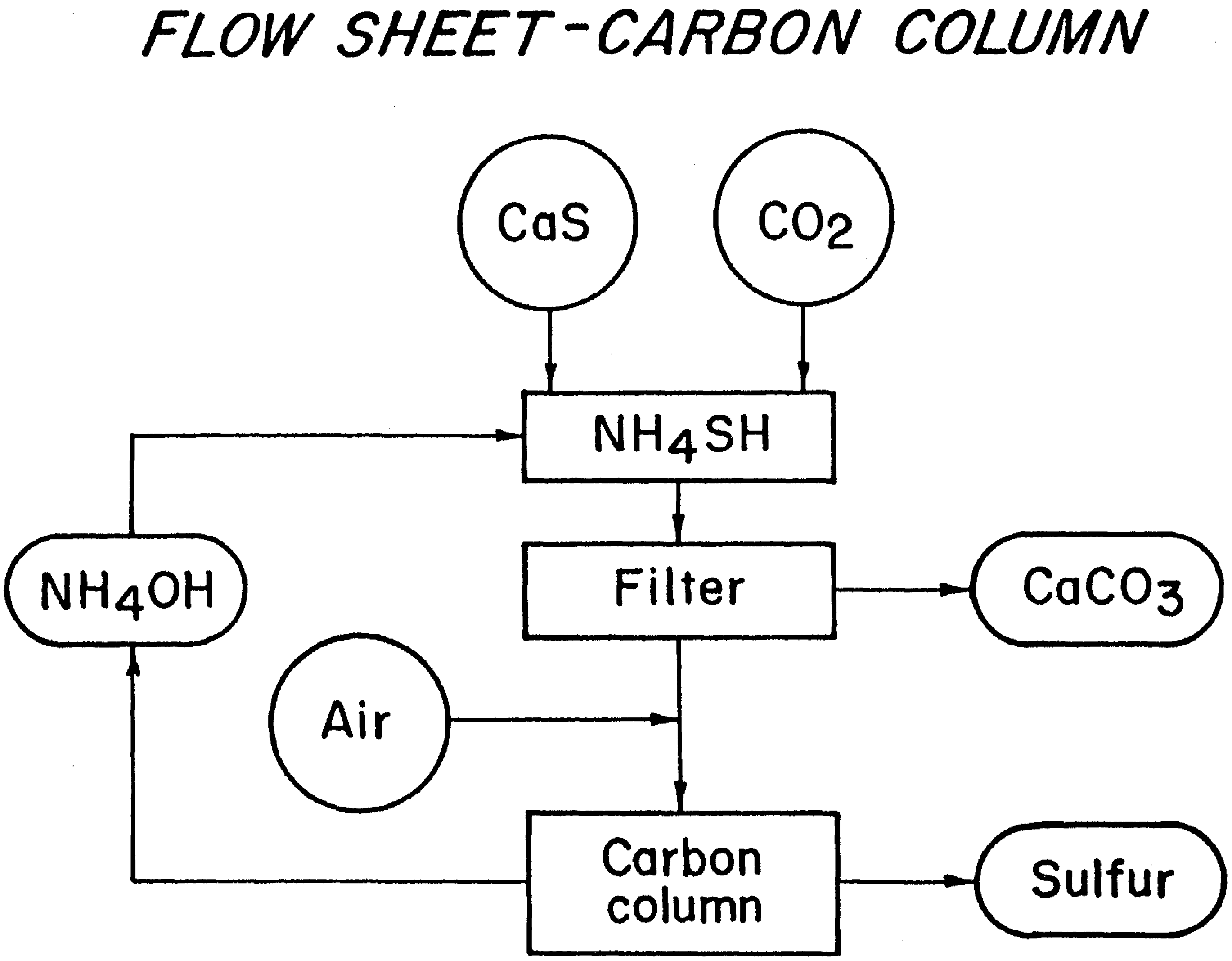

FIGURE 2. - Flow sheet of the improved sulfur from CaS process

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THE MICROBIOLOGICAL RECOVERY OF SULFUR FROM PHOSPHOGYPSUM

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ABSTRACT

The extraction of phosphate ores with sulfuric acid in fertiliser production generates phosphogypsum as a byproduct. Recovery of elemental sulfur from the phosphogypsum is desirable since it is used to manufacture sulfuric acid. The increasing cost of elemental sulfur has re-awakened interest in biotechnological methods for converting gypsum wastes into elemental sulfur. Processes based on natural systems that form elemental sulfur, for example some shallow lakes in Libya, look promising and deserve further investigation, The systems entail sulfate reduction to sulfide by sulfate-reducing bacteria, followed by anaerobic sulfide oxidation to elemental sulfur by photosynthetic bacteria. The process is not entirely solar-powered and will require an organic addition but this could be provided by growing photosynthetic biomass; in Florida the Water Hyacinth is a good candidate. The entire process would then be driven by solar energy. A contribution from genetic engineering might improve the efficiency of the system by transferring genes for anoxic sulfide oxidation to elemental sulfur to a sulfate-reducing bacterium.

INTRODUCTION

Phosphate ores are mined in Central Florida and extracted with sulfuric acid to generate phosphoric acid for the manufacture of phosphate fertilizers. The wet acid extraction process consumes, on a weight basis, about one part of 93% sulfuric acid to produce one part of phosphorus pentoxide with five parts of phosphogypsum as a byproduct.

$$3Ca_{10}(PO_4)_6F_2 + 30H_2SO_4 + SiO_2.58H_2O$$
$$= 30CaSO_4.2H_2O + 18H_3PO_4 + H_2SiF_6$$

Two problems associated with fertilizer production are the increasing costs for elemental sulfur, which is used to make sulfuric acid, and the accumulation of phosphogypsum as a byproduct. There are dumps containing over 400 million tons of phosphogypsum in Central Florida and approximately 30 million tons are added each year. Research is in progress, supported by the Florida Institute of Phosphate Research (FIPR), to examine construction uses for phosphogypsum and also the feasibility of reconverting it into elemental sulfur. Predictions of an eventual shortage of elemental sulfur (20) are being borne out by recent price increases and projections (2,12,14). There is now an economic impetus in developing processes for the recycling of sulfate, as gypsum or phosphogypsum, into elemental sulfur. This paper examines some aspects of microbiological methods for the conversion of phosphogypsum into elemental sulfur.

INTERCONVERSIONS OF INORGANIC SULFUR SPECIES

Figure 1 summarizes the principal biological interconversions of sulfate, sulfide and elemental sulfur. ‘Elemental sulfur is oxidised either aerobically or anaerobically to sulfate. Sulfate, however, cannot be reduced directly to elemental sulfur but must first be completely reduced to sulfide which is then partially re-oxidised, aerobically or anaerobically, to yield elemental sulfur.

SULFATE REDUCTION

Sulfate reduction to sulfide proceeds in Nature by both geothermal and biochemical mechanisms. At mid-oceanic ridges seawater, which contains 28 mM sulfate, is heated to temperatures in excess of 300°C

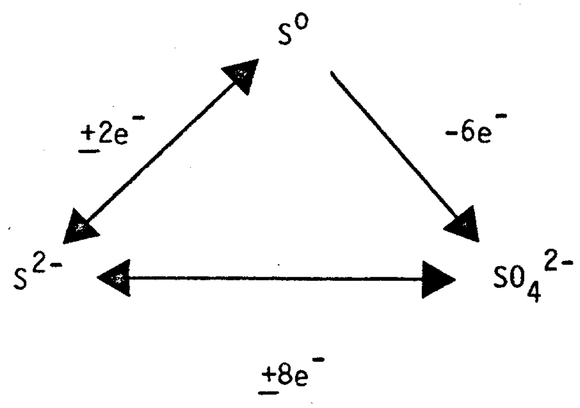

FIGURE 1. Biological Interconversions of Sulfate, Sulfide and Elemental Sulfur.

and the sulfate is reduced to hydrogen sulfide by geochemical reactions (15). Hydrogen sulfide and a variety of insoluble sulfides issue from the hydrothermal vents at the mid-oceanic ridges; the reduced sulfur compounds provide the basis of bacterial-based food chains in dark abyssal regions. Biochemical mechanisms for sulfate reduction are divisible into assimilatory and dissimilatory processes. Assimilatory sulfate reduction is performed, either aerobically or anaerobically, by plants and microorganisms and is essential for the biogenesis of reduced organic sulfur compounds, such as the amino acids cysteine and methionine. A specialised group of anaerobic bacteria, the sulfate-reducers, tarry out dissimilatory sulfate-reduction that provides their metabolic energy. Sulfate-reducers are important for the degradation of organic matter in anoxic environments that contain sulfate. It has been estimated that in coastal environments about equal amounts of organic matter are mineralised by the activities of aerobic and sulfate-reducing bacteria (16).

Until recent years only sulfate-reducers with narrow oxidative capabilities had been isolated. Species of *Desulfovibrio* and *Desulfotomaculum* which attacked mainly C3 and C4 compounds with incomplete oxidation; lactate, for example, was oxidised to acetate. The limited substrate specificity and incomplete oxidation of organics by such isolates was not in accord with the data on the quantitative importance of sulfate-reducers in anoxic sediments. This paradox was resolved by the studies of Widdel and Pfennig in Germany, who described several novel genera and species of sulfate-reducers (19). The sulfate-reducers are broadly divisible into two physiological groups, depending on whether or not they completely oxidise organics to CO_2 and water. Collectively the sulfate-reducers metabolise a wide variety of organic molecules including short to long chain fatty acids, aromatics and glucose (Table I).

TABLE I

Substrates for Sulfate-Reducing Bacteria

A. Incomplete Oxidation

Desulfovibrio desulfuricans, vulgaris, gigas, salexigens, africanus, baculatus, thermophilus	Lactate, pyruvate, malate choline. Some ferment these substrates; some grow on formate or glucose + sulfate
Desulfotomaculum nigrificans, orientis ruminis, antarticum	Lactate or pyruvate. Some ferment pyruvate; some grow on formate or glucose + sulfate
Desulfovibrio sapovorans	Fatty acids (C4-18)
Desulfobulbus propionicus	C3 substrates, ethanol, or H_2 + acetate
Thermodesulfobacterium commune	Up to 85° on lactate, pyruvate or H_2, ferments pyruvate

B. Complete Oxidation

Desulfovibrio baarsii	Fatty acids (C1-18)
Desulfotomaculum acetoxidans	Acetate, butyrate, valerate
Desulfobacter postgatei	Acetate
Desulfococus multivorans	Fatty acids (C1-14), aromatics
Desulfosarcina variabilis	Fatty acids (C1-14), aromatics, H_2
Desulfonema limicola,	Fatty acids (C1-14)
magnum	Fatty acids (C1-10), aromatics

BIOLOGICAL OXIDATION OF SULFIDE TO ELEMENTAL SULFUR

Sulfide is oxidised to elemental sulfur either aerobically or anaerobically by bacteria. Aerobic metabolism is confined to nonphotosynthetic organisms, whereas photosynthetic bacteria are principally responsible for the anaerobic conversion. Table II lists some of the organisms involved in the transformation. Elemental sulfur accumulates either inside or outside the bacterial cells and, when the supply of sulfide is depleted, it is usually further oxidised to sulfate. The elemental sulfur may thus be viewed as an energy reserve that is consumed during times of sulfide deprivation. The energetic value of hydrogen sulfide is such that free-living and symbiotic microorganisms benefit by capturing and oxidising it. Hydrogen sulfide has recently been recognised as an important source of energy for a variety of ecosystems (14,15).

TABLE II

Bacterial Oxidation of Sulfide to Sulfur

Aerobic - Nonphotosynthetic (Chemolithotrophs)	
Thiobacillus, Thiomicrospira	Extracellular S^{o} granules
Beggiatoa, Thiothrix	Intracellular S^{o} granules
Anaerobic - Photosynthetic (Photolithotrophs)	
Chromatium (purple)	Intracellular S^{o} granules
Chlorobium (green)	Extracellular S^{o} granules
Ectothiorhodospira (purple)	
Oscillatoria (blue-green)	

NATURAL FORMATION OF ELEMENTAL SULFUR

Biological sulfate-reduction was responsible for the formation of massive deposits of elemental sulfur on Earth (23). The biological production of elemental sulfur continues and also its deposition. Butlin and Postgate (3) described several shallow lakes in Egypt and Libya in which the bacterial production of elemental sulfur was occurring. They examined Lake Ain-ez-Zauia in detail and some of its characteristics are summarised in Table III. The lake was fed by spring waters that contained about 2% NaCl and were saturated with $CaSO_4$ (the waters issued forth through gypsum deposits). The water column was anoxic and contained significant levels of hydrogen sulfide. Gelatinous masses of green and black material overlaid with red material were also present in the waters and sediment. Butlin and Postgate isolated sulfate-reducing and photosynthetic bacteria from the gelatinous masses; both green, *Chlorobium* sp., and red, *Chromatium* sp., photosynthetic bacteria were secured in pure culture. Elemental sulfur constituted about 50% of the dry weight of the lake sediments and the natives harvested the elemental sulfur during the dry season.

TABLE III

Some Characteristics of Lake Ain-ez-Zauia (Libya)

Waters	Saturated $CaSO_4$ + 2% NaCl
	Temperature 30-32°C
	Maximum depth about 3 m
	Surface area about 5000 m^2
	Collodial sulfur
	H_2S - surface 15-20 mg/l (about 0.5 mM)
	- bottom 108 mg/l (about 3 mM)
Sediment	50% S^o (dry wt) to about 15 cm deep
Bacteria	Sulfate-reducers
	Chlorobium
	Chromatium

BIOTECHNOLOGICAL PRODUCTION OF ELEMENTAL SULFUR

Butlin and Postgate carried out laboratory experiments in which "artificial lakes" were established using crude cultures of sulfate-reducers and gelatinous masses derived from Lake Ain-ez-Zauia. The inorganic composition of the "artificial lake" resembled that of the natural system but the laboratory system received periodic additions of lactate and hydrogen sulfide and was kept at pH 7.5. The "artificial lake" developed gelatinous masses similar to those in the natural lake and elemental sulfur was deposited in the culture vessel. Experiments were also performed with pure cultures of Chlorobium sp. and Chromatium sp. isolated from the Libyan lake and a previously isolated strain of Desulfovibrio desulfuricans. The results suggested that cocultures of the sulfate-reducer and a photosynthetic bacterium could generate elemental sulfur from sulfate without the addition of organic compounds. The system for sulfur production appeared to be driven entirely by solar energy. It seems unlikely that this is possible based on the following stoichiometry:

$$SO_4^{2-} + 8[H] + H^+ = HS^- + 4H_2O$$

$$HS^- + H^+ = S^o + 2[H]$$

$$\text{SUM} \quad SO_4^{2-} + 6[H] + 2H^+ = S^o + 4H_2O$$

Or, alternatively including the oxidation of organic matter (general formula CH_2O) by the sulfate-reducer and CO_2 fixation by the photosynthetic bacterium:

$$2SO_4^{2-} + 4CH_2O + 2H^+ = 2HS^- + 4CO_2 + 4H_2O$$

$$2HS^- + CO_2 + 2H^+ = 2S^o + CH_2O + H_2O$$

$$\text{SUM} \quad 2SO_4^{2-} + 3CH_2O + 4H^+ = 2S^o + 5H_2O + 3CO_2$$

CO_2 fixation linked to photosynthetic sulfide oxidation can only provide one quarter of the organic matter required to drive sulfate-reduction.

A biotechnological process for the conversion of phosphogypsum to elemental sulfur based on the anoxic system of photosynthetic bacteria and sulfate-reducers would thus require an input of organic matter. The additional organic material could be supplied by two methods either the use of waste organic matter or via aerobic photosynthesis. An abundant waste which is rich in organic matter is raw sewage and this was used in a British project just after World War II to drive the reduction of gypsum to sulfide by Desulfovibrio desulfuricans (4,5). The project was scaled up to a pilot plant stage but, in the prevailing economic conditions, the process was not deemed worth further development. In Florida another organic waste that might be considered is that generated by the Citrus Industry.

CO_2 fixation by photosynthetic sulfur bacteria, such as Chlorobium and Chromatium, is limited by the availability of sulfide. Aerobic photosynthesis catalysed by green plants, algae and cyanobacteria uses H_2O as the reductant for CO_2 fixation:

$$CO_2 + 2H_2O = CH_2O + O_2 + H_2O$$

Aerobic photosynthesis generates oxygen (oxygenic), and CO_2 fixation or the generation of organic matter, is limited by light energy rather than the electron donor water which, unlike hydrogen sulfide, is usually in plentiful supply. Some cyanobacteria, Oscillatoria species, can carry out either oxygenic photosynthesis or, in the presence of hydrogen sulfide, anoxygenic photosynthesis (11). In a lake or lagoon system similar to that in Lake Ain-Zauia these organisms might fix CO_2 with H_2O as the electron donor at the surface but lower down in the anoxic region they would fix CO_2 in the same manner as Chlorobium or Chromatium.

Aerobic photosynthesis could also be exploited as a mechanism for providing cheap organic matter for biological sulfate-reduction by growing biomass. Several photosynthetic organisms are currently grown for biomass for example the cyanobacterium Spirulina, the water fern Azolla and the Water Hyacinth. Spirulina is a filamentous cyanobacterium, and therefore relatively easy to harvest from lagoons, that is grown in lagoon systems near Mexico City as a a source of protein (21). The water fern Azolla contains a symbiotic N_2-fixing cyanobacterium, Anabaena azollae, and the plant is cultivated as a green manure in Asia (10). The ideal candidate for biomass production in Florida is probably the Water Hyacinth which is currently being studied as a potential biomass source for methanogenesis. The Water Hyacinth could be grown in aerobic ponds adjacent to anoxic, sulfur-producing ponds near Bartow in Central Florida. Sulfate-reduction might be more efficiently and rapidly carried out in closed reactor systems; even so the Water Hyacinth would be most cheaply grown in open ponds or lagoons. Conversion of the hydrogen sulfide to elemental sulfur would occur in a separate reactor which might be catalysed either chemically (18) or biochemically (6,7,8). A single stage reactor may ultimately be developed if the genes for sulfide oxidation to elemental sulfur can be cloned and transferred to a sulfate-reducer, thereby increasing the efficiency of the process for sulfate conversion to elemental sulfur by packaging the required enzymes in a single organism.

Little has been done on genetic systems in sulfate-reducing bacteria but a start has been made (17,25). Genes coding for selected enzymes in Desulfovibrio vulgaris have been cloned and used to transform Echerichia coli to the expression of the enzymic activity. Thus genes in a sulfate-reducer can be manipulated and studied with cloning systems for E. coli. Genetic systems have been elaborated for thiobacilli (1,13) and photosynthetic bacteria (9,22). Genes for sulfide oxidation could be cloned and used to transform a sulfate-reducer to the characteristic of elemental sulfur production from sulfide. A simpler approach also worth pursuing is the possibility that sulfate-reducers which accumulate elemental sulfur, rather than sulfide, exist in some environments. In habitats where hydrogen sulfide persists and is not detoxified by escape, or reaction with metals, an ability to convert sulfide to elemental sulfur might have survival value. The possibility can be tested by elective culture techniques using inocula from suitable environments.

CONCLUSIONS

The rising cost of elemental sulfur has increased the attractiveness of biotechnological approaches for recovering elemental sulfur from phosphogypsum. Methods based on natural systems that employ sulfate-reducing and photosynthetic bacteria look extremely promising. The processes will require supplementary organic matter and, aside from, sewage which has esthetic and possibly health problems, the cheapest source in Florida is probably the Water Hyacinth. Genetic engineering will allow the development of more energetically efficient systems; specifically the cloning and transfer of genes responsible for the oxidation for sulfide to elemental sulfur from chemo- or photolithotrophic bacteria to a sulfate reducer.

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CALCINATION OF PHOSPHOGYPSUM

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ABSTRACT

The objective of this investigation is to study the conversion of dihydrate phosphogypsum to the hemihydrate form by means of a combination of microwave and convection ovens. Parameters such as the temperature and the calcination period in both ovens types, are investigated. The compressive strength of 2x4 in. (50.8x101 mm) cylinders, made from calcined materials, is tested at 7 and 28 days.

INTRODUCTION

Phosphogypsum, the by-product of the phosphoric acid industry, consists of approximately 93% gypsum and 7% impurities. such as sand, phosphates, fluorides and organic constituens. Previous investigations [1,2] have shown that raw phosphogypsum, can be applied as a construction material in both building and road construction industries.

If part of the total amount of crystalline water contained in dihydrate gypsum ($CaSO_4.2H_2O$), is removed, the material will be converted into hemihydrate ($CaSO_4 1/2H_2O$), which is referred to as plaster of Paris in the construction industry and behaves as a binder in contact with free water.

The objective of this investigation was to study the possibility of the conversion of dihydrate phosphogypsum to the hemihydrate form. A calcination process, combining microwave and convection ovens, was proposed. The parameters of calcination, such as temperature and calcination period in both ovens, were monitored in order to optimize the process. Cylindrical specimens, 2 in. (50.8 mm) in diameter and 4 in. (101.6 mm) in height, were made from the calcined material and their compressive strength was tested at 7 and 28 days. It was proven that calcination of phosphogypsum by the combination of microwave and convection ovens is more effective than using each of the ovens separately.

EXPERIMENT PROCEDURE

The objective of the experiment is to determine the temperatures and the heating periods of both microwave and convection ovens because effectiveness of calcination depends on these parameters.

The microwave oven used for this investigation had a 1.2 cu ft (0.03 m^3) capacity and was manufactured for domestic use. The convection oven used during the experimental work had a capacity of 2.8 cu ft (0.07 m^3) and a temperature selection range up to 300°C with a sensitivety of ±2° c. Constant amounts of dihydrate phosphogypsum, weighing 6.5 lb (2.95 kg) with an initial free moisture content of 13 %, were used throughout this investigation.

Five different experiments were conducted described as follows:

(1) To determine the temperature of dihydrate phosphogypsum in the microwave oven, samples were heated in the oven for a period of five hours.

(2) To determine the optimum heating time in the microwave oven, specimens were first heated in the microwave oven for five different time periods ranging between 0.5 and 2.5 hours, and each sample was subsequently transferred to the convection oven to continue calcination up to total calcination of 5.5 hours. Each sample was weighted every 25 minutes to determine water loss and material temperature was also recorded.

(3) To determine the optimum temperature in the convection oven, specimens were calcined in the microwave oven for two hours and then each sample was transferred to the convection oven to continue calcination for additional 3 hours. The temperature in the convection oven was varied from 100°C to 240°C.

(4) To determine the calcination time of specimens in the microwave oven, specimens were heated in the microwave oven for two hours and were transferred to the convection oven to continue calcination. The time for samples in the convection oven was ranged from 3.5 to 10.5 hours while the temperature in the oven was kept at the optimum temperature of 150°C.

(5) Compressive strength of specimens, calcined 2 hours in the microwave oven and 3.5 hours in the convection oven at temperature of 150°C, were compared to that of specimens calcined

by using the microwave oven and the convection oven separately.

Cylinders for compression testing, 2 in. (50.8 mm) in diameter and 4 in. (101.6 mm) in height, were made from the calcined material. All specimens were cast with a water to gypsum ratio of 0.5 and were subjected to 30 seconds high-frequency vibration for proper consolidation. Specimens were cured under laboratory conditions at approximately a temperature of 75° F (24° C) and a relative humidity of 65 %. Unconfined compressive strength at both 7 and 28 days was tested. The criteria for evaluating the effect of the calcination were the rate of water loss and the compressive strength of the samples. When the calcination parameters, i.e. the temperature in the convection oven and heating times in both ovens, produced the the fastest rate of water loss and the highest compressive strength, they could be regarded as the optimum calcination parameters.

RESULTS AND ANALYSIS

Calcination of phosphogypsum can be defined as the process to remove part or the entire content of crystalline water contained in the dihydrate calcium sulfate by means of heat supply. A temperature between 120°C and 200°C is commonly required for conventional calcination, depending on the impurity content such as P_2O_5 in the phosphogypsum. A higher temperature tends to remove the total water content so that dihydrate is converted into anhydrate [4]. Figure 1 shows the material temperature in the microwave oven. From Figure 1 it can be noted that the temperature of material calcined in the microwave oven quickly raises after 2 hours. Figures 2 and 3 show the relationship between compressive strength and heating time in the microwave oven. Compressive strength of specimens increases as calcination period in the microwave oven increases and reaches to a maximum between 2 and 2.5 hours of heating in the microwave oven. Therefore, 2 hours heating time in the microwave oven is preferred under the given experimental condition.

Phosphogypsum was moved to the convection oven to continue calcination after heating in the microwave oven. The water loss and compressive strength are plotted as a function of temperature changes in the convection oven in Figures 4 and 5, respectively. It can be observed from these figures that a temperature of approximately 150°C yields the best strength results. When the temperature is higher than 150°C, the water loss is faster but a lower compressive strength occurs. In addition to temperature, time of heating in the convection oven was also investigated. Three samples were calcined in the convection oven for 3.5; 7 and 10.5 hours, respectively, after 2 hours heating in the microwave oven. Figures 6 and 7 present the relationships of water loss and compressive strength as a function of calcination time in the convection oven, respectively. As expected, both water loss and compressive strength are increased when calcination time in the convection oven is increased from 3.5 to 10.5 hours. However, improvement of compressive strength is only 12% while the increase in calcination time in the convection oven is 200 %. In other words, the energy consumed by increasing calcination time in the convection oven may be too high for the return in terms of compressive strength. The determination of calcination time in the convection oven obviously depends on economical considerations.

Results of calcination by using the microwave and the convection ovens separately were presented elsewhere [3]. Comparisons between three different calcination methods are given in Figures 8 and 9. Calcination by the microwave oven removes the water held in phosphogypsum quickly, but may induce a low compressive strength. On the contrary, calcination by the convection oven yields high compressive strength, provided that heating time is long. Calcination by a combination of the microwave and the convection ovens possesses the advantages of both techniques and therefore is effective.

CONCLUSIONS

A laboratory investigation shows that calcination of phosphogypsum by the combination of microwave and convection ovens is effective if the adequate calcination parameters are selected. One of the optimum calcination process in microwave oven is to maintain the material temperature between 100° C and 150°C for 2 hours heating. The temperature of the convection oven should be maintained at approximately 150° C during the calcination. The determination of calcination time in the convection oven depends on the choice between energy use and product compressive strength.

The compressive strength of dihydrate phosphogypsum calcined according to the techniques as described above can be considered equivalent to that of mineral plaster of Paris. Therefore, it is conceivable to use the by-product gypsum as a substitute for mineral gypsum in some of its applications in the construction industry.

ACKNOWLEDGEMENT

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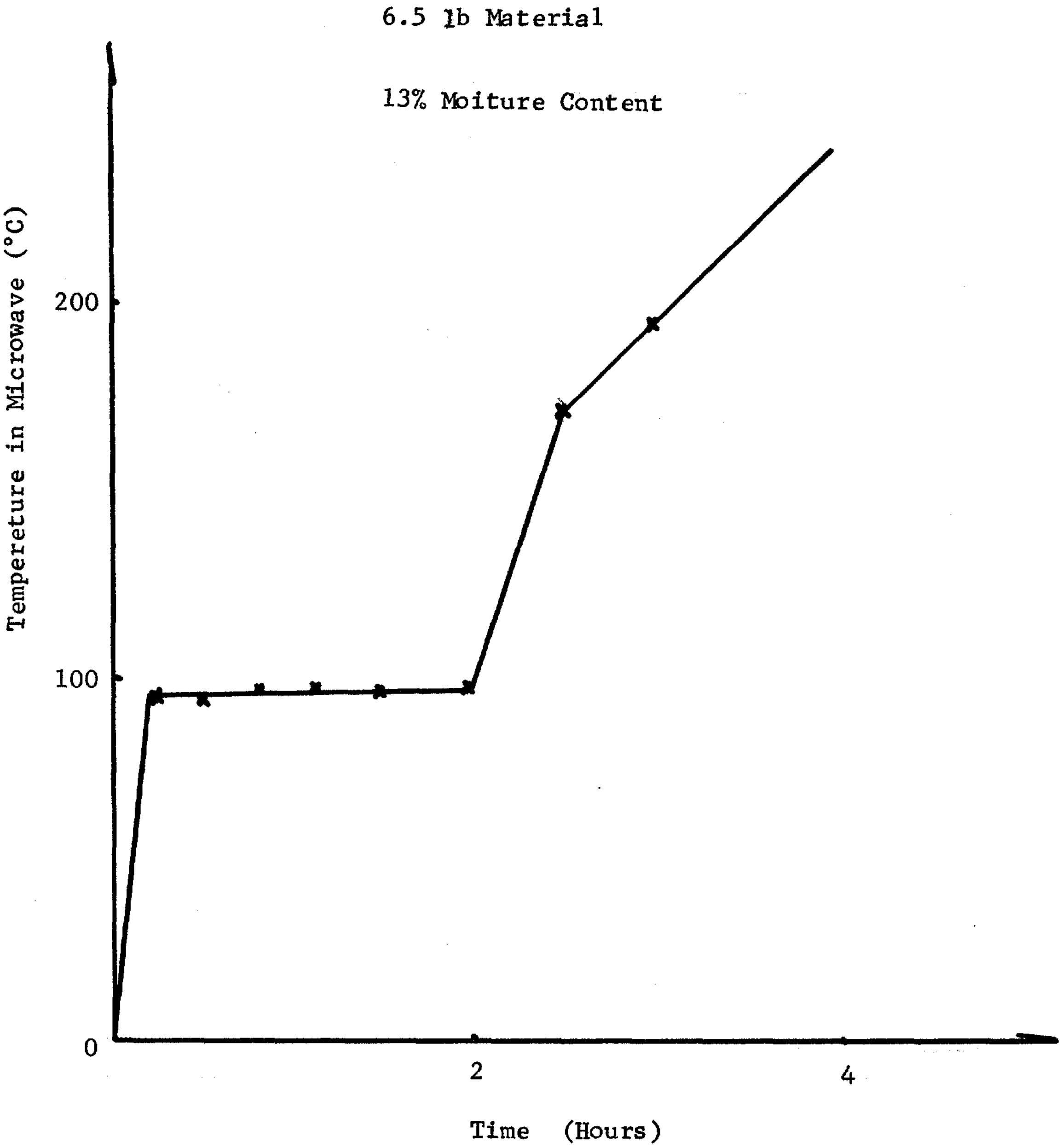

Fig.1 The Tempereture of Material vs. Time in Microwave

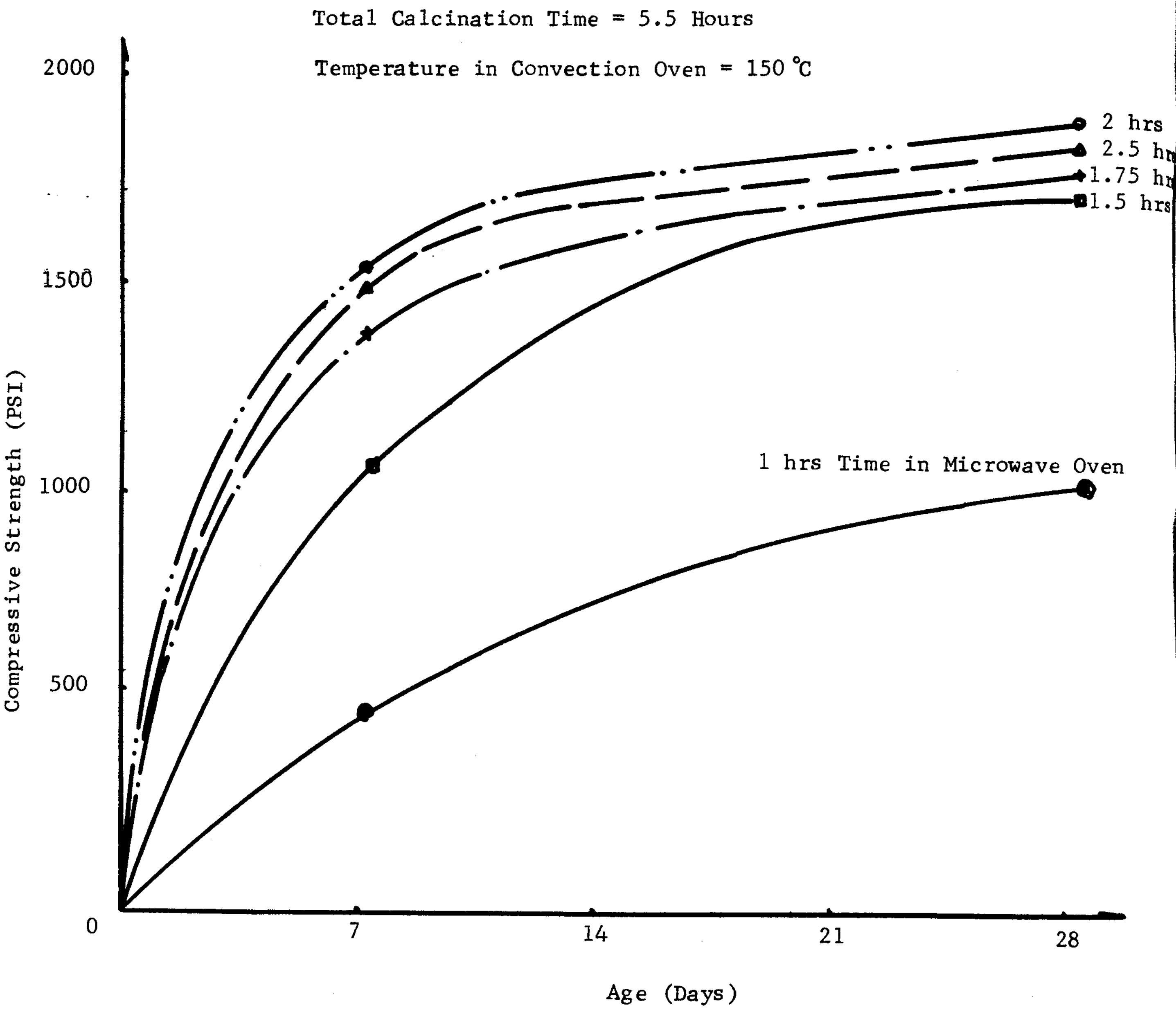

Fig.2 Compressive Strength vs. Specimen Age

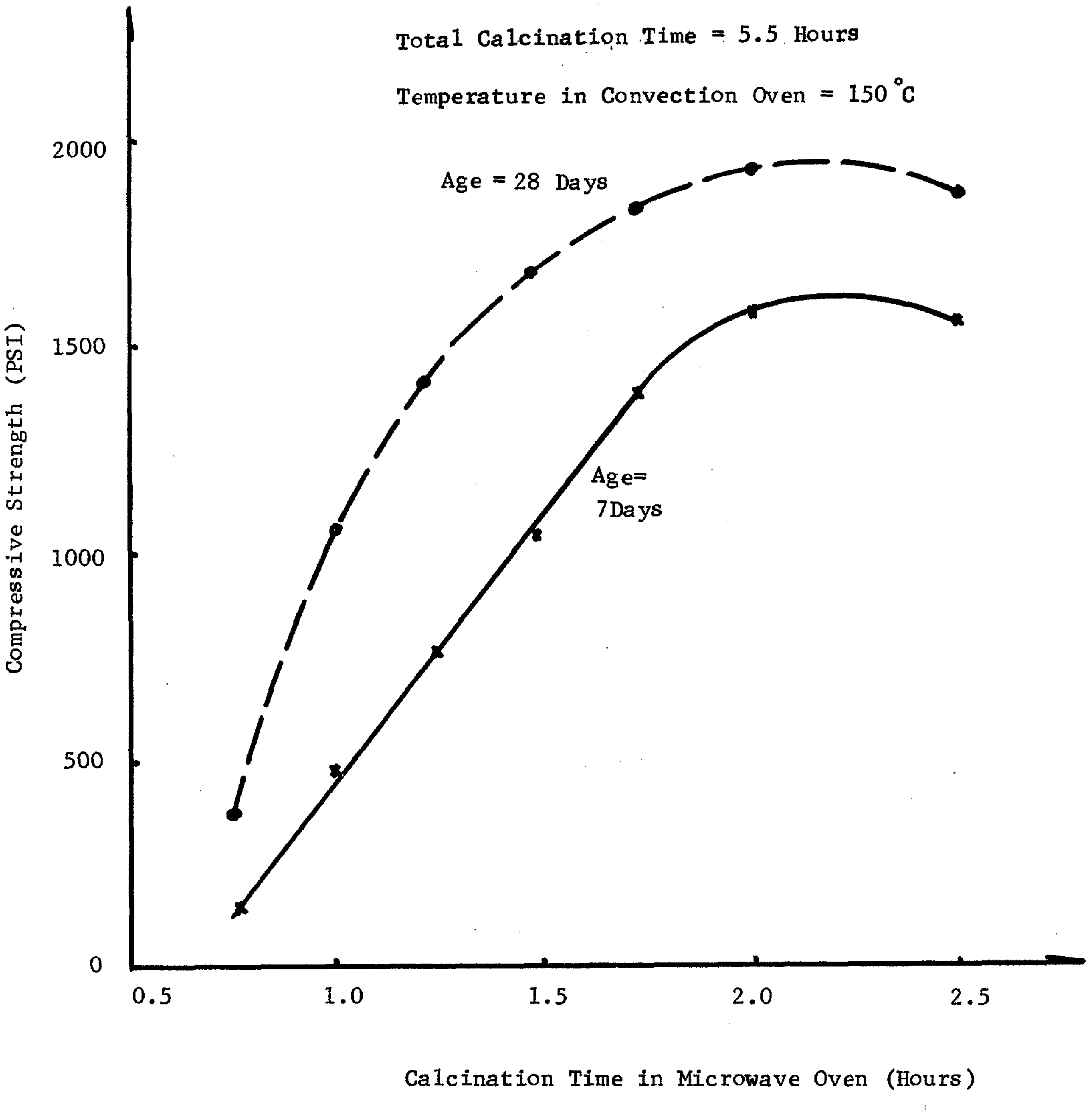

Fig. 3 Compressive Strength vs. Calcination Time in Microwave Oven for Specimens at Different Ages

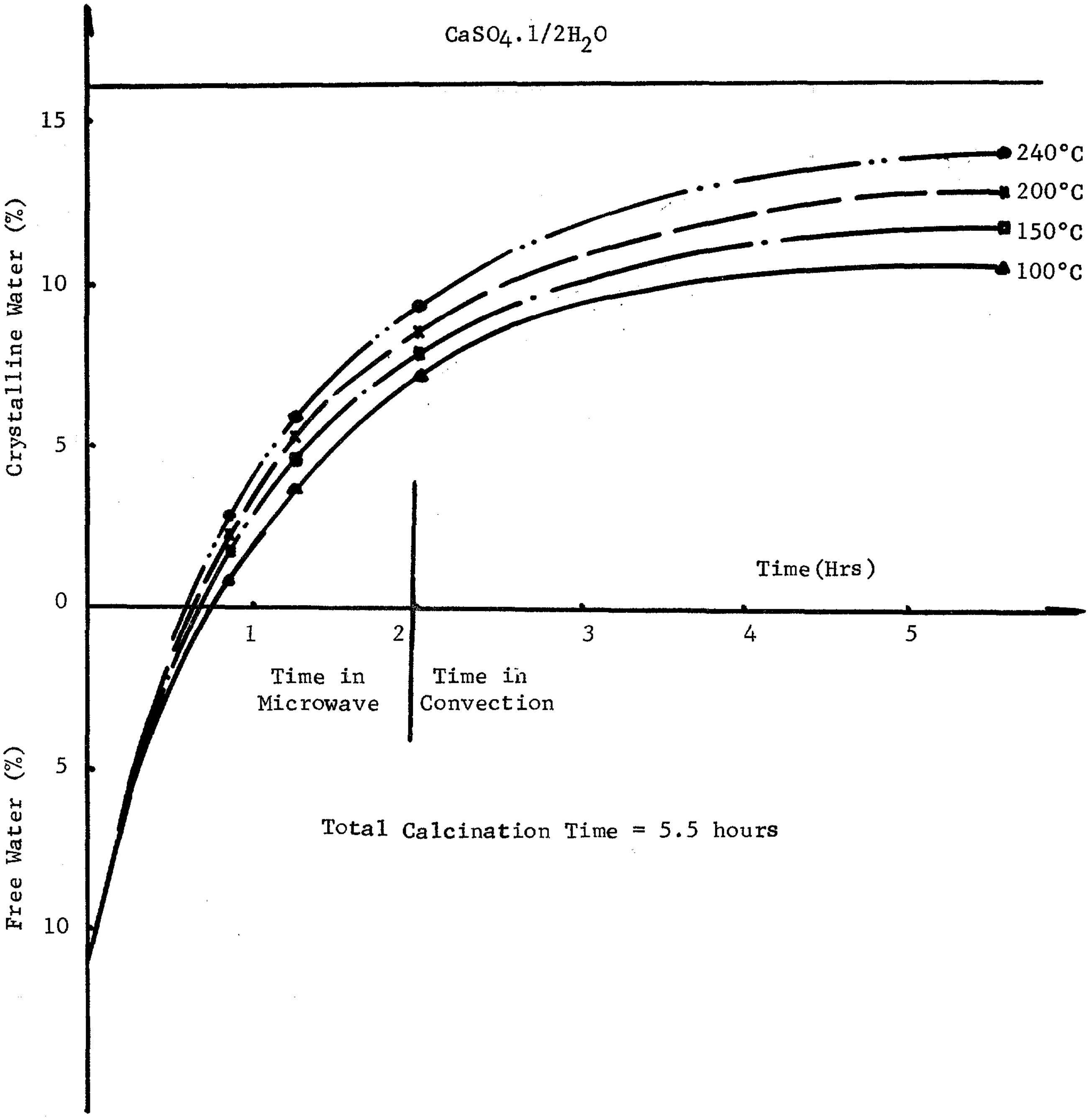

Fig.4 Water Loss vs. Calcination Period for Different Temperatures

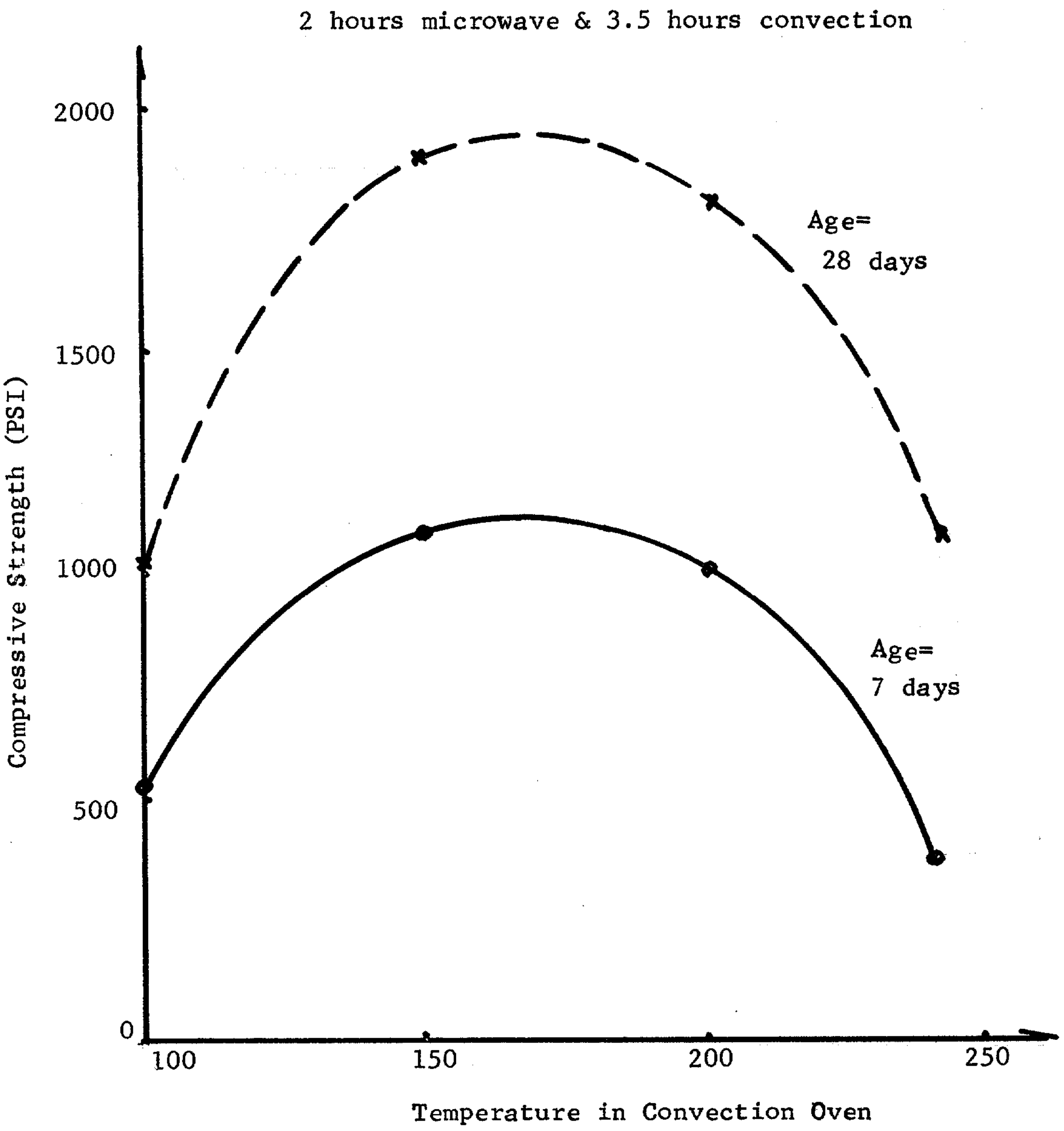

Fig.5 Compressive Strength vs. Temperature in Convection Oven for Different Specimen Ages

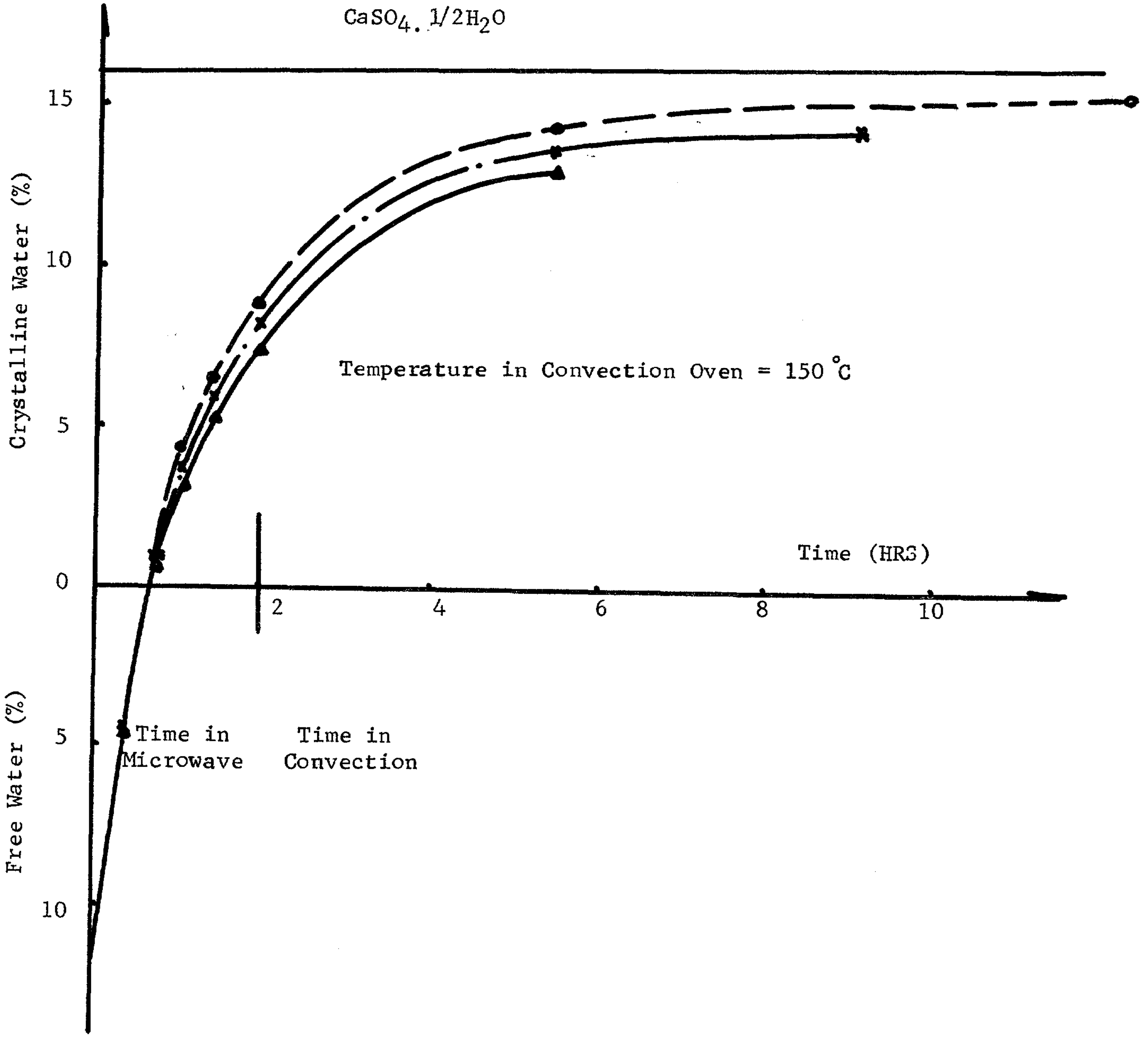

Fig.6 Water Loss vs. Calcination Period

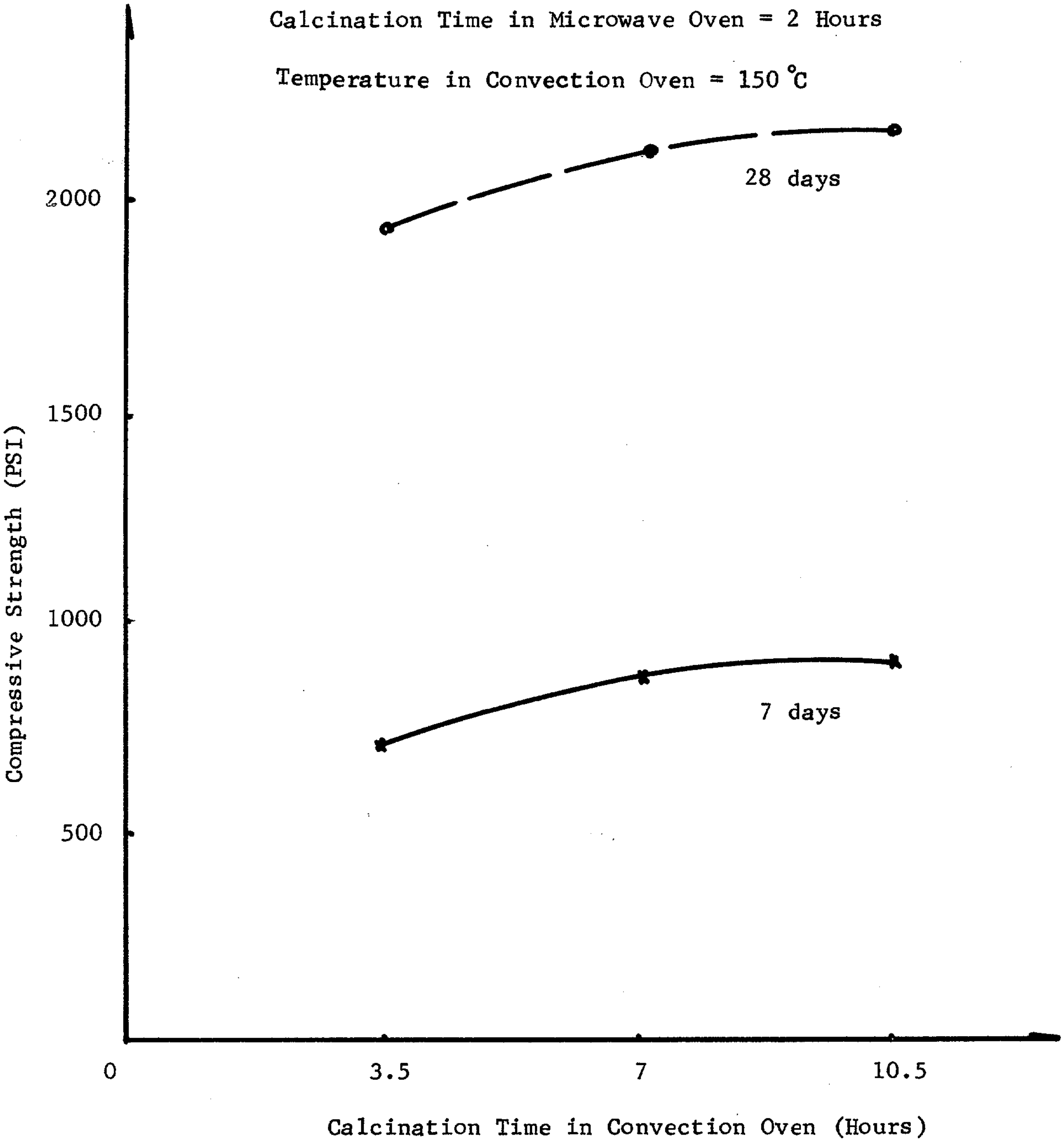

Fig.7 Compressive Strength vs. Calcination Time in Convection Oven

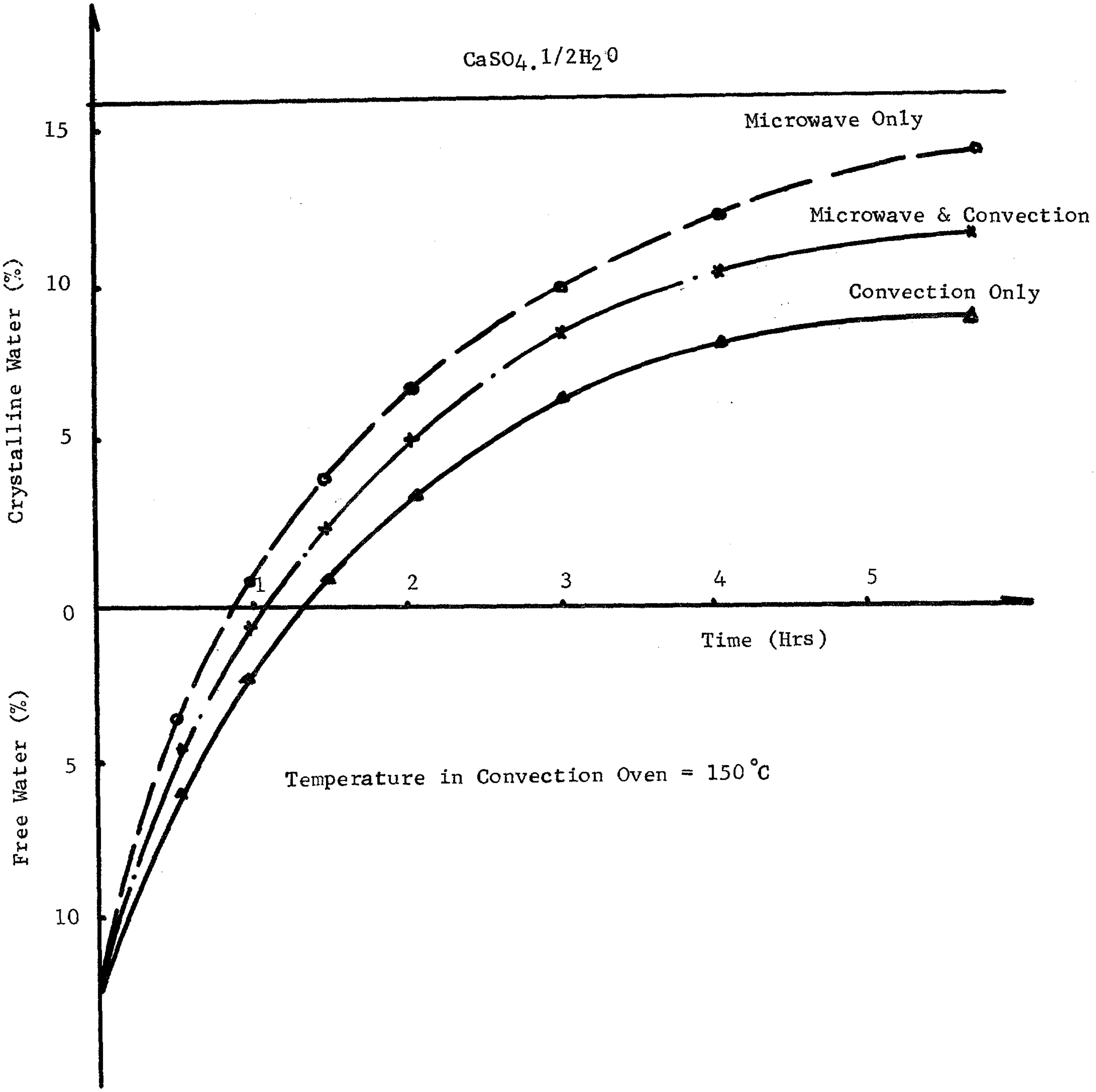

Fig. 8 Water Loss vs. Calcination Period

for Different Calcination Method

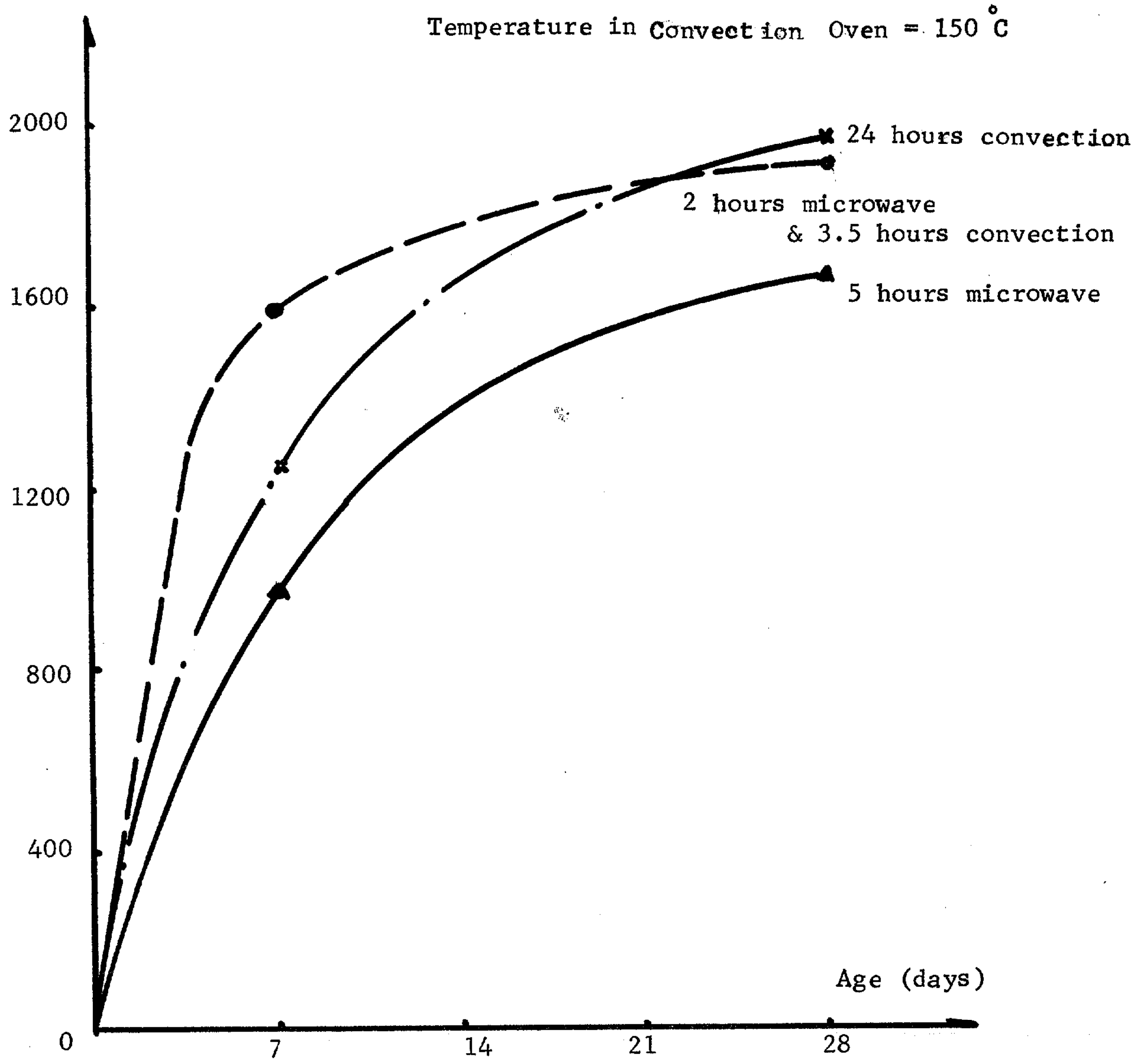

Fig.9 Compressive Strength vs. Age of Specimen for Different Calcination Methods

USE OF PHOSPHOGYPSUM AS AN AMENDMENT FOR HIGHLY WEATHERED SOILS

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ABSTRACT

Many highly weathered soils throughout the world have acid and/or hard subsoils and topsoils which have a tendency to crust formation as a result of their dispersive character. These properties often result in decreased crop productivity as a result of poor root proliferation in the subsoils and reduced water infiltration at the soil surface. Over the past 15 years a number of scientists have been investigating the possibility of utilizing gypsum as an ameliorant for these conditions. To date, there have been many substantial yield responses to gypsum throughout the world on highly weathered soils with a wide variety of crops. Generally, the yield responses have been shown to result from the amelioration of the subsoil acidity syndrome brought about by a reduction in exchangeable Al and its activity in the soil solution and an increase in the level of soluble Ca. The yield responses have been a result of improved utilization of water previously out of the reach of roots due to the inhospitable chemical conditions. In addition to improving the subsoil chemical environment, gypsum has been shown to bring about a reduction in the force required for roots to penetrate hard subsoil layers. At present this seems to be a consequence of the improved chemical conditions which allow roots to explore deeper. They, in turn, improve soil aggregation causing fractures which reduce soil strength. Although highly weathered soils are usually leached of cations such as Na, many soils still contain small quantities sufficient to predispose soil particles at the surface to dispersion which results in crust formation and reduced water infiltration. Addition of small quantities of gypsum at the soil surface counteracts this dispersive tendency as a result of the increased electrolyte concentration in the soil solution which promotes flocculation. As a result, crusting can be considerably reduced allowing free entry of water and better germination of crops.

INTRODUCTION

Crop production on soils with acid, infertile and/or hard subsoils is often severely curtailed because roots of many crop plants fail to penetrate and consequently suffer drought stress. Such problems in topsoils are readily solved by liming and tillage which cannot be used to ameliorate subsoils very readily because lime does not move down the profile of variable charge soils and deep tillage is usually prohibitively expensive. Soils with these characteristics are widespread throughout tropical and subtropical parts of the world and fall, mainly, into three soil Orders, namely, Oxisols, Ultisols and Alfisols which, when well managed, are highly productive. Many soils in these groups also have some poor physical attributes such as low infiltration rates, crusting and low hydraulic conductivities which can in certain circumstances reduce crop yields.

Poor root growth in such subsoils has been associated with Al toxicity and/or Ca deficiency sometimes in association with hard layers which increase resistance to root penetration. Roots are known to be unable to translocate Ca downwards which means that they will not grow into soil low in Ca. Very often soil low in Ca also contains high levels of soluble Al which, when taken up by the root, poisons many enzyme systems resulting in substantially reduced growth. Both Ca deficiency and/or Al toxicity result in reduced water uptake by the crop.

The rate of rainwater intake by field soils is a critical factor in soil management because runoff leads to excessive water loss and often to erosion. Many soils, particularly in the Southeastern United States, exhibit crusting under intense rainfall which results in low infiltration rates. The maintenance of adequate water uptake rates is dependent upon the stability of soil structural units and associated macropores at the soil surface. Gal et al. (13) have shown that crust formation with reduced infiltration involves clay dispersion forming a "washed-in" layer of very low permeability. This dispersion is dependent on soil pH, electrolyte concentration, Na content and raindrop energy. As little as 2-5% exchangeable Na can cause large decreases in infiltration when soil is wetted by high purity water (1). In addition, these levels of Na can reduce hydraulic conductivity of the soil and lead to increased effluent turbidity which further exacerbates the problem.

The solution to these problems lies in reducing the intensity of subsoil acidity and, at the same time, supplying Ca while reducing the hardness of subsoil layers. Increased electrolyte concentration at the soil surface would promote flocculation and possibly increase infiltration. Gypsum, being a sparingly soluble salt, is able to dissolve in the soil solution and move readily in the soil profile, an attribute not possessed by lime which, because it increases the charge on variable charge surfaces, results in the added Ca being held in place as an exchangeable cation. The extent to which gypsum can be used to bring about such amelioration in problem soils will now be reviewed.

GYPSUM AND SUBSOIL ACIDITY

The possibility that gypsum might be able to substitute for lime has been proposed and discussed for a long time (2, 3, 4, 11). The initial observation that gypsum could bring about amelioration of subsoil acidity was made by Sumner (31) who showed that surface applied gypsum leached down the profile and reduced exchangeable Al. Subsequently, Reeve and Sumner (26) studied the effect of gypsum movement, in laboratory soil columns composed of Oxisol profiles, on the exchangeable cations and showed that Ca readily moved down the profile causing a reduction in exchangeable Al. They also clearly demonstrated that lime did not move and caused no improvement in the chemical conditions in the subsoil. Reeve and Sumner (26) postulated that the reduction in exchangeable Al was due to a "self-liming" effect caused by the displacement of hydroxyls from alumino-iron hydrous oxide surfaces by ligand exchange with sulfate. The hydroxyls liberated would react with the Al causing its precipitation as aluminum hydroxide. In a greenhouse experiment, Reeve and Sumner (25) showed that *Sorghum sudanense* cv Trudan responded to gypsum applications which was associated with reduced levels of exchangeable Al. These results were corroborated by Kotze and Deist (16) working with an Ultisol under laboratory conditions who found that the leachate from columns of acid soil contained enhanced levels of Al when the soil had been treated with gypsum.

Pavan et al. (21) studied the effects of gypsum on coffee (Coffea arabica L.) growth in the greenhouse on acid Brazilian topsoils. They obtained significant yield responses to gypsum which markedly reduced the level of Al activity in the soil solution to which growth correlated the best. Although this investigation did not deal with subsoil acidity, it is relevant as they were the first to show the responses to gypsum were likely to be due to reduced Al activity in the soil solution. Subsequently Pavan et al. (22) in a leaching experiment in columns of an undisturbed Oxisol profile confirmed the findings of Reeve and Sumner (26) that surface applied gypsum is a far superior amendment for subsoil acidity than is similarly applied lime. They showed (Figure 1) that gypsum reduced and increased the levels of exchangeable Al and Ca throughout the profile, respectively, while soil pH and CEC were unaffected. The levels of Ca, Al, Mg and SO_4 were far higher in the leachates from the gypsum treated columns than from control or limed treatments.

The first report of subsoil amelioration in the field from surface applications of gypsum was made by Sumner (31) working on a South African Entisol soil. Using the same subsoil in the greenhouse, he showed that alfalfa (Medicago sativa L.) growth was enhanced as a result of reduced levels of exchangeable Al and increased levels of Ca brought about by leaching the soil with a saturated gypsum solution. Subsequently Richey et al. (27) showed that maize (Zea mays L.) rooted deeper in a Brazilian Oxisol as a result of subsoil amelioration from gypsum contained in single superphosphate. This yield response was associated with reduced Al and increased Ca in the subsoil.

Black and Cameron (5) working with a New Zealand Dystrochrept soil in the greenhouse, found that gypsum mixed into the topsoil did not increase B horizon root yields nor those of the associated tops of alfalfa even when the soil columns were leached with a volume of water equivalent to one winter season of rainfall in the field. However, their data showed that there was no difference in the Ca content of the B horizon with or without leaching when the gypsum was placed in the topsoil indicating that the amount of water applied to the columns was probably insufficient to bring about much subsoil amelioration.

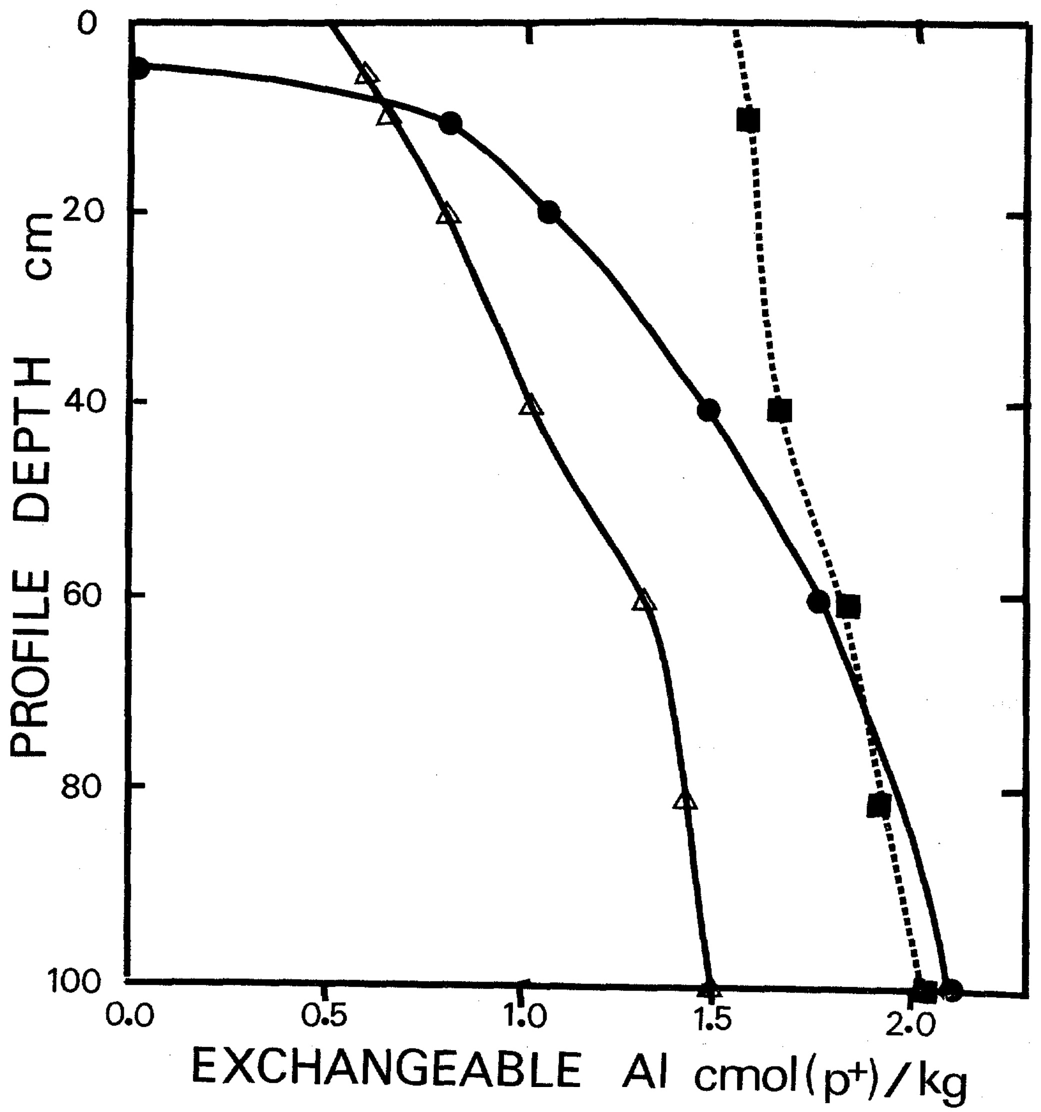


Figure 1. Profile distribution pattern of exchangeable Al as influenced by amendment treatment (■--■, control; ●--●, $CaCO_3$ treatment; △--△, $CaSO_4 \cdot 2H_2O$ treatment).

Chaves et al. (8) in Brazil working with Latosol Roxo and Dark Red Latosol soils containing 1.5 and 0.1 cmol (+) Al/kg respectively, obtained a yield response with coffee to calcium sulfate application which they attributed to the complexation of Al by the sulfate in the soil solution decreasing the toxic effect of the Al. Similar responses were not obtained with applications of calcium nitrate or chloride.

Oates and Caldwell (20) studied the effects of pure gypsum and two by-product materials, phosphogypsum and hydrofluorogypsum, on the acidity of a Fragiudalf subsoil and associated soybean growth. In a short leaching column (20 cm) experiment composed only of the subsoil material, they found that hydrofluorogypsum was more efficient in removing exchangeable Al from the column than was phosphogypsum which, in turn, was slightly better than the pure gypsum. They attributed the increased effectiveness of the by-product gypsums to the fluoride impurity. Data for plant heights and weights did not agree but generally there was a significant growth response to the by-product gypsums but not to the pure material when the soil had been leached after treatment. While not clearcut, the responses are likely to have been a result of reduced levels of exchangeable Al although it is possible that there may have been some response to the P impurity in the by-product materials particularly, as 3 to 10 times as much P was added with the gypsum as was originally applied to the soil.

Wright et al. (33) found that an application of 14.2 Mg gypsum/ha to a reconstituted soil profile of the Gilpin silt loam reduced exchangeable Al throughout a soil column in the laboratory but did not result in improved rooting of barley (Hordeum vulgare L.) or greater rooting depth. The lack of plant response in this experiment could be due to the relatively small quantities of water with which the soil columns were leached. Only 60 cm of water was added to a 55 cm column.

de Sousa and Richey (10) working with Oxisols in Brazil obtained yield responses to gypsum with soybeans (Glycine max Merr.) and maize in the field. These yield responses were particularly marked when drought conditions prevailed which resulted in both crops exhibiting deeper rooting on gypsum treatments (down to 1.4 m) which resulted in better water extraction from the soil profile. This amelioration of

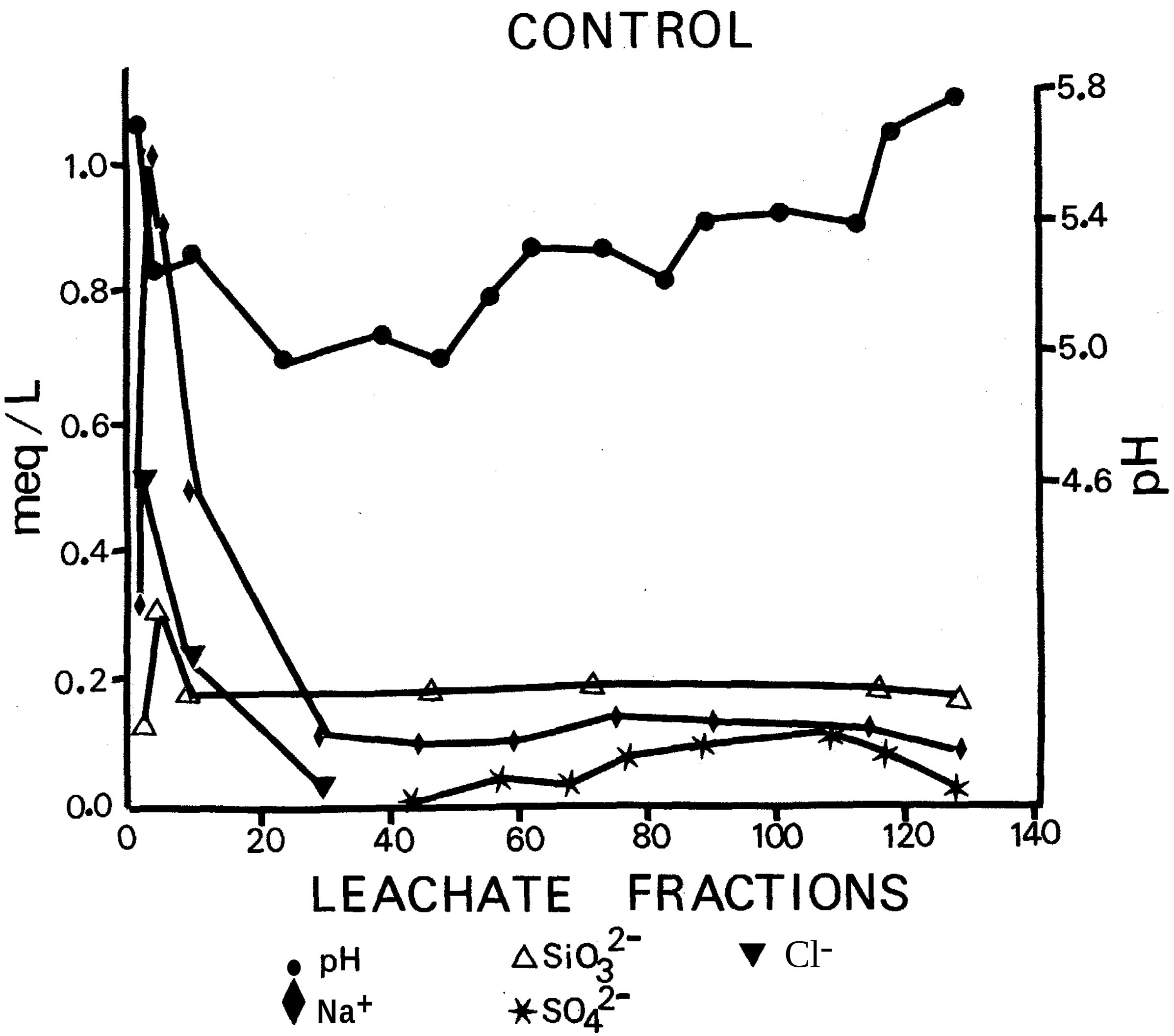


Figure 2(a). **Leachate composition from control column.**

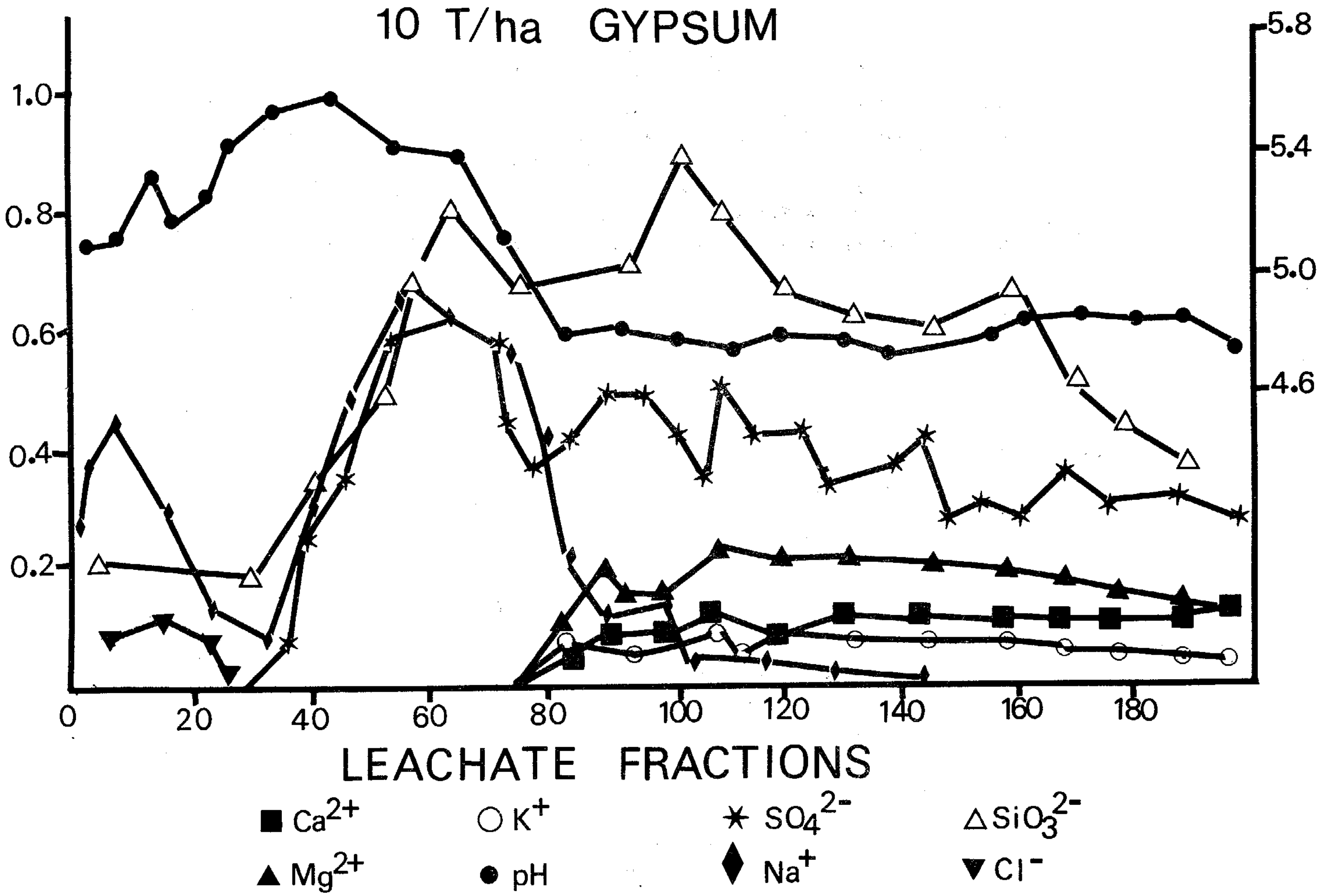


Figure 2(b). Leachate composition from gypsum column.

the subsoil acidity syndrome also resulted in improved extraction of N and other nutrients in the case of maize. In addition, soil pH increased slightly as a result of the gypsum treatments with a corresponding reduction in exchangeable Al and Al saturation while negative charge in the subsoil was also increased. They found substantial movement of K and Mg resulting from the application of large amounts of gypsum and stressed the importance of using dolomitic lime in the topsoil as originally recommended by Reeve and Sumner (26).

