

# FUNDAMENTAL STUDIES OF PORTLAND CEMENT CONCRETE, PHASE II

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BY

S. DIAMOND

D. W. HADLEY

W. L. DOLCH

# JHRP

JOINT HIGHWAY RESEARCH PROJECT

PURDUE UNIVERSITY AND  
INDIANA STATE HIGHWAY COMMISSION



Interim Report

FUNDAMENTAL STUDIES OF PORTLAND CEMENT CONCRETE, PHASE II

TO: J. F. McLaughlin, Director  
Joint Highway Research Project

May 16, 1972

Project: C-36-61E

FROM: H. L. Michael, Associate Director  
Joint Highway Research Project

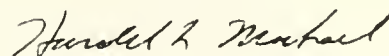
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Attached is an Interim Report on Phase II of the HPR research study titled "Fundamental Studies of Portland Cement Concrete, Phase II". Messrs. Sidney Diamond, D. W. Hadley and W. L. Dolch are the authors and present a summary and detailed description of progress on the study.

A proposal for Phase III, the final phase, of the study to be initiated July 1, 1972, is being submitted under separate cover.

The Interim Report is presented for acceptance as partial fulfillment of the objectives of the study and especially of Phase II. The report will be forwarded to ISHC and HPR for review, comment and similar acceptance.

Respectfully submitted,



Harold L. Michael  
Associate Director

HLM:ms

cc: W. L. Dolch	M. E. Harr	M. B. Scott
R. L. Eskew	R. H. Harrell	J. A. Spooner
W. H. Goetz	M. L. Hayes	N. W. Steinkamp
W. L. Grecco	R. D. Miles	H. R. J. Walsh
M. J. Gutzwiller	J. W. Miller	K. B. Woods
G. K. Hallock	C. F. Scholer	E. J. Yoder

Interim Report

FUNDAMENTAL STUDIES OF PORTLAND CEMENT CONCRETE, PHASE II

by

S. Diamond, Research Associate  
D. W. Hadley, Graduate Instructor in Research  
W. L. Dolch, Research Associate

Joint Highway Research Project

File No.: 5-14-5

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Prepared as Part of an Investigation

Conducted by

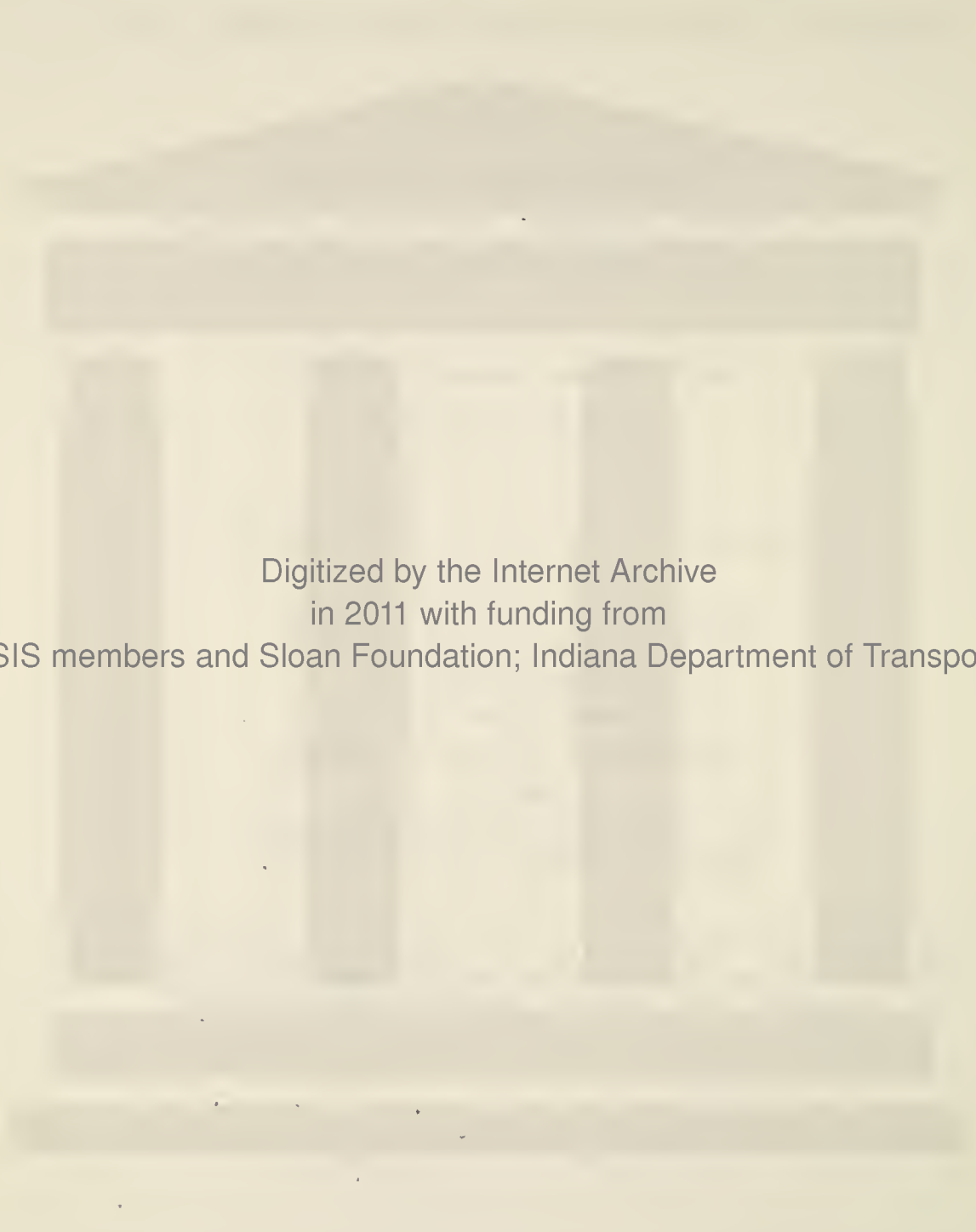
Joint Highway Research Project  
Engineering Experiment Station  
Purdue University

In cooperation with the  
Indiana State Highway Commission  
and the

U.S. Department of Transportation  
Federal Highway Administration

The opinions, findings and conclusions expressed in this publication are those of the authors and not necessarily those of the Federal Highway Administration.

Purdue University  
Lafayette, Indiana  
May 16, 1972



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## INTRODUCTION

This report is a summary and detailed description of progress in Phase II of the above-named project, which was approved in 1969. Phase I of the project was started July 1, 1967, and a final report on Phase I was submitted early in 1969.

