Publication No. 01-028-028

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

Conducted by
Department of Civil & Architectural Engineering
University of Miami
Miami, Florida
under a grant sponsored by the
Florida Institute of Phosphate Research
Bartow, Florida

May, 1985

FLORIDA INSTITUTE OF PHOSPHATE RESEARCH

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

Held at the University of Miami
James L. Knight International Conference Center
Miami, Florida
April, 1984

Sponsored by

UNIVERSITY OF MIAMI
Department of Civil & Architectural Engineering
Miami, Florida

and

FLORIDA INSTITUTE OF PHOSPHATE RESEARCH
1855 West Main Street
Bartow, Florida 33830

Contract Manager: G. Michael Lloyd, Jr.

DISCLAIMER

Preface

The growth of the modern phosphatic fertilizer industry has played a strategic role in the development of U.S. agriculture's ability to supply low cost food products in quantities large enough to more than adequately meet all our needs and still export to the rest of the world.

During much of this time, phosphogypsum, produced as a byproduct of phosphoric acid manufacture, has been stockpiled and largely ignored. When the nature and extent of these stockpiles was realized, the phosphogypsum "problem" began to attract attention.

In recent years the "problem" has been recognized as an unusually attractive "opportunity" for Florida as the potentials for phosphogypsum utilization in agriculture, construction, road building, and as a chemical raw material, have been realized. This publication, reporting on the "Second Workshop on Phosphogypsum" presents the results of some of the recent work in these areas and holds out the promise of even more progress in the future.

CONTENTS

RADIOACTIVITY ASPECTS

ENGINEERING PROPERTIES

HIGHWAY RESEARCH AND APPLICATIONS

ENVIRONMENTAL ASPECTS

KEYNOTE ADDRESS

Dr. Earl M. Starnes

SEMINAR ON PHOSPHOGYPSUM

April 26, 1984

The Florida Institute of Phosphate Research
and
University of Miami

James L. Knight International Conference Center
Miami, Florida

One of the general failings of the human condition is our capacity to see comprehensively the larger state of tomorrow. There are exceptions: Frederick Olmsted's Central Park in New York City, The Biscayne National Monument in Dade County, Florida and Eisenhower's Interstate Highway System. These are very different consequences of public policy taken in the past. Each required a comprehensive vision of tomorrow. Unfortunately they represent peaks in an otherwise unexciting landscape of "muddling through". (Lindblom, 1959) This seminar seems to represent Dr. Chang's capacity to peer above the unexciting and enthusiastically reach for opportunity. His vision is seasoned by the mature skills of a dedicated scholar. Building knowledge through his efforts has the potential for solving several interrelated public and private policies regarding the phosphate industry and Florida.

The Florida Institute of Phosphate Research is in the business of building knowledge. Its purpose is managing research. It is an activity that requires dedication to objectivity and rigor. The kind of dedication we see here in this seminar and the presented papers. Objectivity is one of those elusive terms that we all use. Too often objectivity is couched in a personal context.

To the political activist objectivity is the program or position he or she espouses. Daniel Moynihan in his book "Maximum Feasible Misunderstanding" notes that "Government programs rarely begin with anything like as clear a purpose as the system presupposes." (Moynihan, 1969)

Frances Fox Pevin in 1968 remarks on an earlier Moynihan effort;

> "Similarly, the concrete programs and structures launched under the banner of lofty public goals are in fact formed to deal with the various political circumstances of any agency depends. Through this process government action may become unintelligible to the critic who looks at goals and programs to discover a paradigm for rational action. But the motivating force in government action, the force which shapes public goals and the programs and structures created in their name, reflects another sort of rationalism--the adaptive rationalism through which a political system and its member parts are maintained." (Moynihan, 1970)

FIPR: I prefer to call it the Institute since the acronym reminds me of a popular dolphin; as we have come to know it is one of those programs launched under the banner of lofty public goals. It, however, must deal with another level of objectivity. This level is demanded by the research community; a community to which we owe part or all of our professional allegiance. It is not enough for the scholar to see if it works--he or she must understand why it works--thus building on an empirical base of information paradigms for rational action.

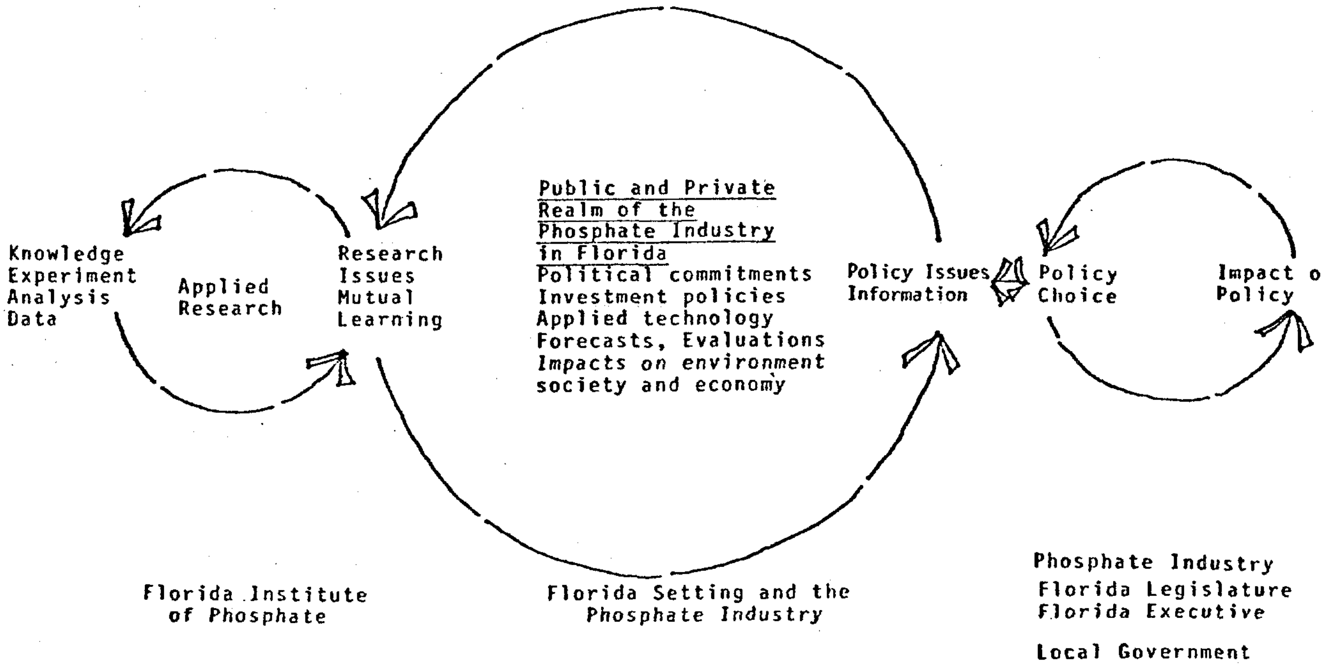
Rigor on the other hand is confined to the means we employ in building these paradigms for rational action. Lawyers call this due process. Researchers call it methodology. Regardless of what it is called, is the rigor of approach to the research proposition, data collection, analysis, findings, conclusions and storage of information. Strict rules exist to channel the flow of data, information and problem solving to guard against extraneous influences and static.

The Institute armed thus with objectivity and rigor and a rationalized purpose is a program hatched in the political arena. It has not yet shed the downy plumage of its beginnings. Hal Scott, a former board member, reminds me of the early administrative problems. Other problems of equal importance had to be coped with in the early years. Thus a few words seem in order as we look to the future of the Institute.

The Institute is builder of knowledge and a transactor of research results into the public and private policy realm. The diagram below explains how I see this role of transaction.

Figure 1

A Diagram which explains the role of FIPR as a major actor in the transaction of research/knowledge to the public and private interests in Florida Phosphate



E. Starnes FIPR 1984
Adapted from J. Friedman's
Transactive Planning Model, 1973.

On the right hand a broken circle represents the cycle of public and private policy. This is meant to illustrate the notion that enacted or adopted policies result in consequences that impact upon the social, environmental, economic, urban and other systems. These consequences tend to alter the behavior of such systems. Let us take for example the 1975 mandatory reclamation act. It is state policy long considered and finally enacted. However, much was to be learned from the consequences of such a policy. We are still learning and continuing to focus on the capacity of industry and public agencies to implement it. We continue to modify the policies even now in the legislature.

As these consequences of these policies impact reality of old lands reclamation and plans are adopted, soon it is discovered the strategies are not always possible thus new issues are raised.

As new policy issues are raised the diagram illustrates a central broken circle. It suggests that policy issues are seasoned by the phosphate industry public realm debate. Issues may be resolved without dedicated research or the confrontations, unresolved conflicts and dialogue in this realm may focus the policy issues into researchable issues or topics. Research issues take on a definitive forms and formats. Questions and propositions for research become clear and research approaches can be designed. The Institute's role here is to fit these research issues into an affordable, a doable and comprehensive on going program.

This requires two levels of effort. The first level is to synthesize statutory prescriptions with public and private research goals into a long range plan for research. The second level of effort requires the fitting of short term research proposals into this comprehensive research plan. What we are about today is organizing these two levels of effort.

The Institute is not a laboratory set apart from the reality of its political life. The cycles illustrated in the diagram above attempt to describe the flow of information. Its research program is laden with social, political, economic and environmental values. We must carve out our goals and objectives by means of participation and dialogue with the public, with the industry and the research community in this often tumultuous market place for knowledge.

Let us see how well this happened in the past few years. In 1981, Professor Joshua Dickenson of the University of Florida assessed the research policy of the Institute. He performed a Delphi using a limited group of knowledgeable respondents. The results of this Delphi prioritized important research issues.

Eighteen issues emerged and the respondents selected six major issues. Three of these deal with reclamation, one singled out radiation hazards, one dealt with dewatering slimes which some like to call clays, and one dealt with ground water impacts of gypsum piles and ponds.

Now how have the funds been allocated in the two subsequent years. The figure below illustrates the applied research program allocated by percent of total funded projects. The five research areas, mining, clay, chemical processing, reclamation and environmental services is the division currently adopted by the Institute. We can see that the efforts of the two years in question reveal:

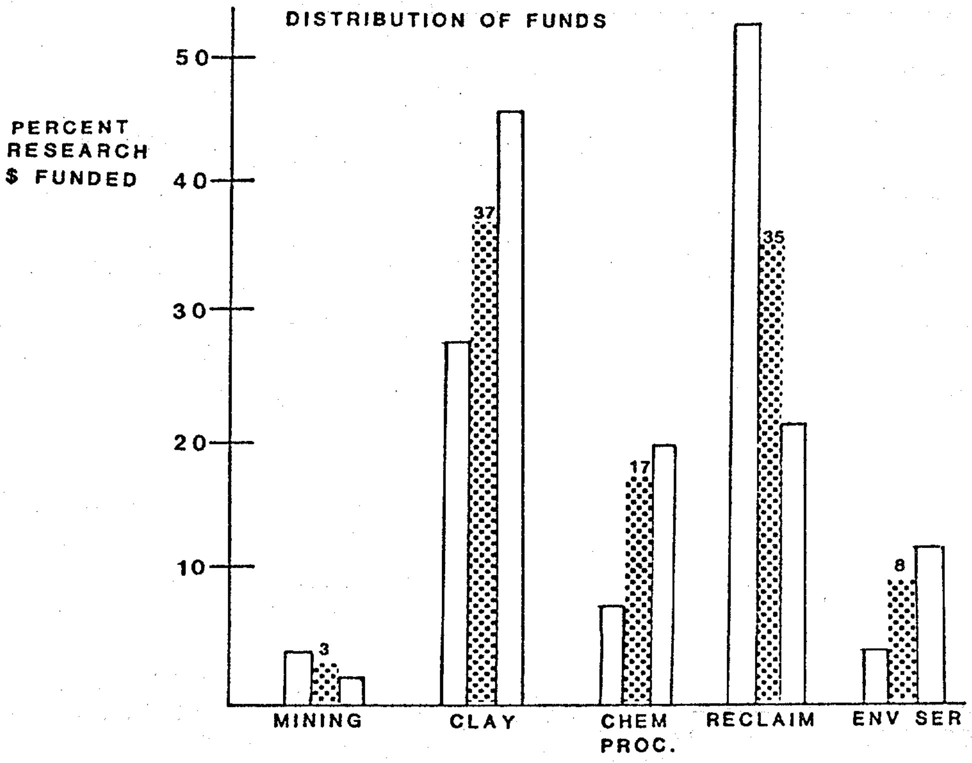
Mining	3% effort
Clay	37% effort
Chemical Processing	17% effort
Reclamation	35% effort
Environmental Services	8% effort

Reclamation efforts appear to be well attended in this cursory analysis. Environmental services certainly appear to be lacking and yet radiation hazards and ground water impacts appeared high in the Dickenson study. It, of course, takes time to adjust the goals of a research program and the Institute is required by law to adjust its priorities from time to time by means of public processes. We have been working on an approach to the public process of developing a new look at the Institute's research agenda. It has been the subject of a great deal of Board attention. It is our belief that we need both an on going process for identifying research goals and a more rigorous process for setting shorter term research objectives and funded programs. The Board has recently taken an action which will renew this process of planning and programming for the Institute.

Figure 3.

APPLIED RESEARCH PROGRAM

TRUST FUND (Aug. 31) .... $13.1 MILLION
TOTAL RESEARCH DOLLARS REQUESTED ...... $32.8 MILLION ($9.5M 82-83)
TOTAL RESEARCH DOLLARS FUNDED .... $ 6.7 MILLION ($3.4M 82-83)



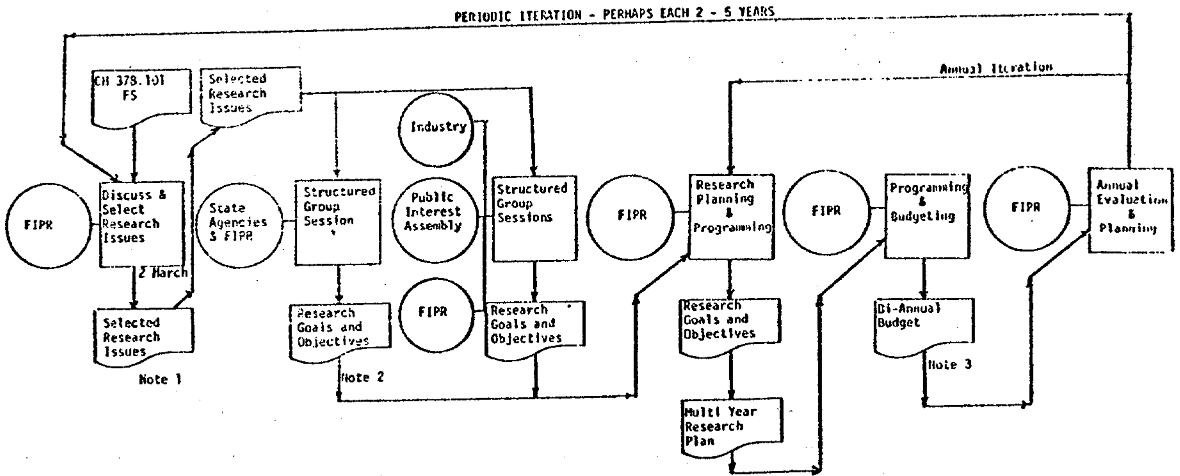
This figure illustrates the Institute's applied research program. The first column in each research area is the 1981-1982 funded research percentage. The third column is the 1982-1983 funded percentage and the shaded column is the average for the two years.

Figure 3 below describes the approach the Board has recently adopted. In addition we have asked the assistance of Dr. Jerome Milliman of the University of Florida and Dr. Larry Gross of the Florida State University faculties to help in this process. Their responsibilities will include gathering information on history of the Institute and clearly documenting its progress. The professors will also gather information on the management of other research institutes. They will assist in the structured group sessions which will be designed to focus clearly on research issues related to the Institute's statutory responsibilities. Focusing clearly means to us definitive concise objective statements of research needs drawn from the environmental community, the industry and state and local permitting agencies. We are also interested in much more comprehensive economic social environmental questions.

Figure 3.

Proposal for Florida Institute for Phosphate Research Planning and Programming

Proposed by: E. Starnes
Chair - FIPR



Note 1: Research Issues - Major subject areas for research consistent with statutory guidelines.

Note 2: Goals - 5 year achievables prioritized
Objective - 2 years or less than 2 years achievables prioritized

Note 3: Subject to annual adjustment

Note 4: A subsidary issue relates to the FIPR research model as opposed to alternative models. Basically: reactive to proposals or seeking out researchers in research plan implemenation.

I am certain that this planning and programming process will be of great value to the Board. It will of course be changed as the University researchers take a harder look at the process.

The Institute's future is rooted in its political origins. It is, however, on its own to reach that plane of objectivity and rigor which is the hallmark of genuine research. The Institute must be relevant to its setting. It should build its record on the sound qualities of its past in this milieu of often conflicting interests with great care. The Institute's goal is to establish itself as a recognized research facility in this field and to make significant contributions to the technology of mining, the understanding of economic and environmental impacts, to the long range realities of a growing Florida and to the knowledge of skills and methods in perfecting the art of policy taking. Finally, the Institute must strengthen its own research management skills and its own research capacities. I am convinced that the Board composed of representatives of the fields of environmental and urban planning, geology and state policy making, education, industry research and reclamation practices and mining management along with its capable staff is dedicated to this purpose. We will, of course, need help through the means of honest research and honest public dialogue.

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Presentation to Seminar on Phosphogypsum
University of Miami
April 26-27, 1984

THE RADIOLOGICAL ASPECTS OF PHOSPHOGYPSUM

C. E. Roessler, Ph.D.
Professor, Environmental Engineering Sciences
University of Florida, Gainesville, FL 32611

This paper has two purposes, 1) to present an overview of the radiological aspects of phosphogypsum and 2) to report an on-going study of radon emissions from phosphogypsum stacks.

AN OVERVIEW

It is well known that uranium and its decay series are associated with phosphate deposits of marine origin, including those in Florida.

The Uranium Decay Series

The major features of the naturally-occurring uranium decay series are shown in Figure 1. This series has fifteen major members and thus undergoes fourteen decay steps to eventually produce nonradioactive lead-206. The series includes isotopes of nine different elements. Some of the radioactive members emit beta particles and others are alpha particle emitters; for some of the radionuclides, particle emission is accompanied by the emission of gamma radiation.

Radionuclides are significant from a human exposure standpoint if they are mobile in the biosphere, tend to concentrate in human tissue, have a long half-life or are constantly replenished from a long half-lived precursor. In general, alpha emitters present a greater hazard when taken into the body than do beta emitters. Those radionuclides that emit gamma rays present the potential for irradiation from outside the body. Various members of the uranium series, singly or in groups, are significant for a variety of reasons as summarized in Table 1 (for a further discussion of the uranium decay series refer to the Appendix at the end of this paper).

Uranium and its decay series are ubiquitous on the earth; concentrations vary with the type of mineral and are significantly elevated in some deposits and ores. Where uranium has remained undisturbed in nature, the various members of the uranium series, at least through radium-226, would be expected to be approximately in radioactive equilibrium - that is all members in equal concentrations of radioactivity. The remaining members of the series would be expected to be in concentrations approaching equilibrium but reduced to whatever extent where is a net loss of the gaseous member, radon-222.

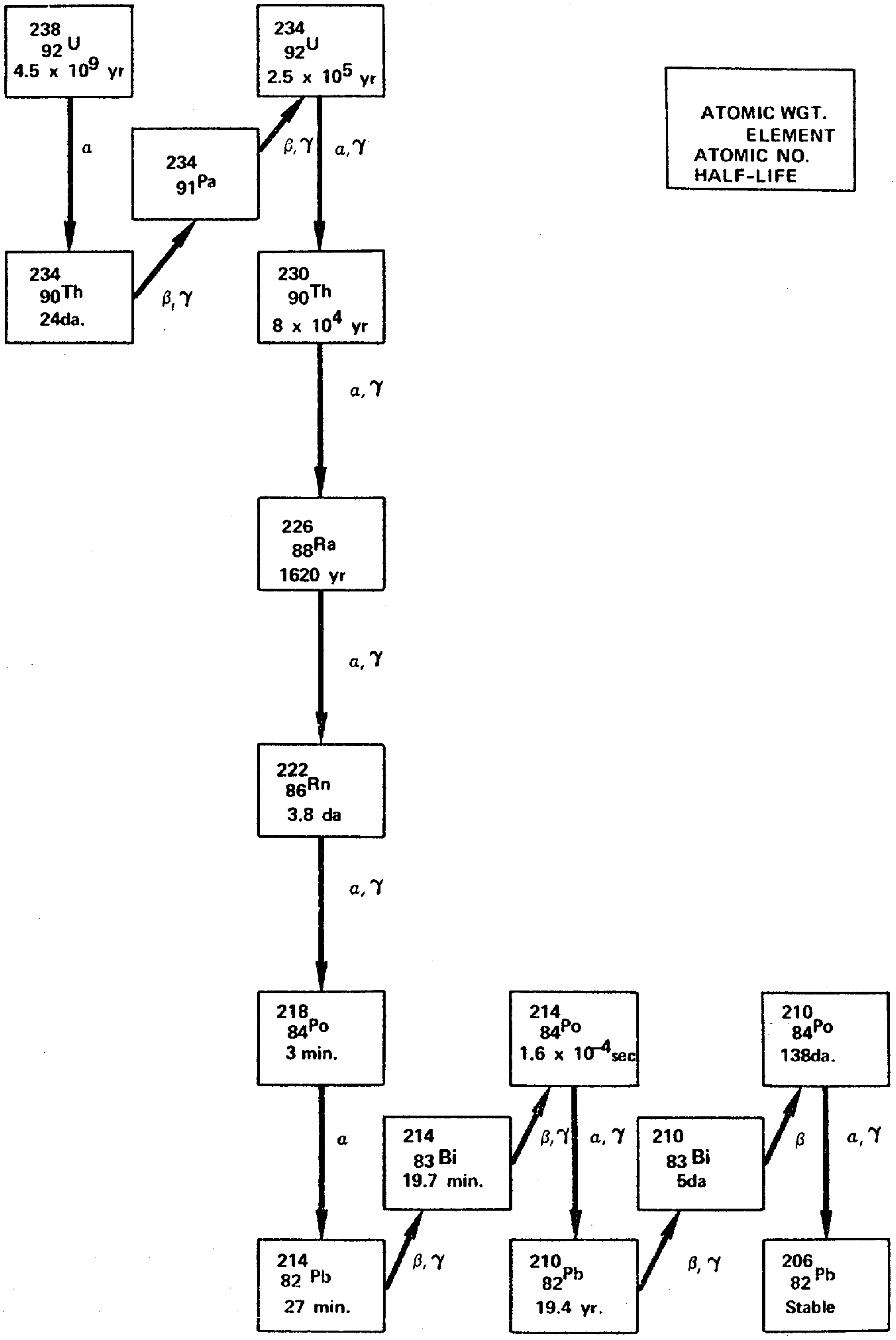


Figure 1. URANIUM-238 DECAY SERIES

Table 1. Significant Members of the Uranium-238 Series

Radionuclide(s)	Member of Series	Half-life	Emission
Uranium and Thorium			
Uranium-238	1st	4.9×10^9 years	alpha
Uranium-234	4th	2.5×10^5 years	alpha
Thorium-230	5th	8×10^4 years	alpha
Significance: Long-lived alpha emitter.			
Radium-226	6th	1622 years	alpha
Significance: Long-lived alpha emitter, chemically similar to calcium, continuous production source for radon-222, gamma radiation source when accompanied by radon and progeny.			
Radon-222	7th	3.8 days	alpha
Significance: Noble gas, continuous production source for radon progeny.			
Short-lived Radon Progeny			
Polonium-218, lead-214, bismuth-214 polonium-214 Decay governed by 26.8 min lead-218 when separated from radon source			2 alpha emitters, gamma emission
Significance: Lung deposition.			
Lead-210/Polonium-210			
Lead-210	12th	22 years	beta
Significance: Biologically mobile, relatively long-lived production source for alpha-emitting polonium-210.			
Polonium-210	14th	138 days	alpha
Significance: Alpha emitter.			

The production and behavior of radon and its short-lived decay products deserves further discussion. Figure 2 presents a simplified diagram of radon formation, radon emanation, and radon progeny formation; the figure also indicates key quantities and units involved. Radium-226 in son-e substrate constitutes a long-lived, continuous production source of radon-222. Only part of the produced radon escapes the mineral grain. The fraction of the radon that is released to the void space in the material is designated the Emanating Fraction. This fraction is then available for transport to the interface between the material and the air. The rate at which radon crosses this interface is known as the radon exhalation rate or radon flux and is expressed in units of picocuries per square meter per second (pCi/m^2-s).

The resulting airborne radon concentration, which depends upon the exhalation rate and the degree of atmospheric dispersion, is expressed in picocuries per liter (pCi/l). The radioactive decay of the airborne radon, in turn, results in the formation of the series of radon decay products. A common unit for expressing the airborne concentrations of radon decay products is the "working level" (WL). This unit was devised to provide a means for expressing the aggregate concentration of the various airborne radon decay products in terms of the ultimate energy given up by the emitted alpha particles.

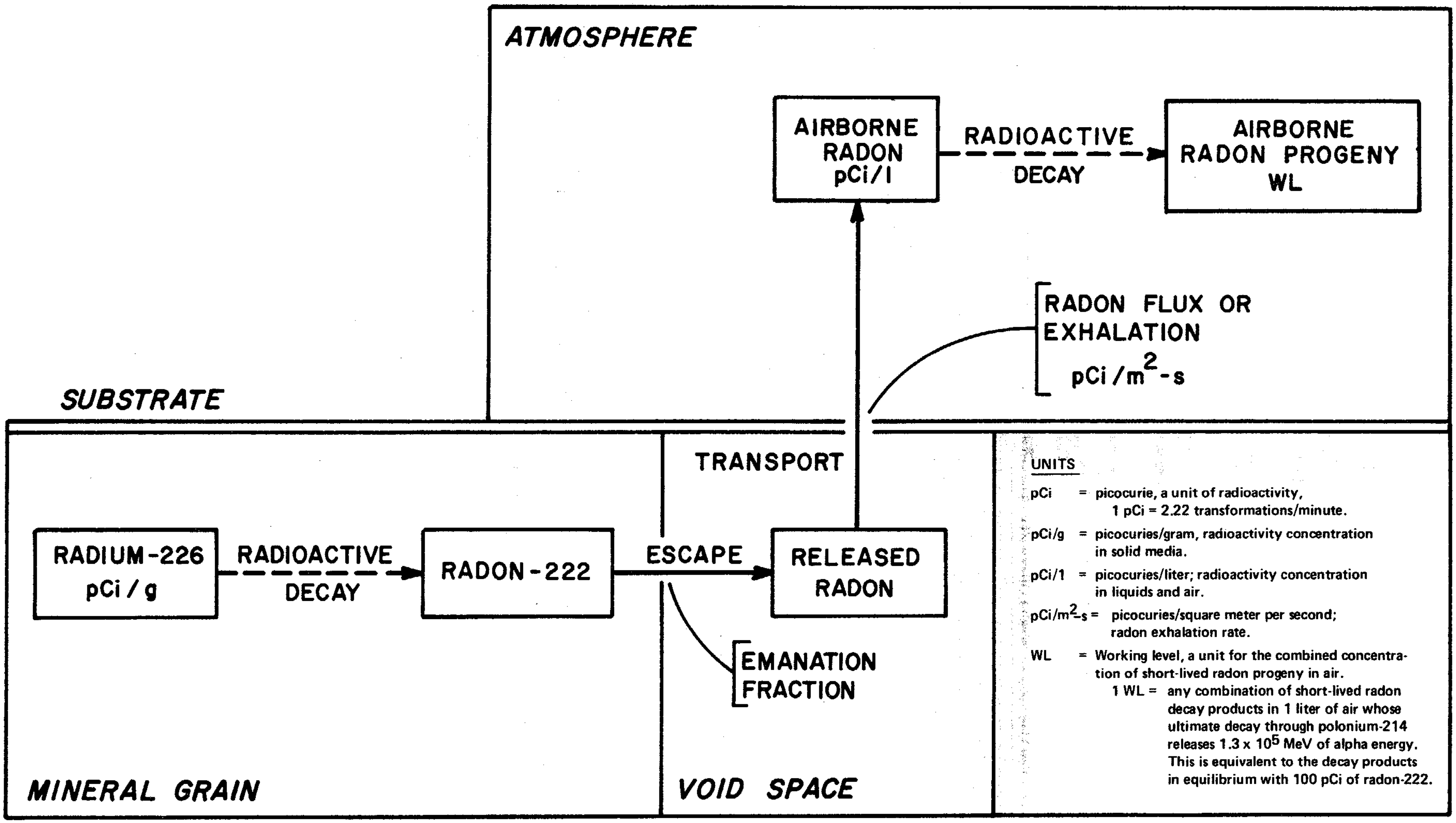
Radioactivity in Phosphate-related Materials

Concentrations of radium-226 in phosphate matrix and beneficiated rock are presented in Table 2 and compared to natural soil. Since approximate radioactive equilibrium is maintained through the beneficiation process, other members of the uranium series would be expected to be present in concentrations comparable to the radium-226 concentrations. The concentrations in matrix and phosphate rock are about 50 times the concentration found in natural top soil but, on the other hand, are one to two orders of magnitude lower than in medium and high grade uranium ores.

In chemical operations such as wet process phosphoric acid production, the various members of the uranium series may follow separate pathways as determined by their chemical properties. As indicated in Figure 3, most of the radium-226 and polonium-210 and a trace of the uranium appear in the phosphogypsum. Typical concentrations of these radionuclides are shown in Table 3.

Radiation and Radionuclide Pathways to Humans

The first step in assessing the potential impact of the phosphogypsum radioactivity is to identify the potential pathways to the environment and to humans. As indicated in Figure 4, candidate pathways away from the gypsum source include direct irradiation by the gamma rays, radon emission, fugitive dust emissions, leaching, and intentional transfer of the gypsum for some further use. Potential modes of exposure to the human include direct irradiation from the stored or relocated gypsum, inhalation of the decay products of radon emitted from the stored and relocated gypsum, inhalation of gypsum dust and ingestion of food or water contaminated through leaching, dust emission or by-product gypsum use. Available information for the various pathways is reviewed in sections that follow.



UNITS

pCi = picocurie, a unit of radioactivity, 1 pCi = 2.22 transformations/minute.

pCi/g = picocuries/gram, radioactivity concentration in solid media.

pCi/1 = picocuries/liter; radioactivity concentration in liquids and air.

pCi/m^2-s = picocuries/square meter per second; radon exhalation rate.

WL = Working level, a unit for the combined concentration of short-lived radon progeny in air.
1 WL = any combination of short-lived radon decay products in 1 liter of air whose ultimate decay through polonium-214 releases 1.3×10^5 MeV of alpha energy. This is equivalent to the decay products in equilibrium with 100 pCi of radon-222.

FIGURE 2. SIMPLIFIED DIAGRAM OF RADON PRODUCTION AND EMANATION AND RADON PROGENY PRODUCTION

Table 2. Radium-226 in Phosphate Matrix and Rock

	^{226}Ra, Avg(range), pCi/g	
	Central Florida	North Florida
Matrix	38(18-34)	9(5-13)
Pebble	57(44-97)	26
Concentrate	37(26-51)	18(16-21)

Notes:

- For comparison, surface soil contains on the order of 0.5 to 1 pCi/g.
- The uranium series will be approximately in radioactive equilibrium in these materials.
- Data from Roessler, et al. (1979b).

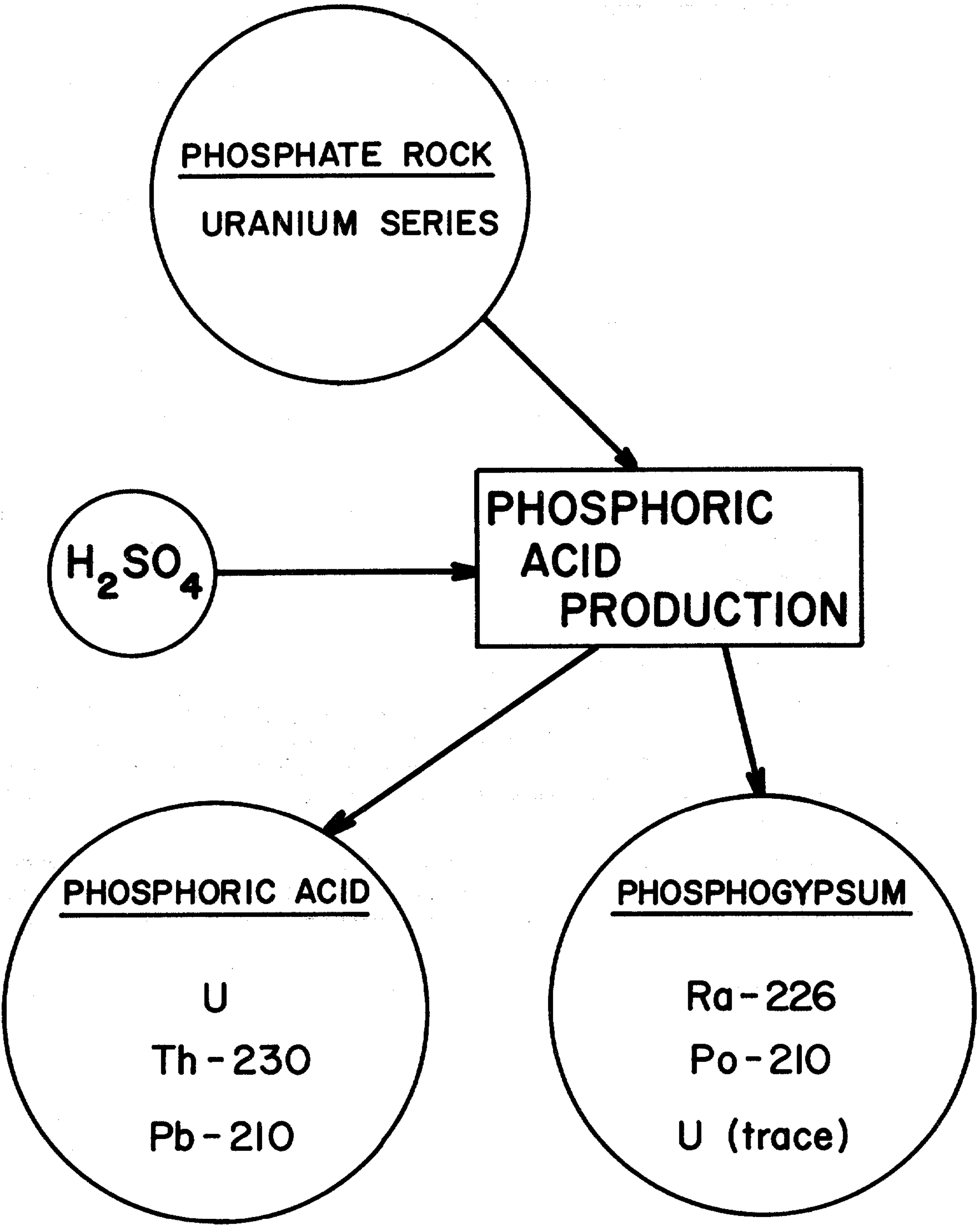


FIGURE 3. PARTITIONING OF RADIOACTIVITY IN WET PROCESS PHOSPHORIC ACID PRODUCTION

Table 3. Typical Radionuclide Concentrations in Phosphogypsum (from Central Florida Rock)

Radionuclide	Concentration[a)] pCi/g	Notes
Uranium-238, 234	4	b), c)
Radium-226	26	b), c), d)
Lead-210	Initially Low	e)
Polonium-210	40	f)

Notes:

a) Concentrations for gypsum originating from North Florida rock are approximately 50% of those in gypsum from Central Florida.

b) From Guimond and Windham (1975).

c) From May and Sweeney (1982).

d) From Roessler, et al. (1979b).

e) Lead-210 concentrations will be low in fresh gypsum but concentrations will increase as lead-210 is produced by decay of radium-226. The ingrowth process is governed by a 22-year half-life - i.e. lead-210 concentration/radium-226 concentration will be about 0.5 in 22 years, 0.75 in 44 years, etc.

f) Polonium-210 concentrations estimated on the basis of the report by Hurst (1982) that from phosphate rock with radium-226 and polonium-210 in equilibrium, 60% of the radium-226 and 99% of the polonium-210 appeared in the gypsum.

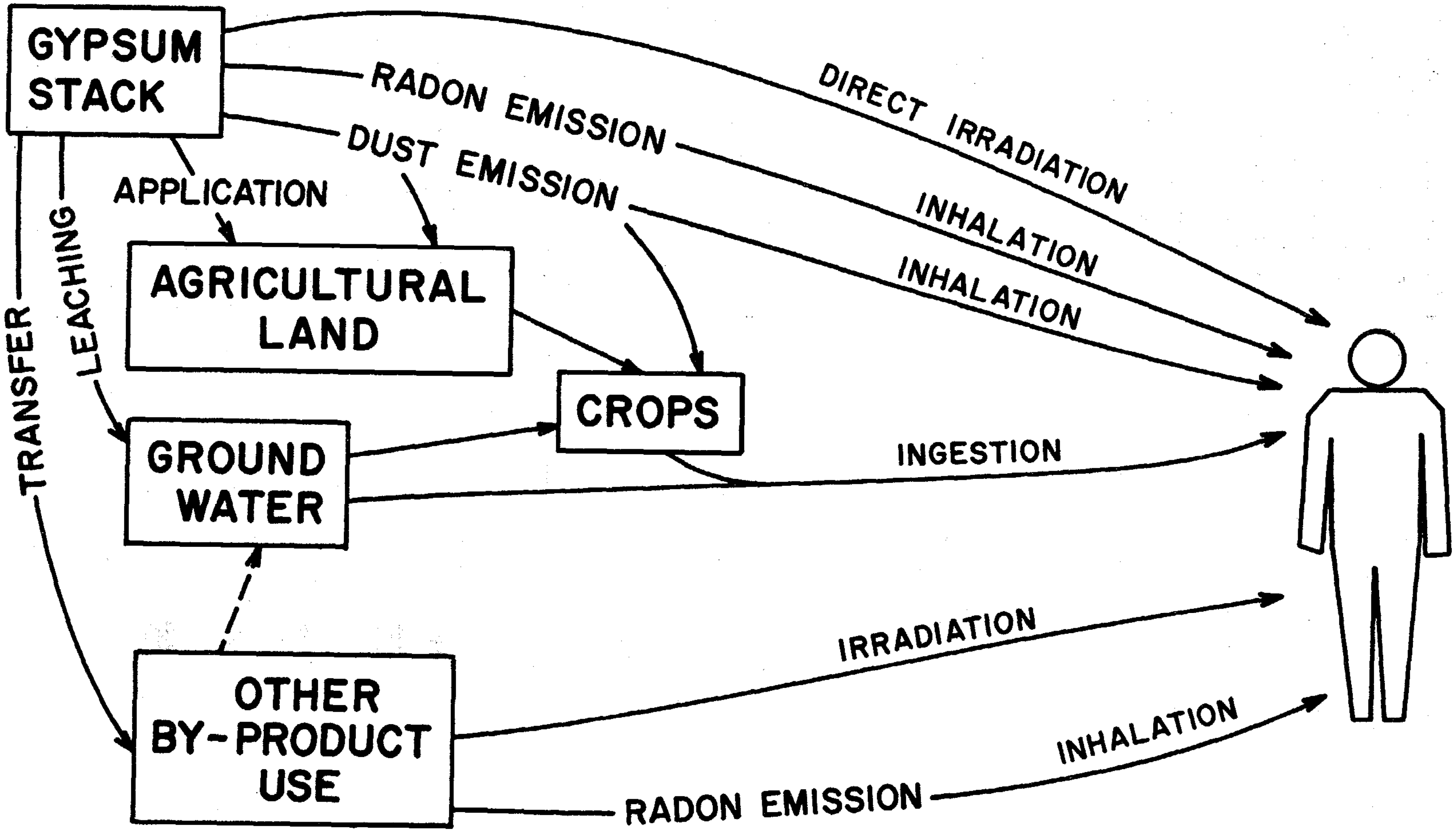


FIGURE 4. POTENTIAL RADIOACTIVITY PATHWAYS TO HUMANS

Direct Gamma Radiation

Table 4 presents data for direct gamma irradiation. The exposure rate directly over a large mass of phosphogypsum, such as a waste gypsum disposal stack, is about 30 microroentgens/hour (µR/hr). An individual working on the top of such a gypsum stack 2000 hrs/yr (40 hours/week, 50 weeks/year) would receive an annual radiation dose of 60 mrem. This is well below the occupational exposure limit of 5000 mrem/yr and also below limits for members of the general public. Exposures to individuals working with smaller amounts, such as in the laboratory, would be considerably lower.

Fulltime occupancy over large masses of phosphogypsum would be contraindicated; however, the radiation intensity drops off very rapidly with distance and levels attributable to the gypsum would be nondetectable within 600 meters (2000 ft).

Leaching

There is little reported in the literature about studies of radionuclide leaching from phosphogypsum. However, May and Sweeney (1983) of the U.S. Bureau of Mines conclude "radium is not leached from gypsum stockpiles".

Radon Emissions

Reported emanating fractions for phosphogypsum and exhalation rates, airborne radon concentrations and indoor radon progeny concentrations attributable to phosphogypsum are summarized in Table 5. As indicated earlier, not all the radon produced in a radium-containing mineral reaches the atmosphere. The process involves two steps - 1) escape from the mineral grain, described by the emanating fraction (E), and 2) -transport to the interface, during which radioactive decay can take place. The table summarizes emanating fraction data reported by Roessler, et al. (1979a). A rule of thumb sometimes employed is that the emanating fraction for these materials is usually less than 0.2.

The literature contains one report of a study of radon emissions from gypsum stacks. Environmental Protection Agency investigators (Horton, 1979; Windham and Horton, 1981) studied radon emanation from two Central Florida gypsum stacks with an average radium-226 concentration of 26 pCi/g. Using the charcoal cannister accumulator method, they studied old and new sections on each stack, deploying 5 cannisters per section for collection periods ranging from 3 to 4 days. They repeated this for two measurement periods on one stack and three measurement periods on the other. Individual measurements ranged from 1.8 to 135 pCi/m^2-s; the average value for fifty measurements between mid-July and early September, 1978, was 26.7 pCi/m^2-s.

These results suggest that individual measurements may be highly variable and that considerable replication may be necessary to obtain good estimates of the average radon exhalation. The results also suggest the following rule of thumb:

$$\text{Avg. radon exhalation (pCi/m}^2\text{-s)} \approx \text{Radium-226 conc. (pCi/g)}$$

Table 4. Direct Gamma Radiation from Phosphogypsum

	Exposure Rate µR/hr a)	Annual Dose mrem/yr b)
- Typical level directly over gypsum stack (including background)	30	60 (2000 hrs/yr) 260 (8766 hrs/yr)
- Vicinity of small quantities	much less	much less
- 600m (2000 ft) from gypsum stack	Not distinguishable from background	
- Typical Florida background	5-10	10-20 (2000 hrs/yr) 44-88 (8766 hrs/yr)
- Occupational standard	--	5000 c)
- Standard for non-restricted areas; individuals of the general public	--	500 c)
- NCRP recommendation for continuous exposures d)	--	100 c)
- Proposed Florida standard, structures over reclaimed phosphate land (Total including background)	20 e)	--

Notes:

a) µR = microroentgen, a unit of exposure. Exposure is a measure of gamma radiation intensity.

b) mrem = millirem, a unit of dose equivalent, the biologically effecitve dose to humans. One roentgen exposure results in a dose equivalent of approximately 1 rem; 1000 µR result in approximately 1 mrem.

c) These standards are for radiation other than medical and natural background.

d) From National Council on Radiation Protection and Measurements (NCRP, 1984).

e) From Florida Dept. of Health and Rehabilitative Services (FDHRS, 1984).

Table 5. Radon Emanation from Phosphogypsum

EMANATING FRACTION:

Material	$\bar{E}$	Relative Std. Deviation
Phosphogypsum	0.12	~30%
Florida soils	0.16	50-60%

From Roessler, et al. (1979a)

RADON FROM PHOSPHOGYPSUM STACKS:

- Measured average exhalation rate	26.6 pCi/m^2-s
Range of 50 measurements	1.8-135 pCi/m^2-s

- Modeled contributions to airborne concentrations 800 m from center of stack in predominant wind direction:

Radon	0.2 pCi/l
Indoor Radon Progeny	0.001 WL

From Horton (1979) and Windham and Horton (1981). Measurements by the charcoal cannister method on 2 stacks; old and new sections on each stack, 2 or 3 measurement periods each, 5 cannisters/section each period, 3 to 4 day collection period.

COMPARISON DATA, INDOOR AIRBORNE RADON PROGENY:

- Typical concentrations in structures over lands without enhanced or elevated radium	0.004 WL	a)
- Recommended level for remedial action, total airborne concentration	0.04 WL	b)
- Proposed Florida standard for new construction on reclaimed phosphate lands	0.02 WL	c)

a) From Johnson and Bailey (1983).

b) Derived from annual cumulative limit in NCRP Report #77 (NCRP, 1984).

c) From FDHRS (1984).

Using the measured radon exhalation rate and meteorological data for Orlando, Florida, these investigators estimated that the airborne radon concentration 800 maters in the predominant wind direction from the center of either pile would be 0.2 pCi/l. They also estimated an indoor radon progeny concentration of 0.001 WL. This value represents an addition of about 25% to the 0.004 WL concentration often quoted as typical for Florida houses that do not have elevated radon levels; the resulting total of 0.005 WL would be 25% of the proposed standard of 0.02 WL.

Uptake from the Soil

Another potential radionuclide pathway to man is through uptake by food or forage plants from soil containing phosphogypsum deposited by fugitive dust or intentionally applied as calcium-containing soil amendment. In evaluating the radiological impact of the direct application of phosphogypsum to agricultural land, Lindeken and Coles (1978) alluded to the low solubility of radium sulfate and stated that because of the excess calcium in the gypsum, the direct application to the soil can be expected to block the plant uptake of radium. For a scenario of 10 applications of 0.66 kg/m^2, tilled to a 15-cm depth, they calculated a soil radium addition of 0.45 pCi/g and predicted a concentration in vegetation of 0.25 pCi/g. They projected that a 50-yr vegetable consumption of 400 g/day would result in a cumulative dose of 160 mrem to the bone and concluded that "there is little basis for concern regarding a radiological hazard from uptake of radium-226 by plants". There should be even less concern about the much smaller contribution by fugitive dust from phosphogypsum storage.

Concentrations of radium-226 and lead-210 in the soil from either intentional or incidental application of phosphogypsum as described above would be much less than the values of 40 pCi/g and 20 pCi/g, respectively, suggested by the NCRP (1984) as guides for agricultural land use.

Other By-product Uses

Other uses of phosphogypsum include use as a road bed material and in the manufacture of construction materials such as cements, blocks, panels and wallboards. There does not appear to be any literature evaluating the radiological aspects of the use of phosphogypsum for road construction. The effects of radioactivity in building materials will be covered by other papers at this seminar.

AIRBORNE RADON EMISSIONS FROM PHOSPHOGYPSUM STACKS - STUDIES IN PROGRESS

Studies of radon emission from phosphogypsum storage are currently being conducted for the Gardinier, Inc. Fast Tampa Phosphate Chemical Plant. Emissions from a proposed new gypsum disposal field have been modeled and measurements are being made for the existing gypsum stack.

Radium-226

Nine phosphogypsum samples were collected from the existing stack during the period 1973-1984, and radium-226 was determined in dried samples by high resolution gamma-ray spectrometry according to the method of Bolch, et al. (1977). The radium-226 concentrations in these nine samples were found to be:

Average:	24.3 pCi/g,
Range:	21-28 pCi/g.

Radon Flux

Radon flux measurements have been in progress at the existing gypsum stack since December, 1983. The method employed is the charcoal cartridge method of Johnson[a], a modification of the charcoal cannister method published by Countess (1976). In this method, charcoal cartridges are deployed in capped standpipes for 48 hours where they collect the emanated radon and the accumulated radon is analyzed by counting the gamma-ray emissions from the radon progeny.

Sample collectors were deployed at seven sites on the stack for each of 5 sampling periods during the interval December, 1983 through February 1984. These results are summarized in Table 6. There is a large amount of variation between sites for any sampling period, considerable variation between site means over continued sampling, and a much smaller variation between the sampling period means. This emphasizes the need for replication in space (i.e., multiple sampling sites) to represent the average over the emanating surface. This also indicates the need for some replication in time; however the cumulative average has stabilized at about 23 pCi/m^2-s after four sampling periods during the first two months[b].

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[a] J. Johnson, Western Radiation Consultants, Ft. Collins, CO.

[b] Note added after the Seminar: With continued sampling, the pattern of variability described above persists but the cumulative average has remained relatively stable. After ten months, the average for 100 samples is 23 pCi/m^2-s with individual samples ranging from 2 to 94 pCi/m^2-s. This represents 12 sampling periods for which sampling period means ranged from 16 to 37 pCi/m^2-s.

Table 6. Radon Flux, Existing Phosphogypsum Stack
December 1983 - February 1984

	Radon Flux pCi/m^2-s
Average	23.0 ± 2.9*
Ranges:	
5 Sampling Period Means	15.6 - 31.1
7 Site Means	4.5 - 49.2
32 Samples	1.7 - 63.7

* ± one standard error of the mean.

The program was modified slightly in March, 1984 to monthly sampling with ten collectors; this program is continuing.

Airborne Radon

Annual average airborne radon concentrations were estimated for the vicinity of the proposed new gypsum disposal field. The proposed field is roughly rectangular in shape, approximately 730 m (2400 ft) East-West by 1050 m (3400 ft) North-South. The calculations were made using Tampa airport meteorological data and a mathematical model presented by Schaiger (1974) for dispersion near an extended plane radon-emanating source.

The modeled locations, described by distance and direction in Table 7, were selected as representative of the nearest occupied off-site locations; occupancy is excluded to much larger distances in the other directions.

As indicated in Table 7, the predicted additions to background as contributed by the pile were in the range of 0.03 to 0.1 pCi/l. If the background is this vicinity is taken to be about 0.2 pCi/l (with a factor of 2 uncertainty), the predicted average total radon concentrations for these locations would be on the order of 0.2 to 0.3 pCi/l with the gypsum stack resulting in a 10% to 50% addition to background.

The maximum predictions are of the same order of magnitude as the 0.2 pCi/l estimated by Horton (1979) for a location in the prominent wind direction 800 m from the center of a Polk County gypsum pile.

A limited airborne radon measurement program was conducted in the vicinity of the existing gypsum stack during the period January 16-26, 1984. Samples were collected at ten sites; these included one on top of the stack, and nine at various distances to the N, NE, and E of the stack. These directions were chosen because they correspond to the directions of the interest around the site of the proposed new stack; furthermore, to the west the stack is bounded by Tampa Bay and to the south results might have been unduly influenced by the presence of the chemical plant and phosphate rock storage. The nine off-stack locations included those that were 1) close-in, 2) further removed but at distances comparable to those used for modeling near the proposed new site and 3) well removed from the stack and hopefully representative of background.

Composite samples were collected by pumping air periodically into an air-sampling bag over a 24-hour period (a 48-hour period in one case). Portions of the composite samples were transferred to scintillation cells and analyzed for radon.*

As expected from theory and the literature, there was considerable day-to-day variation. Average concentrations for the ten-day period are presented in Table 8 and Figure 5. The highest levels, in the range of 0.3 to 0.4 pCi/l,

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* Sampling and Analysis by Eberline Health Physics Services, Albequerque, NM.

Table 7. Predicted Annual Average Radon-222 and Indoor Radon Progeny Concentrations in the Vicinity of the Proposed Gypsum Disposal Field

Location Code	Location From Edge of Stack		Concentration[a)]	
	Distance	Direction	Ambient Radon-222 pCi/l	Indoor Radon Progeny mWL[b)]
N-6	215m (700 ft)	NW	0.120	0.85
N-2	274m (400 ft)	W	0.078	0.55
N-12	490m (1600 ft)	E	0.075	0.52
N-14	550m (1800 ft)	NE	0.027	0.19
N-9	670m (2200 ft)	SE	0.036	0.25

Notes:

a) Contributions from gypsum source; background and contributions from any other source not included. Reported values are for completed pile 60m (200 ft) high, sloped sides, no standing water, negligible radon attentuation by stabilization cover.

During active use of disposal field, radon flux and contributions to airborne radon are estimated to be about 75% of completed pile values.

b) Indoor radon progeny concentrations based on radon progeny/radon equilibrium fraction of 0.7. Values may range from 0.3 to 0.7.

mWL = milli-Working Level 1 mWL = 0.001 WL

Table 8. Measured Airborne Radon Concentrations in the Vicinity of the Existing Gypsum Stack - Jaunary 16-26, 1984

Location Code	Location from Edge of Stack		Concentration, pCi/1*	
	Distance	Direction	Total (Measured)	Addition to Background (Calculated)
E-1	over stack	--	0.31	0.18
E-2	100m (400 ft)	N	0.26	0.13
E-4	100m (400 ft)	NE	0.41	0.28
E-7	300m (1000 ft)	E	0.17	0.04
E-5	600m (2000 ft)	NE	0.18	0.05
E-8	650m (2100 ft)	E	0.16	0.03
E-3	1050m (3400 ft)	N	0.14	0.01
E-6	2.9 km(9500 ft)	NE	0.14	0.01
E-9	6.5 km(4 miles)	N	0.12	0.01
E-10	10.5 km(6.5 miles)	E	0.14	0.01
Estimated Background			0.13	--

*Averages of 8 or 9 samples per station; collected as one 48-hr and eight 24-hr composite samples.

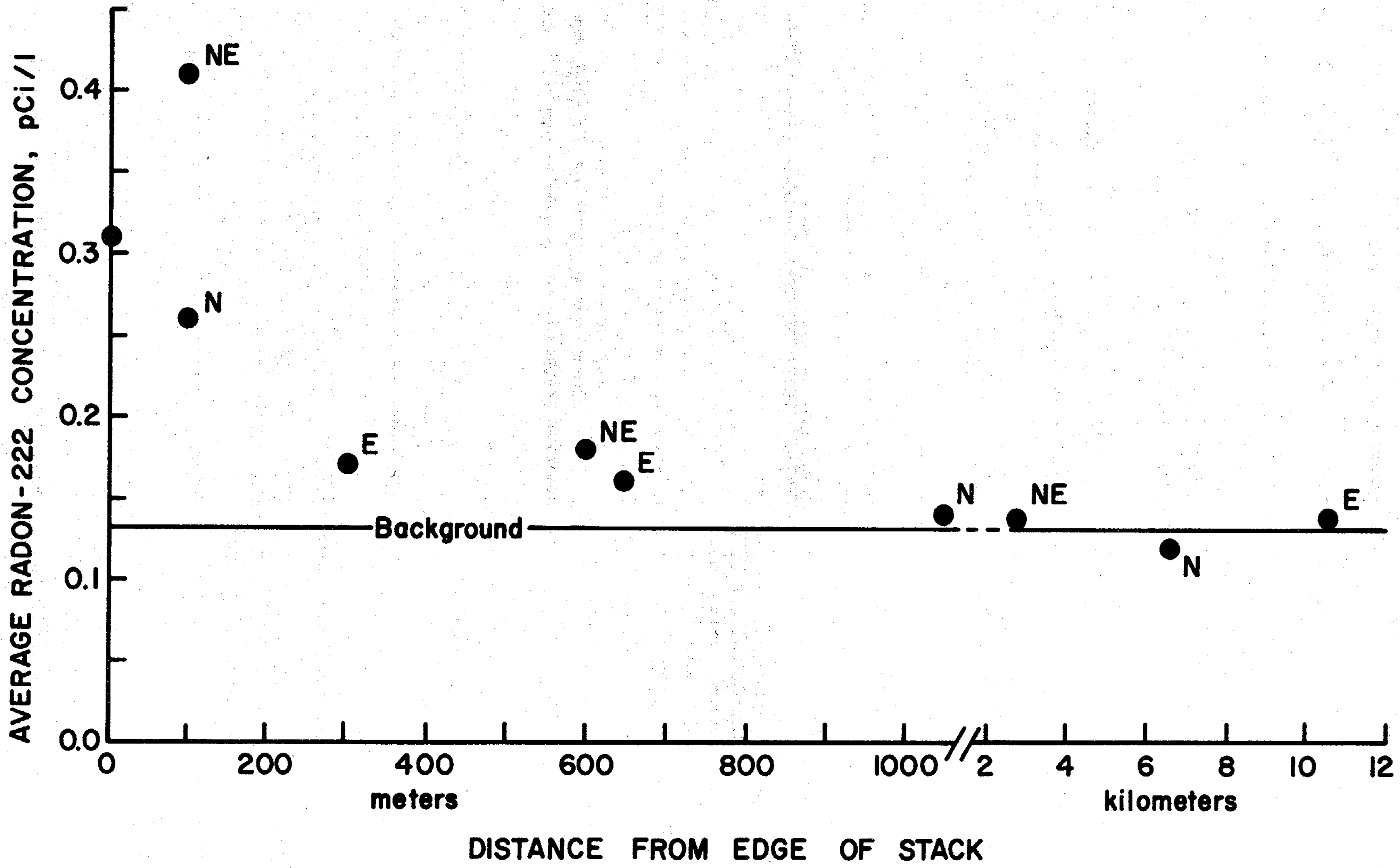

FIGURE 5. MEASURED AIRBORNE RADON CONCENTRATIONS
JANUARY 16-26, 1984

were observed on the top of and near the stack. There was a systematic decrease with distance and levels were not discernable from background (less than 0.01 pCi/l above background) at about 1050 m (3400 ft). The average background was estimated to be about 0.13 pCi/l during this time period.

The measured (existing stack), and predicted (new stack) additions to background are compared as a function of distance, irrespective of direction, in Figure 6. The results compare exceptionally well for environmental data generated by these two methods. However, it must be stressed that the good correlation may be only fortuitous; the air sampling experiment was conducted over a rather short time period and the meteorological data during that time period have not been examined to determine how representative they are of the long-term average. The final answer can be obtained only by additional sampling, preferably with some long-term integrating technique.

Indoor Airborne Radon Progeny

The significance of the radon is not in the ambient radon concentrations themselves but rather in the resulting indoor radon decay product concentrations and these were estimated for the test locations around the proposed new gypsum disposal site. It was assumed that the average annual radon concentrations attributable to the gypsum stack were approximately the same indoors as outdoors. In general, radon and radon progeny concentrations are higher indoors than outdoors. This is due to accumulation of radon emanated from the ground under closely-coupled structures and from indoor sources such as radium-bearing building materials and off-gasing from radon-bearing domestic water. However, for the case of radon transported through the atmosphere from a gypsum stack, there will be no "trapping" and build-up of concentration and the average radon concentrations attributable to the stack were taken to be the same indoors as outdoors. Indoor radon progeny concentrations were calculated in units of working level (WL) using an assumption of 70% equilibrium between radon and radon progeny concentrations (i.e., a radon concentration of 1 pCi/l is equivalent to 0.007 WL or 7 mWL). This is felt to be conservative on the high concentration side since reported indoor equilibrium factors generally range from 0.3 to 0.7.

Results are presented in the last column of Table 7. Predicted indoor radon progeny contributions from the gypsum source were in the range of 0.0002 to 0.0009 WL (0.2 to 0.9 mWL). These values are consistent with the average of 0.6 mWL and range of 0.2 to 1.3 mWL (including background) observed in four short-term measurements over Florida phosphogypsum piles (Roessler and Prince, 1978). The maximum predicted concentration is also comparable to the estimate by Horton (1979) that Central Florida gypsum piles would contribute on the order of 1 mWL to the indoor radon progeny concentrations in structures located in the prevalent wind direction 800 m from the center of the pile.

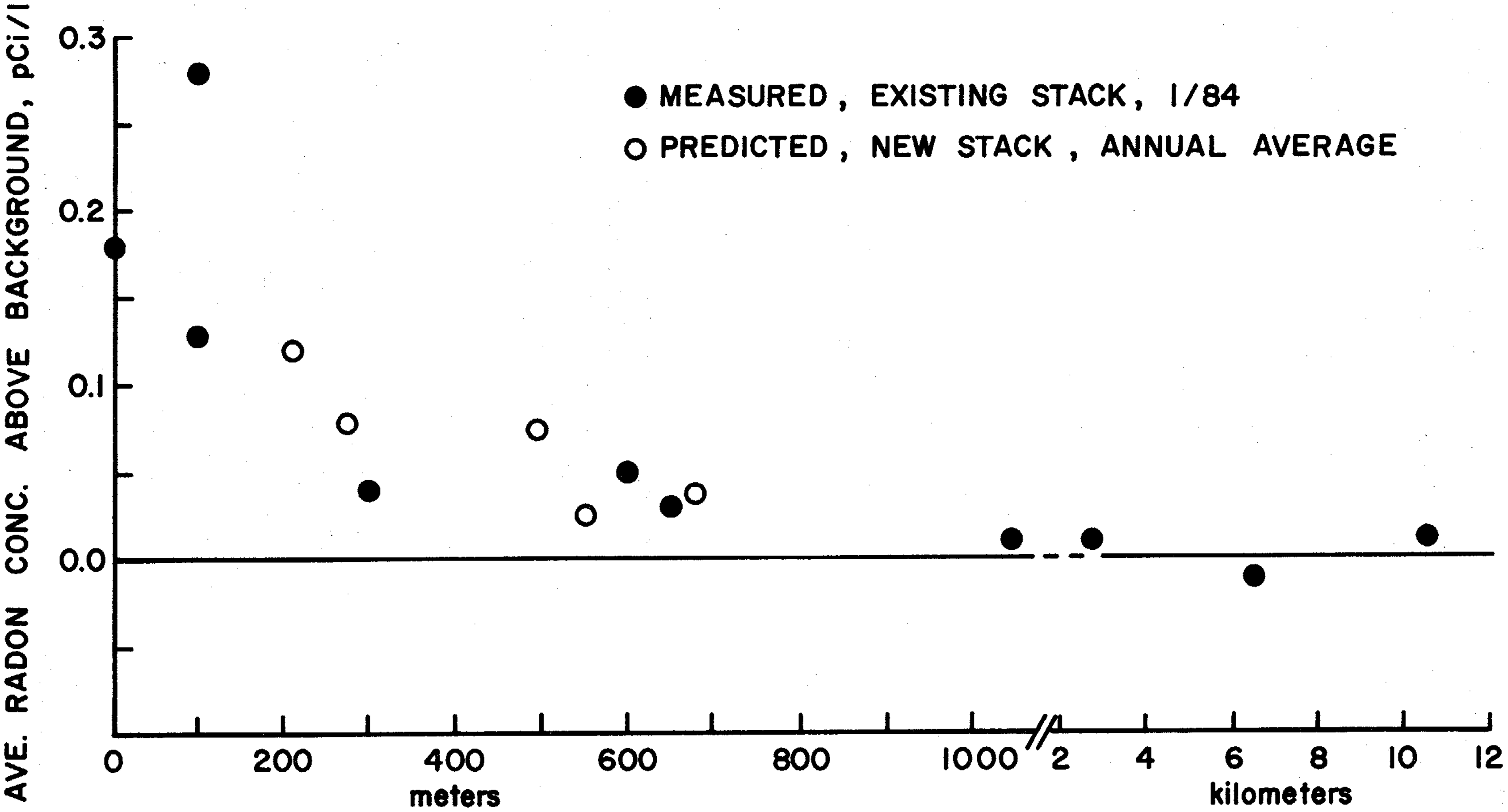

FIGURE 6. COMPARISON OF PREDICTED AND MEASURED AIRBORNE RADON CONCENTRATIONS

Average concentrations of 0.003 WL (Roessler, et al., 1983) to 0.004 WL (Johnson and Bailey, 1983) may be expected for Florida structures constructed over lands without elevated or enhanced soil radium. Thus the total concentration including both background and the gypsum stack contribution at the modeled sites would be on the order of 0.003 to 0.005 WL. By comparison, the National Council on Radiation Protection (NCRP, 1984) has suggested a remedial action value that translates to 0.04 WL total and the Florida Department of Health and Rehabilitative Services has proposed a standard for new construction on reclaimed phosphate mining lands of 0.02 WL total.

SUMMARY AND CONCLUSIONS

Several of the uranium-series radionuclides that occur naturally in phosphate rock appear in phosphogypsum. This a case of a low-level perturbation of the natural radioactivity; a situation that has come to be known as Technologically Enhanced Natural Radiation (TENR). A number of exposure routes have been examined; this radioactivity does not present an acute exposure hazard.

With regard to occupational exposure, phosphogypsum does not present an external radiation exposure problem, either at the disposal site, through handling, or in the laboratory; and ordinarily this material does not present an airborne radioactivity problem. Radon emanating from phosphogypsum would produce significant airborne radon progeny levels only if a large quantity was stored in an enclosed, unventilated space.

The question is one of whether there is undue exposure to the general public from gypsum disposal sites or from the relocation and use of the by-product gypsum. Some applications such as use for construction fill or leveling of gypsum stacks for construction without any gamma radiation or radon-attenuating barrier are to be avoided. On the other hand, the exposure drops off very rapidly with distance from a gypsum source and exposure by most routes appears to be negligible. However, siting of gypsum holding areas and proposed uses of by-product gypsum should be evaluated from a radiation exposure standpoint.

ACKNOWLEDGEMENTS

The on-going gypsum stack studies are being supported by Gardinier, Inc. The other work was a University of Florida effort, supported in part by the Florida Engineering and Industrial Experiment Station. Early phases of the University of Florida natural radioactivity studies were supported by contracts and equipment grants from the Florida Phosphate Council; various phosphate companies have provided information and samples over the years. The author acknowledges Professors W. E. Bolch and J. A. Wethington of the University of Florida for their collaboration in radium and radon analysis. Appreciation is also expressed for the assistance of numerous University of Florida undergraduate and graduate students with the natural radioactivity studies. The contribution of the Florida Institute of Phosphate Research in sponsoring this seminar and other symposia as means of bringing together investigators and information is gratefully appreciated.

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APPENDIX

THE URANIUM DECAY SERIES

By a decay series, we mean that a radioactive species (a radioactive nuclide or radionuclide) undergoes a transformation (undergoes "radioactive decay") to form a radioactive product which in turn forms another radioactive product, etc. until ultimately the process is terminated with the formation of a stable (non-radioactive) atom. One such decay series is the naturally-occurring uranium decay series which begins with the isotope uranium-238 (Figure 1 in text). This series has fifteen major members and thus undergoes fourteen decay steps to eventually produce nonradioactive lead-206. The series includes isotopes of nine different elements. Some of the radioactive members emit beta particles and others are alpha particle emitters: for some of the radionuclides, particle emission is accompanied by the emission of gamma radiation.

Various members of the series, singly or in groups, are significant for a variety of reasons. Properties that make a radionuclide significant from a human exposure standpoint include mobility in the biosphere, tendency to concentrate in human tissue and a long half-life or constant replenishment from a long half-lived precursor. In general, alpha emitters present a greater hazard when taken into the body than do beta emitters. Those radionuclides that emit gamma rays present the potential for irradiation from outside the body.

Uranium-238 and uranium-234 are isotopes of the same element and appear together in the atom ratio of 18,000:1. Both are alpha emitters, contribute equal amounts of radioactivity and persist with the half-life of the uranium-238 "parent", namely 9 billion years. Thorium-230, the fifth member of the series is also a long-lived alpha emitter.

Radium-226, the 5th member of the series, is an alpha emitter that has a chemical and biological behavior similar to calcium; its 1622 year half-life is sufficient for it to persist long after separation from the uranium precursor. One evidence of its biological importance is that it is one of several naturally-occurring radionuclides for which there is a specific drinking water standard. Radium-226 is also important because it is the continuous production source for its radon-222 decay product; thus radium-226 may be the source of constant emanation of gaseous radon to the atmosphere and will also be accompanied by gamma radiation from the decay products of the radon that is retained.

Radon-222, the seventh member of the series, has a half-life of only 3.8 days but it is constantly replenished if the parent radium-226 is present. Being a noble gas, the element radon is not very reactive; however, a portion is often released from the substrate where formed and transported to the interface with the atmosphere where it becomes airborne. Airborne radon by itself is not particularly significant biologically but it serves as a continuous production source for the short-lived decay products.

The term, short-lived radon decay products (or radon "daughters" or radon "progeny") is applied collectively to polonium-218, lead-214, bismuth-214, and polonium-214. They are sometimes identified by their historical names, radium A, radium B, radium C and radium c', respectively. This group consists of two alpha emitters and two beta emitters; several members emit gamma rays as well. When separated from their radon-222 precursor, their radioactive decay is governed by the 26.8 minute half-life of lead-214. When formed in the air from the decay of radon-222, the radon decay products will occur as either free ions or attached to dust particles. If inhaled, some of the airborne radon decay products deposit in the respiratory system where they irradiate bronchial and lung tissues. It has been demonstrated that high concentrations of airborne radon progeny are a cause of lung cancer in uranium miners; it is assumed that lower concentrations of airborne radon progeny present a lung cancer risk in proportion to the cumulative exposure.

The pair, lead-210 and polonium-210 are also potentially significant. Polonium-210 is an alpha emitter and hence a potential hazard inside the body. By itself it is not persistent since the 138 day half-life is relatively short. The beta-emitting lead-210 is less of a hazard in its own right. However, lead is mobile biologically, and lead-210 with its 22 year half-life serves as a persistent production source for polonium-210.

Uranium and its decay series are ubiquitous on the earth; concentrations vary with the type of mineral and are significantly elevated in some deposits and ores. Where uranium has remained undisturbed in nature the various members of the uranium series, at least through radium-226 would be expected to be approximately in radioactive equilibrium - that is all members in equal concentrations of radioactivity. The remaining members of the series would be expected to be in concentrations approaching equilibrium but reduced to whatever extent there is a net loss of the gaseous member, radon-222.

RADIOACTIVITY IN BUILDING MATERIALS

John P. Witherspoon
Health and Safety Research Division
Oak Ridge National Laboratory

Table 1: Average Activity in Soil - 200 U. S. Locations*

	pCi/g	Dose in Air(mrem/yr)
K-40	12	17
U-238	0.6	8
TH-232	1	22
		47
		(Range 15-140)

*Lowder, 1964

Table 2: Activity in Some German Building Materials*
(pCi/g)

Material	K-40	Ra-226	Th-232
Lime Bricks	0.7-8	0.2-0.6	0.2-0.5
Red Slime Bricks	8-13	2.5-6.7	3.9-10
Other Bricks and Clinkers	4-69	0.6-3.1	0.5-3.7
Pumic Bricks	13-30	0.7-3.6	1.1-4.6
Slag Sand and Slag Bricks	3-16	1.2-3.2	0.6-5.6
Cement	0.5-7	0.3-5.3	0.3-5.2
Natural Gypsum	0.7-5	0.7	0.5
By-Product Gypsum	0.8-6	7-28	0.5

*Kolb, 1978

Table 3: Construction Materials in the United Kingdom

Material	Mean Ra Content (pCi/g)
Gypsum (Waste Product)	17.0
Natural UK Gypsum	1.2
Granite Bricks	6.9
Clay Bricks	3.8
Flint Aggregate Bricks	0.3

Table 4: Activity in Polish Building Materials*

	Range of Concentration (pCi/g)	
Material	K-40	Ra-226
Fly Ash	10.4-48.0	1.7-16.5
Slag	6.1-60.2	0.5-12.4
By-Product Gypsum	0.3-3.2	0.7-19.9
Red Brick	19.1-25.5	0.5-0.6
Silicon Brick	3.5-7.5	0.2-0.4
Cement	5.1-82	0.2-0.7
Soil	0.8-7.6	0.1-0.5

*Pensko Et Al., 1978

Table 5: Radon Exhalation rates in Some Danish Building Materials*

Material	Exhalation Rate (Atoms per Kg-sec)
Lightweight Concrete Alum Shale, Old type	210
Lightweight Concrete Alum Shale, New type	71.8
Other Concretes	1.2-2.4
Gypsum Board	0.11
Fiberboard	0.11
Bricks	0.08

*Jonassen and McLaughlin, 1978

Table 6: Relative Radioligical Impact of Selected Construction Materials

Material	Avg. Ra-226 (pCi/g)	Utilization Potential
Phosphogypsum		
Florida	33	High
Morocco	25	High
Idaho	23	High
Khouribga	17	High
Concrete/Alum Shale		
Old Type 1947-75	35	Limited
New Type 1975	9	Limited
Red Mud Bricks	8	Limited
Volcanic Tuff	4-7	Limited
Fly Ash	3-5	High
Phosphorus Slags		
USSR	6	Limited
Florida	56	Limited
Granite	3	High

Table 7: Exposure Rates from Exterior Wall Construction Materials*

Material	Exposure Rate (mrem/y) Range	Average
Brick		
Low	46.4-56.1	50.8
Medium	82.3-140.1	105.1
High	148.9-192.7	175.2
Concrete		
Low	28.9-47.3	35.9
Medium	76.2-113.8	105.1
High		157.6
Concrete Block		
Medium	87.6-122.6	105.1
High	367.9-376.7	372.3

*Eichholz Et. Al., 1978

Table 8:

	Inside Exposure / Outside Exposure
Frame Houses	- 0.7
Brick Veneer	- 1.1
Masonry	- 1.3

Table 9:

Health Effects

150 per 10^6 person-rem or 150 per 10^9 person-mrem

$$\frac{150 \times 20 \text{ mrem} \times 10^6 \text{ persons}}{10^9 \text{ person-mrem}} = 3$$

Table 10: Recommendation for Building materials

USSR	$\frac{C_K}{130 \text{pCi/g}} + \frac{C_{Ra}}{10 \text{ pCi/g}} + \frac{C_{Th}}{7 \text{ pCi/g}} < 1$
Sweden	No Alum Shale in concrete
England	Avoid use of by-product gypsum if significantly over 25 pCi Ra/g

Table 11: Exposure Rate in 30,000 German Dwellings*
(mrem/Y)

	Indoors	Outdoors
Range	46.4-106.0	36.8-69.2
Average	68.3 + 5.7	52.6 + 3.1

*Kolb, 1978

MEASUREMENT METHODS OF RADON LEVELS IN A MODULAR BUILDING MADE FROM A PHOSPHOGYPSUM BASED MIXTURE

Martin Trefler and Riasp Medora
University of Miami Dept. of Radiological Sciences
Miami, Florida.

ABSTRACT:

Two methods of measuring the radon levels in a structure built from phosphogypsum are described in this paper. The two methods are (1) track etch detectors made by TERRADEX COPORATION of California (2) radon gas analyser made by RGA Instruments of Canada. The results obtained to date show the average radon concentration in the structure to be between 2-3 pCi/litre. This value of radon concentration when compared to the values measured in other buildings in the US is within the medium range.

INTRODUCTION:

Phosphogypsum is a waste product of the phosphate industry for which there has been no use until recently. The Phosphate Institute of the University of Miami is trying to use phosphogypsum as a construction material for which it is well suited, except for one major drawback. It is radioactive due to the presence of Radium-226 levels far above background. One of the construction uses of phosphogypsum is its use in the making of panels used in the construction of modular structures.
The ferrocement panels were made using 50% phosphogypsum, 25% cement, and 25% sand. The building made from these panels has dimensions of 14x7x8 feet. All its surfaces the three walls, floor and roof were made from phosphogypsum panels. The house is mounted on a trailer about 2.5 feet above ground level.

The diffusion of radon into the environment as such is not of major concern. It is radon diffusion into a closed place like the structure that creates a problem. Even though the amount of radon diffusing out of the walls may be small, its accumulation over a diffusing out of the walls may be small, its accumulation over a period of time is of concern. Measurements were made using the worst possible conditions as far as ventilation was concerned. This was done by sealing the structure and making it as airtight as possible. Integrated radon measurements were made with two different measuring devices. The first device used was a track etch detector. The second method was a radon gas analyser.

Experimental Techniques: The house in which the readings were taken, as indicated previously was mounted on a trailer about 2.5 feet above the ground with a clear air space between the house and the ground, thus reducing the effect of the radon emitted from the ground, has on the radon levels in the house to a negligible amount. The house had only three walls made from the ferrocement panels. The fourth side was closed using a thick sheet of clear PVC plastic. The plastic sheet was carefully inspected to make sure there were no holes in it. The plastic was attached to the structure so that it was as airtight as possible. The outside of the house was painted with a waterbase emulsion which would effectively act as a barrier for the radon, not allowing it to escape out. The inner walls of the house were left totally unpainted.

Wallpanels: The panels used to construct the house were made in a special way. Hence they need to be looked at in some detail. The panels were of a ferrocement sandwich type. The center of the wall consisted of a slab of polystyrene which was 2-4 inches thick. On both sides of the polystyrene was a facing of mortar (i.e. a mixture of 50% phosphogypsum, 25%cement and 25% sand) 3/8 inch thick, reinforced with agalvanised wire mesh. There were a few parts in the panel where the mortar was solid throughout. The joints connecting the panels again were solid mortar.

INSTRUMENTATION:

The primary method used for the measurement of the radon concentration in the environment of the house was track etch detectors. The detectors used here were the type SF marketed by the Terradex corporation of California. The detectors consisted of a small plastic disc enclosed in a plastic cup with a filter paper at its mouth to prevent radon daughters (non-gaseous) from entering the cup. The detectors were exposed for a period of 30 days and then sent back 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 then counted. Radon concentration is proportional to the track density. The detectors were read in such a way that a level of radon as low as 0.04 pCi/l could be detected fairly accurately. The detectors were placed at each end of the house to get an idea of the average radon concentration in all parts of the house. The house was kept closed for as a 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 the measurements in the house was the RGA 400 radon gas analyser. The RGA-400 radon gas analyser is a microprocessor controlled instrument which is 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 silicon 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 Si-barrier wafer detector is located at the centre of the precipitator and is galvanically connected to ground potential. The primary and the secondary detectors are fed through charge sensitive preamplifiers and main amplifiers to identical spectroscopy grade multichannel analysers. 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 can be measured in pCi/l and in working levels (WL). Secondly the concentration of Radon daughters RaA(Po214) and Rac'(Po214) can also be measured in WL. 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 analyser is placed about 3 feet above the floor level. The house is closed and after 3-4 hours needed for the buildup of radon and radon daughters the analyser is turned on. The sample interval used for the readings shown here is 120 minutes. This sample interval is the time over which the differential and the corresponding integral working levels are calculated. The analyser was kept in the house for a period of 8 days during which time the house was kept sealed. The maximum values obtained during this period are shown in table 2.

RESULTS

As shown in tables one and two, the levels of radon when measured in pCi/l were between 2 and 4 pCi/l depending upon the technique used. The average value obtained over a period of one month using the track etch technique gave a value between 2-3 pCi/l which is considered to be in the medium * radioactivity range. The readings obtained on the other hand using the radon gas analyser varied from 0.4-4.1 pCi/l, which gives an average value of 2.25 pCi/l. These values are measured every 2 hours as opposed to 30 days required for the track etch detector. Even with such frequent measurements the values still remain in the medium activity range.

*(Low is less than 0.5 pCi/l, Medium 0.5-4.0 pCi/l, High greater

TABLE 1.

Readings obtained with TRACK ETCH detector with an exposure period of 30 days

		PCI/L	STD DEV %
(1)	Left side of house	2.87	17.4
	Right side of house	2.24	20.2
(2)	Left side of house	2.61	28.3
	Right side of house	2.04	32.4

TABLE 2.

Readings obtained using the RGA-400 Radon gas analyser with a sample interval of 120 minutes, total counting time 8 days.

Maximum value of Rn concentration	4.1 PCI/L
Minimum value of Rn concentration	0.4 PCI/L
Average value over whole counting period	2.25 PCI/1
Rn integral working level for whole counting period	0.022 WL

than 4.0 pCi/l.)

DISCUSSION

The results presented here indicate that the values obtained in the Phosphogypsum house are in the medium activity range as per the EPA classification. The measurements were made with the inner walls unpainted and the outer walls sealed with paint. It should be noted that the ventilation in the house is not the same as would be existing in a structure used for any sort of business or residence; the air exchanges in such an application would be more -- frequently resulting in a lower radon buildup. Definitive conclusions cannot be drawn at this time since the database is limited but data collection is continuing.

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Engineering Properties of Phosphogypsum

Kuo-Ting Lin
Ph.D. Candidate, Dept. of Civil & Architectural Engineering,
University of Miami, Coral Gables, FL.

J. Ludwig Figueroa
Associate Professor, Dept. of Civil & Architectural Engineering,
University of Miami, Coral Gables, FL.

and

Wen F. Chang
Professor, Dept. of Civil & Architectural Engineering, and
Director Phosphate Research Institute,
University of Miami, Coral Gables, FL.

ABSTRACT

Compressive strength of phosphogypsum under both air dry and moist conditions, effect of moisture content on strength, effect of compaction energy on some engineering properties of phosphogypsum, and the influence of cyclic moisture changes on the strength of phosphogypsum are studied. Results of a tentative method of using tar to improve the water resistance of phosphogypsum are also presented.

1. INTRODUCTION

Phosphogypsum is a by-product of phosphorus fertilizer production. Its main constituent is calcium sulfate dihydrate. In Central Florida, over 400 million tons of phosphogypsum have been stockpiled, and the total tonnage may approach 1 billion tons by the year 2000 (1). This vast volume of phosphogypsum requires disposal, and current consideration has been directed towards the utilization of this waste material.

Research over the past two years has disclosed the suitability of using phosphogypsum as an engineering material, in particular when mixed with other waste and conventional construction materials. Potential application of these mixtures would include highway, building, embankment and fill construction. Somewhat encouraging results have also been found when only phosphogypsum is used, although its application is limited to partially saturated conditions. Moisture susceptibility of phosphogypsum is improved when it is mixed with suitable materials.

Continued research using phosphogypsum as the main aggregate demands the definition of its fundamental engineering properties. Unconfined compression, moisture-density and splitting tension tests were used to evaluate the influence of moisture content at the time of sample preparation, compaction energy, curing time, percentage of added tar and cyclic wetting and drying. Cylindrical specimens 2 inches in diameter and 4 inches in length (prepared under impact compaction) were used during the testing program. The number of blows per layer was adjusted in order to obtain Standard Proctor or Modified Proctor compaction conditions.

2. STRENGTH OF PHOSPHOGYPSUM

Observing the fact that piles of phosphogypsum (over 200 feet high) stand very well by themselves, it would be logical to assume that this material has appreciable shear strength.

The influence of moisture on the unconfined compressive strength of phosphogypsum was examined by allowing specimens to air dry under laboratory conditions (temperature=24°C and relative humidity of 60%) after compaction.

Fig. 1 represents the compressive strength of phosphogypsum varying with air drying time, of specimens prepared by both Standard and Modified Proctor compaction methods. Fairly dry specimens could be obtained in about 5 days under laboratory conditions. It is also seen that a large portion of phosphogypsum strength develops during this period, as shown in Fig. 1. No additional strength development occurs after 2 weeks of curing. It should also be noted that higher unconfined compressive strength resulted from specimens compacted by the Modified Proctor method than those compacted by the Standard Proctor method. Since the compaction energy of the Modified Proctor method is about 4.5 times that of the Standard Proctor method, this implies compactive effort has a marked effect on phosphogypsum strength.

3. EFFECT OF MOISTURE CONTENT ON STRENGTH

Although phosphogypsum possesses significant strength under air dry conditions, very small strength is observed when it contains excessive moisture.

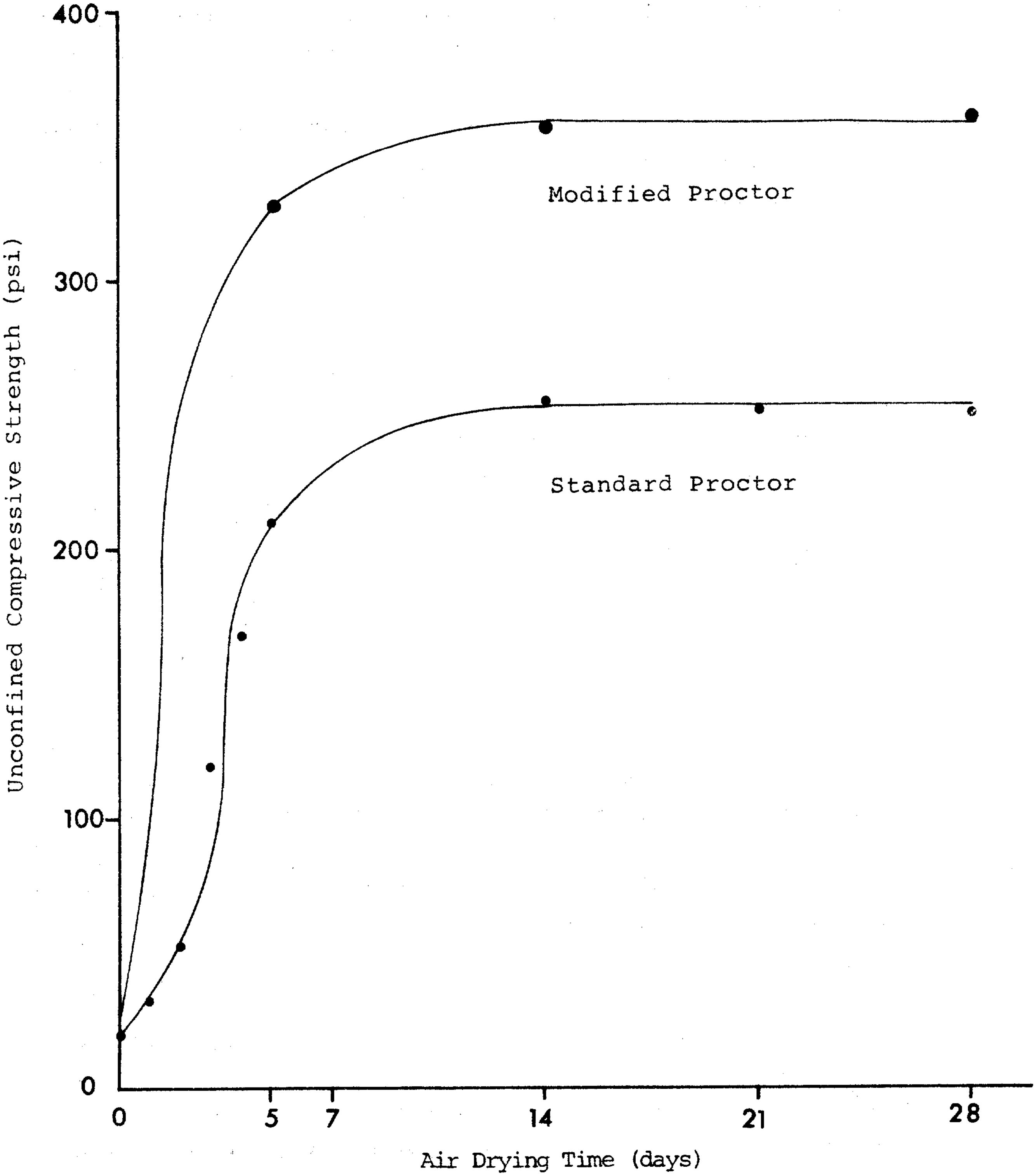

Figure 1. Relationship between strength of phosphogypsum and air drying time.

Moisture susceptibility of phosphogypsum is observed when specimens are tested after placing them in the moisture room for different periods to absorb varying amounts of moisture. Fig. 2 represents the relationship between unconfined compressive strength and moisture content of phosphogypsum. It can be seen that moisture content affects phosphogypsum strength to such extent that even a small increase in the amount of moisture produces a significant drop in strength.

4. EFFECTS OF COMPACTION ENERGY

As stated, phosphogypsum specimens compacted by the Modified Proctor method are stronger than those compacted by the Standard Proctor method. Because of calcium sulfate dihydrate's layered lattice and its monoclinic structure, phosphogypsum particles bind together and lose their original particle sizes and shapes during compaction (2). It is assumed here that this effect is more obvious as more compactive effort is applied. Herein, effects of compaction energy on the maximum dry density, optimum moisture content, and strength of phosphogypsum are presented.

4.1 Maximum Dry Density and Optimum Moisture Content

If the compaction energy is increased from that of the Standard Proctor method to 4 times that of the Modified Proctor method, both the maximum dry density and the optimum moisture content vary. Increased compaction energy increases the maximum dry density and decreases the optimum moisture content of phosphogypsum. This is illustrated in Fig. 3. It is also explicit that the initial energy increase has more effect than any subsequent increases.

4.2 Compressive and Tensile Strengths

Compaction energy has a positive effect on both compressive and tensile strengths of phosphogypsum. Fig. 4 shows the relationship between compressive and tensile strengths of phosphogypsum and compaction energy. Under air dry conditions, phosphogypsum specimens can develop compressive strengths from 250 psi to over 600 psi depending on how much energy is applied during compaction. Likewise, the tensile strength of

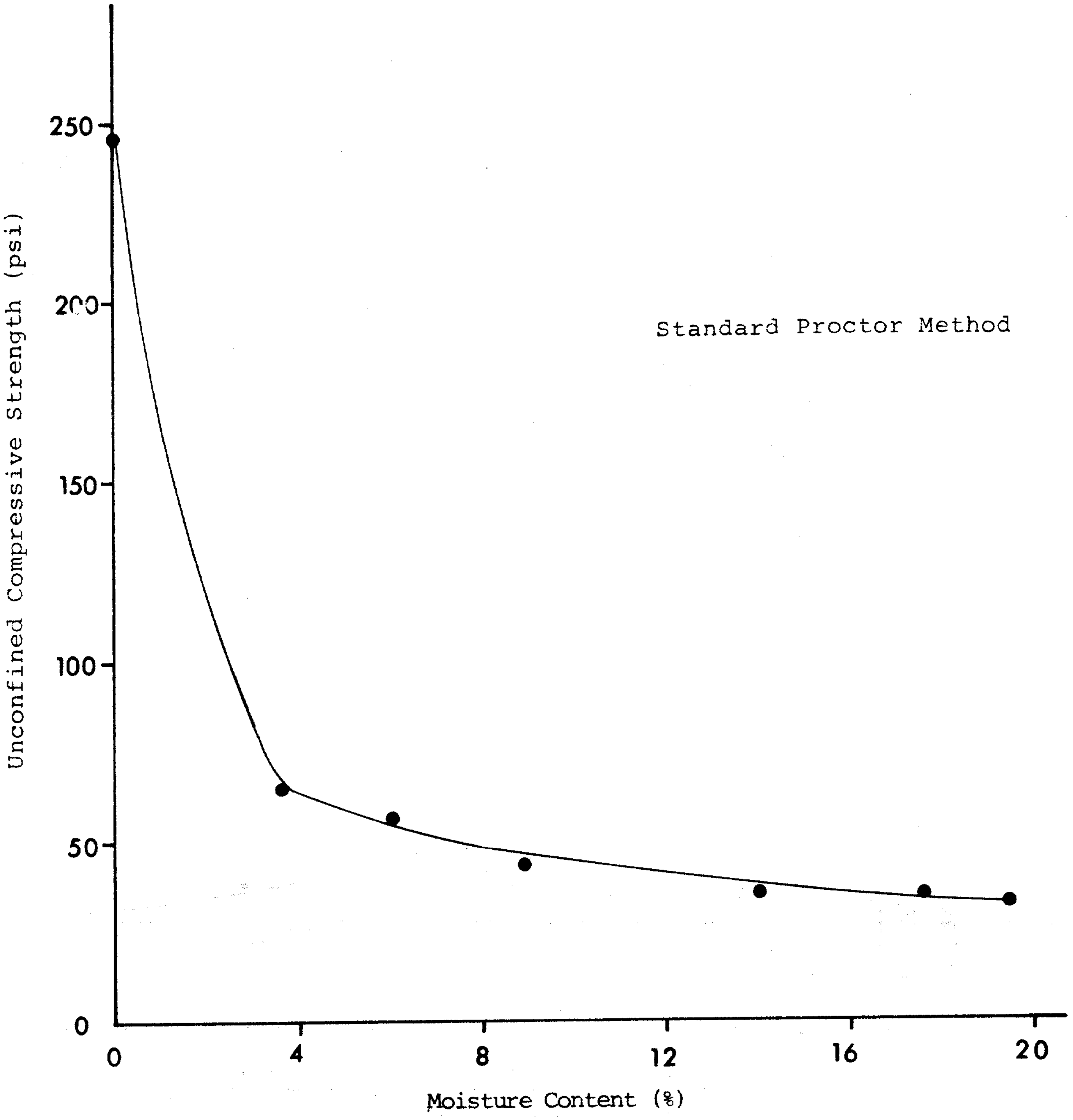

Figure 2. Relationship between strength of phosphogypsum and moisture content.

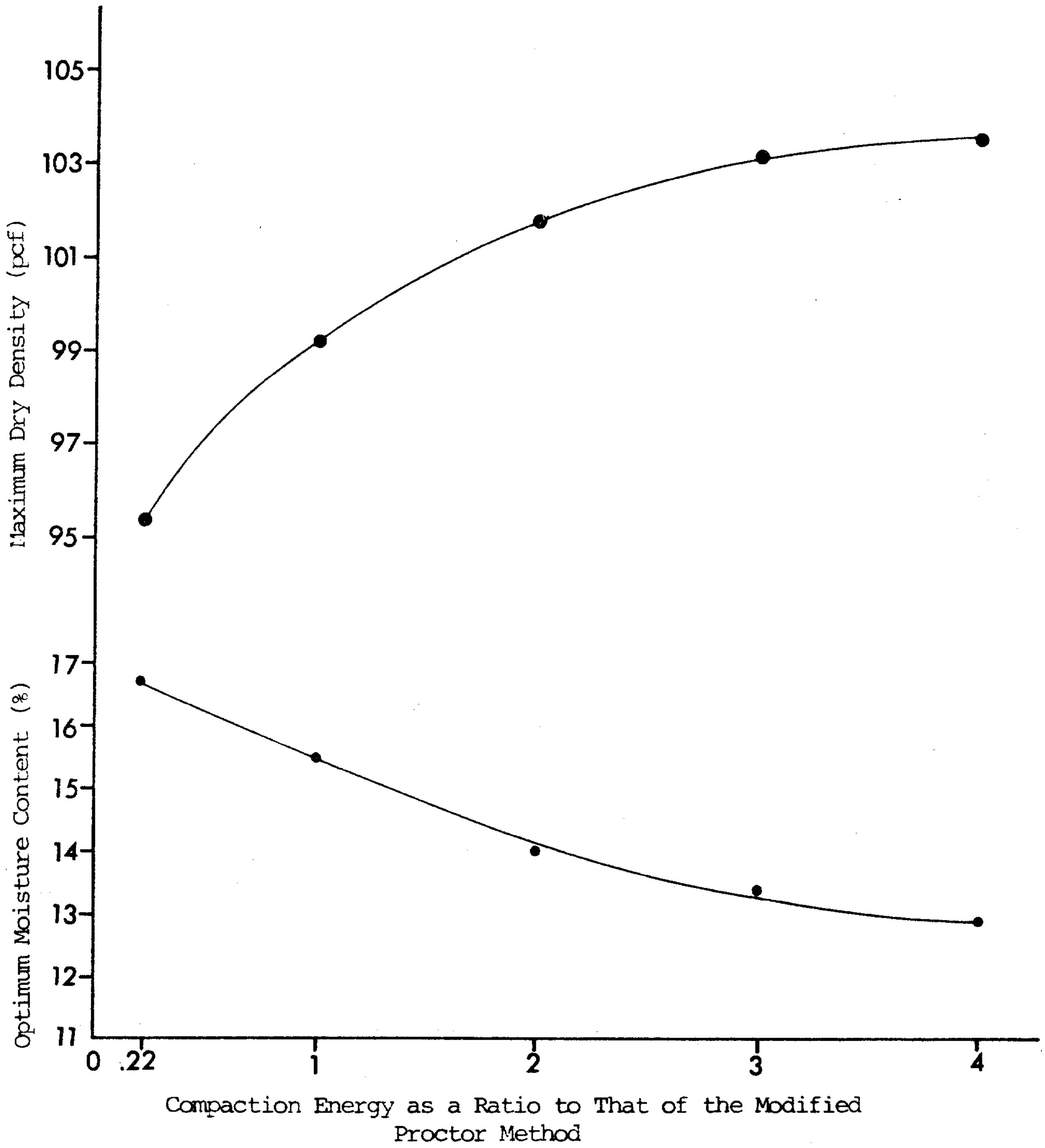

Figure 3. Effects of compaction energy on the maximum dry density and optimum moisture content.

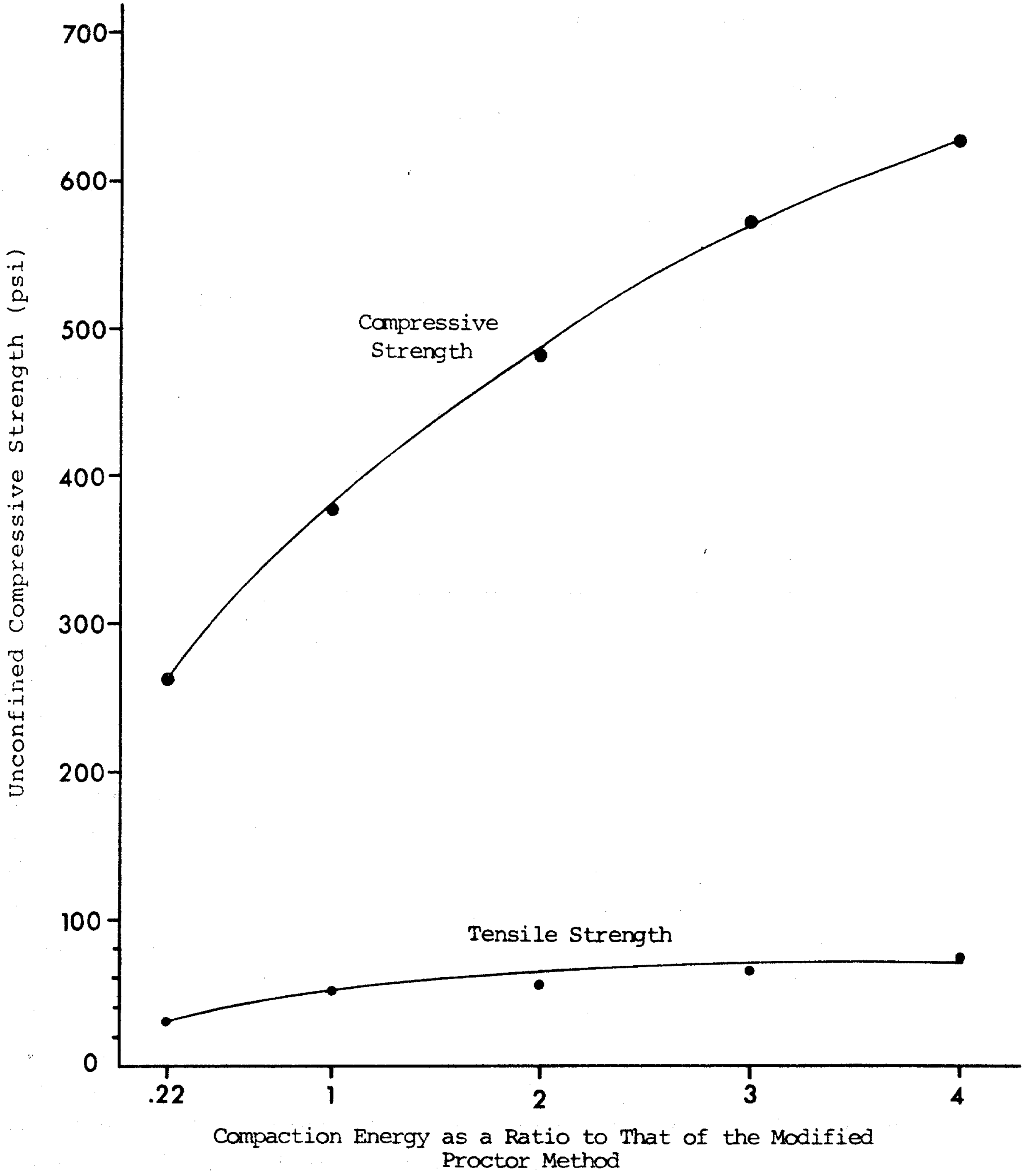

Figure 4. Effects of compaction energy on compressive and tensile strengths.

phosphogypsum increases, although slightly, with the application of higher compaction energy.

