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Characterization of the interface between brick and mortar

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CHARACTERIZATION OF THE INTERFACE BETWEEN BRICK AND MORTAR

Iowa State University PH.D. 1983

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Characterization of the interface
between brick and mortar

by

Gerald Warren Chase

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
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Major: Geotechnical Engineering

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I. INTRODUCTION

The purpose of this investigation was to examine the nature and magnitude of the bond that develops between clay brick masonry and mortar, to examine the effect of factors such as type of mortar and mortar flow on the bond, and to investigate the effect of pretreating the brick with chemicals, such as an acid or base, on the bond.

Although it is true that mortar has been performing its role of holding masonry structures together for hundreds of years, masonry does fail, and the majority of the cases of failure occur at the interface between the mortar and the masonry unit; i.e., brick, stone or concrete block. It is a generally accepted fact that there have been numerous cases of failure of building brick facades (43), brick walls (45), and that the failures frequently initiate in joints (22,55,89).

For this investigation, it was decided to limit the scope to clay brick masonry units only, keeping in mind that the other masonry units such as stone and concrete could be part of continued studies in the future.

The mortar in masonry joints must fulfill three functions; it must be capable of transmitting a compressive load, it must bond the masonry units together, and it must resist moisture penetration.

Generally, there is no problem with the ability of masonry and mortar to transmit allowable compressive loads. For example, the minimum compressive strength required by ASTM Specifications (10) for a commonly used masonry mortar (type S) is 1800 psi. Face brick normally has compressive strengths in excess of 3000 psi (83). In the Uniform Building Code (95) which is frequently incorporated in municipal codes throughout the U.S., the comparable compressive stress allowed for nonreinforced solid brick unit masonry is 160 psi. Thus, it can be seen that the allowable working stress in this case is limited to about 9% of the compressive strength that can be expected from the mortar, and about 5% of the anticipated brick strength.

An examination of the failure of masonry assemblages shows that the preponderant mechanism of failure, when the assemblies are subjected to shear or flexural loading, is a separation of the masonry unit and the mortar at the joints (89). Thus, there is an inherent weakness at this interface. To accommodate this tendency, the allowable "shear or tension" working stress in unreinforced unit masonry is limited to 20 psi (95). This is only 12.5% of the allowable compressive working stress previously mentioned.

It is also generally known that masonry construction is not completely moisture resistant. The bulk of the moisture penetrates the masonry at the joints. According to Anderegg (14) and others (85,96), this leakage occurs at the interface between the brick and the mortar. Current practice to handle the moisture problem is to waterproof the outside of the masonry wall if it is below ground. If it is above ground, the practice is to construct a cavity wall. Moisture can drain to the bottom of the cavity where it is allowed to drain to the outside through weep holes.

Because of the weakness of masonry in tensile bond strength and because moisture appears to penetrate through masonry joints, there appears to be a legitimate need to investigate the fundamental nature of this interface region.

Certain questions come to mind immediately, namely: What is the nature of the bond at the interface? Is there a substance formed at the interface which acts as a chemical glue? Is the bonding mechanical or chemical or a combination of both? What factors favor a good bond? Are there treatments that can be applied to the brick or to the mortar that promote bond?

The purpose of these investigations was to provide answers to these questions within the limits of a reasonable expenditure of time and resources.

Mechanical testing can provide answers with respect to the magnitude of the bond strengths. The most recognized test for direct measurement of tensile bond strength is the crossed brick couplet test, discussed in detail later.

Questions as to the nature of the interface itself and the materials present can be answered by examining the interface with the scanning electron microscope, and by examining blends of powders of the constituents with both X-ray diffraction and the scanning electron microscope.

Research has been performed on bond strength, although it appears to have been limited to physical testing rather than the more fundamental approach. For this reason, this investigation focuses on the fundamental nature of the materials at the interface. The scope of these investigations includes the following:

1. Physical tensile bond tests using a variety of mortars and pretreatments to examine the dependency of bond on these factors.
2. X-ray diffraction investigations of mortar constituents with and without brick powder added, to help determine the presence of any reaction products resulting from the interaction of brick and mortar.
3. Scanning electron microscopy (SEM) examination of brick chips on which mortar paste, without sand, had been applied.
4. Using the above, to attempt to identify the nature of the interface itself and to correlate bond strength to the presence of reaction products, if any, at the interface between brick and mortar.

II. MATERIALS

A. Brick

1. General

One of the two building materials with which this study is concerned is clay brick. Clay brick has been used in construction for centuries. As early as 4000 B.C., the Babylonians used the clay from the banks of the Tigris and Euphrates Rivers to make sun-dried brick, which was used to build their palaces and temples (97). Today, brick is one of society's most popular building materials.

Although there are various end uses of clay brick, this study will address the use of brick in its most common form of construction application where bond strength is a factor, *i.e.*, masonry walls.

2. Brick raw materials and manufacture

The raw material used in the manufacture of brick is clay. The chemical composition of the clay may vary depending on its origin, but typically, it consists of chemically combined silica and alumina, and other free and combined metallic oxides (83).

Table 1, extracted from Plummer (83), represents the chemical compositions of brick clays obtained from 25 sources in 12 states. The free metallic oxides, referred to as "fluxes" affect the freezing point of the clays and the color. The fluxes lower the freezing point of clays and give the burned clay the strength it needs for structural purposes (83). In addition, the oxides affect the color. For example, the iron oxide gives brick its red color after firing.

Table 1. Chemical analysis of clays (from Plummer (83), p. 6)

		Nonvolatile Constituents											
Source	Kind of Clay	SiO_2 %	Total Iron as Fe_2O_3 %	Al_2O_3[a] %	Mn_3O_4 %	P_2O_5 %	CaO %	MgO %	Na_2O %	K_2O %	SO_3 %	Total Loss on Ignition[b] %	Total Flux[c] %
b	Shale	56.0	4.9	20.6	Tr.	0.10	7.2	4.7	0.10	4.7	1.1	12.7	21.70
c[d]	Shale	60.3	6.5	20.4	0.06	Tr.	3.4	2.8	0.92	4.8	0.87	1.8	18.48
c-1[d]	Shale	60.4	6.0	18.5	0.03	0.44	4.9	3.6	0.95	4.5	0.52	1.3	20.42
d	Shale	61.4	8.6	19.2	0.06	1.6	1.1	2.4	0.88	4.3	0.69	6.2	18.94
d-1[d]	Shale	65.2	7.2	18.7	0.03	0.11	0.20	2.2	1.9	4.4	0.27	1.2	16.04
d-2[d]	Shale	67.8	5.8	19.2	0.04	0.06	0.80	1.8	2.4	2.4	0.14	0.40	13.30
d-3[d]	Shale	64.8	7.5	21.3	0.03	0.08	0.80	1.7	1.6	2.8	0.27	0.46	14.51
e	Shale	63.5	6.8	18.7	Tr.	1.6	0.53	4.0	1.1	3.0	0.26	12.3	17.03
f	85% Fire clay 14% shale	63.8	1.9	30.4	Tr.	0.14	0.34	0.89	0.36	1.8	1.2	9.6	5.43
g	50% Shale, 50% fire clay	66.4	5.8	21.3	Tr.	1.4	0.19	1.4	0.50	3.2	0.26	6.4	12.49

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[a] Al_2O_3 figure includes any TiO_2 that may be present.

[b] This figure represents total loss on ignition at the temperature of the blast and is the algebraic sum of the various changes, including loss of CO_2. (See W. F. Hillebrand, U. S. Geol. Surv. Bull. 700, 231 and J. W. Mellor, Treatise on Quantitative Inorganic Analysis, pp. 157-159). The results for samples, k, l, m, n and p are apparently too high, probably owing to the reduction of sulphate to sulphide by the organic matter present.

[c] Total flux includes Fe_2O_3, Mn_3O_4, P_2O_5, CaO, MgO, Na_2O and K_2O.

[d] Analysis made on the burned clay. All others on the raw clay. Organic matter detected in all samples of raw clay. Appreciable amount being present in samples, f, g, h, j, k. l, m, n and p.

Table 1. (Continued)

Nonvolatile Constituents

Source	Kind of Clay	SiO_2 %	Total Iron as Fe_2O_3 %	Al_2O_3[a] %	Mn_3O_4 %	P_2O_5 %	CaO %	MgO %	Na_2O %	K_2O %	SO_3 %	Total Loss on Ignition[b] %	Total Flux[c] %
h	Fire clay	69.6	0.22	29.1	0.08	Tr.	0.22	0.40	0.14	0.33	0.37	9.1	1.39
j	Surface clay	60.8	6.1	16.9	0.04	0.31	6.8	2.9	1.4	3.0	1.2	5.2	20.55
k	Surface clay	64.6	8.2	21.8	Tr.	0.16	0.34	1.3	0.68	1.8	4.1	11.2	12.48
k-1[d]	Surface clay	66.7	6.0	16.7	0.03	0.21	3.0	2.7	2.4	2.7	0.17	0.98	17.04
k-2[d]	Surface clay	70.4	6.6	17.0	0.05	0.12	1.0	1.1	2.6	1.3	0.12	0.40	12.77
k-3[d,e]	Surface clay	67.4	5.7	14.9	0.02	0.18	5.9	2.1	1.6	2.4	0.66	1.1	17.90
l	Fire clay	61.8	4.7	27.9	Tr.	0.37	0.44	0.84	0.60	2.3	3.8	10.5	9.25
l-1[d]	Fire clay	64.4	2.3	28.2	Tr.	Tr.	Tr.	0.96	1.4	3.0	0.19	0.32	7.66
l-2[d]	Fire clay	71.5	3.3	22.4	0.01	Tr.	0.78	0.51	1.3	0.56	0.19	0.26	6.46
m	Fire clay	66.8	1.6	28.9	Tr.	Tr.	0.60	0.40	0.65	0.98	1.2	8.0	4.23
n	Fire clay	72.5	3.8	19.8	Tr.	0.40	0.21	0.56	0.54	1.9	1.2	6.6	7.41
o	Surface clay	57.8	0.81	20.4	0.06	0.40	9.8	5.6	0.76	3.9	0.45	13.9	21.33
o-1[d]	Surface clay	60.9	5.1	12.8	0.04	Tr.	8.8	5.6	2.1	3.9	0.85	1.3	25.54
p	Fire clay	67.8	2.4	25.2	Tr.	Tr.	0.39	0.33	0.38	2.4	2.5	9.4	5.90
p-1[d]	Surface clay	64.6	6.8	24.1	0.03	0.12	0.14	0.94	1.7	1.8	0.14	0.70	11.53
q[d,f]	Surface clay	60.2	5.3	22.8	0.09	0.50	1.5	2.7	2.2	4.0	0.16	4.0	16.29
r[d,f]	Surface clay	75.6	1.9	9.4	Tr.	Tr.	---[g]	0.37	0.97	2.2	0.08	0.44	5.44

[e] Actually a weathered shale.

[f] Actually a mixture of pottery clay, fire clay and fire sand. Analysis applies for tile in tests 40 and 41.

[g] Not detected.

To manufacture brick, the clay is initially mixed with a small quantity of water, then formed into shape and then burned. In the stiff mud process of forming, the clay is extruded to the shape desired, then cut off. In the dry-press method, each brick is individually formed from relatively dry clay material, which has been subjected to very high pressures in a brick press.

After the forming process, the brick is dried in drier kilns, which have temperatures ranging from 38°C to 250°C (90). After drying, the bricks are moved to a burning kiln, where they are fired at temperatures up to 1315°C (90). Firing temperature depends on the vitrification temperature of the particular clay which varies from about 870°C to 1315°C (90). The time for firing varies from 40 to 150 hours, and cooling requires 48-72 hours (90).

3. Physical properties of brick

The primary physical properties of brick include color, texture, strength, absorption and size. As will be discussed later, both texture and absorption affect bond strength between mortar and brick, so each will be discussed here. Brick strength is also discussed; however, it is not a factor in bond strength. There are standards for the physical properties of bricks. Standards published by the American Society for Testing and Materials (ASTM) divide brick into several categories such as facing brick, building brick and hollow brick. Facing bricks are manufactured to strict color and size tolerances because they are used to form the exposed face of a masonry wall. Building brick, on the other hand, is not necessarily exposed, and has less stringent requirements. This study will limit itself to facing brick, since it is the type most commonly used in the exposed surfaces of brick walls.

Fired brick is a very strong material. Depending on firing temperatures, most brick have compressive strength ranging from approximately 1,500 psi to 20,000 psi (90). Brick is considerably weaker in tension, with tensile strength usually 5 to 10 percent of the compressive strength (83). ASTM Specification C-216 (6) requires facing brick to have an average compressive strength of at least 3000 psi for brick classified as SW (severe weathering), and 2500 psi for brick classified as MW (moderate weathering). There is no requirement for the brick to meet a minimum tensile strength. Brick strength generally has no effect on bond strength. In compression, forces tend to force the brick together, so the compressive strength of the brick has no effect on bond.

When a wall is subjected to flexural or to tensile stress, the wall will generally fail because of flexural bond failure. This occurs because the bond strength is so much weaker than the strength of the brick in flexure or tension. For example, brick will fail in tension at a stress in the neighborhood of 600 psi, whereas bond strengths seldom exceed 80 psi (83). Likewise, brick has a flexural strength as measured by the modulus of rupture in the neighborhood of 515 to 2890 psi (83). This is considerably greater than the 96-342 psi ultimate flexural strength measured for composite brick-mortar beams, where failure occurred due to flexural bond failure (80). So, in general, brick strengths are considerably higher than bond strengths, and they have little effect on the composite strength of brick-mortar assemblages.

With respect to texture, two surfaces are of interest, i.e., the top and bottom flat surfaces, which is where the mortar is placed between horizontal courses of brickwork (bed joint), and the vertical surfaces at the end of the brick (head joint). The horizontal surfaces are cut surfaces, caused by slicing the extruded clay as it emerges from the forming die. This surface is relatively rough, compared to the sides and ends of the brick which are smoothed by the sides of the die. It is possible to roughen any of the surfaces by a variety of treatments, to include wire-brushing, scoring, etc. However, this normally is done to provide an architectural effect, and not done to improve bond. Studies performed at Virginia Polytechnic Institute in the 1940s (46) show that the wire cut surface typically has a bond strength about 13% greater than the die formed surface.

Brick absorption has a significant effect on the bond strength. There are various tests for measuring absorption, such as the one hour, two hour, five hour boiling water test, and the initial rate of absorption test, referred to as the "suction" test. These tests are all specified in ASTM Standard C-67, Standard Methods of Sampling and Testing Brick and Structural Clay Tile (5). The absorption which affects bond the most is the initial rate of absorption, known as "IRA", or "suction". It is measured by placing an oven dried brick in a shallow pan so that the water level rises 1/8" above the bottom surface of the brick. The amount of water absorbed in one minute is measured by weighing the brick before and after exposure to the water. This provides a measure of how much water the brick can "suck" out of the mortar when the brick is placed dry.

Brick having an IRA greater than 20 grams per 30 in^2 of absorptive surface area must be wetted prior to laying. Otherwise, the suction will remove water from the mortar so fast that it drastically reduces bond strength. There have been several experiments in which this effect has been measured. They will be discussed later.

B. Mortar

1. General

In the book, Masonry, Materials, Design, Construction, by Smith, Honkala and Andres (90), the authors provide a concise description of what mortar is required to do. They state: "Mortar is designed for several purposes, but it serves primarily to join masonry units together in an integral structure. In addition to that, it is also required to hold the units a specified distance apart, to produce tight seals between units to prevent the passage of air or moisture, to bond metal ties and anchor bolts to the steel joint reinforcement in order to integrate them into the masonry structure, to provide a bed that will accommodate variations in the size of units, and to provide an architectural effect on exposed masonry walls through various styles of mortar joints" (90, p. 57).

The governing specifications for mortar are ASTM C270, "Standard Specifications for Mortar for Unit Masonry" (10) and ASTM C476, "Standard Specifications for Mortar and Grout for Reinforced Masonry." Unit masonry is masonry without vertical and horizontal reinforcing bars, although small diameter joint reinforcing may be encountered. This investigation restricts itself to unit masonry, because the role of bond strength is greater in nonreinforced plain unit masonry. In reinforced masonry the units are partially held together by reinforcing steel with grout occupying some or all of the void spaces.

The masonry mortars included in ASTM C270 are classified according to type. The types, M, S, N, O and K, differ in the proportions of their constituents. Because of this, each type exhibits different properties, and each has different recommended uses.

The basic ingredients from which mortar is made are cement, lime, sand and water. The proportions of each are listed in Table 2.

Table 2. Mortar proportions in parts by volume of cement, lime, sand[a]

Type	Parts by Volume[b] Portland Cement, or Portland Blast-Furnace Slag Cement	Parts by Volume[c] Hydrated Lime or Lime Putty	Aggregate, measured in a Damp Loose Condition
M	1	1/4	Not less than 2 1/4 nor more than 3 times the <u>sum</u> of the volumes of the cements and lime used
S	1	over 1/4 to 1/2	
N	1	over 1/2 to 1 1/4	
O	1	over 1 1/4 to 2 1/2	
K	1	over 2 1/2 to 4	

[a] Extracted from Table 2, Ref. 10, p. 154.

[b] The portland cement may be any of Type I, IA, II, IIA, III or IIIA.

[c] The hydrated lime must meet ASTM specification C207, Type S.

It is possible to prepare mortar by using a commercial masonry cement instead of portland cement. Masonry cement contains lime, hence the proportion of lime which can be used is reduced accordingly. Proportions for mortar prepared using masonry cement are shown in Table 3.

Table 3. Mortar proportions by volume, for mortar prepared with masonry cement[a]

Type	Parts by Volume Portland Cement	Parts by Volume Masonry Cement	Parts by Volume Hydrated Lime or Lime Putty	Aggregate, loose, damp condition
M	1	1	None	Not less than 2 1/4 and not more than 3 times the sum of the volumes of the cements and lime used.
S	1/2	1	None	
N	---	1	None	
O	---	1	None	
K	---	N/A	N/A	

[a] Extracted from Table 2, Ref. 10, p. 154.

Masonry cement is governed by ASTM Standard Specification C91-78 (9). The specification provides the following definition of masonry cement: "...a hydraulic cement used in mortars for masonry construction, containing one or more of the following materials: portland cement, portland blast furnace slag cement, portland pozzolan cement, natural cement, slag cement, or hydrated lime; and in addition usually containing one or more materials such as hydrated lime, limestone, chalk, calcareous shell, talc, slag, or clay, as prepared for this purpose" (9, p. 958).

The ASTM specification C91 contains no limits or ranges for any of these constituents. As a result it is difficult to perform controlled experiments with masonry cement. Accordingly, all experiments in the investigation have used portland cement, specifically Type I portland cement, rather than masonry cement.

2. Mortar raw materials and preparation

As indicated in Table 2, the basic ingredients in unit masonry mortar are cement, lime, sand and water. The role of the portland cement in mortar is much the same as it is in concrete; *i.e.*, when mixed with water, it forms a paste that coats aggregate particles, and in this case, the brick surface. Upon setting, it binds the aggregates and brick together in a rock-like mass. ASTM specification C270 (10) allows the use of portland cement, Types I, IA, II, IIA, or IIIA of ASTM C150, or portland blast-furnace slag cement, Types IS or ISA of ASTM C595 or portland pozzolan cement, Type IP and IPA of ASTM C595 when fly ash is the pozzolanic material.

For this investigation, only Type I portland cement was selected. This is because Type I portland is the most widely used cement, other than masonry cement, in masonry construction. To be classified as a Type I portland cement meeting the requirements of ASTM Specification C150 (11), which is the governing specification, the cement must meet certain minimum standards with respect to air content of the mortar, fineness, autoclave expansion, compressive strength at 3 and 7 days, and time of setting (see Table 4). The cement used for this series of experiments was labeled as meeting the requirements of ASTM Specification C150.

Table 4. Standard physical requirements for Type I portland cement[a]

Air Content of Mortar, volume % (1 part cement, 2.75 parts sand, by wt.)		
	max	12
	min	---
Fineness, specific surface, m^2/kg		
	Turbidity test, minimum	160
	Air permeability test, minimum	280
Autoclave expansion, max %		.80
Compressive strength, psi (1 part cement, 2.75 parts sand, by wt.)		
	3 days	1800
	7 days	2800

[a] From Ref. 11.

The hydrated lime used in masonry mortar is $Ca(OH)_2$, which results from the addition of water to CaO, known as "quick-lime". The process of adding water to quick lime is called "slaking" lime. The resultant product, $Ca(OH)_2$, if left wet is referred to as lime putty. When dried, the result is a white material, which when pulverized and bagged, is the commercial lime with which most persons are familiar. ASTM C51 (4) defines hydrated lime as "a dry powder obtained by treating quick-lime (calcined limestone) with water enough to satisfy its chemical affinity for water under the conditions of its hydration. It consists essentially of calcium hydroxide or a mixture of calcium hydroxide and magnesium oxide or magnesium hydroxide, or both." It is used as an ingredient in plaster and mortar, as well as for soil stabilization, striping of ball fields, etc.

Prior to 1900, the masonry mortar used in the United States was a mixture of hydrated lime, sand and water, without any cement at all. The hydrated lime would gradually absorb carbon dioxide from the air and would be converted to $CaCO_3$, known as limestone. In the process, the mortar would gradually increase in compressive strength until it could support the weight of the masonry above it, plus any weight imparted from roofs and floors. The use of straight lime mortars prevailed in the U.S. until 1890, when portland cement became available in quantity. With the rapid strength gaining properties of portland cement, it was possible to prepare mortars which would obtain a higher early strength. This, in turn, would allow for more rapid construction of load-bearing masonry.

For example, in one set of experiments (90, p. 62) at seven days mortar cubes made from a high lime mixture of 1 part cement and up to 4 parts lime, by volume, had a compressive strength of 45 psi. On the other hand, cubes made from a high cement mixture of 1 part cement and 1/4 part lime, by volume, had a seven day compressive strength of 1600 psi. Figure 1 shows the relationship of 28 day compressive strength and water retentivity of mortar to varying cement-lime ratios.

Although some buildings were built using a pure cement-sand mortar, it was found that this type of mortar exhibited certain undesirable characteristics, such as low workability of the mortar (masons did not care to use it), and the development of cracks in the mortar, possibly created by the rigidity of the cement-sand matrix, and poor bonding in some cases (28,96).