Phase II is scheduled to be completed June 30, 1972, and a proposal for Phase III is being submitted simultaneously with this report. It is hoped that approval of Phase III will permit uninterrupted progress in this productive research area.

The plan of study for Phase II was divided for convenience into two distinct but related areas of research: (a) the micro-structure of hydrated cement paste, and (b) interaction between paste and aggregate. Many of the techniques used are common to both areas, and interaction between work in the two areas has been helpful.

### MICROSTRUCTURE OF PORTLAND CEMENT PASTE

Progress in this area has been extensive. Three papers have been presented at technical society meetings, as follows:

1. "Effects of Hydration Temperature on Pore Structure and Microstructure of Hydrated Cement Paste" by Sidney Diamond, American Ceramic Society Symposium on Cements, 72nd Annual Meeting, Pittsburgh, May 1970.
2. "Examination of Cement Paste Constituents by X-Ray Spectrometer Attachment to the SEM" by Sidney Diamond, American Ceramic Society Symposium on Cements, 73rd Annual Meeting, Chicago, April 1971.

3. "Modes of Occurrence of Calcium Hydroxide in Hydrated Cement Paste" by Sidney Diamond, Annual Meeting, American Society for Testing and Materials, Atlantic City, June 1971.

Of these papers, one has been submitted for approval for publication, and the others will be submitted in the near future. Abstracts of the papers are provided in the Appendix.

The results so far obtained in this portion of the project are discussed below under several specific headings. The general objective was to develop new and if possible quantitative methods of examining the microstructure of hydrated cement paste and to explore the influence of the microstructure on the behavior of the material.

- (1) Pore-Size Distribution and Coordinated Studies of the Same Pastes

This was the primary subject of Phase I of this research, the results of which were earlier presented in final report form ("The Pore Size Distribution of Portland Cement Paste", D. N. Winslow, J.H.R.P. Report No. 31, Dec. 1968) and published as "A Mercury Porosimetry Study of the Evolution of Porosity in Portland Cement Paste", D. N. Winslow and S. Diamond, J. Materials 5, 564-585 (1970). The evaluation of pore size distributions has continued in Phase II, and the kinds of cement pastes examined have been broadened to include pastes hydrated at high and low temperatures and pastes to which commercial retarders and accelerators have been added. Particularly critical study has been made of the effects of temperature, in that many other parameters in addition to pore

size distribution were evaluated for the same specimens. These include x-ray diffraction investigations of the content of lime,  $C_3A$ ,  $C_3S$ ,  $C_2S$ , ettringite, and calcium aluminate monosulfate-12-hydrate, measurements of total pore space, density, degree of hydration, "threshold diameter", and percentage of pore space intrudable at 15,000 psi pressure of mercury. At the same time examinations were carried out on the pastes by scanning electron microscopy.

The samples included pastes with water/cement ratios of 0.4 and 0.6 and hydrated for periods of from one day to two years.

The water:cement ratio seems to be the criterion that most strongly influences the paste structure. Pastes of 0.4 W:C were much more compact, less porous, and less intrudable to mercury than companion 0:6 W:C pastes of similar ages. The effect of temperature seems to be less pronounced than had been anticipated. Specimens hydrated at higher temperatures had a pore size distribution keyed to a finer size range, a lower mean pore size, a lower "threshold diameter", less pore space intruded, and lower densities than similar specimens hydrated at lower temperatures. However, the magnitude of the differences decreased with time. Some of the differences were directly relatable to the degree of hydration attained in a given time, which was of course higher for samples hydrated at higher temperatures. But the differences in pore size distributions do not quite disappear even when samples are compared at equal degree of hydration; when this is done, the differences in pore size distribution between samples hydrated



at low temperature (6°C) and "normal" temperature (24°C) disappear, but samples hydrated at higher temperature (40°C) seem to have a more open and coarser-textured pore system. It should be noted that by "equal degree of hydration" is meant equal amount of non-evaporable water. It is apparent from the x-ray diffraction results that hydration does not proceed uniformly for the several cement constituents at different temperatures, but rather that the pattern of hydration is conditioned by the temperature used. Overall, the rate of hydration of  $C_3S$  was slower than that found by some other workers, and the hydration of  $C_2S$  was very much slower. In fact, after six months the hydration of  $C_2S$  at 6° was barely detectable, in terms of a reduction of the height of the x-ray peak of  $C_2S$  that was used as a criterion.

It was found impossible, except for the lime, to quantify the accumulation of the hydration products, since their x-ray peaks were, as expected, weak and broad. It was definitely indicated that the same hydration products (calcium silicate hydrate gel, ettringite, and calcium aluminate monosulfate-12-hydrate) were produced at all temperatures. As expected, the content of ettringite diminished with time, and it all but disappeared after 60 days at all temperatures. However, it was not expected that the content of the "monosulfoaluminate" would also be substantially reduced by 60 days, even at low temperature. It appears that much of the sulfate eventually finds its way into the calcium silicate hydrate gel phase.

The pattern of deposition of lime with time and temperature was also different from that expected. The x-ray diffraction peak for lime was found to be essentially as strong after two days as it was for periods of continued hydration, even up to 180 days; this was true for all temperatures. The significance of this finding is not clear, since it conflicts with the microscopical observations of the growth of massive crystals of lime through the paste structure at later ages.

Examination of the pastes by scanning electron microscopy suggested that there were no drastic differences in the morphologies of the products produced at the different temperatures. The main differences noted were that the "cold" pastes seemed to have a greater tendency to generate calcium silicate hydrate of the short-fibered cluster morphology than did the others.

The effect of various admixtures on the structure of the paste was examined by pore-size distribution studies and by scanning electron microscopic examination. The admixtures were two commonly-used retarders, one of the hydroxycarboxylic acid type, and the other a reducing sugar, and a commonly used accelerator, calcium chloride. The focus of the investigation was not the effect on early periods incident to the retardation or acceleration of set, but rather any influence the admixture might have on the structure developed in the pastes over a longer term. All the pastes were mixed at a W:C of 0.6 and were hydrated at room temperature.

In general, the pore-size-distribution data indicated that the pastes with the admixtures developed pore structures not greatly different from those of ordinary paste. The two retarders yielded pore size distributions that were almost duplicates of each other. Initially these were somewhat "tighter", i.e. somewhat finer-pored, than untreated pastes. By two weeks of age this difference had disappeared. The curves for older retarder-bearing pastes were similar to those for pastes of a corresponding age that had no admixture.

The effect of calcium chloride was more difficult to characterize. At early ages, up to a week or so, the pore size distribution of these pastes was broader than that of untreated paste. There was a greater content of relatively large pores (diameters from about 1  $\mu\text{m}$  down to about 1500 A) and also a greater content of the finer sizes (500 A to about 85 A). The tendency toward the greater content of the larger pores diminished and more or less disappeared after a few months, but the tendency toward a greater proportion of the finer sizes was maintained indefinitely, indicating that some permanent difference in structure persists with time in pastes containing calcium chloride.