5. EFFECT OF CYCLIC MOISTURE CHANGES

It has been indicated that under air dry conditions phosphogypsum has a strength of several hundred pounds per square inch, while under moist conditions it has little strength. If phosphogypsum specimens compacted by the Standard Proctor method are placed in the humidity room for one week and then air dried for another week (constituting a wet and dry cycle), their resistance to cyclic moisture changes can be determined.

Fig. 5 illustrates how the compressive strength of phosphogypsum is affected by cyclic moisture changes. As it can be observed, the number of wet and dry cycle does not change the strength of phosphogypsum under both air dry and moist conditions, as long as moisture content is kept below saturation.

6. IMPROVEMENT OF WATER RESISTANCE OF PHOSPHOGYPSUM

Although compacted phosphogypsum specimens can withstand cyclic moisture changes, they disintegrate when soaked in water. Several methods could be used to improve the water resistance of phosphogypsum. In general, it requires mixing it with binding agents such as cement, fly ash plus lime, tar, and others. The results of mixing phosphogypsum with the first two binders are presented in other articles contained in these Proceedings (3,4). If phosphogypsum is mixed with a small amount of tar (3 to 5%) and compacted using the Standard Proctor method, its water resistance is largely improved. Although compressive strength under soaked conditions is lower than under air dry conditions, specimens do not disintegrate when completely submerged, as indicated in Fig. 6. It should be noticed that the amount of tar (from 3 to 5%) seems not to affect the strength of the mixture. Moreover, the addition of tar into phosphogypsum reduces the strength of phosphogypsum under air dry conditions, but provides phosphogypsum with the capability of being water resistant.

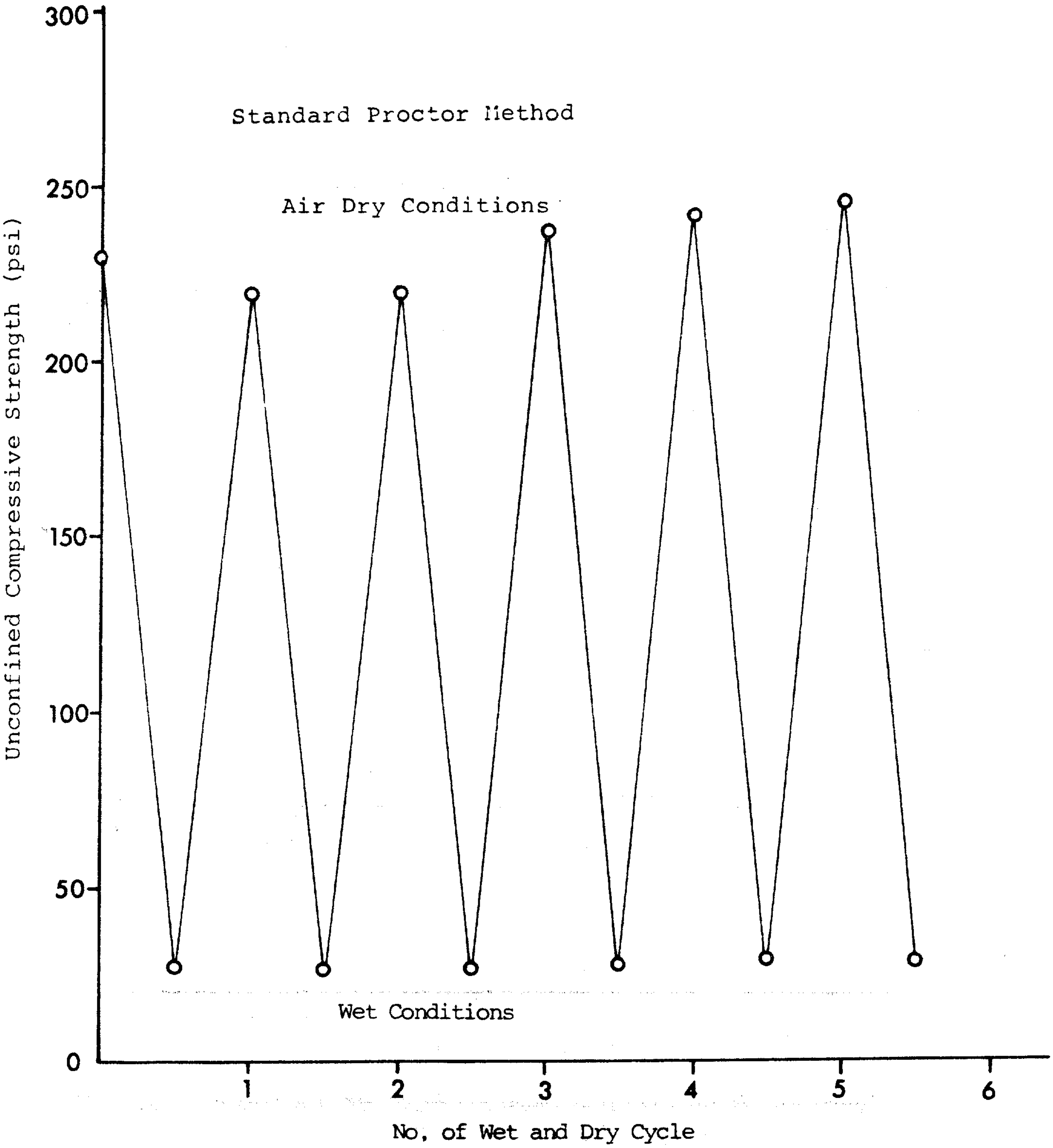

Figure 5. Effect of cyclic moisture changes on phosphogypsum strength.

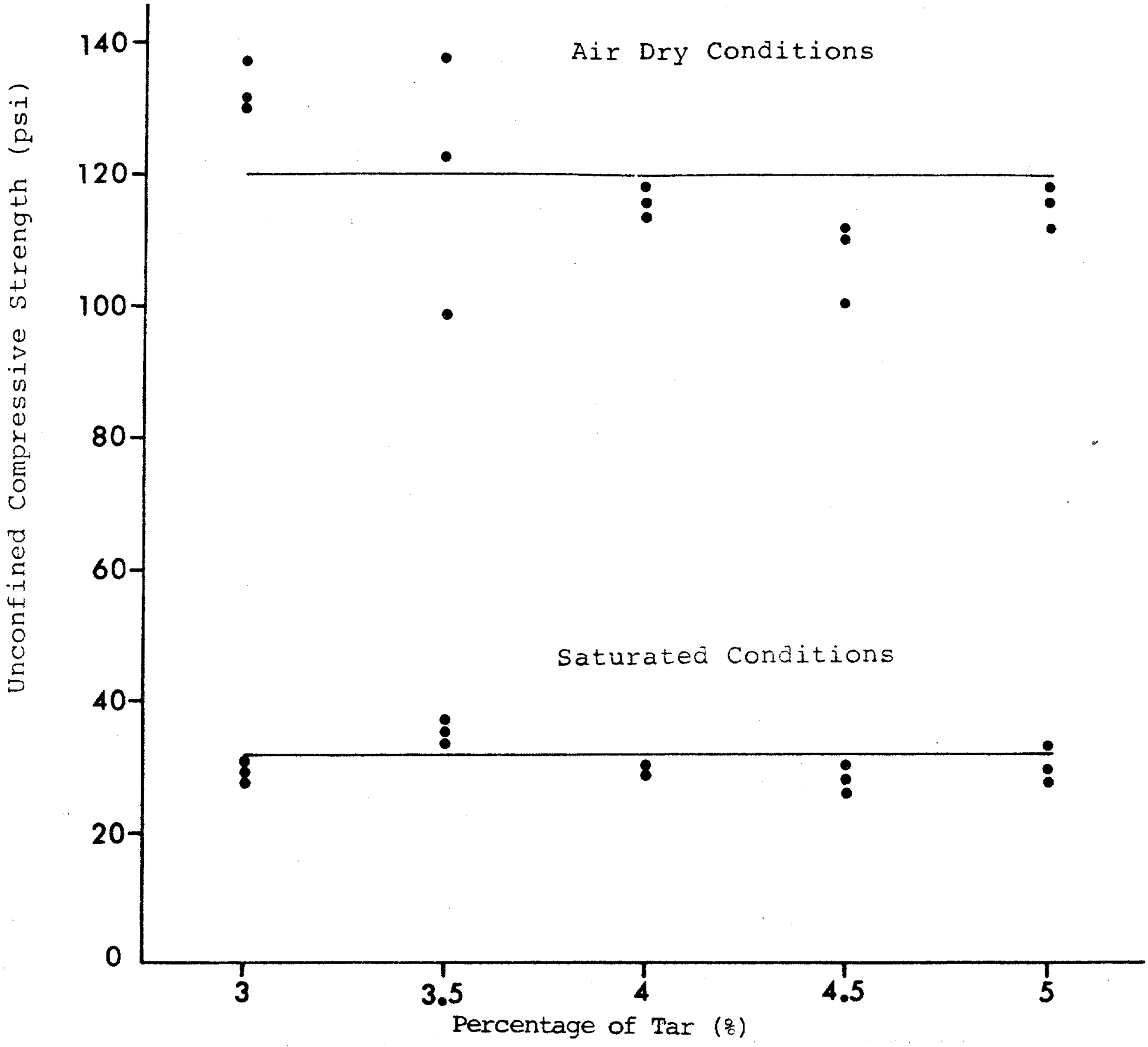

Figure 6. Relationship between strength and the amount of tar of the phosphogypsum-tar mixture.

7. CONCLUSIONS

Some engineering properties of phosphogypsum have been studied. Phosphogypsum shows its potential to be an engineering material, although more research needs to be undertaken. Phosphogypsum has some significant strength under air dry conditions but loses it under saturated conditions. Cyclic moisture changes do not have a negative effect on the strength of phosphogypsum as long as moisture content stays below saturation. Due to its latticed and monoclinic structure, phosphogypsum exhibits better engineering properties when higher compaction energy is applied. Phosphogypsum is not water resistant by itself, but it becomes a water resistant product of adequate engineering properties after mixing it with tar.

ACKNOWLEDGEMENTS

The research has been funded by the Florida Institute of Phosphate Research, Bartow, Florida. The authors would also like to express their gratitude to Agrico Chemical Co. and Gardinier Inc. for providing the samples used in this research.

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ENGINEERING PROPERTIES OF PHOSPHOGYPSUM AND PORTLAND CEMENT MIXTURES

Antonio Nanni
Ph.D. Candidate, Dept. of Civil & Architectural Engineering,
University of Miami, Coral Gables, FL.

Kuo-Ting Lin
Ph.D. Candidate, Dept. of Civil & Architectural Engineering,
University of Miami, Coral Gables, FL.

and

Wen F. Chang
Professor, Dept. of Civil & Architectural Engineering, and
Director Phosphate Research Institute,
University of Miami, Coral Gables, FL.

ABSTRACT

Mixtures containing portland cement as a binder, and raw phosphogypsum in combination with coarse limerock sand as fillers have been investigated. Specimens were prepared by three different methods: dynamic compaction (modified proctor), static compaction and high-frequency vibration.

It was found that for preparation by compaction and low cement content, phosphogypsum contribution to strength was remarkable when testing air-dried specimens. Such characteristic is due to the self-adhesive property of gypsum when subjected to a compressional force.

Strength characteristics in compression and tension were studied with different moisture contents at the time of testing. In the case of specimens prepared by high-frequency vibration, the properties of hardened mixes were found to be functions of the constituent materials and the mathematical relationships were derived.

1. INTRODUCTION

Portland cement is the most common binder used in the construction industry. Its applications range from high strength concrete to soil stabilization, depending on the cement content and aggregate properties.

Raw phosphogypsun, a by-product of the wet phosphoric acid industry, can be used as an aggregate in cement based mixtures. The characteristics of the product obtained, primarily depend on mix ratios and placement technique. The latter plays an important role because it is closely related to the water demand and the properties of phosphogypsun. Previous studies have demonstrated that phosphogypsun has self-adhesive properties after compaction (1). Such desirable behavior of calcium sulphate dihydrate is due to its layered lattice and monoclinic structure, which allow the individual particles to lose their original shape and melt together under compaction (4). However, this consistency is lost as soon as phosphogypsum is submerged in water. The advantage of self-adhesion is particularly evident in the case of low cement content and air-dry testing conditions, where both materials, cement and phosphogypsum, can be effectively considered as binders.

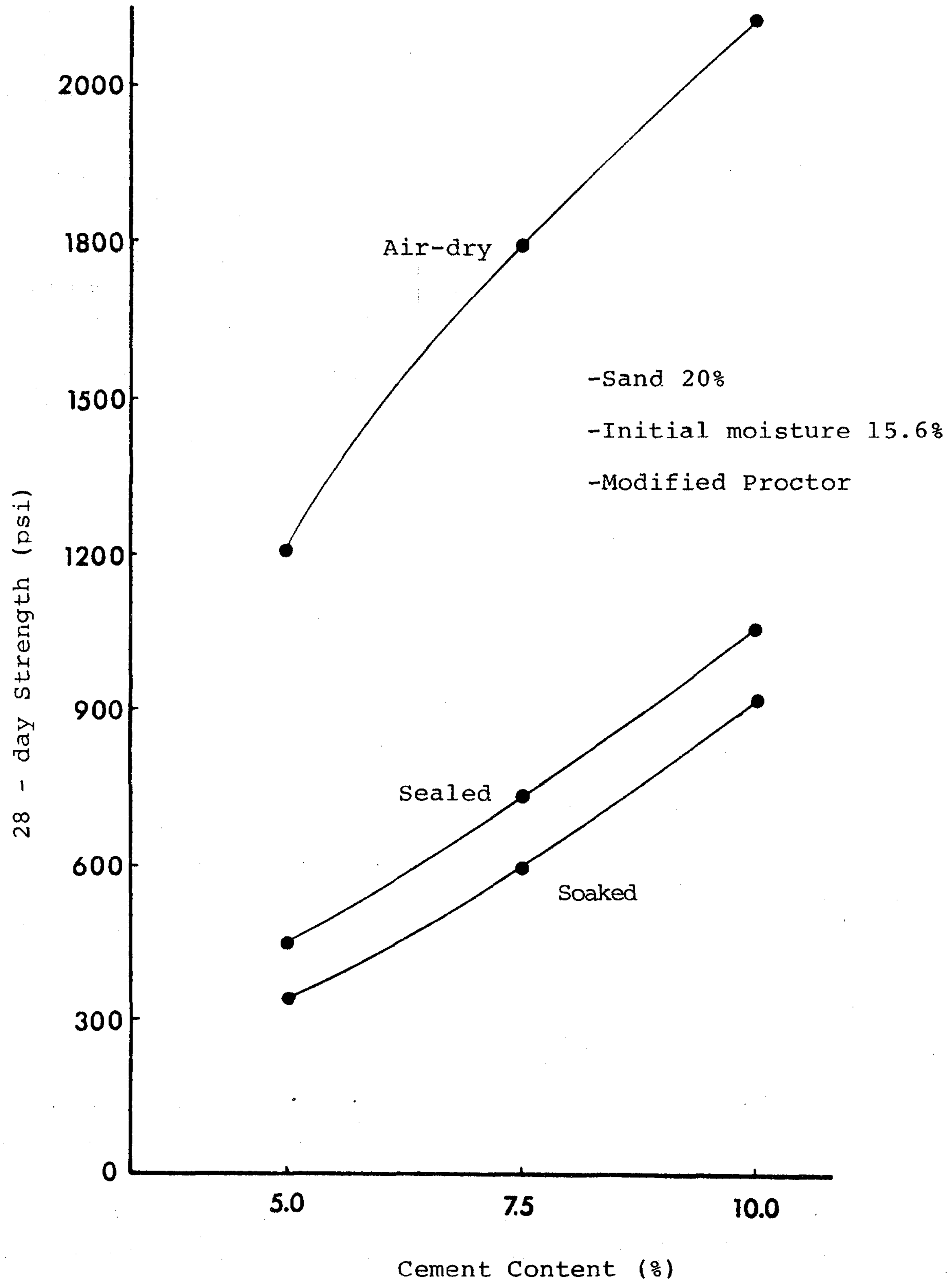
The emphasis of this paper is placed upon determining strength properties in unconfined compression and tension (splitting or modulus of rupture) of phosphogypsum-cement-sand mixtures with particular attention to testing conditions in terms of water content. Previous studies have established that not only plain phosphogypsun (1), but also phosphogypsum-based mixtures (2) are highly influenced by the moisture content at the time of testing. The following specimen conditions at the time of testing will be addressed during this investigation:

1) Air-Dry: indicating that the specimen had been removed from the curing environment (sealed or 100% humidity room) and maintained in open-shelf, laboratory conditions for 2 days. The resultant moisture content of all specimens was below 3%.
2) Sealed: indicating that the specimen was tested with the moisture content resulting from sealed curing. Sealed curing was obtained by tightly wrapping the specimen with a plastic membrane after removal from the mold. The 28-day moisture content was approximately 2.5% lower than the moisture content of the mix at the time of compaction.
3) Soaked: indicating that the specimen was removed from the curing environment (sealed or 100% humidity room) and submerged in water for a 2-day period.

2. DYNAMIC COMPACTION PREPARATION

The 28-day unconfined compressive strength of cylindrical specimens containing variable amounts of phosphogypsum and 20% of sand as aggregates, is plotted in Figure 1 as a function of cement content for different moisture levels at the time of testing. Specimens compacted by the modified Proctor technique and cured under sealed conditions,

Figure 1
Compressive Strength vs. Cement Content
(1000 psi = 6.89 MPa)



were 2 in. (50.8 mm) in diameter and 4 in. (101.6 mm) in length. An optimum initial moisture content of 15.6% (obtained during a moisture-density test) was used in the mixes presented in this Figure. As expected, strength is directly proportional to cement content. In addition, air-dry values are consistently higher than the corresponding soaked conditions: for a 5% cement content the ratio between air-dry and soaked compression is approximately 4, and drops to approximately 2 when the amount of cement is increased to 10%. It should be indicated that the air-dry unconfined compressive strength of the mixture with a 5% cement content is over 1200 psi. It is expected that higher compaction energy would lead to an even higher compressive strength. Further testing also showed that at a cement content as low as 3% and for a properly blended mix, specimens maintain their consistency when submerged in water for 7 days after being cured for 7 days under sealed conditions.

The effect of varying sand content, for a constant cement content of 7.5%, on the 28-day compressive strength is presented in Figure 2. The optimum moisture content obtained in moisture-density tests and used in specimens preparation, decreased from 18.6 to 14.5 as the percentage of sand increased. It is shown that the addition of sand improves the compressive strength particularly under air-dry testing conditions. This can be explained by the fact that limerock sand is a stronger aggregate than phosphogypsum and that coarser particles decrease the surface area to be bound by cement hydration. However, extremely high sand percentages have a detrimental effect as the mix loses its ability to be compacted properly.

The effect of curing time under sealed conditions on cylinder unconfined compression is shown in Figure 3. The behavior of the phosphogypsum-cement-sand mixtures is equivalent to that of conventional mortars with respect to hardening: the longer the curing period the higher the strength. It is noticed that sealed conditions preserve enough water to fully develop the hydration process. Moreover, Figure 3 also shows that compressive strength reaches a plateau after a curing period of approximately 7 days when soaked specimens are tested.

Mixes discussed in this section may find suitable applications in

Figure 2

Compressive Strength vs. Sand Content

(1000 psi = 6.89 MPa)

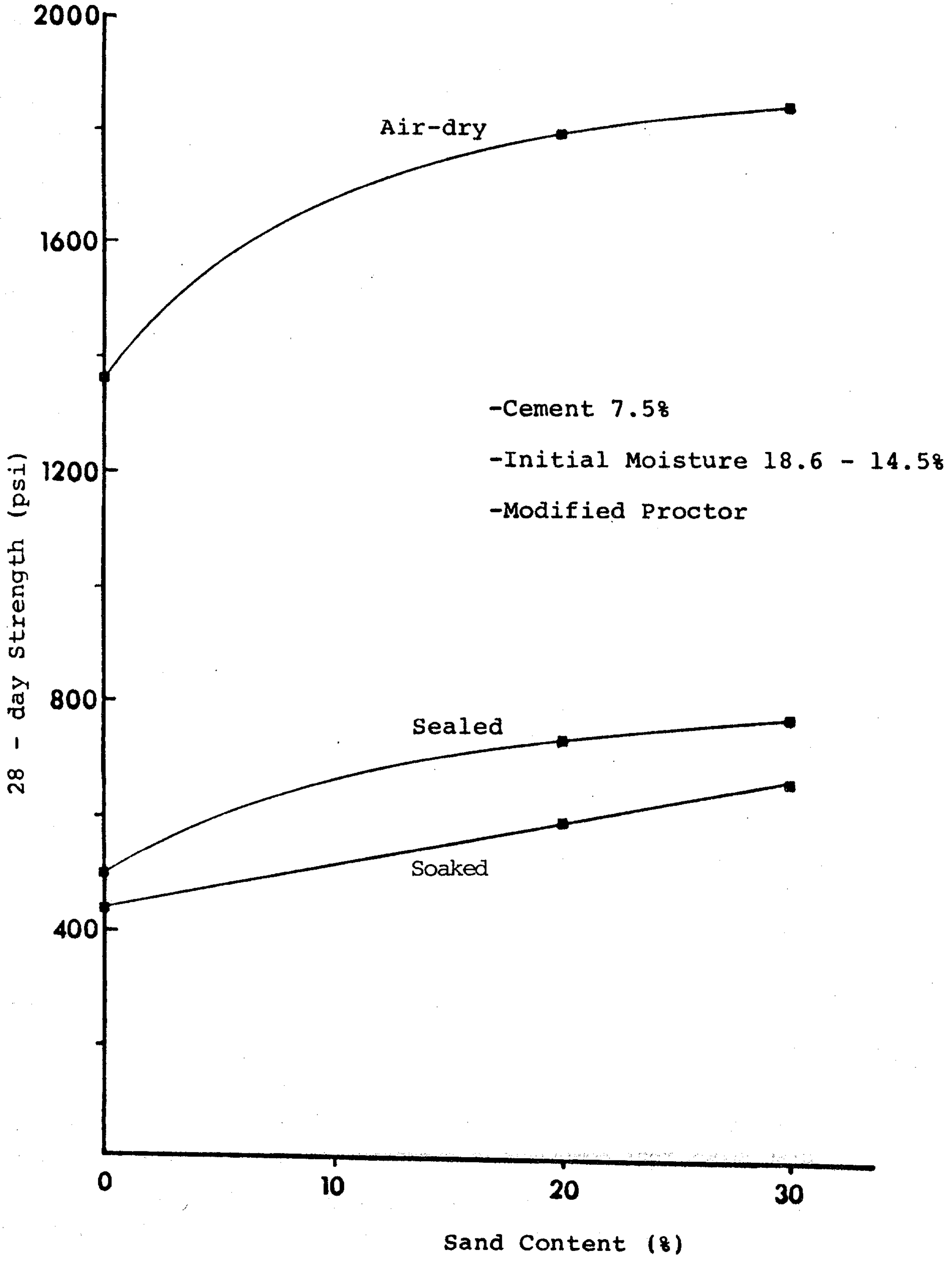
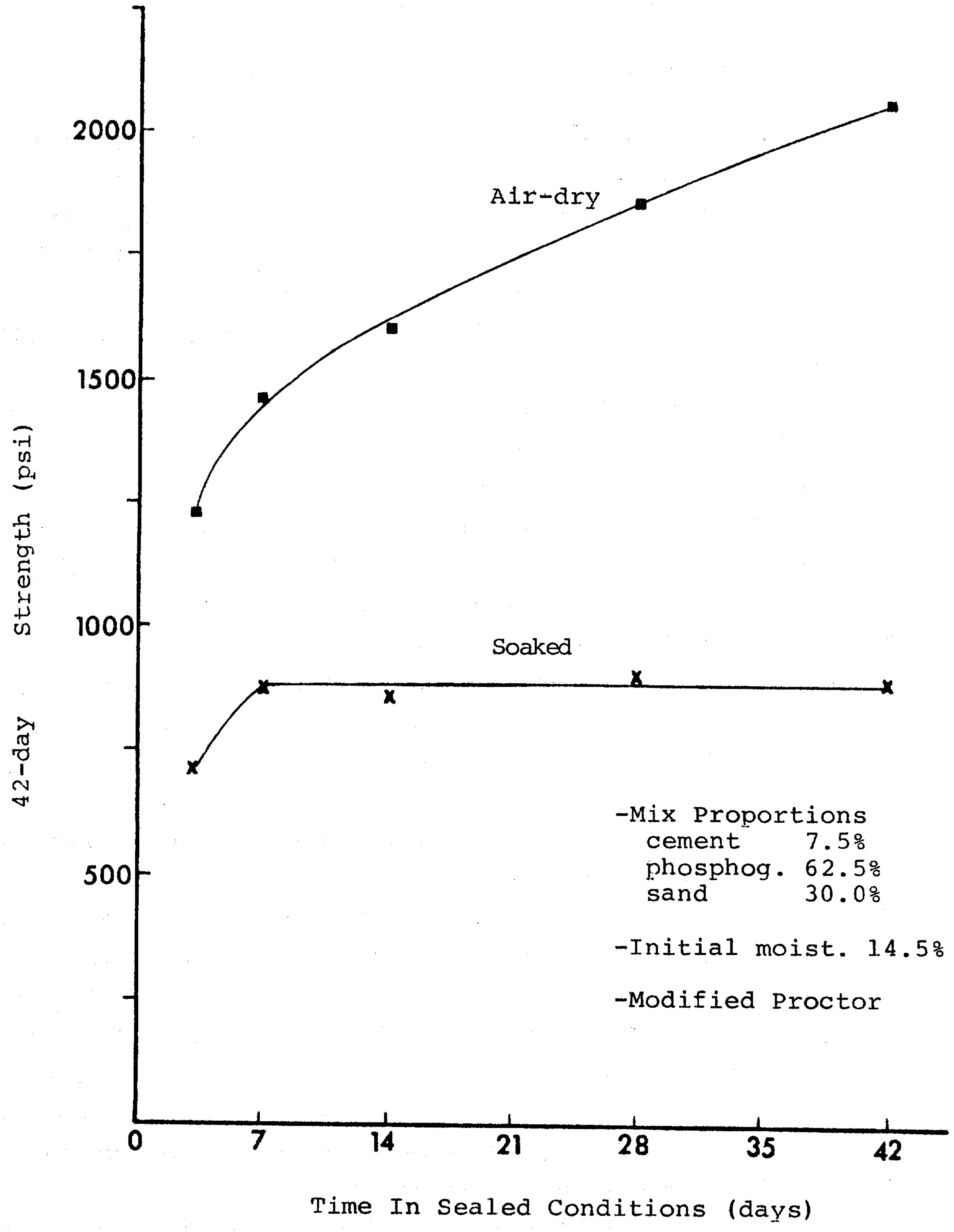


Figure 3

Compressive Strength vs. Time in Sealed Conditions
(1000 psi = 6.89 MPa)



road construction. An experimental highway, containing a base course with similar composition, has already been constructed in the State of Texas (3) with very encouraging results.

3. STATIC COMPACTION PREPARATION

The remarkable behavior of phosphogypsum when compacted can also be utilized in the development of building products as shown by strength results presented in this section, where mixtures with higher cement content were also studied. Brick specimens, 3.75x8x2.5 in. (88x203x64 mm), were produced by static compaction applying a static force of 30 kip (13,620 kg), which resulted in a pressure of 1000 psi (6.89 MPa).

Specimens thus prepared and cured in a 100% humidity room for 25 days, were cut into halves to be tested in compression under both air-dry and soaked conditions. Twenty eight-day compressive strength results are presented in Figures 4 and 5 for mixes with and without the addition of sand and for initial moisture values of 14% and 16% respectively.

Increasing cement content proved to be more beneficial to the compressive strength under soaked conditions than under air-dry conditions for mixes containing phosphogypsum and cement only, as shown in Figure 4. In fact, soaked compressive strength increased 105% when the cement increased from 10% to 30%, while air-dry compressive strength gain was only 53% for a similar increase in cement content.

A 10% addition of sand to the mix components produced even higher strength gains when the cement content was increased from 10% to 25%, as shown in Figure 5. Soaked compressive strength improved 157% and air-dry compressive strength improved 85% over the same cement increase of 15%.

Results of bending tests on specimens aged for 28 days are plotted in Figures 6, 7 and 8 as a function of cement or sand content. The test setup consisted of a concentrated load applied at the centerline of a beam specimen having 7 in. (178 mm) of free span and 3.75 in. (88 mm) of width. Testing was performed in accordance with the American Society for Testing and Materials (ASTM) standard C-67.

Results presented in Figures 6 and 7, relate to the 28-day modulus of

Figure 4

Brick Compressive Strength vs. Cement Content
(1000 psi = 6.89 MPa)

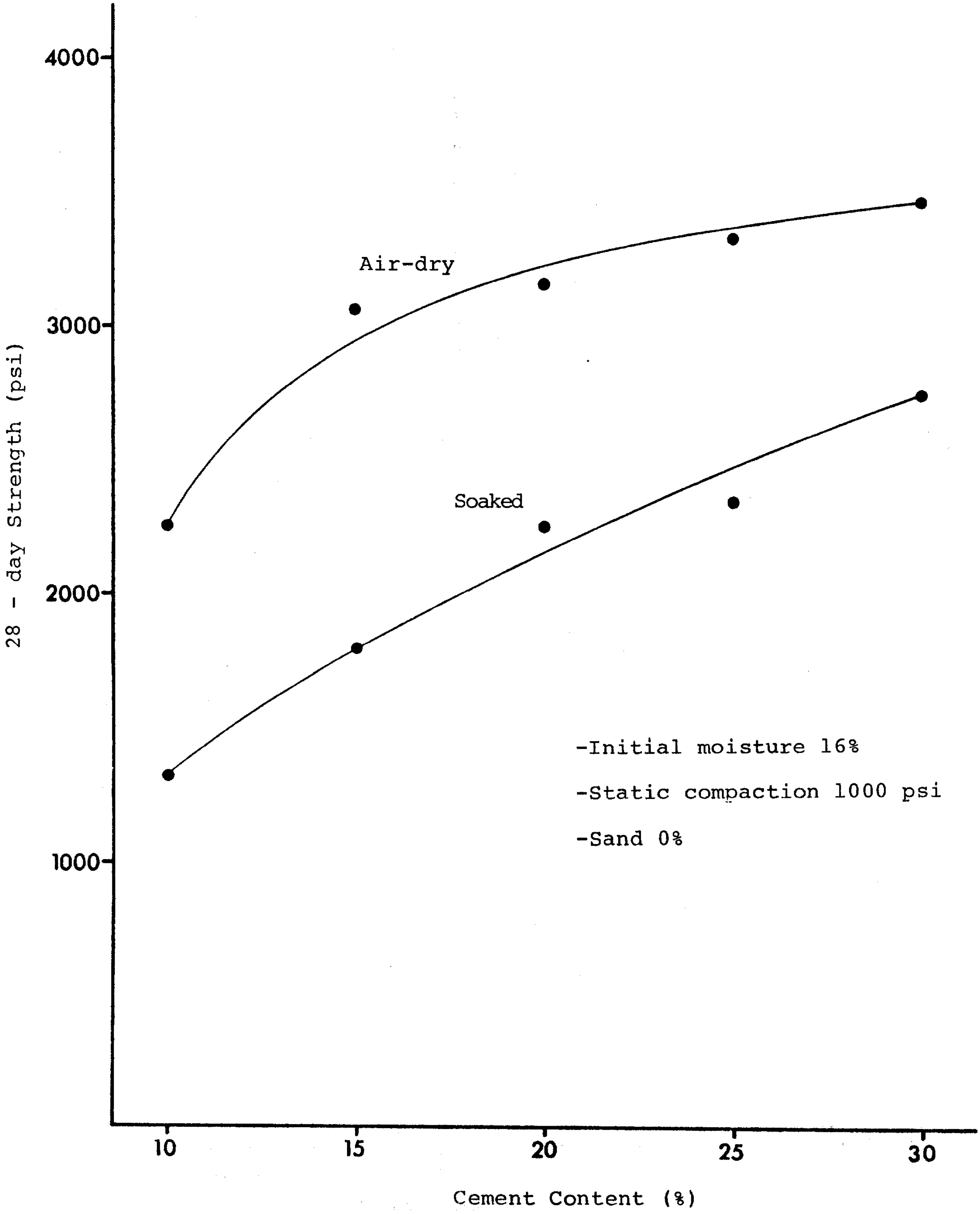
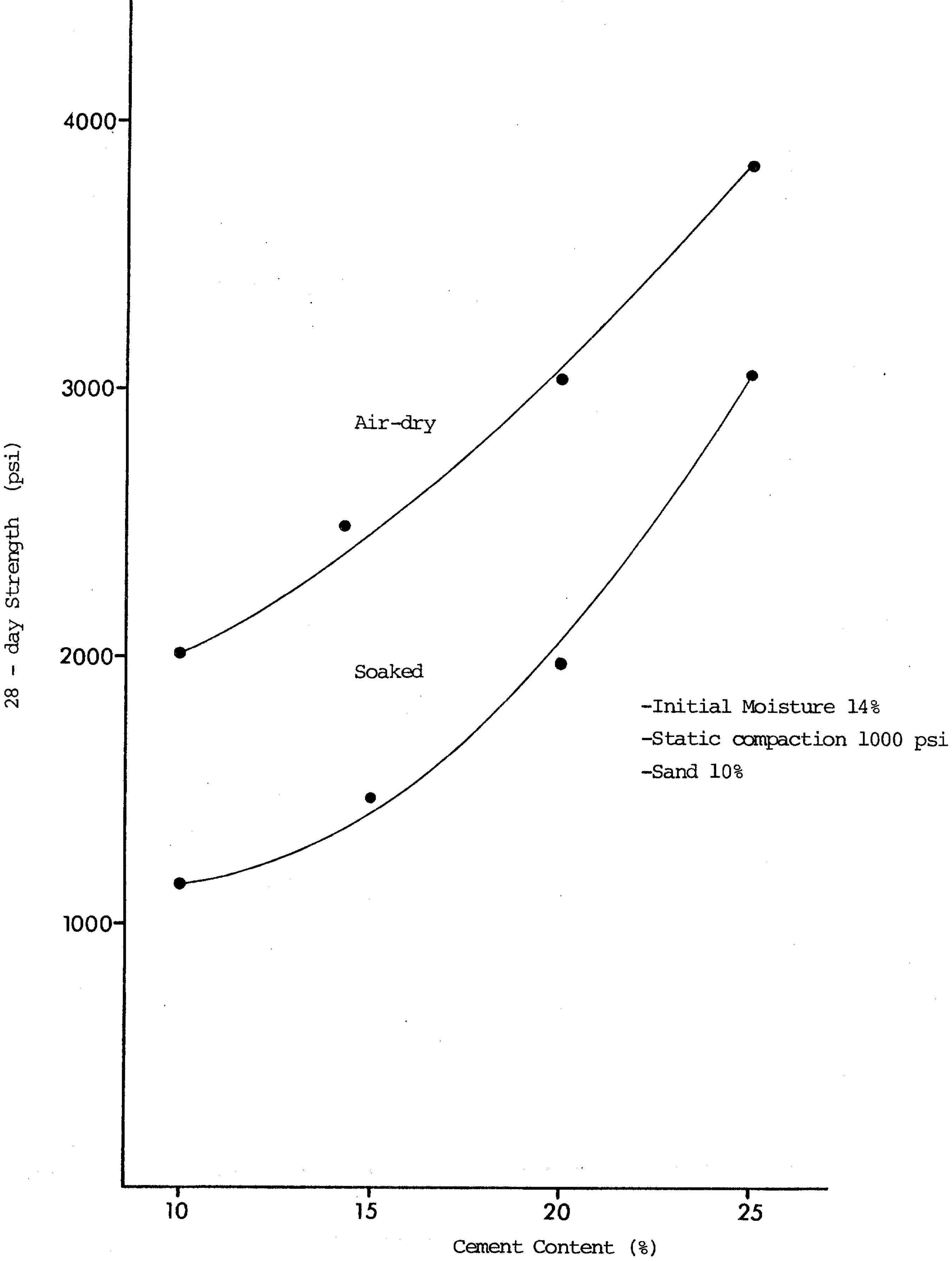


Figure 5

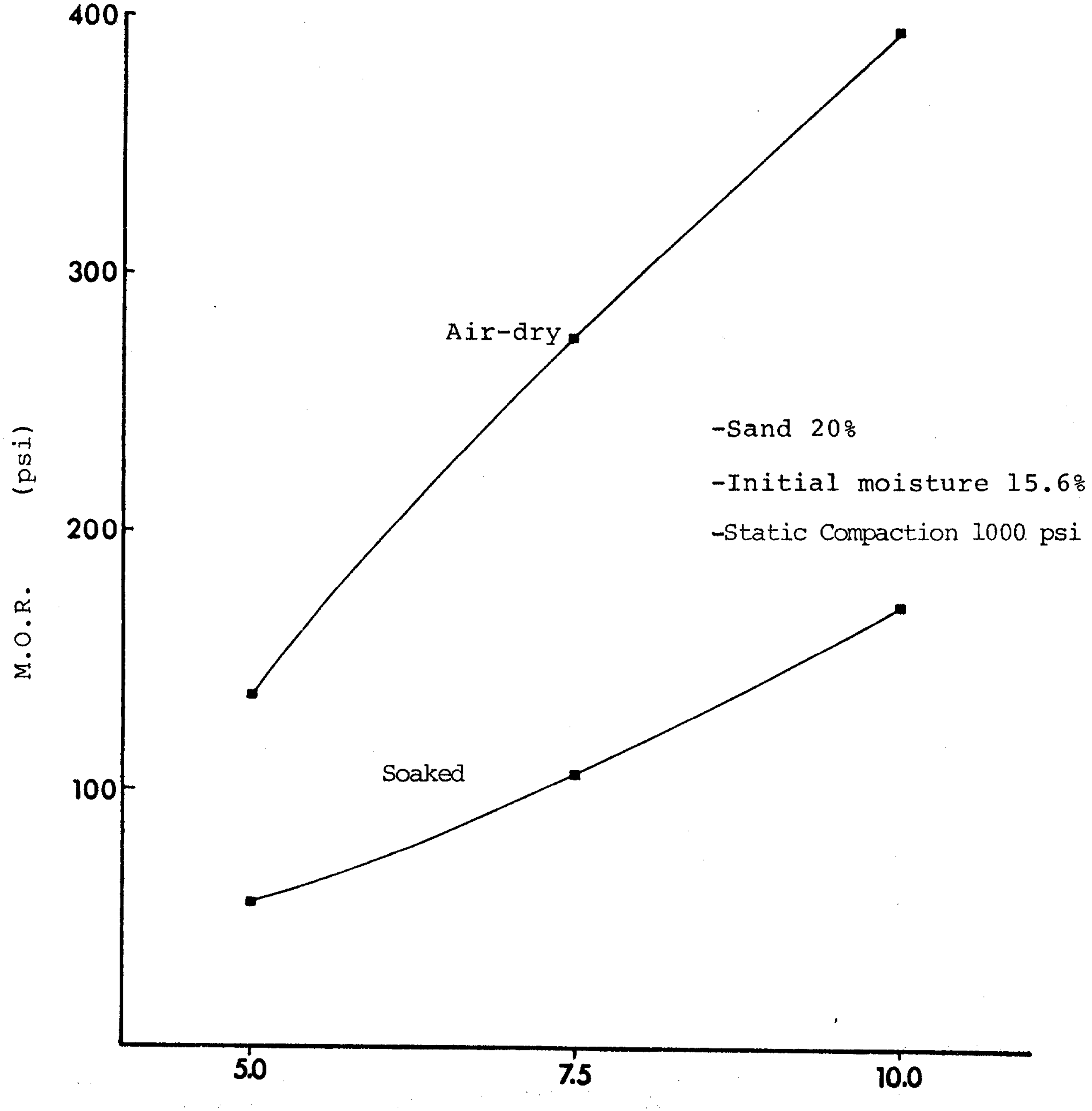
Half-Brick Compressive Strength vs. Cement Content
(1000 psi = 6.89 MPa)



-Initial Moisture 14%
-Static compaction 1000 psi
-Sand 10%

Figure 6

Modulus Of Rupture vs. Cement Content
(1000 psi = 6.89 MPa)



Cement Content (%)

Figure 7

Modulus Of Rupture vs. Sand Content
(1000 psi = 6.89 MPa)

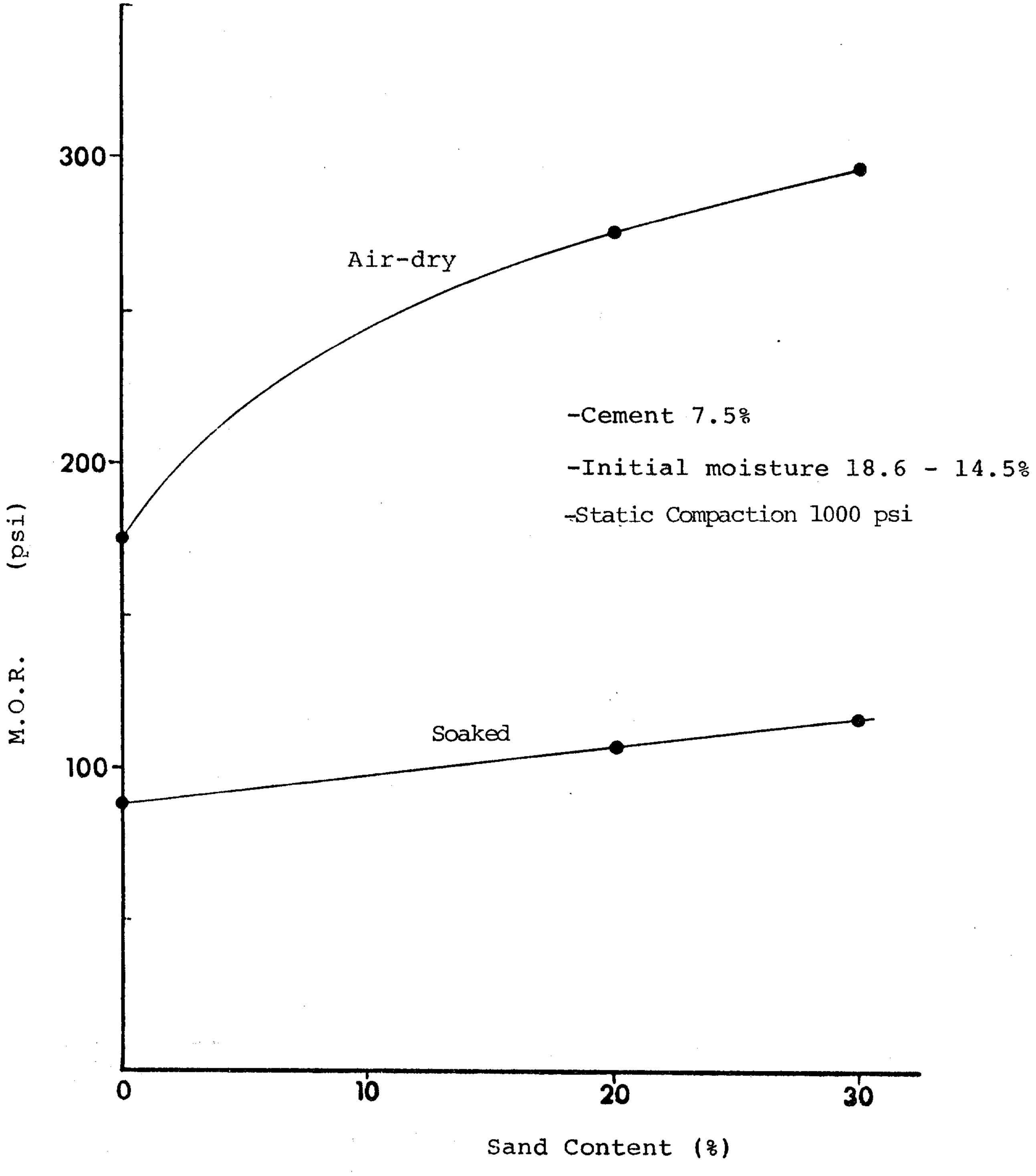
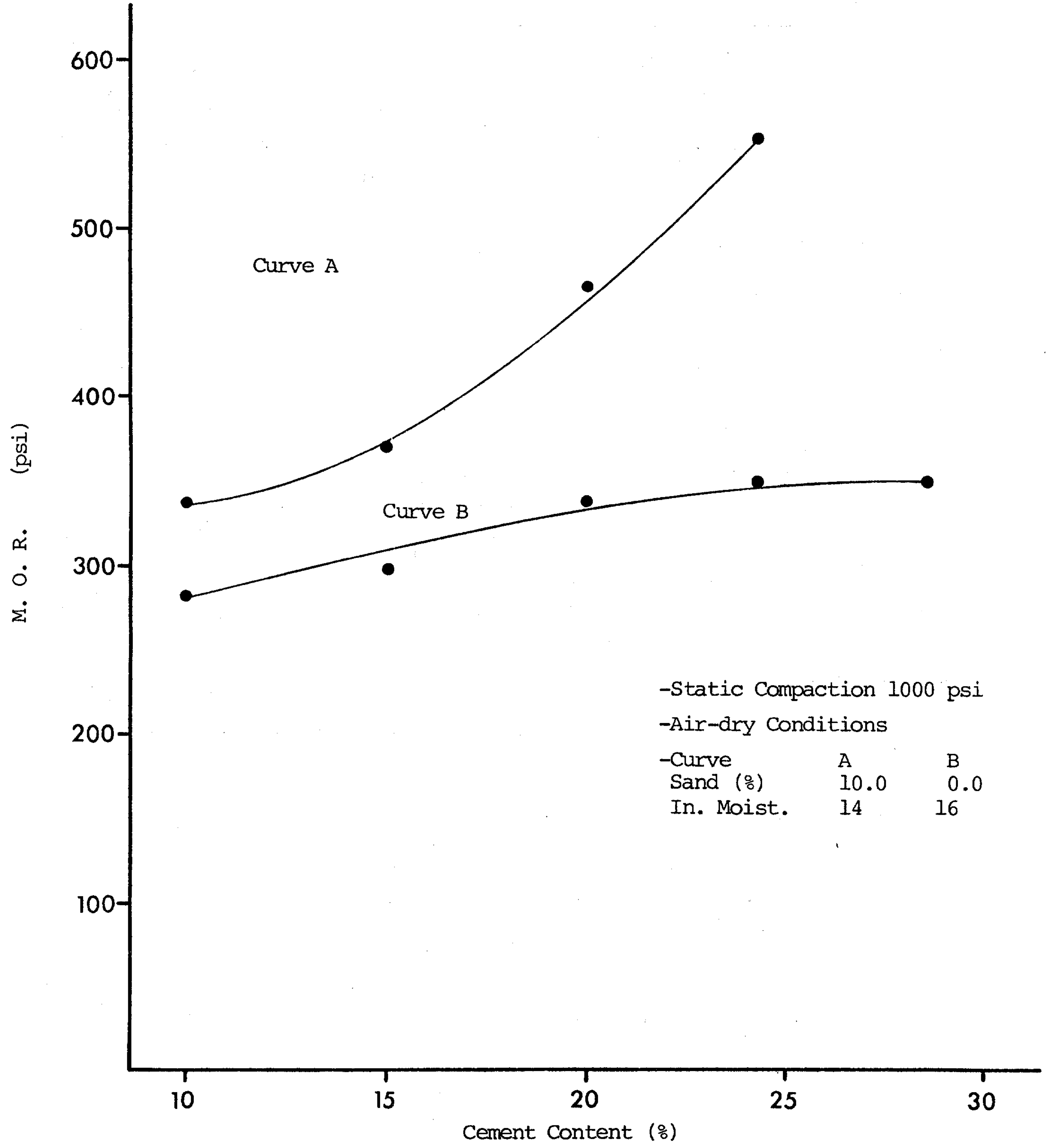


Figure 8

Modulus of Rupture vs. Cement Content
(1000 psi = 6.89 MPa)



rupture as a function of cement and sand content respectively for both soaked and air-dry testing conditions. These values show similar trends to compressive strength data previously discussed for specimens with identical mix proportions as shown in Figures 1 and 2.

The modulus of rupture as a function of higher cement content is presented in Figure 8 for specimens tested under air-dry conditions. Curve A (corresponding to phosphogypsum-cement mixtures) shows a more pronounced strength gain than curve B (corresponding to phosphogypsum-cement-sand mixtures) when the cement content varies from 10% to 30%.

4. HIGH-FREQUENCY VIBRATION PREPARATION

Phosphogypsum-cement-sand mixtures become workable under vibration when a suitable amount of water is added to the mix. Table or pen vibrators can be used to induce mix flow into the mold and remove entrapped air bubbles.

The conventional parameter, water over cement ratio (W/C), used to describe workability of cement-based mixtures had to be modified into the water over cement plus phosphogypsum ratio (W/(C+P)) due to the high fineness and absorption of the phosphogypsum. However, the principal controlling factor of strength is still the W/C ratio as in conventional concrete, even if the presence of phosphogypsum has to be accounted for. Statistical analyses performed on compressive and split tensile strength results follow a material law of the exponential type, derived from the one suggested by Powers (2) for conventional concrete, and expressed by:

$$f = a R^b \qquad ......(1)$$

Where: f = Compressive or split tensile strength
a,b= Constants depending on age and type of test
R = Composite Ratio

The composite ratio R results from a linear combination of the W/C ratio and phosphogypsum over dry solid ratio (P/S) as follows:

$$R = W/C + m\,P/S \quad . . . . . .(2)$$

Where: $m=0.4$ for compression
$m=0.5$ for splitting tension

The values of m are independent of specimen age and only depend on the type of test.

Results of specimens prepared with 35 different mix proportions are presented in Figures 9 and 10, for the cases of 28-day compression and indirect tension respectively. Values were obtained by testing 2 by 4 in. (50.8 by 101.6 mm) cylindrical specimens, table-vibrated for a period of 30 seconds, cured under sealed conditions and tested immediately after the removal of the plastic wrap.

The constants a and b, as defined in equation (I), were calculated by regression analysis and the appropriate correlation equations for each case are also presented in these Figures.

The influence of preparation technique on compressive strength was examined comparing the results of specimens with identical solid proportions. Dynamically compacted specimens (containing 10% cement, 70% phosphogypsum and 20% sand) reached 1060 psi, while specimens prepared by vibration produced 780 psi. Part of this difference is due to the self-adhesion of phosphogypsum. However, this effect decreases as the cement content increases.

The relationship between split tension and compression is presented in Figure 11. Results show a distribution similar to that of conventional concrete and also confirm the fact that the tensile to compressive strength ratio decreases as age (or compressive strength) increases. For a compression of 500 psi the ratio f_t/f_c is approximately 0.15 and drops to 0.13 when the compressive strength reaches 5000 psi.

Finally the cylinder compressive strength at 3, 7 and 28 days of age is plotted in Figure 12 as a function of the composite ratio R as defined in equation (2). These relationships become linear on a log-log plot and can be directly used for design purposes.

Figure 9: Cylinder Compressive Strength vs. Composite Ratio
(1000 psi = 6.89 MPa)

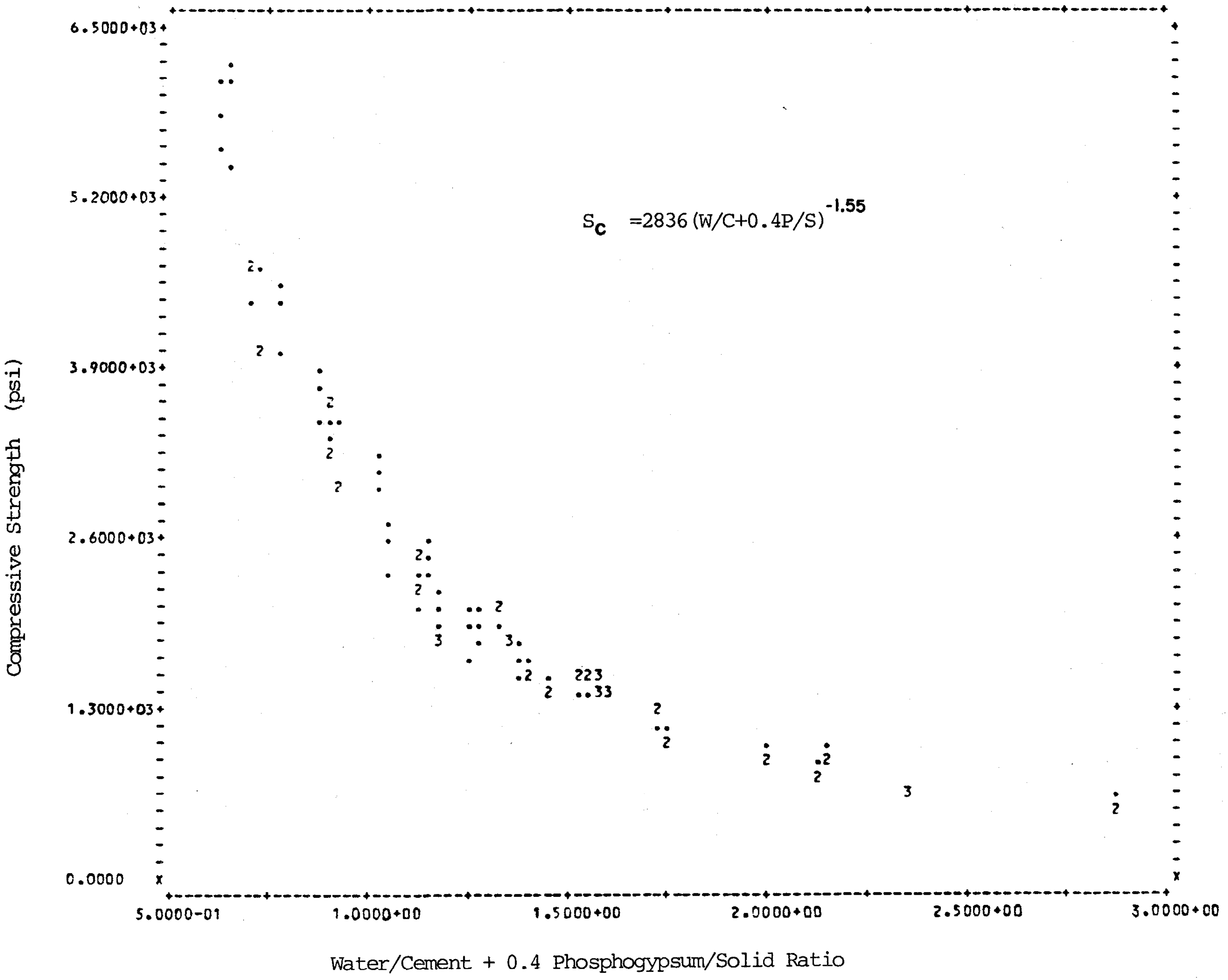


Figure 10: Split Tensile Strength vs. Composite Ratio

(1000 psi = 6.89 MPa)

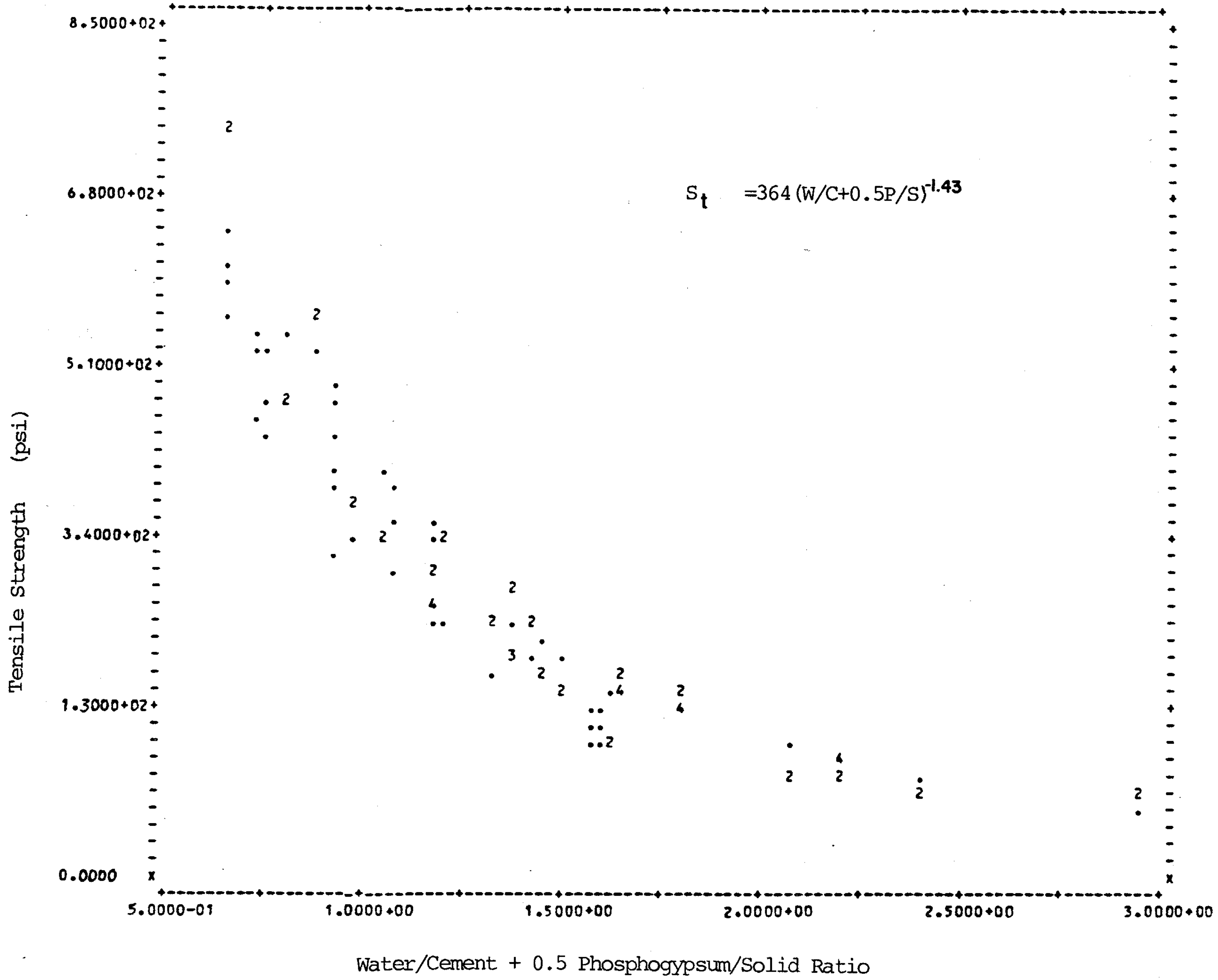


Figure 11: Split Tension vs. Cylinder Compression

(1000 psi = 6.89 MPa)

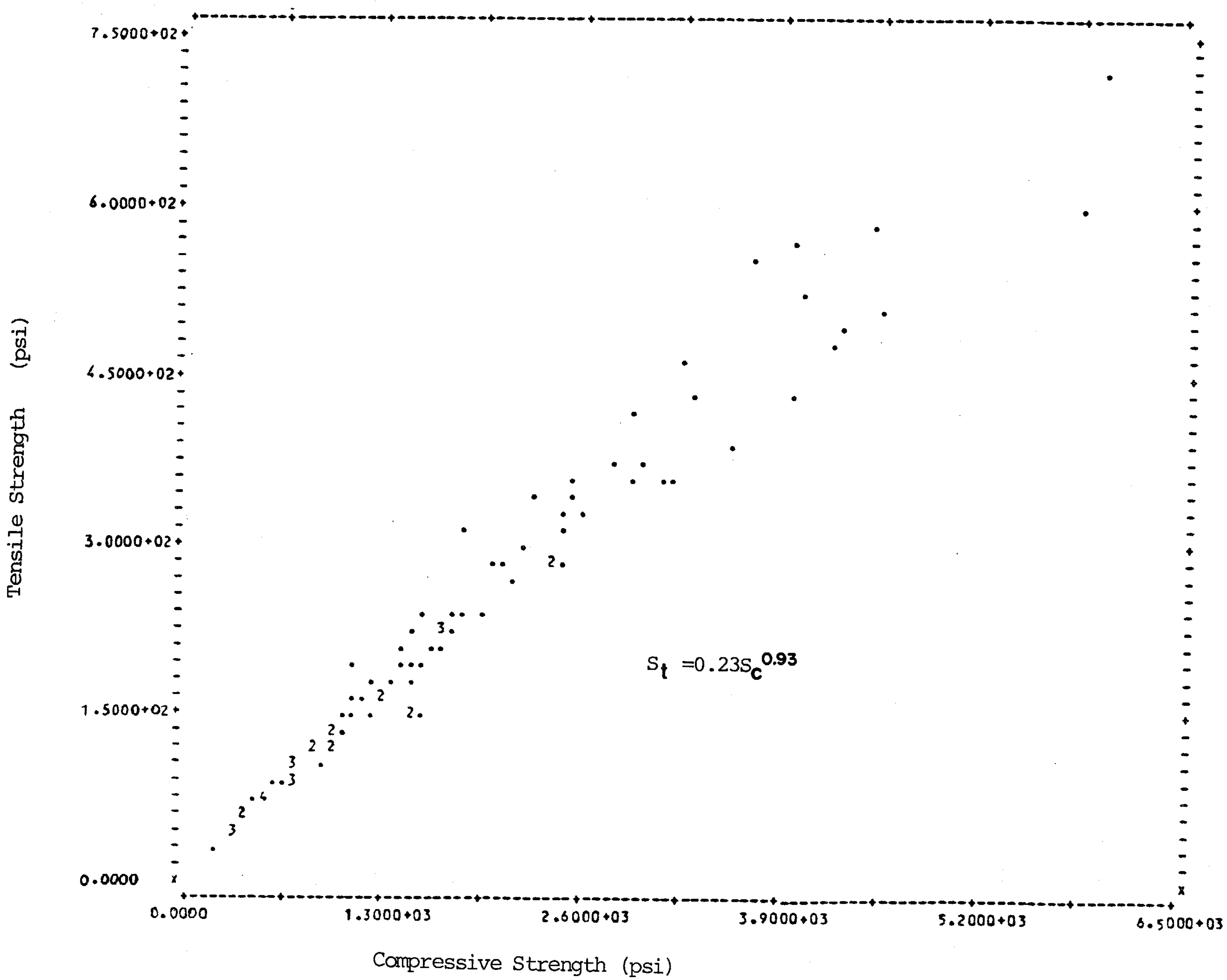
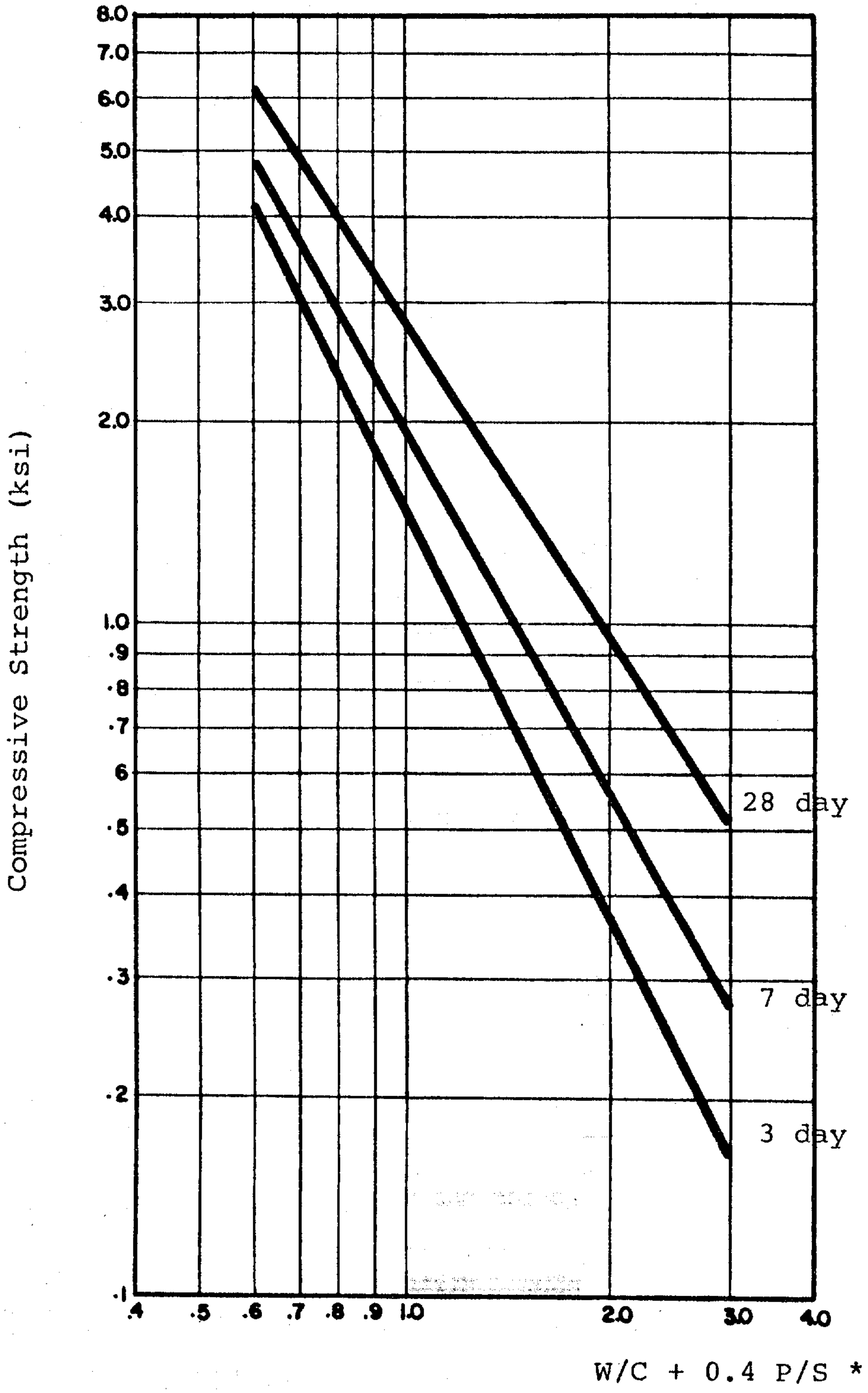


Figure 12

Cylinder compressive strength vs. composite ratio

(1000 psi = 6.89 MPa)



*W = Water P = Phosphogypsum

C = Cement S = Total Solid

4. CONCLUSION

Results of this investigation lead to the following conclusions:

1) Raw phosphogypsum can directly be used in cement-based mixtures. Cement content primarily determines mix strength. However, for low cement content and preparation by compaction, phosphogypsum (with its ability of self-adhesion) plays an important role as a binding agent when the material is in air-dry conditions.
2) Compressive and tensile strength of specimens prepared by high-frequency vibration vary in a similar fashion to those of conventional concrete and both properties can be expressed as functions of the constituent materials.
3) Moisture content at the time of testing was found to strongly affect strength values.
4) Each of the three preparation techniques investigated in this study, namely: dynamic compaction, static compaction and high-frequency vibration, has its own characteristics. Phosphogypsum-based products for building and highway construction can benefit from the appropriate choice according to specific requirements of the application.

ACKNOWLEDGEMENTS

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

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ENGINEERING PROPERTIES OF PHOSPHOGYPSUM, FLY ASH AND LIME MIXTURES

Hernan D. Velarde
Ph.D. Candidate, Dept. of Civil & Arquitectural Engineering, University of Miami, Coral Gables, FL.

J. Ludwig Figueroa
Associate Professor, Dept. of Civil & Arquitectural Engineering, University of Miami, Coral Gables, FL.

Wen F. Chang
Professor, Dept. of Civil & Arquitectural Engineering, and Director, Phosphate Research Institute, University of Miami, Coral Gables, FL.

ABSTRACT

The availability of by-product Phosphogypsum in the state of Florida and the expected increase of coal use to produce electricity indicates that phosphogypsum and fly ash along with lime can be combined to form a stabilized mixture such that a construction material containing more than 90% waste be obtained. Several mixes with different proportions of lime - fly ash and phosphogypsum content have been tested with very encouraging results. A water resistant matrix with compressive strengths of over 2500 psi have been obtained which will yield suitable mixtures for pavement bases and furthermore the development of building products in the future. The effect of different curing conditions has been studied and the optimum lime to fly ash ratio has been determined.

1.- INTRODUCTION

Phosphogypsum, a waste product from the phosphate industry primarily containing calcium sulfate, is a material composed of fine particles which develops strength when compacted but becomes unstable when saturated (1). It is the objective of this research to study the possibility of using phosphogypsum as an aggregate in a stabilized mixture to improve its strength and obtain a water resistant matrix with wide applications in the construction industry.

As a result of the availability of waste materials in local areas and the shortage of suitable aggregates a great effort has been placed on the utilization of these wastes in highway and landfill construction over the past twenty years.

Lime and fly ash have been used to stabilize soils and aggregates during the construction of pavement bases and subbases since the early 1950's. General specifications for lime - fly ash mixtures are currently available from the Federal Highway Administration (2).

Calcium Sulfate waste, in combination with lime and fly ash, has been used in road base construction since the early 1970's. The Transpo 72 parking lot at Dulles Airport near Washington D.C. (3) was built with this mixture. The results obtained from this pavement structure indicated that waste sulfates could be successfully used along with lime and fly ash but provisions needed to be taken to seal the compacted matrix to prevent exposure to adverse weather conditions prior to strength development.

Great interest developed after this experience in using waste sulfates as base course materials. Recently, an experimental base course test section was built at West Virginia University including several calcium sulfate - lime - fly ash mixtures (4).

The pozzolanic reaction between lime and fly ash has been widely studied (5,6). The cementitious properties of lime - fly ash mixtures make them desirable for soil and aggregate stabilization.

Fly ash is primarily composed of pozzolans such as silica and alumina which will react with lime in the presence of moisture. Certain types of fly ashes, containing high percentages of calcium oxide, will react by themselves in the presence of moisture.

Lime - fly ash reactions are time dependent such that strength development continues for several months. Increases in strength of lime - fly ash - aggregate mixtures used in pavement bases have been documented for 10 years after construction (7).

One of the advantages of stabilizing phosphogypsum with a lime - fly ash mixture is that two waste products (phosphogypsum and fly ash) are combined in the matrix. As a result, a construction material containing more than 90% wastes can be obtained.

Preliminary testing indicated that lime - fly ash - phosphogypsum mixtures (LFP) strength characteristics depended upon several factors:

a) chemical composition of the constituents
b) mixtures proportions
c) lime to fly ash ratio
d) moisture content
e) compaction energy
f) curing time, and
g) curing conditions

In light of the many factors involved, it is very difficult to predict the performance or characteristics of an LFP mixture. Nevertheless, LFP mixtures seem to follow typical trends observed in other types of lime - fly ash mixtures (8,9,10).

It concerns pavement designers to obtain the appropriate combination of materials that would provide suitable pavement performance according to the intended application. When waste products are to be used, the selection of the material proportions has the objective of utilizing as much of these waste products as possible provided the resulting mixture is economical and technically feasible.

Unconfined compressive strength testing is commonly used in the evaluation of LFA mixtures and other soil stabilization alternatives. A similar approach was adopted in the evaluation of LFP mixtures.

2.- MATERIALS CHARACTERISTICS

PHOSPHOGYPSUM.- Phosphogypsum is a by-product obtained from the dihydrate process used in the production of phosphoric acid from the phosphate rock. The chemical composition of phosphogypsum varies depending on the different storage piles and the location within the pile itself. These variations are mainly due to its exposure to the environment and the age of the pile. An average of 90% calcium sulfate in the dihydrated form ($CaSO_4$-$2H_2O$) is found in Florida's phosphogypsum. A typical chemical composition of phosphogypsum is shown in Table 1.

The grain size distribution (fig 1) shows that phosphogypsum particles are very fine with 80% of them passing the #200 sieve. No significant reaction was observed when phosphogypsum was mixed with lime alone.

TYPICAL ANALYSIS of PHOSPHOGYPSUM

$CaSO_4 \cdot 2H_2O$	85 - 95%
P_2O_5	0.2 - 1.7%
F	0.4 - 1.3%
SiO_2	1.4 - 8.4%
Soluble salts	0.1 - 5.3%
ph	3.1 - 5.3

TABLE 1

CHEMICAL COMPOSITION of FLY ASH

Principal Constituents	Percents
SiO_2	53.47
Al_2O_3	20.62
Fe_2O_3	16.00
K_2O	3.16
CaO	2.20
MgO	1.00
SO_3	0.66
P_2O_5	0.30

TABLE 2

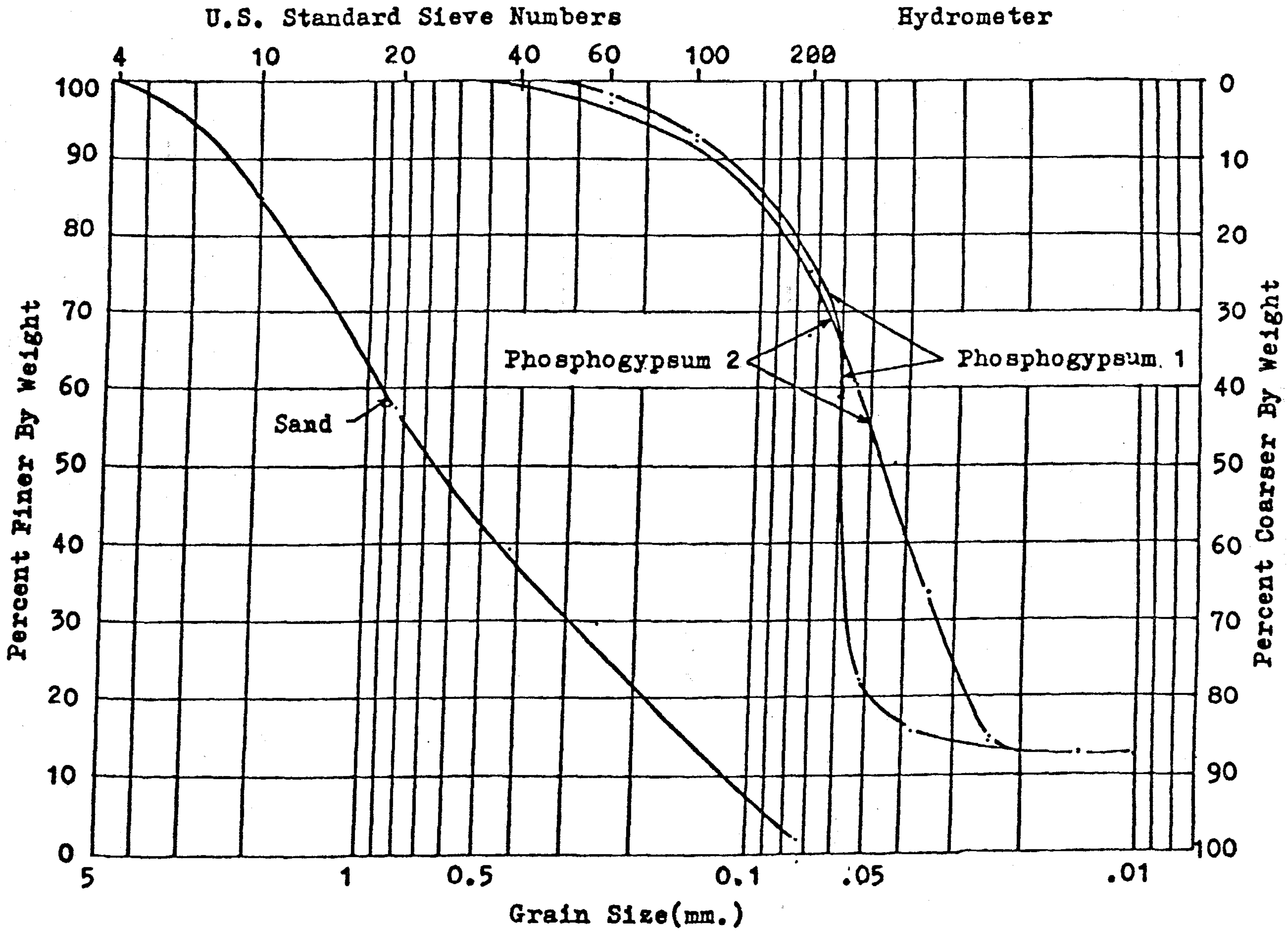

FIGURE 1 **Grain size distribution curves for sand and phosphogypsum 1 & 2.**

FLY ASH.- Fly ash is a waste product obtained from burning coal. Its composition varies depending on the type of coal used as well as the burning process. The chemical composition of the fly ash used in this research is presented in Table 2 in which 90% of the total constituents are silicious, aluminous and ferrous components. This composition makes this fly ash very desirable for the development of the pozzolanic reaction with lime. Although a low percentage of calcium oxide (2.2%) was found in the fly ash; no appreciable development of the pozzolanic reaction was noticed in the fly ash alone.

LIME.- Roth hydrated lime $Ca(OH)_2$ and quick-lime CaO were used during the investigation. Either type of lime was first grinded and sieved through the U.S. #40 standard mesh before mixing with fly ash and phosphogypsum. The type of lime used in each mixture is identified along with tests results.

3.- EXPERIMENTAL PROGRAM

The main objective of this study was to evaluate the strength characteristics of LFP mixtures. Typical compositions of LFP mixtures are shown in figure 2. Mixtures contained 50% to 90% of phosphogypsum, whereas lime to fly ash ratios varied between 0.04 and 0.50.

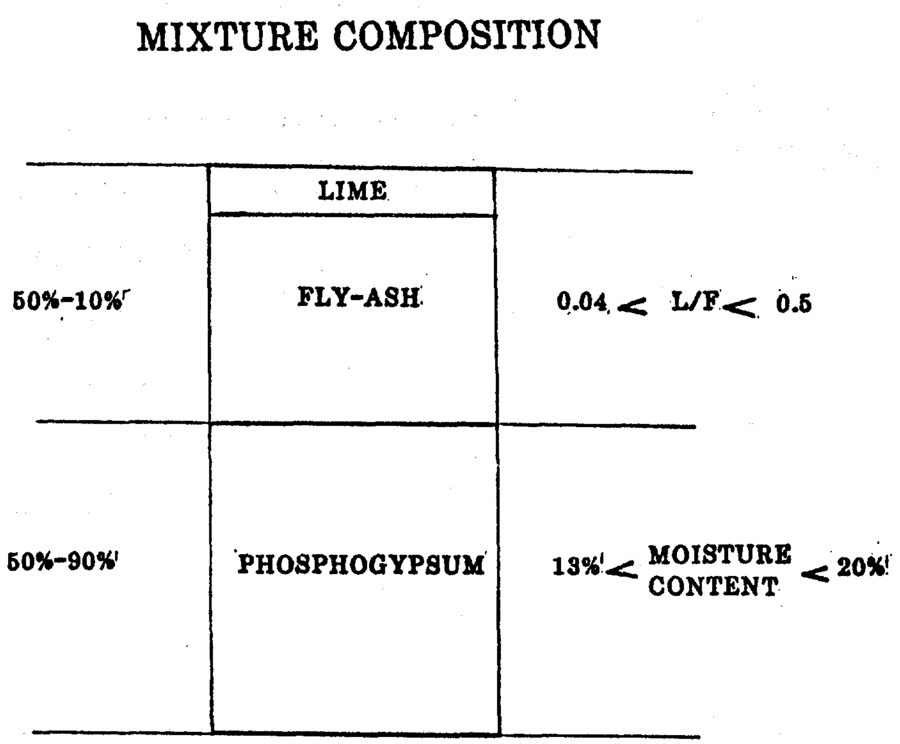

FIGURE 2

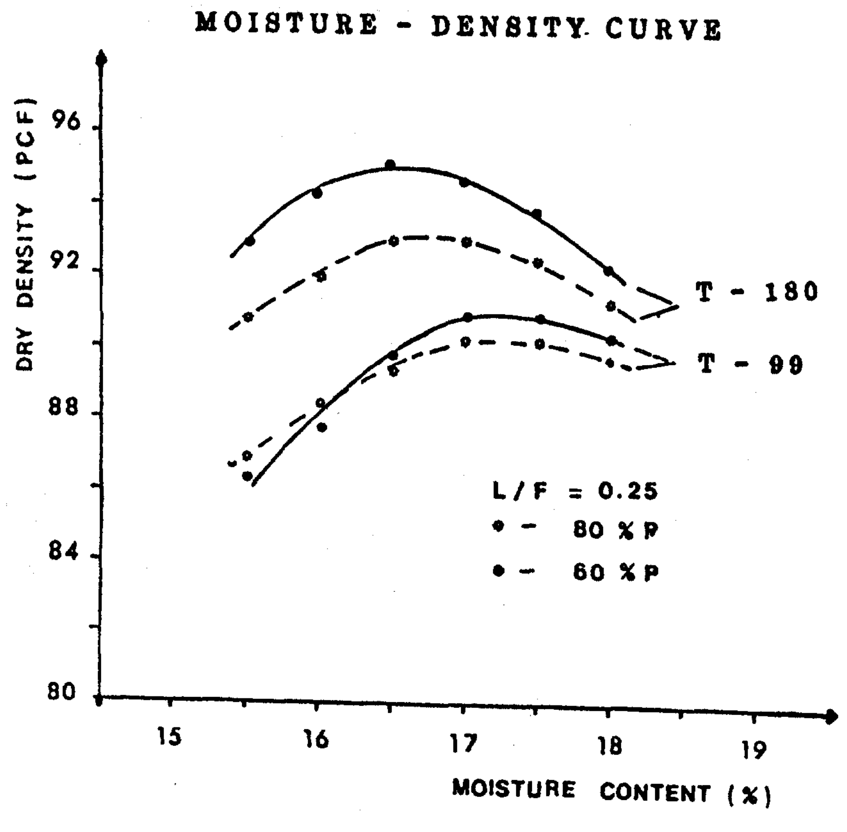

FIGURE 3

Specimens were prepared using either the Standard or Modified Proctor compaction methods. Different mixtures were prepared to obtain the optimum moisture content. Figure 3 shows typical moisture - density curves for both compaction methods. Optimum moisture contents ranged between 16.5% and 17.5% for different proportions of phosphogypsum and different lime to fly ash ratios. Subsequent specimens were prepared at the corresponding optimum moisture content .

Preparation moisture content is of fundamental importance in strength development. Figure 4 shows the effect of preparation moisture content on the compressive strength for a mixture with 60% phosphogypsum and a lime to fly ash ratio of 0.25. A distinctive peak is observed indicating the sensitivity of strength development to the preparation moisture content.

Cylindrical specimens 2" in diameter and 4" in length were compacted in plastic molds with an impact compactor. All specimens were wrapped in plastic sheets and cured at room temperatures until test time, unless otherwise stated. Unconfined compression tests were performed on all mixes for different curing periods.

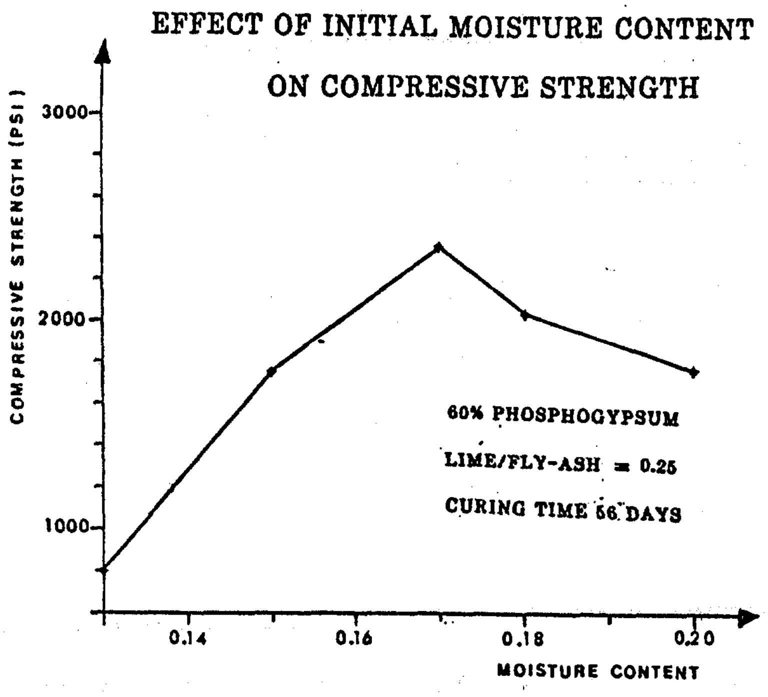

FIGURE 4

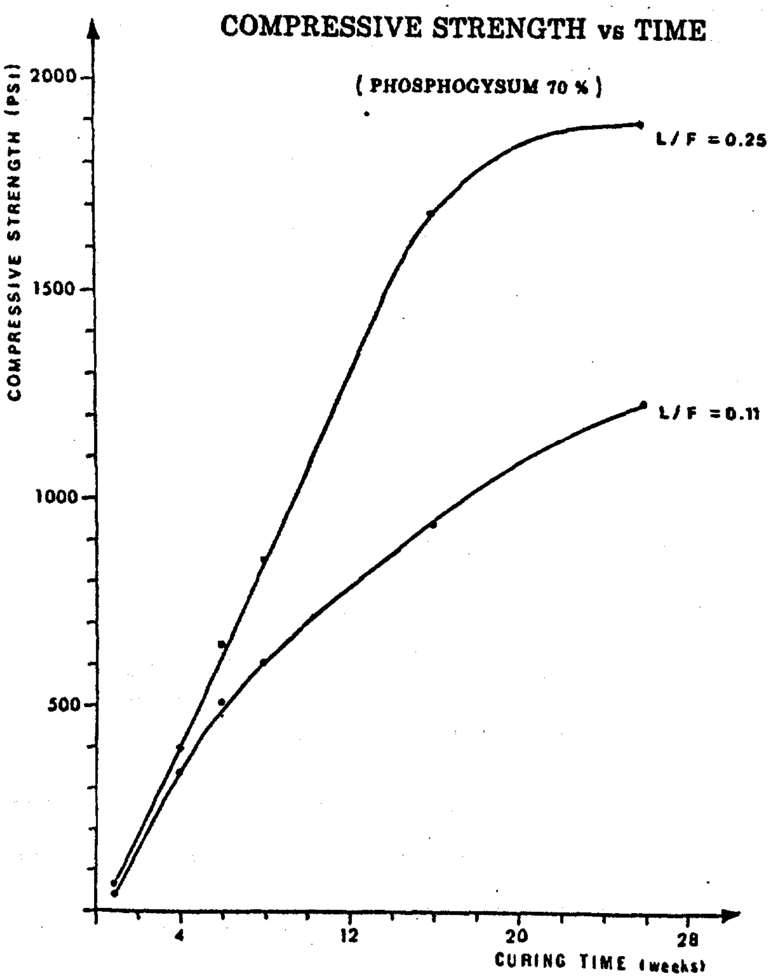

FIGURE 5

4.- PRESENTATION OF TEST RESULTS

The unconfined compression test was utilized to evaluate the different factors affecting the strength of LFP mixtures. The following results have been obtained from the average of three specimens for each point.

Compressive Strength vs. Time Curve

The time dependent reaction between lime and fly ash can be observed in figure 5 which represents two typical mixtures containing 70% of phosphogypsum and different lime to fly ash ratios. Compressive strength increases at a higher rate for the mixture with a lime to fly ash ratio of 0.25. Strength gains continue to occur even after 26 weeks of curing but at a decreasing rate. Specimens were compacted by the standard proctor compaction method and contained hydrated lime.

Lime to Fly Ash Ratio

One of the most important factors affecting compressive strength of a lime - fly ash mixture is their relative ratio. Several mixtures were prepared in order to determine the optimum L/F ratio. Lime to fly ash ratios varying between 0.04 and 0.50 were considered during the investigation. Figure 6 represents the relationship between the compressive strength and the lime to fly ash ratio of specimens prepared according to both standard and modified

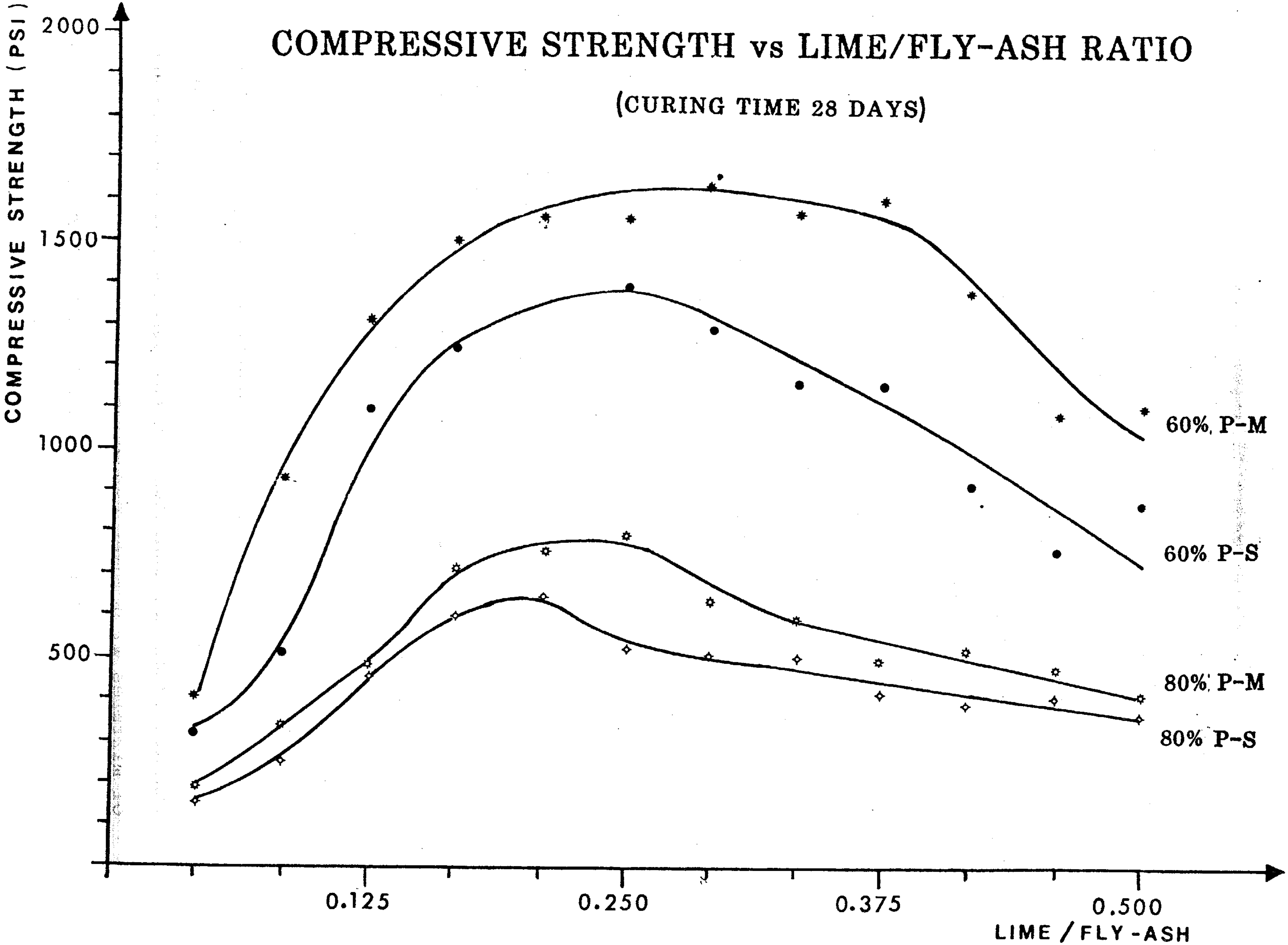
COMPRESSIVE STRENGTH vs LIME/FLY-ASH RATIO
(CURING TIME 28 DAYS)
COMPRESSIVE STRENGTH (PSI)
2000
1500
1000
500
0.125
0.250
0.375
0.500
LIME / FLY-ASH
60% P-M
60% P-S
80% P-M
80% P-S

FIGURE 6

proctor compaction methods and containing quick lime.

The analysis of these results reveals that the compressive strength of mixtures with higher amounts of phosphogypsum is more sensitive to the L/F ratio. Lime to fly ash ratios higher than 0.125 result in acceptable 28-day unconfined compressive strengths. A generalized optimum could be selected at a L/F ratio of 0.25 which will yield a conservative mixture and will be economical due to the relatively small amount of lime needed. Mixtures containing 60% of phosphogypsum require 8% of lime. The lime requirement is reduced to 4% when the amount of phosphogypsum is increased to 80%.

Effect of Compaction Energy

Specimens were compacted according to Standard and Modified Proctor specifications and tested at different curing time periods. The percentages of phosphogypsum considered in this research were of 60% and 80% as indicated in Figure 7. As expected, compressive strength increases with higher compaction energy.

Compressive strength of mixtures with high percentages of phosphogypsum is more suceptible to the different compaction energy applied. On the other hand, the strength of mixtures with lower percentages of phosphogypsum depends mostly on the cementitious agent and the difference in the

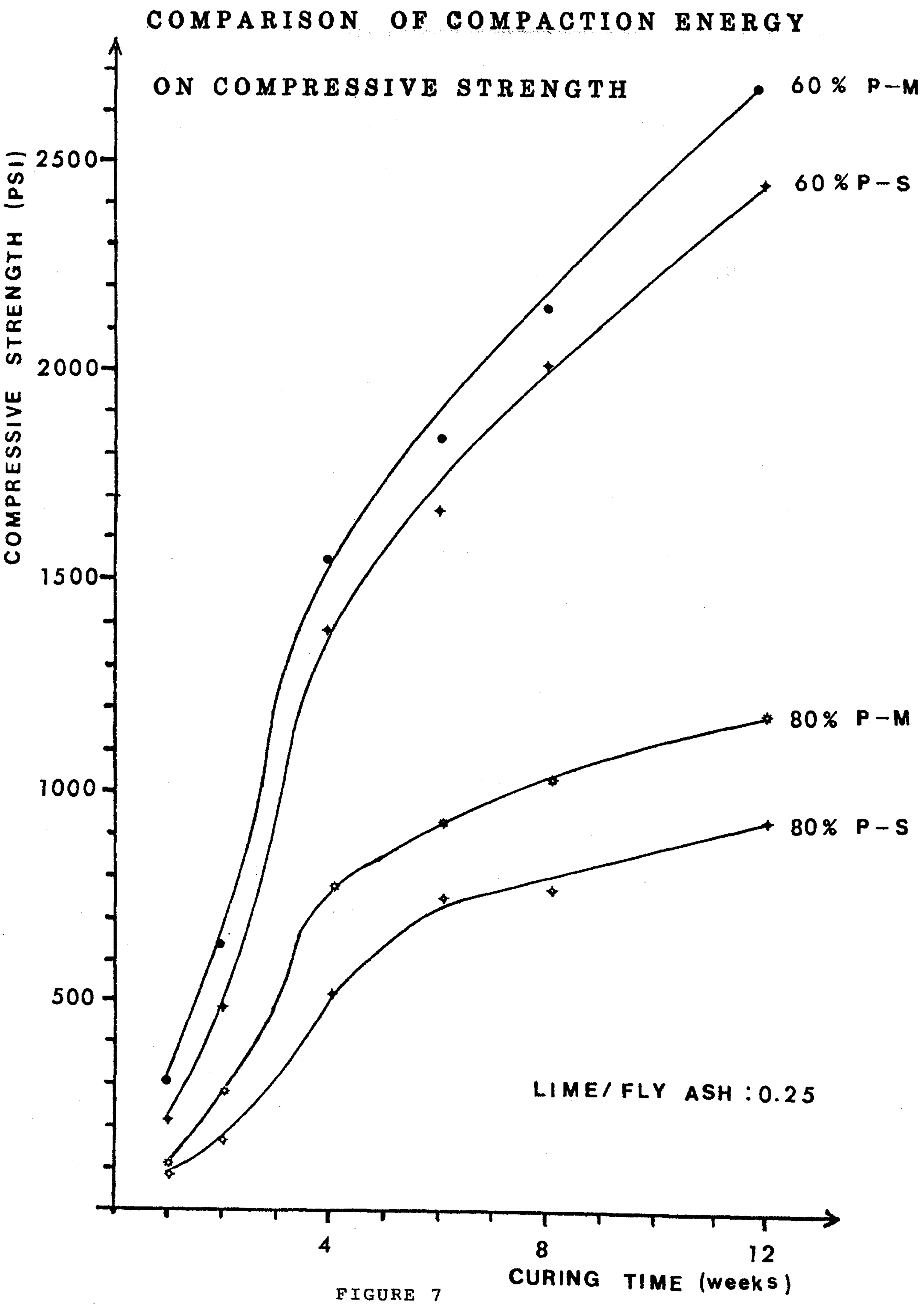
COMPARISON OF COMPACTION ENERGY
ON COMPRESSIVE STRENGTH
COMPRESSIVE STRENGTH (PSI)
2500
2000
1500
1000
500
4
8
12
CURING TIME (weeks)
60 % P-M
60 % P-S
80 % P-M
80 % P-S
LIME/ FLY ASH : 0.25

FIGURE 7

long term strength development of specimens compacted by the modified and standard proctor methods is approximately 10%.

Effect of Curing Conditions on Compressive Strength

Several mixes with different lime to fly ash ratios were tested after 130 days of curing to evaluate the performance of LFP mixtures under soaked conditions. Figures 8 and 9 represent the effect of different curing conditions on the compressive strength for mixtures containing 50% and 70% phosphogypsum. Soaking was achieved by submerging specimens in water for two days prior to testing. Tests were also performed on specimens dried for two days in an oven at a temperature of 40 degrees centigrade. The behavior of both mixes are very similar. A reduction in strength is observed in the soaked condition. Dry specimens developed an increase in strength. Specimens were compacted according to standard proctor compaction specifications and hydrated lime was used in these series.

5.- CONCLUSIONS

i) The compressive strength of LFP mixes increases with time. Results show that it continues to increase for more than six months after compaction.