Lemus-Grob (17) studied the effect of phosphogypsum treatments on the movement of cations and anions in 1 meter long columns of a Georgia Ultisol in the laboratory. Composition of the leachate solutions are presented in Figure 2. His data indicate that only very small quantities of ions are removed from the control columns in contrast to the much larger concentrations coming out of the gypsum treatment. Initially, Na, Cl and Si dominate in the gypsum columns but when SO_4 appeared, only Na, SO_4 and Si continued to be removed until virtually all the Na had been removed whereupon low levels of Ca, Mg and K replaced the Na while substantial levels of SO_4 and Si continued to appear. From these data, it seems clear that gypsum enhances the level of Si in the soil solution. It is pertinent to note that no Al was removed from the columns.

Hammel, Sumner and Shahandeh (14) obtained significant soybean grain and corn silage yield responses to gypsum on a Georgia Ultisol (Table I). They compared surface applied gypsum with lime incorporated to 1 meter depth and found that gypsum was better than the control but not as good as the deep lime treatment. In the first year, no significant response to gypsum was obtained, despite a positive trend, because insufficient time had elapsed to allow for substantial movement down the profile. This supports the lack of response observed by Black and Cameron (5). Although gypsum had no significant effect on subsoil pH, exchangeable Ca and Al were increased and decreased, respectively, as illustrated in Figure 3. This amelioration resulted in deeper root penetration which was reflected in the water extraction patterns where plants growing on the gypsum treatment removed more water down the profile than in the control.

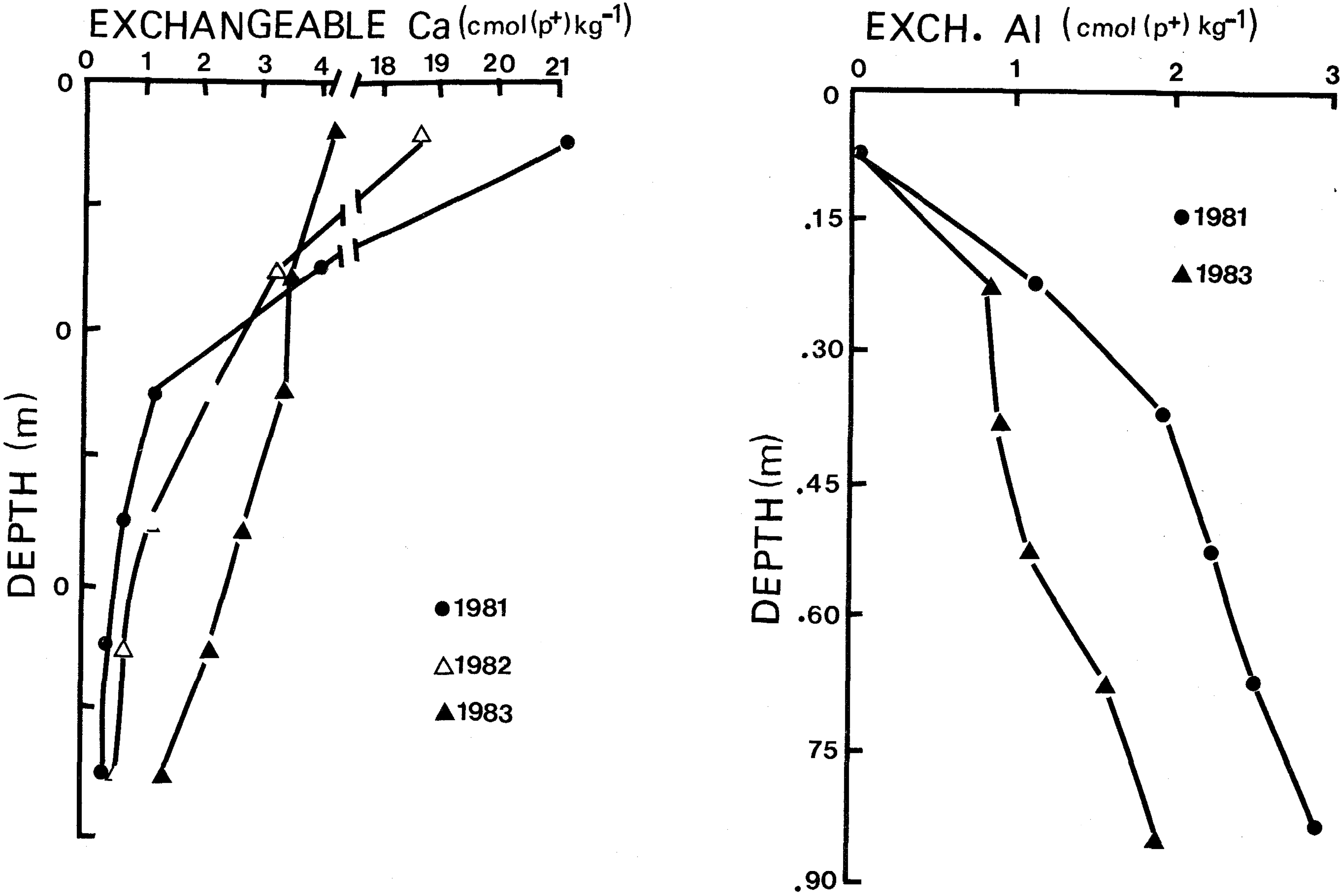


Figure 3. Effect of time on the levels of exchangeable Ca and Al in the profile of the gypsum treatment.

TABLE I

Effects of Surface Applied Gypsum and Deep Liming on Soybean and Corn Yields (14)

Treatment	Yields			
	Soybean			Corn
	1981	1982	Mean	1983
	Mg/ha			
Control	0.941	1.283	1.112	26.2
Gypsum	1.216	1.613	1.415	35.4
Deep Lime	1.761	2.007	1.884	41.0
LSD (0.05)	0.304	0.223	0.128	5.4

Farina et al. (12) working with maize in South Africa obtained significant yield responses to surface applied gypsum and found phospho- to be better than natural gypsum because of the growth promoting effect of the P impurity in the former. The gypsum treatment caused a reduction in exchangeable Al and Al saturation probably as a result of precipitation while Mg and K leached downward. Root development on the gypsum plots extended to 600 mm whereas on the control plots, roots were limited to the top 200 mm of soil.

Howeler (15) obtained substantial cassava (*Manihot esculenta*) yield response to gypsum in the highly weathered Llanos area of Colombia but unfortunately did not measure the resultant changes in soil properties.

Buyeye et al. (6), working with a South African Ultisol in the greenhouse in reconstituted profiles, found that phosphogypsum significantly increased maize shoot yields and considerably improved root penetration in the subsoil. Gypsum treatments reduced the level of exchangeable acidity and increased exchangeable Ca and extractable sulfate in the upper subsoil. Increased levels of Ca in topsoils treated with gypsum resulted in the downward movement of significant amounts of Mg which could be overcome by the use of dolomitic lime in the topsoil. Soil solution composition of the upper subsoil (Table II) showed that increasing gypsum levels increased pH and ionic strength but had little effect on the activity of Al which remained constant while the activity of Ca increased. They suggested that, while part of the response observed could possibly be ascribed to the detoxification of Al by the formation of an $AlSO_4^+$ ion pair, the term $1/2\log(a_{Ca})-1/3\log(a_{Al})$ where a_{Ca} and a_{Al} refer to the calculated activities of Ca^{++} and Al^{+++} in the soil solution, might prove to be a more meaningful index by which the rooting performance of plants growing in an acid soil can be anticipated.

TABLE II

Effect of Gypsum on Subsoil Solution Composition of an Ultisol (6)

Gypsum Mg/ha	pH	Ionic Strength	Activity Al	 Ca	$1/2\log(a_{Ca})-1/3\log(a_{Al})$
		----------mmol/L----------			
0	4.1	8.3	0.014	0.47	-0.05
3	4.5	19.4	0.011	1.20	0.18
6	4.5	35.6	0.012	1.80	0.27
9	4.4	45.0	0.013	2.40	0.32
12	4.5	46.8	0.011	2.20	0.32

Sumner et al. (32) studied the effect of surface applied gypsum and deep liming on the growth of alfalfa on a Georgia Ultisol over a four-year period (Table III).

TABLE III

Response of Alfalfa to Surface Applied Gypsum and Deep Liming

Subsoil Treatment	Alfalfa yield 1982	 1983	 1984	 1985
	----------Mg/ha----------			
Control	9.73	7.18	10.67	3.29
Gypsum	10.36	9.08	13.59	7.16
Deep lime	12.81	11.13	15.71	7.92
LSD (0.05)	2.18	0.72	1.24	1.07

In the first year, no significant yield response to gypsum was obtained probably because insufficient time had elapsed for downward movement to have taken place. In subsequent years, highly significant yield responses of more than 30% above control were recorded. In the 1985 season, yield on the gypsum treatment was no different to that of the

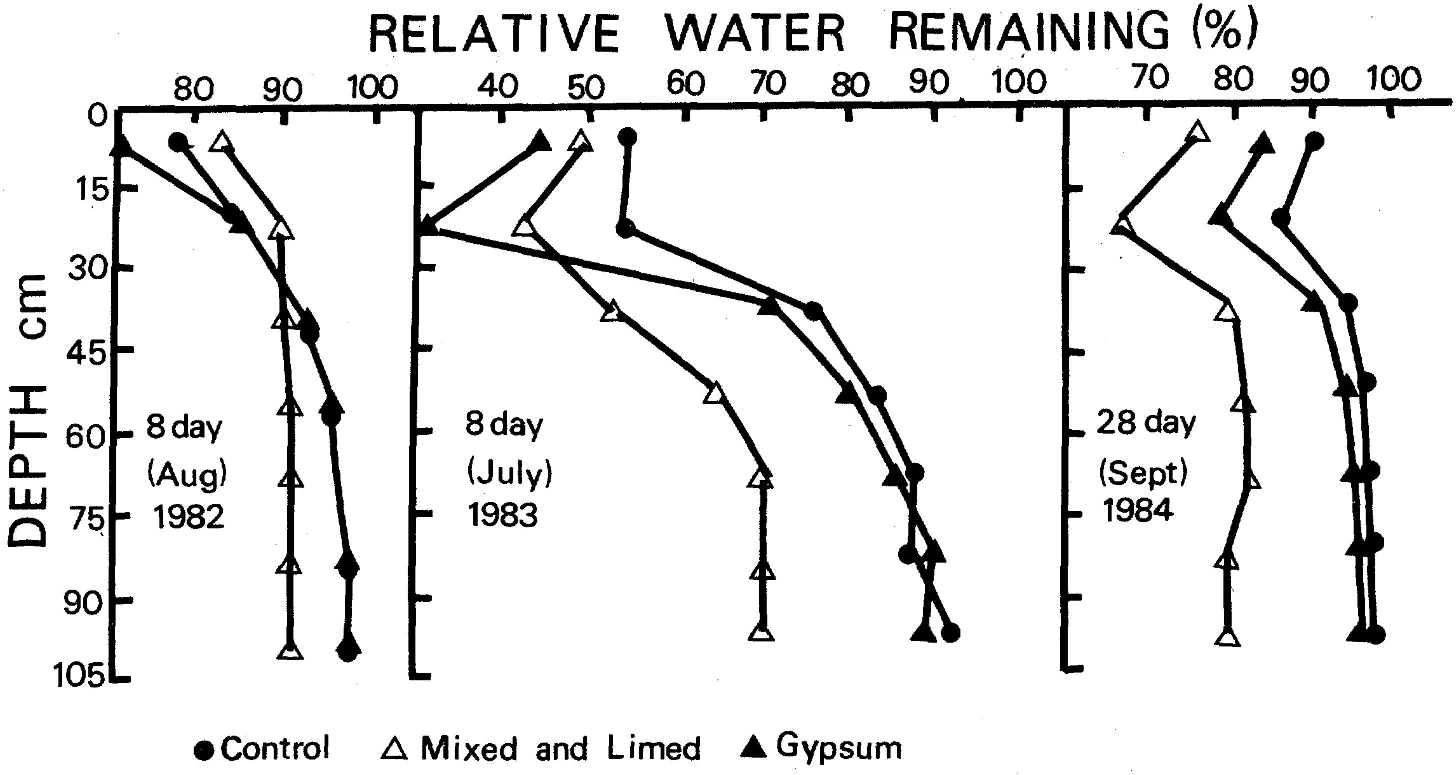


Figure 4. Water extraction patterns during drydown periods.

deep liming treatment indicating that given sufficient time, gypsum can emulate lime as originally claimed by Albrecht (3). These yield responses to gypsum are attributable to the improved chemical conditions in the soil profile as illustrated in Table IV. The gypsum treatment has lowered the levels of exchangeable and soil solution Al while substantially increasing those of Ca without changing the soil pH value appreciably. There is also evidence that the gypsum has caused K to begin moving down the profile. The combined effect of Al and Ca can readily be seen in the drastic change in the value of $1/2\log(a_{Ca})-1/3\log(a_{Al})$ in the gypsum treatment. This agrees with the views of Buyeye et al. (6).

TABLE IV

Effect of Surface Applied Gypsum on Soil Chemical Properties (32)

Soil depth	Soil	Exchangeable cations			Soil solution activities		
	PH	Al	Ca	K	Al	Ca	$1/2\log(a_{Ca})-$
cm	N KC1	-----cmol (+)/kg-----			-----µM-----		$1/3\log(a_{Al})$
		Control					
o-15	5.03	0.00	3.75	0.28	0.0	1120	--
15-30	4.40	1.40	0.95	0.16	5.4	330	0.015
30-45	4.10	1.52	0.75	0.07	5.6	320	-0.003
45-60	4.06	1.70	0.60	0.05	5.2	210	-0.078
60-75	4.12	1.86	0.30	0.04	4.9	140	-0.157
75-90	4.10	1.98	0.35	0.03	4.6	60	-0.332
90-105	4.08	2.24	0.24	0.02	5.4	40	-0.443
		Gypsum					
o-15	5.34	0.00	6.70	0.15	0.0	3630	--
15-30	4.18	0.82	2.65	0.13	2.2	2460	0.581
30-45	4.04	0.94	2.05	0.09	2.9	1470	0.429
45-60	3.96	1.18	1.60	0.06	3.7	1100	0.331
60-75	4.02	1.36	1.21	0.05	4.3	750	0.226
75-90	4.01	1.69	0.95	0.04	4.0	590	0.185
90-105	4.00	1.73	0.78	0.03	4.0	420	0.111

Sumner et al. (32) showed that the improved growth was due to deeper rooting of the alfalfa on the gypsum treatment as illustrated by the water removal patterns in Figure 4. This is further corroborated by the data of Carter et al. (7) who studied the rooting distribution in the same experiment 4 years after planting (Table V). With the exception of the plow layer (0-15 cm), there are more roots down the profile in the gypsum than control treatments which is in total agreement with the water removal patterns.

Pavan and Volkweiss (23) have discussed possible explanations for the beneficial effects of gypsum applied to Oxisols. They come to the conclusion that Al^{+++} is detoxified to some extent as a result of the formation of the ion pair $AlSO_4^+$ which they claim is less absorbed by roots. In addition, raised levels of Ca^{++} promote root growth.

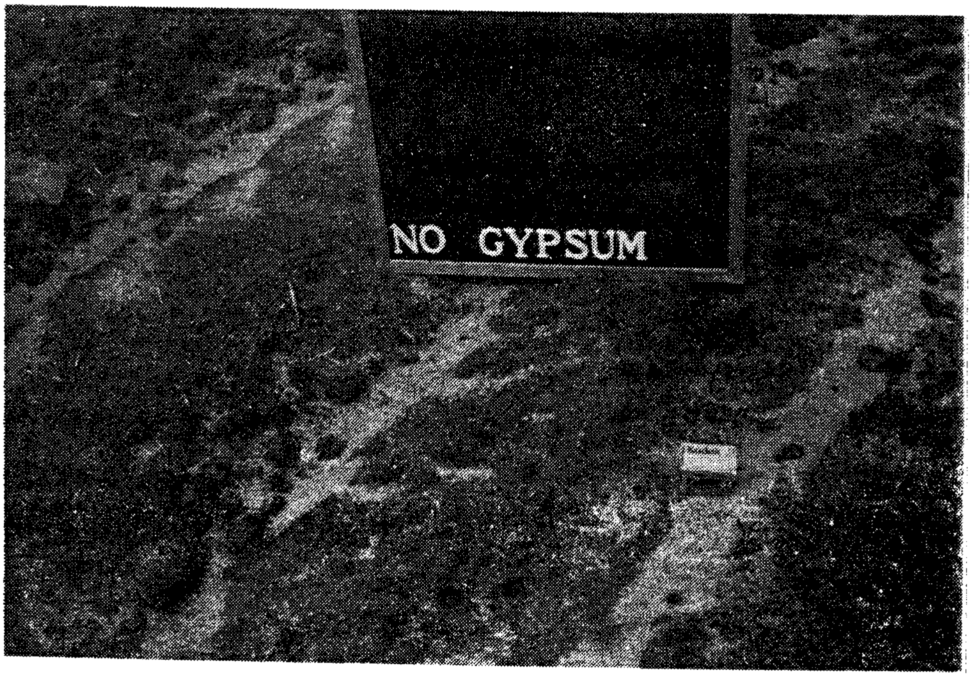
TABLE V

Effect of Gypsum on Root Mass in a Georgia Ultisol (7)

Depth	Control			Gypsum		
	Tap root	Fibrous root	Total root	Tap root	Fibrous root	Total root
cm	----------g/m^3----------			----------g/m^3----------		
0-15	64.2	60.0	124.2	70.7	44.2	114.9
15-30	5.6	8.5	14.1	19.6	10.5	30.1
30-45	0.7	5.4	6.1	8.5	9.9	18.4
45-60	0.5	3.8	4.3	4.1	6.0	10.1
60-75	0.1	1.4	1.5	1.6	4.0	5.6
75-90	0.0	0.2	0.2	2.3	6.3	8.6
90-105	0.0	0.1	0.1	0.0	0.3	0.3
Total	71.1	79.4	150.5	106.8	81.2	188.0
Total (15-105)	6.9	19.4	26.3	36.1	37.0	73.1

GYPSUM AND WATER INFILTRATION

Miller (18) has shown that, in soils of the Southeast, the ravages of clay dispersion can be readily seen at the soil surface where, after a rainfall event, a pronounced crust forms with "naked" sand grains washed free of fine particles scattered over the crust (Figure 5). This observation is somewhat surprising in that these soils are acid and non-sodic unlike soils usually exhibiting this phenomenon.



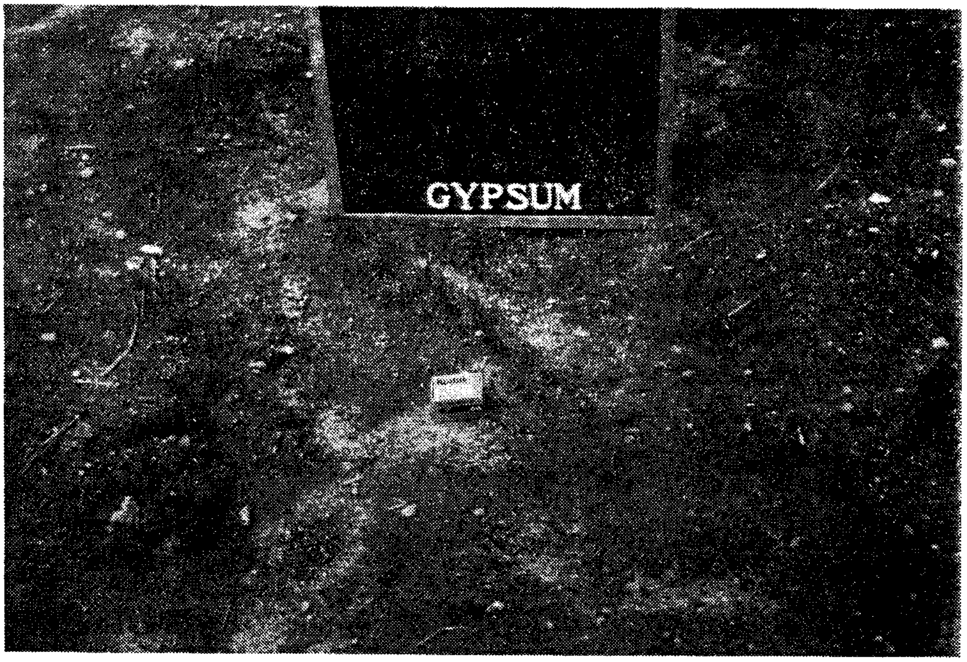


Figure 5. Effect of gypsum in preventing clay dispersion at soil surface.

Shaking such soils in distilled water for 36 hours caused significant clay dispersion (Table VI) and kinetic studies showed that much of the clay was dispersed after only 2 to 10 minutes (19). The exchangeable Na percentage (ESP) levels in these soils are low but lie within the range of 3-10% considered to have an effect on dispersion (Table VI). In addition, the considerable amounts of exchangeable K and Mg, as well as the low ionic strength, promote dispersion reflecting the inability of these highly weathered soils to maintain sufficient salt in solution to keep the soil flocculated. The infiltration and soil loss data, collected using soil in runoff trays under a rainfall simulator, showed a wide range of values with final infiltration rates being less than 1 cm/hr. They showed that dispersible clay was highly correlated with both infiltration and soil loss and the degree of dependence for the latter was $r^2 = 0.78^{**}$. Thus clay dispersion exerts a controlling influence over the processes of water intake and soil loss and any treatment causing a reduction in dispersion should lead to improved water entry into the soil.

TABLE VI

Soil Dispersion and Some Related Values for 15 Selected Georgia Soils (19)

Parameter	Units	Range	Mean
Dispersion	% of clay	6-60	38
Sum of cations	cM(+)/kg	1.4 -10.8	4.7
Sodium	% of sum	1-9	3
Potassium	% of sum	3-20	11
Magnesium	% of sum	8-29	16
Calcium	% of sum	53-82	69
Ionic strength	mM	1.8-7.5	3.7
Infiltration	cm/hr	0.1-4.9	2.0
Soil loss	Mg/ha	0.59-3.5	2.3

In field experiments on a steeply sloping Ultisol, Miller (18) showed that low rates (2 Mg/ha) of surface applied phosphogypsum significantly increased and maintained infiltration (Table VII) over the control during a rainstorm event but the effect on soil loss failed to reach significance. On a highly weathered Israeli soil, Agassi et al. (1) found that phosphogypsum applications (5 Mg/ha) resulted in final infiltration rates 2-4 times higher than the control even after 20 cm of simulated rainfall.

TABLE VII

Effect of Phosphogypsum (2 Mg/ha) on Infiltration and Soil Loss from a Cecil Sandy Loam Soil in a 10% Slope (18)

	Soil loss			Infiltration		
Run	Control	Gypsum	Sign.	Control	Gypsum	Sign.
	-------kg/ha------			---% of rainfall---		
Dry	365	412	ns	46	71	**
Wet	288	302	ns	28	43	*

GYPSUM AND HYDRAULIC CONDUCTIVITY

Many studies (28, 30) have demonstrated the well known decrease in hydraulic conductivity that occurs as the Na adsorption ratio (SAR) (closely related to ESP and numerically almost equal) increases and total salt content decreases. Chiang et al. (9) studied the effects of varying SAR and electrolyte concentration at 3 pH levels on the relative hydraulic conductivity of a Georgia Ultisol (Table VIII). Increasing levels of Na in the soil resulted in a pronounced reduction in relative hydraulic conductivity but increased electrolyte concentration provides a means of counteracting this deleterious effect. The effect of soil pH was minimal but increasing pH favored reduced conductivity. Percolate turbidity as a measure of clay dispersion was lowest at high salt and low pH and SAR and vice versa. This relationship strongly suggests that ionic strength, SAR and pH control hydraulic conductivity by regulating clay dispersion which results in the blockage of water transmission pores.

The potential of gypsum to improve water movement in soil lies in its relatively high saturation electrolyte concentration (28 mM) and the ability of Ca to replace Na on the exchange sites. Chiang et al. (9) studied the effect of gypsum on the hydraulic conductivity of a

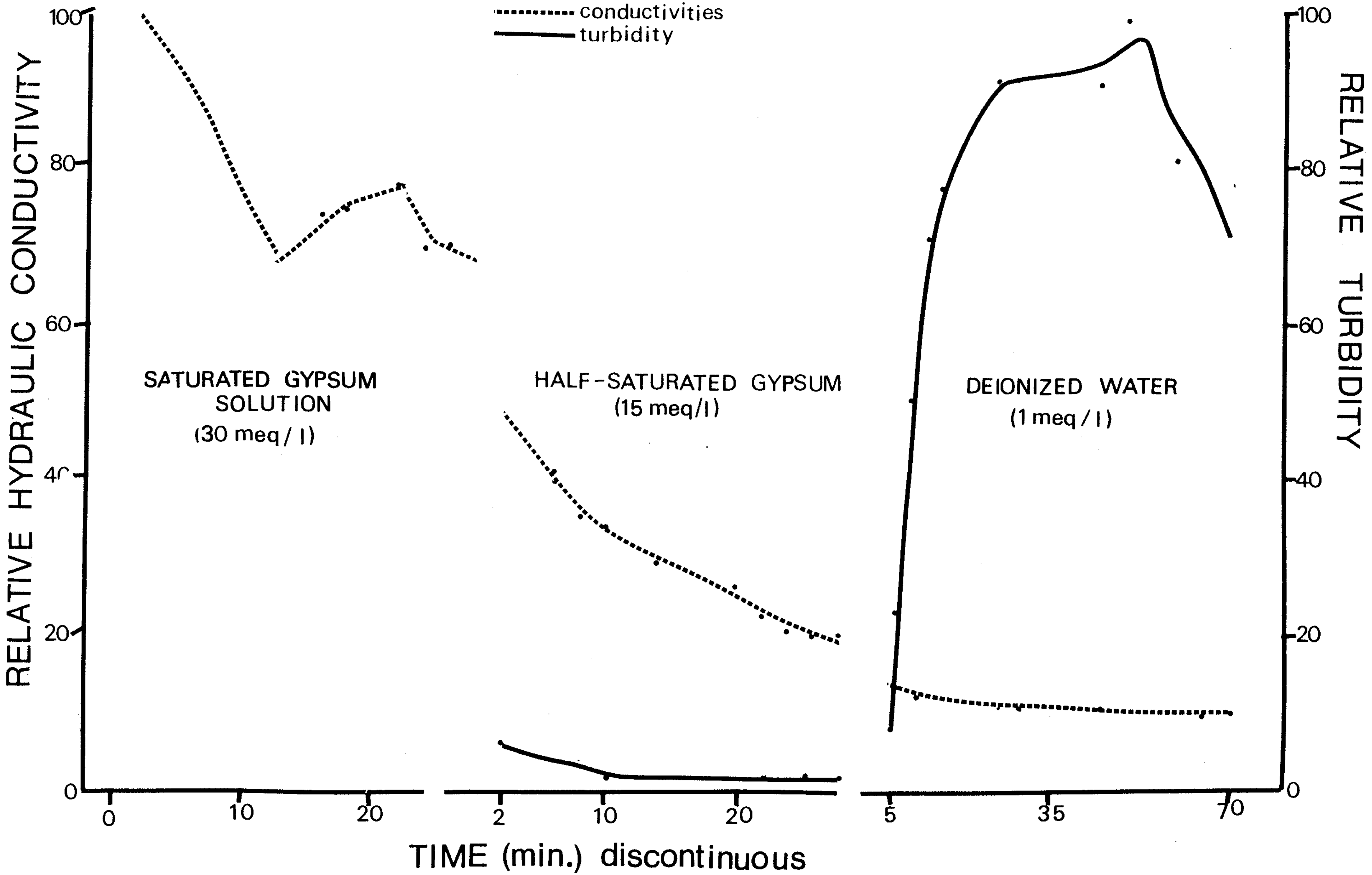


Figure 6. Effect of gypsum on hydraulic conductivity and clay dispersion.

Georgia Ultisol (Figure 6). The saturated gypsum solution maintains a relative conductivity of 80% with no turbidity detectable in the percolate while with the half saturated gypsum solution, hydraulic conductivity declines to 20-30% with a slight increase in turbidity. With deionized water, conductivity declines to less than 15% with a large increase in turbidity that signals the onset of clay dispersion and pore blockage. In a field situation, this mobile clay would move downward and accumulate in pore constrictions with disastrous results.

TABLE VIII

Relative Hydraulic Conductivities* of a Cecil Sandy Loam Topsoil as a Function of pH, SAR and Electrolyte Concentration (9)

SAR	Total electrolyte concentration (mM(+)/L)		
	0	2	5
		pH 4.5	
0	63	78	95
1	55	79	92
5	48	65	75
15	24	51	66
		pH 5.4	
0	48	90	97
1	38	78	85
5	30	39	56
15	31	40	50
		pH 7.9	
0	44	78	90
1	30	48	68
5	50	54	63
15	23	29	43

*Relative hydraulic conductivities calculated as conductivity after 10 pore volumes of indicated solution divided by initial conductivity in 0.2M.

GYPSUM AND HARDPANS

Subsoils in the Southeast frequently have layers of high bulk

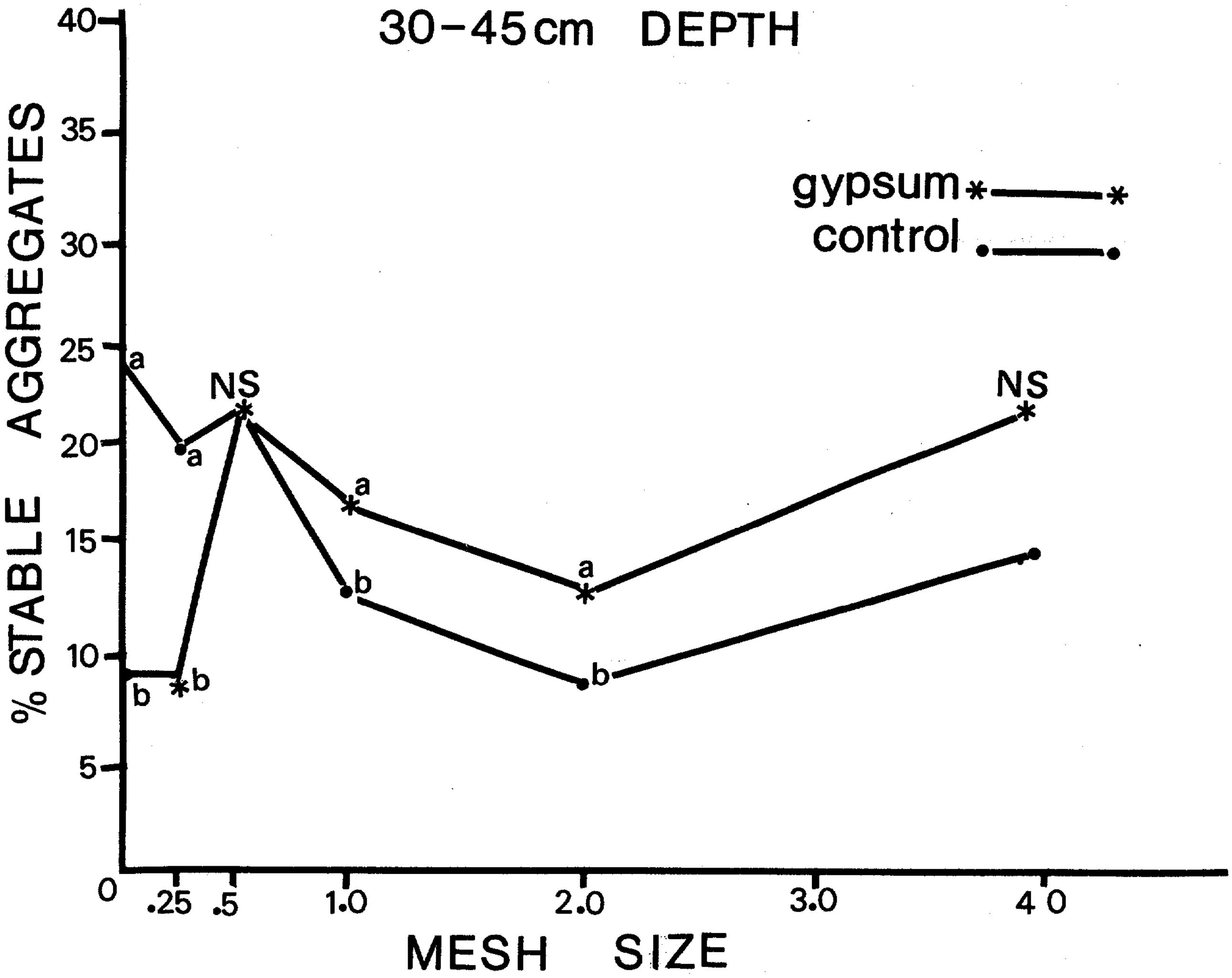


Figure 7. Effect of gypsum on subsoil aggregation.

density and soil strength which severely inhibit root penetration. Radcliffe et al. (24) have studied the effect of gypsum, initially applied on the surface of a Georgia Ultisol, on the subsoil mechanical impedance to roots measured using a tractor mounted hydraulically driven, computerized cone penetrometer. Their results (Figure 7) clearly show the beneficial effects that gypsum has had on subsoil penetrability, five years after the treatment was applied. It is not clear whether the reduction in mechanical impedance is a direct effect of the gypsum or whether it results from improved root activity made possible by the improved chemical conditions in this subsoil (Table IV). Dry root mass below 15 cm in the gypsum treatment is about three times that of the control (Table V). That roots are probably causing some of the improvement in subsoil physical condition is corroborated by the data in Figure 8 showing the percentage of water stable aggregates of different sizes at the 30-45 cm depth. Gypsum has clearly facilitated root proliferation and aggregation.

CONCLUSIONS

Phosphogypsum is an amendment of potentially great benefit to highly weathered soils. Not only does it ameliorate subsoil acidity by causing the precipitation of toxic Al and supplying Ca needed for root extension but also promotes the infiltration of water into the soil surface resulting in a reduction in runoff and thus soil loss. Furthermore, the increased electrolyte concentration in the soil solution provided by the gypsum improves the hydraulic properties of the profile. This overall amelioration allows acid sensitive crops to extract water from soil horizons seldom exploited by roots thereby circumventing, to some extent, drought conditions often prevalent during the growing season.

A number of research programs, notably in Brazil, South Africa and Georgia, on the use of phosphogypsum in acid soils are currently in progress and the prospects for a rapid increase in the information available on gypsum reactions with acid soils are high.

ACKNOWLEDGEMENTS

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STABILIZATION OF OIL FLYASH AND LIME SLUDGE UTILIZING PHOSPHOGYPSUM

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ABSTRACT

A current disposal method of oil flyash and lime sludge consists of storing in sealed stockpiles. The recovery of vanadium from oil flyash, which used to be a method of reuse, is no longer economical. Environmental safety concerns, increased production of wastes, and inappropriate use of valuable land are some of the reasons to provide an alternative solution to current disposal methods.

Tests results indicate that oil flyash and lime sludge could be stabilized and used in construction, but due to their poor binding properties, may only be utilized as fillers. On the other hand, phosphogypsum (by-product of the fertilizer industry), and Portland cement could be utilized as binders to obtain useful construction materials.

Specimens were prepared using the Modified Proctor compaction method on different combinations of oil flyash or lime sludge and the above mentioned binders. The main purpose of this research was to utilize as much waste products as possible, and cement to a limited quantity.

INTRODUCTION

Waste by-products have always created problems to their producers. Without any exception, Florida Power and Light Co., is facing some problems in disposing the oil flyash and lime sludge which are produced at their power plants. Since the recovery of vanadium from oil flyash is no longer economical, and the conversion of the lime sludge back into quick lime is also uneconomical, these by-products keep piling up. Therefore, it is highly important to seek an alternate solution to current disposal procedures.

Tests conducted used the waste products mentioned above as fillers, and phosphogypsum (by-product of the fertilizer industry) and cement as binders. Initial results indicate that the oil flyash and the lime sludge can be stabilized using phosphogypsum.

DESCRIPTION OF THE WASTE BY-PRODUCTS

1. Oil Flyash

Oil flyash consists of both the light ash fraction entrained in the flue gas and the denser fraction that settles at the bottom of the boiler after combustion. The material itself is composed of colloidal particles which are black in color and have little binding property. Oil flyash as obtained from the disposal pond had a very high water content.

2. Lime Sludge

Lime sludge results from water softening in the boiler using quick lime. It consists of minute colloidal particles which are yellowish brown in color. This waste by-product seemed to have a better binding property than that of the oil flyash but it is still relatively poor. The dry and wet densities of lime sludge compacted using the Modified Proctor method were found to be 88 lb/cu. ft and 115 lb/cu. ft, respectively. The specific gravity was found to be about 2.58. Lime sludge as obtained from the disposal pond possessed a very high water content.

3. Phosphogypsum

Phosphogypsum, a by-product of the phosphate industry, consists primarily of calcium sulfate. Two different types of phosphogypsum, hemihydrate and dihydrate, were utilized in this study, but more emphasis was placed on the dihydrate which is abundantly available in Central Florida.

SPECIMEN PREPARATION

The specimens were prepared in accordance with the Modified Proctor method. Each specimen was made in a mold 2 in. in diameter and 4 in. in height. The cylindrical specimen was made in 5 layers with a total compaction energy of 56,250 lb.-ft/cu. ft. Once the compaction was obtained, the specimen was extruded from the mold. Some specimens were cured under sealed conditions, while others were cured under open shelf laboratory conditions at 75°F and 60% relative humidity.

All specimens were allowed to cure for about 28 days prior to testing. Only compression tests were conducted on these specimens.

The dry components of the mixtures were first mixed in a pan mixer with a grinding wheel. Then, the appropriate amount of water was added. A uniformmixture is a very critical factor in the sample preparation.

TEST RESULTS

1. Oil Flyash and Phosphogypsum Mixtures.

When several mixtures of various proportions of oil flyash and phosphogypsum were tested, the maximum compressive strength was obtained for mixtures having moisture contents between 18% and 24%. Using the maximum compressive strength of the different compositions, several graphs were plotted to show the development of strength as a function of the constituents percentage. Figure 1, presents the compressive strength versus the oil flyash content relationship for mixtures cured under air-dry conditions. It was found that the mixtures using hemihydrate phosphogypsum yielded higher compressive strength as compared to that of the mixtures using dihydrate phosphogypsum. As predicted, the strength decreases with the increase of the oil flyash content. For instance, the strength of the hemihydrate-based mixtures dropped from 600 psi (10% oil flyash) to 325 psi (30% oil flyash), whereas the strength of dihydrate-based mixtures dropped from 500 psi (10% oil flyash) to 300 psi (30% oil flyash). Figure 2, presents the compressive

Compressive strength Vs. Oil Flyash content

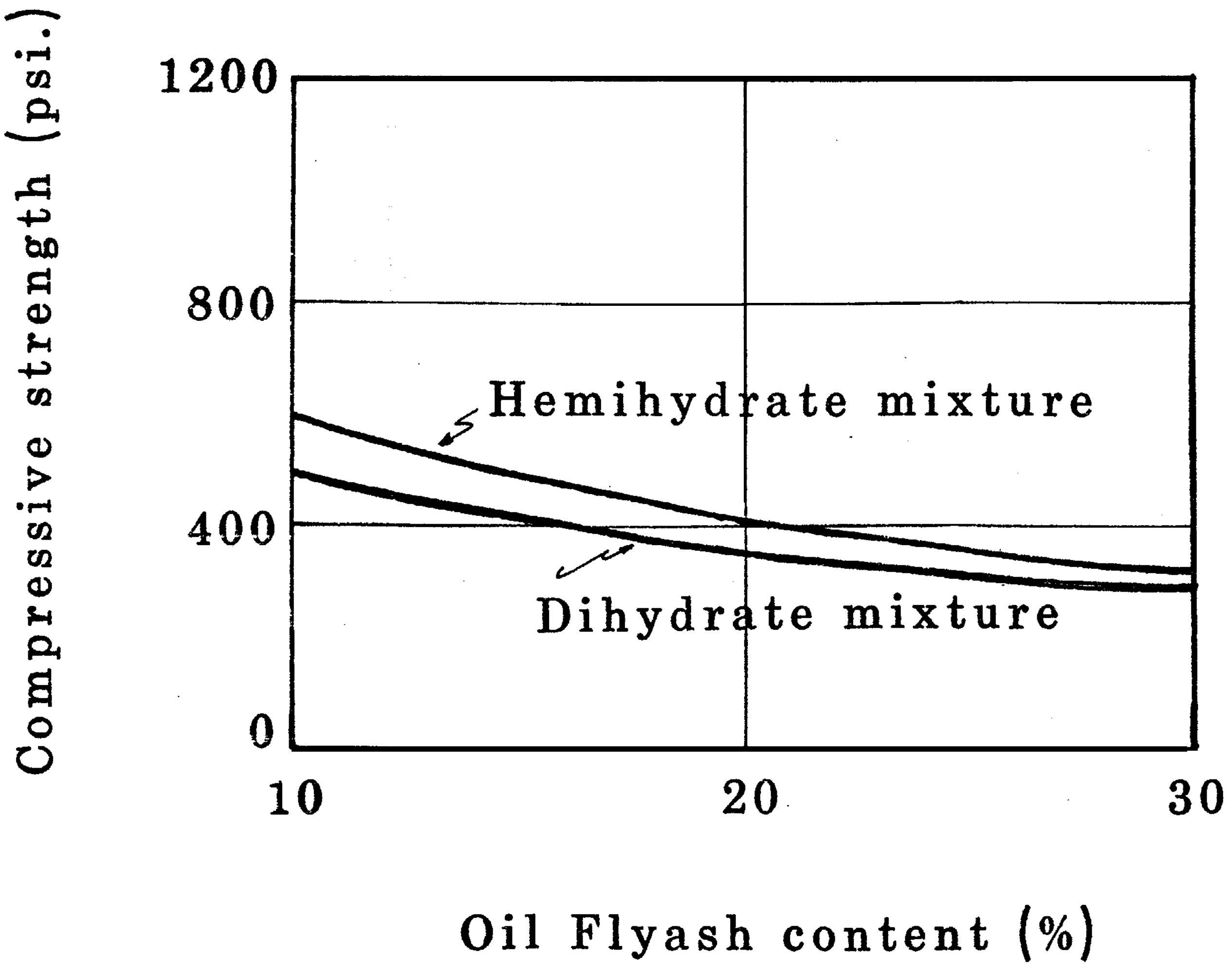
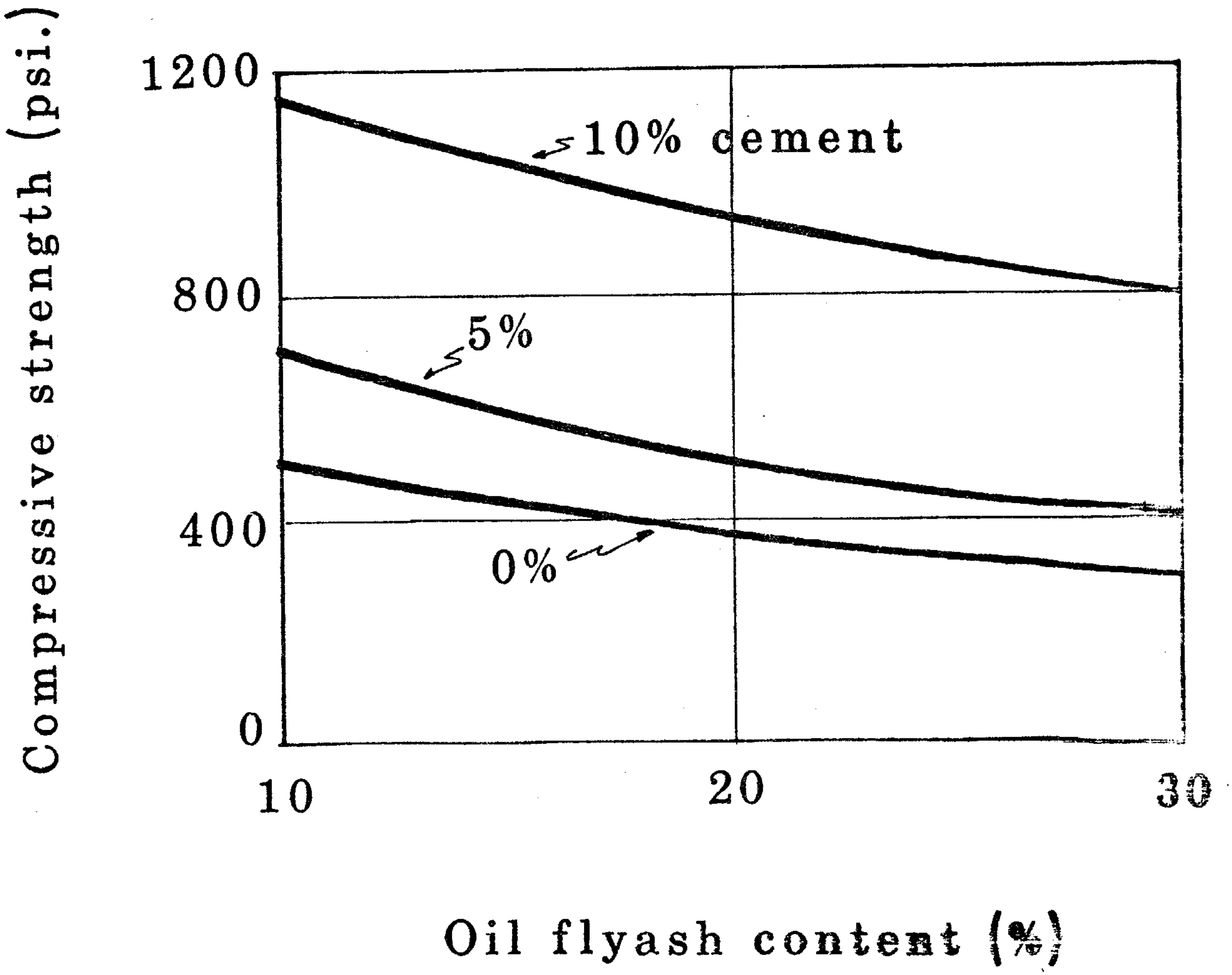


Figure 1



Oil Flyash, Phosphogypsum, and Cement mixture

Figure 2

strength versus oil flyash content for mixtures with different cement percentages. As expected, a compressive strength, higher than in the previous case, was obtained because of the addition of cement. The compressive strength of the mixtures containing 10% oil flyash with no cement was found to be 500 psi while the strength of mixtures with the same oil flyash content and a 10% cement addition was found to be 1150 psi. As it can be observed from Figure 3, there strength is plotted as a function of cement content, the slope of the curves, with different flyash content is almost identical, which indicates that the oil flyash content is a major factor governing the compressive strength of the mixtures. Higher compressive strength was also obtained with higher cement content as shown in the figure,

2. Lime Sludge and Phosphogypsum Mixtures

Specimens consisting of lime sludge and phosphogypsum were also cured in dry and sealed conditions for 28 days prior to testing. Figure 4 presents the relationship between the compressive strength and the lime sludge content for mixtures cured under air-dry conditions. Similar to the oil flyash mixtures the strength of lime sludge mixtures is reduced by the increase of lime sludge content. The strength reduces linearly for mixtures containing no cement. With the addition of some cement, the compressive strength was significantly improved. For instance, the mixture containing 10% lime sludge with no cement had a compressive strength of 225 psi while the mixture with the same lime sludge content and a 10%

Oil Flyash, Phosphogypsum, and Cement mixture

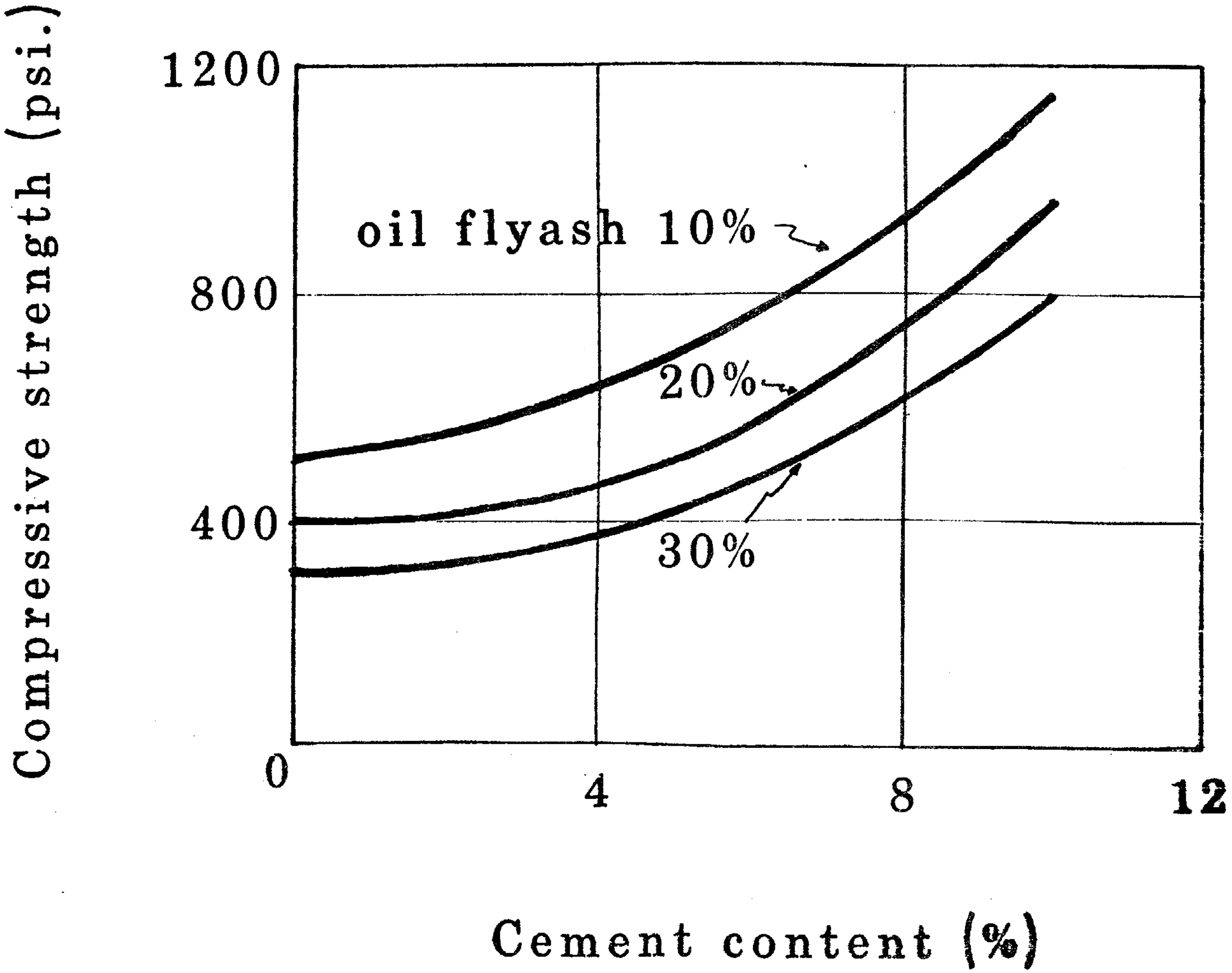


Figure 3

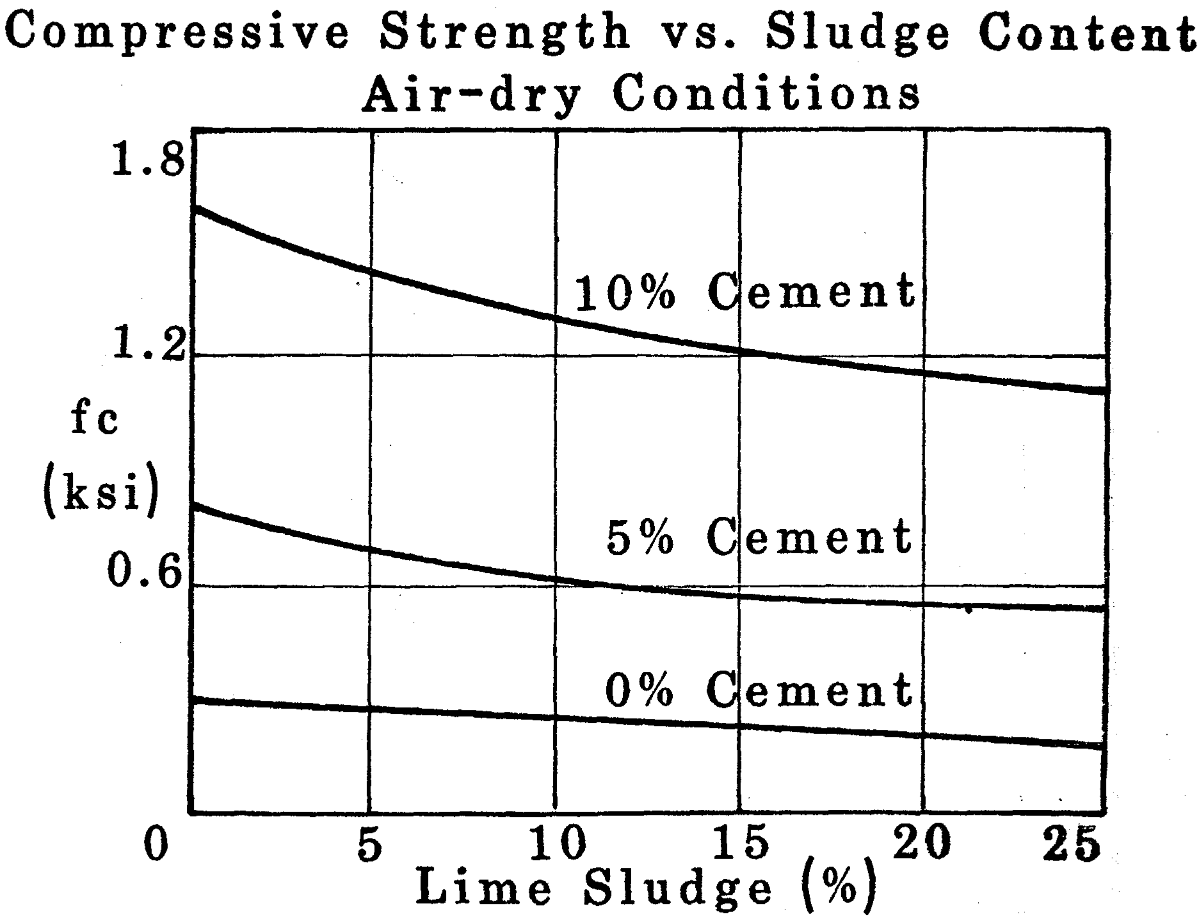

Compressive Strength vs. Sludge Content
Air-dry Conditions
1.8
1.2
0.6
0
fc
(ksi)
10% Cement
5% Cement
0% Cement
5
10
15
20
25
Lime Sludge (%)

Figure 4

cement addition had a compressive strength of 1300 psi. Figure 5 presents the relationship between the compressive strength and the lime sludge content for mixtures cured under sealed conditions. It was found that the compressive strength of the specimens cured under the sealed conditions was lower than those under air-dry conditions. For instance, a mixture containing 10% lime sludge and 10% cement had a compressive strength of 725 psi for sealed conditions as compared to that of 1300 psi for air-dry conditions. The curves in Figure 5 have relatively small gradient thus meaning that the increase in the lime sludge content is not critical.

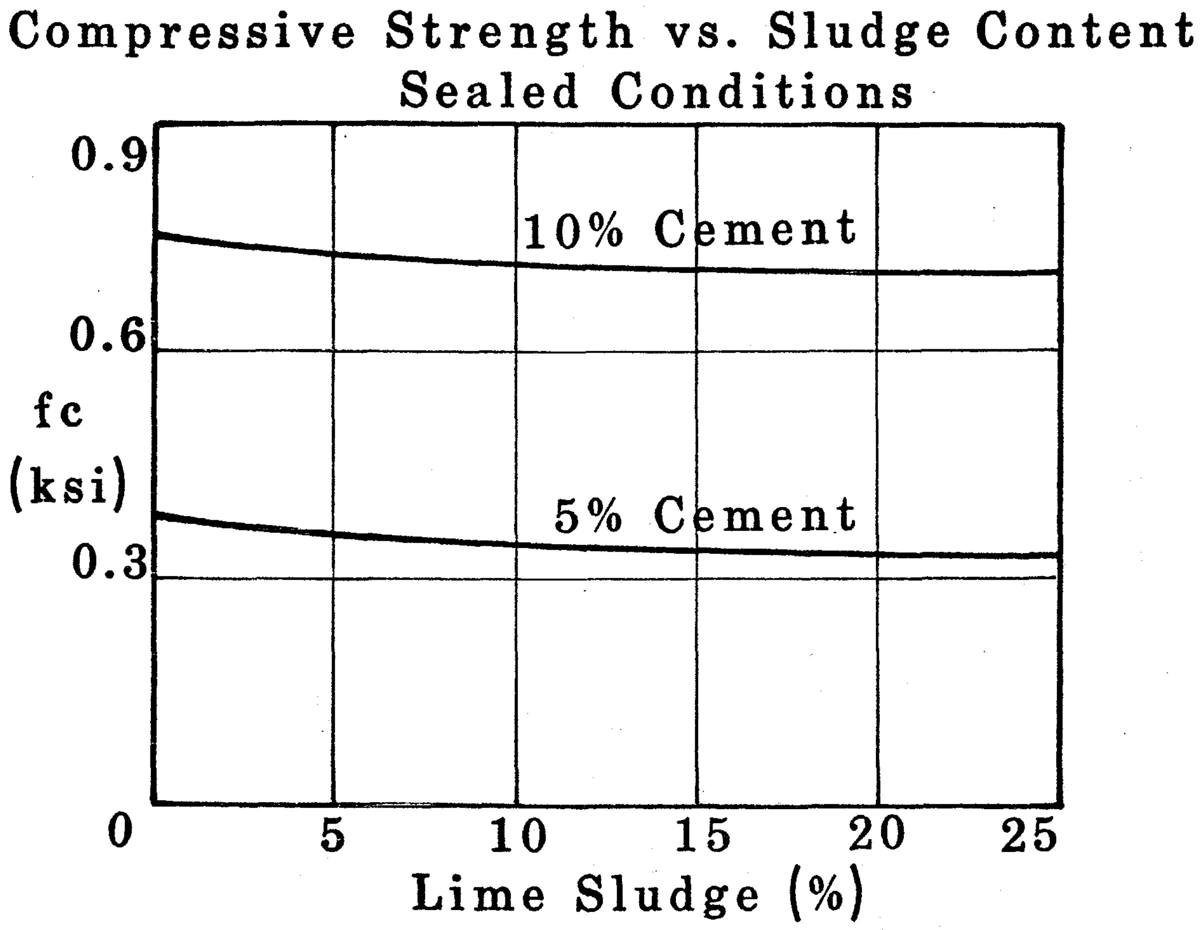
CONCLUSION

1. The data obtained from the reported tests indicate that waste by-products such as oil flyash and lime sludge can be stabilized utilizing phosphogypsum.

2. Mixtures of oil flyash and phosphogypsum compacted using the Modified Proctor method achieved a maximum compressive strength of 600 psi.

3. Mixtures of lime sludge and phosphogypsum compacted using the Modified Proctor method achieved a maximum compressive strength of 300 psi.

4. The compressive strength of both mixtures as mentioned in items 2 and 3 were significantly improved with the addition of a small quantity of cement.



Compressive Strength vs. Sludge Content
Sealed Conditions

Figure 5

ACKNOWLEDGEMENT

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ENGINEERING PROPERTIES OF HEMIHYDRATE PHOSPHOGYSUM

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ABSTRACT

Phosphogypsum in hemihydrate form (like dihydrate) is a by-product of the phosphoric fertilizer industry. The patented hemihydrate process by the Occidental Chemical Company produces hemihydrate phosphogypsum (Oxy-HPG) with more desirable engineering characteristics than dihydrate (DPG). After curing, compacted Oxy-HPG achieves higher compressive strength than DPG under the air-dry testing conditions. Moreover, Oxy-HPG is water resistant and possesses valuable compressive strength under soaked conditions.

The aim of this study is to investigate the feasibility of utilizing this material in road construction and in the development of building products.

Both the impact (Modified Proctor) and static compaction methods were used for the preparation of testing specimens. Laboratory studies concentrated on the following:

a) moisture-strength relationship for specimens under both air-dry and soaked conditions;
b) effect of soaking specimens in fresh water on strength;
c) effect of cyclic wetting-and-drying on strength;
d) effect of curing age on strength; and
e) effect of static compaction pressure on strength.

Test results indicate the high potential of Oxy-HPG for construction applications. Compressive strengths of up to 1800 psi were attained on cylindrical specimens under air-dry conditions and prepared according to the Modified Proctor compaction specifications. Using the static compaction approach, high pressure applications lead to increased strength. **In** addition, Oxy-HPG mixtures gain strength under sealed curing conditions.

INTRODUCTION

Traditionally, the dihydrate process has been adopted by the fertilizer industry for the production of the phosphoric acid (P_2O_5) of strength 28-32%) the by-product calcium sulfate. being essentially precipitated as dihydrate ($CaSO_4.2H_2O$). Recently, however, the desire to produce high strength acid (40-52% P_2O_5) has motivated a number of companies to accept the hemihydrate technology.

In Florida, the Occidental Chemical Co. (Oxy) is one of the companies using the hemihydrate process, and the patented process by Oxy results in the calcium sulfate as a mixture of both dihydrate and hemihydrate ($CaSO_4. 1/2H_2O$).

While researches over the past have been conducted on the utilization of dihydrate phosphogypsum (DPG), the objective of this study is to introduce some basic engineering properties of this particular hemihydrate phosphogypsum (Oxy-HPG), with the expectation that this material, in addition to DPG, could beneficially be utilized for construction uses.

Data presentation of this study consists of compressive strengths of Oxy-HPG specimens subjected to different environmental conditions (air-dry, soaked, and wetting and drying). Generally, test specimens prepared using the impact (Modified Proctor) and the static compaction methods were cured under the air-dry conditions. In addition, effect of sealed curing age on strength was also investigated.

One of the outstanding properties of Oxy-HPG is its water resistance in addition to its valuable strength under air-dry conditions. It is herein hypothesized that this excellent quality comes from the hemihydrate content in the product.

Due to the industrial process variation, this hemihydrate content in Oxy-HPG may not be a constant. Laboratory test results did indicate some strength variation of Oxy-HPG supplied in different drums. Nevertheless, so far gathered information indicates that Oxy-HPG is a promising material for the road as well as building applications.

STRENGTH OF OXY-HPG

Herein, effects of compaction moisture content, curing age, wetting and drying, and soaking period on compressive strength of Oxy-HPG under impact compaction (Modified Proctor) are investigated. Moreover, compressive strength of Oxy-HPG subjected to static compaction is also presented.

Effect of Compaction Moisture Content

Oxy-HPG specimens gain strength under the air-dry curing conditions. The drying rate depends on the shape and size of specimens and also on the environmental conditions. For 2 in. by 4 in. cylindrical specimens, fairly dry samples could be obtained in about five days under the laboratory conditions (temperature of around 25°C and relative humidity 60%). Further drying has no apparent effect on the strength of specimens.

Figure 1 is the relationship between compressive strength of

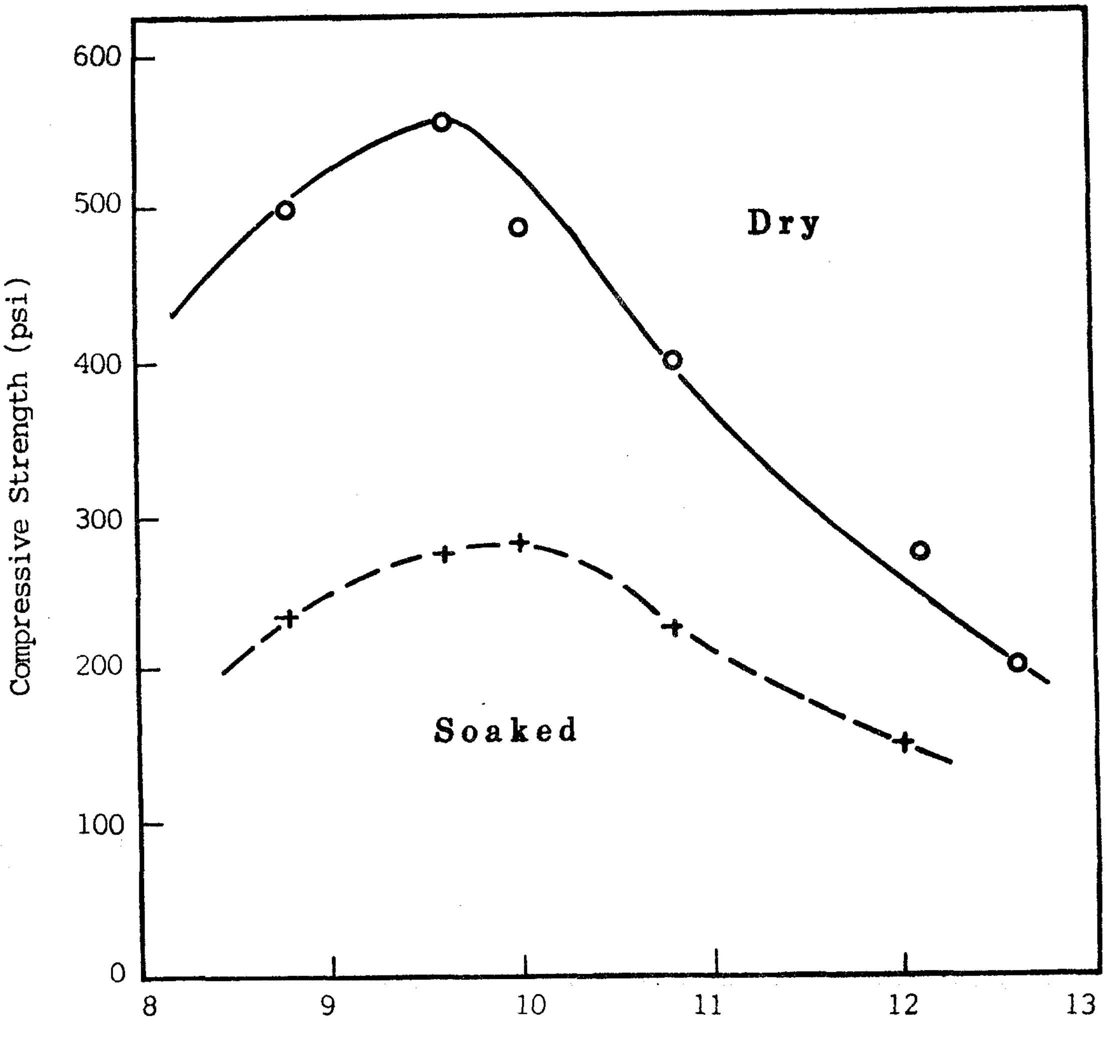

Figure 1. Compressive strength of HPG under air dry and soaked testing conditions as a function of compaction moisture content.

Oxy-HPG and compaction moisture content when the air-dry curing applies. HPG specimens possess strength under both air-dry and soaked conditions. The strength depends on the compaction moisture content. If the moisture content around optimum is used, adequate strength for the road application can be obtained (Figure 1). When under soaked testing conditions, Oxy-HPG specimens retain quite certain strength as compared to that under air-dry conditions. This water resistance of Oxy-HPG is of great value for the road construction where the disintegrating effect of water on basecourse material can be avoided or greatly reduced.

Effect of Curing Age

Under air-dry conditions, as has been mentioned, the strength of Oxy-HPG does not increase after drying for five days. The strength increases continuously, however, when specimens are cured under sealed conditions. Figure 2 is a plot of the compressive strength of Oxy-HPG as a function of the sealed curing age. It can be seen that considerable strength gain is obtained even after four months of curing. This tremendous strength increase adds to the advantage of using Oxy-HPG as a road basecourse material.

Effect of Cyclic Wetting and Drying

Figure 3 illustrates the compressive strength of Oxy-HPG subjected to cyclic wetting and drying. Oxy-HPG specimens were first cured under air-dry conditions for a period of one week, followed by one day soaking in water and one day drying in oven at 60°C,

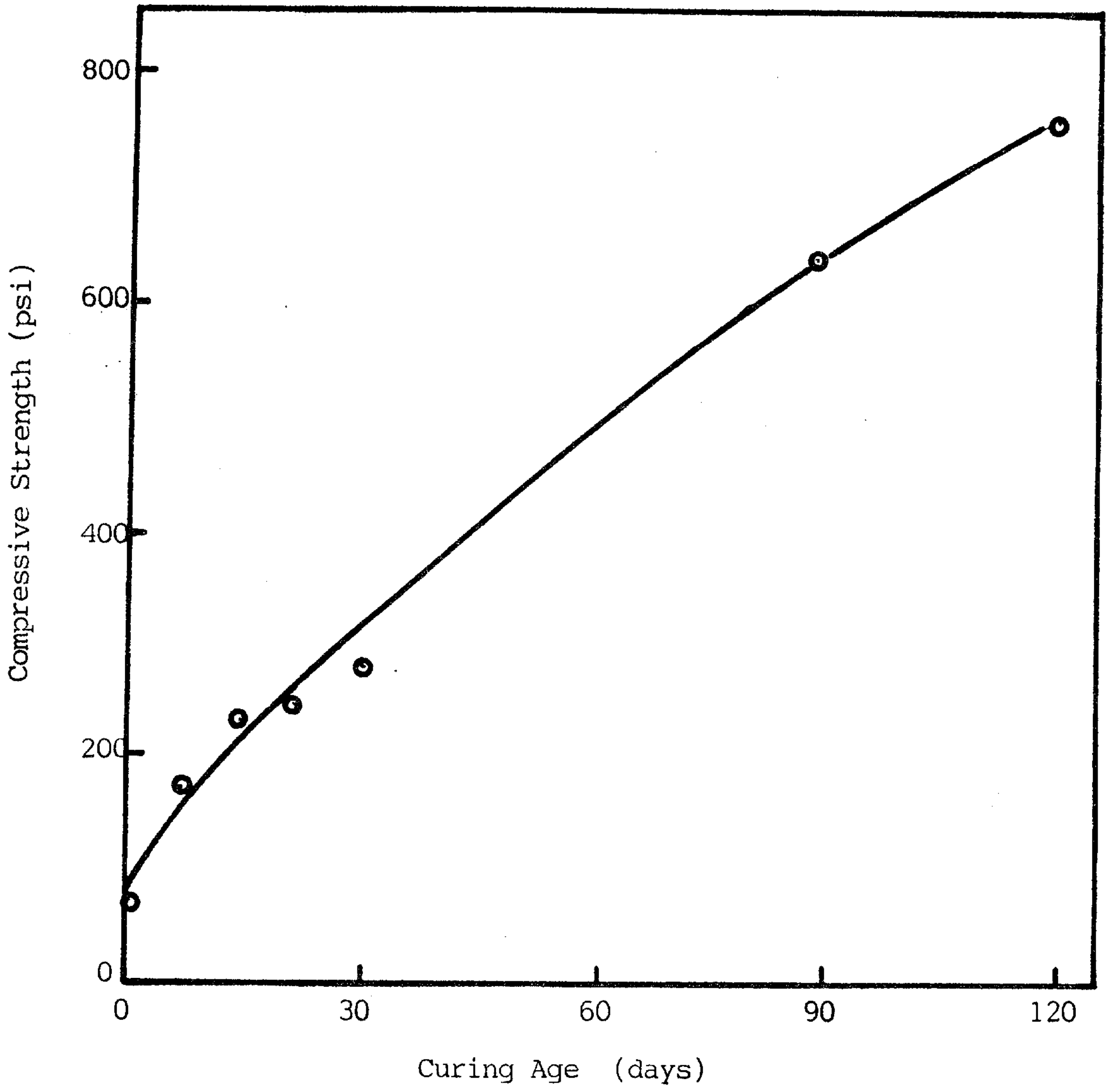

Figure 2. Effect of curing age on strength of HPG cured and tested under sealed conditions.

constituting a cycle of wetting and drying. From Figure 3, it can be observed that the number of wetting and drying cycles (after 10 cycles) does not affect the strength of Oxy-HPG under both air-dry and soaked conditions. In other words, when under fluctuating moisture conditions, Oxy-HPG is a durable material, and the strength would not be affected.

Effect of Soaking Period

Figure 4 represents the effect of soaking period on strength of Oxy-HPG. Specimens were first air dried for one week and subsequently soaked in water for differing durations. As can be seen from Figure 4, when the soaking period extends, a slight decrease in strength of Oxy-HPG exists. Except for under-water structures, this gradual strength decrease is insignificant as long as the soaking conditions do not extend over months.

Oxy-HPG under Static Compaction

Static compaction is meant by statically applying pressure to a mixture confined in a rigid mold. The applied pressure can be varied depending on the capacity of the loading machine and the strength of the rigid mold. The study of Oxy-HPG under static compaction was aimed at the application of precast building elements, such as bricks and blocks. As shown in Figure 5, strength of Oxy-HPG specimens increases continuously with the static compaction pressure. This reveals the potential of using Oxy-HPG for the production of precast building elements.

Variation of Strength of Oxy-HPG

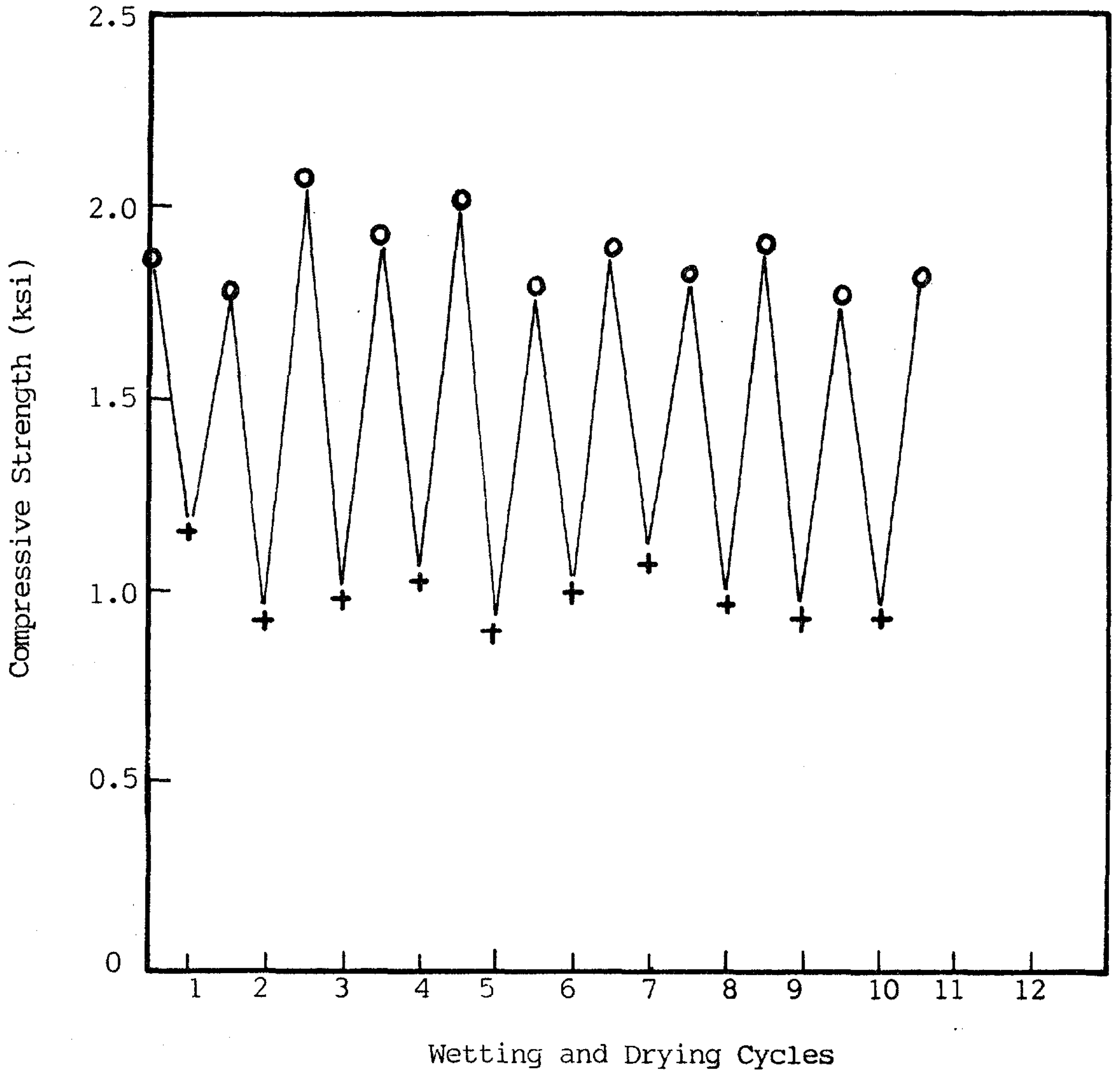

Figure 3. Effect of wetting and drying on strength of HPG.