Observation of these pastes by scanning electron microscopy was carried out to a limited extent to see if any major differences could be detected. Tentatively, it was found that comparatively little difference could be detected between the retarder-treated pastes and non-treated pastes, but that the young  $\text{CaCl}_2$ -treated pastes showed a somewhat greater proportion of field in which the peculiar "reticulated network" morphology

was prominent. This microstructure consists of intertined fibrous structures growing together in a mesh arrangement, leaving holes of the order of several thousands of Angstroms. Presumably these holes show up in the pore size distribution curves as the relatively coarse pores found in excess with  $\text{CaCl}_2$ -treated pastes at young ages. As the paste matures, these holes presumably get plugged by material deposited continuously through the paste (mostly lime), and they diminish in size. It should be stressed that the above interpretations are tentative, and much work needs to be done in terms of viewing additional fields before they can be considered experimentally valid. Only a comparatively small number of micrographs were taken of these samples.

(2) Studies of the Microstructure Using the Scanning Electron Microscope and the Energy-Dispersive Spectrometer Attachment

Considerable time was spent in attempting to define the characteristic microstructural units comprising hydrated cement and in analyzing these units with the energy-dispersive x-ray spectrometer attachment. The morphology is exceedingly complex and variable, and only a summary of the results can be provided here.

At early ages (of the order of a day or two) the paste consists of residual grains of cement, largely covered by spines of hydration product, and with large spaces (of the order of several microns) left essentially vacant. A few fields show the presence of large rod-shaped particles, many microns long,

that were originally interpreted as being ettringite crystals; subsequent analysis has cast doubt on this identification. Many of the spiny growths projecting from the residual cement grains are branched, dendritic structures. These are identified as one form of calcium silicate hydrate gel. Other particles tend to be rod-shaped with blunt ends, and may be ettringite. The dendritic structures are also found as small (one to two micron) clusters that seem to be deposited in the water-filled spaces between the positions of the original cement grains. Most lime in pastes of this age seems to be confined to relatively thin crystals and films. There are areas of "reticulated network" structure, which presumably are regions where growing dendritic branches have overlapped each other and joined. The result is a region of open network structure with a spongy appearance and large volume of more or less equal-sized pores of the order of 2000 to perhaps 5000 A diameter.

Noteworthy changes take place as the cement paste matures. The small globular clusters and the spines surrounding the original cement grains tend to grow together. The residual content of voids progressively diminishes. Deposits of filmy material, largely lime, forming on the surfaces of these particles fill in the holes in the reticulated network. The lime crystals increase in size and visibility. They grow through regions of gel and of residual cement grains and incorporate and encapsulate regions of paste. The appearance of these crystals is distinctive; they are smooth-textured and have parallel edge directions, which indicates they are

basically growths of single-crystal orientation.

As growth proceeds there is evidence that some of the residual cement grains dissolve from within their shells of hydration products. Also, mechanical disturbance during the fracturing of the sample causes other changes. In consequence, regions that appear to be relict portions of hydration rims are occasionally observed, and regions that are identified as porous relicts of the inner cement grains, presumably now partly or fully hydrated as the so-called "inner hydration product" may be found. Thin, hexagonal plates identified as calcium aluminate monosulfate-12-hydrate are occasionally observed at intermediate ages. Occasionally a rounded grain of non-porous residual unhydrated cement, often  $C_2S$ , is uncovered.

As the paste continues to mature, observation of the microstructure becomes increasingly difficult. Secondary deposits tend to fill in the cavities. The texture approaches a more massive appearance. However, the distinction between areas of massive lime crystals, with gel and other constituents incorporated locally, and regions of gel is always readily made; it is the gel that becomes more difficult to characterize.

There is one point of seeming conflict between these observations and those recorded previously under the section devoted to pore size distribution. This has to do with the deposition of lime in the paste. So far as the x-ray diffraction results are concerned, it appears that the calcium hydroxide content after about two days of hydration is as

large as it ever gets. In contrast, the qualitative appearance observed in microscopy suggests that more and more calcium hydroxide deposits with time, and lime growth continues for weeks or months. Obviously, further work is required to resolve this apparent anomaly.

The identification of particular kinds of particles rests largely on studies of the chemical composition of selected small areas by means of the element-dispersive x-ray spectrometer attachment. This is the first time such a device has been applied to this field of work, and problems arose. Fortunately it was found that the ratio of x-ray counts for particular pairs of elements was linearly related to the mole ratio of these elements in materials of known composition. The materials used were cement compounds, pure compounds of hydrates of calcium aluminates and aluminate sulfates, tobermorite, and several related materials. Calibration curves were constructed, the use of which provided the means for determining the ratios of calcium to silicon, sulfur, etc. on the small areas in the cement paste samples.

It was found difficult precisely to specify the size of the areas contributing to the analysis. Theoretical developments are available relating areal and depth spread of the region being excited to the voltage of the electron beam, the density of the material, and the chemical elements present. However, these interpretations do not take into account sample roughness, tilt of the specimen surface, and the presence of voids in the region under analysis. It appeared that the region contributing

to the x-ray analysis is a bulb-shaped zone perhaps 1 1/2 microns wide and 2 microns deep surrounding the point of impact of the electron beam. Useful analyses of features on a micron scale is therefore possible, but there are many features in cement pastes (particularly needles, thin plates, etc.) that seemingly cannot be analyzed unequivocally by this method owing to the spread of the excited zone to adjacent microstructural units.

Despite these difficulties, hundreds of analyses were carried out and a number of conclusions can be drawn. The universal content of sulfur in the calcium silicate hydrate gel was confirmed, and the general level found was in accord with expectations derived from the work of others. The calcium:silica ratio of the calcium silicate hydrate gel was found almost always to be between 2 and 3, rather than between 1.3 and 1.8 or so, as had been indicated previously on the basis of indirect measurements on hydrated  $C_2S$  and  $C_3S$  pastes. The presence of gel can be detected even encapsulated in massive lime crystals by the content of sulfur and silica that appears in the analysis for such regions. Conversely, other regions may contain relatively pure lime, and essentially no sulfur or silica is detectable.

As one of the many special studies that came out of this general line of research, a catalogue was made of the many shapes and morphologies assumed by calcium hydroxide in cement pastes. These ranged from thin, amorphous-looking films and



thin plates at early ages, to thicker, tabular hexagonal crystals and massive anhedral crystals marked by many parallel face intersections at later ages. Special morphologies included thick columnar crystals showing excellent development of prism surfaces that were found in more porous, hydrous regions that develop next to glass or other surfaces in contact with the paste.