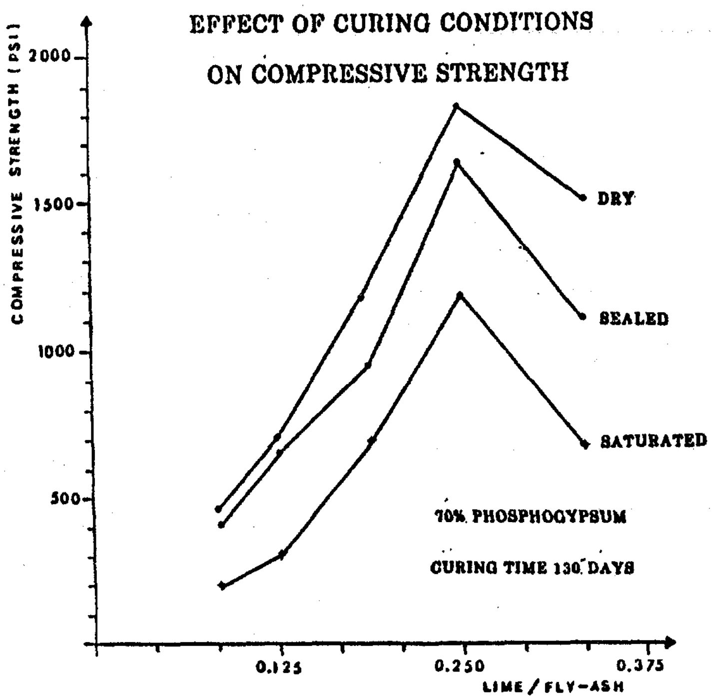

FIGURE 8

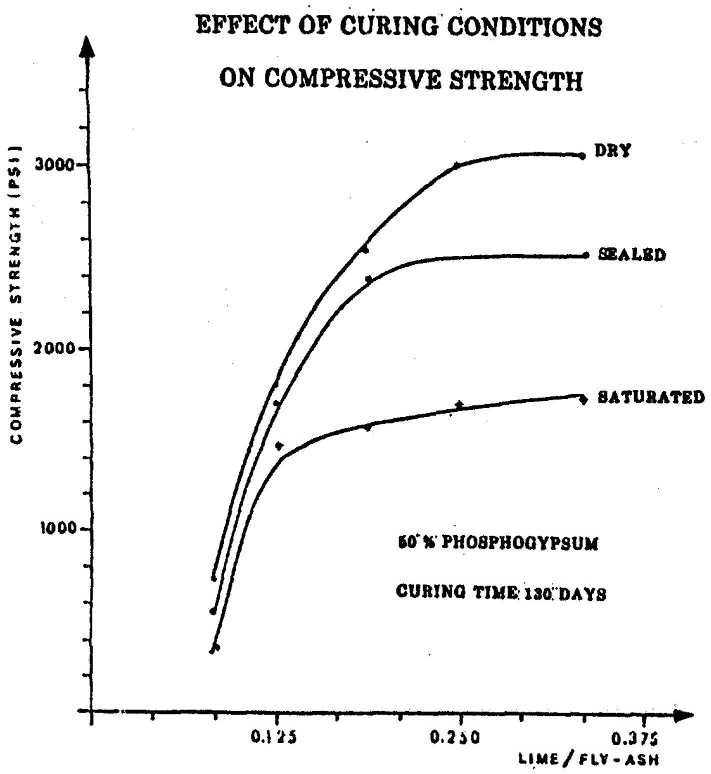

FIGURE 9

ii) LFP mixtures are very suceptible to preparation moisture content and sufficient moisture has to be provided in order to develop the lime - fly ash pozzolanic reaction Moisture contents lower than optimum should be avoided, as specimens' strength below optimum is more sensitive to moisture variations.

iii) Mixtures with high percentages of phosphogypsum are much more sensitive to the L/F ratio. The general optimum ratio is between 0.15 and 0.25. This provides, suficient lime to fully react with the fly ash.

iv) LFP mixtures are stable under soaked conditions. However a decrease in strength between 20% and 35% is observed as compared to the unsoaked condition.

vi) The moisture content of specimens at the time of testing has a great influence in the compressive strength.

vi) Mixtures with 80% phosphogypsum will provide suitable materials for base road construction, reaching 28-day strengths of over 500 psi.

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MICROWAVE AND THERMAL, RESISTANCE OVEN CALCINATION OF PHOSPHOGYPSUM

Antonio Nanni
Ph.D. Candidate, Dept. of Civil & Architectural Engineering,
University of Miami, Coral Gables, FL.

and

Wen F. Chang
Professor, Dept. of Civil & Architectural Engineering, and
Director, Phosphate Research Institute,
University of Miami, Coral Gables, FL.

ABSTRACT

Microwave and thermal resistance oven calcination of phosphgypsum, by-product of the wet phosphate industry, is studied in laboratory conditions. The effects of varying parameters such as calcination period, temperature (where applicable), amount of material and initial moisture are investigated. The raw material used in this study was supplied by six different producers. The cylinder compressive strength of calcined phosphogypsum is dependent on the source of supply, but the better qualities match the values of mineral gypsum (commercial plaster of paris). Microwave heating, tested up to a maximum period of 5 hours, is more effective than traditional heating in removing the free moisture content and also in the early calcination phase. In addition it speeds up the process and allows for considerable energy savings.

1. INTRODUCTION

Phosphogypsum, the by-product of the wet phosphoric acid industry, has the potential to be used as a viable building material. At present it is not considered economical by the manufacturing industry to substitute the waste for the mineral gypsum, due to the high cost of removing impurities not only present in the calcium sulphate crystals but also mixed with them. Such impurities are claimed to have detrimental effects on the quality of gypsum boards.

The scope of this paper is to present series of laboratory results on the conversion of dihydrate calcium sulphate to the hemihydrate form, by means of microwave and thermal resistance (convection) ovens. The attention of this study is focused on:

a) Dewatering (free moisture and chemically bound water removal)
b) Compressive strength of cylindrical specimens tested at various ages

c) Comparison between the effectiveness of the two heating methods

The experimental investigation is subdivided into three sections: microwave oven calcination, thermal resistance oven calcination and comparison between the two. The raw material used for most of this research was supplied by Agrico Chemical Co., Mulberry, Florida. Strength comparison of specimens prepared with waste material provided by six different phosphate producers is also presented in this study.

In the course of the article it is proved that, at least in terms of density, strength and setting time, calcined phosphogypsum from the wet process phosphate industry can be considered equivalent to mineral plaster of paris. Furthermore, the use of microwave oven for free moisture removal or partial calcination is very effective in the laboratory environment.

2. PHOSPHOGYPSUM AND CHEMISTRY OF CALCIUM SULPHATE

2.1 Production and Nature of By-Product Gypsum

In the wet process of production of phosphoric acid, ground phosphate rock is reacted with sulphuric acid and water to produce a slurry of phosphoric acid and by-product gypsum. For each ton of phosphoric acid there is a simultaneous production of 4.7 tons of waste gypsum. The gypsum by-product, discharged from the filter and slurried with water, is pumped to large piles, where the final moisture content stabilizes between 20% and 30%. The nature of the rock, the degree of digestion and filtration determine the chemical composition of phosphogypsum. Chemical analyses (2) show that approximately 93% of the waste material consists of gypsum ($CaSO_4.2H_2O$) and the remaining 7% is classified as impurities such as sand, phosphates, fluorides and organic constituents. Among the impurities, radium from the original ore, remains and coprecipitates with the calcium sulphate. The granular size also depends on the process and degree of grinding prior to the reaction. Size and chemical analyses indicate that the typical phosphogypsum particles are approximately 50-100 microns, the coarser sizes mostly consisting of silica sand and unprocessed ore, while the remaining impurities are concentrated in the fraction below 30 microns.

2.2 Hydratable Calcium Sulphates

When part of the total amount of crystalline water contained in gypsum ($CaSO_4.2H_2O$) is removed, the material becomes hydratable, i.e. the addition of free water to the powdered matter forms a paste or slurry which upon setting yields a solid mass of interlocking crystals of considerable strength. The two products of interest are the hemihydrate ($CaSO_4 . \frac{1}{2} H_2O$) , and the anhydrite ($CaSO_4$). The former is also known in the construction industry as plaster of paris and is prefered to the latter, whose reaction with water is much slower.

From an industrial point of view there are several methods to obtain hemihydrate from gypsum:

a) Thermal calcination. The most common and traditional technique, in which many types of kilns might be used (flash calciner, rotary, autoclave, etc.). The calcination conditions (temperature and pressure) affect the final characteristics of the product. A temperature of approximately 120°C is required to calcine pure gypsum into hemihydrate. Higher temperature will produce anhydrite, which becomes the stable composition for values above 250°C.

b) Addition of dilute sulphuric acid. A portion of water of crystallization is removed by adding dilute sulphuric acid. If the acid concentration is increased (up to 98%), anhydrite will result from the reaction.

3. EXPERIMENTAL WORK

3.1 Calcination by Microwave Oven

Microwave ovens function on the principle that certain materials (dielectric) heat up uniformly under the influence of high-frequency fields, by the rapid reversal of polarization of individual molecules which create internal friction and hence heat (4). Frequencies used by industrial equipment manufacturers are in the ranges from 13.56 to 27.12 MHz (RF= radio frequencies) and 896 to 2450 MHz (MW= microwaves) .

Although RF and MW heating rely on the same basic principle of generating molecular friction within receptive materials, they differ in the method of generating the operating frequency. The former is the more commonly adopted by manufacturers. A survey of industrial practice shows that microwave heating techniques are well established in various processes dealing with rubber and plastics, textile, wood and paper, food processing and ceramics. In most applications the major benefit of the technique is drying. In fact, water is sought out in preference to other materials so that a virtually uniform moisture removal, with a great reduction in time and energy use, is ensured. Ideally, the wave frequency should be matched to the material dielectric loss factor and therefore each application should be considered separately, provided band allocations for industrial usage are respected. The use of microwave heating in conjunction with a fuel-fired oven is also common practice.

Effectiveness of MW oven calcination was investigated after varying oven time, amount of raw material and initial free moisture content. The effect of these three parameters on amount of water removal and on unconfined compressive strength of specimens prepared with the calcined material was also studied. The MW oven used for this investigation had a 1.2 cu ft (0.03 m^3) capacity and was manufactured for domestic use. The cylinders for compression testing had a diameter of 2.0 in. (50.8 mm) and a height of 4.0 in. (101.6 mm). All, specimens were cast with a water/gypsum ratio of 0.5 and were subjected to high-frequency vibration to remove all voids for a period of 30 sec . Specimens were demolded the following day and cured under laboratory conditions at approximately 75°F (24°C) and a relative humidity of 65%. After capping, compression tests were conducted with a 10,000 lb (44.5 KN) capacity Universal Testing Machine. A thermocouple was used to measure the temperature of the material, when removed from the oven at predetermined intervals of time.

a) Effect of Oven Time.

Constant amounts of material weighing 7.5 lb (3.4 kg), with an initial moisture content of 1%, were calcined for various time periods ranging between 1 and 5 hours. Calcination had to be limited to a relatively short time, in order to prevent possible damages due to overheating of the MW oven designed for regular domestic use only. The amount of water removal, expressed as a percentage of the total dry weight, is plotted in Figure 1 as a function of the heating time. After approximately 45 min the material was completely dry, i.e. only the water chemically bound to the calcium sulphate remained at this point. After a period of 5, hours, 14.7% of the nominal 20.9%, total percentage of crystal water, had been driven off.

The rate of water loss, which represents the speed of water removal, is plotted as a function of oven time in Figure 2. Fran this Figure, it can be noticed that the most effective period for water removal is approximately between l/2 and 2 hours. The material temperature varied according to the calcination time. It should be observed that temperature measurement varied according to the recording position within the phosphogypsum mass. It was determined that the material core was approximately 15-20°C warmer than the corner positions when the gypsum was spread in a rectangular container. Figure 3 shows the highest corner-average reading approaching 218 °C, which indicates the probable presence of anhydrites at the time. Finally, the compressive strength values of specimens prepared with material calcined for 3, 4 and 5 hours are given in Figure 4 as a function of curing time up to 28 days. As expected, longest calcination period and curing yielded the highest strength value, up to 1666 psi (11.5 MPa).

b) Effect of Amount of Material.

The amount of material placed in the oven varied between 7.5 and 1.5 lb (3.4 and 0.7 kg). As expected, drying time decreased with decreasing the amount of material as shown in Figure 5. This leads to conclude that calcination is directly proportional to wave emission power per weight of phosphogypsum in oven. The effects of varying the amount of material on gypsum temperature and 14-day compressive strength are presented in Table 1.

Figure 1

Water Loss Vs. Time In Microwave Oven.

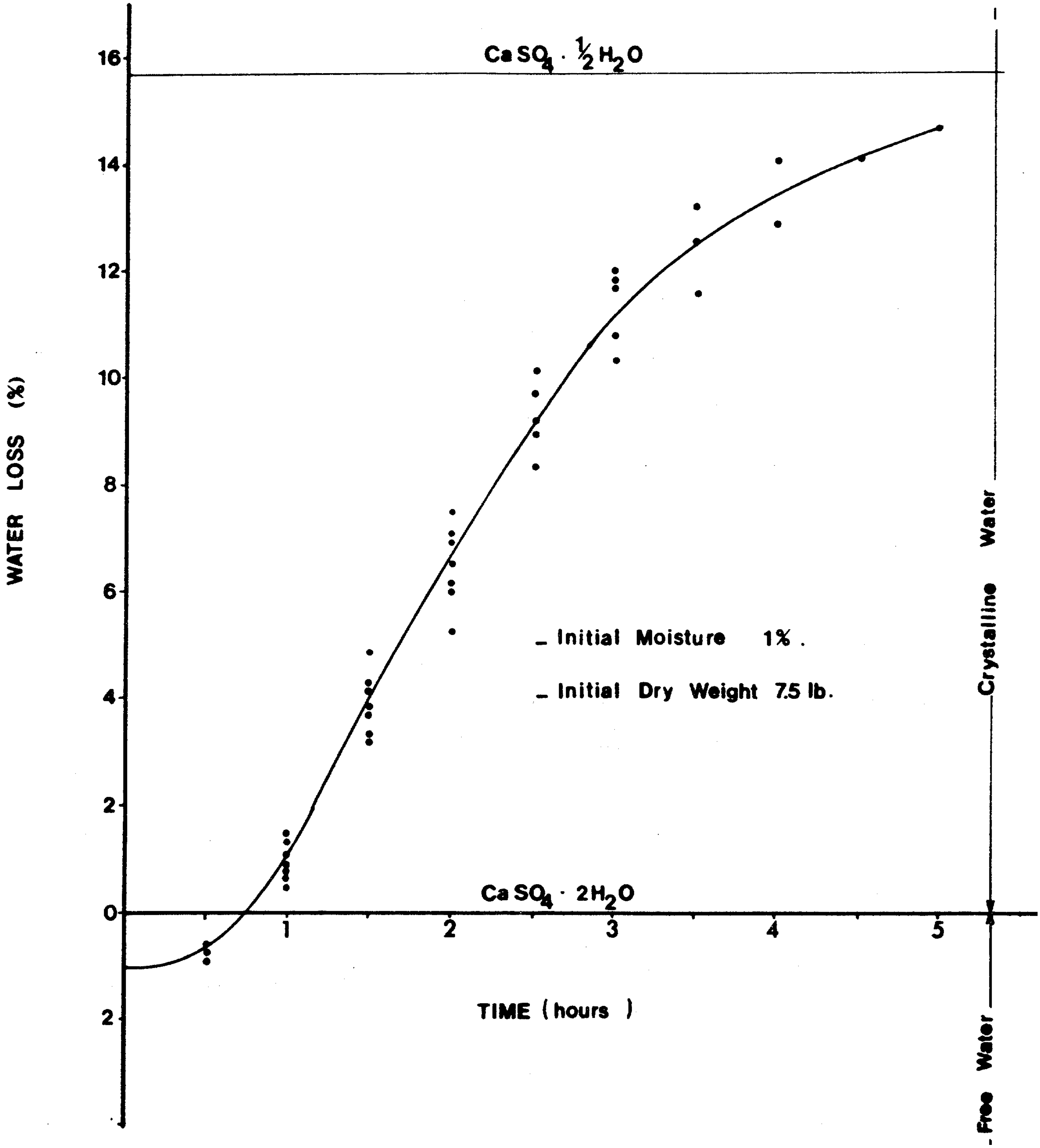


Figure 2

Rate Of Water Loss Vs. Time In Microwave Oven.

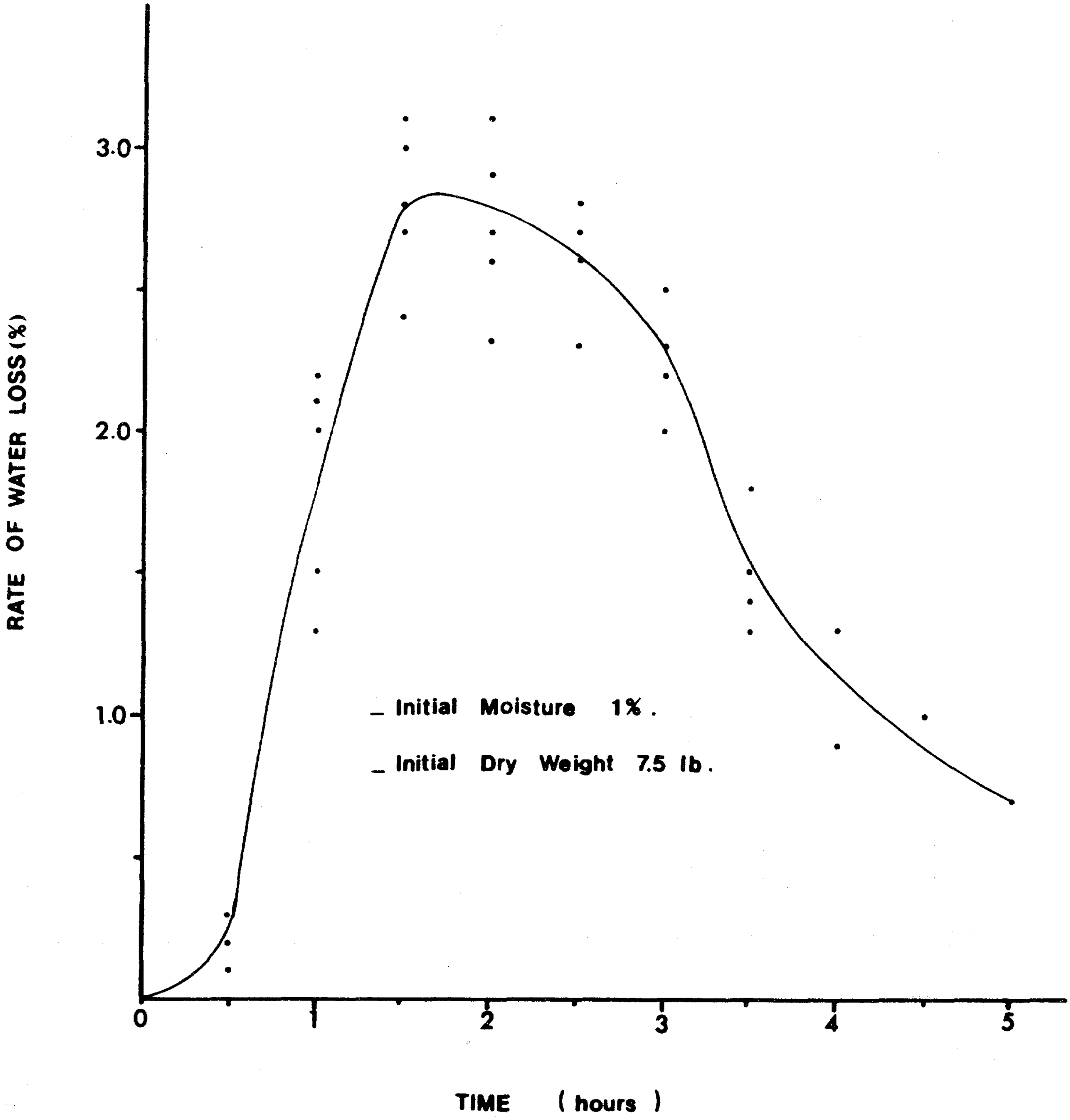


Figure 3

Material Temperature Vs. Time In Microwave Oven.

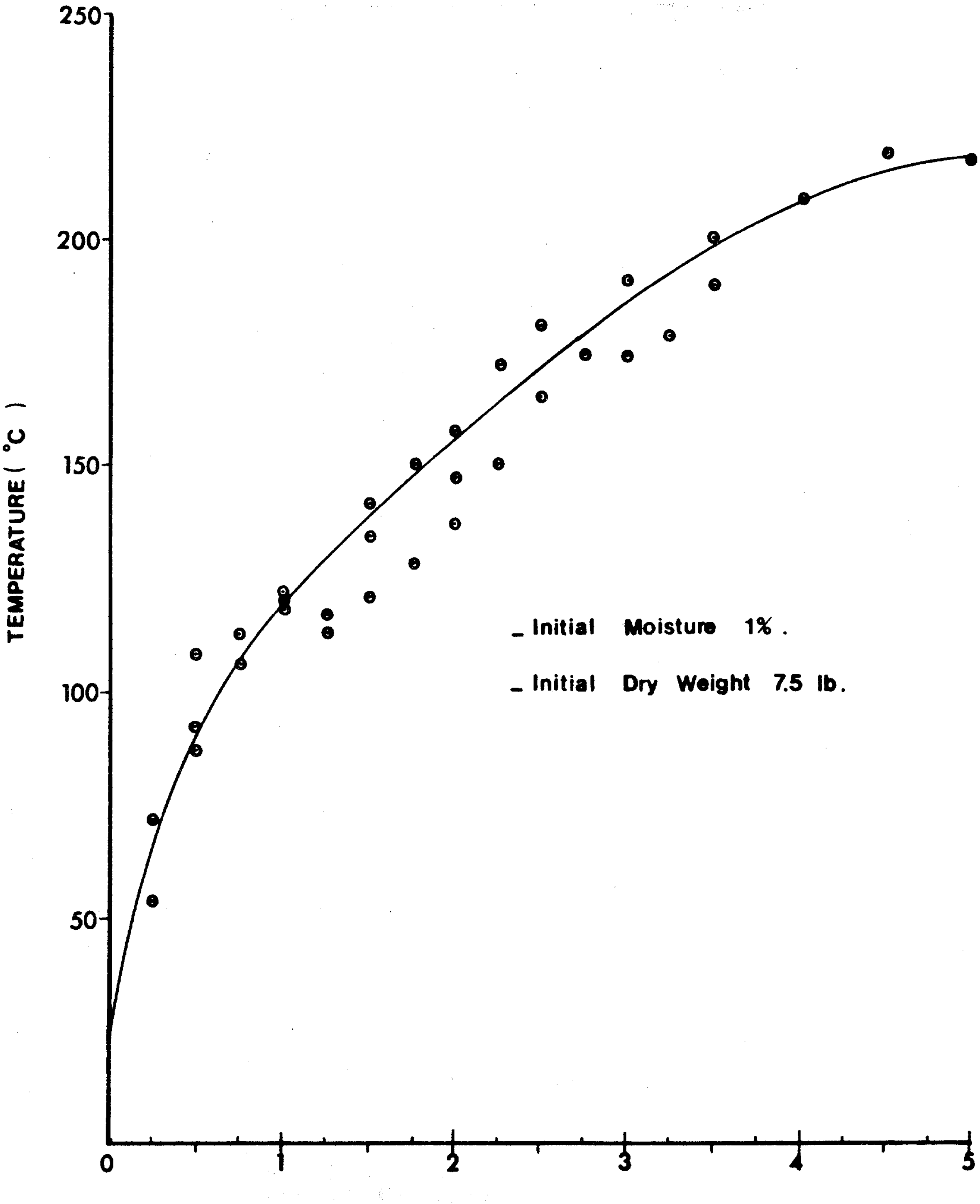


Figure 4

COMPRESSIVE STRENGTH VS SPECIMEN AGE FOR DIFFERENT CALCINATION PERIODS IN MICROWAVE OVEN

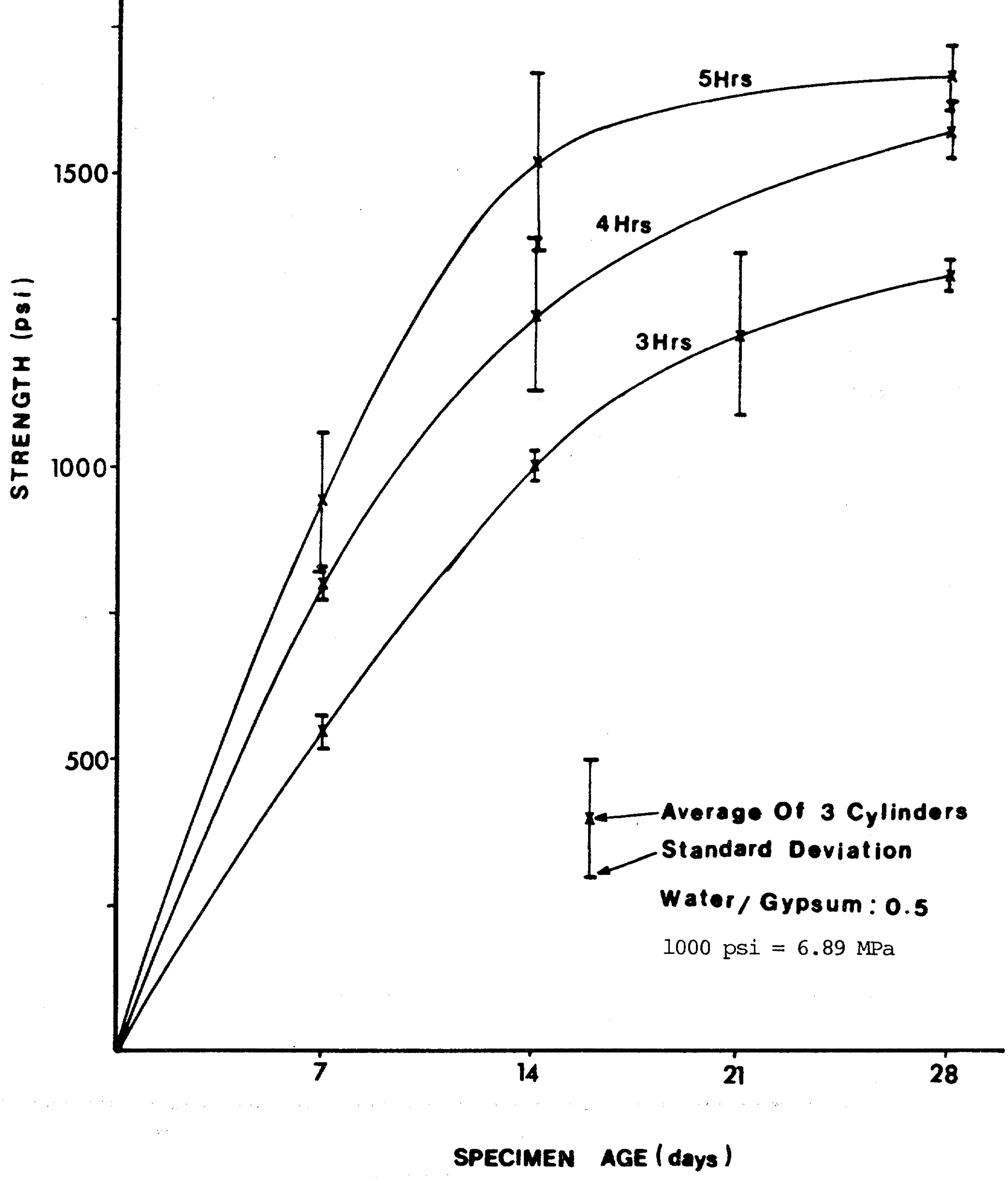


Figure 5

Water Loss Vs. Time In Microwave Oven For Different Initial Dry Weight.

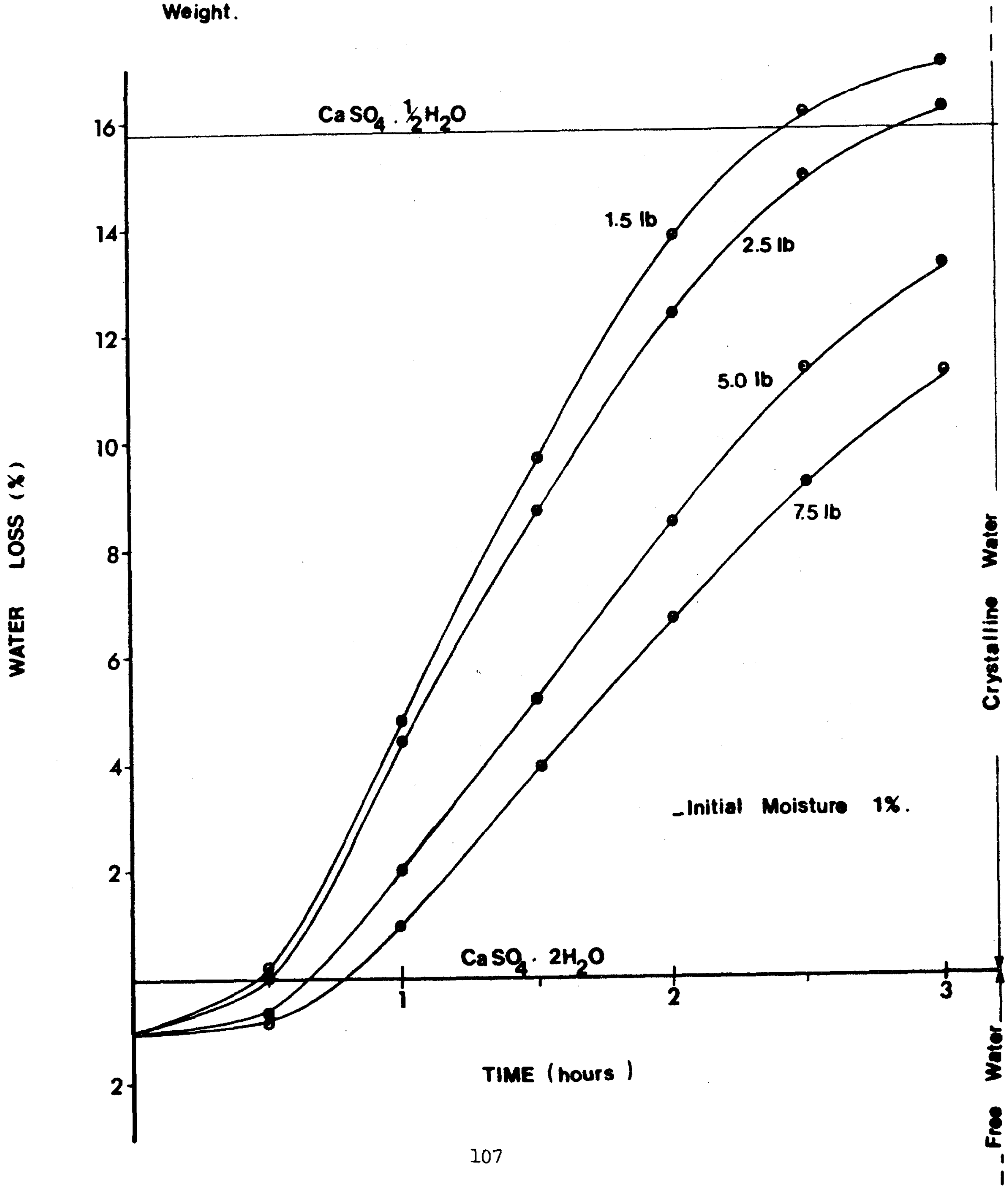


Table 1: Control Parameters for Samples of Different Weight Calcined in a Microwave Oven for 3 Hours

Amount of Material (lb)	Temper. @ 3 hrs (°C)	Crystal Water Loss (%)	14-day Strength (psi)
1.5	275	17.1	n/a
2.5	245	16.2	1535
5.0	185	13.3	1168
7.5	183	11.3	1008

Note: 1000 psi=6.89 MPa

c) Effect of Initial Material Moisture.

The higher the initial free water content, the longer the time to completely remove it. This hypothesis was confirmed when the effect of varying the initial moisture content from 1% to 30% was investigated. The results are summarized in Table 2, where for a calcination period of 3 hours the 14-day compressive strength decreased 7.6 times, when the initial moisture increased from 1% to 30%. It should be indicated that phosphogypsum stacks contain between 20% and 30% of free water; therefore, this phase of the study is of great importance in practical applications.

Table 2: Control Parameters for Samples of Different Initial Moisture Calcined in Microwave Oven for 3 Hours

Moisture Content (%)	Temper. @ 3 hrs (°C)	Crystal Water Loss (%)	14-Day Strength (psi)
1	183	11.3	1008
10	173	9.5	555
20	168	7.3	249
30	157	5.8	132

Note: 1000 psi=6.89 MPa

3.2 Calcination by Thermal Resistance Oven

The thermal resistance oven used during the experimental work had a capacity of 2.8 cu ft (0.07 m3) and a temperature selection range up to 300°C with a sensitivity of ±2°C. General procedures and specimen preparation techniques have already been described in the previous section. During the course of the study three parameters, namely: sample origin, heating temperature and period, were varied and their effect on compressive strength was monitored.

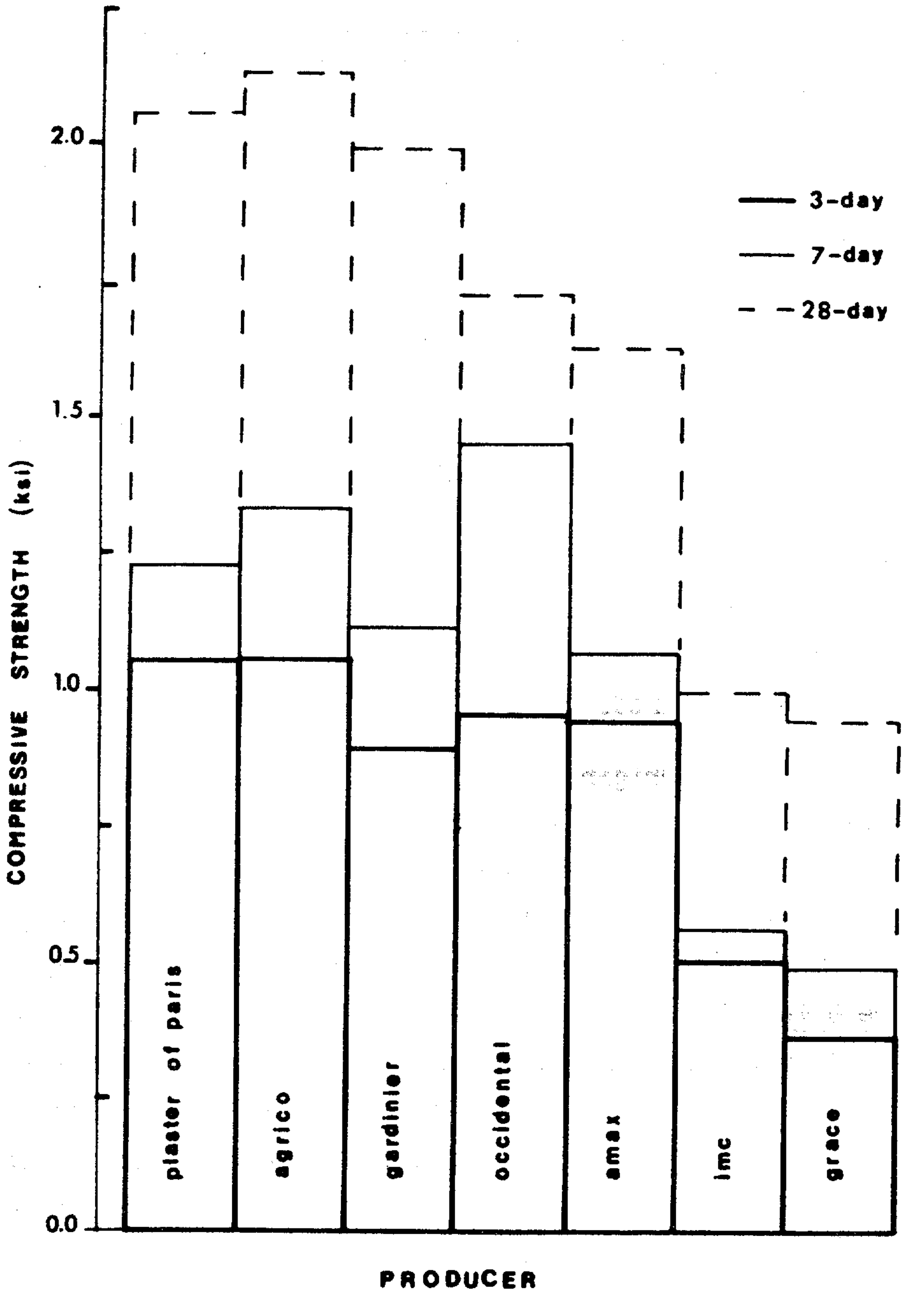
a) Effect of Sample Origin.

Samples of dihydrate phosphogypsum from different producers, received without specification of age and position in the stack, were calcined for a period of 24 hours at a temperature of 175°C. The 3, 7 and 28-day strength of the different samples is shown in Figure 6 together with values obtained for commercial plaster of Paris. It is found that there was a great difference between producers, unfortunately it could not be established if the variations were enhanced by phosphogypsum age and position in the pile. The strength of commercial plaster of paris is almost equivalent

Figure 6

Cylinder Compressive Strength at 3, 7 and 28 Days vs. Producer

Calcination at 175°C for 24 hrs
Water/Gypsum : 0.5
1.0 ksi = 6.89 MPa



to the best phosphogypsum batches and no difference was noticed in the setting time, which for all mixes, was approximately 5 to 8 minutes. In addition, the dry density of phosphogypsum is approximately 80 lb/cu ft (1283 kg/m^3), while plaster of paris yields a slightly higher value of 82 lb/cu ft (1315 kg/m3).

b) Effect of Temperature.

The 3, 7 and 28-day compressive strength, as a function of oven temperature for a calcination period of 24 hrs, is presented in Figure 7. For this assigned period, the highest compression values are obtained at 175°C. The curves have the expected bell shape to indicate that for low temperatures some calcium sulphate is still dihydrate, while at high values some has become anhydrite.

c) Effect of Time.

The 7-day compressive strength, of material calcined at various temperatures, is given in Figure 8 as a function of oven time. This diagram suggests some interesting results: the low temperature shows a continuously increasing curve, indicating that with time all molecules loose their crystalline water. Medium temperatures show a flat peak, indicating that the transition di-hemi-anhydrite is continuous. Finally, high temperature tests show a steep peak and strength values are lower than in previous cases.

3.3 Comparison between Oven Types

A comparison of the results presented in the previous two sections shows that the MW oven is more effective than the convection oven particularly in removing high quantity of free moisture. This conclusion is visualized by the slope of the curves presented in Figure 9, where water loss is plotted as a function of time for samples with different initial moisture content using both ovens. Specimen temperature variations are given in Figure 10 showing again the more rapid effect of MW oven. However, the development of relatively high temperatures in microwave oven (see Figure 1) leads to the formation of anhydrite, which explains the limited gain in strength when extending calcination from 4 to 5

Figure 7

Cylinder Compressive Strength at 3, 7 and 28 Days vs. Oven Temperature for a 24-hr Calcination Period

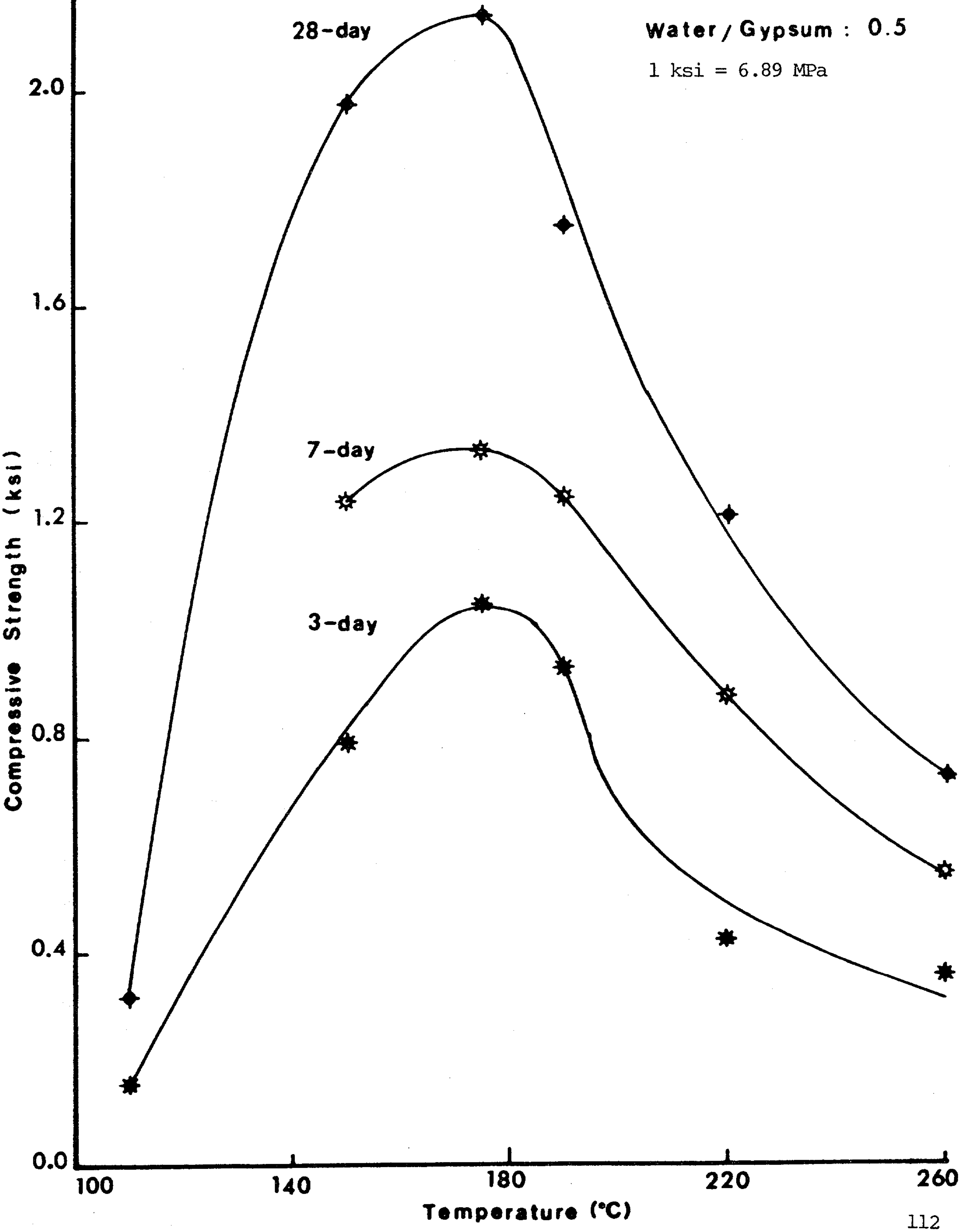


Figure 8

Cylinder Compressive Strength at 7 Days vs. Oven Time for Different Calcination Temperature

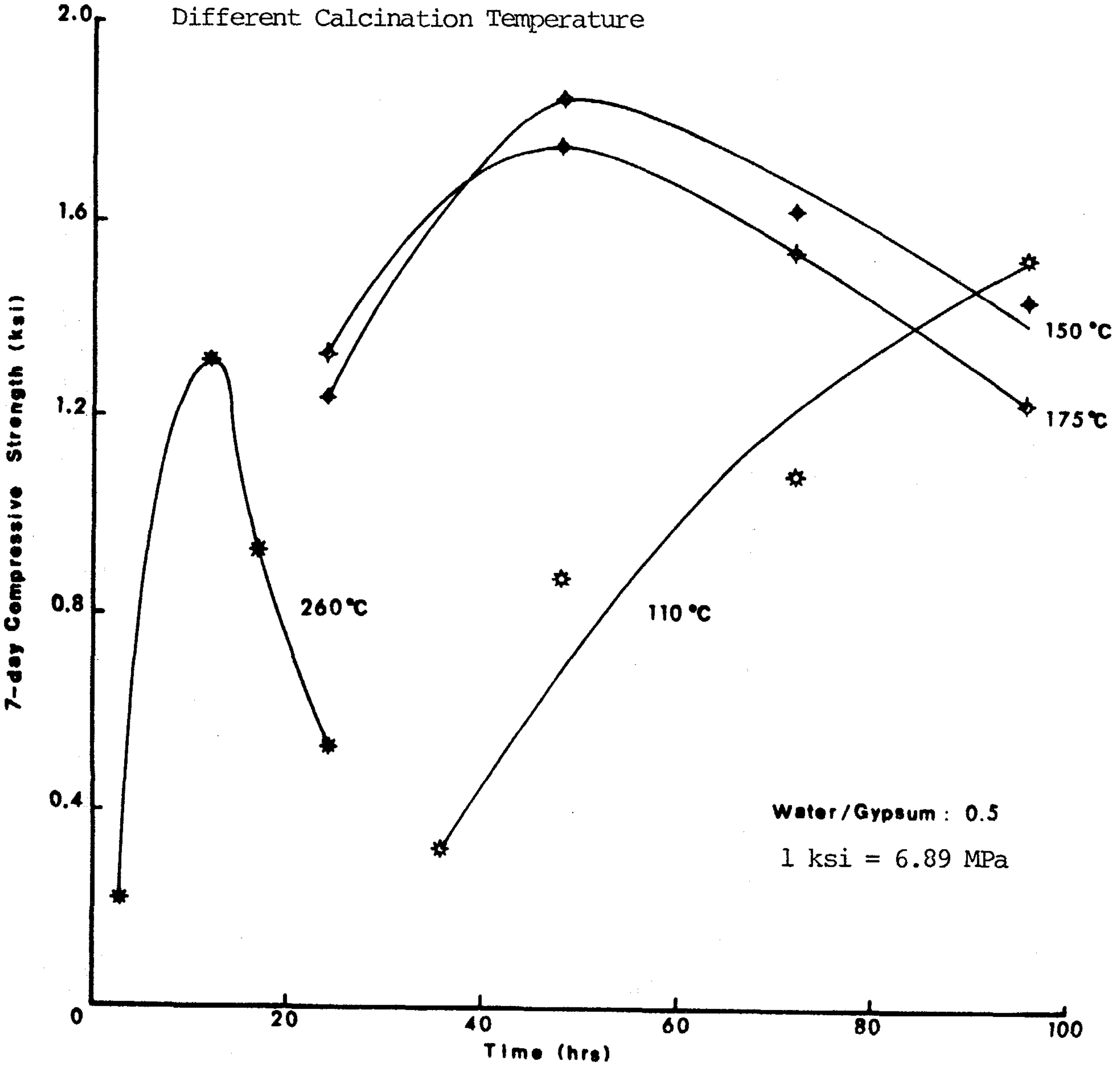


Figure 9

Water Loss Vs. Time In Microwave Or Regular Oven For Different Initial Moisture Content.

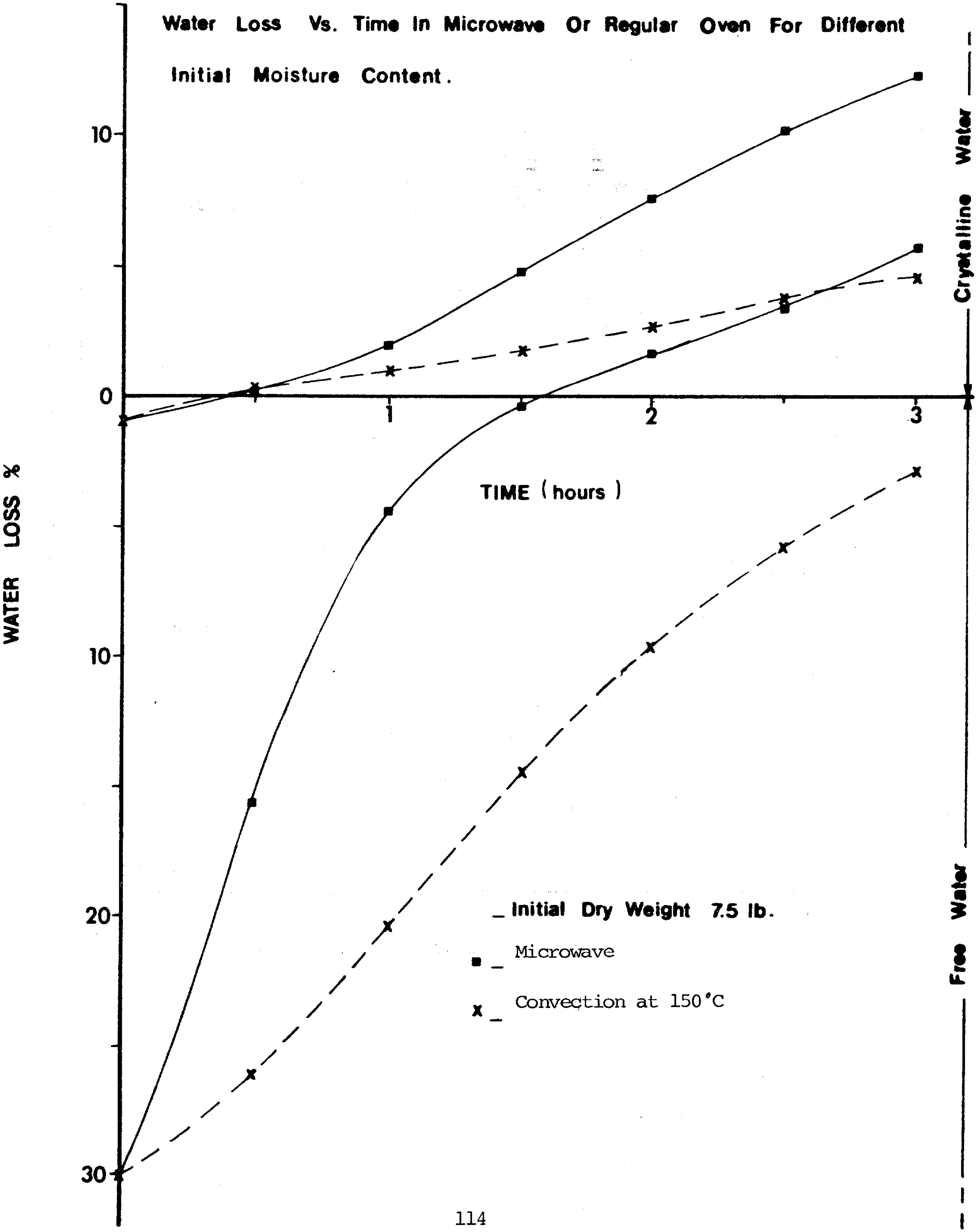
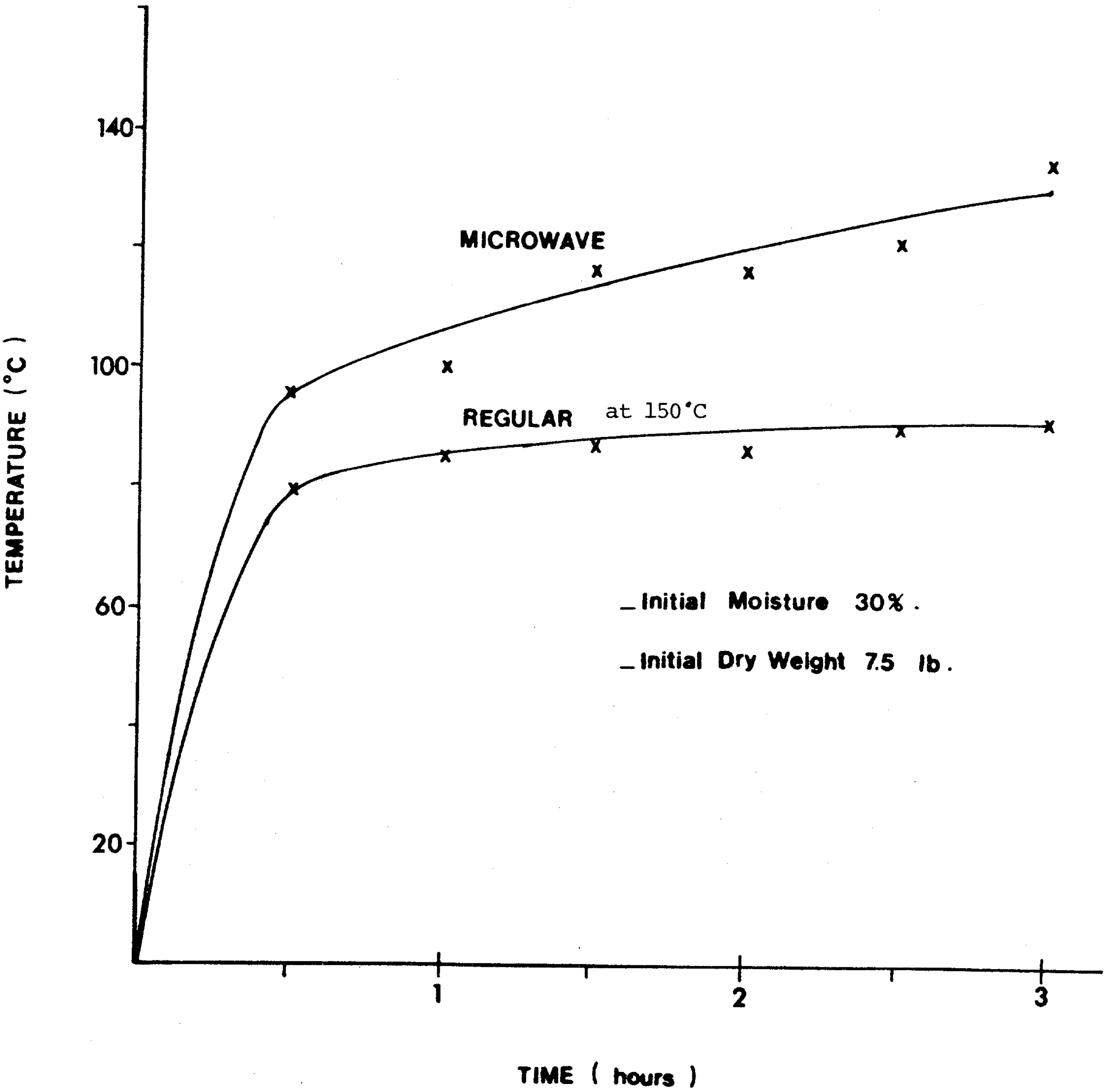


Figure 10

Material Temperature Vs. Time In Microwave And Regular Oven.



hrs (see Figure 4) . Finally, the results arranged in Table 3 indicate that microwave is not only faster, but allows for consistent energy savings.

Table 3: Comparison between Microwave and Thermal Resistance Oven (7.5 lb of Material at 1% Initial Moisture).

Oven Type	Temper. (°C)	Time (hrs)	28-day Strength (psi)	Energy Consumpt. (kJ)
Microwave	not-cnst.	4	1550	18,000
Microwave	not-cnst.	5	1650	22,500
Convection	175	12	1412	34,560
Convection	150	24	2008	62,280

Microwave : 0.03 m^3, 120 V, 60 Hz, Domestic Use
Convection: 0.07 m^3, 120 V, 60 Hz, 1600 W, Forced Draft
1000 psi=6.89 MPa

4., CONCLUSION

Laboratory calcination of phosphogypsum yields results that are comparable with commercial plaster of paris in terms of density, compressive strength and setting time.

Microwave ovens could represent an alternative or a supplement to thermal resistance oven calcination. MW ovens dry the free water more rapidly and uniformly, particularly for high initial moisture contents. The reduction in operating time is accompanied by energy savings.

ACKNOWLEDGEMENTS

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

The cooperation of the six phosphate producing companies (Agrico, Amax, Gardinier, Grace, IMC and Occidental), which supplied the raw material, is greatly appreciated.

The authors also wish to extend their appreciation to M. Alfagiri, M. Badaoni, G. Beltran, G. Boisson and C. Chabbi, who enthusiastically contributed to the data collection.

APPENDIX.-REFERENCES

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ABACA FIBER REINFORCED PHOSPHOGYPSUM CONCRETE PANELS

Selcuk Yetimoglu
Engineer, Herbert S. Saffir, Consulting Engineer
Miami, Florida

and

Wen F. Chang
Professor, Dept. of Civil & Architectural Engineering, and
Director Phosphate Research Institute,
University of Miami, Coral Gables, FL.

ABSTRACT

This paper presents the results of an experimental study to investigate the possibilities of utilization of phosphogypsum, a by-product of the phosphate industry, in the production of thin concrete panels reinforced with abaca vegetable fibers. The effects of varying the phosphogypsum content on the properties of concrete were examined. The phosphogypsum concrete properties investigated were flexural, tensile and compressive strengths, energy absorption capacity, toughness, maximum post-cracking load, and unit weight. In particular, the flexural behavior of abaca fiber reinforced phosphogypsum concrete panels was extensively studied.

Panels and cylinders were cast using 16 different concrete mixes consisting of portland cement, phosphogypsum, sand, abaca fiber and water. These mixes consisted of varying amounts of fiber, phosphogypsum and water contents, and panel thickness. Specimens were tested in bending, tension and compression. Fiber content ranged from 0.0 to 0.8% of the total weight. Phosphogypsum content varied from 0.0 to 75% and water/(cement + phosphogypsum) ratio varied from 0.46 to 0.60. Tested panel thicknesses were 3/8 in., 1/2 in. and 5/8 in.

Test results indicate that phosphogypsum can be used in concrete as a fine aggregate. High strength capacity can be obtained when phosphogypsum in a mix is less than 50% of the total solid weight. Phosphogypsum increases the mixing water demand and reduces the unit weight of concrete.

1. INTRODUCTION

Pollution abatment and preservation of natural areas for a variety of activities are key conservation issues that have had an important impact on phosphoric acid industry and the utilization of by-product materials.

An extensive study on utilizing phosphogypsun for building and marine applications and for highway base course has been underway at the University of Miami since 1981. In this particular study, fibrous phosphogypsun concrete consisting of portland cement, phosphogysum, sand and short randomly distributed abaca fibers was developed.

A lightweight concrete with fairly good structural properties can be produced with the combination of fiber reinforcement and phosphogypsum. The primary benefit of fiber inclusion is seen in the postcracking behavior even if plain concrete can reach higher strength values. Fibers affect the materials after cracking occurs, by bridging cracks, such that concrete does not fail in a brittle fashion. Therefore, fibers make concrete pseudo-ductile and increase its toughness.

The work reported herein consists of an experimental study of the flexual behavior of fibrous phosphogypsum concrete panels. Compressive and splitting tensile strengths of each concrete mix used in panel construction have also been obtained and analyzed.

2. MATERIALS

Phosphogypsum: The phosphogypsum used in the preparation of the complete set of specimens was supplied by the Agrico Chemical Mining Co., Mulberry and Gardinier Inc., Tampa, Florida. Phosphogypsum, a by-product of the phosphate industry, results from extracting phosphoric acid from the phosphate rock. Central Florida is the location of the phosphate industry where the resulting by-product, phosphogypsum, has been piling up for years. It is reported that there are over 400 million tons of phosphogypsum in existing piles.

Phosphogypsum used throughout the experiments was sieved and stored in a sealed drum. Its moisture content was in a range between 18 and 19 percent.

Cement: Portland cement type I was used throughout the experimental program.

Sand: The sand used throughout the test program was concrete sand passing sieve no. 10, and commonly available in south Miami quarries. Its moisture content ranged between 5.0 and 6.0 percent, based on readings before mixing.

Abaca Fiber: Abaca fiber is a very strong vegetable fiber produced in very large quantities in countries such as the Philippines and Ecuador. It is obtained from the plant called Musa Textiles, belonging to the

Banana family. Abaca fibers were cut into 2 in. long pieces, a desirable length for phosphogypsum concrete mix,

3. MIXES

In this experimental study, 16 different mixes were made as shown in Table I. Mixes were prepared changing the following variables:

(a)Fiber content: Four mixes with different fiber contents as shown in Mix Nos. 6,7,8 and 13 were made to observe the effects of varying fiber content in phosphogypsum concrete. Fiber amounts used in the mixes were 0.0 , 0.4 , 0.6 and 0.8 percent of the total dry weight while the mix proportions, the water/(cement + phosphogypsum) ratio and thickness of panels were kept constant.

(b)Phosphogypsum content:

(i) Four mixes with different phosphogypsum contents (Mix Nos. 6, 14, 15 and 16) were made to observe the effects of varying phosphogypsum content in the phosphogypsum concrete while the cement content, the amount of aggregates (sand + phosphogypsum), the water/(cement + phosphogypsum) ratio and thickness of panels were kept constant. The amount of phosphogypsum used in the mixes was 0, 25, 50, and 75 percent of the total dry weight.

(ii) Four mixes with different phosphogypsum contents, as shown in Mix Nos. 2, 3, 5 and 6, were also compared. The water/(cement + phosphogypsum) ratio and thickness of panels were kept constant in these mixes. The phosphogypsum content used in the mixes was increased from 33.3 to 66.7 percent while both cement and sand contents were decreased from 33.3 to 16.7 percent.

(c)Water/(cement + phosphogypsum) ratio: Five mixes with different water /(cement + phosphogypsum) ratios as shown in Mix Nos. 1, 4, 9, 11, and 12 were compared. Water/(cement + phosphogypsum) ratio was varied from 0.46 to 0.60 while the mix proportions, the fiber content and the thickness of panels were kept constant.

(d)Panel thickness: Tested panel thicknesses were 3/8", 1/2" and 5/8"

TABLE 1 - LIST OF MIXES

Mix Number	Mix proportion (Cement:Sand: Phosphogypsum)	Fiber content $\frac{\text{Fiber weight}}{\text{Total weight}}$ (%)	$\frac{\text{Water}}{\text{Cement+Phosphogypsum}}$	Thickness of panels (in.)	Curing period (days)
1	1:1:2	0.4	0.46	1/2	20
2	1:1:3	0.4	0.50	1/2	20
3	1:1:1	0.4	0.50	1/2	20
4	1:1:2	0.4	0.52	1/2	20
5	1:1:4	0.4	0.50	1/2	20
6	1:1:2	0.4	0.50	1/2	20
7	1:1:2	0.6	0.50	1/2	20
8	1:1:2	0.8	0.50	1/2	20
9	1:1:2	0.4	0.50	3/8	20
10	1:1:2	0.4	0.50	5/8	20
11	1:1:2	0.4	0.55	1/2	20
12	1:1:2	0.4	0.60	1/2	20
13	1:1:2	-	0.50	1/2	20
14	1:2:1	0.4	0.50	1/2	20
15	1:0:3	0.4	0.50	1/2	20
16	1:3:0	0.4	0.50	1/2	20

as shown in Mix Nos.6,9 and 10. The fiber content, water/(cement + phosphogypsum) ratio and mix proportions for the panels were kept constant.

4. TEST SPECIMENS

The dimensions of the fiber reinforced phosphogysum concrete panels tested were 28 in. long and 6 in. wide. Panel thicknesses were 3/8 in. , l/2 in. and 5/8 in. Cylindrical specimens used to determine compressive and splitting tensile strengths of phosphogypsum concrete were 2 in. in diameter and 4 in. in height.

5. TYPE OF TEST

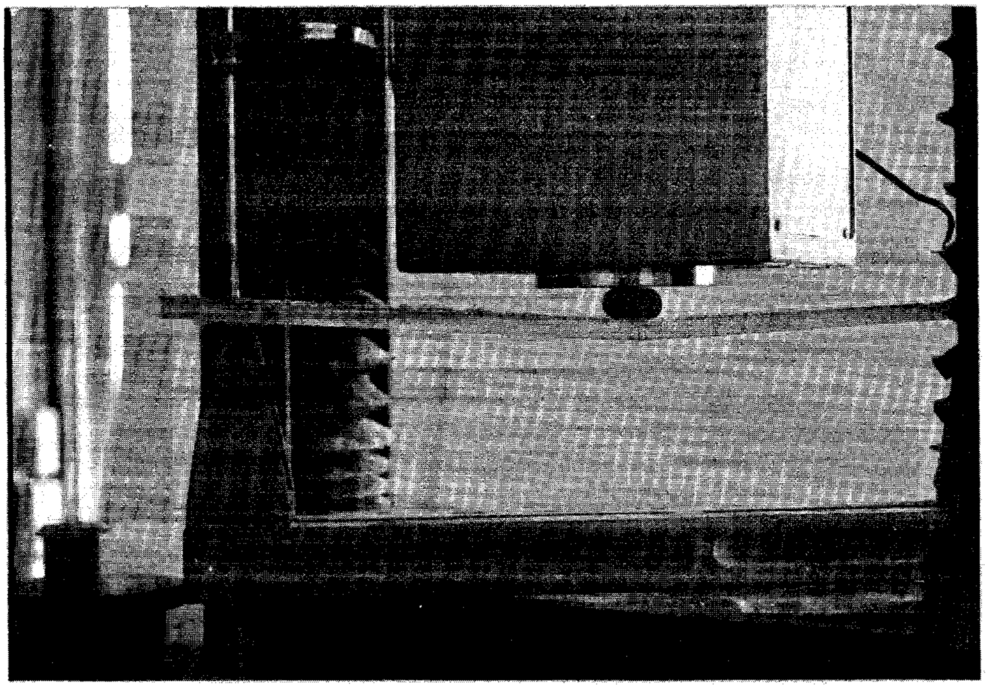
Three different tests were performed during this experimental study.

l.)Bendinq Test: Tested panels were simply supported and subjected to a concentrated load applied at midpoint of the 24 in. long span as shown in Figures 1 and 2. The main purpose of the bending test is to determine the flexural strength, energy absorption capacity, toughness and maximum postcracking load of fibrous phosphogypsum concrete for different mixes with varying phosphogypsum and fiber contents.

Flexural strength is expressed in terms of the modulus of rupture. Its computation is based on the assumption that fiber reinforced phosphogypsum concrete is a linear elastic material up to the moment of failure.

Energy absorption capacity is the ability of the material to absorb energy in the plastic range and is an indication of the degree of occurrence of crack propagation. For evaluating test results, the area under a load- deflection curve up to 0.75 in. of central deflection was considered as the measure of energy absorption capacity for evaluating test results. Load-deflection curves for fiber reinforced phosphogypsum concrete panels are shown in Figure 3.

Toughness index is another parameter related to energy absorption measurements. It is calculated as the area under a load-deflection curve up to 0.75 in. of central deflection, divided by the area under the



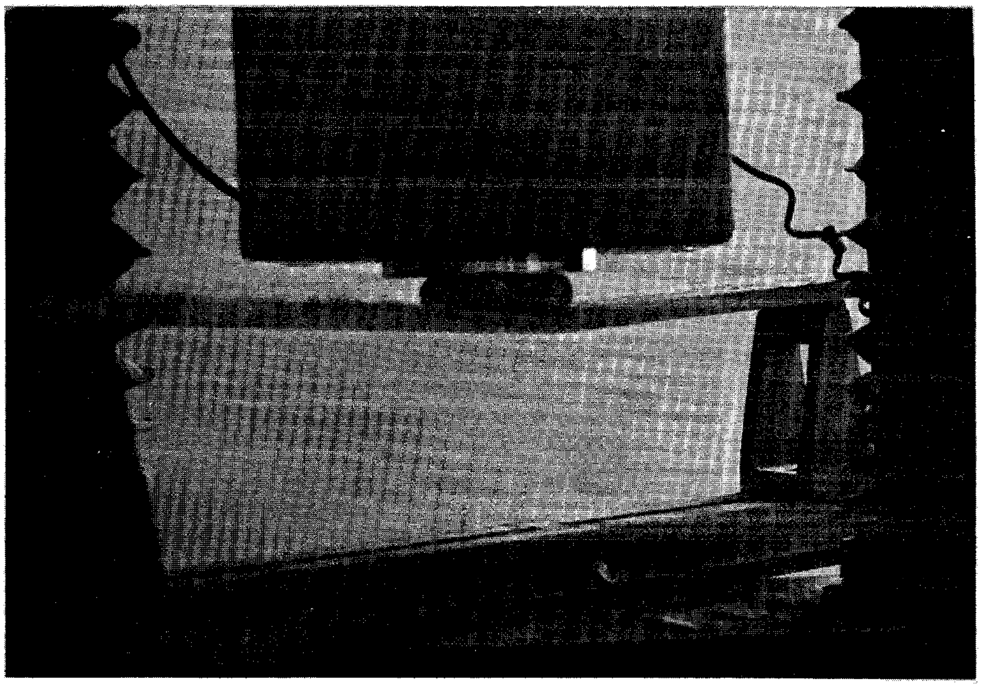


FIG. 3.6- FIBROUS PHOSPHOGYPSUM CONCRETE PANELS IN BENDING.

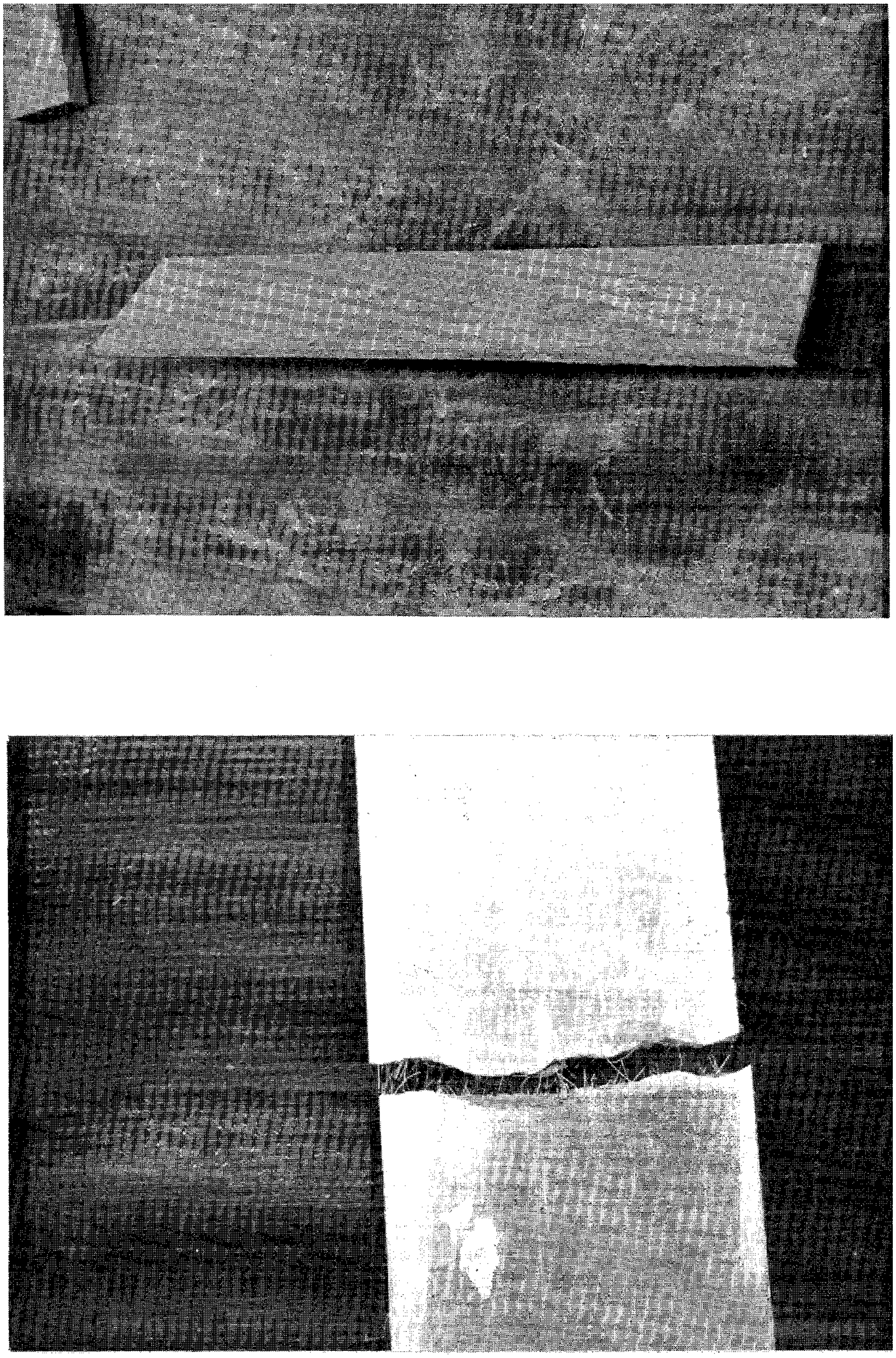


FIG. 3.7- ABACA FIBER REINFORCED PHOSPHOGYPSUM CONCRETE PANELS TESTED.

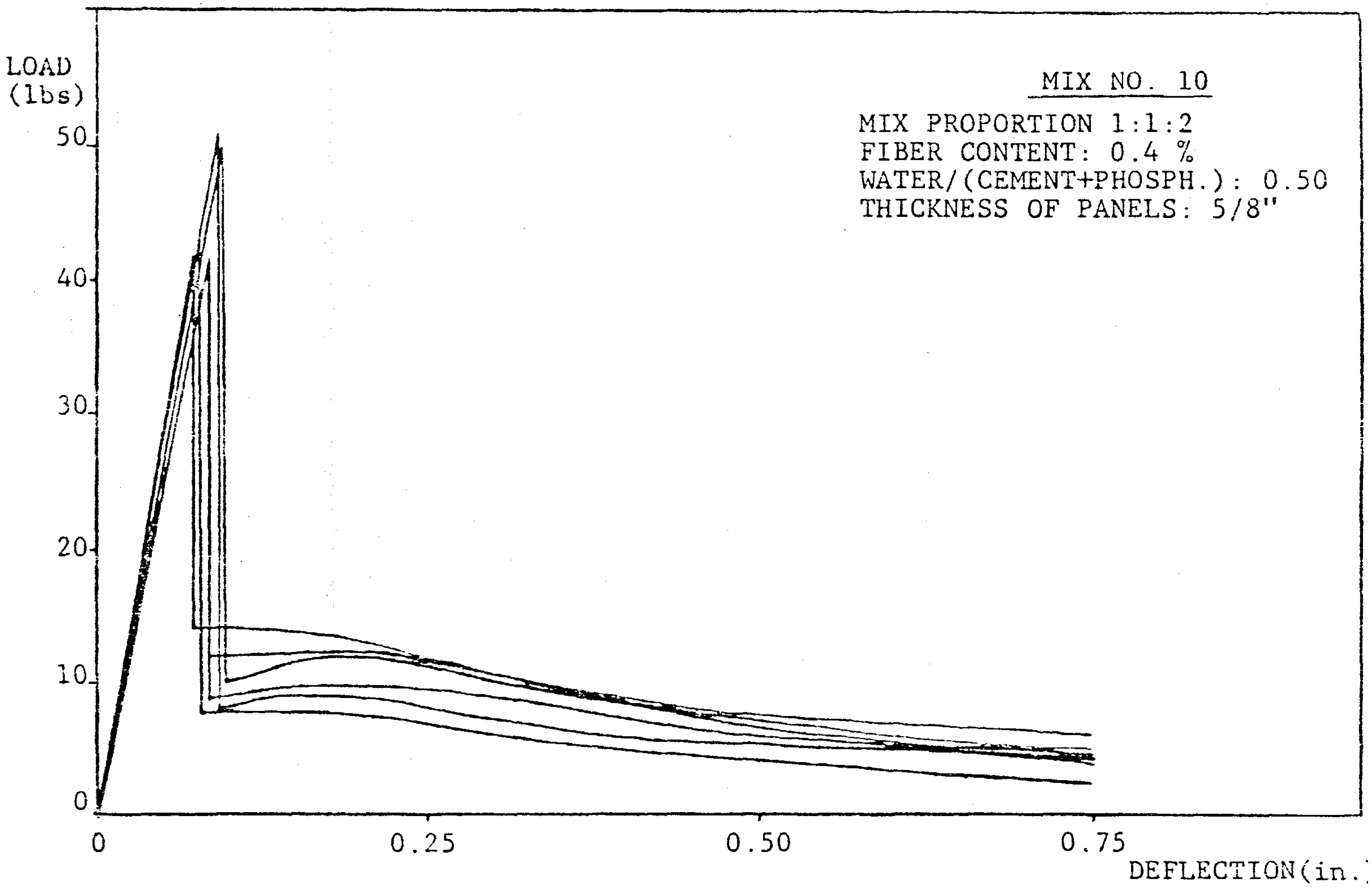

LOAD
(lbs)
50
40
30
20
10
0
0
0.25
0.50
0.75
DEFLECTION(in.)
MIX NO. 10
MIX PROPORTION 1:1:2
FIBER CONTENT: 0.4 %
WATER/(CEMENT+PHOSPH.): 0.50
THICKNESS OF PANELS: 5/8"

FIGURE 3

load- deflection curve up to the first crack load as shown in Figure 4.

Maximum postcracking load is defined as the maximum load that fibers carry after concrete cracks.

2.)<u>Split-Cylinder Test</u>: Tensile strength of concrete is usually determined by split-cylinder test. The test was performed according to ASTM Standards as shown in Figure 5. The maximum applied load at failure, P, was recorded during the experiments. The splitting tensile strength is then calculated as follows:

$$T = 2P/ 3.14 \times d \times 1$$

where

1 = length of specimen
d = diameter of specimen
T = splitting tensile strength
P = maximum applied load

3.)<u>Compression Test</u>: Cylindrical specimens, 2 in. in diameter and 4 in. long, for determining compressive strength of phosphogypsum concrete, were used. All the cylinders were capped before testing. Photographs of test specimens taken during compression tests are shown in Figure 6.

6. EXPERIMENTAL TEST RESULTS

(a)<u>Effect</u> of <u>phosphogysum content</u>: Concrete strength decreased as phosphogypsum content increased as shown in Figures 7, 8, and 9. There was a slight decrease in energy absorption capacity and toughness of the panels when phosphogysum content was in the range from 0 to 50%. Considerable decrease in energy absorption capacity and toughness was noticed in the mixture containing 75% of phosphogypsum, as shown in Figures 10 and 11. The modulus of rupture decreased from 770 psi to 240 psi; whereas the compressive strength decreased from 4850 psi to 1770 psi as Phosphogypsum content increased from 0 to 75%. Unit weight of concrete considerably decreased from 129 pcf to 101 pcf as phosphogypsum

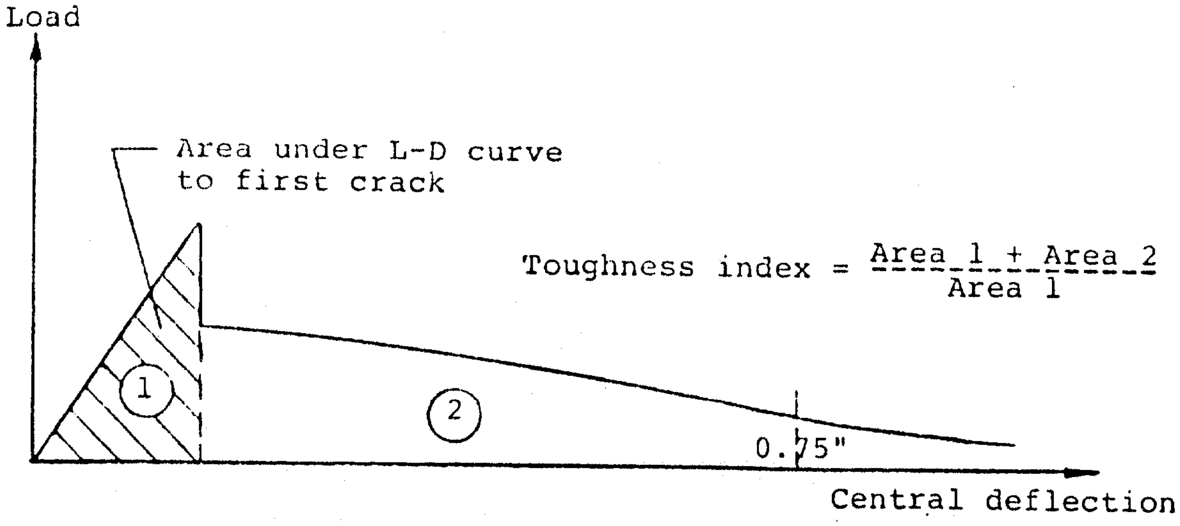


Figure 4 Determining the toughness index

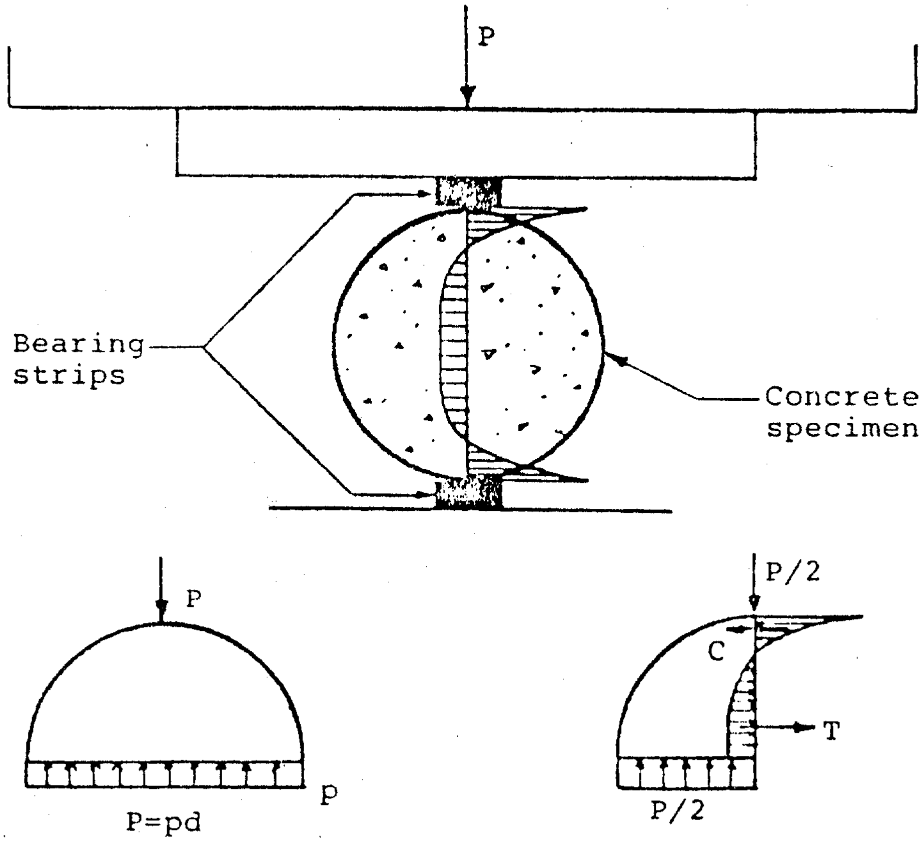


Figure 5 Finding tensile strength of concrete by split-cylinder test

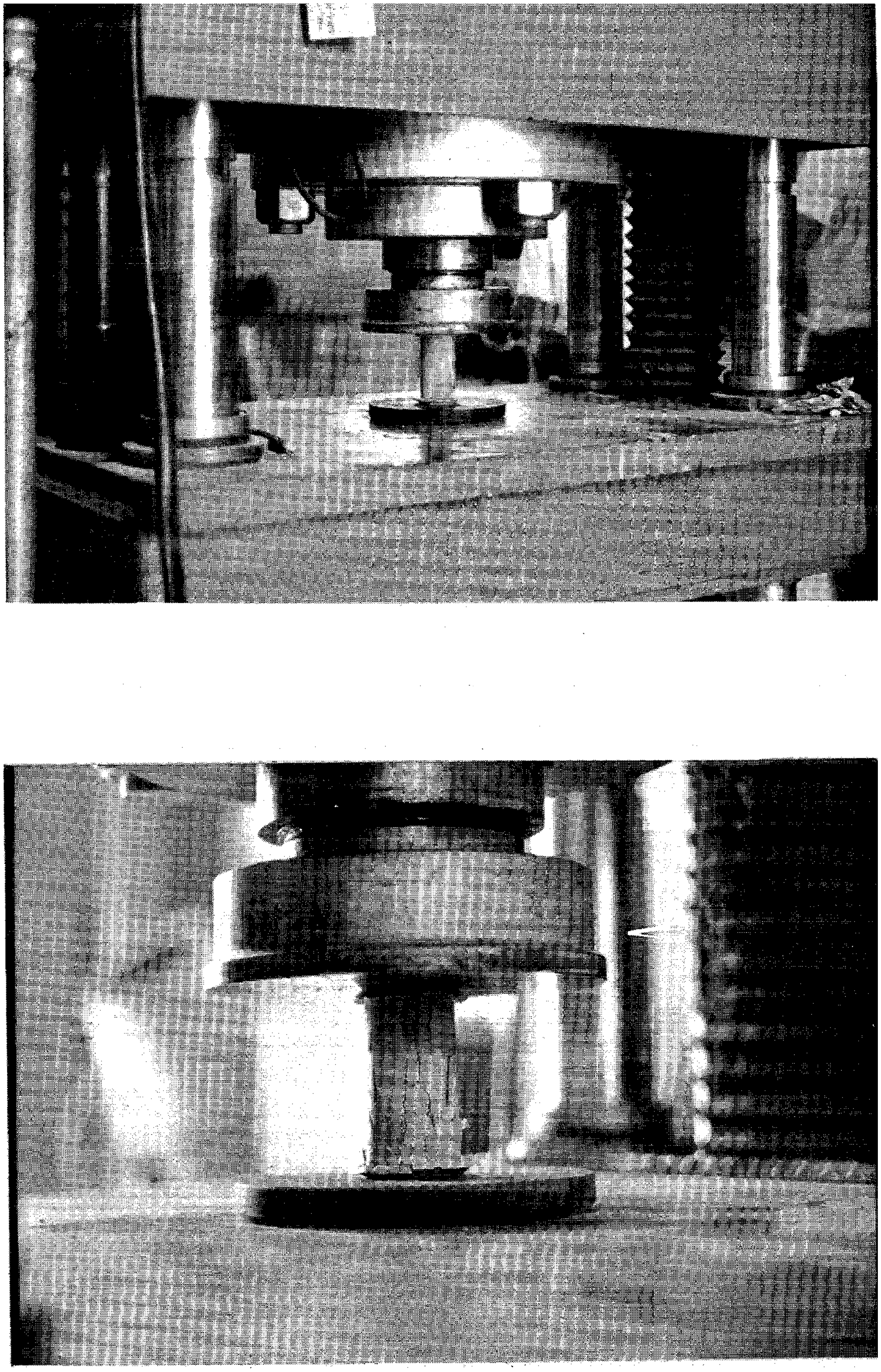


FIG. 3.9- COMPRESSION TEST.

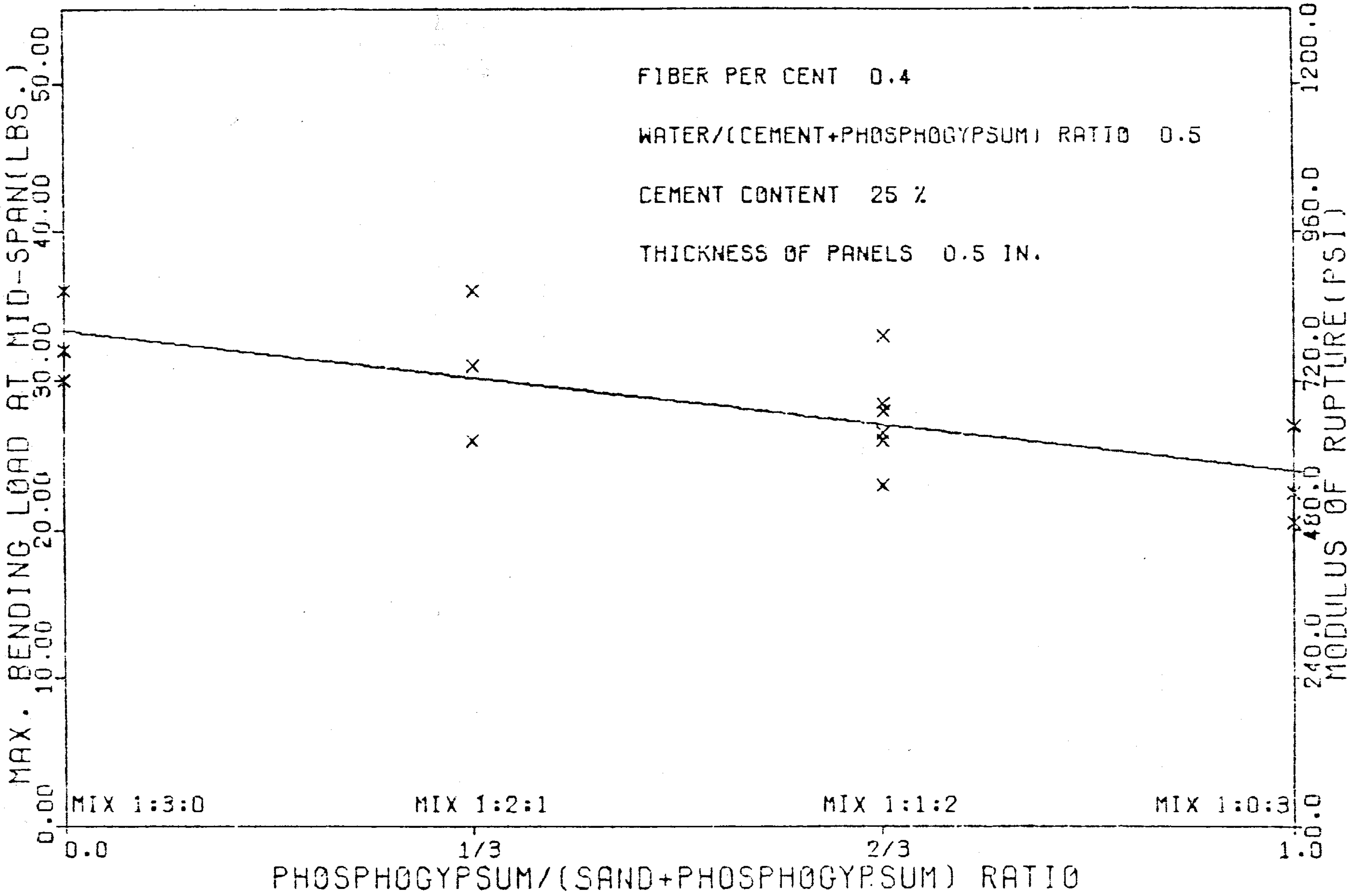


FIG. 7 - BENDING LOAD CAPACITY AND MODULUS OF RUPTURE OF FIBROUS CONCRETE PANELS AS FUNCTION OF PHOSPH./(PHOSPH.+SAND) RATIO.

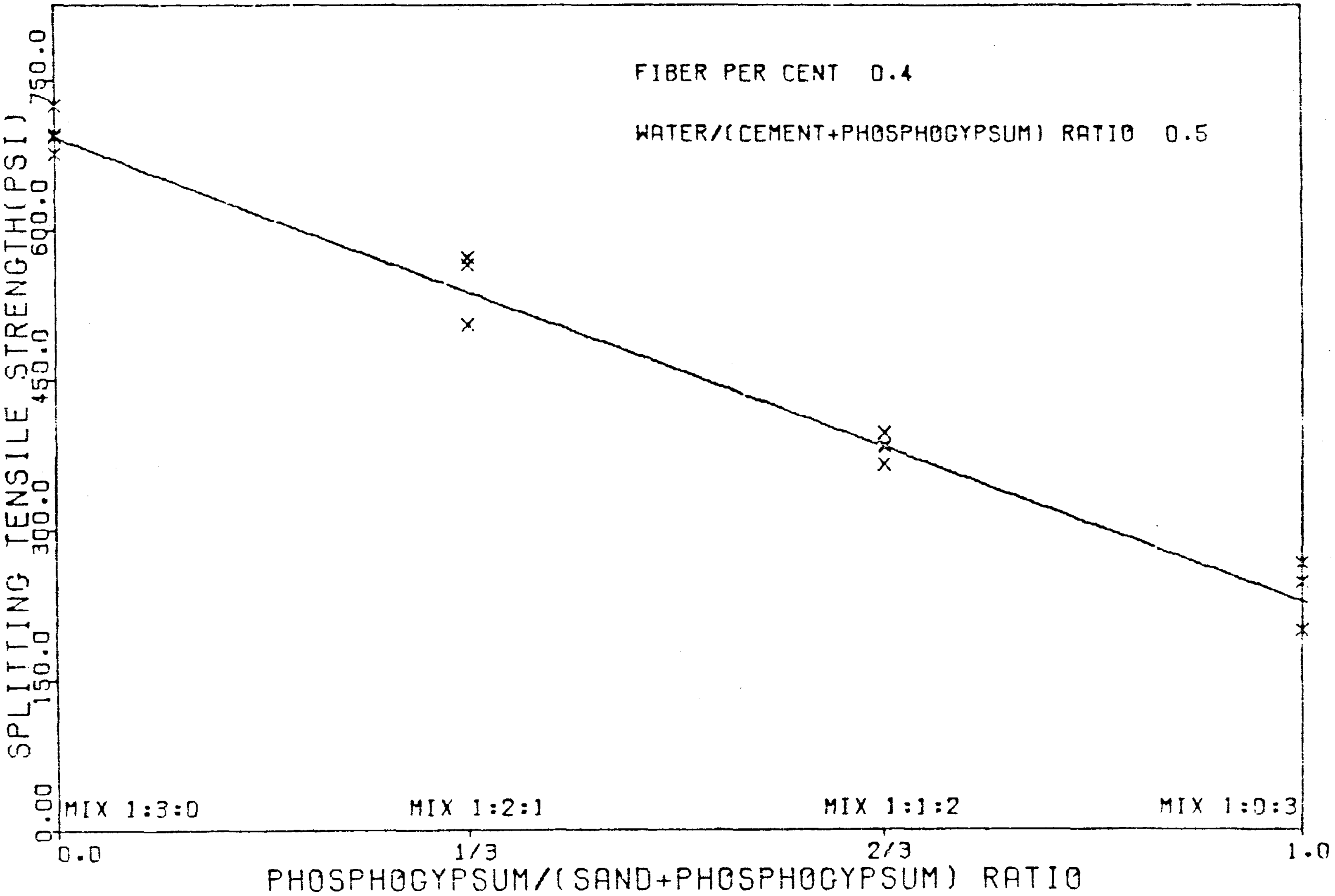


FIG. 8 - SPLITTING TENSILE STRENGTH OF FIBROUS CONCRETE AS FUNCTION OF PHOSPH./(PHOSPH.+SAND) RATIO.

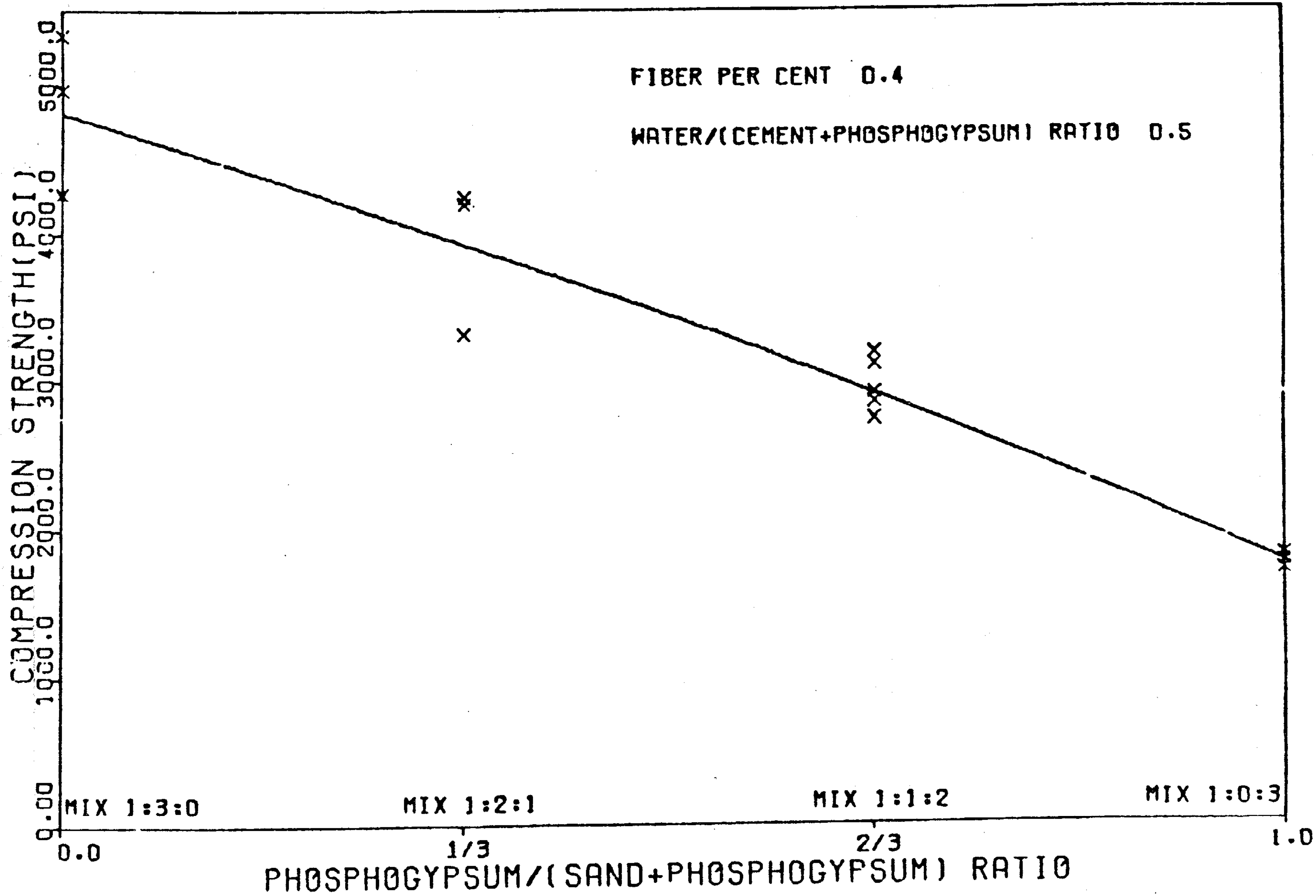


FIG. 9 - COMPRESSIVE STRENGTH OF FIBROUS CONCRETE AS FUNCTION OF PHOSPH./(PHOSPH.+SAND) RATIO.

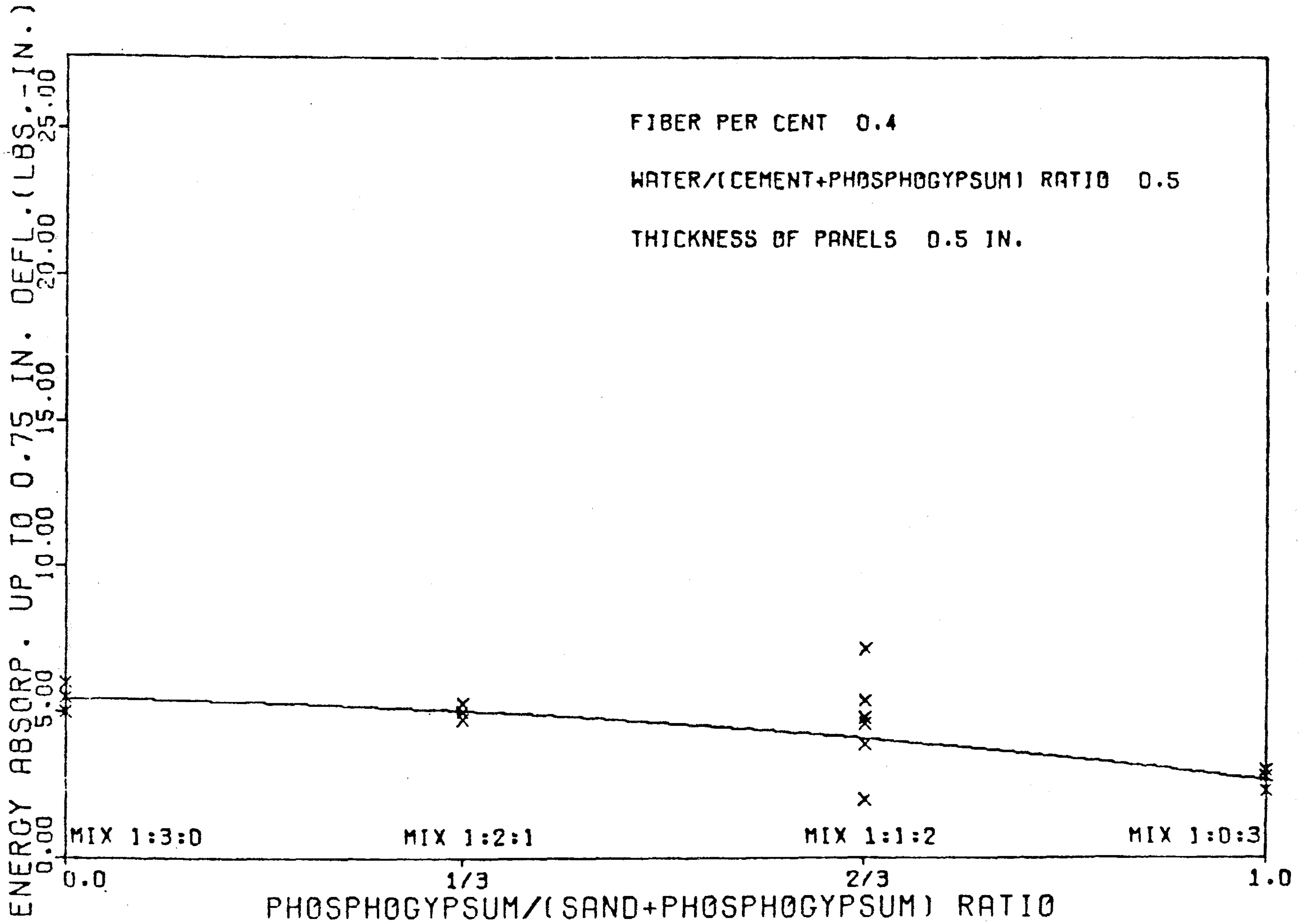


FIG. 10 - ENERGY ABSORPTION CAPACITY OF FIBROUS CONCRETE PANELS AS FUNCTION OF PHOSPH./(PHOSPH.+SAND) RATIO.