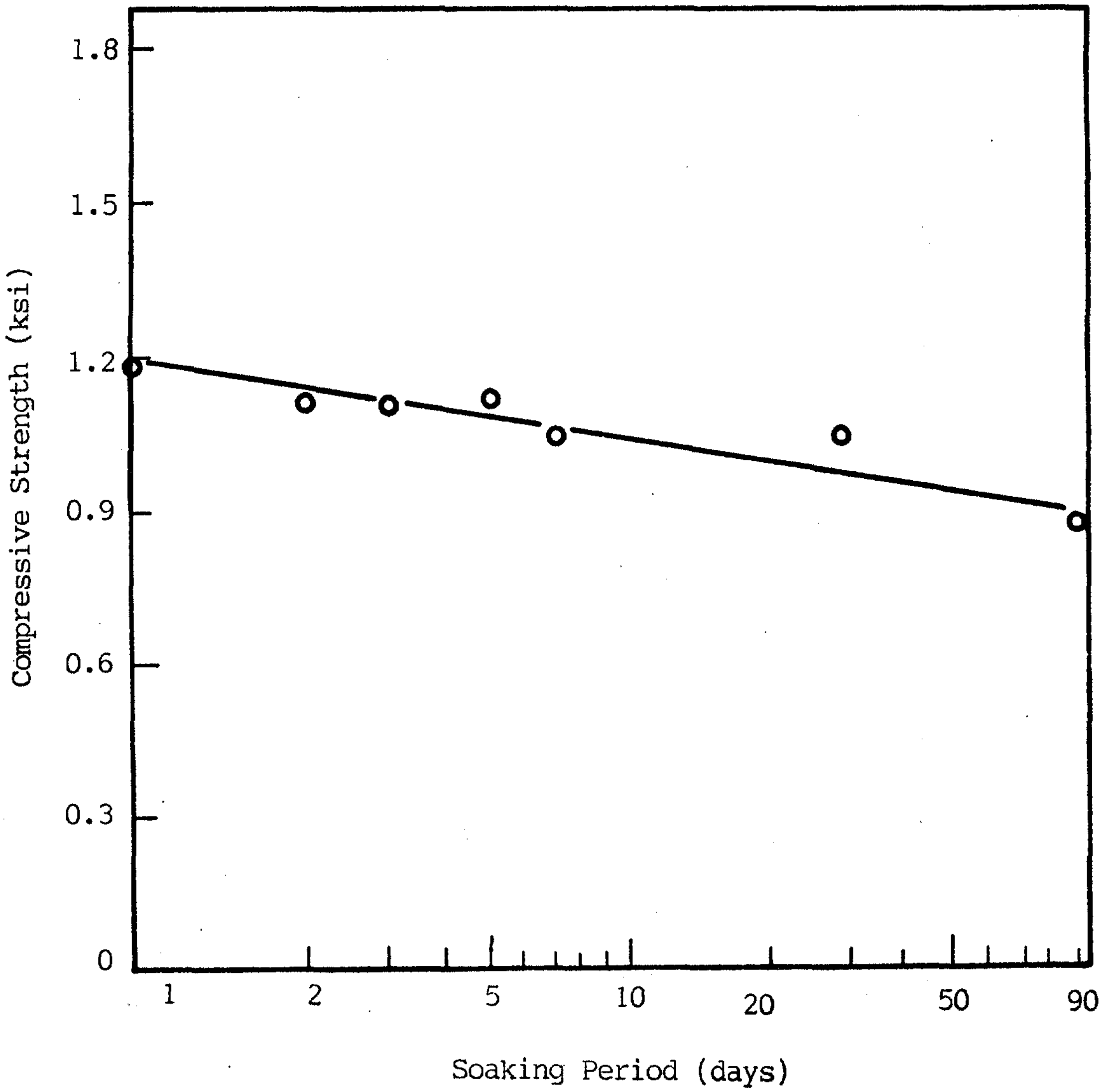

Figure 4. Effect of soaking period on strength of HPG.

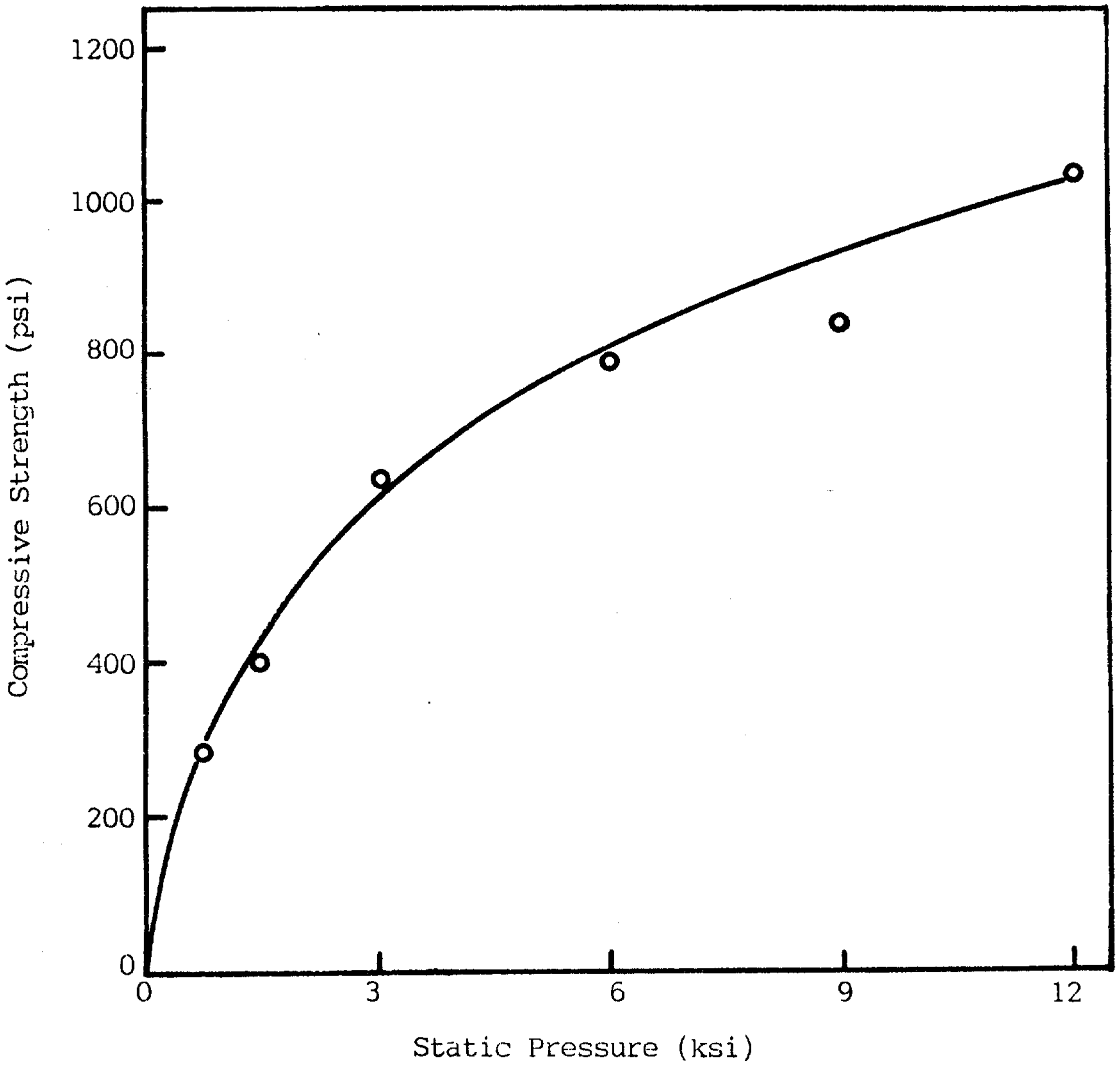

Figure 5. Effect of static compaction pressure on strength of HPG.

As previously explained, the hemihydrate content of Oxy-HPG might vary and thus affect the strength of the product. As a matter of fact, strength variation of Oxy-HPG was observed in the course of the experiment (compare Figure 1 with Figures 3 and 4). Although promising results have been obtained both in the laboratory and in the field [1], this suggests the necessity of conducting the chemical analysis correlating with the strength results for the further understanding of the material properties.

CONCLUSIONS

1. Oxy-HPG possesses appreciable strength under both air-dry and soaked conditions. The water resistance of Oxy-HPG is considered important particularly for the road application.

2. Strength of Oxy-HPG increases continuously with age under sealed curing conditions. The long-term and sizable strength gain can be used to advantage for embankment and road constructions, where the sealed conditions would apply.

3. Cyclic wetting and drying has no effect on strength of Oxy-HPG. The gradual and slight strength decrease of Oxy-HPG under extended soaking period is considered insignificant except for under-water constructions.

4. Chemical analysis in correlation with strength results is essential for the further understanding of the material

properties of Oxy-HPG.

5. The potential of Oxy-HPG for precast building products is indicated by the continuous strength increase with the applied pressure under the static compaction.

ACKNOWLEDGEMENT

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ENGINEERING PROPERTIES OF DIHYDRATE PHOSPHOGYPSUM, PORTLAND CEMENT AND FINE AGGREGATE MIXTURES

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ABSTRACT

The objective of this paper is to present an in-depth investigation on engineering properties such as compressive and splitting-tensile strength, modulus of rupture and modulus of elasticity of dihydrate phosphogypsum, portland cement type I and fine aggregate (crushed limerock) mixtures. Mix proportions at optimum moisture content for specimens prepared by the Modified Proctor compaction method were the variables to be studied under the following testing conditions: different moisture contents at the time of testing (air dry, sealed and soaked), and different curing (sealed or wet). Data presentation and discussion focus on:

a) relationship between mix proportions and strength characteristics when varying environmental conditions at testing;
b) relationships between compressive, splitting-tensile and bending-tensile strength under similar testing conditions; and
c) effects of curing condition and age on strength properties.

Laboratory strength results encourage the utilization of dihydrate phosphogypsum-based cement mixtures for construction purposes. Compressive strengths above 3000 psi become readily accessible for specimens containing at least 7.5% cement under air dry conditions. Despite the fact that strength increases with cement content, dihydrate phosphogypsum mixtures with low cement content achieve excellent compressive strength under compaction.

INTRODUCTION

Research over the past revealed that dihydrate phosphogypsum (DPG) based cement mixes, when using the conventional vibration placement method, showed no superior strength properties to the traditional fine aggregate-cement mixtures [1]. The reasons for this are possibly: the fineness of DPG particles, which requires more water in a workable mix thus increasing the water/cement ratio; and the incapability of developing the binding property of DPG by the vibration technique. Therefore, in order to acquire quality DPG mixes, approaches other than the vibration method may have to be adopted.

Soil-cement has long been used for the constructions of highway and airport runway basecourses. By the use of road construction equipment, the no-slump soil-cement, in plant or on site mixed, is evenly spread and well compacted, resulting in a quality mixture on site. Construction industries have recently begun to utilize this concept to the constructions of mass concrete structures. In fact, several dams have been constructed using the roller compacted concrete (RCC), and the outcomes are: fast construction, low cost, and high strength products [2,3].

In the laboratory, the Modified or Standard Proctor compaction method (impact compaction) is commonly used to simulate the field compaction. Under laboratory compaction, two observations of DPG mixtures have been noticed. First, compacted DPG alone possesses useful unconfined compressive strength [4], which is inaccessible to other traditional aggregates. Second, in the case of DPG based cement mixtures, mixing water is greatly reduced since dry, or no-slump, mixtures are to be compacted, thereby beneficially decreasing the water/cement ratios. With these two advantages, the improvement in strength properties of DPG based cement mixtures should be anticipated by compacting no-slump mixures.

The main scope of this paper consists of investigating the compressive strength properties of mixtures containing a complete range of portland cement type I, DPG , and sand (crushed limerock). The Modified Proctor compaction procedure was applied for the preparation of test specimens. Other engineering parameters, such as splitting-tensile strength, bending-tensile strength, and modulus of elasticity; and effects of curing conditions, ages, and compaction energy, on strength properties are also presented. Laboratory test data have indicated that compaction greatly improves the strength of DPG based cement mixtures, and the excellent binding property of DPG under compaction makes these mixtures superior to the conventional fine aggregate mixtures for the low cement mixture utilization. It is foreseeable that with appropriate construction techniques subsequently developed, DPG will become tangible assets to the community and the industry in the near future.

SPECIMEN PREPARATION

DPG , sand, and portland cement type I constitute the mixtures investigated under this study. Figure 1 shows the particle size distribution of DPG and sand. It can be seen that most DPG particles lie in the range of 30-100 microns, and the maximum size of sand is 4.75 mm. (.187 in.), allowing the 2 in. diameter samples to be used [5]. Thus test samples were prepared according to

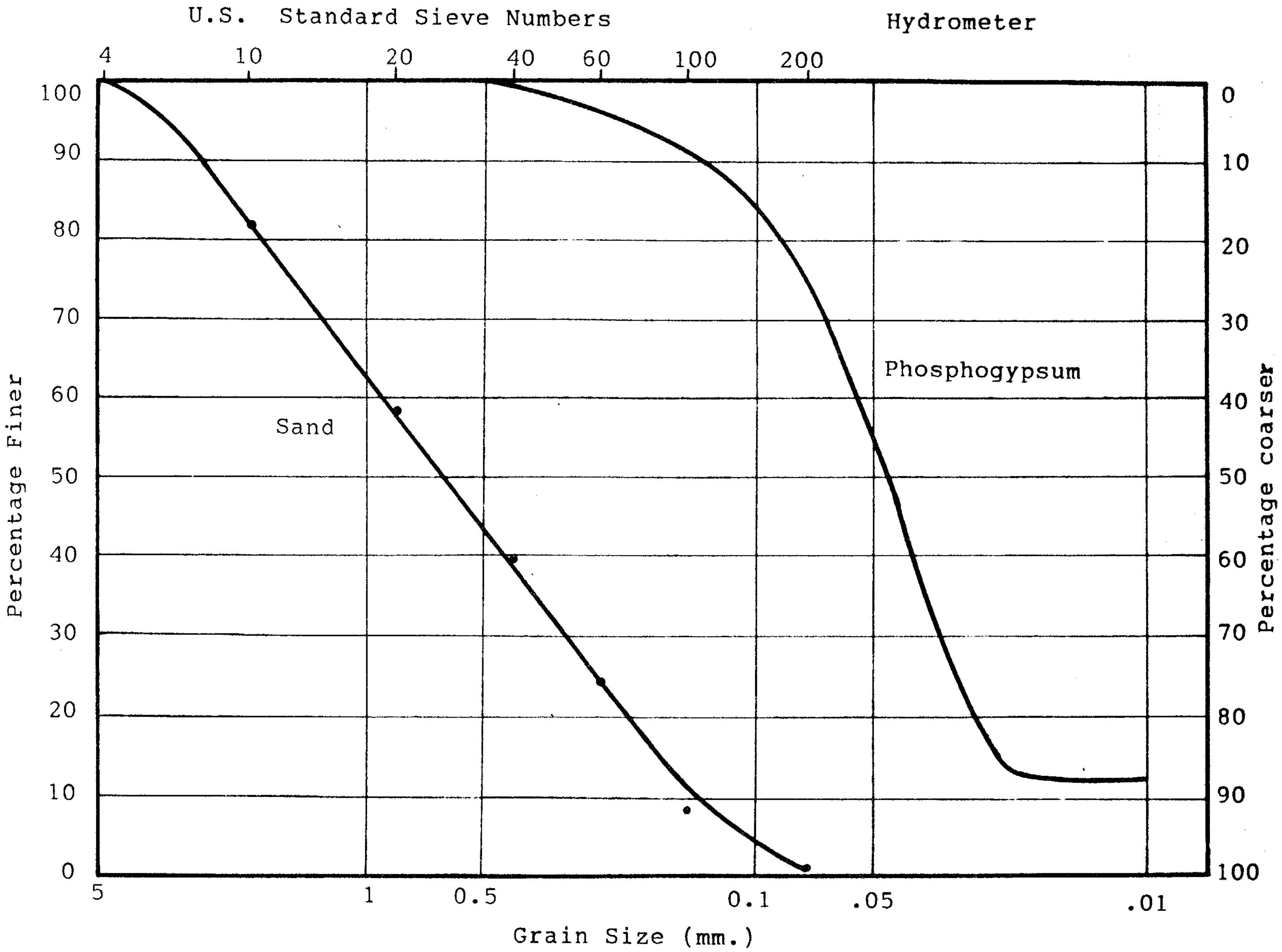

Figure 1. Grain size distribution curves for sand and DPG.

ASTM (American Society for Testing and Materials) C192 and D1632 with the following notices:

1) 2 in. by 4 in. cylinders were used for molding test specimens.

2) A manually operated dropping-weight compactor fitting the 2 in. by 4 in. molds was used for compacting test specimens.

3) The compaction energy of the Modified Proctor procedure (ASTM D1557) was applied.

4) Specimens were cured under sealed conditions, i.e. closely wrapped in plastic membranes, and tested under air dry, Sealed, and soaked conditions.

Mixtures were mixed by the use of a pan mixer provided with the grinding roller. DPG lumps easily broke under the action of the grinding roller, and uniform mixing was at all times obtained.

COMPRESSIVE STRENGTH

Effect of Mix Proportion

One of the major objectives of the study is to investigate the compression behavior of mixtures under compaction when varying the mix proportions. Considering the fact that strength of DPG based mixtures is affected largely by the moisture content of the specimen at the time of testing [1,6], specimens were tested under three moisture conditions defined as follows:

a) Sealed conditions: specimens tested immediately after the removal of the plastic membrane.

b) soaked conditions: specimens immersed completely in water prior to testing for at least a period of 48 hours.

c) air dry conditions: specimens air dried under laboratory conditions for five days.

Seven families of mixtures containing cement varying from 2.5 to 25% and different proportions of DPG and sand were investigated. Figures 2 to 4 presents the 28-day compressive strength of specimens under air dry, sealed, and soaked conditions respectively as a function of the sand content for these families of mixtures. From these test results, several observations should be noticed:

1) All mixtures possess considerable compressive strength. Compressive strengths above 3000 psi could readily be acquired for specimens under air dry conditions, using at least 7.5% cement (Figure 2). Although specimen strength decreases when tested under sealed and soaked conditions (Figures 3 and 4), compressive strengths above 2000 psi can still be retained for specimens containing at least 7.5% cement.

2) Strength of DPG based cement mixtures depends greatly on the cement content and mix proportions in the mixtures. Based on the different characteristics of these strength curves, two types of mixtures can be distinguished. For mixtures with cement content above a certain value (around 15% for air dry testing conditions and 10% for sealed and soaked conditions), specified here as high cement content mixtures, the strength increases with the sand content, meaning that the contribution of DPG to strength is not observed. However,

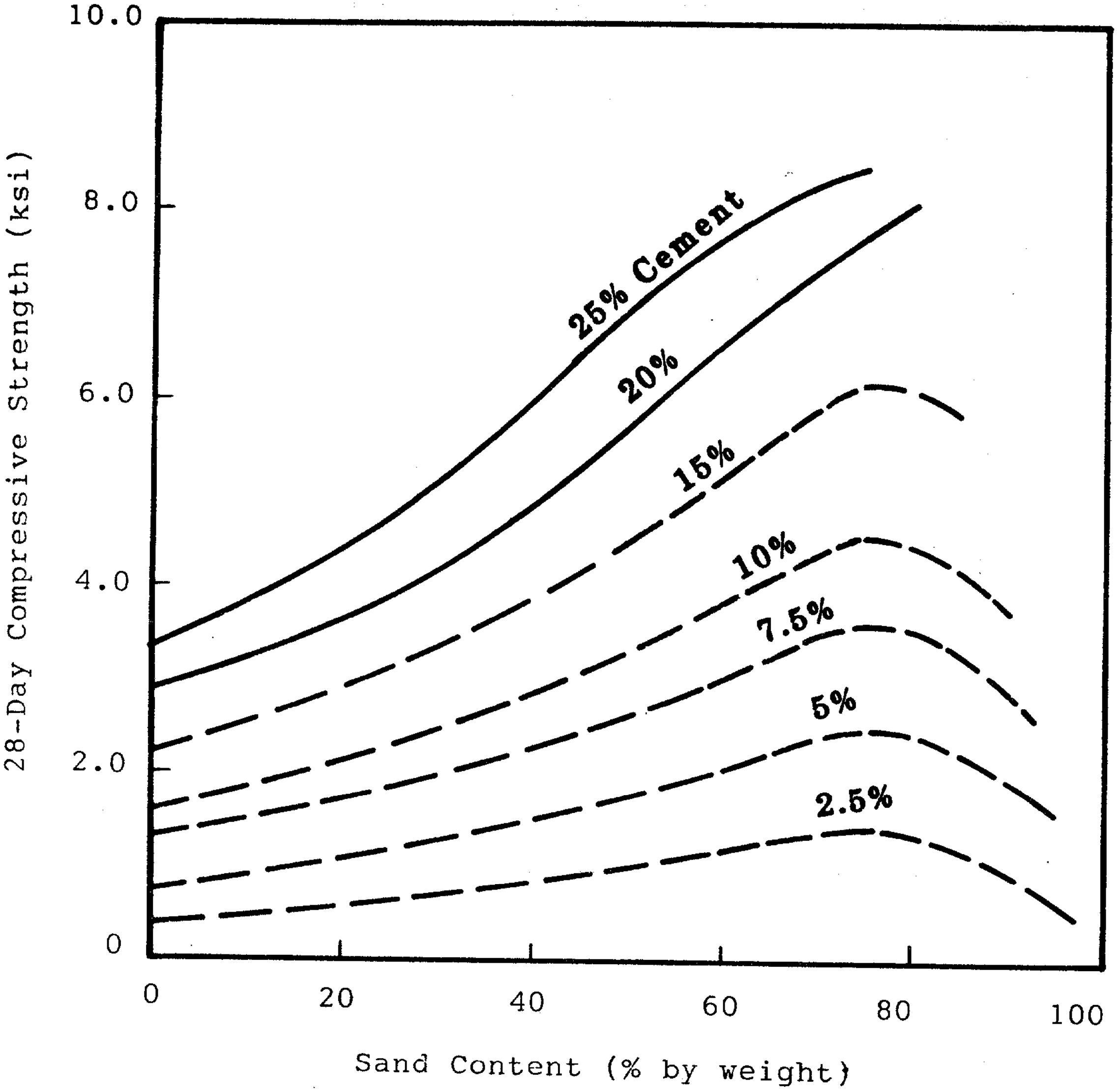

Figure 2. 28-day compressive strength (tested under air dry conditions) of DPG based cement mixtures as a function of sand content.

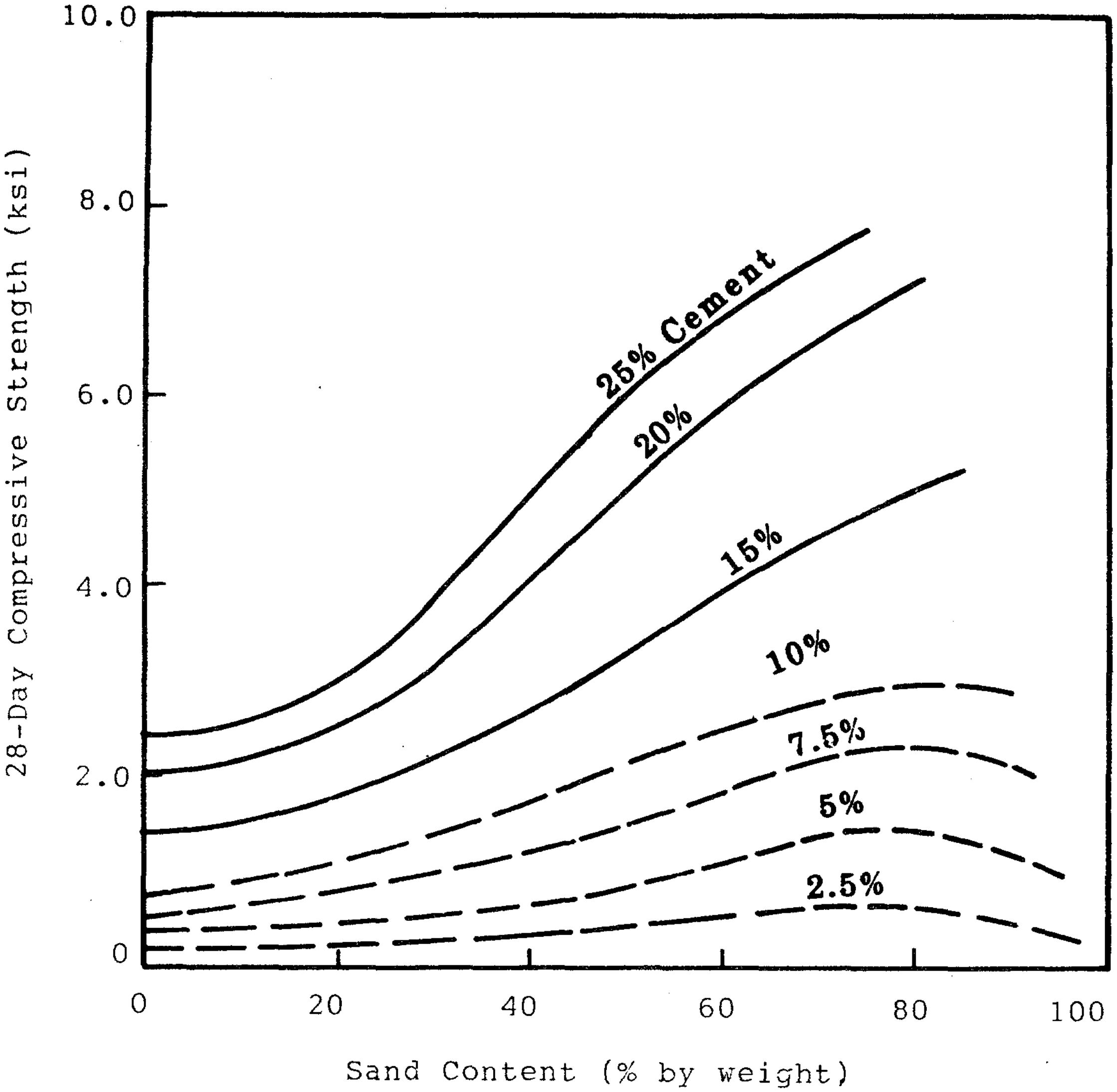

Figure 3. 28-day compressive strength (tested under sealed conditions) of DPG based cement mixtures as a function of sand content.

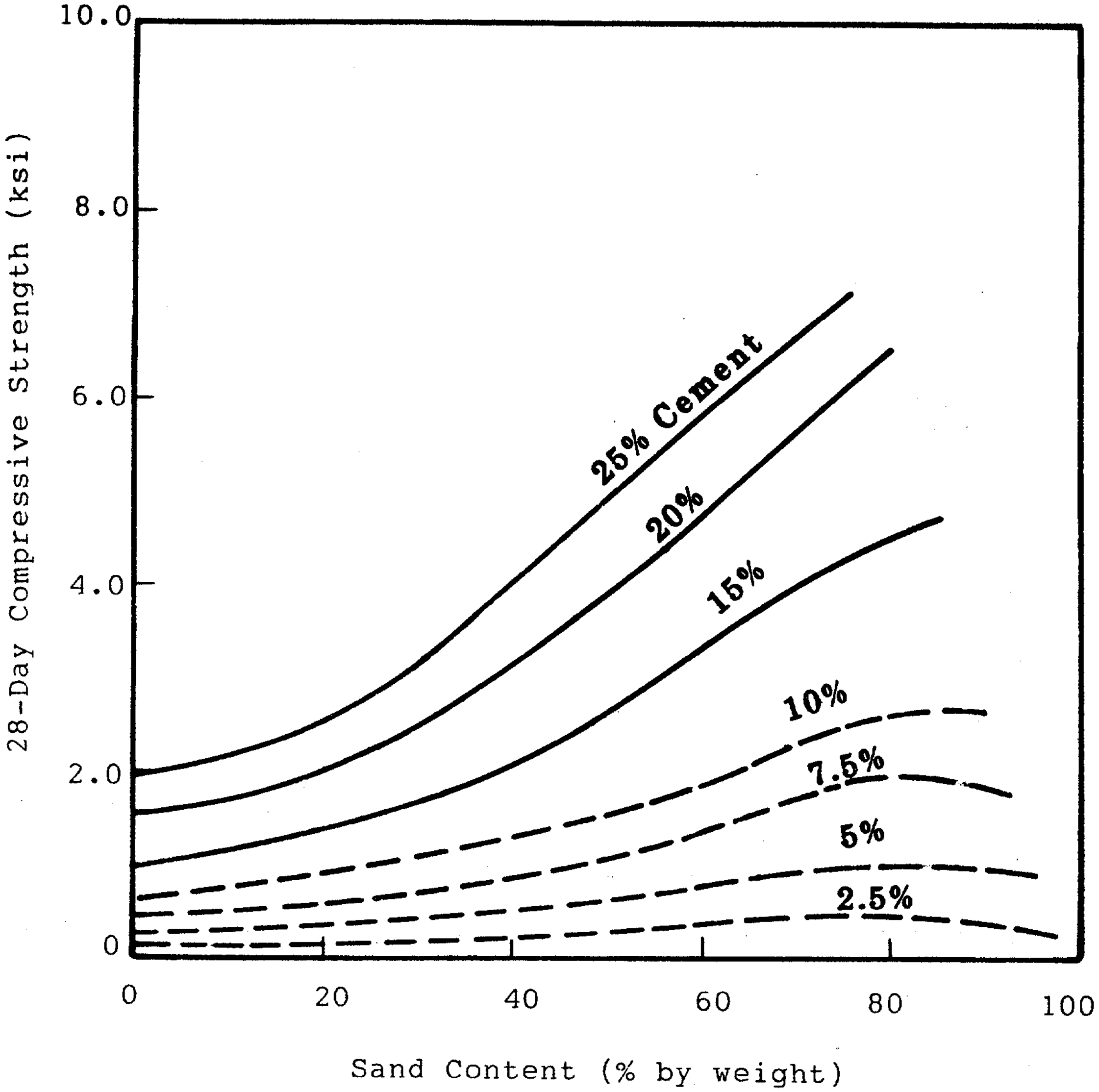

Figure 4. 28-day compressive strength (tested under soaked conditions) of DPG based cement mixtures as a function of sand content.

for mixtures with less than the aforementioned cement content, specified as low cement content mixtures, peaks of strength curves develop, reflecting the strength contribution of' DPG to low cement content mixtures. It is thus for the low cement content mixtures that DPG can be utilized most beneficially. To see this more clearly, for example, consider the strength curve of the 7.5% cement mixtures in Figure 2. The inclusion of DPG at about 40% (sand at 50%) leads to the same compressive strength as when sand alone is incorporated. The strength further increases until a peak develops at the DPG content of approximately 20%. This excellent strength behavior of the low cement content mixtures springs from the useful binding properties of DPG under compaction and probably the fineness of the DPG particles, which contributes to the compaction of no-slump mixtures [7].

3) All DPG based cement mixtures containing at least 2.5% cement are water resistant. Compressive strength of about 400 psi can be obtained under soaked conditions for specimens with 2.5% cement content (Figure 4).

Effect of Testing Condition

As has been pointed out, strength of DPG based cement mixtures is affected by the moisture conditions of the mixtures at the time of' testing. Figure 5 compares the 28-day compressive strength of specimens under air dry, sealed, and soaked conditions. It can be observed that when the testing conditions change from the sealed to the soaked, only a slight decrease in strength results. On the

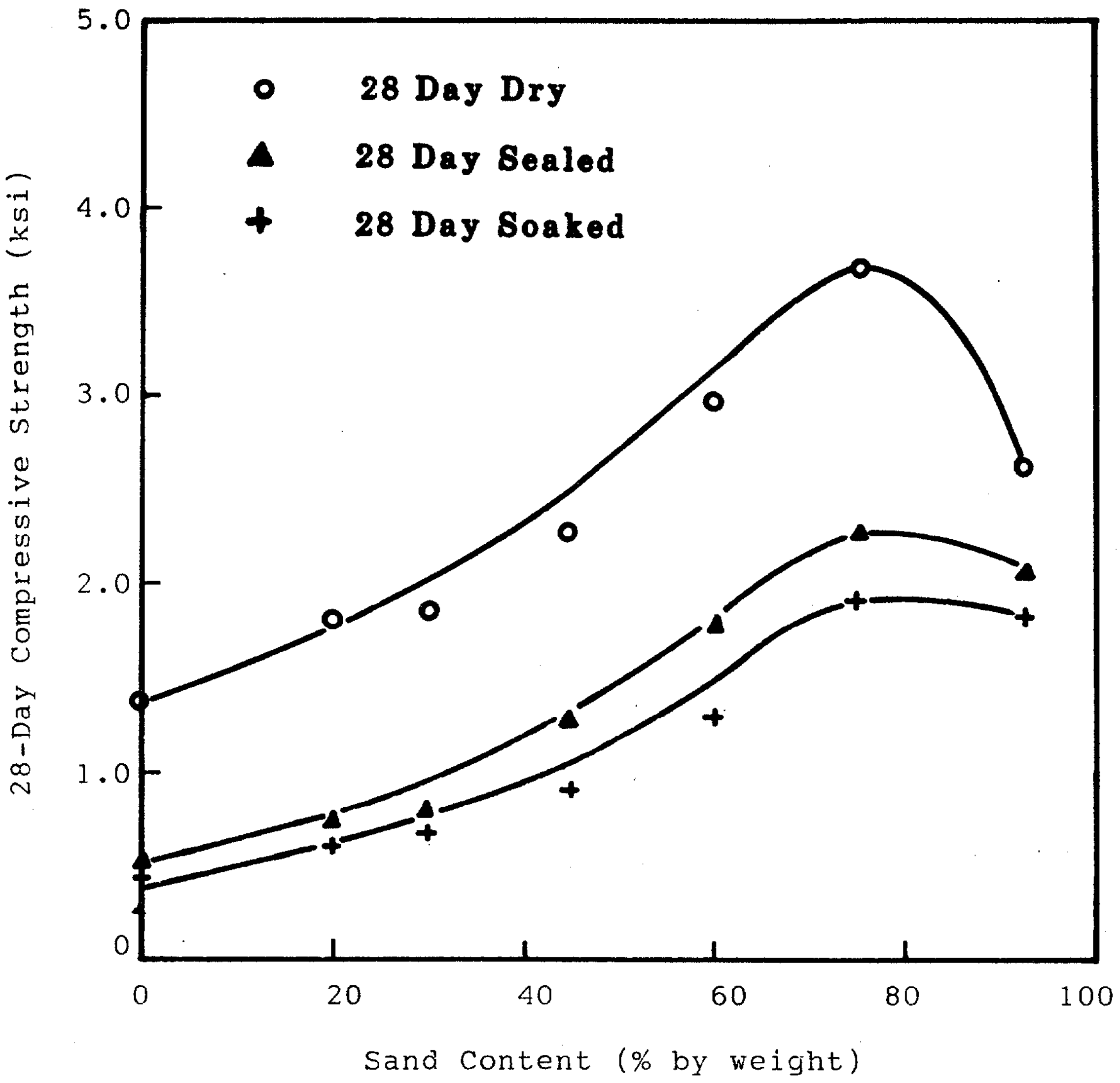

Figure 5. Comparison of 28-day compressive strength of DPG based cement mixtures (with 7.5% cement) tested under air dry, sealed, and soaked conditions.

other hand, considerable strength increase could be gained as the dry conditions apply. This strength gain can be fully utilized in the application of building products where the air dry conditions prevail.

Effect of Curing Age

Strength of' DPG based cement mixtures increases with the curing age similarly to the conventional concrete mixtures. Figure 6 represents the compressive strength of two mixtures containing 7.5% and 25% cement respectively versus the curing age. Specimens were tested under soaked conditions, and test data from two curing conditions (sealed and wet) were obtained, as indicated in Figure 6. It is consistent that the strength of both mixtures (7.5% and 25% cement) cured under either condition (sealed or wet) increases continuously with specimen age, and the negligible strength difference resulting from two curing conditions implies that both the sealed and wet curings provide the same effect on the strength development of DPG based cement mixtures.

Effect of' Soaking Period

The compressive strength of DPG based cement mixtures under soaked conditions increases with cement content as shown in Figure 4. The soaked conditions are encountered in the applications of mass concrete dams, roads under flood conditions, under water constructions, and so on. Then it would be of concern if the DPG based cement mixtures can maintain the strength when subjected to a sustained soaking period. Table 1 presents the compressive strength of two mixtures containing 7.5% and 25% cement respectively subjected to different soaking periods: one day, and

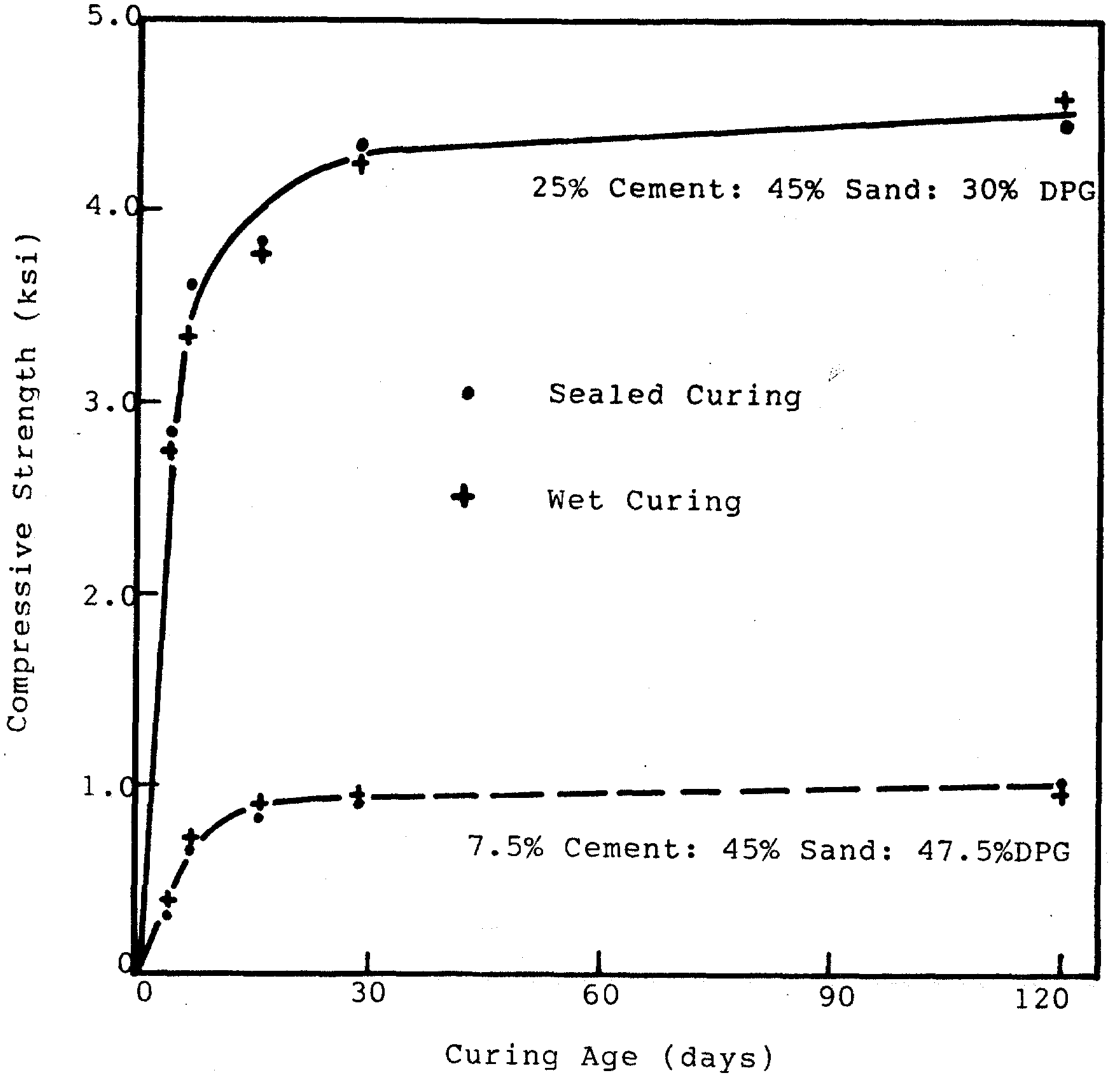

Figure 6. Comparison of effect of sealed and wet curing on strength with respect to curing age.

Table I : Effect of soaking in water on strength

Mix Proportions C : S : DPG	Compressive Strength (psi)		
	Soaking Period		
	1-Day	4-Month	8-Month
7.5:45:47.5	914	891	788
25 :45 :30	4364	4667	5252

Note: C=Cement, S=Sand, DPG=Dihydrate Phosphogypsum four and eight months. For the 7.5% cement mixture, a slight decrease In strength was observed after a soaking period of eight months, suggesting that the soaking period has only a minor effect on the strength of low cement content mixtures. For the 25% cement mixture, however, Increase in strength can be observed, indicating that strength of high cement content mixtures is unaffected by the soaking period, and in fact is increased continuously by the moist curing from the soaking environment.

Summary

All DPG based cement mixtures show useful strength values. In particular, the excellent strength properties of low cement content mixtures can be advantageously utilized. Like the conventional concrete mixes, strength of DPG based cement mixtures increases continuously with curing time. Although strength of low cement content mixtures decreases slightly when subjected to long extended soaking period, it is considered immaterial especially for the road construction where very rarely a flooding period over months would happen.

BENDING AND SPLITTING TENSILE STRENGTH

The bending and splitting tensile strength of DPG based cement mixtures, similar to ordinary concrete mixes, can be related to the compressive strength. Figure 7 represents the relationships between the bending-tensile, splitting-tensile and compressive strength. To construct these relationships cylindrical specimens sized 2 in. by 4 in. were tested for splitting-tensile strength, and beam specimens dimensioned 2 in. by 2 in. by 7 in. were

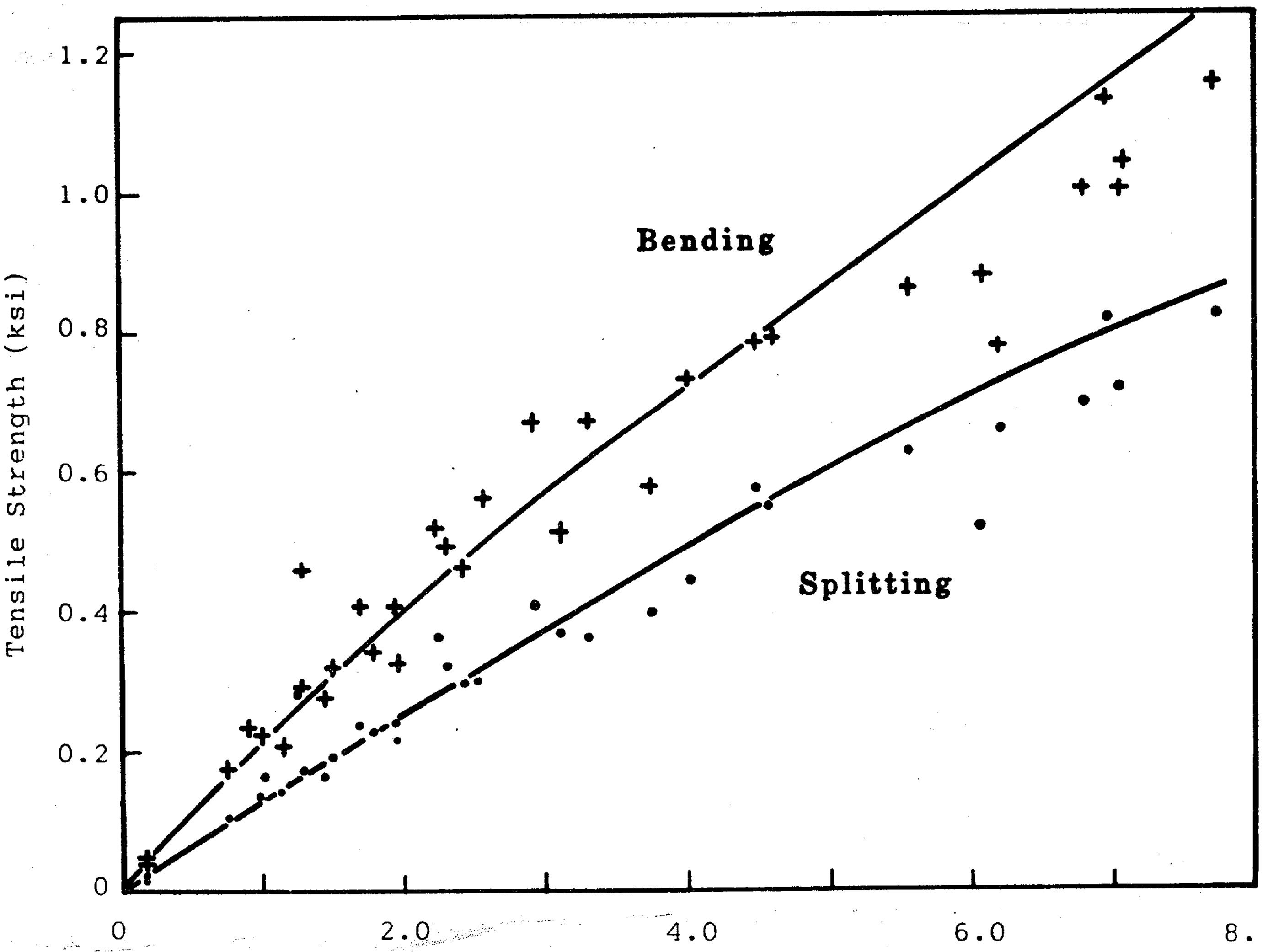

Figure 7. Splitting tensile-compressive and bending tensile-compressive strength relationships of DPG based cement mixtures.

tested for bending-tensile strength. All specimens were tested under sealed and soaked conditions so that a more uniform moisture distribution within the specimen could be assumed. From Figure 7, It can be seen that in general the bending-tensile strength of DPG based cement mixtures Indicates higher values than the splitting-tensile strength, as is the case for conventional concretes. Further, the statistical analysis yielded the following equations for the estimation of bending-tensile and splitting-tensile strength respectively based on the compressive strength.

a) For bending-tensile strength:

$$Ft = 0.54*(Fc**0.87)$$

b) For splitting-tensile strength:

$$Ft = 0.19*(Fc**0.94)$$

A similar equation of the splitting tensile-compressive strength relationship of the DPG based cement mixes was previously established where the conventional vibration method was utilized [1], and the equation was:

$$Ft = 0.23*(Fc**0.93)$$

MODULUS OF ELASTICITY

In concrete, usually the modulus of elasticity is expressed in relation to the compressive strength. The ACI (American Concrete Institute) suggests an equation of the form:

$$Ec = A*(W**1.5)*(Fc**0.5)$$

where EC is the secant modulus at from 25% to 50% of the compressive strength, A is a constant to be determined, W is the air dry density of specimens at the time of testing, and Fc is the cylindrical compressive strength under the air dry testing conditions.

Applying the same model, Figure 8 plots EC (at 0.45 Fc) of DPG based cement mixtures as a function of (W**1.5)*(Fc**0.5). The DPG contents of these mixtures vary from 15 to 50%, considered a range In which DPG will be utilized most frequently. Using the method of least squares the constant A was obtained to be 24. The constant suggested by the ACI is 33 for ordinary concretes. Thus, when the DPG based cement mixtures are compared with the ordinary concretes of the same air dry density and compressive strength, about 30-40% more deformations would be expected from the DPG based cement mixtures.

EFFECT OF COMPACTION ENERGY

The strength of compacted plain DPG increases proportionally to the applied compaction effort [4]. To examine the effect of compaction effort on strength of DPG based cement mixtures, test results from two compaction methods are compared: Modified Proctor vs. Standard Proctor. The energy input of the Modified Proctor method is 56250 foot-pounds per cubic foot, approximately 4.5 times that of the Standard Proctor method.

Figure 9 compares the 28-day compressive strength of the DPG-cement mixtures in terms of the cement content, using these two compaction methods. Specimens were tested under both the air dry and soaked conditions. It can be seen from Figure 9 that

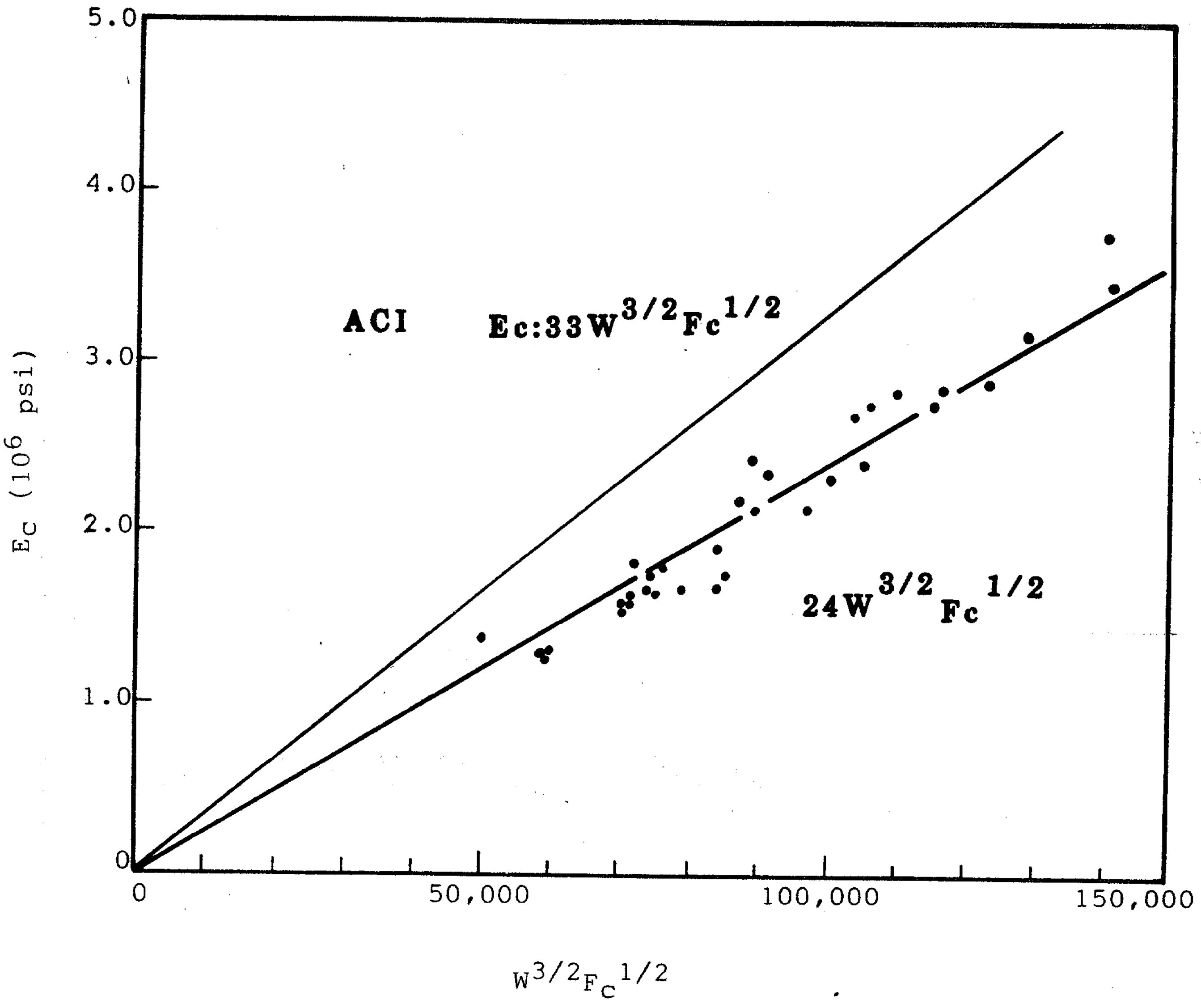

Figure 8. Modulus of elasticity of DPG based cement mixtures (DPG content: 15-50%).

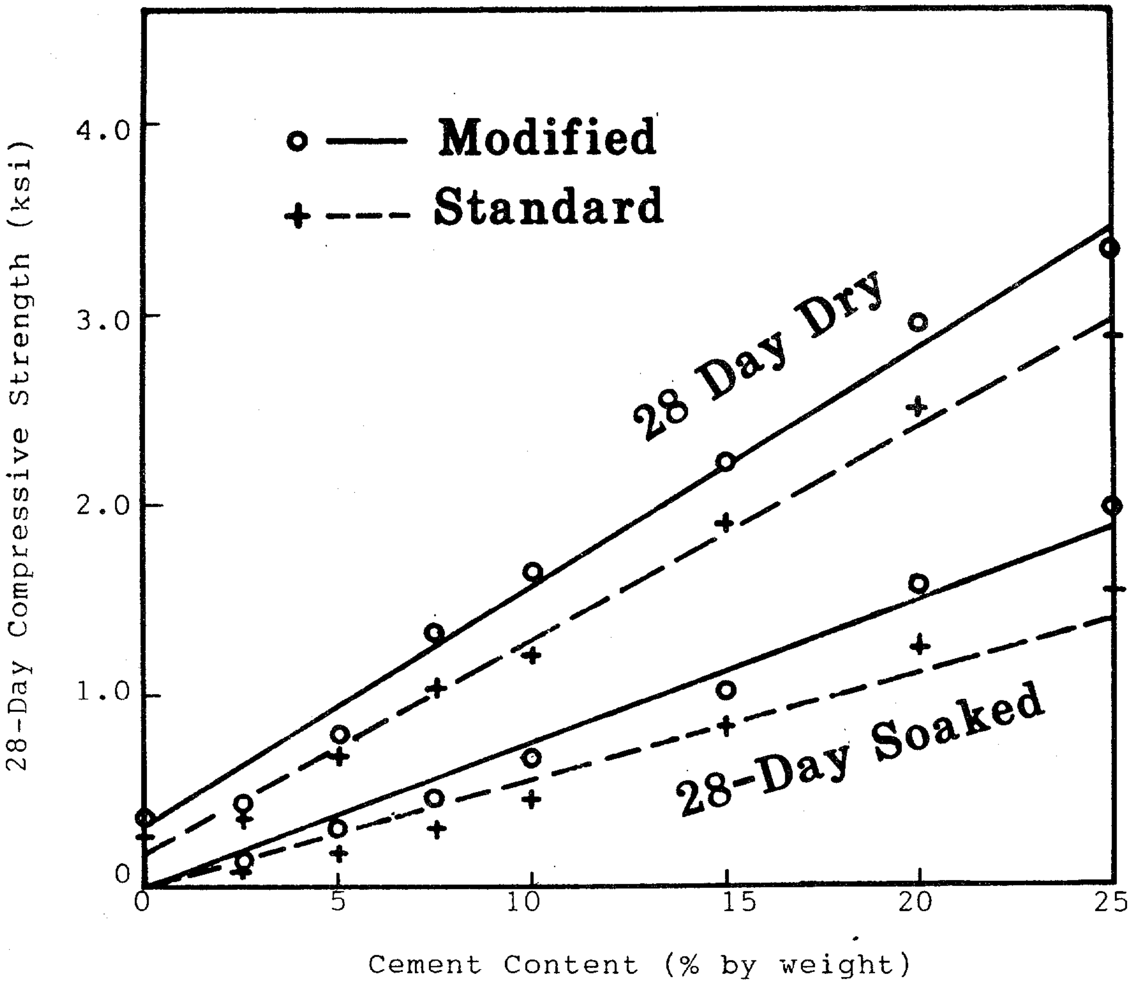

Figure 9. Effect of compaction energy on strength of DPG based cement mixtures: Modified vs. Standard Proctor compaction.

strength of mixtures using the Modified Proctor method is consistently higher than that using the Standard Proctor method, indicating that the compaction energy is a factor affecting the strength of DPG based cement mixtures.

CONCLUSIONS

The compressive strength, bending and splitting-tensile strength, and modulus of elasticity of the DPG based cement mixtures have been presented. Experimental results lead to the following conclusions:

1) Strength of DPG based cement mixtures depends on the cement content and mix proportion. Mixtures containing low cement content possess excellent strength characteristics attributed to the significant binding properties of DPG. Compressive strengths over 3000 psi under air dry conditions are accessible to mixtures having 7.5% cement content.

2) Long-term soaking has a minor effect on strength of low cement content mixtures; while strength of high cement content mixtures is unaffected.

3) DPG based cement mixtures are more deformable as compared with the conventional concrete mixes. In general, mixtures containing 15-50% DPG will undergo displacements 30-40% larger than the conventional concrete mixes of identical strength and densities.

4) Compaction energy is a factor affecting strength of DPG based cement mixtures. More compaction energy leads towards strength increase.

ACKNOWLEDGEMENT

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ENGINEERING CHARACTERISTICS OF DIHYDRATE PHOSPHOGYPSUM-BASED CONCRETE

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ABSTRACT

Phosphogypsum-based concrete consists of dihydrate phosphogypsum, cement, sand and gravel. With proper moisture content the mixture can be compacted into a product that has a smooth surface appearance and can offer an acceptable compressive capacity. The objective of this paper is to present an in depth investigation on the fundamental Engineering characteristics of compacted dihydrate phosphogypsum-based concrete.

Using impact compaction technique (Modified proctor method), mixes having cement content ranging from 5 to 25% and gravel contents between 10 and 40% were prepared. Most specimens were cured under sealed curing condition and tested immediately after removal of the plastic covering membrane.

Results indicate that, with proper mixture of phosphogypsum, sand and gravel, an air-dry strength of roughly 4500 psi can be achieved at cement content as low as 7.5%. This strength is considered sufficient for applications such as road costruction. Furthermore, it can be concluded that the binding strength contribution Of dihydrate phosphogypsum and effectiveness of the impact compaction technique are critical parameters only in mixtures of low cement content.

1. INTRODUCTION

The huge quantity of waste product generated by the phosphate-fertilizer industry has created a tremendous waste-disposal problem. This is very noticeable not only in State of Florida but in many other phosphate-fertilizer producing States. Apart from United States, undoubtedly, this is a world-wide problem.

The logical solution of this waste material disposal is to find’ ways to convert it into a usable product. This reproduction conserves natural resources, abates further pollution and preserves the environment.

Past studies have suggested that raw phosphogypsum, a by-product of the wet phosphoric acid industry, has a potential to be used as an aggregate in cement-based mixtures with application in building product and road construction (1). Its remarkable behavior under compaction is an additional advantage to the development of compaction concrete by utilizing the mixtures of portland cement, phosphogypsum, sand and gravel.

The scope of this paper is to present a series of laboratory results on the basic Engineering characteristics of dihydrate phosphogypsum-based concrete, consolidated by using impact (dynamic) compaction technique. The moisture-density, unconfined compression and splitting tension are among the basic engineering properties that are determined. In addition, the influential elements affecting these Engineering properties such as moisture at time of testing, compaction energy, curing time and curing types were also investigated during this research program.

2. MATERIALS

Phosphogypsum: The phosphogypsum used in this study as one of the matrix constituents was supplied by Gardinier Inc., Tampa, Florida. It is finely graded material where nearly 80% of its particles pass through the # 200 sieve (as shown in Figure 1). A typical chemical composition of raw phosphogypsum in State of Florida has about 90% calcium sulfate as a major composition element.

Cement: Portland cement type I (ASTM.C-150) was used throughout the experimental program.

Sand: The sand used during the test program was a finely crushed limerock obtained from south Miami quarries. it has an average specific gravity of 2.7 and fineness modulus of 2.6 . Its grain size distribution is shown in Figure 1.

Gravel: Limerock pea gravel with a maximum nominal size of 3/8 inches commonly available in Miami was used throughout this research experiment (specific gravity = 2.69). Its typical grain size distribution is shown in Figure 2 .

Figure 1: Phosphogypsum and Sand Grading

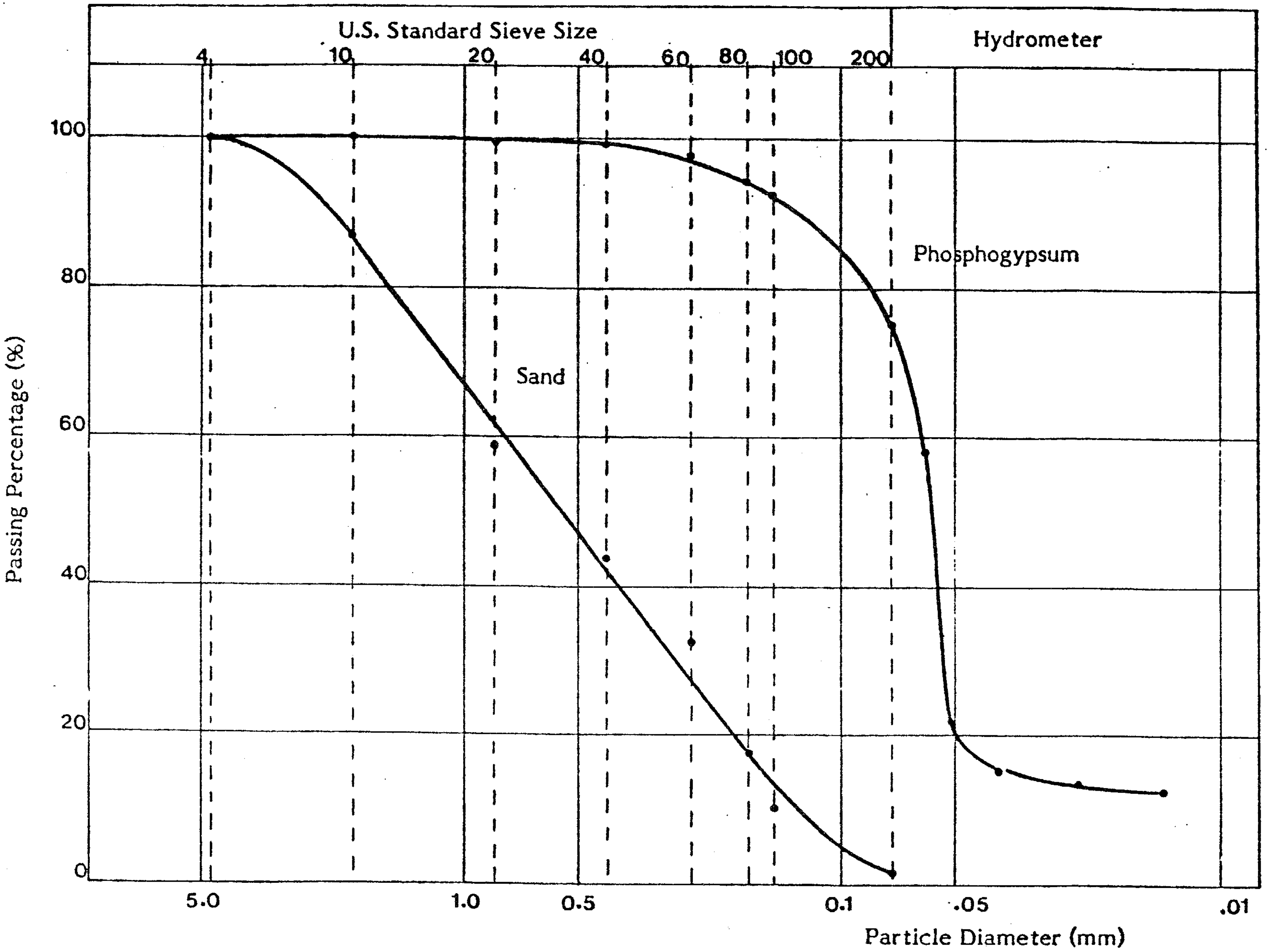
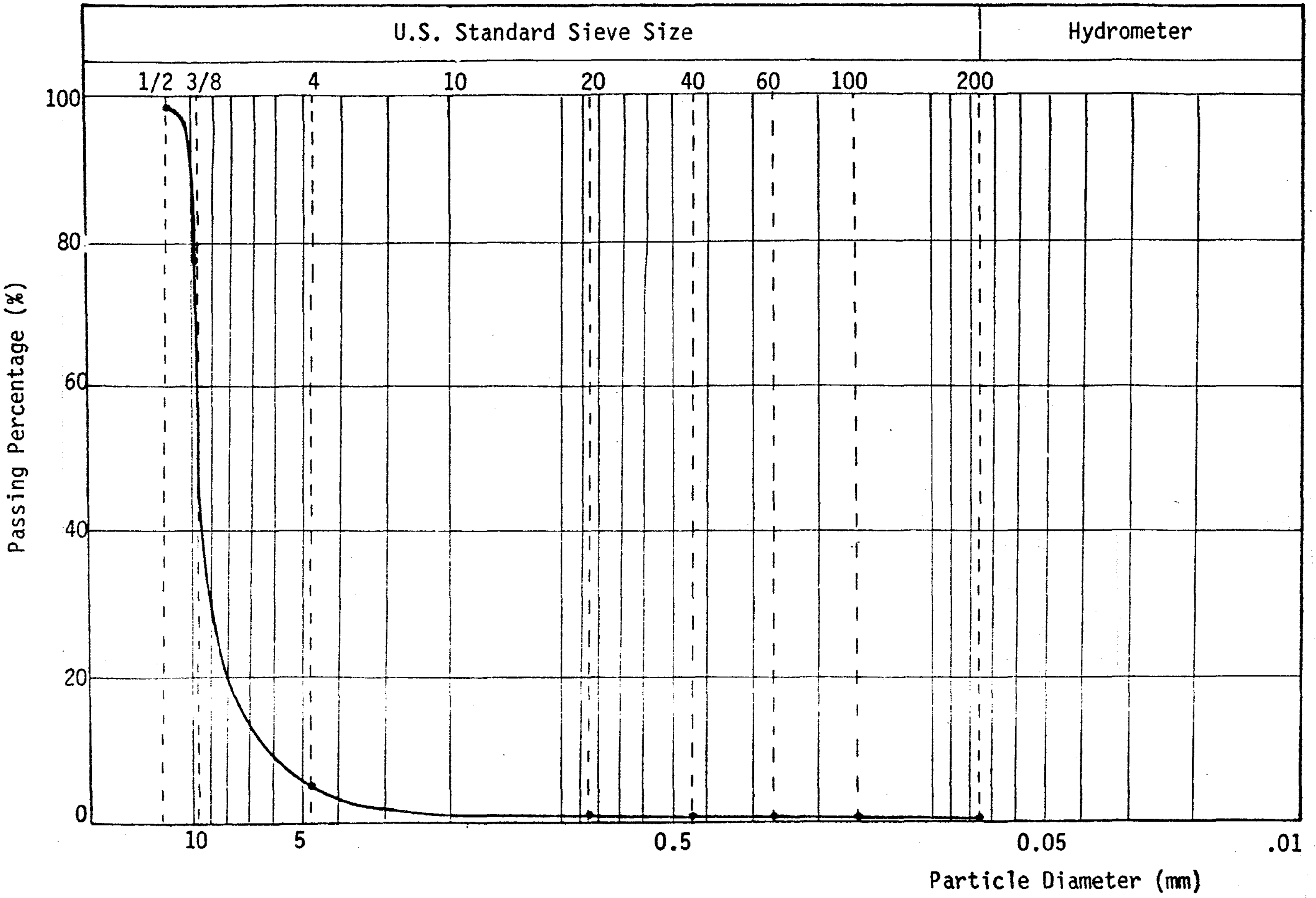


Figure 2: Gravel Grading



3. SPECIMEN PREPARATION

The dry components of the matrix, in order of cement, limerock sand and dihydrate phosphogypsum, were first mixed in a conventional pan mixer for a period of ten minutes; then, the appropriate amount of water was added. Finally the adequate amount of pea gravel was placed in the mixer till a homogeneous mix was obtained. The amount of water used in all samples herein presented corresponds to the optimum moisture content which is referred to as a quantity of water that yeilds to maximum dry density for the given compacted energy and mix proportion.

Cylindrical specimens two inches (51 mm) in diameter and four inches (102 mm) in length were used in the evaluation of compression and split-tension capacity. The standard size beam of 2x2x7 inches (51x51x178 mm) were utilized exclusively for flexural testing. All specimens were compacted using impact compactor where the energy input, number of blows and layers, was adopted in accordance with the Modified and Standard Proctor compaction methods.

After compaction, all samples were wrapped in plastic sheet and cured at room temperature (77-F, R.H.60%) for different curing time (sealed curing condition). All specimens were tested immediately after the removal of the plastic covering membrane, unless otherwise stated (sealed at testing).

4. EXPERIMENTAL RESULTS

4.1. Moisture-Density Curve It was necessary to evaluate the moisture-density relationship, since all mix designs throughout this experimental program were to be compacted nearly at their corresponding optimum water content. Figure 3 presents the dry density as a function of free water content for two different mix proportions. The small changes in magnitude of dry density indicate that compacted phosphogypsum-based concrete is less sensitive to optimum moisture content as that of conventional concrete is to water-cement ratio.

The required nominal optimum moisture content for two classes of mix proportion, 20% and 40% of gravel content, is shown in Figure 4 as a function of sand content. The increase in sand content decreases the moisture requirement (from 17.5% to 10.5 percent for 20% gravel content and from 14.25 to 9.65 percent for 40% gravel content respectively). The cement percentage does not significantly affect the value of optimum water content (average reduction of 0.5% when phosphogypsum is replaced by cement from 5 to 25% by weight).

4.2. Compression and Splitting Tension Strength: A nearly 140 mix proportions, divided into four classes

Figure 3: Moisture-Density Relationship (Modified Proctor)

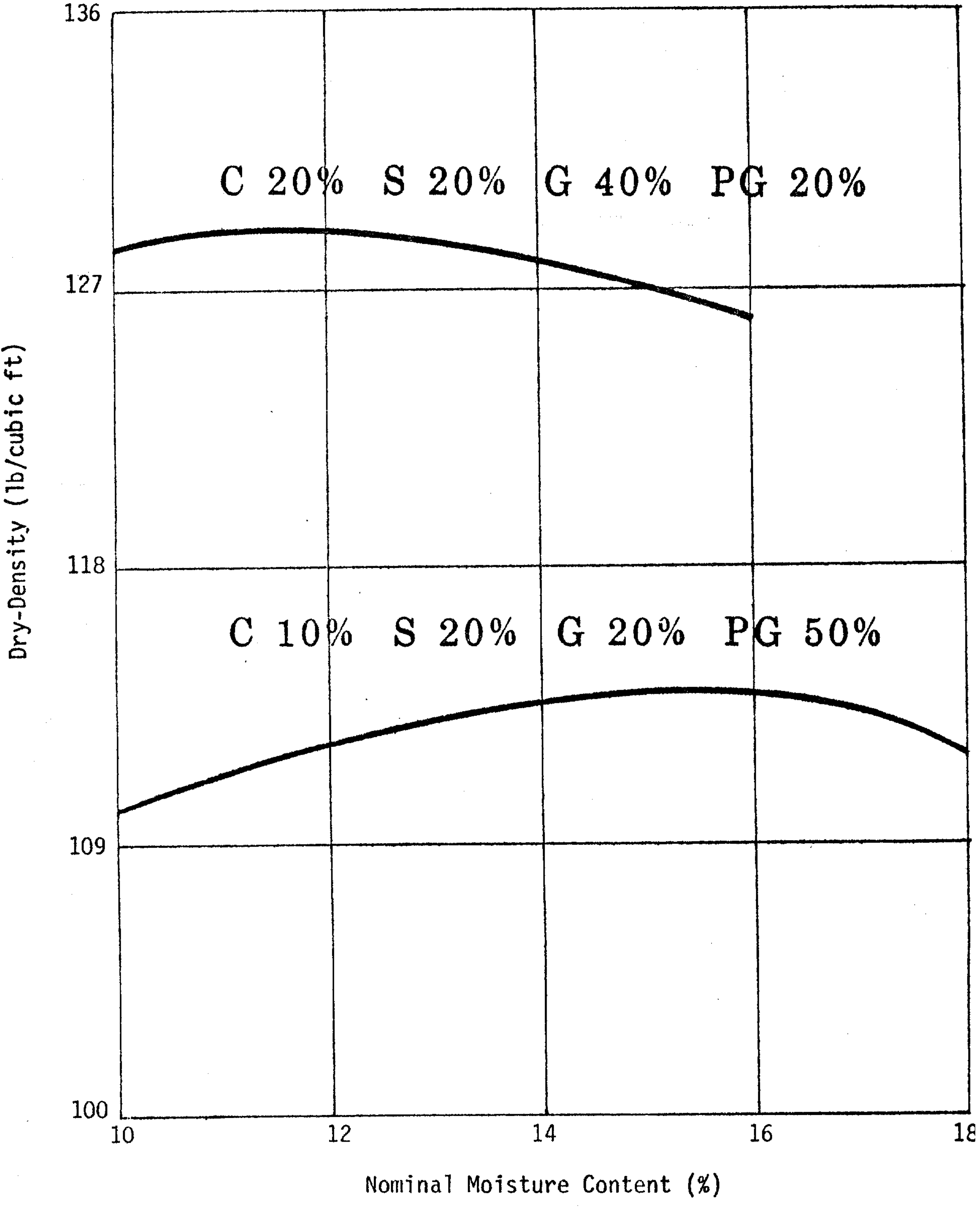
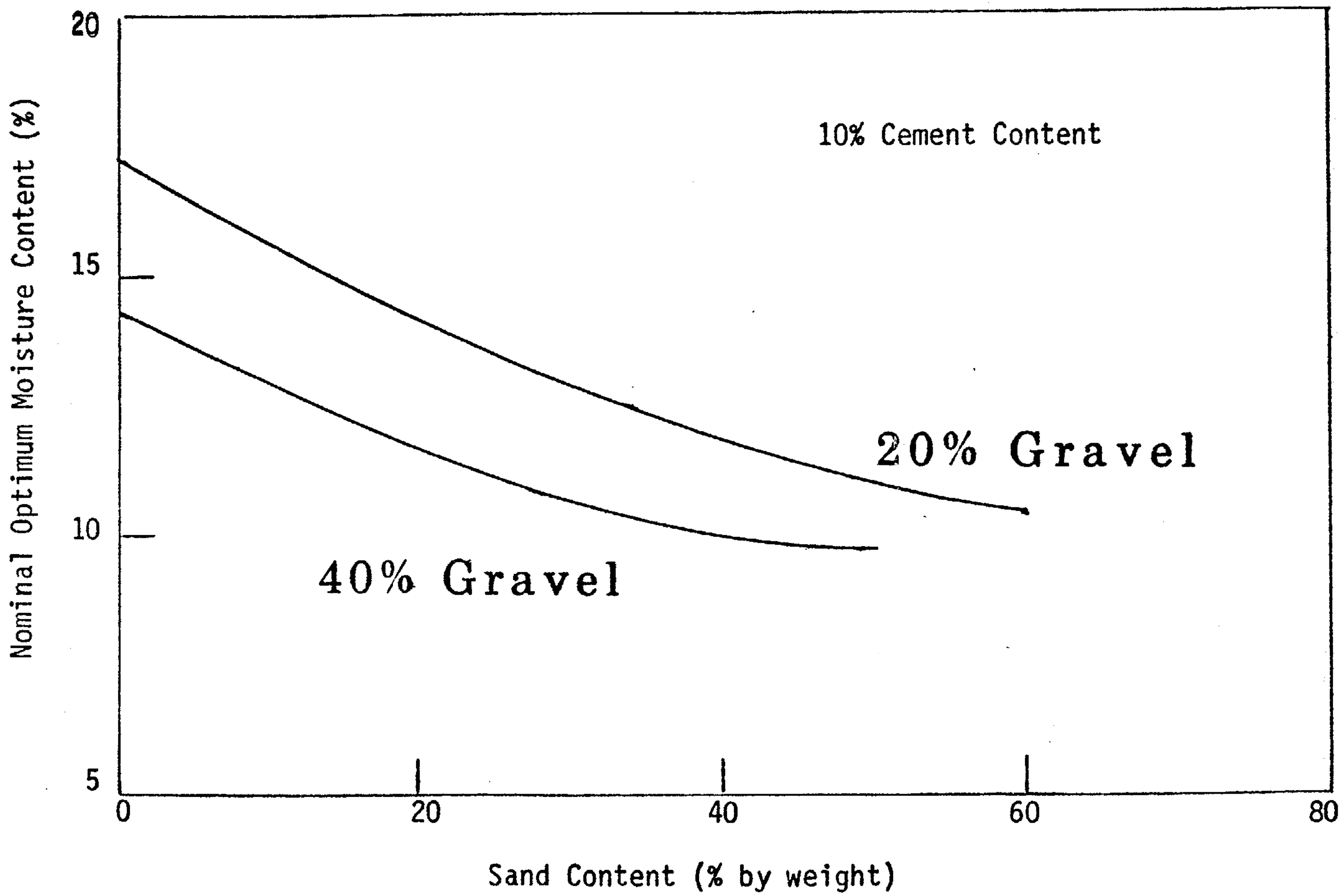


Figure 4: Optimum Moisture Content vs. Sand Content
(Modified Proctor)



of mixtures with gravel content varying from 10 to 40% by weight, were used in investigation of compressive and splitting tension capacity of phosphogypsum-based concrete. All cylindrical specimens were compacted using Modified Proctor compaction energy and tested at seven and twenty-eight days after their fabrication.