(3) Relationship Between Microstructural Character and Physical Behavior of Cement Paste

It was hoped that more would have been accomplished along these lines than has been done to date. The difficulty has been partly the unavailability of a graduate student qualified to carry out this aspect of the research.

There are two aspects under consideration with respect to "physical properties" - mechanical behavior and permeability. The mechanical behavior of pastes include shrinkage on drying, creep, elastic properties, and mechanical strength. The permeability of a porous body is related to its pore size distribution. A few permeability studies have been made on hardened cement pastes, and conclusions have been drawn from the results concerning the structure. It was hoped to get further information in Phase II by making more such measurements. But progress has been confined to the construction of the instrument.

Measurement of the permeability of paste presents some difficulties. The permeant must be water, because drying causes irreversible structural changes. But the permeability is so small that in order to make a determination in reasonable time a relatively large pressure gradient must be used. A permeameter has been built that is of stainless steel, with a suitable sample holder for thin discs of hardened paste, and with the accessories to permit application of a sufficiently high hydraulic pressure. The equipment has been tested and does perform properly, but it has not been yet used on a suite of paste samples.

Both these aspects - mechanical properties and permeability - are the subjects of the proposed Phase III of this project.

## THE PASTE-AGGREGATE INTERFACE

This summary of the work on the nature of the paste-aggregate interface necessarily omits many details. The object of the study was to investigate the nature of the region at or close to the interface between the paste and another solid, i.e., the "aggregate" and to try to determine how this structure develops and how it is influenced by the nature of the solid and the pertinent variables in the paste composition.

The main tool of the investigation has been scanning electron microscopy, although conventional microscopy and x-ray diffraction have also been used.

### Materials and Sample Preparation

Most of the work has been done with cement pastes deposited on the surface of a solid and later removed and studied. For the most part a water/cement ratio of 0.5 was used. The cement was a Type I of ordinary composition.

The pastes were mixed by hand and applied to the surface of the solid as a small pat. The solid most used was glass, in the form of a microscope slide, because of its smoothness as well as its chemical similarity to many silicious aggregates. Other solids used have been quartzite, a high-calcium marble, and various metals and plastics. Some pastes were made with alite and alite plus gypsum and  $C_3A$ . Some studies were also done with mortars made with Ottawa sand and crushed marble. Most of the following summary concerns the results with the glass surfaces.

The pats of paste were cured for various times from one hour to 28 days and then were removed from the slide. Originally the samples were cleaved from the slide by a light blow on a chisel, but it was found that even this comparatively gentle treatment gave a surface so shattered that details were obscured. So it was decided to remove the samples by drying the slide and attached pat in a desiccator over magnesium perchlorate. When this was done, the differential shrinkage produced a crack near the interface and the pat was removed spontaneously with little distraction of detail in the region of the crack. This "shrink-off" method proved to be entirely satisfactory; indeed it was necessary to the production of an appropriate specimen. The method is also probably similar to the processes by which bond separation between paste and aggregate actually occur in field concrete under drying and thermal gradients.

The mortar samples were simply fractured by cleavage. The final sample was prepared for viewing by metal-coating in the usual way. The surfaces of both the removed paste sample and the residual film on the glass were examined. Identification of phases was done both by x-ray diffraction and by the use of the spectrometer attachment to the scanning electron microscope, in the way previously described in this report. The results of this latter process are, therefore, subject to the uncertainty that was discussed earlier in some detail.

Based on these results, a scenario can be constructed that shows typical behavior and structure at various times. This follows, and reference is made to the figures, which are

simplified drawings made to show the generalities that can reasonably be asserted.

### Results

Figure 1 shows a drawing of a typical view along the surface of the glass slide and a portion of the original flocculated plastic paste. Note the scale. The spaces between the individual cement grains are water-filled. A bridging action results in extensive spaces adjacent to the slide that contain only a few isolated grains of cement.

Figure 1 and Figure 2, which is on a larger scale, emphasize that a water film exists between all the cement grains and the glass surface.

Figure 3 shows the situation in the interfacial region after 1-2 hr of hydration. A thin layer, considerably less than a micron thick, of calcium hydroxide has formed on the glass surface. This layer is perfectly oriented with the c-axis normal to the glass surface. Small crystals of lime are also forming on the cement grains and they also, at least in the interfacial region, form with their basal planes parallel to the interface in the same orientation as that of the lime adjacent to the surface. A few small amounts of C-S-H gel are deposited on the paste side of the interfacial lime layer, but not on the lime attached to the grain, nor on the grain itself.

Figure 4 shows the same region after about 8 hr. The oriented lime film on the glass surface is complete and has been covered with C-S-H gel particles to make a compound film perhaps a micron thick. This orientation is independent of the original position of the glass surface; it forms the same way if the slide is vertical. The same is true of the lime that deposits on the cement grains. The compound film seems to contain no sulfur.

The oriented lime on the cement grain is now contiguous and still has no deposits of gel. This lime, in contrast to that on the glass, does contain "impurities" of aluminum, sulfur, and silicon.

The cement grain is becoming small as its outermost regions are consumed by the chemical reaction with the water. A thin empty space is seen between the surface of the unhydrated cement and its original outline, which is now the inner surface of the oriented lime layer. A few columnar crystals are seen to bridge this gap between the unhydrated cement and the lime shell.

Figure 5 shows that after 24 hr the compound film remains unchanged, and now the gel has been deposited liberally on the lime film covering the cement grain. The unhydrated portion is smaller, and the empty space between it and the lime shell is occupied only by the lengthening columnar crystals.

After three days hydration the situation is shown in Figure 6. The compound film on the glass and on the original cement grain are relatively unchanged. If the grain was small it may be completely hydrated, leaving an empty space within

the shell except for the now relatively long columnar crystals. A new crystal form is also seen. Long acicular crystals have appeared and extend out from the surface of the compound film that outlines the original grain. The nature of these new crystals is problematical. They have the appearance of ettringite, but contain no sulfur or aluminum detectable by the method used. These are, of course, constituents of ettringite. On the other hand, in the pastes made with alite, these crystals were not observed unless the paste also contained  $C_3A$  and gypsum, a result that supports the possibility of the crystals being ettringite.

Figure 7 shows the appearance of the sample at one day, on the same larger scale as Figure 1. The glass is covered with the compound lime and gel film, as are the individual cement grains. Here and there are also seen large massive growths of lime crystals, randomly oriented as a group but parallel to each other within the group. These crystals seem to grow in a pervasive manner and to encapsulate cement grains and hydration products that are in their way. When the pat is removed by drying shrinkage from the slide at this age the fracture goes through either the void space close to the slide, cleaving the few cement grains in the region, or through the lime portion of the compound film on the slide itself if the void space has been filled by the massive lime.