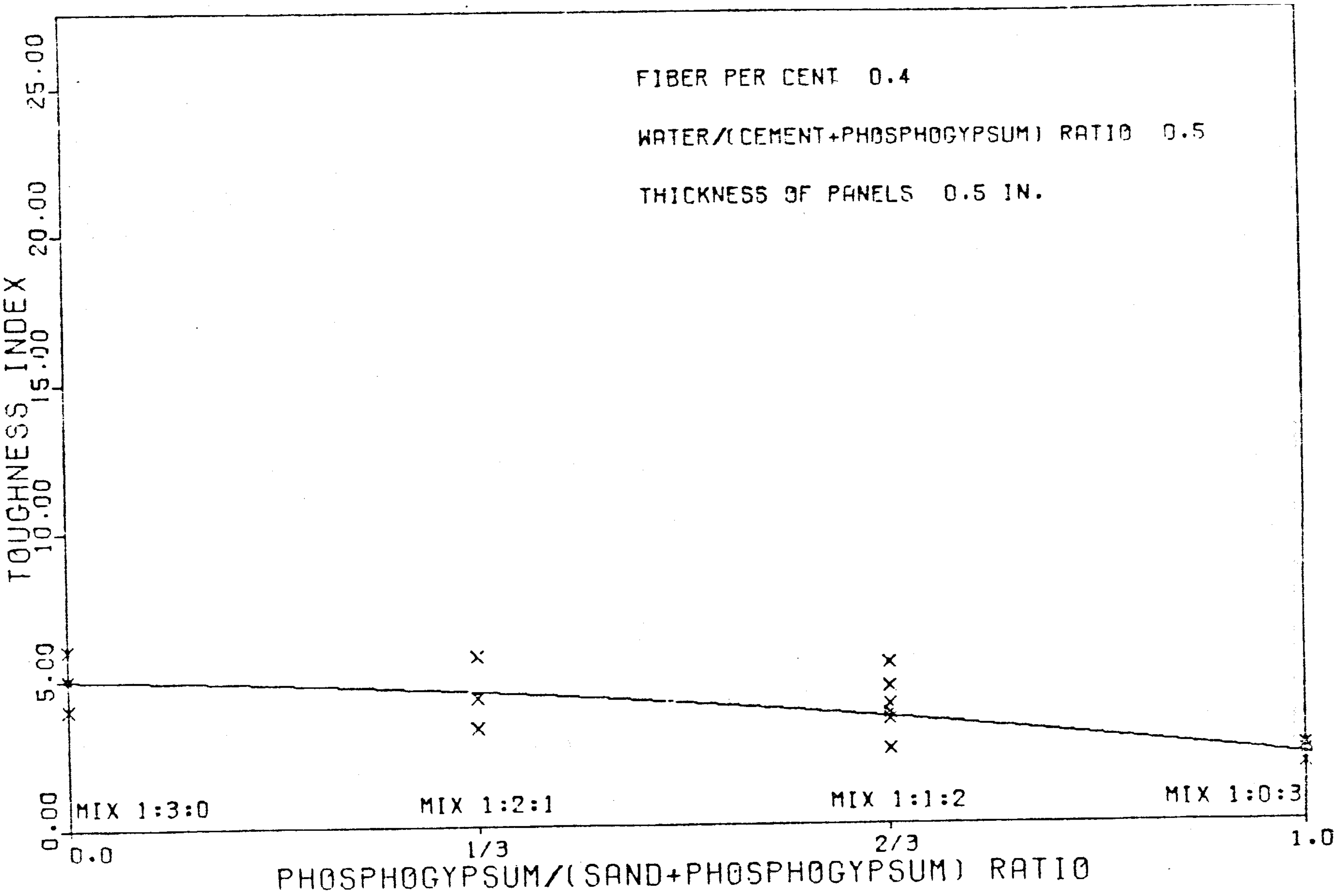


FIG. 11 - TOUGHNESS OF FIBROUS CONCRETE PANELS AS FUNCTION OF PHOSPH./(PHOSPH.+SAND) RATIO.

content increased from 0 to 75% of the total solid weight. Cement content was kept constant (at 25%) in all cases. Average test results including the above mentioned parameters are summarized in Tables 2 through 6.

(b)Effects of abaca fibers: Test results show that the inclusion of abaca fibers provide added ductility to concrete. Abaca fibers considerably increased energy absorption capacity and toughness as shown in Figures 12 and 13. Increasing fiber content slightly decreased modulus of rupture, splitting tensile strength and compressive strength as shown in Figures 14, 15 and 16. Average modulus of rupture and splitting tensile strength decreased about 20%, whereas compressive strength decreased a little more than 10% when the fiber content was changed from 0.0 to 0.8% of the total weight. Average test results are summarized in Tables 2 through 6.

(c)Effect of Water Content: It was observed that a concrete mix with a water/(cement + phosphogypsm) ratio of 0.46 was too dry to be properly placed into the forms without having an excessive amount of voids. This explains the descending portion of the curves for values lower than 0.5, as shown in Figures 17 through 20.

Test results showed that modulus of rupture and splitting tensile strength decreased by about 20% and compressive strength decreased by about 35% as the ratio increased from 0.5 to 0.6. Maximum postcracking load, energy absorption capacity and toughness also decreased as the water content increased.

(d)Effects of panel thickness: The modulus of rupture of phosphogypsum concrete increased as the panel thickness increased. Bending test results and calculated modulus of rupture for three different thicknesses are shown in Figures 21 and 22. The ultimate strength should not have been a function of the cross-sectional depth for the same constituent materials according to the assumption of elastic linearly distributed stress. However, test results showed that the thickness of panels had a beneficial effect on ultimate resistance. This can be explained by the fact that the material under consideration in not per-

TABLE 2 - EFFECT OF FIBER CONTENT ON POSTCRACKING BENDING LOAD

CATEGORY I

Mix ratio 1:1:2 , Water/(Cement+Phosphogypsum)=0.5 , Thickness=0.5 in.

Fiber content (%)	Average bending load(lbs)	Average postcracking load(lbs)	$\frac{\text{Postcracking Load}}{\text{Max. bending Load}}$ (%)	$\frac{\text{Postcracking Load}}{\text{Max. bending load of non-fibrous concrete}}$ (%)
0.0	32.0	0.0	0	0
0.4	27.5	7.4	27	23
0.6	25.4	11.0	43	34
0.8	24.5	15.0	61	47

TABLE 3 - AVERAGE ENERGY ABSORPTION CAPACITY AND TOUGHNESS INDEX OF FIBROUS PHOSPHOGYPSUM CONCRETE PANELS

	Category I				Category II					Category III				Category IV			
	Mix ratio 1:1:2 $\frac{\text{Water}}{\text{Cement+Phosph}}$: 0.5				Fiber content:0.4% Mix ratio 1:1:2					Fiber content:0.4% Cement content:25% $\frac{\text{Water}}{\text{Cement+Phosph}}$: 0.5				Fiber content:0.4% $\frac{\text{Water}}{\text{Cement+Phosph}}$: 0.5			
	FIBER CONTENT(%)				W/(C+P) RATIO*					P/(P+S) RATIO*				PHOSPH. CONTENT(%)			
	0.0	0.4	0.6	0.8	0.46	0.5	0.52	0.55	0.60	0	1/3	2/3	1	33	50	60	67
Average Energy Absorption Capacity (lbs.-in.)	1.5	5.2	6.9	9.7	3.5	5.2	4.0	3.3	2.1	5.4	5.2	5.2	2.6	8.3	5.2	2.0	0.6
Toughness index	1.0	4.2	6.3	8.0	3.0	4.2	3.7	3.0	1.9	5.0	4.7	4.2	2.2	6.5	4.2	1.4	1.1

* W: water
C: cement
P: phosphogypsum

TABLE 4 - AVERAGE MODULUS OF RUPTURE AND SPLITTING TENSILE STRENGTHS

	Category I				Category II					Category III				Category IV			
	Mix ratio 1:1:2 $\frac{\text{Water}}{\text{Cement+Phosph}}$: 0.5				Fiber content:0.4% Mix ratio 1:1:2					Fiber content:0.4% Cement content:25% $\frac{\text{Water}}{\text{Cement+Phosph}}$: 0.5				Fiber content:0.4% $\frac{\text{Water}}{\text{Cement+Phosph}}$: 0.5			
	FIBER CONTENT(%)				W/(C+P) RATIO*					P/(P+S) RATIO*				PHOSPH. CONTENT(%)			
	0.0	0.4	0.6	0.8	0.46	0.5	0.52	0.55	0.60	0	1/3	2/3	1	33	50	60	67
Average modulus of rupture (psi)	768	660	610	588	622	660	612	571	526	770	730	660	560	734	660	548	400
Average splitting tensile strength (psi)	420	390	380	370	353	390	373	350	310	698	548	390	237	581	390	275	226

* W: water
C: cement
P: phosphogypsum

TABLE 5 - AVERAGE COMPRESSIVE STRENGTHS

	Category I				Category II					Category III				Category IV			
	Mix ratio 1:1:2 $\frac{\text{Water}}{\text{Cement+Phosph.}}$:0.5				Fiber content:0.4% Mix ratio 1:1:2					Fiber content:0.4% Cement content:25% $\frac{\text{Water}}{\text{Cement+Phosph.}}$: 0.5				Fiber content:0.4% $\frac{\text{Water}}{\text{Cement+Phosph.}}$: 0.5			
	FIBER CONTENT(%)				W/(C+P) RATIO*					P/(P+S) RATIO *				PHOSPH. CONTENT(%)			
	0.0	0.4	0.6	0.8	0.46	0.5	0.52	0.55	0.60	0	1/3	2/3	1	33	50	60	67
Average compressive strength (psi)	3230	2970	2930	2800	2585	2970	2770	2450	1940	4850	3910	2970	1770	4100	2970	2000	1870

* W: water
C: cement
P: phosphogypsum

TABLE 6 - AVERAGE UNIT WEIGHTS

Mix number	Mix proportion	Fiber content (%)	$\frac{\text{Water}}{\text{Cement+Phosph.}}$	Average unit weight after 20 days (pcf)
1	1:1:2	0.4	0.46	112
2	1:1:3	0.4	0.50	104
3	1:1:1	0.4	0.50	114
4	1:1:2	0.4	0.52	106
5	1:1:4	0.4	0.50	103
6	1:1:2	0.4	0.50	109
7	1:1:2	0.6	0.50	108.5
8	1:1:2	0.8	0.50	106
9	1:1:2	0.4	0.50	109.5
10	1:1:2	0.4	0.50	109
11	1:1:2	0.4	0.55	104
12	1:1:2	0.4	0.60	101
13	1:1:2	-	0.50	109
14	1:2:1	0.4	0.50	121
15	1:0:3	0.4	0.50	101
16	1:3:0	0.4	0.50	129

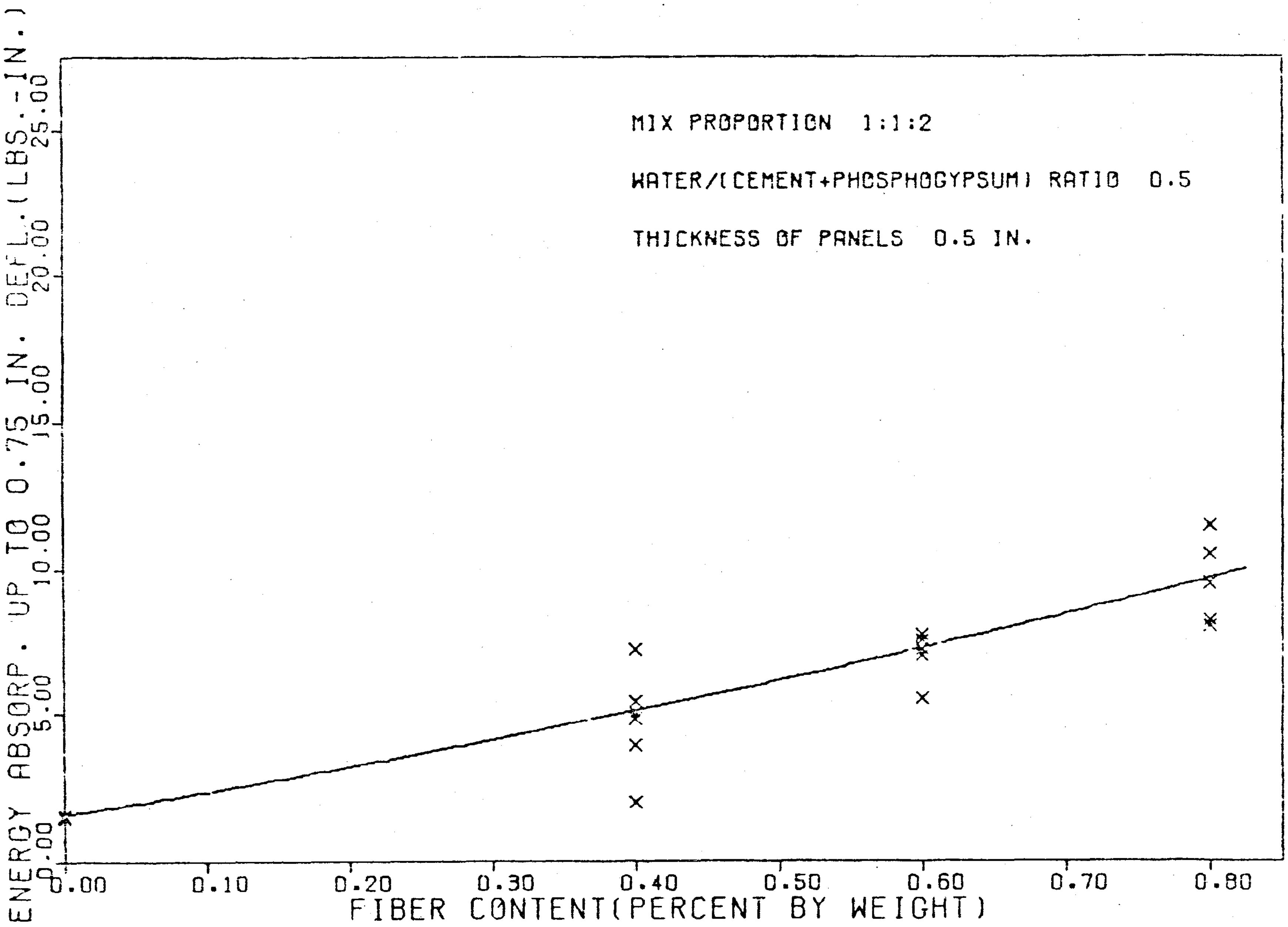


FIG. 12 - EFFECT OF FIBER CONTENT ON ENERGY ABSORPTION CAPACITY OF PHOSPHOGYPSUM CONCRETE PANELS.

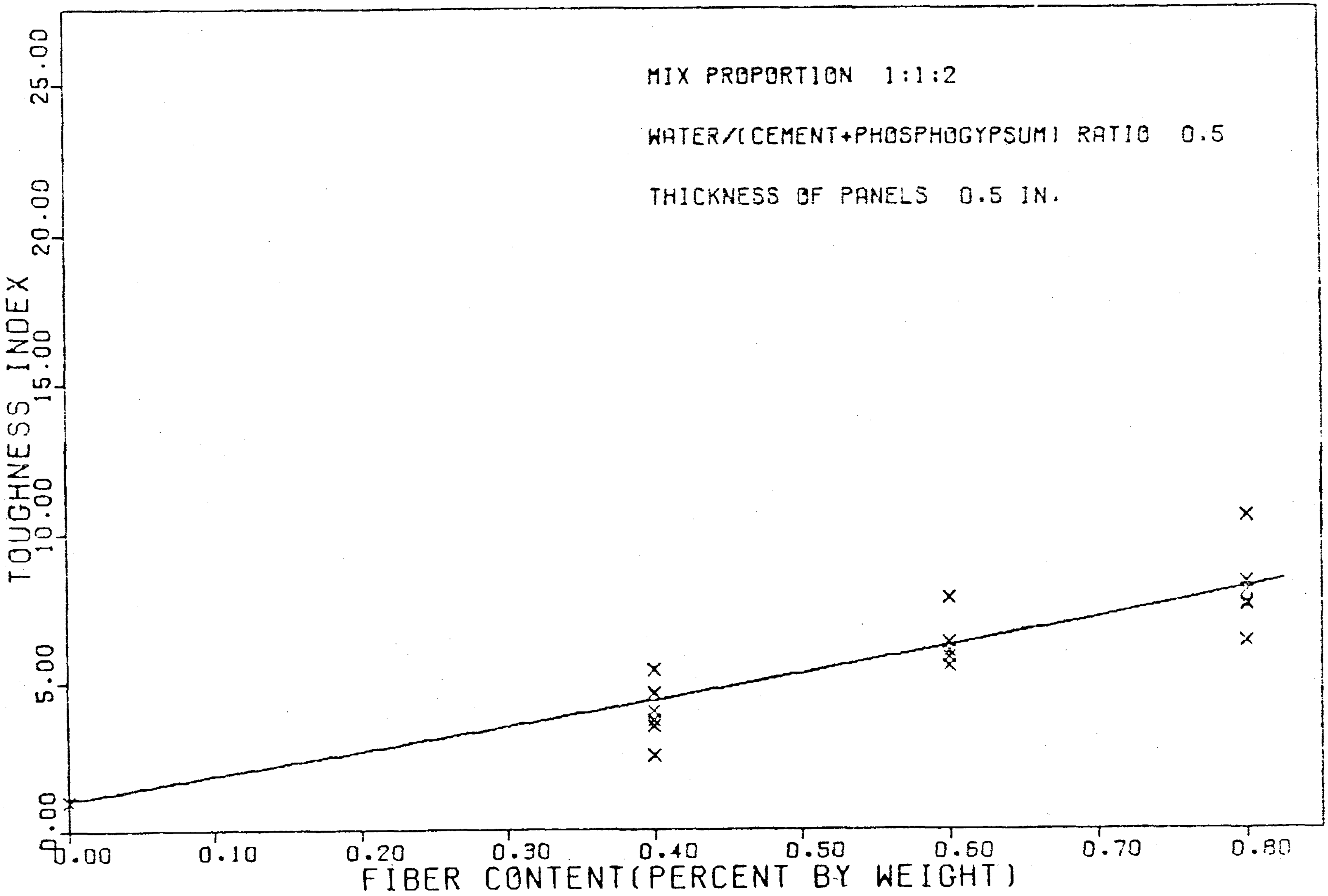


FIG. 13 - EFFECT OF FIBER CONTENT ON TOUGHNESS OF PHOSPHOGYPSUM CONCRETE PANELS.

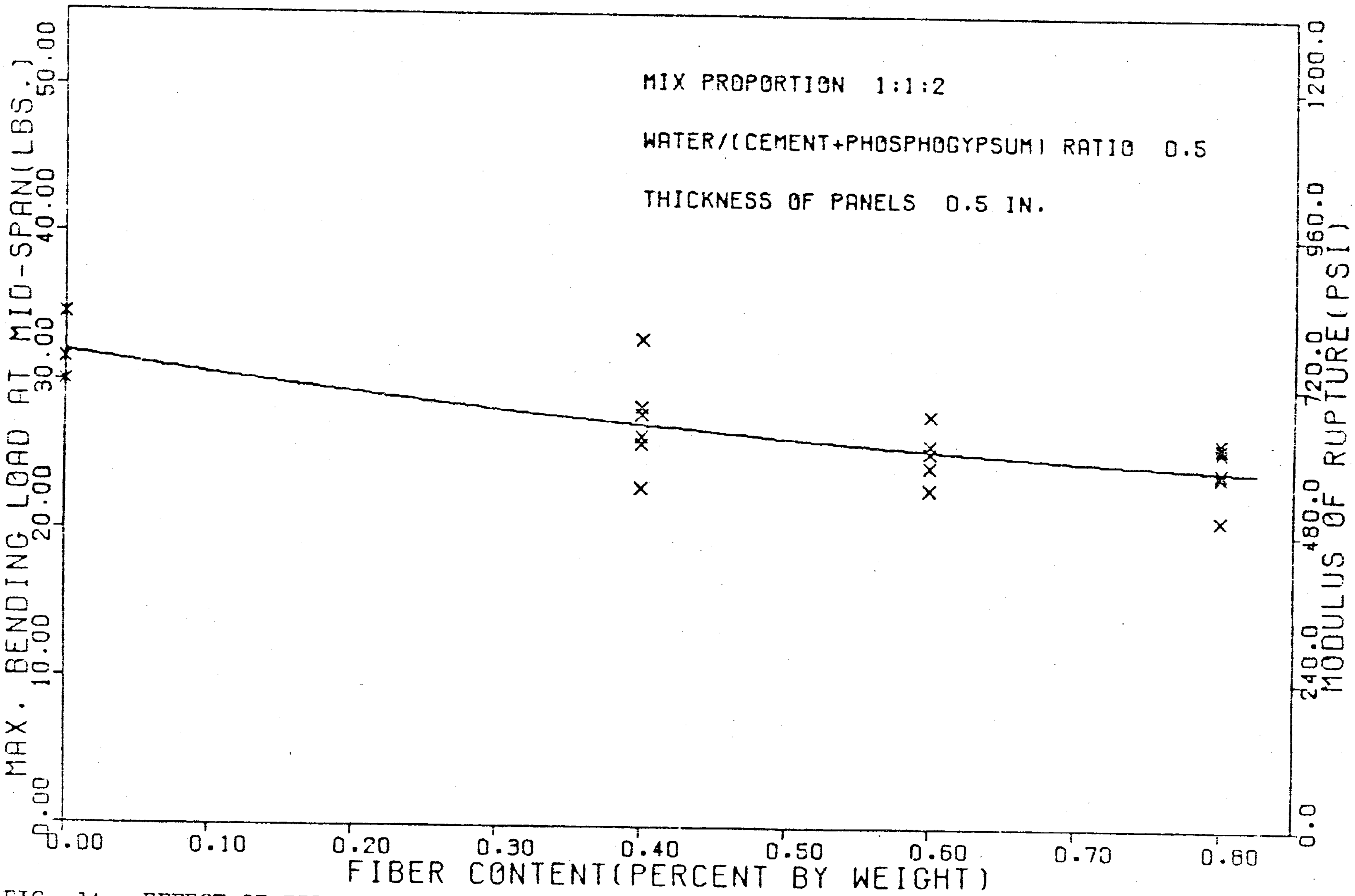


FIG. 14 - EFFECT OF FIBER CONTENT ON BENDING LOAD CAPACITY AND MODULUS OF RUPTURE OF PHOSPHOGYPSUM CONCRETE PANELS.

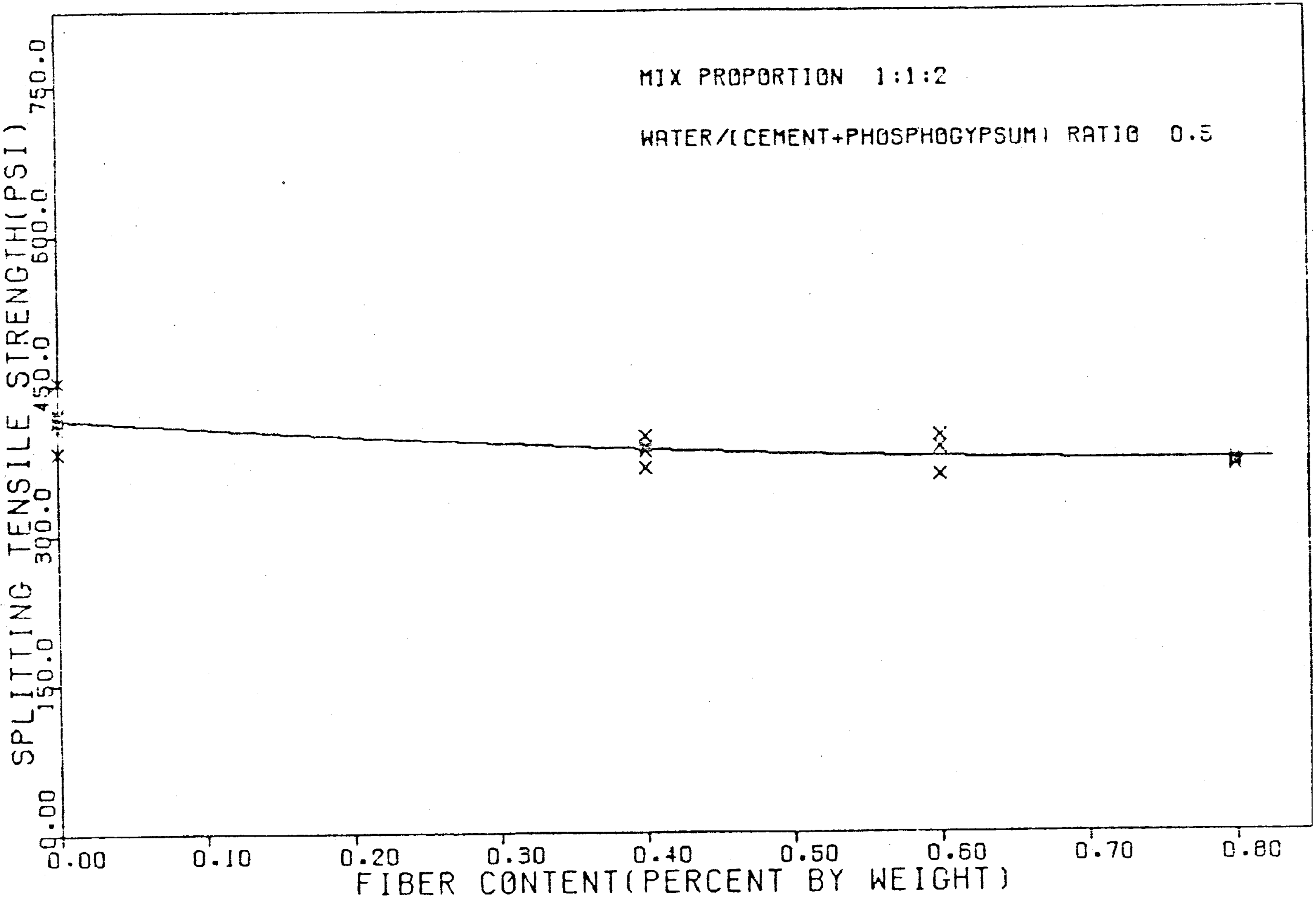


FIG. 15 - EFFECT OF FIBER CONTENT ON SPLITTING TENSILE STRENGTH OF PHOSPHOGYPSUM CONCRETE.

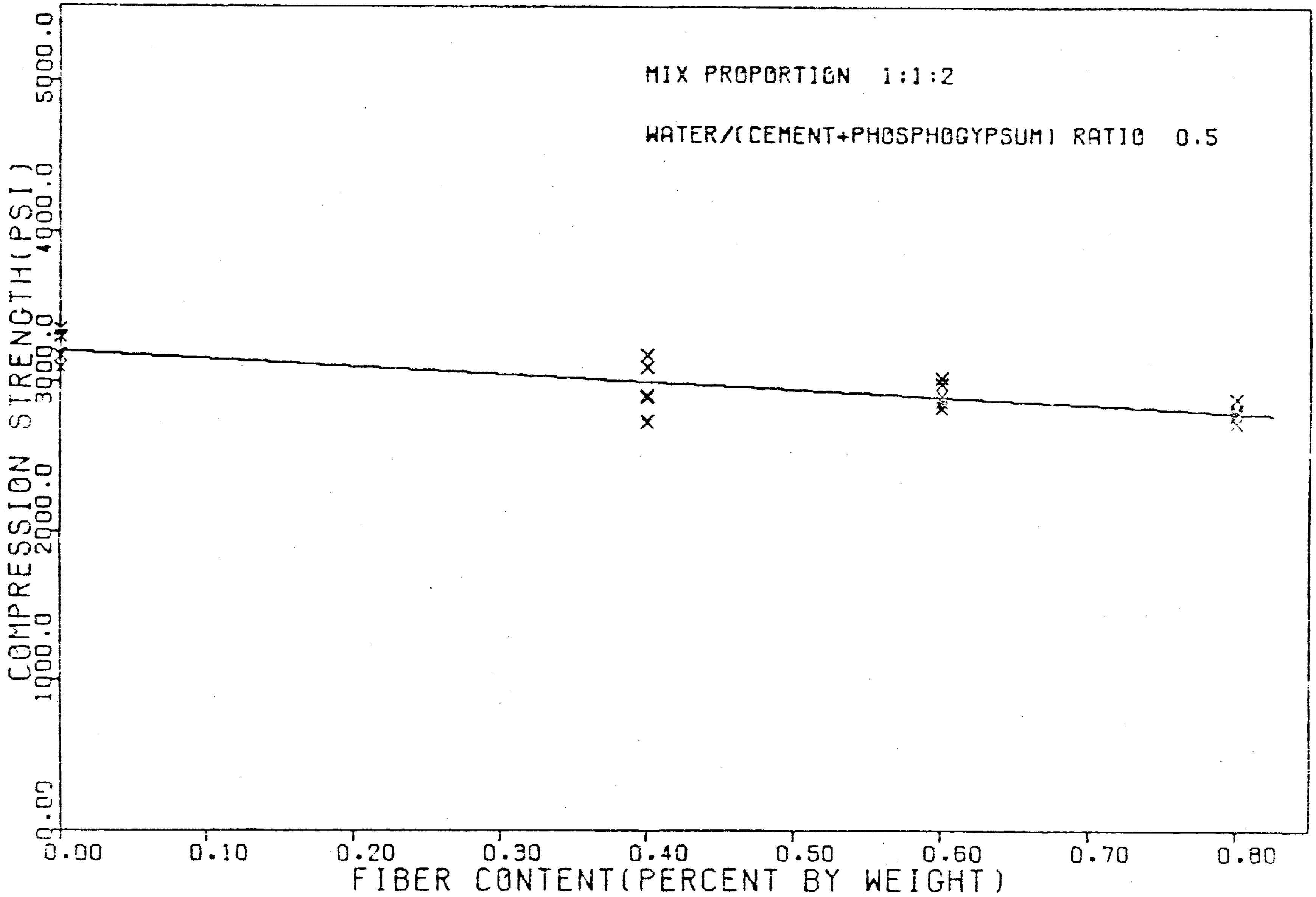


FIG. 16 - EFFECT OF FIBER CONTENT ON COMPRESSIVE STRENGTH OF PHOSPHOGYPSUM CONCRETE.

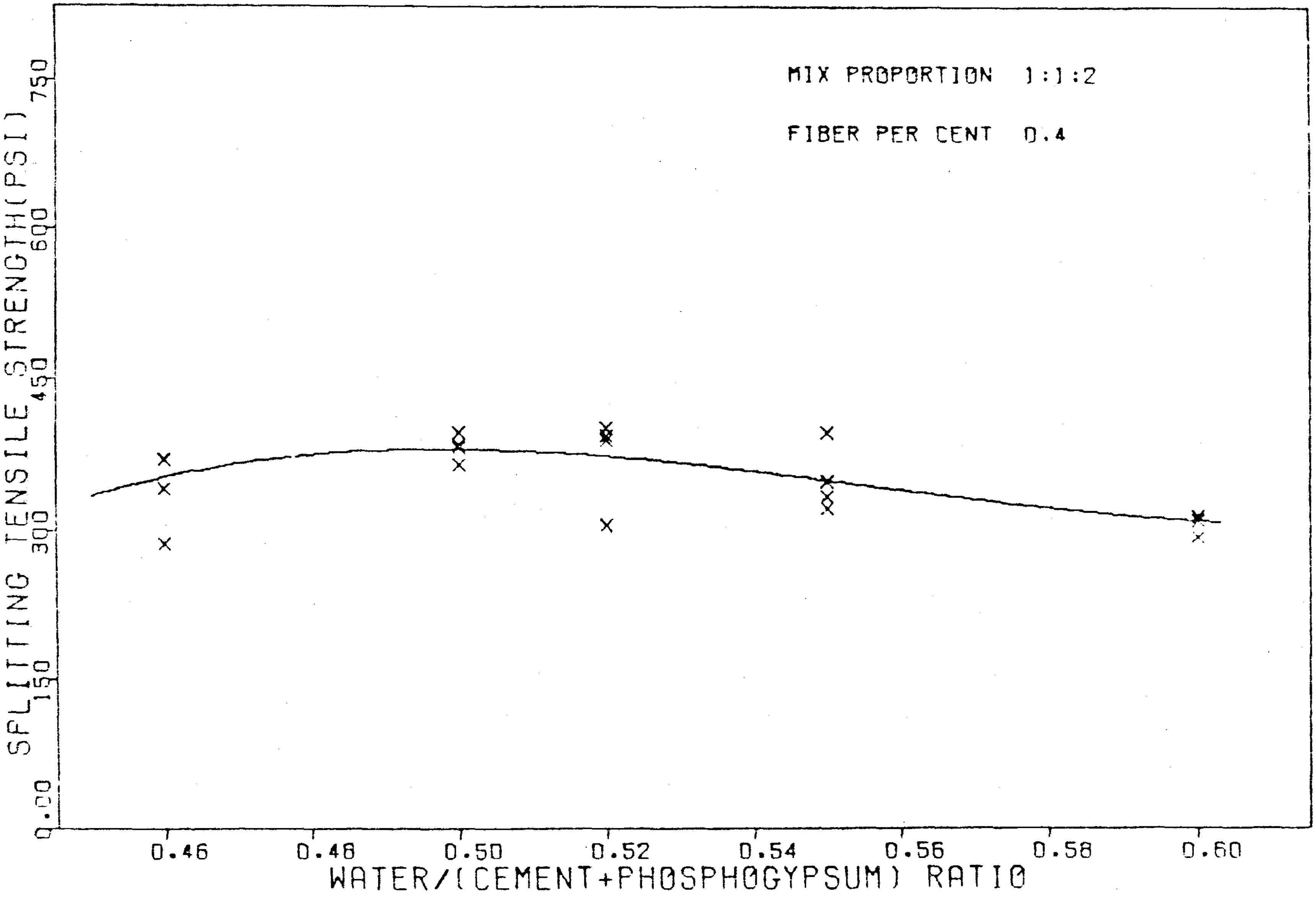


FIG. 17 - SPLITTING TENSILE STRENGTH OF FIBROUS PHOSPHOGYPSUM CONCRETE AS FUNCTION OF WATER/(CEMENT+PHOSPH.) RATIO.

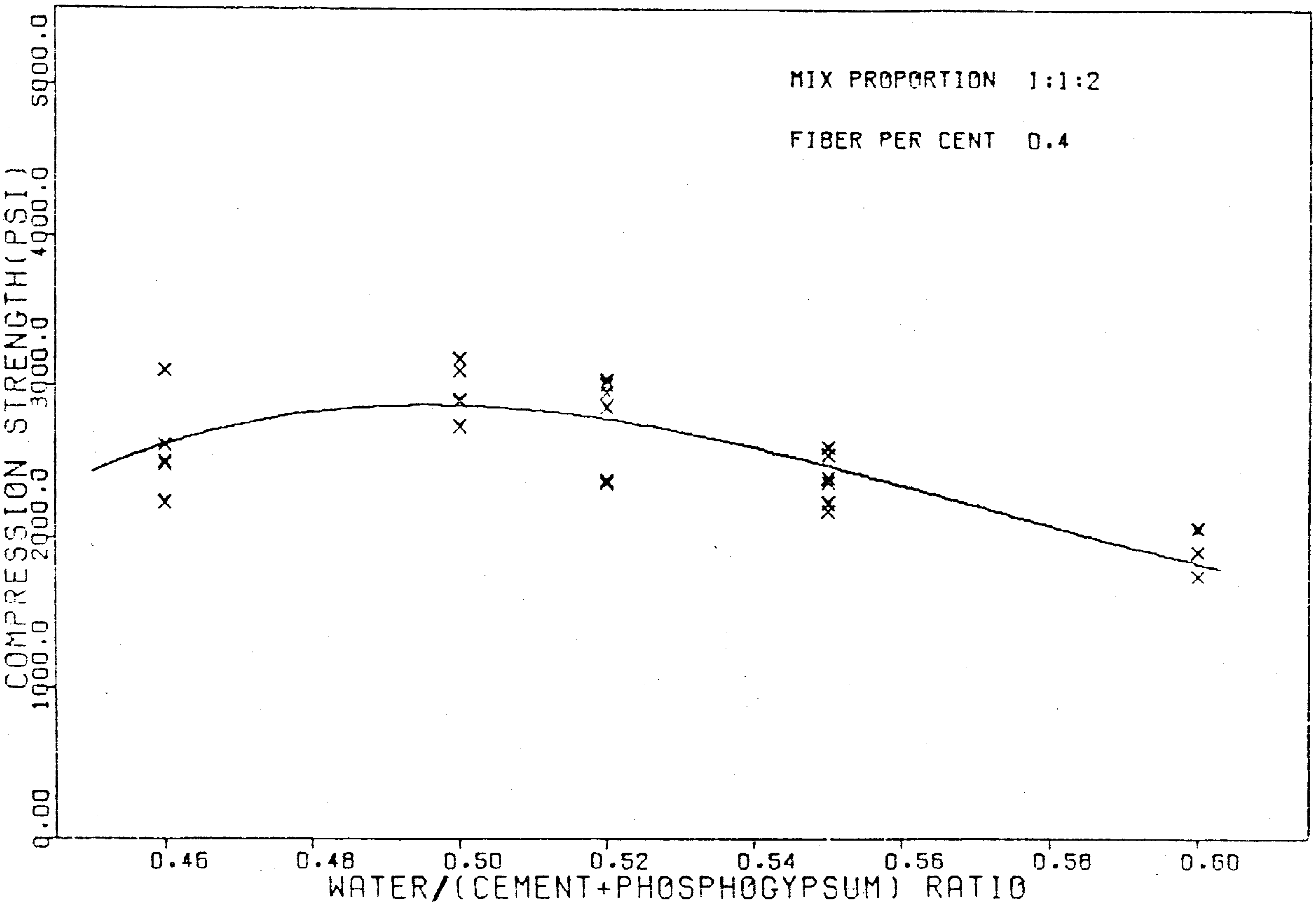


FIG. 18 - COMPRESSIVE STRENGTH OF FIBROUS PHOSPHOGYPSUM CONCRETE AS FUNCTION OF WATER/(CEMENT+PHOSPH.) RATIO.

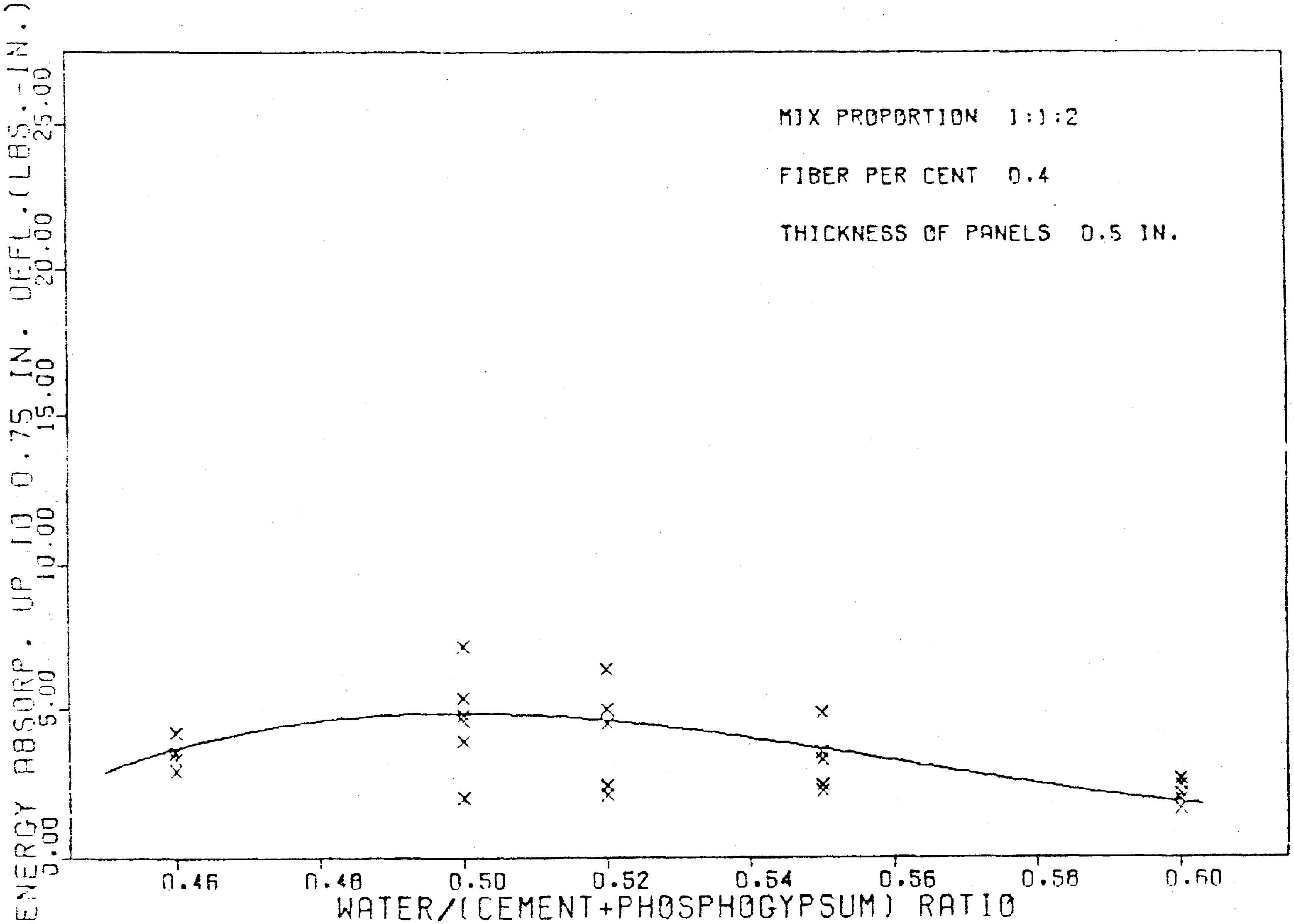


FIG. 19 - ENERGY ABSORPTION CAPACITY OF FIBROUS PHOSPHOGYPSUM CONCRETE PANELS AS FUNCTION OF WATER/(CEMENT+PHOSPH.) RATIO.

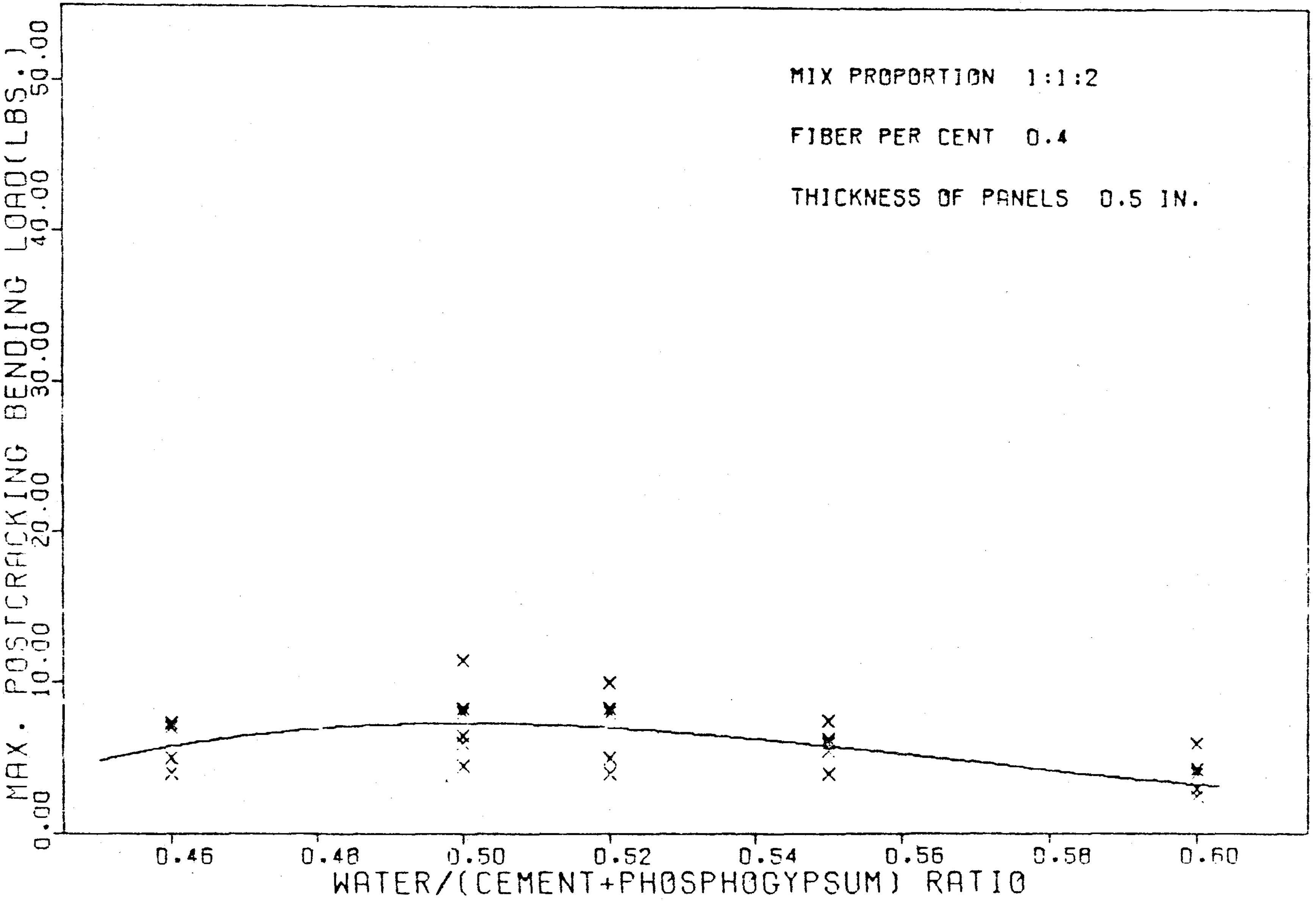


FIG. 20 - POSTCRACKING LOAD CAPACITY OF FIBROUS PHOSPHOGYPSUM CONCRETE PANELS AS FUNCTION OF WATER/(CEMENT+PHOSPH.) RATIO.

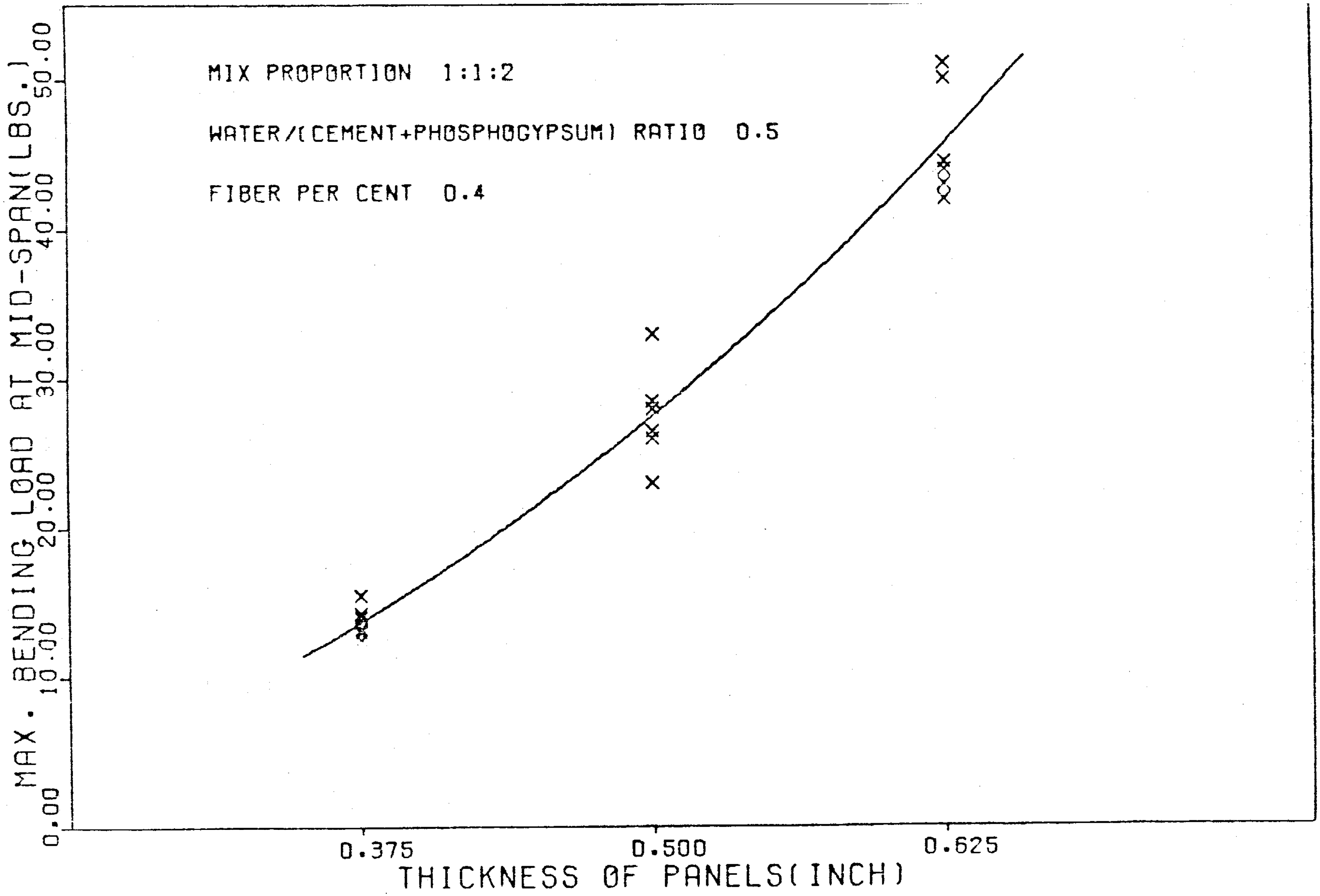


FIG. 21 - BENDING LOAD CAPACITY OF FIBROUS PHOSPHOGYPSUM CONCRETE PANELS AS FUNCTION OF THICKNESS.

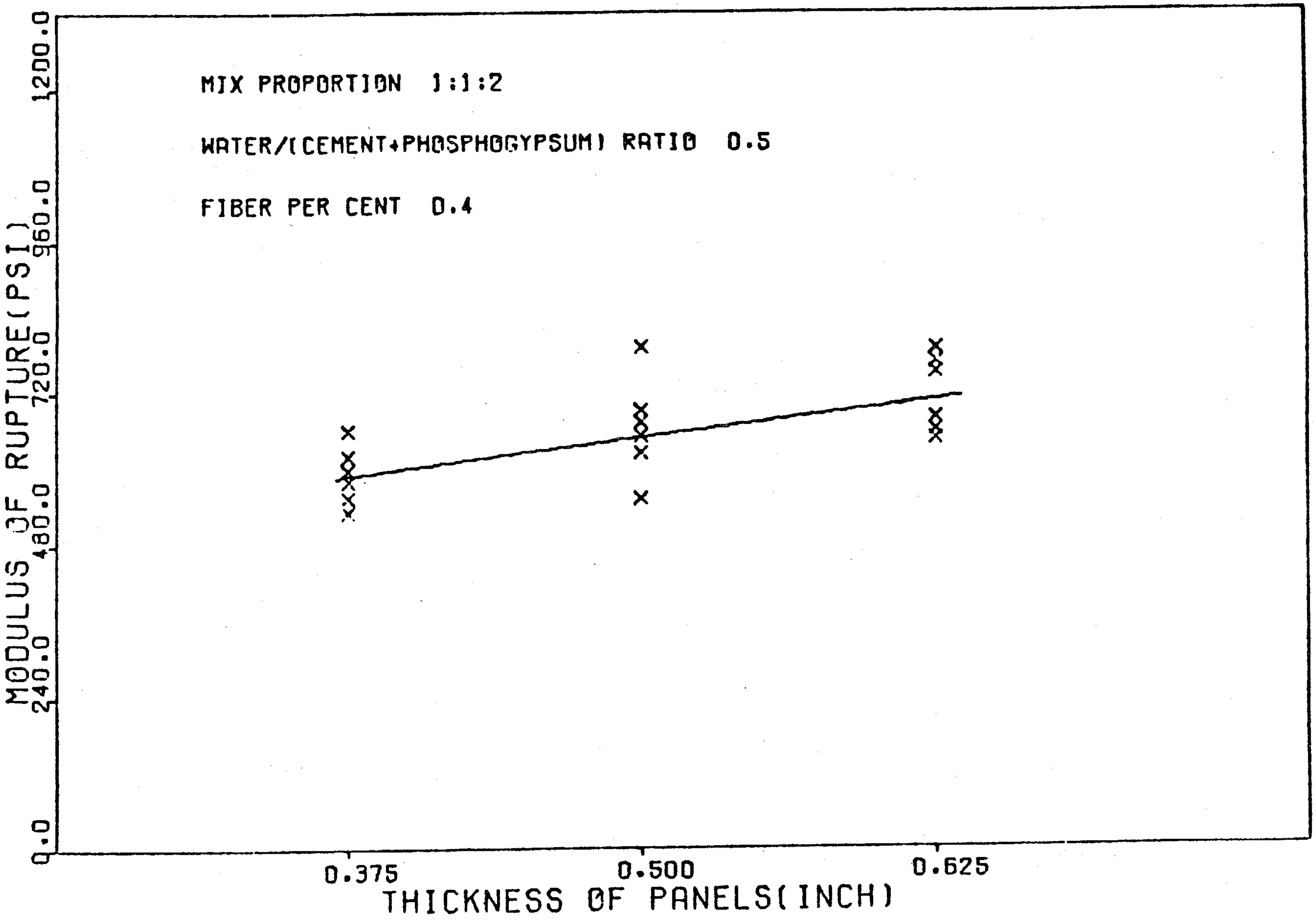


FIG. 22 - MODULUS OF RUPTURE OF FIBROUS PHOSPHOGYPSUM CONCRETE PANELS AS FUNCTION OF THICKNESS.

fectly homogenous and the presence of voids and imperfections is more detrimental within a thinner section.

7. CONCLUSION

The following conclusions were reached on the basis of observations gathered during the experimental program:

1. High bending, splitting and compressive strengths can be obtained if the phosphogypsum content is less than 50 percent of the total dry weight of the mixture.

2. Phosphogypsum is found to be a suitable material to be used in thin concrete panels as an aggregate because of its fineness, which also improves surface finishing of the thin phosphogypsum concrete panels.

3. Increased phosphogypsum content requires increased water content in order to have a workable mix. Therefore, water/(cement + phosphogypsum) ratio is found to be a suitable parameter to describe workability. Results of mixing trials show that 0.5 is the lowest practical water/(cement + phosphogypsum) ratio for mixes reinforced with abaca fibers.

4. Abaca fibers considerably increase energy absorption capacity of phosphogypsum concrete panels since they improve concrete postcracking behavior.

5. Inclusion of abaca fibers in phosphogypsun concrete slightly decreases the flexural strength, the splitting tensile strength and the compressive strength of concrete.

6. Fiber failure in panels was due to bonding between fibers and concrete rather than a tensile failure of the fibers themselves.

7. Phosphogypsum concrete is lighter than regular concrete. Therefore, it can be concluded that the combination of two new materials, phosphogysum and abaca fiber with cement, will lead to suitable mixtures to be used in the production of thin concrete wall panels.

Acknowledgements

The research has been funded by the Florida Institute of Phosphate Research, Bartow, Florida. The authors would like to extend their gratitude to the Agrico Mining Co. and Gardinier Inc. for supplying the phosphogypsum for this research.

PHOSPHOGYPSUM PRODUCTS FOR THE CONSTRUCTION INDUSTRY

Antonio Nanni
Ph.D. Candidate, Dept. of Civil & Architectural Engineering,
University of Miami, Coral Gables, FL.

and

Wen F. Chang
Professor, Dept. of Civil & Architectural Engineering, and
Director Phosphate Research Institute,
University of Miami, Coral Gables, FL.

ABSTRACT

Building products containing phosphogypsum as the main constituent material, in the form of either binder or filler, are described. Emphasis is placed on the wide range of applications, while specific publications are referenced for detailed mechanical properties. Calcined and raw phosphogypsum cement and fly-ash based mixtures are the four categories of products presented.

1. INTRODUCTION

Recycling of phosphogypsum, by-product of the wet process phosphoric acid industry, is investigated with regard to practical applications in the construction industry.

The scope of this paper is to introduce several building products, developed at the Phosphate Research Institute (PRI), University of Miami, after close to two years of study. The term ‘building product’ is herein used with the broad meaning of an element which can be readily used as manufactured product, e.g. brick for housing, or of material for on-site manufacturing, e.g. plaster or road base-course mix. This presentation is of a descriptive type and reference is made to other publications included in the Proceedings of the Second Seminar on Phosphogypsum, Miami, April 1984, for a full explanation of the technical characteristics.

A discussion of the general problem of reusing solid wastes as construction materials and the approach adopted at the PRI is introduced first. Subsequently, a description of the building products, subdivided into two sections, is given. According to the nomenclature in use, also adopted in leading publications on waste recycling (2), composite materials contain a filler and/or a reinforcement surrounded by a binder (matrix), which performs chemical adhesion. Following this classification, the first section is devoted to products where phosphogypsum acts as a binder, while the second one deals with products containing phosphogypsun as a filler, enclosed in a cementitious matrix.

Display and characterization of building products, whose main component is phosphogypsum, should make the reader aware of the potential of this waste material for engineering use.

2. SOLID WASTES AS BUILDING MATERIALS

The United States is both a major consumer of natural resources and a major producer of mining, industrial, agricultural and municipal waste materials. As an alternative to the traditional methods of solid waste disposal, recycling, in the forms of direct use as or conversion into viable construction materials, allows the conservation of natural resources and mitigates the harmful effects of wastes. on the environment. So far only relatively small amounts of wastes have been utilized by the construction industry, but in the past decade federal and state government agencies have been sponsoring and supporting a significantly growing number of programs and research, which should facilitate their use. In addition the business sector and learned societies are taking an active role in promoting new technologies in this field.

With regard to Florida, the phosphate industry is certainly the major source of mining (sand tailings and phosphate slimes) and industrial (phosphogypsum) wastes. However it is important to recall that this type of industry is present all over the world arising the same type of problems. The Phosphate Research Institute at the Department of Civil and Architectural Engineering, University of Miami, has the goal of promoting research and development on the reuse of phosphate industry wastes, particularly of the by-product gypsum. The philosophy of the Institute is to investigate the basic material properties and the feasible applications in all sectors of the construction industry. A versatile approach not only ensures a better understanding of the material mechanics, but also provides a number of viable applications with different degrees of feasibility according to the location and needs of the industry. Moreover, construction materials obtained from wastes could in some instances have better performance than their existing technological counterparts and also constitute a novelty. The seminar sign, presented in Figure 1, does a little more than just indicate the way to the meeting room: calcined phosphogypsum letters of different colors are glued to a phosphogypsum-cement-sand panel reinforced with abaca fibers (vegetable by-product).

As a final remark it must be reminded that the optimism on the research results is blended with the conservative caution of dealing with health safety. If there is concern about chemical or radiation pollution of the envirownent when wastes are disposed, this aspect certainly becomes the major issue when products related to every-day and all-day exposure are considered. For this reason, applications will be ready for the public use only at the conclusion of favorable health-related studies.

2. PHOSPHOGYPSUM AS A BINDER

3.1 Raw Phosphogypsun

Without any doubt the most appealing way of utilizing phosphogypsum is as it is received from the stockpile, with no additional treatment. The properties of raw phosphogypsum (3) indicate that there is room for direct application in road base-courses as long as the material is mantained at a low moisture content. In fact, the compressive strength, which is a function of the dry density and therefore of the compaction energy, is totally lost when the material is submerged. In order to overcome this deficiency, waterproofing agents have been added to phosphogypsum resulting in water resistant mixtures, samples of which are shown in Figure 2. These agents can be divided into three groups according to the application method:

1) Mixed with phosphogypsum to form a uniform blend

Figure 1

Seminar Sign Made of Elements
Containing Phosphogypsum

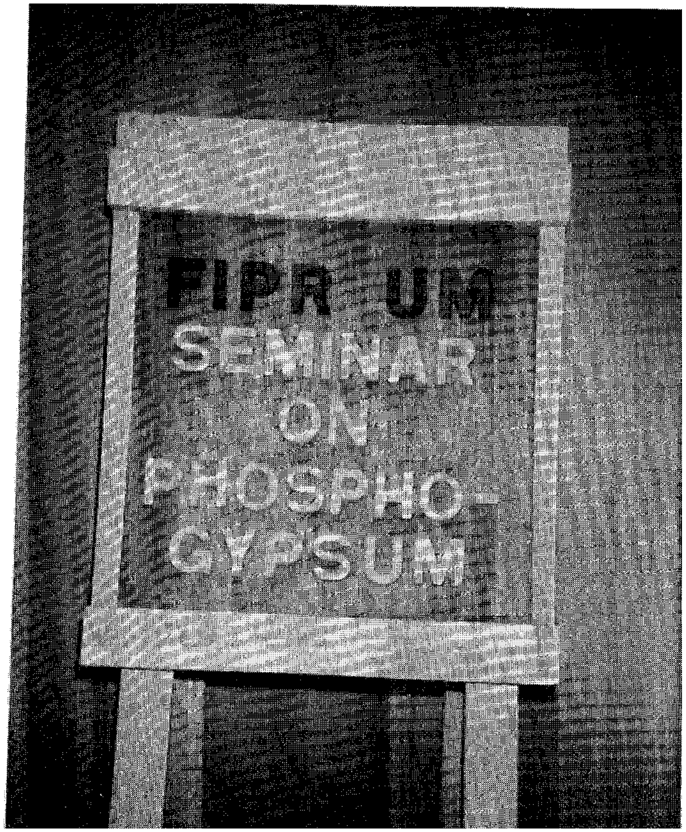
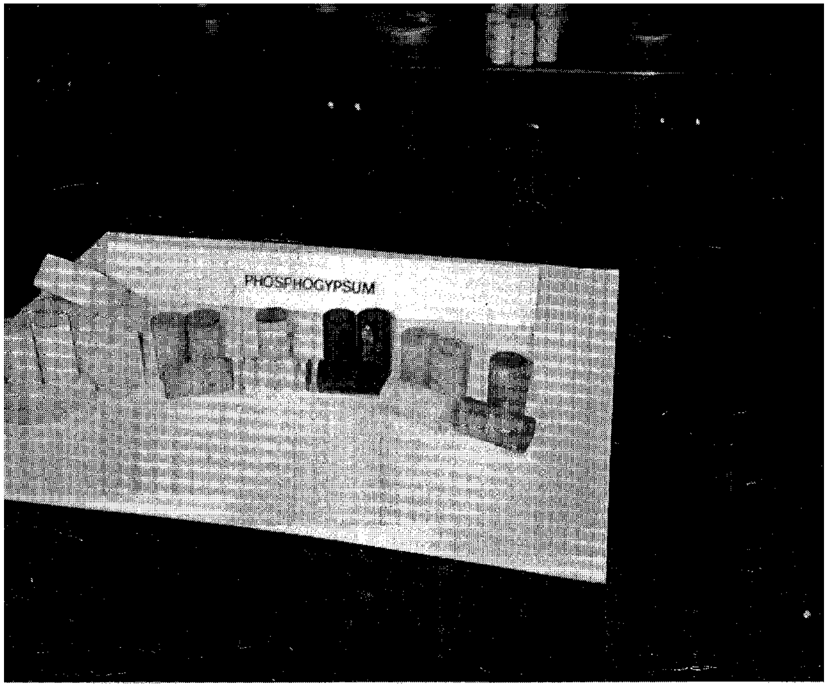


Figure 2

Products with Raw Phosphogypsum as Binder.
From Left, with Asphalt Cutback, with Asphalt Emulsion, with Tar, with Paraffin and with Resin.



2) Painted or sprayed as coatings on the finished product to give a surface treatment
3) Melted on or used as a dipping bath for partial/total penetration

The followings are brief descriptions of each waterproofing agent as used:

1) Asphalt. Rapid curing cutback as well as anionic and cationic emulsions were investigated. These petroleum derived products were added in small percentages to the phosphogypsum in a pan-type mixer, as to obtain a uniform distribution. While emulsified asphalts are found ineffective, rapid curing cutback produces positive results. Waterproofing can be obtained at values as low as 1% of the total dry weight without affecting the air-dry compression resistance, which remains approximately the same as that of phosphogypsum alone.

2) Tar. Coal or petroleum by-product obtained by destructive distillation and commonly used as a roofing material, presents very much the same behavior shown by the cutback asphalt. Waterproofing is obtained at a concentration of 1% of the total dry weight.

3) Resin. Organic polymers can be used as regular paint coatings. They have the characteristic glossy look after drying and do not affect phosphogypsum strength when used as surface treatments. High cost is their major limitation.

4) Paraffin. Macrocrystalline paraffin, petroleum residue with melting point below 60°C, was used to fully saturate phosphogypsum cylinders and also, in liquid form after melting, was added to the mix. Research in progress shows very encouraging results, which indicate not only waterproofing, but also positive effects on strength properties.

3.2 Calcined Phosphogypsum

The methods of obtaining calcined phosphogypsum, together with the material mechanical properties, have been discussed elsewhere (4). The advantages of gypsum building products are well-known in the construction industry and they can be summarized as follows:

1) Excellent fire protection far superior to concrete
2) Heat insulation
3) Air-borne sound insulation
4) Condensation-free surfaces
5) Capacity of exchanging moisture with the surrounding environment and therefore good habitability conditions
6) Crack-free, high-quality surfaces with no need for plastering
7) Ease of coloring and machining
8) Ease of installation, 1.75 times lighter than concrete

These properties make gypsum products particularly suitable for interior and non-structural applications where no reinforcement and waterproofing is required. The products developed at the PRI, presented in Figures 3 and 4, are described next.

1) Decorative Tile and Wall-Board (Figure 3, Left).
   The product is cast on a flat mold and can be colored according to the desired application. If tensile strength needs to be improved the panel can be topped on one or both sides with cardboard sheetings or reinforced with vegetable fibers.

2) Sandwich Brick (Figure 3, Right).
   These bricks were produced using two different mixtures: calcined phosphogypsum with dye for the facings and calcined phosphogypsum containing 2% in weight of sodium sulphate and 2% in weight of calcium carbonate for the core. The presence of the two chemicals causes a reaction leading to the formation of carbon-dioxide bubbles, which create voids in the fresh mixture. An inexpensive way to provide calcium carbonate is simply to add limerock powder, a waste product too fine to be used for road base-courses or fill material. The main advantages of the sandwich brick are to decrease the weight and to improve the insulation value without modifying its exterior appearance. The properties of expanded phosphogypsum are presented in Figure 5, where 7-day strength, dry

Figure 3

Products with Calcined Phosphogypsum as Binder, From Left: Decorative Tile-Wall Boards, Sandwich Bricks and Solid Bricks

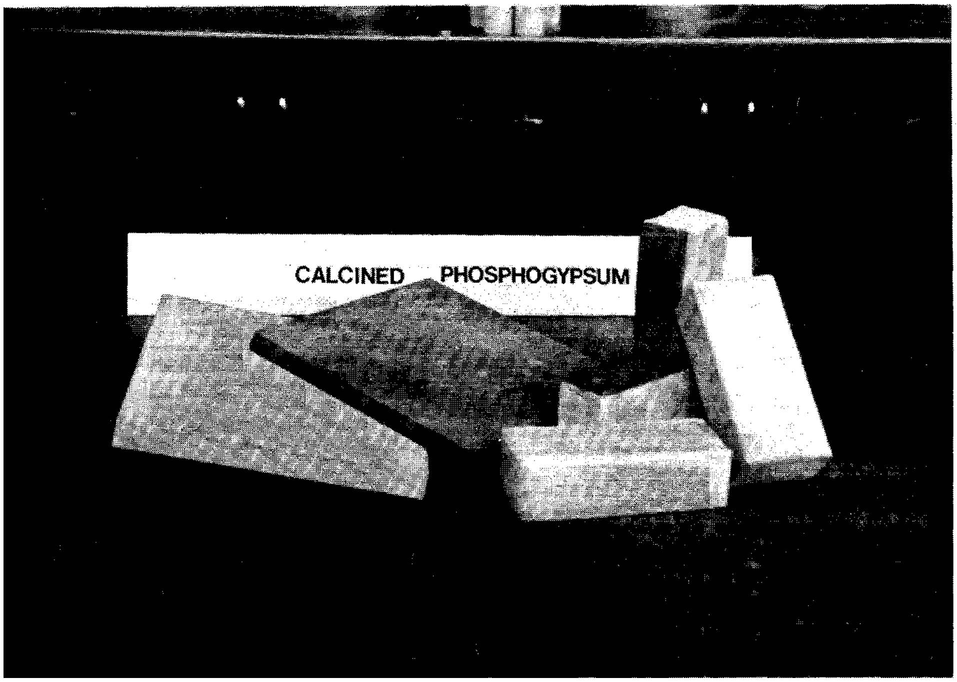


Figure 4

Products with Calcined Phosphogypsum as Binder, From Left: Block, Sandwich Blocks, Floor Tiles, Lettering and Cylinders

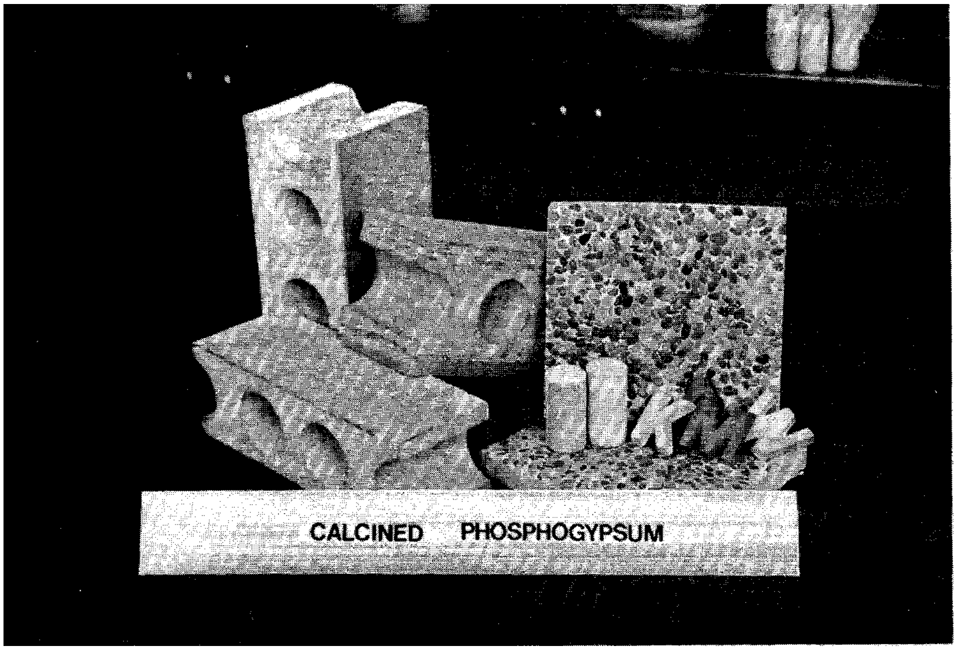
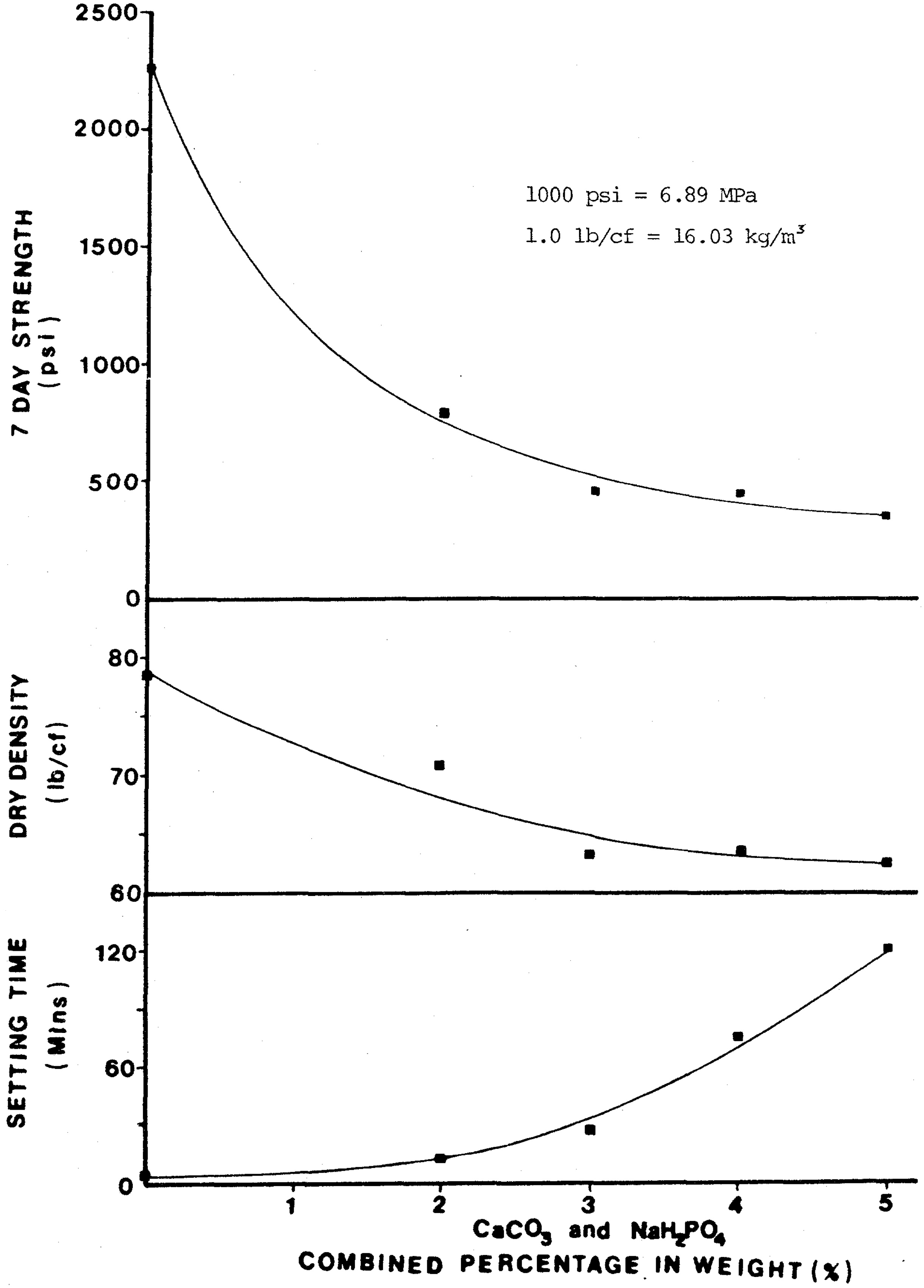


Figure 5

Effects Of Addition Of Sodium Phosphate And Calcium Carbonate In Equal Amounts



1000 psi = 6.89 MPa

1.0 lb/cf = 16.03 kg/m^3

density and setting time are plotted as a function of the content of equal amounts of sodium sulphate and calcium carbonate, expressed as a percentage of the total dry weight.

3) Blocks (Figure 4, Left).

Three types of blocks were produced. The first block (bottom left) consists entirely of calcined phosphogypsum and is suitable for interior walls. The second block (center) has a calcined phosphogypsum core exactly the same as the previous one, with the addition of phosphogypsum concrete facings, which make it usable for exterior applications improving at the same time its bearing capacity. Finally the third type is a sandwich, with expanded phosphogypsum core and calcined, colored facings similar to the bricks described in section 2.

4) Floor Tiles (Figure 4, Right) .

Floor tiles with exposed aggregates on the top side were produced according to the well-established technique of reverse casting adopted for the production of concrete tiles.

5) Lettering (Figure 4, Right).

Decorative, colorful items and unlimited shapes can be easily obtained as shown with these letters. A slight shrinkage of the calcined phosphogypsun product during the hydration phase facilitates the removal from the molds.

As a conclusion to this section devoted to calcined phosphogypsum, it is relevant to mention among other applications the gypsum plaster. It is a mixture of equal amounts of calcined phosphogypsum and fine sand which is used for plastering walls. From a mechanical stand-point the 28-day cylinder compressive strength is approximately 1000 psi (6.89 MPa) for a water/gypsum ratio of 0.66 .

4. PHOSPHOGYPSUM AS A FILLER

4.1 Cement Binder

One of the most exciting applications of phosphogypsum is its use as aggregate for cement based mixtures. Mechanical properties of phosphogypsum-cement-sand have been reported elsewhere (6). Under current investigation is the addition of gravel for the development of a “compaction concrete” to be used for a wide range of applications spanning from road courses to precast building products. This would represent an important novelty for the construction industry which could take advantage of the fineness of phosphogypsum and its remarkable property of self adhesion when subjected to compaction. Moreover, in the field of soil stabilization, the advantage of phosphogypsum-cement mixtures consists in the homogeneity of phosphogypsum as compared to soil and the possibility of plant mixing which can guarantee proper blending at low cement content.

Products developed with phosphogypsum mortar are presented in Figure 6 and described below.

1) Compaction Brick (Figure 6, Front Left and Center).
   These three sets of bricks were produced by static compaction using different component proportions. As mentioned, the use of compaction as placement technique is favored by the presence of phosphogypsum and its high fineness. In addition, since workability is not a relevant parameter anymore, the amount of optimum mixing water is lowered with beneficial effects on strength and density. The appearance of the products obtained by compaction is of high quality. Moreover, bricks may be demolded immediately after placement since they maintain their shape. From an industry stand-point this is a tremendous advantage in terms of savings in man-power, operation-time and storage facilities.
2) Vibration Bricks (Figure 6, Front Right).
   These elements were obtained by pouring phosphogypsum-cement-sand mixtures into plywood molds subjected to external high-frequency vibrations. Specimens were cured for a 28-day period at a room temperature of approximately 75°F (24°C) and relative humidity of 60%. The results of six different mixes, tested in accordance to American Society for Testing and Material (ASTM) standards, are summarized in Table 1. The values obtained satisfy all ASTM requirements. As a result, phosphogypsum brick production was ap-

proved by the Metropolitan Dade County and Zoning Department on July 11, 1983. Other results, presented in Table 2, show the effects of wetting and drying cycles for bricks tested in air-dry conditions. It can be seen that after two cycles the steady state is reached.

3) Abaca Fiber Reinforced Panel (Figure 6, Back).
The properties of this composite product and its application as an alternative to gypsum wall-boards are dealt with in reference 8.

As additional building products with cement binder, ferrocement panels and sandwich ferrocement panels, as described in reference 5, are also to be considered as viable applications for the precast industry in particular.

Table 1: Summary of Brick Test Results According to ASTM C-67.

	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6
Phosphog./Cement	1.85	1.82	1.50	1.50	1.50	1.50
Sand/Cement	0.5	0.5	0.5	0.5	0.5	0.5
Water/Cement+Phph.	0.31	0.33	0.32	0.31	0.34	0.36
Compression (psi)	3093	3500	5140	4730	3866	3554
Modulus of Rupture (psi)	774	846	1200	1026	902	801
Saturation Coeff.	1.04	1.06	1.08	1.03	1.10	1.03
Suction (%)	1.0	0.5	0.4	0.36	0.56	0.5

Note: 1000 psi= 6.89 MPa

Table 2: 28-Day Compressive Strength after Wetting and Drying Cycles.

Compression (psi)	Mix 1	Mix 2	Mix 3	Mix 4	Mix 5	Mix 6
No Drying	3093	3500	5140	4730	3866	3554
Drying @ 60°C	2795	3302	4438	3616	3431	2840
Drying @ 110°C	1698	1800	2713	2895	2462	1742
110°C + Saturation	4380	4900	5429	5222	4715	4027
110°C +Sat.+ 110°C	3013	3637	5211	3893	4062	3622

Note: 1000 psi= 6.89 MPa
Drying in convection oven for 24 hrs
Wetting for 7 days in 100% humidity room

4.2 Fly-Ash Lime Binder

Hydration products resulting from the reaction of fly-ash, lime and water are similar to those produced by cement and water. Specimens using the combination of these two materials are presented in Figure 7. Considering that the long term characteristics of the two binders are similar, there is a self-evident advantage in substituting cement with the by-product of the coal burning industry. However, the hydration rate, and therefore hardening and early strength, of fly-ash lime mixtures is remarkably slower than in cement. This factor has determined a preference to use it in road construction as discussed in Reference 7.

A fly-ash lime binder could profitably be used in the building industry in combination with cement in order to have acceptable early strength and improved compactability. Another attractive possibility is to accelerate curing by subjecting specimens to heat after casting. The results of pilot testing, presented in Figure 8, clearly show the beneficial effect of heat. For a 24-hour period, the best results are obtained at a temperature of 70°C.

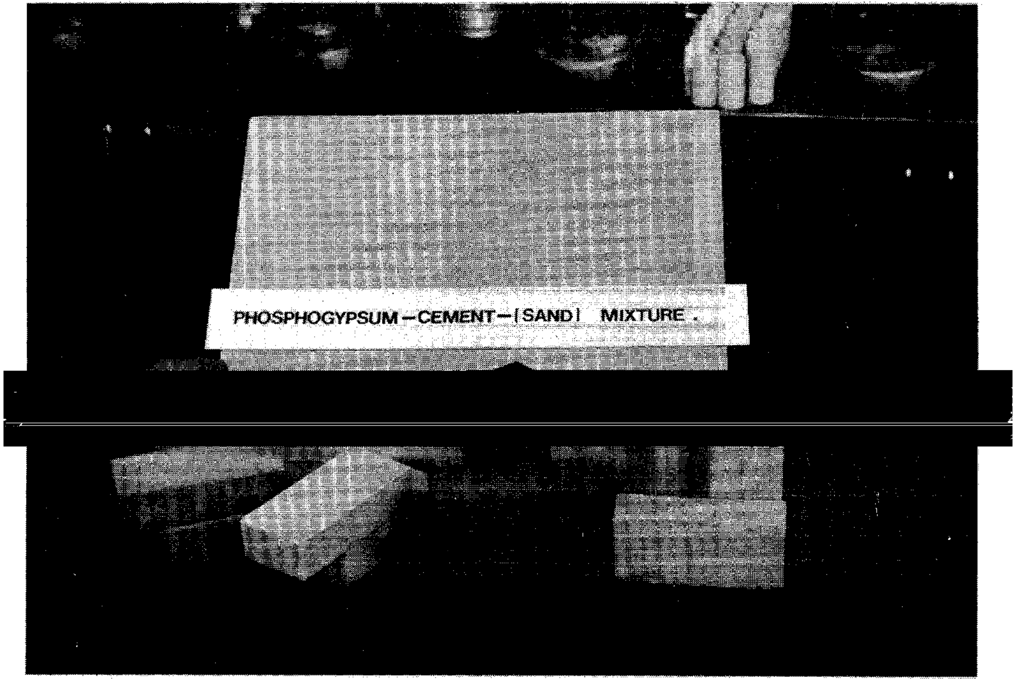
5. CONCLUSION

The phosphogypsum building products developed at the PRI indicate that this waste material can satisfactorily be used by the construction industry.

Figure 6

Phosphogypsum as Filler in Cement Based Materials.

Panel Reinforced with Abaca Fiber (Back) and Bricks Produced by Static Compaction (Left and Center) or High-Frequency Vibrations (Right)



Phosphogypsum as Filler in Fly-Ash Lime Based Materials

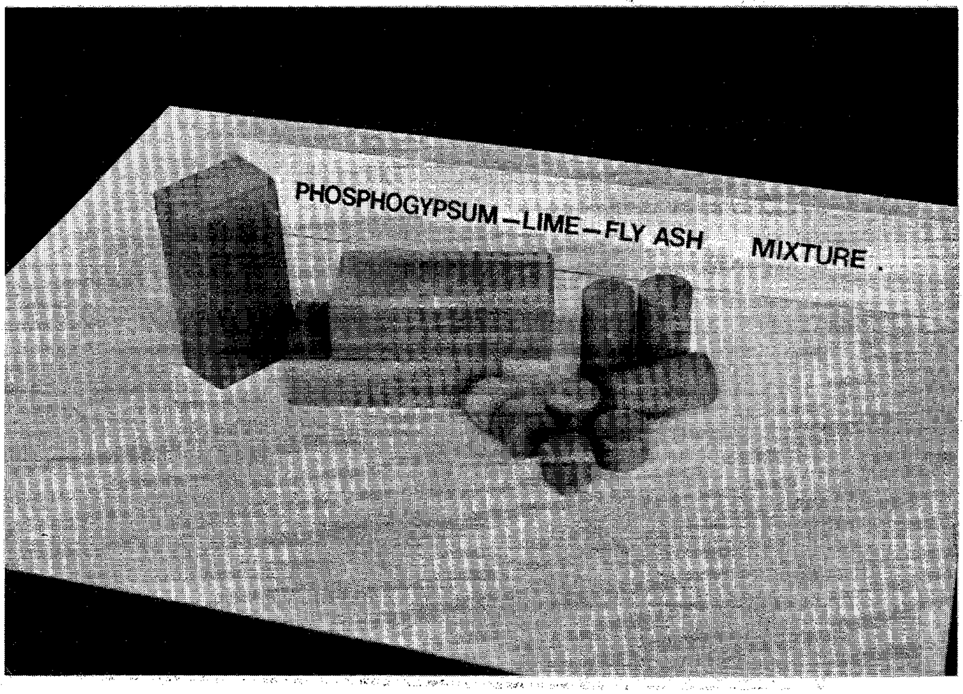
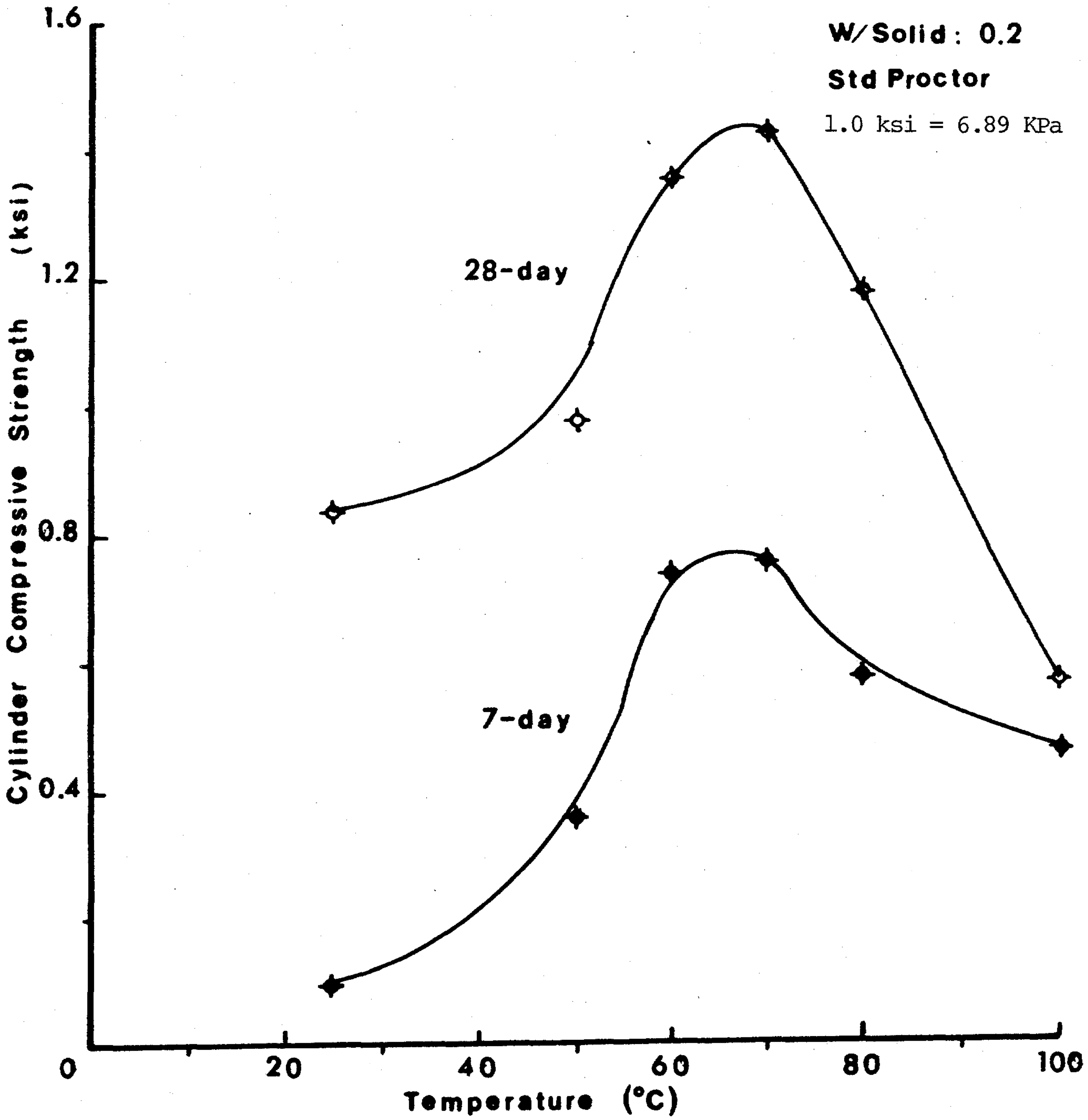


Figure 8

Compressive Strength of Phosphogypsum, Fly-Ash and Lime Mixture (0.60:0.32:0.08) vs. Curing Temperature for a 24-Hour Heating Period under Sealed Conditions



It was the intent of the Institute to explore the various areas of application in Civil Engineering, ranging from road construction to precast components. In the opinion of the authors, this search has been very successful and should be continued.

ACKNOWLEDGEMENTS

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

The phosphogypsum mortar bricks produced by vibration and the sandwich blocks are the result of work done by Mr O. Blanco, as part of his M.S. thesis. The help of Mr K.T. Lin in the preparation of some of the samples is also greatly appreciated.

APPENDIX.-REFERENCES

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PHOSPHOGYPSUM CANOES AND MODULAR BUILDING CONSTRUCTION

Antonio Nanni
Ph.D. Candidate, Dept. of Civil and Architectural Engineering,
University of Miami, Coral Gables, FL.

and

Wen F. Chang
Professor, Dept. of Civil and Architectural Engineering, and
Director Phosphate Research Institute,
University of Miami, Coral Gables, FL.

ABSTRACT

Current research at the Phosphate Research Institute of the University of Miami, is aimed to investigate the potential of phosphogypsum for building and marine constructions.

Two racing canoes and a modular building unit were constructed using phosphogypsum as their main component material. The canoes constructed for nation-wide racing projects, consist of folded ferrocement plates 1/4 in. and 3/16 in. (6.4 and 4.8 mm) thick respectively. The transportable building module side-walls, roof and floor are made of precast ferrocement sandwich panels assembled with cast-in-place joints. Panels consist of a polystyrene core of variable thickness, which separates two ferrocement facings, each 3/8 in. (10 mm) thick. It is shown that phosphogypsum can satisfactorily be used as an aggregate in cement-based mixtures since its small grain size particles improve surface finishing as swell as improve penetration through closely spaced reinforcement and minimum thickness control as required in ferrocement products.

The advantages of this technique are numerous; strong, light-weight, durable constructions can be built in factories resulting in cheaper labor cost and better quality control.

1. INTRODUCTION

During the Summer of 1982, the first precast ferrocement canoe was constructed using a phosphogypsum-cement-sand mixture to be used in the American Society of Civil Engineers (ASCE) student chapters racing competitions. This event coincided with the beginning of an extensive study on the use of by-product gypsum for building, marine and highway constructions at the University of Miami. Recently, important results have been obtained in the understanding of the phosphogypsum mechanical behaviour and in the assessment of its potential as a new construction material. The production of a second racing canoe (Spring 1983) and a modular building unit (Spring 1984), made of precast ferrocement sandwich panels assembled with rigid joints to form a 14x7x8 ft (4.3x2.1x2.4 m) module, were other important landmarks. They are not only relevant achievements from a technical standpoint, but also are evidence of a growing involvement of the student body in research, which has contributed to an extended educational and practical experience.

In the following sections a presentation of the techniques adopted in the construction of the canoes and the building module are given along with a detailed description of the geometrical characteristics of these prototypes and the physical properties of the materials used. Results and evaluation of laboratory tests of sandwich panels in edge-wise compression and bending and of cast-in-place joint effectiveness will be reported in future publications.

The prototypes discussed herein represent the first attempt ever to use phosphogypsum as a structural mix component in building and marine constructions. Furthermore the use of precast, cement-based modular systems is proposed as a viable alternative to conventional construction for low-cost housing.

2. MATERIAL AND CONSTRUCTION TECHNIQUES

2.1 Phosphogypsum-Cement-Sand Mixtures

The characteristics of phosphogypsum as well as the mechanical properties of phosphogypsum-cement-mixtures, adopted as matrix in the project, have been reported elsewhere (5,6). However it should be mentioned that for both constructions the by-product gypsum content was at least 50% in weight and the sources were Agrico Co. (for the canoes) and Gardinier Inc. (for the building unit).

2.2 Ferrocement

Ferrocement is a type of thin wall reinforced concrete commonly constructed of hydraulic cement mortar reinforced with closely spaced layers of continuous and relatively small wire diameter usually metallic mesh (1). Particularly advantageous in spatial structures, ferrocement has better mechanical properties and durability than ordinary reinforced concrete. Its good performance is greatly affected by the uniform distribution and high surface-area to volume ratio of its reinforcement from which matrix ultimate strain is improved and cracking propagation develops in a controlled manner.

Mixtures containing phosphogypsum are particularly suited to ferrocement applications. In fact, the small grain size of phosphogypsum improves ease of penetration through closely spaced reinforcement, as well as wall thickness control and quality of surface finishing.

2.3 Sandwich Panels

Structural sandwich construction is a laminar construction comprising a combination of alternating, dissimilar, simple or composite materials assembled and intimately fixed in relation to each other such that the advantageous properties of each are used to attain specific structural advantages for the complete assembly (2). The principal reason for using this construction approach is the structural efficiency that may be achieved. The combination of thin, rigid facings firmly connected by ribs interspaced by light-weight cores was used in this research to create a geometry which provides great strength and rigidity with a fraction of the weight otherwise necessary. The facings provide the internal couples resisting bending, the resistance to edge-wise loading and the resistance to racking, while the ribs resist shear and stabilize the facings against buckling. One of the most attractive features of sandwich construction is the ability to provide high thermal insulation efficiency and control of sound transmission with minimum thickness of 'structural' material. Low density cores such as expanded plastics are very desirable in providing these characteristics.

The use of ferrocement as a facing material for sandwich construction was first investigated in the early 1970's by Chang (4) for a structural application similar to the one presented herein.

3. CANOES

The, racing canoes were built using mortar with mix proportions (expressed as percentage of the total dry weight): phosphogypsum 50%, cement 28% and sand 22% (3). The water-cement plus phosphogypsum ratio, which describes workability more appropriately than the traditional water-cement ratio, was .30. Panels were cast horizontally on a platform, where the reinforcement, consisting of two layers of 2x2 22 gauge (spacing= 10 mm, diameter= 0.73 mm) galvanized welded wire mesh, was placed according to the layout shown in Figure 1. Precast panels (Figure 2) were folded after hardening following premarked joints, and finally assembled together to complete the canoe as shown in Figure 3. Joints were filled with phosphogypsum mortar containing additive before painting.

This technique of flat casting allows high quality control of matrix penetration, thickness and finishing. Both canoes are 16 ft (4.9 m) long and have wall-thicknesses of 1/4 in. (6.4 mm) and 3/16 in. (4.8 mm) respectively . The thinner wall resulted in a reduction in weight of 200 lb (91 kg) to 150 lb (68 kg).

4. MODULAR BUILDING

A modular building is the result of the on-site assemblage of modular, factory-built, transportable units.- Concrete-made housing utilizing this technology, benefits from a mechanized, industrial operation with the consequent advantages of automation, repetition, year-round production and quality control. This type of construction also preserves resistance, durability and low-maintenance requirements proper of concrete products. A single-modulus, multi-unit building system was designed following this approach. This construction represents the first attempt in the use of gypsum by-product as a principal mix component in housing applications.

The mix proportions adopted in the project were: 50% phosphogypsum, 25% cement and 25% sand, expressed as percentages of the total dry weight. The water-cement plus phosphogypsum ratio was equal to 0.33 whereas the mix unit weight was 122 lb/cu ft (1,980 kg/m^3). Average strength values in compression and indirect tension are given in Table 1 for different testing ages.