Figures 5 and 6 present the 28-day compressive strength (sealed at testing) as a function of sand percentage for the mixtures of 20% and 40% gravel content respectively . Both figures contain five groups of portland cement type I varying from 5 to 25% by weight. It can be seen that, as the cement content increases the compressive strength increases. It is also noticed, as phosphogypsum is replaced by sand , compressive strength continuously increases for the mixtures having cement content of 15% or more, whereas a peak value is reached for cement content of 10% or less. It is therefore concluded that the combined effects of impact compaction and binding resistance of phosphogypsum is only significant in the mixtures of low cement content. Furthermore for the same low cement mixtures, the use of only limited amount of phosphogypsum is beneficial for strength characteristics of phosphogypsum-based concrete.

Similar trends were observed for the case of split-resistant evaluation. Figure 7 presents the indirect tension strength as a function of sand content for the

Figure 5: 28- Day Compressive Strength vs. Sand Content
(Sealed Curing, Sealed at Testing)

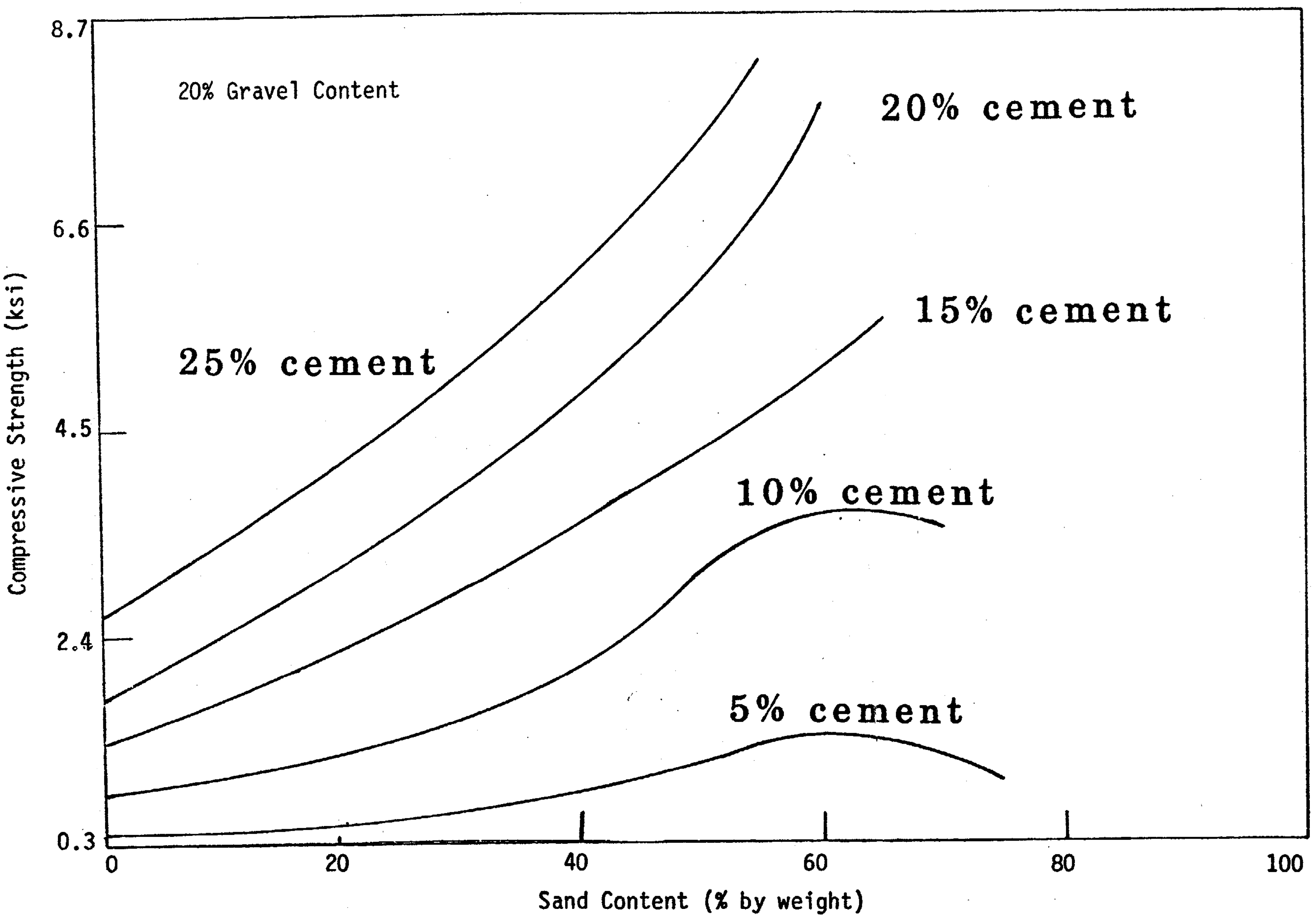


Figure 6: 28-Day Compressive Strength vs. Sand Content
(sealed Curing, Sealed at Testing)

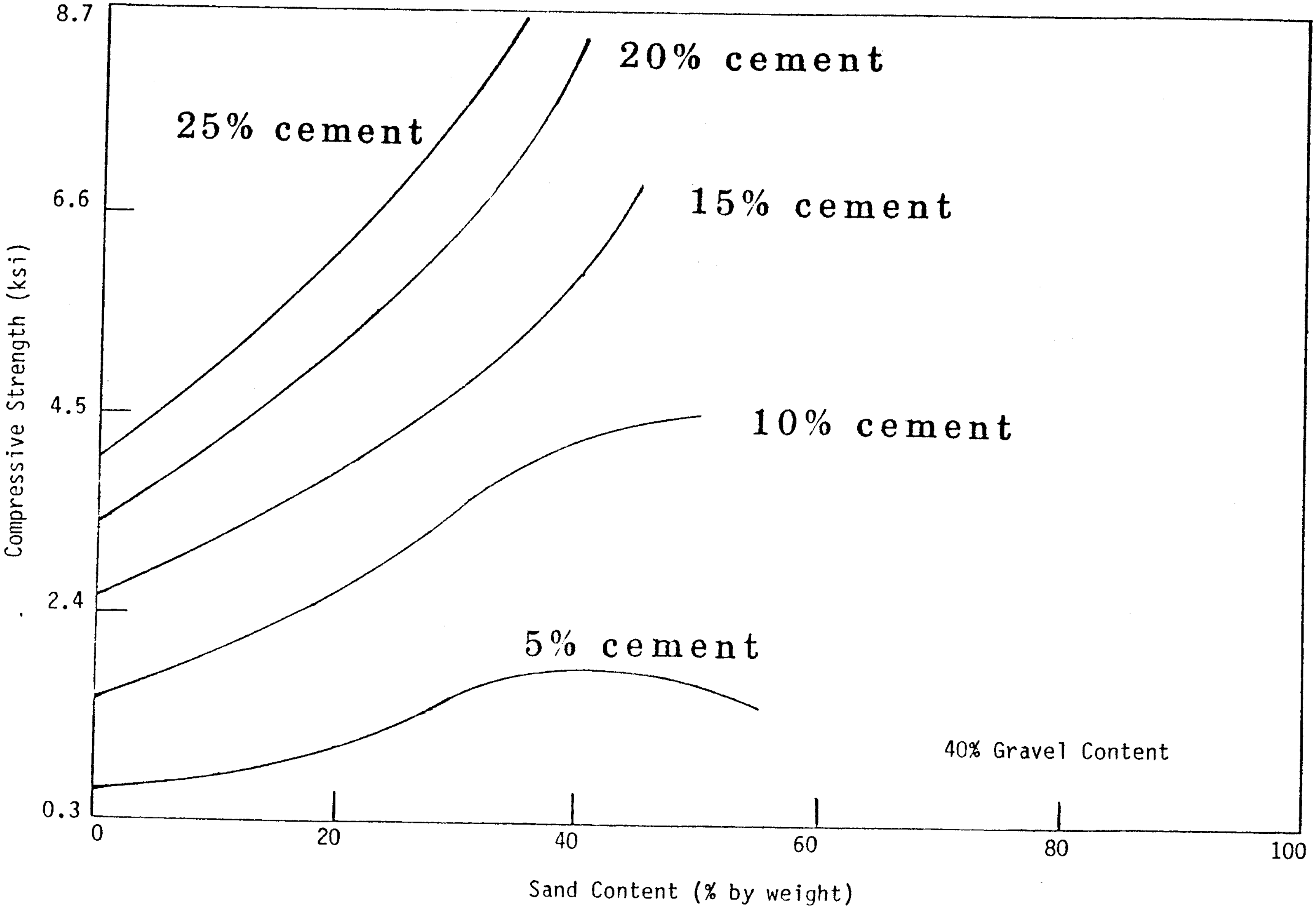
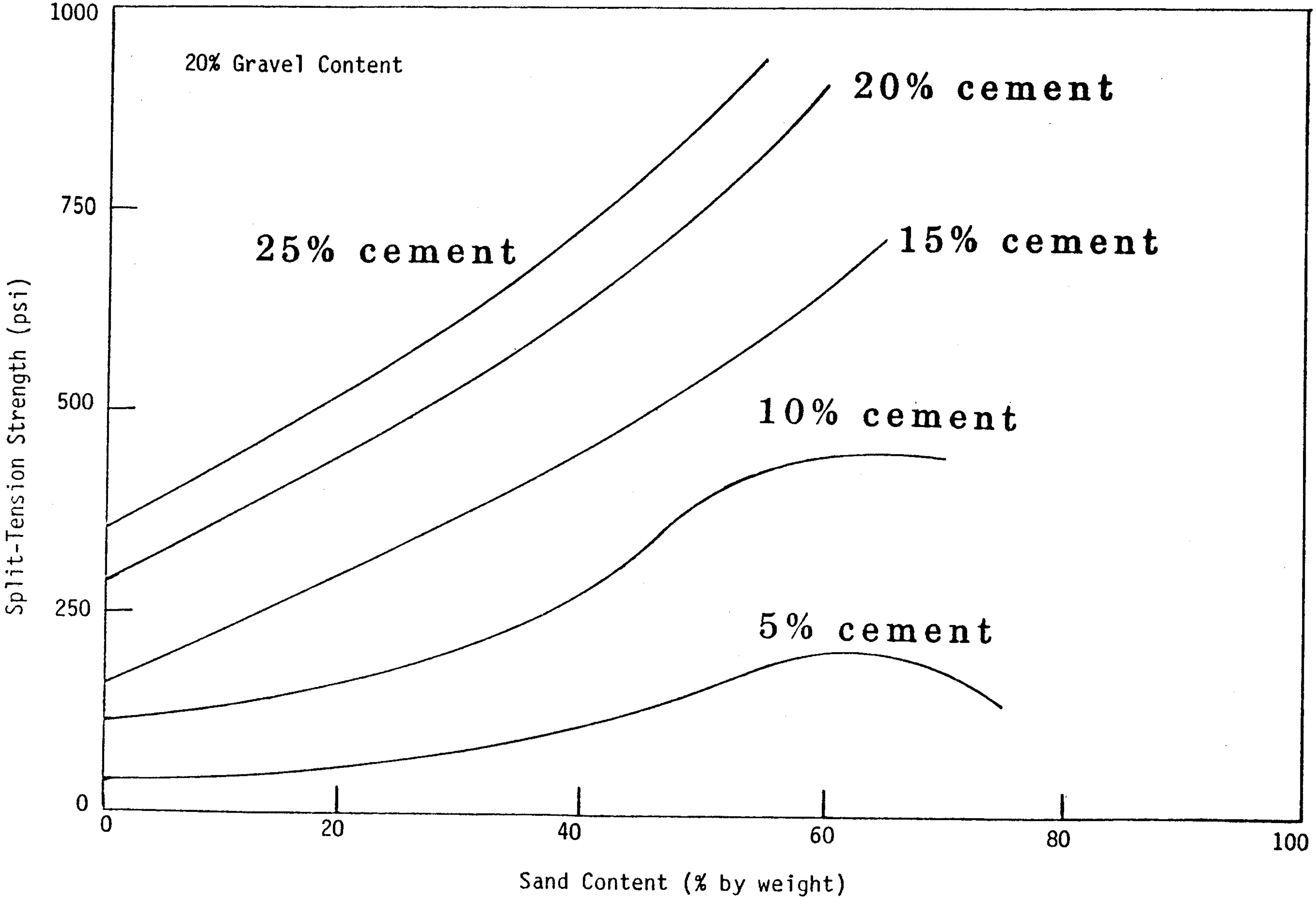


Figure 7: 28-Day Split-Tensile Strength vs. Sand Content
(Sealed Curing, Sealed Testing)



mixtures containing twenty percent gravel.

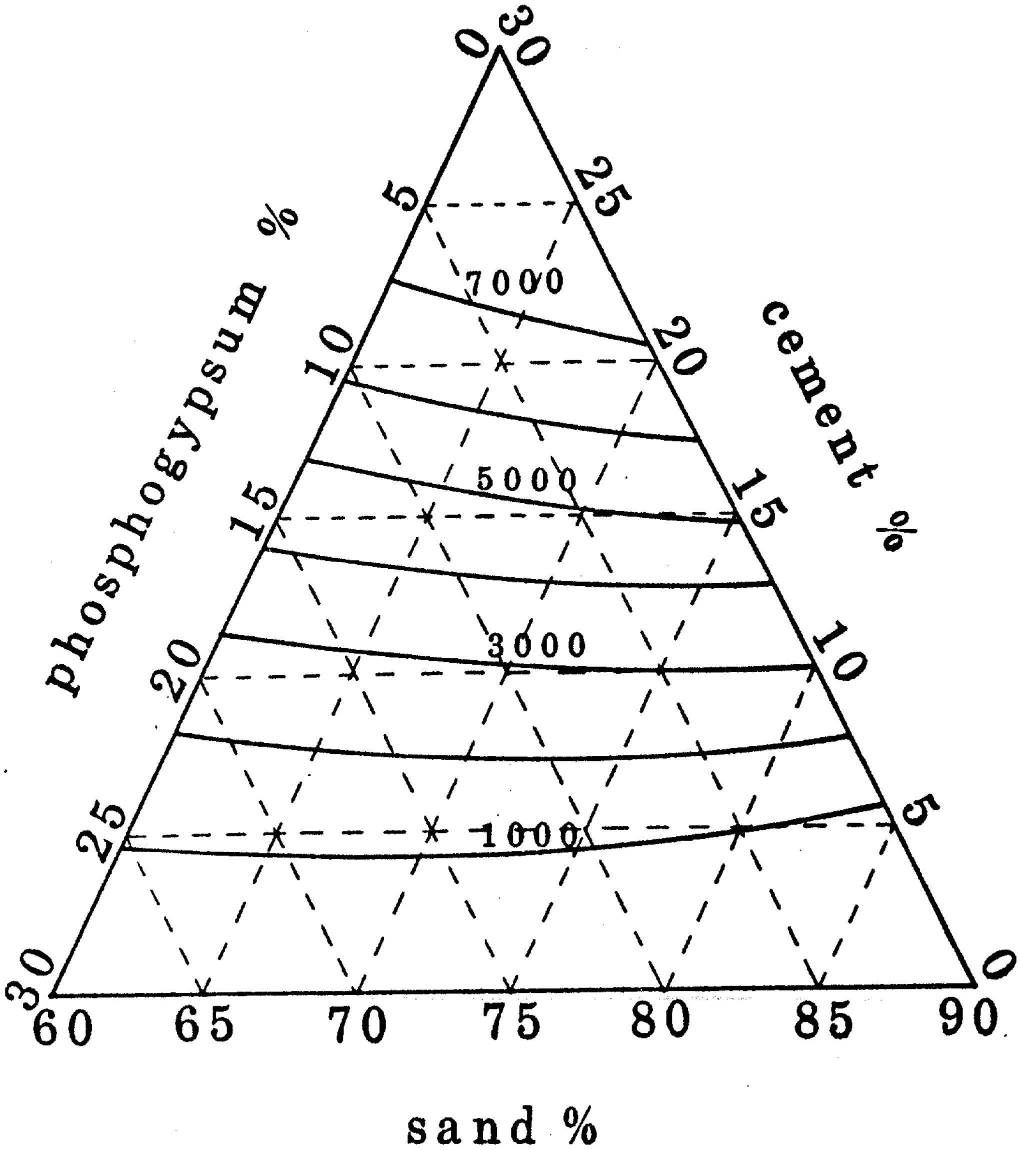
Figures 8 and 9 illustrate the 28-day sealed compressive strength as a function of mix proportions by means of contour lines for the mixtures of low (10%) and high (40%) gravel content respectively .

4.3. Strength Development and Effect of Curing:

Temperature, time and moisture are the important parameters that control the curing condition and strength development of cement- based mixtures. Figure 10 presents the compressive strength as a function of testing age for the mixtures having 20% gravel content. As it is observed, the strength development with time of compacted phosphogysum-based concrete is similar to those of conventional concrete. The range of the 7-day to 28-day compressive strength ratio lies between 0.55 and 0.79 which is similar to that of conventional concrete.

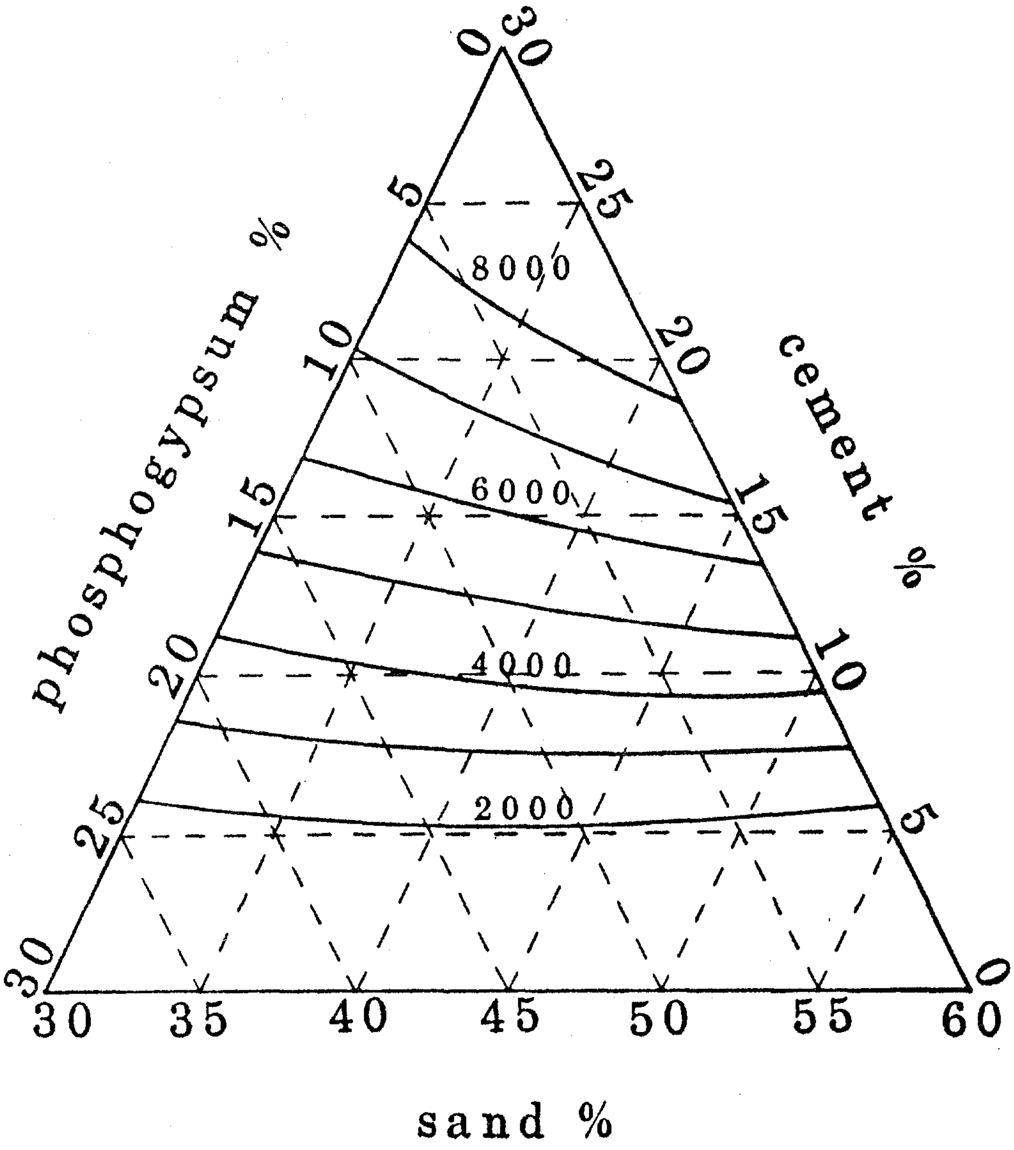
Figure 11 illustrates the soaked compressive strength as a function of sand content for two types of curing conditions (sealed and wet). All cylindrical specimens were cured for four weeks and then submerged in water for a period of two days prior to testing. It is concluded that both curing types have equivalent effect on the development of strength. It is also important to notice that sealed curing condition preserve enough water to fully develop the hydration

Figure 8:
28-Day Compressive Strength of Phosphogypsum-based Concrete Mixture Containing 10% Gravel Content (Modified Proctor, Sealed Curing, Sealed at Testing)



Note: Strength in psi

Figure 9:
28-Day Compressive Strength of Phosphogypsum-based Concrete Mixtures Containing 40% Gravel Content (Modified Proctor, Sealed Curing, Sealed at Testing)



Note: Strength in psi

Figure 10: Compressive Strength vs. Testing Age
(Sealed Curing, Sealed at Testing)

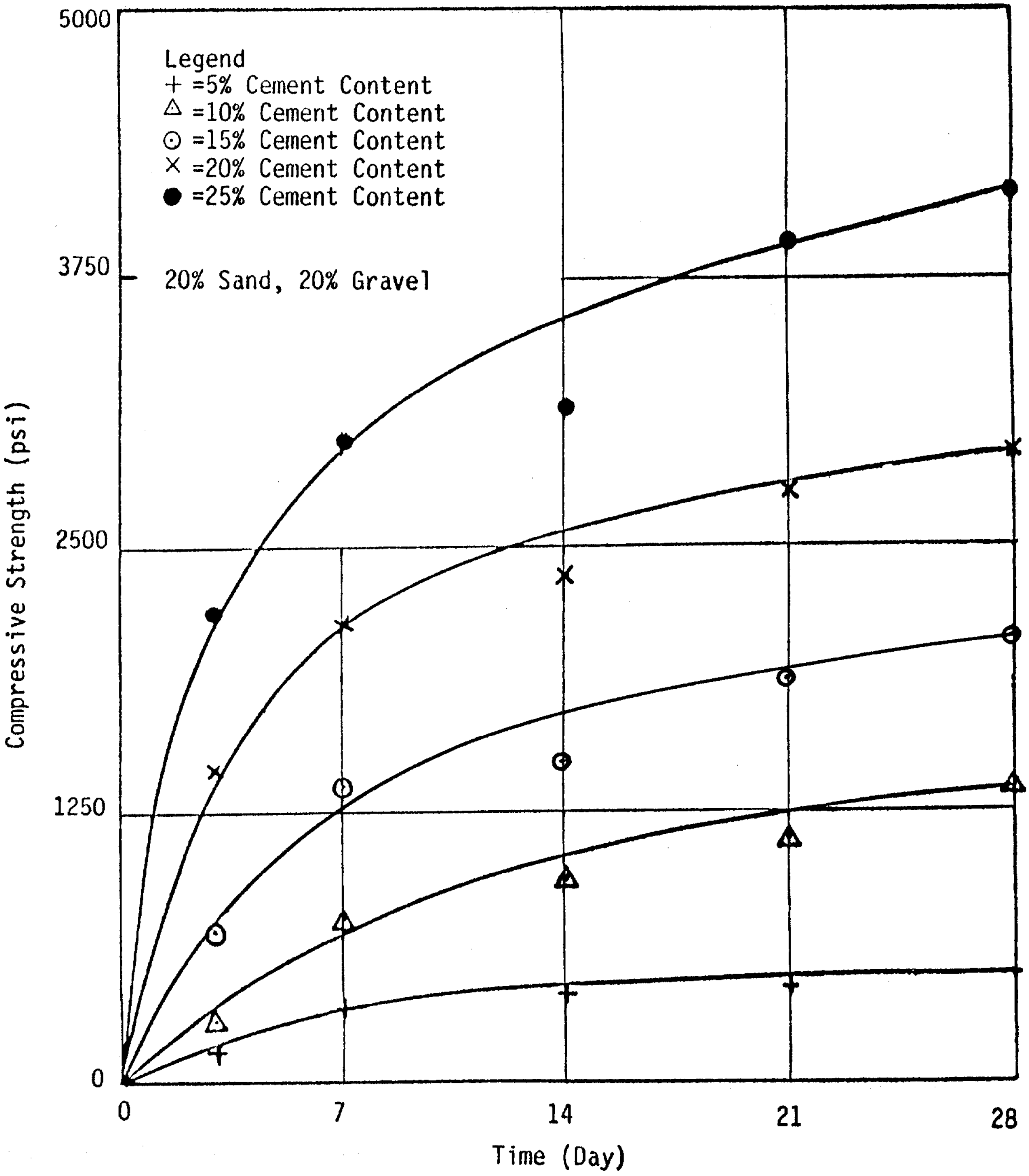
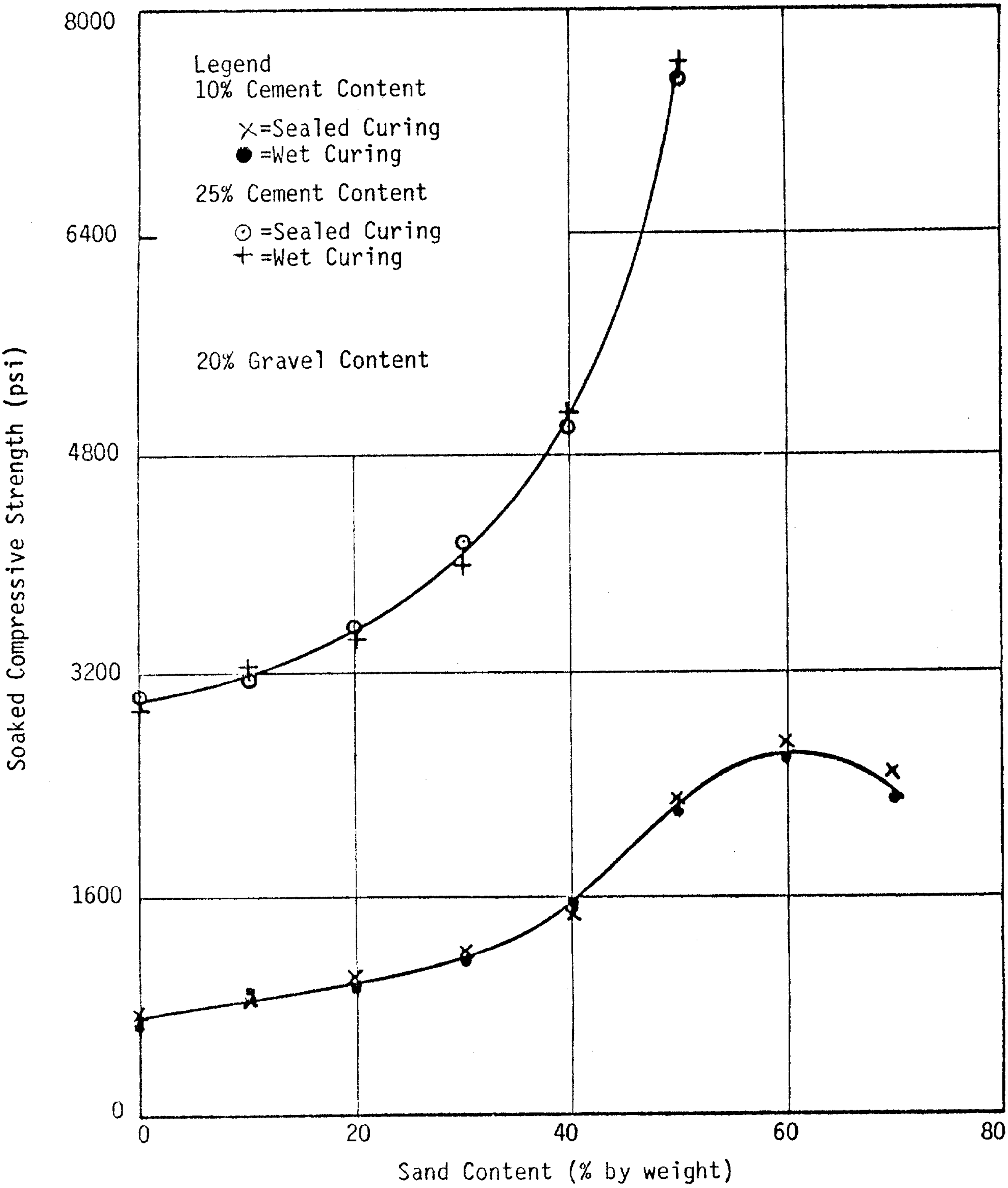


Figure 11: Compressive Strength vs. Sand Content
(Modified Proctor, Soaked at Testing)



process in phosphogypsum-based concrete mixtures.

4.4 Effect of Moisture Content at the time of Testing: Previous studies have suggested that phosphogypsum-based mixtures are highly influenced by the degree of moisture content at the time of testing (1,2). The following testing conditions were adopted during this investigation:

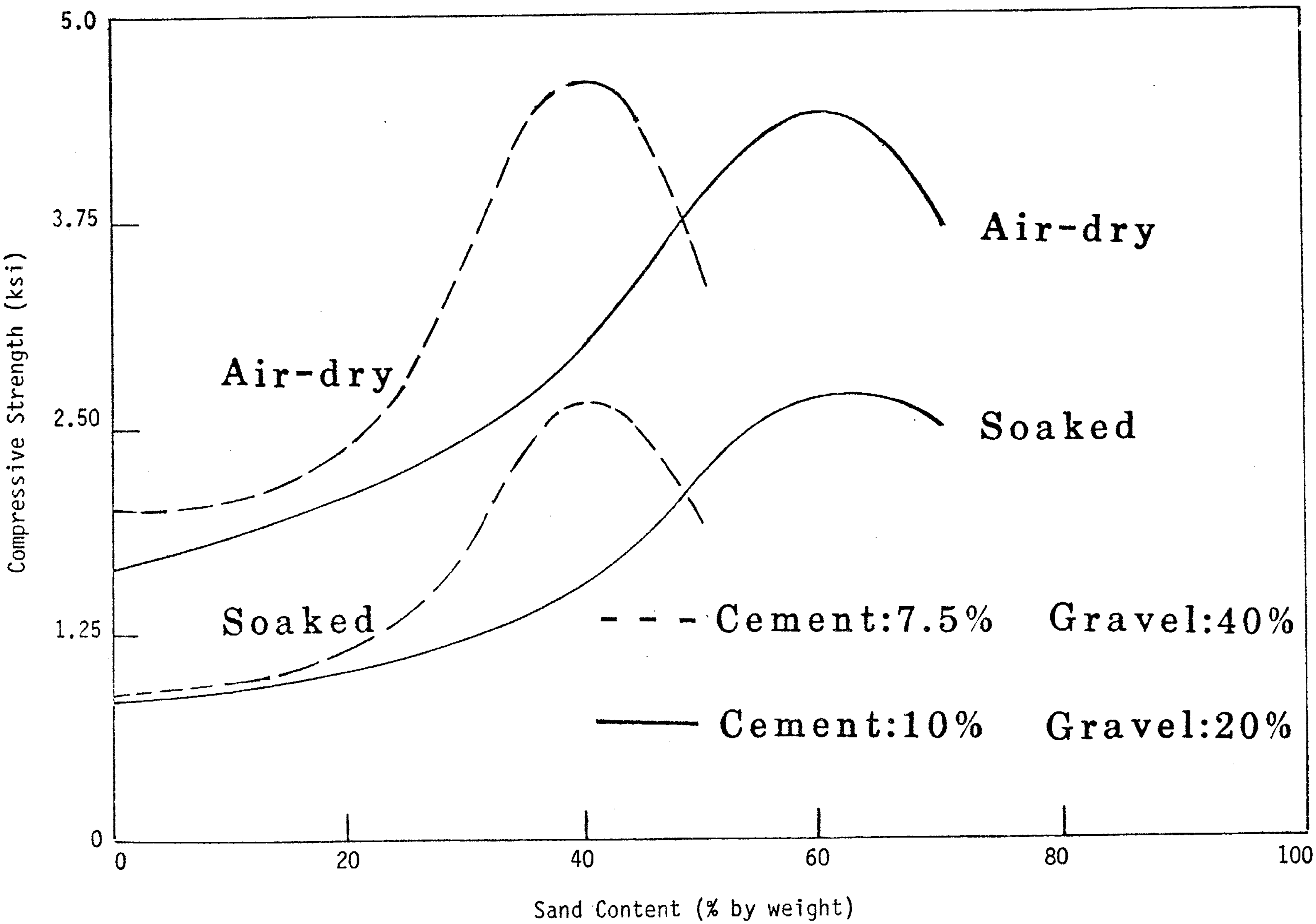
1) Sealed: this condition indicates that the sample was tested immediately after removal of curing plastic sheet. The moisture in the sample after 28-day sealed curing was approximately 2 to 2.5% lower than mixing moisture content at the time of compaction.

2) Soaked: this condition indicates that specimen was submerged in water for a period of two days after removal from the curing environment (sealed or humidity room).

3) Air-dry: this condition indicates that after proper curing period, the specimens were maintained inside the laboratory (77 F, R. H. 60%) for a period of five days prior to testing. The moisture content remained in samples were below 3% at the time of testing.

Figure 12 illustrates the effect of moisture at

Figure 12: 28-Day Compressive Strength vs. Sand Content
(Modified Proctor, Sealed Curing)

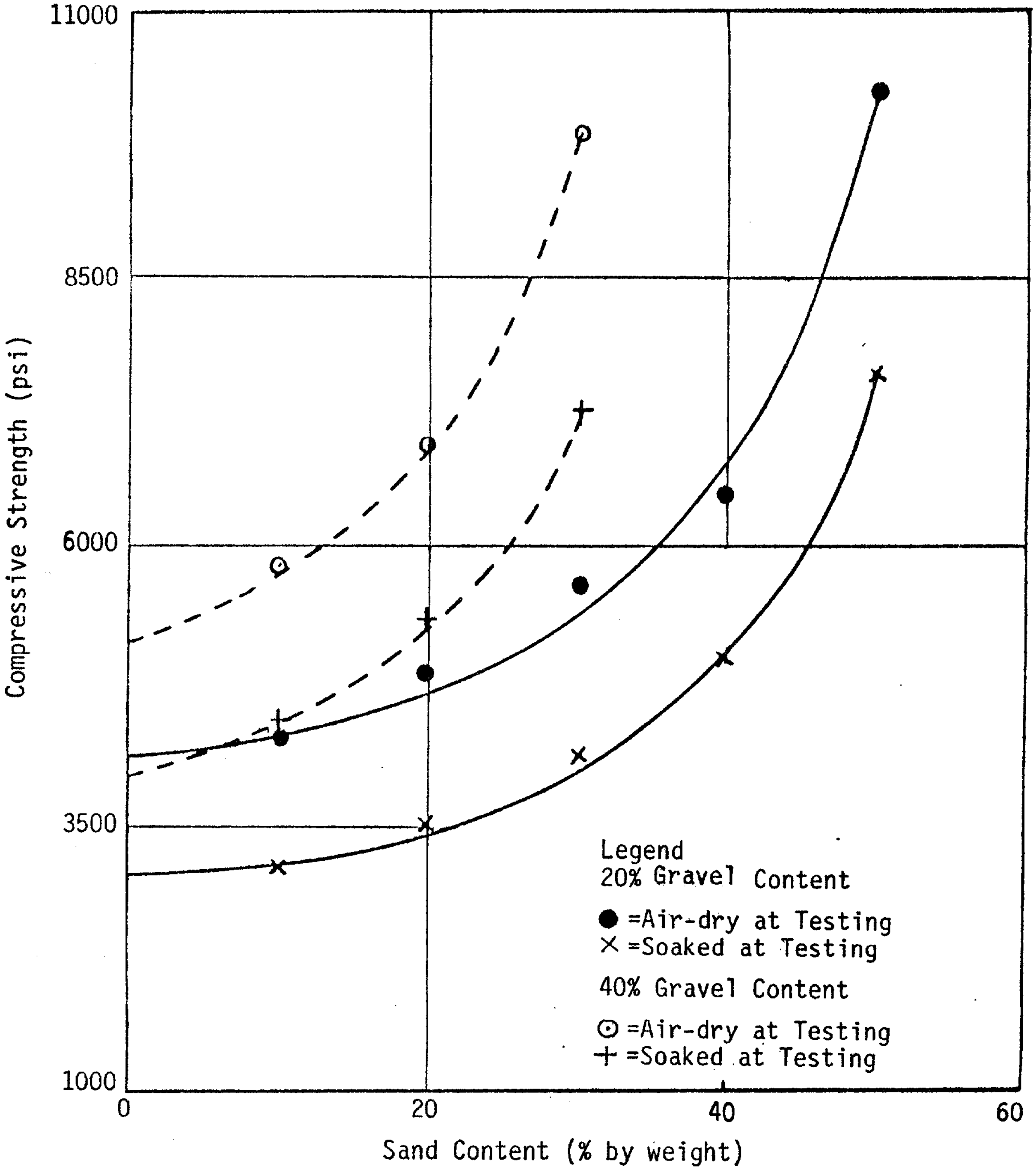


time of testing for the mixtures having 7.5 and 10% cement content. The results in all selected proportions indicate that the concrete mixtures containing phosphogypsum exhibit the higher compressive capacity in air-dry as opposed to soaked testing condition. In addition, as phosphogypsum is replaced by limerock sand, the percent difference in compressive strength of air-dry condition over the equivalent soaked condition reduces. This reduction ranges from 112 to 49% and 142 to 71% for the mixtures of 20% and 40% of gravel content respectively.

Figure 13 presents the evaluation of moisture at the time of testing for the phosphogypsum concrete mixtures containing high cement content (25%). A fairly constant percent difference in compressive strength between the specimens of two moisture content levels is noticed (30 to 38% for the mixture of twenty percent gravel content and 29 to 36% for the design proportions containing fourty percent gravel content by weight). The foregoing results indicate that besides the quantities of phosphogypsum, the percentage of the cement content in the mixtures is also an influential element in evaluation of strength properties under different environmental conditions.

4.5 Effect of Compaction Energy: It is expected that due to the fineness of phosphogypsum particles, the

Figure 13: 28-Day Compressive Strength vs. Sand Content
(Sealed Curing, 25% Cement Content)



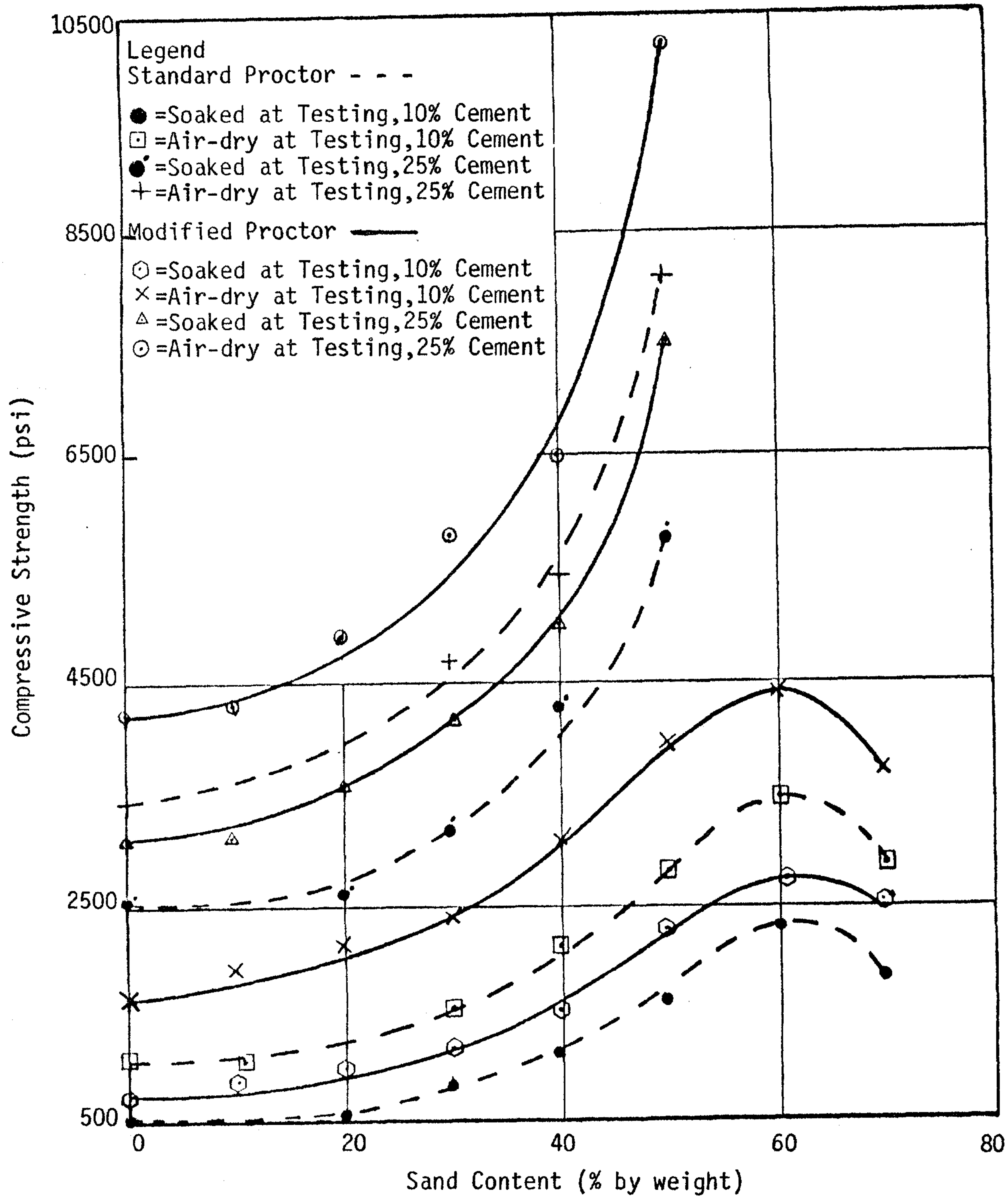
strength capacity of final product increases as compaction energy increases. Figure 14 illustrates the 28-day compressive strength as a function of sand for the tested specimens which were compacted in accordance with the Standard and Modified Proctor specifications. As expected, the compressive strength increases with higher compaction energy for both low and high cement content mixtures. In addition, from obtained results , it is clearly evident that the mixtures with higher percentage of phosphogypsum are more susceptable to applied impact energy. This finding is particularly significant in the mixtures of low cement content. For example, using 10% of cement, the percentage difference in compressive strength between two energy levels is increased from 26% to 82% in air-dry condition and 15 to 87% in soaked testing condition, whereas in the mixtures containing 25% cement content, the percentage difference in compressive strength varied from 21% to 39% and 17% to 30% for air-dry and soaked testing conditions respectively.

5. CONCLUSION

The following conclusions can be drawn based on the results of this investigation:

1) Concrete consolidated by dynamic compaction uses less cement and water as compared to conventional concrete of

Figure 14: 28-Day Compressive Strength vs. Sand Content
(20% Gravel Content, Sealed Curing)



the same strength.

2) Binding resistance contribution of phosphogypsum is significantly effective in the mixtures of low cement content.

3) The strength properties of phosphogypsum-based concrete containing low percentage of cement meet the strutural requirement in applications such as road construction.

4) The strength values of cement mixtures containing high percentage of phosphogypsum are strongly affected by the moisture content at the time of testing.

5) The increased in compaction energy improves the engineering characteristics of phosphogypsum-based concrete.

6) Strength of compacted phosphogypsum concrete mixtures are function of their corresponding optimum moisture content instead of water-cement ratio.

7) Both sealed and wet (100% humidity room) curing conditions have shown similar effect on strength development of phosphogypsum-based concrete.

ACKNOWLEDGEMENT:

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A COMPARATIVE STUDY ON STRENGTH PROPERTIES OF CEMENT MORTARS USING PHOSPHOGYPSUM: HEMIHYDRATE VS DIHYDRATE

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ABSTRACT

Hemihydrate alone shows better engineering properties than dihydrate phosphogypsum under compaction. Research over the past few years has found encouraging results from dihydrate phosphogypsum based cement mortars; the main objective of this paper is to conduct a study on strength properties of hemihydrate phosphogypsum, type I portland cement, and fine aggregate (crushed limerock) mixtures.

Cylindrical specimens prepared by both the impact (Modified Proctor) and static compaction methods were tested under air dry, sealed, and soaked conditions after 28 days of sealed curing. Comparative studies were based on:

a) effect of mix proportion on strength (lab impact compaction), and
b) effect of applied pressure on strength (lab static compaction).

According to test results, two important aspects of strength behavior of hemihydrate phosphogypsum based cement mortars were observed. First, utilization of hemihydrate produces higher strength than using dihydrate phosphogypsum. Second, with 7.5% cement content, the inclusion of hemihydrate in combination with fine aggregate results in higher strength values than when fine aggregate alone is being used. Cement mortars containing 40-60% hemihydrate and 7.5% cement achieve compressive strengths around 4000 psi under air dry conditions.

INTRODUCTION

Under compaction dihydrate phosphogypsum (DPG) possesses good binding properties [1]; also, excellent strength properties have been found when portland cement, along with sand (crushed limerock), is mixed with it and compacted [2]. Compacted hemihydrate phosphogypsum (HPG), on the other hand, exhibits even better strength properties than DPG. Compressive strength as high as 1800 psi was attained for compacted HPG under air dry conditions [3]. The goal of this study is therefore to investigate the strength performance of cement mortars using HPG under compaction, and compare it with mortars using DPG.

To compare the strength properties of cement mortars using HPG and DPG respectively, two different sample preparation techniques to achieve compaction were applied: laboratory impact compaction (Modified Proctor) and laboratory static compaction. Cylindrical specimens sized 2 in. by 4 in. were prepared. Under the impact compaction both mortars show excellent strength properties for the low cement content utilization, although in general HPG based mortars possess better strength than DPG based mortars. Under the static compaction consistent and sizable strength gain was obtained for both mortars as the applied static pressure was continuously increased; this excellent property reveals the suitability of both mortars for the application of precast building products.

PREPARATION AND TESTING OF SPECIMENS

Test specimens 2 in. in diameter and 4 in. in height were prepared for the two compaction approaches: laboratory impact and laboratory static compaction. Selected proportions of portland cement type I, phosphogypsum (HPG or DPG) , and sand were investigated for each compaction approach. A pan mixer with a grinding roller was used for the mixing of materials. The existence of the grinding roller eliminated the particle lumps of DPG and HPG; however, due to the large size and hardness of some of the HPG lumps, extra effort had to be applied to break these lumps so that a uniform mixing could be obtained. Compacted specimens were cured under sealed conditions and tested under air dry, sealed, and soaked conditions (For definitions of these conditions see [2]).

LABORATORY IMPACT COMPACTION

The Modified Proctor procedure was employed for the preparation of test specimens. Compressive strengths of mortars having two cement contents (7.5% and 25% by weight) and varying proportions of HPG and sand are presented. In addition, strengths of these mortars are compared with those of DPG based cement mortars.

Strength of HPG Based Cement Mortars

The strength characteristic of HPG based cement mortars differs as the cement content varies. To illustrate the difference, strength results of mortars with two cement contents are presented. Figure 1 is a plot of the 28-day compressive strength of HPG based cement mortars as a function of the sand content, for a given cement content of 7.5%, under air dry, sealed, and soaked testing conditions. It can be observed that under the air dry conditions a peak strength approximately of 4000 psi exists at a sand content somewhere between 40% and 60% (HPG content 30% to 50%). In addition, the HPG and cement (no sand) mortar possesses somewhat higher strength than the sand and cement (no HPG) mortar. When tested under sealed and soaked conditions (Figure 1), the strength of HPG based cement mortars decreases, implying that the strength is sensitive to moisture conditions.

At a higher cement content (25%), different strength characteristic of HPG based cement mortars is obtained. Figure 2 represents the compressive strength of HPG based mortars using 25% cement with respect to the sand content. Unlike the case of low cement content mortars, the strength of these mortars increases continuously with the sand content in the mixture. The different strength characteristics from mortars with different cement contents (7.5% and 25%) can be reasoned as follows:

When the high percentage of cement (25%) is present, both HPG and sand function as fillers. While the low percentage of cement (7.5%) is used, the strength contribution of HPG as a binder becomes significant. Thus, it is for the low cement content mortars that HPG can be utilized most advantageously.

Comparison with DPG Based Cement Mortars

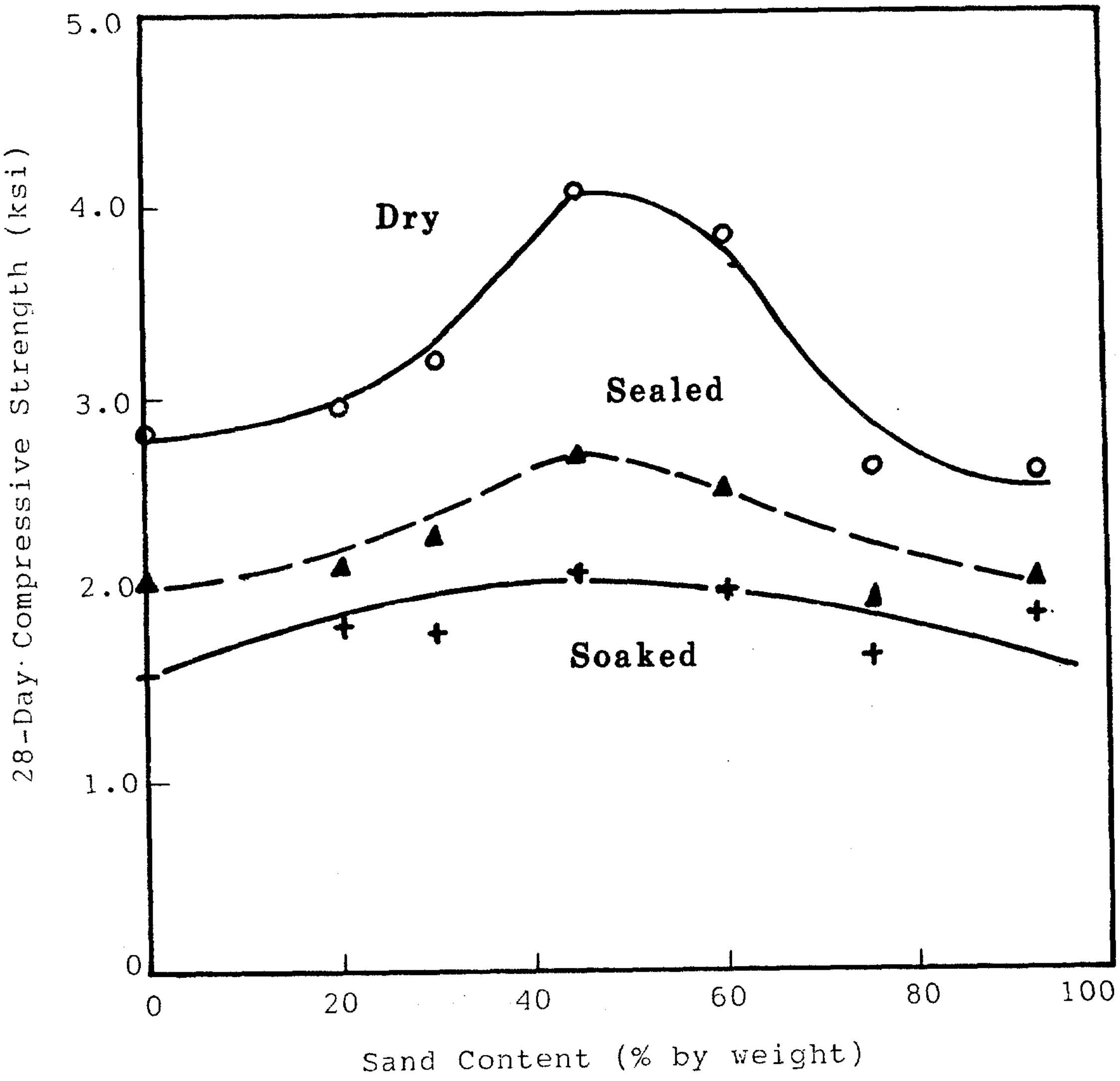

Figure 1. 28-day compressive strength (tested under air dry, sealed, and soaked conditions) of HPG based cement mortars (7.5% cement) as a function of sand content.

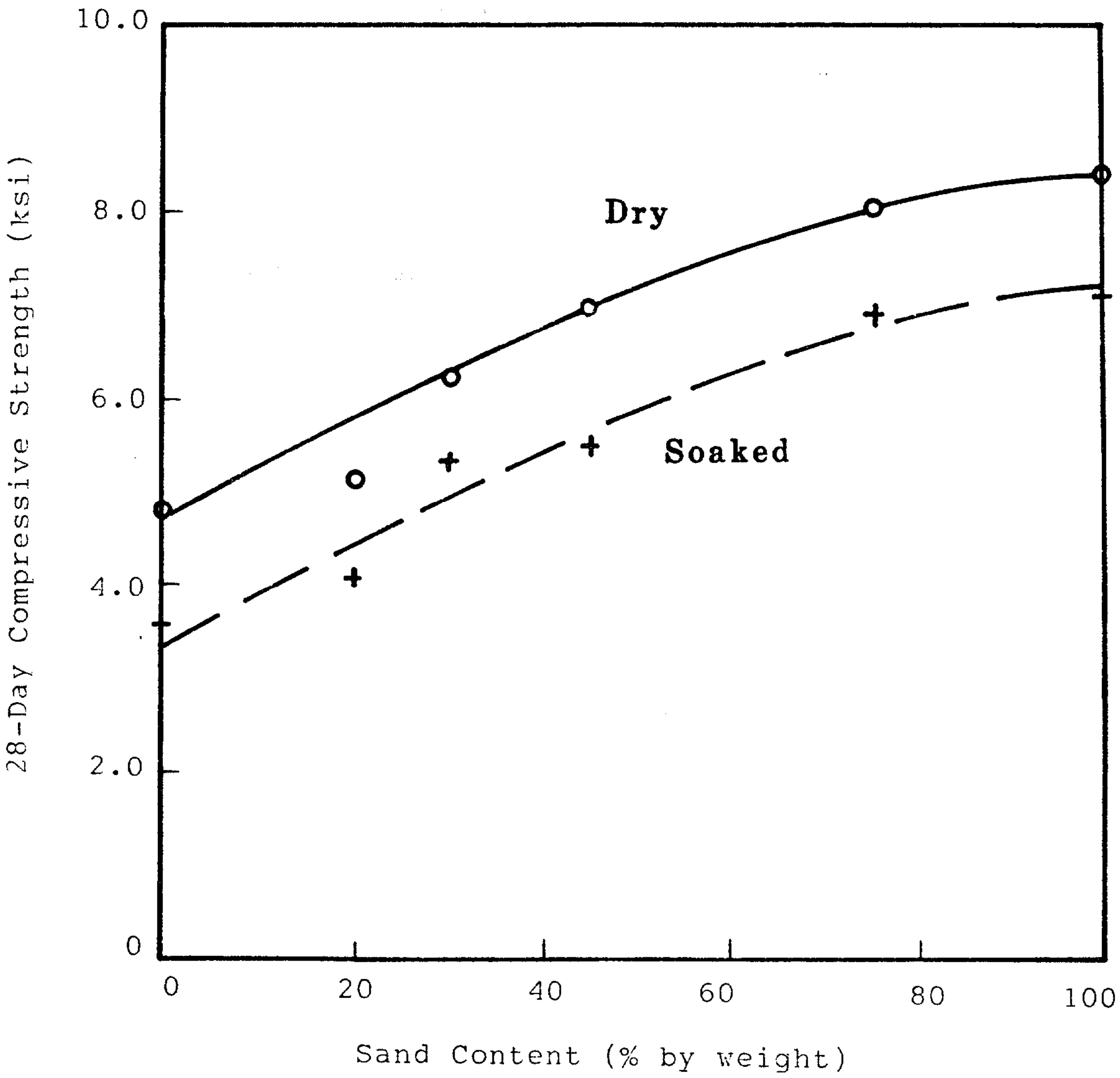

Figure 2. 28-day compressive strength (tested under air dry and soaked conditions) of HPG based cement mortars (25% cement) as a function of sand content.

The strength of DPG based cement mortars under laboratory impact compaction was found adequate for construction applications [2]. The emphasis of this study is therefore put on comparison of the strength parameters between HPG and DPG based cement mortars. Figure 3 compares the strength curves of HPG and DPG based cement mortars in terms of sand content for given percentages of cement content (7.5 and 25%). Although data as presented are based on the air dry testing conditions, similar observations exist for the sealed and soaked conditions. From Figure 3, basically the same trend of strength curves can be observed for both HPG and DPG based cement mortars. It should be noticed, however, that utilization of HPG as compared with DPG increases the compressive strength in general, and shifts the occurrence of the peak strength to a lower sand content (approximately from 75% to 50%) for the case of' 7.5% cement usage. Thus to obtain the optimum strength, more phosphogypsum can be used in HPG based than in DPG based cement mortars.

LABORATORY STATIC COMPACTION

Laboratory static compaction consists of the application of direct pressure at a slow rate (statically) to a matrix confined in a rigid mold. Previous research on DPG based cement mortars has shown that the effectiveness of compaction is enhanced if specimens are compacted in layers [4]. The aim of this study is therefore focused on the effect of the magnitude of applied pressure on strength of specimen. Specimens were compacted in two equal layers at five levels of pressure: 750, 1500, 3000,

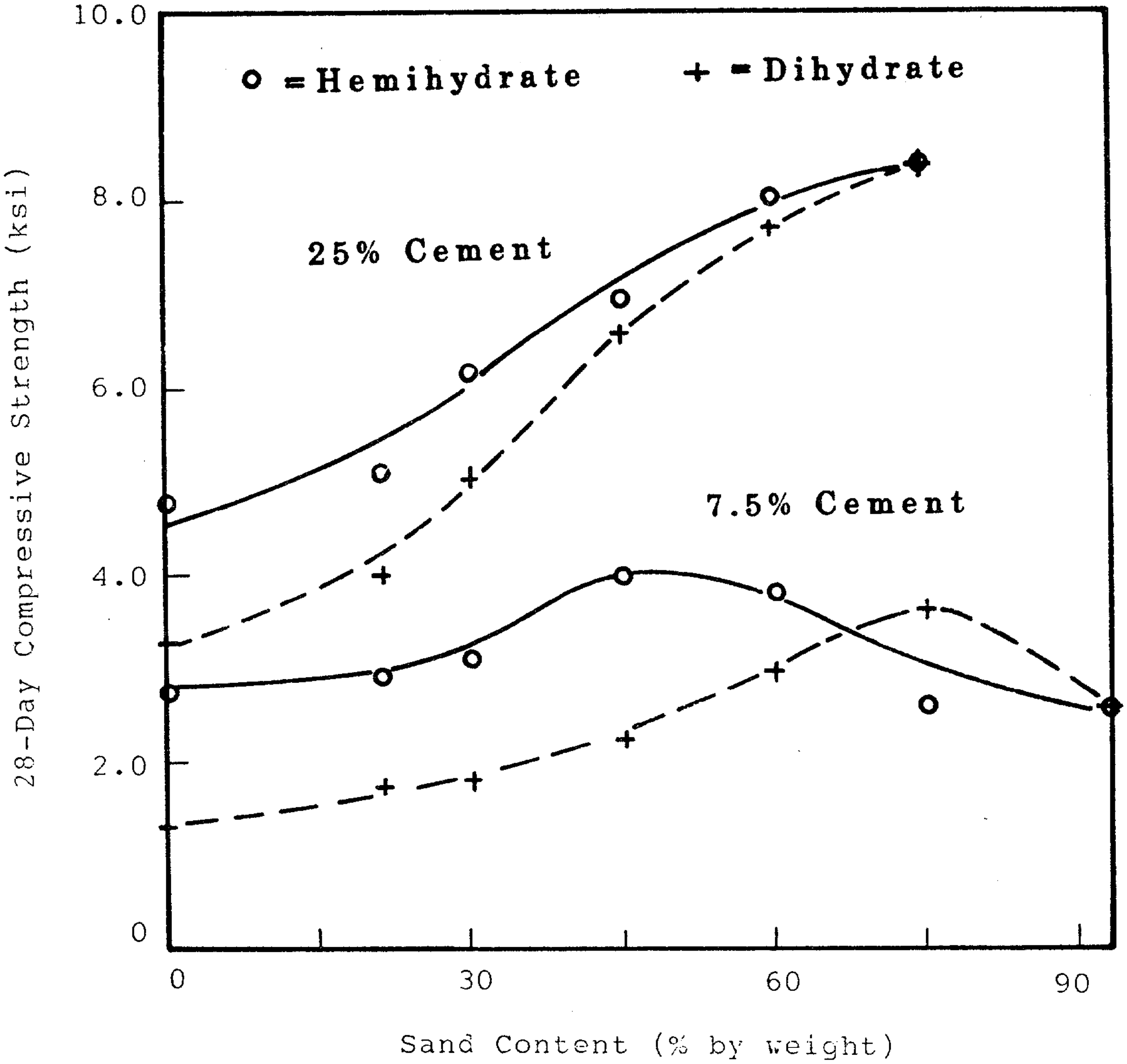

Figure 3. Strength comparisons between HPG and DPG based cement mortars tested under air dry conditions.

6000, and 12000 psi. Experimental data were obtained for cement mortars using HPG sand DPG respectively, and results compared.

Dry density and compressive strength were the parameters to evaluate the effectiveness of compaction. Data shown in Figure 4 for the mortars having 7.5% cement, 45% sand, and 47.5% HPG or DPG, indicate that dry densities of both HPG and DPG based cement mortars Increase as the level of pressure is raised. Although higher densities result for HPG based cement mortars due to the greater specific gravity value of HPG than DPG [3], the same trend of density increase is observed for both HPG and DPG based cement mortars.

In Figure 5, the 28-day compressive strength of mixtures proportioned as mentioned is presented in relation to the applied static pressure. Specimens were tested under both air dry and soaked conditions. Considerable and continuous strength improvement of HPG and DPG based cement mortars is accomplished by increasing the pressure level. This excellent property can be utilized to advantage for the application of precast building products where the supply of great pressure could be managed.

CONCLUSIONS

The compressive strength characteristics of both HPG and DPG based cement mortars have been presented. Based on these strength results, the following conclusions can be drawn:

1. Under the impact compaction, both HPG and DPG based cement

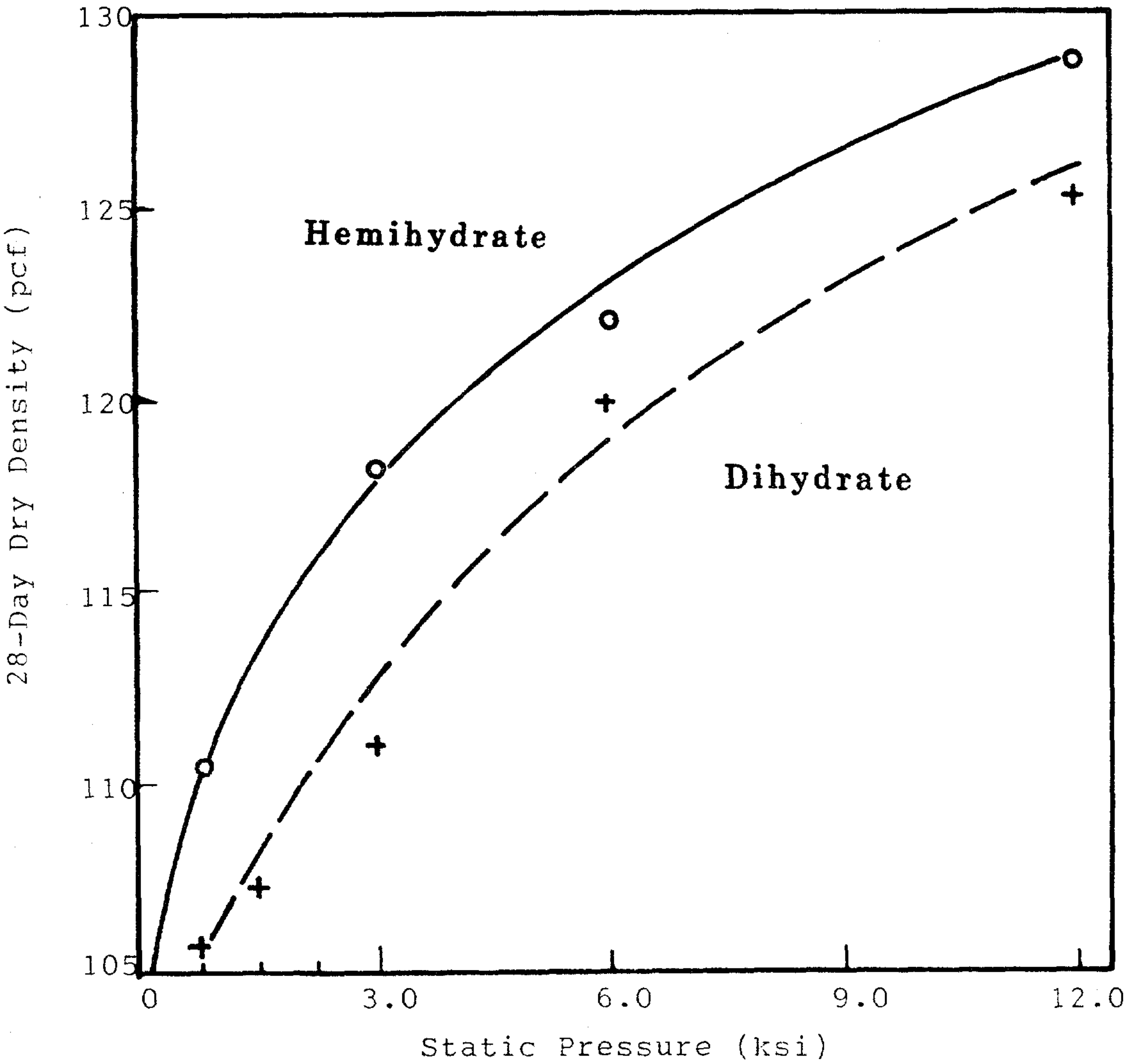

Figure 4. Effect of static compaction pressure on densities of HPG and DPG based cement mortars (7.5% cement: 45% sand: 47.5% phosphogypsum)

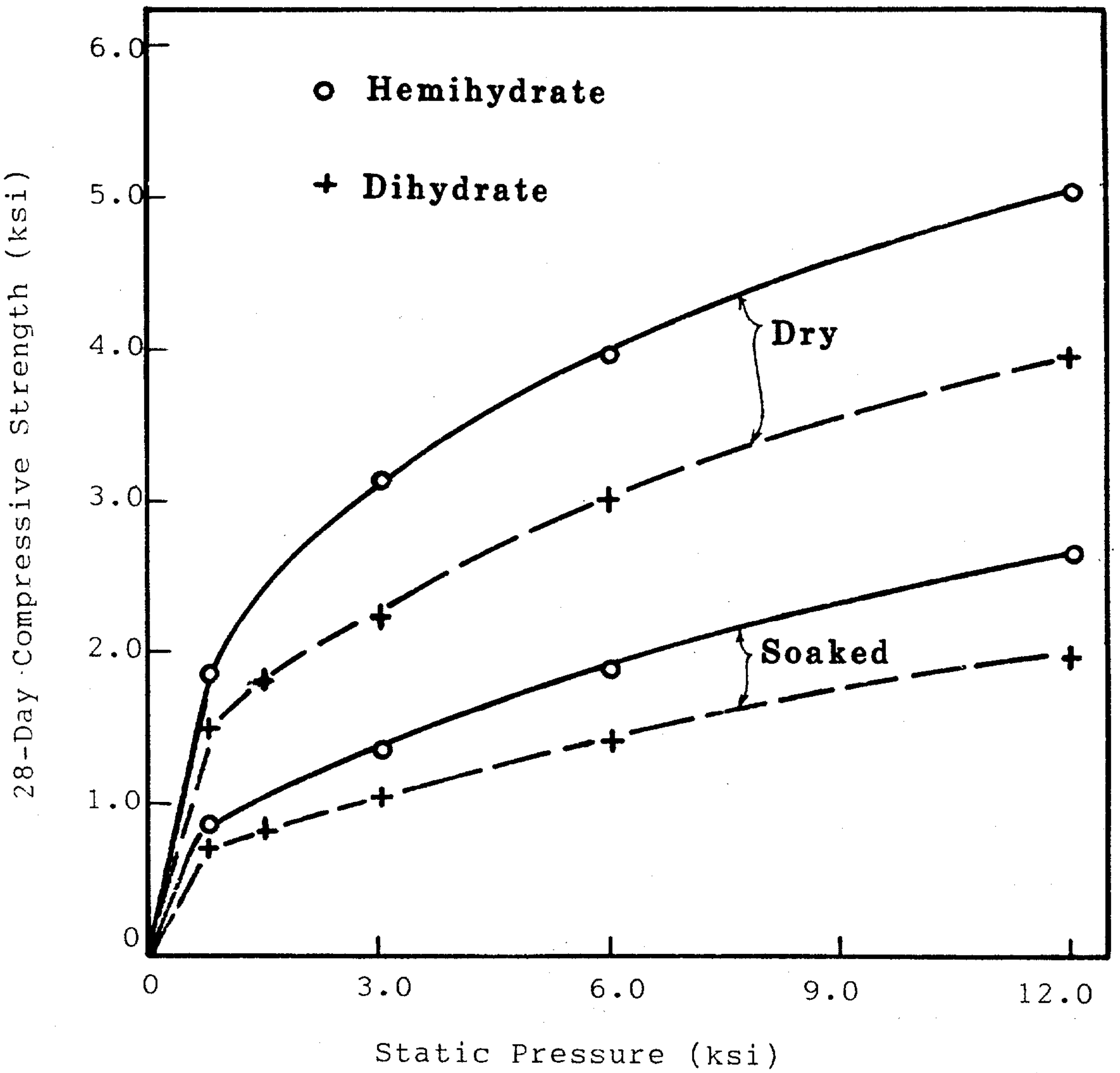

Figure 5. Effect of static compaction pressure on 28-day compressive strength (tested under air dry and soaked conditions) of HPG and DPG based cement mortars (7.5% cement: 45% sand: 47.5% phosphogypsum).

mortars demonstrate excellent strength properties for the low cement application. When using 7.5% cement, both mortars possess optimum strength at different phosphogypsum contents, approximately 40% for HPG and 20% for DPG based cement mortars.

2. Under the static compaction, strength of both mortars increases continuously and considerably with increase in the applied static pressure. This excellent property indicates the suitability and potential of both materials for the application of precast building products.

3. Using low cement content, both. mortars possess. adequate strength for construction applications.

ACKNOWLEDGEMENT

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LABORATORY CONSOLIDATION OF PORTLAND CEMENT-BASED MORTARS CONTAINING PHOSPHOGYPSUM

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ABSTRACT

Laboratory consolidation of portland cement-based mixtures containing dihydrate phosphogypsum and fine aggregate (crushed limerock) can be obtained in at least three different ways: static compaction, impact compaction (Modified Proctor method), and external high-frequency vibration. The objective of this paper is to compare the effectiveness of these three methods based upon the compressive strength criterion. All specimens were cured under sealed conditions and tested at 28 days immediately after the removal of the plastic membrane, or air-dried, or soaked.

Information gathered in this paper makes the user of cementitious mortars containing phosphogypsum aware of the fact that strength characteristics are not only influenced by mix constituents and proportions, but also, and to a great extent, by the selected consolidation technique. In particular, for low cement percentages, phosphogypsum contributes to strength development of the mortar in the case of consolidation by compaction because of its nature and fineness, and also as a consequence of the reduced amount of mixing water required by compaction methods.

INTRODUCTION

If a mass of freshly mixed portland cement-based mixture is deposited in a form and allowed to harden, the resulting solid will be extremely weak due to the presence of numerous voids. It is therefore necessary to densify the mixture in order to develop the desired engineering properties. This process of densification is termed consolidation and, according to ACI Committee 309, can be defined as: "...the process of removing entrapped air from fresh concrete in the form" (2).

Several consolidation techniques are available and commonly used according to the specific application. For conventional concrete these methods are considered equivalent provided that entrapped air can be removed and a homogeneous system obtained. It is known that strength properties of concrete decrease approximately 5% for each percentage increase in voids (3).

In the case of cement-based mixtures containing phosphogypsum, the consistency of the system (i.e., the ability of the mix to flow) and consequently its suitable consolidation technique, have a great influence on the mechanical properties of the hardened product as a consequence of the gradation and nature of phosphogypsum.

As a result of phosphogypsum's extremely fine gradation, most particles being between 50 and 100 microns (5), a plastic mixture can only be obtained with extremely high water content which adversely affects strength properties. Furthermore, the nature of phosphogypsum is such that densification by directly applied pressure produces a molecular modification of the calcium sulfate particles yielding to a rocklike body (6). Under these circumstances it can be speculated that extremely dry mixtures using static or impact compaction as consolidation techniques, are bound to provide better hardened mix properties.

The objective of this paper is to present and compare the compressive strength results of mixtures consolidated according to three different methods, namely: static. compaction, impact compaction (Modified Proctor method), and external vibration. Conclusions are drawn upon data collected under laboratory conditions; however, the evaluation can be extended to the practical methods applying similar consolidation principles.

A description of the production, composition, and properties of phosphogypsum by-products is outside the scope of this paper. More information can be found in other articles collected in this publication and in Reference 5.

CONSOLIDATION METHODS

According to ACI Committee 116 (1), consolidation and compaction are synonyms; however, in the course of this paper the term consolidation will be used to indicate the general process of densifying concrete, whereas the term compaction will refer to the consolidation methods that specifically make use of direct pressure application. A brief description of the consolidation methods adopted during this experimental program will follow.

Static Compaction

As shown in Figure 1, static compaction is obtained by surcharging the matrix confined in a steel cylinder by means of a press. The consolidation method is qualified as static because the surcharge is produced at a speed of the press ram in the order of magnitude of in./min (25 mm/min) without

Static Compaction

Features:

1. Any Compaction Pressure at inch/min.
2. Influence of Mold (Arching Effect)

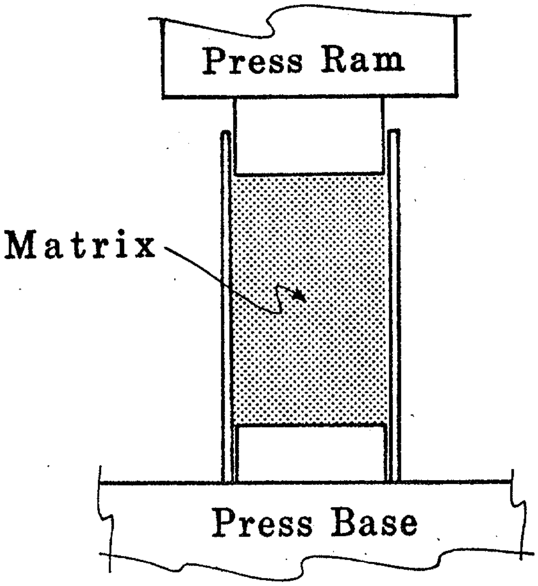

Figure 1: Skematic of Static Compaction

Impact Compaction

(Modified Proctor)

Features:

1. Falling Weight
2. Energy Input vs. Material Amount

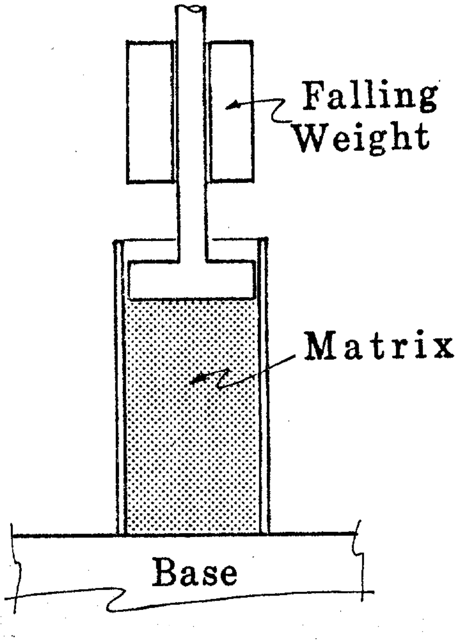

Figure 2: Skematic of Impact Compaction

therefore any energy release. The applied pressure is only limited by the load capacity of the press and the resistance capacity of the mold.

Effectiveness of static compaction may be influenced by the size of the mold. In fact, for deep and narrow forms the friction between the matrix and the wall of the form may produce an arching effect, so that the pressure applied by the ram is transferred to the press base through the form rather than the matrix with consequent loss of matrix consolidation.

The action of static compaction consists of forcing the solid particles together. Best results are obtained under the condition of matrix constituent proportions with a sufficient number of fine particles to fill the voids and sufficient mixing water to lubricate the particles interface. If excessive water is provided, it will seep through the openings between form and press; however, some of the very fine particles, including cement, may escape during the process.

Impact Compaction

Impact compaction is obtained by repeatedly dropping a guided weight upon a steel dish in contact with the matrix contained in a rigid mold (see Figure 2). The consolidation action is a function of the energy input provided during compaction, in other words, the kinetic energy of each blow times the number of blows.

For this particular experiment the total amount of energy prescribed in the Modified Proctor method (ASTM.D-1557) was selected. The reason for this choice rests in the fact that densities obtained in the laboratory under these specifications can be matched in the field, with conventional road construction equipment.

The action of impact compaction, similarly to the static case, consists of forcing the solid particles together and therefore matrix constituents have to be of the appropriate gradation. However, the water content is of extremely critical importance for the reason that lower than optimum moisture percentage will prevent particles from sliding on one another, and higher than optimum moisture content will result in wasting the compaction energy by hammering on an incompressible body, since all the voids will be filled with water.

External Vibration Consolidation

Consolidation of concrete by vibration consists of drastically reducing the internal friction between matrix solid particles (i.e., concrete liquefaction) so that they can settle under the action of gravity forces. When vibration is terminated, friction is reestablished.

Figure 3 shows the type of external vibration adopted in the course of the experiments. The vibrating table on top of which the molds were held for a period of 30 sec., was electrically driven (CV 60) and operated with a frequency of 3,600 rpm.