Figure 8 shows the same region after 3 days hydration. More massive lime is seen. The needles radiating from the grains are bridging across to others and tying the whole mass into a firmer network. On this scale, a new crystal form

is also seen at this age. Tabular crystals, arranged about a common edge somewhat as are the leaves of a book, are seen in the larger void spaces close to the glass. These crystals seem to be a calcium aluminate phase that contains sulfur and silicon.

As time goes by more and more massive lime appears. The fracture goes increasingly through the oriented lime on the glass, until at 14 days this is the only position of the fracture, and therefore no more detail can be seen of the paste structure.

These results for the glass substrate are also observed with the quartzite surfaces. With the calcitic marble the situation is different. The structure development in the paste is similar, but the fracture tends to occur in the substrate, and after 2 weeks hydration it is exclusively there. The same thing happened whenever the paste was cast on any mineral with a cleavage plane parallel to the interface, calcite, galena, etc. The same fracture modes occurred in the mortars as in the pat-on-surface samples.



## APPENDIX

### Abstracts

1. "Modes of Occurrence of Calcium Hydroxide in Hydrated Portland Cement"

Studies of hydrated Portland cements with a scanning electron microscope incorporating an element-dispersive x-ray spectrographic attachment indicate the presence of calcium hydroxide in a variety of morphological forms. Micrographs are presented showing examples of these, with accompanying analytical x-ray data to document the identification of each as lime. The local microstructural and positional relationships of each of the varieties with respect to other microstructural elements (voids, calcium silicate hydrate gel formations, surfaces, etc.) are indicated, and possible genetic relationships explored. Implications drawn by various workers concerning the influence of lime on the strength of hydrated cements are assessed in the light of the present results.

2. "Effects of Hydration Temperature on Pore Structure and Microstructure of Hydrated Cement Paste"

The process of hydration of cement paste at 6° and at 40°C is compared with that occurring at room temperature (24°C). Scanning electron microscopy of pastes after various periods of hydration suggest that the microstructures of the hydration products are similar, except that a consistently greater tendency toward the formation and retention of fibrous globular clusters of CSH gel is noted for the higher temperature. Pore size distribution curves and X-ray diffraction data are presented for samples of various ages.

3. "Analysis of Hydrated Cements Using A Scanning Electron Microscope - Energy Dispersive X-Ray Spectrometer Combination"

Preliminary studies of the chemical composition of individual particles and other local microstructural units in hydrated Portland cement pastes were carried out using a scanning electron microscope-energy dispersive x-ray spectrometer combination. Calibration curves were prepared in terms of gross peak heights for calcium as compared with silicon, sulfur, and aluminum K $\alpha$  peaks, for a series of pure homogeneous cement and hydrated cement compounds used as standards. The count ratio was in each case found to be linearly related to the compositional (mole) ratio. The analysis of small (approximately 1 1/2  $\mu$ m diameter) areas of fracture surface of specimens observed in the SEM was carried out for hydrated cement pastes of various ages. It was confirmed that sulfur is universally distributed throughout calcium silicate hydrate gel regions. Local calcium to silica ratios of the gel ranged generally between 2 and 3 considerable higher than had been expected. A number of morphological features found in hydrated cement pastes were interpreted in the light of the chemical compositions determined.

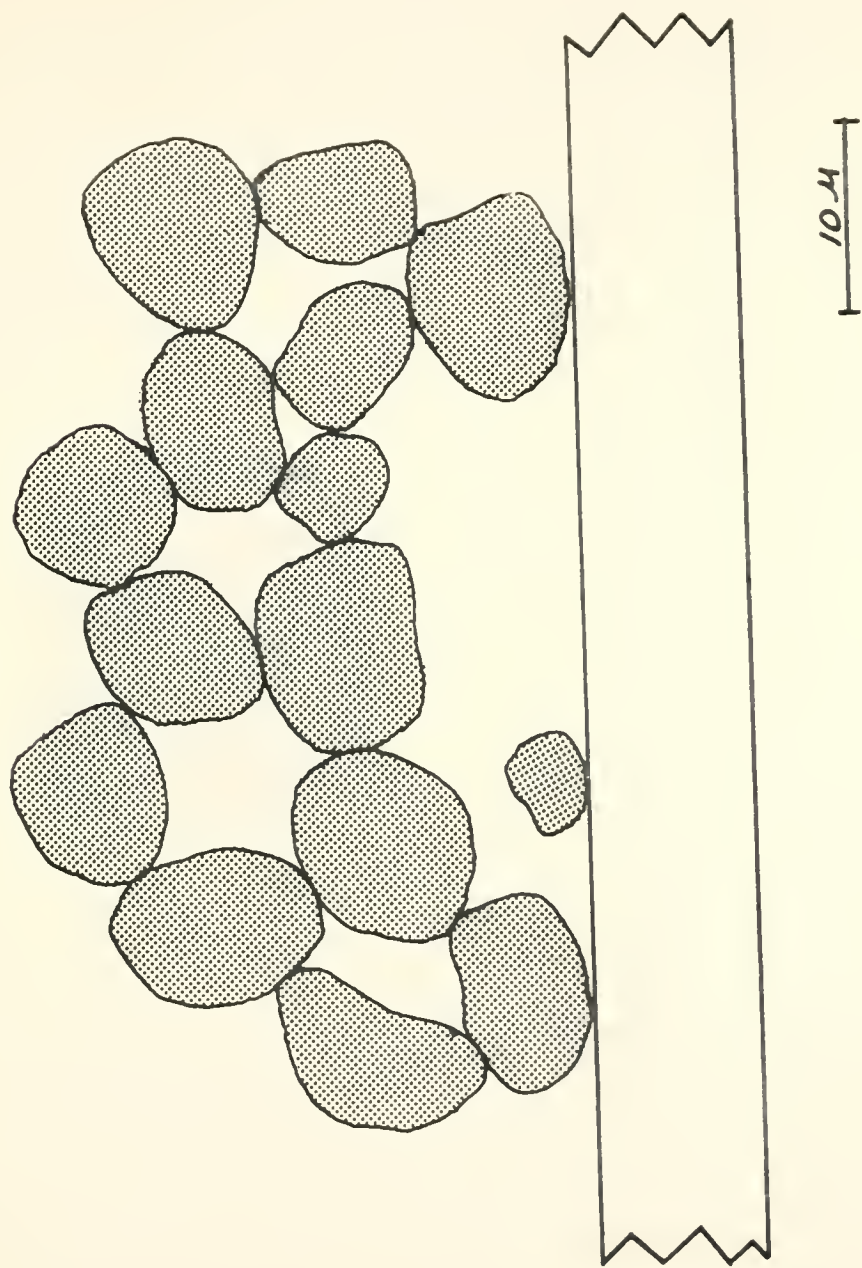


FIGURE 1.