Hydrated lime used in masonry mortars today is covered by ASTM Specification 270 (10). Hydrated lime imparts certain properties to masonry mortar which are desirable. Specifically, lime increases the workability of the mortar, so that it is more plastic, and easier to spread. In addition, lime increases the water retentivity of the mortar, so that brick with high suction will not draw the moisture as rapidly from the mortar. This is discussed in more detail later. In addition, lime delays the time of set of the mortar, so that mortar can be used up to 2 1/2 hrs, depending on the weather, after it is initially mixed, before it must be thrown out (87). ASTM C270 (10) requires that the lime used in masonry mortar be type S lime and that it meet the requirements of ASTM C207. ASTM C207 (8) refers to a type S hydrated lime as one which

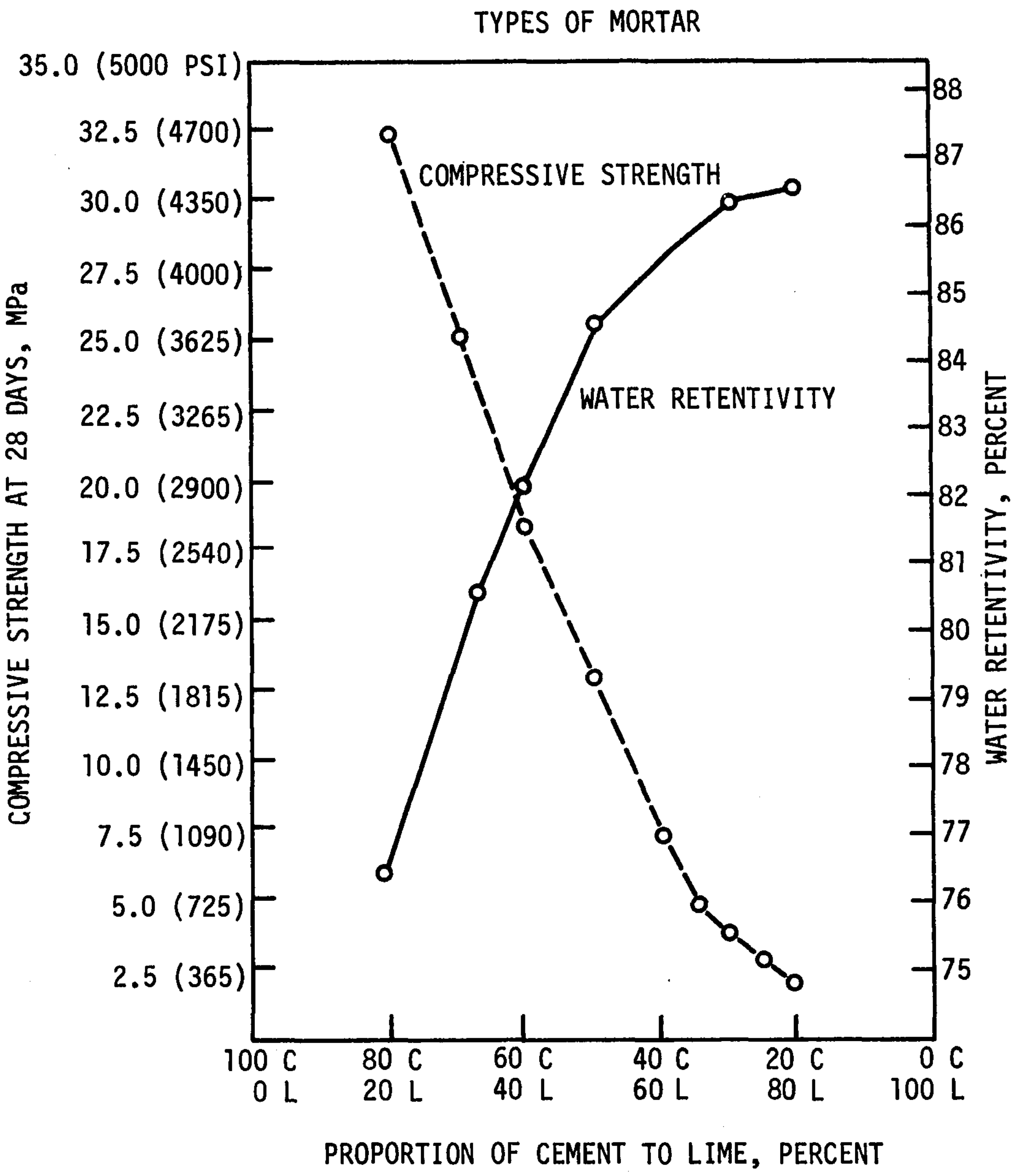


Figure 1. Relationship among mortar composition, compressive strength and water retentivity (90)

develops high early plasticity and high water retentivity and which permits no unhydrated oxide content. The lime used for these investigations was a type "S" hydrated lime, for masonry purposes.

The purpose of the sand aggregate in mortar is to provide body and to economize on the quantity of cementitious materials used. There is a range for the proportion of sand that can be added to mortar, in accordance with ASTM C270 (10). The minimum quantity is 2.25 times the amount (by volume) of the cementitious materials (cement, lime) used. The maximum quantity is 3.0 times the amount of the cementitious materials used. The governing specification for sand used in masonry is ASTM C144, 1981. This specification places limitations on the gradation and impurities, and specifies minimum resistance to disintegration by saturated solutions of sodium or magnesium sulfate.

For these investigations, standard sand meeting the requirements of ASTM C778, 1980, was used. This sand is a natural silica sand from Ottawa, Illinois, and meets strict gradation requirements. Use of this sand provided for uniformity of the aggregate during these investigations.

3. Mortar properties

There are three basic properties of masonry mortar which are addressed by ASTM C270 (10). They are compressive strength, flow, and water retentivity.

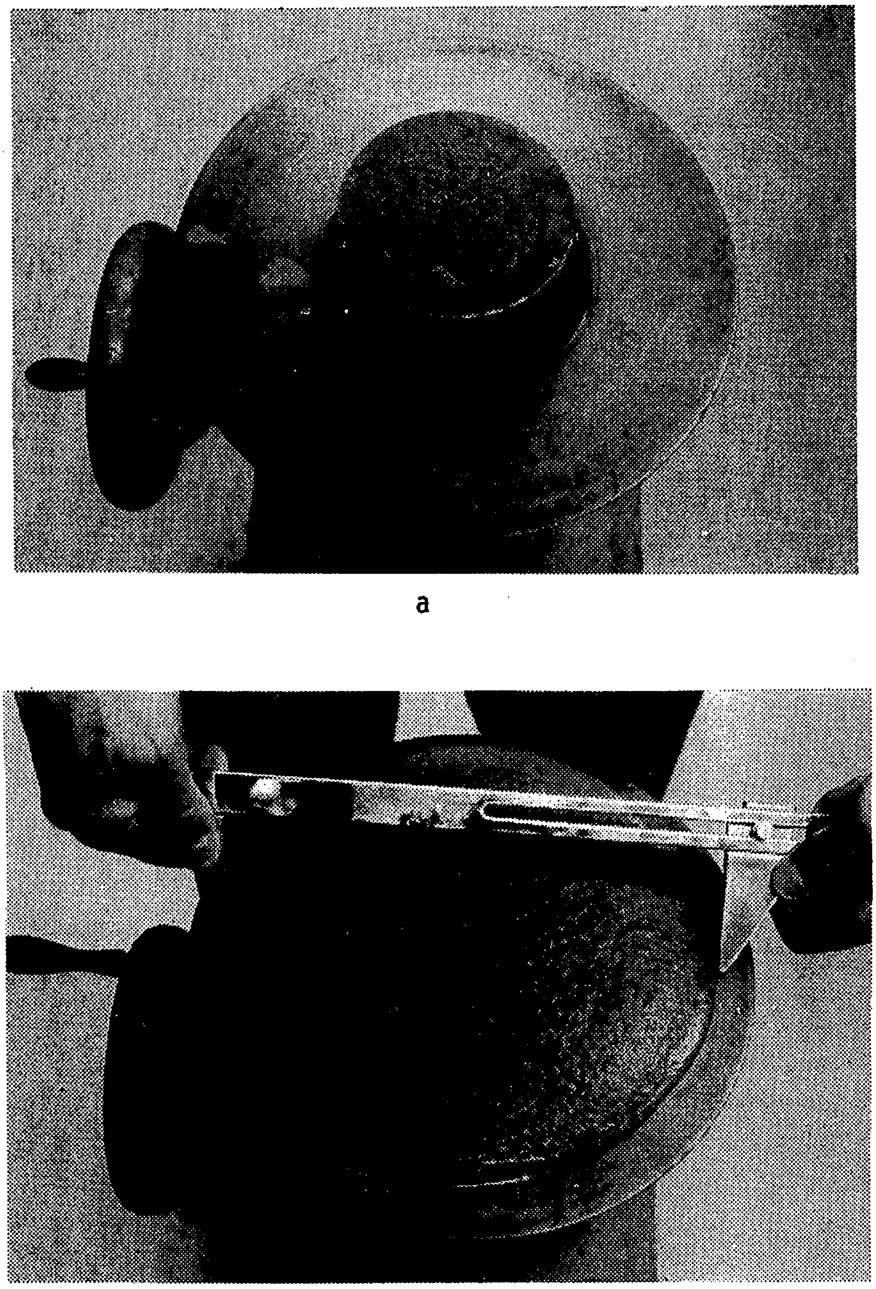
Compressive strength is a measure of the ability of the mortar to carry a compressive load. The 28 day compressive strengths required by the different types of masonry mortar are shown in Table 5. A comparison with Table 2 shows that the high cement/low lime mortar exhibits a higher compressive strength than the low cement/high lime mortar. The compressive strength is measured by preparing 2 inch mortar cubes and testing them to failure by compressive load, after 28 days of curing.

Table 5. Compressive strengths for mortar[a]

Mortar Type	Average Compressive Strength, 28 days, psi
M	2500
S	1800
N	750
O	350
K	75

[a] From Ref. 10.

One of the measures of consistency and workability of mortar is a parameter known as "flow". The flow of a mortar is determined by placing prepared mortar in a mold, which has the shape of a truncated cone, see Figure 2. The cone sits in the center of a steel platform which can be raised, then dropped. When the mold is removed, the table is allowed to rise and drop 25 times in 15 seconds. The difference between the original



a

b

Figure 2. Apparatus for measuring flow

a - Truncated brass cone containing leveled mortar, centered on flow table

b - Measuring diameter of mortar after 25 falls of the table and final average diameter of the mortar is compared to the original diameter. The result is expressed in percent flow. ASTM C270 requires that the mortar flow be between 110 and 115 for measurement of water retention and compressive strength. However, that range is used to standaradize the flow for testing purposes only. No minimum or maximum flow is specified for actual construction. Instead, the specification limits the amount of water used to the "maximum amount of water to produce a workable consistency in a mechanical batch mixer".

Water retentivity is the ability of a mortar to retain water and prevent it from being drawn into the air or the porous brick above and below the joint. To test for water retentivity, the flow of a fresh sample is measured. Then the mortar is placed over filter paper in a funnel with a porous bottom. Suction is applied to the mortar for 60 seconds, drawing water out of the bottom of the sample. The flow of the mortar is again measured after suction. The retentivity is calculated as the flow after suction, divided by the flow before suction, times 100. The minimum acceptable water retentivity for mortars in accordance with ASTM C270, is 75. The governing specification for performing the retentivity test on mortar is ASTM C91 (9).

Figure 1, previously referred to with respect to compressive strength, also shows the variation in water retentivity with mortar composition. High lime content favors high retentivity.

III. CEMENT AND MORTAR HYDRATION

The chemistry of cement is very complicated, and has involved the efforts of many researchers over the years. Neville (75), Bogue (24), and Lea (70) are three of the leading current sources on cement chemistry.

Reduced to its simplest form, portland cement consists primarily of four principal compounds, with the percentages of some American cements as follows (70):

1. C_4AF, or $4CaO \cdot Al_2O_3 \cdot Fe_2O_3$, tetra-calciumaluminoferrite (celite), makes up approximately 6-9% of Type I portland cement.

2. C_3A, or $3CaO \cdot Al_2O_3$, tri-calcium aluminate, makes up approximately 7-14% of Type I portland cement.

3. C_3S, or $3CaO \cdot SiO_2$, tri-calcium silicate, also known as alite, makes up approximately 33-55% of Type I portland cement.

4. βC_2S, or $2CaO \cdot SiO_2$, di-calcium silicate, also known as belite or felite, makes up approximately 18-35% of Type I portland cement.

The percentages associated with portland cement used by other researchers, such as Berger et al. (23) and Akaiwa and Sudoh (1), fall within these limits. There are other compounds present in lesser quantities. These might include Na_2O, K_2O, TiO_2, SO_3, MgO and free CaO. Usually their percentages are below 3%. The chemical formulas above show both the long and shorthand notation for cement components. This shorthand notation is used by cement chemists to reduce the complexity of the formulas that would otherwise result. The common substitutions are as follows (70):

C = CaO

A = Al_2O_3

S = SiO_2

F = Fe_2O_3

T = TiO_2

M = M_gO

K = K_2O

N = Na_2O

H = H_2O

Thus, $C_3AH_6 = 3CaO \cdot Al_2O_3 \cdot 6H_2O$

Mortar and concrete derive their strength from the products that form when the cement constituents hydrate upon the addition of water.

According to Lea (70), the hydration of the individual cement constituents at room temperature passes through several phases, C_3S and C_2S pass into an aqueous solution first, then form a calcium silicate hydrate (C-S-H) gel plus free calcium hydroxide. The final stable form of the calcium silicate hydrate may be afwillite, $3CaO \cdot 2SiO_2 \cdot 3H_2O$, but that is not certain. The intermediate, metastable forms of C-S-H are probably CSHI (CSHβ) and CSHII (C_2SH_2). These are poorly crystallized, tobomorite-like compounds. In solutions saturated with lime, CSHII is the more likely interim product. Lea indicates that at room temperature, these poorly crystallized hydrates probably consist of a continuous range of phases, with varying calcium/silicate ratios, basal spacing and degree of crystallinity.

According to Bogue (24), the C_3A hydration occurs very rapidly. To slow the hydration, gypsum is normally added to the cement. The result is the formation of a sulphoaluminate, which shows up as needles. Ultimately, the excess C_3A that does not precipitate out as sulphoaluminate becomes the cubic C_3AH_6, in the shape of small round particles which form a gelatinous mass. Lea adds that a final form of the sulphoaluminate may be a hexagonal plate solid solution with the formula $3CaO \cdot Al_2O_3 \cdot Ca(SO_4,(OH)_2) \cdot aq$ (70, p 237).

Diamond (40) makes no mention of the C_3AH_6. He states, "Ettringite (6-calcium aluminate trisulfate-32 hydrate) and calcium aluminate monosulfate-12 hydrate are both found...," but in small proportions, showing small X-ray diffraction peaks (40, p 5). The ettringite occurs as needles and the calcium aluminate monosulfate-12 hydrate as a layered structure. Neville (75) indicates that the C_3A and gypsum ($CaSO_4 \cdot 2H_2O$) form an insoluble calcium sulpho-aluminate ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$), which eventually forms a tricalcium aluminate hydrate, but this is preceded by a metastable $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ (75, p 17). The rate of hydration of C_3A also appears to be retarded by $Ca(OH)_2$ which reacts with C_3A to form C_4AH_{19}, which then coats the surface of unhydrated grains of C_3A. Neville confirms that the stable form of the aluminum hydrate is probably C_3AH_6, a cubic crystal.

According to Lea, the C_4AF reacts initially with gypsum and lime to form a solid solution of the high-sulphate sulphoaluminate and sulphoferrite. This later becomes a low-sulphate aluminoferrite solid solution and/or a more complex solid solution phase in which sulphate ion is replaced by hydroxyl ion (70, p 236).

In summarizing the possible hydration reactions, Lea indicates a great degree of uncertainty still exists as to the whole scheme of reactions and products formed.

Diamond also says that phases of lesser crystallinity include the calcium silicate hydrate gel. He points out that few actual X-ray diffraction traces of C-S-H gel in portland cement paste have appeared in literature. He attributes the characterization of CSHI and CSHII structure as "weakly crystallized tobermorite" to speculation and wishful thinking rather than experimental results. According to Diamond, the weakness of the C-S-H gel peaks in X-ray diffraction suggest that the gel is almost amorphous or totally amorphous.

He has identified four distinctive forms of C-S-H gel, which he classifies as Types I, II, III, IV. The Type I C-S-H gel particles are fibrous, usually less than 2 μm across, and vary from 0.5 to 2 μm in length, tapering to a point at their end. The Type II C-S-H gel particles have a reticular network. The particles are similar to Type I particles, however, there is more extensive branching. The result is an interconnected reticular network. The Type III C-S-H gel particles consist of small irregularly equant or flattened particles, not more than 0.3 μm across. Type III gel is common in hardened cement pastes and represents a reasonable proportion of hydrated cement. The Type IV C-S-H gel particles have a dimpled "brain-like" appearance. They are not very common, and generally form as an interior product.

Diamond says the Type I morphology dominates immature paste. Type II and III particles appear as hydration proceeds. With increased maturity, it becomes difficult to see detail, and in most cases no individual particle morphology is evident, except in pores and thin spots.

Diamond summarizes by saying that the hydration products consist of some form of C-S-H gel, plus crystalline forms of calcium hydroxide, ettringite, calcium aluminate monosulfate hydrate, perhaps C_4AH_{13}, and residual, unhydrated cement compounds. Estimates of approximate percentages by weight are: C-S-H gel, 70%; $Ca(OH)_2$, 20%; ettringite and $CA\bar{S}H_{12}$, 7%; other 3% (40, p. 4).

Neville summarizes the hydrated products as being calcium silicate hydrates, tricalcium aluminate hydrate, both together referred to as gel, crystals of $Ca(OH)_2$, some minor components, and unhydrated cement. These hydration products, then, are the materials which interact with and bond to the surface of the masonry units when assembled. The primary difference in the case of masonry mortar is that calcium hydroxide, one of the cement hydration products, is mixed with the cement at the time the mortar is prepared. Thus, any of the hydration reactions which are dependent on the amount of calcium hydroxide present would be affected. Lea indicates that at room temperature, the stable hydration products for hydrated cement mortars with a high ratio of CaO to SiO_2 in the initial mix would be C-S-H II and $Ca(OH)_2$.

IV. THE BONDING MECHANISM

A. The Nature of Bond Strengths

Bond strength is probably a combination of several different types of forces, *i.e.*, primary bonds, such as ionic and covalent bonding, and secondary bonds such as van der Waals bonds, as well as mechanical interaction and interlocking.

Of the primary bonds, the strongest is the ionic bonding. NaCl is an example.

In covalent bonding, the forces are also strong. Atoms may group together to form molecules by sharing their valence electrons. Water is an example of a molecule bonded by covalent bonds. Quartz is also formed with partially covalent bonds. The Si^{+4} shares its four outer electrons with four oxygen atoms forming a stable, strong tetrahedron. Each oxygen still has one electron left to share, which is available to combine with another silicon atom. This pattern continues to form the stable network of quartz.

The third type of force, van der Waals bonds, are intermolecular forces. These bonds are approximately 1000 times less than ionic bonding.

B. Cement Paste Strength

A point of departure for examining the bond between mortar and clay brick is to examine the nature of the strength of cement paste itself. Lea cautions that "when we turn to the actual mechanics of the bonding action, there is still room for divergence of opinion, and we have yet to reach any firm conclusion (70, p. 263).

With respect to bonding within portland cement paste itself, Lea cites investigations by others that would indicate that failure in tension is probably a failure in van der Waals bonds. He also cites an alternative theory in which the particles are held together at solid to solid points of contact by bonds which cannot be classified simply as chemical or van der Waals bonds. He refers also to the possibility of mechanical interlocking of crystals as they grow together. Lea says that the contribution of calcium hydroxide cannot be dismissed. The $Ca(OH)_2$ crystals may contribute to strength by filling voids and increasing the density of the paste.

Phileo (81), in his paper, "The Origin of Strength of Concrete", states that the strength of the hardened cement paste, without aggregate, is a combination of chemical bonds and secondary bonds, but primarily secondary. He cites work by Powers and Brownyard in which they report that the strength of the hardened paste increases as the cube of the gel-space ratio, where gel-space ratio is the ratio of gel volume to gel volume plus capillary space.

Alford (2) cites research by others that shows that there is an inverse relationship between tensile strength of cement paste and the total porosity of the paste. He maintains that the relationship is largely fortuitous, and that the true relationship is not between porosity and strength, but instead, between the pore size and strength. "The pores in cement paste act as stress concentrators, and a reduction in their size will reduce the size of their stress intensity field" (2, p. 609). To illustrate his point, he cites the results of experiments which show a nonlinear relationship between tensile strength and flaw size. The resulting curve, Figure 3, closely approximates the theoretical Griffith curve, defined by

$$\sigma = \sqrt{\frac{2E\gamma}{\pi c}}$$

where E is Youngs modulus, γ is the surface energy and c is one-half the flaw length, in this case, the largest pore diameter.

C. Paste-Aggregate Bonding

When aggregate is added, the cement-aggregate bond becomes a factor. Phileo states that "...one of the important and most interesting bonds, that between paste and aggregate, has been neglected. Most of the work has dealt with measurement of bond strength rather than explanation of bond strength, although the conclusion is frequently reached that rough surfaces bond better than smooth surfaces since the bond area is greater" (81, p. 183). Phileo cites work by Jones and Kaplan that concluded that failure in compression and in tension are essentially the same mechanism, both being initiated by a local failure in bond between aggregate and paste. Phileo concludes by saying, "The principal areas in which research is now needed to further our understanding of concrete strength are paste-aggregate bond and the propagation of cracks following the first local failure" (81, p. 184).

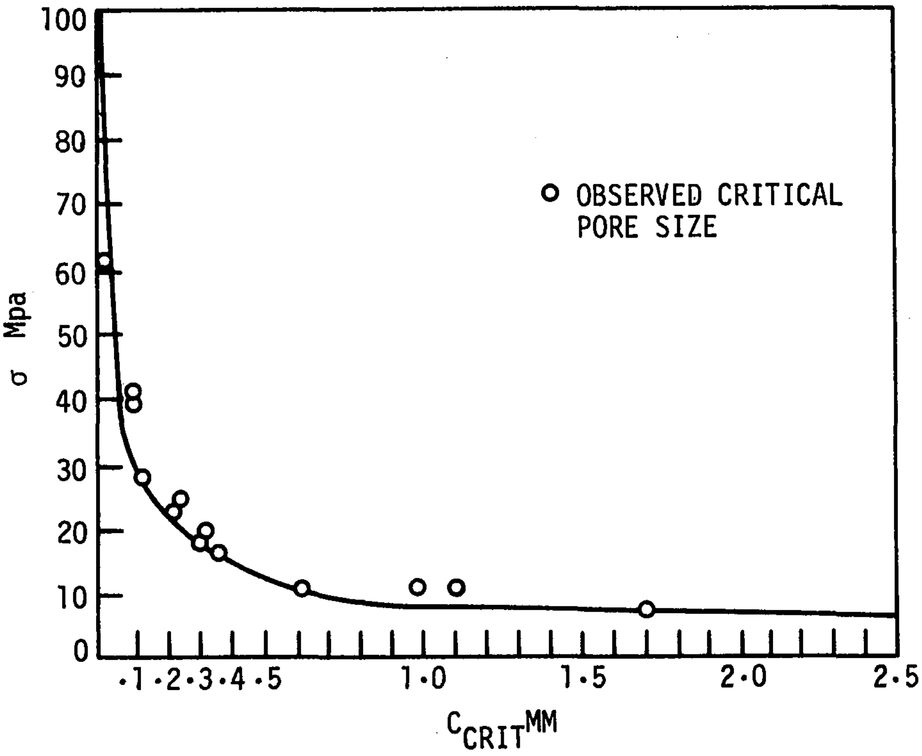


Figure 3. Tensile strength (σ) of cement paste vs. flaw size (C_{CRIT}) (2)

With respect to the cement-aggregate bond, Lea (70) says that chemical interaction is possible between lime and limestone aggregate. He cites investigations by Farran in which calcium hydroxide crystals formed a contact layer between the cement paste and a limestone aggregate in an epitaxial arrangement, forming a solid solution. The failure surface at the cement-calcite interface occurred through the calcite particles, whereas, with quartz, the failure occurs at the interface. This would tend to show a greater bond between $Ca(OH)_2$ and limestone than $Ca(OH)_2$ and quartz.