Figure 1

Layout of Boat Panels. Internal Lines Represent Joint Positions

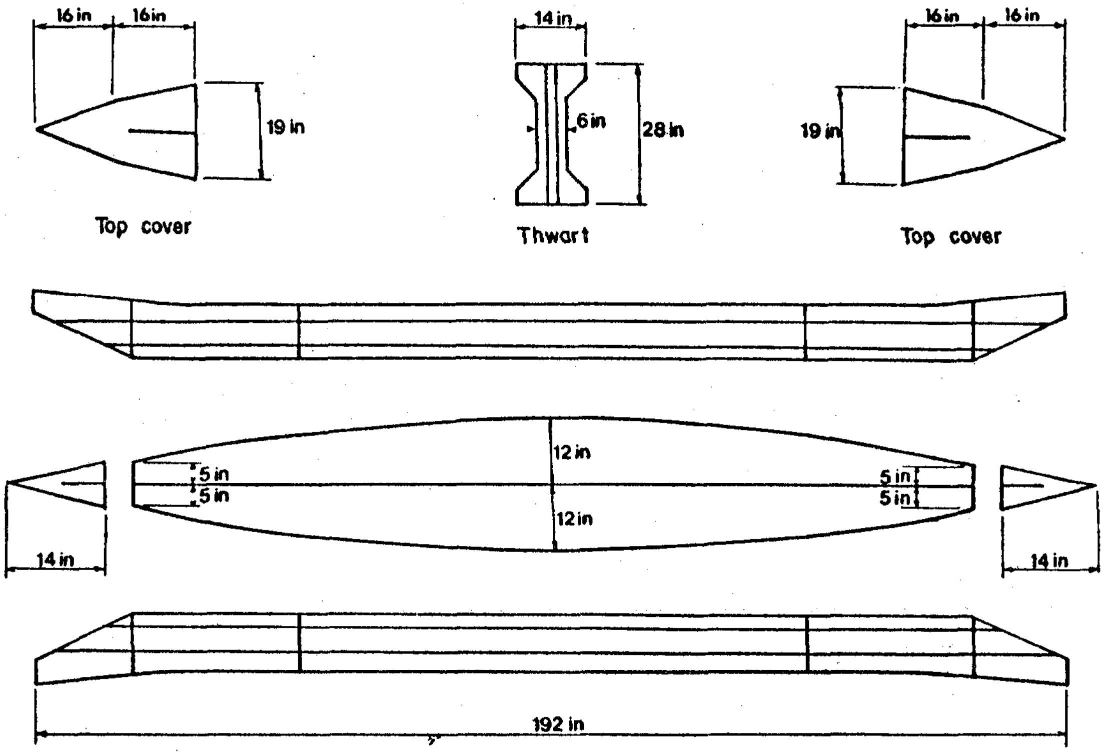


Figure 2

Ferrocement Precast Panels

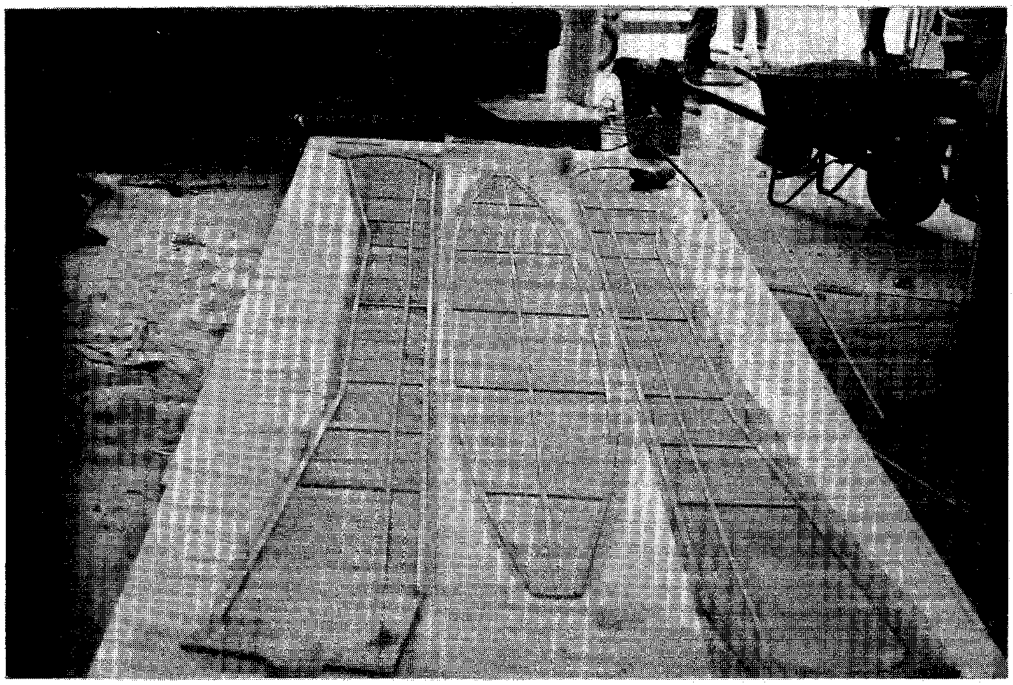


Figure 3

Completed Boat after Joint Filling

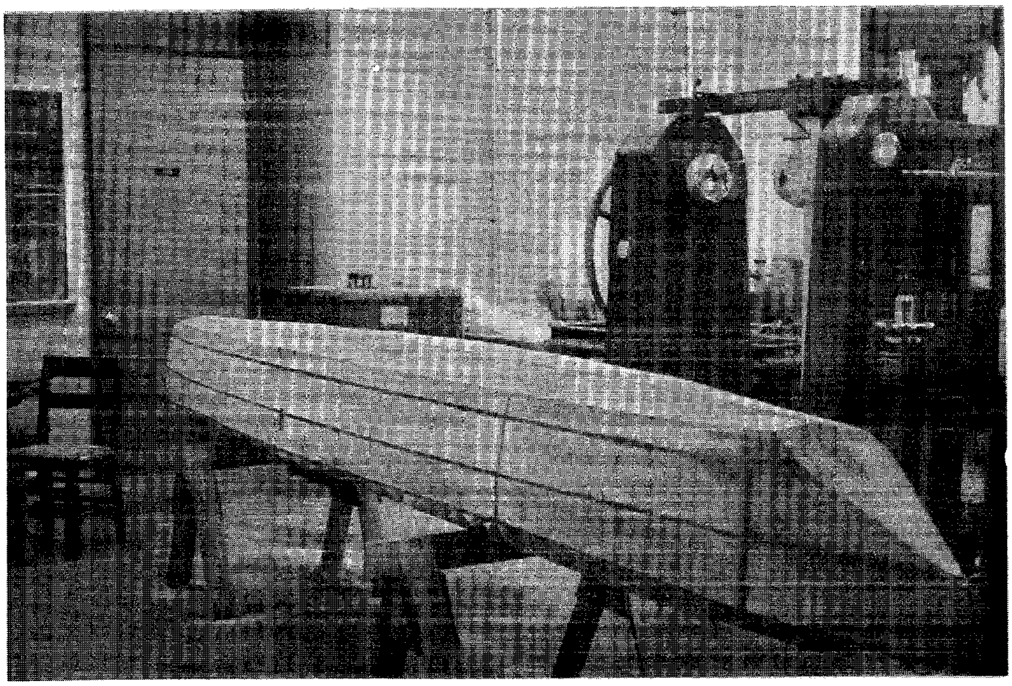


Table 1: Compressive and Indirect Tensile Strength

Testing Age (days)	3	7	28
Compressive Strength (psi)	982	1806	2726
Standard Deviation	(72.7)	(166.2)	(261.5)
Splitting Strength (psi)	144	186	264
Standard Deviation	(10.8)	(16.6)	(26.7)

Note: 1000 psi = 6.89 MPa

The top and bottom ferrocement facings of the sandwich panels used in the project were 3/8 in. (10 mm) thick and were reinforced with woven galvanized steel wire mesh, gage 19 (diameter=1.04 mm), with a spacing of 1/2 in. (13 mm). A single layer of mesh was used except for the top facing of the floor panels, where 2 layers were utilized in order to provide better ductility and punching resistance. Tensile testing on mesh samples showed an ultimate strength equal to 64.9 ksi (447.4 MPa).

Ferrocement facings were separated by a core consisting of polystyrene with a density of 0.98 lb/cu ft (15.7 kg/m^3). Commercial-size sheets, 4 by 8 ft (1.2x2.4 m) , were cut into 16 in. (0.3 m) wide strips and placed in the panel forms 1.0 or 1.5 in. (25 or 48 mm) apart. This scheme permitted the formation of solid mortar ribs which provided suitable connection and bonding between the two facings. The ribs were reinforced with longitudinal W2 grade 40 and D5 grade 60 (diameter= 4.04 or 6.40 mm) steel wires in both roof and floor panels. Polysterene thicknesses of 2, 3, 4 in. (50, 75, 100 mm) were adopted for side-walls, floor and roof respectively . The typical panel cross-section is shown in Figure 4, while the module plant-view and cross-section are given in Figure 5.

Constraints in terms of facilities, labor, time of execution, transportation and budget, limited the design of the unit to a minimal 98 sq ft (11 m^2) area. However, it was possible to show the potential of this technique to its full extent and it is expected that practical distributions can be assembled as the ones shown in Figure 6. Construction was completed in 3 months utilizing unskilled personnel on weekends. The various construction phases are presented in Figures 7 to 11.

Figure 4: Typical Panel Cross-Section (1 in.= 25.4 mm)

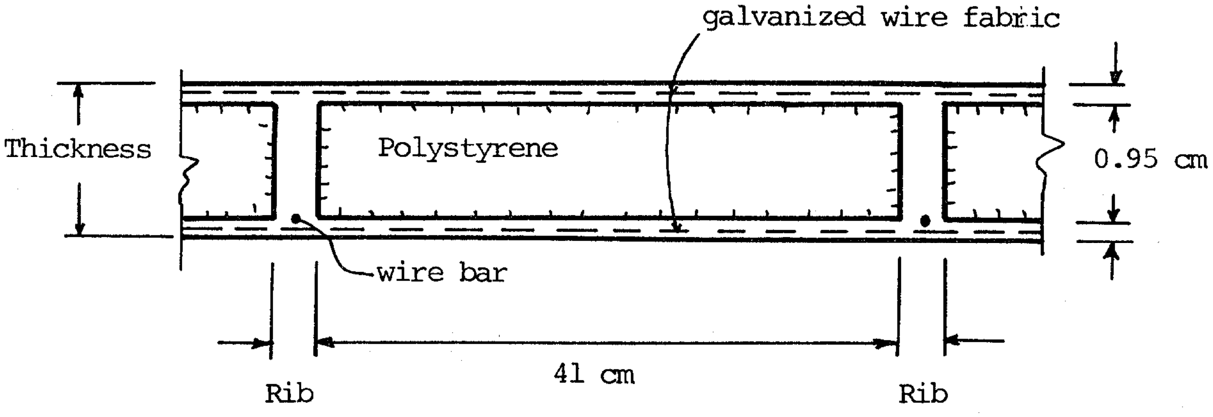
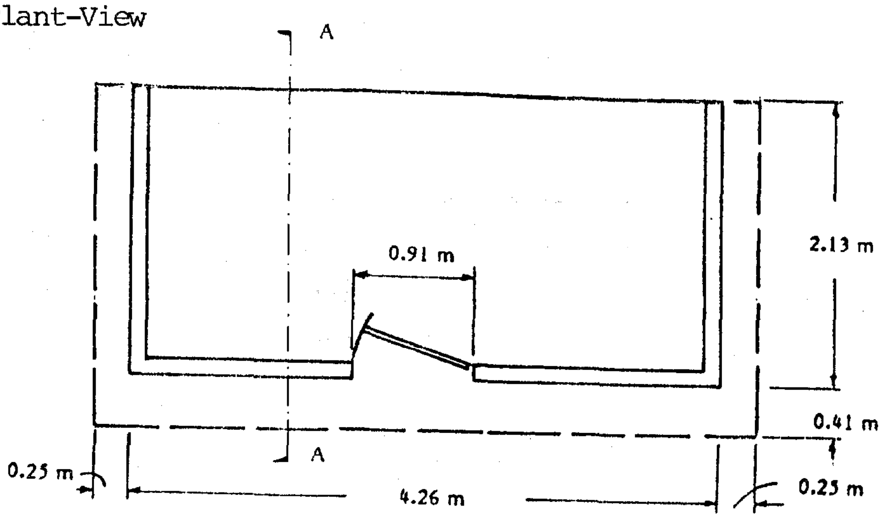


Figure 5

Module Plant-View and Cross-Section

(a) Plant-View



(b) Cross-Section

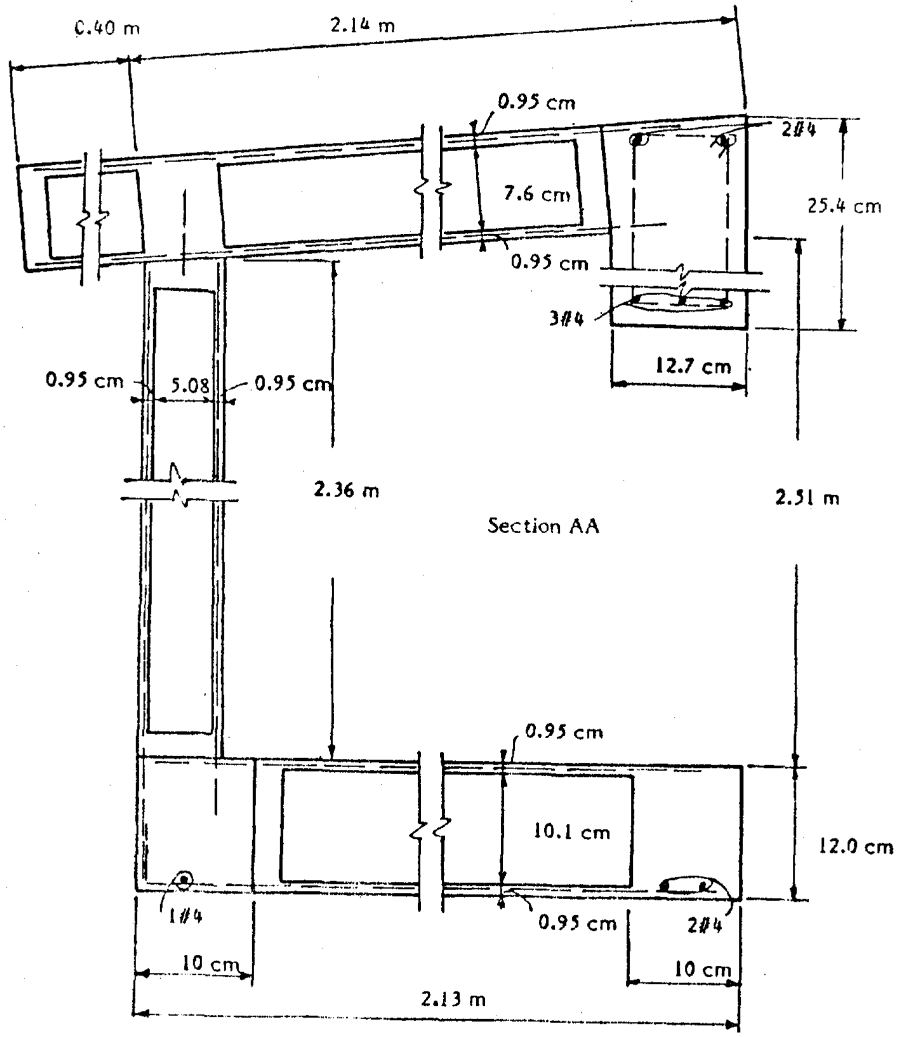


Figure 6

Plant View of 2-Unit Combinations

(1 in. = 25.4 mm, 1 ft = 0.305 m)

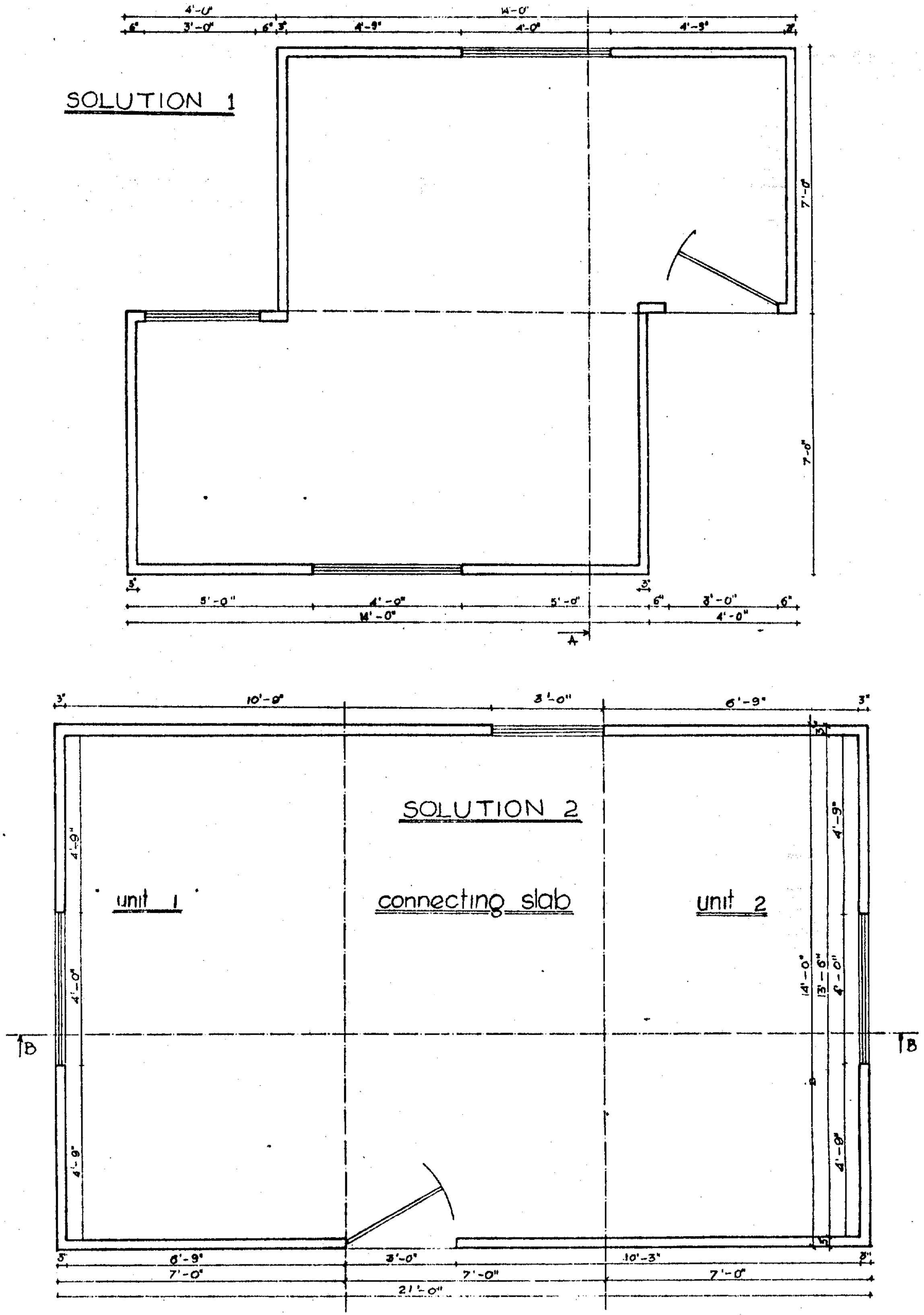


Figure 7

Panel Fabrication. Casting Solid Ribs between Polystyrene Strips

Figure 8

Lifting and Positioning Side-Wall Panels

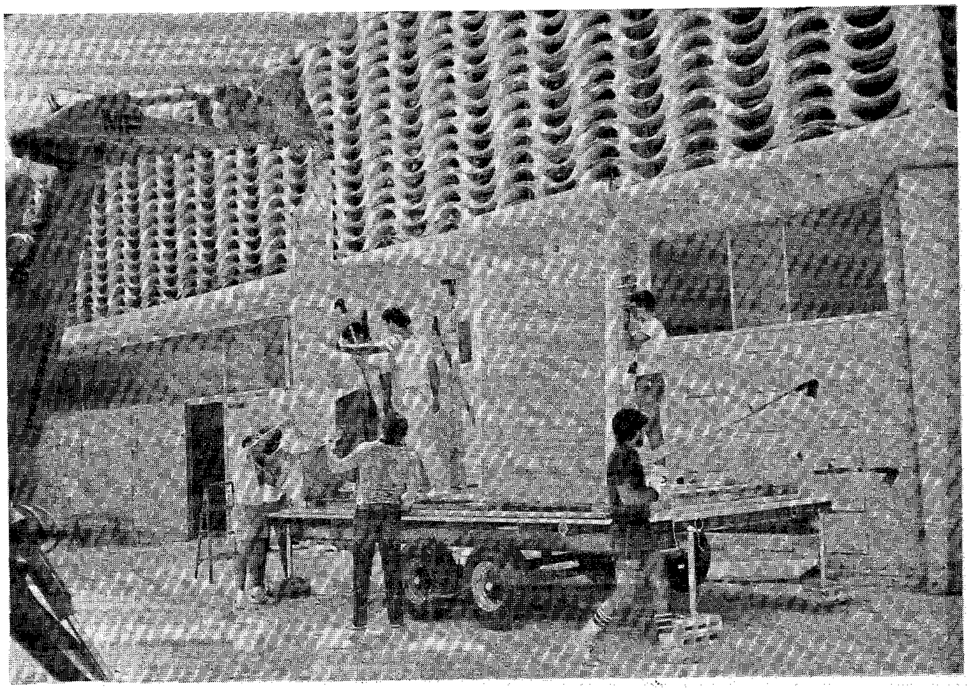


Figure 9

Cast-in-Place Joint Connecting Side Wall Panels to Floor

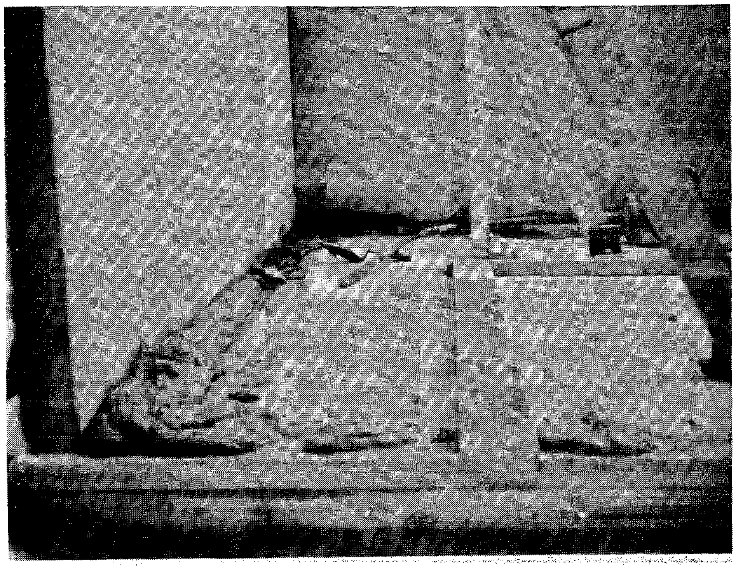


Figure 10

Lifting and Positioning Roof Panels

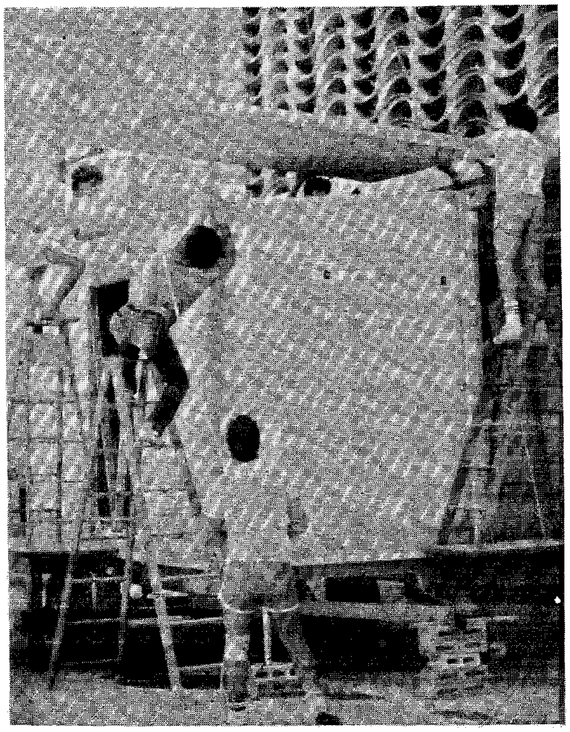
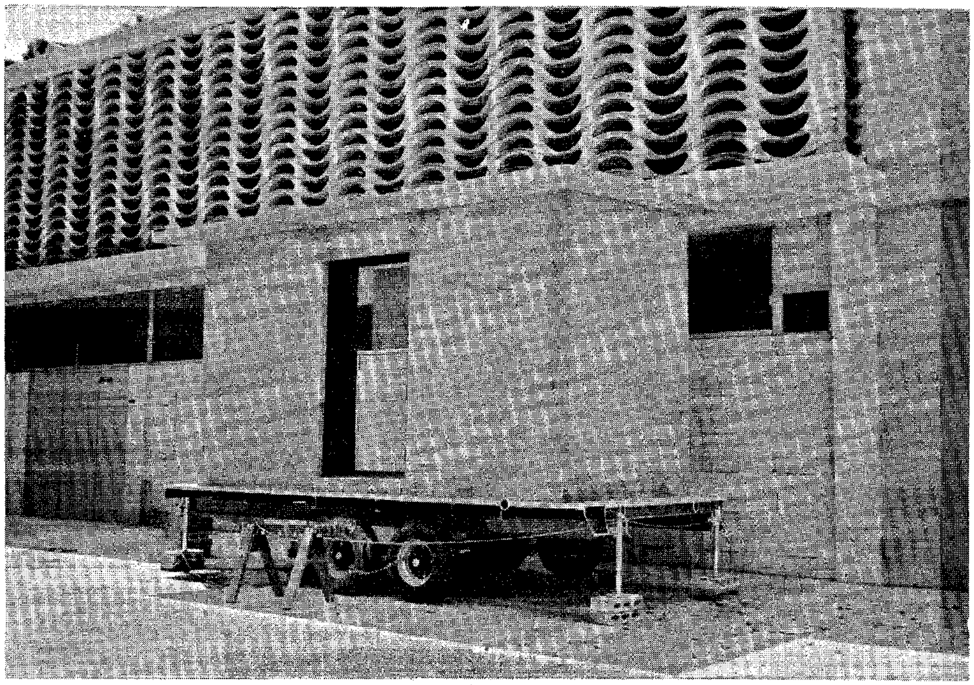


Figure 11

Complete Unit



5. CONCLUSION

The main objective of these projects was to prove that, from a structural point of view, phosphogypsum could be considered a viable construction material when used as filler in cementitious mixes and in particular in applications with thin cross-sections and industrialized procedures.

Having established that the 'strength' requirements are met, the expectation of seeing this by-product disappear from the undesirable list of the waste materials, is one step closer to reality.

ACKNOWLEDGEMENTS

The project was funded by a grant from the Florida Institute of Phosphate Research, Bartow, Florida, and the material was provided by Agrico Co., Lakeland, Florida, and Gardinier Inc., Tampa, Florida.

Credit for the construction of both canoes and modular unit is entirely given to the Student Chapter of the American Society of Civil Engineers (ASCE) at the University of Miami.

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STATE OF FLORIDA
DEPARTMENT OF TRANSPORTATION
Bureau of Materials and Research
P.O. Box 1029
Gainesville, Florida
32602

RESEARCH REPORT FL/DOT/BMR-84-276

COMMENTS ON THE INVESTIGATION OF PHOSPHOGYPSUM FOR EMBANKMENT CONSTRUCTION

by

Robert K. H. Ho
Soils Materials and Research Engineer
Bureau of Materials & Research

and

W. H. Zimpfer
Associate Professor
Department of Civil Engineering
University of Florida

Presented at Seminar on Phosphogypsum
J. L. Knight International Conference Center
University of Miami
April 26 & 27, 1984

April, 1984

ACKNOWLEDGEMENTS

The Florida Department of Transportation sincerely appreciates the cooperation and assistance of the six phosphate companies, W. R. Grace, Gardinier, Amax, Conserv, Occidental, and International Materials and Chemical Corporation (IMC), who supplied the phosphogypsum material necessary to conduct this study.

The writers are also grateful to the engineers and technicians in the Soils Section of the Bureau of Materials and Research, Gainesville, who contributed to the preparation of this report.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF PLATES

LIST OF FIGURES

INTRODUCTION

A recent research study was performed at the Florida Department of Transportation (FDOT) Bureau of Materials and Research on the use of waste materials in highway pavement and embankment construction. A cooperative research program between the FDOT and the University of Florida Department of Civil Engineering was established to evaluate the potential application of phosphogypsum, fly ash, incinerated garbage, and bottom ash as roadway material. This report deals entirely with the laboratory evaluation of seven phosphogypsum sources.

SOURCES OF PHOSPHOGYPSUM

In 1982, the Bureau of Materials and Research initiated a preliminary investigation of the use of phosphogypsum, which is a solid waste by-product of phosphoric acid production, for use in highway construction as a flexible pavement base or subbase and as embankment material. Phosphogypsum, also referred to as gypsum, is calcium sulfate dihydrate, $CaSO_4 \cdot 2H_2O$. This waste product has been used as base for haul roads and as embankment soil on some local phosphate mining sites.

Since phosphogypsum is available in abundant quantities and could be an economical source of material for roadway construction, it was decided to evaluate its potential as a pavement material. The selected sources were: W. R. Grace, Gardinier, Amax, Conserv, Occidental (two locations), and International Materials and Chemical Corporation (IMC). A total of seven sources of phosphogypsum have now been investigated. Five of these sources are located between Tampa and Bartow in Polk, Hillsborough, and Manatee Counties, as shown in Figure 1. The remaining two sources are from Occidental, which is located in White Springs, North Florida,

LABORATORY TESTING PROGRAM

A comprehensive laboratory testing program was performed on all seven sources of gypsum. These tests were:

1. Grain Size Analysis (Sieve and Hydrometer)
2. Atterberg Limits
3. Specific Gravity
4. Moisture-density Relationship
5. Limerock Bearing Ratio
6. Permeability
7. Triaxial Compression Test
8. Gypsum Content and pH

Materials from each source were transported by the Bureau of Materials and Research personnel in a five-yard dump truck. Locations of these materials were determined by the respective plant personnel.

Most tests were conducted in replicates of three to determine the inherent variability between samples. Average values and their ranges are presented for the physical and engineering properties in Table I and II. Since gypsum is

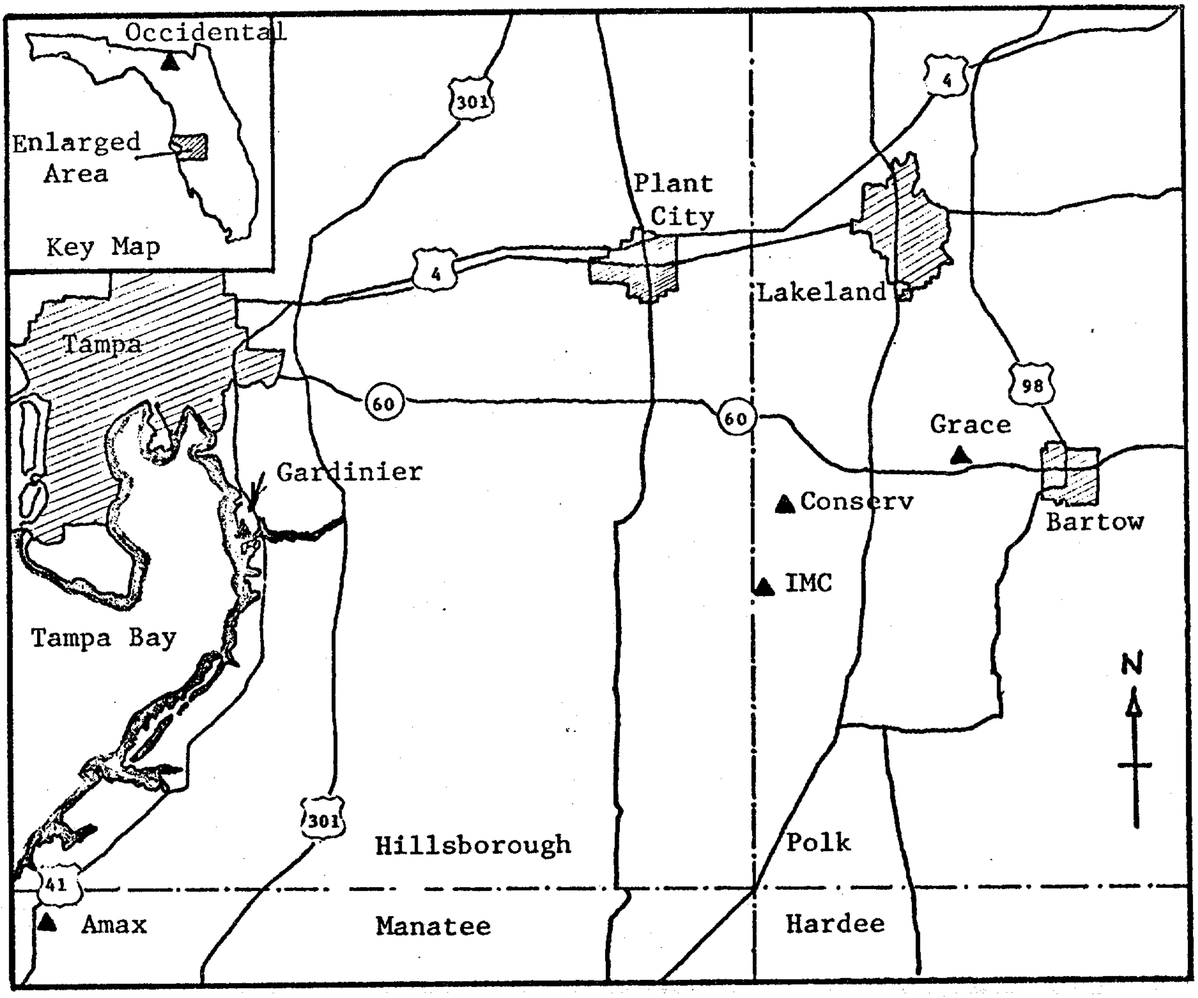


Figure 1. Location of Phosphogypsum Sources.

TABLE 1. LABORATORY TEST SUMMARY

SOURCE		SPECIFIC GRAVITY	SIEVE SIZE (% PASS)			PH	% GYPSUM	PERMEABILITY cm/sec	
			40	60	200			MOD. DENSITY	STD. DENSITY
W. R. GRACE	Avg.	2.39	100	99	55	3.5	92.5	3.2×10^{-5}	3.5×10^{-4}
	Range	2.35-2.42	100	99	53-58			$3.7\text{-}2.7 \text{x} 10^{-5}$	$3.8\text{-}3.3 \text{x} 10^{-4}$
AMAX	Avg.	2.33	100	99	72		89.0	6.3×10^{-5}	1.7×10^{-4}
	Range	2.33	100	99	71-72	3.5-5.4		$7.8\text{-}5.4 \text{x} 10^{-5}$	$2.4\text{-}1.0 \text{x} 10^{-4}$
OCCIDENTAL 1	Avg.	2.35	100	98	79	2.5	96.7	1.5×10^{-5}	3.5×10^{-5}
	Range	2.33-2.36	100	98	77-82			$1.9\text{-}1.3 \text{x} 10^{-5}$	$4.3\text{-}2.9 \text{x} 10^{-5}$
GARDINIER	Avg.	2.40	93	88	51	4.3	81.3	4.5×10^{-5}	5.9×10^{-5}
	Range	2.40	93	87-88	49-53			$4.7\text{-}4.3 \text{x} 10^{-5}$	$7.6\text{-}4.2 \text{x} 10^{-5}$
OCCIDENTAL 2	Avg.	2.34	100	98	80	4.9	98.7	4.1×10^{-5}	7.5×10^{-5}
	Range	2.31-2.38	99-100	97-98	79-81			$5.9\text{-}2.5 \text{x} 10^{-5}$	$8.0\text{-}7.0 \text{x} 10^{-5}$
CONSERV	Avg.	2.44	100	96	31	6.0	99.3	9.7×10^{-5}	4.6×10^{-5}
	Range	2.39-2.53	100	96-97	30-33			$1.0\text{-}.93 \text{x} 10^{-4}$	$5.1\text{-}4.1 \text{x} 10^{-5}$
I.M.C.	Avg.	2.34	100	98	69	5.2	95.0	5.0×10^{-5}	6.8×10^{-5}
	Range	2.33-2.35	99-100	98-99	66-71			$5.1\text{-}4.8 \text{x} 10^{-5}$	$7.1\text{-}6.1 \text{x} 10^{-5}$

TABLE II LABORATORY TEST SUMMARY (continued)

SOURCE		MAXIMUM DRY DENSITY (PCF) & OPTIMUM MOISTURE		LBR	TRIAXIAL
		MODIFIED	STANDARD		
W. R. GRACE	Avg.	97.1 @ 15.0	91.7 @ 12.8	40.2	$\bar{\phi} = 50.0^\circ$ $\bar{c} = 0$
	Range	96.3 - 97.6 @ 14.6-15.5		37.0 - 41.0	
AMAX	Avg.	90.3 @ 18.4	83.0 @ 19.2	5.0	$\bar{\phi} = 47.5^\circ$ $\bar{c} = 0$
	Range	90.2 - 90.4 @ 18.2-18.4		4.5 - 5.5	
OCCIDENTAL 1	Avg.	92.2 @ 17.3	91.7 @ 18.9	13.5	$\bar{\phi} = 45.0^\circ$ $\bar{c} = 0$
	Range	91.8 - 92.5 @ 17.1-17.4		13.0 - 14.5	
GARDINIER	Avg.	101.0 @ 14.1	95.0 @ 16.8	26.0	$\bar{\phi} = 49.0^\circ$ $\bar{c} = 0$
	Range	100.0-102.7 @ 14.0-14.1		22.0 - 29.0	
OCCIDENTAL 2	Avg.	91.6 @ 17.7	84.6 @ 21.6	7.5	$\bar{\phi} = 43.5^\circ$ $\bar{c} = 0$
	Range	91.4 - 91.7 @ 17.3-18.0	84.0-85.0 @ 19.7- 22.7	6.5 - 9.0	
CONSERV	Avg.	94.9 @ 15.0	90.4 @ 19.1	21.7	$\bar{\phi} = 47.5^\circ$ $\bar{c} = 0$
	Range	94.2 - 95.3 @ 14.1-15.6		20.0 - 22.5	
I.M.C.	Avg.	96.9 @ 16.4	91.9 @ 18.4	17.2	$\bar{\phi} = 46.5^\circ$ $\bar{c} = 0$
	Range	95.0 - 99.7 @ 16.0-16.8		16.0 - 19.0	

soluble in water, gypsum-saturated solutions were used to prevent the dissolution of gypsum crystals during testing.

Drying of Gypsum

Since gypsum contains both chemically bound and free water, higher drying temperatures will expel the chemically bound water. Based on our laboratory study (Figure 2), it was decided. to dry gypsum samples for moisture content determination at approximately 120° F. At this temperature, moist samples took about five days to dry to a constant weight.

Specific Gravity

The average specific gravity of the seven sources varied between 2.33 and 2.43, with individual test values varying between 2.31 and 2.53.

Grain Size Distribution

Figure 3 shows the band of grain size distribution of all the samples. All sources were classified as A-4 soils according to AASHTO classification system excepting one source, Conserv, which was five percent short of the A-4 classification. The samples consisted of mostly silt size particles (nonplastic) and were rated as fair to poor subgrades.

Permeability

Falling head permeability tests were performed on compacted test samples using both AASHTO T-99 and AASHTO T-180 methods of compaction. The average and range of permeability values, presented in Table I, indicate values varying from approximately 3×10^{-4} to 2×10^{-5} cm/sec. Permeability decreases

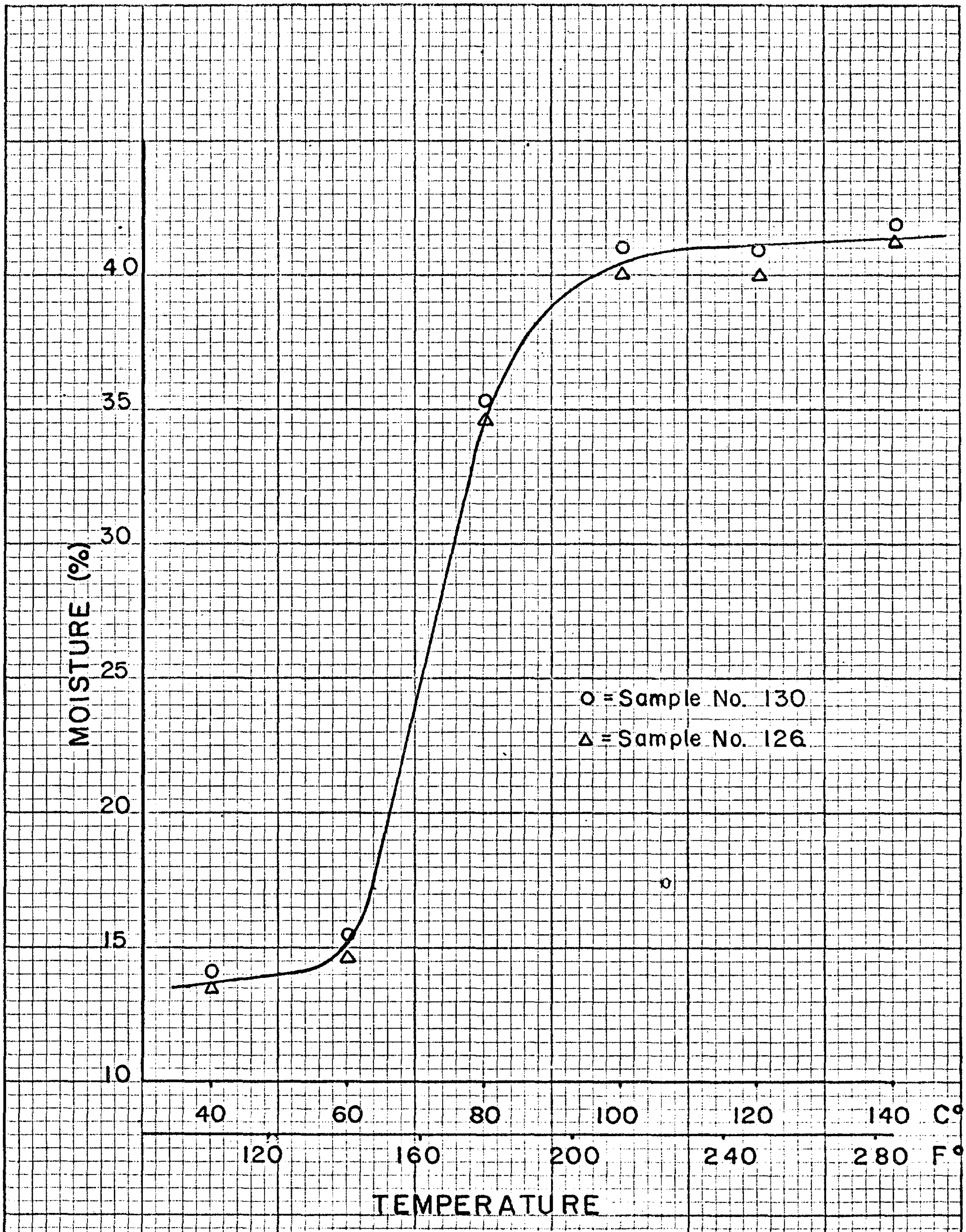


FIG. 2 GARDINIER GYPSUM

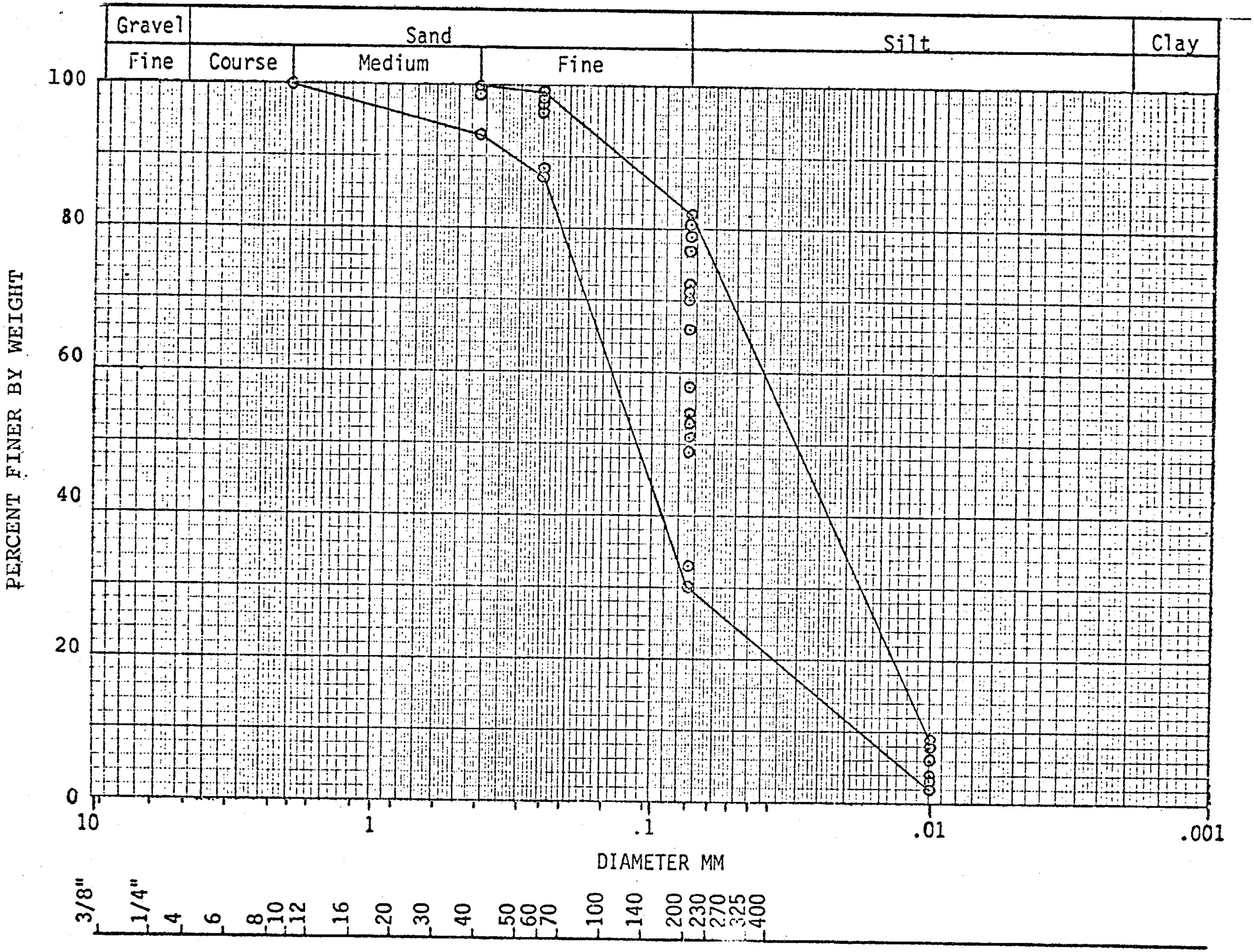


FIG. 3 GRAIN SIZE DISTRIBUTION OF SEVEN GYPSUM SOURCES

with increasing fines (that is, percentage of material passing No. 200 sieve) and also with increasing compaction effort.

Moisture-Density Relationship and Limerock Bearing Ratios

The ranges of maximum dry densities based on AASHTO T-180 compaction method varied between approximately 90.3 pcf and 102.7 pcf (see Table II), with moisture contents varying between 18 percent and 14 percent respectively. Maximum dry densities based on the AASHTO T-99 compaction method were always lower, with differences as much as 7 pcf.

Limerock bearing ratio (LBR) values obtained on samples compacted by AASHTO T-180 showed generally low values. With the exception of one source, all values were less than 30.

Triaxial Compression Tests

All gypsum samples were compacted at optimum moisture and consolidated under confining pressures of 10, 20, and 30 psi overnight. They were then sheared under drained conditions. Mohr-Coulomb envelopes yielded $\bar{c} = 0$ and $\bar{\phi}$ varying from 43.5° to 50°.

Gypsum Content and pH

The percentages of gypsum in the sources obtained ranged from 81.3 to 99.3, with pH varying from a low of 2.5 to a high of 6.0. Florida DOT corrosion engineers consider pH values of less than 6.0 to be extremely corrosive not only to metal but also to concrete structures.

Gypsum is not considered hazardous by the State of Florida Solid and Hazardous Waste Bureau. According to Mr. Raoul Clarke of that Bureau, the criteria for the materials to be considered hazardous would be a pH equal to or less than 2.0 or equal to or greater than 12.5. The limits noted above appear to be very permissive. A pH of 7.0 is considered neutral, and 2.0 is associated with fairly strong acids, whereas 12.5 is associated with a strong base.

One of the sources was monitored for radiation hazard by Dr. C. E. Roessler's graduate students from the University of Florida and was given a safe rating. Radiation does not appear to be a hazard, but it does warrant monitoring when working with all unknown sources.

STOCKPILE VARIABILITY

To determine the variability of gypsum within a stack, ten samples from different locations in a stockpile at Occidental of White Springs were obtained.

Physical and chemical tests were run and included: gradation, specific gravity, percent gypsum, and pH-Hydrogen Ion Content. Table III summarizes the test results and includes average values for all ten samples. Variability in test results did exist, and for some tests this could be considered significant.

There is a wide variation in grain size distribution or gradation. Considering the limits shown in Table III, the

TABLE III

VARIABILITY OF GYPSUM $CaSO_4$ $2H_2O$

OCCIDENTAL STACK, WHITE SPRINGS, FLORIDA

	SAMPLE NUMBERS										
	NORTH	1	2	3	4	5	6	7	8	9	
GRADATION											AVERAGE
% PASS NO. 10	100	100	100	100	100	100	100	100	100	100	100
% PASS NO. 40	88	85	78	97	94	97	92	96	86	98	91
% PASS NO. 60	75	80	73	91	85	95	88	93	82	95	86
% PASS NO. 200	38	66	47	49	43	58	59	50	52	52	51
SPECIFIC GRAVITY	2.37	2.36					2.48				2.4
GYPSUM $CaSO_4$ $2H_2O$	96.1	98.8	97.7	94	81.0	96.2	96.2	95.3	97.1	92.6	94.5
pH	5.8	5.9	5.9	5.9	6.0	6.0	6.0	6.0	4.0	5.5	5.7

following ranges in percent passing selected sieve sizes were as follows:

Percent Passing No. 40 sieve	78 to 98%
Percent Passing No. 60 sieve	73 to 95%
Percent Passing No. 200 sieve	38 to 66%

The physical and engineering properties of soils, including gypsum, vary with the silt content. A variation from 38% to 66% would contribute in a major way to the variable performance and stability of gypsum embankments and pavement layers. All of these samples would be classified as A-4, nonplastic silty soil.

Variability from stack to stack is also important and may be significant. The only data available, as shown in Table III, indicates an average value of 51% passing the No. 200 sieve. The latest Occidental (OXY No. 2) test pit sample had a value of 80% passing the No. 200 sieve. This is an additional variable that also appears to be significant as it would definitely affect the performance of the gypsum.

We have not checked the variability of other sources of gypsum but suspect that variation in stacks would also exist. The degree of variability, however, is unknown.

The apparent specific gravity of the three samples tested had an average value of 2.4.

The percent gypsum dihydrate $CaSO_4$ $2H_2O$ for the ten samples was fairly consistent. Sample No. 4 had a low water content, which accounted for the one low value. In general, the average percent gypsum was 94.5 percent.

The pH value was fairly constant, with the exception of one sample, No. 8. Values ranged from 4 to 6, with an average value of 5.7.

The most significant characteristic is the gradation of the A-4 silty soil. Silts may present problems in handling, compaction, and water retention. As such, each source should be sampled and tested to establish variability and the potential suitability or unsuitability for use as an embankment material.

TEST PIT STUDY

The FDOT Test Pit No. 2 consists basically of a concrete pit 8 feet wide by 24 feet long and 7 feet deep; The bottom layer consists of 12 inches of gravel and 12 inches of builder's sand separated by a filter fabric. This is then covered with 36 inches of A-3 sand subgrade (Figure 4). The sand has an LBR value of 29 and a resilient dynamic plate modulus of about 12,000 psi when soaked. Flexible pavement base sections 10% inches thick are usually placed and compacted above the sand subgrade. The upper portion of the pit can be bulkheaded and three base types tested during a typical testing sequence. Plate 1 shows the over-all arrangement of the pit and two gypsum sources after completion of testing.

A major feature of the test pit is that it permits testing of materials under different environmental conditions. These conditions may be simulated by raising or lowering the water level in the pit. Connecting galleries permit efficient control of the water level. The three environmental conditions that have been used in the past and were again used to evaluate the gypsum were:

1. As Constructed (Optimum) -At or near optimum moisture. Water level 12 inches below bottom of “base."
2. Drained and Dried - Relatively dry condition. Water level lowered to 36 inches below base and drained for seven days.
3. Soaked Condition - Essentially saturated. Water level one-half inch below surface.

Materials are tested in each of these conditions which simulate different field conditions. The most critical condition is the (3) Soaked Condition. This is emphasized when discussing and rating the performance of the materials.

Twelve-inch diameter rigid plate tests are conducted on most materials which are evaluated in the test pit. This simulates typical circular single wheel load contact area and has been used in all FDOT test pit and field studies. The loading and recording system is a new (1981) Materials Testing Systems (MTS) unit with a loading capacity of 20 kips. Load magnitude and sequences of loading may be programmed. Vertical deformations are measured with Linear Variable Displacement Transducers (LVDT). The basic series of tests begins with a static load test which is repeated three times and then is automatically repeated 10,000 times. One complete cycle consists of a 50 psi load duration for 0.5 second followed by zero load for 2 seconds. Ten thousand cycles can be applied in an 8-hour day. The loading rates are relatively fast and

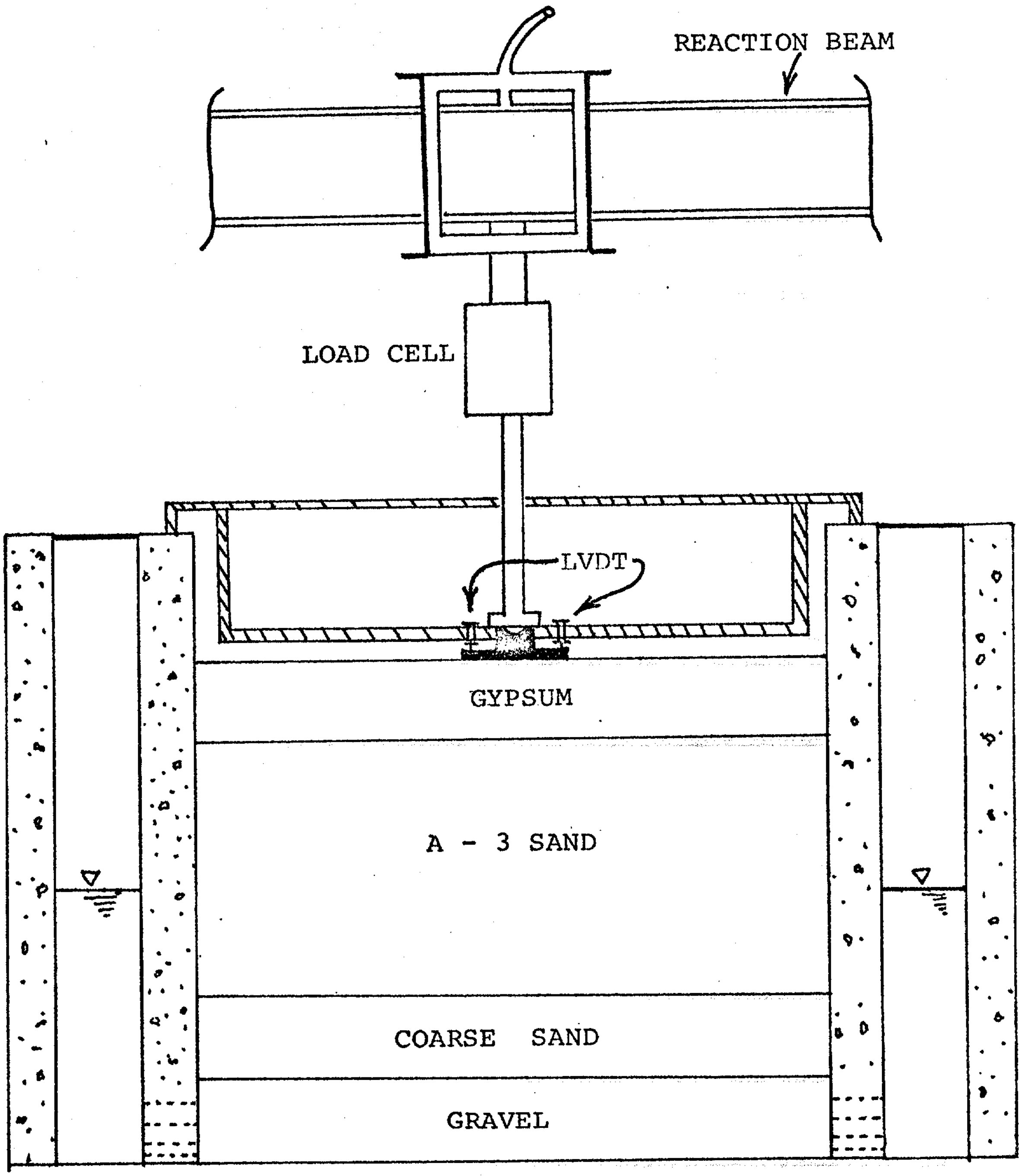
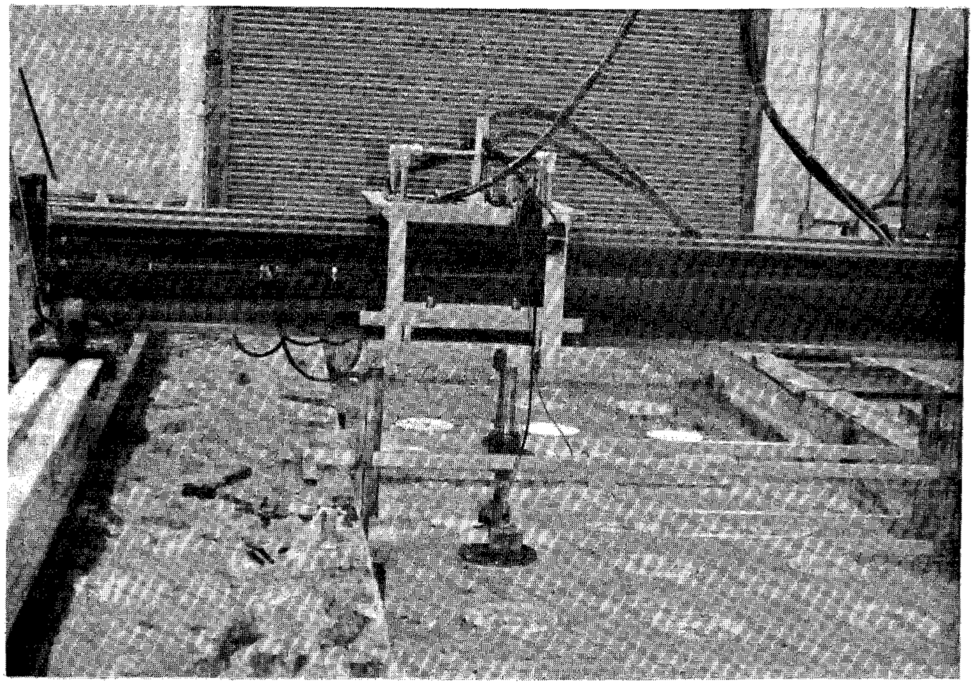
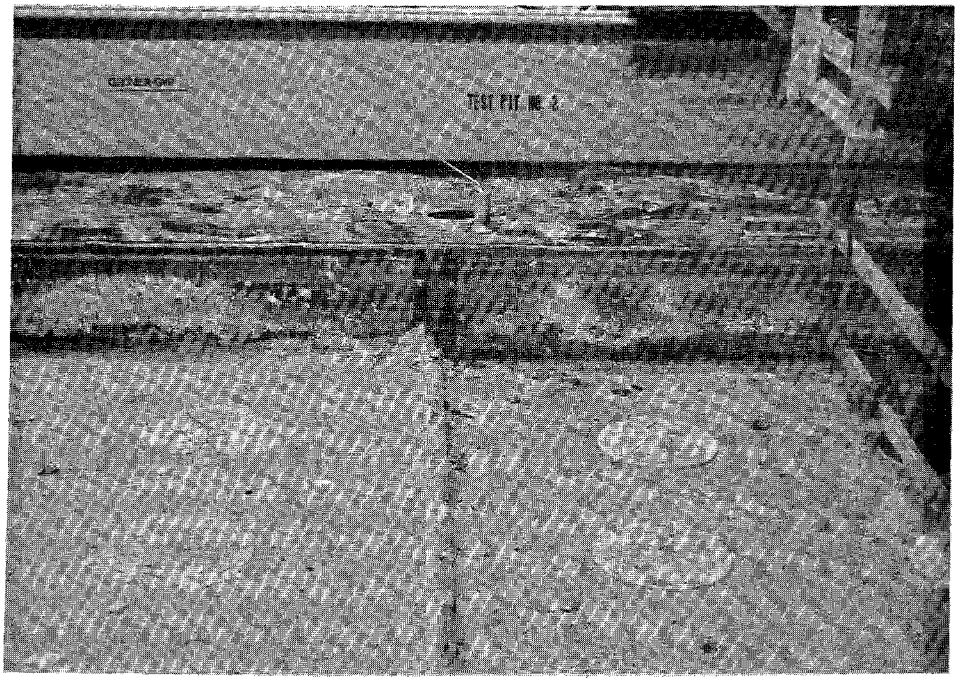


FIGURE 4. CROSS SECTION OF TEST PIT & LOADING SYSTEM

PLATE 1



FDOT TEST PIT NO. 2



GYPSUM

PLATE 2

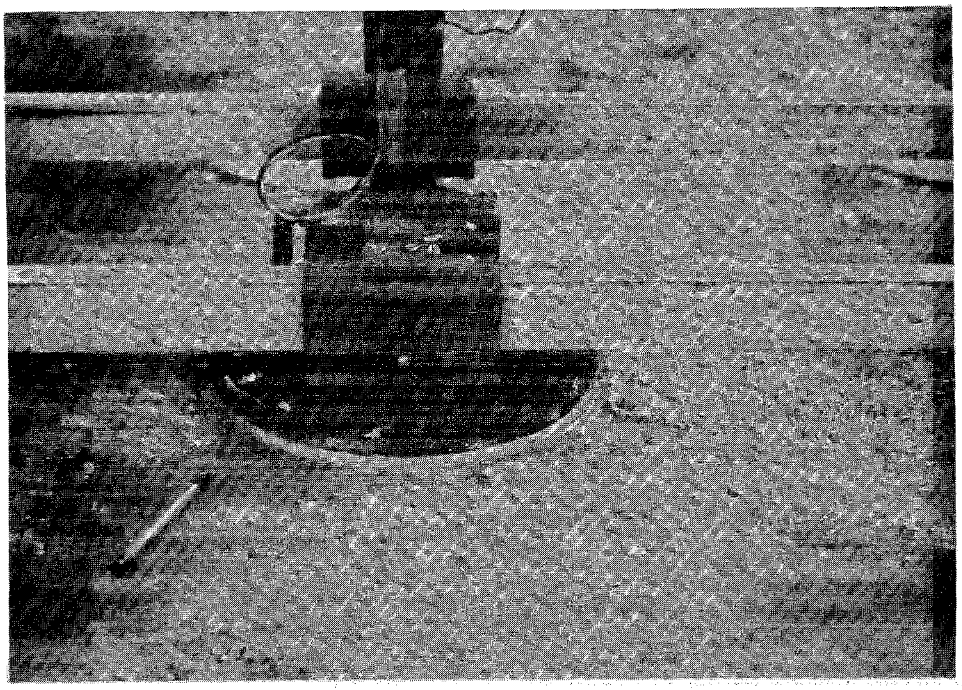


PLATE TEST - GYPSUM

simulate a moving wheel load at about 30 miles per hour. This plate stress was used for static and dynamic tests on gypsum. The stress level corresponds to the stress on top of a pavement base and is not associated with stress at lower depths of the pavement structure. This is a moderately high level of stress when imposed on weak materials. However, since we do have materials such as limerock which can withstand this level of loading, we used it as a FDOT standard for comparison. Plate 2 illustrates the plate test and the accumulated deformation of the material after 10,000 repetitions of stress.

STRENGTH AND PERFORMANCE TEST PIT EVALUATION

Gypsum sections of 10 1/2 inches in thickness were compacted in the FDOT Test Pit No. 2 and tested using standard FDOT Plate Test Methods. The stress level used for static and dynamic plate tests was 50 psi. This level is associated with stresses imposed on bases.

Table IV presents a summary of the results of strength, deformation, and accompanying density and moisture, for the seven gypsum sources tested. The data is arranged according to the soaked strength plate modulus E_{eR} at the fourth repetition of stress. This is a stable test parameter and has been used in all previous studies as a reliable measure of modulus.

As can be noted, the soaked values of E_{eR} are significantly less than the drained and dried E_{eR} values and optimum E_{eR} values. However, they do represent the worst environmental conditions which can occur. Soaked conditions also correspond "directly" to the LBR, a soaked sample laboratory test, used by the FDOT to evaluate granular materials. As such, these measures of strength can be correlated. We again found that soaked E_{eR} plate modulus and LBR were related. This is clearly seen by noting the similar array of LBR values which decrease as plate modulus decreases. Considering the seven sources tested and the LBR limits encountered, we found that the equation relating E_{eR} and LBR is:

$$\text{Soaked } E_{eR} \text{ (psi)} = 700 \text{ LBR}$$

This is the same equation presented in 1983 for the initial test series. Besides being related to the modulus values, LBR also seems to indicate some linear relationship with the percentage of fines (Figure 5) with the exception of one source (W. R. Grace).

The LBR ranged from 8 to 40 with the highest value obtained for W. R. Grace gypsum. The plate modulus (soaked condition) varied significantly, ranging from a low of about 8,500 psi for IMC to a high of 28,700 psi for W. R. Grace. Plate modulus of 28,700 psi are associated with good base materials whereas 12,000 psi is associated with typical subgrades.

The value of 8,500 psi was much lower than the sand subgrade modulus on which it was placed. The corresponding repeated load performance was also poorer than that of the sand.

Table V is a summary of the soaked condition test results. This table presents a direct comparison of static strength and repeated stress performance data. Excellent correlations resulted when comparing the plate modulus E_{eR} at $N = 4$ with total deformation and permanent deformation after 1,000 repetitions of stress

TABLE IV
SUMMARY OF RESULTS

SOURCE	% GYP.	LBR	PLATE MOD. EeR N=4	DEN. (DRY) p.c.f.	% MOIST.	TOTAL DEF. @1000 REP. inches	PERM. DEF. @1000 REP. inches
Grace Gypsum	92.5	40	OPT. 38,417 psi	93.6	17.5	.0468	.0351
			SOAKED 28,700	92.3	24.0	.0543	.0368
			DRIED 45,619	100.5	13.4	.0328	.0239
Gardinier Gypsum	81.3	26	OPT. 28,941	99.1	15.8	.0869	.0729
			SOAKED 22,615	95.4	23.9	.2173	.1586
			DRIED 38,847	98.9	12.7	.0496	.0398
Amax Gypsum	89.0	22	OPT. 21,286	90.8	21.4	.0918	.0752
			SOAKED 16,902	89.2	26.1	.2719	.2463
			DRIED 34,478	93.7	15.4	.0368	.0472
Conserv Gypsum	99.3	22	OPT. 20,491	88.1	16.9	.1074	.0895
			SOAKED 14,774	88.3	27.3	.3625	.3311
			DRIED 25,383	87.5	14.7	.0722	.0579
Occidental Gypsum No. 1 OXY	96.7	14	OPT. 15,196	94.1	17.3	.4249	.3971
			SOAKED 10,424	88.8	27.3	1.378	1.330
			DRIED 23,486	91.8	18.6	.1569	.1370
Occidental Gypsum No. 2 OXY	98.7	08	OPT. 19,679	87.4	22.8	.3650	.3356
			SOAKED 10,338	89.3	28.7	N = 500 1.236	N = 500 1.184
			DRIED 20,379	90.4	19.7	.1170	.0985
IMC Gypsum	95.0	17	OPT. 19,199	87.8	21.6	.6463	.6213
			SOAKED 8,463	89.8	28.0	N=10 .8010	N=10 .7615
			DRIED 25,263	95.9	18.8	.2216	.2026

Results shown are the average of 3 tests.

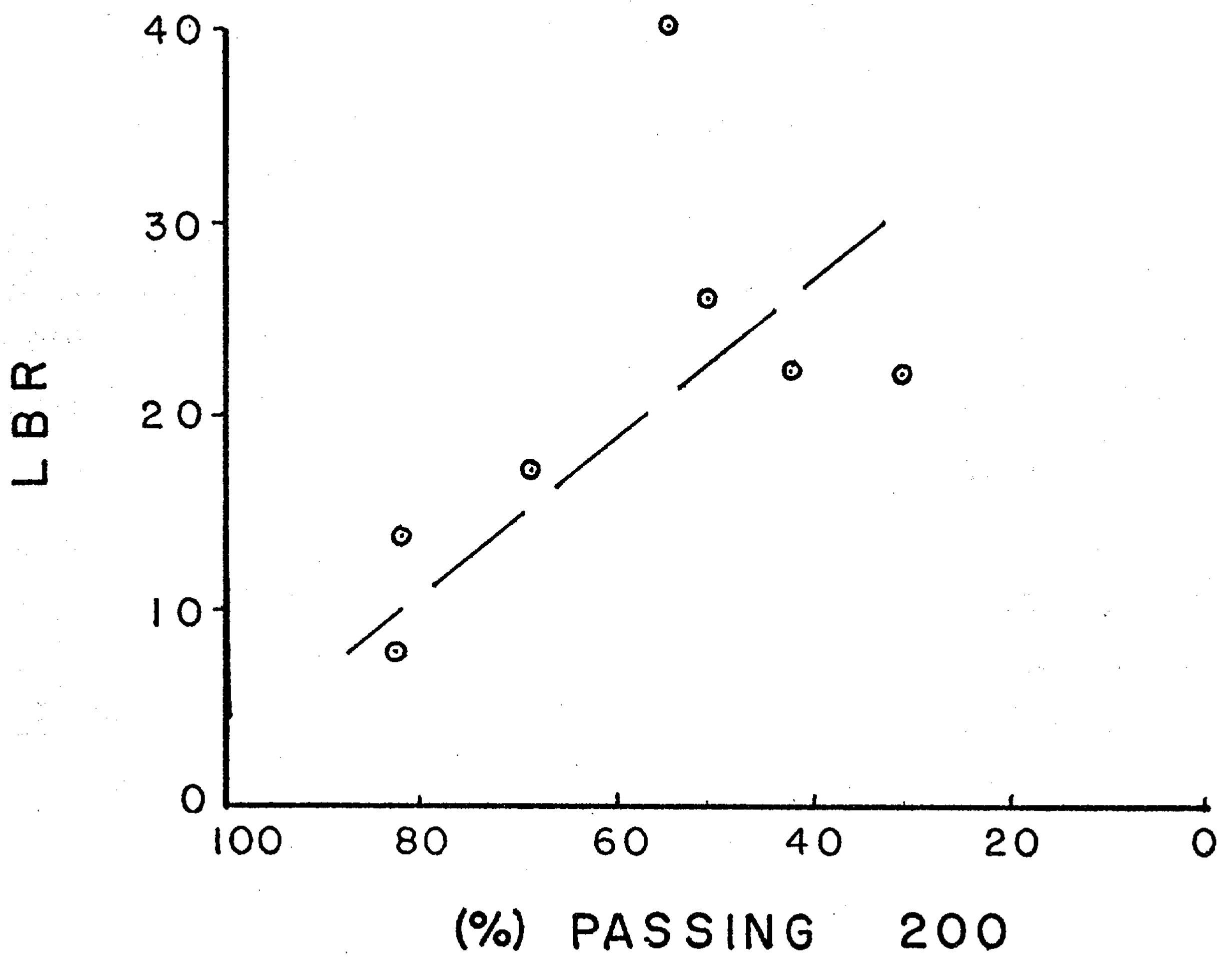


FIG. 5 LBR vs. PERCENTAGE OF FINES

TABLE V

SUMMARY OF STRENGTH AND TEST PIT PERFORMANCE TESTS

GYPSUM, $Ca\ SO_4 \quad 2H_2O$

(SOAKED LBR, AND TEST PIT CONDITIONS)

SOURCE	% GYPSUM	% PASS #200	LBR	SOAKED E_{eR} N = 4 p.s.i.	TOTAL DEF. @ 1000 REP. inches	PERM. DEF. % 1000 REP. inches
Grace	92.5	55	40	28,700	.0543	.0368
Gardinier	81.3	51	26	22,615	.2173	.1586
AMAX	89.0	42	22	16,902	.2719	.2463
Conserv	99.3	31	22	14,774	.3625	.3311
OXY No. 1	96.7	82	14	10,424	1.378 N=500	1.330 N=500
OXY No. 2	98.7	80	8	10,338	1.236 N= 10	1.184 N= 10
IMC	95.0	69	17	8,463	.8010	.7615

or failure if it occurred by excessive settlement before 1,000 repetitions. LBR was also related to modulus as well as accumulated deformations under repeated stress. These findings agree with our investigation of other granular materials conducted during the past five years.

Figures 6 and 7 are similar in that they present the complete picture of the effect of repeated stress on the material deformation under the loaded plate. Figure 6 shows the relationship between all seven sources, which are identified and clearly show the cumulative <u>permanent</u> plate deflection of these gypsum materials under repeated stress. The curves also indicate the corresponding tabular values in Table V. Accumulated deflection curves of this type are most helpful in observing and rating the performance of granular materials when used in the roadway structure. Permanent deflection also represents settlement and has been associated with "rutting" potential,

Figure 7 is very similar to Figure 6 except that it shows the cumulative <u>total</u> plate deflection. The curves of all gypsum sources are very similar in shape to the permanent plate deflection, but with greater deflection. This is clearly evident in Table V and can be noted when comparing Figures 6 and 7. Total cumulative plate deflection was adopted years ago as a criteria for comparing and rating flexible pavement bases. Figure 7 includes this rating which is shown as Group 1, 2, and 3. Group 1 is a zone which generally includes very good bases. Group 2 includes good to fair bases. Group 3 includes fair, poor, and unsuitable bases. As can be seen, the seven sources

FIG. 6 CUMULATIVE PERMANENT PLATE DEFLECTION VS. NUMBER OF LOAD APPLICATIONS (SOAKED MOISTURE CONDITIONS)

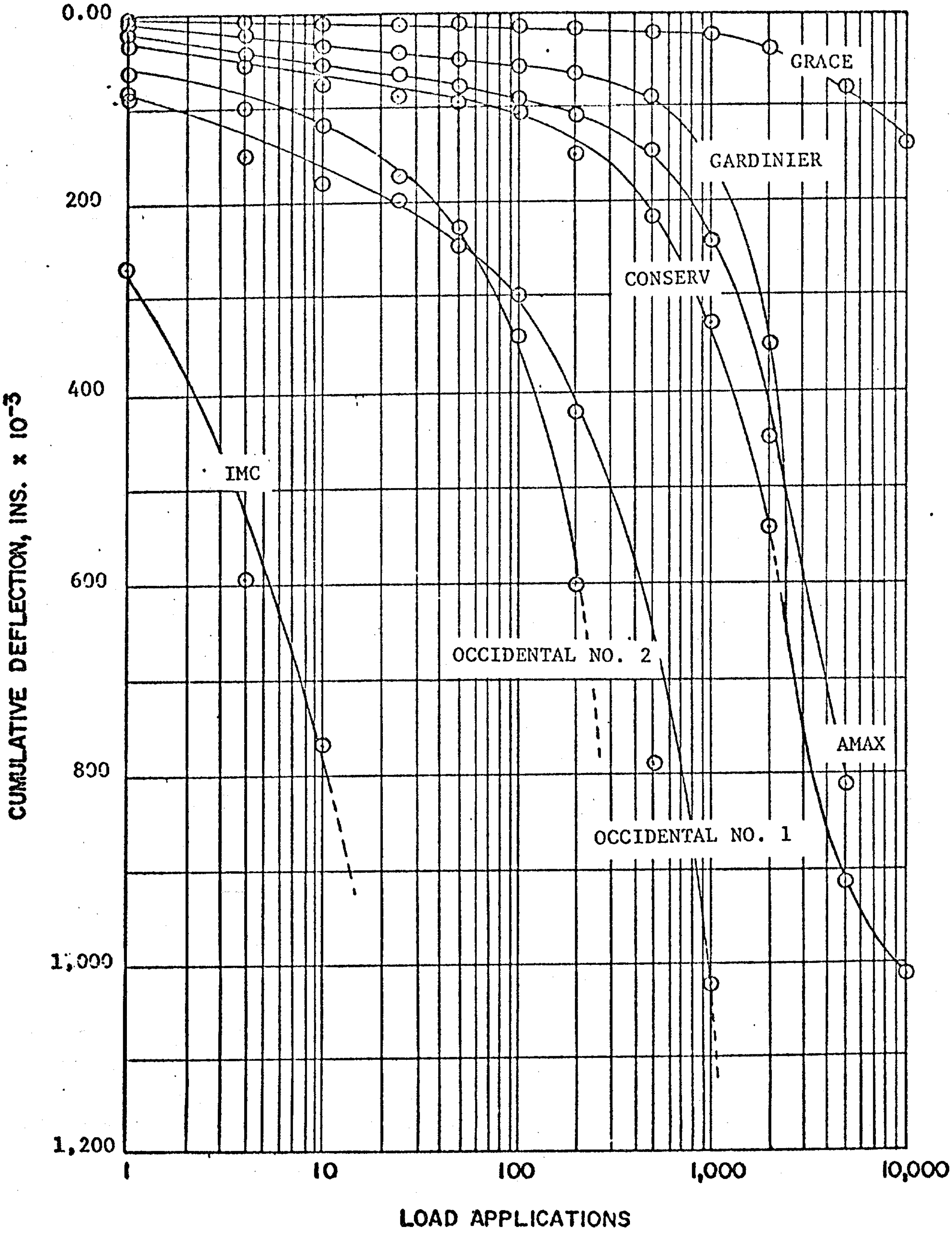
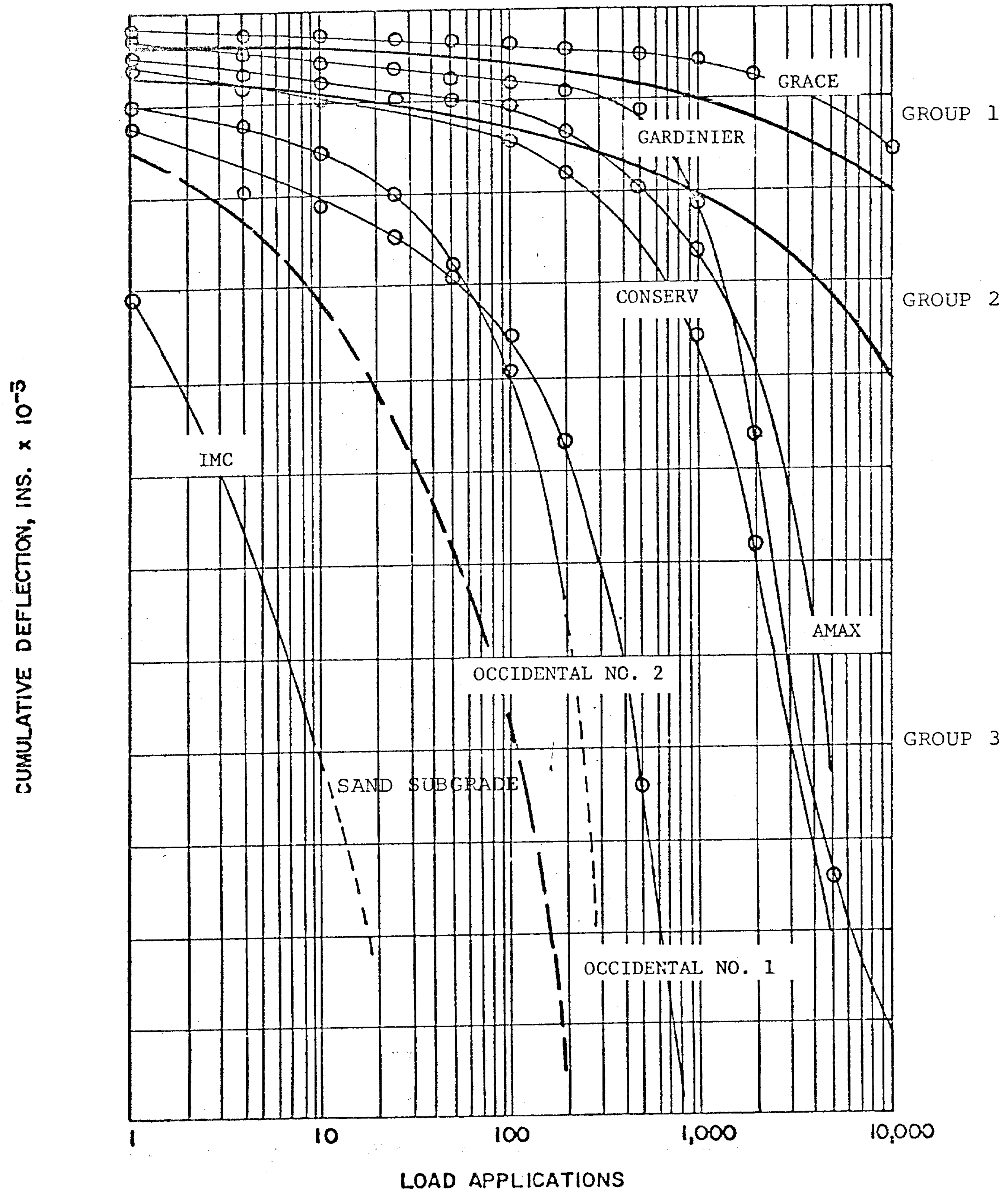


FIGURE 7

CUMULATIVE TOTAL PLATE DEFLECTION VS. NUMBER OF LOAD APPLICATIONS (SOAKED MOISTURE CONDITIONS)



of gypsum which were supplied by the mines fall into all of the groups and categories used to rate materials.

Since sources and stacks are variable, it could be expected that if we were to research and test other samples, we could expect to obtain different results. However, it appears that we have examined a reasonable cross-section of sources and can rely on the range of results obtained to identify important characteristics of gypsum-dihydrate.

POTENTIAL USE OF GYPSUM AS EMBANKMENT MATERIAL,

All the sources investigated are classified as A-4 soils containing silt size particles varying from about 30 to 70 percent. Generally, such soils are rated as fair to poor subgrades.

Based on FDOT design standard Index No. 505, "Embankment Utilization," an A-4 soil may be used in an embankment only above the water level and 48 inches below the bottom of the base. This does not take into consideration the possible effect of leachate on water quality in the vicinity of gypsum embankments. Therefore, monitoring wells should be installed around such embankments to determine this effect on the environment, particularly on groundwater.

One problem which has not been investigated is the field handling and compaction of large quantities of gypsum in a construction project. Compaction, to over 97 percent of maximum laboratory density was achieved in the test pit by using a combination of vibratory and impact compactors. However, in an actual construction project, the use of a sheepsfoot or pneumatic roller rather than a vibratory type may be more beneficial because of the gradation or gypsum. The material would probably be easier to handle if the moisture content is on the dry side of optimum. The material could become spongy when compacted near a high water table. Handling of the gypsum would be a problem during the rainy season.

Based on this laboratory study, the W. R. Grace gypsum appears to have the best potential for use in embankment construction. Other potential sources would be Gardinier, Amax, and Conserv. One property of gypsum which has not yet been determined is the cementation effect on its shear strength.

This laboratory and test pit study revealed considerable variation in the properties of the various gypsum sources. Each source of phosphogypsum should be evaluated prior to any consideration for use as an embankment material. Future studies should include experimental field test sections to compare the engineering properties of gypsum and other conventional Florida embankment materials, and pavement structure materials. All experimental sections using gypsum should also include sufficient "monitoring" programs which need to be developed in cooperation with the Department of Environmental Regulations (Groundwater Section) and the Health and Rehabilitative Services (HRS).

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BARTOW TEST ROAD UTILIZING PHOSPHOGYPSUM AND PHOSPHOGYPSUM MIXTURES

J. Ludwig Figueroa
Associate Professor, Dept. of Civil and Architectural Engineering
University of Miami, Coral Gables, F1.

and

Wen F. Chang
Professor, Dept. of Civil and Architectural Engineering, and
Director, Phosphate Research Institute,
University of Miami, Coral Gables, F1.

ABSTRACT

Road construction using stabilized and waste materials has been common practice in recent decades. Materials such as lime, cement, bitumen, flyash and furnace slag, among others have been successfully combined with existing soils and used in transportation facilities construction.

The abundance of phosphate mining waste in Central Florida in combination with the problems generated during its disposal and handling, have encouraged researchers to find suitable uses for this material. A pilot study, funded by Gardinier Inc. has disclosed the suitability of phosphogypsum-cement as well as phosphogypsum-flyash-lime mixtures for base road costruction. It is proposed to build a test road containing bases composed of these mixtures. Both rigid and flexible pavement surface layers are to be included in the test study. Pavement sections are expected to be subjected to severe traffic conditions and their performance monitored for a period of up to five years. Results of pavement monitoring will serve as the basis for the development of a design procedure for pavements containing phosphogypsum-based layers.

1. INTRODUCTION

Road construction using stabilized and waste materials has been common practice in recent decades. Materials such as lime, cement, bitumen, fly-ash, and furnace slag among others, have been successfully used in road as well as railroad construction.

Road sections containing one or more or combinations of these stabilizers and waste materials have been carefully monitored to determine their performance with time as well as with respect to sections containing non-stabilized materials.

The abundance of phosphate mining waste in Central Florida in combination with the problems generated during its disposal and handling, have encouraged researchers to find suitable uses for this material. A study currently in progress at the Department of Civil and Architectural Engineering of the University of Miami, on the Reclamation, Reconstruction and Reuse of Phosphogypsum Wastes for Building Materials has produced several advances mainly in the characterization of cement-phosphogypsum wastes-aggregate mixtures as well as on the development of a binder agent (phosphogypsum) and other products of possible commercial use. The initial results of this study are contained in a report submitted to the Florida Institute of Phosphate Research FIPR (1) in August of 1983.

A recent study completed by Usmen and Moulton (2), involved the construction and monitoring of road test sections using base course sections containing 5% lime, 20 to 65% fly-ash, and 75 to 30% fine calcium sulfate. These authors concluded that "...the results obtained so far indicate that these mixtures show very good promise for use in pozzolanic bases and subbases in secondary roads, and relatively large percentages of waste calcium sulfate can be successfully used in such mixtures". Due to the similar composition of phosphogypsum it is expected that base courses, built with this material would perform identically, if not better, under the influence of traffic loads and weathering agents.

It is the main objective of the proposed research to design, build and monitor a test road to determine the suitability of phosphogypsum-based admixtures as road construction materials. If phosphogypsum is proven to be adequate road construction material, rational design procedures will be developed for pavement sections consisting of rigid or flexible surface layers.

2. BACKGROUND

A pilot study funded by Gardinier Inc., East Tampa, Florida and FIPR to determine the suitability of using phosphogypsum for airport and highway pavement base courses and building foundations has produced encouraging results. Different admixtures containing cement, sand and phosphogypsum as well as containing lime, fly-ash and phosphogypsum were tested. Cylindrical specimens 2" in diameter by 4" in length were compacted according to AASHTO T-99 and T-180 specifications an tested under unconfined compression.

Figure 1 shows the variation of compressive strength with curing time for several cement-sand-phosphogypsum specimens compacted according AASHTO T-99 specifications. It should be observed that about 80% of the strength development occurs during the first seven days of curing. Compressive strength also depends on the proportions used in specimen preparation, as shown in Figures 1 and 2.

The effect of curing conditions on the development of compressive strength is presented in Figure 2. Identically prepared specimens were exposed to various moisture conditions during curing. Air-dry specimens developed about 2.5 times the strength of sealed (constant moisture) and saturated specimens.

Preparation moisture content was also an important factor in strength development. Lin (3), after testing concrete-sand-phosphogypsum specimens prepared at different moisture contents, obtained an optimum preparation moisture content (preparation moisture content for maximum strength) of about 18% as shown in Figure 3. This optimum preparation moisture content was consistent regardless of the specimen curing time and was somewhat lower than the optimum moisture content obtained during a compaction test on the same mixture.

Comparable compressive strength values were reached on specimens prepared (according to ASSHTO T-99) with several lime-flyash-phosphogypsum mixtures but at a slower rate. Furthermore strength continues to increase even after the seventh week of curing, as shown in Figure 4. Lin (3) as well as Chang et al. (4) reported that strength gains continue to occur in some cases for about four months after specimen preparation.

These results clearly indicate that admixtures reasonably strong for base course construction can be obtained from phosphate mining waste. It is expected that this research will expand the findings of this preliminary study, determine the performance of phosphogypsum-based road test sections and set the basis for the development of a pavement design procedure for this type of roads.

The study, to be carried out over a period of 3 years, with a probable extension of 2 years (depending on road performance), will include several stages:

-Laboratory and Field Testing

-Pavement Analysis and Design

-Test Section Construction

-Field Monitoring

-Data Analysis and Design Procedure Development

The proposed test road to be built in Polk County, will consist of both flexible and rigid pavement sections ranging in length between 400 and 500 feet. A total of 11 pavement sections with different profiles will be constructed within Gardinier Inc. property and will be used as a service road by loaded and unloaded trucks from the same company.

3. RESEARCH METHODOLOGY

The combined field and laboratory study encompasses several phases leading to the development of the design procedure.

PHASE 1. Laboratory and Field Testing.

Material characterization is fundamental for the appropriate design of both flexible and rigid pavements. Preliminary field sampling and testing indicated that six of the proposed pavement sections will be located on disturbed subgrade soil consisting of a ligth to dark brown clayey fine sand with phosphate fines fill. The remaining five sections will be located on undisturbed clayey sand subgrade soil. The presence of both disturbed and undisturbed subgrades will allow to determine the performance of phosphogypsum-based pavements when built on either embankments or cut sections.

California Bearing Ratio and plate load testing carried out at both locations indicated that the disturbed section offered better support values that the undisturbed section. It is expected however, that the disturbed subgrade soil will experience long term deformations since no compaction control was exercised during fill operations. Both disturbed and undisturbed subgrades will need to be proof-rolled in order to obtain a minimum Limerock Bearing Ratio greater than 40% and a modulus of subgrade reaction greater than 200 pci. Experience by local contractors indicates that these support values can be achieved without difficulty on both subgrade types.

The laboratory testing program in progress at the Soils and Materials Laboratory of the University of Miami encompasses index property determination tests for proper identification and classification of subgrade soils. Repetitive load tests will also be performed in order to determine the subgrade soils' resilient moduli and their behavior with the number of load repetitions will be recorded. These tests will be performed using an electro-pneumatically operated testing system and their results will be the basis for the development of a rational design procedure for phosphogypsum-based flexible pavements. The same testing equipment will also be used to determine fatigue curves for the phosphogypsum-based admixtures. A more detailed explanation of the fundamentals of the proposed design procedure will be presented later. Other tests of common use in pavement design and construction such as Standard Proctor Compaction, soaked CBR and “static” compression will also be performed in order to correlate the results of resilient modulus tests with these parameters.

The modulus of rupture will be determined for the admixtures composing the surface slab in the rigid pavements.

PHASE 2. Pavement Analysis and Design.

Results from laboratory and field tests, carried out during the previous stage, were used in combination with the projected traffic to determine the composition and profile of the proposed pavement sections. Advanced mathematical models (5) in combination with generally accepted analysis and design techniques (including the Florida Department of Transportation (FLDOT) design procedure) were used to design suitable pavement profiles. Among these, a finite element computer program for flexible pavement analysis, originally developed by Wilson (6) and later modified by Raad and Figueroa (7) was used to provide a more rational assessment of the state of stress of pavement materials approaching failure; according to the Mohr-Coulomb theory of failure. This finite element computer program, termed ILLI-PAVE, has the capability of considering stress-dependent material models (Resilient modulus is a function of the stress level). Traylor (8) showed that the ILLI-PAVE program adequately predicted flexible pavement response to loading, when the results of the computer modeling and field test data were compared.

Figure 5 shows the distribution of the eleven pavement sections within Gardinier's mining site. The western location will include five profiles with a length of 400 ft. per section to be built on an undisturbed subgrade soil. The eastern location will consist of six profiles with a length of 500 ft. per section to be built on a disturbed subgrade. Both locations will be joined by an existing haul road and will carry the same amount of traffic.

A generalized pavement profile, following FLDOT specifications, is shown in Figure 6. A 3-foot deep drainage ditch is to be provided along the road in order to maintain the underground water level below the subbase soil. A 5/8 of an inch thick non-structural friction course (FC-2) will also be placed on all asphalt concrete pavements as specified by the Florida Department of Transportation.

Pavement layer thicknesses as well as compositions are given in Table 1 for the six projected pavement sections. A control section containing limerock as a base course material has been included in order to establish a relative performance between pavement sections built with this commonly used material and those containing suitable phosphogypsum-based mixtures as developed during the laboratory testing. Identical base layer thicknesses for profiles 1 to 3 have been suggested in order to obtain a direct comparison. Minimum bearing and strength requirements have also been given in Table 1 in order to exercise careful construction control.

Two alternatives, containing different layer thicknesses, have been presented in order to offer the opportunity of selecting the most economical one according to the local availability of required components. It is expected, according to the parameters used for design, that either choice will perform similarly under the expected traffic.

PHASE 3. Test Section Construction.

The proposed test road will be built within Gardinier Inc. property in Polk County and will have a total length of 5000 ft. and a width of 24 ft. (2 way traffic). Eight foot wide shoulders will also be built along each side of the road. Figure 6 shows a detailed pavement profile for the proposed pavement sections given in Table 1. The road will used by Gardinier Inc. trucks to haul phosphate matrix 7 days a week and 16 hours a day during 10 years. Mini-wheeler trucks carrying a loaded gross weight of 72 kips on 4 axles and weighing 26 kips while empty will travel the haul road.

Water quality monitoring wells will be installed at locations to be determined and following an alignment perpendicular to the road axis. These wells, placed perpendicular to the road axis, will determine if any significant leaching of phosphate mining waste solubles has occurred. The number of well lines will correspond to the number of different phosphate-based admixtures used in the road construction project.

Periodic maintenance of the road surface and shoulders will be provided by Gardinier Inc. Gardinier Inc. will also deliver a finished subgrade surface.

It should be indicated that due to the difference in layer thickness of the proposed test sections it will be required to prepare the subgrade at different elevations in order to provide a uniformly finished grade.

PHASE 4. Field Monitoring.

Pavement performance will be monitored periodically during the investigation. Both non-destructive and destructive testing will be performed on each pavement section. At the same time, weather-related data including amount of rainfall and temperature will be gathered daily. Both destructive and non-destructive tests as well as pavement surface evaluation will be performed every two months or at higher frequency if the amount of traffic applied to the road, so requires.

Experience gained by researchers during similar research projects such as the AASHO Road Test (9) and others found in the literature, in combination with recently developed non-destructive testing techniques will be used in the performance evaluation of each pavement section with the number of load repetitions and climatological factors.

Before any testing is done a surface condition survey will be performed along the test road. The Pavement Condition Index proposed by Shahin and Kohn (10) will be used to evaluate pavement performance with time and with the number of applied loads.

The non-destructive testing will include:

- Measuring surface deflection with the Benkelman Beam.
- Measuring surface deflection with the Dynaflect
- Determination of the roughness index.

Data thus gathered will also be helpful in evaluating pavement performance with traffic and time. It will also be of great interest in selecting the mathematical models that more closely represent the behavior of phosphogypsum-based pavements. Automatic traffic counters will be required on both road lanes to obtain an accurate reading of the number of applied axles previous to pavement evaluation.

Cores and undisturbed samples will be taken at the same locations where any non-destructive testing was done. After determining the properties of each material composing the pavement profile in the laboratory, a prediction could be made as to the remaining life of the pavement section. These properties which include resilient modulus, modulus of elasticity and Poisson's ratio, will serve as input parameters in the available mathematical models.

Field CBR and plate load tests will also be performed, although less frequent, to determine whether there have been any significant changes in base material and subgrade soil properties.

PHASE 5. Data Analysis and Design Procedure Formulation.

Data gathered during the previous stage will be carefully analyzed in order to set up the basis for the development of a design procedure for pavements containing phosphogypsum-based admixtures. The methodology used in this development will be similar to that used by Figueroa (5), Figueroa and Thompson (11) and Thompson and Figueroa (12), to develop design procedures for secondary roads including granular bases or soil-lime layers.

Thompson and Figueroa (12) used the ILLI-PAVE finite elements computer program to develop a simplified procedure to calculate the soil flexural stress of pavements containing lime-stabilized layers. Multi-variable regression analyses led to a simple algorithm that can be used to predict the resilient response of this type of pavements in terms of material properties and layer thicknesses. This algorithm was expressed in graphical- form, as shown in Figure 7, which can be very easily used by neophites in the subject following a similar path to the one indicated by the segmented arrows. The end result of this graph is the soil-lime flexural stress which in combination with the fatigue curve, obtained for cured soil-lime mixtures as shown in Figure 8, can be used to design lime-stabilized pavements.

Similar graphs could be developed during the proposed research project. They would provide a quick and accurate way to determine the required pavement. layer thicknesses for the projected traffic once the material properties are known.

4. SUMMARY

Suitable mixtures of pavement based materials containing phosphogypsum as their main component have been developed. Some of the mixtures tested in the laboratory containing cement , sand and phosphogypsum as well as lime, flyash and phosphogypsum have reached unconfined compressive strengths of more than 1,000 psi. These mixtures have also been found to posses adequate durability when subjected to cyclic wetting and drying.

A test road using phosphogypsum-based mixtures is to be built in Central Florida within a phosphate mining site in order to determine the pavement performance with time when subjected to severe traffic loading conditions.

Eleven pavement sections consisting of six different pavement profiles will be built and monitored for up to five years. Pavement monitoring will consist of periodic condition surveys, field destructive and non-destructive testing as well as laboratory testing of pavement material samples obtained during the field destructive testing. Results of monitoring, in combination with theoretical analysis will be fundamental in the development of pavement design procedures for pavements containing phosphogypsum-based mixtures.

ACKNOWLEDGEMENT

The authors would like to extent their gratitude to both the Florida Institute of Phosphate Research (FIPR) and Gardinier Inc. for their continued interest and support in making this research possible.

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Table 1. Pavement Sections Composition

Profile No.	Surface Layer Type	Base Layer Type	Surface Layer Thickness (in)	Base Layer Thickness (in)	Stabilized Subbase Thickness (in)
1	Asphalt Concrete (a)	Cement Sand Phosph.(c)	2	10	12
			3	8	12
2	Asphalt Concrete (a)	Lime Flyash Phosph.(d)	2	10	12
			3	8	12
3	Asphalt Concrete (a)	Limerock (e)	2	10	12
			3	8	12
4	Portland Cement Concr.(b)	Cement Sand Phosph.(c)	6.5	8	12
5	Portland Cement Concr.(b)	Lime Flyash Phosph.(d)	6.5	8	12
6	Asphalt Concrete (a)	Phosph. (f)	2	26	12
			3	20	12

Notes:
a. Type S (FLDOT)
b. fc=4,000 psi
c. 7.5% cement/ 20% sand/ 72.5% Phosphogypsum
d. 6% Lime/ 24% Flyash/ 70% Phosphogypsum
e. LBR>100%
f. LBR>40%
g. LBR>40%

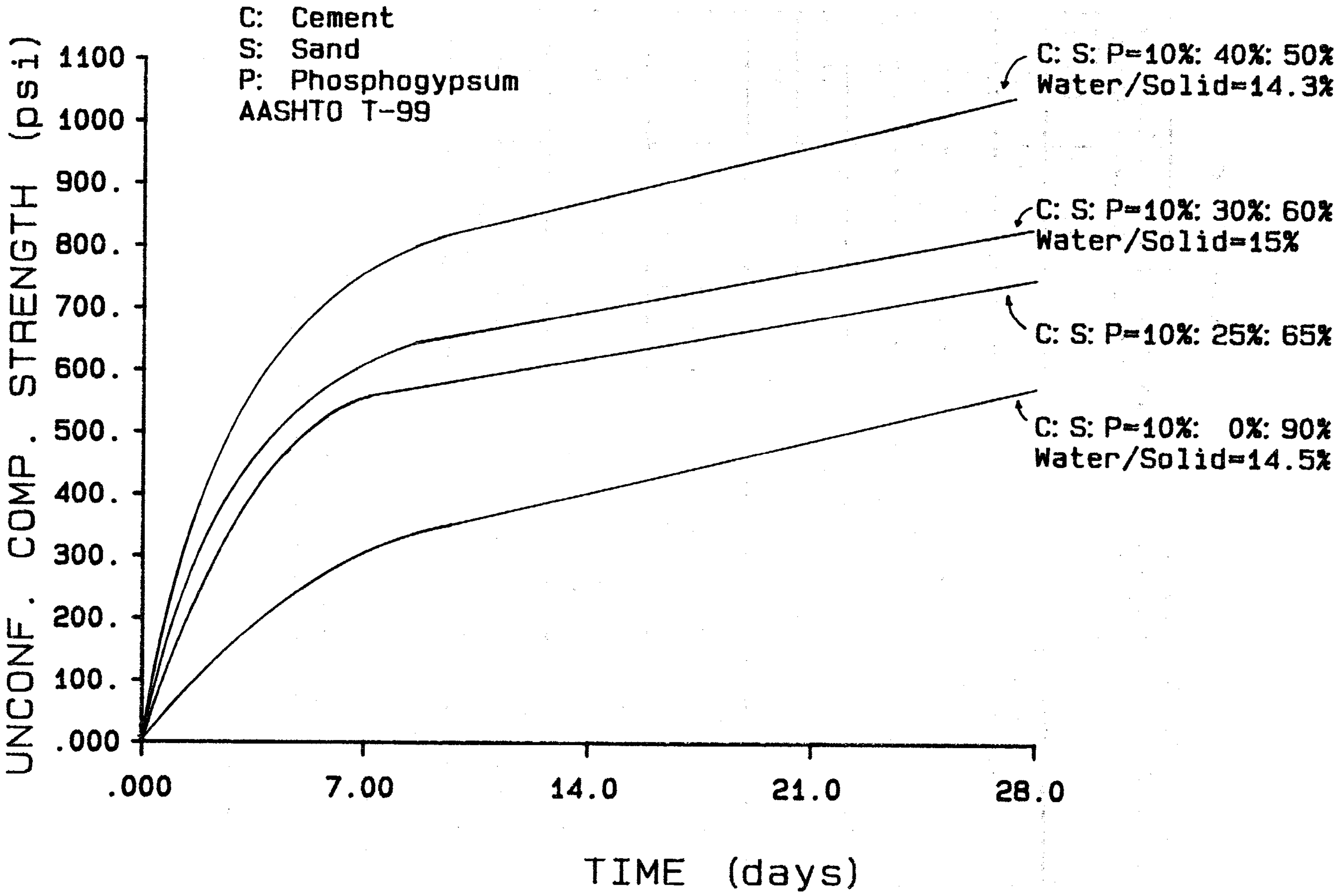


FIGURE 1. Unconfined Compressive Strength of Several Cement-Sand-Phosphogypsum Mixtures.