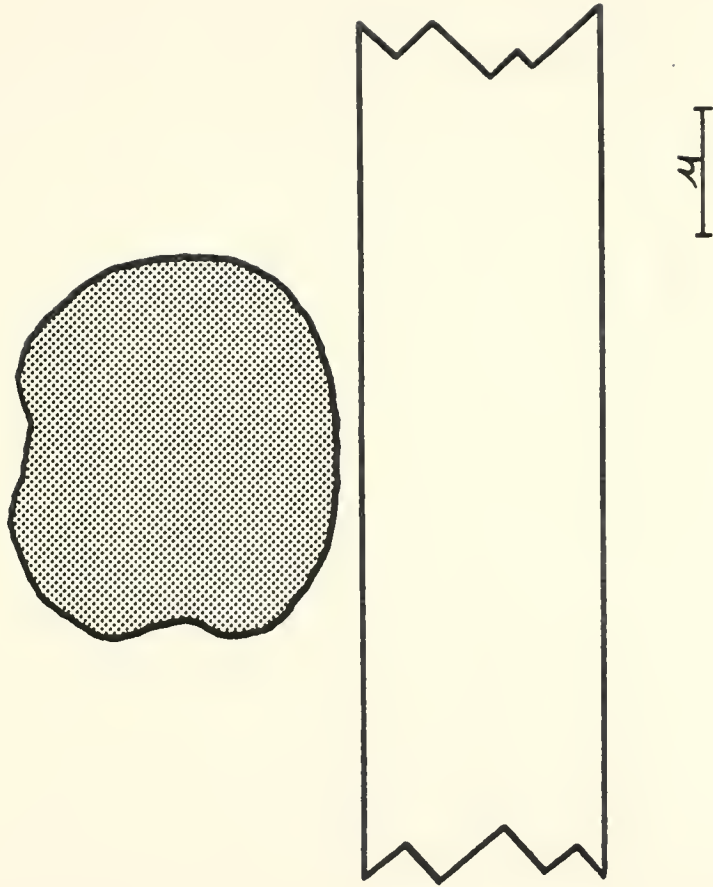


FIGURE 2.

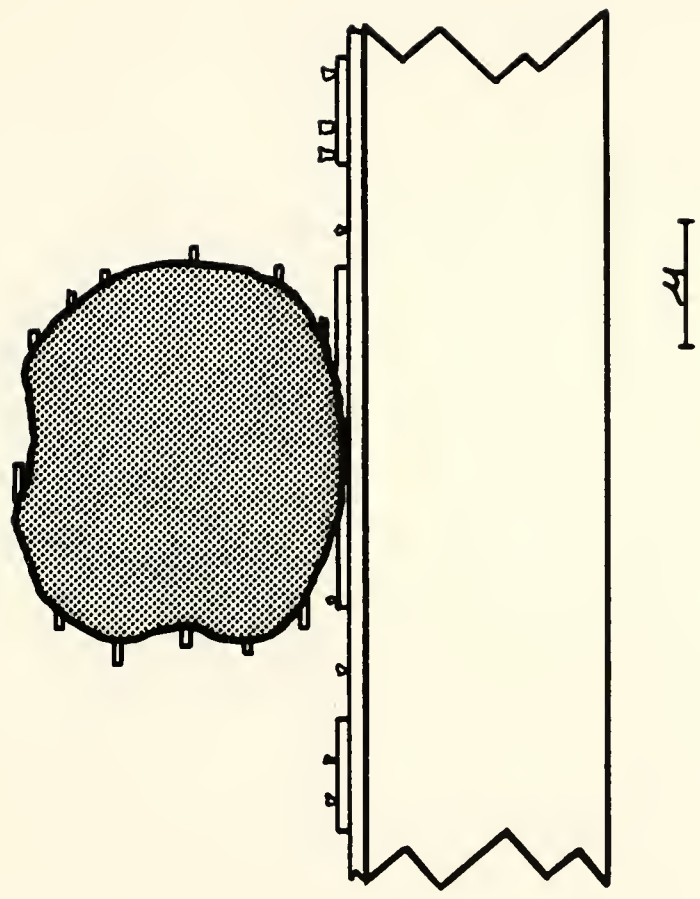


FIGURE 3.

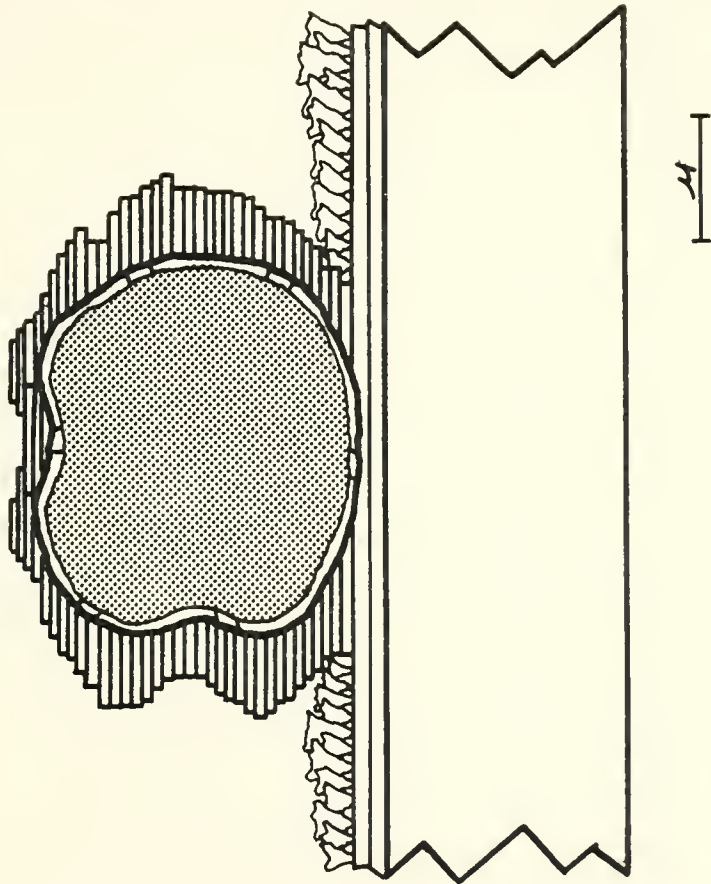


FIGURE 4.