EXPERIMENTAL RESULTS

Static Compaction

Two different mix proportions were adopted for testing the effect of static compaction on compressive strength; both mixtures had a finely crushed limerock (from now on referred

External Vibration

Features:

1. Vibration Frequency
   2,000–6,000 rev./min.
2. Influence of Vibration
   Time

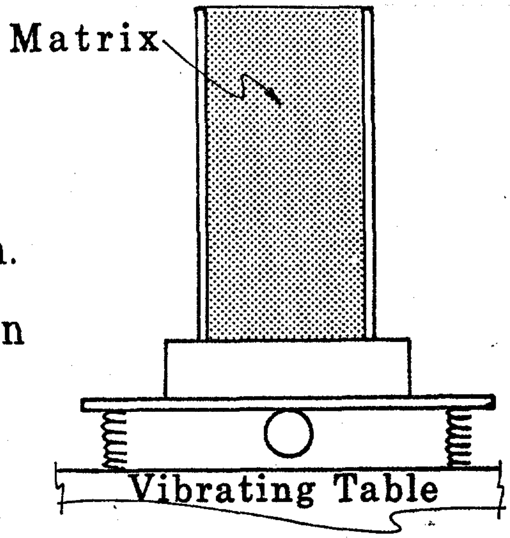

Figure 3: Skematic of External Vibration Consolidation

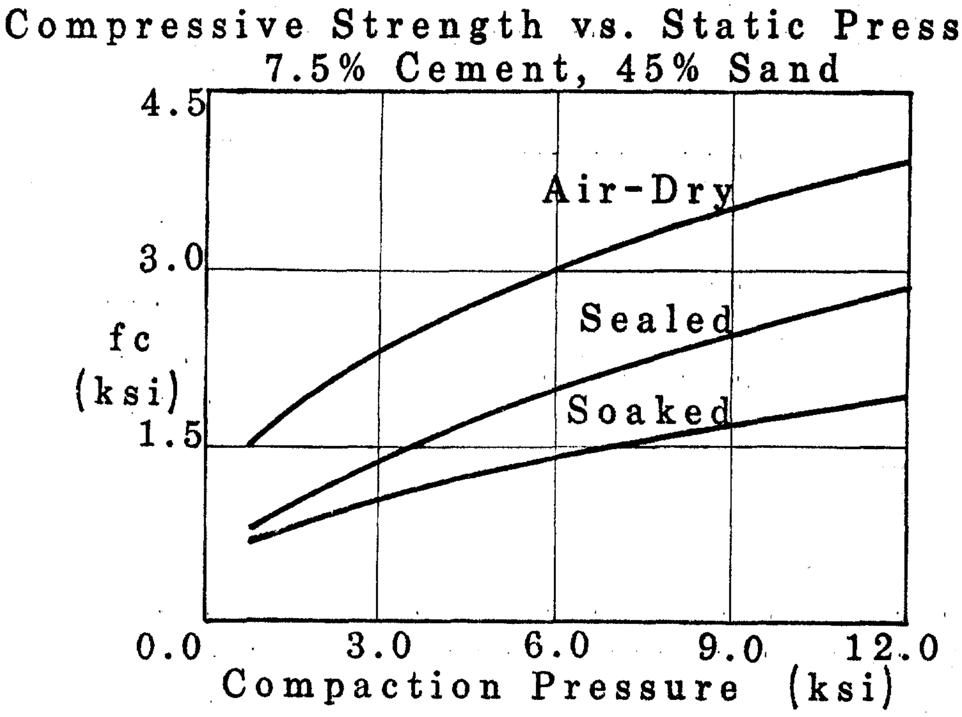

Figure 4: 28-day Compressive Strength Curves under Various Testing Conditions

to as sand) content of 45% by weight, whereas the cement content was 7.5 and 15%, respectively. The remaining solid constituent consisted of phosphogypsum (47.5 and 40%, respectively). The mixing water content, as discussed later, was dependent on the compaction pressure and varied approximately between 11% (high pressure) and 18% (low pressure).

Five pressure levels were used starting at 750 psi (5.17 MPa) up to 12,000 psi (82,68 MPa), each increment being equal to the previous pressure value. Specimens were cured under sealed conditions and tested at 28 days under air-dry, sealed , and soaked conditions. Figures 4 and 5 report the compressive strength curves as a function of the static pressure for the two mixes.

The strength ratios between the three moisture testing conditions are as expected (5), and also as expected is the improvement in strength as a function of the cement content. With reference to these two diagrams the most relevant observation is based upon the relationship between compressive strength and compaction pressure. It is seen that as the static compaction pressure increases so does the resulting 28-day compressive strength and the two parameters are related by an exponential law as indicated by the straight lines of the log-log diagram presented in Figure 6. In fact, exponential relationships of the type $Y=aX^b$ become linear in a log-log representation.

Future research on this consolidation method will establish the relationship density-compaction pressure and relate it to strength results.

Comparison of Consolidation Methods

A detailed presentation of strength results obtained for

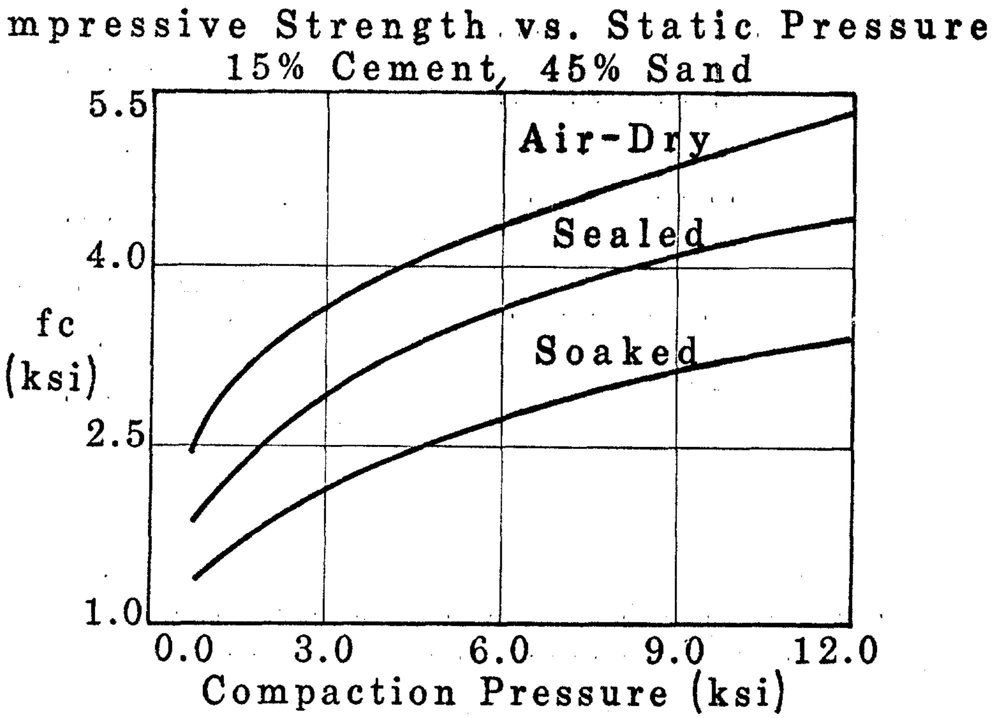

Figure 5: 28-day Compressive Strength Curves under Various Testing Conditions

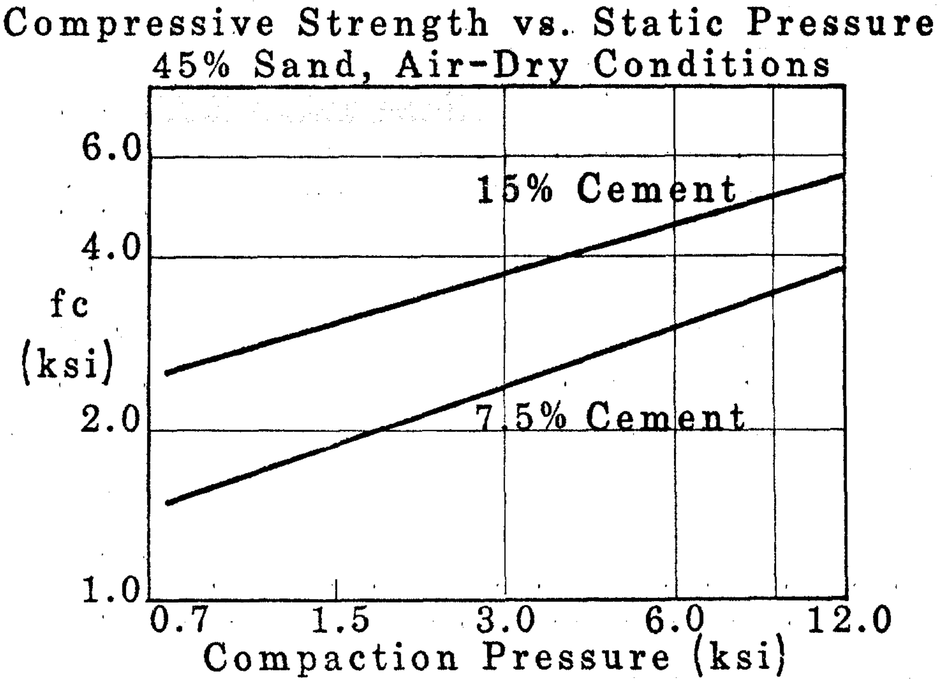

Figure 6: 28-day Compressive Strength Curves in a log-log Representation for Different Cement Contents

specimens prepared by external vibration consolidation and impact compaction have been given elsewhere (5,4). For specimens cured and tested under sealed conditions the 28-day compressive strength is plotted in Figure 7 as a function of cement content, when the sand percentage is-held constant at 45%, for the three different methods of consolidation.

The shaded area of the diagram in this figure represents the experimental and projected strength results for mixtures subjected to static compaction under pressures varying from 750 psi (5.17 MPa), lower limit, to 12,000 psi (82,68 MPa), upper limit. It is seen that the results obtained by impact compaction using the Modified Proctor method are well inside the fuse, whereas strength data resulting from plastic mixes subjected to external vibration are substantially lower.

Figure 8 is a caption of the previous figure where the curves for static and impact compaction between 7.5 and 15% cement content are shown in detail. In this cement percentage interval the Modified Proctor method is equivalent to static compaction pressures varying between 2,000 and 6,000 psi (13.78 and 41.34 MPa) depending on the cement content.

For the case of constant cement amount (10% by weight) the 28-day compressive strength of specimens tested under air-dry conditions is plotted in Figure 9 as a function of sand content for the three different consolidation methods. Static compaction data were available for a pressure of 1,500 psi (10.33 MPa) only. It is to be noted that both compaction methods, as opposed to external vibration, have a compressive strength peak for mix compositions which contain phosphogypsum. This is to say that, for proper proportioning and consolidation method, the use of phosphogypsum improves strength characteristics.

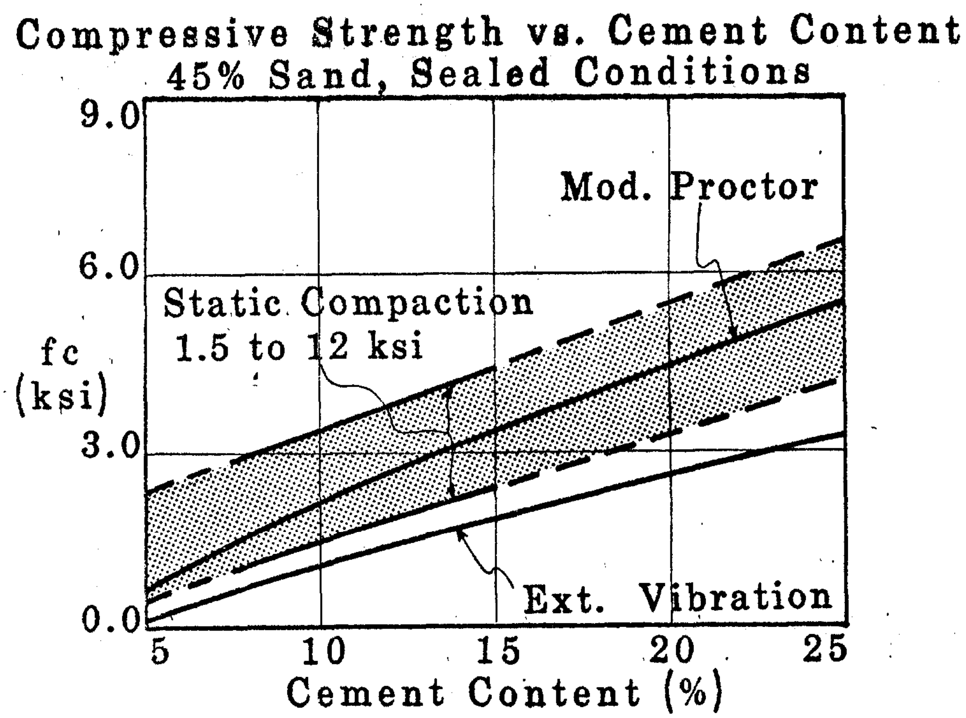

Figure 7: 28-day Compressive Strength Curves for Different Consolidation Methods

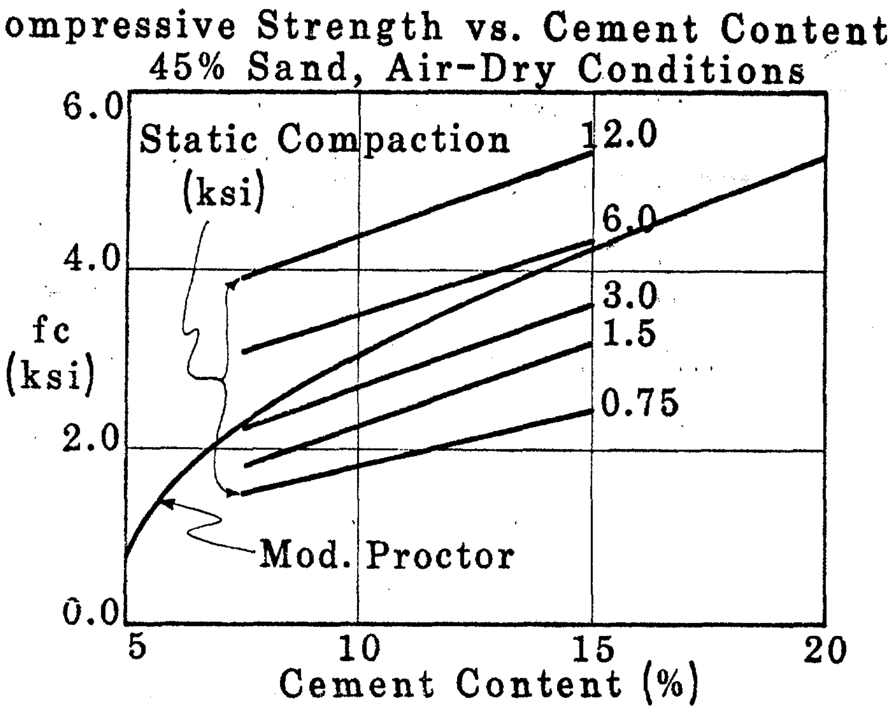

Figure 8: 28-day Compressive Strength Curves for Static and Impact Compaction

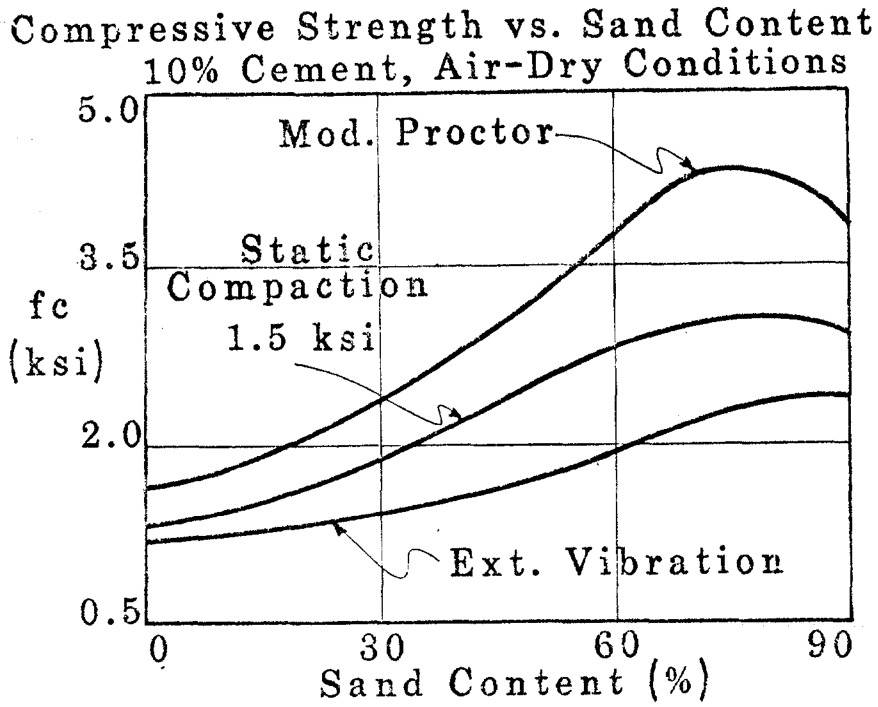

Figure 9: 28-day Compressive Strength Curves for Different Consolidation Methods

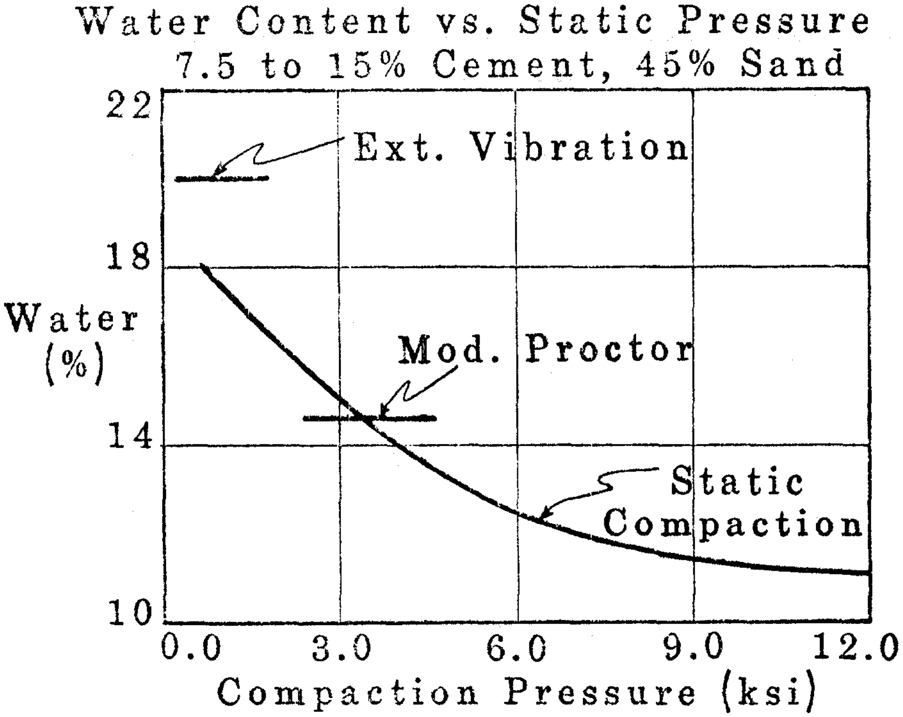

Figure 10: Mixing Water Content of Samples Prepared according to Different Consolidation Methods

Water Content

Better strength properties obtained by the compaction methods rather than external vibration can be partially explained by considerations on the mixing water content.

The mixing water content is plotted in Figure 10 as a function of the static compaction pressure for cement content of 7.5 or 15%, indifferently. It is seen that as pressure increases, the water content as used is decreased. The reported amounts of water were selected on an empirical base as the quantities for which seepage would begin to appear between the mold and the press base at the adopted maximum pressure level. Obviously, the higher the pressure, the lower the amount of water that would cause initial seepage.

In the same figure the average water contents used for external vibration and impact compaction are also shown. It appears that as external vibration consolidation requires mixing water amounts higher than the other methods, corresponding strength results are consequently lower. Furthermore, as the optimum water content for the Modified Proctor method is approximately the middle value of the water content interval used for static compaction, so are the corresponding strength values for both 7.5 and 15% cement content.

These observations lead to the conclusion that consolidation methods requiring the lower amounts of mixing water are also the ones that provide the higher strength.

CONCLUSIONS

A summary of the relevant observations reached in the course of this paper are as follows:

1) For portland cement-based mixtures that make use of phosphogypsum consolidation methods using direct force application (i.e., static or dynamic compaction) are to be preferred to external vibration under the criterion of maximum compressive strength.

2) One of the reasons that make static and dynamic compaction more effective than external vibration is the reduced amount of mixing water that they require.

3) Consolidation by compaction requires the presence of very fine particles and therefore a limited amount of phosphogypsum enhances strength properties when the third component of the cementitious mixture is crushed limerock, conventionally graded and with a maximum size of 0.25 in. (5.1 mm).

4) Static compaction has an edge over impact compaction because it is less dependent on accurate determination of water content (i.e., excessive water can be driven out of the matrix) and also because high static pressure is more easily obtained than high kinetic energy.

ACKNOWLEDGEMENTS

Grateful acknowledgement is made to the Florida Institute of Phosphate Research, Bartow, Florida, for funding the project. Thanks are also due to Gardinier, Inc., Tampa, Florida, for supplying the phosphogypsum.

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COMPACTION PHOSPHOGYPSUM-BASED CEMENT MORTAR REINFORCED WITH STEEL FIBER

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ABSTRACT

The purpose of this experimental study is to investigate engineering properties and practical applications of compaction phosphogypsum-based mortar, consisting of phosphogypsum, fine aggregate and portland cement, reinforced with steel fibers.

Like conventional portland cement mortar, phosphogypsum-based mortar is high in compressive strength while low in tensile strength. Steel fibers were added to resist tensile cracking and the effects of varying the fiber content and the aspect ratio on flexural, tensile and compressive strengths and ductility of mortar were studied.

Specimens were produced by static compaction. Different compaction pressures were used when preparing specimens to study this effect on the specimen properties.

Three point flexural tests were performed on beams and panels of different thickness to obtain modulus of

rupture and load-deflection curves. Cubes (obtained by sawing beam samples) were used for compression tests and splitting tension tests.

Experimental results were interpreted as a function of compaction pressure, steel fiber volume percentage and aspect ratio.

The experimental results showed that compacted phosphogypsum-based mortar reinforced with steel fibers has improved tensile strength and pseudo-ductility. These two properties considerably extend composite material potential for practical applications such as building system precast elements.

INTRODUCTION

As of today, about 400 million tons of phosphogypsum, a dust like by-product of the phosphorus fertilizer production, have been stockpiled in central Florida. The stockpiled tonnage is increasing at a rate of 30 million tons per year [l].

Since 1983, a series of research works on the properties of phosphogypsum and phosphogypsum products for use in construction have been undertaken. According to previous works [2], it is evident that phosphogypsum-based mortar behaviors like conventional mortar and, therefore, there is a need to improve properties associated with tensile resistance.

The use of short, randomly distributed fibers as a reinforcement for concrete is well established in several areas of civil engineering. For some specific applications such as refractory, shotcrete and repairs, fiber reinforced concrete is among the most appropriate products [3,4]. The function of the fibers in the matrix is to provide a crack arrest mechanism and pseudo-ductility.

Compaction concrete has some advantages when compared with conventionally vibrated concrete and has progressed rapidly in the last few years, particularly in the form of roller compacted concrete (RCC) for water retaining structures [5] and pavements[6]. The main advantages of compaction concrete are strength properties higher than those of conventional concrete at the same cement content, and handling and placing are simpler and faster. In addition, phosphogypsum is conducive to compaction because of its fineness and self-adhesive properties.

Fiber reinforcement is appropriate for use in compaction concrete for the reasons that fiber mixing and distribution in the zero-slump matrix, are greatly facilitated, whereas the conventional steel bar reinforcement is not practically feasible.

This paper reports the results obtained by testing specimens of phosphogypsum-based mortar reinforced with steel fibers and produced by static compaction.

MATERIALS AND FABRICATION OF SPECIMENS

The phosphogypsum-based matrix of this investigation consists of three construction materials: portland cement type I (ASTM, c-150), dihydrate phosphogypsum, and finely crushed limerock (fineness modulus=2.59) referred as sand from hereafter.

There are four types of steel fibers used in this investigation as listed in Table 1.

TABLE 1

Characteristics of Steel Fibers

Fiber Reference Code	Cross-Section Side-Side or Diam. (in.)	Length (in.)	Aspect Ratio	Production Method
F22	0.010x0.044	0.75	22	Slit Sheet
F45	0.010x0.022	0.75	45	Slit Sheet
F60	0.010x0.022	1.00	60	Slit Sheet
F90	0.010x0.022	1.50	90	Slit Sheet

Phosphogypsum and steel fibers, were first mixed in a conventional pan mixer. After about 8 minutes, the appropriate amount of water was then added. The material was well mixed and removed from the mixer about 15 minutes later. Specimens were prepared by filling a steel mold (the amount of loose material was determined during several trial tests) and the consolidating pressure was applied at a stroke rate of 0.1 in./min. As required by the static compaction method, the free water content of the mix was so low that the mix was zero-slump. After compaction, specimens were removed from the steel mold and cured in a 100 % relative moisture room at a temperature of 75 F. Fourteen days later, they were removed from the moisture room and stored in laboratory condition for another 14 days. The specimens were finally tested at age 28-days.

TYPES OF SPECIMENS AND EXPERIMENTS

Two mixtures of different constituent proportions were used in this investigation. The first proportions were 10% portland cement, 15% phosphogypsum, 75% sand and 13±0.5% water. The type and amount of steel fibers and the compacting pressure were varied. The following specimens were made of mixture of the first proportions:

a) Standard Beams with dimensions 4x4x14 in. (ACI 544.2R-78) with 5 different fiber contents and 5 aspect ratios made by 5 different compaction pressures were tested in flexure using three-point loading with the loading span 12 in. apart.

b) Standard size (4x4x14 in.) sandwich beams, i.e. top and bottom layers of fibrous concrete, 1.0 in. thick, and plain matrix core, 2.0 in. thick, were tested in flexure under the same testing conditions as undertaken for standard beams.

c) Standard beams of 4x4x14 in. consolidated by vibration (initial moisture content 17±0.5 %) were also tested in flexure under the same testing conditions as undertaken for compacted beams. The purpose of this was to compare the two fabrication methods.

d) Cubes 4x4x4 in. as cut from beams which had been tested in flexure were used for compressive and splitting tensile strength tests.

The other set of specimens consists of thin panels exclusively for three point flexure testing. These specimens were made of a mixture with proportions 25% cement, 25% sand, 75% phosphogypsum and 17±1% water. The panels of dimensions 0.5x4x14 in. were fabricated at a compaction pressure of 1500 psi, varying fiber type and fiber content.

EXPERIMENTAL RESULTS

The typical load-deflection curves of standard beams reinforced with steel fibers under three point flexure testing is presented in Figure 1. It is shown in the figure that after first crack the fibers provide partial tensile resistance capacity. The value of Modulus of Rupture was defined as the strength at first crack.

Two beam strength parameters, which are Modulus of Rupture (MOR) and Toughness Index (TI), are presented in Figures 2 to 9 as functions of three independent variables: consolidating compaction pressure, fiber content and fiber aspect ratio. The strength parameters increase when each of the three factors increases. This behavior is a consequence of a better consolidated matrix due to higher compaction pressure, and a better crack

$$\text{Modulus of Rupture} = \frac{\text{Moment(first cracking)}}{\text{Section Moduli Z}}$$

$$\text{Toughness Index} = \frac{\text{Area 1}}{\text{Area1} + \text{Area2}}$$

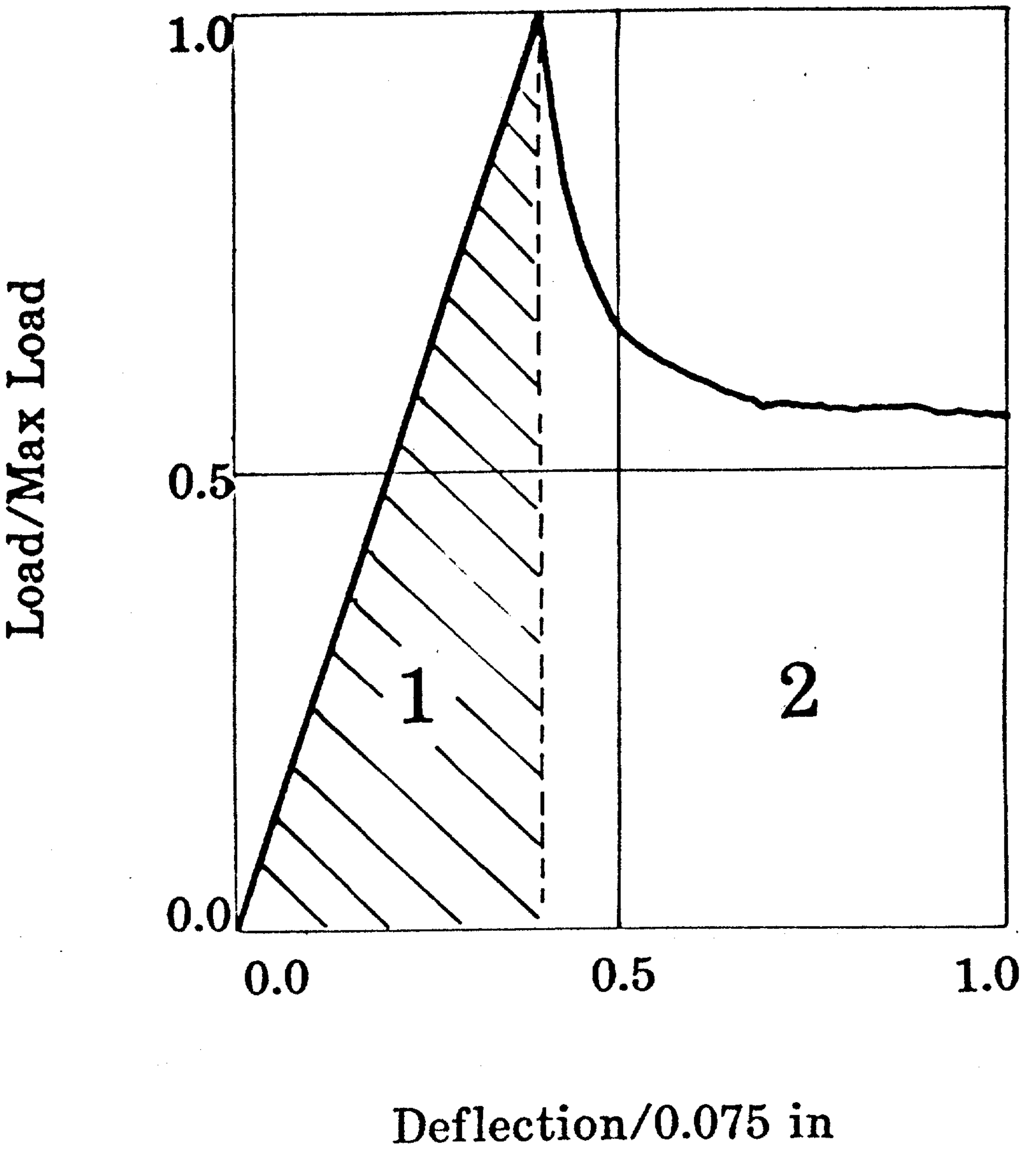


Figure 1 Typical Load-Deflction Curves of Standard Beam

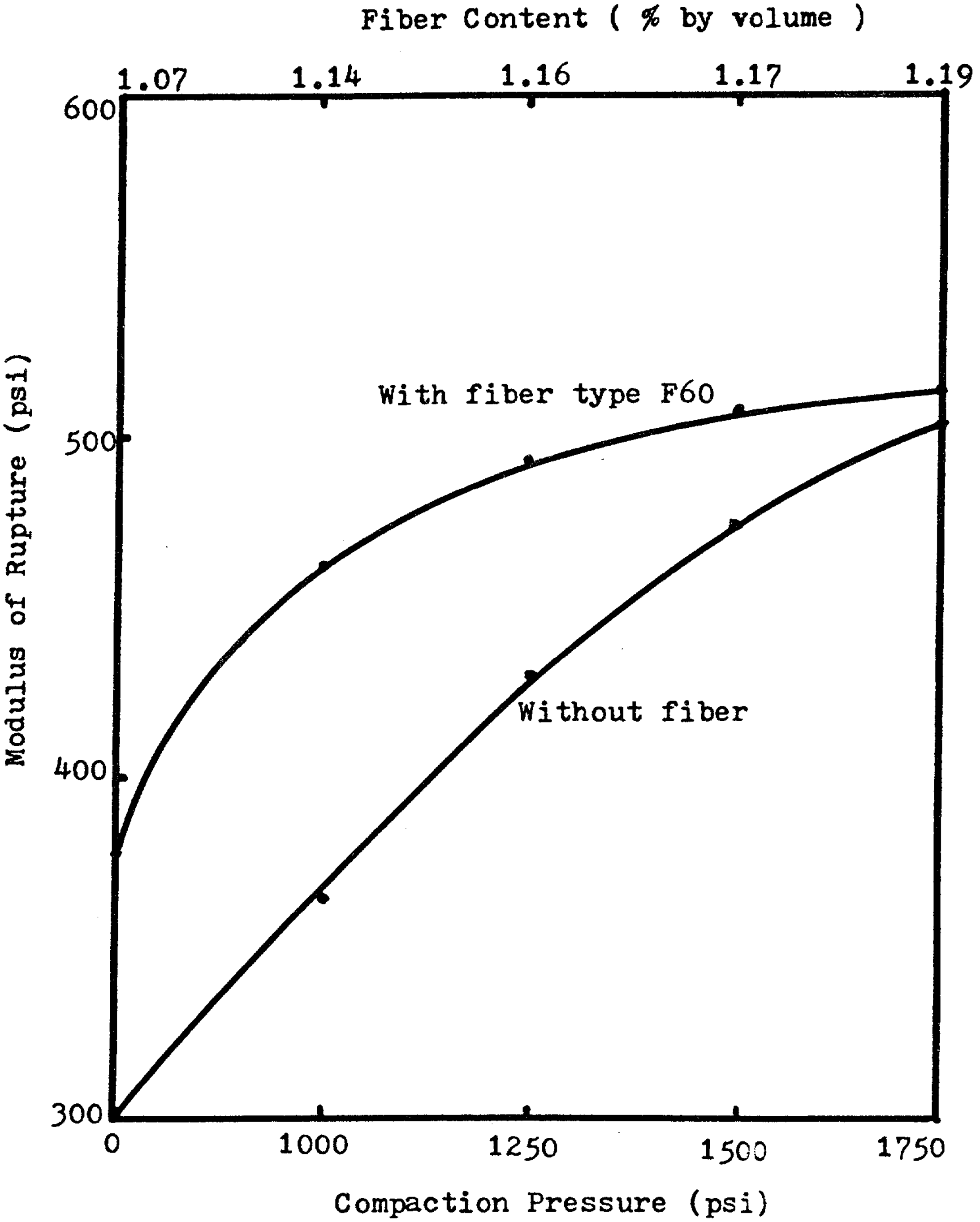


Figure 2 Modulus of Rupture of Standard Beams vs. Compaction Pressure

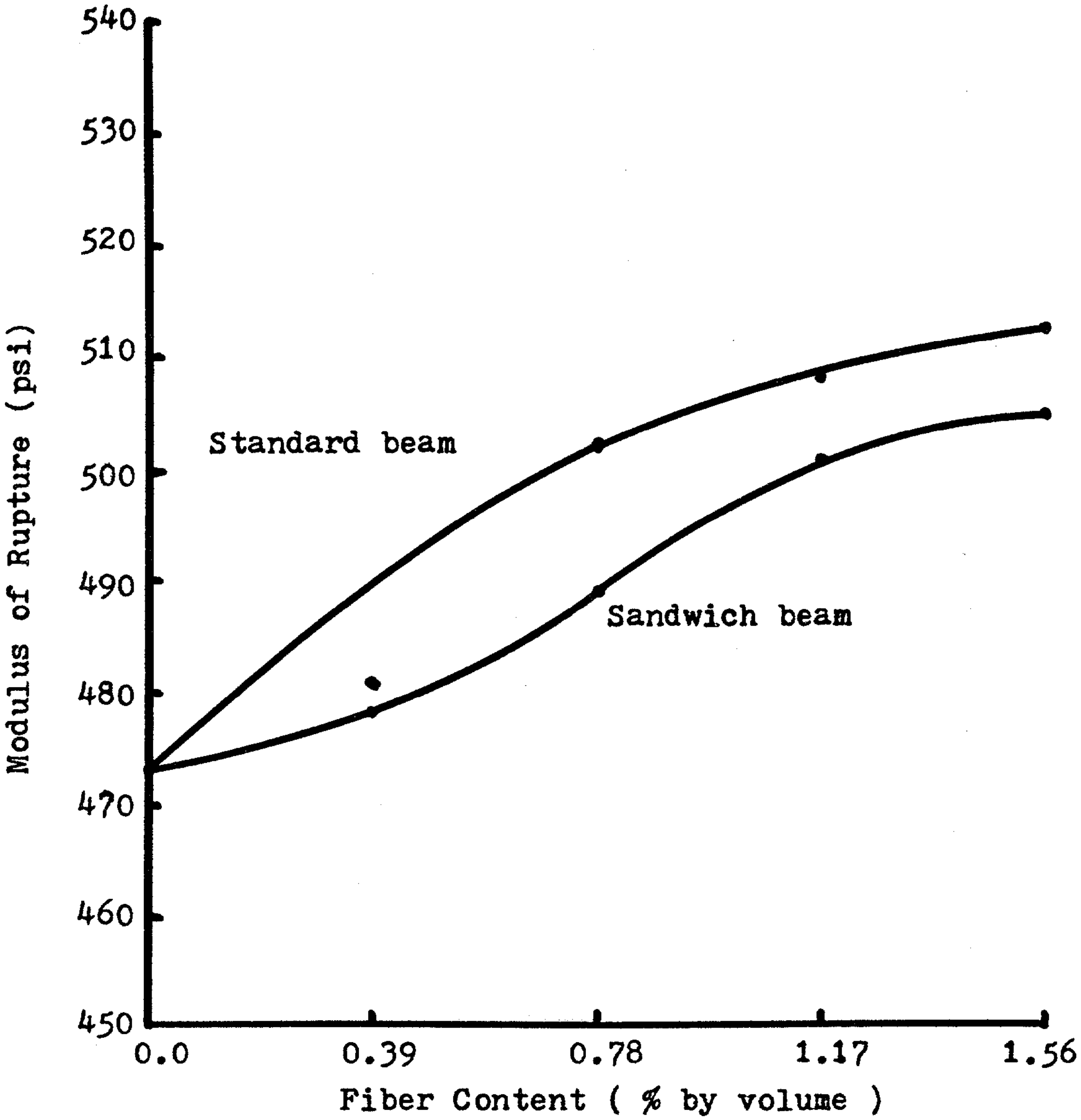


Figure 3 Modulus of Rupture vs. Fiber Content of Standard and Sandwich Beams

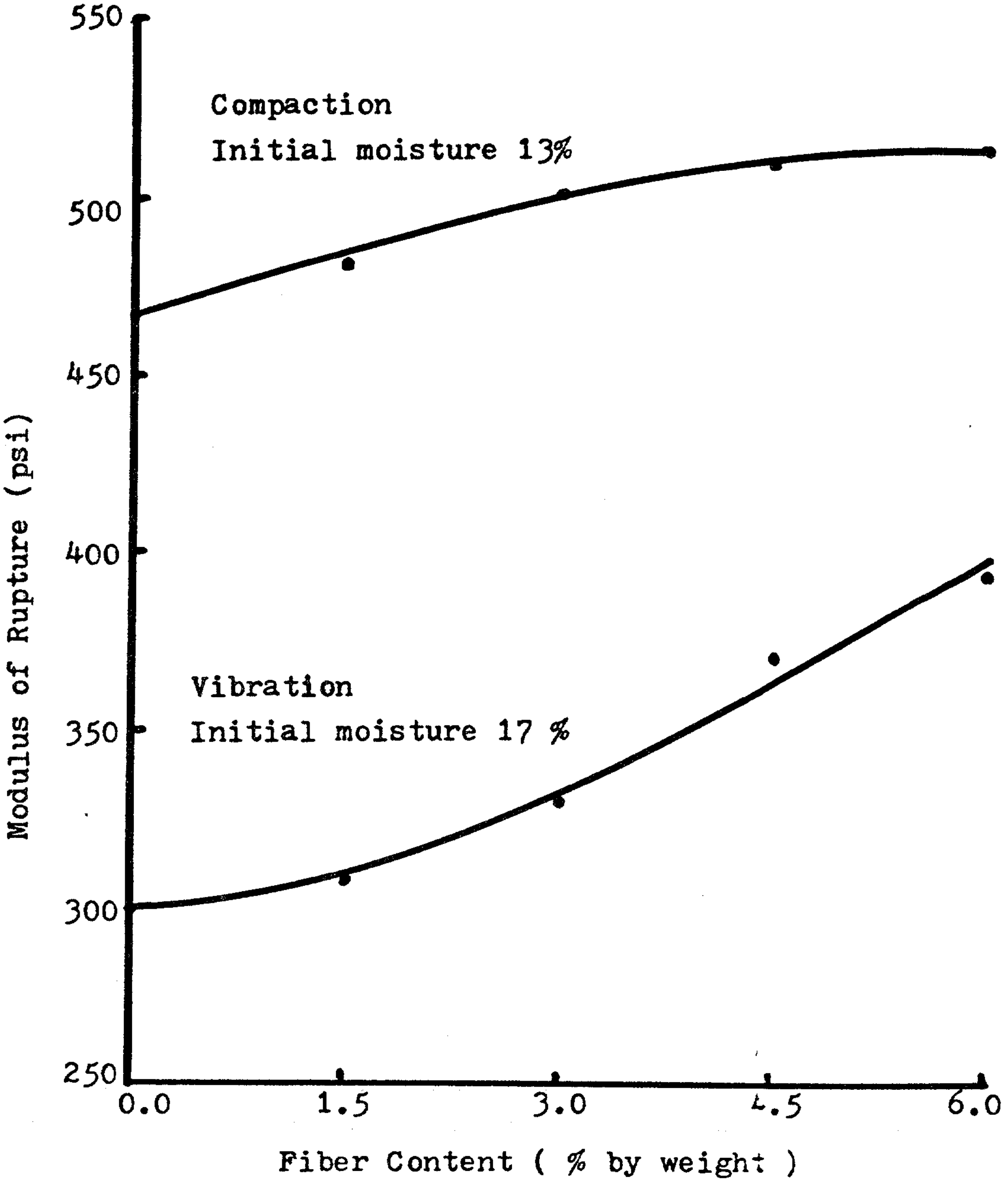
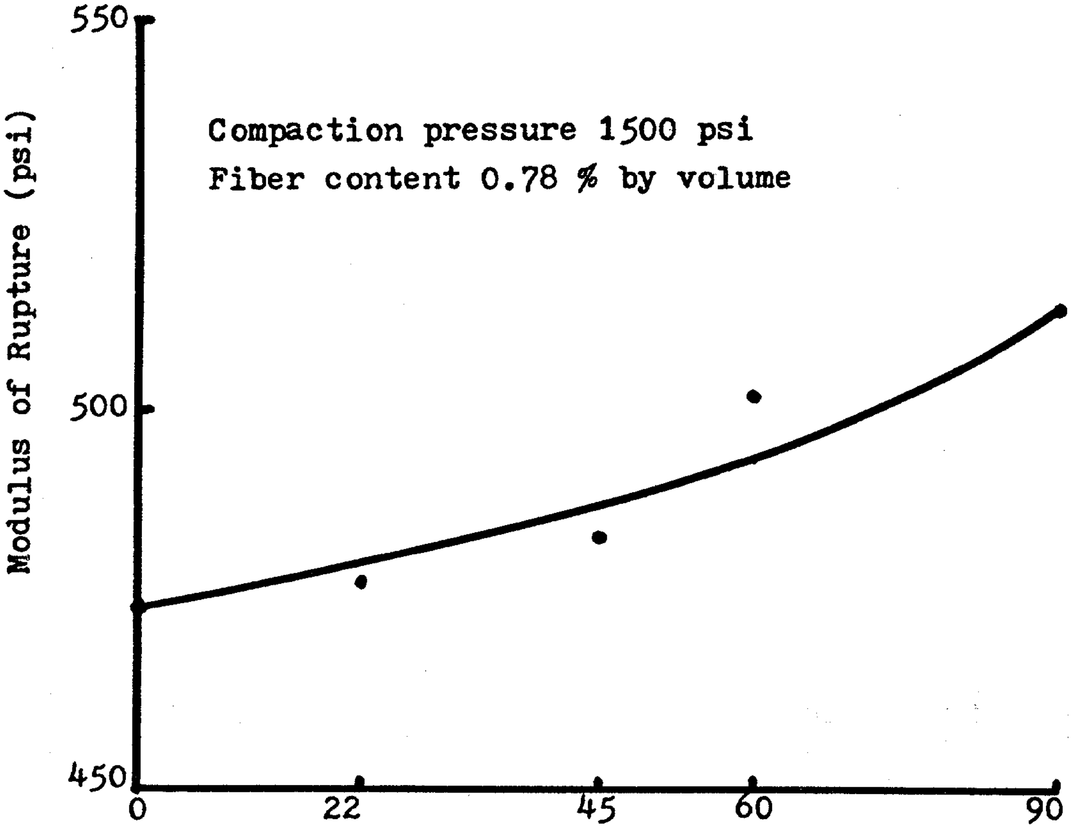


Figure 4 Modulus of Rupture vs. Fiber Content
(Beams consolidated by static compaction and vibration)



Fiber Aspect Ratio

Figure 5 Modulus of Rupture vs. Fiber Aspect Ratio of Standard Beams

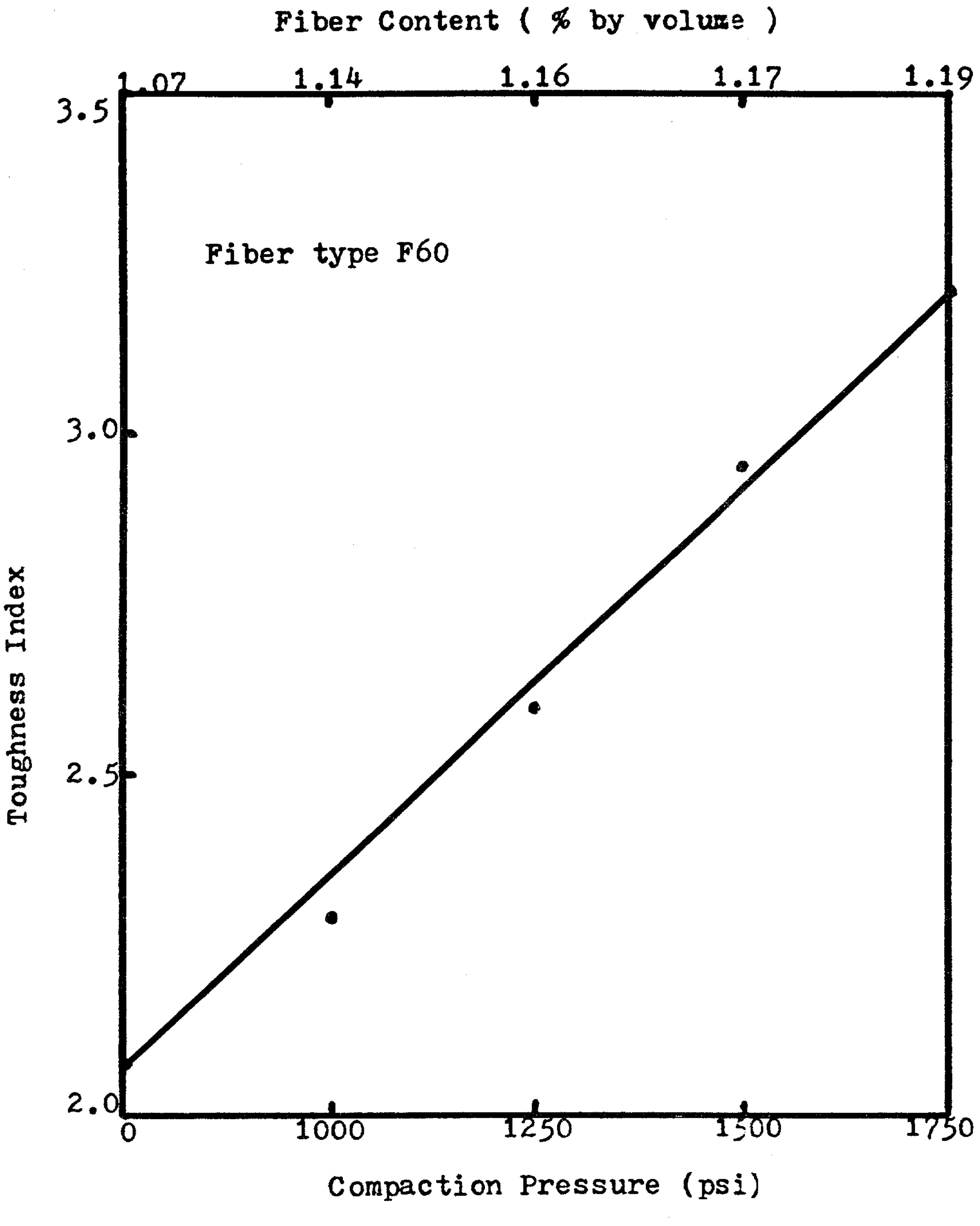


Figure 6 Toughness Index of Standard Beams
vs. Compaction Pressure

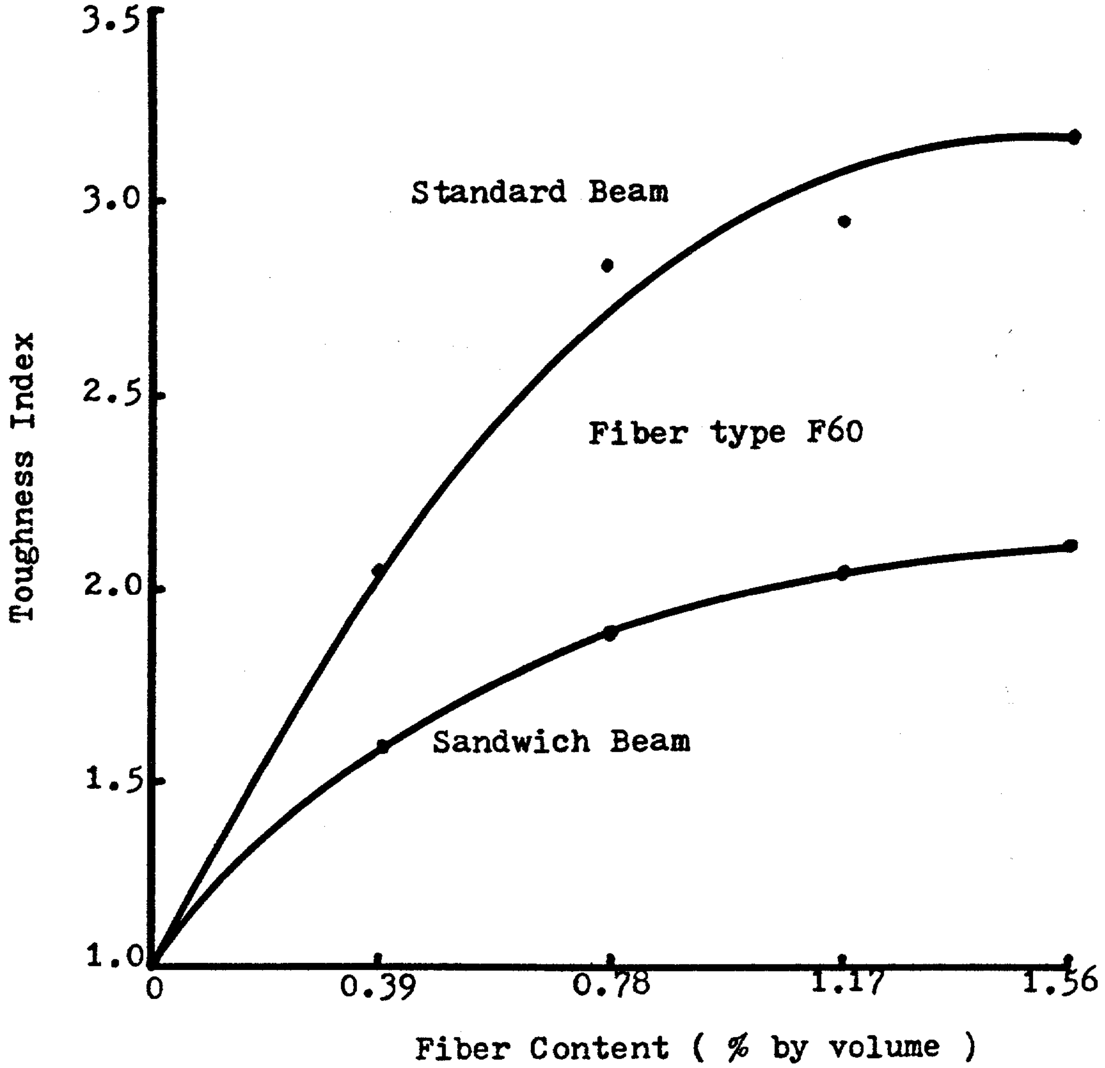


Figure 7 Toughness Index of Beams vs. Fiber Content

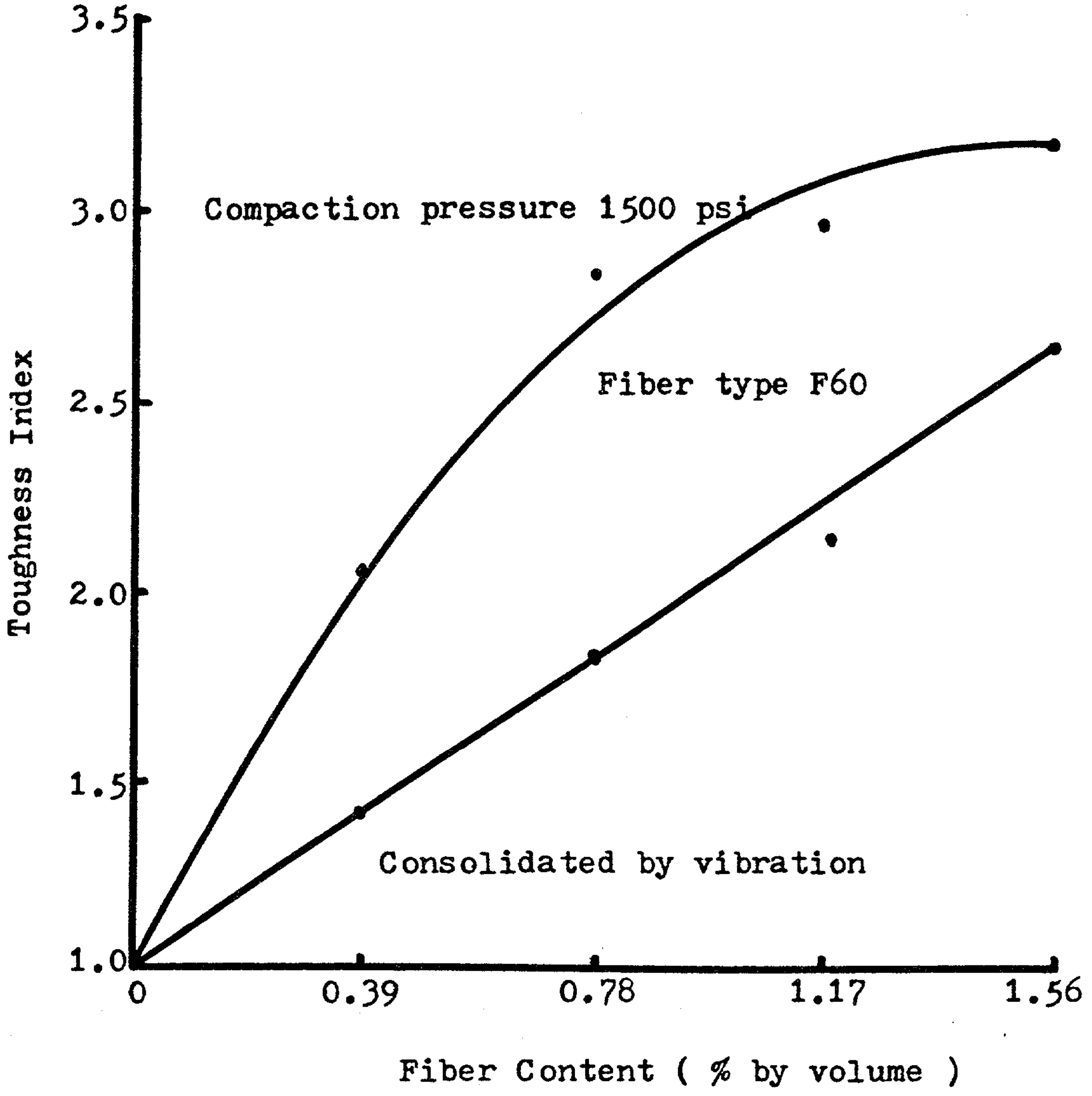


Figure 8 Toughness Index of Beams vs. Fiber Content

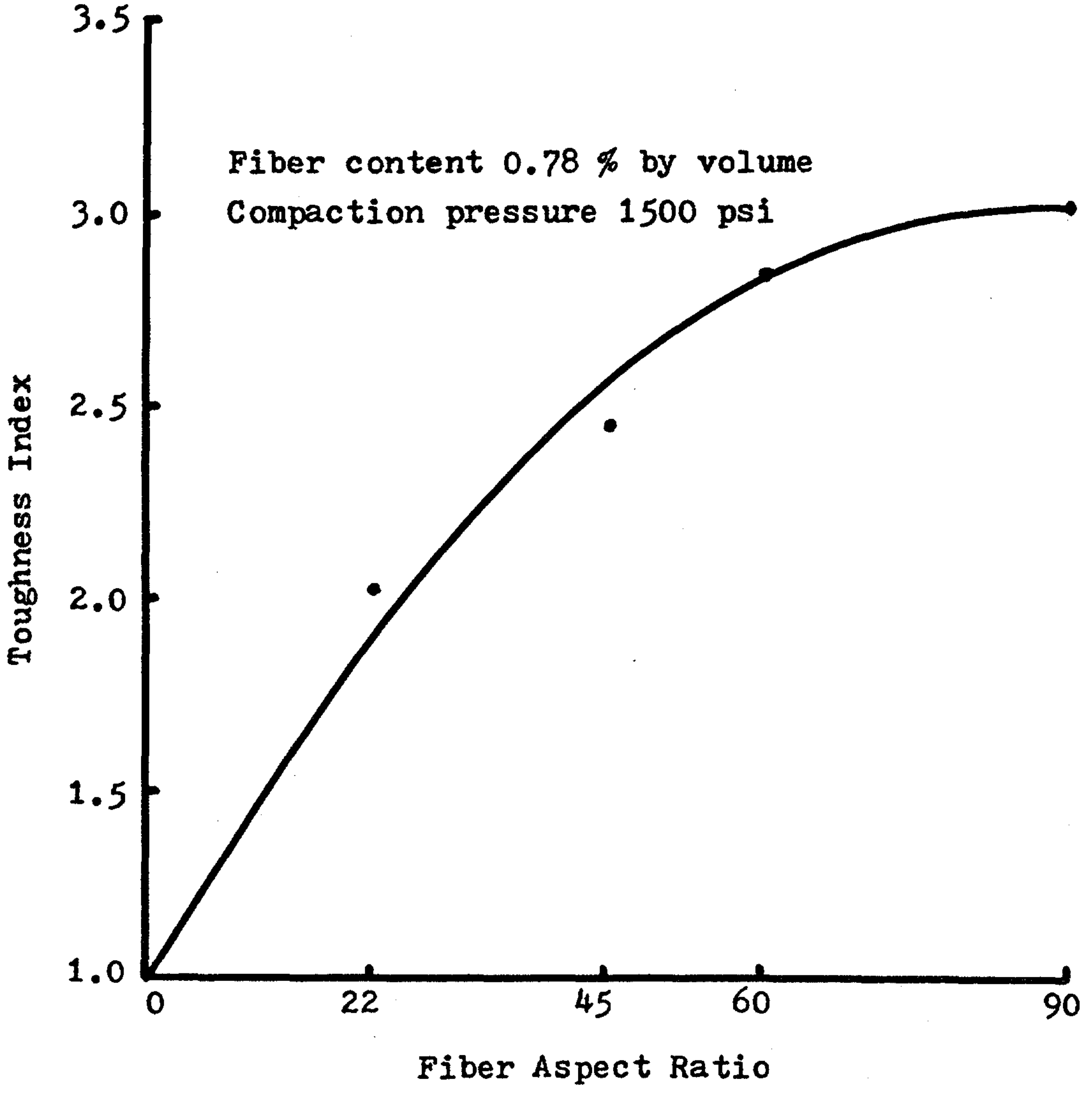


Figure 9 Toughness Index of Standard Beams vs. Fiber Aspect Ratio

arrest mechanism due to higher fiber content and higher aspect ratio. It also can be observed in Figures 2 and 6 that the percentage of fiber content (by volume) increases as a consequence of increased specimen density due to increasing compaction pressure. All values presented in figures are the average of three specimens. Compressive strength and splitting tensile strength of cubes are presented in Figures 10 to 13 as a function of compaction pressure and fiber content. The strength parameters increase when the values of compaction pressure and fiber content increase.

The testing results from sandwich beams with layered construction are compared with the results from uniform cross-section beams in Figures 3 and 7. It can be observed that the MOR of sandwich beams is about 96% of that of uniform cross-section beams whereas the average fiber content of sandwich beams is only half of that of uniform cross-section beams with the same dimensions (the fiber content in the top and bottom layer of sandwich beams is the same as that in the uniform cross-section beams).

The results relative to thin panels under bending are indicated in Figures 14 to 18, the typical panel load-deflection curve shows that the contribution of fibers to the ductility of thin panels is very explicit (plateau is approximately 70% of the first crack strength). The MOR and TI of the panels increase as the fiber content