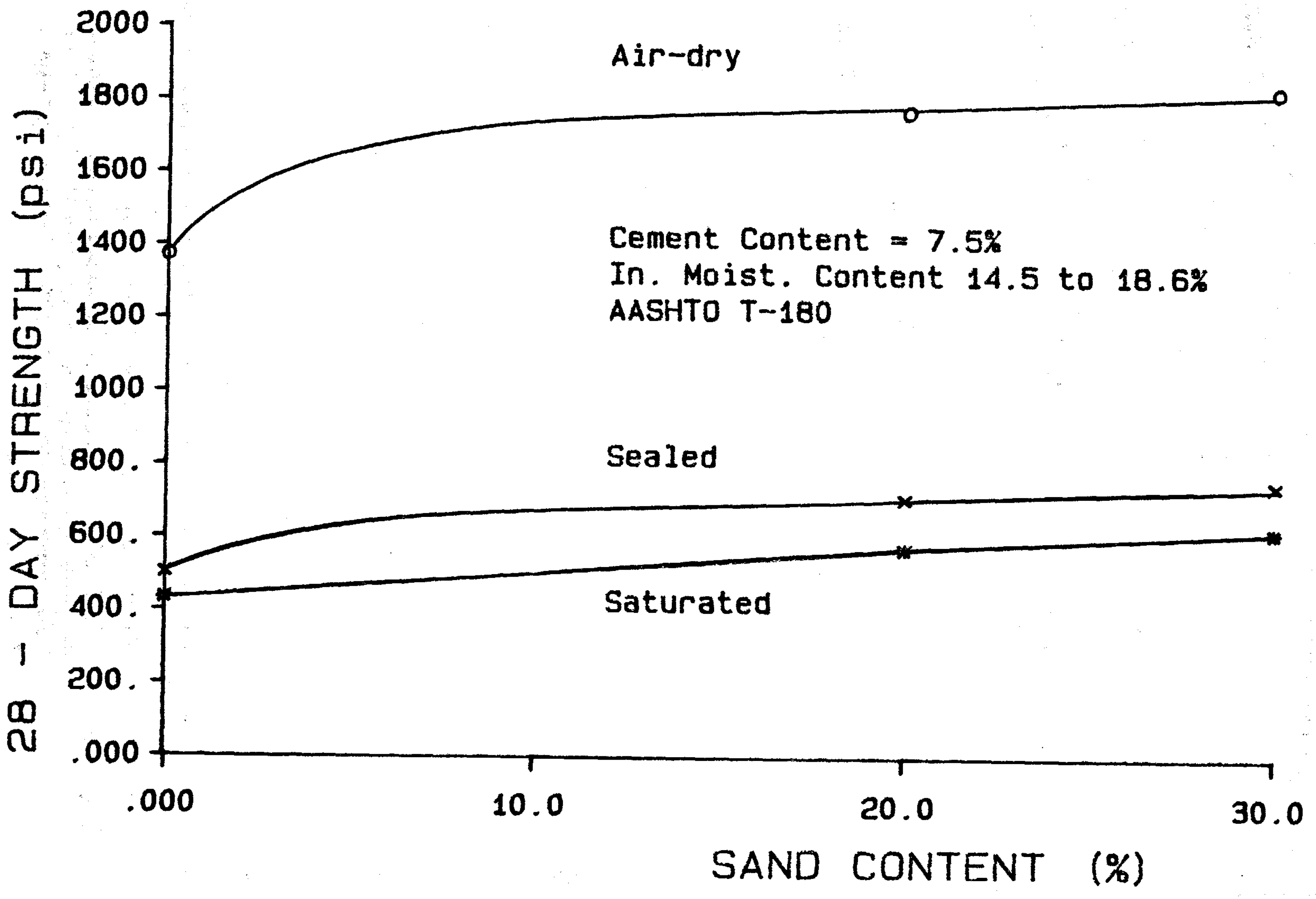
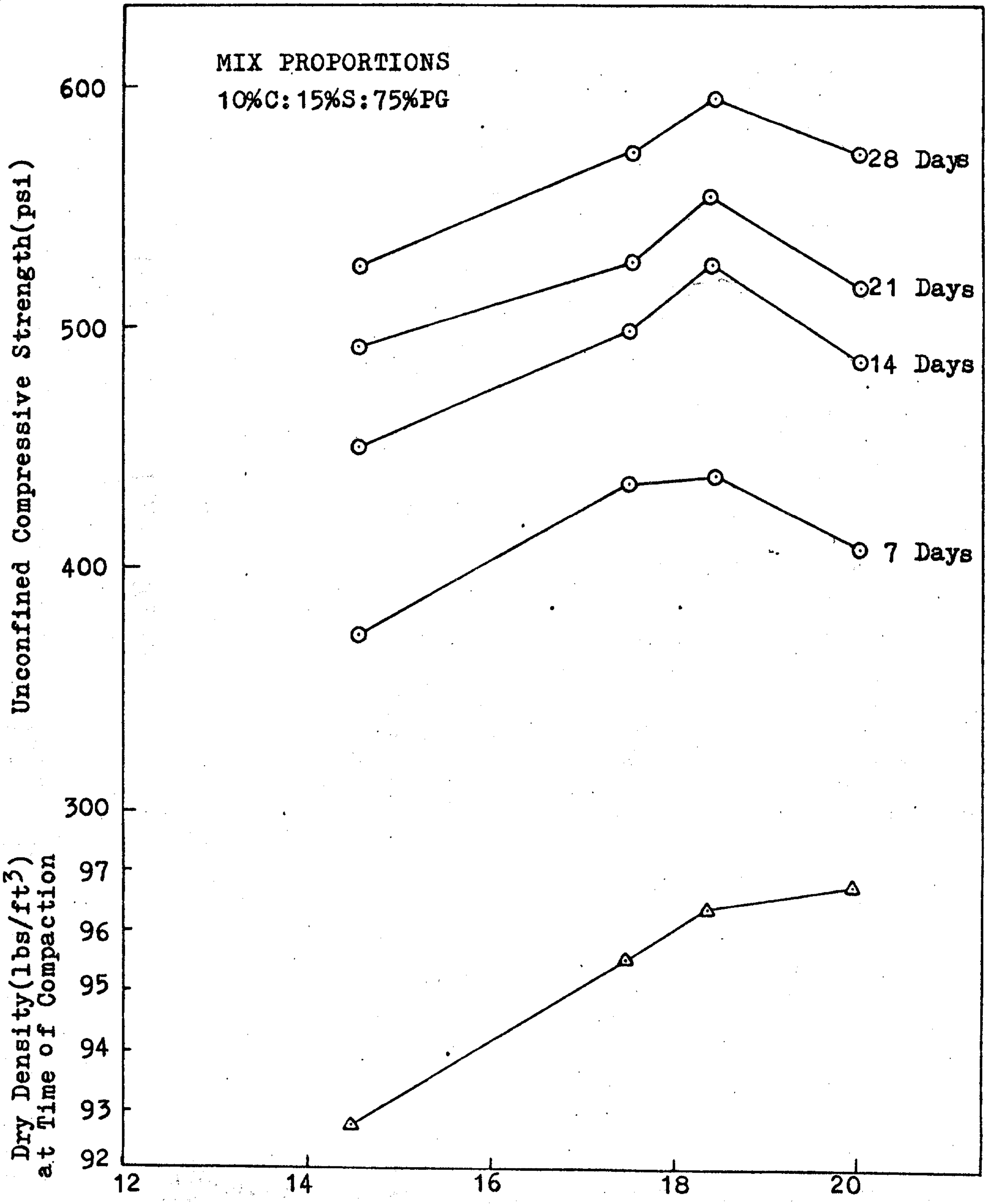
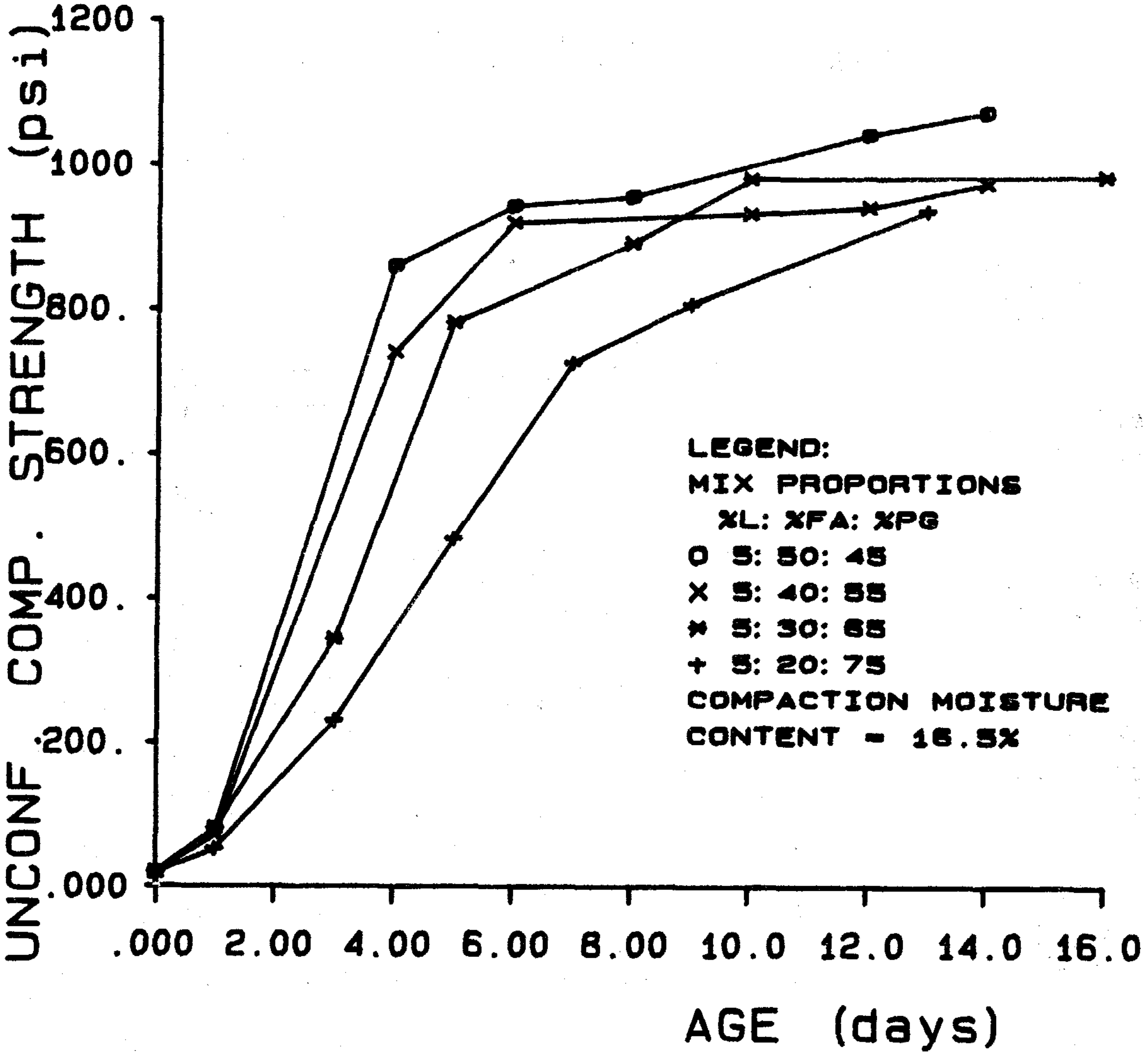


FIGURE 2. Unconfined Compressive Strength vs. Sand Content for Different Curing Conditions. (Cement-Sand-Phosphogypsum Mixtures).



Compaction Moisture Content(%)

Figure 3. Effects of compaction moisture content on the strength and dry density of the 10% cement-15% sand-75% phosphogypsum mixture. (Ref. 3)



GURE 4. Comparison of the Unconfined Compressive Strength of Various Lime-Flyash-Phosphogypsum Mixtures.

MATERIALS:

Asphalt Concrete: Type S (FLDOT)

Portland Cement Concrete f'_c=4,000psi

Limerock LBR≥100

7.5% Cement/20% Sand/72.5% Phosphogypsum/

6% Lime/24% Flyash/70% Phosphogypsum/

Stabilized Subbase: min LBR=40

Concrete Slabs : Jointed @ 15' - Preformed Seal
Dowel Bars
Tiebars along Longitudinal Joint

5/8" Non-structural Friction Course FC-2 on Asphalt Concrete Pavement Sections.

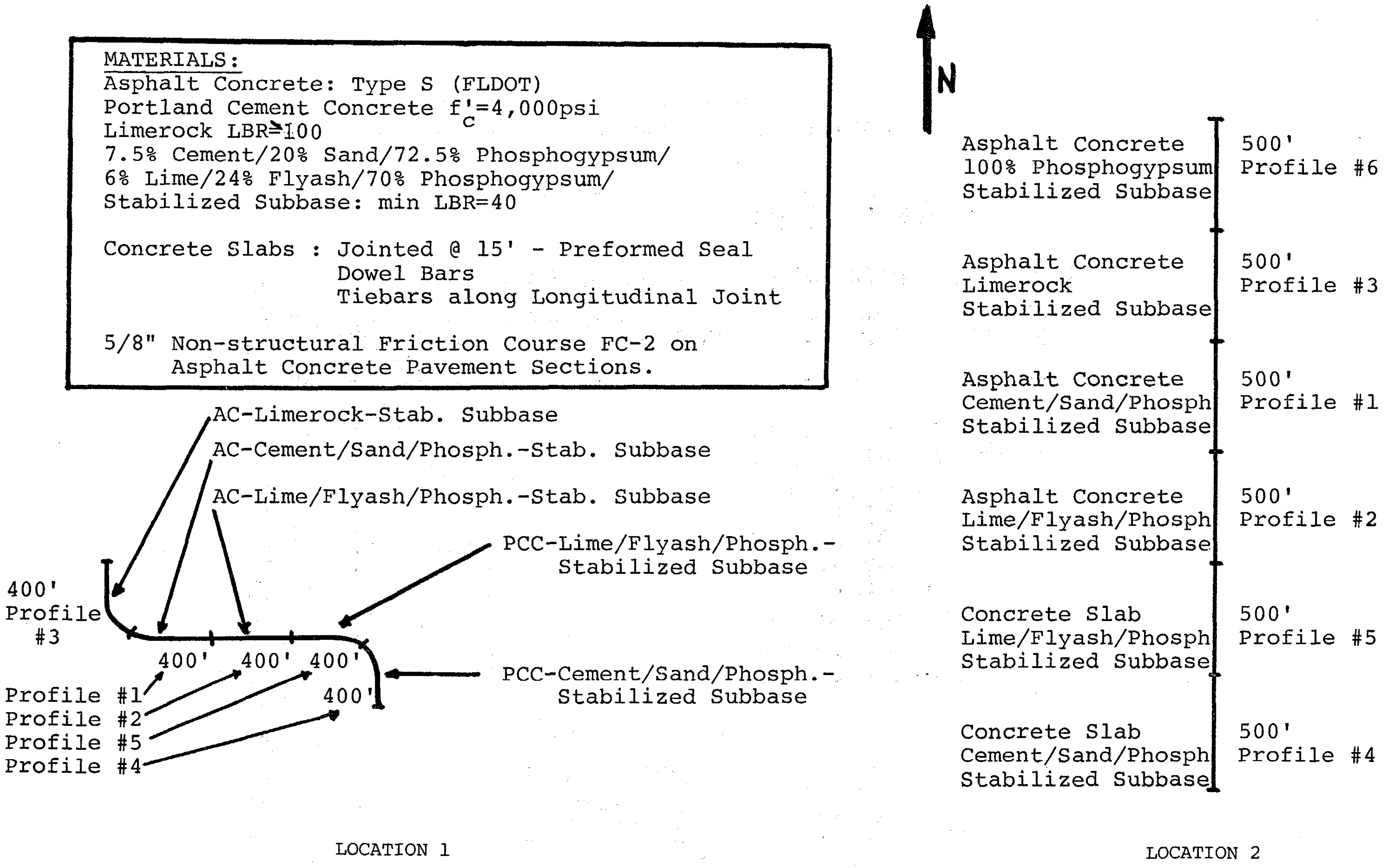
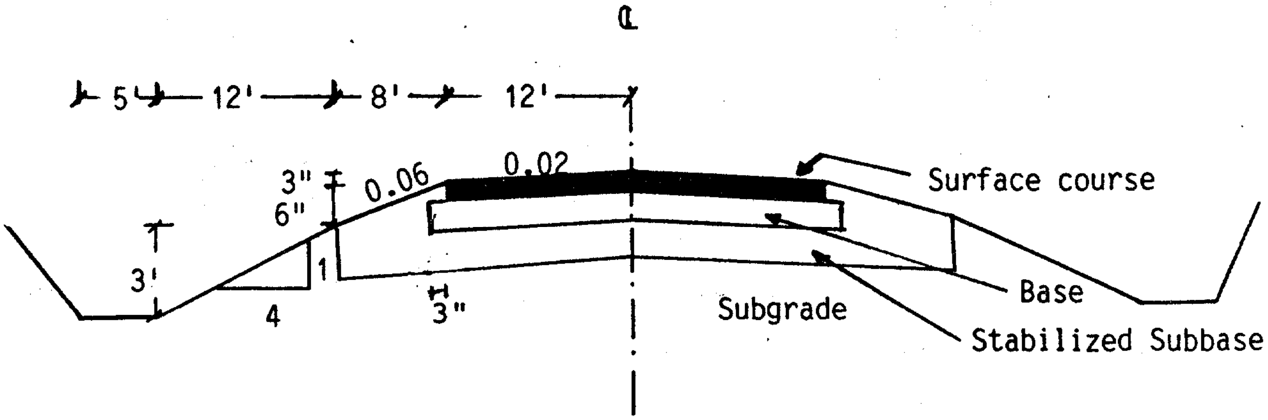


FIGURE 5. Distribution of Pavement Profiles.



5/8" Non-structural Friction Course FC-2

Required A.C. Layer

Specified Base

Stabilized Subbase (min LBR=40)

FIGURE 6. Detailed Pavement Cross-Section

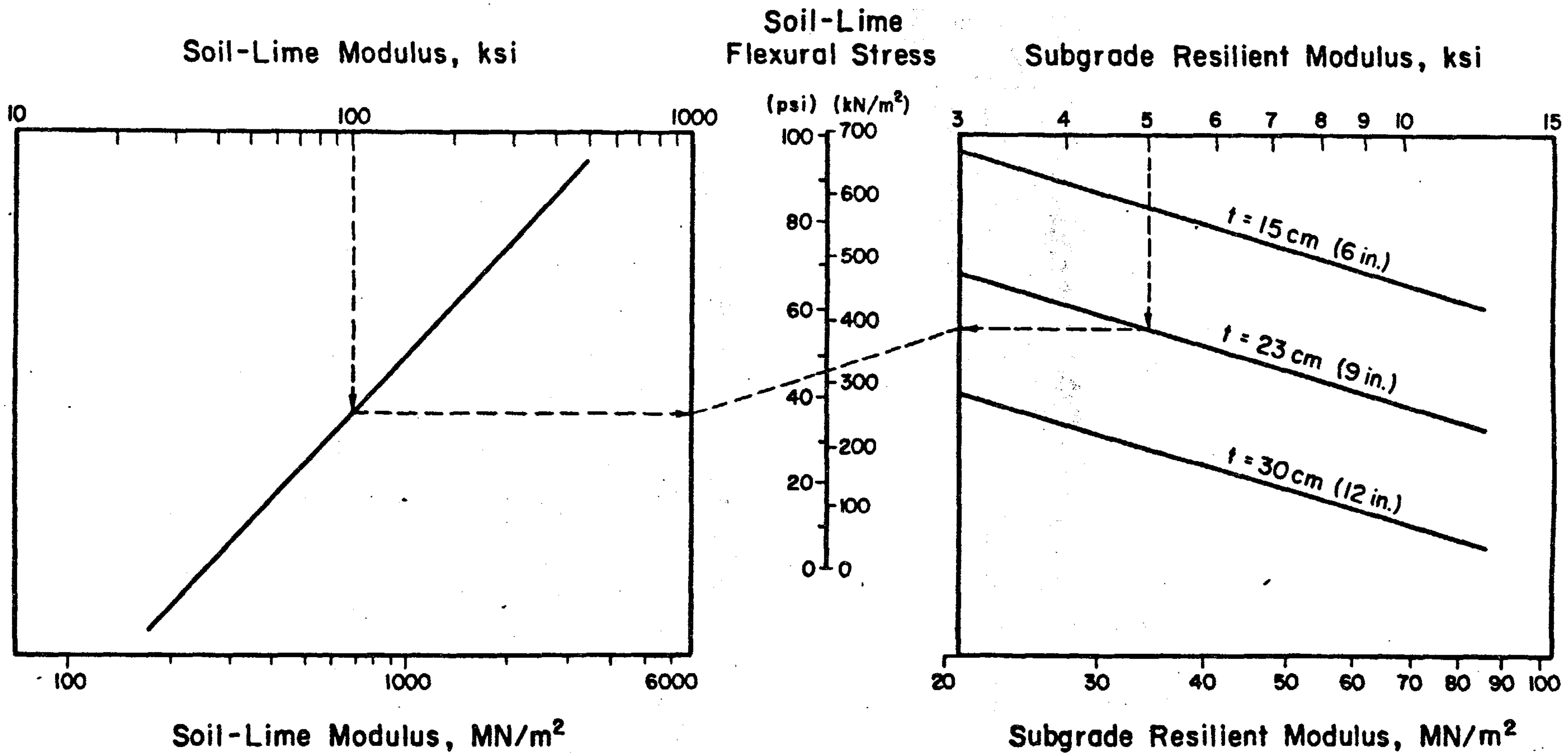


FIGURE 7. Soil-Lime Flexural Stress Nomogram. (from Ref. 12)

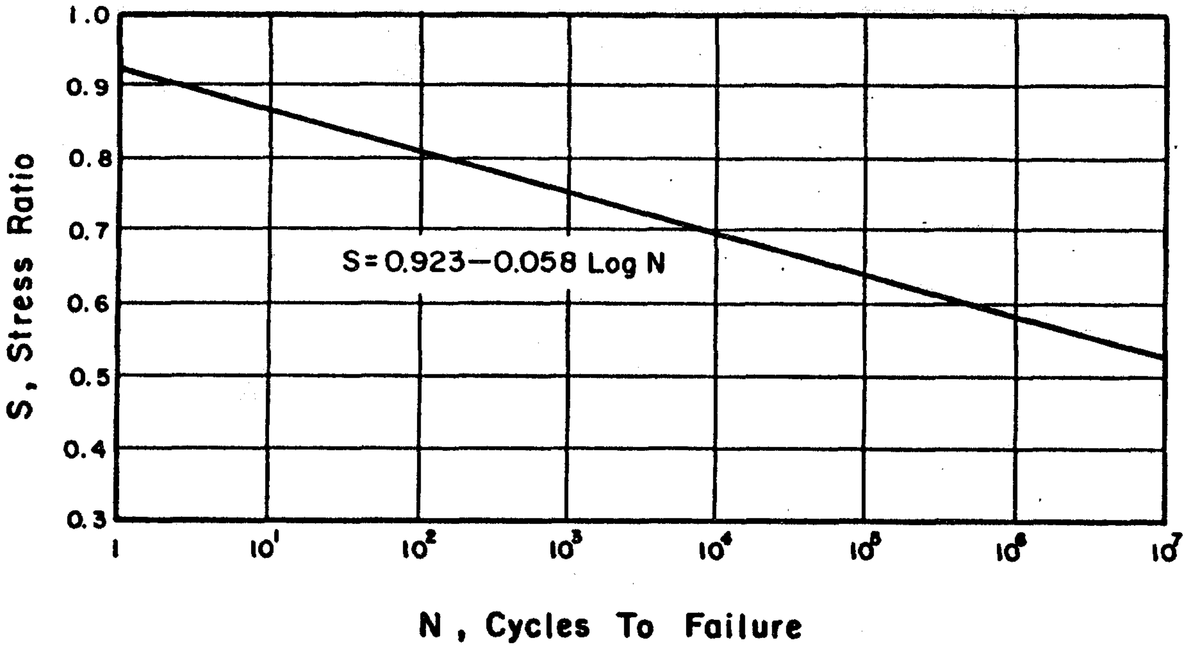


FIGURE 8. Fatigue Response for Cured Soil-Lime Mixtures (Ref. 12).

ENGINEERING PROPERTIES OF PHOSPHOGYPSUM, SAND AND CLAY MIXTURES

Arup Maji
Graduate Assistant, Dept. of Civil and Architectural Engineering
University of Miami, Coral Gables, FL.

J. Ludwig Figueroa
Associate Professor, Dept. of Civil and Architectural Engineering
University of Miami, Coral Gables, FL.

Wen F. Chang
Professor, Dept. of Civil and Architectural Engineering, and
Director, Phosphate Research Institute
University of Miami, Coral Gables, FL.

ABSTRACT

This pilot study was undertaken in order to provide alternate methods of rebuilding county and other secondary roads using phosphogypsum (a phosphate mining waste) as an aggregate. Current construction practice of these roads consists of mixing and further compacting the generally granular soil subgrade with fine-grained soils transported to the site. These mixtures tend to be largely affected by changes in the moisture regime.

Several phosphogypsum-sand mixtures have been studied under unconfined compression as well as CBR testing. Most of these mixtures yield acceptable strength and bearing values. However, they also become unstable when soaked. A Rapid Curing cutback asphalt RC-70 has been added to the mixtures in order to provide water resistance. It has been found that a very small percentage of RC-70 is required for specimens to develop such water resistance. Several alternatives that would give acceptable performance when used in the construction of secondary roads are presented.

INTRODUCTION

The pilot study to be described was undertaken in order to provide alternate methods of rebuilding county and other secondary roads using phosphogypsum (a phosphate mining waste) as an aggregate.

Current construction practice of these secondary roads consists of mixing the generally granular soil subgrade with fine-grained soils transported to the site. The on-site mixing operation is followed by appropriate compaction. It has been found, however, that roads built in this fashion tend to be greatly affected by changes in the moisture regime. They tend to be soft and muddy during long rainy periods and become dusty during dry spells, with the consequent inconveniences to users.

The Polk County Highway Department has taken the initiative of finding alternate methods of rebuilding these roads that would improve their life expectancy and rideability.

In light of the abundance of phosphogypsum in this county, attempts were made to develop suitable mixtures that would render phosphogypsum insensitive to moisture changes. Other criteria considered in selecting suitable mixtures included strength, on-site mixing, inexpensive components and any other factors that would expedite construction. Florida's dominance as a producer of phosphogypsum, its ready availability and low handling cost has provided added incentive for its use.

A rapid curing cutback asphalt (RC-70), in combination with commonly found granular subgrade soils, phosphogypsum and other fine-grained soils, were mixed in different proportions in order to obtain suitable materials meeting the criteria given above.

It is expected that the results of this pilot study serve as the basis for full-scale tests to be undertaken within the next three years. Roads rebuilt with these mixtures will be subjected to actual traffic conditions and their performance monitored periodically.

SAMPLE TESTING

Unconfined compressive strength, moisture density and field and laboratory California Bearing Ratio tests were mainly used to ascertain the suitability of the proposed mixtures as pavement materials. Small pavement sections 2x3 ft. in area by 5 inches in thickness were compacted outdoors with direct exposure to rain and sun. Periodic field testing has allowed the determination of the variation of mechanical properties of soils with time and weather conditions. The results of this phase of the study will be given at a later date.

The effect of a varying moisture regime was also investigated in the laboratory by periodically soaking and drying compacted specimens. Samples achieved a steady state regardless the number of wetting and drying cycles, as it will be shown later.

Unconfined compressive strength testing of the proposed mixtures required the compaction of specimens 2" in diameter by 4″ in length, according to equivalent modified Proctor compaction specifications. Moisture-density tests were also performed according to identical compaction specifications (ASTM D-1557-70) (Ref. 1). Specimens prepared for this purpose were 4" in diameter by 4.58″ in length. Moisture content was obtained after subjecting mixture samples to a temperature of 60 degrees C in a convection-type oven for at least 24 hours. The lower temperature (as compared to ASTM specification D2216-71) was required in order to prevent the calcination of phosphogypsum, as shown in Ref. 2. Identically, samples subjected to cyclic wetting and drying were exposed to a maximum temperature of 60 degrees C.

Samples tested for unconfined compressive strength were capped with CYLCAP in order to provide smooth and parallel plane surfaces that would assure a uniform distribution of load within the specimen. A constant rate of loading equal to .05 in/min was used in all compression tests. Stress-strain relationships were also obtained during compression tests in order to ascertain whether or not the proposed mixtures could be considered as elastic materials at least within a certain range. This characterization will be of great use in future flexible pavement analyses using the Theory of Elasticity.

No attempt was made to evaluate Poisson’s ratio for these mixtures. However, this parameter will be investigated in the near future.

PHOSPHOGYPSUM-CLAYEY SAND-SAND MIXTURES

Several basic soil laboratory test were performed on each of the components of the proposed phosphogypsum - clayey sand - sand mixture. The grain size distributions along with the specific gravity of the three materials (obtained as per ASTM D422) are shown in Figure 1. As it can be observed, phosphogypsum possesses the grain size characteristics of a silt and its specific gravity is appreciably lower that that of the two sands.

Figures 2 and 3 show the unconfined compressive strength and moisture-density relationships respectively, of specimens prepared at different moisture contents and containing different proportions (as indicated in the figure index) of sand, phosphogypsum and clayey sand. All specimens were compacted according to the modified Proctor compaction procedure.

Replacement of the clayey sand with phosphogypsum increases the dry density up to a maximum shown by line III in Figure 3. Any further increase of phosphogypsum content decreases the dry density. Hence, the 1.5:l.0:0.5 clayey sand, sand, phosphogypsum mixture is considered to be the most favorable.

Phosphogypsum tends to fill in the voids in the clayey sand-sand mixture increasing dry density to the level shown by line III in Figure 3. Any excess phosphogypsum (a lower specific gravity material) thereafter, causes a reduction in the dry density. Thus, research efforts have been concentrated towards the study of the engineering properties of the 1.5:1.0:0.5 clayey sand, sand and phosphogypsum mixture.

The effects of increased phosphogypsum content on several parameters have been summarized in Figure 4. Maximum dry density and unconfined compressive strength simultaneously increase with increased phosphogypsum content, up to a maximum of 1/6 of the total mixture. Any further increase in the amount of phosphogypsum leads to decreases in both parameters. Optimum moisture content, on the other hand, initially decreases to a minimum (at a phosphogypsum content of 1/6 of the total weight) and increases thereafter.

Curing conditions largely affect the development of unconfined compressive strength. Results of unconfined compressive strength testing of specimens initially dried in the oven at 60 degrees C for 24 hours (to accelerate curing), and thereafter left out exposed to room temperature (25 degrees C) and relative humidity of 60%, are shown in Figure 2. Specimen moisture content at the moment of testing was in general below 1.0%. Unconfined compressive strength values of specimens tested 2 to 3 hours after removal from the oven are shown in Figure 5. Specimen moisture content at the moment of testing was less than .1%. Their strength values are somewhat higher than in the previous case, where the influence of the absorbed moisture content, when exposed to room conditions, is noticed. These results may be indicative of the moisture susceptibility of the mixture. Again, the 1.5:1.0:0.5 clayey sand, sand and phosphogypsum mixture yielded the best results. This mixture was also found to be of superior quality as compared to the 2.0:l.0 clayey sand-sand mixture currently used in the construction and rehabilitation of secondary roads.

California Bearing Ratio tests (4″ mold) were conducted on the proposed optimum (1.5: 1 .0: 0.5) mix using phosphogypsum and the mix currently in use (2 parts of clayey sand to 1 part of sand). Tests were conducted on specimens after compacting the mixture according to the modified Proctor compaction method. Two different series of tests were run on each mix to simulate different curing conditions:

- First, specimens were tested immediately after compaction, and
-Second, specimens were tested after soaking in water for 4 days.

Results of these tests are depicted in Figure 6. It should be observed that the addition of phosphogypsum tends to increase the Bearing Ratio of the mixture, and to lower the critical preparation moisture content.

USE OF RC-70 FOR WATER RESISTANCE

Different proportions of a Rapid Curing cutback asphalt (RC-70) .25 to 2.0% by weight of the total mix consisting of 1.5 parts of clayey sand, 1.0 part of sand and 0.5 parts of phosphogypsum were used to prepare samples to be tested under unconfined compression. Figures 7 and 8 show that the strength of samples prepared with different cutback asphalt contents is not significantly different when specimens are tested after oven drying for 24 hours at 60 degrees C and allowing them to remain at room temperature for 2 to 3 hours before testing. However, the addition of RC-70 becomes highly beneficial as soaked specimens are able to maintain their stability, and increased strength results with increased cutback content as shown in Figure 8.

Dry and wet cycles were run on specimens containing cutback asphalt. These cycles consisted of alternate drying at 60 degrees C for 24 hours and soaking in water for 24 hours . Results presented in Figure 9 show that specimen water resistance is possible even with a percentage RC-70 content as low as .25%. However, in order to obtain appreciable strength after soaking the percentage of RC-70 should be at least equal to 2.0%. Unconfined compressive strength values of at least 200psi may be obtained even after 24 hours of soaking. The variation of unconfined compressive strength between the dry and wet condition is considerably less with the use of higher percentages of RC-70. The results also show no trends of gradual degradation with subsequent wet and dry cycles, as specimens reach a steady state of strength as shown in Figure 9. The dry unconfined compressive strength remains basically unaltered with increased RC-70 content, while the soaked strength greatly increases with higher percentages of RC-70.

As a result of this phase of the study, it can be concluded that the addition of the cutback asphalt RC-70 to mixtures of clayey sand, sand and phosphogypsum prevents the collapse of soils when saturated. This laboratory testing intended to simulate environmental cyclic wetting and drying during actual field conditions.

SAND-PHOSPHOGYPSUM MIXTURE AND THE EFFECTS OF RC-70

Moisture-density relations were obtained for different mix ratios of sand and phosphogypsum. General trends are shown in Figures 10 and 11. An increase in the proportion of phosphogypsum beyond 1:1 tends to decrease the dry unit weight. As a result, subsequent studies were limited to mixtures containing 50% or less of phosphogypsum. Moisture-density curves for additional combinations of sand and phosphogypsum are presented in Figure 11. The mixture containing 2 parts of sand to 1 part of phosphogypsum yielded the highest dry unit weight and the lowest optimum moisture content.

Results of CBR tests conducted immediately after compaction on different mix ratios are presented in Figure 12 and 13. The examination of these figures shows no definite trend in the critical moisture content with respect to phosphogypsum content of the mixture.

Figure 14 compares the unconfined compressive strength of the 1:1

sand:phosphogypsum mixture in the dry and wet condition for specimens prepared at different moisture contents. As expected, dry compressive strength is higher than the compressive strength of specimens tested after soaking. The effect of adding RC-70 to the sand-phosphogypsum specimens tested after oven drying is imperceptible. The influence of RC-70 becomes important when specimens are tested under compression after soaking.

Values of the modulus of elasticity of sand-phosphogypsum specimens prepared at different moisture contents and containing different amounts of RC-70 are shown in Figure 15. These results, after testing soaked specimens, demonstrate that the amount of RC-70 influences the determination of the elastic properties of the mixture producing increased modulus of elasticity with an initially higher cutback asphalt content. The modulus of elasticity is expected to decrease at excessively higher RC-70 contents.

SUMMARY

This research has been directed towards the use of mixtures of available clayey sand, sand and phosphogypsum as improved road construction materials. Considering the clayey sand, sand, phosphogypsum type of mixture the ratio 1.5:1.0:.5 respectively, was determined to be the most effective way of using these three components. Further investigation will be directed towards the total replacement of the clayey sand from the mixture, and the examination of the effects of adding cutback asphalt in several proportions to these resulting mixtures.

Figures 16 and 17 compare the dry density and compressive strength of these two suggested alternatives to the original combination not containing phosphogypsum. The clayyey sand, sand, phosphogypsum mixture emerges as the best alternative. Figure 18 compares the soaked CBR of three mixtures. The sand-phosphogypsum mix along with 2.0% of RC-70 leads to the most desirable results under soaked conditions. Finally, Figure 19 shows a comparison between the CBR values obtained on specimens compacted in the 4 and 6-inch diameter molds. It should be observed that at low moisture content the arching effect is evident in the 4” mold. However, at high moisture content the difference in the results becomes negligible.

Soaked CBR tests on clayey sand, sand, phosphogypsum and RC-70 mixtures are currently under way. Considering the beneficial effects of RC-70 on this mix, CBR resultsare expected to be of fundamental importance before a final choice is made between the possible alternatives. The evaluation of mixture properties will continue with the use of both field and laboratory testing. Efforts will be made to correlate laboratory and field testing results and to develop design criteria leading to the construction of improved secondary roads using phosphogypsum as an important pavement component.

ACKNOWLEDGEMENT

The authors would like to express their gratitude to the Florida Institute of Phosphate Research (FIPR) as the funding agency for the project, Mr. Kenley from the Polk County Highway Department and Gardinier In. for their continued interest and support in making this research possible.

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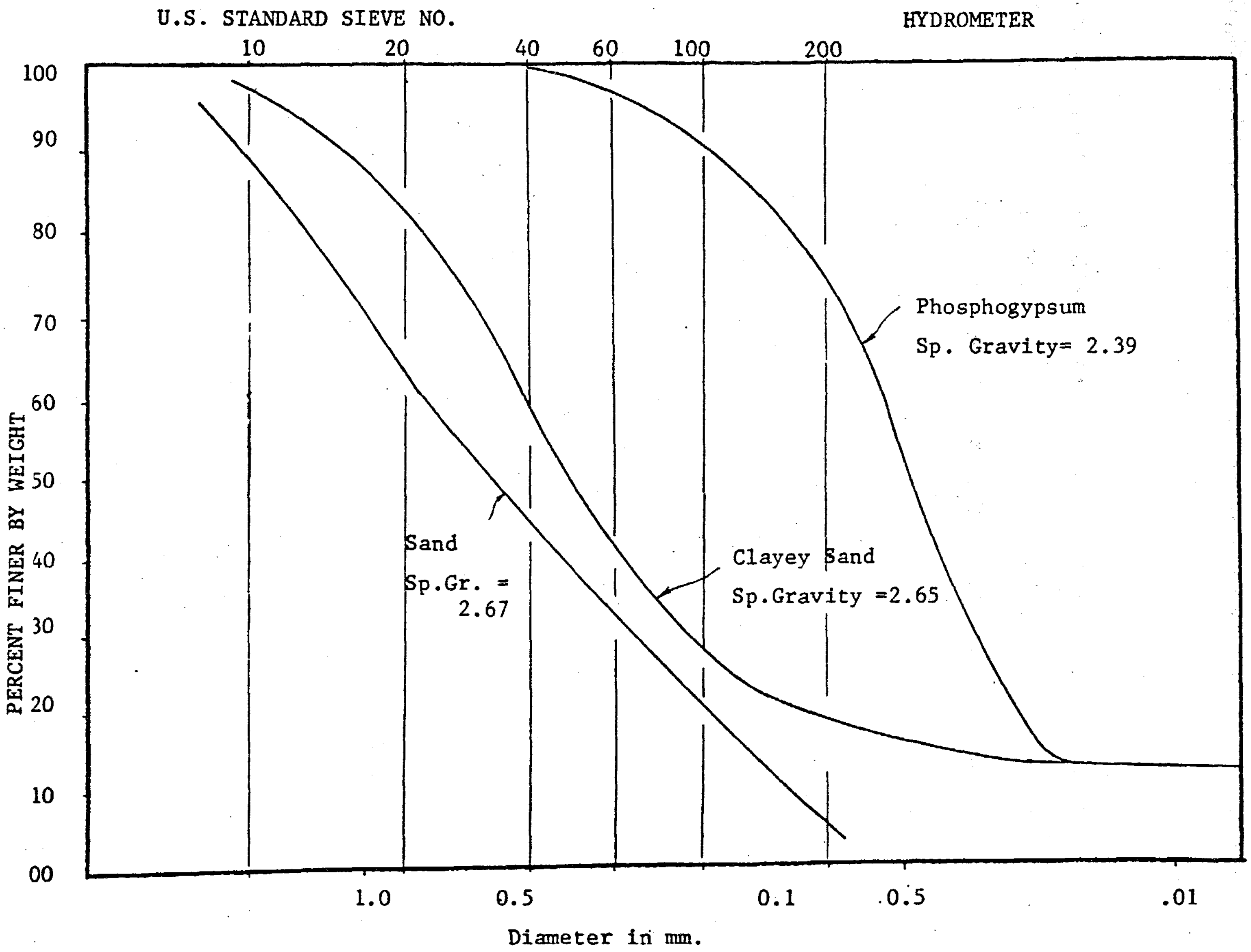
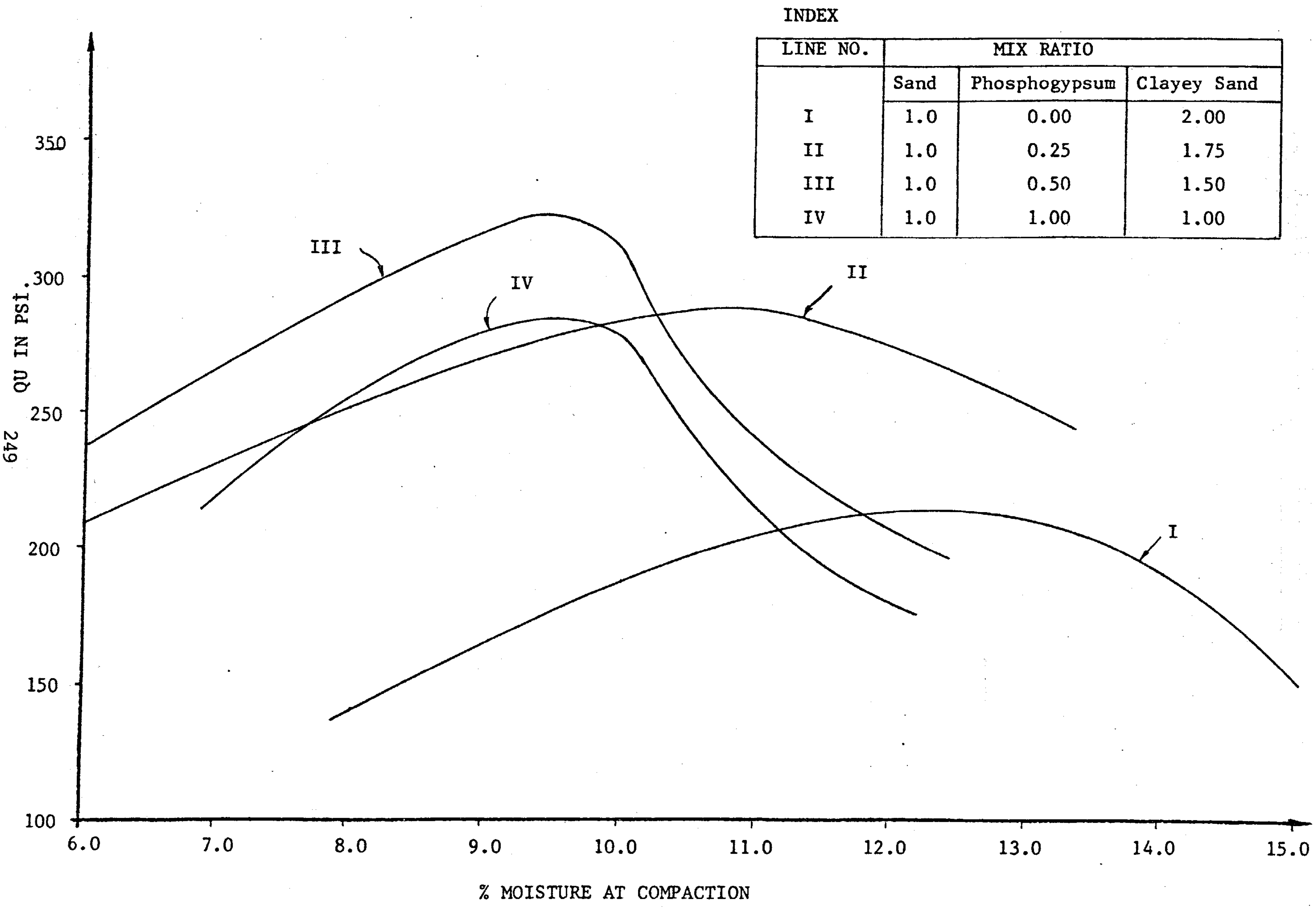


GRAIN SIZE DISTRIBUTION OF SAND, CLAYEY SAND AND PHOSPHOGYPSUM AND SPECIFIC GRAVITY.

FIGURE 1.



INDEX

LINE NO.	MIX RATIO		
	Sand	Phosphogypsum	Clayey Sand
I	1.0	0.00	2.00
II	1.0	0.25	1.75
III	1.0	0.50	1.50
IV	1.0	1.00	1.00

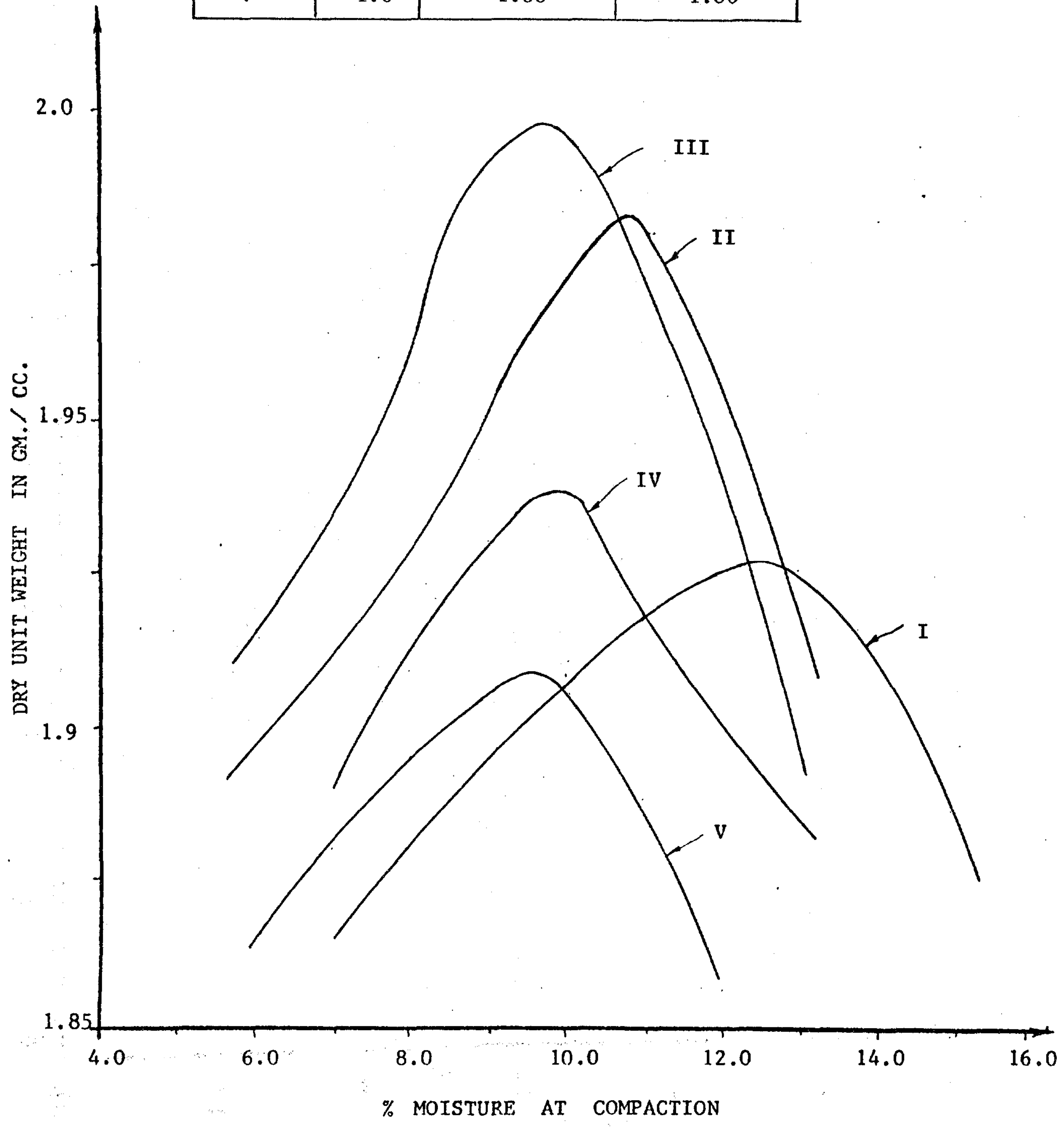
UNCONFINED COMPRESSIVE STRENGTH OF DIFFERENT MIXTURES OF SAND, PHOSPHOGYPSUM AND CLAYEY SAND. FIGURE 2.

MOISTURE DENSITY RELATIONS OF CLAYEY SAND, SAND AND PHOSPHOGYPSUM MIXTURES.

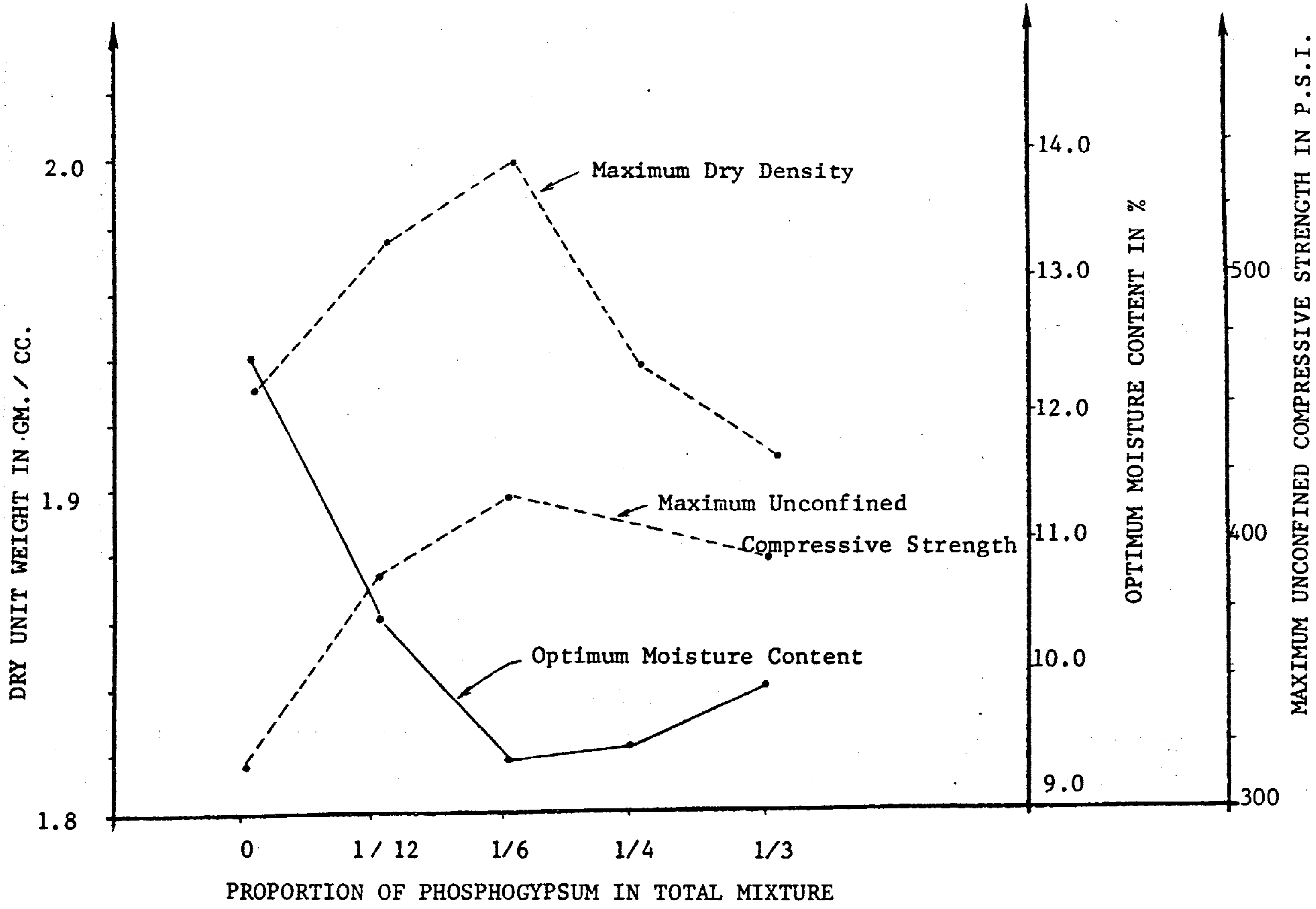
FIGURE 3

INDEX

LINE NO.	MIX RATIO		
	Sand	Phosphogypsum	Clayey Sand
I	1.0	0.0	2.0
II	1.0	0.25	1.75
III	1.0	0.50	1.50
IV	1.0	0.75	1.25
V	1.0	1.00	1.00

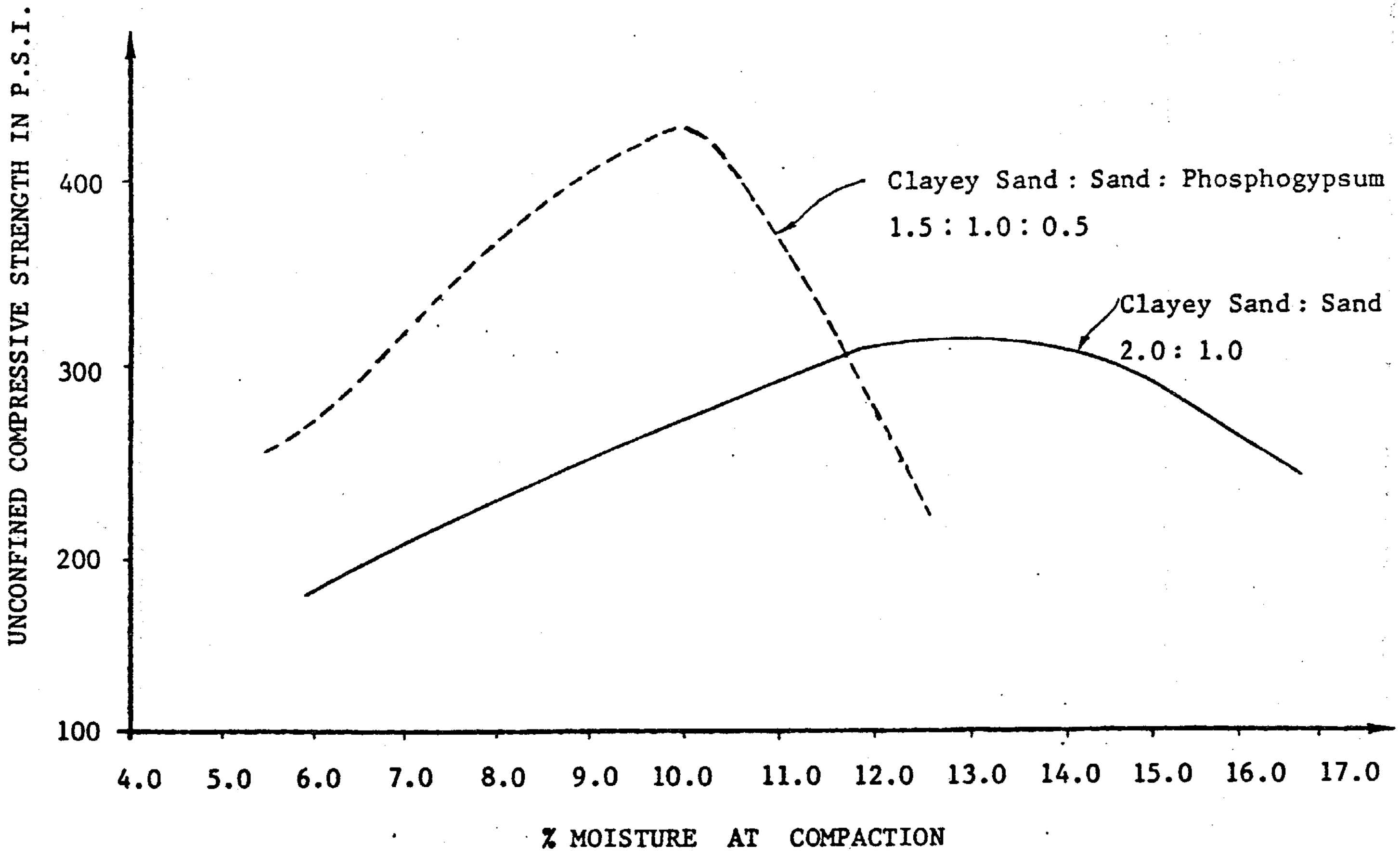


VARIATION IN THE MAXIMUM UNCONFINED COMPRESSIVE STRENGTH, OPTIMUM MOISTURE AND MAXIMUM DRY UNIT WEIGHT WITH CHANGE IN THE PROPORTION OF PHOSPHOGYPSUM IN THE VARIOUS MIXTURES OF CLAYEY SAND, SAND AND PHOSPHOGYPSUM. FIGURE 4.



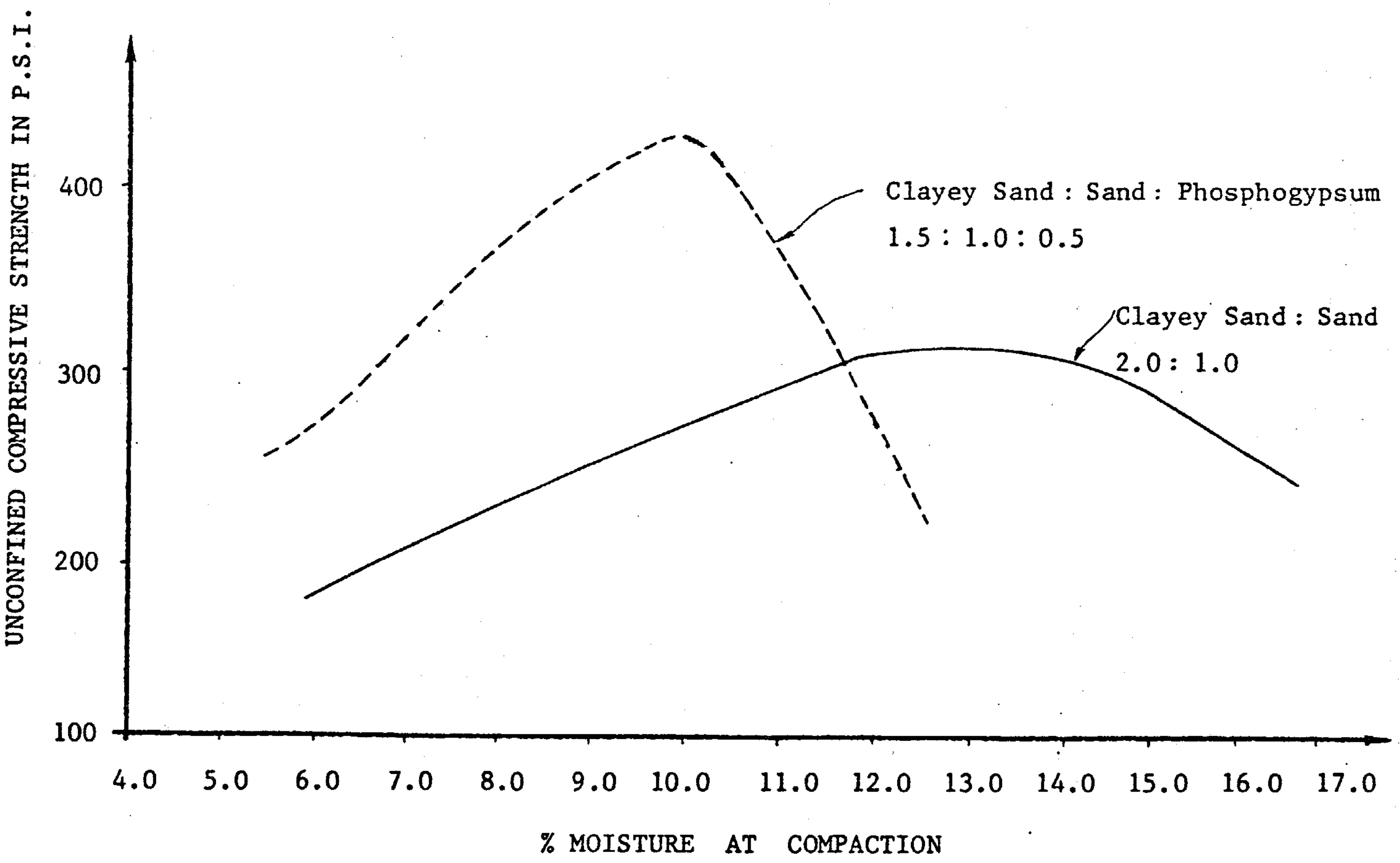
UNCONFINED COMPRESSIVE STRENGTH OF OVEN DRIED SAMPLES VS. % MOISTURE AT COMPACTION

FIGURE 5.



UNCONFINED COMPRESSIVE STRENGTH OF OVEN DRIED SAMPLES VS. % MOISTURE AT COMPACTION

FIGURE 5.



SOAKED AND UNSOAKED CBR vs.COMPACTION MOISTURE CONTENT

FIGURE 6.

INDEX

LINE NO.	TYPE	INGREDIENTS			TEST CONDITION
		Clayey Sand	Sand	Phosphogypsum	
I	————	2.0	1.0	0.0	Tested after Compaction
II	————	2.0	1.0	0.0	Tested after Soaking
III	--------	1.5	1.0	0.5	Tested after Compaction
IV	--------	1.5	1.0	0.5	Tested after Soaking

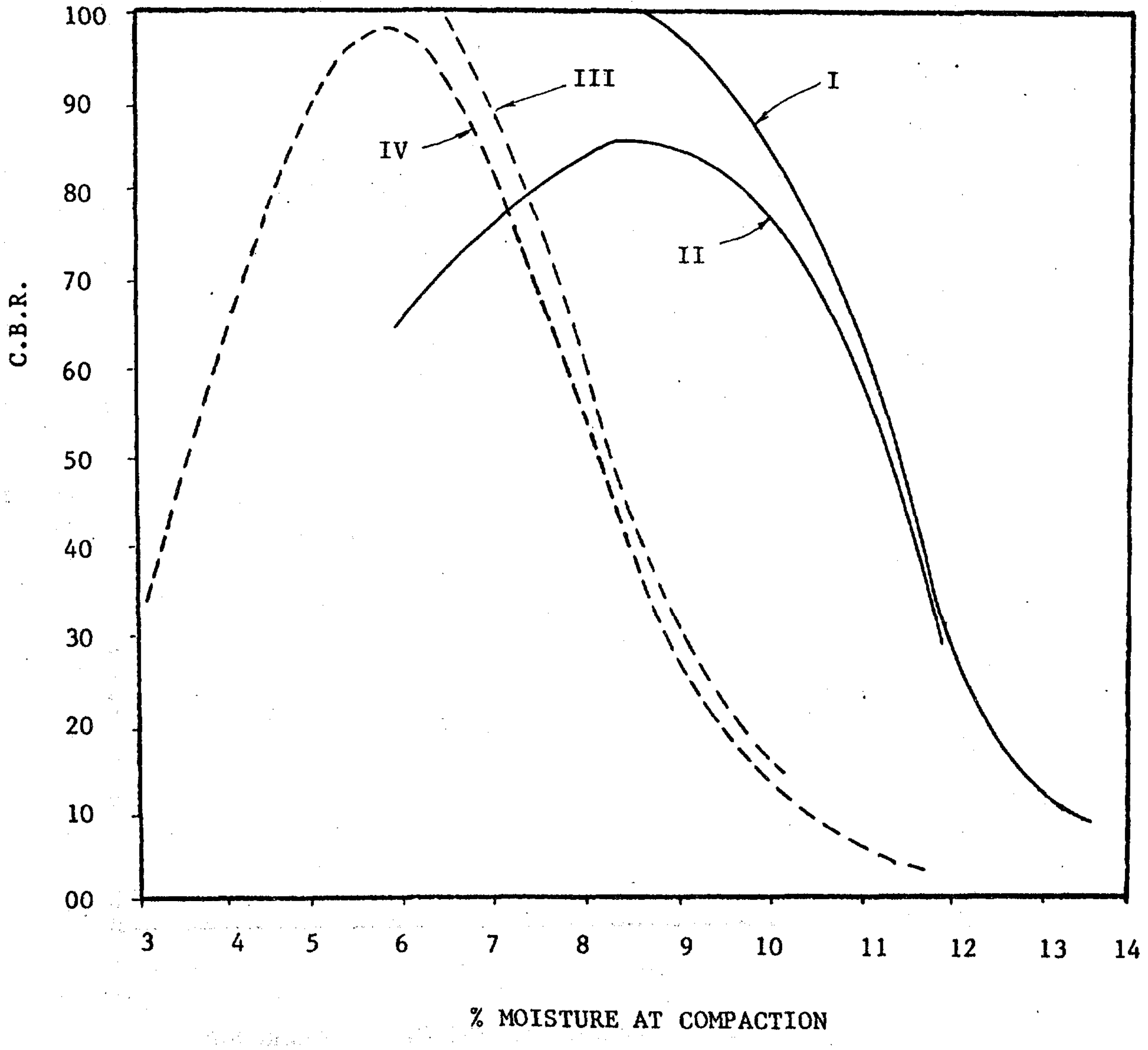


FIGURE 7. UNCONFINED COMPRESSIVE STRENGTH VS. COMPACTION MOISTURE CONTENT OF OVEN DRIED SAMPLES.

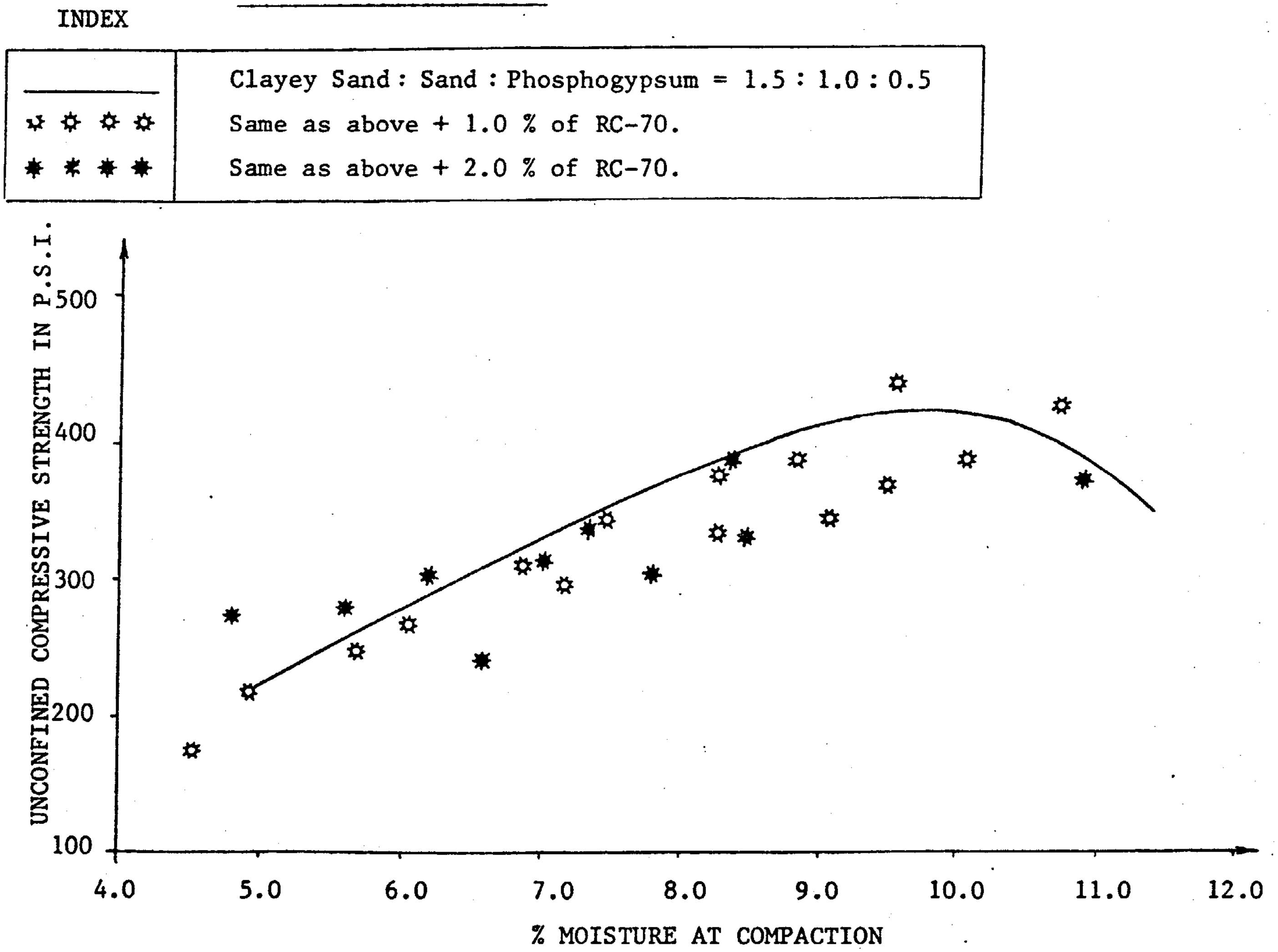
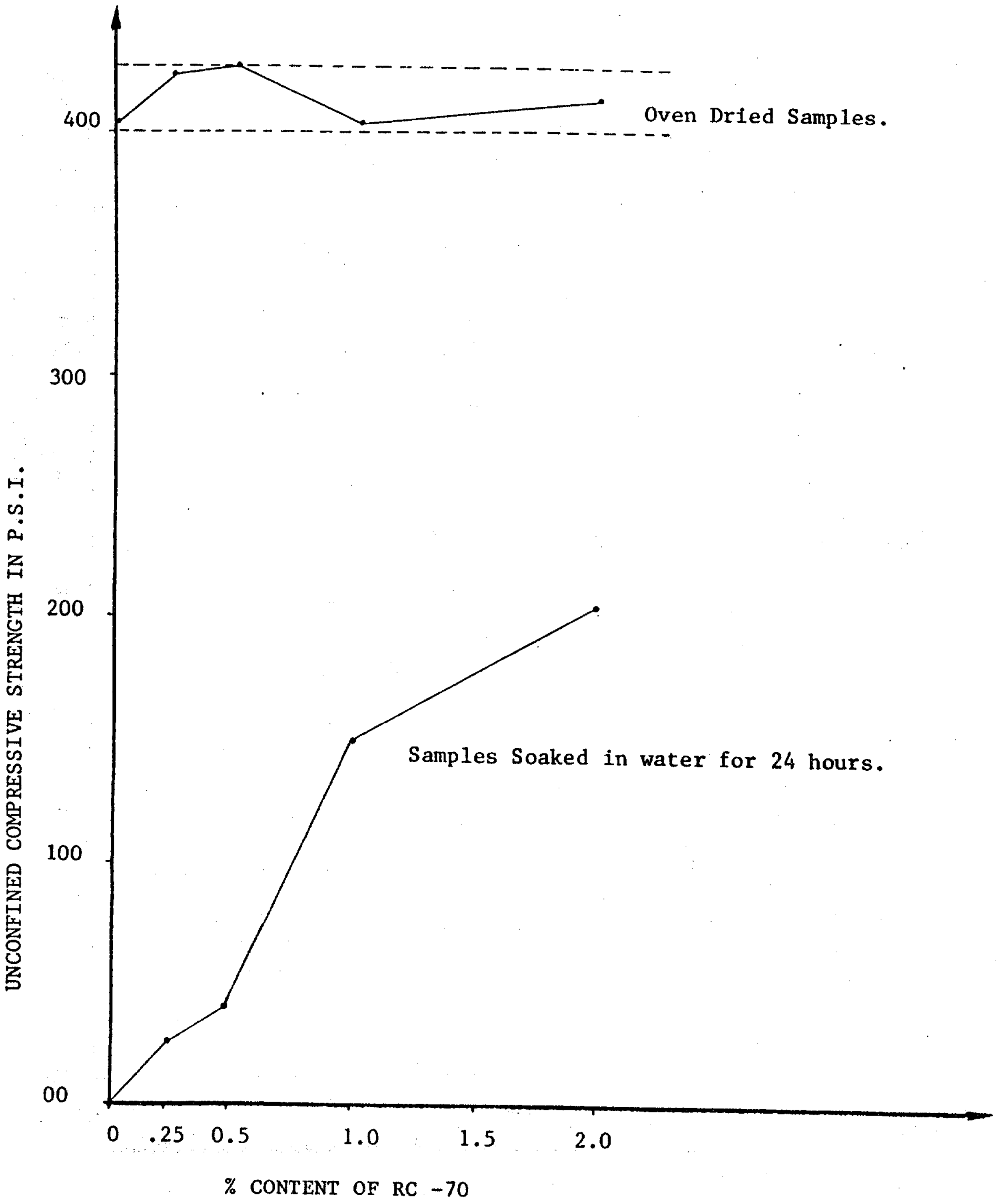
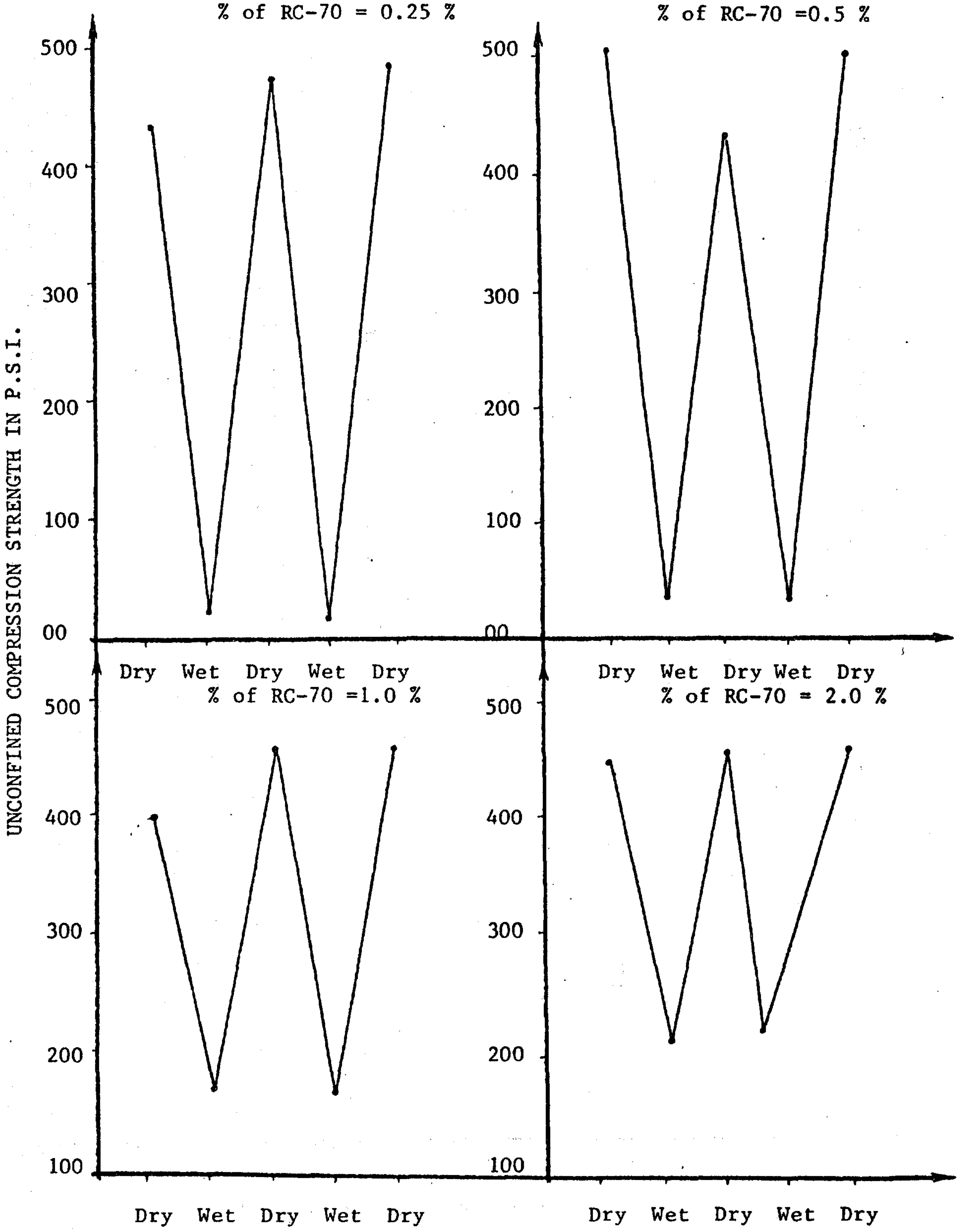


FIGURE 8.
VARIATION OF UNCONFINED COMPRESSIVE STRENGTH OF THE 1.5:1.0:0.5 MIXTURE OF CLAYEY SAND SAND PHOSPHOGYPSUM WITH RC - 70 CONTENT.



ALTERNATE DRY-WET CYCLES ON PHOSPHOGYPSUM, SAND AND CLAYEY SAND MIX (0.5:1.0:1.5) + RC-70 COMPACTED AT OPTIMUM MOISTURE. FIGURE 9.



MOISTURE DENSITY RELATIONS OF SAND AND PHOSPHOGYPSUM MIXTURES FIGURE 10.

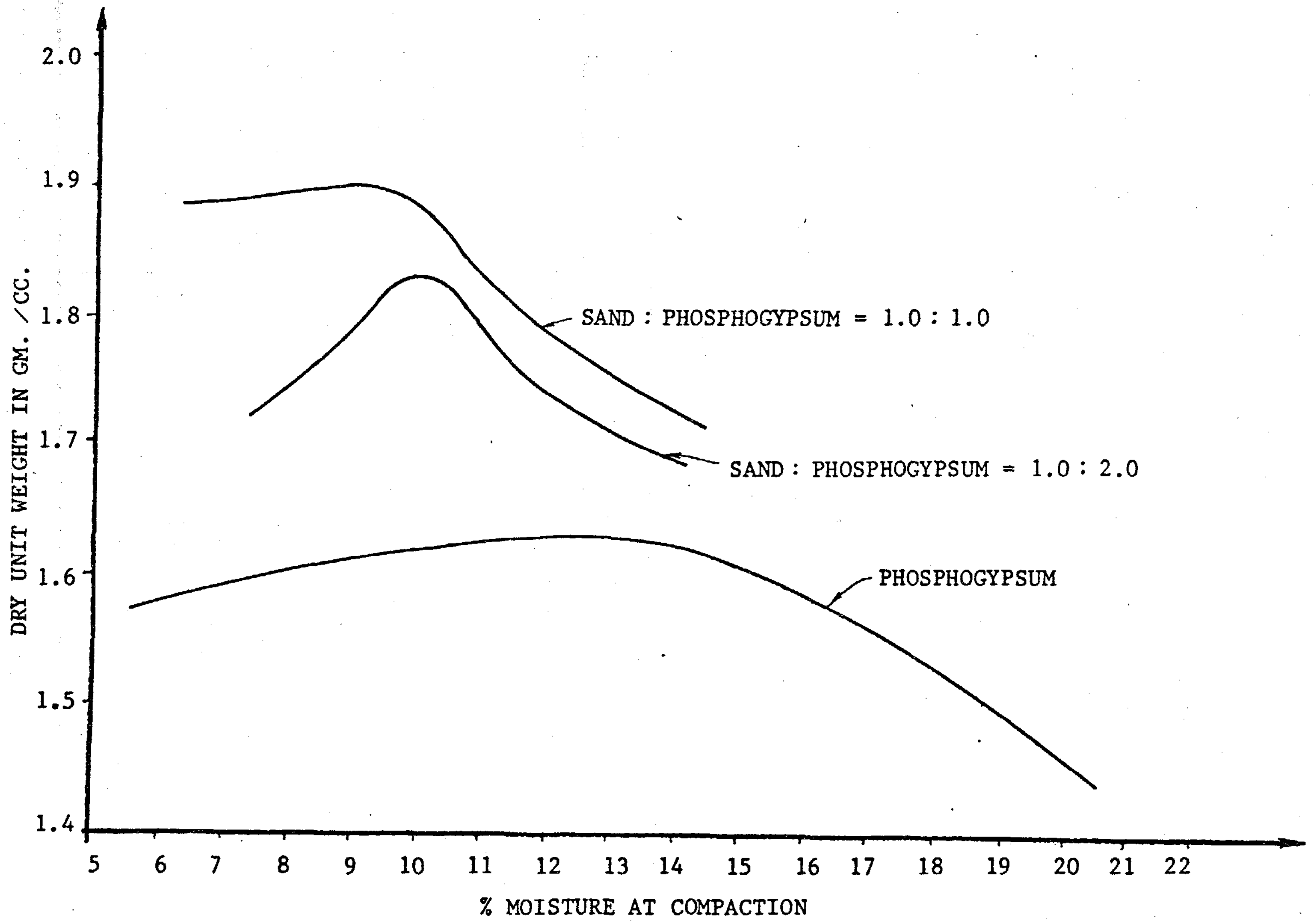
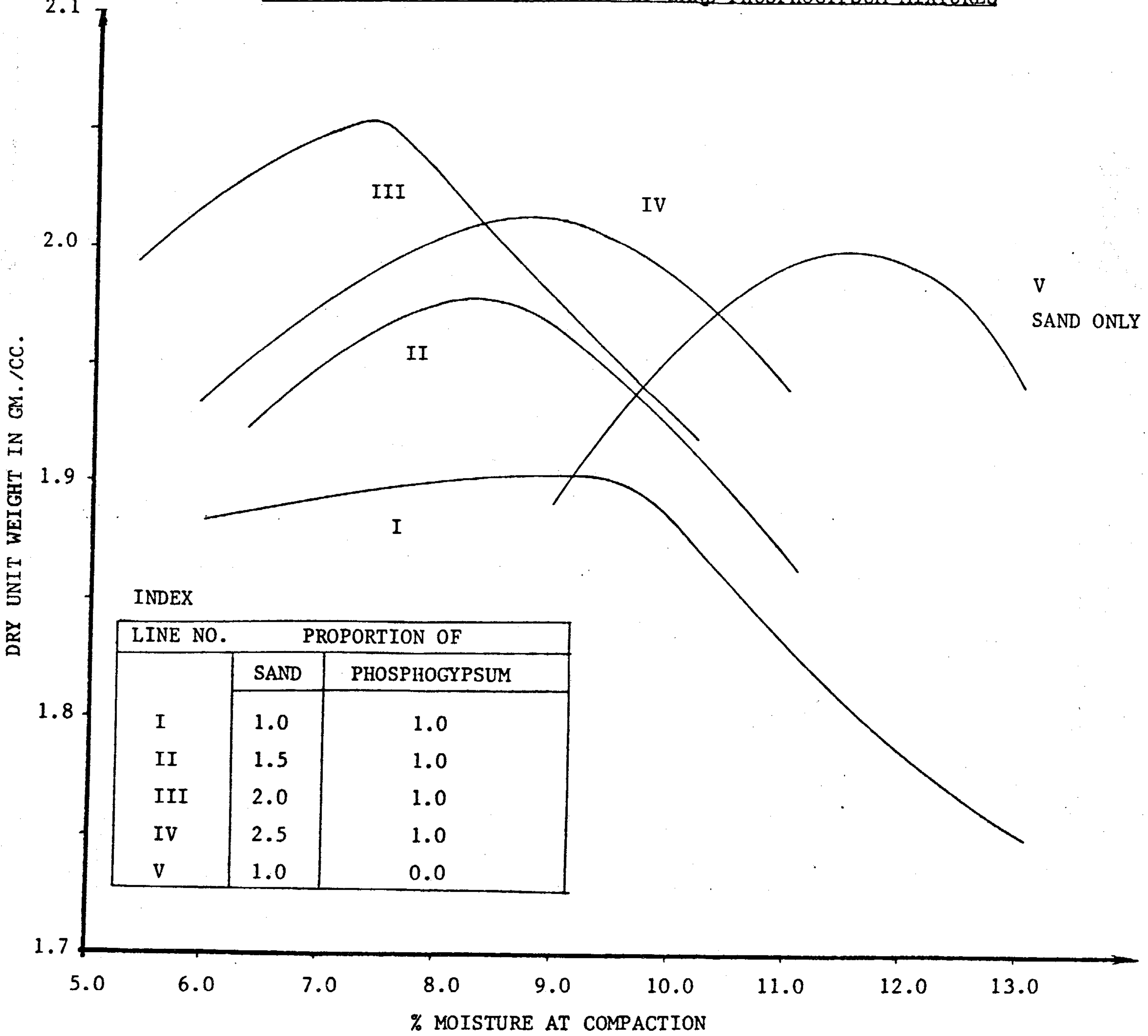
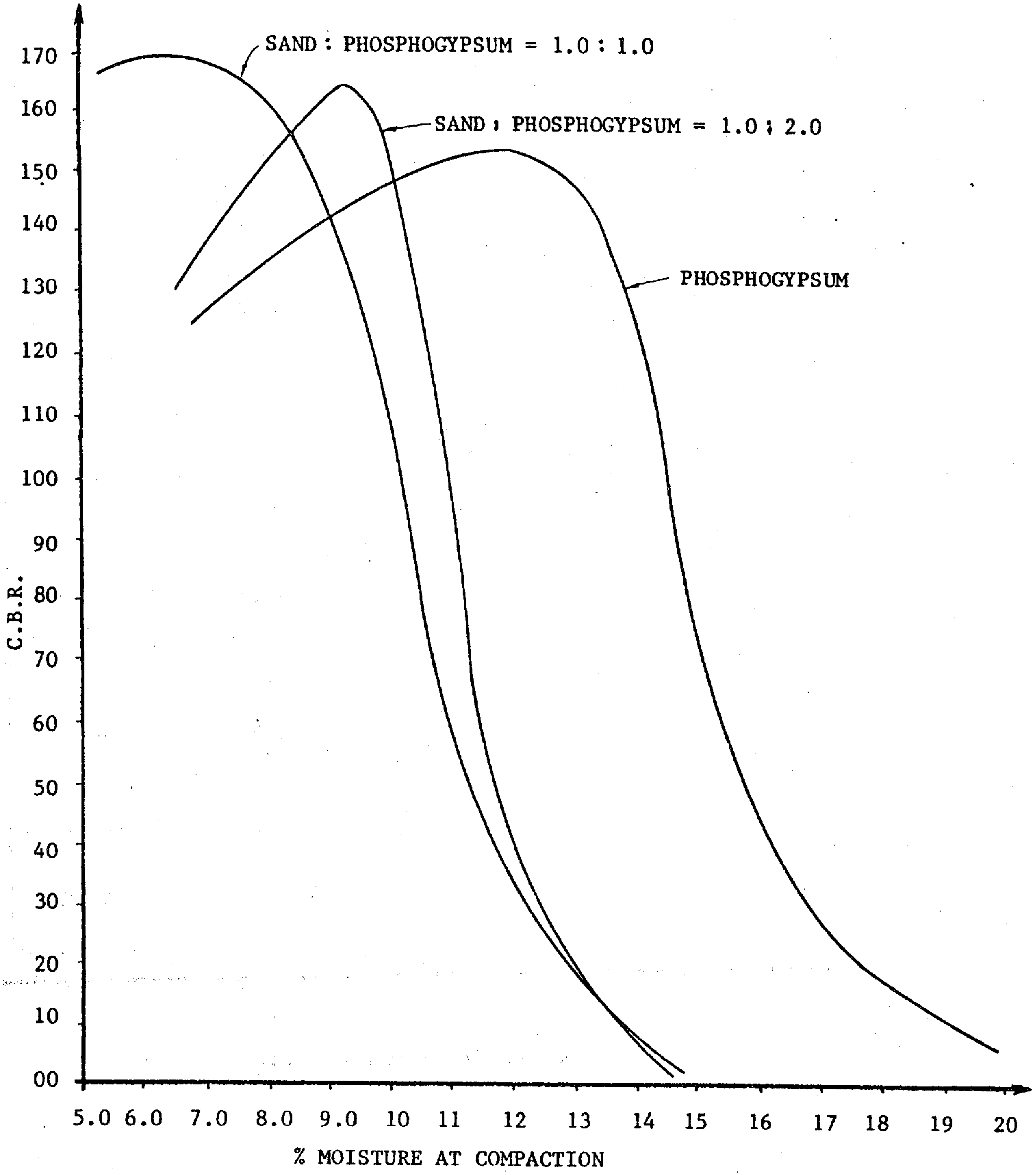


FIGURE 11. MOISTURE DENSITY RELATIONSHIP OF SAND-PHOSPHOGYPSUM MIXTURES



LINE NO.	PROPORTION OF	
	SAND	PHOSPHOGYPSUM
I	1.0	1.0
II	1.5	1.0
III	2.0	1.0
IV	2.5	1.0
V	1.0	0.0

C.B.R. TESTS CONDUCTED IMMEDIATELY AFTER COMPACTION ON SAND AND PHOSPHOGYPSUM MIXTURES. FIGURE 12.



RESULTS OF C.B.R. TESTS CONDUCTED ON SAND AND PHOSPHOGYPSUM MIXTURES IMMEDIATELY AFTER COMPACTION.

FIGURE 13.

INDEX

LINE NO.	PROPORTION OF	
	SAND	PHOSPHOGYPSUM
I	1.0	1.0
II	1.5	1.0
III	2.0	1.0
IV	2.5	1.0

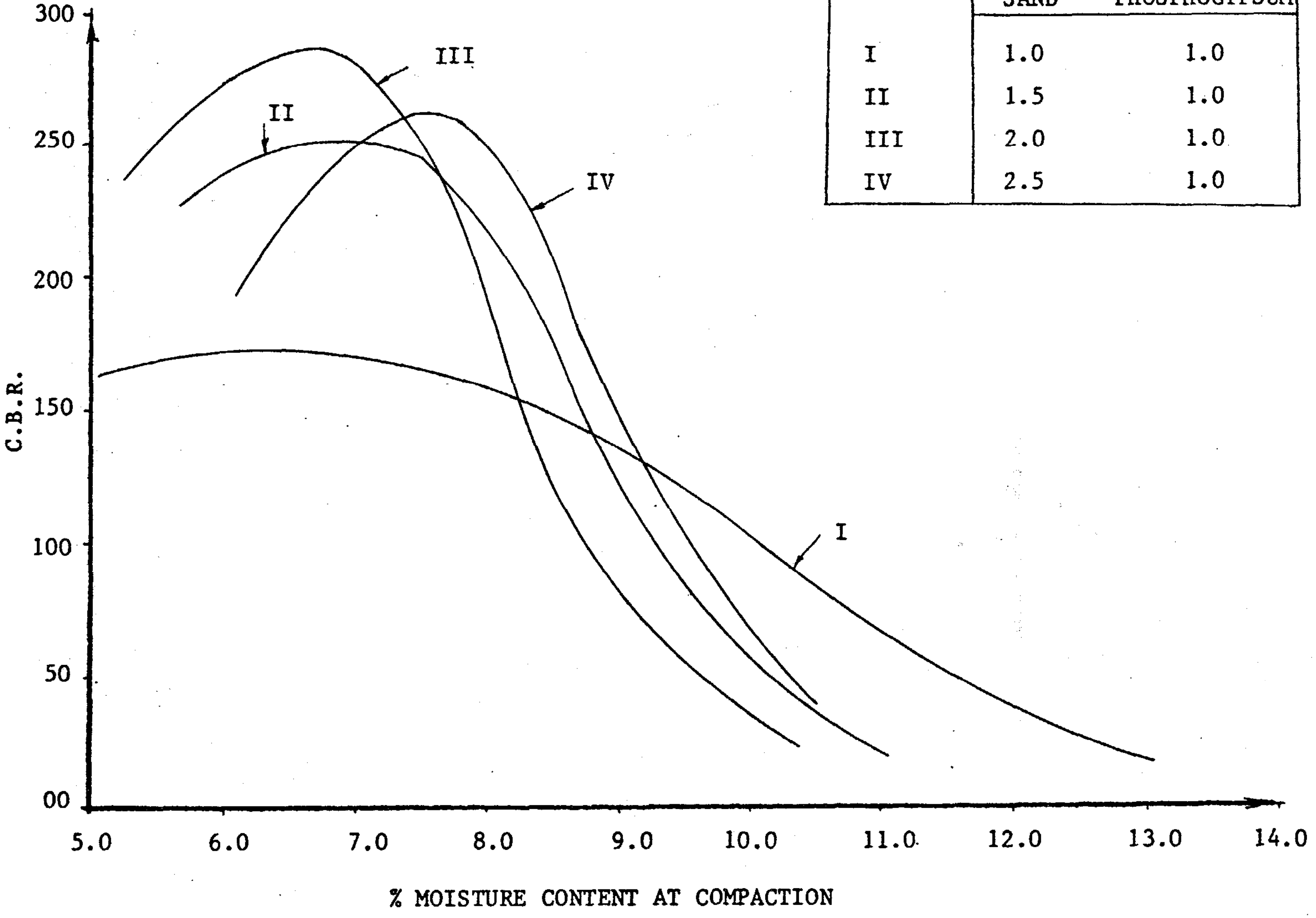
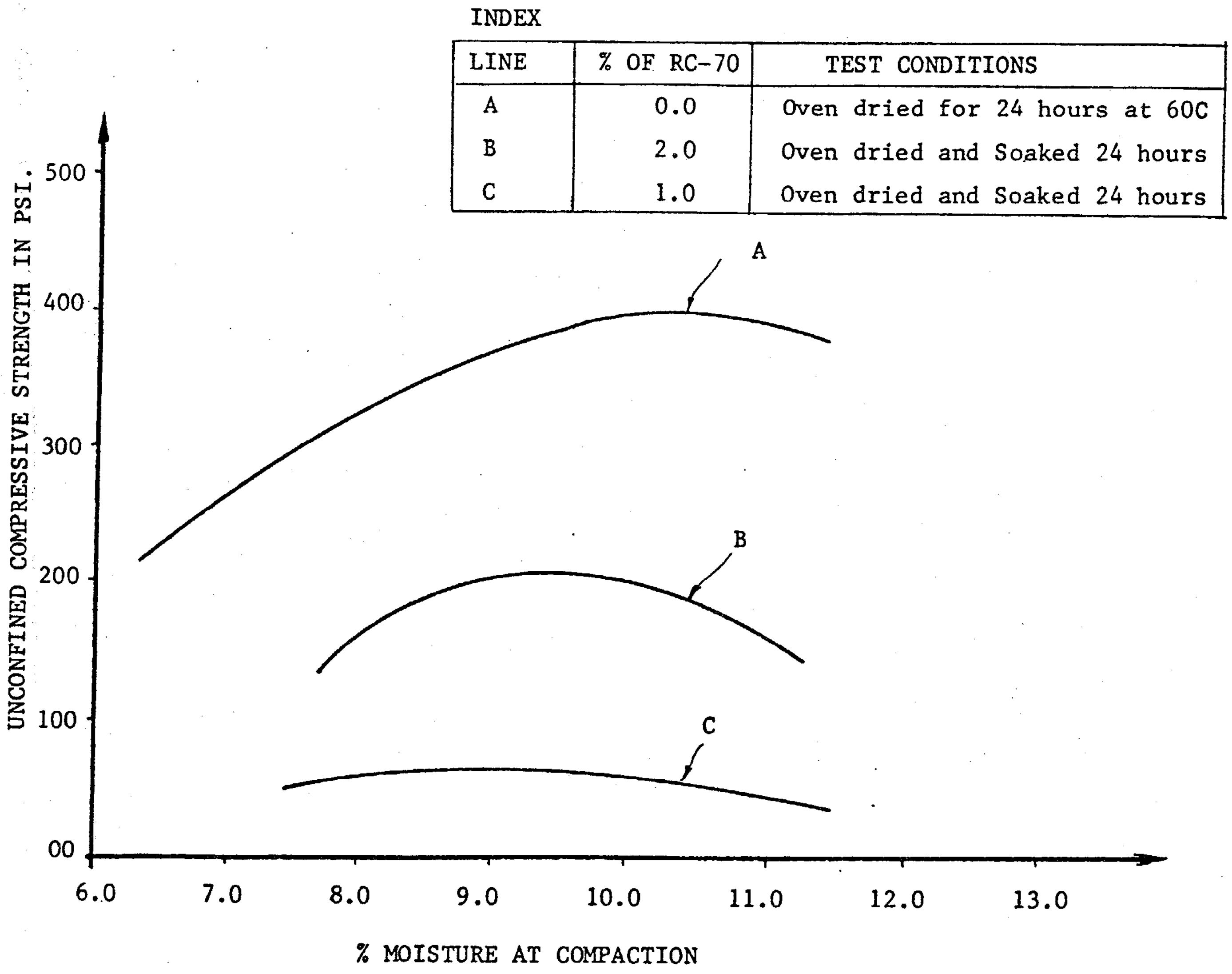


FIGURE 14.