Hsu and Slate (56) performed approximately 1000 tests to determine the tensile bond strength between four types of aggregate and cement paste. They reiterate the lack of published information on bond strength. Their test results show that the bond strength of cement paste to aggregate is increased by: a) decreasing the water/cement ratio, b) wet curing rather than air drying the specimens, c) increasing the cement-sand ratio, d) prewetting the aggregate, and e) increasing the surface roughness of the aggregate (56, p. 483). They found that the bond strength varied between 41 and 95 percent of the paste tensile strength. Four aggregates were chosen, namely, sandstone, granite, New York limestone and Indiana limestone. New York limestone is generally harder and less porous than Indiana limestone. Figure 4 is an illustration of the mold which was used. It is patterned after ASTM C190 for measuring the tensile strength of mortar. Tables 6, 7 and 8 show the results in tabular form. Figures 5 and 6 show the results in graphical form. Table 6 shows that mortar with a cement:sand ratio of 1:2 has a higher bond

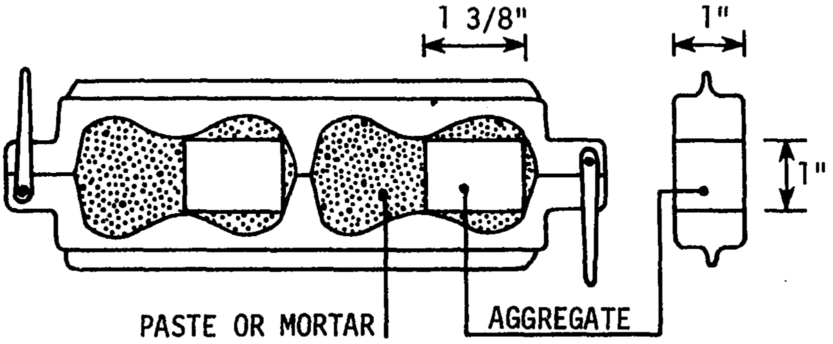


Figure 4. Diagram of mold device used to prepare tensile bond strength specimens (56)

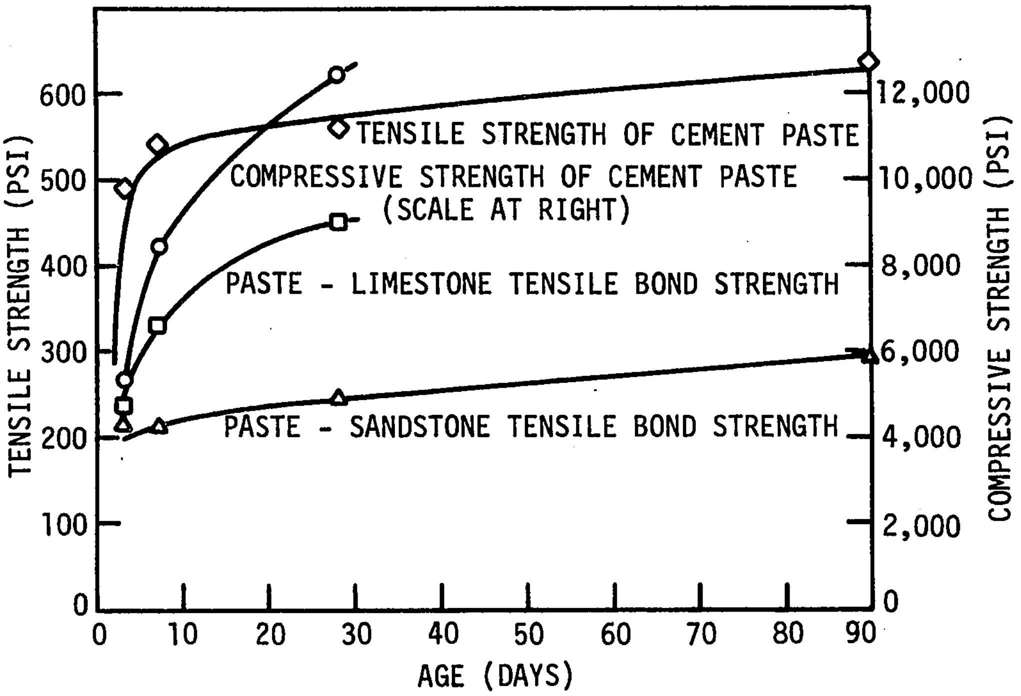


Figure 5. Paste-aggregate tensile bond strength, and tensile and compressive strength of cement paste as functions of age (56)

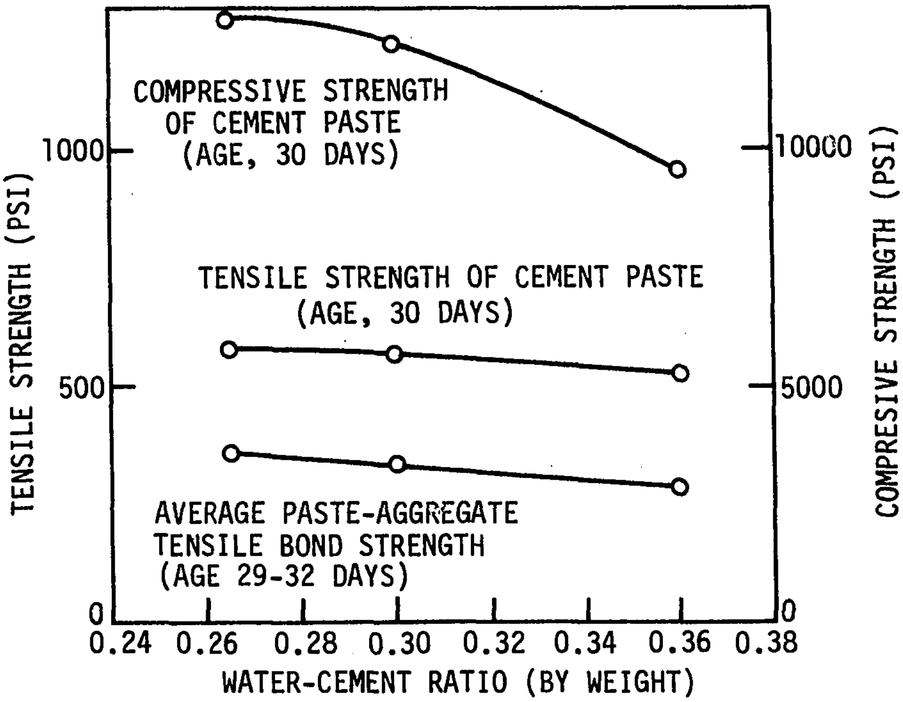


Figure 6. Average paste-aggregate tensile bond strength, and tensile and compressive strength of cement paste as functions of water-cement ratio (56)

Table 6. Mortar-aggregate tensile bond strength with three variables (rock type, water-cement ratio, and cement-sand proportion) (56)

Rock type	C/S W/C	 0.36	1:2 0.45	 0.55	 0.55	1:3 0.65	 0.75
New York limestone	(1)[a] psi	313	329	304	266	219	246
	(2)[b] psi	288	311	295	241	207	239
	(3)[c] percent	8.6	5.9	3.2	11.4	5.4	3.0
	(4)[d] percent	19.3	17.6	17.1	12.5	11.0	7.9
Granite	(1)[a] psi	201[e]	211[e]	235	193	186	171
	(2)[b] psi	191	205	234	180	175	166
	(3)[c] percent	5.0	2.8	0.50	7.6	6.2	2.9
	(4)[d] percent	8.0	9.2	13.6	11.3	17.2	15.0
Sandstone	(1)[a] psi	224	219	196	153	124	130
	(2)[b] psi	206	209	192	132	116	125
	(3)[c] percent	8.6	4.8	1.9	16.2	6.9	4.4
	(4)[d] percent	7.5	12.1	15.9	13.9	21.5	18.7

[a] (1) = Corrected value of tensile bond strength.

[b] (2) = Uncorrected value of tensile bond strength.

[c] (3) = Percentage of area occupied by air voids, according to which the tensile bond strength were corrected (percent).

[d] (4) = Coefficient of variation (percent). Each value of tensile bond strength is the average of nine specimens, with 29-31 days and tested on saw-cut surface of aggregate.

[e] These two values seem low.

Table 7. Paste-aggregate tensile bond strength with three variables (rock type, water-cement ratio of cement paste, and surface roughness of aggregate) (56)[a]

Surface roughness	Rock type	Sandstone			Granite			New York limestone			Indiana limestone		
	W/C	0.265	0.39	0.36	0.265	0.36	0.36	0.265	0.30	0.36	0.265	0.30	0.36
Polished	Strength, psi	234	240	223	---	347	307	433	338	271	264	222	237
	Range of deviation, %	+20 -22	+9 -13	+20 -15	--- ---	+6 -9	+14 -12	+45 -23	+27 -36	+35 -37	+6 -4	+51 -18	+11 -11
Saw-cut	Strength, psi	308	275	234	---	396	363	520	506	376	342	277	239
	Range of deviation, %	+13 -7	+13 -26	+24 -12	--- ---	+25 -19	+23 -40	+12 -16	+40 -50	+29 -28	+5 -8	+18 -13	+37 -25
Naturally-fractured	Strength, psi	361	367	319	---	402	354	486	439	355	322	355	288
	Range of deviation, %	+18 -9	+11 -14	+57 -12	--- ---	+7 -11	+12 -16	+26 -36	+20 -13	+33 -20	+9 -9	+8 -20	+26 -19
Number of specimens for each value			6			6			9			4	

[a] Age: 29-32 days. Tensile bond strengths between granite and paste of W/C = 0.265 were eliminated due to testing mistake.

Table 8. Effect of age on paste-aggregate tensile bond strength, and on tensile strength of cement paste (56)[a]

	Age, days	3	7	28	90
Sandstone - paste bond	Bond strength, psi (1)	216	214	244	294
	Coefficient of variation, percent	16.5	19.1	21.6	13.6
	(1)/(3)	44	39	44	46
Limestone - paste bond	Bond strength, psi (2)	238	333	453	---
	Coefficient of variation, percent	29.8	27.2	27.3	---
	(2)/(3)	48	61	82	---
Paste	Paste strength, psi (3)	489	546	550	641
	Coefficient of variation, percent	11.0	11.6	13.5	17.0

[a] Number of specimens for each value: 14 for bond strength, 18 for paste strength. Limestone-paste bond of 90 days was eliminated because of curing error.

strength than mortar with a 1:3 ratio. It also shows that New York limestone had the highest bond strength of the three aggregates shown, and that bond strength may be affected by water-cement ratio. Table 7 shows that New York limestone has a higher bond strength than Indiana limestone, and shows that a rough surface appears to give better bond strengths than a smooth surface. Table 8 and Figure 5 show that bond strength and cement paste tensile strength increase with age. The authors theorize that the bond strength for New York limestone, as shown in Table 6, is higher than the nonlimestone aggregate because of a chemical reaction between limestone and cement, previously reported by Farran _et al._ in 1956 (44, p.

475). They also theorize that the reason the New York limestone shows a higher bond strength than the Indiana limestone is because of the porosity and calcite inclusions in the latter (44, p. 475). The authors did not attempt to explain the fundamental mechanism of bonding.

D. Published Information on Mechanism of Brick-Mortar Bonding

The mechanism of bonding between brick masonry and mortar is not treated to any significant degree in the literature. Many experiments have been performed to examine the effect of various parameters on masonry bond strength, and these are discussed in Section V. However, there appears to be little published in the area of the fundamental mechanism of bonding between mortar and brick.

In addressing bond in his publication, Exterior Masonry Construction, Voss (96) claims that lime promotes the bond between brick and mortar through two processes. In the first process, he claims that because lime containing mortars harden slower than mortars which do not contain lime, they can accommodate slight movements during construction without degradation of bond. The second process, according to Voss, is one of chemical reconstitution, due to "autogenous healing". In this process, the lime, which is slightly soluble in water, migrates into areas where there are voids, and through the action of air and water, forms $CaCO_3$, the stable form of limestone. The $CaCO_3$ in turn is acted upon by air and water to form calcium bicarbonate. This material also migrates to fill voids and promote bond. The reaction is reversible as follows: $CaCO_3 + H_2O + CO_2 \rightleftharpoons Ca(HCO_3)_2$. Thus, lime rich mortars, according to

Voss, have the capability of bridging small gaps and increasing bond due to this autogenous healing. Lea (70) confirms the effect of lime in strengthening mortar. He states that experiments on lime-sand mortar have shown that exposure to CO_2 in an atmosphere of 50% relative humidity increases the 28 day tensile strength of the mortar from 19 psi (with no CO_2) to 167 psi (with pure CO_2) (70, p. 252). The calcium carbonate formed is crystalline, and the interlacing of the slowly growing crystals binds the whole mortar into a hard and coherent mass, although the process is confined to the outer layers. "Mortar taken from buildings many hundred years old, if uninjured, is found to consist mainly of calcium hydroxide, only the external portion having been converted to carbonate" (70, p. 252).

E. Interfacial Compounds

Several researchers have been successful in identifying some of the compounds which exist at the interface between cement paste and aggregate. As previously mentioned, Lea cites work of Farran in which Farran determined that a contact layer of calcium hydroxide is formed at the interface between limestone and cement paste and that a solid solution $Ca(OH)_2$-$CaCO_3$ was probably formed. This bond is apparently quite strong, inasmuch as the failure at the interface occurred inside the limestone.

Barnes, Diamond and Dolch (20) investigated the interface zone between cement paste and an artificial aggregate consisting of a glass slide. They found that a duplex film approximately 1 μm in thickness was deposited on the glass. The film layer in immediate contact with the glass consists of a continuous film of calcium hydroxide. This layer is "overlain by rod-shaped C-S-H gel particles projecting normal to the interface. After a few days, the pores of the near by cement paste become partly filled with a deposit of platelets of $Ca(OH)_2$" (20).

These same researchers later investigated the interface zone between cement paste and a sand aggregate. The sand was a standard silica sand from Ottawa. They found that the sand grains were never cleaved when samples were broken, but that the fracture followed the outside of the grains (20, p. 21). On the sand grains they found evidence of the same duplex films that they observed with glass, i.e., a smooth continuous layer of $Ca(OH)_2$ closest to the sand grain, with CSH above. As with the glass, $Ca(OH)_2$ plates formed between the duplex layer and the remainder of the paste (20, p. 23).

Farran, Grandet and Masso (44) investigated the interfacial region between porous fired clay and portland cement paste. Samples were cured at a relative humidity of 55% for two days, then broken and examined. The researchers conclude that the primary crystalline product formed at the interface with fired clay is ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ whereas, with other aggregates the crystalline product is primarily portlandite, $Ca(OH)_2$. The results of their X-ray analysis are shown in Figure 7. Figure 7a is the pattern of the cement paste. The peaks correspond to portlandite, $Ca(OH)_2$, (4.90 Å, 2.62 Å), ettringite (9.73 Å, 5.61 Å, 4.98 Å), tricalcium silicate (2.77 Å, 2.74 Å) and tricalcium aluminate (2.70 Å). Figure 7b is the X-ray pattern of the fired clay with a thin film of residual cement paste. The peaks are those of the quartz and feldspar of the brick, plus primarily ettringite in the adhered cement paste. $Ca(OH)_2$ is not present. Figure 7c is the X-ray pattern of a glass sample with a residual film of the cement mix. The primary crystalline component is $Ca(OH)_2$, and the secondary component is ettringite. The authors hypothesize that the reason the ettringite is found in quantity in the brick is that the sulfate ions from the gypsum instantaneously dissolve along with tri-calcium aluminate and are quickly adsorbed by the porous brick surface. Hence, there is a higher concentration of ettringite in the zone where the sulfate ions concentrate, which is in the immediate vicinity of the fired brick.

The formation of $Ca(OH)_2$ is a slower process, and its concentrations will be higher where the water has not been sucked from the paste (44). The researchers do not make any statements with regard to the effectiveness or lack of effectiveness of the ettringite in promoting bond.

Figure 7. X-ray diffraction chart traces for cement paste in contact with fired clay brick and glass (44).
a - Cement paste at the interface with brick
b - Fired clay brick with adhered mortar
c - Glass with adhered film of cement paste

P = Portlandite, $Ca(OH)_2$

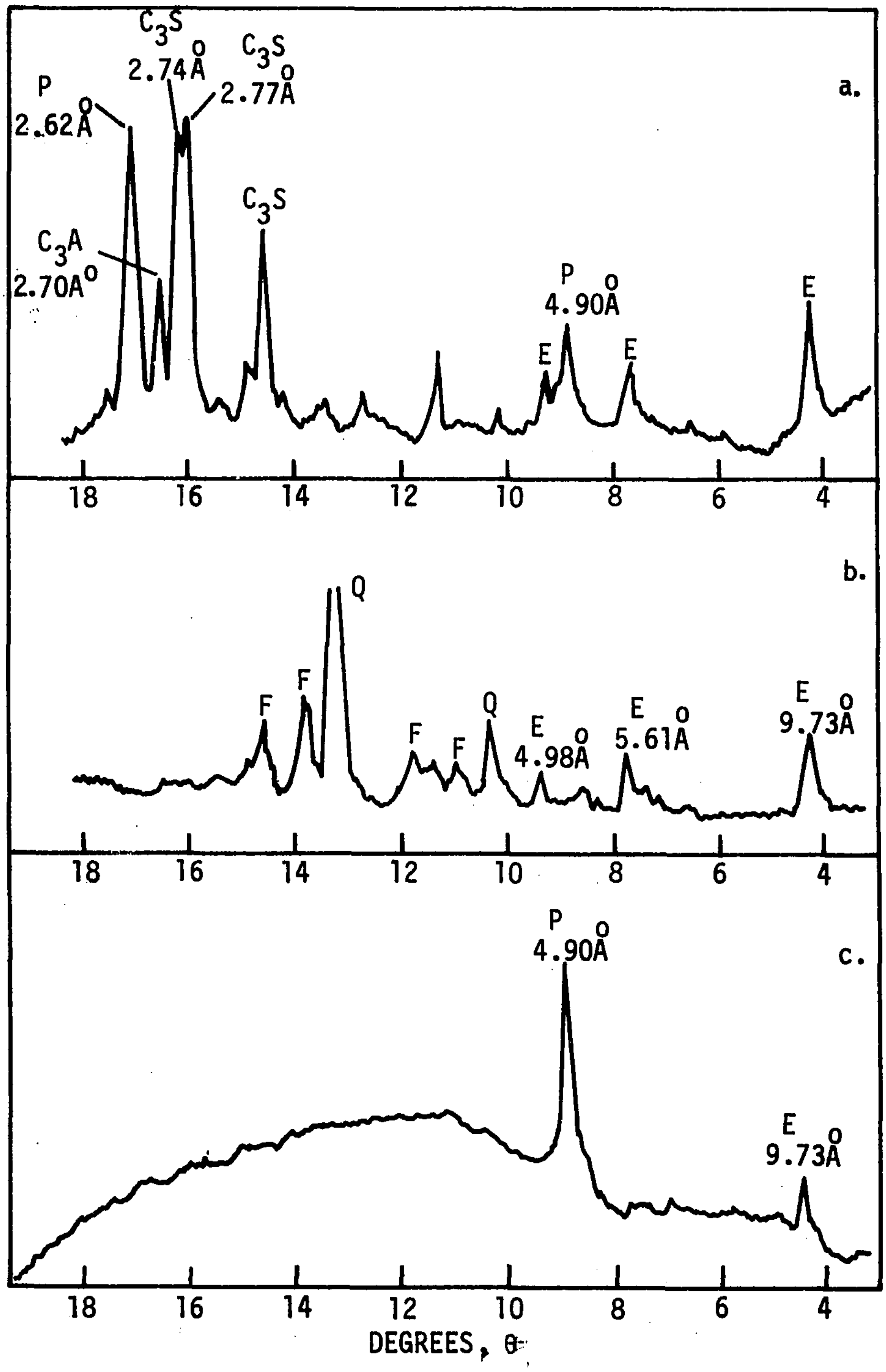
C_3S = Tri-calcium silicate, $3CaO \cdot SiO_2$

C_3A = Tri-calcium aluminate, $3CaO \cdot Al_2O_3$

E = Ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$

Q = Quartz, SiO_2

F = Feldspar (probably one of the feldspar groups of minerals. Not otherwise identified by the authors


a.
P
2.62Å
C$_3$S
2.74Å
C$_3$S
2.77Å
C$_3$A
2.70Å
C$_3$S
P
4.90Å
E
E
E
18
16
14
12
10
8
6
4
b.
Q
F
F
F
F
Q
E
4.98Å
E
5.61Å
E
9.73Å
18
16
14
12
10
8
6
4
c.
P
4.90Å
E
9.73Å
18
16
14
12
10
8
6
4
DEGREES, θ

V. PREVIOUS INVESTIGATIONS OF MASONRY BONDING

A. General

In contrast to the fundamental mechanism of bonding of mortar to brick masonry, where few published articles are available, the subject of tensile bond strength, and its variation with several factors, has been well researched and published. Bond strength can be easily measured, and conclusions can be drawn with respect to which factors, such as brick suction and mortar flow, affect bond strength, without addressing the fundamental mechanism of the bonding itself.

The investigations which are summarized in this section have done precisely that. They are valuable investigations, because they have provided quantitative evidence on which factors enhance and which factors lessen bond strength. However, they did not address the mechanism of bonding nor the interfacial compounds formed at the interface. The results of these investigations have been considered in the preparation of the specifications which govern masonry materials and masonry construction.

B. Investigations by Palmer and Hall (1931)

1. General

L. A. Palmer and J. V. Hall were both research associates with the American Face Brick Association. The results of their investigations are included in the paper (79) entitled "Durability and Strength of Bond Between Mortar and Brick."

In their experiments, the authors investigated the strength between brick and mortar for a total of 1296 brick-mortar units. Each unit was composed of two bricks placed together with a mortar joint in between. Half of the units underwent a freeze-thaw durability test; half underwent a simple tensile bond strength test.

2. Durability tests

The units tested for durability were cured for two months before testing. They were then immersed in water for 48 hours, then subjected to 50 repetitions of alternate freezing and thawing. Failure was judged to have occurred when, upon attempting to lift the specimen, the top brick separated from the bottom brick. The failure rate at the end of 50 freeze-thaw cycles, varied between 67% and 100%, depending on the type and absorption of the brick used, and the degree of saturation of the brick prior to laying the brick. Most of the bond failures occurred in the first ten cycles. Table 9 is a listing and description of the types of brick used, along with the range of absorption of the brick and their rate of absorption. Brick type #2 had the highest total absorption, *i.e.*, 17.0%, whereas type #3 had the lowest total absorption, *i.e.*, 4.8%. Type #1 had the highest rate of absorption, *i.e.*, 30 minutes to wet from one end to the other after immersion of one end in water. Type #4 had the lowest rate of adsorption; *i.e.*, 8-12 hours to wet from one edge to another.

Tables 10-15 summarize the results. Table 10 shows by brick type the durability versus degree of saturation of the brick when set. The lowest failure rate was associated with type #1 brick, which was 80% saturated at

Table 9. Brick types used by Palmer and Hall (79)

Brick Type	Description	Range of Absorption, 48 hr immersion, % of dry wt.	Rate of Absorption, end to end
1	Made from surface clay, molded dry-press	9.5 - 15.5	30 min
2	Made from surface clay, molded dry-press	11.5 - 17.0	1 hr
3	Made from fire clay, extruded	4.8 - 9.8	4-6 hrs
4	Stiff mud-shale, extruded	5.2 - 10.7	8-12 hrs
5	Stiff mud-shale, extruded	6 - 11.5	4-6 hrs

Table 10. Durability of bond versus degree of saturation at time of laying brick (79)

Brick Type	Total Absorption Range (%)	Rate of Absorption, Hrs	Total # of units tested	Failure rate of bonded units, 1:1:6 mortar		
				Brick dry	Brick 50% saturated	Brick 80% saturated
1	9.5 - 15.5	Very rapid, 0.5 hr	36	97	97	67
2	11.5 - 17.5	Rapid, 1 hr	36	100	94	92
3	4.8 - 9.8	Slow, 4 hrs	108	78	86	81
4	5.2 - 10.7	Very slow, 8-12 hrs	108	89	89	97
5	6 - 11.5	Slow, 4-6 hrs	108	75	77	83

the time of preparing the couplets. Type #1 brick had a high rate of absorption and a high total absorption. The highest failure rates were experienced in brick types #1 and #2, the high absorption brick, when set dry. The authors, therefore, conclude that the absorption properties of the brick were not of any considerable importance when due regard was given to the necessity of thoroughly wetting the rapidly absorbing brick. The conclusion appears to ignore the much lower failure rate of the high absorption brick, brick #1, when properly wetted.