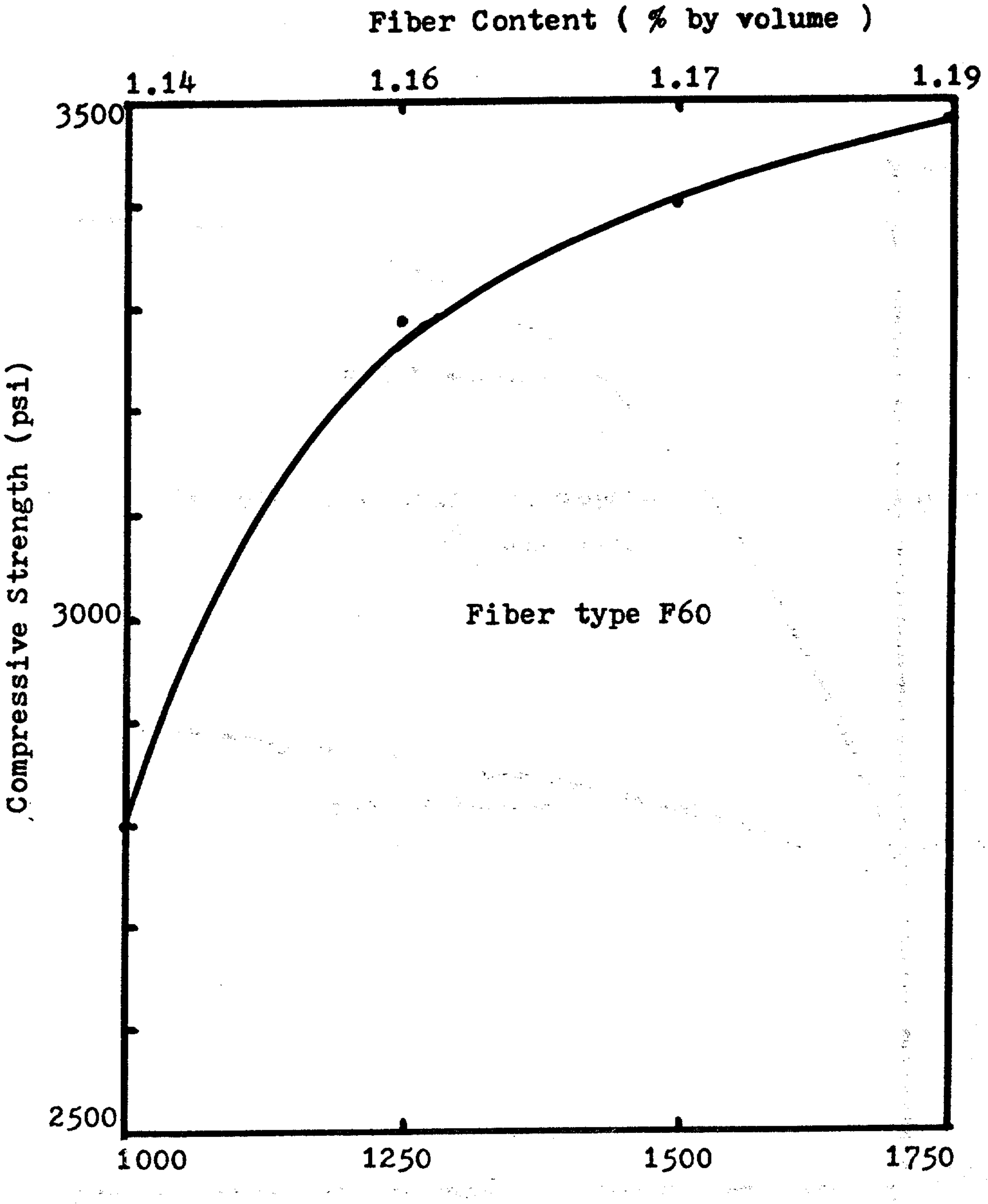


Figure 10 Compressive Strength of Cubes vs. Compaction Pressure

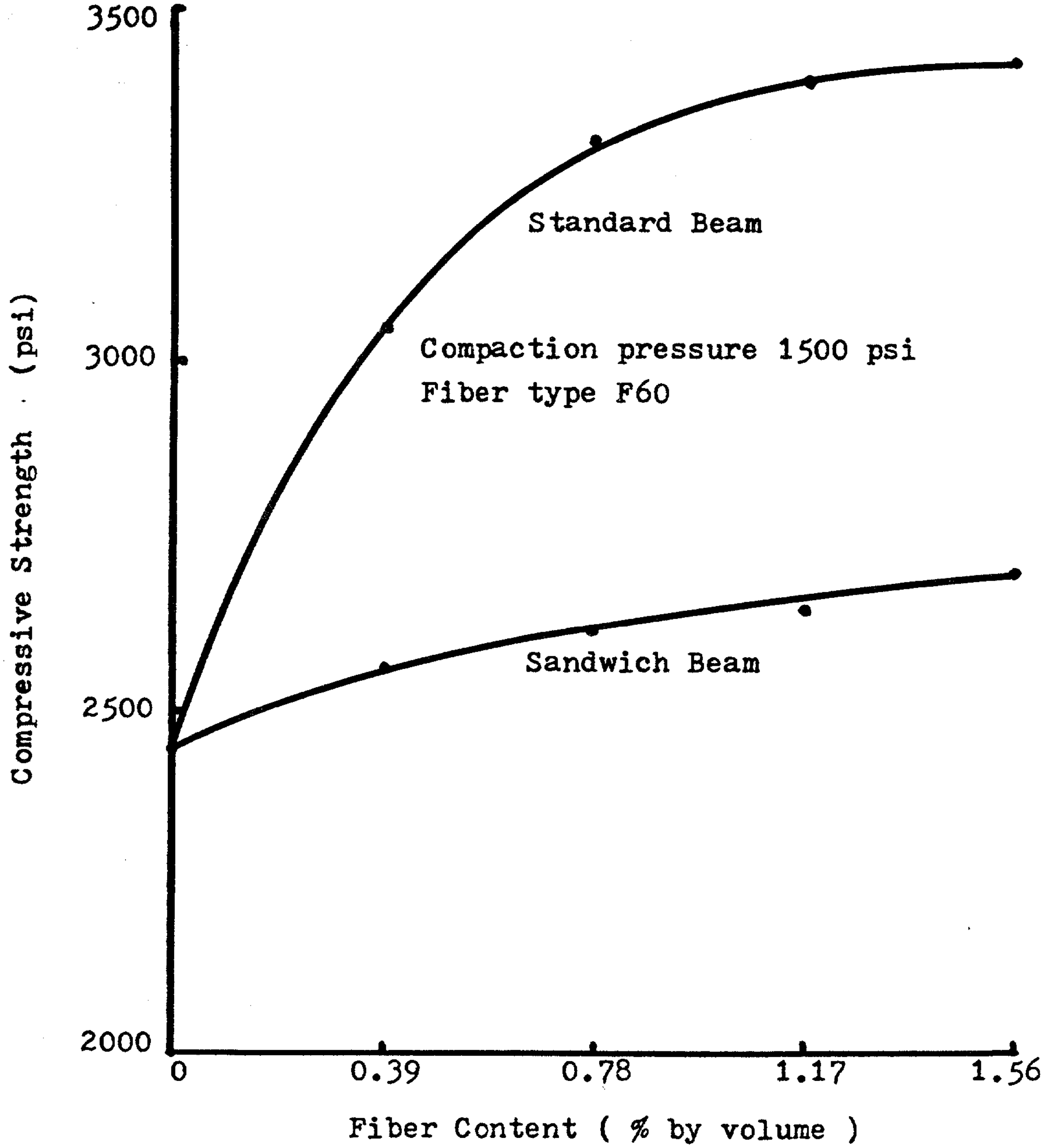


Figure 11 Compressive Strength of Cubes vs. Fiber Content

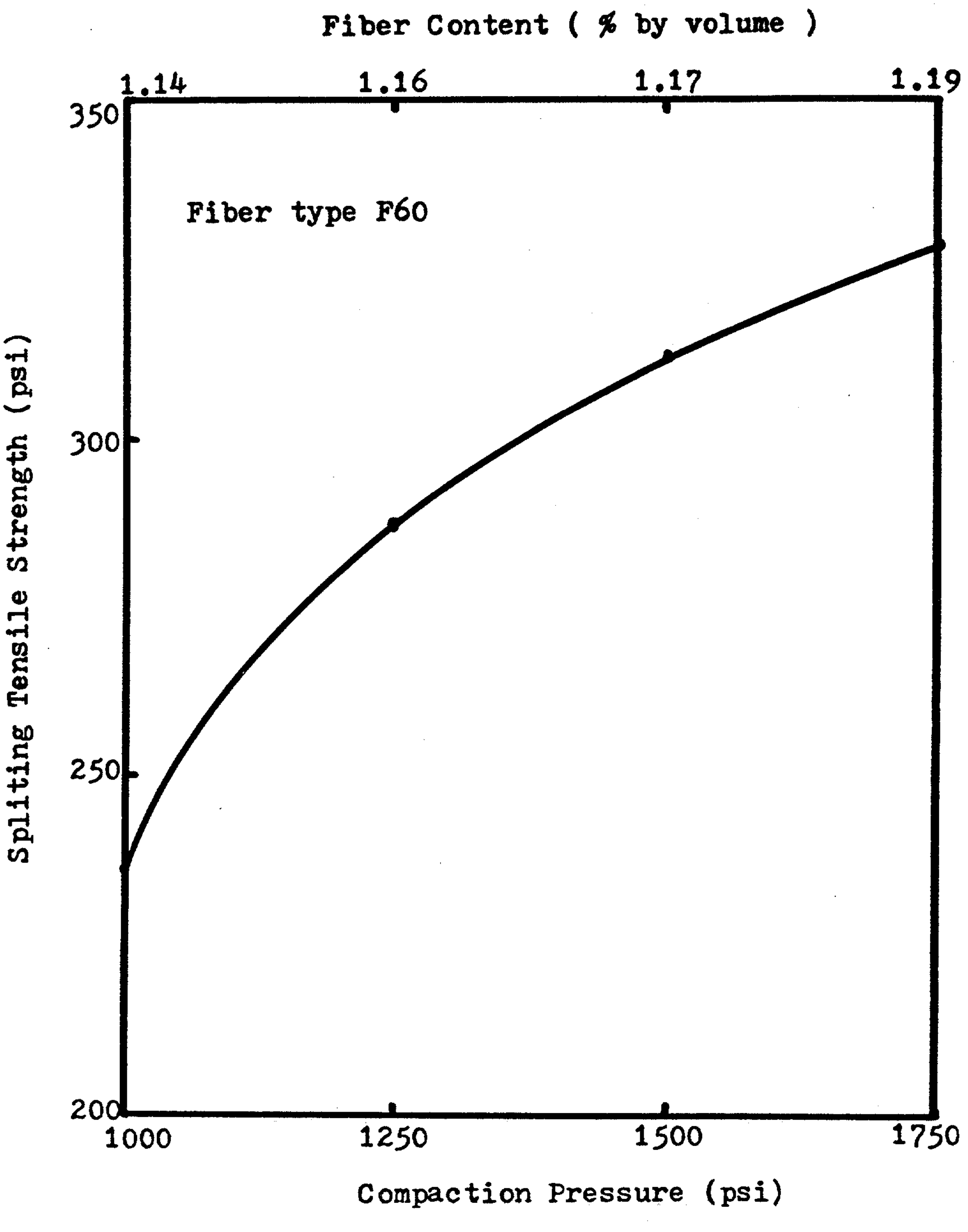


Figure 12 Spliting Tensile Strength of Cubes vs. Compaction Pressure

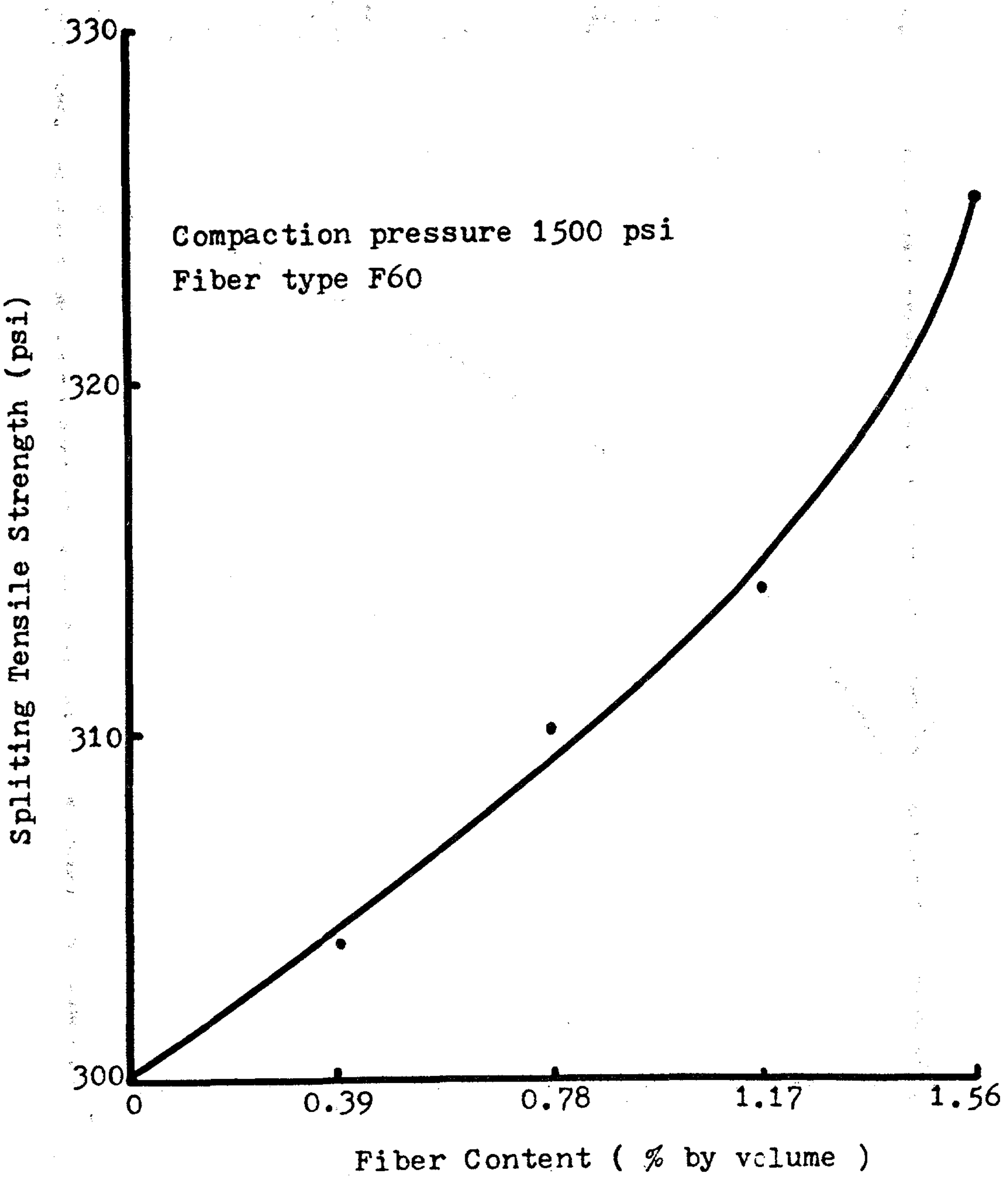


Figure 13 Spliting Tensile Strength of Cubes vs. Fiber Content

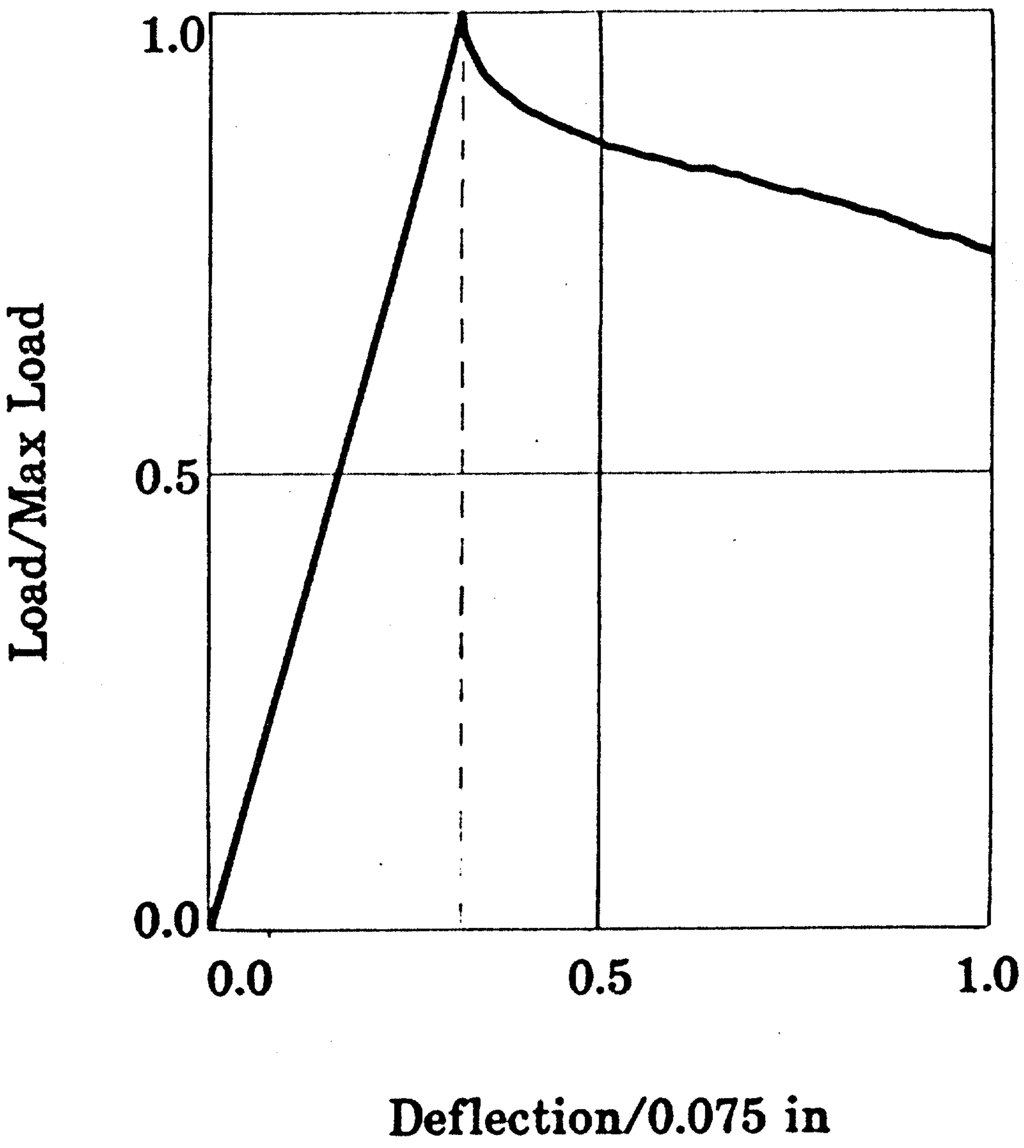


Figure 14 Typical Load-Deflection Curve of Thin Panel

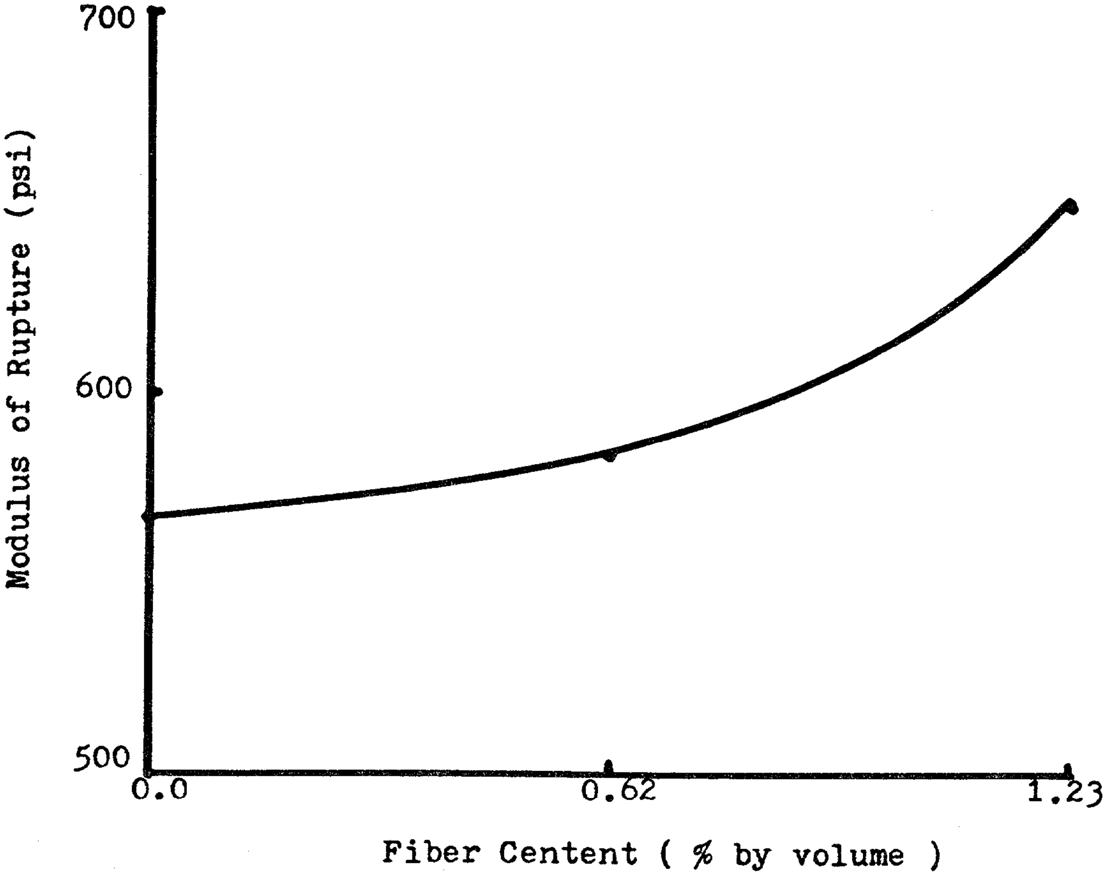


Figure 15 Modulus of Rupture of Panels vs. Fiber Content

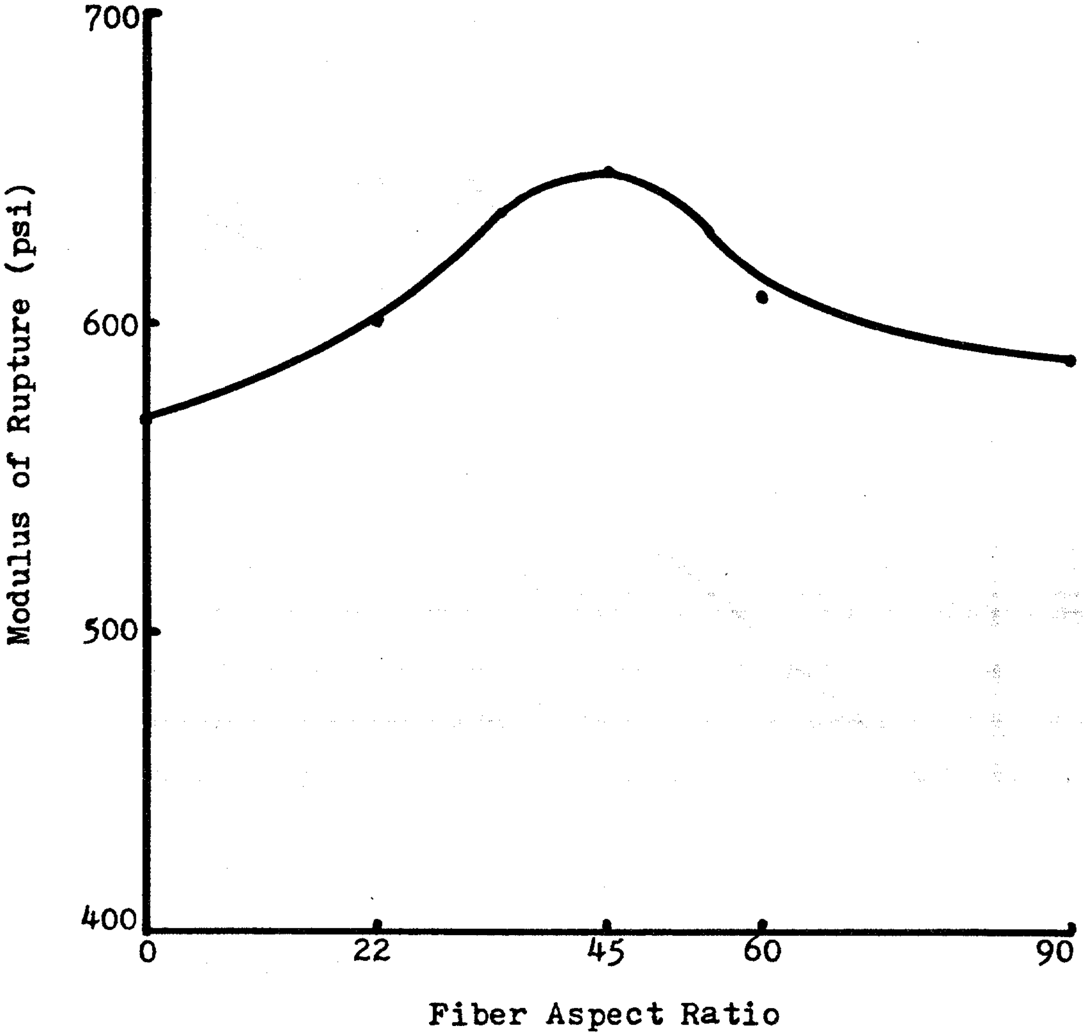


Figure 16 Modulus of Rupture of Panels vs. Fiber Aspect Ratio

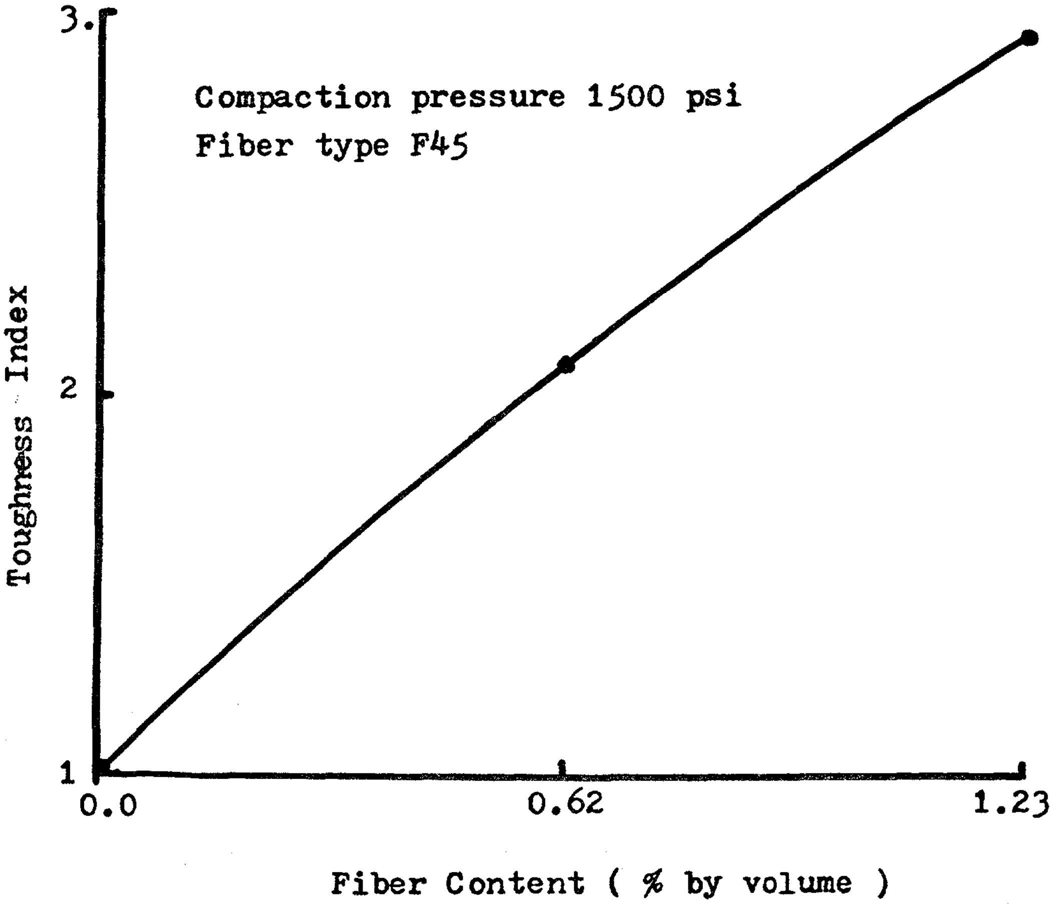


Figure 17 Toughness Index of Panels vs. Fiber Content

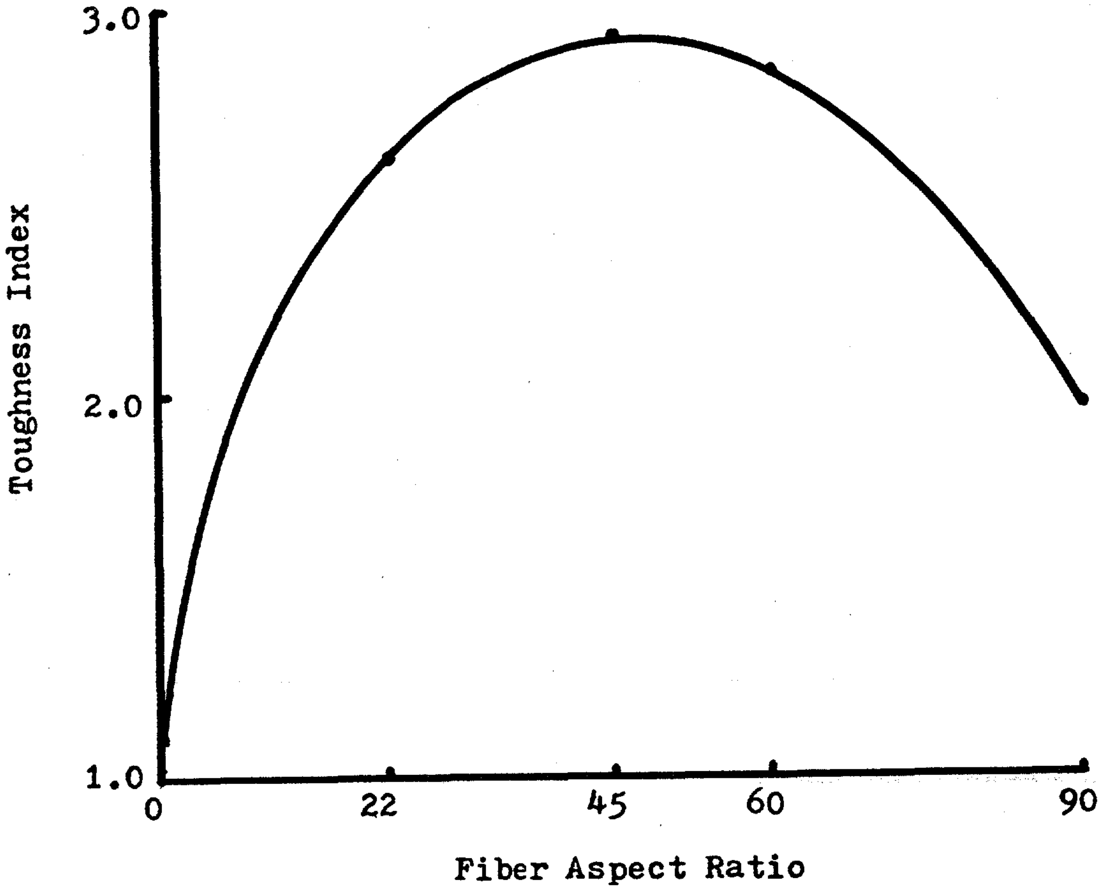


Figure 18 Toughness Index of Panels vs. Fiber Aspect Ratio

increases. However it is shown that there are peak values of MOR and TI at the fiber aspect ratio of 45. The reason for that is that in-plane orientation of fibers is not attainable by static compaction and, therefore, long fibers as compared to panel thickness (aspect ratio over 45 in this case) may be bent during the compaction process.

CONCLUSIONS

Experimental results obtained from this investigation lead to the following conclusions:

a) Mechanical properties of phosphogypsum-based mortar, such as tensile strength and ductility (Toughness Index), are improved by the use of fiber reinforcement, as for the case of conventional concrete with low volume steel fiber reinforcement.

b) Mechanical properties are improved with increasing compaction pressure.

c) There is potential for applications of phosphogypsum-based compaction mortar or concrete as a consequence of adequate mechanical properties for structural uses achieved at a low cement content.

ACKNOWLEDGMENTS

Grateful acknowledgment is made to the Florida Institute of Phosphate Research, Bartow, Florida, for funding this project. Thanks are also due to Mitchell Fibercon Inc., Pittsburgh, Pennsylvania, and Ribbon Technology Corporation, Gahanna, Ohio, for providing the steel fibers, and Gardinier Inc., Tampa, Florida, for supplying the phosphogypsum.

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EFFECT OF MIXING PROCEDURE ON ENGINEERING PROPERTIES OF PHOSPHOGYPSUM- BASED CONCRETE

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ABSTRACT

Raw phosphogypsum, as available from stockpiles, consists mostly of small particles bound together in lumps, varying in size from fractions of an inch to several inches, and having the same consistency. When phosphogypsum is used in combination with cement, sand and gravel the extent to which these lumps are crushed affects the homogeneity of the mixtures and its properties in the hardened state.

The aim of this paper is to report on the strength characteristics under compression, splitting tension and bending of various field-compacted mixtures prepared in three different mixing procedures: pan mixing (using pan mixer), drum mixing (using drum mixer) and hand mixing (using spades) directly on the ground.

Results indicate that the highest strength is obtained when using the pan mixer with grinding wheels. The drum mixer is not capable of crushing phosphogypsum lumps and, in addition, increases the tendency to balling of the fine constituents. As a result, strengths drop to approximately 2/3 of the corresponding mixes prepared with the pan mixer. Finally, hand mixing yeilds to lowest result (approximately half of the maximum value).

1. INTRODUCTION

It is clearly evident that the mixing procedure can play an important role in uniformity of the mix through disintegration of phosphogypsum lumps. As part of strength investigation of the phosphogypsum-based concrete it is necessary to examine the various mixing techniques in order to evaluate the extent to which these lumps of raw phosphogypsum are crushed and eliminated during the mixing.

The objective of this paper is to present a series of results obtained from various mixes consisting of portland cement type I (7.5 and 15% by weight), dihydrate phosphogypsum (45 and 52.5%), limerock sand (20%) and limerock pea gravel (20 and 40%). All mixes were prepared by using different mixing procedures and then compacted, by a field vibratory roller. into the concrete slab sections.

The results of this investigation is intended to provide the reader with information on two major topics:

a) strength comparison for three different mixing procedures.

b) strength comparison for laboratory and field samples.

All strength evaluations are based on the Engineering characteristics such as compression, splitting tension and bending strengths.

2. EXPERIMENTAL PROGRAM

2.1 Materials: Materials used during this investigation consisted of portland cement type I (ASTM.C-150), dihydrate phosphogypsum, finely crushed limerock (specific gravity = 2.7 and average fineness modulus of 2.6) and limerock pea gravel (maximum nominal size of 3/8 inches and specific gravity of 2.69). Raw phosphogypsum was supplied by Gardinier Inc., Tampa, Florida. Both limerock sand and pea gravel were obtained from Miami area.

2.2 Mixing Method and Fabrication: Three different mixing procedures were used in the preparation of the matrices, shown in Figures 1 and 2 :

a) pan mixing with grinding power of pan roller in the pan mixer (vertical rotation);

b) drum mixing (horizontal rotation); and

c) hand mixing directly on the ground.

Dry components of the design proportion were first mixed for a period of fifteen minutes; then the appropriate amount of water was added until a homogenous mix was obtained. The matrix constituent proportions of

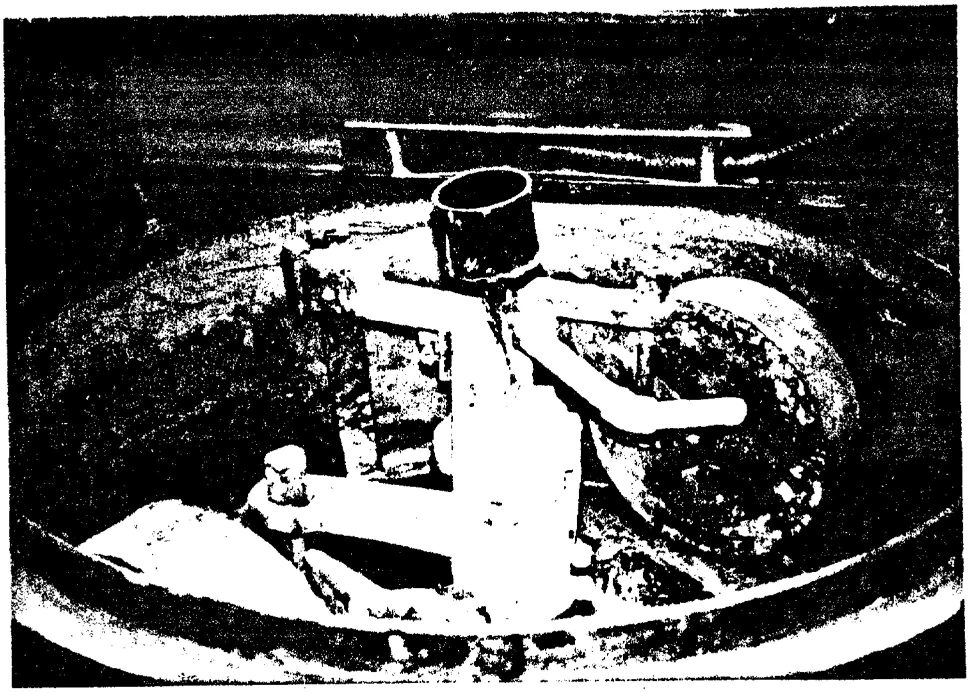

Figure 1: Pan Mixer

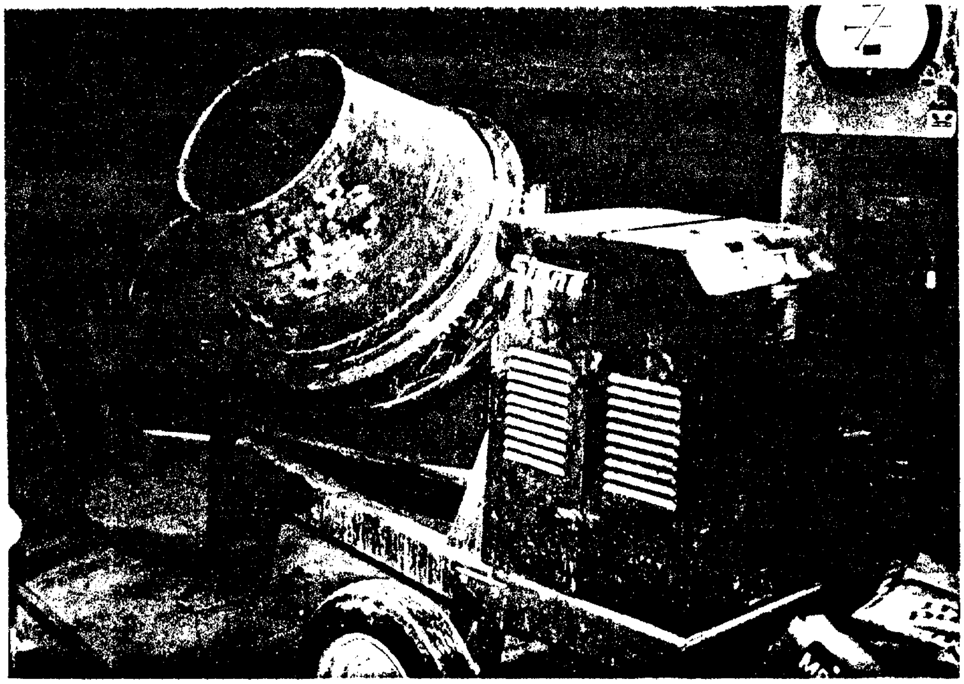

Figure 2: Drum Mixer

different phosphogypsum concrete mixtures selected for this investigation are shown in Table 1.

All phosphogypsum concrete slabs were 3 ft long and 2 ft wide. The final thickness of all sections, 6 inches , was the result of 9 inches deep loose material compacted in three layers (six passes per layer) using road-construction vibratory roller. The dry density of the cored samples , extracted from slab sections, were similar to those obtained from laboratory specimens (as shown in Table 2). This results attest to the fact that the energy-input using conventional vibratory roller was equivalent to that of laboratory Modified Proctor compaction.

2.3. Specimens Types: The cylindrical cores obtained from slab sections were 2.75 inches in diameter and 5.5 inches in height. They were primarily used in evaluation of compression and splitting tension capacity. The standard size beams of 2"x2"x7" (51x51x179 mm) were also cut from concrete slabs and tested in flexure using third point loading system. All beams were simply supported at 6 inches apart.

3. EXPERIMENTAL RESULTS

The results of compression, splitting tension and flexural capacities of the samples obtained from the field compacted phosphogypsum concrete slabs, using three different mixing procedures as stated earlier, are

Table 1 : matrix constituent proportions of field compacted slabs

Mix proportion				Mixer type	Lift (in)	Layers	Passes
C	S	G	P				
7.5	20	20	52.5	pan	2	3	6
7.5	0	40	52.5	pan	2	3	6
15	20	20	45	pan	2	3	6
7.5	20	20	52.5	drum	2	3	6
7.5	0	40	52.5	drum	2	3	6
7.5	20	20	52.5	hand-mix	2	3	6
10	40	30	20	pan	6	1	10

C = cement , S = limerock sand , G = limerock pea gravel

P = dihydrate phosphogypsum

Table 2 : comparison of air-dry density & dry density of field and laboratory samples

Mix proportion*				Field air-dry density & dry density(lb/ft^3)	Laboratory air-dry & dry density (lb/ft^3)	
C	S	G	P		Modified	Standard
7.5	20	20	52.5	114.47 & 113.61	113.7 & 112.56	108.85 & 107.51
7.5	0	40	52.5	115.75 & 114.0	114.1 & 113.26	109.7 & 108.46
15	20	20	45	123.83 & 122.3	123.2 & 120.85	116.74 & 113.56
10	40	30	20	129.23 & 127.07	134.6 & 132.37	128.54 & 126.80

C = cement , S = limerock sand , G = limerock pea gravel , P = phosphogypsum

* pan mixing

shown in Table 3 (air-dry strength) and Table 4 (soaked strength). From comparison of these results, it is clearly evident that the mixing procedure influences the strength properties of the final product. Furthermore, the results indicate that pan mixing provides the most desirable strength, as compared to other mixing techniques. As is shown in Tables 3 and 4, the average compressive strength obtained from drum and hand mixing were 64.5% and 46% of those obtained from pan mixing respectively. In the splitting tension test, the strength obtained from drum mixing provided 63.9% of its equivalent pan mixing procedure, while hand mixing 40%. The values of modulus of rupture were 60% and 43.2% of those of pan mixing.

The explanation of the above results rest in the fact that the grinding power of the pan mixer does effectively disintegrate the phosphogypsum lumps. As a result, it provides the proper dispersion of cement within the matrix and offers the most desirable strength capacity of the final product. The significance of this finding is important for application such as road construction where for the selected mixing technique, the design consideration should allow for proper strength parameters.

Tables 5 and 6 present the comparison of results for the field and laboratory samples in air-dry and

Table 3 : Air-dry strength properties of field compacted phospogypsum-based concrete slabs

Mixing procedure	Compression (psi)	Split-tension (psi)	Modulus of rupture (psi)
Pan-mix	1495 (1.0)	227 (1.0)	383 (1.0)
Drum-mix	962 (0.643)	152 (0.669)	233 (0.608)
Hand-mix	689 (0.461)	81 (0.361)	148 (0.390)

**** Cement: 7.5% Sand: 20% Gravel: 20% Phosphogypsum: 52.5%

Pan-mix	1609 (1.0)	247 (1.0)	370 (1.0)
Drum-mix	1029 (0.640)	157 (0.636)	211 (0.567)

**** Cement: 7.5% Gravel: 40% Phosphogypsum: 52.5%

Table 4 : Soaked strength properties of field compacted phosphogypsum-based concrete slabs

Mixing procedure	Compression (psi)	Split-tension (psi)	Modulus of rupture (psi)
Pan-mix	621 (1.0)	100 (1.0)	163 (1.0)
Drum-mix	396 (0.637)	63 (0.630)	93 (0.571)
Hand-mix	284 (.457)	44 (0.440)	77 (0.473)
**** Cement: 7.5% Sand: 20% Gravel: 40% Phosphogypsum: 52.5%			
Pan-mix	661 (1.0)	114 (1.0)	151 (1.0)
Drum-mix	436 (0.660)	71 (0.622)	96 (0.635)

**** Cement: 7.5% Gravel: 40% Phosphogypsum: 52.5%

Table 5 : Air-dry strength comparison of field and laboratory samples

C:	S:	G:	PG:	Compression (psi)	Split-tension (psi)	Modulus of rupture (psi)
Air-dry strength of field compacted specimens						
7.5	20	20	52.5	1495	227	383
7.5	0	40	52.5	1609	247	370
15	20	20	45	3378	424	643
Air-dry strength of laboratory compacted specimens **						
7.5	20	20	52.5	1824 (M) 1142 (S)	272 (M) 134 (S)	447 (M) 308 (S)
7.5	0	40	52.5	2058 (M) 1457 (S)	280 (M) 182 (S)	440 (M) 288 (S)
15	20	20	45	3945 (M) 3195 (S)	485 (M) 381 (S)	728 (M) 676 (S)

C: cement S: limerock sand G: limerock pea gravel PG: phosphogypsum

(M): Modified proctor (S): Standard proctor

** 2x4 in. cylindrical specimens

Table 6 : Soaked strength comparison of field and laboratory samples

Soaked strength of field compacted specimens

C:	S:	G:	PG:	Compression (psi)	Split-tension (psi)	Modulus of rupture (psi)
7.5	20	20	52.5	621	100	163
7.5	0	40	52.5	661	114	151
15	20	20	45	2171	278	465

Soaked strength of laboratory compacted specimens**

C:	S:	G:	PG:	Compression (psi)	Split-tension (psi)	Modulus of rupture (psi)
7.5	20	20	52.5	763 (M) 522 (S)	99 (M) 56 (S)	199 (M) 138 (S)
7.5	0	40	52.5	952 (M) 622 (S)	133 (M) 81 (S)	212 (M) 137 (S)
15	20	20	45	2084 (M) 1527 (S)	285 (M) 221 (S)	469 (M) 337 (S)

C: cement S: limerock sand G: limerock pea gravel PG: phosphogypsum

(M): Modified proctor (S): Standard proctor

** 2x4 in. cylindrical specimens

soaked testing conditions, respectively. As it can be seen, the field compaction can provide satisfactory and favorable results as compared to those of compacted laboratory specimens. It is therefore concluded that strength characteristics of site consolidation samples can be predicted by using laboratory data of the specimens prepared in accordance with the Modified and Standard Proctor compaction.

A phosphogypsum concrete ramp was constructed at the parking lot of University of Miami on September 1, 1985 (5). The results of core samples extracted from this ramp along with their equivalent tested laboratory samples are shown in table 7 for both air-dry and soaked testing conditions. The encouraging results, i.e. a compressive strength of nearly 4000 psi from field concrete ramp, re-emphasize the advantage of compaction consolidation particularly for the mixtures of low cement content. It also reconfirms the earlier finding that with careful planning, a satisfactory field results comparable to those of laboratory can be easily obtained.

4. CONCLUSION

Based on the results of this investigation the following conclusion can be drawn:

1) Mixing procedure is an important parameter in the

Table 7 : Comparison of strength for field compacted phosphogypsum concrete ramp specimens and their equivalent laboratory samples

(Air-dry strength)

		(Laboratory) **	
	(Field)	Modified	Standard
Compression (psi)	3801	4960	3783
Split-tension (psi)	441	607	473
Modulus of rupture (psi)	----	980	918
(Soaked strength)			
Compression (psi)	2007	2659	2202
Split-tension (psi)	291	398	317
Modulus of rupture (psi)	----	518	494

** 2x4 in. specimens

strength characteristics of phosphogypsum-based concrete.

2) The use of pan mixing, over other mixing methods, results in the highest strength properties for the concrete mixtures containing phosphogypsum.

3) The field compacted phosphogypsum-based concrete slab can provide satisfactory results and its core samples compare favorably with those obtained from laboratory tests.

ACKNOWLEDGEMENT

Acknowledgement is greatly given to the Florida Institute of Phosphate Research, Bartow, Florida, for funding this project. Thanks are also due to Gardinier Inc., Tampa, Florida, for supplying the dihydrate phosphogypsum.

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ENGINEERING PROPERTIES OF PHOSPHOGYPSUM AND SAND MIXTURES FOR SECONDARY ROADS

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ABSTRACT

This study is focused towards finding suitable sand-phosphogypsum mixtures to be used in secondary road pavement construction. Phosphogypsum, whose particles bind together when subject to compaction, is used as binder for the mixtures. The laboratory and field tests are used to investigate the engineering properties of different phosphogypsum-sand mixtures. Unconfined compressive strength, moisture-density and both field and laboratory California Bearing Ratio tests were used to ascertain the suitability of the proposed mixtures as pavement materials. Laboratory and field test results indicated that phosphogypsum-sand mixtures show good promise for use in the construction of secondary roads and highway pavement base.

INTRODUCTION

The main objectives of this research are to study the engineering properties of phosphogypsum-sand mixtures to be used in the construction of the experimental roads in both Polk and Columbia Counties in Florida, and to provide alternate methods of rebuilding county and other secondary roads. This investigation involves the use of the phosphogypsum as a road building material with the possibility of replacing currently used materials (such as clay and limerock) for road construction.

Present construction practice for secondary roads generally consists of mixing fine-grained soils transported to the site with the existing granular subgrade soil. Granular soil is abundantly available throughout Florida. However, the lack of an adequate source of fine-grained soil, such as clay, has been a major concern for the road builder. Phosphogypsum, also a fine-grained binder, is abundantly stockpiled in Central and North Florida and possibly serves as an economical replacement for clay.

The materials used in this research include granular (sandy) soil widely available in Polk and Colombia Counties, Florida, and phosphogypsum, a by-product of the phosphate industry.

Both the unconfined compression and the California Bearing Ratio tests were used to investigate the engineering properties of phosphogypsum-sand mixtures consisting of different proportions of phosphogypsum and sand, thereafter, the selected mixtures were studied for their application under actual site conditions.

Small sections of pavement were compacted outdoors with a hand compactor to compare laboratory results with field tests.

It is anticipated that the results of this investigation will serve as the basis for the design, construction and monitoring of experimental roads to be built in both Polk and Columbia Counties, Florida. In addition, the results will be used to help determine the suitability of phosphogypsum-sand mixtures as secondary road construction materials.

MATERIALS

Phosphogypsum:

Wet process phosphoric acid is manufactured by mixing ground phosphate rock with sulfuric acid. After separation by filtration, the phosphoric acid is the liquid product and dihydrate phosphogypsum (calcium sulfate) is the solid by-product waste. For each ton of wet process phosphoric acid, there are approximately 5 tons of dihydrate phosphogypsum produced.

Phosphogypsum from two different places was used in this research program. The dihydrate phosphogypsum was stockpiled in Central Florida, Florida. The hemihydrate phosphogypsum was from Occidental Chemical Company site White Spring, Florida. Figures 1 and 2 show the grain size distribution curves and specific gravity for the phosphogypsums and sands used in this investigation.

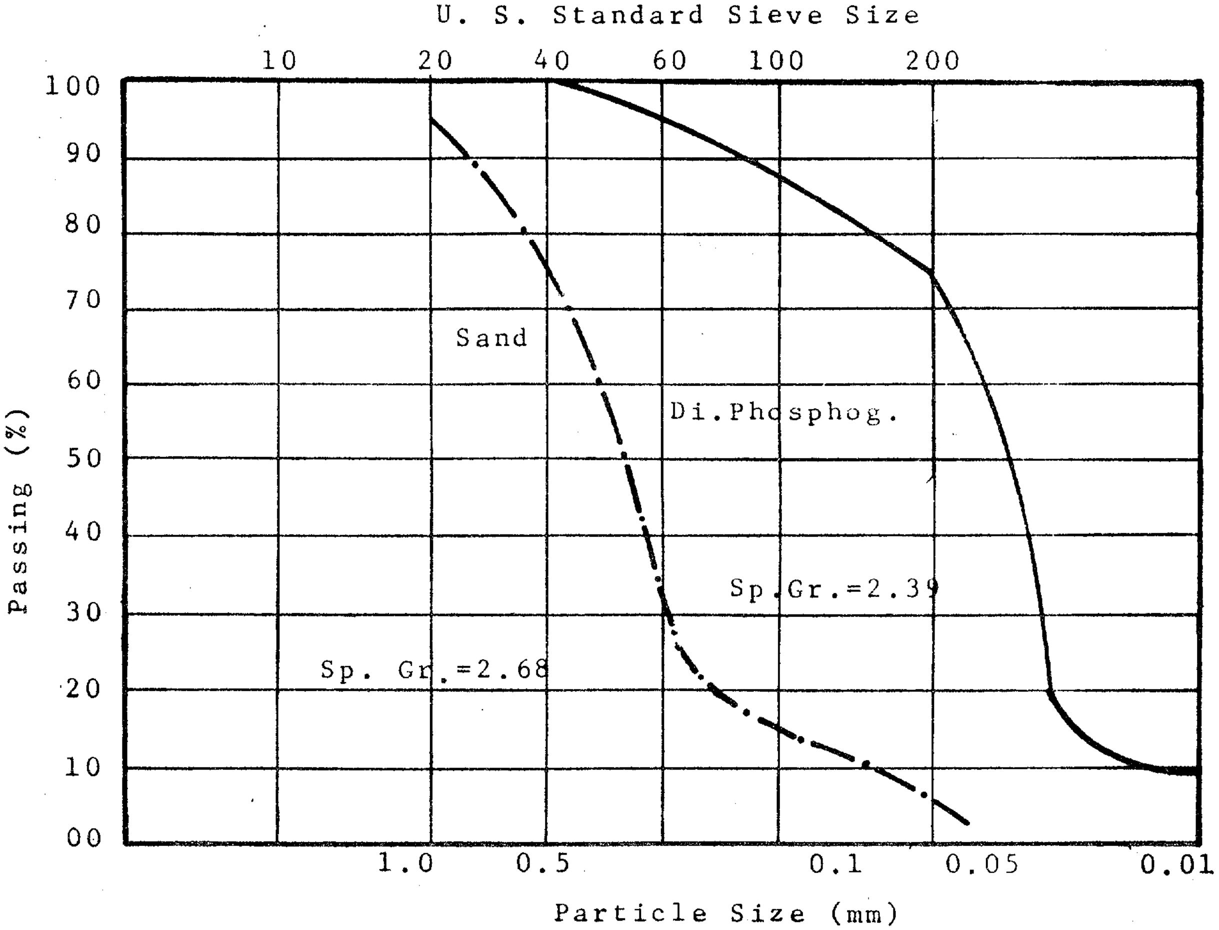


Figure 1 Grain Size Distribution of Dihydrate Phosphogypsum and Polk County Sand and Their Specific Gravity

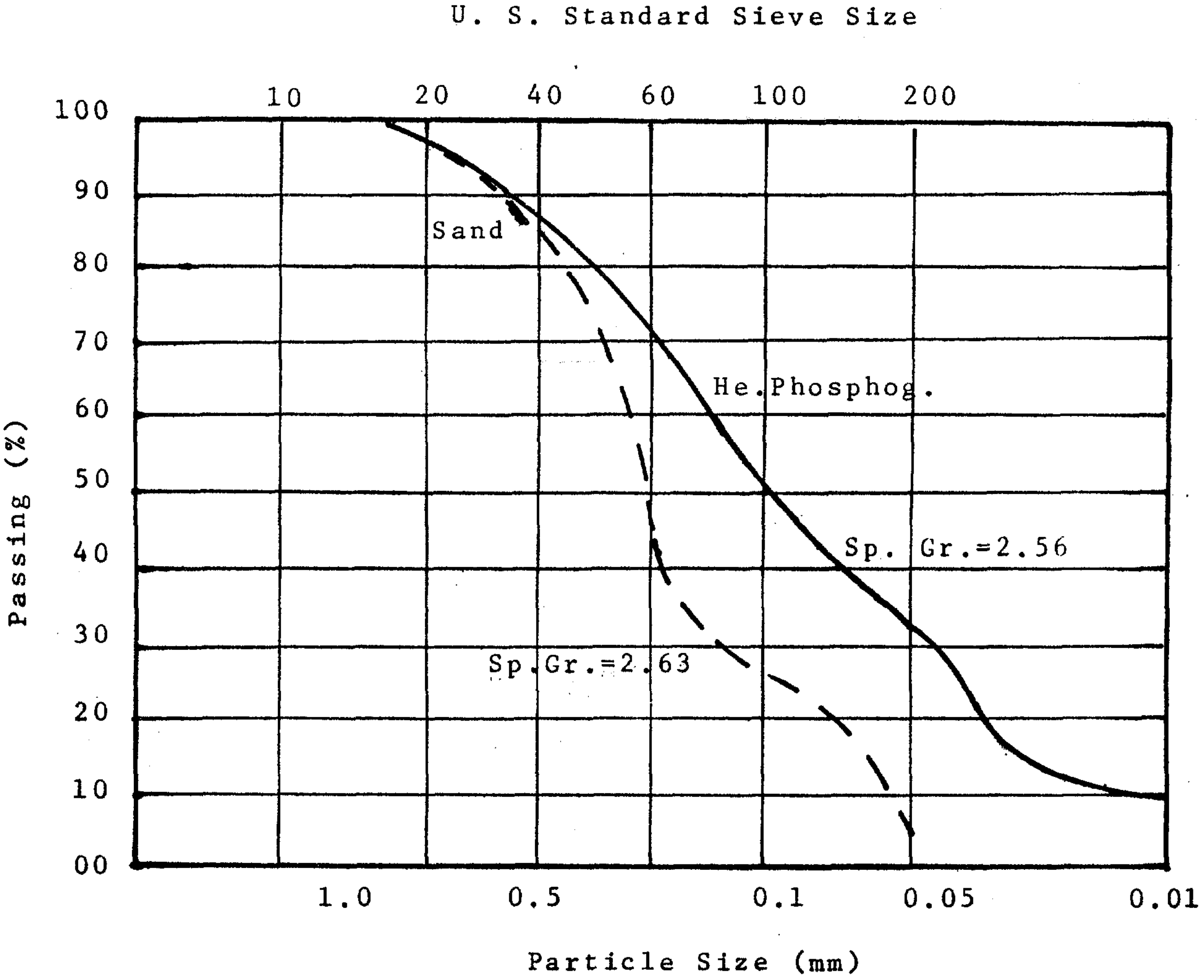


Figure 2 Grain Size Distribution of Hemihydrate Phosphogypsum and Columbia County Sand and Their Specific Gravity.

Sand:

Two different kinds of sand were used in the phosphogypsum-based mixtures. These sands were obtained from the actual construction sites at Polk County and Columbia County in order to simulate actual field conditions as close as possible. The grain size distribution curves and specific gravities are also shown in Figures 1 and 2. The results as shown in the Figures 1 and 2, indicated that these two different kinds of sand were classified as A-3 soils according to the AASHTO soil classification system.

ENGINEERING PROPERTIES OF PHOSPHOGYPSUM AND SAND MIXTURES

This section introduces the methodology to determine appropriate percentages of phosphogypsum and sand with desirable engineering characteristics for experimental road construction. On the basis of strength and density criteria consisting of moisture-density, unconfined compression, both laboratory and field California Bearing Ratio Tests, the suitability of the proposed mixtures as pavement materials was ascertained.

Mixtures compacted in accordance with the Modified Proctor method and consisting of phosphogypsum content between 25% and 66% and sand between 33% and 75% were studied.

Moisture Density Relation

The moisture density test was performed according to the Modified Proctor Method (ASTM D 1557-70) The Modified Proctor method of compaction was chosen for its compatibility to modern field compaction equipment.

The determination of the optimum mixture involved the use of six different combinations were listed in Table 1.

Specimens prepared for this purpose were 4.0 in. in diameter and 4.58 in. in length (ASTM D 1557-70).

Moisture content was obtained after subjecting samples from the mixture to a temperature of 60 degrees Celsius in a convection oven for 24 hours. This low temperature was selected on the basis of ASTM Specification (D 2216-71) and was required to prevent the calcination of Phosphogypsum. Three samples were used in all cases to obtain an good average of the moisture content.

From Figure 3, it can be observed that the dry density of the mixtures increases from the ratio 1:3 to the ratio 1:2 where it reaches a maximum dry density of about 2.01 (g/cm^3). Further reducing the amount of sand in the mixture to the ratio 1:1 causes a decrease in the dry density. This decrease can be attributed to the fact that excess of phosphogypsum (which has a lower specify gravity) causes an opposite trend with the consequent reduction in the dry unit weight.

Moisture-density relationships for hemihydrate phosphogypsum and Columbia County sand mixtures are

Table 1. Mixture Proportions

Mixture No.	Di. Gypsum (%)	Polk Sand (%)	He. Gypsum (%)	Columbia Sand (%)
1	25	75	-	-
2	33.3	66.6	-	-
3	50	50	-	-
4	-	-	33.3	66.6
5	-	-	50	50
6	-	-	66.6	33.3

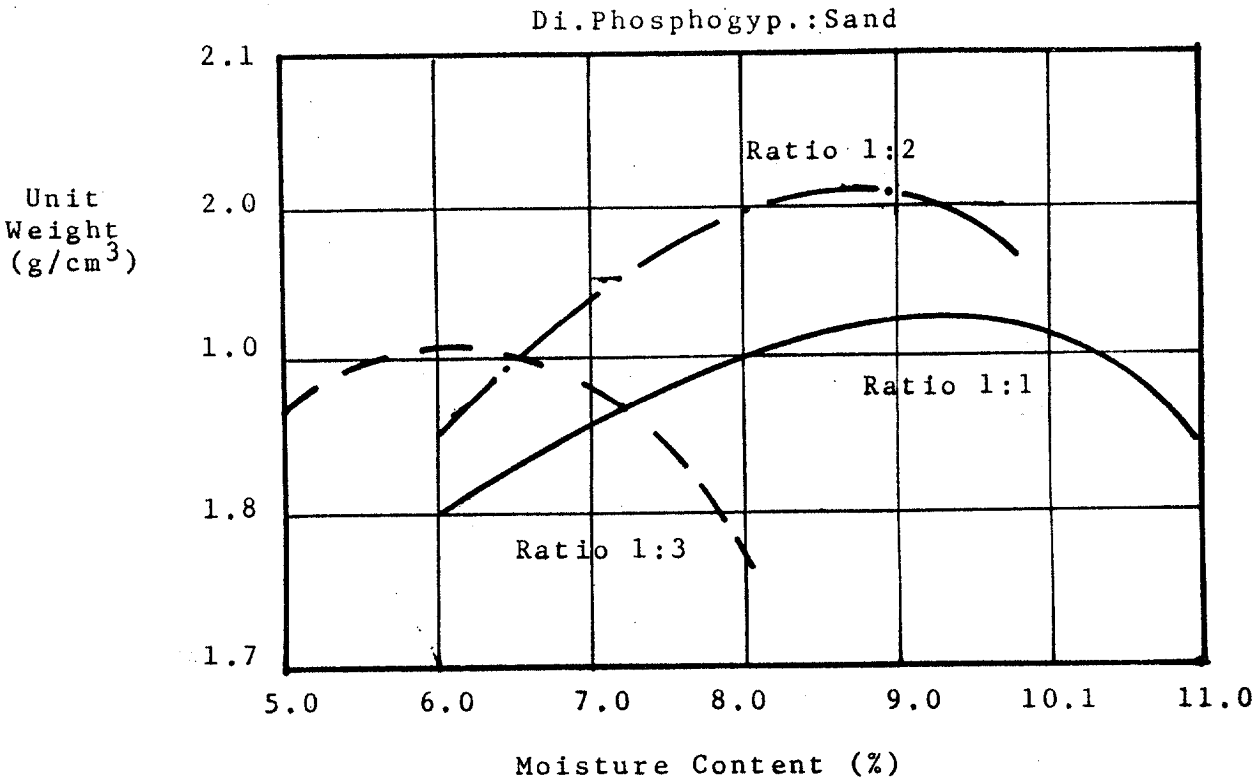


Figure 3 Moisture Density Relation of Dihydrate Phosphogypsum and Sand Mixture

shown in Figure 4. In these mixtures, it can be observed that the higher amount of hemihydrate phosphogypsum, the higher the dry density of the mixture. For a ratio of 2:1 of hemihydrate phosphogypsum to sand mixture, the optimum moisture content is around 9.5%, whereas the maximum dry density is 2.07 (g/cm^3).

Unconfined Compression

The testing of the proposed mixtures for unconfined compressive strength was performed on specimens 2.0 in. in diameter and 4.0 in. in length, according to the Modified Proctor compaction specification. (ASTM D 2166-65:. The mixtures studied in this section correspond to those in density test.

Results of the unconfined compression tests conducted on the above mentioned mixtures were as follows:

a) Unconfined Compressive Strength Immediately after Compaction

To study the strength of the mixture without any curing, the specimens were tested immediately after compaction as shown in Figure 5. Prom these results, the strength of the subbase using this mixture immediately after compaction can be predicted.

b) The Unconfined Compression under Sealed Curing Condition

The unconfined compression under sealed curing conditions were performed at different time intervals.

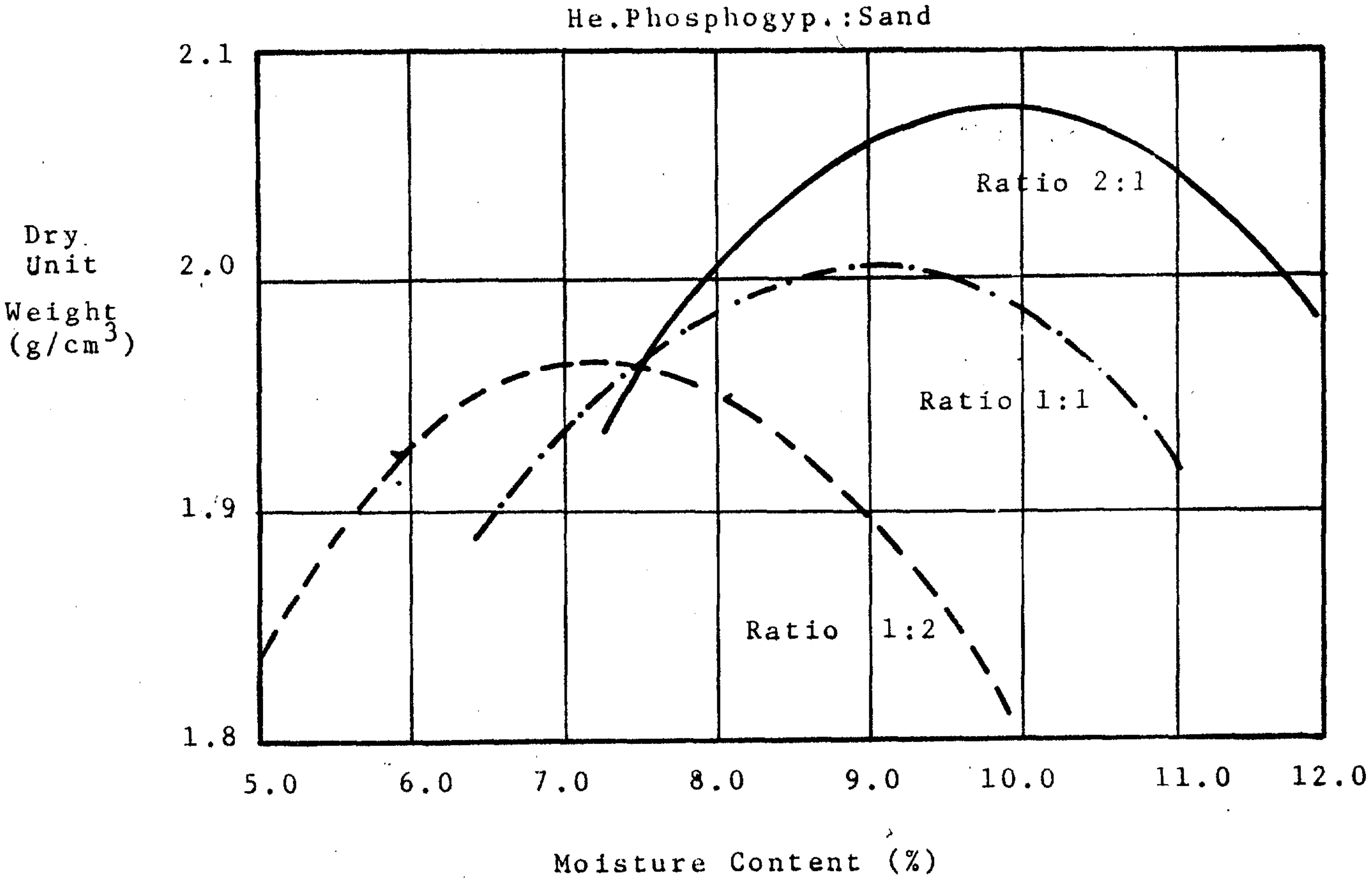


Figure 4 Moisture Density Relation of Hemihydrate Phosphogypsum and Sand Mixtures

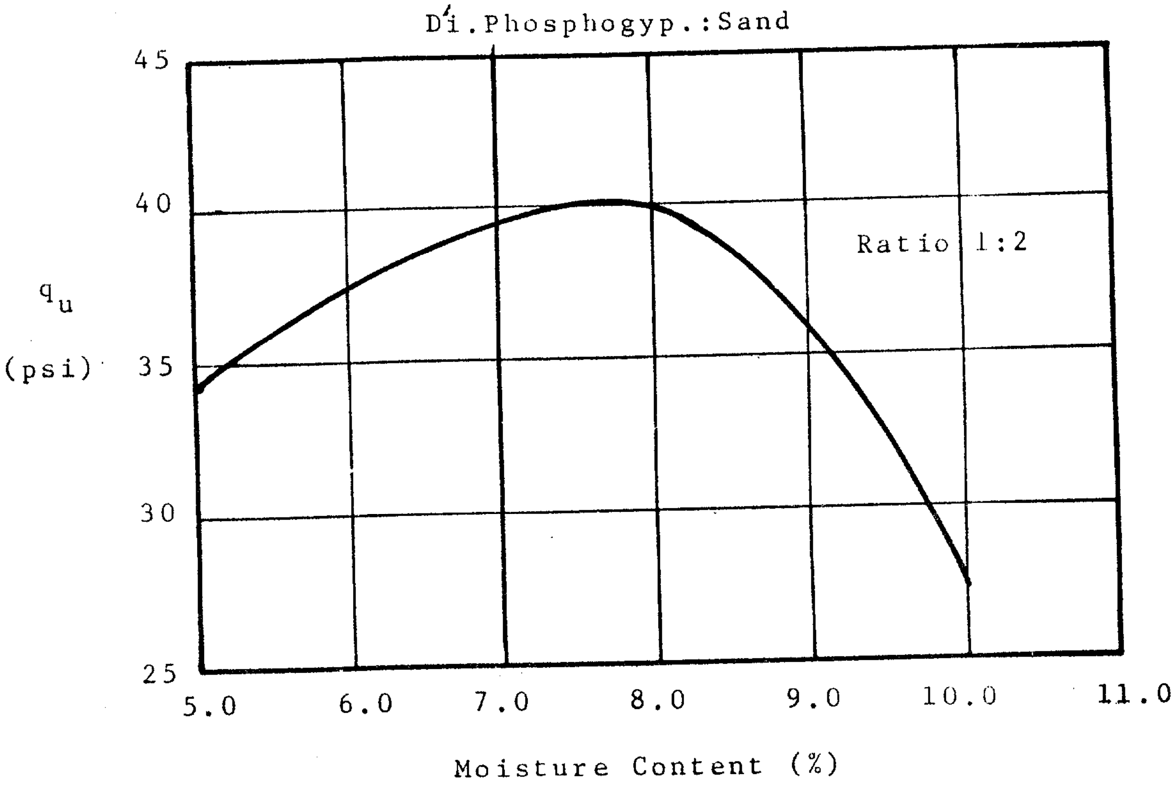


Figure 5 Unconfined Compressive Strength of Samples vs. Moisture Contents at Compaction for Dihydrate Phosphogypsum and Sand Mixture (Test Conducted Immediately after Compaction).

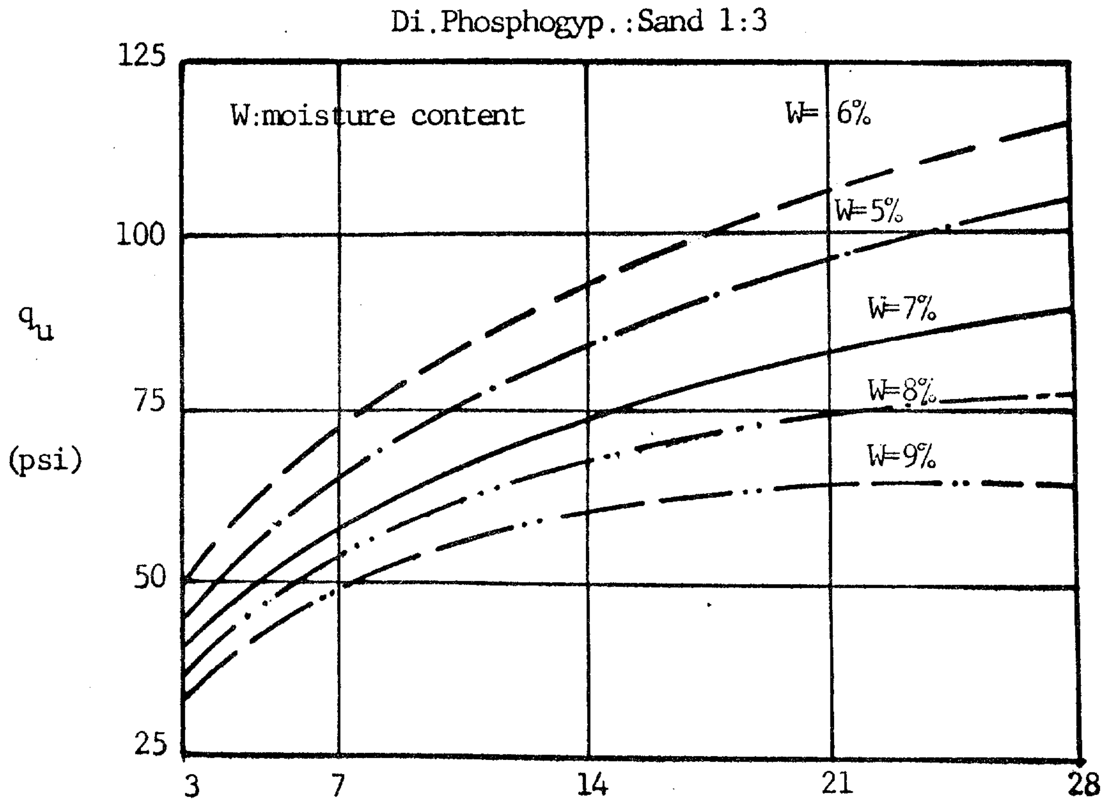
The material strength, under sealed curing conditions, was considered to simulate the on site condition. Figures 6, 7 and 8 represent the unconfined compressive strength of dihydrate phosphogypsum and Polk County sand mixtures under sealed curing conditions at different intervals. Analysis of these curves suggests that the strength increased continuously with curing time. After comparing the strength of different mixtures, it is observed that the 1:2 of phosphogypsum-sand mixture with moisture content 7% has the highest strength. Higher contents of phosphogypsum in the mixture decrease unconfined compressive strength.

c) Unconfined Compressive Strength under Soaked Conditions

The unconfined compressive strength of the specimens under soaked conditions were studied. The results indicated that the dihydrate phosphogypsum and sand cylindrical specimens were not water resistant, hence, they collapsed when they were immersed in water. As shown in Figure 9, the mixtures of hemihydrate phosphogypsum and Colombia County sand showed good water resistance under soaked conditions. It can be observed that the higher the hemihydrate phosphogypsum content in the mixtures the higher the soaked strength of the specimens.

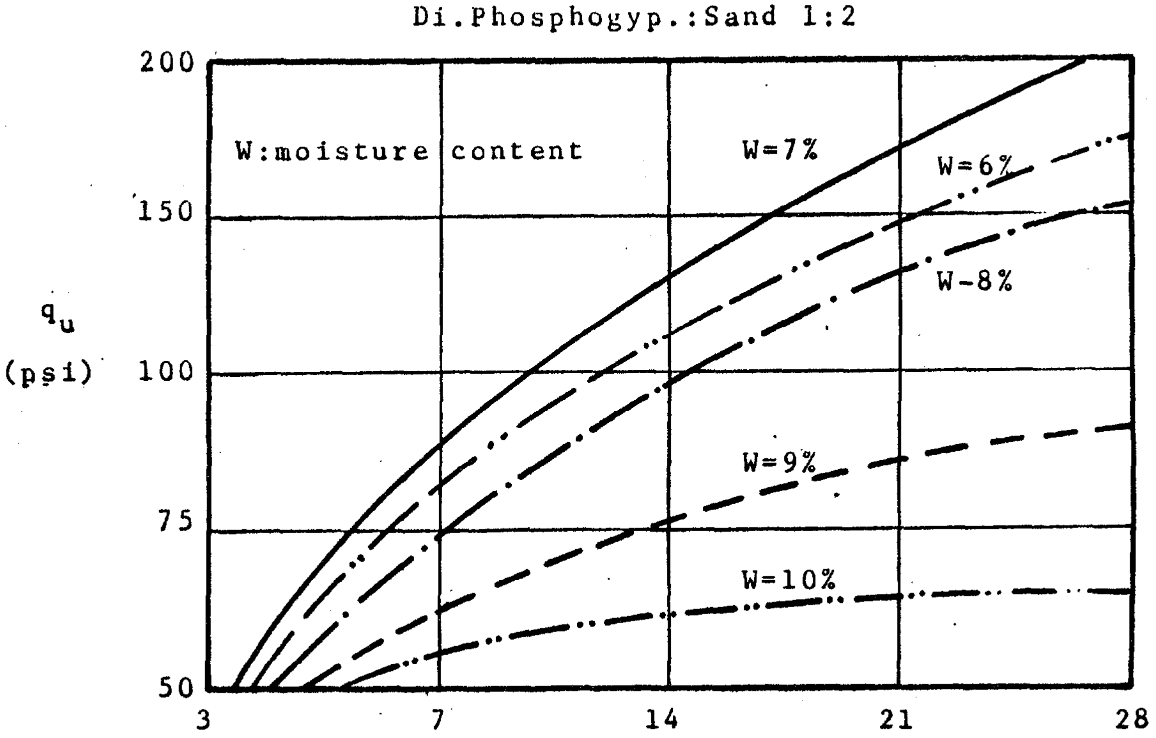
Effect of Compaction Energy

In order to study the effect of the compaction in the



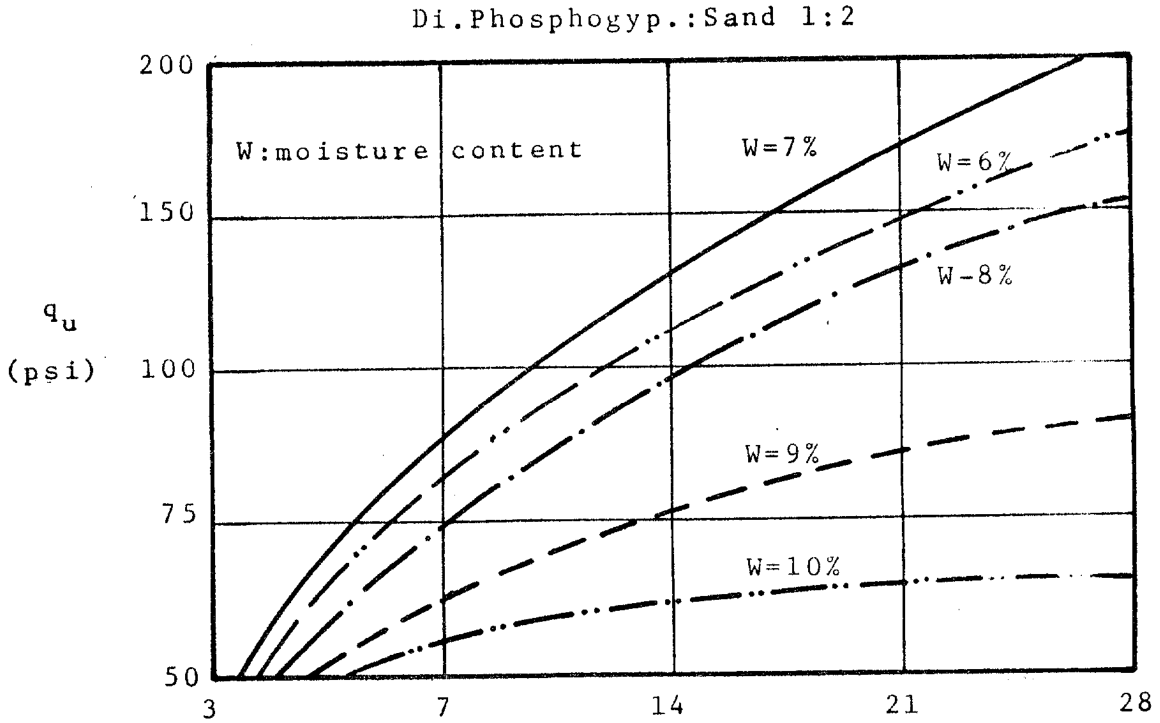
Time of Curing (days)

Figure 6 Unconfined Compressive Strength of Samples vs. Time of Curing for Different Moisture Contents at Compaction, Under Sealed Curing Condition for a 1:3 Ratio of Dihydrate Phosphogypsum and Sand Mixture



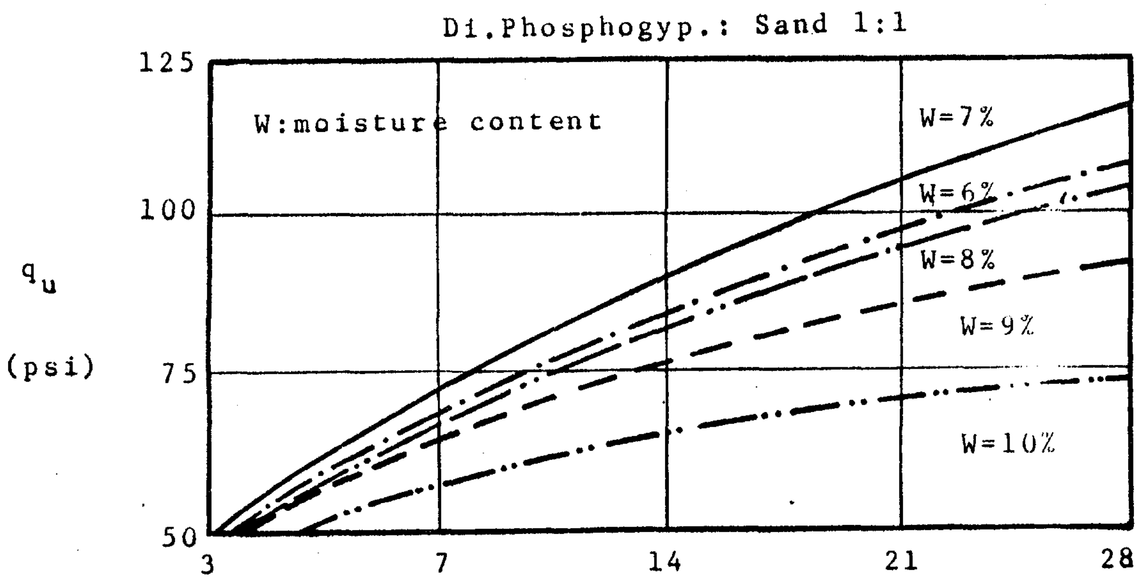
Time of Curing (days)

Figure 7 Unconfined Compressive Strength of Samples vs. Time of Curing for Different Moisture Contents at Compaction, under Sealed Curing Condition for 2:1 Ratio of Dihydrate Phosphogypsum and Sand Mixture



Time of Curing (days)

Figure 7 Unconfined Compressive Strength of Samples vs. Time of Curing for Different Moisture Contents at Compaction, under Sealed Curing Condition for 2:1 Ratio of Dihydrate Phosphogypsum and Sand Mixture



Time of Curing (days)

Figure 8 Unconfined Compressive Strength of Samples vs. Time of Curing for Different Moisture Contents at Compaction, under Sealed Curing Condition for 1:1 Ratio of Dihydrate Phosphogypsum and Sand Mixture.

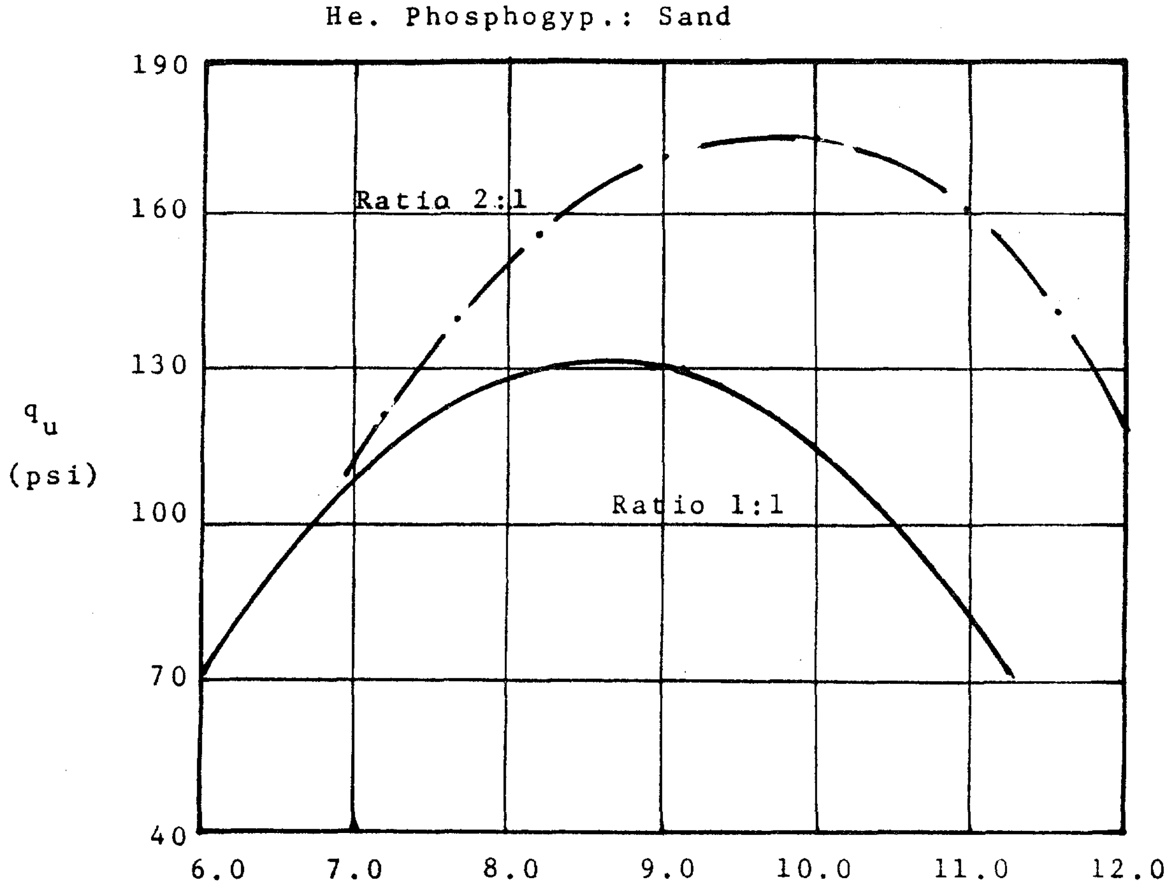


Figure 9 Unconfined Compressive Strength of Samples vs. Moisture Content for Different Ratio of Hemihydrate Phosphogypsum and Sand Mixtures at Optimum Moisture Contents Under Soaked Curing Condition.

road construction process, the relationship between compaction energy and strength of phosphogypsum and sand mixtures was studied.

For this phase of the research, the specimens were compacted separately according to Standard or Modified Proctor compaction method, but subjected to the same curing condition (air dry).

Based upon the experimental results studied previously, the 1:2 mixture of dihydrate phosphogypsum and Polk County sand was chosen to represent the material characteristics. Figure 10 shows that higher unconfined compressive strength resulted, as expected, from specimens compacted according to the Modified Proctor method than compacted according to the Standard Proctor method. The results of this study indicate that compaction effort has a marked effect on strength in the construction of the secondary road.

Laboratory CBR Test

The CBR value of the materials was evaluated from tests conducted immediately after compaction according to the Modified Proctor method (ASTM D 1883).

Results of CBR tests are shown in Figures 11 and 12. It is possible to observe from Figure 11, that the mixtures of dihydrate phosphogypsum and sand in ratio of 1:2, give the highest CBR value when compared with other mixtures ratios.

In the Figure 12, the CBR values increase with the

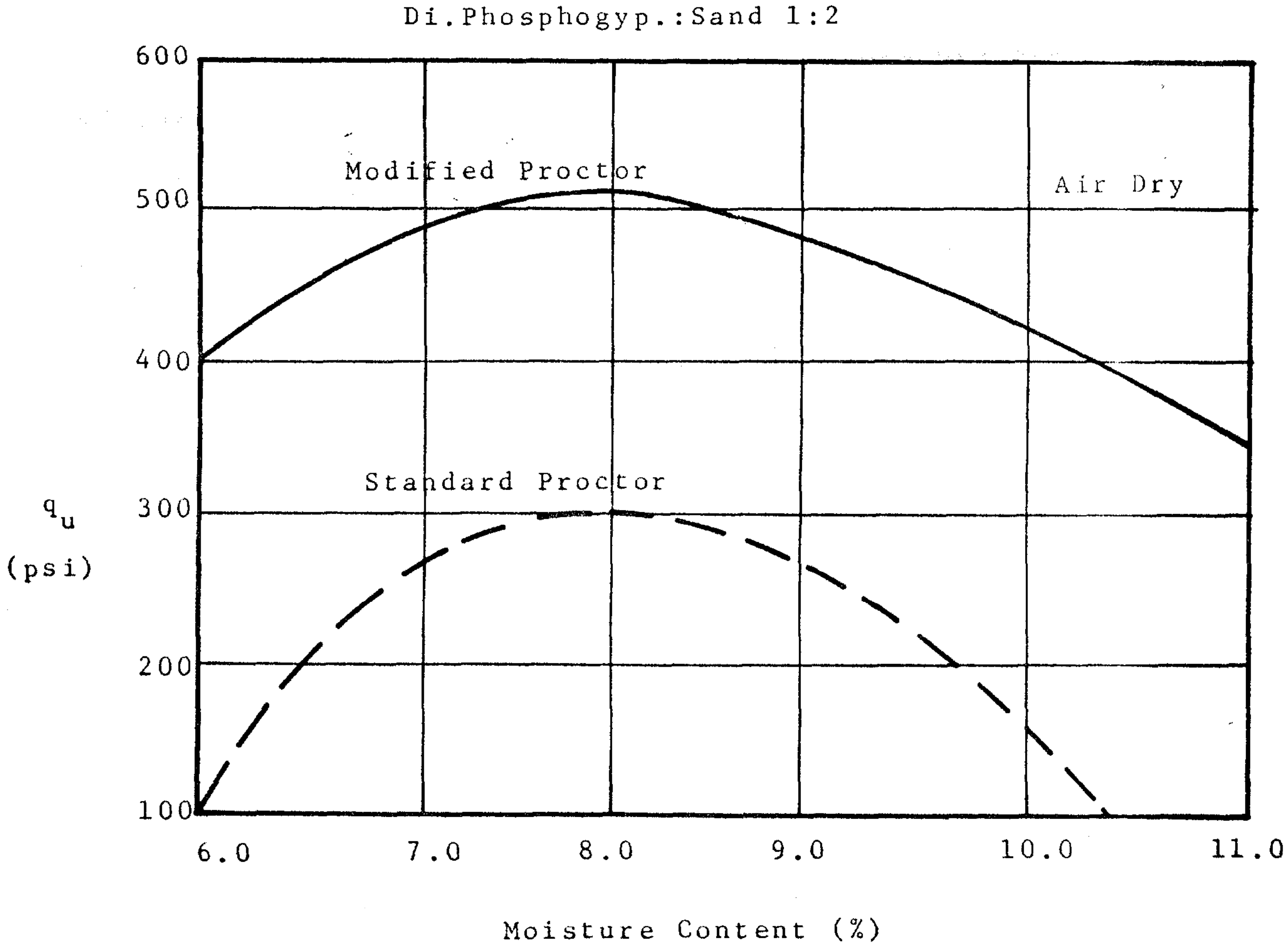


Figure 10 Unconfined Compressive Strength of Samples vs. Moisture Contents at Compaction for Dihydrate Phosphogypsum and Sand Mixture (1:2) under Air Dry Condition With Different Compaction Methods

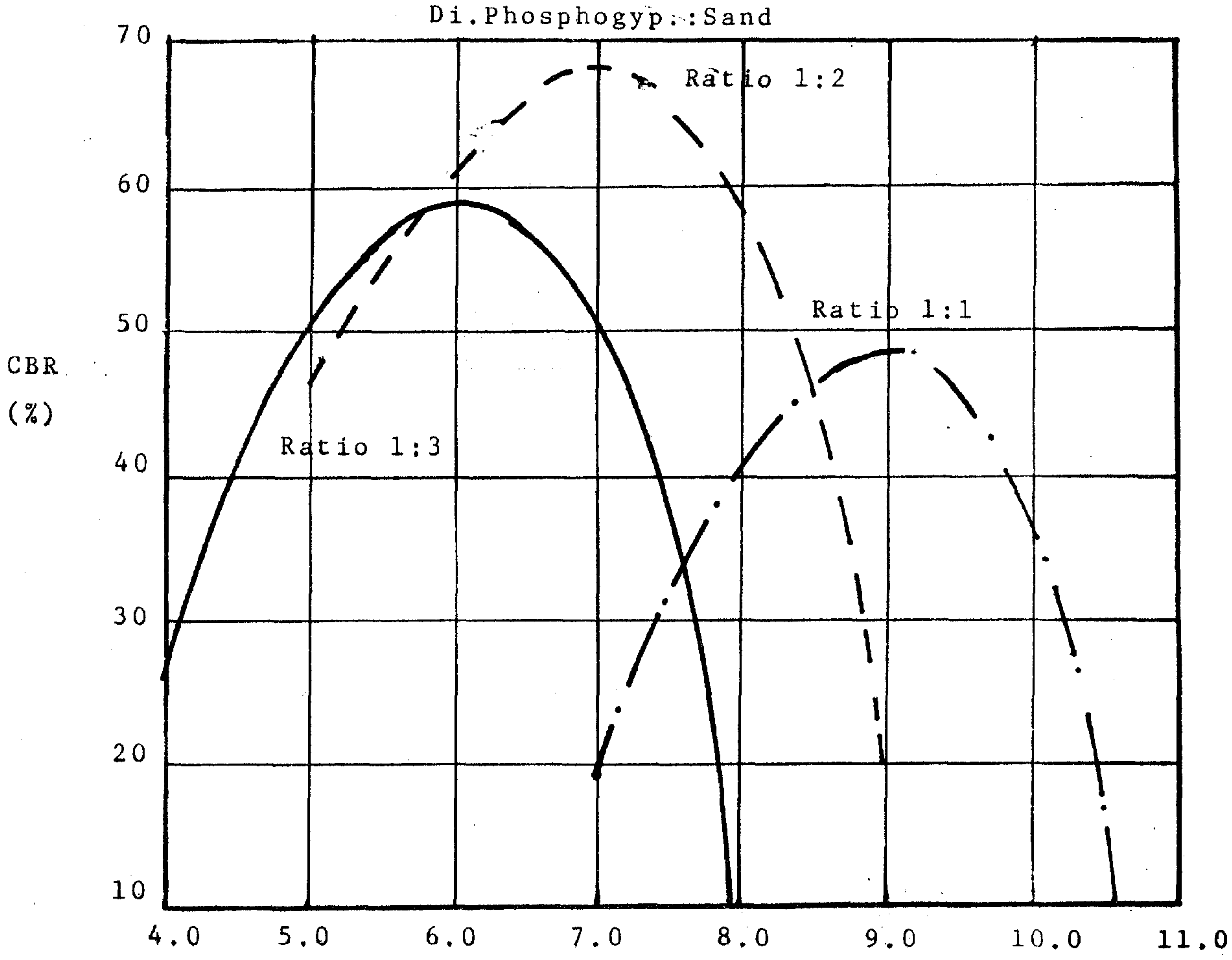


Figure 11 Modified CBR Test Conducted Immediately after Compaction on Dihydrate Phosphogypsum and Sand Mixtures.