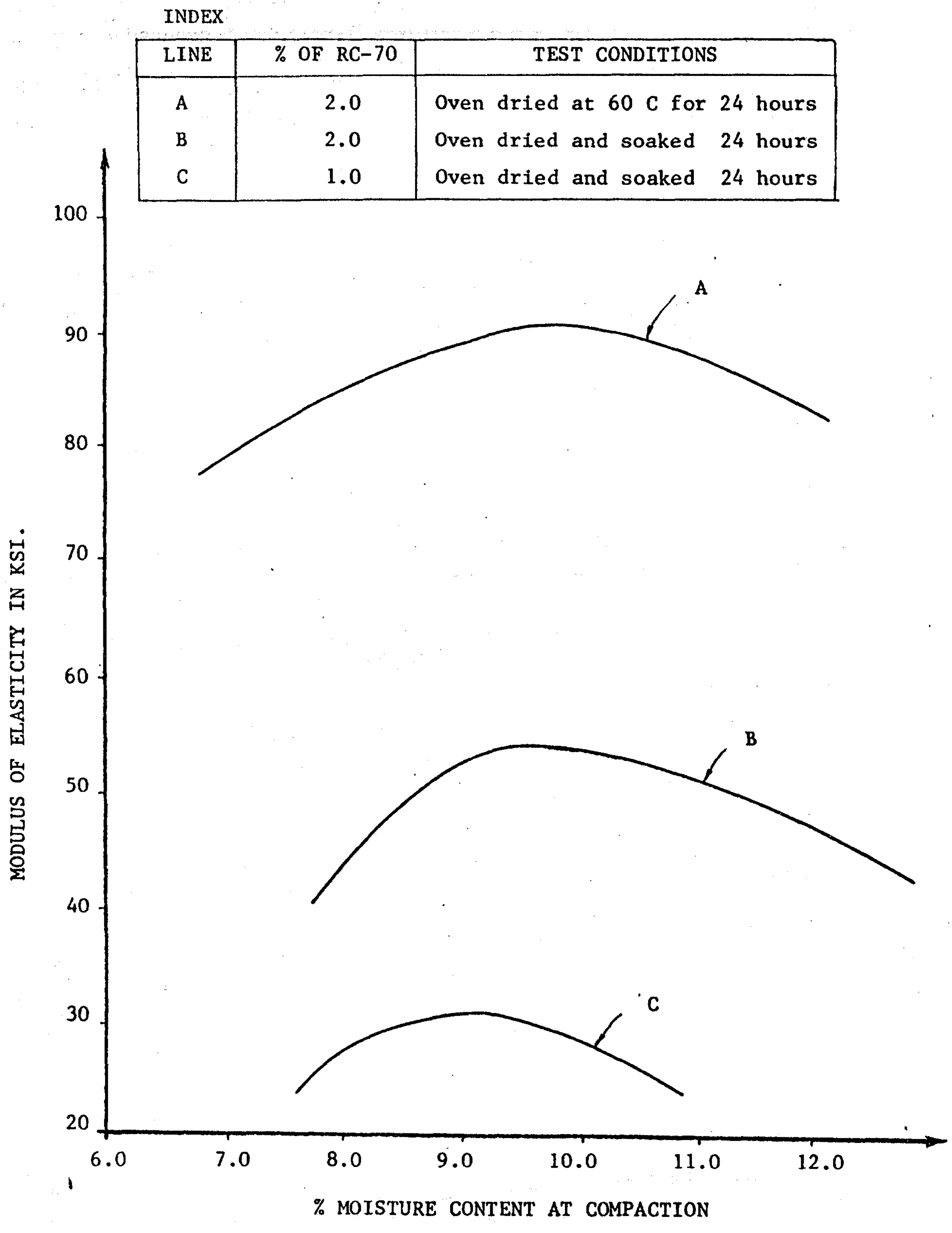
VARIATION OF THE UNCONFINED COMPRESSIVE STRENGTH OF SAND AND PHOSPHOGYPSUM MIXTURES(1.0 : 1.0) WITH CURING CONDITIONS AND PERCENTAGE OF RC- 70.



INDEX

LINE	% OF RC-70	TEST CONDITIONS
A	0.0	Oven dried for 24 hours at 60C
B	2.0	Oven dried and Soaked 24 hours
C	1.0	Oven dried and Soaked 24 hours

VARIATION OF THE MODULUS OF ELASTICITY OF PHOSPHOGYPSUM AND SAND MIXTURES (1.0 : 1.0) WITH CURING CONDITIONS AND PERCENTAGE OF RC-70. FIGURE 15.



INDEX

LINE	% OF RC-70	TEST CONDITIONS
A	2.0	Oven dried at 60 C for 24 hours
B	2.0	Oven dried and soaked 24 hours
C	1.0	Oven dried and soaked 24 hours

COMPARATIVE RESULTS OF STRENGTH AND DENSITY OF THE ORIGINAL MATERIAL AND SUGGESTED ALTERNATIVES. FIGURE 16 & 17.

INDEX

————	Clayey Sand : Sand = 2.0:1.0 Original Material
– – – – – –	Clayey Sand:Sand:Phosphogypsum = 1.5 : 1.0 : .5
–·–·–·–	Sand:Phosphogypsum = 1.0 : 1.0 + 2.0 % of RC70

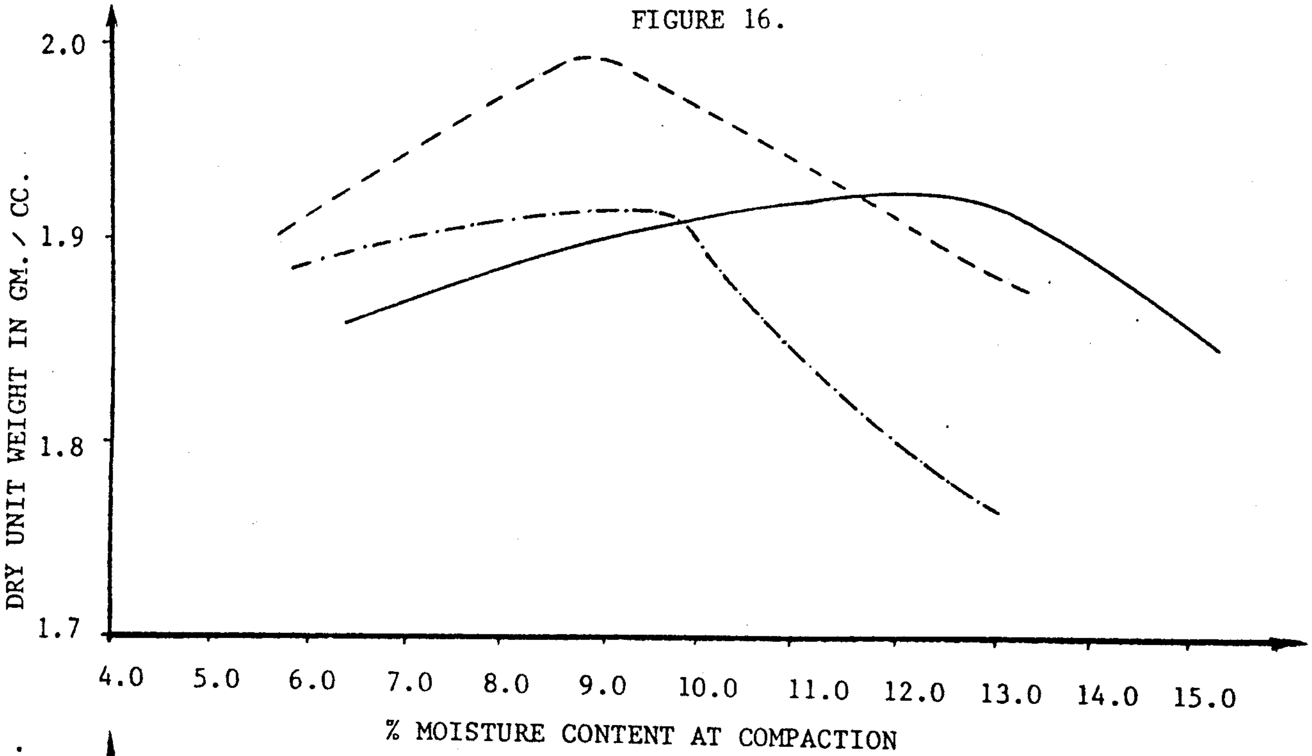


FIGURE 16.

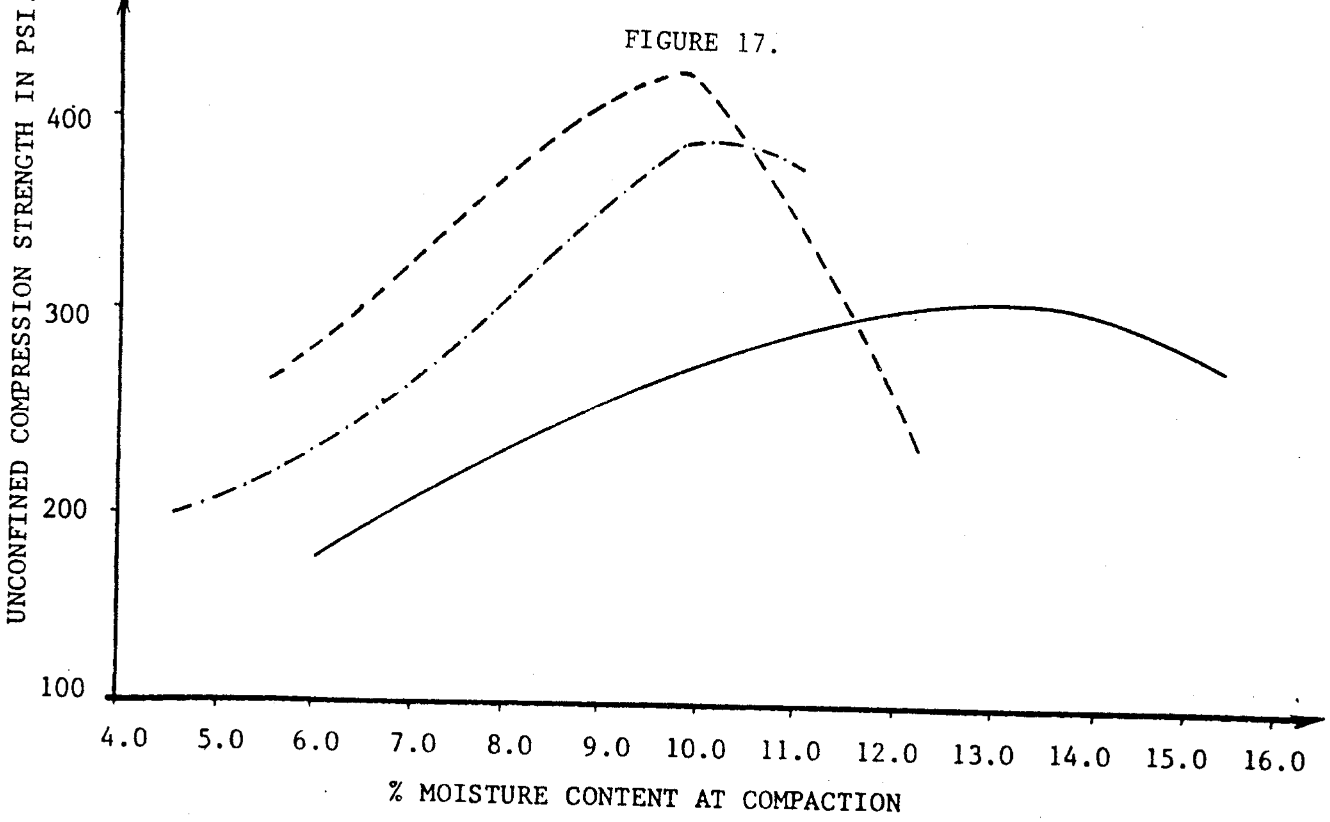
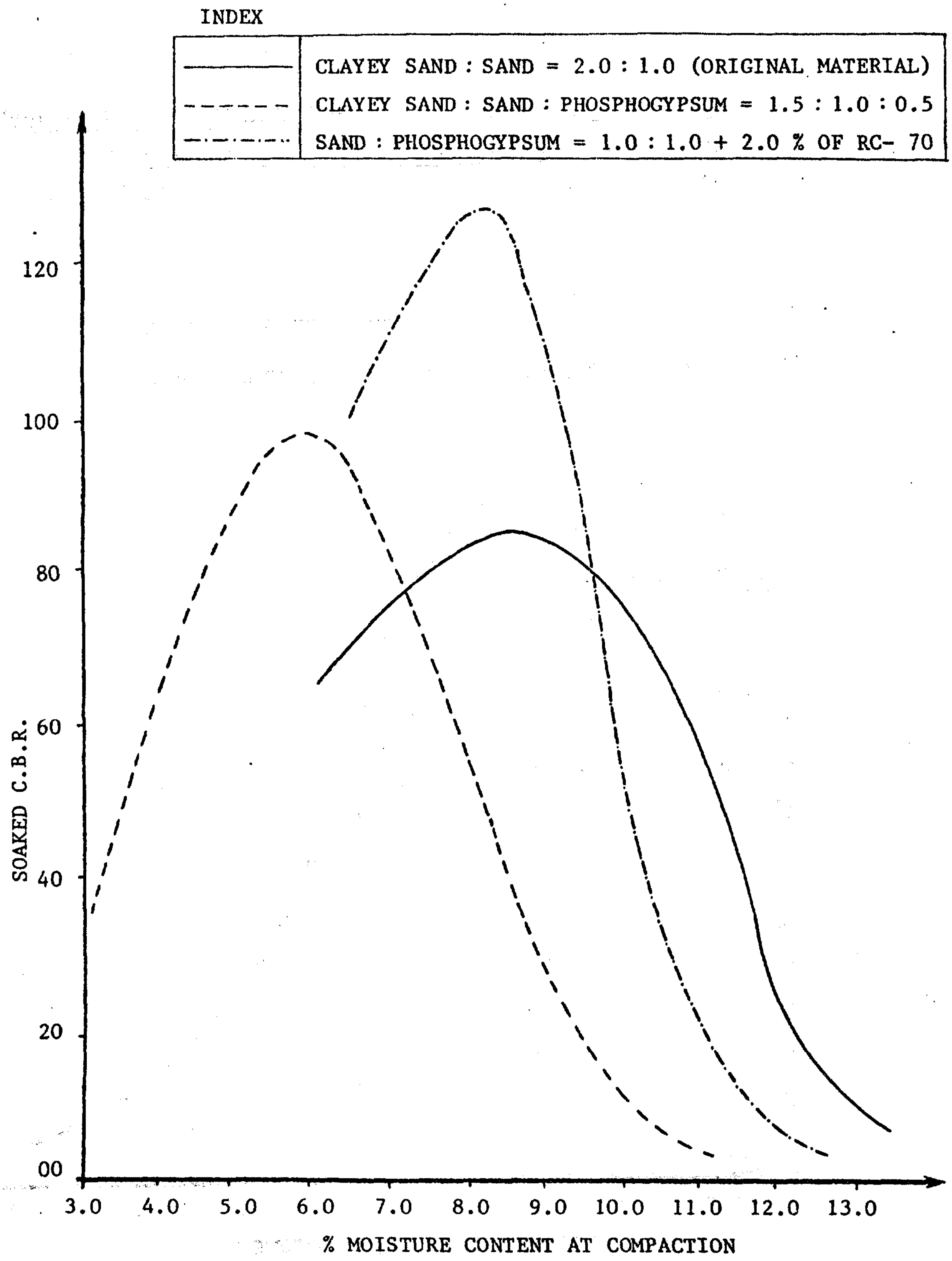


FIGURE 17.

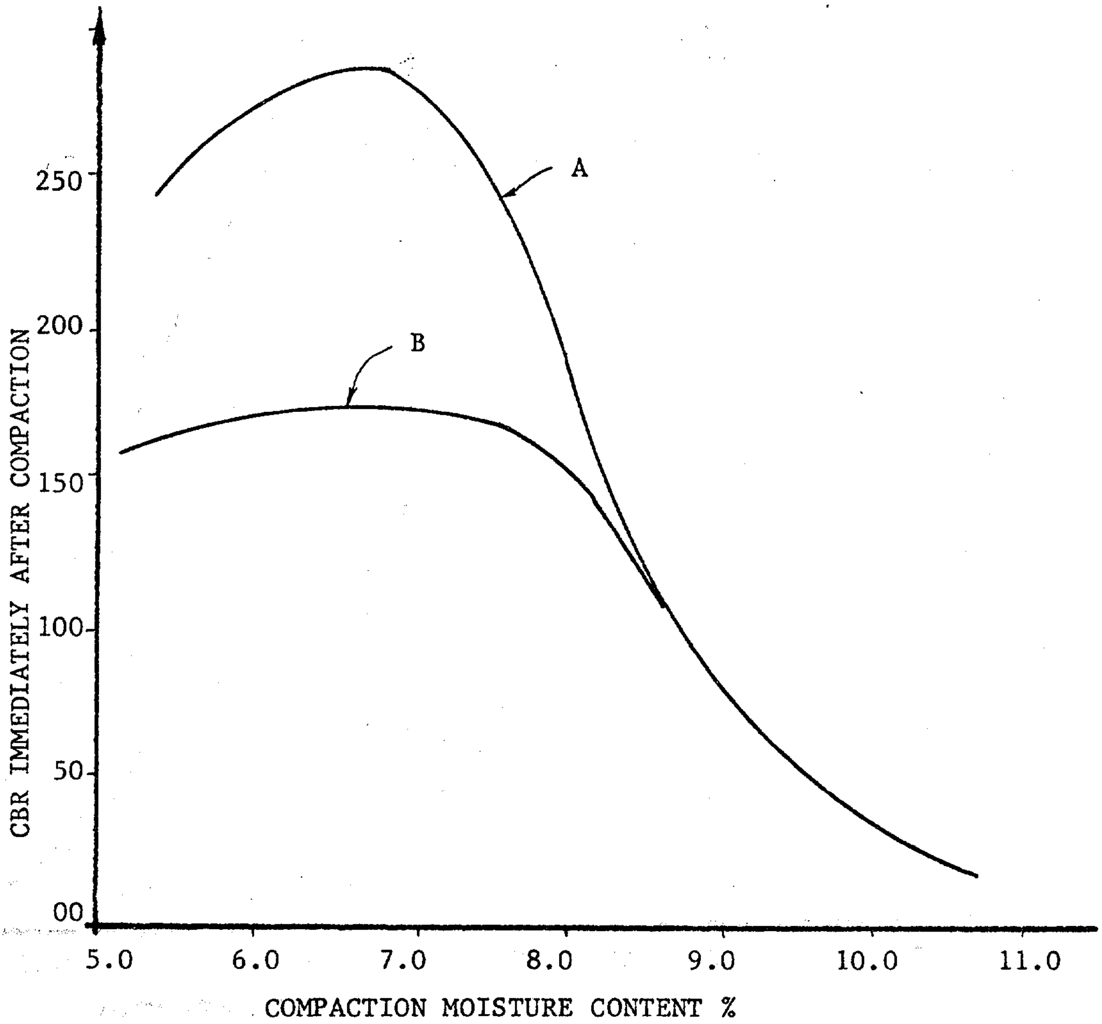
COMPARATIVE RESULTS OF SOAKED C.B.R. TESTS CONDUCTED ON THE ORIGINAL MATERIAL AND SUGGESTED ALTERNATIVES. FIGURE 18.



COMPARATIVE RESULTS OF CBR TESTS CONDUCTED ON THE 2.0:1.0 MIXTURE OF SAND AND PHOSPHOGYPSUM WITH 6.0" AND 4.0" DIAMETER MOULDS. FIGURE - 19.

LINE A - CBR VALUES FROM THE 4.0" DIAMETER MOULD.

LINE B - CBR VALUES FROM THE 6.0" DIAMETER MOULD.



SLIMES WASTE SOLIDIFICATION
WITH
HYDRATABLE CALCIUM SULFATE(1)

By

DR. JAY W. PALMER - U.S. GYPSUM CO.

and

MR. A. P. KOULOHERIS - ZELLARS-WILLIAMS, INC.

PAPER
TO BE PRESENTED AT THE UNIVERSITY OF MIAMI
CIVIL ENGINEERING DEPARTMENT SEMINAR ON PHOSPHOGYPSUM
HELD ON APRIL 25-27, 1984

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1.0 PURPOSE AND SCOPE OF PAPER

The purpose of this paper is to present a novel process (1) for the solidification of slimes waste recently developed by the U.S. Gypsum Company. The primary scope of this presentation is to provide the main physico-chemical parameters of this process as well as the preliminary engineering and economics as they apply to the solidification of phosphatic slimes. However, on a secondary basis, the process potential as it may apply to the treatment of other mining, industrial and municipal slimes waste is equally projected (see 8.0 Appendix).

2.0 INTRODUCTION AND BACKGROUND

Industry in general and more specifically the Phosphate Industry has been confronted in the last decade with serious and costly pollution abatement problems. As a typical example, the permitting of a new phosphate mine in Florida may entail the development of an environmental impact study requiring a period of about five years to complete and an expenditure of out-of-pocket money of 5 to 6 million dollars. Similarly, the establishment of a new conversion chemical plant to produce phosphoric acid and associated fertilizer products is equally complicated. In the last seven years no new chemical plant has been built in a new location in Central Florida.

Among the many environmental requirements specified for a new phosphate mine and chemical plant, it appears that the disposal of plant wastes-phosphate slimes and gypsum are receiving critical review by permitting agencies.

It should be pointed out here that for each ton of phosphate rock produced, approximately one ton of dry slimes requiring appropriate disposal is co-produced. The problem is the slimes, even after ultimate compaction in an operating settling pond, commonly carry a solids content of 20 to 25 percent. A typical 2,000,000 TPY mine may require the design and construction of a 400 acre above grade impoundment to contain the slimes produced every two to three years. A capital cost of several million dollars for such a pond is not unusual. In addition, when the pond itself is filled, it has to be abandoned for years, so that by a combination of evaporation and drainage/dewatering, it can solidify as part of a costly and difficult land reclamation program.

In a similar manner, a conversion chemical plant producing one ton of P_2O_5 co-produces about 4.7 tons of waste gypsum. The latter, after dewatering, is stacked in large piles. Some basic statistics may show quantitatively the magnitude of this problem the industry is facing. This is given in Table I below.

Table I
Total Waste Products Distribution in an
Operating Mine/Chemical Plant
Basis: 500,000 TPY P_2O_5 Product

Rock Required	:	1,750,000	TPY (Dry Basis)
Slimes Waste Produced	:	1,750,000	TPY (Dry Basis)
Wet Slimes Prod. (15% solids)	:	11,666,666	TPY Wet Slurry
Approx. Slimes Pond Volume Req'd	:	24,000	Ac. Ft. (3 yr. life)
Slimes Pond Life	:	2-3	Years
Gypsum Waste Produced	:	2,350,000	TPY (Dry Basis)
Wet Gypsum Waste Produced	:	2,764,705	TPY (Wet Basis)
Gypsum Pile Volume	:	40,000	Ac. Ft.
Gypsum Pile Life	:	∼15	Years
Sand Tails Produced	:	1,750,000	TPY (Dry Basis)
Wet Sand Tails	:	2,058,824	TPY (Wet Basis)

The disposal of sand tails is not a major problem as this waste is used to construct dikes surrounding slimes ponds or is used as backfill for mined-out pits.

In the past 20 years, a considerable amount of research has been carried out individually by the Industry companies as well as the State of Florida and the Federal government. Practical and economic solutions to these problems have yet to be developed, but progress is being made. It is to the credit of both the Government and the Industry, that research and development and field experimentation is being vigorously pursued.

Some typical examples of slimes and sand tails are described below; however, very little field work has been done with phosphogypsum.

2.1 Flocculation Techniques

The U.S. Bureau of Mines successfully developed a method(2) of treating slimes with polyetheylene oxide (PEO) to produce a strong floc that can be further dewatered either by the use of a hydrosieve apparatus or a trommel. The final dewatered product was a compacted material of between 18 to 20 percent solids. Pilot plant and semi-industrial tests are under study by a number of phosphate producers. In a similar fashion a “super flocculation” technique(3) was developed by Alstom Atlantic Inc. and piloted at the Gardinier mine. This method showed that under certain conditions an overflocculated slimes slurry can be further slowly dewatered in a mined-out area reaching a final compaction of about 40 percent solids. Another flocculation system(4) utilizes the enviroclear thickener which was successfully tested by Gardinier and Estech Inc., the former on a pilot scale and the latter on an industrial scale. This scheme consisted of admixing sand tailings with pre-flocculated slimes. Reportedly, a non-segregated mixture of sand and slimes was produced at 30 to 40 percent solids which was further dewatered in a mined-out cut to a semi-solid consistency.

2.2 Sand Spraying Operation

A number of phosphate producers are still experimenting on a large scale with this method(5). Slimes are first placed in mined-out cuts and allowed to thicken to about 12 to 18 percent solids. Periodically, sand tailings are dispersed or sprayed over the filled cuts producing a mixture that reportedly assists in further dewatering without segregating slimes from sand particles. This scheme is being tested by Brewster Phosphate.

2.3 Sand Capping

Another variation(6) of the above described method is being tested by IMC, Agrico and Mobil. In this semi-industrial application, a floating barge reclaims partially consolidated slimes from a slimes pond discharging them into a proper disposal area. A sand-clay mix station mixes the preconsolidated slimes with cyclone-dewatered sand tails and the mixture is fed into a mined-out disposal area. Additional sand can be further added by spraying the consolidated area to provide a final cap. Reportedly, the success of these methods requires a sand/clay mixture ratio of over 1.5:1 on a dry basis.

2.4 Sand/Clay Mixtures

A similar variation(7) practiced by CF Industries involves mixing preconsolidated clay of about 18 percent solids with dewatered tails in a mix tank, which is hydraulically pumped into a mined-out area.

3.0 CHARACTERIZATION OF PHOSPHATE WASTES

Previously, the nature of the slimes problem and its magnitude as it relates to the operation of a phosphate mine/chemical plant complex was described. Prior to presenting the U.S. Gypsum Process, a physico-chemical characterization and identification of the phosphate wastes is warranted.

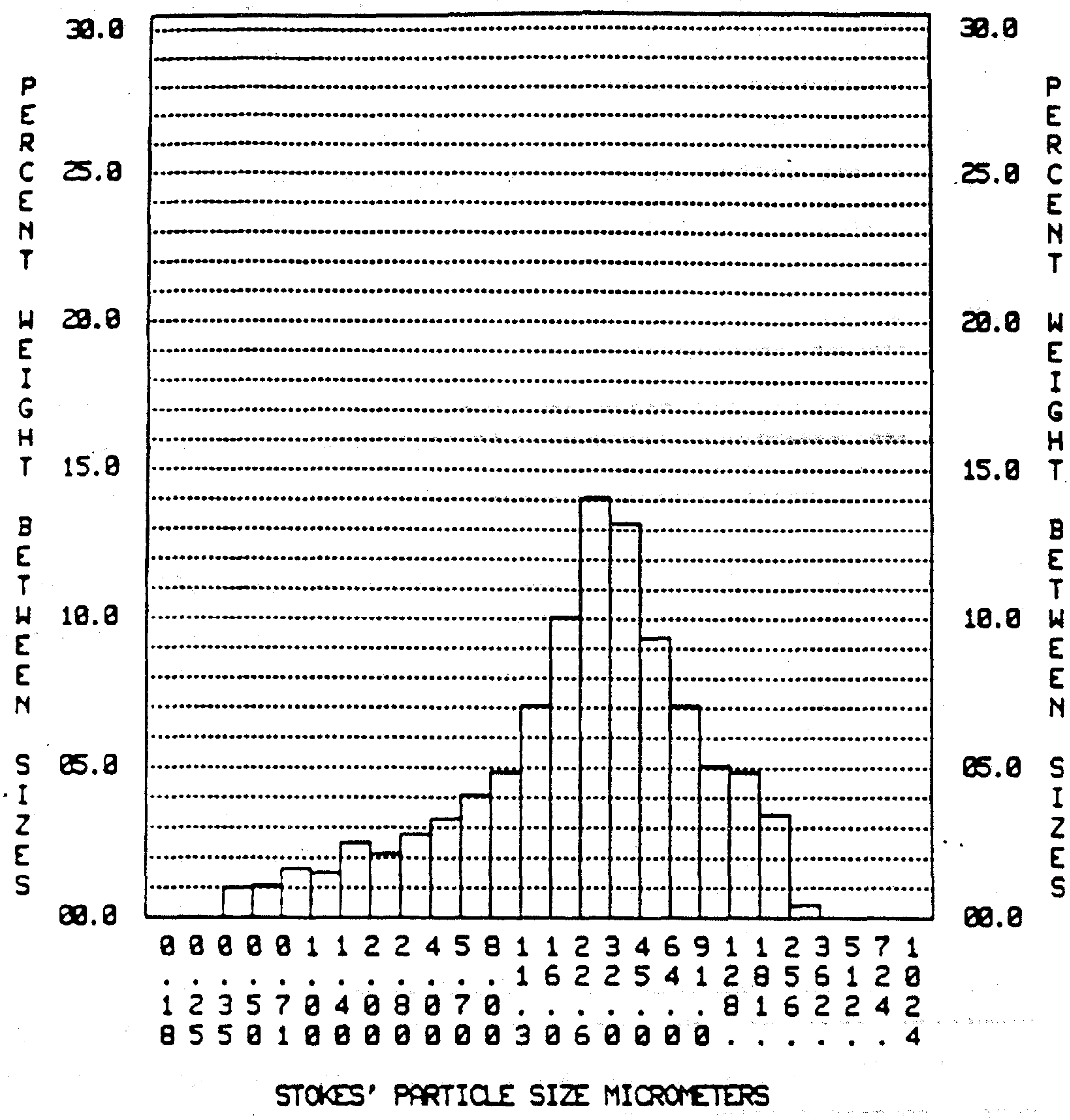
3.1 Sand Tails

This waste by-product is found mostly in the form of quartz at a particle size range of -30 x +150 mesh which is actually the range of cell, spirals and belt flotation carried out normally in a beneficiation plant. Sand is usually dewatered by hydrocyclones and the final waste is readily compacted to about 80 percent solids.

3.2 Slimes

This waste consists of a nominally defined -150 mesh fraction. However, its actual size distribution is that of a colloidal suspension of clays (montmorillonite, attapulgite and others) with finely divided phosphate and silt. A typical sub-sieve analysis of dried slimes is shown in Figure 1. Many of the slimes particles, especially the clay components, are colloidal in nature, electro-

TYPICAL CENTRAL FLORIDA DRIED SLIME



SMALLEST SIZE = 0.35 MEAN SIZE = 27.73 TOP SIZE = 300.00

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LOGARITHMIC PARTICLE SIZE DISTRIBUTION HISTOGRAM

FIGURE 1.

negative and hydro-philic; however, no bimodal distribution is seen in the figure indicating that the colloidal particles have coalesced onto the larger particles. Natural settling of slimes is very slow with consolidation in a few weeks or months to about 15 percent solids and further consolidation to perhaps 20 to 30 percent as a result of settling, evaporation and seepage. A typical chemical/mineral composition of slimes is shown in Table II. The physico-chemical structure and nature of the clay components are discussed in more detail in another section of this paper.

3.3 Phosphoqypsum

The origin of this waste is the reaction by-product of H_2SO_4 with phosphate rock to produce phosphoric acid, In a dihydrate process, this waste reports as a gypsum ($CaSO_4 \cdot 2\ H_2O$). In a hemihydrate process, this waste reports as a hemihydrate ($CaSO_4 \cdot 1/2\, H_2O$).

Depending on the process and the degree of grinding of the rock used in the process, the size analysis may vary. A typical sieve analysis is shown in Figure 2. A bimodal distribution is seen in the figure indicating some coarser silica sand in the sample.

The degree of digestion, the nature of the rock, and the degree of filtration and washing of this waste will determine its chemical composition. A typical chemical analysis is shown in Table III.

Phosphate rock contains uranium and radium as impurities. During rock digestion, most of the uranium (over 90 percent) is dissolved and reports with the product phosphoric acid. Radium, due to its ionic size, co-precipitates with the calcium in the $CaSO_4$ finer size fraction. As a result of this, radium reports into the gypsum pile. A decay product of radium is the well-known radon-222 gas. Table IV presents some radium-226 data on phosphate materials of various origin(8). Present disposal methods consist of using a gypsum field where gypsum is dewatered by gravity, the hot acidic water is cooled in pond and returned to the plant for recycle, while gypsum is stacked

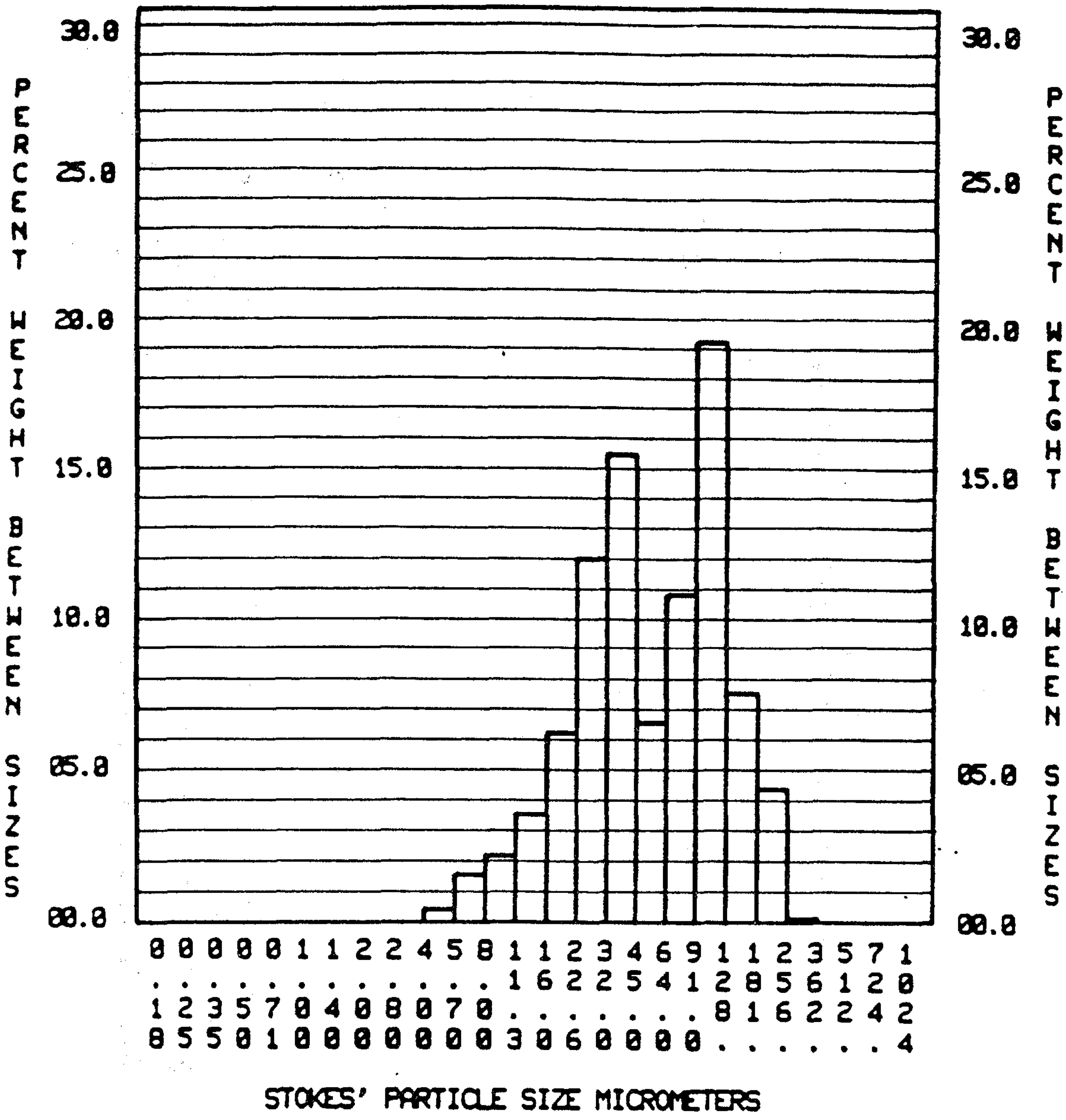
Table II
Typical Chemical/Mineral Composition of Slime

	CaO	SO_3	MgO	SiO_2	Fe_2O_3	Al_2O_3	CO_2	P_2O_5	Na_2O	K_2O	LOI	Free H_2O	Chem H_2O	pH
North Florida Dried Slimes	10.09	0.32	1.79	40.36	2.50	18.12	3.00	8.27	0.16	0.72	14.21	0.69	4.99	6.77
Hardee County Dried Slimes	14.68	0.26	1.98	38.63	2.18	16.04	2.93	10.59	0.19	0.48	12.30	0.63	3.73	7.66
Central Florida (Polk) Dried Slimes	16.38	0.52	1.27	40.69	5.15	11.03	2.62	10.93	0.41	1.50	8.86	0.53	3.61	7.53

Mineralogical content varies considerably from site to site. In general, the minerals present occur in the following descending order:

1. Smectite (mainly montmorillonite)
2. Carbonate-fluorapatite
3. Palygorskite (attapulgite)
4. Illite
5. Interstratified Clay Minerals
6. Kaolinite
7. Quartz
8. Wavellite
9. Crandallite
10. Dolomite/calcite

TYPICAL PHOSPHOGYPSUM



SMALLEST SIZE = 5.00 MEAN SIZE = 69.00 TOP SIZE = 290.00

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LOGARITHMIC PARTICLE SIZE DISTRIBUTION HISTOGRAM

FIGURE 2.

Table III
Chemical Composition of a Phosphogypsum Sample

Chemical Analysis

Chemical analysis performed on sample after drying at 45°C and passed through 100 mesh screen.

Combined Water, 45-230°C	19.34
CaO, %	30.75
SO_3, %	42.99
MgO, %	0.05
SiO_2, %	2.79
Fe_2O_3, %	0.75
Al_2O_3, %	0.16
P_2O_5, %	0.30
F, %	.31
Excess LOI, 230-950°C, %	3.21
Total Sum, %	100.65

Possible Chemical Reconstruction:

$CaSO_4 \cdot 2\ H_2O$, %	92.42
SiO_2, %	2.79
R_2O_3, %	0.91
Excess CaO, %	0.64
F, %	0.31
Excess LOI, %	3.21
MgO, %	0.05
P_2O_5 %	0.30
Total, %	100.63

with the proper structural slopes. Because of the acidic leach, radioactivity concerns and aesthetic appearances of the gypsum piles, pressure has increased for eliminating or reducing this problem.

Table IV
Radium-226 Analysis of Florida
Phosphate Materials

	Central Florida ^{226}Ra, pC$_1$/g Average	North Florida ^{226}Ra, p C$_1$/g Average
Mining and Rock Operations		
Matrix	37.6	8.6
Pebble	57.4	25.8
Rock Concentrate	37.1	17.5
Clays (Old Settled Areas)	23.8	---
Tailings	5.2	2.7
Phosphoric Acid Plant		
Gypsum	25.9	---
Hemihydrate	---	13.5

4.0 THE PHYSICO-CHEMICAL MECHANISM OF THE U.S. GYPSUM SLIMES SOLIDIFICATION PROCESS

The physical and chemical properties of the phosphatic clay slimes in Central Florida are primarily determined by the smectite clay, montmorillonite. This is because: one, montmorillonite is the predominent mineral in the slime; two, it has a platelet-like structure; three, it has a very small size, less than 1 micron, and thus a very large surface area; and four, it has a net negative electrical charge on its platelet surfaces and a net positive electrical charge on its edges. These properties allow the small montmorillonite platelets to coat the other larger minerals in the slime with a thin layer, so that they behave as if they were larger montmorillonite particles.

As the solid concentration in a slime increases, there is a greater interaction of particles with the positive edges of the montmorillonite platelets being attracted to the negative surfaces of the platelets. This results in a "house of cards" structure having "quasi" solid properties (see Figure 3). The water in the slime is trapped within the compartments or pores of the structure, so that further solid concentration is severely restricted. Since the attractive forces between the platelets are not great, agitation can break this "house of cards" structure; however, it will reform in time.

Researchers at the U.S. Gypsum Research Center in Libertyville, Illinois, probably the largest laboratory in the world conducting gypsum research and development, have found that hydratable calcium sulfate can be used to destroy this slime structure resulting in solidification of the slime into a load bearing mass.

The probable mechanism of this solidification is several fold. First, the agitation and incorporation of a large amount of hydratable calcium sulfate particles into the slime breaks the "house of cards" structure and physically separates the montmorillonite platelets from one another with calcium sulfate particles. Second, soluble calcium ions from the calcium sulfate are attracted to the negative surface of the montmorillonite platelets, partially nullifying the negative charge. Third, the calcium sulfate hydrates by using up slime water and forms an interlocking mass of gypsum crystals. Fourth, pressure resulting from the growth of hydrating calcium sulfate collapses any "house of cards" structure remaining in the mixture. On completion of the calcium sulfate hydration, a hard, strong load bearing mass is formed.

Two general types of hydratable calcium sulfates can be used for solidification of slime. One is the hemihydrate and the other the

SLIME "House of Cards" Structure

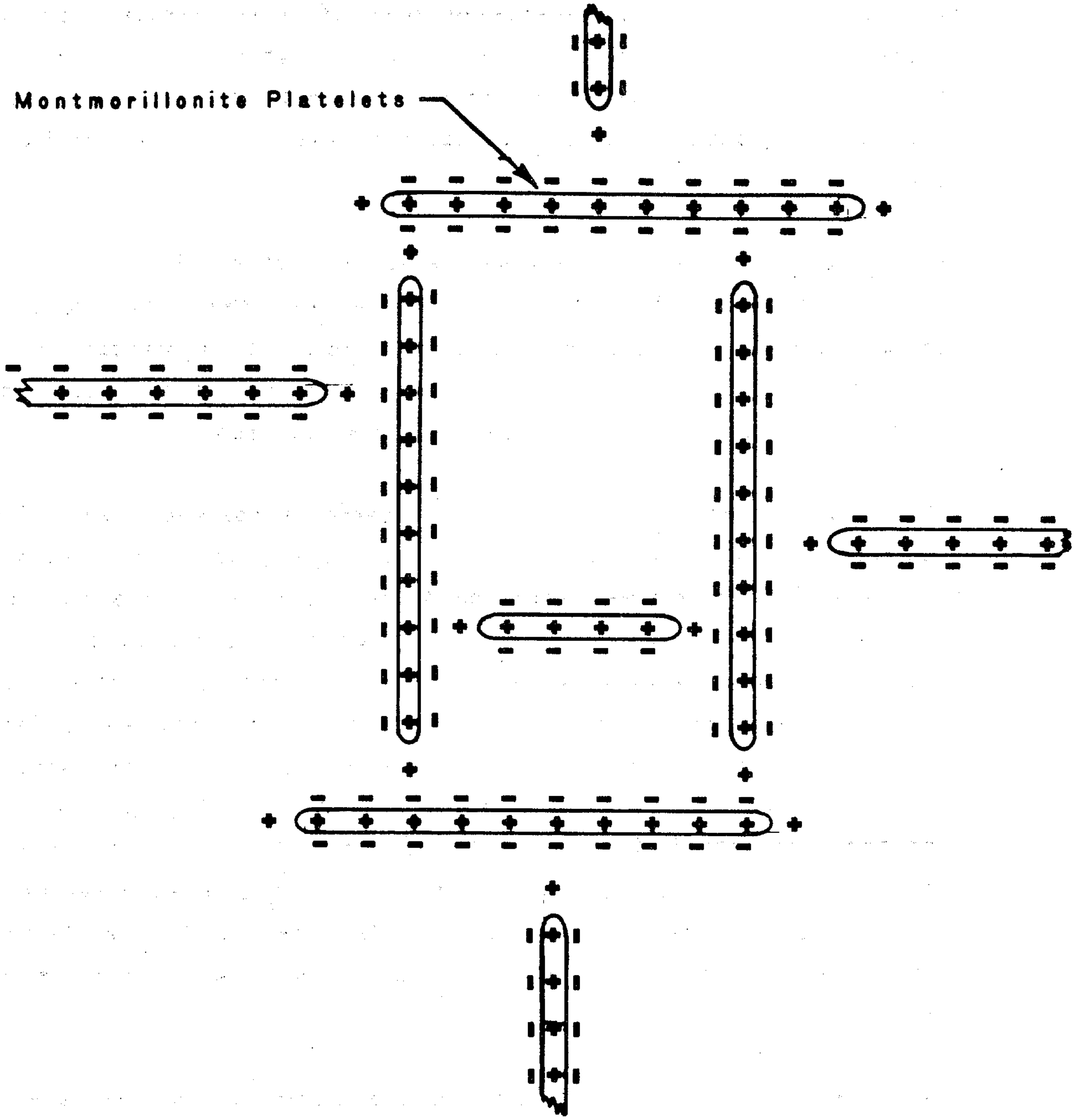

FIGURE 3.

anhydrite. Their hydration equations are shown below:

$$\underset{\text{hemihydrate}}{CaSO_4 \cdot 0.5\ H_2O} + 1.5\ H_2O \longrightarrow \underset{\text{gypsum}}{CaSO_4 \cdot 2\ H_2O}$$

$$\underset{\text{anhydrite}}{CaSO_4} + 2\ H_2O \longrightarrow \underset{\text{gypsum}}{CaSO_4 \cdot 2\ H_2O}$$

The hemihydrate can be obtained from: one, hemihydrate-phosphoric acid process; two, thermal calcination (dry or autoclave) of phosphogypsum; and three, dilute sulfuric acid dehydration of phosphogypsum, while the anhydrite can be obtained from the concentrated sulfuric acid dehydration of phosphogypsum, thermal calcination, or natural and other by-product sources. Processes for removal of radium-226 from phosphogypsum leave waste hemihydrate and anhydrite which can be used for the solidification of slime. (9,10,11,12)

Laboratory work has consisted of mixing different phosphatic clay slimes with different types and modifications of hydratable calcium sulfate. The, mixtures were transferred to small cups or pans and the rate of solidification followed using a standard vicat needle or penetrometers. Final load bearing strengths of the strongest compositions were determined with the penetrometer or by the California soil test analysis (mass compacted by ASTM D1557 procedures and tested for load bearing and unconfined compressive strength under ASTM D1883 procedures) .

Vicat sets (less than 4 hours) and a number of penetrometer readings are shown in Figure 4 for a number of slimes-hemihydrate compositions. The maximum value obtainable with the penetrometer is 4.5 T/Ft^2, so many of the compositions may have much greater strengths than that.

This figure also shows those compositions that do not solidify to any great degree and those compositions that are too dry for the solidification process to readily take place.

Since the anhydrite type of calcium sulfate is much slower to hydrate, some separation of water from the mass can take place during

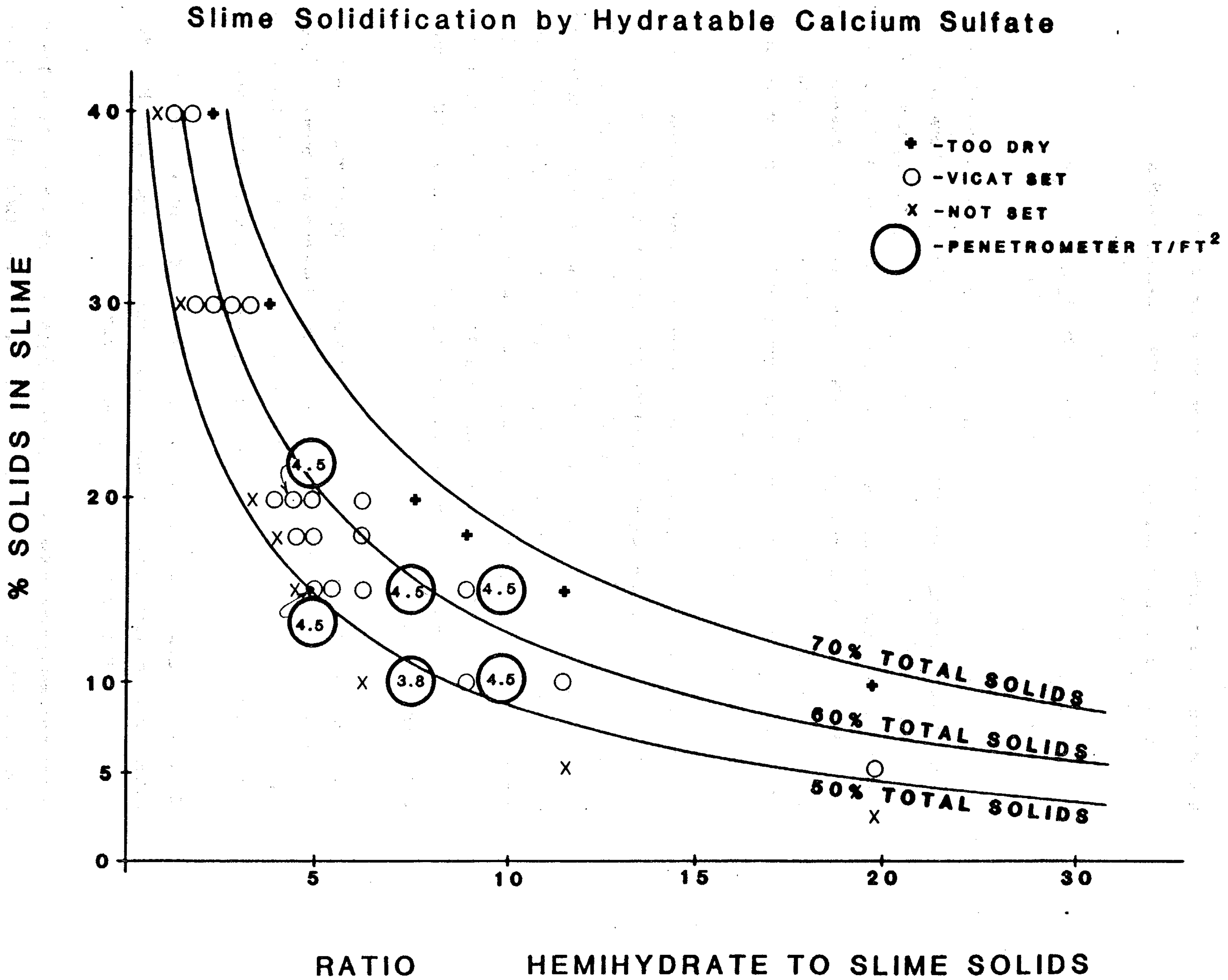
Slime Solidification by Hydratable Calcium Sulfate
% SOLIDS IN SLIME
RATIO HEMIHYDRATE TO SLIME SOLIDS
0
5
10
20
30
40
5
10
15
20
30
✚ -TOO DRY
○ -VICAT SET
X -NOT SET
◯ -PENETROMETER T/FT²
4.5
4.5
4.5
4.5
3.8
4.5
70% TOTAL SOLIDS
60% TOTAL SOLIDS
50% TOTAL SOLIDS

FIGURE 4.

solidification. This results in long-term, load bearing strengths that may be greater than the hemihydrate compositions.

Among the preferred embodiments of this patent pending process(1) are: one, using the now available hemihydrate residue from a hemihydrate phosphoric acid plant, or two, using sulfuric acid dehydration of phosphogypsum. The latter method has the additional benefit of recovering phosphate value from the phosphogypsum (see Table V).

Table V
Comparison of Typical By-Product Calcium Sulfates

Analysis (% by Weight)	Dihydrate	Hemihydrate Residue	Hemihydrate from Dihydrate	Anhydrite from Dihydrate
% P_2O_5	0.57	0.94	0.01	0.01
% F	0.10	0.25	0.01	0.08
% Fe_2O_3	0.37	0.19	0.04	0.05
% Al_2O_3	0.11	0.49	0.04	0.10
% SiO_2	5.10	4.80	5.80	7.23
Mean Particle Size (μ)	69	51	30	5

Acid retained in the solidified mass may be neutralized in time by carbonate-fluorapatite or calcite/dolomite present in the slimes, while soluble ions may be trapped in the solid matrix.

5.0 AVAILABLE PROCESS SCHEMES RESULTING FROM THE U.S. GYPSUM SLIMES SOLIDIFICATION PROCESS

The solidification process has been proven on a laboratory scale for several sources of hydratable calcium sulfate. Sources tested to date include:

- o hemihydrate residue as a waste by-product from phosphoric acid production
- o hemihydrate. produced from by-product dihydrate via dilute sulfuric acid dehydration
- o anhydrite produced from by-product dihydrate via concentrated sulfuric acid dihydration

All three have been tested with thickened slime slurries representative of what is achieved through natural settling. Mixtures were done at various ratios of slime to $CaSO_4$ yielding load-bearing abilities of well over 4.5 tons per square foot.

The process alternates provide essentially the same end result; however, each has its own variations which can make the choice of alternates somewhat site specific. For example, a solidified mix can be obtained in a very short time (less than 1 month) using either of the hemihydrate sources. Hemihydrate residue remains stable for some period of time allowing for haulage to a remote site; whereas, the hemihydrate from dihydrate reacts very quickly and must be mixed with the slime on site. For operations where chemical conversion is necessary, yet the $CaSO_4$ must be hauled some distance, the anhydrite option would be chosen due to its slow reaction rate.

This solidification process also has the potential for rapid land reclamation utilizing sand tails and/or sand tails/slimes mixtures.

5.1 Slime Solidification Process from Hemihydrate Residue Produced by a Hemihydrate Chemical Plant

The hemihydrate residue process is the simplest process in that no treatment at the chemical plant is necessary. The material is used, as is, transferred to the mine site via conveyor, mixed with the waste clay and disposed of in a mined out area (see Figure 5).

The hemihydrate filter cake is taken directly from the pan filter in the acid plant and discharged onto a long transfer conveyor which transports the hemihydrate to the mine site.

At the mine site, naturally thickened slime is recovered through a dredge which pumps the material to a small head tank located next to the settling area. The head tank provides surge capacity and is used, With proper instrumentation, to feed the appropriate amount of slime to the hemihydrate/slime mix tank.

GENERALIZED SLIME/$CaSO_4$ SOLIDIFICATION FLOWSHEET

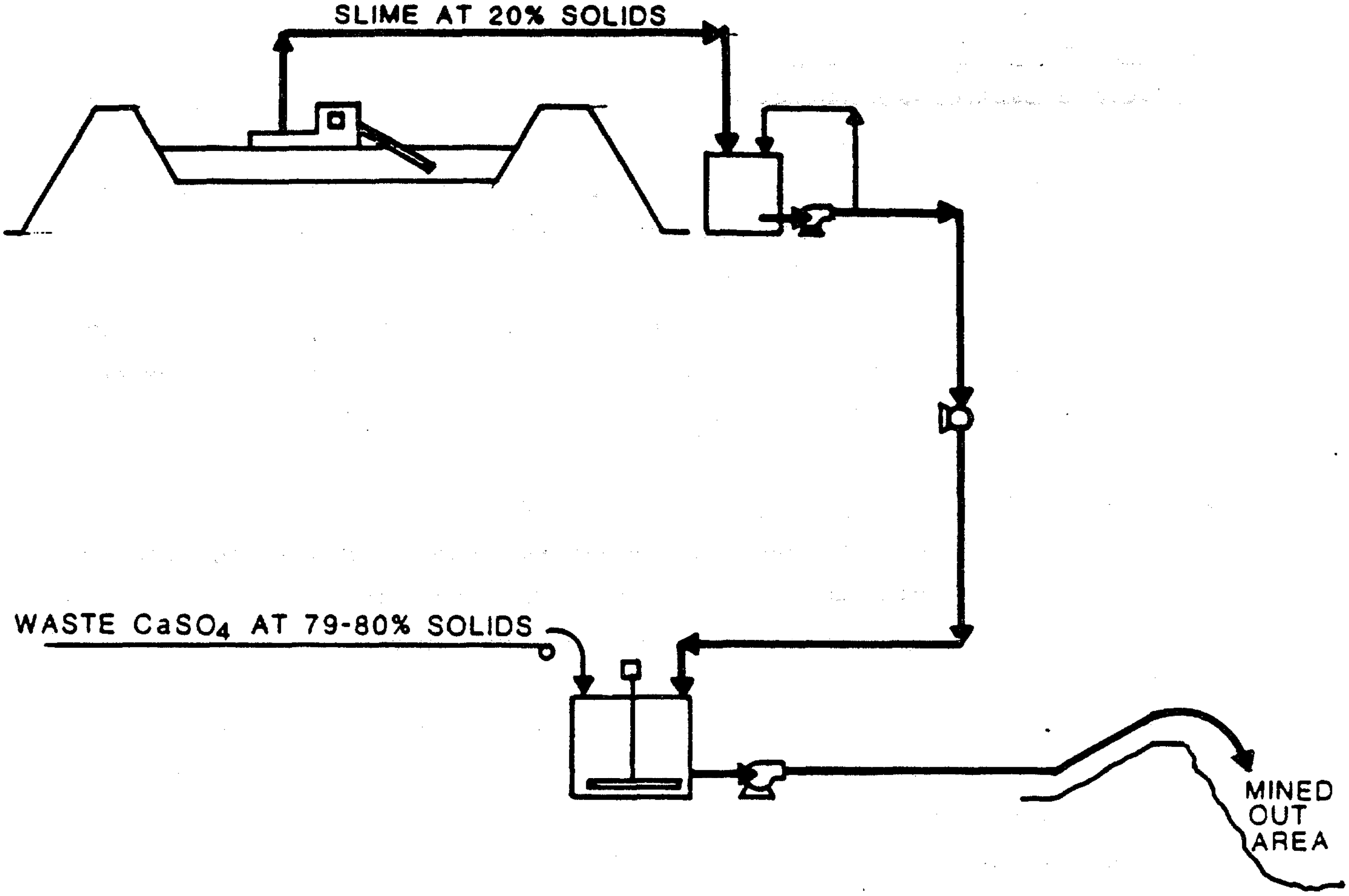

FIGURE 5.

The transfer belt from the chemical plant discharges the hemihydrate directly into the mix tank located near the below-grade storage area. The slime slurry is pumped to this same mix tank where the combined waste streams are vigorously mixed for two to three minutes. The mixture is then pumped to a mined-out area where the slurry can dewater and eventually solidify.

5.2 Capital and Operating Cost Estimate

Both a capital and operating cost estimate were prepared based on the generalized flowsheet and equipment list. These estimates were. based on assumptions made due to lack of specific data; however, they showed great potential for application to the phosphate industry.

These estimates are being refined further taking into account additional disposal costs of slimes, anticipated material conveyance distances, and credit for reduction of retention areas.

5.3 Hemihydrate Process - Advantages and Disadvantages

Being the simplest of the aforementioned disposal processes, this is readily adaptable to an existing hemi-plant in relatively close proximity to a mine waste disposal site. Advantages include:

- o disposal of all waste $CaSO_4$ below grade,
- o significant reduction of required retention area for the mining operation, and
- o disposal of slime in such a manner as to provide a stable solidified mixture in a very short time.

The majority of construction work would be done in the field, with the only required modification at the chemical plant being conversion to a dry discharge system.

The predominant disadvantage in the process is the material being handled. It is both acidic and abrasive yielding a mixture which could cause higher than normal maintenance cost for all material handling equipment.

5.4 Slimes Solidification Process by a Hemihydrate Conversion of a Dihydrate By-Product Via Sulfuric Acid Dehydration

A hemihydrate production be made from waste dihydrate using a dilute sulfuric acid dehydration process. In this process, a port ion of the water of crystallization is removed while liberating unreacted rock and other P_2O_5 tied up in the dihydrate cake. The hemihydrate is dewatered via pan filter and then dry discharged to the mix station. Here, slime is added as in the other cases and the mixture is pumped away for disposal below grade. The dilute sulfuric acid is recovered and recycled back to the phosphoric acid plant for addition into the operating system (see Figure 6). Additional data are now being obtained for refining the process and for making capital and operating cost estimates.

This process has the combined advantages of P_2O_5 recovery, solidification in a short time frame, and the maximum consumption of slimes. The disadvantages would include modification of the phosphoric acid plant and close proximity to the mine site to keep slimes transportation from being cost prohibitive.

5.5 Slimes Solidification Process by an Anhydrite Conversion of a Dihydrate Chemical Plant Via Concentrated H_2SO_4 Acid Use

The anhydrite process combines chemical conversion at the phosphoric acid plant with waste disposal at the mine site. The phosphogypsum is dehydrated, filtered and conveyed to the mine site where it is mixed with waste clay and disposed of below grade (see Figure 7).

The dihydrate filter cake is first diluted with approximately 60 percent sulfuric acid and dumped into the anhydrite reactor. Here concentrated (98%) sulfuric acid is added and the mixture is allowed to react for a short period of time. The anhydrite slurry is pumped to a bank of centrifuges and dewatered to recover the residual P_2O_5 value and diluted H_2SO_4. The dry cake is discharged onto a conveyor belt for transfer to the mine site. At the mine site, the mixing operation is done in the same manner as the preceding cases.

HEMIHYDRATE PREPARATION FLOWSHEET

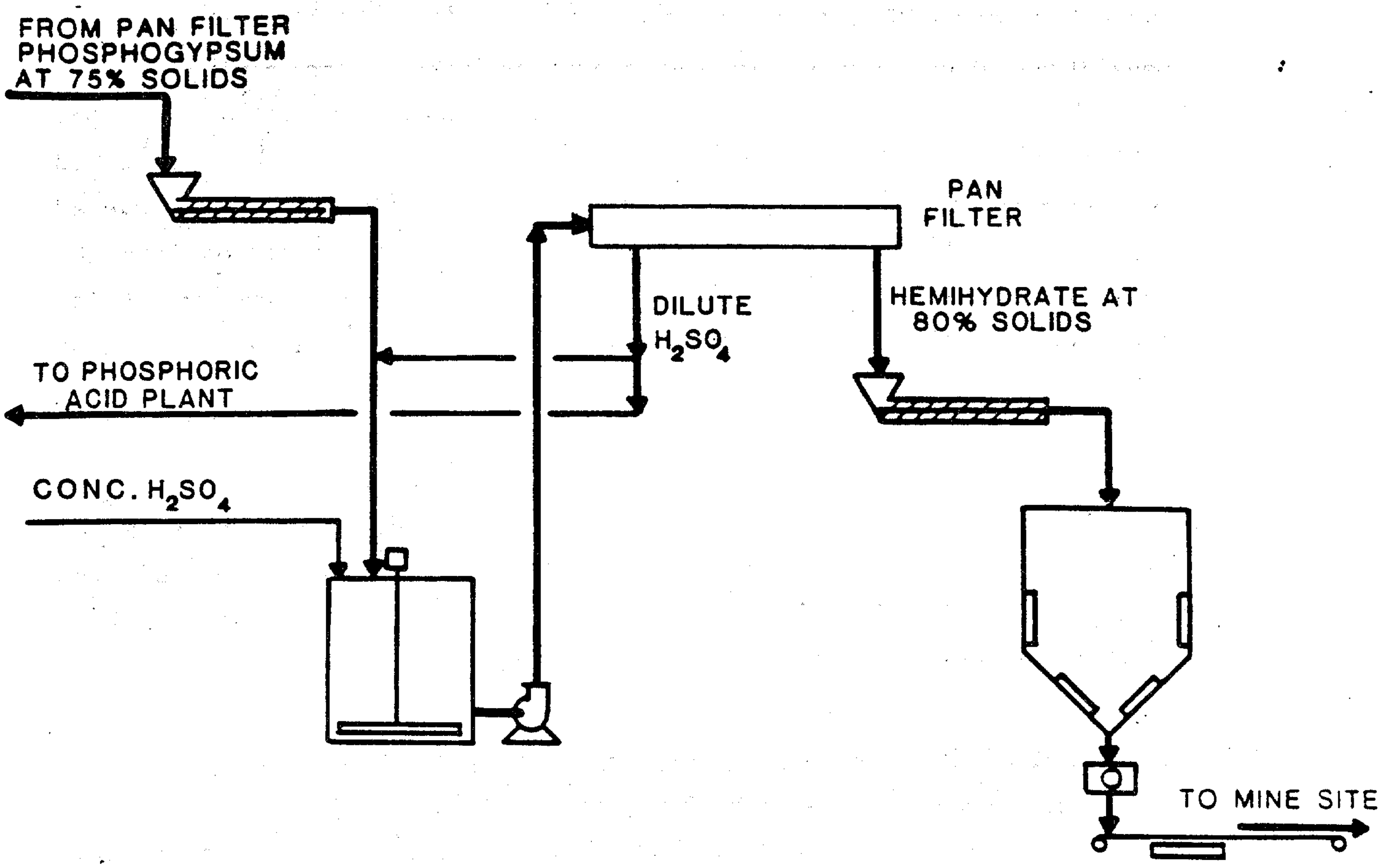

FIGURE 6.

ANHYDRITE PREPARATION FLOWSHEET

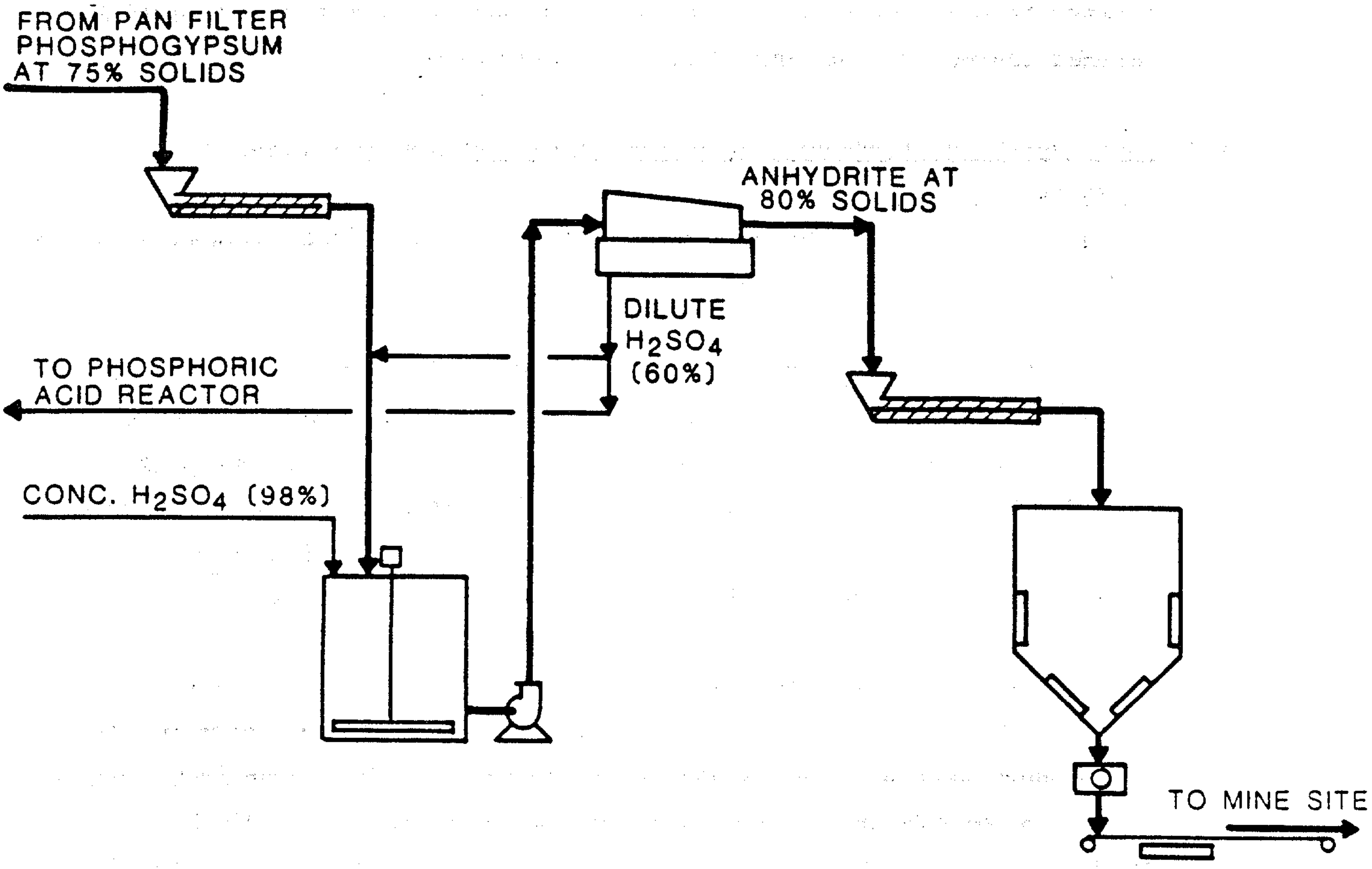

FIGURE 7.

5.6 Capital and Operating Cost

Estimates were prepared in the same manner as the hemihydrate (residue)/slime process estimate. These are also being further refined taking into account credit for P_2O_5 recovery.

5.7 Advantages and Disadvantages of the Solidification Process Via Anhydrite/Slime

There are certain advantages and disadvantages in the process where chemical conversion is included.

The anhydrite preparation process will provide a hydratable calcium sulfate product for solidification with clay waste while recovering a significant amount of the P_2O_5 which is normally lost. P_2O_5 losses in the waste $CaSO_4$ can be cut by almost 70 percent while the $CaSO_4$ mass itself is reduced by 20 percent. Both values have a significant impact on the plant operation and are definite advantages.

Some potential disadvantages also arise from this conversion process. The dewatering of the anhydrite product is a critical point in the design and successful operation of the process. The anhydrite crystal formed is very fine and does not dewater easily, as in the case of dihydrate and hemihydrate. Also, certain modification to the phosphoric acid plant would be necessary for maximum P_2O_5 and H_2SO_4 recovery.

5.8 Slimes Solidification Process by Conversion of an Old Dihydrate Plant to a Hemihydrate Process

This alternate leads to a mixing scheme identical to the one described in 5.1 (slime disposal with a hemihydrate residue). This would be appropriate for companies wishing to upgrade an existing facility to a more energy efficient operation while taking care of the $CaSO_4$ waste problem.

5.9 Slimes Pond Savings from an Operation Using the U.S. Gypsum Solidification Process

By dredging thickened slime from inactive retention areas, this process allows the "recycling" of retention ponds as opposed to constructing new ones. Using a conservative ratio determined in the initial laboratory work, it is estimated that the required retention area over the life of the mine can be reduced by at least 15 percent utilizing anhydrite and 20 percent with hemihydrate residue. In the case of hemihydrate from dihydrate, current laboratory work indicates a lower working ratio of $CaSO_4$ to slime raising the reduction in retention areas considerably as compared to what is seen with the hemihydrate residue solidification process.

6.0 COMMERCIALIZATION REQUIREMENTS OF THE PROCESS

The U.S. Gypsum Slimes Solidification Process is the product of an extensive laboratory and bench scale work done in the last couple of years at the U.S. Gypsum Company's Research Center in Libertyville, Illinois. As soon as the technical viability of the process was verified by static and dynamic tests, a process flowsheet was established. Zellars-Williams, Inc., a division of Jacobs Engineering Group, Inc., was involved at that point to provide a preliminary engineering and cost profile of the process. To specify and accurately define the unit operations involved in the process, additional laboratory tests were carried out at Zellars-Williams in Lakeland, Florida. Finally, it was decided that process flow diagrams (PFD), equipment sizing and list, and other engineering documents had to be produced to specify the various alternatives or options available to specific producers with specific problems. Similarly, capital and operating costs for each alternative will be established.

Further development of this project will require the installation and operation of a pilot plant unit on site at an operating mine and plant. The necessity for this pilot plant development was warranted by the need for collecting continuous data, operating with varying and fresh raw materials, and collecting equipment sizing data for further optimization.

Equally important is that such a pilot plant can also be a demonstration plant for the Industry to see and evaluate its full potential based on their experience and input.

It is important to emphasize here that such a pilot plant has to be installed in a specified site confronted with the specific requirements of the mine and chemical plant under consideration. Thus, the above scenario indicates that possibilities exist for joint ventures with either an operating company or State agencies or a combination of both.

Assuming successful operation of a pilot plant, the further development of this project may entail the design and installation of a prototype plant, again either as a joint venture or as a one-party venture.

7.0 ACKNOWLEDGEMENT

Acknowledgement is gratefully given to J. C. Gaynor and G. M. Staniszewski at the U. S. Gypsum Research Center, Libertyville, Illinois and J. R. Moon and M. E. Zellars of Zellars-Williams, Inc., Lakeland, Florida, for their help in preparing this paper.

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9.0 APPENDIX

Process Potential Application to the Treatment of Other Mining, Industrial and Municipal Wastes

Throughout the United States and the World there are many operations that generate slime wastes which are contained in holding ponds (see Table VI). The mining industry alone generates over 600 million tons/year of slimes on a solid basis. Oil and gas well drilling produces 7,000 tons of 20 percent drilling mud for each 7,000 feet of well.

There are unknown quantities of slimes produced in the chemical industry by electric utilities and by municipal water and sewage treatment. Many of these slimes are amenable to treatment with hydratable calcium sulfates(1). Many slime pond areas are located near natural anhydrite deposits or other waste anhydrite stacks such as fluoroanhydrite(13) co-produced in the manufacture of hydrogen fluoride. All of these operations need looking into.

Production of Holding Pond Slimes in the United States

Industry	Million Tons/Year (Dry Basis)	Type
A. Mining	over 600	Clays - Other Minerals
Copper	260	Clays - Other Minerals
Taconite & Other Iron Ores	129	Clays - Other Minerals
Coal	100	Clays - Other Minerals
Phosphate	60	Clays - Other Minerals
Lead and Zinc	17	Clays - Other Minerals
Uranium	7	Clays - Gypsum
Gold	6	Clays - Organic
Other	?	
Oil & Gas Well Drilling	?	Clays - Other Minerals
B. Industrial		
Aluminum (Red Muds)	6	Clay-like Iron Hydroxides
FGD and Other Scrubbers	?	Lime, Calcium Sulfite, Gypsum
Waste Paper Recycling	?	Clay, Calcium Carbonate
Chemical Effluent	?	Acid Pickle Liquers, Organic Chemicals, Electrolytic Solutions
C. Municipal		
Water Treatment	?	Clay-like Basic Aluminum Sulfate, Lime - Calcium Carbonate
Sewage	?	Organic

ENVIRONMENTAL ASPECTS OF PHOSPHOGYPSUM DISPOSAL

Presented at

Seminar on Phosphogypsum
April 26 and 27, 1984
University of Miami, Florida

Seminar Sponsored by

The Florida Institute of Phosphate Research
The University of Miami

Paper Presented by

Anwar E. Z. Wissa
and
Nadim F. Fuleihan

Ardaman & Associates, Inc.
Consulting Geotechnical Engineers
8008 South Orange Avenue
Orlando, Florida 32809

Environmental Aspects of Phosphogypsum Disposal

by

Anwar E. Z. Wissa[1] and Nadim F. Fuleihan[2]

Abstract

The groundwater environmental aspects of phosphogypsum disposal are a function of the hydrogeologic conditions at the disposal site and the leachate attenuation characteristics of subsurface strata.

The hydrogeology in Central Florida is briefly described and some historic water quality records from monitoring wells at existing phosphogypsum disposal sites are presented. The data indicate that contamination is limited to the surficial aquifer and to a distance of a few hundred feet only from the disposal facilities.

The effect of process water leaching on permeability and water quality is presented for typical Floridian soils and geologic formations. Mechanisms contributing to treatment and attenuation of the leachate including chemical reactions (such as neutralization, precipitation, ion exchange, and sorption), radioactive decay, biological reduction, and dispersion are identified via results from laboratory leaching tests. Long-term leaching of the various stratigraphies indicates that some materials are very effective in treating the process water and, hence,. minimizing the impacts on groundwater resources.

[1] President, Ardaman & Associates, Inc., Orlando, Florida.
[2] Principal Engineer, Ardaman & Associates, Inc., Orlando, Florida.

Introduction

About five tons of by-product phosphogypsum are generated for every ton of phosphoric acid produced. While some of this phosphogypsum is being consumed as a soil conditioner in agriculture, as a road base material, and in the manufacture of plaster boards, most of it has to be disposed of by stacking and occasionally by discharging into oceans and rivers.

The most common method of gypsum disposal is by “wet” stacking. The gypsum filler cake is slurried with acid process water and then pumped to a settling pond where it is allowed to settle. The gypsum is then stacked usually using draglines and the upstream method of construction. These stacks can cover several hundred acres and reach 200 feet or more in height, as illustrated in Figure 1. Process water decanted from the gypsum stack is generally collected in process ponds abutting the gypsum stack. The process ponds act as surge ponds to temporarily store rainfall for subsequent evaporation, and as cooling ponds to allow recirculation of process water to the plant for reuse. Water stored in these cooling ponds as well as water entrained in the gypsum pores is highly acidic with a pH on the order of 2, and contains high levels of various contaminants such as fluoride, phosphorus and sulfate with concentrations for these parameters generally ranging from 3,000 milligrams per liter (mg/l) to as much as 9,000 mg/l. Leachate from these facilities is therefore a potential source of contamination.

Another method of disposal less commonly used is "dry" stacking. In this method the gypsum filter cake is transported by conveyor belts or trucks to the disposal facility. Even though this paper discusses the groundwater and environmental aspects of wet stacking, dry stacks, especially in wet climates, can have similar impacts.

Hydrogeology

The hydrogeology of the site is of major importance in assessing the impact on groundwater resources. This paper presents groundwater impact data from three phosphogypsum case studies in the State of Florida. Figure 2 shows a generalized geologic cross section through Polk County, Florida. The surficial deposits average approximately 50 feet in thickness and consist of overburden soils, silty sands and clayey sands, overlying the phosphate matrix of the Bone Valley Formation which is mined. Together these deposits comprise the surficial aquifer. The Hawthorn Formation and underlying Tampa Limestone which together average approximately 120 feet in thickness comprise the Secondary Artesian Aquifer. The producing zone of this aquifer is limited mostly to the lower portion of these formations. The upper portions of the Hawthorn Formation act as a confining unit between the Surficial and Secondary Artesian Aquifer.

Underlying these formations is the Tampa Clay Unit which averages approximately 40 feet in thickness, and acts as a confining unit between the Secondary Artesian and underlying Floridan Aquifer system. A useful way of determining the extent of the various aquifers and confining units is to measure and plot the piezometric water level versus depth from piezometers tapping sealed zones within the subsurface profile, as illustrated in Figure 3. On these plots a sloping line implies a hydraulic head loss from one point to the other while a vertical line implies an aquifer system in which no head loss is observed. As shown, there are three distinct aquifers at this location in Central Florida. The Surficial Aquifer, the Secondary Artesian Aquifer, and the Floridan Aquifer. The upper portion of the Hawthorn Formation acts mostly as a confining layer with some producing zones in it, and the Tampa Clay Unit acts as a confining layer between the Secondary Artesian and Floridan Aquifers. The head loss from the Surficial to the Secondary Artesian Aquifer at this location is on the order of 45 feet, while that between the Secondary Artesian and Floridan Aquifer is on the order of 10 to 15 feet.

Groundwater Impact Assessment Methodology

Process water from gypsum stacks and cooling ponds seeps laterally in the Surficial Aquifer system and migrates slowly downward through confining layers to the Secondary Artesian and Floridan Aquifers, as schematically illustrated in Figure 4. During this slow downward migration, the leachate is effectively treated and purified to a large extent by subsurface soils. Additional “treatment” occurs via leachate dilution with the waters flowing in the confined aquifers.

In assessing the impact of future gypsum stacks and process ponds on groundwater resources, one can make use of historic water quality records measured in monitoring wells at existing sites in a similar hydrogeologic environment as that of the proposed facility. Alternatively, one can predict the impact based on similations of hydrogeology and leachate attenuation characteristics determined from laboratory leaching tests on subsurface strata. This method is particularly useful where historic data is lacking and/or if one wishes to extrapolate the historic record. Roth methods will be illustrated in the following sections.

Historic Water Quality Records

Figure 5 shows pH, phosphorus, and fluoride concentrations as a function of time in a Secondary Artesian Aquifer well located some 200 feet downstream from a mature gypsum stack. As shown, no monotonic trends with time are observed. Moreover, concentrations for fluoride and phosphorus are less than one part per million and the pH is on the order of seven. The lack of contamination in this Secondary Artesian Aquifer well is typical of many wells tapping the Secondary Artesian and Floridan Aquifers in the vicinity of gypsum stacks and cooling ponds.

The impact on groundwater in the Surficial Aquifer will be illustrated via a case study of a 20-year old gypsum stack located, as shown in Figure 6, within a mined-out pit with a pervious layer of tailings debris and silty sands underlying the stack. The seepage ditch at the edge of the facility contains process water that is of similar quality as the gypsum stack and cooling pond water. Wells were located at various depths within the surficial aquifer at distances of 50, 100, 200, and 400 feet from the seepage collection ditch. pH concentrations versus distance are shown in Figure 7 for three sets of wells, namely wells tapping the surficial silty sands, underlying clayey sands, and phosphate matrix layer of the surficial aquifer. Wells located at a distance of 50 feet from the seepage ditch indicate pH concentrations ranging from about 4 to 6 which is well above that measured in the seepage collection ditch where the pH is on the order of 2. Rackground pH concentrations of 6 to 7 were measured some 200 feet from the seepage collection ditch. Figure 8 presents plots of specific conductance versus distance. Again wells closest to the seepage collection ditch exhibited specific conductance values on the order of 1,000 to 5,000 µmhos/cm compared to 36,000 µmhos/cm for the process water. The conductivity decreased to less than 1,000 µmhos/cm at a distance of about 200 feet reaching background conditions beyond that.

Fluoride at this site was very effectively treated by the foundation soils mostly via precipitation at a pH in excess of 4 or 5. As shown in Figure 9, none of the wells at this particular site exhibited a fluoride concentration in excess of one part per million, compared to a process water fluoride concentration on the order of 9,000 mg/l. Sulfate is also treated although less effectively than other contaminants. In wells closest to the seepage collection ditch, sulfate concentrations were as high as 1,000 mg/l compared to values on the order of 6,000 to 7,000 mg/l in the process water (see Figure 10). Sulfate concentrations were also somewhat elevated at a distance of about 200 feet indicating that the leachate front at this site has already passed this particular location.

Figures 11 through 14 present monitor well data from another gypsum stack site in Florida. At this site, collection zones A and B are located in the Surficial Aquifer, while collection zones C and D are located at the top of the Secondary Artesian Aquifer. As shown in Figure 11, the set of wells closest to the gypsum stack indicates depressed pH concentrations in shallow wells abutting the facility but the pH increases rapidly to background concentrations within a distance of 1,000 feet. pH values in Secondary Artesian Aquifer wells are at background level.

Fluoride is also very effectively treated, as illustrated in Figure 12. Only one surficial aquifer well abutting the facility had a fluoride concentration of about 100 mg/l compared to a process water fluoride concentration on the order of 4,000 mg/l. All other fluoride concentrations are well within background.

Phosphorus is effectively treated, although to a lesser extent than fluoride. Two surficial wells at this location exhibited concentrations ranging from 100 to 1,000 mg/l, compared to a process water concentration on the order of 6,000 mg/l, but as shown in Figure 13, the concentrations quickly fall back to background levels with distance from the stack. Gross alpha radiation profiles in Figure 14 are all within background in spite of the fact that the process water exhibits a gross alpha concentration on the order of 4,000 pCi/l.

Profiles of pore fluid pH and specific conductance versus depth under a gypsum stack are presented in Figure 15. The pH reached background levels on the order of 6 to 7 some 20 feet to 30 feet below the gypsum, and the specific conductance decreased down to about 300 or 500 µmhos/cm at the same depth, inferring that at this site downward contamination has not progressed beyond this depth in spite of the fact that the stack has been in operation for over 20 years.

Elements of Predictive Model

The elements of a predictive model include defining the hydrogeologic conditions at the site and assessing the leachate attenuation characteristics of subsurface strata. Hydrogeologic conditions in Central Florida were addressed in a preceding section. In addition to determining the hydraulic characteristics and hydraulic heads of aquifers, confining beds and semi-confining beds, one has to consider the long-term effect of process water seepage on the permeability of the various subsurface soils. This effect can be determined via laboratory leaching type tests which are also used to establish the leachate attenuation characteristics of subsurface strata.

Effect on Long-Term Permeability

As illustrated in Figure 16, leaching tests on relatively impermeable soils are performed under backpressure in a battery of stainless steel permeameters fitted with pore pressure monitoring probes to document changes in permeability as a function of process water flow and time. The leachate is collected in sampling burettes for water quality monitoring. Also depicted in the figure is a controlled hot temperature bath used to accelerate the reaction of the soil with process water. Typical long-term permeability test results on clay soils are shown in Figure 17. As can be seen, some soils are not affected by process water leaching; some are favorably affected as a result of cementation and/or ion exchange causing a reduction in the coefficient of permeability with continued acid water flow; while others are adversely affected by dissolution and/or ion exchange. For example, if sodium montmorillonite is leached with a water containing elevated calcium concentrations, the cation exchange of sodium to calcium could lead to an increase in the coefficient of permeability.

For relatively pervious-type soils, leaching tests are performed in specially designed column tests (see Figure 18) that allow determination of the head loss and changes in permeability as well as leachate quality with time. Figure 19 presents permeability test results from two fine sand samples leached with process water. Whereas one of the soils is not affected by acid water leaching, the other became cemented with time and exhibited a substantial reduction in the coefficient of permeability. Figure 20 illustrates a cemented cake that developed in drain material surrounding a collector drain pipe in an actual field situation. This cementation prevented performance of the drain and hampered its intended use. More than five types of gels and crystals causing cementation and clogging have been identified so far with process water seepage. Scanning electron photomicrographs of one such cementing agent is presented in Figure 21. The figure depicts calcium-aluminium-sulfur octahedral crystals forming on a quartz grain. Hydrous gel-type and honeycomb-type cementations have also been observed.

Leachate Attenuation Mechanisms

There are several mechanisms that act favorably to attenuate or treat the leachate. These mechanisms are based on: (i) chemical reactions such as neutralization, precipitation, ion exchange and sorption; (ii) radioactive decay; (iii) biological reduction; (iv) dispersion; and (v) dilution.

The dissolution of calcium from limerock is an example of an effective chemical reaction. This process causes neutralization of the acid water. When the pH rises to about 4 or 5, several chemicals such as fluoride are precipitated. Metals are also precipitated. Ion exchange and sorption are effective in clay minerals resulting in lower fluoride, phosphorus and metal concentrations. Laboratory leaching type tests are ideally suited to evaluate the effect of these and other processes such as radioactive decay, biological reduction and dispersion. Dilution is a contributing factor to attenuation but cannot be modeled in the laboratory. Bather, it has to be accounted for in the theoretical modeling technique used.

Figure 22 presents a plot of normalized concentrations versus time (or pore volume flow) to illustrate how laboratory leaching tests can be used to determine dispersion in a given material, in this case a fine sand. An unreactive tracer, sodium chloride, was used in this leaching test. Because soils have preferential flow paths, non-uniform seepage occurs, and an attenuated contaminated front actually reaches at an arrival time closer than one would expect based on the arrival of an undispersed front, i.e., a slug. Dispersion is also responsible for retarding the arrival of the fully contaminated front. At the expected arrival of the undispersed front, the concentration in the leachate is approximately 60 percent of the tracer concentration.

Leaching tests are most useful in determining the leachate attenuation or treatment provided by soils. Figure 23 presents leaching test results illustrating leachate fluoride concentrations for flow through a fine sand which does not normally exhibit substantial treatment. In spite of the limited treatment capacity of the sand, the front is retarded behind the anticipated arrival of the non-attenuated slug and even behind the anticipated arrival of a dispersed front. Attentuation is effective until the treatment capacity of the soil is exhausted.

Figre 24 illustrates the mechanism of biological reduction of sulfate by desulfovibrio. These micro-organisms which can only live in a relatively basic, neutral to slightly acidic environment are highly active in Central Florida and can reduce sulfate concentrations by taking up the oxygen tied up in the sulfate. They multiply in the presence of sulfate by 100 fold or more.

Leachate Attenuation Characteristics and Impact on Groundwater

Typical leaching test results for two surficial sands and a clayey sand are presented in Figure 25. As shown, the fine sands have very little treatment potential, but the clayey sand is very effective in neutralizing the leachate and attenuating fluoride concentrations. It is somewhat less effective in treating phosphorus except at low void volumes of flow. Sulfate concentrations are not significantly attenuated.

Figure 26 presents leaching test results for a dolomitic limestone from the Hawthorn Formation. As shown, the fluoride is substantially attenuated; even after four pore volumes of process water flow, fluoride concentrations are on the order of 100 mg/l only. Phosphorus is attenuated to a lesser extent. Sulfate attenuation occurs mainly at low pore flow volumes. Specific conductance reflects attenuation of the various chemicals. pH remained in excess of 6 after 3 pore volumes of flow due to effective neutralization.

The relative fluoride treatment capacity of various materials, namely a fine sand, a phosphate matrix and a limestone from the Hawthorn Formation is depicted in Figure 27. As shown, the limestone is most effective in treating fluoride mainly due to precipitation. The matrix which has some calcareous material is also effective in precipitating fluoride. The surficial fine sand is the least effective. As process water seeps through limestone, precipitation products tend to coat the limestone surface causing it to become relatively less effective with continued extensive leaching.

Once the treatment capacity of the soils has been established, a flow net can be constructed as illustrated in Figure 28 to determine the progress of the leachate plume in the surficial aquifer and, hence, the quality of the leachate with time and distance from the facility.

For downward percolation into the Secondary Artesian and Floridan Aquifers, it is desirable to perform a column leaching test on a stratigraphy modeling prevailing conditions at the site. Leaching tests on the model stratigraphy will allow for determining the cumulative treatment provided by all stratigraphic units underlying the site. Figures 29 and 30 present leaching test results on model stratigraphies of the surficial aquifer deposits and the Hawthorn Formation, respectively. As shown, the Hawthorn Formation stratigraphic model is highly effective in treating contaminants.

Long-term leaching effects can be predicted by determining the pore volumes of flow that will occur through the life of the facility. At retirement, recharge will continue to occur but with natural water sources replacing process water as the source of recharge. A gradual decay of the various contaminant levels will then occur as illustrated in Figure 31. Clean water in this case leaches through soil that has absorbed some contaminants and, hence, additional contamination will occur beyond retirement although at lower contaminant concentrations. These data can be used in conjunction with theoretical seepage models to predict the progress of the leachate plume during the life of the facility and beyond. For several sites investigated in Florida, all concentrations of contaminants, including sulfate concentrations, were predicted to be within drinking water standards when aquifer dilution and treatment were taken into account.