3. Effect of lugs on durability

One-half of all specimens were prepared with a metal spacing lug inserted in the mortar, between the top and bottom brick. An average of 95% of the specimens with lugs failed; an average of 69% of those without lugs failed. The authors relate the failure to shrinkage of the mortar, and conclude that this helps explain the greater incidence of cracks in the vertical head joints of masonry walls where the brick are not free to move to accommodate mortar shrinkage.

4. Effect of type of mortar on durability

Two types of mortar were used with brick type #5 only. One mortar was a straight cement-sand mortar in the volume proportions 1:3. The other mortar was a 1:1:6 mortar (cement-lime-sand). The results are shown in Table 11. The authors concluded that there was a slightly greater percentage of failure of bond with the 1:1:6 mortar rather than 1:3 mortar.

Table 11. Durability of bond as related to mortar (79)

Mortar Type	Failure Rate %	Number Averaged
1:3 (portland cement:sand)	48	216
1:1:6 (Cement:lime:sand)	61	216

5. Effect of loading on durability

The samples made with brick #5 were examined not only for the effect of type mortar, but also for the effect of applying a load to the specimens during the curing period. The load was applied by placing steel plates over and under the specimens and tightening the bolts connecting the plates. The initial pressure was light, but after 48 hrs, the bond was tightened so as to impose a pressure between 500 and 800 lbs. The results are shown in Table 12.

Table 12. Durability of bond as increased by a vertical load on bonded units (79)

Loading	Failure Rate %	Number Averaged
Units loaded	36	216
Units not loaded	73	216

The data in Table 12 include all of the brick #5 samples, both with and without lugs, and those prepared with 1:1:6 mortar as well as those prepared by 1:3 mortar. Seventy-six percent of the nonloaded specimens failed and 36% of the loaded specimens failed. Palmer and Hall conclude that the percentage failure of nonloaded units was twice that of the loaded ones, and therefore bond failure is most likely to occur in vertical joints in masonry, where there is no vertical loading.

6. Bond strength tests by Palmer and Hall - general

Half of the units made by Palmer and Hall were subjected to the tests described in paragraphs 1-5 above. The other half were subjected to a variety of storage conditions, then tested for tensile bond strength after six months in storage. The survivors of the durability tests in paragraphs 1-5 above were also included among those tested for bond strength.

The manner of testing was to grip the top and bottom bricks in a set of jaws and pull the specimen apart. A universal testing machine was used to apply the load. The load at failure was divided by the area of the mortar contact surface to determine the failure stress in psi.

7. Effect of storage conditions on bond strength

The units were stored in three conditions; namely, outdoor storage (winter), laboratory storage, and humid room storage. Table 13 shows the results.

Table 13. Effect of storage conditions on bond strength (6 months, 1:1:6 mortar, with and without lugs) (79)

Brick type	# of Couplets Tested			Average strength (psi)		
	Outdoors	Lab	Humid Room	Outdoors	Lab	Humid Room
1	12	12	12	19.3	21.1	25.3
2	12	12	12	51.8	32.7	29.0
3	36	36	36	34.0	16.3	39.4
4	36	36	36	21.0	5.6	28.0
			Average:	31.7	18.9	30.4

The authors make no conclusions with respect to the effect of storage conditions. It would appear, however, that the drier laboratory conditions resulted in lower bond strengths than the outdoors and humid room conditions.

8. Effect of brick total absorption on bond strength

To investigate the effect of total absorption on bond strength, Palmer and Hall grouped the data for all brick into two ranges of absorption for each brick. The low ranged from 4.8 to 14.5 percent and the high ranged from 7 to 17.5 percent. The results of the bond tests indicated an average of 29.1 psi for the lower absorption range, and 25.0

psi for the higher absorption range. The authors conclude that there is no significant difference.

9. Effect of degree of wetting brick on bond strength

Three conditions were evaluated to test the effect of degree of wetting of the brick on bond strength. Samples were made up with the units 80% saturated, 50% saturated and with the brick dry. Table 14 shows the results. The lowest strengths result from setting brick with high absorption rates dry. The highest strengths result from a) setting high absorption rate brick 80% saturated, and b) setting dry brick type #3, which has a very low total absorption, and low absorption rate.

Table 14. Effect of degree of wetting brick on strength of bond (1:1:6 mortar, with and without lugs) (79)

Brick Type	Absorption Range (%)	Time to wet end to end	Average Bond Strength (psi)		
			Set 80% Saturated	Set 50% Saturated	Set Dry
1	9.5 - 15.5	1/4 - 1/2 hr	21.9	9.6	6.8
2	11.5 - 17.5	3/4 - 1 hr	37.8	16.0	0.5
3	4.8 - 9.8	4 - 6 hrs	25.6	29.1	35.0
4	5.2 - 10.7	6 - 12 hrs	20.1	17.1	18.0

The authors comment that it is the rate of absorption, not the total absorption that must be given primary consideration.

> "A rapidly absorbing brick tends to dry the wet mortar very quickly when it is first applied. When so quickly dried, the mortar loses plasticity and does not make intimate contact with the entire surface as it should. At the same time a brick when laid should not be so thoroughly saturated that it can absorb no water. A little suction is necessary to form the best bond", (79, p. 489).

The authors conclude that dense, impervious brick which absorb water very slowly (Brick types 3,4) can be bonded satisfactorily. They conclude that the strength of bond using relatively porous brick is slightly greater than that using relatively impervious brick. They also concluded that there was nothing to be gained by wetting brick which did not wet through from edge to edge in less than 4 hours.

10. Effect of metal lugs on bond strength

The placement of lugs in the mortar beds prevented movement of the brick to accommodate any mortar shrinkage. The result was that the average bond strength for units with spacing lugs was 15.2 psi whereas the average bond strength without lugs was 38.8 psi. The authors draw no conclusions, but it appears that the use of lugs had a deleterious effect on bond strength because of the inability of the brick to accommodate mortar shrinkage.

11. Effect of mortar type and loading on bond strength

Units made with brick type #5 were the only ones made up with both 1:3 (cement:sand) and 1:1:6 (cement:lime:sand) mortars. They were also the only units subjected to loading during curing. Furthermore, all of the brick #5 units were subjected to the freeze-thaw durability tests. Data for those which survived the durability tests are shown in Table 15. The authors comment that although the loading of the units appeared to improve survivability, it did not appear to affect the bond strength. The authors go on to mention that very little mortar remained on the failed brick surface in the case of the 1:3 mortar, whereas a considerable amount of the 1:1:6 mortar remained adhered to the brick surface. This would indicate a bond failure with the 1:3 mortar, and a mortar failure with the 1:1:6 mortar. They conclude that the ratio of bond strength to mortar tensile strength was greater in the 1:1:6 than the 1:3 mortar.

12. Summary

The tests and observations above in the Palmer-Hall study are amongst the most comprehensive in the literature. Two of the most important conclusions relate to the importance of pre-wetting highly absorptive brick and the effect of loading on durability.

The experiments provided useful data with regard to the degree to which bond strength and durability are affected by loading, use of lugs, type of mortar, pre-wetting of brick, and storage conditions. However, there was no attempt to investigate the nature of the bond itself or to investigate the effect of any chemical pretreatment of the brick on the bond strength.

Palmer and Hall do not make mention of the consistency, or flow, of their mortar. However, they do say that the water content, by weight, of the prepared mortar was 16.2% for the 1:1:6 mortar and 15.2% for the 1:3 mortar. Based on investigations made as part of this dissertation, this

Table 15. Tensile bond strength of units made with brick type #5, for two different mortars, for two loading conditions, all units subjected to 50 freeze-thaw cycles. Data are for units with and without lugs (79)

	Units Loaded					Units not loaded				
			Bond Strength (psi)					Bond Strength (psi)		
Mortar	No. of Units Made	No. of Survivors	Ave.	Indiv. Maximum	Indiv. Minimum	No. of Units Made	No. of Survivors	Ave.	Indiv. Maximum	Indiv. Minimum
1:3	108	76	27.3	84	1.9	108	37	31.3	69.9	5.4
1:1:6	108	63	15.5	71.6	2.0	108	21	22.7	60.9	7.4

would result in a flow of 130% for the 1:1:6 mortar. Couplets using 1:3 mortar were not prepared as part of this investigation, hence no estimate of that flow can be made.

C. Investigations by McBurney (1942)

1. General

Robert S. McBurney was a research associate in Mechanics at the University of Wisconsin. He performed a series of tests on brick and mortar, the results of which appeared in an unpublished paper in 1942 (71). It has not been possible to obtain a copy of the paper in spite of queries to McBurney himself, the University of Wisconsin, and the sponsor, the Structural Clay Products Institute. Instead, the results reported here are those reported by Plummer in his book (83).

McBurney tested 467 couplets. He varied mortar composition, flow and brick suction. Couplets were cured in laboratory air for 28 days. The mortars he used were portland cement/lime mortars. Flows varied from 95 to 135.

2. Test Results

Table 16 shows the results obtained by McBurney. The bond strengths shown are the averages of 5 to 15 couplets. Within each mortar, one can see that flows between 125 and 135 provide the highest bond strengths. Mortars 1, 2, and 3 utilize lime putty. Mortar 4 utilized a pressure-hydrated dolomitic lime, and mortar 5, a commercial hydrated lime. It would appear, in comparing mortars #2, 4 and 5 that the commercial hydrated lime and lime putty might be better in providing maximum bond

Table 16. Tensile bond strength of mortars (83)

Mortar No. & Mix[a]	Initial Flow, %	Flow after Suction, Percent of initial flow	Compressive Strength, psi	Tensile Bond Strength, psi Brick Suction, grams 5-10	 10-20	 20-40
1	125-135	87	4830	49	76	45
1:1/4:3	110-125	87	5153	49	49	10
	95-110	87	5492	18	11	2
2	125-135	89	2175	54	77	67
1:1/2:4 1/2	110-125	88	2408	43	58	44
	95-110	88	2758	22	23	14
3	125-135	92	793	47	72	59
1:1:6	110-125	93	905	49	56	53
	95-110	91	1173	14	36	23
4	125-135	80	2938	64	62	56
1:1/2:4 1/2	110-125	80	3215	41	46	34
	95-110	80	3488	28	21	6
5	125-135	63	3290	66	70	49
1:1/2:4 1/2	110-125	64	3503	70	57	32
	95-110	66	3642	50	44	8

[a] Proportion: cement, lime, sand by volume. Note: 1 gram equals 0.035 oz. approximately.

strength and compressive strength. It also appears that brick suction in the range 10-20 provided better bonding than suctions greater or lesser than that range. An exception appears to be mortar 5 at intermediate flow, when used on low suction brick.

The effect of quantity of lime on water retentivity of mortar is also shown in Table 17. Water retentivity was highest in the 1:1:6 mortar, which contains the greatest quantity of lime. Note, however, that the tensile strength of the 1:1:6 mortar was lower.

Table 17. Compressive and tensile strengths of mortars (83)

Mortar		Initial flow, Percent	Water retention Percent	Strength, psi[a]	
Type	Mix[b]			Tension	Compression
M	1:1/4:3	100	87	457	5492
		120	87	425	5153
		133	87	420	4830
S	1:1/2:4 1/2	100	89	300	2758
		120	88	277	2408
		133	88	268	2175
N	1:1:6	100	92	180	1173
		120	93	165	905
		133	91	145	793

[a] Tension specimens, briquets; compression, 2-in cubes; both cured in water, tested at 28 days.

[b] Proportions: cement, lime, sand by volume.

3. Summary

McBurney's tests provide a considerable amount of useful information on the effects of mortar type, flow, brick suction and type of lime on bond strength. Generally, higher flows, moderate suction brick and type "S" mortar resulted in the highest bond strengths. The lowest bond strengths occurred with high suction brick and low flows. However, where a high retentivity mortar was used, this reduction in bond strength was lessened.

D. Investigations by Pearson (1943)

1. General

J. C. Pearson was Director of Research for the Lehigh Portland Cement Co., Allentown, Pennsylvania. The results of his investigations are included in a paper entitled "Measurement of Bond Between Bricks and Mortar", published in 1943 (80).

The thrust of his investigations was to seek the best way to test for bond strength. All of the methods Pearson tried will not be discussed here. However, he did perform crossed couplet tests, and the results are pertinent to this investigation.

2. Test procedure

The crossed couplet test procedure used by Pearson to test for bond strength was the crossed brick couplet test as described by ASTM Committee C-12 on Mortar for Unit Masonry in the ASTM Bulletin, October 1938. The apparatus and procedures are similar to those used for the crossed couplet tests performed as part of this investigation. Two bricks were mortared together at 90° to each other. After suitable curing time, the couplet was placed in a jig in a testing machine, where the bricks were forced apart.

To force the break in bond to occur at the top brick, Pearson coated the bottom brick with a grout of high-early strength cement before applying the mortar. This almost always caused failure to occur in the top joint.

The bricks used had a one minute absorption "suction", between 35 and 60 grams which is very high. The bricks in the couplets were initially forced together by a steady pressure of 20 lbs. The ASTM specifications now require a sharp blow to the top brick at time of assembly, using a special drop hammer. One week of damp curing preceded the testing.

Mortar consistency was measured by using a 6 inch slump cone. The slump was maintained to within 1/2 inch of any particular range. This was accomplished by periodically retempering (adding water to) the mortar. A companion test was also conducted using a wall test in which the top most bricks could be pried up, and the modulus of rupture of bond could be measured. Although there is no direct comparison between modulus of rupture bond strength, which is a flexural phenomena, and the couplet test, which measures tensile bond strength directly, there were some interesting comparisons.

3. Results

Unfortunately, Pearson does not indicate the composition of his mortars. Although he uses some designations which were in use at the time, he also uses some designations which were not. Therefore, the possibility exists that the designations he is using are his own, and should not be assumed as being those in practice at the time. However, certain observations are possible.

The range in bond strength for his couplet specimens ranged from 54.9 psi to 77.8 psi, based on 310 couplets tested.

Mortar consistency as measured by slump did affect bond strength. For example, the average bond strength for ten couplets in which the mortar had a slump between 3 1/4 and 3 inches was 68 psi. The average bond strength for another ten couplets in which the mortar had a slump between 2 3/4 in and 2 3/8 in was only 44 psi. The author concludes that the consistency of the mortar must be closely controlled because of the significant effect it has on bond strength.

Retempering did not appear to significantly affect bond strength. According to the authors, "If re-tempering affects the bond strength materially, it should cause the average of the first ten couplets of a set to be higher or lower than the average of the second ten, in the long run. The grand average difference from all...sets...is less than 2 percent, in favor of the first ten" (80, p. 863).

Although the brick were joined by pressure only without impact in the case of the couplet tests, both pressure only and impact were used on specimens placed in the wall. The test results showed that there was a considerable difference in the modulus of rupture of bond between those two methods. "The effect of tapping the bricks is, therefore, to increase the bond strength from 50 to 100 percent, which suggests that the contact between mortar and brick is much improved by impact or by vibration resulting from impact" (80, p. 864).

With respect to statistical variation, the number of couplets required for P = 0.9, according to Pearson, is six, based on his data (80, p. 865).

4. Summary

Pearson made an important contribution to the body of knowledge with respect to testing for bond strength. He endorsed the crossed couplet test as a measure of tensile bond strength; he showed the importance of consistency and "tapping", and the relative unimportance of re-tempering the mortar. Unfortunately, conclusions cannot be drawn with respect to mortar type (compared to present mortar types) because of his failure to explain his designations.

E. Investigations by Forkner *et al*. (1948)

1. General

H. R. Forkner and associates performed this work at Virginia Polytechnic Institute in the 1940s. The results are included in a paper entitled "Mortar Bond Characteristics of Various Brick", published in 1948 (46).

The purpose of these tests was to examine brick from different parts of the country to determine the effect of surface texture, bond strength, suction rate and raw materials on tensile bond strength. Also examined were the effect of mortar type and mortar flow. Six different types of brick, each with a varying suction rate, were used. Three mortars, which correspond to present day types M, S, and N were used, and mortar flows ranged from 67% to 130%.

2. Test procedure

Crossed brick couplets were prepared to test for tensile bond strength. No pretreatment, or presoaking of the brick was accomplished except in one experiment where the authors desired to adjust brick suction by presoaking. Couplets were formed using two methods. In the first method, the bricks were set by hand without any mechanical help for alignment or leveling and were given three sharp taps with the butt of a mason's trowel on the top brick. The second method of forming used a special jig to insure proper 90° alignment of the brick, and a strap which held the top brick level as it was placed on the mortar bed. This method was also used by Pearson. Instead of tapping the brick together, a uniform 12 pound pressure was applied to the top brick for several minutes. All specimens were cured for 28 days.

3. Results

a. Effect of mortar flow The flow of the mortar mixes was varied in each of several investigations. The overall results, irrespective of type of brick or brick suction, are shown in Table 18. An analysis of variance by the authors for each investigation showed the effect of mortar flow on bond strength to be highly significant (F> tabular value for 1% level). Generally, as mortar flow increases toward 125%, so also does

Table 18. Effect of mortar type and flow on bond strength. Summary of investigations by Forkner and associates (46)

Investigation	Type Mortar	Average Flow	Average Bond Strength
1	S	71.5	9.6 psi
1	S	119.3	34.4
2	M	103	18.8
2	M	124	39.6
2	S	103	40.2
2	S	124	41.5
2	N	103	35.2
2	N	124	41.1

Table 18. (Continued)

Investigation	Type Mortar	Average Flow	Average Bond Strength
3	S	(95-105)	26.8
3	S	(115-125)	37.2
3	S	(130-140)	36.3
4	S	(100-110)	16.8
4	S	(115-125)	24.7
4	S	(125-135)	26.2
5	S	(95-100)	23.0
5	S	(115-125)	44.0
5	S	(125-135)	23.8 (Probably too low)
6	S	(110-120)	28.6
6	S	(125-135)	36.2

bond strength. The authors conclude: Mortars in the range of 125% give better tension bond strength than lower or higher mortar flows (46, p. 6).

b. Effect of type of mortar on bond strength The investigation compared 3 different types of mortars at two different flows. The results are shown in Table 19.

Table 19. Effect of type of mortar on tensile bond strength at 28 days (46)

Type Mortar	Average Tensile Bond Strength (psi)		
	Mortar Flow		Grand Average
	100-110	120-130	
M (16 couplets	18.8	39.6	29.2
S (15 couplets)	40.2	41.5	40.4
N (16 couplets)	35.2	41.1	38.2

Type S mortar appears to result in the highest bond strength for both flow situations, although to a lesser extent at higher flow. Analysis of variance for this investigation shows the effect of mortar type on bond strength to be highly significant. The authors conclude: "The strength superiority of the type S and N mortars over the type M mortar is striking at the lower flow of 100-110%. At the higher flow of 120-130%, however, all mortars are essentially the same in regard to tension-bond strength" (46, p. 25).

c. Effect of surface texture on bond strength Two separate investigations were used to evaluate the effect of surface texture on bond. The smooth surface was provided by the sides of extruded brick. This surface is smoothed by the steel die surface as the clay is extruded. The rough surface is formed as the individual brick are cut off by a wire as they are extruded.

Table 20 shows the effect of surface texture on bond strength.

Table 20. Effect of surface texture on bond strength (46)

Mated Surfaces	# of Couplets	Average Bond Strength (psi)
	Flow = 67-75	
Rough-Rough	16	14.8
Smooth-Smooth	16	4.4
	Flow = 95-110	
Rough-Rough	36	32.1
Smooth-Smooth	12	20.4

Table 20. (Continued)

Mated Surfaces	# of Couplets	Average Bond Strength (psi)
	Flow = 105-115	
Rough-Rough	8	32.8
Smooth-Smooth	8	24.6
	Flow = 116-125	
Rough-Rough	52	39.9
Smooth-Smooth	28	32.1
	Flow = 126-140	
Rough-Rough	20	47.1
Smooth-Smooth	20	32.24

The rougher wire cut surface, which is the normal bonding surface for brick, resulted in higher bond strengths than the smooth extruded surfaces. The authors conclude: "The rough to rough surface combination...shows a consistency and overall higher average tension-bond strength than the smooth to smooth combination."

d. Effect of type of brick Six different types of brick based on raw material and absorption (suction) were evaluated. Two were stiff-mud shales, with suctions of 10-20 and 2-5 grams per minute. Two were stiff-mud clays with suctions of 10-20 and 2-5 grams per minute, and two were soft mud clay, with suctions of 50-60 grams per minute each. The results of this investigation are shown in Table 21.

Table 21. Effect of type of brick and suction rate on bond strength (46)

Brick Raw Material:	Stiff-Mud Shale			Stiff-Mud Clay			Soft Mud Clay		
Suction, gms of H_2O/min	5g/min	10-20	50-60	5g/min	10-20	50-60	5g/min	10-20	50-60
Tensile Bond Strength, psi	29.4	39.3	---	47.1	40.8	---	---	---	22

With no prewetting of the bricks before assembly, it appears that stiff-mud clay brick resulted in generally higher bond strengths than the stiff-mud shale or soft mud clay. The authors conclude, "Of the brick types studied, the stiff-mud clay group shows the highest tension bond strength, followed by stiff-mud shale and soft-mud clay. The bricks in the 10-20 gram per minute suction rate group do not vary significantly in their tension bond strength, whereas those in the 5 gram per minute group do. This may suggest that in the 10-20 gram/minute group it is a matter of indifference as to the type of brick" (46, p. 32).

e. Effect of presoaking brick with a high suction rate One kind of brick, stiff-mud shale, with a high suction rate of 45-55 grams per minute, was presoaked until its suction rate was reduced to two ranges of suction, 30-40 grams per minute and 15-20 grams per minute. Couplets made from these brick were then tested to determine the effect of presoaking on the bond strength. The results are presented in Table 22.

Table 22. Effect on bond strength of reducing suction by presoaking (46)

Mortar Flow *	Tensile Bond Strength (psi) Suction Rate 45-55 Original	30-40 Adjusted	15-25 Adjusted	Grand Average
100-110	13.7	13.3	23.3	16.8
115-125	16.0	27.3	30.7	24.7
125-135	22.0	22.7	34.0	26.2

The effect of presoaking brick with a high suction rate appears to be beneficial. Also, the same investigation shows the increase of bond strength with increasing mortar flow. The authors conclude, "Adjustment of relatively high (45-55 grams/min) suction rate brick to lower suction rates (30-40 and 15-25 gms/min) operates to increase the tension bond strength. For the three flows of mortar used, tension-bond strength increases as the flow of mortar is increased" (46, p. 35).

f. Summary The work of Forkner and his associates was very extensive. It provided valuable confirming data with respect to the effect of surface texture, brick suction, mortar type and mortar flow on bond strength.

F. Investigations by Thornton (1953)

1. General

John C. Thornton was the architect for the Detroit Edison Company at the time he performed these investigations (94). Many masonry structures had been built for Detroit Edison over the years, to include brick chimneys for their power plants and buildings with brick walls. Some of these structures exhibited a variety of problems. In investigating cases of unsound masonry, Detroit Edison had found that certain brick showed a tendency to leak, and certain brick did not. Specifically, they found that structures constructed of sand-finished brick were more prone to leak than those constructed of smooth brick. As a result, they initiated a series of experiments to determine the effect of surface texture on bond and on water penetration.

Surface texture in this case pertains to the texture applied for architectural purposes to the sides of the extruded column. This would include the face that one would see exposed in a brick wall, and might include the other three concealed faces. However, the top and bottom surfaces of the brick are normally wire cut perpendicular to the extruded column, and are not considered textured. An exception would be brick which is pressed in a mold, where the mold has been given a sand coating to aid in the release of the brick from the mold. Such brick would have a thin coating of sand on all faces.