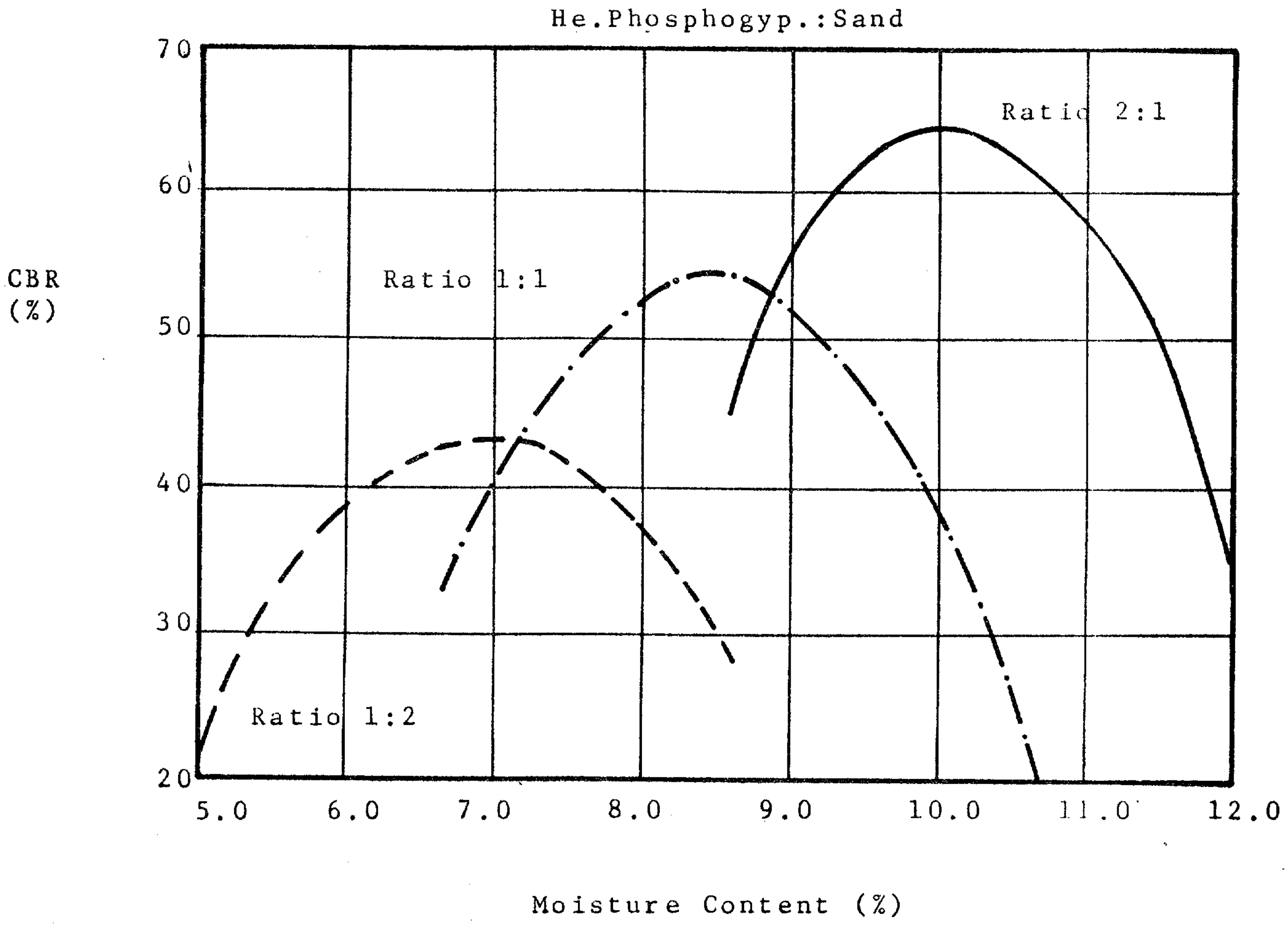


Figure 12 Modified CBR Test Conducted Immediately After Compaction on Hemihydrate Phosphogypsum and Sand Mixtures.

hemihydrate phophogypsum content in the mixtures. Therefore, it can be concluded that the higher the hemihydrate phosphogypsum content in the mixture, the higher the CBR value will be.

Field CBR Test

It is desirable to check the laboratory CBR value with those actually obtained during construction. To accomplish this, field tests were conducted. Small pavement sections 2 ft by 3 ft and 5 in. in thickness were compacted outdoors with a hand compactor.

The testing equipment consisted of a forklift truck fitted at its rear with CBR equipment. This set up provides a mobile unit that could monitor CBR at different location on the pavement.

Based on laboratory test results, a few mixtures were selected to study the field CBR value. Field CBR test results are shown in Figure 13 for the characteristic mixtures specified in Table 2.

Results presented in Figure 13 show that the value of CBR of dihydrate phosphogypsum and Polk County sand mixture is much higher than that of sand or phosphogypsum. Because the RC-70 improves the water resistance of the dihydrate phosphogypsum and sand mixture, the addition of small amount RC-70 in the mixture further increases the value of CBR, thereby, improving the quality of the pavement.

Table 3 summarizes the composition of mixtures covered

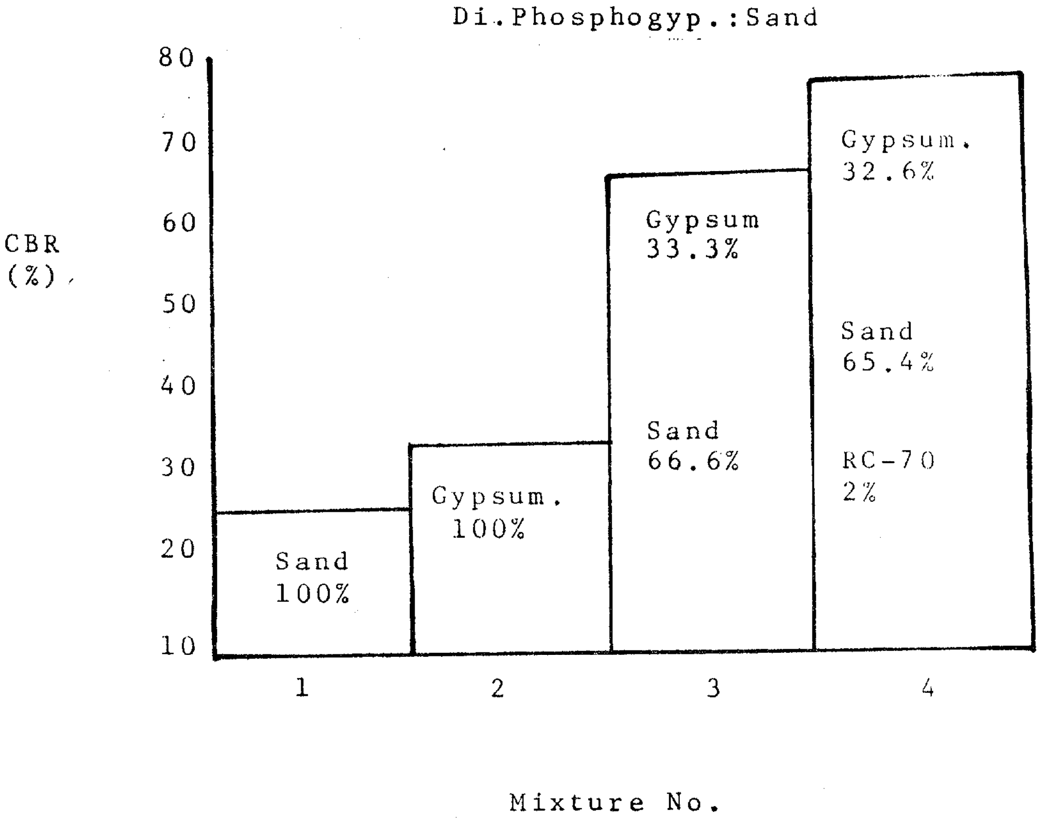


Figure 13 Variation of Field CBR Test on Dihydrate Phosphogypsum and Sand Mixtures

Table 2 Mixture Proportions of the Pavement and Tneir Moisture Contents at Compaction and Test Time for Dihydrate Phosphogypsum and Sand Mixture

Mixture No.	Di.Gypsum (%)	Polk Sand (%)	RC-70 (%)	Moisture at Compact (%)	Moisture at Test (%)
1	-	100	-	-	-
2	100	-	-	18	4.5
3	33.3	66.6	-	10	3.2
4	32.5	65.4	2	10	3.2

Table 3 Mixture Proportions of Pavement and Their Moisture Contents at Compaction and Test Time for Hemihydrate Phosphogypsum and Columbia County Sand Mixtures

Mixture No.	He.Gypsum (%)	Columbia Sand (%)	Moisture at Compaction (%)	Moisture at Test (%)
1	-	100	-	4.0
2	50	50	11	3.6
3	66.6	33.3	12.5	3.6
4	100	-	22	4.0

in Figure 14 as well as their moisture content immediately after compaction and during testing. Examining Figure 14, the trend of field CBR values seems to be no different from that of laboratory tests. These results show that pavements under actual weather conditions behave satisfactorily. Both field and laboratory CBR tests are source of the basic parameters for experimental road design.

SUMMARY

The following conclusions are reached for this paper on the basis of observations gathered during the experimental program.

a) Based on the test results obtained from unconfined compressive strength under different curing condition and CBR values, the following mixtures are recommended for the Polk County and Columbia County road projects.

Polk County road project:

The optimum mixture contains 33% dihydrate phosphogypsum and 67% sand by dry weight

Columbia County road project:

From the testing, it was determined that higher content of hemihydrate phosphogypsum in the mixture results in higher strength, a phosphogypsum mixture composed of 66% or higher hemihydrate phosphogypsum and 33% or lower Columbia County sand was considered suitable.

b) Higher compaction energy results in higher compressive strength. Applying these results to road

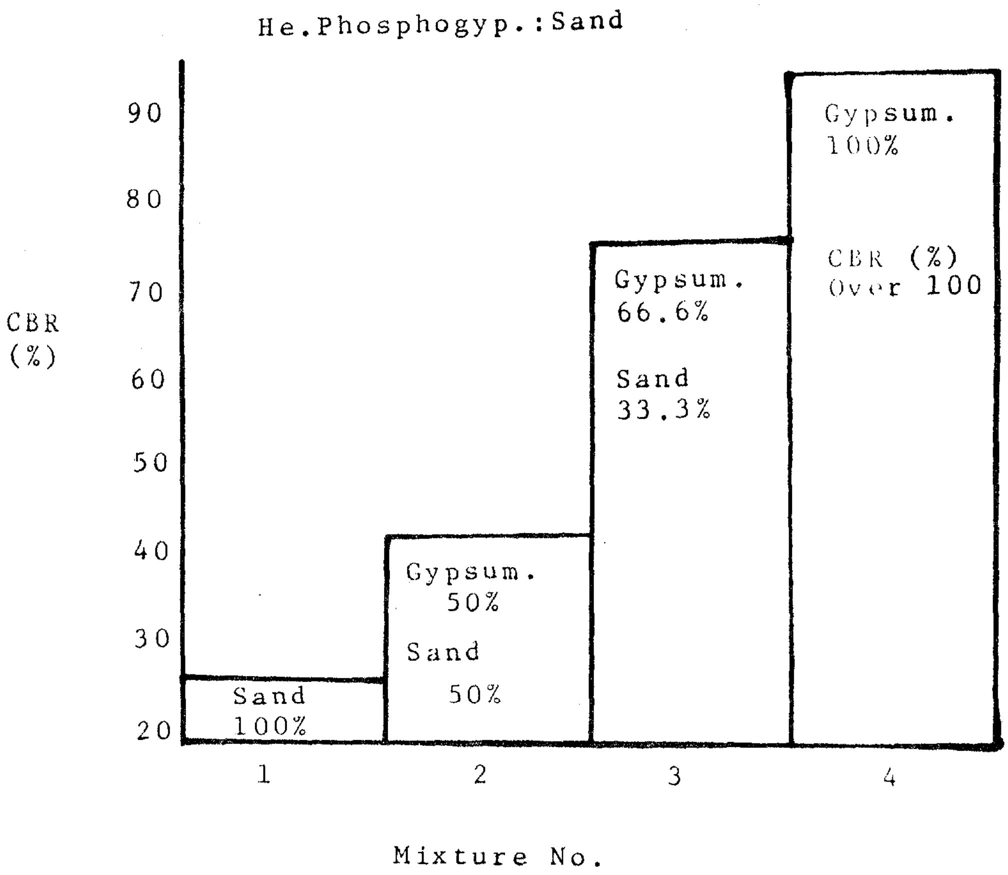


Figure 14 Variation of Field CBR Tests on Hemihydrate Phosphogypsum and Sand Mixtures

construction, the more compactive effort on the mixture, the better the quality of the road.

ACKNOWLEDGEMENTS

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NEUTRALIZATION AND STABILIZATION OF PHOSPHOGYPSUM FOR ROAD CONSTRUCTION

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Abstract

Neutralization curves using NaOH, $Ca(OH)_2$, NH_4OH and reclaimed fly ash were compared to determine the most effective means for reducing acidity which adversely effects strength development in stabilized phosphogypsum mixtures. Various amounts of NaOH and $Ca(OH)_2$ were used to achieve different pH values before a Type I portland cement and a high lime (Type C) fly ash were used as stabilizers. Unconfined compressive strength measurements after curing for 3, 7 and 28 days were generated. At low cement contents the difference in strength development following neutralization with NaOH and $Ca(OH)_2$ was not significant. At all cement contents and with 20% fly ash, the addition $Ca(OH)_2$ consistently increased the strength. On the other hand, at cement contents above 6% the addition of large amounts NaOH yielded lower strengths and produced premature cracking. A possible explanation is offered in view of the salts produced.

Phosphogypsum acidity was also lowered by water leaching to avoid salt formation. The acidic, (pH -2.5) natural material developed higher strength than the leached material when both were stabilized with cement. The reverse behavior was observed with fly ash. These results were explained as a consequence of leaching out the fine particles essential for good compaction. It was demonstrated that shape and size distributions of particles may be more important than acid level in achieving higher strength.

INTRODUCTION

Inactive (aged) phosphogypsum stockpiles in Florida and Texas were found to possess higher acidity than active ones (1,2,3). The pH of the material in the upper 18 inches of an inactive pile at Mobil Chemical Company's facility in Pasadena, Texas varied from 4.5 to 6.0 while the pH of material from an inactive source in Florida varied from 3.7 to 4.4. The lower acidity in the aged piles can be attributed in part, to the progressive leaching of P_2O_5 by rain water. Previous studies on a large numbers of stockpiles in Florida using Analysis of Variance, revealed no significant difference in free water content or in the concentration of the elements with depths. However, more recent studies carried out by the Texas Transportation Institute (TTI) on both active and inactive stockpiles indicate otherwise (1,2), Mineralogical examination of material from Mobil's active pile showed that, although the particle size distribution was relatively homogenous throughout the pile, the moisture content tended to vary over a wide range. While no consistent pattern was displayed by the moisture content, the acidity and the dissolved uranium appeared to increase with depth.

May and Sweeney reported that the residual radioactivity in Florida PG averaged 21 pci/g (3). This value approximates that found in the Mobil PG. In 1983, the Environmental Protection Agency issued its recommended standards to govern residual reactivity at inactive uranium processing sites. These standards restrict the allowable radium activity to 5 pci/g in the top layer and 15 pci/g at depths below 15cm. May and Sweeney (3) and Gadalla, Saylak and Rozgonyi, (4) showed that residual radium in the PG produced by the dihydrate process is concentrated in the fine particle size fractions. On the other hand, the uranium concentrates itself in the large particles (4,5).

Historical Background

Using EPA recommended standards May, et al. (6) calculated the maximum amounts of PG which could be safely used in road construction. They concluded that compositions containing up to 23.8 percent PG may be used in surface layers while mixtures with up to 71.4 percent PG may be used in subsurfaces at depths exceeding 6 inches. These figures may be conservative since higher fractions may be permitted when the PG mixtures are covered with a dense material with a low permeability such as asphalt or portland cement concrete.

Results from on going research at TTI to utilize PG as a base *course* and subbase in roads, parking lots and storage yards continue to be very promising. Cement and fly ash stabilized PG systems were developed and successfully demonstrated as base courses on several streets for the city of La Porte, Texas (7). Post-construction evaluation, now in its third year indicates that the streets are performing well with no signs of structural failure. Cost savings up to 50 percent over conventional road base materials were realized during this project. Since that time, over 70 additional projects using cement-stabilized PG have been completed (8).

Phosphogypsum stabilized with either a high-lime fly ash or with portland cement exhibits sufficient unconfined compressive strength to satisfy specifications established by the Texas SDHPT (State Department of Highways and Public Transportation) (1,2,4,9). Allowable 7-day strength levels required to satisfy these specifications (i.e. 650 psi) were met with 10 percent portland cement (9). A modified Proctor compaction technique (ASTM D-1557-Method A) using a free-fall, kneading-type compacting action was used to achieve this strength. This procedure requires nearly 2.5 times the energy (32.6 ft-lb/in^3) and a smaller specimen size than that specified by SDHPT for its cement stabilized soils. It should be noted that mixture densities associated with this additional compactive effort were easily achieved in the field during the La Porte, Texas project using conventional construction equipment.

Initially, the acidity, as reflected by pH, appeared to be the primary factor responsible for retarding strength in stabilized PG materials. Test results indicated that compressive stress tended to increase with pH. The PG obtained from a 10-year old, inactive pile (Pile 2) at the Mobil Chemical Company in Pasadena, Texas proved to be less acidic (pH=5.5) and generated a significantly greater load carrying capability than their active Pile 3 (pH=2.3) at the same plant. Washing the acid out of the active pile material to achieve a pH corresponding to that in the inactive pile yielded a significant improvement in strength when fly ash was used for stabilization (See Figure 1). However, contrary to what was expected, the strength obtained was much lower than that obtained with naturally aged material at the same pH. Similar results were obtained using portland cement as stabilizer (See Figure 2).

As a result of research conducted by the Bureau Mines studies (6), PG was not recommended for use with asphalt-concrete, not only because this mixture consumes a relatively low percentage of gypsum (20 percent), but because none of the mixes achieved the strength required for wearing courses. The Bureau's study utilized aggregates containing 50 percent PG and 50 percent ball clay or clay from phosphate rock. The asphalt-aggregate briquettes were fired at 1000°C for one hour and achieved compressive stresses of 1000 psi. The results were very sensitive to both temperature and reaction time. May, et al. (3,6) also used a blend of lime and a low-line fly ash to stabilize their PG. To determine the effect of the PG/fly ash ratio on strength, mixtures of 50 percent PG and 6-10 percent lime were blended with fly ash at fly ash/lime ratios ranging from 3:1 to 10:1. After curing for 28 days, compressive strengths exceeding 1000 psi were obtained. In these tests, strength tended to decrease with PG content and increase with fly ash content. A comparison of the chemical compositions of the fly ash used by May and Sweeney and that used by TTI indicated the former to be much lower in lime content and richer in SiO_2 and Fe_2O_3. However, the optimum fly ash/lime ratios in the Bureau's stabilized PG approximated that used in the the TTI study.

This paper presents the results of a study sponsored by the Bureau of Mines (10) which investigated neutralization and stabilization as a means of enhancing the load carrying capability of phosphogypsum to that required for use in road construction.

Technical Program

The primary objectives of this study were to define those chemical and physical parameters which effect the development of strength in stabilized phosphogypsum.

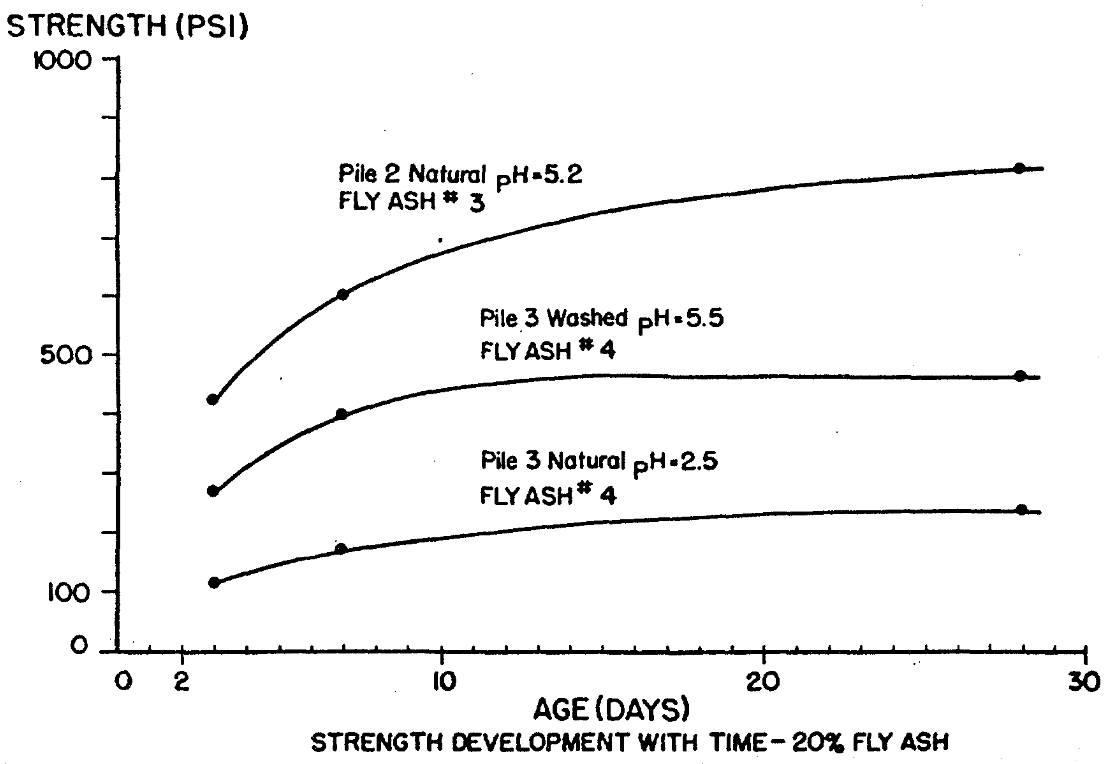

Figure 1. Influence of acidity (pH) on strength development in fly ash stabilized phosphogypsum.

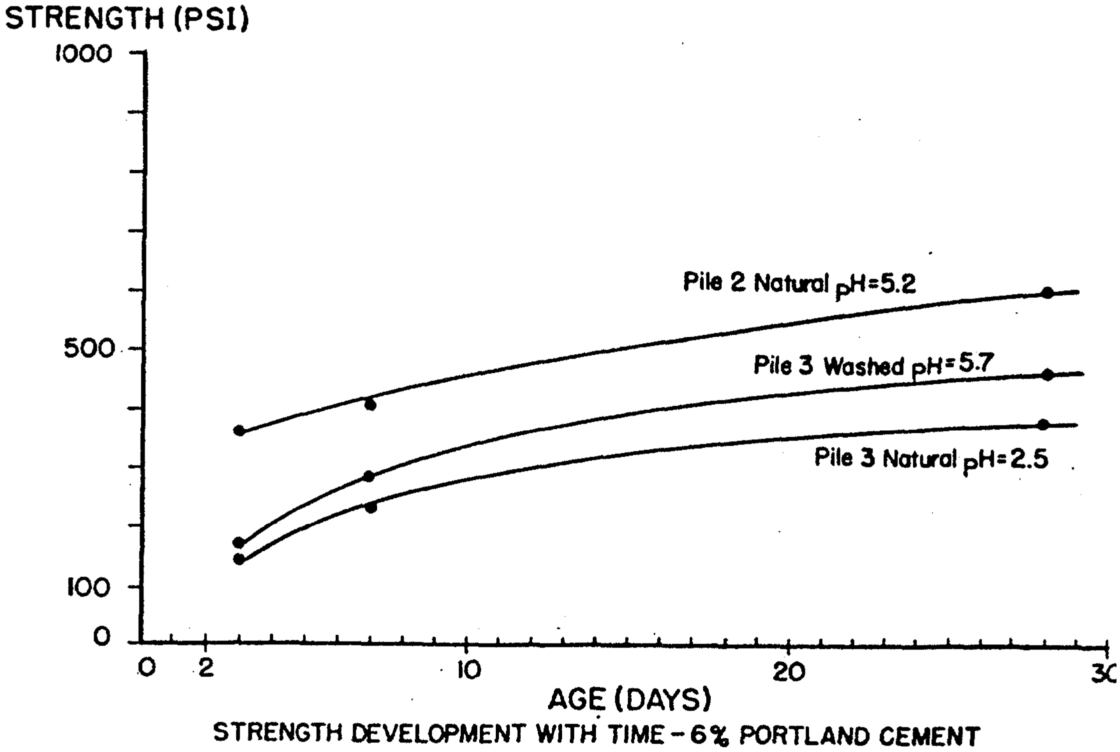

Figure 2. Influence of acidity (pH) on strength development in portland cement stabilized phosphogypsum.

Two phosphogypsum materials considered to be representative of that currently being stockpiled in the United States were selected for study. A series of chemical, physical and mineralogical analyses were first carried out on unstabilized PG. Mineralogical analyses include X-ray diffraction, thermal analysis and microscopic examination of thin-sections using petrographic microscopy. Particle morphology (shape, size and texture) were examined by scanning election microscopy (SEM). Finally, suitable stabilizers and/or neutralizers were investigated as to their ability to enhance strength development. Strengths were measured using the unconfined compression test and evaluated as to their compliance with acceptance criteria set forth by the Texas State Department of Highways and Public Transportation.

Materials Selection

Phosphogypsum

Two types of PG were selected for use in this study. The first was a dihydrate gypsum obtained from Mobil Chemical Company (MCC) stockpiles located in Pasadena, Texas. This plant uses a dehydrate modification of the "Wet Process" to produce phosphate fertilizers. To determine the influence of stockpile age on performance, material was obtained from a 10 year old (inactive) pile (designated Pile 2) and from one which is currently in use (active) and designated Pile 3. All material was taken from the top 18 inches of each pile and stored in plastic lined 55-gallon drums prior to testing.

The other PG used in this study was produced by a hemihydrate process and was furnished by Occidental Chemical Company (OCC) of White Spring, Florida. Only a limited supply of this material was made available and was not included in any of the strength tests. A comparison of the chemical make up of the Mobil and Occidental phosphogypsum is given in Table 1.

The OCC material was taken from the wet cake, dried at 8°C to eliminate free moisture and stored in a sealed dessicated container. The hemihydrate was gray in color, sand-like in texture but much finer than Mobils dihydrate. The Occidental Chemical Company stockpiles contain some PG in large lumps which forms when the hemihydrate absorbs water from the atmosphere and changes to dihydrate. Therefore, much of the material, as received, had to be crushed before it could be used.

Table 1. Chemical composition of Mobil dihydrate and Occidental Chemical Company hemihydrate phosphogypsum.

	Dihydrate	Hemi-dihydrate
CaO	32.50%	32.30%
SO_3	44.00	46.50
P_2O_5	0.65	0.25
F	1.20	0.50
SiO_2	0.50	0.40
Fe_2O_3	0.10	0.05
Al_2O_3	0.10	0.30
Cryst. H_2O	19.00	20.00

Portland cement

The portland cement used in this study was a commercial grade, Type I which met the requirements of ASTM C-150. The cement was purchased in bulk from General Portland, Inc. of Houston, Texas.

Fly ash

The fly ash was supplied by the W.A. Parrish Power Plant of Richmond, Texas. This ash exhibited the chemical make up and cementitious properties associated with a high quality, Class C fly ash as specified by ASTM C-618. The ash is tan in color, a distinguishing characteristic of fly ashes produced from sub-bituminous and lignite coals. Total calcium oxide (CaO) content, as determined by the CaO heat evolution test (11), ranged from 22 to 25 percent, which is well above the 15 percent minimum usually associated with Class C ashes. The fly ash was also checked for fineness in accordance with guidelines set forth in ASTM C-311. Fractions retained on the No. 325 sieve ranged from 10 to 18 percent, which is significantly below the specified maximum of 25 percent associated with Class C ashes.

Neutralizer

Four neutralizers were initially considered for use in this study; $Ca(OH)_2$, NaOH, NH_4OH and a reclaimed fly ash. The latter two were subsequently dropped from consideration as not being effective. The other materials were of commercial grade.

Materials Characterization

Chemical analysis

Free water, combined water, SO_3 and CaO contents were determined using the analytical procedures set forth in ASTM C-471-76; "Method of Analysis of Gypsum and Gypsum Products".

To determine the moisture content, the material was dried at 45C (113F) for 2 hours in accordance with ASTM C-471-76. It was noticed that drying for longer periods caused a further loss in weight. Therefore, drying was subsequently carried out irrespective of time until a near constant weight was attained. X-ray examination of undried PG from Mobils active pile (Pile 3) failed to show the presence of any hemihydrate. However, after drying for 2 hours, the hemihydrate pattern was detected, implying that the acidity of the active pile enhanced dehydration. Therefore, although ASTM C-471-76 has been used successfully with natural gypsum and its products, these results indicate that it may not be satisfactory for drying acidic by-product material.

In view of the above, to determine moisture content it is recommended that PG first be washed with water, then with alcohol, followed again with an acetone wash before drying at $45^{o}C$. This operation will remove the acid while keeping the original ratio of dihydrate to hemihydrate constant. The chemical composition of Mobil's Pile No. 3 over a range of depths from surface to 35 feet is shown in Table 2.

The composition for Pile 2 was found to be essentially the same as Pile 3. It was observed that PG taken from Pile 2 during 1985 had physical characteristics different from that taken during 1983 and 1984 from the same pile. The pile had undergone some excavation during 1985. Therefore the more recent samplings came from deeper within the pile. This material was whiter and screening showed the presence of organic matter such as roots, grass, etc. in measurable quantities.

Table 2. Chemical Composition at various depths of phosphogypsum samples from Mobil Chemical Company Stockpile No. 3.

Parameters	Boring Sample[a] 1(0-5ft) %	 3(0-5ft) %	 3(25-30ft) %	 5-(0-5ft) %	 5(30-35ft) %
SiO_2	6.8	1.5	1.5	1.2	1.6
PO_4	2.3	1.9	2.2	2.1	1.8
Mg	0.1	0.1	0.1	0.1	0.1
Ca	20.4	21.2	20.1	20.8	21.6
SO_4	46.0	54.8	56.7	52.4	55.8
H_2O	18.9	21.6	19.6	19.8	20.2
Total	94.5	100.1	100.1	96.4	101.1

[a]Sample were known to contain varying quantities of Li, Al, Fe and F. These were not quantified due to incomplete dilute mineral acids.

Physical analysis

Particle Size and Shape: Figures 3 and 4 showed SEM micrographs at 450X magnification for Mobil's phosphogypsum obtained from the surface of an inactive pile (Pile 2-Figure 3) compared with that obtained from an active pile (Pile 3-Figure 4). Several micrographs taken at random locations in the samples consistently indicated that the particles of the aged pile were smaller in size, more uniformly graded and tended to have rounded corners whereas those in the active pile were larger, more single-size with sharp edges and corners. Some of the crystals in the old pile seem to have been delaminated or shattered.

It is hypothesized that the rounded corners were produced by the effect of leaching. Rain water as it migrates through a pile will dissolve some crystals until the saturation point is reached. Corners or sharp edges have higher surface energy than crystal faces. Therefore dissolution rates at the corners would be expected to be more pronounced. When ambient conditions are dry (i.e. low humidity), evaporation takes place. Precipitation of gypsum from the supersaturated solution will take place to give a system with lowest possible energy. Since a sphere has the minimum surface energy per

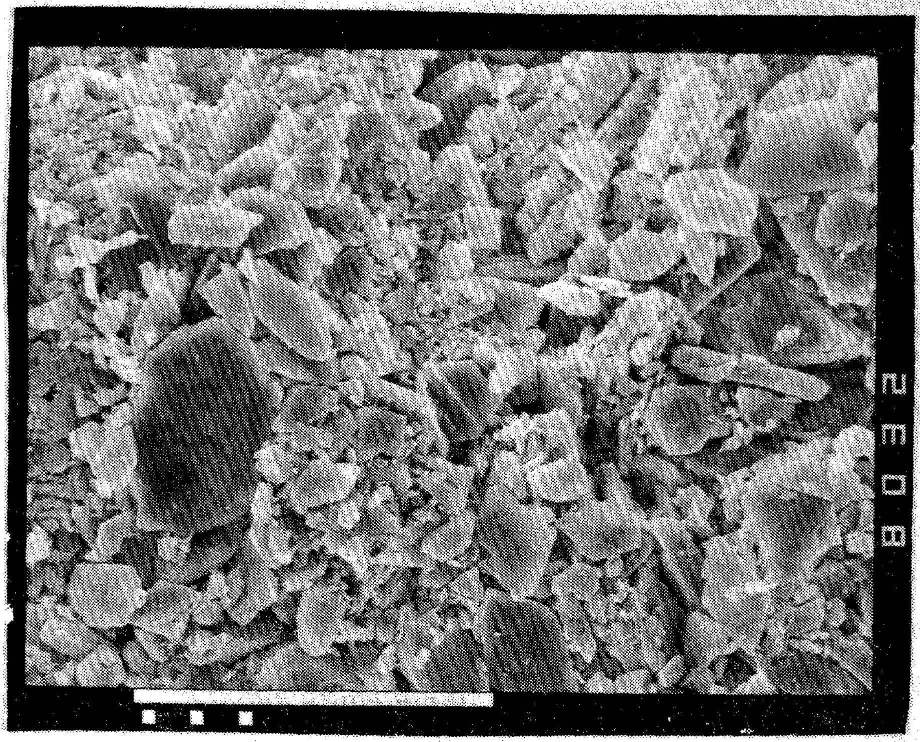

Figure 3. Mobil phosphogypsum - Pile 2 (Aged) 450 X.

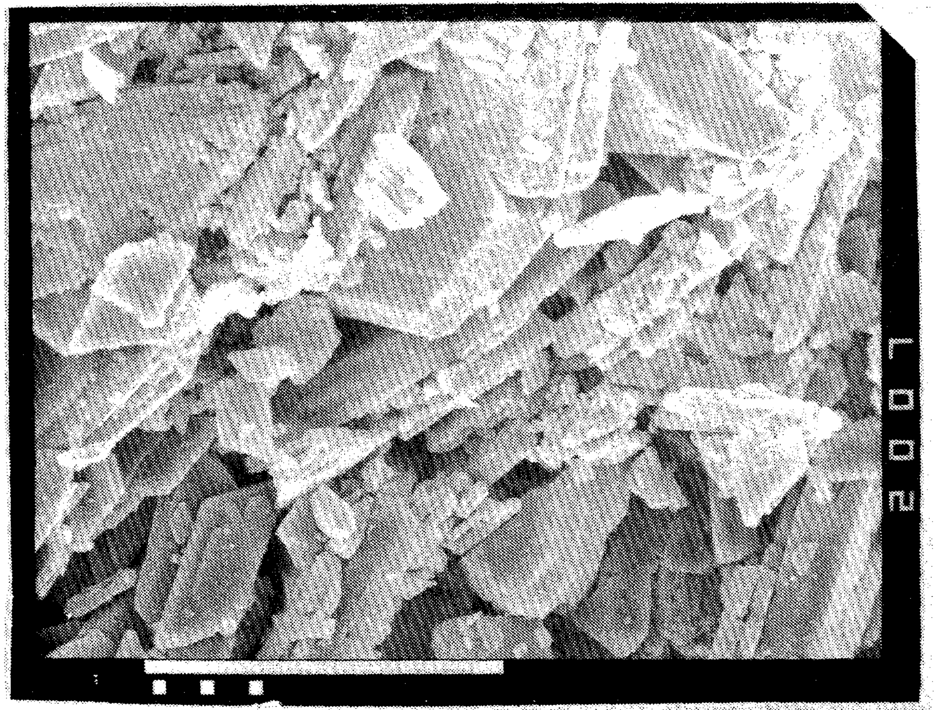

Figure 4. Mobil phosphogypsum - Pile 3 - (Active) 450 X.

unit volume, the tendency toward spheroidization would be indicated. On hot days some dehydration of the dihydrate to hemihydrate may take place due to the influence of the acidity of the pile. Sudden evolution of part of the water of crystallization can induce a delamination or fragmentation of some of the crystals. This could explain the presence of fine crystals along with partially broken or delaminated crystals. The two micrographs illustrate microscopically one of the primary reasons for the inherently lower strength capability in active piles. The aged Pile 2 material shown in Figure 3 consists of large crystals with the fine crystallites filling the voids between the larger ones in the manner of a dense graded aggregate system. Such a system can be expected to have a higher bulk density, to allow better aggregate interaction during compaction and therefore generate higher strength. Figure 4, on the other hand, shows that Pile 3 material consists of relatively larger crystals with a more single-size particle distribution. Therefore, the lower bulk density and poor interparticle interaction should reduce strength.

Neutralization Of Phosphogypsum With Bases

As discussed above, acidity, as dictated by concentration of water soluble P_2O_5, is considered one of the main factors which inhibits compressive strength development in compacted PG materials. The phosphogypsum used in these tests was taken from Mobil's active, Pile 3, which had an initial pH of around 2.6. Initially, four neutralizers were studied; $Ca(OH)_2$, Na(OH), NH_4OH and a reclaimed fly ash. The first two were selected to represent strong bases, $Ca(OH)_2$ is a dibasic, weakly soluble alkali and NaOH is a soluble monobasic alkali. The third represents a dibasic, relatively cheap, water-insoluble alkali. The reclaimed fly ash is an industrial waste. Prior to neutralization, 500 g of PG were homogenized to minimize variability in pH and moisture content. For each test, 10 g of the homogenized material were mixed with 10 ml of deionized water using a magnetic stirrer. After the initial pH was recorded, 2 ml of one of the neutralizers of known normality was added and mixed for 15 seconds after which the pH was remeasured. The procedure was repeated until a pH above 9 was reached.

The ability to change acidity and, hence, strength using four neutralizers is depicted in Figures 5 and 6 and designated as "master curves". Each curve indicates the amount of neutralizer required per mole (or per unit weight) of dry PG to achieve a certain pH. Figure 5 shows the master curves for NaOH, NH_4OH and $Ca(OH)_2$. Figure 6 shows the effect of using reclaimed fly ash.

The NaOH curve shows features typical for titrating phosphoric acid in which two fairly well defined end points (vertical rise in the curve) can be observed. These end points correspond to the condition at the end of each of the following two reactions:

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O \qquad (1)$$

$$NaH_2PO_4 + NaOH \rightarrow Na_2HPO + H_2O \qquad (2)$$

indicating the consumption of two equivalents of base. The end point for the third reaction:

$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O \qquad (3)$$

could not be detected since HPO_4"is only slightly dissociated. This is reflected by its dissociation constant

$$K = \frac{[H^+]\,[PO^{-3}4]}{[HPO_4^{--}]} = 4.2 \times 10^{-13} \qquad (4)$$

This value is extremely low compared to the dissociation constants of $H_3PO_4 \rightarrow H^+ + H_2PO^-_4$ and $H_2PO^-_4 \rightarrow H^+ + HPO_4^{--}$ which are 7.1×10^{-3} and 6.24×10^{-8}, respectively.

To achieve the same pH, larger amounts of weak neutralizer are needed. The lower amount of $Ca(OH)_2$ required to achieve the same change in pH is due to the fact that this neutralizer is dibasic, producing $2(OH)^-$per mol.

The "master" neutralization curves were difficult to reproduce. Even with the premixing of the PG to achieve homogenity, sample-to-sample variations in material taken from the same general location in the stockpile, still tended to make the curves move either to the right indicating higher

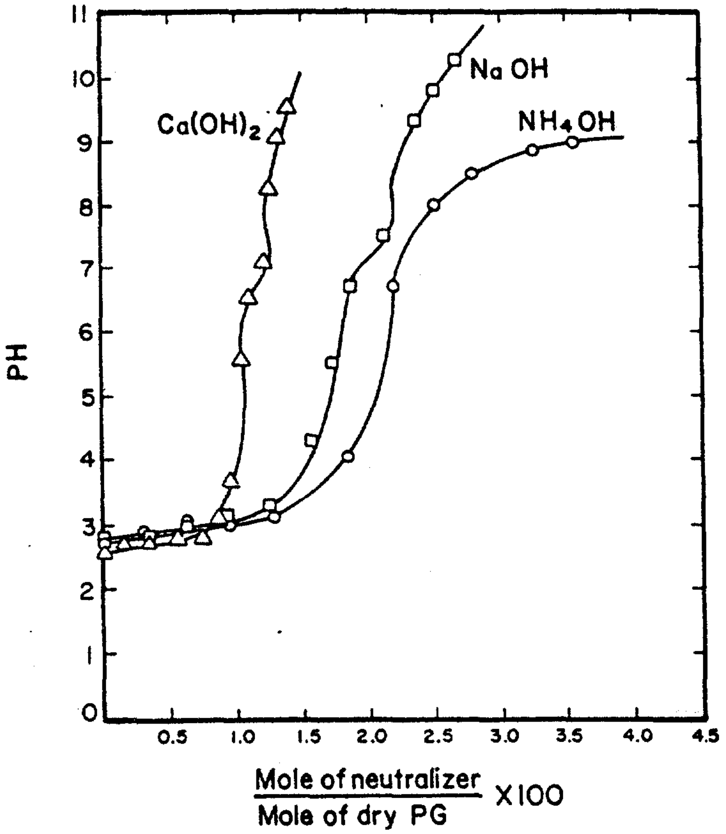

Figure 5. Effectiveness of neutralization by NaOH, NH_4OH, and $Ca(OH)_2$.

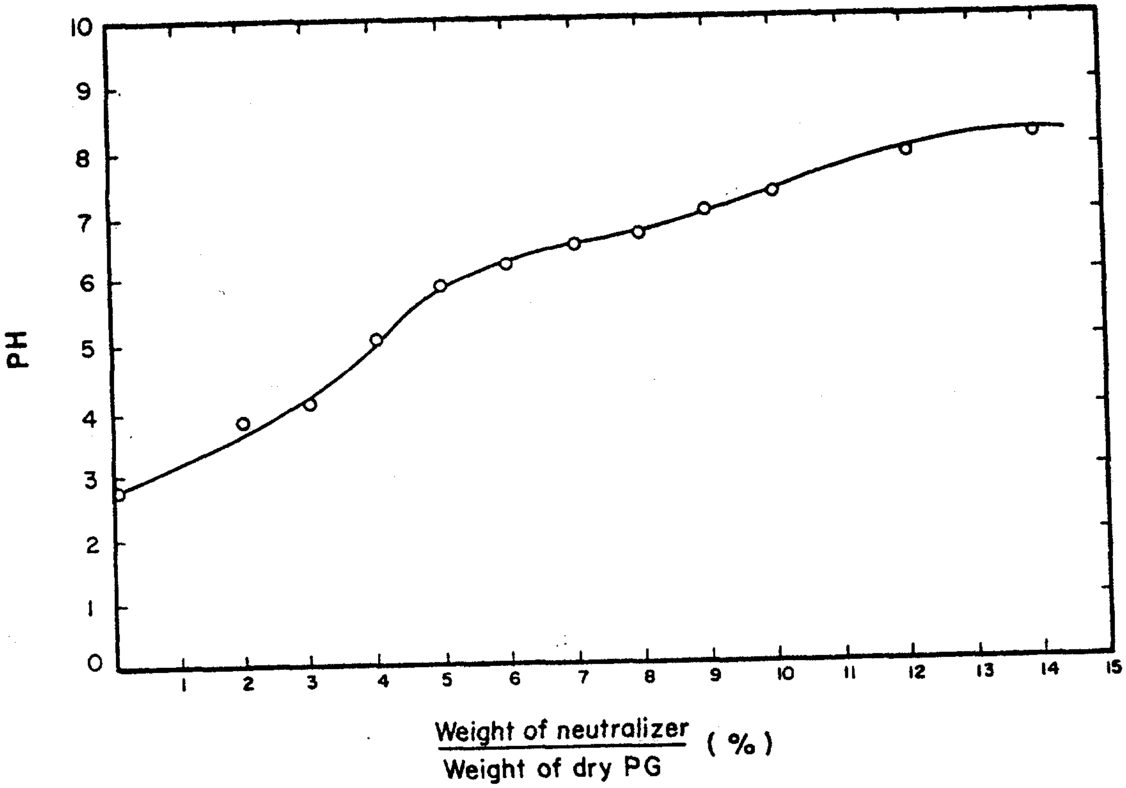

Figure 6. Effectiveness of neutralization using reclaimed fly ash.

acid content, (i.e. requiring greater amounts of neutralizers), or to the left, indicating a lower acid content. This was attributed to an inability to eliminate the high degree of heterogeneity inherent the material. Test results showed that moisture content (which carries the P_2O_5) varied over a wide range. Fine particles with high surface area and fine capillaries will normally retain more water (and hence P_2O_5).

Stabilization Of Neutralized Phosphogypsum

Unconfined compression strength tests were conducted on neutralized PG following stabilization with varying amounts of portland cement and fly ash. The NH_4OH and reclaimed fly ash were not included in these series of tests since they were the least effective of the four neutralizers studied. $Ca(OH)_2$ were used in various amounts and the equilibrium pH for each blend NaOH and $Ca(OH)_2$ were used in various amounts and the equilibrium pH for each blend was determined. Untreated PG specimens along with partly neutralized PG, and PG with excess neutralizer were stabilized with 3, 6, and 10 percent commercial grade Type I portland cement and 20 percent fly ash. All PG used in these tests were obtained from Mobil's active Pile 3.

Sample preparation and testing was carried out in accordance with ASTM D-1557-Method A. All samples were compacted in 5 layers in 4 in. diameter x 4.5 in. cylinders using a 10-lb. hammer with an 18 in. free fall. The number of blows per layer was adjusted so that the dry density of the samples containing the same stabilizer were reproduced within ± 2 pcf. The optimum moisture content was established at 14 percent. Compacted cylinders were cured for 3, 7, and 28 days in sealed plastic bags which produced an environment with 100 percent relative humidity. This was preferred to curing in a moist room which tended to adversely affect sample integrity during the initial curing stages.

Figure 7 shows 3-day-unconfined compressive strengths versus equilibrium pH for neutralized PG mixtures. Each data point represents the average value for 3 specimens. Typically, the range of accuracy for compressive strength data is ± 15 percent. Applying these limits of accuracy in an Analysis of Variance, the strength was shown to depend on both pH prior to the addition of the cement as well as the amount of cement added. At the

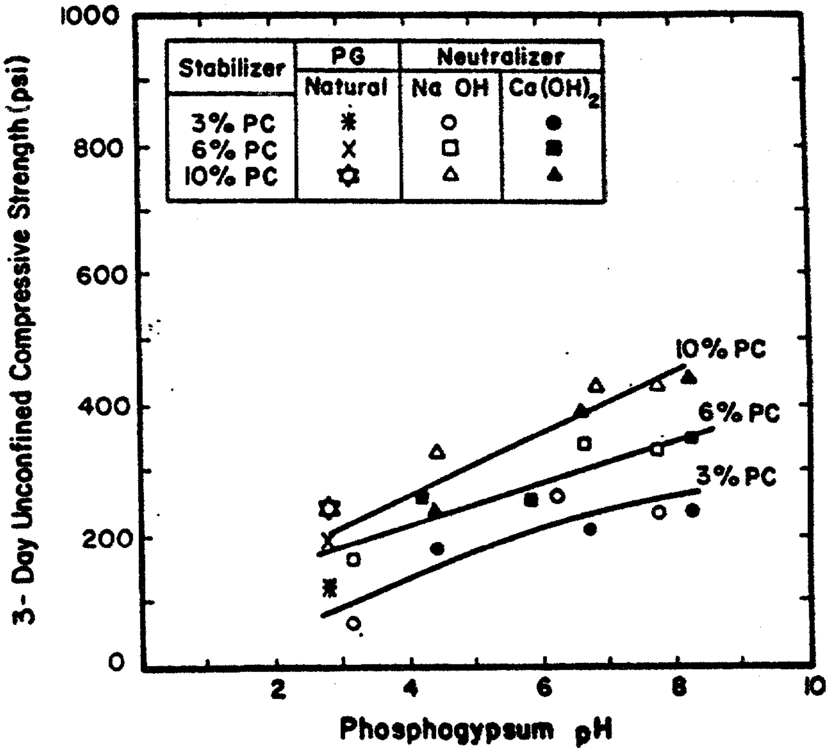

Figure 7. Three-day unconfined compressive strength versus pH of cement stabilized phosphogypsum.

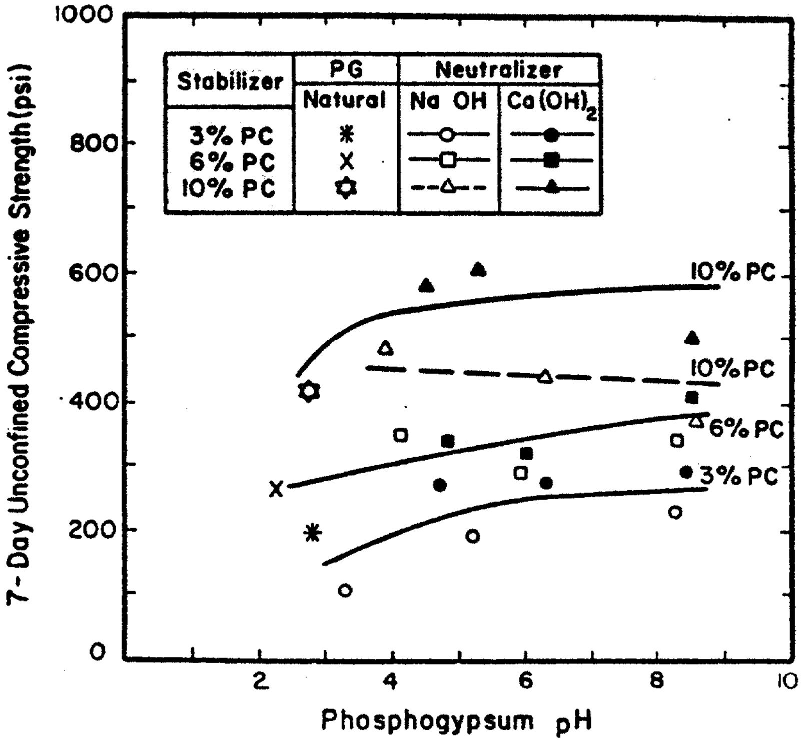

Figure 8. Seven-day unconfined compressive strength versus pH of cement stabilized phosphogypsum.

same pH level strength tends to increase with cement content. Also, at the same cement content, an increase in pH likewise increases strength. An effect on strength due to the type of neutralizer used was not apparent after curing for only 3 days.

The 7-day, unconfined compressive strength are shown in Figure 8. There still appears to be little or no difference between the ability of either of the neutralizers to alter strength for cement contents up to 6 percent. However, with 10 percent cement, the strength achieved by neutralization with $Ca(OH)_2$ was much higher than that obtained with NaOH. In fact, a decrease in strength with pH <u>may</u> be indicated for the NaOH system (as shown by the dotted line). An explanation for a strength reversal with NaOH neutralized material will be discussed along with the 28-day cured material later. These curves were drawn taking into account a ± 15 percent range of accuracy for unconfined compression testing. Similar to the results shown in Figure 7 the 7-day strengths also increase with neutralizer and/or cement content.

Figure 9 shows the 28-day unconfined compressive strengths versus pH for both natural and neutralized PG material after stabilizing with 3, 6, and 10 percent Type I cement. The strengths continued to improve with little or no effect due to type of neutralizer used up to a cement content of 6 percent. The strengths achieved using 10 percent cement following $Ca(OH)_2$ neutralization were higher than those obtained with NaOH. The experimental data for $Ca(OH)_2$ neutralized PG are plotted as a nearly horizontal solid line. On the other hand, those corresponding to NaOH neutralized PG as indicated by the dashed line indicate a trend towards decreasing strength.

When sodium hydroxide is used as a neutralizer, several sodium phosphates can form, depending on the amount added. These phosphates are produced in accordance with the following reactions:

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O$$
$$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O$$
$$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$$

In addition, $Ca(OH)_2$ produced during hydration will react with any residual acids present. The excess $Ca(OH)_2$ will react with the sodium

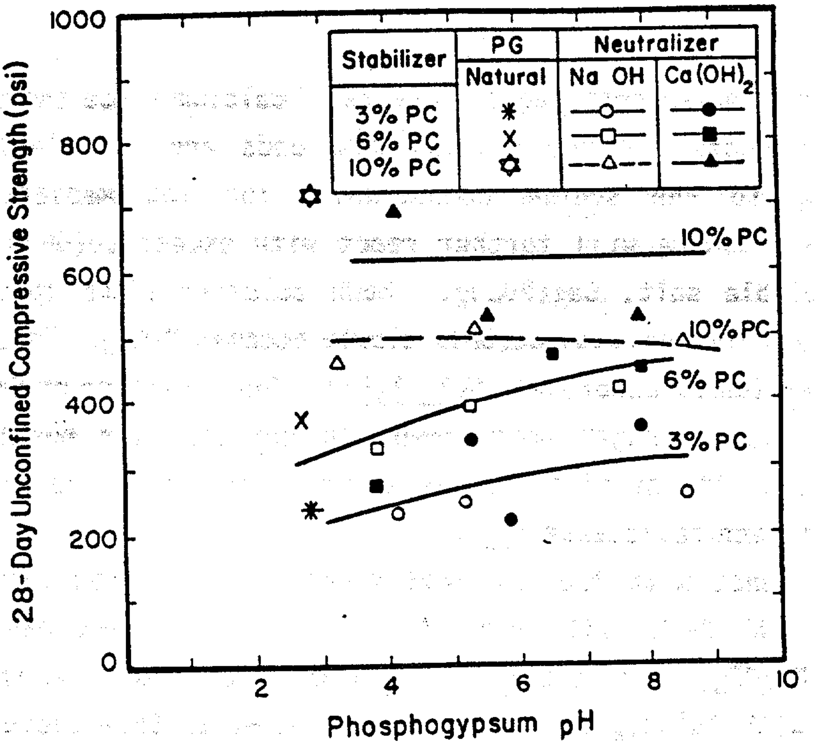

Figure 9. Twenty-eight day unconfined compressive strength versus pH of cement stabilized phosphogypsum.

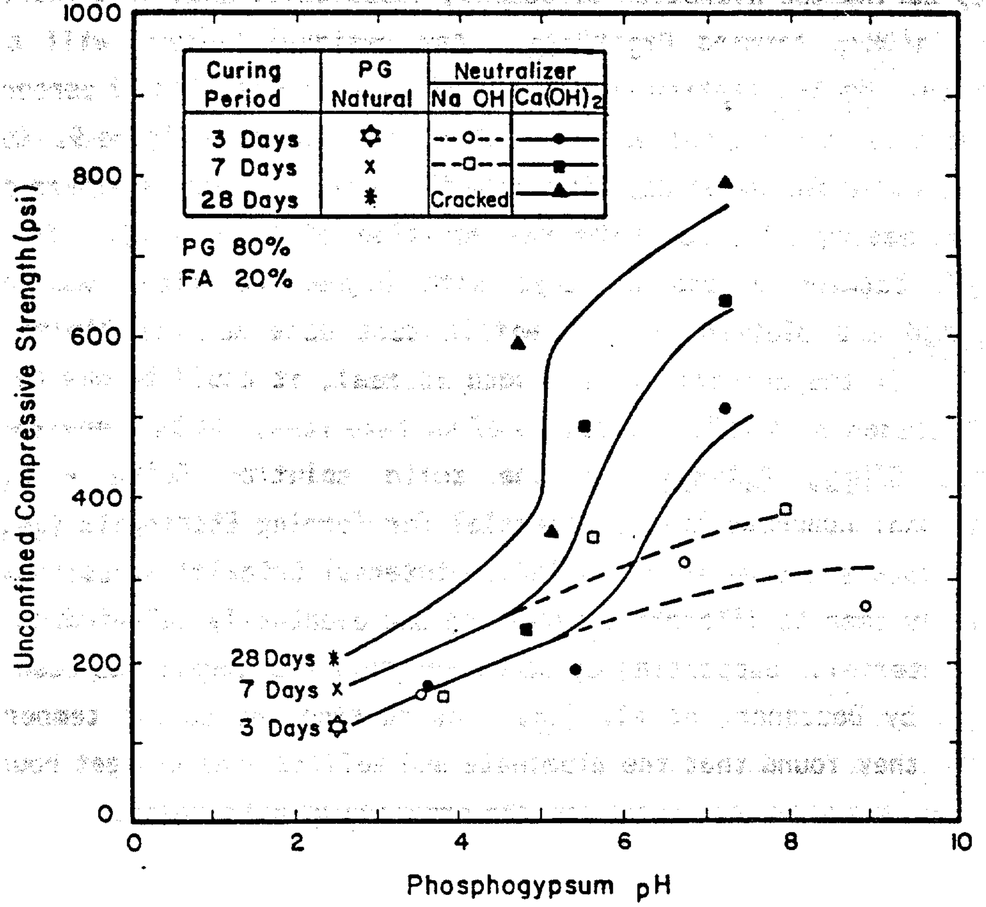

Figure 10. Unconfined compressive strength versus pH at 3, 7 and 28 days for fly ash stabilized phosphogypsum.

phosphates to form the corresponding salts of calcium since the values of the solubility products for the calcium compounds are much less than those corresponding to the sodium compounds. The intermediate compounds, $Ca(H_2PO_4)$, and $CaHPO_4$ will further react with excess $Ca(OH)_2$ forming the sparingly soluble salt, $Ca_3(PO_4)_2$. NaOH solution picks up CO_2 from the atmosphere, and the residual $Ca(OH)_2$ slowly becomes $CaCO_3$. This is referred to as "carbonation of concrete" (12,13,14). The formation of $CaCO_3$ has been shown to enhance strength development in cement, lime mortars and lime paints (12,13). It has also been established that the carbonation process improves corrosion resistance (14).

In accordance with the chemical reactions mentioned above, mixtures neutralized with NaOH will eventually form a stabilized mass containing $Ca_3(PO_4)_2$, Na_2CO_3, and $CaCO_3$. On the other hand, mixtures partly neutralized with $Ca(OH)_2$ consist of mono-, di-, or tri-calcium phosphate, depending on the pH at which the reactions take place. With the evolution of $Ca(OH)_2$ during the hydration of cement, these salts undergo a reaction with excess $Ca(OH)_2$ forming $Ca_3(PO_4)_2$. Any residual $Ca(OH)_2$ will also form carbonate. Neutralization curves for mixtures containing 10 percent cement after 28 days in cure, reflect this behavior as shown in Figure 9. Curves for mixtures cured for seven days indicate that $Ca(OH)_2$ induces higher strengths with increasing pH (i.e. with the addition of hydroxide). The drop in strength between 7 and 28 days with higher additions was purposely designated and plotted to stay within test data scatter limits of ± 15 percent. If the decrease in strength is real, it could be due to the fact that PG presents an infinite source of sulfate ions. In this environment the hydrates CAH_{13}, C_4ASH_{12} and the solid solution C_2AH_8 - C_4AH_{19} in conventional concrete have a potential for forming Ettringite (14,15). As these crystals expand they can induce internal triaxial stresses which can eventually lead to dilatative weakening and eventually self-induced failure of the material. Supporting evidence for this hypothesis has been recently reported by Deussner, et al. (16). By raising the curing temperature of concrete they found that the aluminate and sulfate ions can get bound to the CSH phases and serve as source for the creation of Ettringite.

Any strength reversal at the higher pH values, due to Ettringite formation will be made even more significant as the curing process continues. The reactions could be accelerated: (a) if a cement rich in tricalcium aluminate (C_3A) is used, since it is one of the constituents of Ettringite or (b) if a finer cement is used such as a high early strength (Type III). On the other hand, cements low in C_3A (Type V Sulfate Resistant) should retard the formation of Ettringite but at the sacrifise of early strength development. This point needs further study and verification.

When NaOH was used as a neutralizer, hairline cracks were observed on the surface of specimens subjected to prolonged curing. These specimens contained Na_2CO_3 (as explained earlier), which is soluble in water. As the excess water moves to the surface during drying, the dissolved salt moves with it. When this water evaporates, the salt is recrystallized, causing efflorescence (12). The salt and. its hydrates will cause stress concentrations within the mixture which may also adversely effect strength. As the sodium content and, hence, pH increases more salt will form causing the compressive strength to decrease further. This phenomenon explains the slight decrease in strength with increasing pH for specimens neutralized with NaOH and stabilized with 10 percent cement. This decrease becomes even more pronounced after curing for 28 days as shown in Figure 9. The migration of salts, as explained above, was found to occur in cement cubes with one face in contact with saturated solutions of salt. This phenomenon was used by previous researchers to explain staining and failure of paint films on concrete (14).

Another explanation for the presence of the hairline cracks could be the formation of alkali silicate gels containing a certain amount of lime, which tend to exert surface tensile strains during absorption of water (12).

Fly Ash Stabilization Of Partially And Fully Neutralized Phosphogypsum

Unconfined compressive strengths were determined on partially and completely neutralized phosphogypsum materials following stabilization with 20 percent of a Class C fly ash. Strengths after 3, 7, and 28 days curing versus equilibrium pH achieved are shown in Figure 10. After curing for 28 days numerous hairline cracks were observed in the NaOH neutralized materials. These cracks and other defects were responsible for either lowering the 28-day strengths or for premature failure. It could be concluded that similar to cement PG mixtures an increase in the amount of neutralizer or curing time will also increase the strength in the fly ash system. Moreover, there was a more significant increase in strength in $Ca(OH)_2$ - neutralized specimens than in specimens neutralized with NaOH.

As previously mentioned, the type of sodium phosphate formed depends on the pH level attained. With the addition of fly ash, excess $Ca(OH)_2$ is liberated which reacts with salts to form $Ca_3(PO_4)_2$ and Na_2CO_3. Any residual $Ca(OH)_2$ present slowly forms $CaCO_3$ which apparently adds to the strength.

Stabilization Of Clashed Phosphogypsum

Since stockpiled PG, under the leaching action of rain, achieved higher strengths than the more acidic unaged material, the investigation was directed towards the study of strength development in "washed" phosphogypsum. By subjecting natural PG to a continuous flow of tap water through a vertical column the leaching action of rainfall on a stockpile was simulated. Washed PG specimens containing various amounts of PC and 20 percent fly ash were prepared and tested for unconfined compressive strengths. For cement stabilized specimens, the unconfined compressive strength after washing was consistently less than that for the natural material even though the latter was more acidic. This is shown in Figure 11 where solid lines refer to samples prepared with washed PG and dashed lines refer to those prepared with natural material. A probable reason for this difference in strength development is that some fines in the PG were washed away with the water. X-ray analysis carried out on both materials indicated a higher fines content in the PG before washing.

Unlike the comparatively low strength improvement exhibited in washed PG stabilized with portland cement, the strengths in washed, fly ash - stabilized specimens were significantly higher than in specimens prepared with natural PG (Figure 12). This could be attributed to the fine fly ash particles (i.e. minus #300 Sieve) which substitute themselves for the fines removed by washing. The fly ash which fills the voids, thus, reestablished the high densities required for strength development. From Figure 12, it

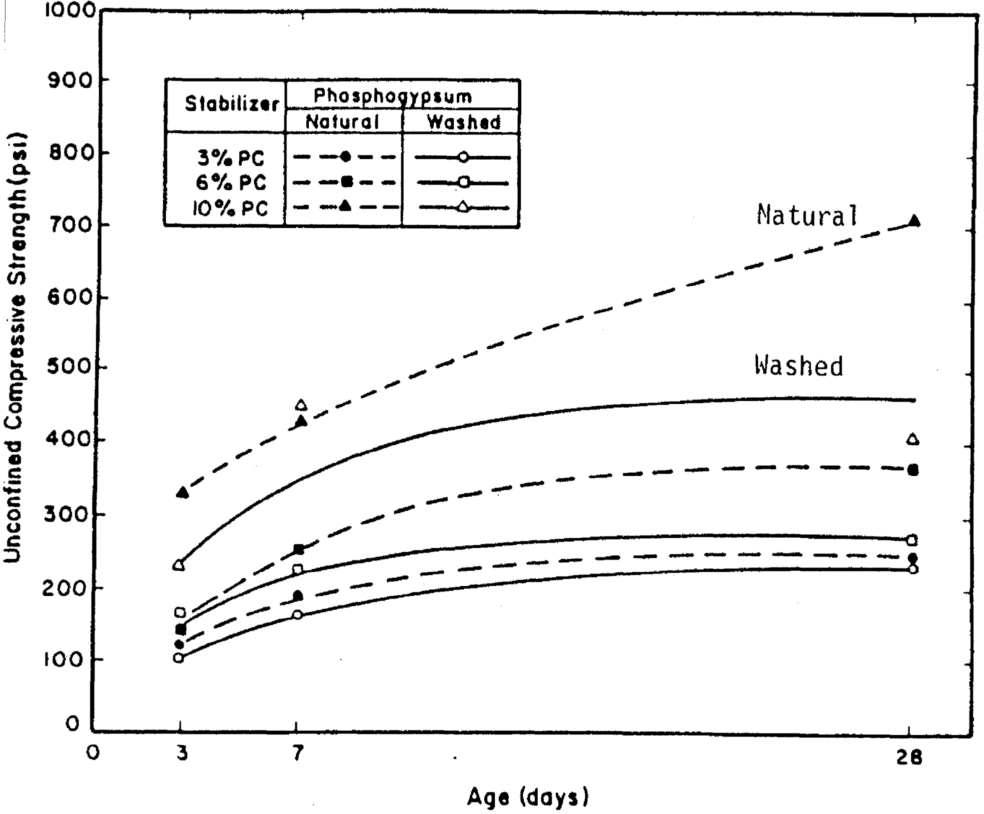

Figure 11. Unconfined compressive strength of portland cement stabilized natural and washed phosphogypsum versus curing age.

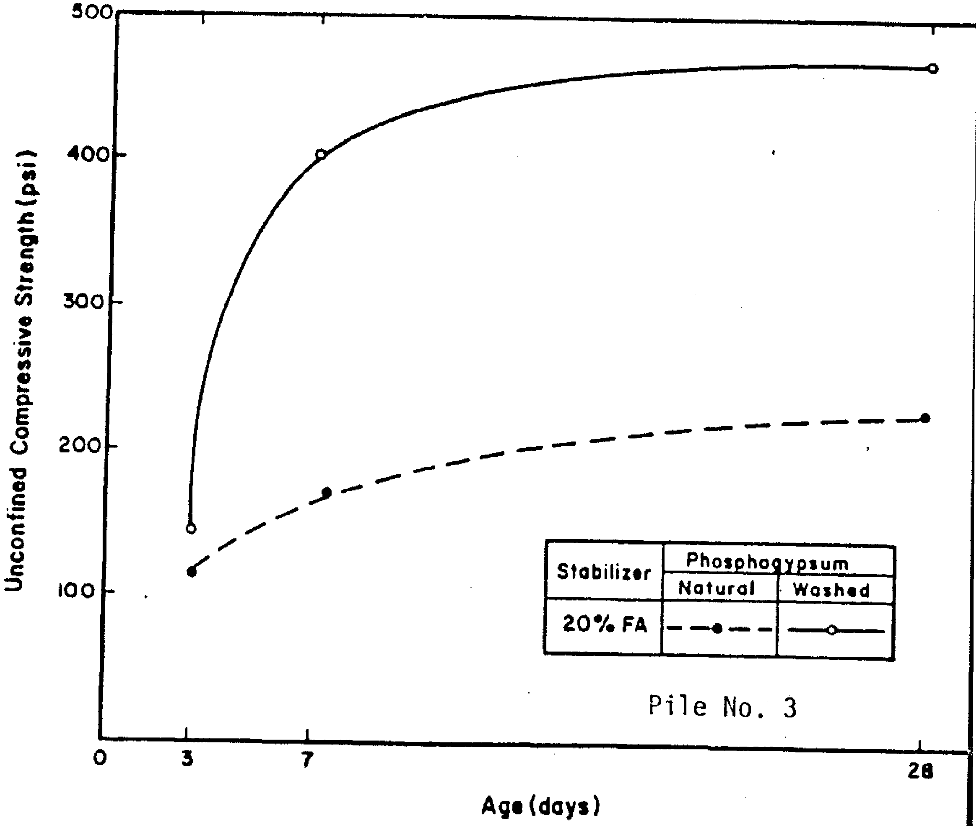

Figure 12. Unconfined compressive strength of fly ash stabilized natural and washed phosphogypsum versus curing age.

would seem that the effect of particle size distribution on strength development may be even more important than acidity.

CONCLUSION

Aged and unaged Phosphogypsum were studied so as to elucidate the chemical and physical factors responsible for strength development following stabilization with either portland cement or a high-lime fly ash. The prime factors which affect strength appear to be acid level (pH) and particle size, shape and distribution.

Acid levels were altered by neutralization with $Ca(OH)_2$ and NaOH. The former proved to be more effective on the basis of mols of neutralizer used per unit change in pH. The $Ca(OH)_2$ systems continued to show strength improvement after 28 days curing. Na(OH) systems also showed strength improvement with age for cement contents up to 6 percent. Within allowable experimental limits of accuracy, a possible trend towards strength reversal was indicated for the 10 percent cement stabilized mixtures. This requires further study and verification. In addition, the NaOH neutralized mixtures stabilized with fly ash experienced hair line cracking and, in some cases, premature failure.

Another means for the simulation of aging in stockpiled PG was by washing. When residual acidity was lowered by washing, portland cement-stabilized material was found to be inferior in strength to the unwashed natural material. This seems to be due to the removal of fine particles in the leachant during washing. These series of experiments tended to add support to the conclusion that particle size and distribution may be more important contributors to strength than the level of residual acidity.

On the other hand, fly ash stabilization generated higher strengths in the washed material. In this case the ultrafine fly ash particles tended to correct the particle size distribution disturbed by washing. Thus particle size, geometry and distribution tends to enhance compaction efficiency which in turn produces a material with a higher density and strength.

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WATER RESISTIVITY OF PHOSPHOGYPSUM MIXTURES

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ABSTRACT

Compacted dihydrate phosphogypsum (DPG) develops adequate strength for road construction under air-dry conditions. The strength can be further increased by mixing DPG with proper amounts of fine aggregate. The consistency of specimen is not maintained, however, under soaked conditions. It is the objective of this paper is to provide approaches towards improving the water resistivity of DPG and of fine aggregate-DPG mixtures; or, more clearly, to avoid severe strength losses when the material is subjected to soaked conditions.

Water-resistance developing additives were used in DPG-based mixtures to achieve this purpose: tar, RC-70 (a rapid curing asphalt), and sodium silicate. In addition, paraffin wax was used to water-proof DPG specimens. Cylindrical specimens prepared by the Standard or Modified Proctor compaction method were tested under soaked and air-dry conditions.

Two strength aspects were investigated in the course of the experiment:

1) soaked strength enhancement, and

2) influence on air-dry strength when varying the amount of additives in the mixtures.

Based on test results, around two percent of RC-70 or tar proves sufficient to obtain DPG and fine aggregate-DPG mixtures of adequate soaked strength for road constructions. An insignificant strength reduction occurs under air-dry conditions when these water-proofing agents are added to DPG-based mixtures. The use of

sodium silicate also leads to water resistant products but its use is limited due to its blooming effect. Paraffin treatment produces water-proof specimens with suitable applications to building construction.

In contrast, the hemihydrate phosphogypsum from the Occidental Chemical Co. (Oxy-HPG) is water-resistant itself; furthermore, it retains this property when mixed with a fine aggregate. As much as fifty percent of the fine aggregate could be used although test results indicate that better strength parameters are achieved with a lower percentage of the fine aggregate.

INTRODUCTION

In pavement constructions, the water resistance of basecourse or subgrade materials, though not required, will be favorable when under adverse moisture conditions. On the other hand, building elements, generally not subjected to extremely moist conditions, will be preferred if they are water resistant or even waterproof.

Dihydrate phosphogypsum (DPG), which has appreciable strength under air-dry conditions, is water susceptible. The main purpose of this study is, therefore, to improve the water resistance of DPG-based materials, making DPG a more suitable material for the road and building constructions.

Binding agents such as tar, RC-70, sodium silicate, and paraffin wax were employed to strengthen DPG-based mixtures under soaked conditions. The compressive strength of 2 in. by 4 in. cylindrical specimens was tested under air-dry as well as soaked conditions.

THE USE OF TAR AND RC-70

Asphalt and tar are both bituminous materials and widely used for the constructions of highways, airport and other paving. They are strongly cementitious, readily adhesive, highly water-proof, and thus of particular interest to road engineers.

RC-70, a rapid curing cutback asphalt, is derived from the liquefaction of asphalt cement with naphtha or gasoline--type diluent of high volatility. And tar, also in the liquid form, is obtained from the distillation of coal or petroleum. Both materials can be cold mixed and compacted with aggregates, i.e., heat is not required during the process.

When uniformly mixed with DPG and subjected to compaction, tar and RC-70 make the resulting products water resistant. Figures 1 and 2 represent the compressive strength, under both air-dry and soaked conditions, of DPG-tar and DPG-RC 70 mixtures respectively as a function of the tar and RC-70 content. DPG-tar specimens were prepared by the Standard Proctor, and DPG-RC 70 specimens by the Modified Proctor compaction procedure. From these figures (1 & 2). it is observed that by adding a small amount of tar or RC-70 (2-3%) the strength under soaked conditions is greatly enhanced. Although the strength under air-dry conditions is somewhat reduced, the improvement in water resistance makes DPG a more desirable material when subjected to moist conditions.

The water-proofing property of RC-70 can likewise be utilized to improve the water resistance of sand-DPG mixtures. In Polk

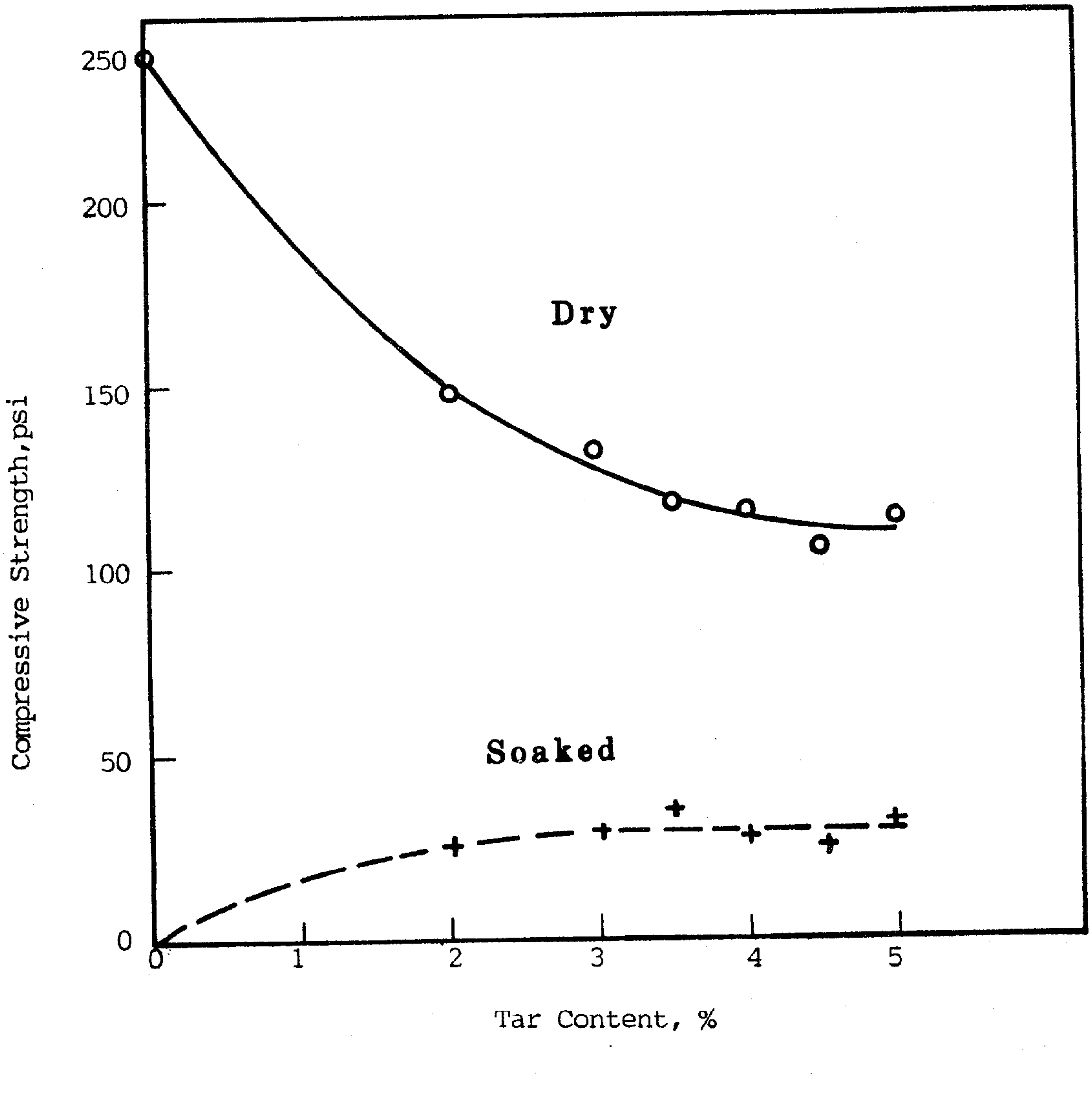

Figure 1. The effect of tar content on the strength of DPG-tar mixtures under air-dry and soaked conditions.