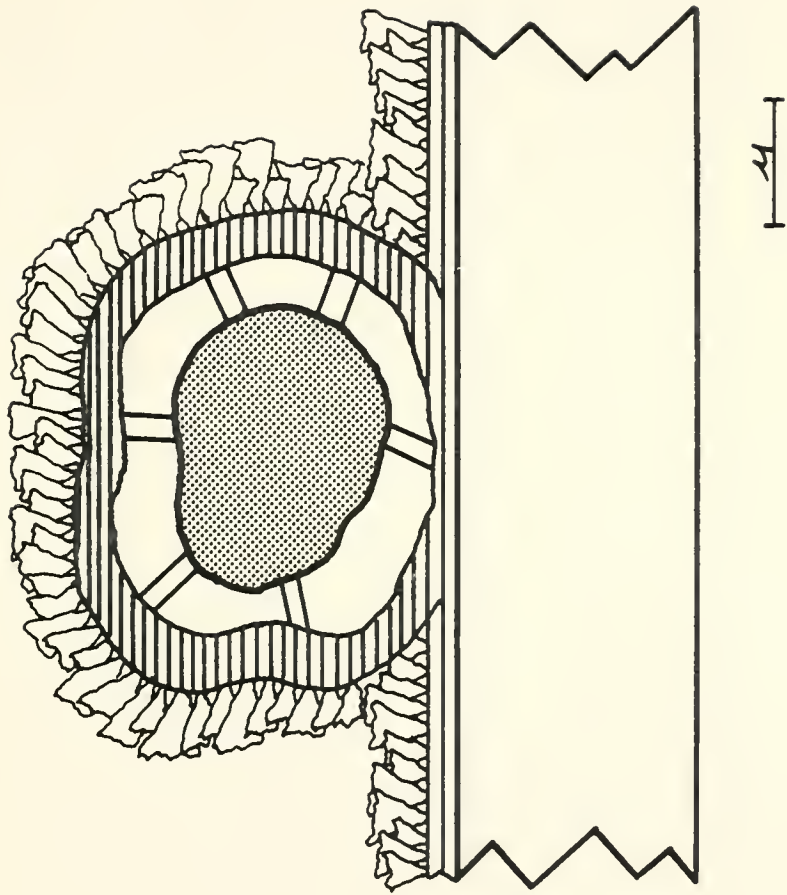


FIGURE 5.

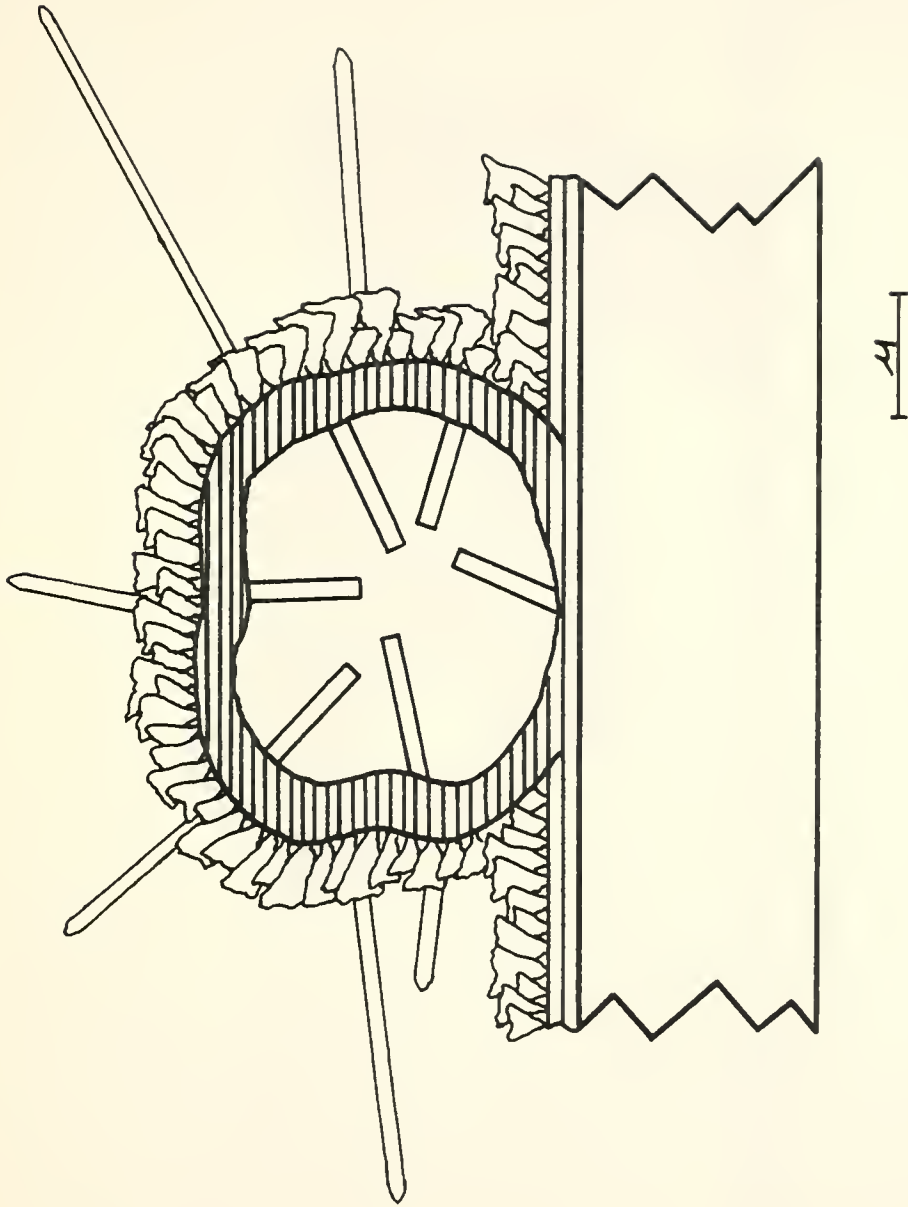


FIGURE 6.