2. Test procedures

Three sets of experiments were run; one to test the brick surface for capillarity; one to test for bond, and finally a series of "chimney" experiments to test for both. In the capillarity tests, bricks were set on end in 5/8 in of water. The rise on the brick surface in a period of 15 minutes was noted. This surface capillarity was then compared to the brick suction. In the bond tests, bricks were covered with mortar, then knocked loose at the end of four hours. A visual rating from 0 to 100 was given the bonding, based on the amount of adhered mortar. Comparisons were also made to test the effect of waterproofing, and prewetting on the bond. A comparison between 4 hrs and 4 days was also made, and it was determined that the 4 hr test gave a good indication of bond.

In the chimney test, 4 sided wells, about 48" x 48" x 18" high were made of brick and filled with water after a 30 day curing period. The amount of leakage to the outside was observed and a comparison of the leakage rate for various brick surfaces was made. Dye was also introduced in order to determine the extent of penetration into areas where bond was not complete.

3. Test results

The results of these investigations are probably best discussed in a qualitative rather than a quantitative manner. The reason for this is that bond tests were not made by a testing machine. Rather, the bricks were knocked loose and the quantity of mortar which adhered was rated to be between zero and 100% of the surface area.

In the capillarity tests, it was found that bricks with a rough or scored surface showed a rise of moisture along the rough face that was considerably more rapid than the rise through the brick itself. When bricks were placed so that grooves in the surface run vertically, the rise up the scores on the surface was rapid. When bricks were placed so that the grooves ran horizontally, the rise was slowed. Surface capillarity appeared to be independent of brick suction. Brick with a high suction could exhibit low surface capillarity, and vice versa. Sand finish brick exhibited the highest surface capillarity. However, when the excess sand was brushed or scraped off, the capillarity dropped.

The results of the bond tests showed that surface roughness, instead of improving bond, actually weakened it. The tests were made of the head (end) joints after the brick had set 4 hrs (later 4 days). Sand mold brick showed poor bond. A textured "matt" brick was rather poor. The bond on vertically scored brick was fair. The mortar had adhered to the smooth surfaces between scores, but had not filled the scores. With smooth surfaced brick, mortar covered the entire surface, and the bond appeared to be good. The effect of waterproofing on capillarity and bond was also examined. The ends (heads) of brick were treated with a silicone and wax-base waterproofing compound. This stopped entirely the surface capillarity, i.e., water would not rise on the treated vertical surface. When coated with mortar and later knocked loose, the treated ends showed better bonding than the untreated areas. In placing smooth brick against rough brick, the mortar would usually break away from the rough brick and would adhere to the smooth brick.

Premoistening brick significantly improved bonding for the sand-mold brick and had less effect on the other finishes.

In the well or chimney tests, there were 250 leaks in 8 chimneys. Not one of those leaks occurred in the mortar used with smooth brick. The time for water to appear on the outer surface of the brick from inside the well was also measured. The bulk of all leaks appeared between 5 and 25 minutes after filling the wells.

To further examine the lack of bond which probably was accounting for the leaks, a dye was introduced into the water. The extent of dye penetration into joints made with smooth brick was negligible. On the other hand, the extent of dye penetration into joints made with sand-mold brick was very extensive.

Further tests with the sand-mold brick indicated that if the surface sand was removed by wire brushing or scraping, capillarity decreased and bond increased. A second series of tests included a vertical scored brick, where the scoring on the ends runs vertically, or 90° to the direction of water penetration. The leakage was practically nil, which indicated that the bond to the smooth portions in between scores was good. In the second series, sand-mold brick which was prewetted exhibited a drop in the area of dye penetration from 905 in^2 to 368 in^2, indicating that prewetting of sand-molded units with a high surface capillarity aids bonding. This was indicated in their first series of tests also.

Figure 8 offers a possible explanation for the effect of the sand on preventing good bond. The authors propose that the sand provides a path for the water, which not only leaves the mortar, but travels along the

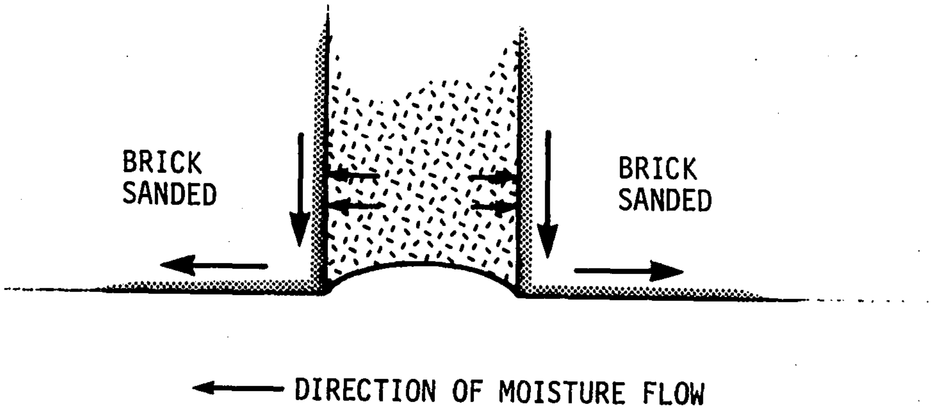


Figure 8. Illustration of the capillary effect of a sand coating on brick in wicking away moisture from the joint. Arrows indicate direction of flow of moisture (94)

series of capillaries formed by the sand to the sanded front face of the brick, where it rises and evaporates. Moisture continues to be removed from the mortar in this fashion.

4. Conclusions

The conclusions of the author follows (94, p. 20):

a) "Mortar does not get into the voids of rough brick, regardless of whether the voids are large,...or small, as in sand finish brick.

b) Capillary action of some brick surfaces draws moisture from the mortar before perfect bond can take place.

c) Loose or removable sand on any faces of brick raises capillarity and reduces bond considerably....

d) For rough brick a mortar is needed with sufficiently high workability to fill the voids on the face of the brick and sufficient water retention to nullify the surface capillarity.

e) Time in tooling is important. Tooling too quickly breaks the bond.

f) You should advocate wetting mortar boards or advise using metal or treated wood boards. Keep the water in the mortar as long as possible.

g) Some brick of low suction (sanded brick) require wetting to obtain proper bond."

5. Summary

This investigation by Thornton indicates that surface texture can increase surface capillarity, which, in turn, can reduce bonding and increase leakage through a wall.

Head joints do not benefit from the tap of the mason's trowel; they are shoved together. Further, they are not loaded, so they do not benefit from the weight of the brick above them. As a result, the bond can be expected to be poorer at head joints. These experiments showed that a textured surface at the head joint serves to weaken this already potentially weak bond and to increase water penetration through the head joint. In the case of sand-mold brick, the sand is often on the face of the brick also, and thus bed joints would be affected also. The experiments showed this.

G. Investigations by Fishburn (1961)

1. General

Cyrus C. Fishburn was a researcher with the National Bureau of Standards. The results of his investigations, involving the testing in compression, flexure and racking of over 114 full scale masonry walls and a corresponding number of bond test specimens, were published in National Bureau of Standards Monograph #36, "Effect of Mortar Properties on Strength of Masonry", published in 1961 (45). The type of brick was not a variable in these investigations. Twenty thousand bricks were used from a single source in North Carolina, and according to the author, were "unusually uniform in dimension, absorptive properties, and strength" (45,

p. 5). The primary thrust of the research was to investigate how different mortars affect the structural behavior of walls under different loading conditions.

2. Test procedures

Twenty-six walls were tested in compression; 24 in racking, and 64 in flexure. Of these, approximately half were of hollow concrete masonry units and the other half were a brick veneer over a concrete masonry back-up (a composite wall). For each wall unit corresponding bond test specimens, using the same mortar, were made.

Two primary types of mortar were used; *i.e.*, type N and type S; however, the type of cement used to make them was varied. Four different types of masonry cements were used to make four different type N mortars. In preparing the type S mortars, however, approximately 40% of the volume of the same four masonry cements was replaced by portland cement. The consistency of each batch was as wet as possible, yet it could still be handled by a mason. Four crossed brick couplets were prepared for each wall sample. Couplets were cured 14 days and were tested with the panels they represented. The crossed brick couplet test used was similar to that required by today's ASTM E-149-76 (12).

3. Test results

The testing of the large wall specimens vividly demonstrated that the bond between masonry units and mortar is the weak link in masonry construction. In almost all loading conditions, the failure took place by separation of mortar from the masonry unit. In the compression testing of composite block and brick walls, failure was initiated by crushing of the concrete block. This was followed by debonding at the brick-mortar interface.

The crossed couplet test results are shown in Table 23 for the mortar used.

Table 23. Tension bond strength, crossed brick couplets (45)

Mortar Designation	Ave. Flow (%)	Ave. Water Retention (%)	Ave. 15 day Compressive Strength (psi)	Ave. 15 day Tensile Bond Strength (psi)
BN	145.3	84.4	676.7	31.3
CN	154.2	75.1	842	44.8
DN	134	85	1180	25
EN	145	87	1070	55
BS	146.7	83	1773	37.7
CS	155.8	76.8	2203	51.3
DS	143	83	2370	40
ES	144	87	3030	69

One is tempted to infer that type S mortars give greater bond strength than type N mortar. Unfortunately, the author used straight masonry cement for the type N mortar and replaced approximately 50% of the masonry cement with portland cement in the type S mortars. This makes it difficult to make a meaningful comparison of type S and type N mortars because the cementing materials used are not the same.

Within each type mortar, types N and S, four different types of masonry cement were used. These were called blends B, C, D, and E, resulting in the mortar designations shown. Types B and C and D were blends of commercially available masonry cements. Type E, on the other hand, was a blend made in the laboratory, probably using portland cement and hydrated lime. The exact composition was not reported. Some of the physical properties of mortars made with these cements are shown in Table 24. A brief description of each of the mortar types follows:

Type N - These mortars contained one part cementing materials (masonry cement) plus three parts of sand, by volume.

Type S - These mortars contained one and one-half parts of cementing materials and 4 parts of sand. (One-half of the masonry cement was replaced with portland cement.)

Table 24. Properties of mortars made from masonry and portland cements (45)

Cement Designation	Water Retention (%)	Air Content by Volume (%)	28 day Compressive Strength (psi)
	Type N Mortars		
B	83.0	20.4	1610
C	77.5	15.0	1965
D	88.5	22.7	2480
E	86.0	5.1	2340
	Type S Mortars (50% portland cement)		
B	82.0	18.9	2730
C	76.0	13.9	3285
D	83.0	17.7	3610
E	80.0	5.4	4080

A comparison of Tables 23 and 24 shows that type E mortar not only had the highest bond strength, but had the highest or near the highest compressive strengths. It also had the lowest air content of all the mortars. This would imply that low air content mortars would improve bonding. However, it could also be due to the percentage each of lime and cement used in the mortars. These percentages are unknown for the commercially prepared types B, C, D masonry cements, and were not reported for the type E masonry cement prepared in the laboratory. This makes it difficult to interpret the results except to infer that low air content mortar possibly promotes better bonding.

4. Summary

Fishburn's results, standing alone, are valuable in showing the behavior and failure mechanism of walls under a variety of loading conditions. Almost all the failures were initiated by a debonding. The series also demonstrated that masonry cements provide satisfactory mortars. However, no comparisons between mortars is possible except to infer that air content may affect bond strength.

H. Investigations by Ritchie and Davison (1962)

1. General

Ritchie and Davison were researchers with the Division of Building Research, National Research Council, Ottawa, Canada. Their research was reported in several papers, but their paper "Factors Affecting Bond Strength and Resistance to Moisture Penetration of Brick Masonry", published in 1962 (85), is the most comprehensive, and includes the testing of nearly 1000 brick panels. The testing program was designed to test for those conditions which affected bond strength and moisture penetration of brick walls. Parameters evaluated included brick suction, prewetting of brick, mortar flow, manner of assembly, mortar water retention, type of mortar, and time of assembly (after spreading mortar), retempering the mortar, and thickness of the mortar bed.

2. Test procedure

Small panels were made which consisted of five bricks in stack bond (one brick directly over the one below...no staggering). After two weeks of curing at 50% relative humidity and 70°F, the panels were placed in a special frame where they were tested for water penetration through the wall. The quantity of water that penetrated the wall in 24 hrs was measured. The panels were then allowed to cure an additional two weeks before testing for bond strength. Unlike the couplet test, where each brick is crossed 90° with respect to its partner, and where roughly only half the brick surface is in contact, the bricks in the panels used by Ritchie and Davison had the entire surface of each brick in contact. The bricks were gripped by a set of special clamps, which gripped the bottom brick and the one above it. By applying a load to the clamp, the bricks were forced apart. This procedure would be repeated until all of the bricks (5 bricks, 4 joints) in each panel were separated. The bond strengths were then averaged for each panel. The mortar used was principally a masonry cement mortar. As mentioned earlier, the constituents of masonry cement are not as rigidly controlled as they are in cement-lime mortars. As a result, it is possible that the researchers did not have the degree of uniformity of and control over materials that they would have had if they had prepared their own portland cement-lime mortar.

After mixing, the mortar was placed on each brick and allowed to stand for one minute before the next brick was placed. The method of bedding the brick used a 4 lb hammer dropped 1 1/2 in.

3. Results

a. Effect of brick suction on bond strength The authors found that high rates of absorption led to poor bonding and high leakage rates. Very low rates of absorption also tended to decrease bond strength. Brick suctions around 20 grams per minute seemed to maximize bond strength and practically eliminated wall leakage. Figure 9 is a graphical representation of the data. The mortar used was a masonry cement mortar mixed to a flow of 120%. The authors conclude that, "bond strength increased to a maximum value at a brick suction between 10 and 20 grams, and decreased sharply when the suction exceeded 30 grams, thus substantiating...that optimum bonding occurs when brick suction is less than 20 grams" (85).

b. Effect of prewetting bricks on bond strength High suction bricks, with suctions between 38 to 75 grams per minute, were used for this part of the investigation. The test bricks were soaked for 10 minutes before assembly of the panels. Again, a masonry cement mortar, one part masonry cement to three parts sand, with a flow of 115% was used. Panels were also made up without prewetting the brick, and a

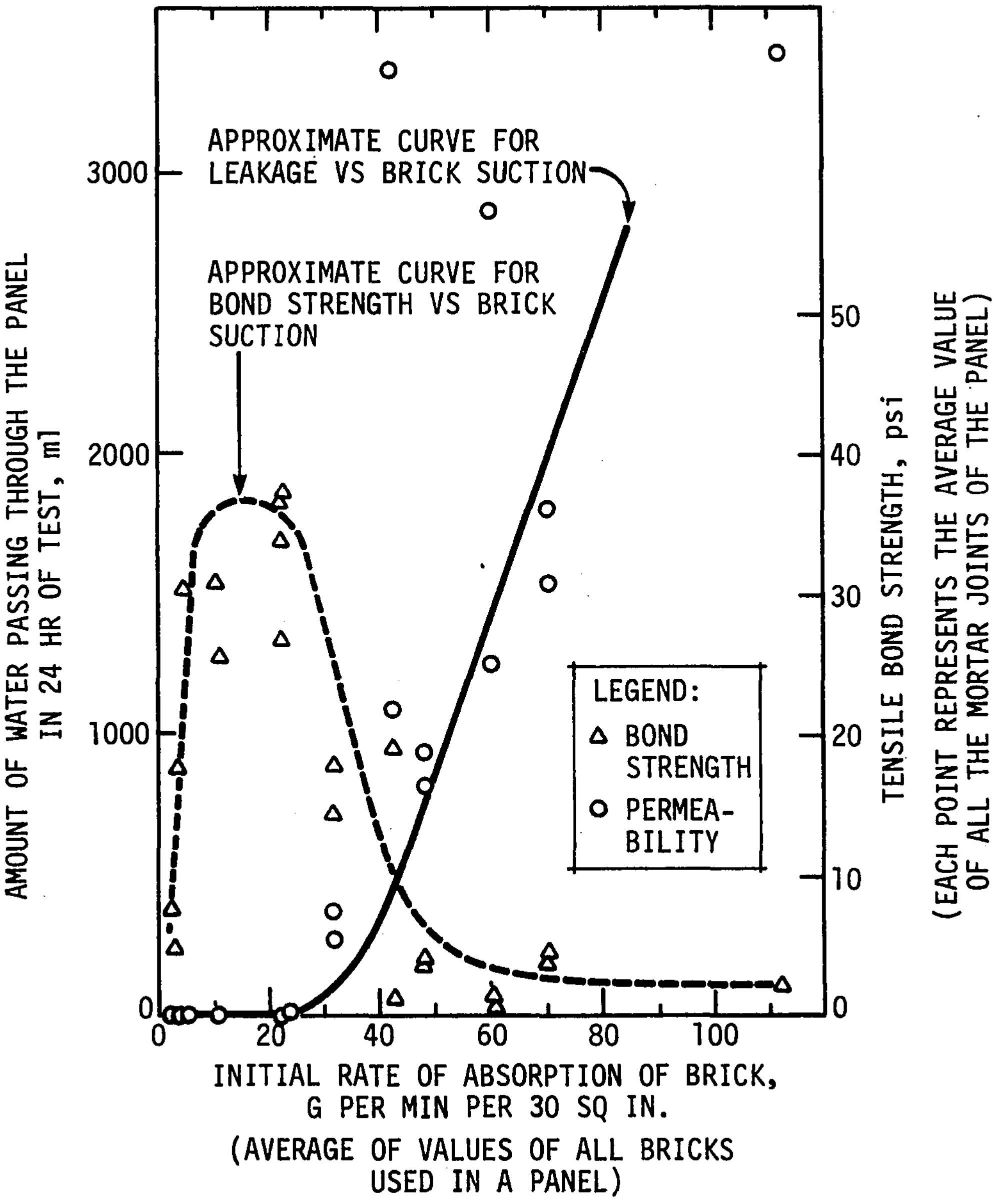


Figure 9. Influence of brick suction on bond strength and permeability (85)

comparison of bond strengths was made. The prewetted bricks were soaked in water for 10 minutes. The results are shown in Table 25.

Table 25. Effect of prewetting bricks on bond strength and water penetration (85)

Condition of brick	Time for Leakage to start, min	Total Leakage in 24 hrs, ml	Tensile Bond Strength, (psi)
Dry	2	5441	11.3
Dry	2	4948	14.6
Wet	47	436	20.7
Wet	47	514	36.4

As can be seen, the prewetting of the brick appeared to improve bond strength when the brick was in the 38-75 gram suction range, and when the mortar flow was approximately 115%. Although the authors do not mention it, the same conclusion was reached by Forkner et al. (46). The authors conclude, "Wetting high-suction bricks can be an effective method of reducing moisture penetration by lowering the suction of bricks to a level at which better bonding with mortar will occur".

c. Effect of mortar flow on bond strength The authors recognize that previous studies have shown that bond improves as flow increases. The results of their tests on six panels are shown in Figure 10. The brick had a suction of 22-30 gms/min, the mortar was type N cement-lime mortar in the proportions 1 cement:1 lime:6 sand, by volume. The flow

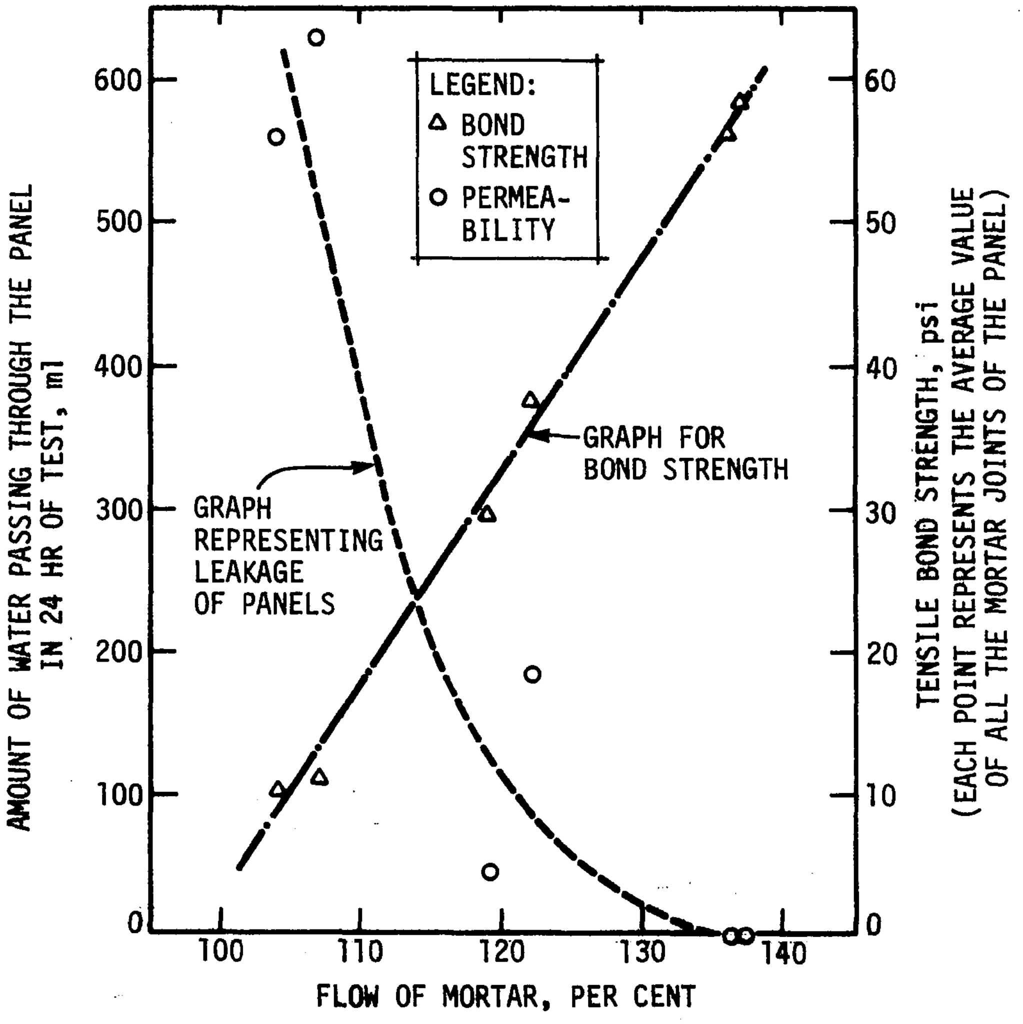


Figure 10. Influence of flow of mortar on resistance to moisture penetration and strength of bond (85)

of the mortar varied from 104 to 136%. The graph clearly shows the beneficial effect of high flow on both bond strength and resistance to water penetration.

d. Effect of water retention on bond strength   Six panels were fabricated with bricks having suctions from 42-44 gms/min. The constitution of the mortar was varied so that part of the masonry cement was replaced by lime. Lime serves to increase water retention of mortar. There were three water retention values used in six panels. The results are shown in Table 26. Increased water retention for this combination of brick suction and initial mortar flow (116-119%) increased the bond strength.