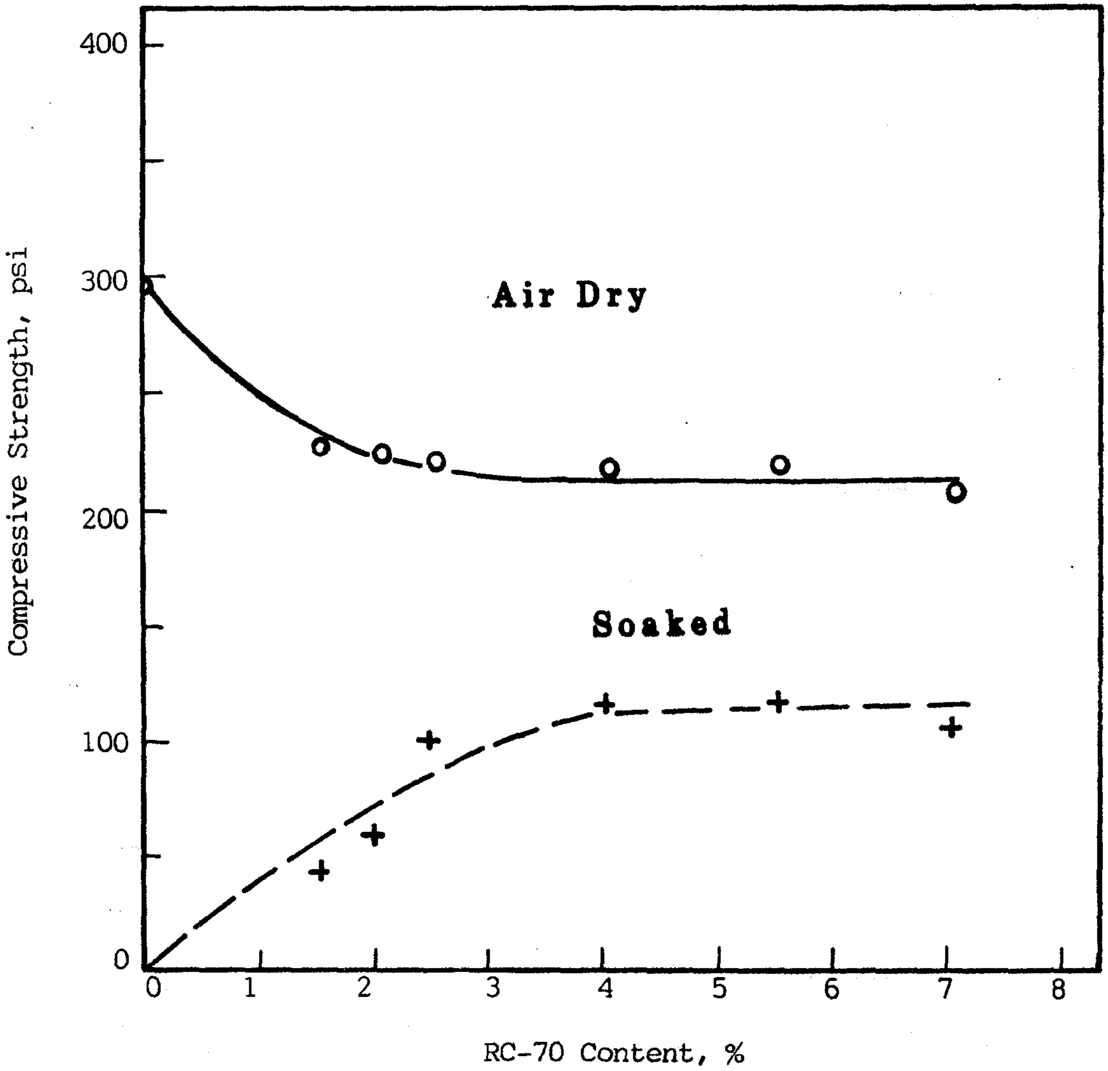

Figure 2. The effect of RC-70 content on the strength of DPG-RC-70 mixtures under air-dry and soaked conditions.

County, Florida, the conventional construction practice for secondary roads generally involves mixing fine-grained soils (usually clays) transported to the site with the existing granular subgrade soil. However, due to the lack of sources of clays and also the abundant stockpiling of DPG, a fine-grained binder, current secondary road projects point towards mixing DPG with sand on site.

Like DPG or sand alone, the combination of sand and DPG does not have strength under soaked conditions. Mixing the mixture with RC-70, as expected, induces water resistant products. Figure 3 illustrates the effect of RC-70 on the Polk County sand-DPG (2:1) mixtures, prepared according to the Modified Proctor specifications, under soaked conditions. It can be seen that the addition of 1-2% of RC-70 imparts the property of water resistance to the mixture.

THE USE OF SODIUM SILICATE

Sodium silicate has been used successfully in the injection and grouting techniques employed to increase the stability of excavations and tunnel walls in cohesionless soils. In addition, it can be used in the road construction to stabilize soils, usually containing soluble calcium salts, to form insoluble calcium silicates.

When reacting in small quantities with DPG, sodium silicate improves the water susceptibility of the material. The use of various commercial sodium silicates available from the PQ

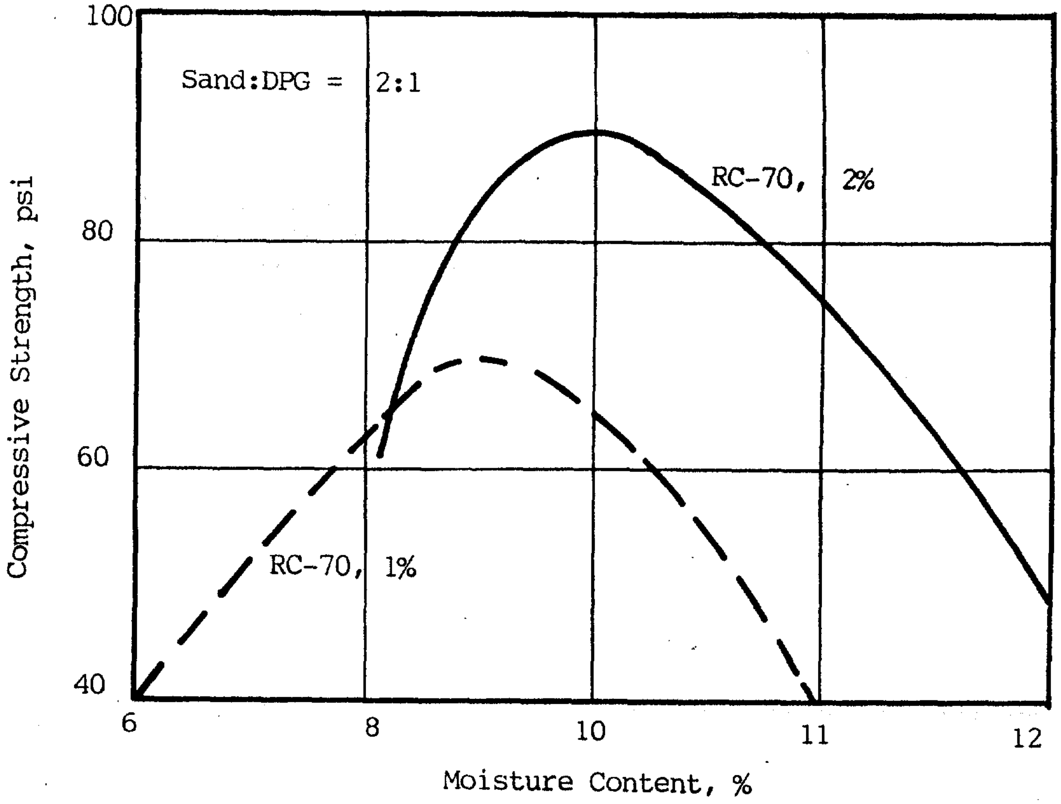

Figure 3. The effect of RC-70 content on the strength of sand-DPG mixtures under soaked conditions.

Corporation, Pennsylvania, indicates the following:

1) At the content of 1%, sodium silicate treated DPG mixtures obtain cylindrical compressive strengths in the range of 30-50 psi under soaked conditions.
2) The reactions among sodium silicate, DPG, and moisture generate the accompanying dust-like powdered material, which is undesirable for environmental and esthetical consideration.

Due to this “blooming effect”, the use of sodium silicate in the DPG-based mixtures is limited.

THE APPLICATION OF PARAFFIN WAX

Paraffin wax is a generally used material, when coated on the surface of an object, for water-proofing purpose. At elevated temperatures, it is a liquid-like material and becomes solid at ambient (room) temperatures.

Maintained in the liquid form (at 60°C), paraffin wax can be absorbed by air-dried DPG specimens after compaction. The extent of absorption depends on the soaking period and the dimensions of the specimens. For 2 in. by 4 in. cylindrical specimens, almost complete absorption can be attained in a period of several minutes. After cooling in the air, paraffin soaked DPG specimens become even more solid and completely water-proof. Table 1 compares the compressive strengths of DPG specimens, compacted according to the Modified Proctor procedure, with and without the application of paraffin. It is clear that the use of paraffin

Table I : Strength of water-proofed DPG by paraffin application.

Material	Strength, psi	
	Air-dry	Soaked
DPG	290	0
DPG & paraffin	1034	1008

extraordinarily increases the strength of DPG under air-dry and particularly soaked conditions. When subjected to soaked conditions, the strength of paraffin soaked DPG specimens does not decrease due to the completely water-proof property of the products.

OTHER POTENTIAL BINDERS

Other materials like resins, sulfur, sulfur/asphalt, plasticized sulfur etc., are either conventional or newly developed binding materials for pavement and building constructions [1,2,3,4]. The use of resins and sulfur in the DPG-based mixtures is being conducted at the University of Miami. It is believed that subsequent research findings will contribute to a variety of uses of phosphogypsum in the construction area.

WATER RESISTANCE OF OXY-HPG BASED MIXTURES

The hemihydrate phosphogypsum (HPG) produced by the Occidental Chemical Co. (Oxy) is a water resistant material itself; considerable strength has been found for Oxy-HPG alone, after compaction, under soaked conditions [5]. When mixed with fine-aggregate (sand), moreover, the property of water resistance remains. This excellent material property can be utilized to stabilize the aggregate materials on site for the secondary road constructions.

Figures 4 and 5 demonstrate the effect of Oxy-HPG content on the strength of sand-Oxy-HPG mixtures under air-dry and soaked condi-

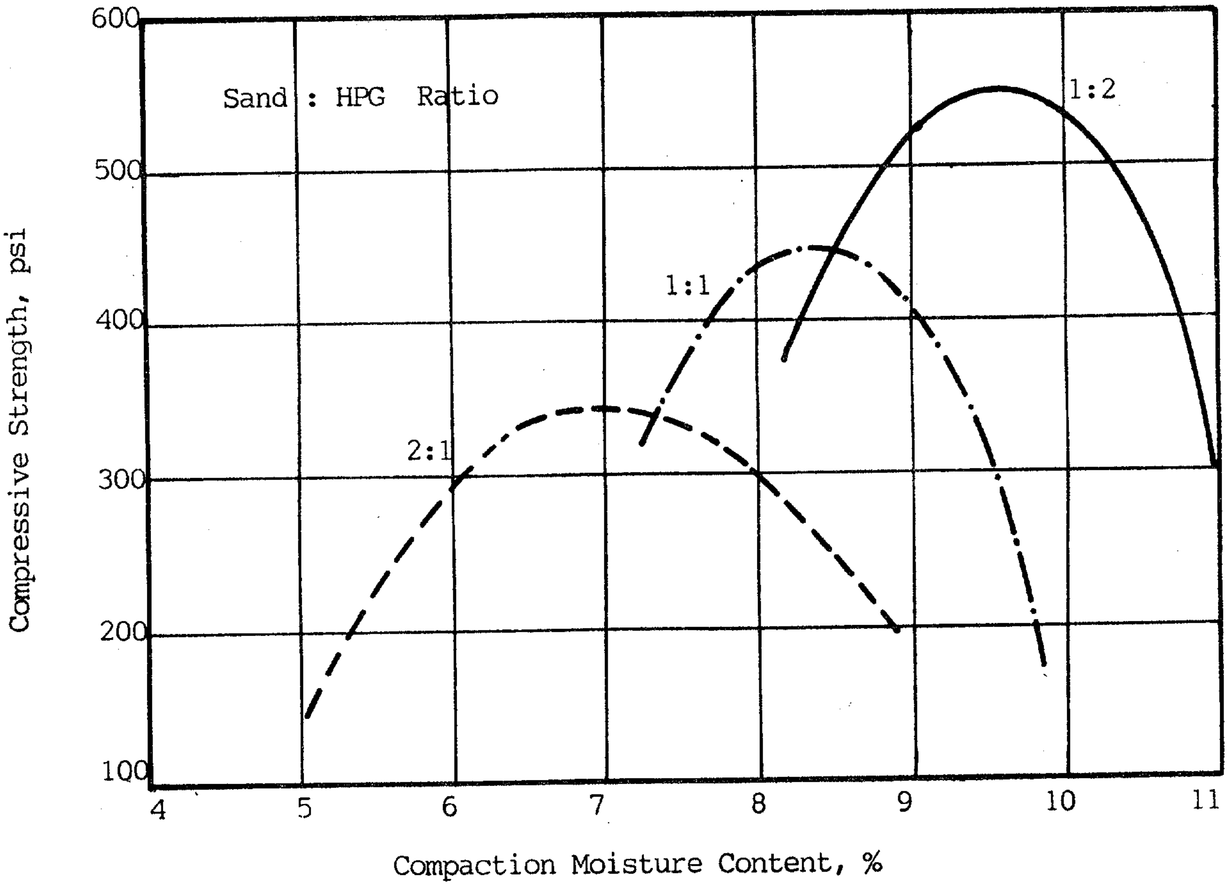

Figure 4. Strength-compaction moisture relationships for various sand-HPG mixtures under air-dry conditions.

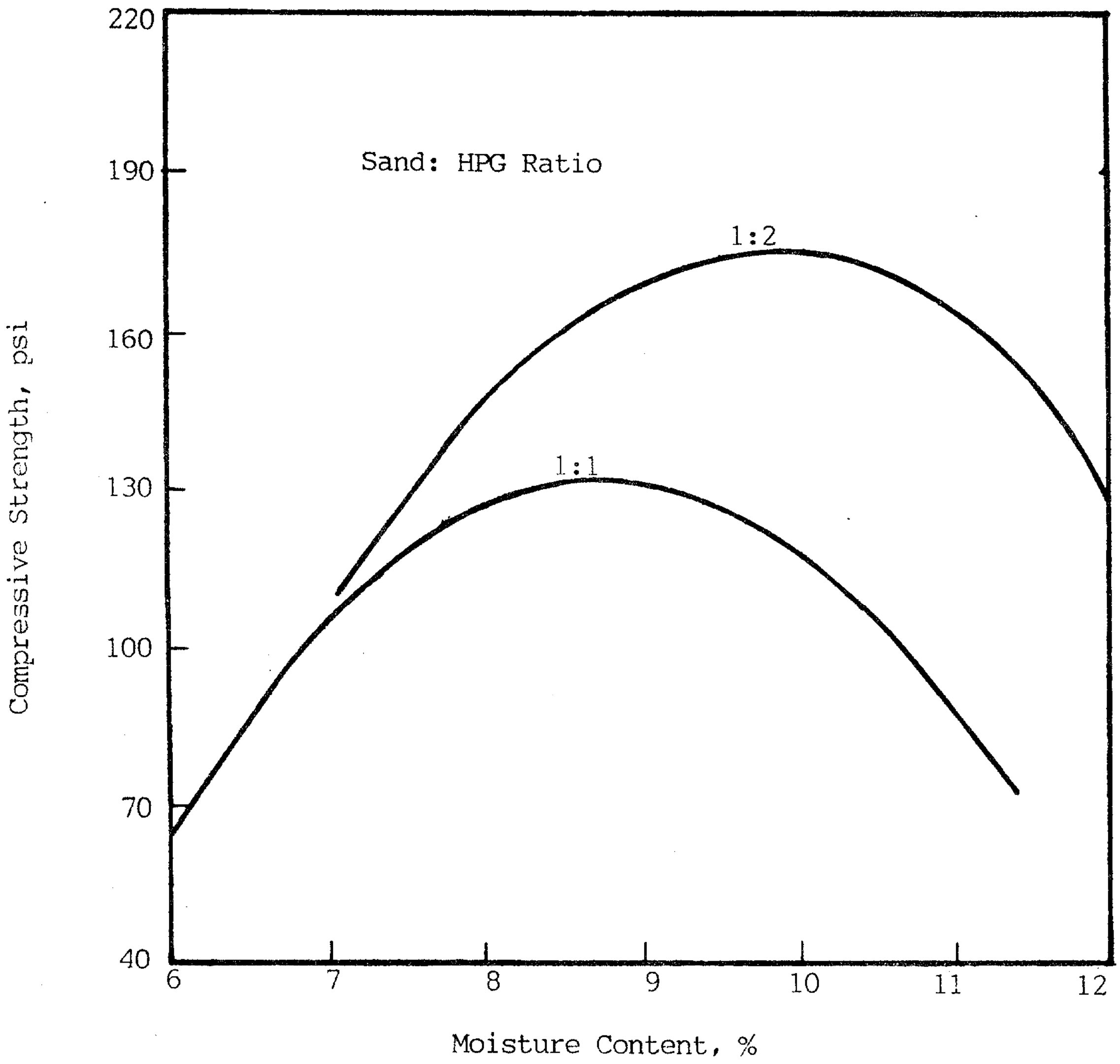

Figure 5. Strength-compaction moisture relationships for sand-HPG mixtures under soaked conditions.

tions respectively. The sand used is widely available in the Columbia County, Florida, where secondary roads using Oxy-HPG and sand on site will soon be built. From Figures 4 and 5, it can be seen that the addition of Oxy-HPG continuously strengthens the material under both air-dry and soaked conditions. In order to maintain the water resistance of the product, however, at least fifty percent of Oxy-HPG has to be used in the mixture.

CONCLUSIONS

Test results on the stabilizing agent treated DPG mixtures lead to the following conclusions:

1) RC-70 and tar in small quantities (around 2%) prove sufficient to improve the water resistance of DPG-based mixtures.
2) Paraffin wax soaking improves greatly the strength of DPG. Due to the water-proof property of the product, this strength is not moisture-affected.
3) Sodium silicate is effective in improving the water susceptibility of DPG, but its use is limited because of the "blooming effect".
4) Other materials like resins and sulfur have the potential of improving the engineering parameters of DPG, and continued researches in this area are currently under way.

In addition, Oxy-HPG when mixed with a fine aggregate (sand) improves the strength of the mixture under both air-dry and soaked conditions, thus providing an effective way to stabilize the existing fine aggregate on site.

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PHOSPHOGYPSUM TEST ROAD

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ABSTRACT

Occidental Chemical Company constructed a test road with phosphogypsum on Company controlled property on the road between Suwannee River Chemical Complex and Suwannee River Mines at its White Springs, Florida Facilities.

The road was 200 feet long and consisted of four (4) different design cross sections, 50' long each constructed as follows:

1) 50' section of road constructed with 12" thick layer of loose hemi-hydrate gypsum, from Swift Creek, compacted to 98% density.

2. 50' section of road constructed with 7" of loose hemi-hydrate gypsum, from Swift Creek, mixed with 5" of sand tailings compacted to 98% density.

3. 50' section of road constructed with 5" of loose dihydrate gypsum, from Dorr-Oliver Gypsum Stack, mixed with 7" of sand tailings. Added 2% by volume emulsified asphalt Fla. D.O.T. AEP-1 and compacted to 98% density.

4. 50' section of road constructed with 12" thick layer of loose dihydrate gypsum, from Dorr-Oliver Gypsum Stack, compacted to 98% density.

After construction completion the road surface was coated with asphalt prime coat. The road is being monitored for durability and performance.

INTRODUCTION

The Phosphogypsum Test Road was constructed by Oxy to study the structural durability and construction feasibility of the different mixtures of gypsum and sand.

TEXT

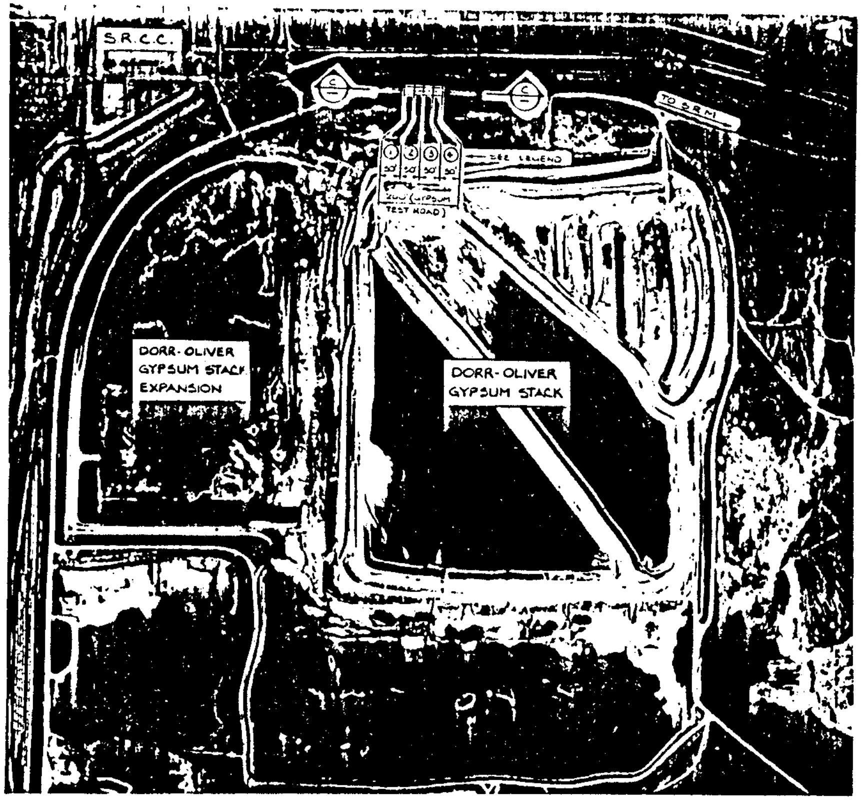
The test road was constructed with phosphogypsum at the White Springs Plant on September 17, 1985.

The site selected is a service road between the Chemical Plant and the Suwannee River Mine, subjected to routine plant traffic including heavy trucks and loaded pans. (Figure 1)

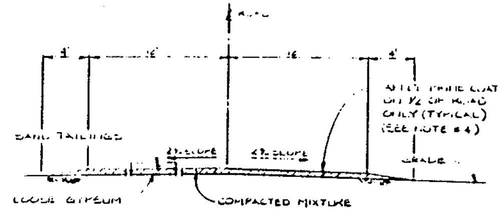
The road is 24 feet wide and 200 feet long and consists of four sections (Fig. 2) constructed as follows:

1. The first section was constructed with 100% hemi-hydrate gypsum. (Fig. 3)
2. The second section was constructed with 60% hemi and 40% sand. (Fig. 4)
3. The third section was constructed with 40% dihydrate gypsum and 60% sand. (Fig. 4)
4. The 'last 50' section was constructed totally of dihydrate gypsum with 2% asphalt emulsions mixed with the gypsum. (Fig. 3)

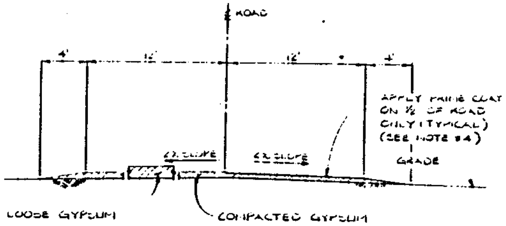
Sections 1 and 4 were built with 12 inches of loose gypsum compacted down to about 8 inches. Sections 2 and 3 were constructed in two layers, a



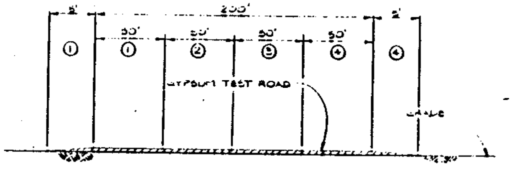
PLAN
SCALE: 1"=250'



SECTION Ⓐ
SCALE 1"=5'



SECTION Ⓑ
SCALE: 1"=5'



SECTION Ⓒ
N.T.S.

LEGEND

① 50' SECTION OF ROAD CONSTRUCTED WITH 12" THICK LAYER OF LOOSE HEMI-HYDRATE GYPSUM, FROM SWIFT CREEK, COMPACTED TO 98 % DENSITY. SEE SECTION Ⓑ

② 50' SECTION OF ROAD CONSTRUCTED WITH 7" OF LOOSE HEMI-HYDRATE GYPSUM, FROM SWIFT CREEK, MIXED WITH 5" OF SAND TAILINGS. MIXTURE SHALL BE COMPACTED TO 98% DENSITY. SEE SECTION Ⓐ

③ 50' SECTION OF ROAD CONSTRUCTED WITH 5" OF LOOSE DIHYDRATE GYPSUM, FROM DORR-OLIVER GYPSUM STACK MIXED WITH 7" OF SAND TAILINGS. ADD 2% BY VOLUME RC-70 CUTBACK ASPHALT. MIXTURE SHALL BE COMPACTED TO 98% DENSITY. SEE SECTION Ⓐ

④ 50' SECTION OF ROAD CONSTRUCTED WITH 12" THICK LAYER OF LOOSE DIHYDRATE GYPSUM, FROM DORR-OLIVER GYPSUM STACK, COMPACTED TO 98% DENSITY. SEE SECTION Ⓑ

NOTES:

1. INPLACE MIXING SHALL BE ACCOMPLISHED BY USING AN INPLACE ROTOMIXER TO MIX THE LAYER OF GYPSUM WITH THE LAYER OF SAND TAILINGS
2. COMPACT THE ROADWAY MATERIAL BY USING A ROLLER COMPACTOR. COMPACTED THICKNESS IS APPROX. 7" THICK.
3. INPLACE DENSITY TESTS SHALL BE TAKEN DURING CONSTRUCTION TO MONITOR THE COMPACTION.
4. SURFACE TREATMENT PRIME COAT SHALL BE CUTBACK ASPHALT GRADE RC-70. APPLICATION SHALL BE 0.25 GALLONS PER SQUARE YARD. THE TEMPERATURE OF THE PRIME MATERIAL SHALL BE BETWEEN 100° AND 150°(F) TO INSURE UNIFORM DISTRIBUTION.

NOT FOR CONSTRUCTION

FIGURE 1

MARK	REVISION	BY	DATE
A	ISSUED FOR APPROVAL	[illegible]	[illegible]

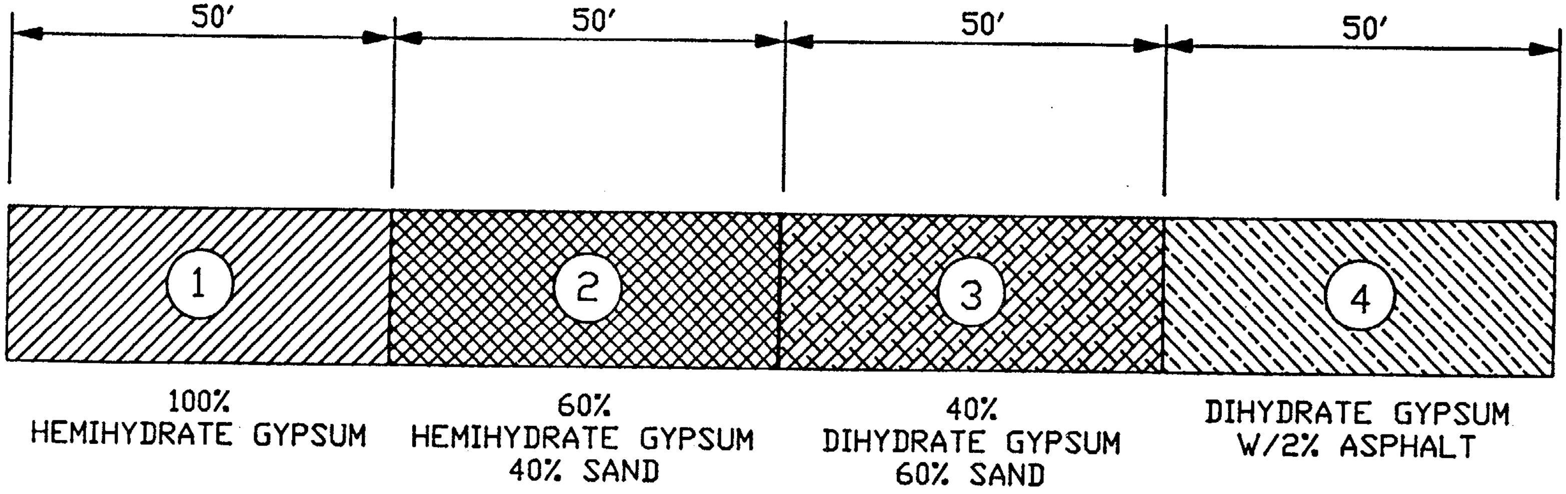
SCALE: AS NOTED
DRAWN BY [illegible] SCHAETZE 5-9-85
CHECKED BY S. ANLY [illegible]
APPROVED BY S. ANLY [illegible]
APPROVED BY
APPROVED BY

OCCIDENTAL CHEMICAL
AGRICULTURAL PRODUCTS, INC
FLORIDA OPERATIONS
WHITE SPRINGS, FLORIDA

TITLE
SUWANNEE RIVER CHEMICAL COMPLEX
GYPSUM TEST ROAD

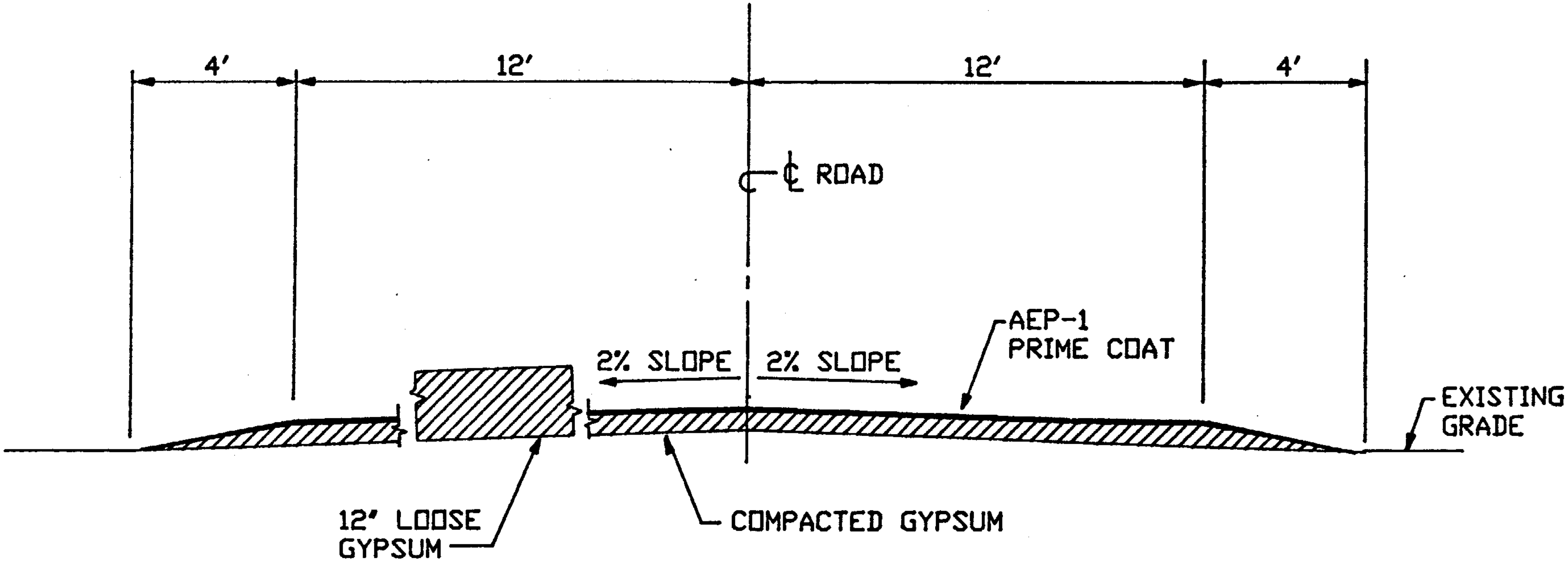
PLANT S.R.C.C.
JOB NO 256-40-[illegible]
CHARGE NO
REVISION NO. A
DWG NO 4[illegible]

WORK SAFELY



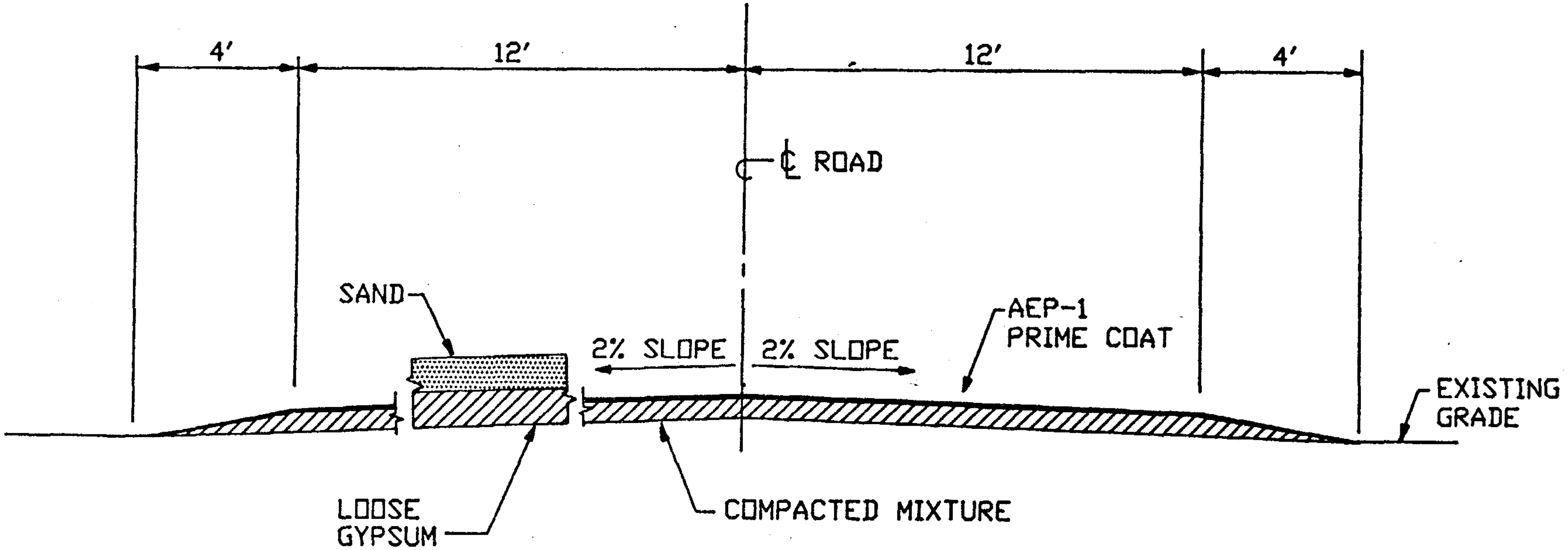
DESIGN SECTIONS
GYPSUM TEST ROAD

FIGURE 2



SECTIONS ① & ④

FIGURE 3



SECTIONS ② & ③

FIGURE 4

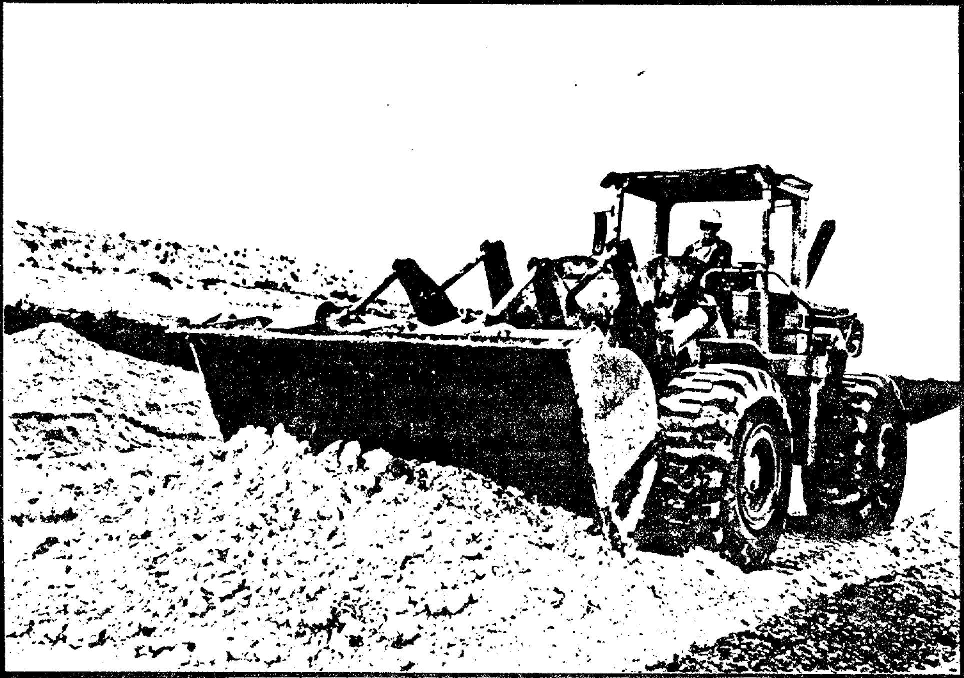
layer of gypsum and a layer of sand to a total thickness of 12". The gyp and sand were mixed in place with a rotomixer and then compacted down to about 7 1/2 inches. (See Figures 3 and 4).

Dihydrate gypsum from the Dorr-Oliver Gypsum Stack was loaded and transported to the road site by pans. The hemi-hydrate gypsum was excavated from the Swift Creek Gypsum Stack and transported to the road site by dump trucks. The sand was transported to the site by pans.

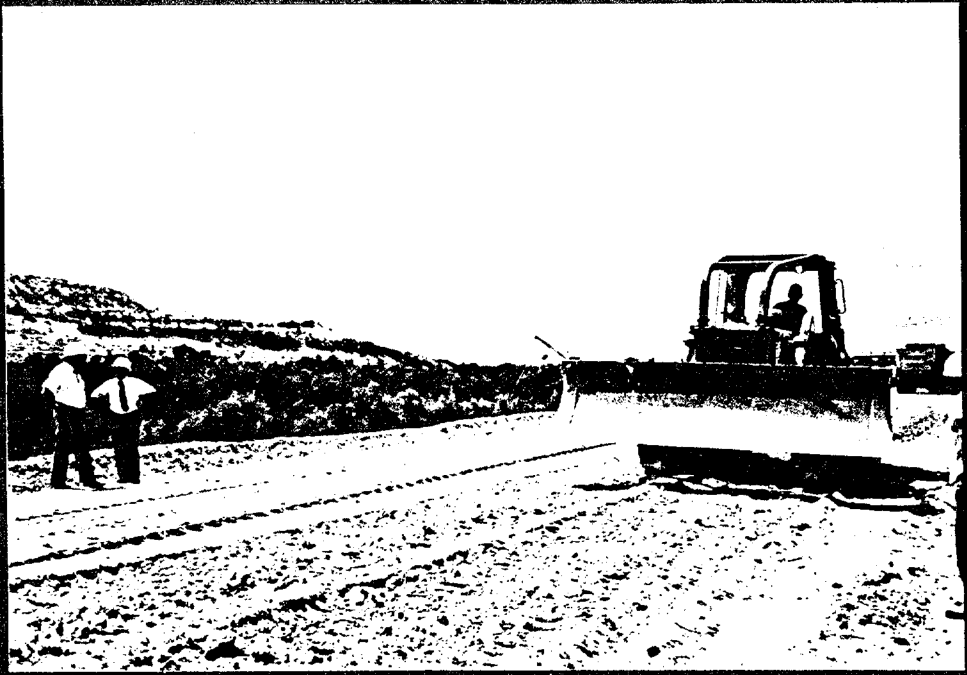
The hemi-hydrate gypsum was spread with a loader and a bulldozer. The dozer was tracked across the gypsum to break up the hard lumps. The gyp was then leveled to the designed thickness with a motorgrader. The dihydrate gypsum was then spread with a loader. There were no lumps encountered in the dihydrate gypsum. Lime was added to these sections to neutralize the pH. The sand was then spread on sections 2 and 3 and graded to the design thickness.

With the asphalt applied to section 4, the rotomixer mixed the materials in Sections 2, 3 and 4. Checks of the material thickness were made following the rotornixing. Checking the material following the rotornixing in Section 4, it was apparent that a homogenous mix of the dihydrate gypsum and asphalt was not achieved.

Following the completion of the mixing a bulldozer was used for the initial compacting. The surface was then bladed smooth with a motorgrader and the final compacting was achieved with a 15 ton steel wheeled roller running 10 passes over the entire road. Asphalt was then sprayed and hot sand applied to seal the surface. See photographs of the actual road construction on Figures 5 thru 11.

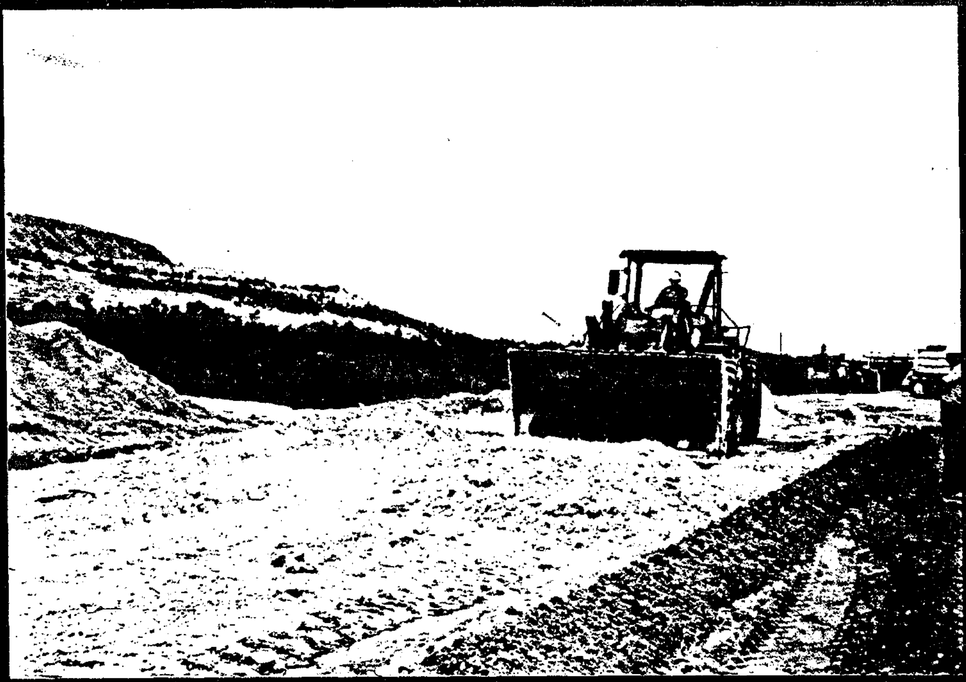


GYPSUM SPREAD WITH LOADER

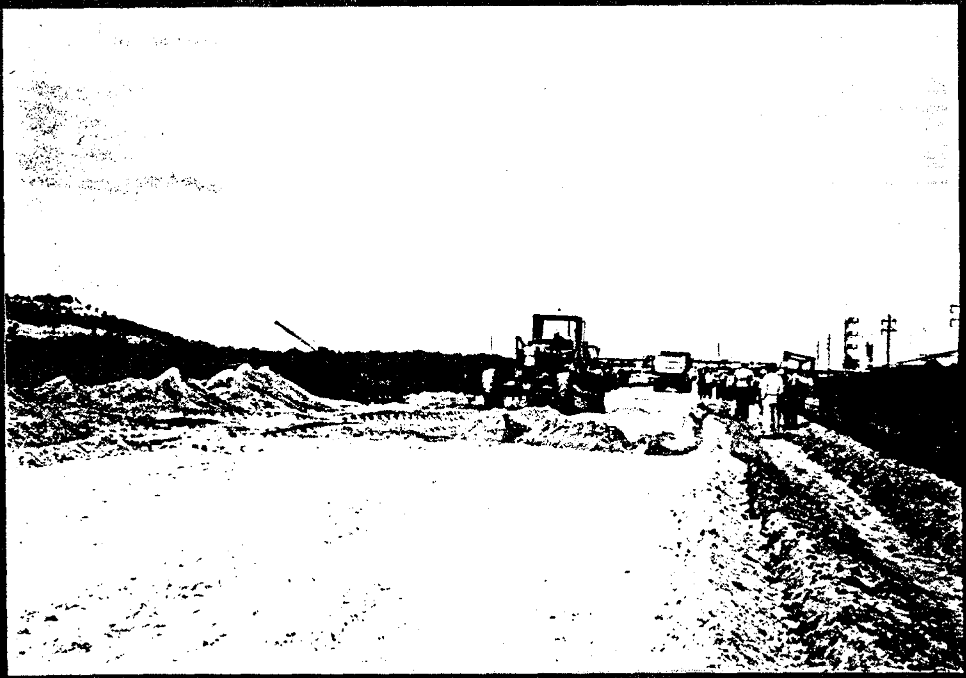


INITIAL COMPACTION AND SPREADING

OF GYPSUM WITH DOZER

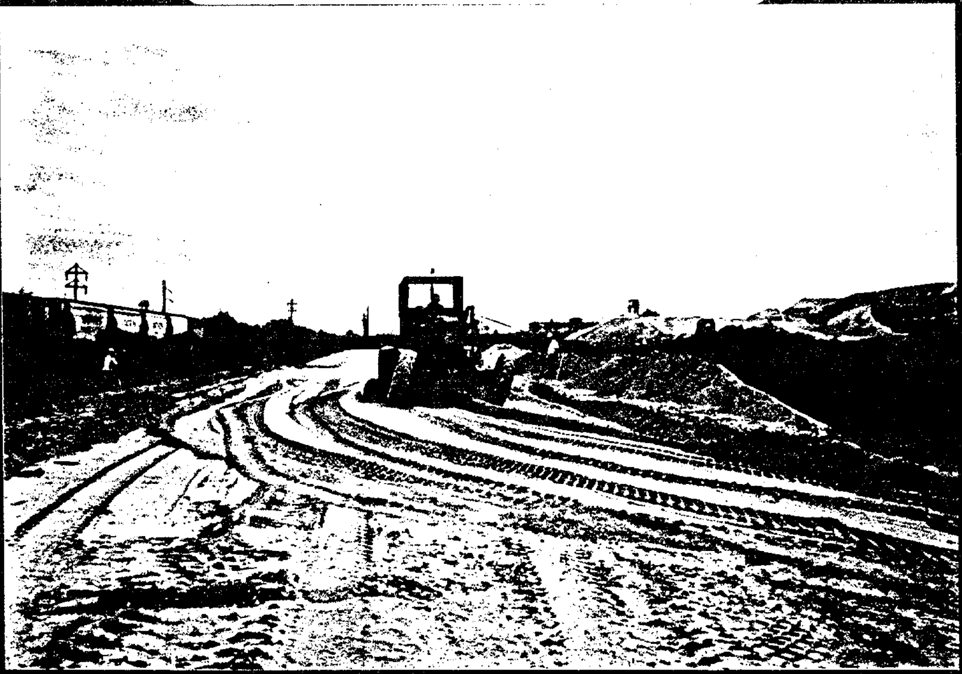


LOADER SPREADING SAND & GYPSUM



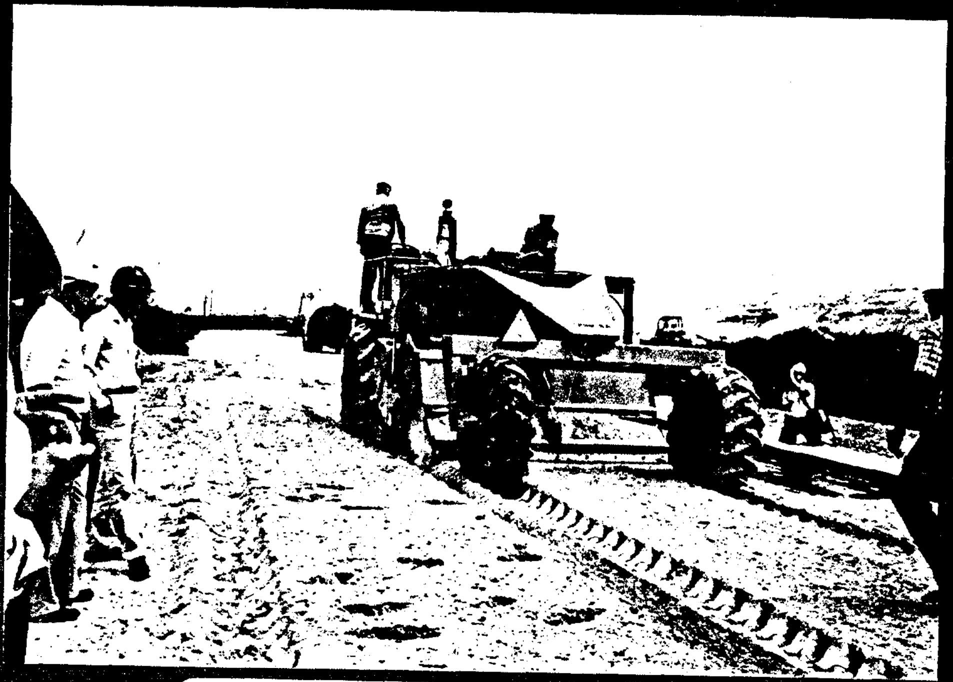
MOTOR GRADER BLADING ROAD

MOTOR GRADER BLADING ROAD

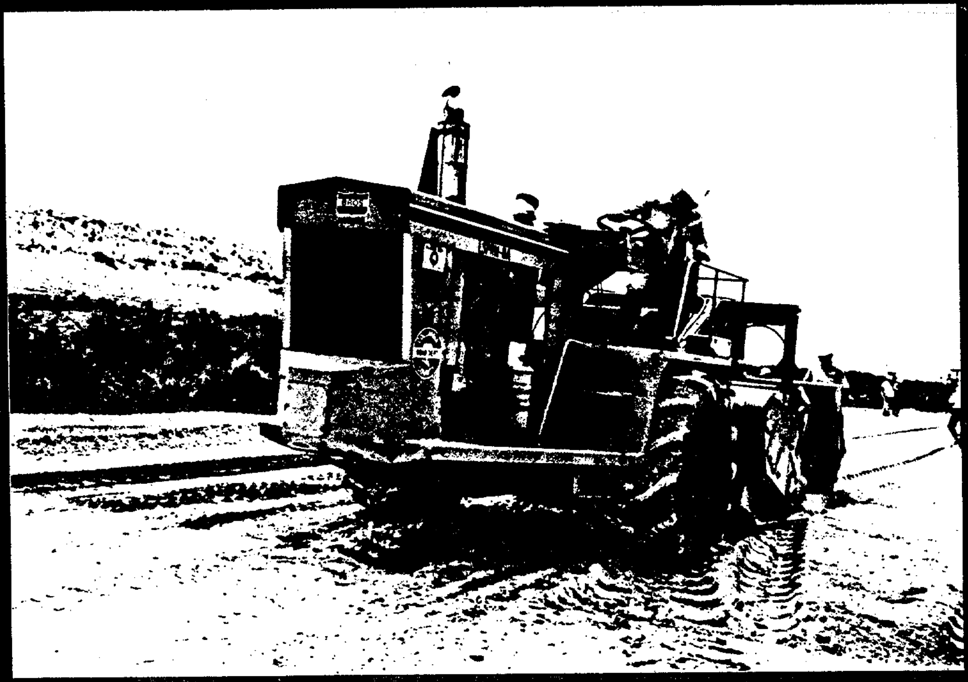


MOTOR GRADER BLADING ROAD

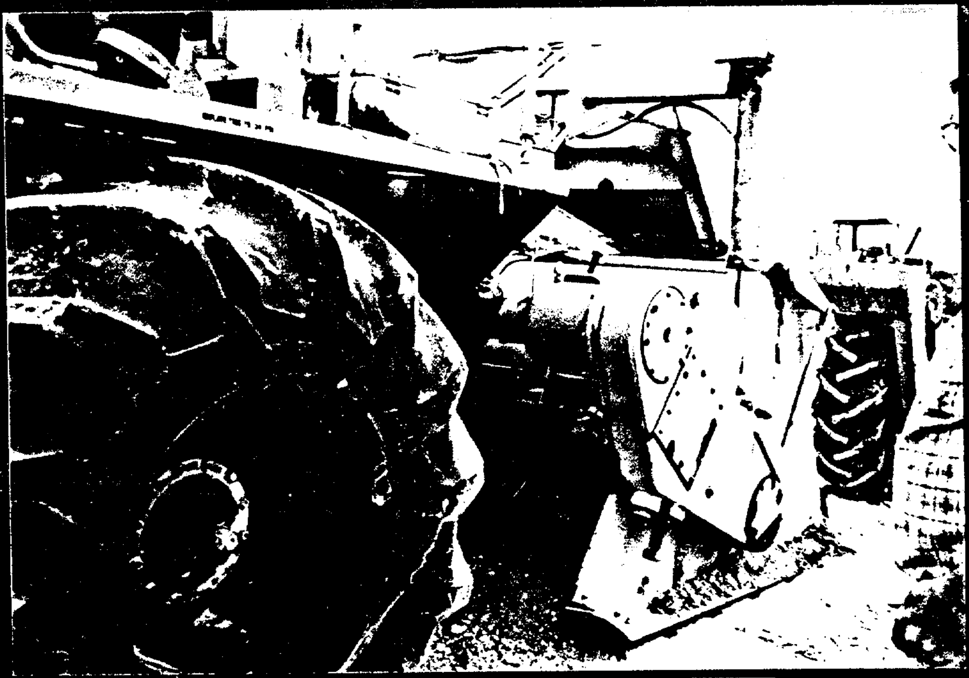
BULLDOZER PASSING OVER ROAD TO BREAK LUMPS IN GYPSUM



ROTOMIXER MIXING GYPSUM AND SAND LAYERS

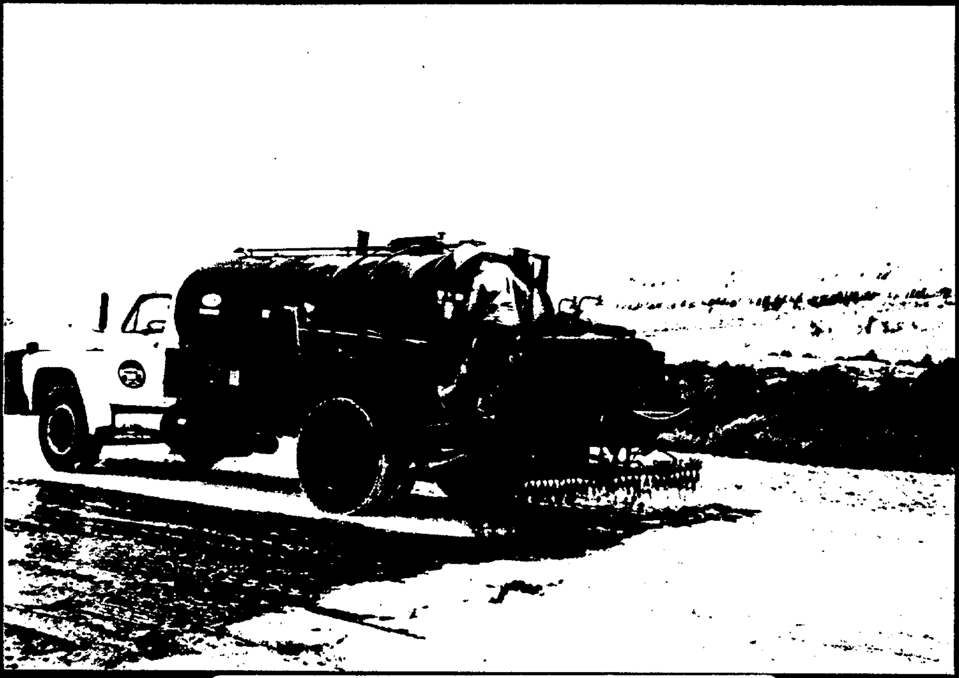


ROTOMIXER



ROTOMIXER

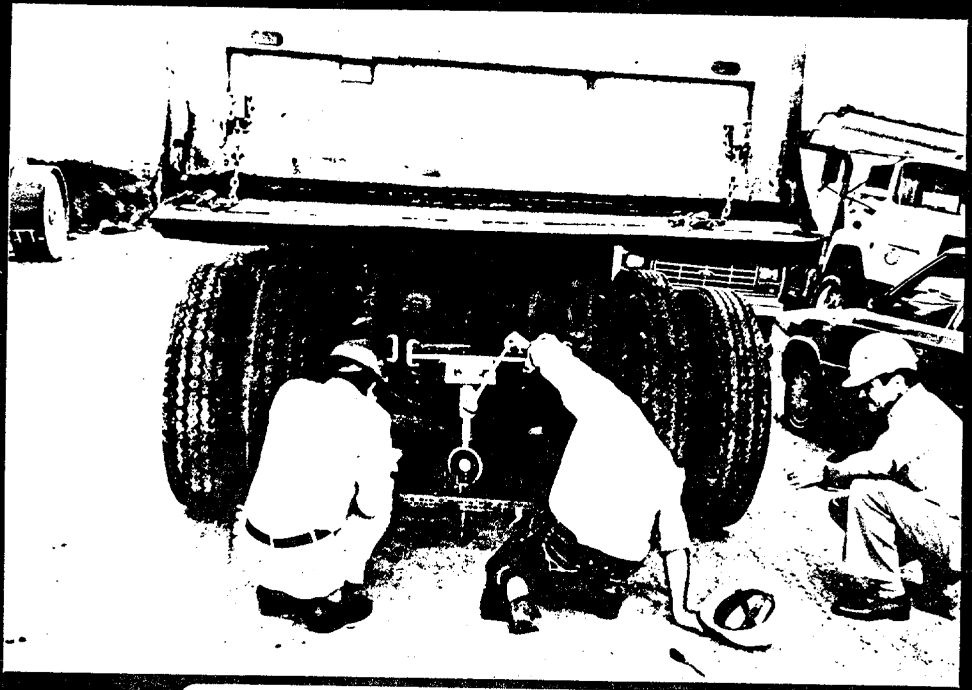
FIGURE 9



ASPHALT SPRAY SURFACE

ASPHALT SPRAY SURFACE

FIGURE 10



-CBR- TEST ON ROAD

FIGURE 11

The asphalt sealer on the road surface provided a good skid resistant surface as well as protecting the surface against erosion. The asphalt also eliminated the dust problem.

The test road was opened to traffic immediately after completion. The road has been subjected to extremely heavy traffic and construction equipment.

CONCLUSION

Preliminary results indicate that the section of the road built with the 100% hemihydrate gypsum section 1 appears to be superior to the other three combinations. The surface treatment is a very important factor in extending the life of the road. Also, it reduces dust, improves skid resistance and protects the gypsum from erosion, The road will be monitored and tested periodically for performance and durability.

ACKNOWLEDGEMENTS

I extend my appreciation to Mr. Lincoln Olson, Training Superintendent, Occidental Chemical Company, for his contribution in taping and editing the video presentation of the road construction.

The gypsum-sand mixtures were the result of laboratory tests on gypsum from Occidental performed by Dr. Chang and his staff at the University of Miami.

PHOSPHOGYPSUM-BASED CONCRETE RAMP

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ABSTRACT

A parking lot ramp utilizing a phosphogypsum-based concrete mixture was built at the University of Miami on September 1, 1985. The ramp measured 24 feet wide and 14 feet long, was divided into two equal sections of 12 feet by 14 feet each. The mixture used, consisted of phosphogypsum, fine and coarse aggregates and cement. One of the sections was built with plain phosphogypsum-based concrete and the other was built with the same mixture reinforced with steel fibers. Materials were mixed in a pan type mixer in the laboratory and transported to the site. A small road compactor was used to compact the mixtures in place. The ramp has been subjected to traffic loads consisting mostly of automobiles and occasionally truck loads since September 10, 1985 and is in good condition.

INTRODUCTION

Phosphogypsum, when subjected to proper compaction, becomes a smooth-surfaced, strong solid, two desirable engineering properties for a construction material. The unique properties have enabled the development of compaction concrete utilizing phosphogypsum. Laboratory tests indicate that compressive strength of concrete increases as much as 50% by replacing a portion of fine aggregate with phosphogypsum [1] . In other words, phosphogypsum can be used as a binder for the mixtures containing low cement content.

A parking lot ramp was built at the University of Miami to demonstrate the possible application of using phosphogypsum-based concrete in rigid pavement construction. The ramp has performed satisfactorily under traffic loads.

THE CONCRETE RAMP

The ramp as shown in Figure 1 is 24 feet wide and 14 feet long and, the slope of the ramp is about 0.04. The thickness of the ramp slab as constructed was 6 inches minimum. The ramp was divided into two equal sections of 12 feet by 14 feet each. One of the sections was built with plain phosphogypsum-based concrete consisting of phosphogypsum, fine and coarse aggregates and, cement. The other section was built with the same mixture reinforced with steel fibers.

MATERIALS

The phosphogypsum-based concrete used for the construction of the ramp, consisted of 20% of phosphogypsum, 40% of fine crushed limerock aggregate, 30% of coarse limerock aggregate with a maximum nominal size of 3/8 inch and 10% of type I port land cement. Moisture content at the time of mixing was 12% of the total mixture measured by weight. Phosphogypsum was supplied by the Gardinier Inc., Tampa, Florida.

Steel fibers used in the mixture, were 3/4 inches Fibercon “44” manufactured by the Michell Fibercon, Inc., Pittsburgh, Pennsylvania. The dimensions of the fibers are 0.010 inches by 0.044 inches and 3/4 inches long.

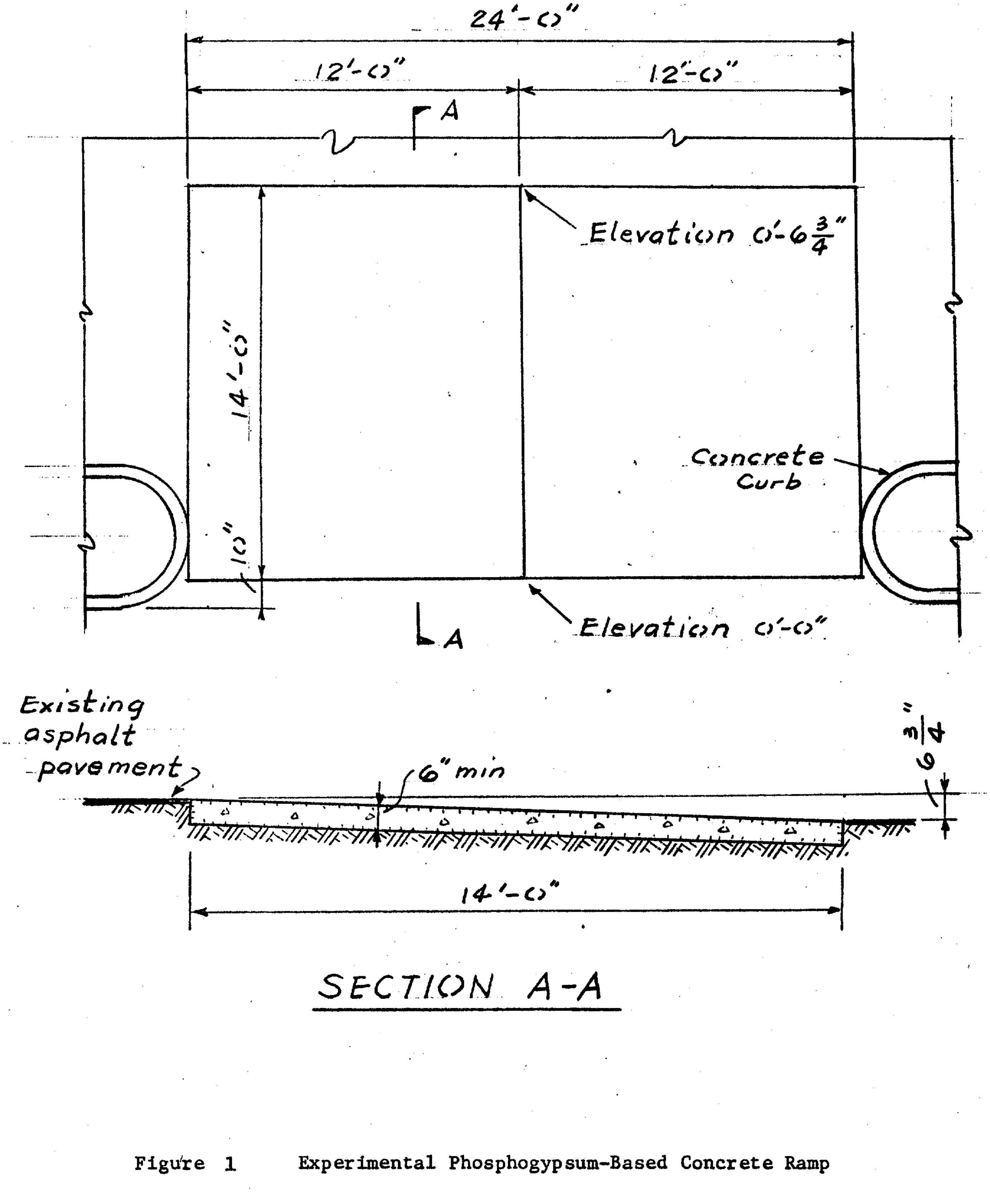

Figure 1 Experimental Phosphogypsum-Based Concrete Ramp

CONSTRUCTION PROCEDURE

Materials for phosphogypsum-based concrete were mixed in a conventional pan mixer with grinding wheels as shown in Figure 2 in the order of phosphogypsum, fine aggregate, coarse aggregate and water until the materials were well mixed. Steel fibers were then added to the mixture.

The mixtures were transported and placed on the job site as shown in Figure 3. A road compactor was used to compact the mixtures as shown in Figures 4 and 5. After the phosphogypsum-based concrete pavement was cured for ten days, the ramp was opened to traffic loads as shown in Figure 6.

FIELD TESTING

Core samples, 2.75" in diameter and 5.5" in height, were taken from the ramp after 28-days. The average compressive strength of the core samples was 3,890 psi.

PHOSPHOGYPSUM-BASED COMPACTION CONCRETE VERSUS CONVENTIONAL CONCRETE

The mix design used in the ramp is compared with a conventional concrete design used in South Florida as shown in Table I.

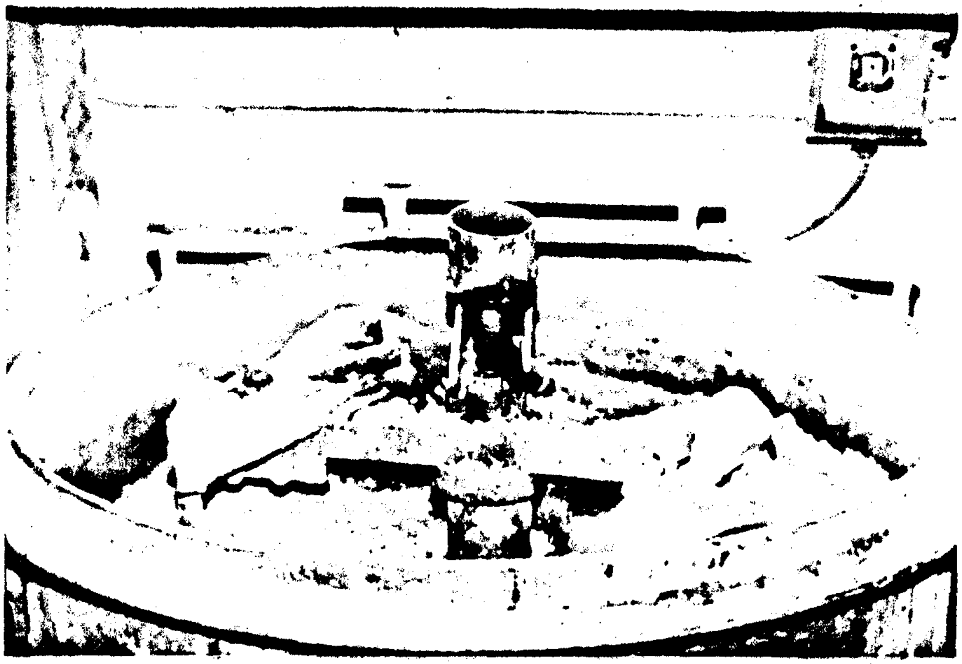

Figure 2

Figure 3

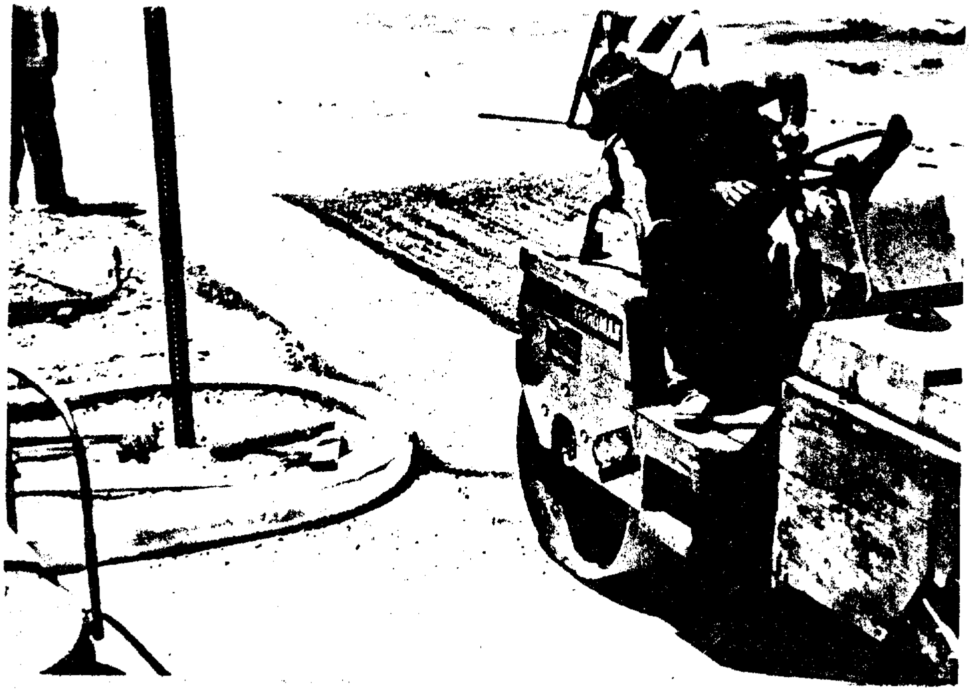

Figure 4

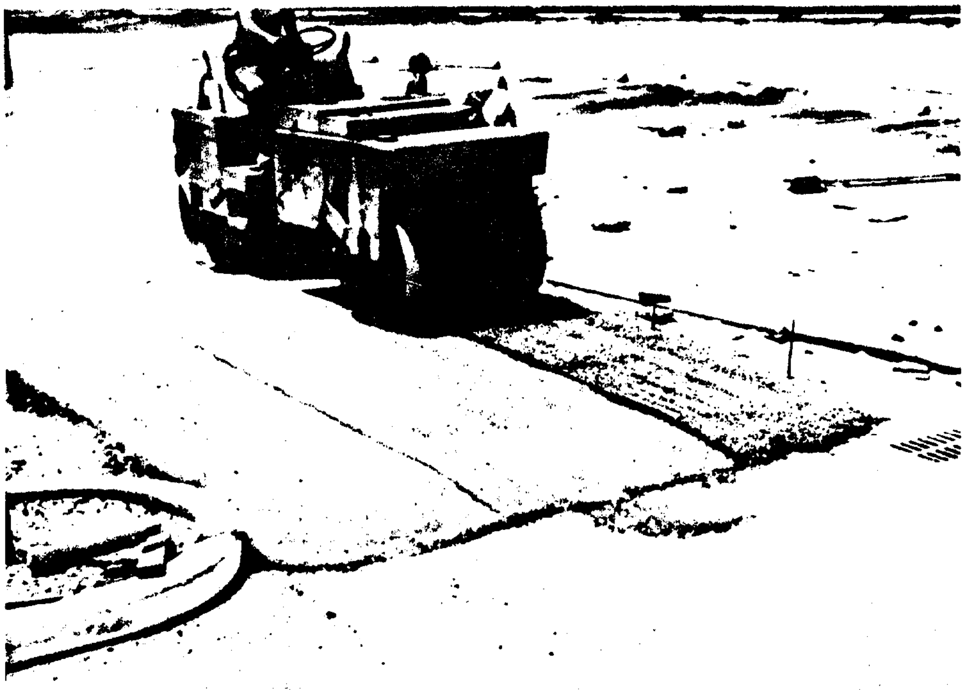

Figure 5

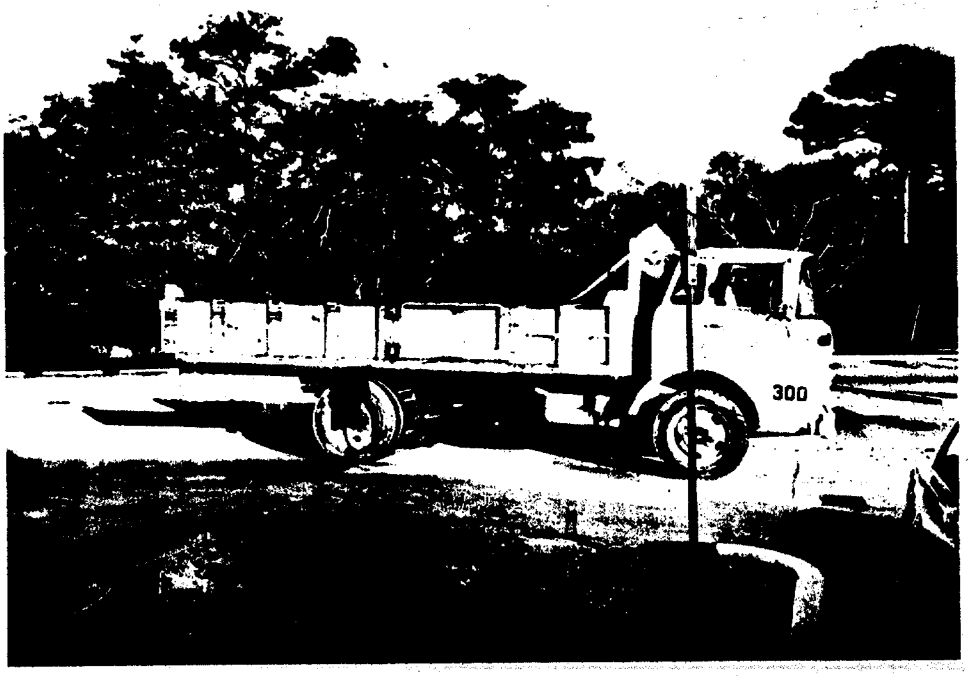

Figure 6

TABLE 1

A COMPARISON OF MIX DESIGN BETWEEN PHOSPHOGYPSUM-BASED CONCRETE AND CONVENTIONAL CONCRETE COMPRESSIVE STRENGTH: 3,500 PSI AT 28-DAYS

Materials Per Cubic Yard of Concrete	Conventional Concrete in Lb.	Phosphogypsum-Based Compaction Concrete
Cement	517	340
Phosphogypsum	0	675
Fine Aggregate	1,338	1,350
Coarse Aggregate	1,520	1,000
Admixture	16 oz.	0

The advantages of using phosphogypsum-based concrete as compared to that of the conventional concrete, are described as follows:

1) The saving of cement in per cubic yard of concrete is 177 lbs.

2) Although the total amount of aggregates used in both types of concrete is almost unchanged, it is more economical in the State of Florida to substitute phosphogypsum for lime rock.

3) No admixture is used in phosphogypsum-based compaction concrete as compared to that of conventional concrete which requires 16 oz. of admixtures.

4) Phosphogypsum-based concrete is a zero-slump concrete. The natural moisture contents in the phosphogypsum and aggregates generally provide a quantity of mixing water very close to the required moisture content of the mixture. On the other hand, the conventional concrete is a wet mix which requires about 250 lbs. of water per cubic yard of concrete.

CONDITION OF THE RAMP

The ramp has been subjected to traffic loads consisting mostly of automobiles and occasional truck loads since September 10, 1985. The ramp is in good condition.

CONCLUSION

1. The ramp as constructed has demonstrated the potential application of using phosphogypsum-based concrete in highway surface course.

2. It is economically feasible to use phosphogypsum-based concrete for highway construction as compared to that of using conventional concrete.

3. Construction method as presented, requires only conventional road construction equipments.

ACKNOWLEDGEMENT

The research is funded by a grant from the Florida Institute of Phosphate Research, Bartow, Florida.

REFERENCE

1. Lin, K. T., Nanni, A., and Chang, W. F., “Engineering Properties of Dihydrate Phosphogypsum, Portland Cement and Fine Aggregate Mixtures”, Proceedings of the Third Workshop on By-Products of Phosphate Industries, Florida Institute of Phosphate Research, 1986.