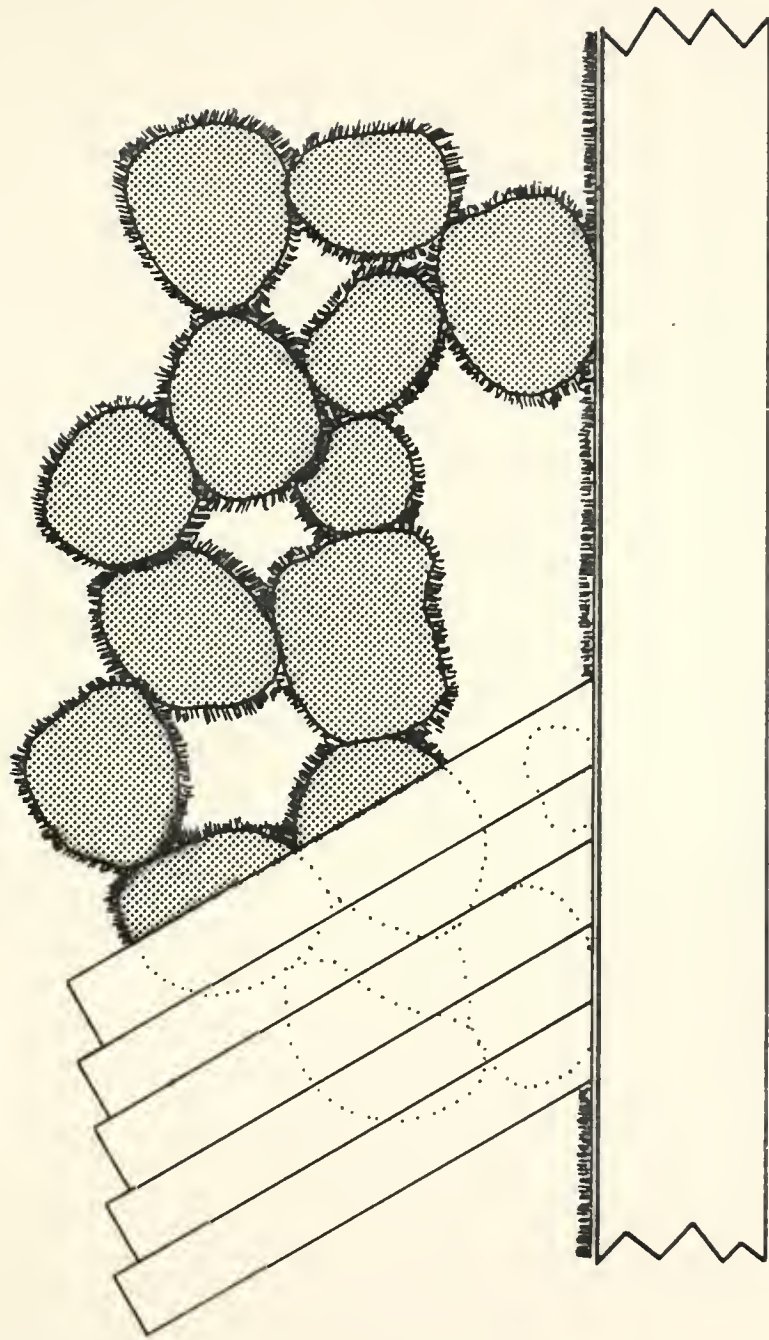


FIGURE 7.



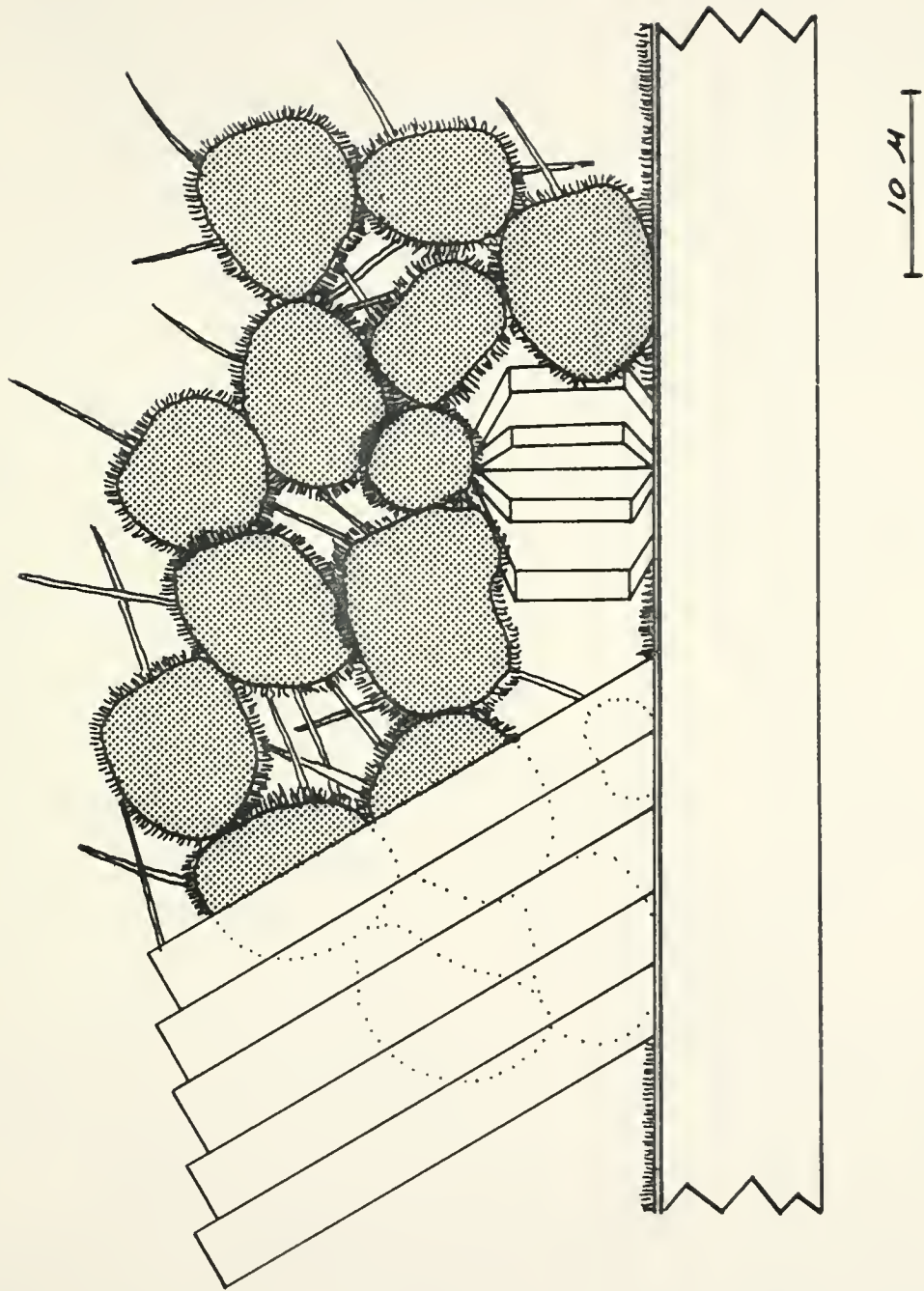


FIGURE 8.