Table 26. Effect of change in water retention on wall leakage and bond strength (85)

	Water Retention (Flow after suction)	Average Amount of Water Passing through in 24 hrs, ml	Average Bond Strength (psi)
Panels 1,2	70.5	1127.5	9.5
Panels 3,4	74.3	337.5	12.7
Panels 5,6	78.0	46.5	13.55

e. Effect of time interval on bond strength Six panels were made from brick having a range of suction between 11 and 17 gms/min. The mortar was type N (1 cement:1 lime:6 sand) with a flow of 110%. For two of the panels, the time between placing the mortar and placing the next brick was 30 sec. For two other panels, it was 60 sec, and for the last two panels the time was 90 sec. The purpose here was to evaluate the effect of the length of time elapsed between spreading the mortar and placing the next brick. Figure 11 shows the results. There was an increase in water penetration and a decrease in bond strength with increased time interval between placing mortar and setting brick.

f. Effect of tapping impact on bond strength The purpose of this investigation was to see how various impact schemes affect permeability and bond strength. Most bricklayers tap the brick they are setting into the mortar with several sharp blows with the butt end of the trowel. This method does not necessarily provide for uniform results, and the researchers were looking for a method that could be used successfully in the laboratory and which could be replicated exactly for each brick. One method involved dropping a 2 lb weight through a distance of 1 1/2 in. Another method involved dropping a 4 lb hammer through the same distance. A total of 9 panels were used for each of these methods, i.e., the 4 lb hammer, the 2 lb hammer, and a bricklayer using the handle of a trowel. In addition to testing for the tapping method, this series of panels was also used to determine the effect of mortar type and type of brick on bond strength.

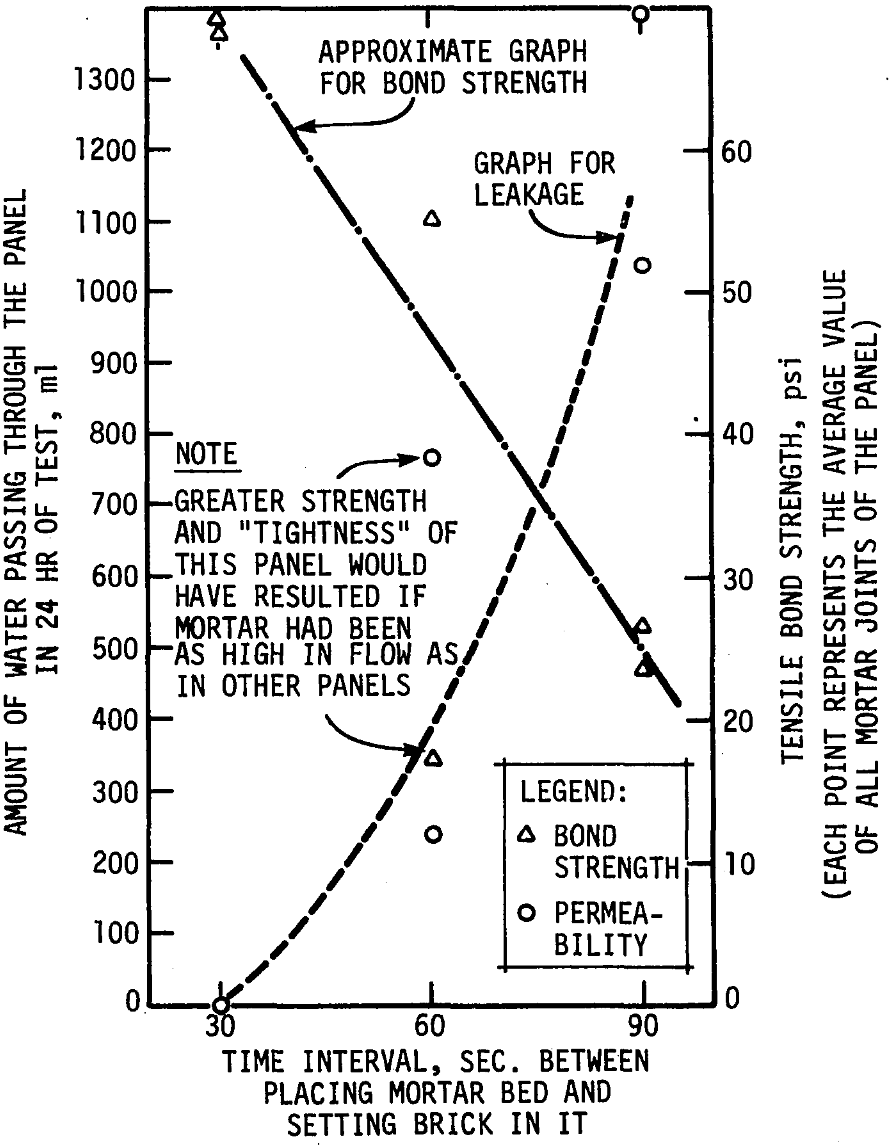


Figure 11. Effect of time variation on properties of masonry (85)

The results are shown in Table 27. The sharp taps of the mason's trowel were more effective in every instance. Notwithstanding these results, the current ASTM procedures for crossed couplet tests require a 3.5 lb hammer to be used (12). This is conservative, because the strength of masonry made in the field would probably be stronger.

Table 27. Effect of variation in method of bricklaying on bond strength (85)

Type of Brick	Mortar Composition by Volume[a]	Conditions of Construction	Bond Strength (psi)[b]
Extruded	1:3MC:S	2-lb hammer[c]	22.5
Extruded	1:3MC:S	4-lb hammer[c]	26.8
Extruded	1:3MC:S	bricklayer	46.5
Extruded	1:1:6C:L:S	2-lb hammer	19.6
Extruded	1:1:6C:L:S	4-lb hammer	27.4
Extruded	1:1:6C:L:S	bricklayer	36.9
Dry press	1:1:6C:L:S	2-lb hammer	7.5
Dry press	1:1:6C:L:S	4-lb hammer	14.2
Dry press	1:1:6C:L:S	bricklayer	19.2

[a] MC = masonry cement, S = sand, C = portland cement, L = lime.

[b] Average of all joints of three panels.

[c] Dropped 1 1/2 in.

g. Effect of retempering mortar To investigate the effect of retempering (adding water to) the mortar, a series of 8 panels was prepared. A 1:1:6 mortar was used, mixed to a flow of 120%. The bricks used had a suction range of 13 to 17 gms per min. Two panels were made up immediately after the mortar was mixed. Water was added to the mortar after 2 hrs to restore the flow to 120%, and then another two panels were prepared. This procedure was repeated with the time to retempering extended to three and then to four hours. The results are shown in Table 28. There was a decrease in bond strength with increasing time to retempering. This is a particularly important test because in practice it could take an hour or so to use all of the prepared mortar on a mortar board. Masons will usually retemper the mortar as it stiffens. The results above indicate that the shorter the interval between initial mixing and final use the better the bond strength.

Table 28. Effect of retempering on bond strength (85)

Time of Retempering	Average Bond Strength (psi)
0 hr	45.7
2 hrs	42.7
3 hrs	30.8
4 hrs	19.4

h. Effect of thickness of mortar bed on bond strengths To evaluate the effect of variations in the thickness of the mortar bed, the authors performed several tests in which the mortar bed thickness varied from 5/8 to 1/4 inch. Their results are not shown in tabular form; however, they state that, "The result of decreasing the thickness of the mortar joint was, in general, a decrease in strength of bond and an increase in permeability of the panel".

4. Summary

This was a rather comprehensive series of investigations that evaluated most of the parameters that were considered worthy of investigation. The investigations showed that bond strength is promoted by using brick with suctions in the vicinity of 20 gms per minute, by pre-wetting high-suction bricks, by increasing mortar flow, by increasing water retentivity, by setting the brick immediately after the mortar is laid, by tapping the brick sharply with the handle of a mason's trowel at the time of laying, by retempering the mortar within 2 hrs after initial mixing, and by using a thicker (5/8") rather than a thinner (1/4") mortar bed.

VI. METHODS OF INVESTIGATION AND RESULTS

A. General

Three principal means of investigations were used. The first, crossed couplet bond tests, was used to measure the tensile bond strength between brick and mortar. This provides a quantitative measure of the effect of a variety of treatments on bond strength.

The second method used was X-ray powder diffraction. In this method, powders of mortar constituents without sand were mixed with treated and untreated brick powder, moistened, then allowed to hydrate. The purpose of examination of these samples using X-ray diffraction was to obtain information on the crystalline products that form at the interface between brick and mortar. Reaction products caused by NaOH, limewater, and H_3PO_4 treatment of the brick could possibly be identified using this technique.

The third method was to examine residual cement and cement plus lime paste on treated and untreated brick chips using the scanning electron microscope (SEM). In this manner, the extent and nature of the interfacial material can be determined.

B. Crossed Couplet Bond Tests

1. General

The crossed couplet tensile bond test is the generally accepted test method for determining the tensile bond strength between brick and mortar. The test requirements and procedures are covered in detail in ASTM Specification E-149-76 (12).

The purpose of this portion of the investigation was three-fold; namely, to familiarize this investigator with the procedures, to obtain results consistent with other investigators, and to obtain data on the effect of various treatments on the tensile bond strength.

A photograph of the crossed couplet testing device is shown in Figure 12. A couplet consists of two bricks at right angles to each other, bonded together by a 1/2 inch thick square of mortar at this common intersection. After curing, the couplet is placed in the testing jig shown and inserted in a universal testing machine. The top brick is suspended from the three prongs of the lower jig. The upper jig has three prongs which span the upper brick and contact the lower brick. When the device is inserted in the testing machine, the compressive load applied to the jigs forces the two bricks apart. The tensile bond strength is calculated from the relationship

$\sigma_T \text{psi} = P/A$

where P = total applied load in lbs

A = cross sectional area in bond, in^2.

2. Test procedure

a. Materials

1) Brick The bricks used in this series were obtained from the same source, i.e., CANTEX Industries, Des Moines, Iowa. The bricks have nominal dimensions of 3 7/8" x 7 7/8" x 2 1/4". Solid face brick were selected. Face brick are those normally used on the exterior face of buildings. The selection of solid brick allows an examination of bond strength without having to consider the effect of cores.

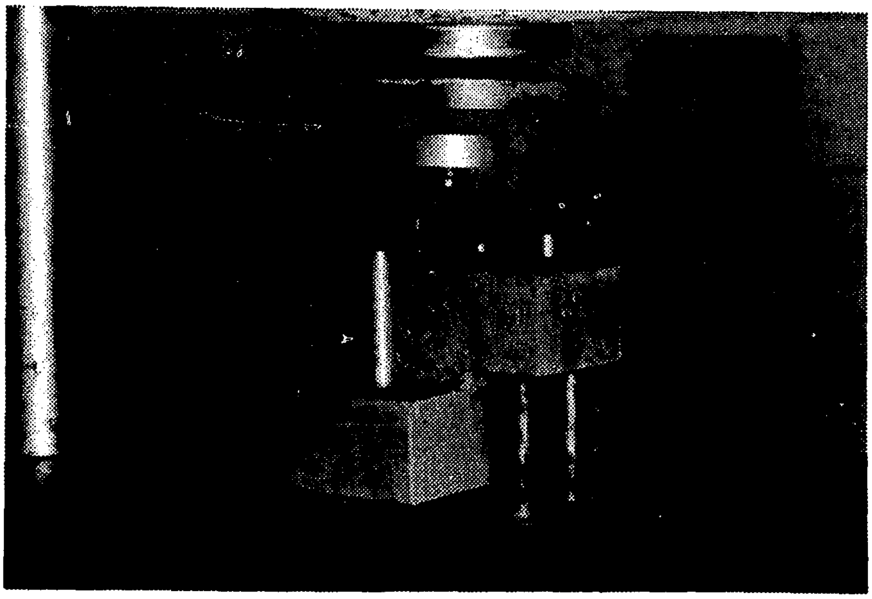


Figure 12. Crossed couplet testing device, with bricks in place

Prior investigations have shown that tensile bond strength is sensitive to the absorption characteristics of the brick, with an initial rate of absorption (IRA) between 10 and 20 grams giving the highest bond strengths.

The bricks used in this investigation were tested for IRA in accordance with ASTM specification C67-78 (5). IRA is measured as grams of water absorbed in one minute per thirty square inches, and is normally expressed as X gms per minute. The average IRA for the bricks used in this investigation, based on two samplings of five bricks each, is 12.1 gms/minute.

2) Sand It was desired to eliminate as much variation as possible in the test results by using a sand which is generally uniform from one batch to another. For this reason, Ottawa sand was used which meets the requirements of ASTM specification C109 (13). This sand was purchased in 50 lb bags from the Bellrose Silica Company, Ottawa, IL.

3) Cement The cement used was a Type I Portland Cement, meeting the requirements of ASTM specification C150 (11), manufactured by the Monarch Cement Company, Des Moines, IA. The cement was obtained in early 1981, and was stored in the laboratory in an open original sack, stored within a sealed 30 gallon container. X-ray diffraction tests reveal no change in the crystal structure of the stored cement during the time it was in storage.

4) Hydrated lime The lime used was a type S hydrated lime, manufactured by the Ash Grove Cement Co., Springfield, MO, and meeting ASTM specification C207 (8). The lime was stored in the same manner as

the cement. X-ray diffraction tests show a very slight increase in the $CaCO_3$ content of the lime over the year it was in storage.

5) Water The water used to make the couplets was normal tap water.

b. Preparation, curing, testing The steps used in preparing the specimens are as follows:

1) Preparation of the brick All brick were washed in plain water to remove surface dirt. They were then allowed to dry in laboratory air for a minimum period of 48 hours.

2) Preparation of the mortar Mortar ingredients were weighed and mixed in accordance with ASTM E-149 (12).

At the end of the mixing period the mortar flow was measured in accordance with ASTM E-149. The flow test apparatus is shown in the photographs of Figure 2. The procedure involves placing a truncated brass cone in the center of a 10 inch diameter steel table. The freshly mixed mortar was placed in the cone to a height of one inch. It is then tamped 20 times with a rod-shaped tamper. This procedure is repeated a second time, and the excess mortar is struck off even with the top of the cone. The cone is then lifted from the mortar.

The table is designed so that it will rise when a cam on a shaft contacts the table and pushes it up. As the shaft continues to turn, the cam allows the table to free fall 1/2 inch. This raising and falling occurs once in every revolution of the shaft.

After the cone is removed, the table is subjected to 25 drops in a 15 second time period, which causes the mortar to spread out. The ratio of the final to original diameter, expressed in %, is termed the "flow", a measure of the consistency.

During the time that the flow was being measured, the metal mixing bowl containing the mortar was covered with plastic wrap to prevent evaporation.

After measuring the flow, the mortar used to make the flow measurement was returned to the mixing bowl. It was mixed in with the rest of the mortar by hand, using a large spoon.

3) Preparation of couplets Couplets were prepared immediately after the flow test. The maximum number of couplets made from one mix was ten. The time required to make ten couplets was approximately twenty minutes. The bowl containing the mortar was covered to prevent evaporation during this time. A 3.5 pound drop hammer, dropped a distance of 4 inches, was used to seat the top brick in the mortar.

4) Curing conditions After assembly, the couplets were transferred to a humid room for storage. Care was taken not to disturb the specimens during transportation to the storage shelves. The majority of the specimens were stored in the humid room for 28 days. The average temperature in the humid room was between 70°F and 90°F, and the relative humidity was maintained at 100%.

5) Testing The couplets were removed from the storage room on the 28th day of storage and were tested immediately. The area in contact was measured and the tensile force applied to the specimen was recorded.

c. Treatments A variety of treatments were used to determine their effect on bond strength. The treatments used in this investigation consisted of the following:

Presoaking brick for one minute in:

a) limewater

b) 1 normal solution of phosphoric acid

c) 1 normal solution of sodium hydroxide

d) plain tap water.

A total of 173 couplets were made, varying the treatments, and mortar types.

1) Treatment with limewater Fired brick contains the elements present in its raw clay form, although they have changed structure. The illite in the Pennsylvania clay shale undergoes a transformation to the mineral mullite, an aluminum silicate, during the firing process. Because the same elements are present in both brick and clay, i.e., silicon in tetrahedral coordination, and aluminum, in octahedral coordination, it appears that some of the agents which stabilize clay soils might also be used to enhance the cementing reaction between brick and mortar. Calcium hydroxide is frequently used for the stabilization of clay soils. Although calcium hydroxide makes up a considerable portion of the mortar, its use as a pretreatment for the brick surface was considered to be reasonable. Accordingly, hydrated calcitic lime, type S, was added to water to form a saturated "lime-water" solution. The faces of the brick to be joined were immersed in this solution for one minute, then removed and blotted. Twenty-two couplets

were made with this treatment; five with type N mortar; seventeen with type S. Nine of the couplets were made immediately after the treatment; thirteen were made after allowing the bricks to dry in laboratory air for two days. Those brick allowed to dry after pretreatment had their joining faces soaked in water for one minute just prior to assembling the couplets.

2) Treatment with sodium hydroxide (NaOH) Sodium hydroxide is a caustic that etches the surface of glass. Furthermore, Davidson, Mateos and Katti (34) had found that NaOH had a significant effect on promoting the early compressive strength of clay soils treated with lime and fly-ash. They theorized that the NaOH might serve as a catalyst by first reacting with siliceous material to produce an intermediate sodium silicate which would subsequently react with the calcium hydroxide to form sodium hydroxide and cementitious calcium silicates.

Mullite and a glass phase compose the surface of the fired brick. Therefore, it appeared possible that the pretreatment with NaOH might etch the glass surface and might interact with the mullite. This, in turn, might enhance the bond strength with mortar. The treatment solution was prepared by mixing sodium hydroxide with water in a one liter flask to obtain a one molar solution. The proportions used were 40 gms of NaOH and sufficient water to make one liter. The solution was placed in a plastic dishpan so that the level of liquid would rise approximately 1/4 inch up the side of the brick when it was placed in the solution.

Seven couplets were prepared using type M mortar. Of these, two were prepared immediately and five were prepared after allowing the treated faces to dry. In the latter case, the brick faces were soaked in water for one minute just prior to assembly. Twenty-one couplets were prepared using type S mortar. Of these, thirteen were prepared immediately, and eight were prepared after allowing the treated faces to dry, as described for type M mortar.

3) Treatment with dilute solution of phosphoric acid

Reactions between phosphoric acid and clay minerals have been examined by several researchers. Demirel, Benn and Davidson (37) reported on the use of phosphoric acid in soil stabilization. They found that clay minerals treated with phosphoric acid exhibited cement-like properties, the probable product being a complex amorphous aluminum phosphate in the form of a gel. In recent experiments, Boybay and Demirel (25) have shown that phosphoric acid reacts with fly-ash to form a complex crystalline product. Upon mixing with water, a hydrated gel is formed with compressive strengths comparable to portland cement. The principal constituents of fly-ash are oxides of iron, aluminum and silicon, and these are also the structural constituents of fired brick. Also, phosphoric acid is commonly used as a bonding agent in refractory concretes, especially high alumina types. Therefore, it appeared reasonable that a reaction between phosphoric acid and brick might be anticipated, and that the products might enhance the bonding with mortar.

A one molar solution of H_3PO_4 was prepared by combining 115.3 grams of 85% strength H_3PO_4 with sufficient water to make one liter of solution. The brick faces were soaked in this solution for one minute. Eight couplets were prepared using type M mortar. Of these, three were made up immediately after treatment and five were made up after allowing the treated faces to dry for two days. Twenty-one couplets were prepared using type S mortar. Of these, thirteen were made up immediately and eight were prepared after the treated faces had dried.

4) Treatment with water Several references suggest that brick be wetted prior to laying up a brick structure when the initial rate of suction of the brick is excessive. For example, the Brick Institute of America (29) recommends prewetting when brick suction exceeds 20 grams per minute. The ASTM states the following in Note 2 to their specification on facing brick (6):

> "Both laboratory and field investigations have shown that strong and watertight joints between mortar and masonry units are not achieved by ordinary construction methods when the units as laid have excessive initial rates of absorption....Hence, the initial rate of absorption of the units should be determined....Units having initial rates of absorption exceeding 30 grams/minute should be well wetted prior to laying."

Although the IRA of the brick in this investigation averaged 12.1 gms/min, prewetting was adopted as one of the treatments so that the other treatments could be compared to the water treatment. Prewetting was accomplished by placing sufficient water in a plastic dishpan so that the water would rise approximately 1/4 inch up the sides of the brick when the brick was placed face down in the dishpan. The brick faces of the two brick to be joined were soaked in this manner for one minute. At the end of one minute, the bricks were removed, excess surface water blotted, and the couplets were immediately assembled. As mentioned earlier, this treatment was also used for those brick which had been previously treated with limewater, NaOH, or H_3PO_4 and which had been allowed to dry for two days, i.e., these brick were soaked in water for one minute immediately prior to assembly. This, then, permitted a comparison between brick assembled with a water pre-soak only, and those which had been pretreated with limewater, NaOH or H_3PO_4.

For example, the faces of the H_3PO_4 treated (dry) brick, Table 29, were soaked in the H_3PO_4 solution for one minute. They were then allowed to dry for 48 hours. At the time of assembly, they were soaked in water for one minute and then blotted.

5) No treatment In each set of treatments, one couplet was made by assembling the bricks dry, i.e., without soaking in water. This provided a basis of comparison of bond strength between wet and dry brick surfaces.

3. Results

Tables 29 and 30 show the variation of bond strength with the various treatments for selected ranges of flow.

A casual perusal of these data in Tables 29 and 30, and the graphs of bond strength in Figures 13-15 show that the bond strength values ranged from a high of 94.7 psi for a limewater treated brick using type S mortar at a flow of 125-135 to a low of 43.4 psi for water treated brick at a flow between 95 and 104.

Figure 13 compares bond strength at various ranges of flow, for type S mortar, for two treatments, i.e., brick dry and brick wet when assembled. The bond strength is greater in the range of 115-124%. This

Table 29. 28 day crossed couplet tensile bond test results

Treatment ↓		Mortar Type					
		Type M			Type S		
	Flow →	105 to 114	115 to 124	125 to 135	105 to 114	115 to 124	125 to 135
Dry-Untreated (Immediate)[a]	$\bar{\sigma}$, psi		68.5	45.5	44.4	58.1	45.9
	n		7	3	10	5	3
	s		20.7	7.2	15.3	19.9	4.9
Water (Immediate)	$\bar{\sigma}$, psi		86.2	77.9	55.2	60.1	48.7
	n		8	25	10	17	6
	s		24.9	29.3	14.4	27.8	8.5
Lime Water (Immediate)	$\bar{\sigma}$, psi				49.7	68.9	
	n				4	5	
	s				4.44	21.4	
Lime Water (Dried)[b]	$\bar{\sigma}$, psi		73.4		59.1		94.7
	n		5		5		3
	s		9.2		5.7		2.9
NaOH (Immediate)	$\bar{\sigma}$, psi			68.5	60.6	74.2	65.7
	n			2	5	5	3
	s				16.0	30.0	15.6
NaOH (Dried)	$\bar{\sigma}$, psi		83.3		67.6		91.6
	n		5		5		3
	s		17.7		13.6		11.5
H_3PO_4 (Immediate)	$\bar{\sigma}$, psi			74.1	45.4	68.6	66.3
	n			3	5	5	3
	s			8.0	8.8	16.6	12.9
H_3PO_4 (Dried)	$\bar{\sigma}$, psi		80.9		70.0		82.8
	n		5		5		3
	s		15.5		7.7		17.5

[a] The "immediate" designation indicates that the couplets were assembled immediately after treatment.

[b] The "dried" designation indicates that the brick were treated, then allowed to air dry in the laboratory for 2 days. They were then resoaked in water for one minute at the time of assembly.