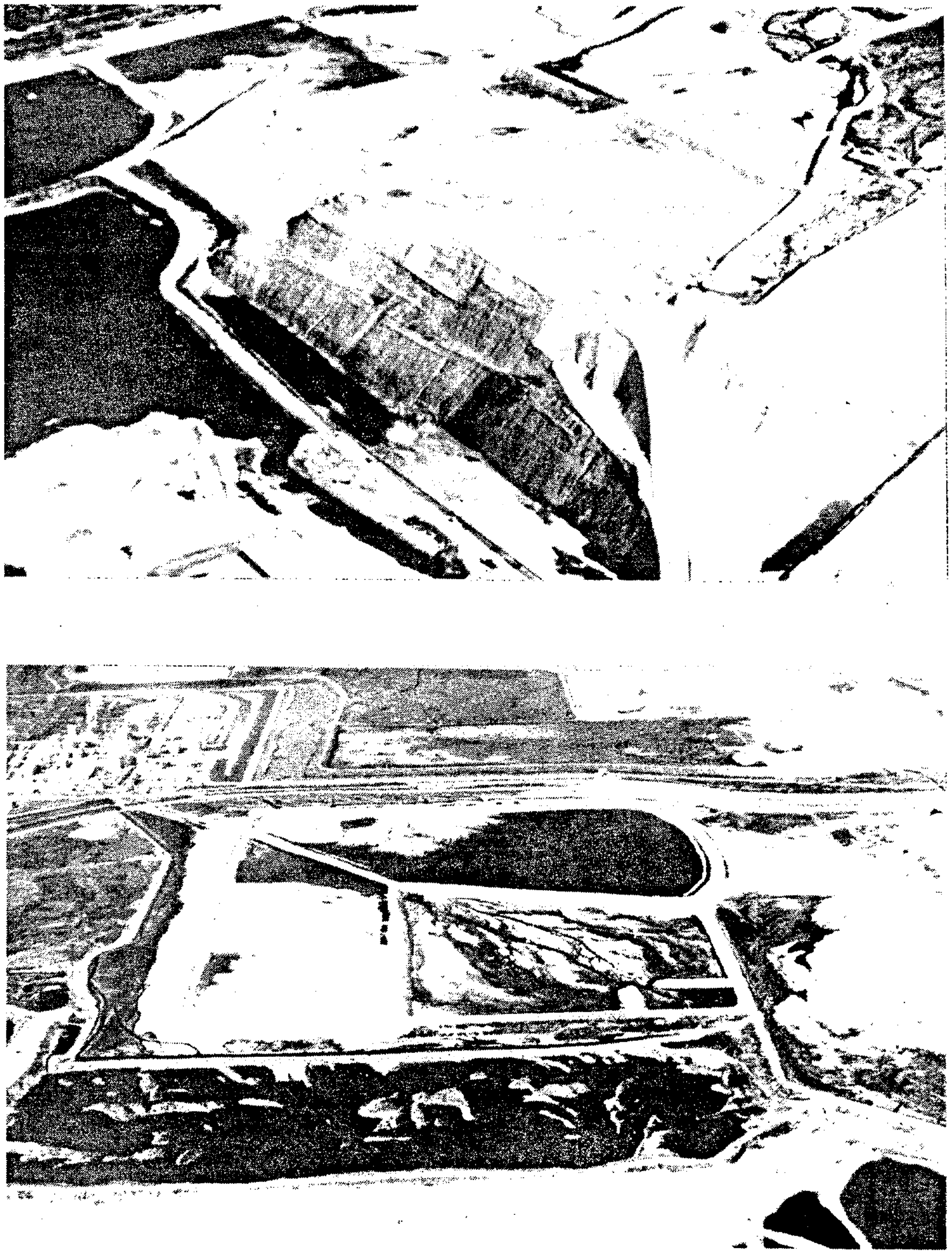

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FIGURE 1
TYPICAL GYPSUM STACKS AND
ASSOCIATED PONDS

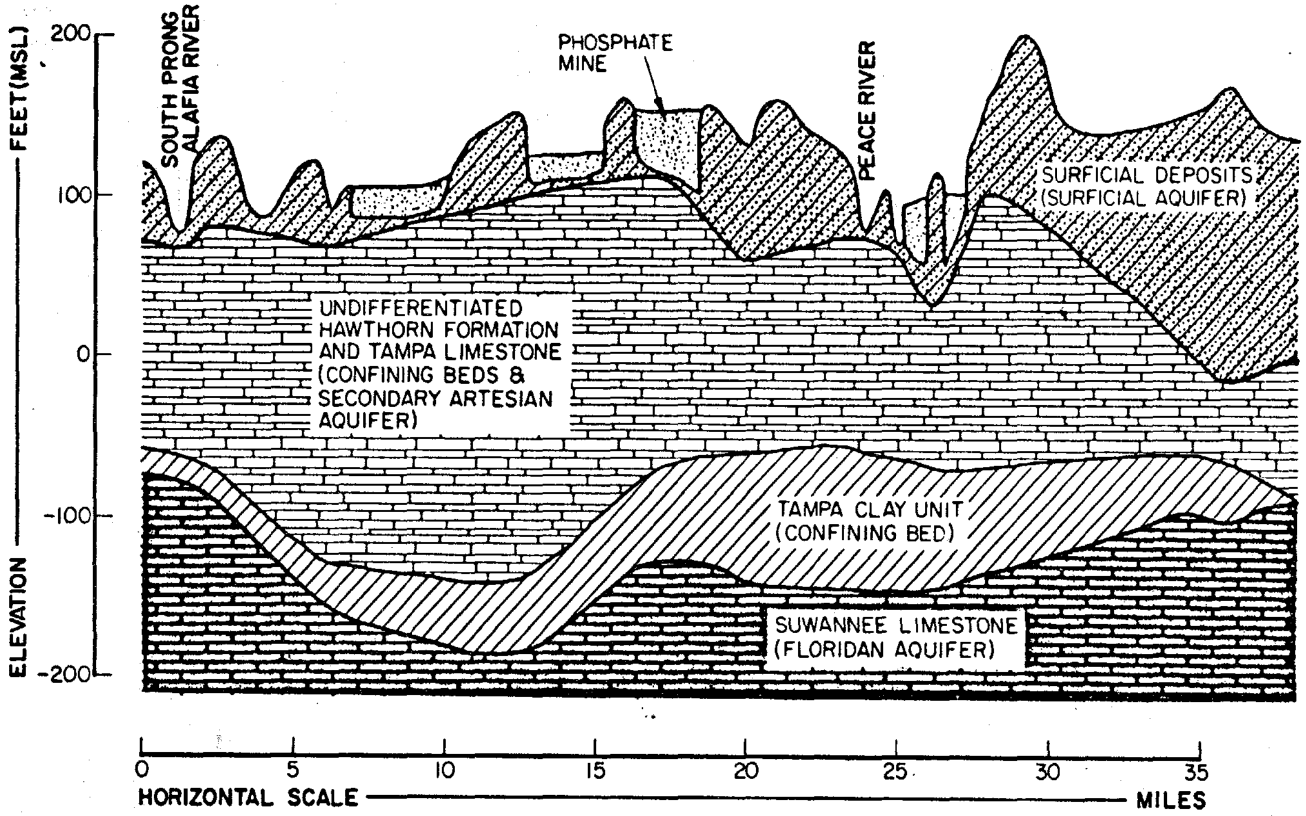

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FIGURE 2
CENTRAL FLORIDA REGIONAL HYDROGEOLOGY

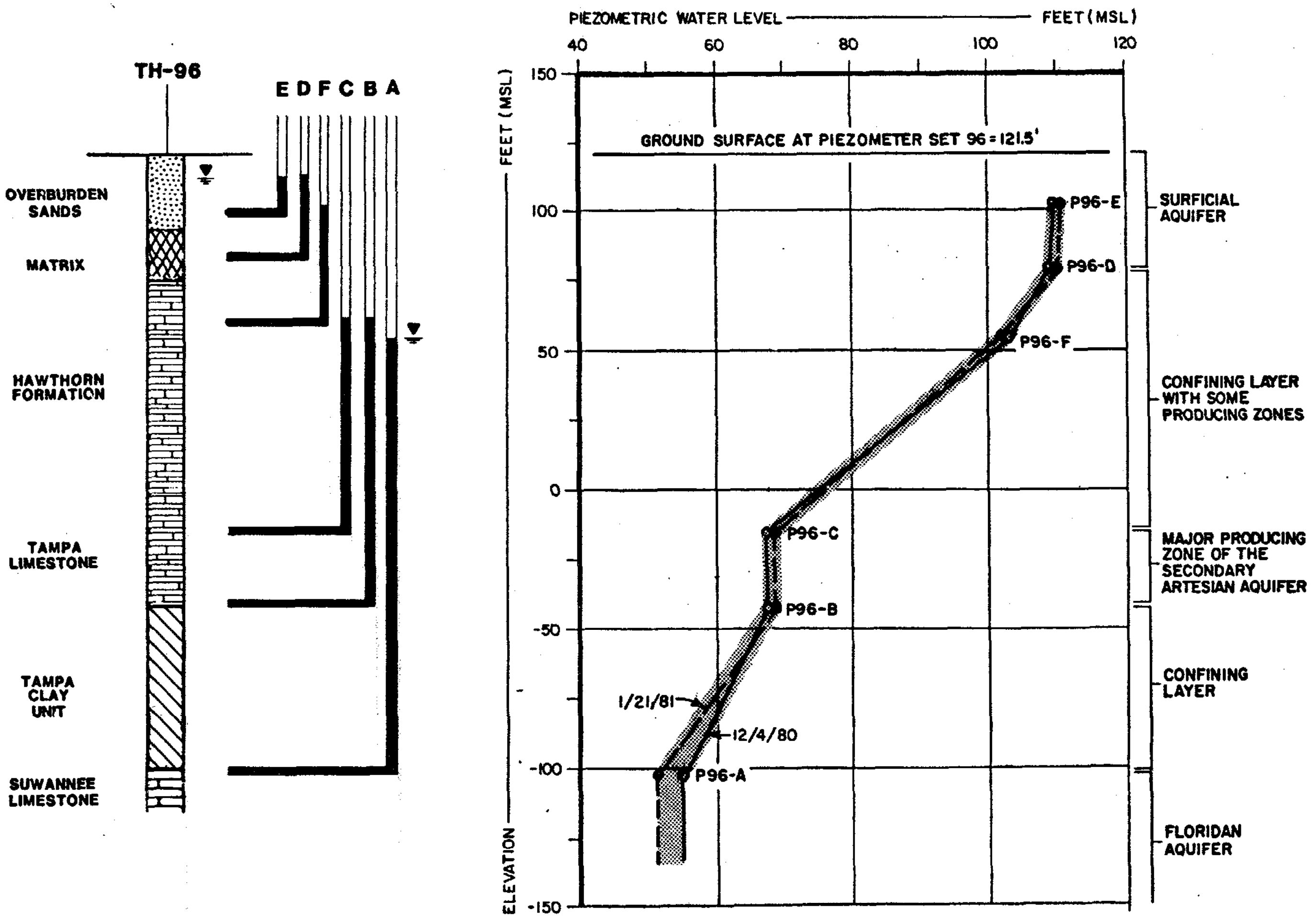

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FIGURE 3
PIEZOMETRIC WATER LEVEL VERSUS DEPTH

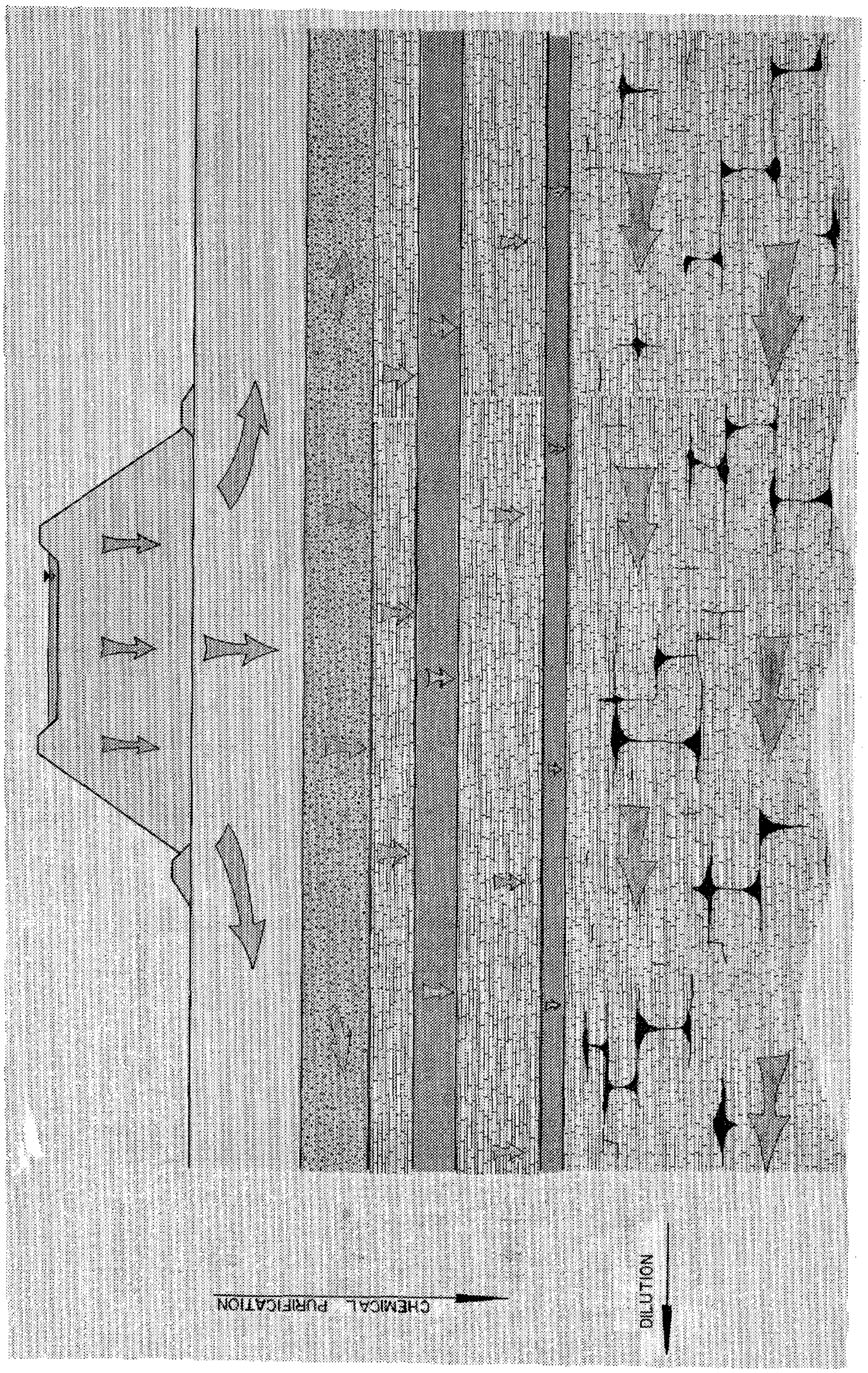

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FIGURE 4
EFFECT OF LEACHATE ON CONFINED AQUIFER
IN A FAVORABLE HYDROGEOLOGIC ENVIRONMENT

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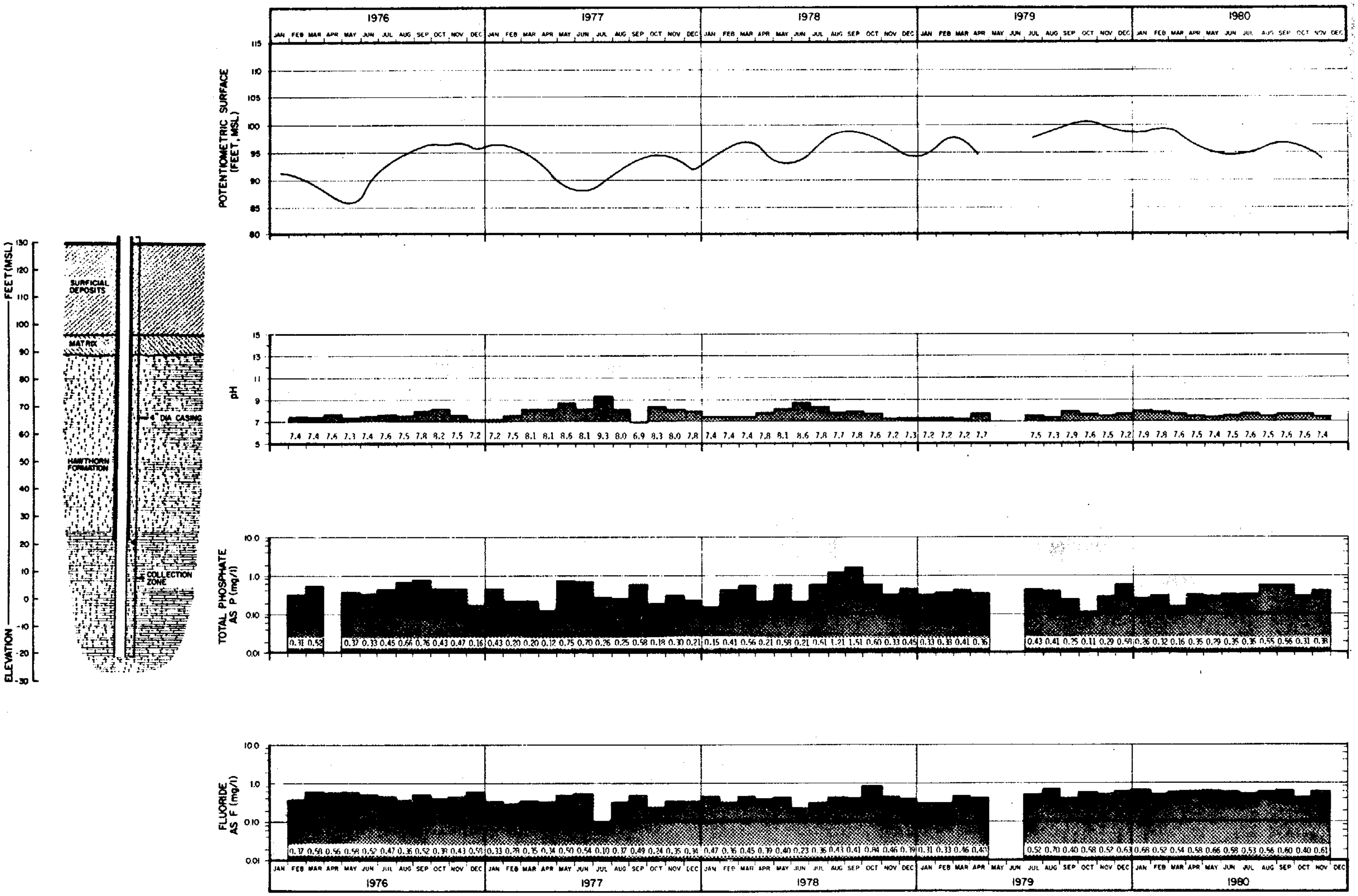
FIGURE 5
HISTORIC WATER QUALITY OF SECONDARY ARTESIAN AQUIFER



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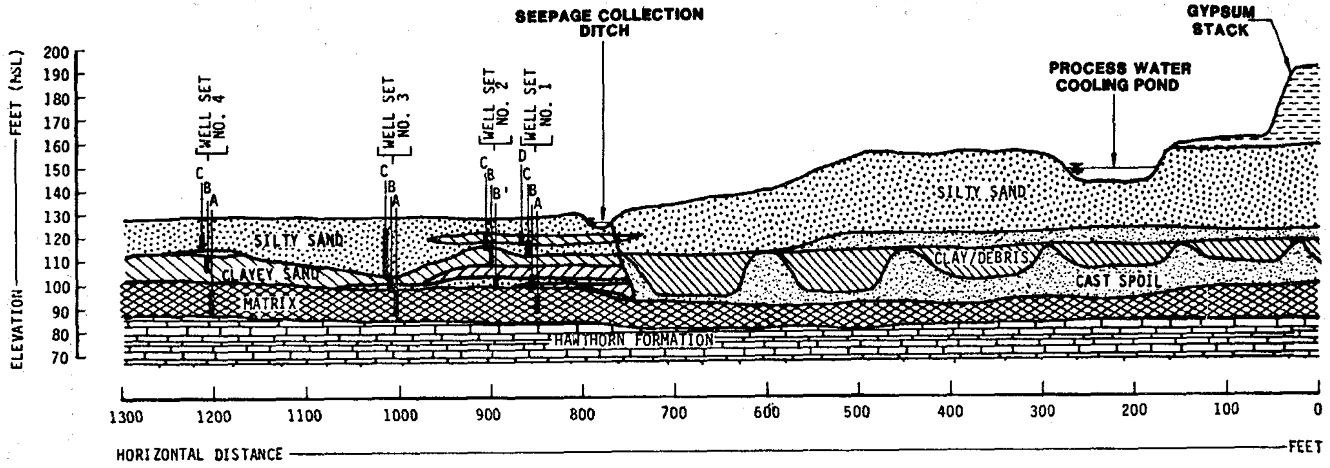

FIGURE 6
GEOLOGIC SECTION AT SURFICIAL AQUIFER MONITORING WELLS

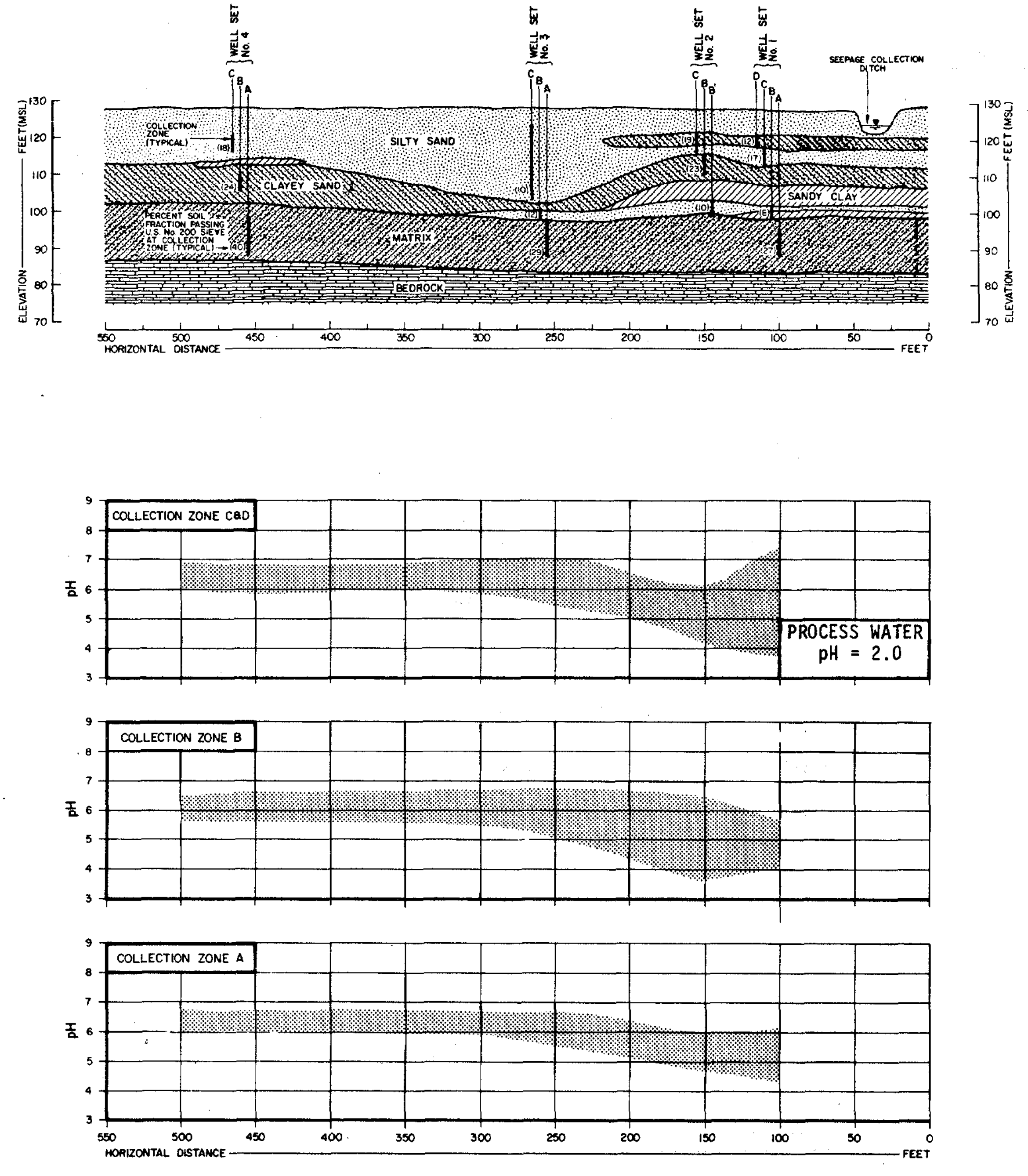

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FIGURE 7
GROUNDWATER pH VS.
DISTANCE FROM PROCESS PONDS

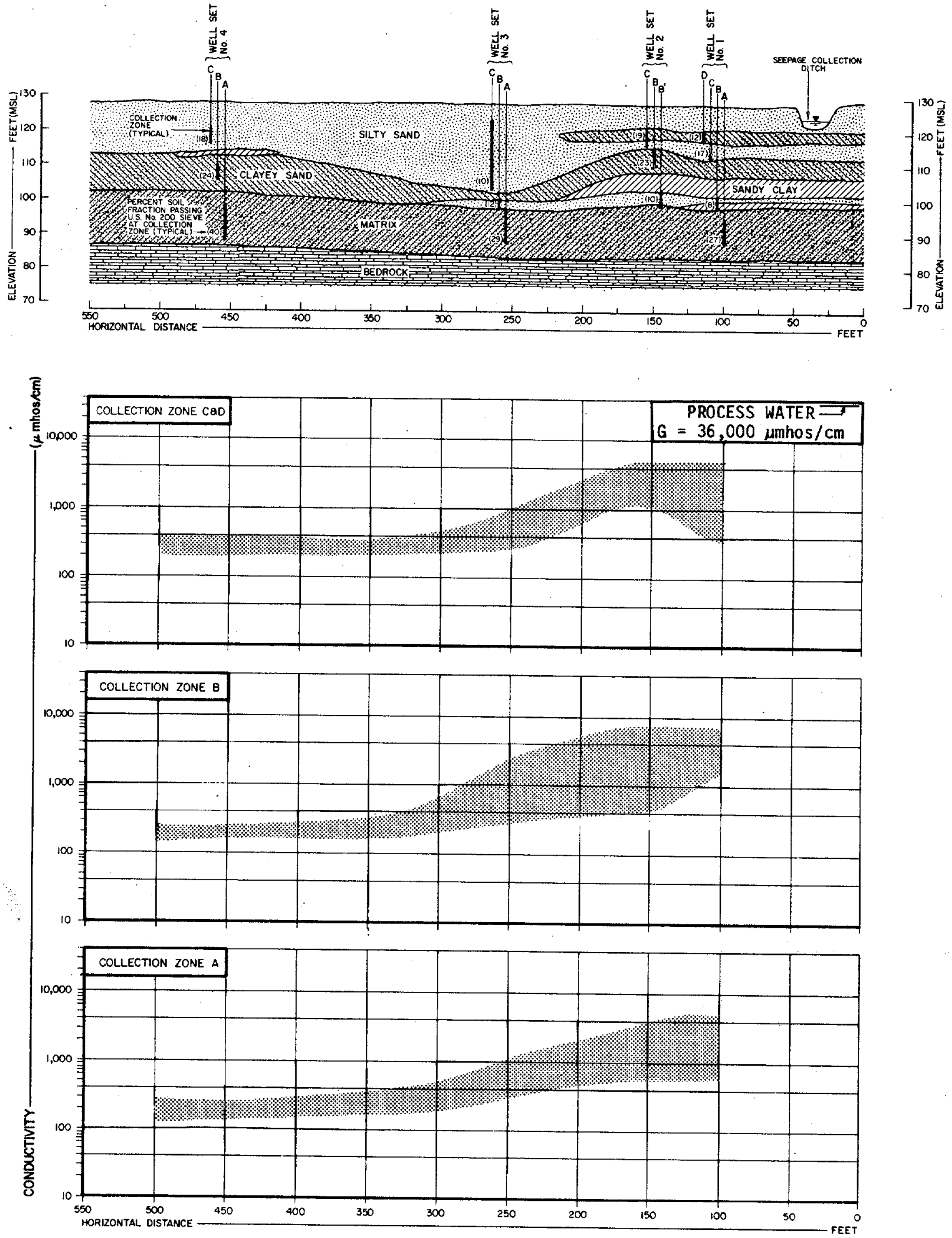

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FIGURE 8
GROUNDWATER CONDUCTIVITY VS.
DISTANCE FROM PROCESS PONDS

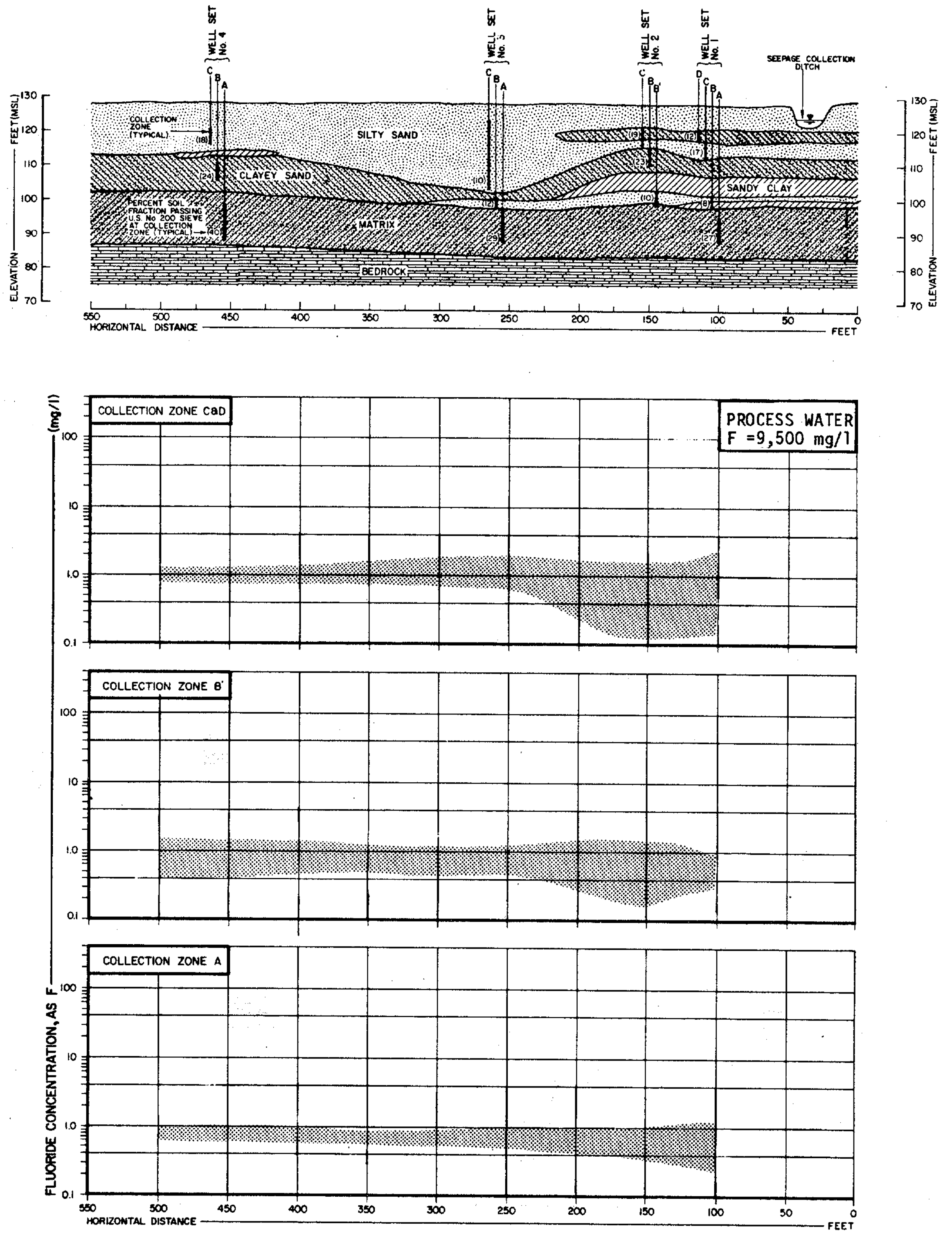

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FIGURE 9
GROUNDWATER FLUORIDE CONCENTRATION VS. DISTANCE FROM PROCESS PONDS

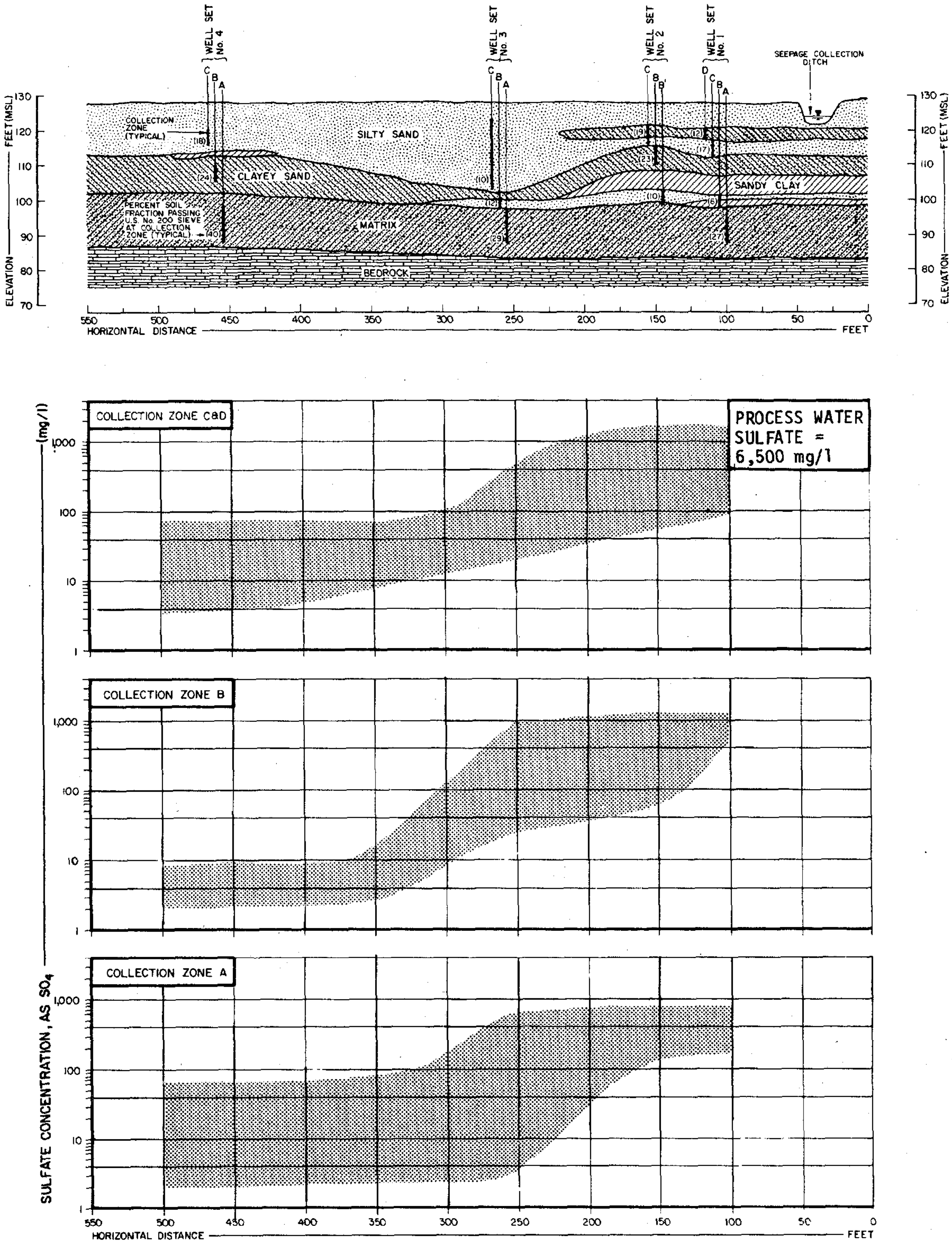

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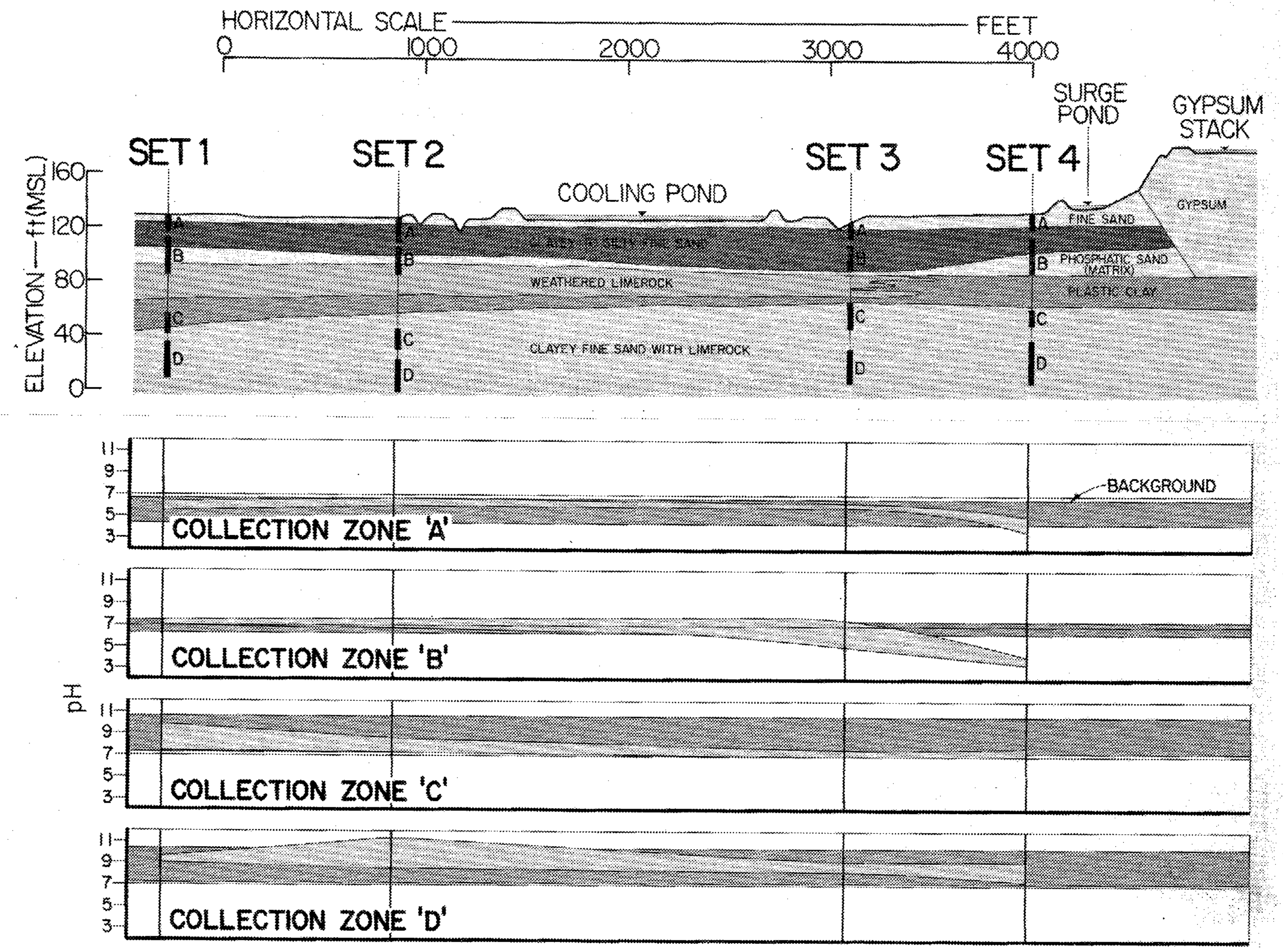
FIGURE 10
GROUNDWATER SULFATE CONCENTRATION
VS. DISTANCE FROM PROCESS PONDS



pH PROFILES

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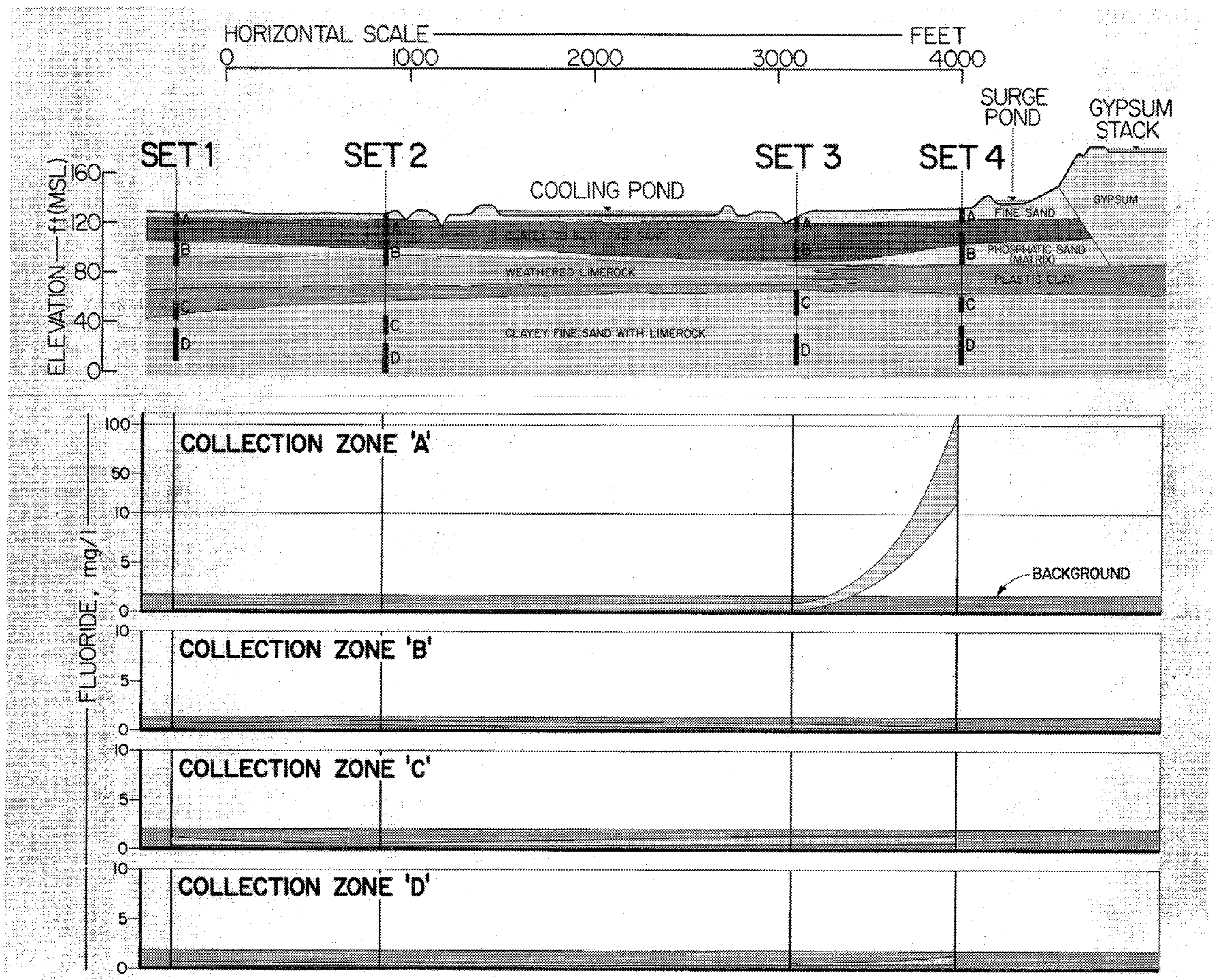
FIGURE 11
pH PROFILES WITH DEPTH AND DISTANCE
FROM GYPSUM STACK AND COOLING POND



FLUORIDE CONCENTRATION PROFILES

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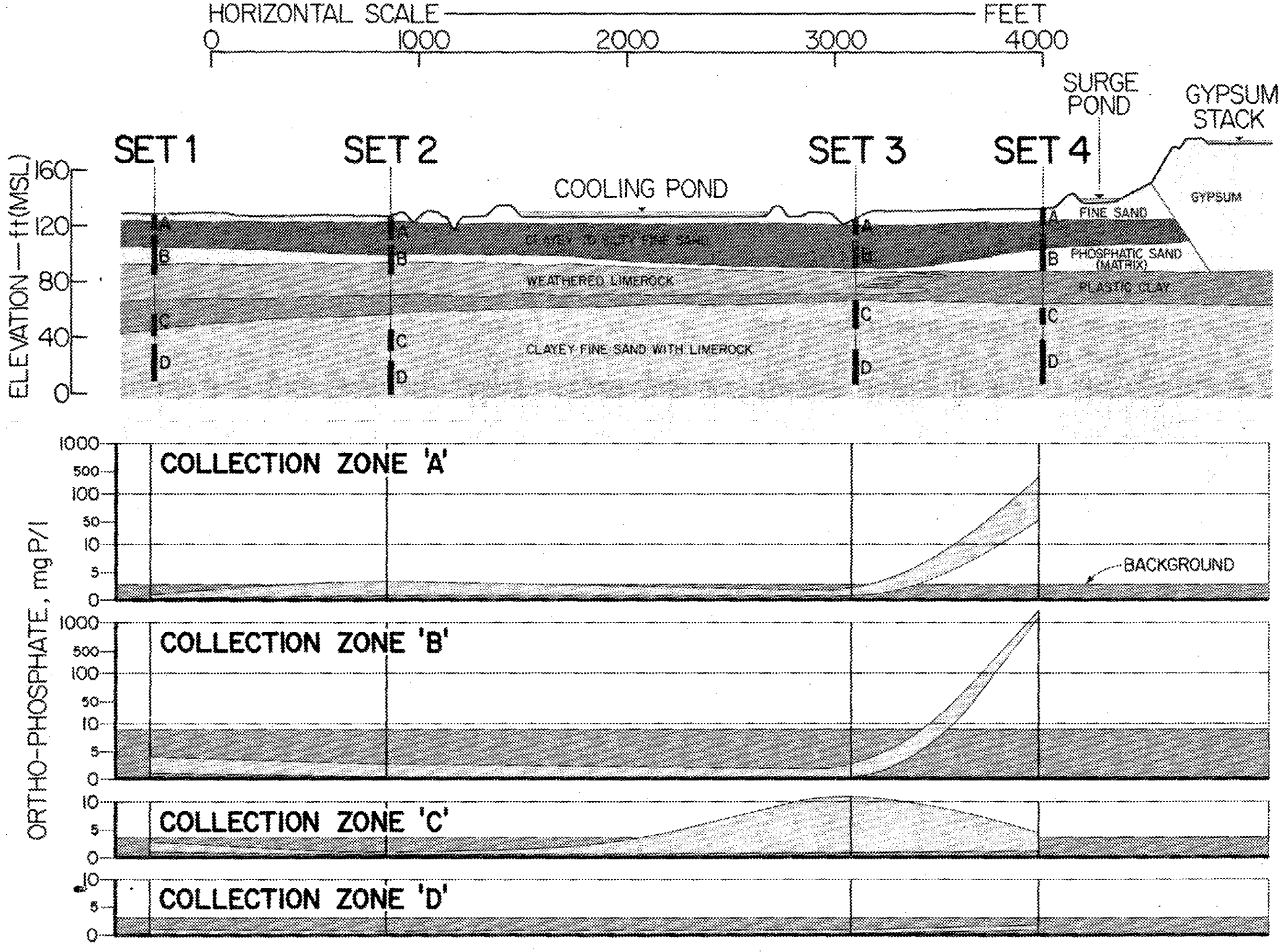
FIGURE 12
FLUORIDE CONCENTRATION PROFILES WITH DEPTH
AND DISTANCE FROM GYPSUM STACK & COOLING POND



ORTHO-PHOSPHATE CONCENTRATION PROFILES

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FIGURE 13
ORTHO-PHOSPHATE CONCENTRATION PROFILES WITH DEPTH
AND DISTANCE FROM GYPSUM STACK AND COOLING POND

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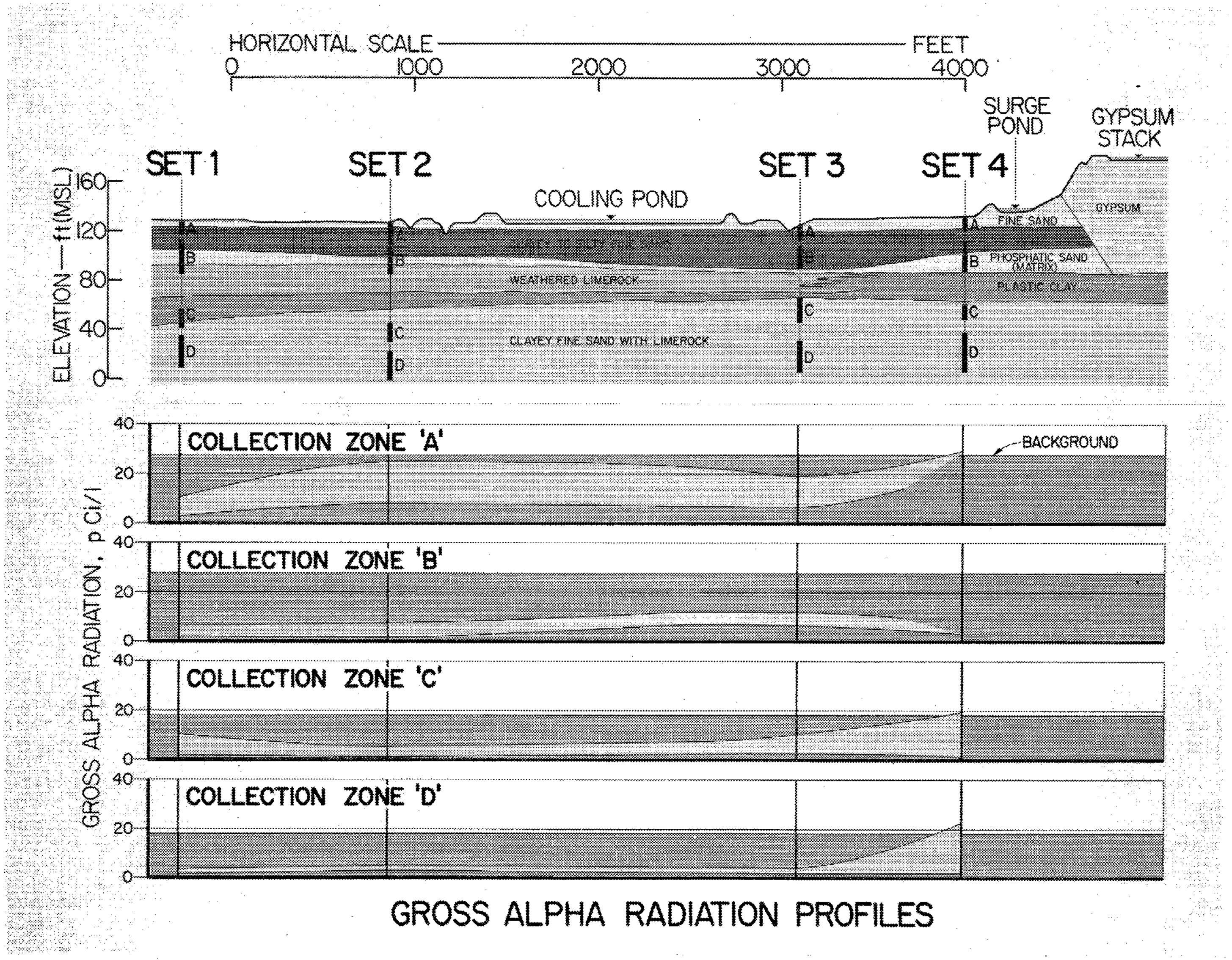

FIGURE 14
GROSS ASPHA RADIATION PROFILES
WITH DEPTH AND DISTANCE
FROM GYPSUM STACK AND COOLING POND

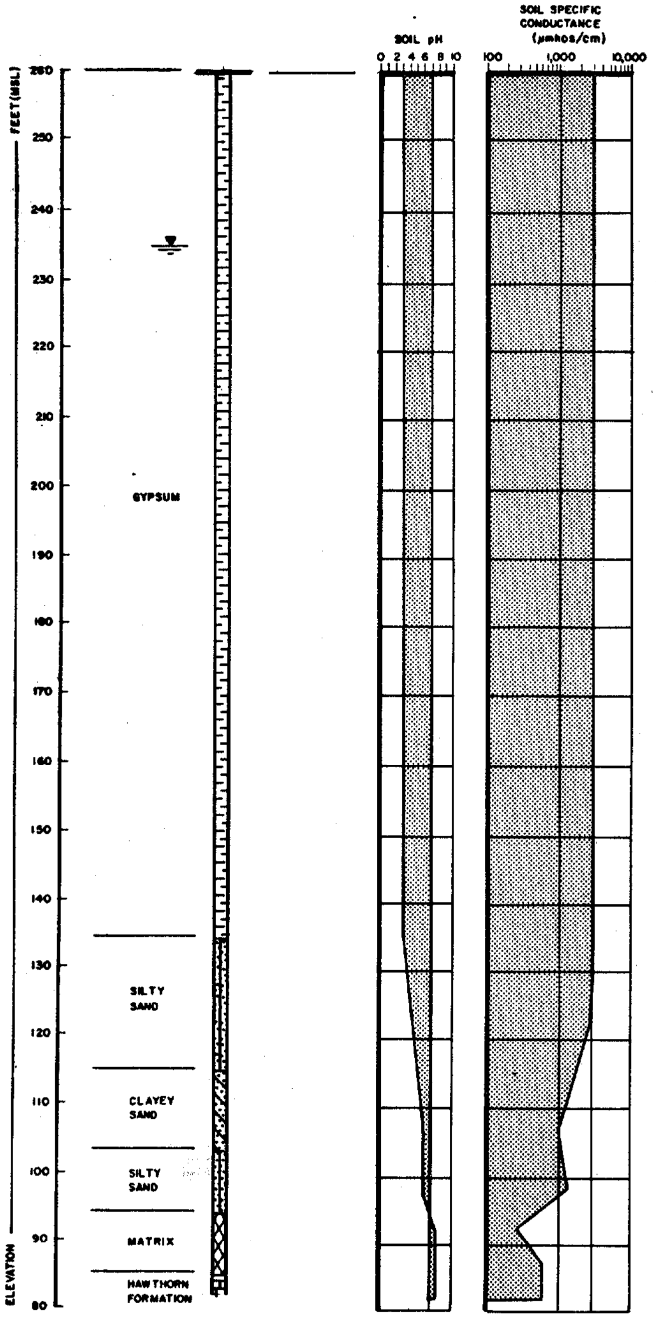

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FIGURE 15
PORE WATER pH AND SPECIFIC CONDUCTANCE
BELOW GYPSUM STACK

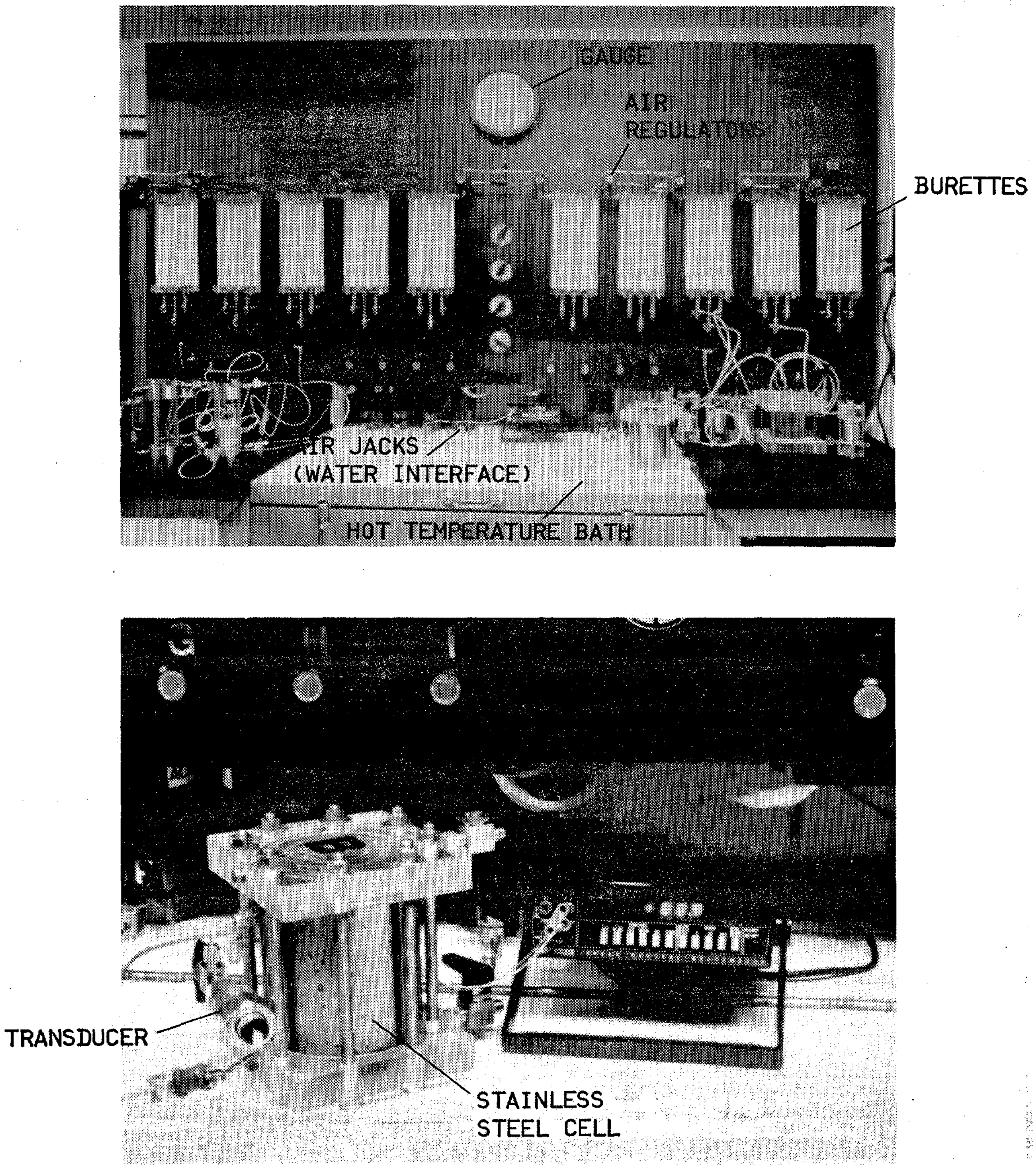

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FIGURE 16
PERMEABILITY/LEACHING TEST EQUIPMENT
STAINLESS STEEL PERMEAMETERS

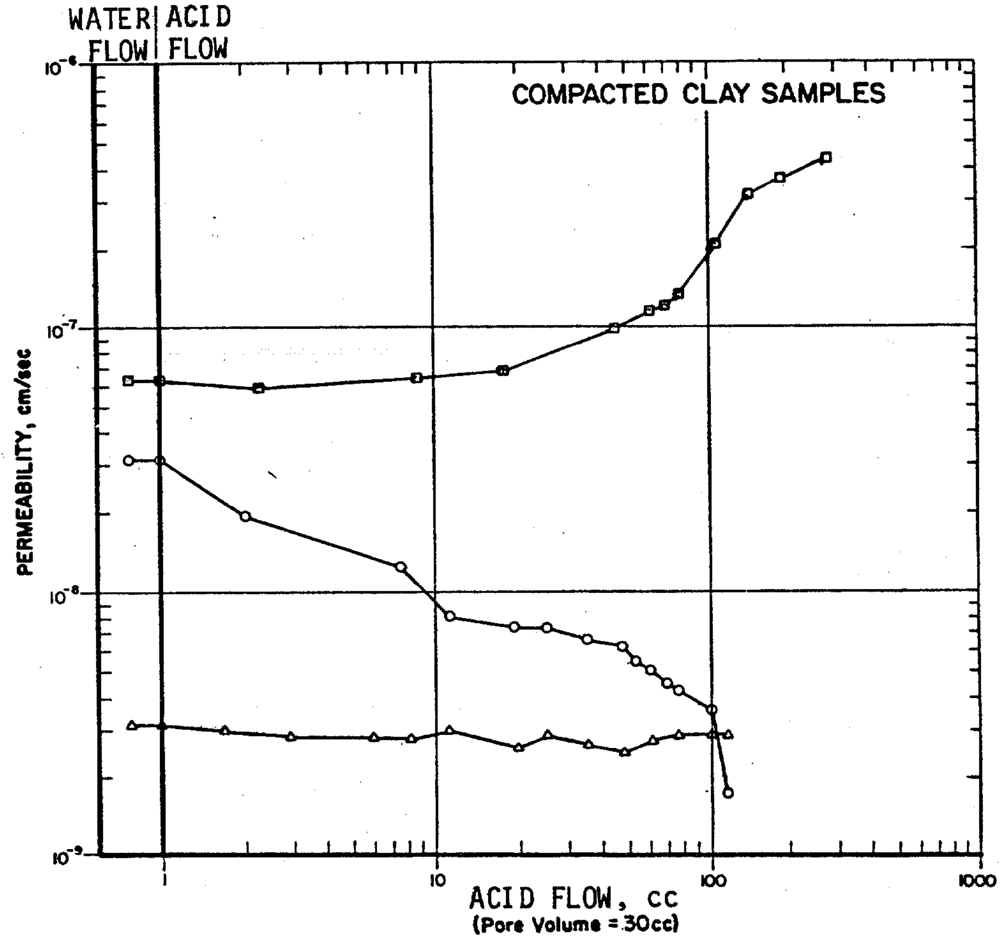

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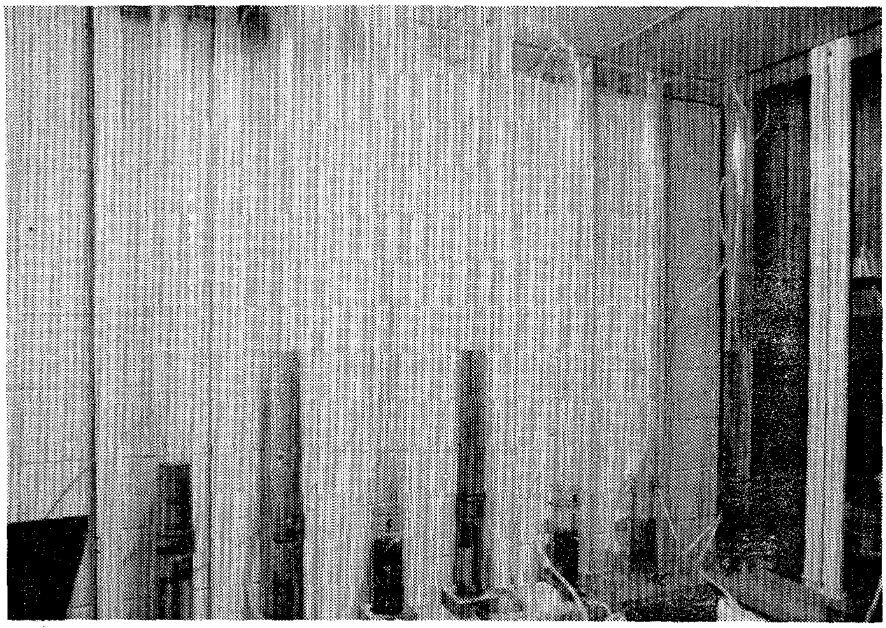
FIGURE 17
EFFECT OF ACID LEACHING ON PERMEABILITY
OF VARIOUS COMPACTED CLAY SAMPLES



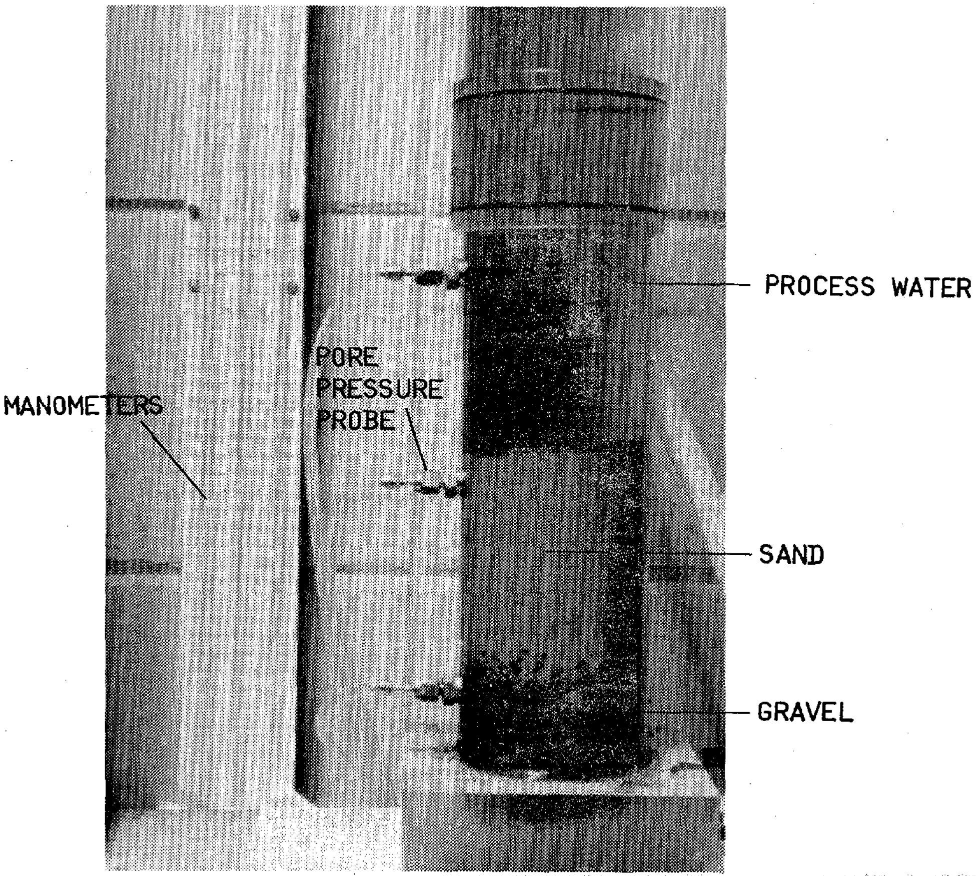


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FIGURE 18
PERMEABILITY/LEACHING TEST EQUIPMENT
FOR DRAIN MATERIAL EVALUATION

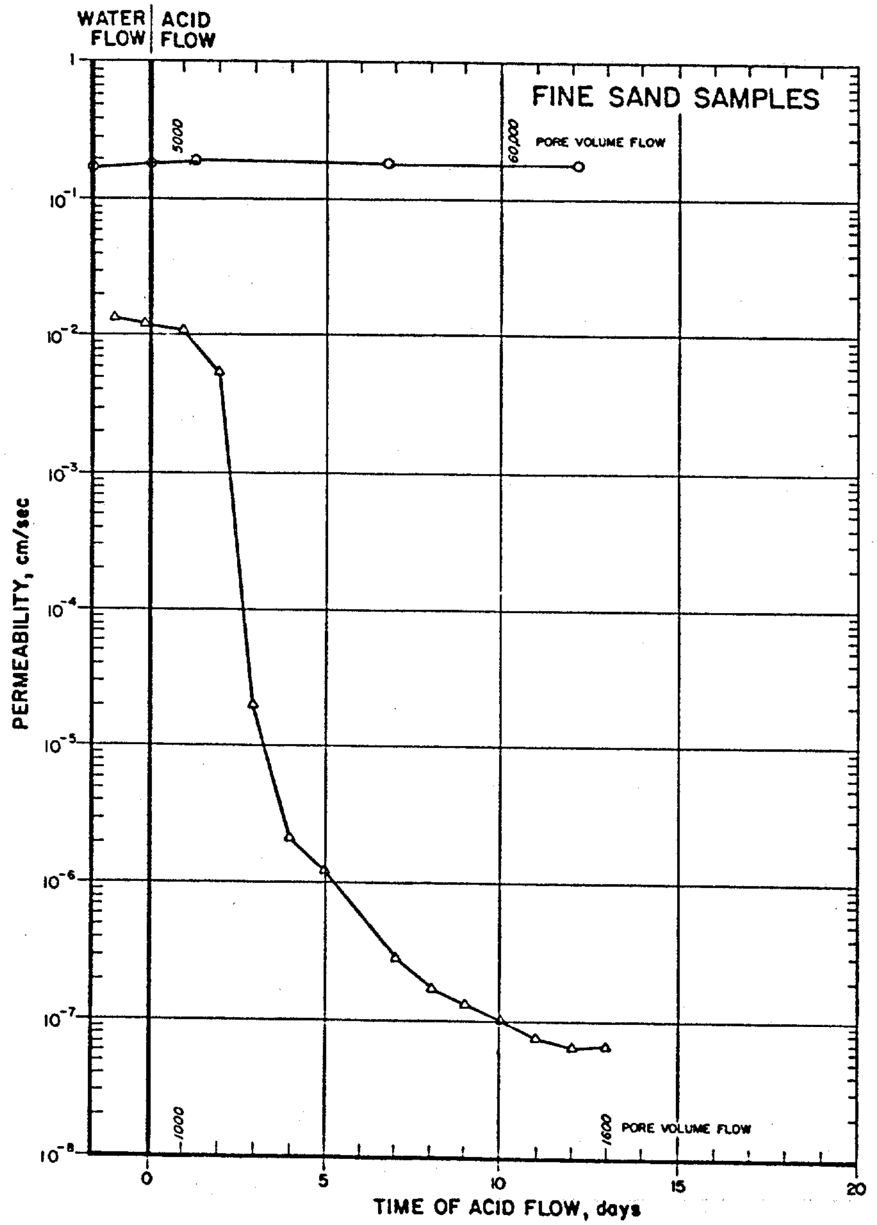

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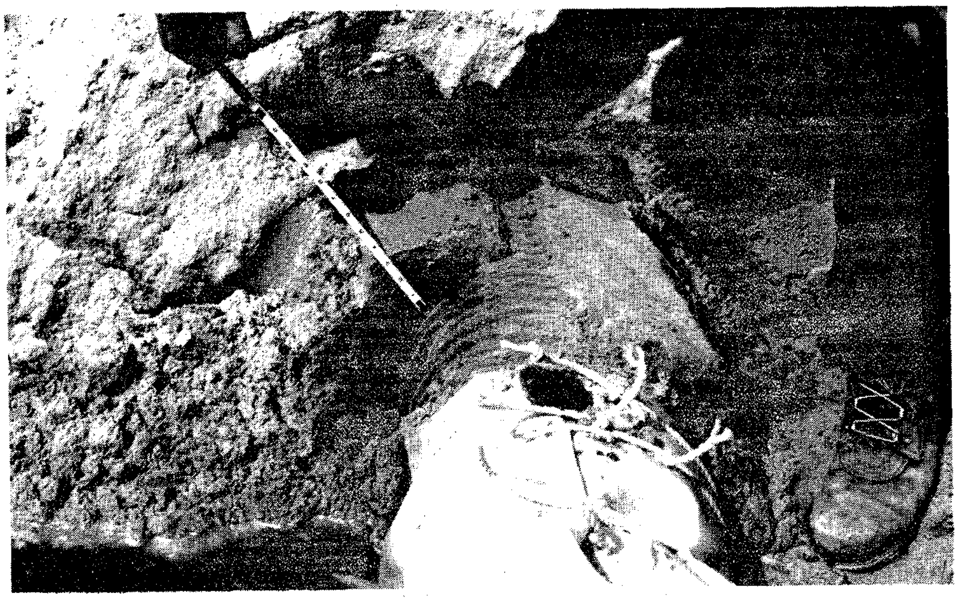
FIGURE 19
EFFECT OF ACID LEACHING ON PERMEABILITY
OF TWO DIFFERENT DRAIN MATERIALS



(a) CEMENTED CAKE FORMED AROUND DRAIN PIPE

(b) CEMENTED MATERIAL

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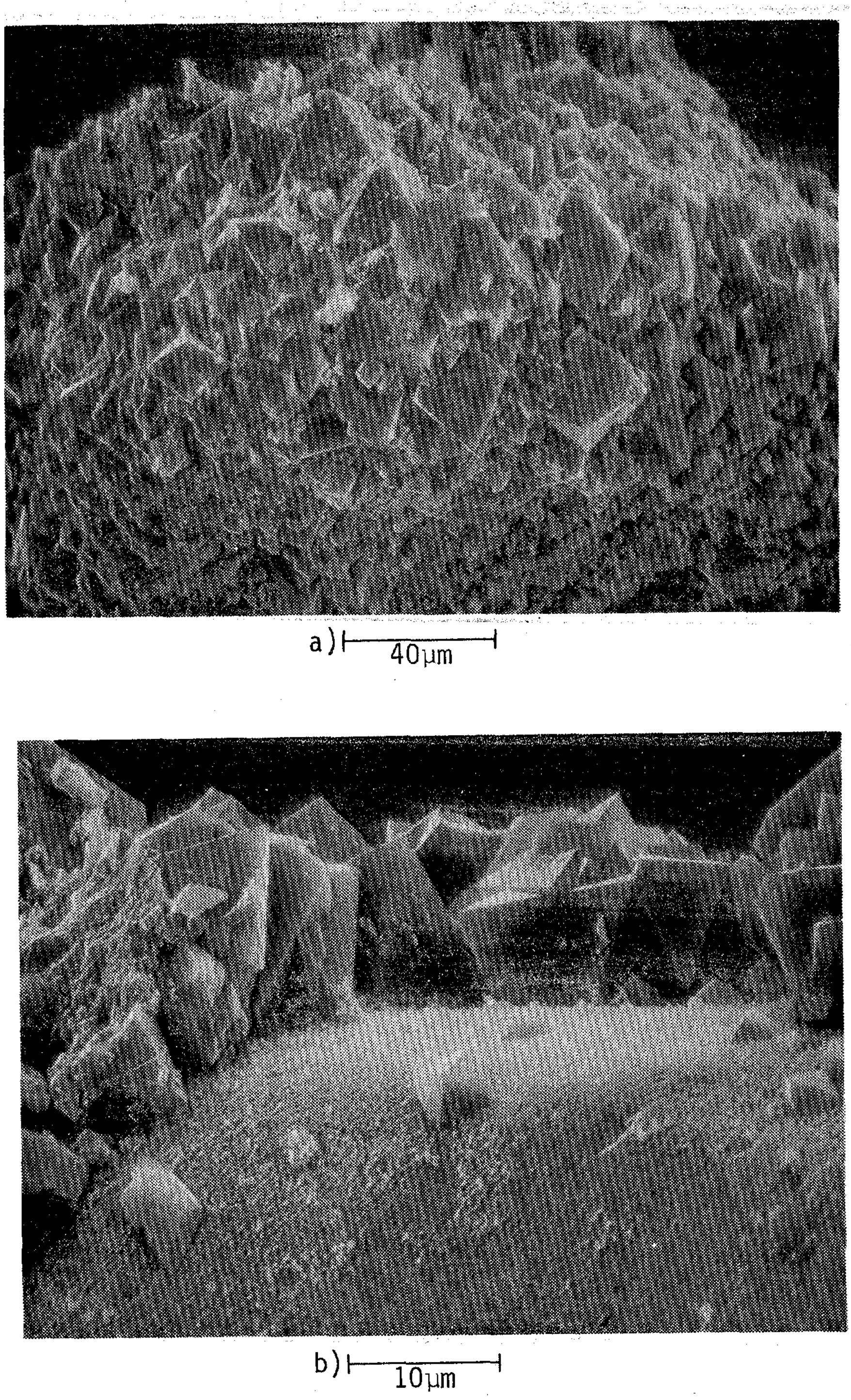
FIGURE 20
CEMENTATION OF DRAIN MATERIAL



Scanning Electron Photomicrographs Showing Ca-Al-S Octahedral Crystal with Silicon Dust on a Quartz Grain.

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FIGURE 21
SCANNING ELECTRON
PHOTOMICROGRAPHS

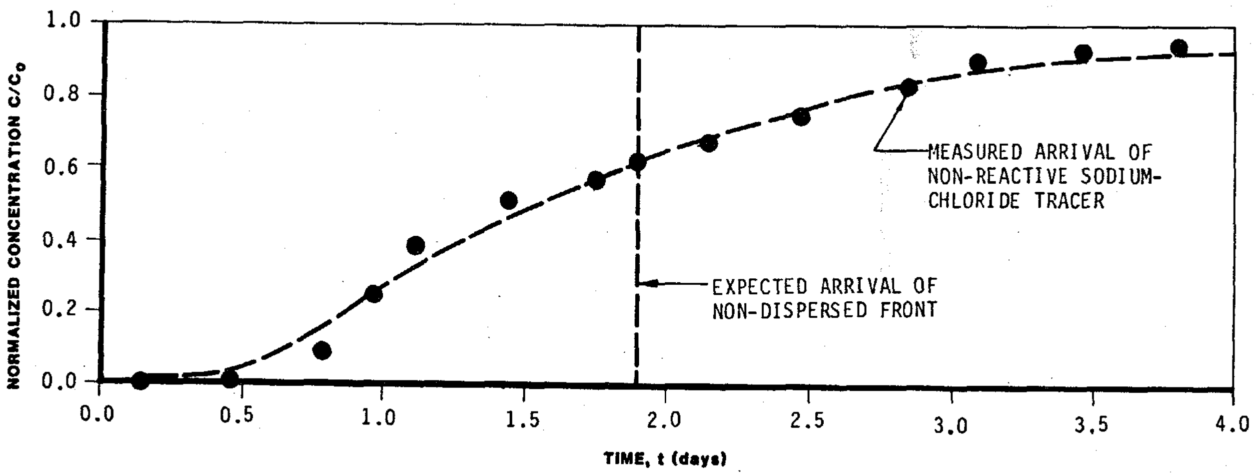

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FIGURE 22
MEASUREMENT OF DISPERSIVITY IN A FINE SAND

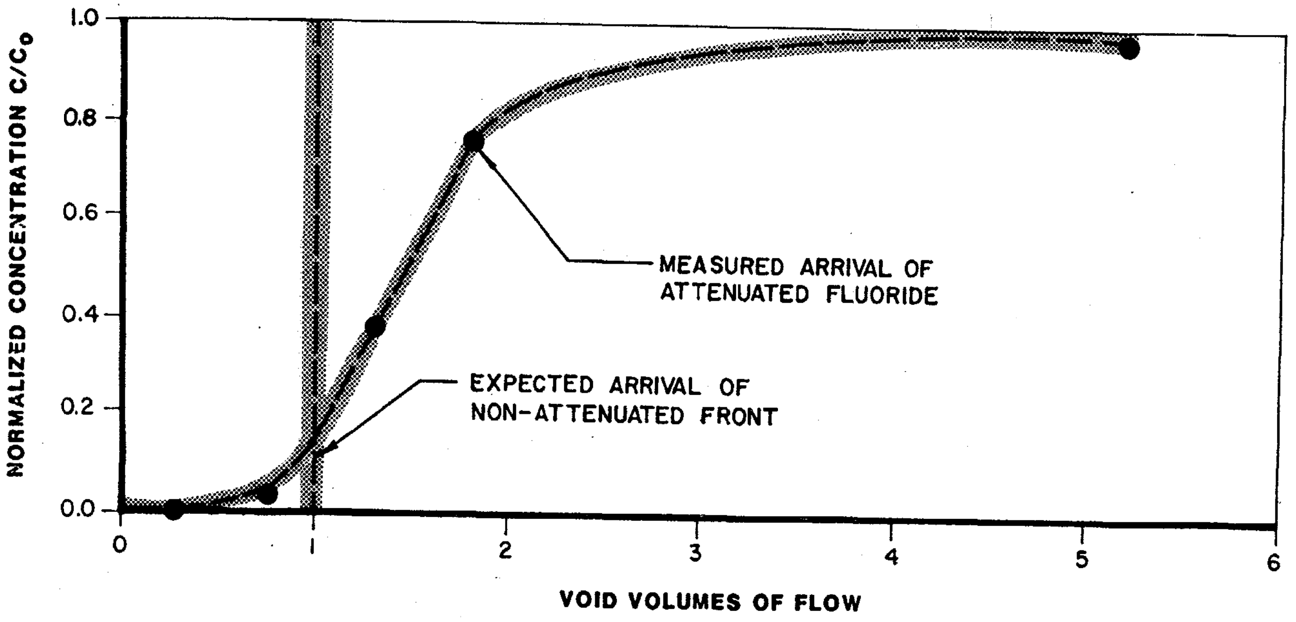

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FIGURE 23
MEASUREMENT OF FLUORIDE ATTENUATION
CAPACITY OF A FINE SAND

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FIGURE 24

BIOLOGICAL REDUCTION OF SULFATE
BY DESULFOVIBRIO

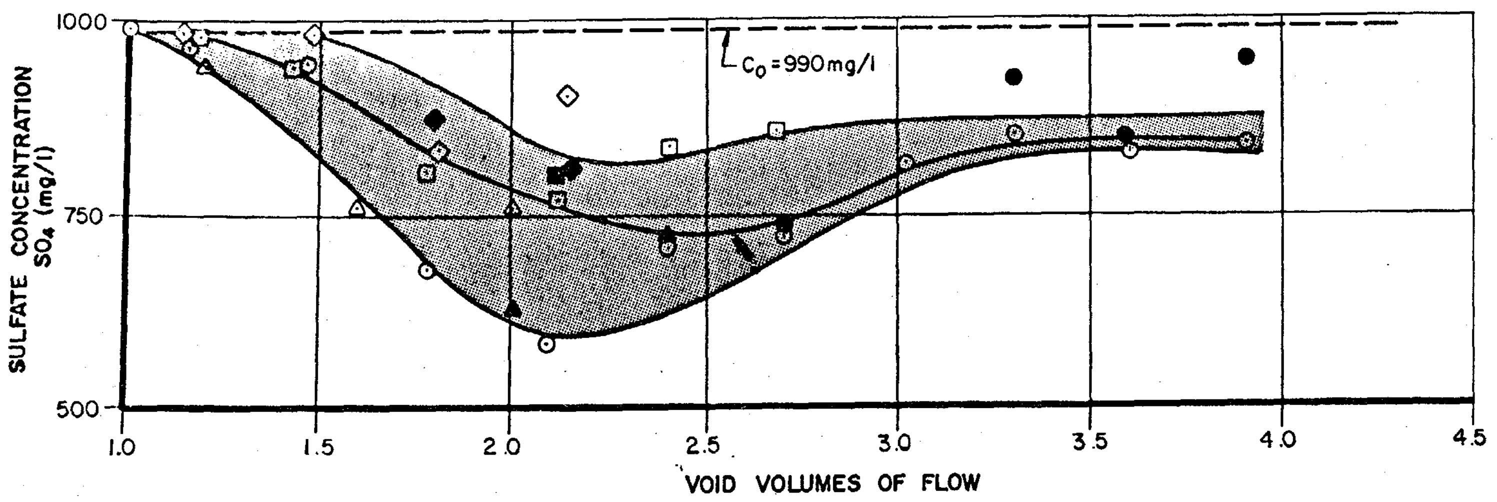

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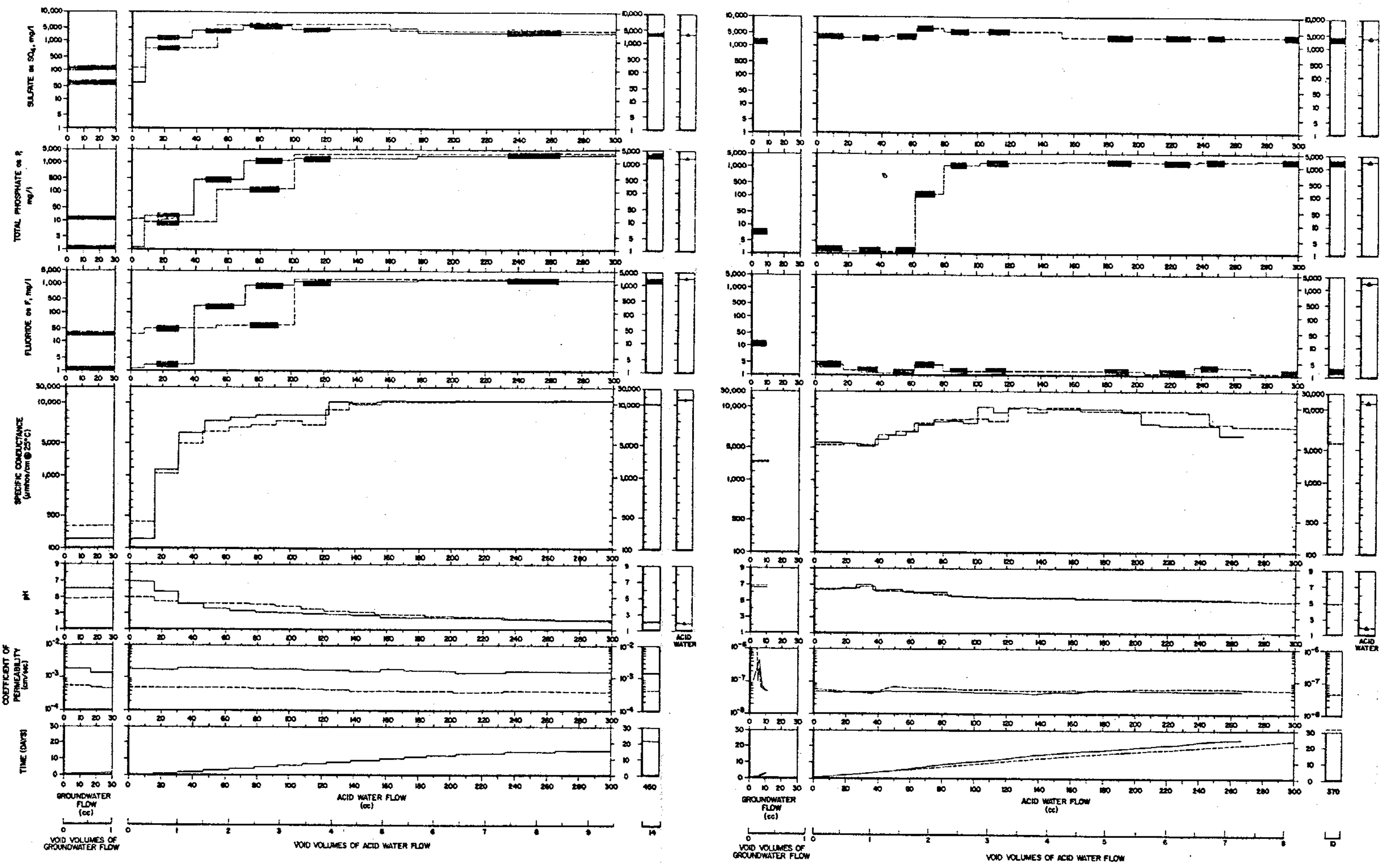
FIGURE 25
LEACHING STUDY RESULTS
FOR SANDY AND CLAYEY SOILS



LEACHING STUDY RESULTS FOR SANDY SOILS

LEACHING STUDY RESULTS FOR A CLAYEY SAND

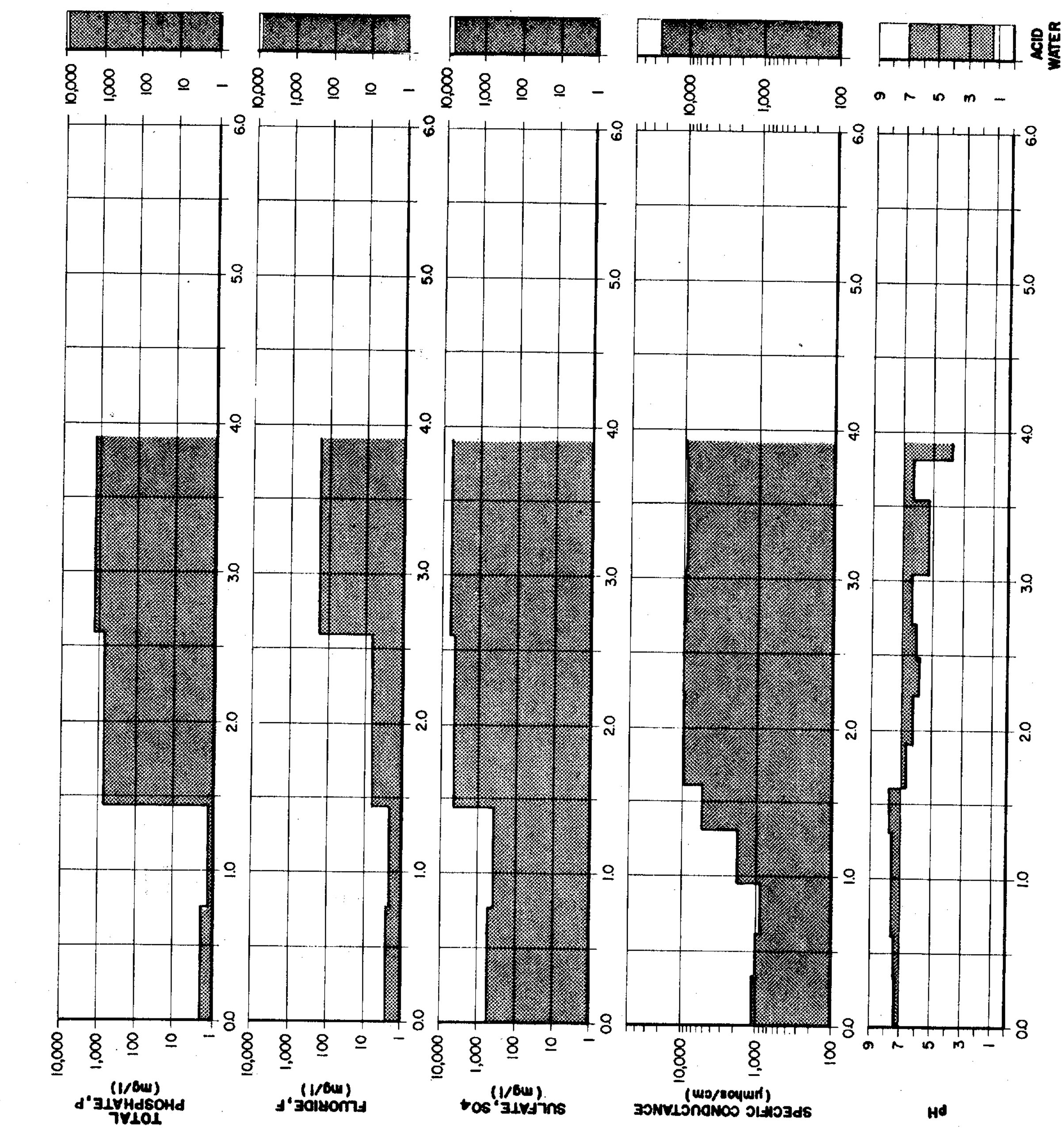


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FIGURE 26
LEACHING TEST ON DOLOMITIC LIMESTONE
FROM HAWTHORN FORMATION

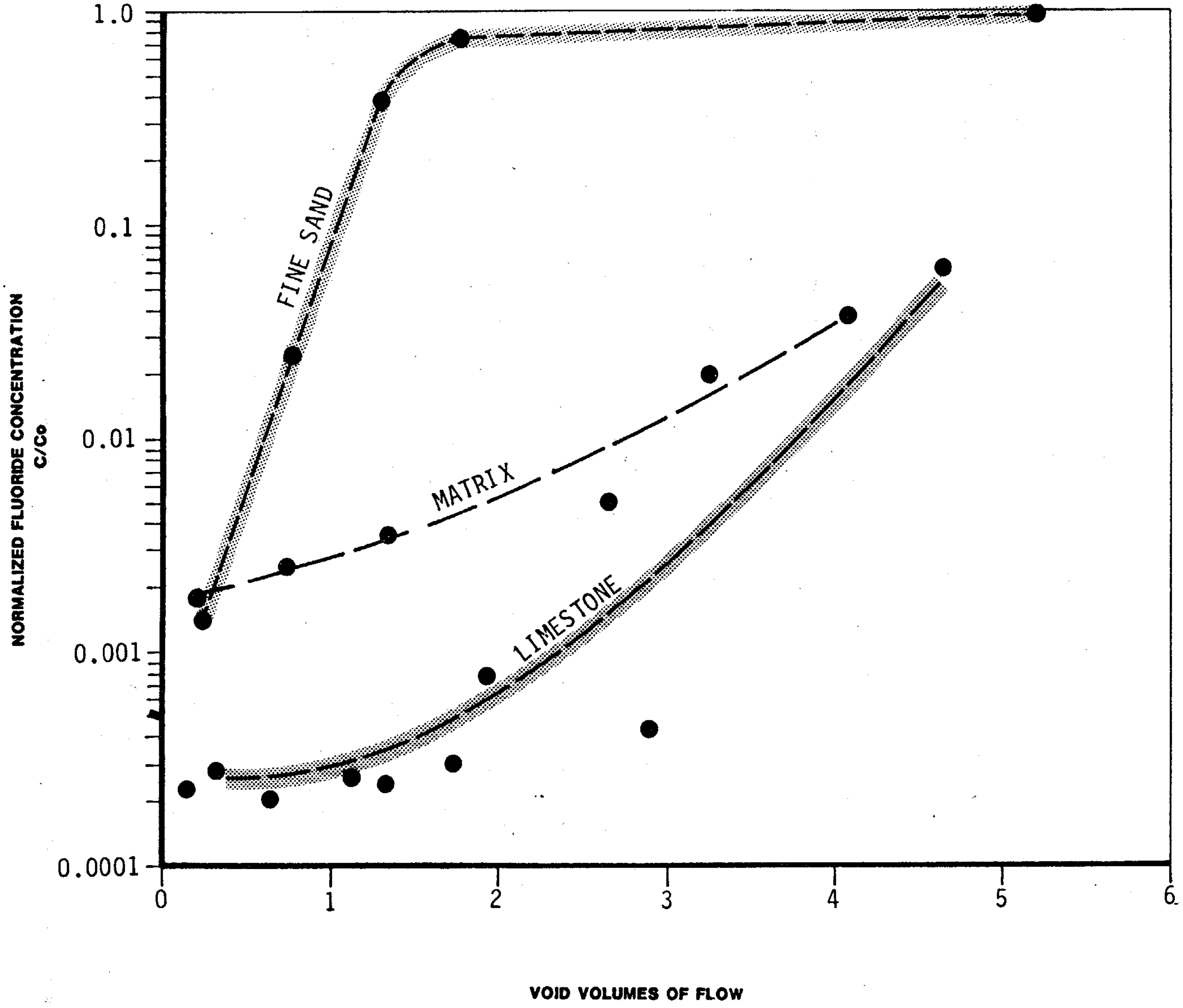

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FIGURE 27
MEASURED FLUORIDE ATTENUATION
CAPACITY OF VARIOUS MATERIALS

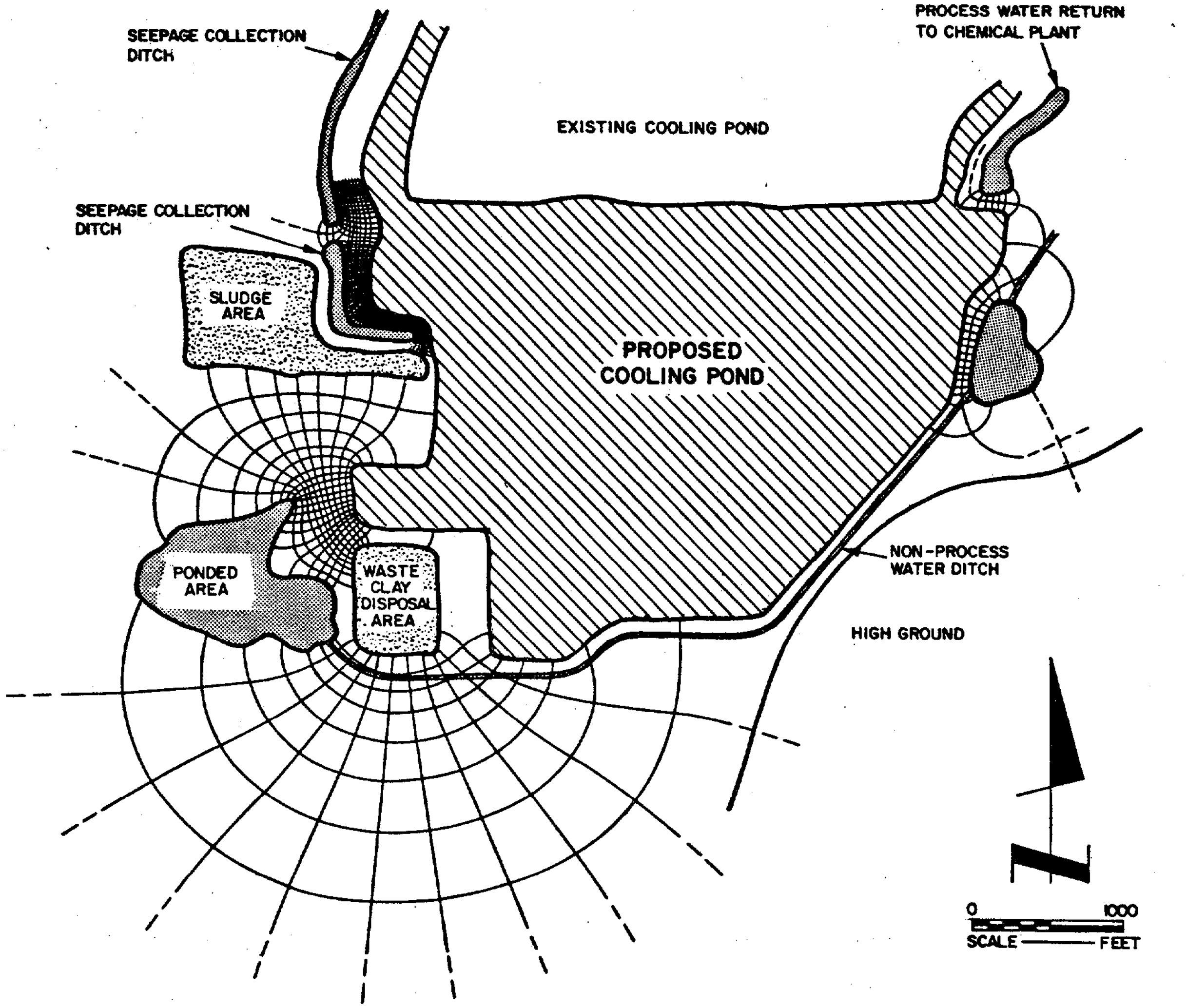

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FIGURE 28
FLOW PATTERN FOR SEEPAGE
WITHIN THE SURFICIAL AQUIFER

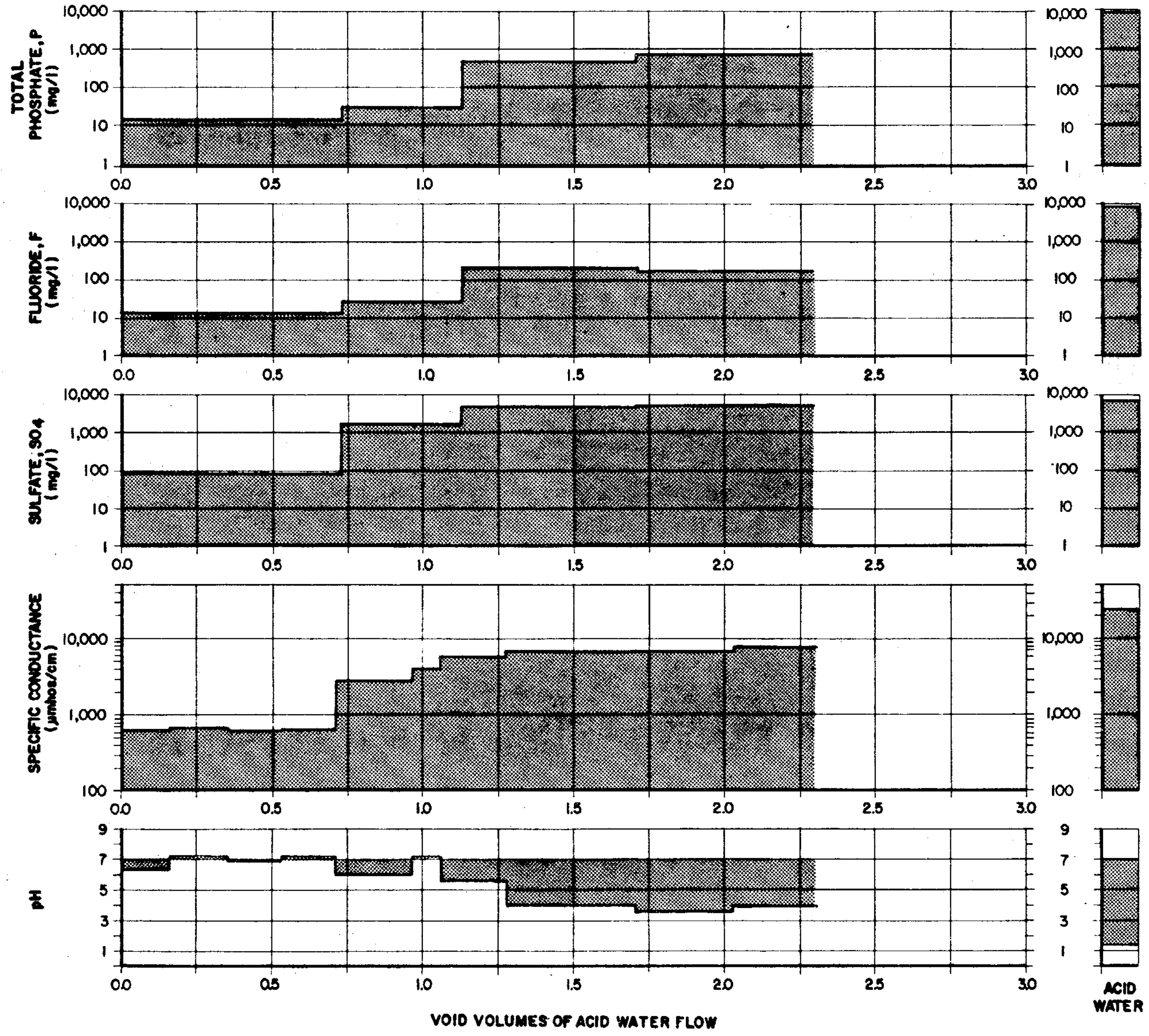

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FIGURE 29
LEACHING TEST ON MODEL STRATIGRAPHY
OF SURFICIAL DEPOSITS

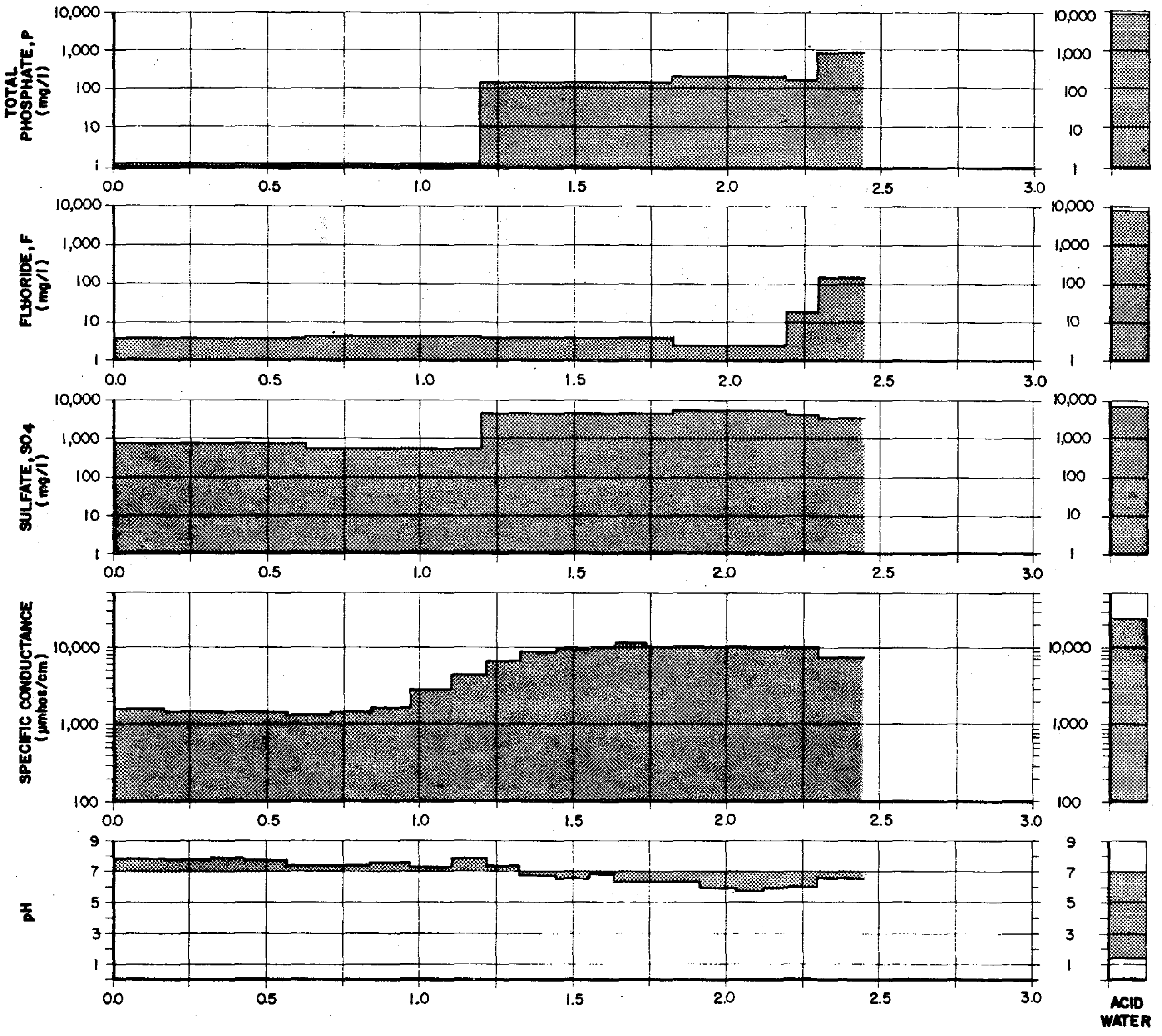

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FIGURE 30
LEACHING TEST ON MODEL STRATIGRAPHY
OF HAWTHORN FORMATION

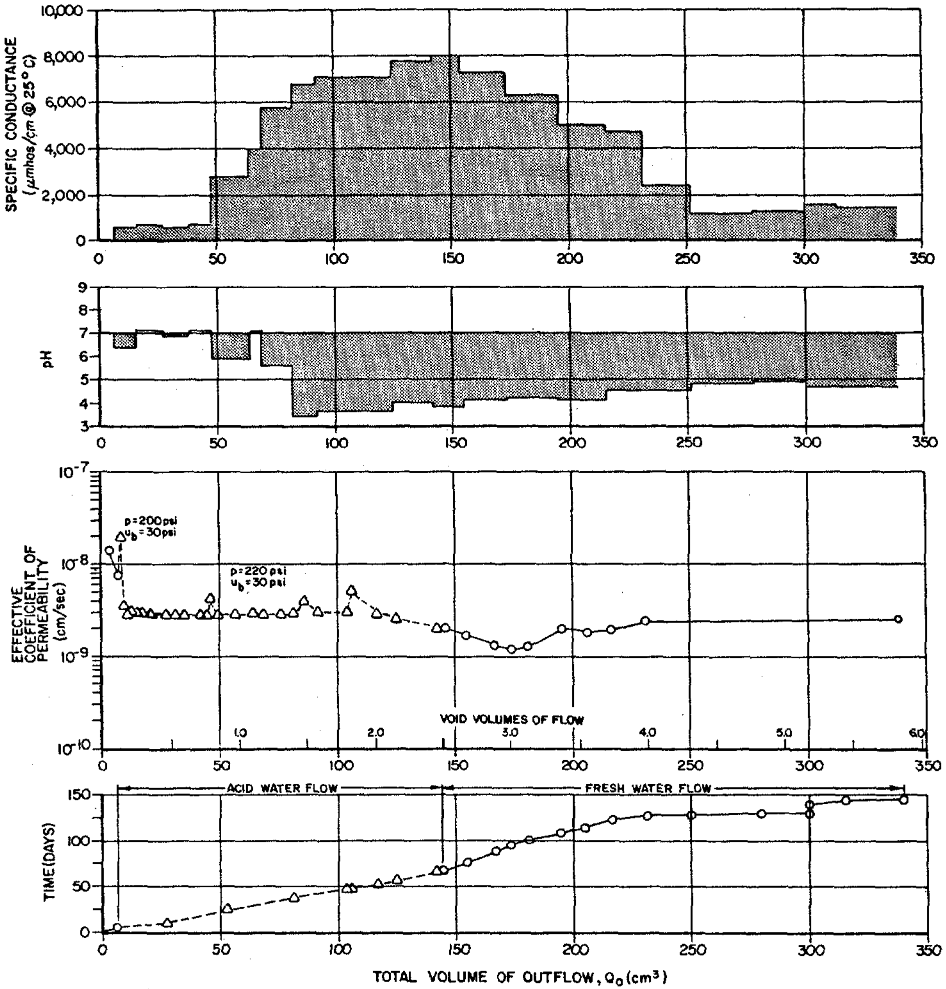

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FIGURE 31
LEACHING STUDY RESULTS SIMULATING
LONG-TERM EFFECTS OF LEACHATE SEEPAGE
AND SUBSEQUENT FRESH WATER FLUSHING