Table 30. 28 day crossed couplet tensile bond strength test results

Water Treatment Only

Type M Mortar

Flow →	70 to 94	95 to 104	105 to 114	115 to 124	125 to 135
$\bar{\sigma}$, psi	46.7	56.9	---	86.2	77.9
n	12	13	---	8	25
s	23.2	11.8	---	24.9	29.3

Type S Mortar

Flow →	70 to 94	95 to 104	105 to 114	115 to 124	125 to 135
$\bar{\sigma}$, psi	49.1	43.4	55.2	60.1	48.7
n	3	3	10	17	6
s	18.4	9.6	14.4	27.8	8.5

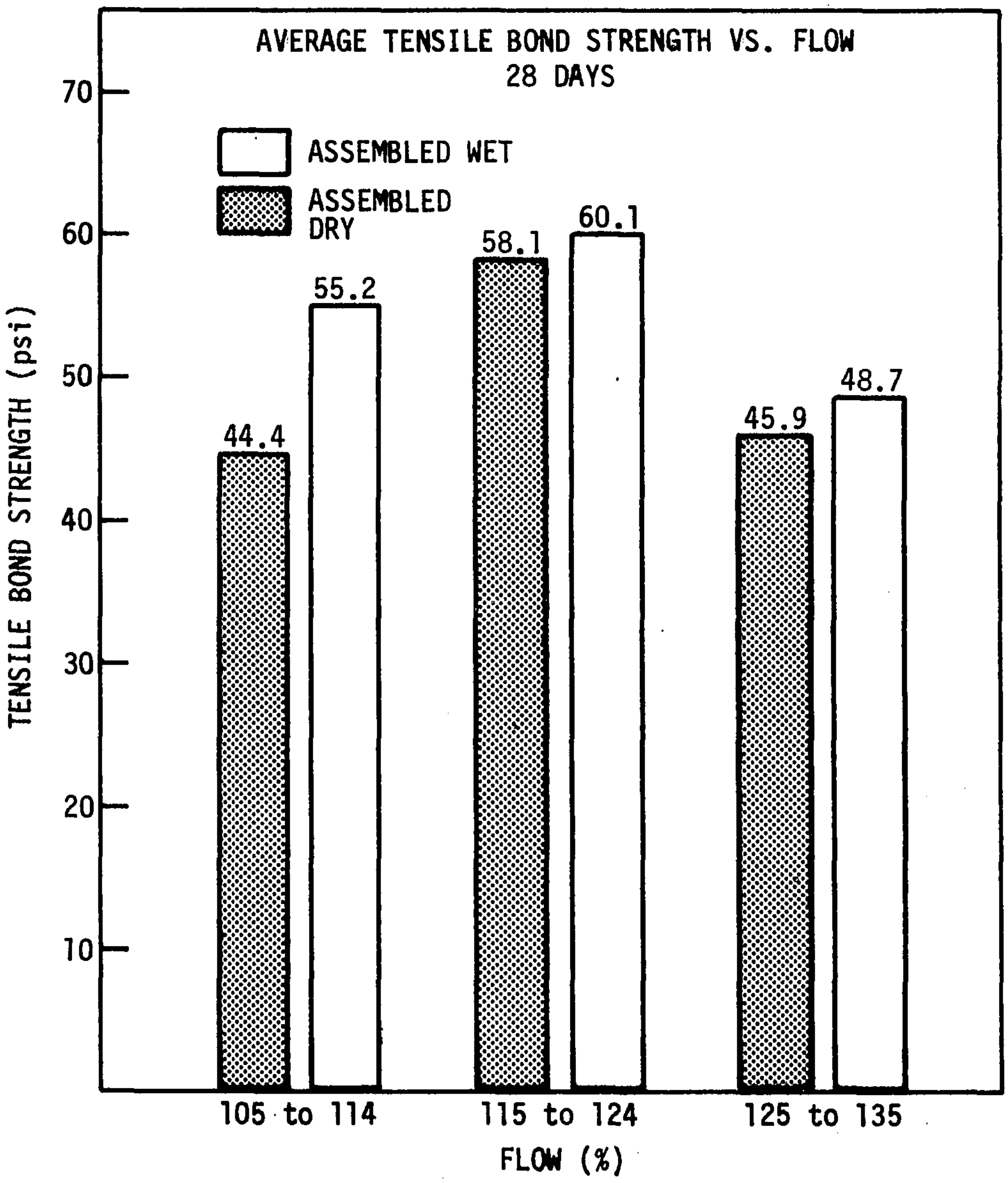


Figure 13. Variation of tensile bond strength vs. mortar flow for type S mortar

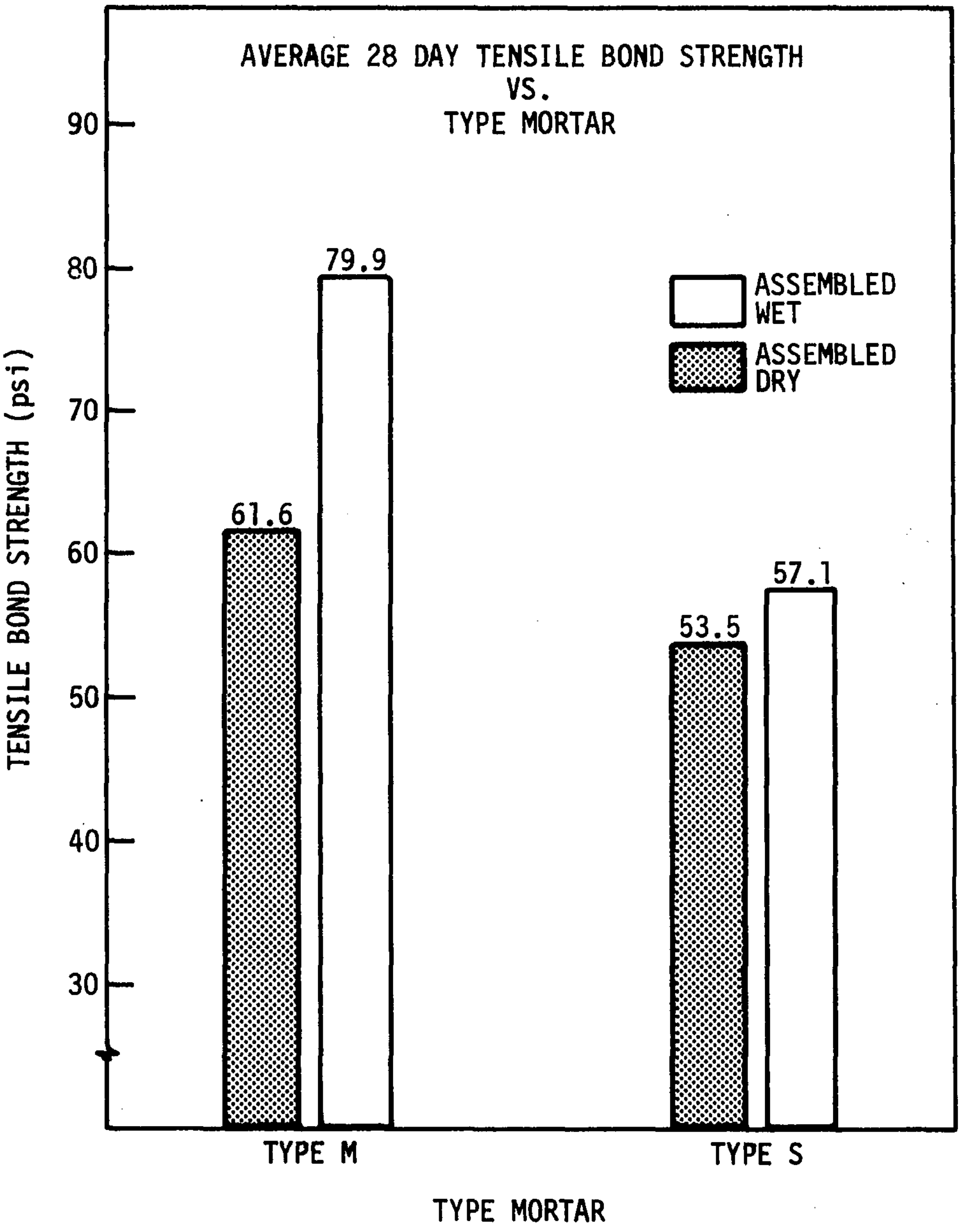


Figure 14. Effect of type mortar and prewetting brick on tensile bond strength, for flows from 115-135%. Only water and dry treatments are considered

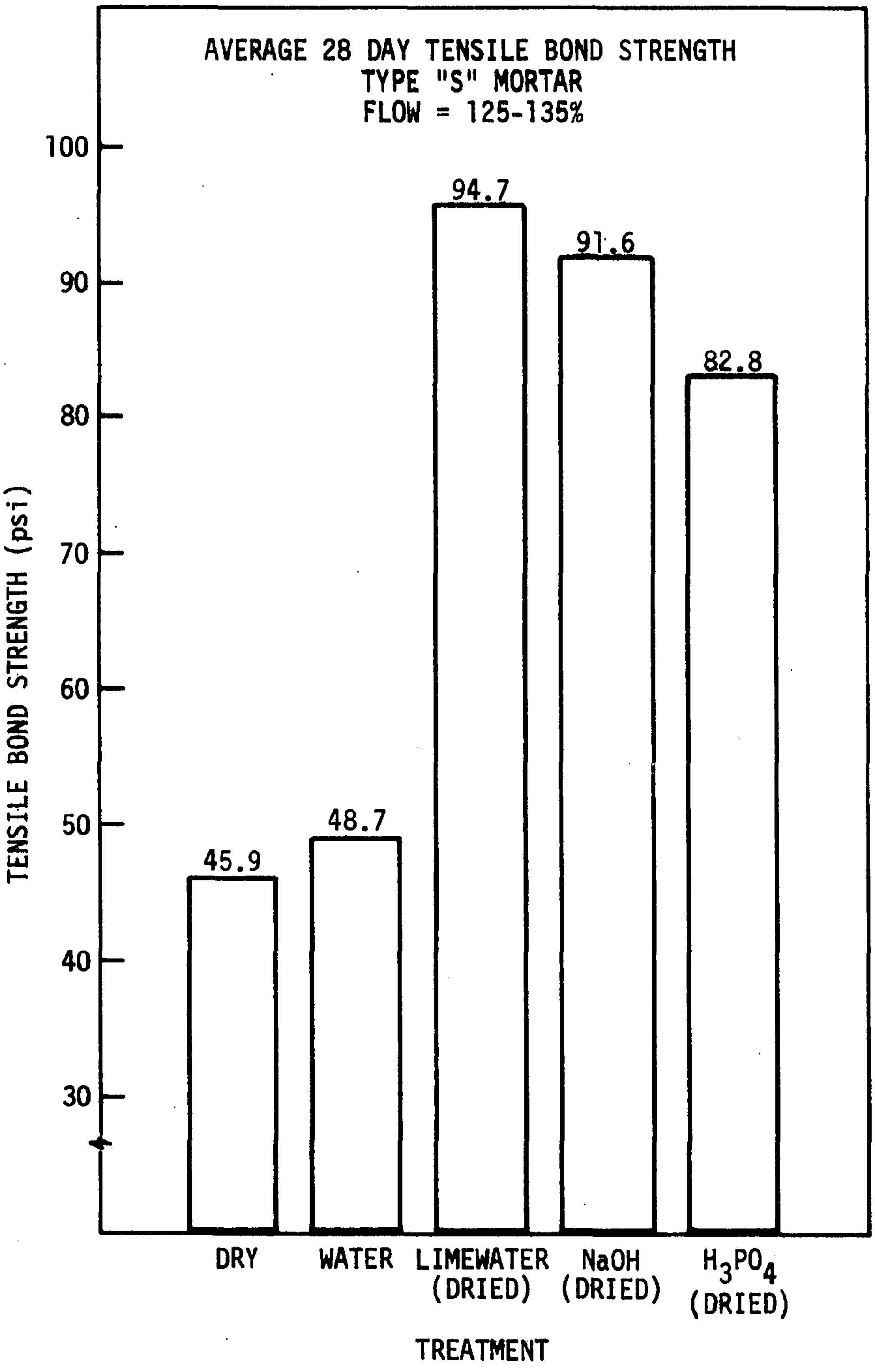


Figure 15. Tensile bond strength vs. several treatments

is in agreement with Forkner et al. (46). The beneficial effect of pre-wetting the brick is also evident, the effect being most pronounced for flows between 105-114.

Figure 14 compares the bond strength of type M mortar to type S mortar for the same two treatments, i.e., for brick assembled wet and dry. The values are for flows between 115-135%. Type M mortar provides better bond strength at these flows. Pre-wetting the brick is beneficial, and has a more pronounced effect on type M mortar.

Figure 15 compares tensile bond strengths for the various treatments, using type S mortar, at flows between 125-135%. This particular combination has the greatest amount of data available, and corresponds to the last column of Table 29. Only those chemical treatments where the brick were allowed to dry after treatment were included in Figure 15. That is because the greatest effect on bond strength occurs when the bricks are allowed to dry after treatment. The beneficial effects of the limewater, NaOH and H_3PO_4 pretreatment are quite pronounced, for this set of conditions.

Table 29 shows that with type M mortar the limewater, NaOH, and H_3PO_4 treatments do not appear to be any better than water in promoting bond strength. However, with type M mortar all of the treatments appear to be more beneficial than dry brick at these particular flows.

5. Statistical interpretation of results

The data used to prepare Tables 29 and 30 and Figures 13-15 involved 113 observations over a range of flows from 100.8% to 133%. There were a total of eight treatments, as follows: dry, water only, limewater, dried and wet, NaOH dried and wet and H_3PO_4 dried and wet. A comparison of the means of all the treatments, adjusted to the overall mean flow value, for type S mortar, provides the following ranking:

Treatment	Number of Observations N	Tensile Bond Strength Mean
NaOH (dry)	8	76.6
H_3PO_4 (dry)	8	74.8
Limewater (dry)	8	72.4
NaOH (wet)	13	67.0
Limewater (wet)	9	60.3
H_3PO_4 (wet)	13	59.1
Water only	36	55.5
No treatment (dry)	18	48.4

From just this descriptive set of data, it appears that the most promising treatments are the H_3PO_4, NaOH and limewater, dried after treatment, and re-wetted at the time of assembly. A general linear model was investigated in which the effect of flow and treatment on strength were evaluated. The details of the analysis are shown in the Appendix.

The results of the general linear model (GLM) analysis show the following:

a. There is no significant interaction between flow and treatment;

b. The effect of flow in tensile bond strength is highly significant;

c. The effect of the chemical treatments on bond strength is highly significant;

d. All treatments have a significant beneficial effect on bond strength compared to no treatment (dry);

e. There is a significant difference between the wet and dry NaOH, H_3PO_4 and limewater treatments

f. There is no significant difference between the limewater and both the H_3PO_4 and NaOH treatments taken together;

g. There is no significant difference between the H_3PO_4 and NaOH treatments.

From the conclusions above, it appears that the chemical pretreatment of brick has a significant effect on bond strength, and that brick in this suction range should be prewetted, rather than assembled dry, when using type S mortar.

6. Discussion of results

The increase of bond strength with mortar flow shows that adequate moisture is necessary for good bond. The moisture may be essential for several reasons. Sufficient moisture is required to permit complete hydration of the cement particles in the mortar, it permits the migration of the hydration products into the pores of the brick and it permits intimate contact between hydrating products and the brick surface. To the extent that the bond is mechanical in nature, good penetration of mortar into the brick pores is essential. To the extent that the bond is chemical, intimate contact is also essential.

Presoaking brick in limewater immediately prior to assembly promoted higher bond strength than water alone at the two highest flows. This would indicate that the presence of the calcium hydroxide in solution in the brick at the time of assembly promoted the interaction between the brick and mortar. Calcium hydroxide does interact with fired clay products at room temperature. This was shown by Kondo and Oshawa (69) in a series of experiments designed to test the reactivities of various silicates with calcium hydroxide and water. They found that $Ca(OH)_2$ reacted with pozzolan, silica gel, metakaolin, clinoptilolite, granulated blast furnace slag, a Japanese pozzolan called Hakuko, which is made from porous opal, silica glass and other silicates. The end product was preponderantly calcium silicate hydrates. It is therefore possible that soaking the brick in limewater allowed for a more complete penetration of the pores of the brick by calcium hydroxide, which formed calcium silicate hydrates and tri-calcium aluminate hydrates through interaction with the siicates and alumina in the brick. These products could then link with the hydration products in the mortar, thus producing a better bond.

The increased bond strength shown by brick treated with NaOH, and which had then been allowed to dry first, indicates some type of beneficial interaction between the brick and mortar. Silicates do react with sodium hydroxide. This was shown by Oshawa and Kondo (77). They examined the reactivity of various silicates with NaOH when the temperature was elevated to 97°C for one hour. The silicates used were the same used in their studies of reactions between $Ca(OH)_2$ and silicates (69). The researchers found a close relation between pozzolanic activity and reactivity with NaOH. The NaOH dissolves SiO_2. The order of reactivity of the three most reactive silicates was opal, borosilicate glass, silica gel and Hakudo. Based on the above, it is possible that a sodium silicate may form on or in the brick. This, in turn, may react with the calcium of the mortar to form a calcium silicate of a more continuous nature than that normally formed when mortar is placed on untreated brick. The scanning electron microscope investigations, discussed later, show the formation of calcium silicate hydrates with some sodium content at the interface.

The same comments apply to the H_3PO_4 treated brick. The results give some indication that this treatment may increase bond strength. The scanning electron microscope studies show that a dense growth of a variety of crystals containing Ca, P, K, Si, Al and Fe, in a variety of ratios, exists at the interface. The better bonding of H_3PO_4 treated brick is also demonstrated in magnified photos (4X magnification) of the residual mortar on a H_3PO_4 treated chip.

7. Summary

The data of Tables 29 and 30, in which only some of the possible combinations have been investigated, show a need for more research in this area. The beneficial effect of increasing flow and prewetting the brick has been demonstrated. The beneficial effect of pretreating the brick with limewater, NaOH and H_3PO_4 is indicated, especially if the brick is allowed to dry after pretreatment. For untreated brick, assembled wet or dry, type M mortar appears to provide better bond than type S, and the question of which is superior when the chemical treatments are used remains to be answered in the future.

Additional experiments in this area should be accomplished to increase the data on the three chemical treatments, limewater, NaOH and H_3PO_4, for all of the three ranges of flow and for varying lime content of the mortars; not necessarily restricted to types M and S mortar. The concentration and time and temperature of exposure of the treatments could also be varied.

Consideration should also be given to a simpler type of bond test where the specimen size is smaller. The separated specimen could then be used for both X-ray diffraction studies and SEM studies after the bond tests are performed.

C. Scanning Electron Microscope Studies

1. General

The purpose of using the scanning electron microscope (SEM) was to provide a visual examination of the micromorphology of the interface region. Reaction products, if any, might be identifiable. Beyond that, the micrographs would provide for a characterization of the interface region.

The SEM in use in the materials laboratory at Iowa State University is a JEOL, model JSM-03, purchased in 1971. The SEM is equipped with a TRACOR NORTHERN TN-2000 energy dispersive X-ray analyzer, which can be used for quantitative elemental analysis.

Magnification of 100,000X with 100 Å resolution is theoretically possible, but this researcher has been unable to obtain sharp, clear photographs at magnifications above 10,000X.

Most of the samples were prepared by placing a paste of cement or cement plus lime on small brick chips, allowing these to cure for 7 or 28 days, then removing the droplet and examining the surface. A companion series of 4X magnification photographs of the chips after the paste had been removed was also prepared. This provided for a more macroscopic comparison of the various treatments.

Several samples were also prepared by spreading paste on one side of the thin brick chip, curing, then breaking the chip and examining the edge.

2. Preparation of samples

The chips were prepared by cutting thin slices from a regular brick, using a circular masonry saw blade. The slices were approximately 1/16" thick. Grooves were then cut in the back of the slices using a carbide coated masonry hacksaw. The slices were then broken along the grooves into chips, approximately 1 inch x 1/2 inch in area.

One sample was prepared by spreading a thin layer of cement paste on one side of a thin brick chip. This particular chip was not polished, but it was thoroughly washed with water and a bristle brush before applying paste. The back side of the chip was grooved to provide for a relatively clean break. A thin layer of cement paste approximately 1/64" thick was spread over one surface of the chip. The water/cement ratio of the paste was not observed. The chip was not prewetted. The chip was then placed in a desiccator jar over water, with a 20% by weight solution of NaOH in the bottom to retard carbonation. The chip was allowed to cure for 7 days, then was removed and placed in a covered Petri dish for another 7 days. It was then broken, revealing an edge with cement paste on one side and brick on the other. The chip was then coated with approximately 154 Angstroms of gold and examined. The micrographs are in Figure 16. Another sample was prepared in the same manner; however, it was cured for

42 days in the desiccator, then for 2 days in a dry Petri dish. The micrographs are in Figure 17.

Twenty-six samples consisted of brick chips on which a paste droplet was placed. The chips were prepared as above, except that they were polished on the side that was to receive the paste. This was accomplished using successively finer papers on a polishing wheel until the chip had been polished with a #600 grit. Water was used with the polishing wheel. After polishing, each chip was scribed with a diamond scribe to reveal a small V which served as a point of reference in the photographs. After scribing, each chip was placed on a small piece of screen placed in water in an ultrasonic cleaner, and was cleaned with the polished side down for one minute. The purpose of the cleaning was to remove the debris of polishing and any other extraneous matter that might clog the pores of the brick.

There were twenty chips prepared in this manner. Of these, five were selected for each treatment, i.e., dry, water only, limewater, NaOH, and H_3PO_4. Within each treatment, two were to receive cement only and two to receive cement and lime. Then within each of those categories, one was cured 7 days and the other 28 days.

The water treatment consisted of immersing the chip in water for one minute, then removing and blotting the chip surface-dry. The paste was then immediately applied.

The limewater treatment consisted of soaking the chip in limewater for one minute, then removing, blotting surface-dry, then allowing it to dry in a covered Petri dish for two days before applying the paste.

The same procedure was also followed for the NaOH and H_3PO_4 treatments, using the 1 molar concentrations prepared for the couplet and X-ray investigations.

The cement paste was prepared by mixing several grams of cement and water to a syrup-like consistency. The cement-lime paste was prepared by mixing several grams of cement and $Ca(OH)_2$ together in a 50/50 proportion by weight. To this was added sufficient water to obtain a similar syrupy consistency. The paste was lifted with a toothpick and applied to the chip. All of these chips were wetted with water at the time of applying the paste. This was accomplished by soaking the chip in water one minute then blotting surface-dry.

After the paste was applied, each sample was placed in the desiccator jar over water containing 20% NaOH by weight. The relative humidity in the jar varied between 70% and 75%. All operations were conducted at room temperature.

At the end of the curing period, samples were removed from the jar and were dried by vacuum evaporation. After drying, the paste droplets were removed by prying them off with a small screwdriver. The chips were then mounted on one inch diameter carbon stubs. After mounting, the samples were sent to the Iowa State University Photo Service where they were photographed, in color, at a magnification of 4X. After being photographed, the samples were given a coating of gold, approximately 154 Å thick in a vacuum sputter-coater. The samples were then stored in a desiccator, with desiccant added, until examined in the Scanning Electron Microscope (SEM).

3. Examination procedures

Samples were examined in the JEOL SEM. A voltage of 15 kV and a scanning speed of 50 seconds per frame were normally used.

Brick is a nonhomogeneous mixture. It contains inclusions of several different minerals, each of which can react differently with mortar. An attempt was made to have the micrographs be as representative as possible, and not concentrate on any features which were not representative. The samples were carefully scanned at low magnification to select uniform areas. After an area was selected, magnification was raised to 1,000, then 3,000, and a search within the selected area was made to select a uniform sub-area.

When it was suspected that charging might be a problem, the higher magnification photographs were taken first. In some cases, charging was enough of a problem that it was necessary to apply another 150 Å gold coating. This did not appear to mask any detail.

The JEOL SEM is equipped with an energy dispersive X-ray analyzer, EDXA, which permits the determination of elements present in a sample. Individual spots may be analyzed as well as the entire area covered by the picture. Based on the counts obtained, a rough approximation can be made of the relative quantities of the element present, *i.e.*, 2 parts silicon, 3 parts calcium, etc. The results of three picture scans, averaged, for untreated brick, are listed in Table 31. This type of analysis was useful for determining which particles were paste and which were brick, as well as for providing some information on their composition.

Table 31. Elemental analysis for brick, as determined by X-ray energy dispersive analysis. Average of three samples

Element	Approximate quantity in parts (moles)
Al	0.9
Ca	0.3
Fe	1.0
K	0.5
Si	4.8
Ti	0.16

4. Results and discussion

a. Edge views of interface region Figure 16 shows views of the broken edge of the sample with cement paste on one side, cured 7 days. Upon examination, it appeared that a separation had occurred at the interface, and it was assumed that this occurred at the time the chip was broken. Micrographs a, b and c clearly show the region of separation. The interface region is not uniform. In a, the morphology is blocky, showing stacked plates of crystals on the cement side of the interface, with some fibrous particles. In b, the fibrous material, which is probably ettringite or C-S-H, is more abundant. In examining the length of the broken edge, the type of morphology shown at b is more prevalent. Micrograph c shows the growth of the fibrous materials on the brick.

Unfortunately, EDXA was not used to assist in the identification, but EDXA on similar fibrous growths shows them to contain calcium and silicon, indicating a calcium silicate hydrate of some type. The micrograph at d shows the fibrous material in more detail. It appears similar to the C-S-H gel structure identified by Diamond (40) as Type I C-S-H. According to Diamond, Type I gel particles may be anywhere from 0.5 μm to about 2 μm in length, and usually less than 0.2 μm across. "Their outlines are usually not quite parallel, but narrow slightly toward the outer end; often they branch into two or more portions at the outer tip" (40, p. 13). This branching is evident in d.

It appears that this fibrous C-S-H is the preponderant material at the line of separation between the brick and paste, and that it forms a zone that is weaker than the more blocky gel mass evident in the upper left side of b. Diamond refers to this latter type of gel as Type III C-S-H gel (40).

Figure 17 shows views of the broken edge of another sample with cement paste on one side, this time cured 42 days. The cement did not separate from the brick as with the previous sample. At a, the region to the left of A-A, appears to be cement paste with little fibrous material present. The gel appears to be mature and integral. Between lines A-A and B-B, shown both in photos a and b, the region appears to contain both gel and brick. To the right of line B-B, the material is all brick. At the limit of penetration of the paste into the brick, which appears to occur at the line B-B in photos c and d, there is material which looks like the reticulated C-S-H gel, Type II, referred to by Diamond (40). It appears to be attached to the surface of the brick and it may be a more mature form of the Type I gel shown in Figure 16.

There is no separation of the brick and paste in this case. It may be that the additional curing time allows the fibrous C-S-H gel to change form and that the reticulated gel form bonds better; hence, no separation. The additional curing time may also have assisted in the penetration of the paste into the brick, accounting for the zone containing both gel and brick, between lines A-A and B-B. However, this may also have been caused by a difference in water content between the paste of Figure 16 and that of Figure 17 when applied. The moisture content of the paste was not quantitatively controlled. This should be done in future experiments.

b. 4X magnification photos of treated and untreated chips

Figures 18 and 19 show the photographs taken of 16 sample chips prior to gold coating. The photos provide a good visual contrast of the effect of the treatments in causing the paste to adhere better to the chips. The scribe marks used for a reference when viewing the samples with the SEM are clearly visible, except where covered by paste. Each figure contrasts two types of paste, namely cement paste and cement plus lime paste. Figure 18 shows samples cured 7 days and Figure 19 shows samples cured 28 days. The cement droplet, 7A-1 on the untreated 7 day sample popped off with very little effort, leaving very little residual paste. The bond did not appear strong. The limewater sample, 7B-1, left more residual cement. This may have been because the limewater increased the quantity of $CaCO_3$ formed on the surface and edges of the paste. However, most of the droplet popped off leaving a clean surface. A white residue, probably

Figure 16. Edge view of the interfacial region, cement paste on brick, hydrated 7 days

a - Interface region; cement on left, brick on right

b - Interface region, different location; cement on left, brick on right

c - Magnified view of fibrous material on brick

d - Detail of fibrous material; probably C-S-H gel, Type I, according to Diamond (40)

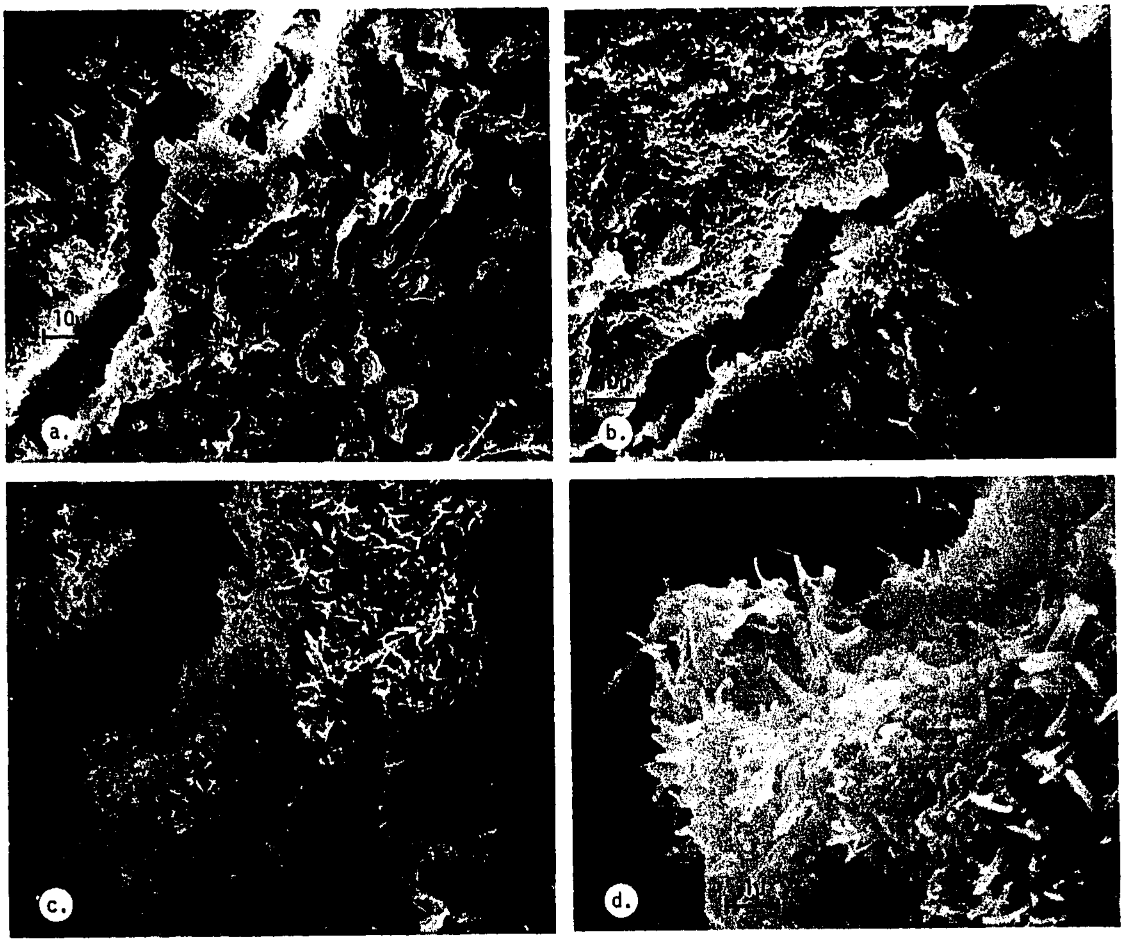

10
a.
b.
c.
d.

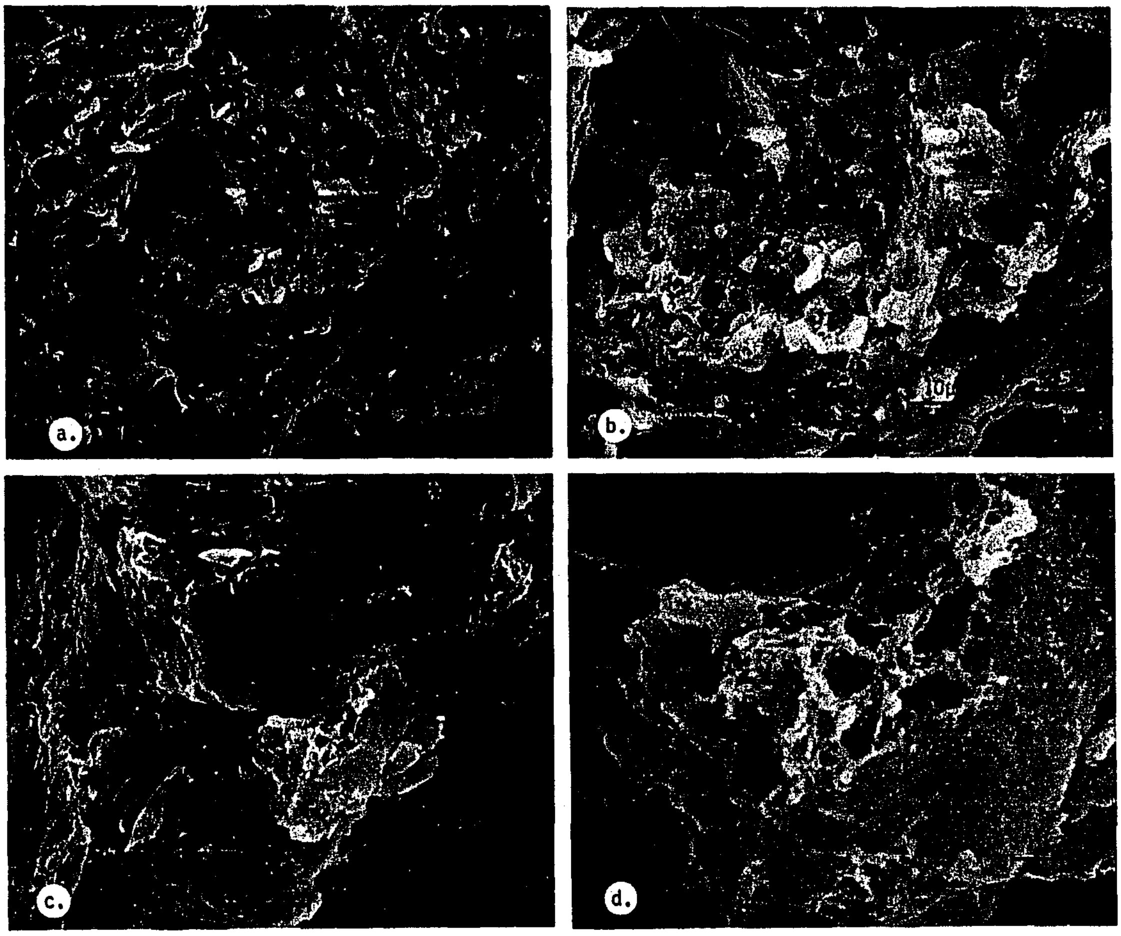
Figure 17. Edge view of the interfacial region, cement paste on brick, hydrated 42 days

a - Probable interface region, showing cement left of A-A, a zone of paste penetration between A-A and B-B, and brick to the right of B-B. Square shows approximate region covered by c

b - Magnified view of a. Shows probable limit of penetration of paste within brick, represented by B-B

c - Magnified view of b. C-S-H gel, Type II, according to Diamond (40), attached to brick

d - Magnified view of c, showing reticulated C-S-H gel in more detail


a.
b.
10
5
c.
d.

$Ca(OH)_2$, remains on the surface. The NaOH treated sample, 7C-1, shows a great amount of residual paste. It was not possible to remove the paste without excessive scraping.

The H_3PO_4 treated sample, 7D-1, did not present a great amount of resistance, although there remain well-bonded areas of paste.

The results using lime and cement paste instead of cement show more residual paste on the NaOH and H_3PO_4 treated chips, 7C-2 and 7D-2, than on the untreated and limewater treated chips, 7A-2 and 7B-2.

The results at 28 days were approximately the same, with greater bonding shown with the NaOH and H_3PO_4 treated samples, 28C-1, 28C-2, 28D-1, 28D-2. Figures 18 and 19 provide visual evidence that the NaOH and H_3PO_4 pretreatments promote better bonding between brick and paste. However, there is insufficient detail to provide any clues as to why. The micrographs which follow examine the chip surfaces in more detail.

c) Micrographs of untreated chips, cement paste Figure 20 shows the micrographs for two sample chips. Micrographs a through d show the surface of a chip from which the cement paste droplet has been removed at 7 days. The chip at a and b was not wetted before applying the cement. The chip at c and d was wetted before applying the cement. This latter chip is 7A-1 in Figure 18. The residual paste particles can be clearly seen in both cases. The paste particles in a and b show less hydration and appear more angular than those in c and d. There does not appear to be an appreciable penetration of the paste into the pores of the brick in either chip. A comparison of a and c with e, which is a plain, polished brick surface at the same magnification, shows that the paste is

Figure 18. Residual paste on brick chips after paste droplet has been removed at 7 days hydration

a - Chips untreated

b - Chips treated with limewater

c - Chips treated with NaOH

d - Chips treated with H_3PO_4

Left column - Cement paste

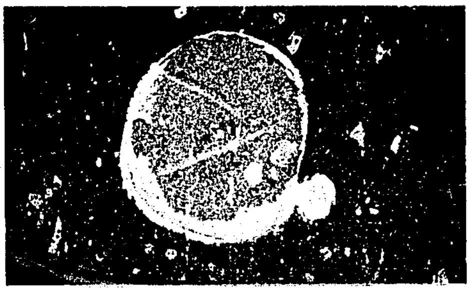
Right column - Cement plus $Ca(OH)_2$ paste

7 DAY HYDRATION

CEMENT PASTE

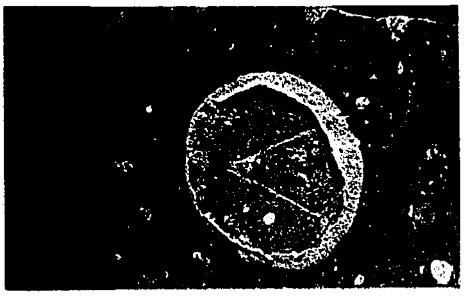
CEMENT AND LIME PASTE

7A-1.

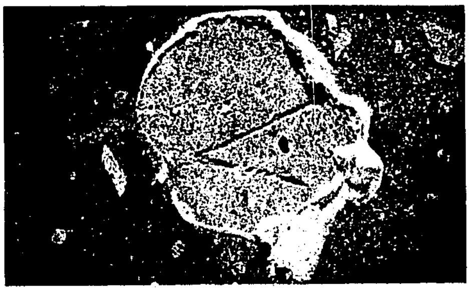


7A-2.

a. UNTREATED



7B-1.



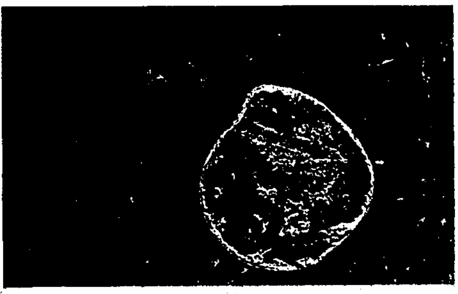
7B-2.

b. LIMEWATER

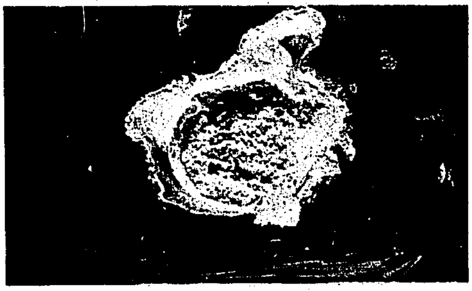
7C-1.

7C-2.

c. NaOH



7D-1.



7D-2.

d. H_3PO_4

1 cm

Figure 19. Residual paste on brick chips after paste droplet removed at 28 days hydration

a - Chips untreated

b - Chips treated with limewater

c - Chips treated with NaOH

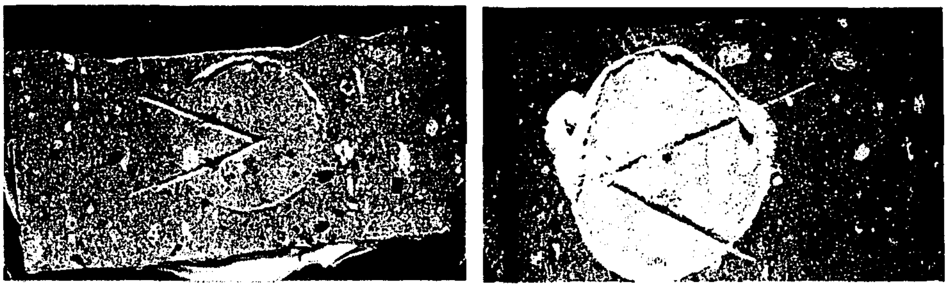
d - Chips treated with H_3PO_4

Left column - Cement paste

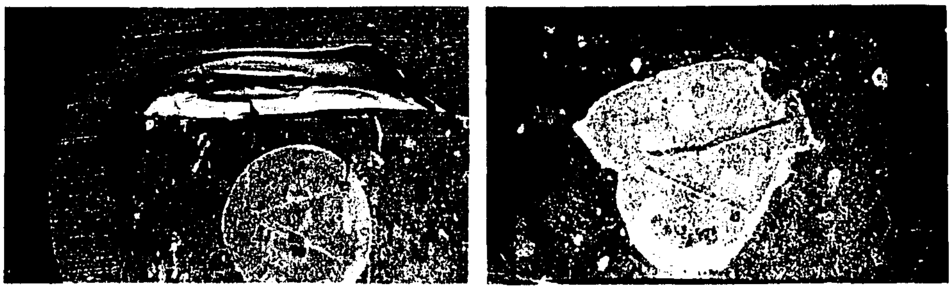
Right column - Cement plus $Ca(OH)_2$ paste

28 DAY HYDRATION

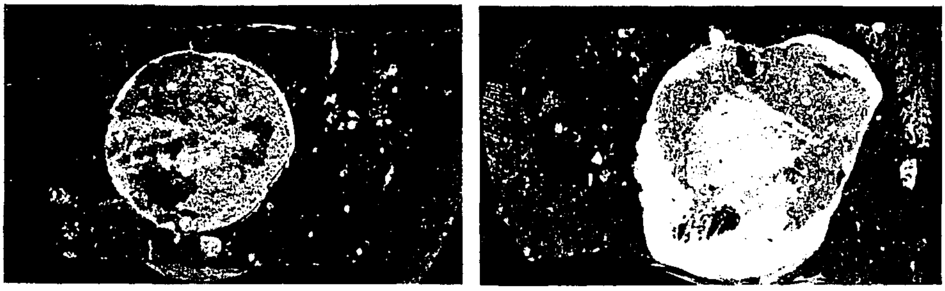
CEMENT PASTE CEMENT AND LIME PASTE



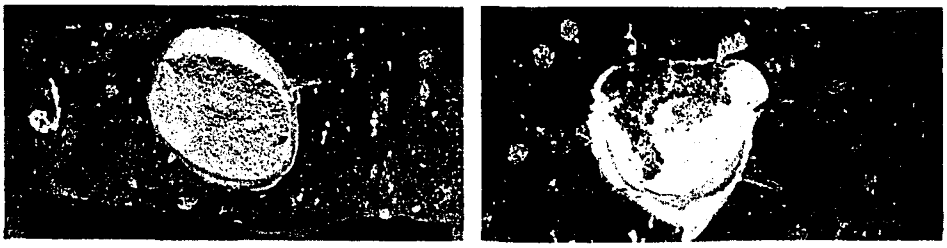
28A-1. a. UNTREATED 28A-2.



28B-1. b. LIMEWATER 28B-2.



28C-1. c. NaOH 28C-2.



28D-1. d. H_3PO_4 28D-2.

1 cm

Figure 20. Micrographs of chip surfaces with no chemical treatment after removal of cement paste, 7 days

a - Residual paste, placed on dry chip

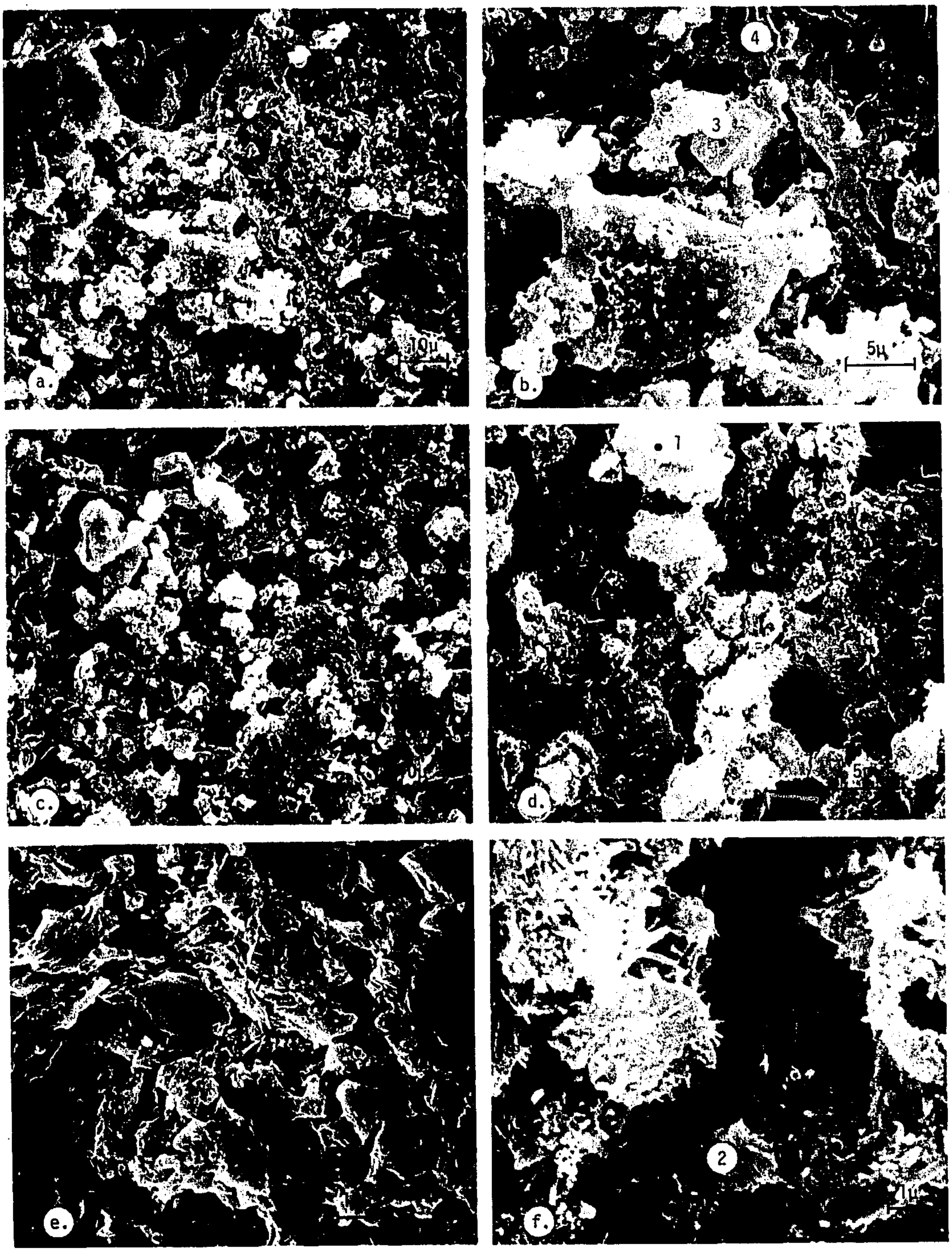
b - Magnified view of a

c - Residual paste placed on wetted chip

d - Magnified view of left center part of c

e - Untreated, polished brick surface

f - Magnified view of d, showing possible C-S-H growth on brick surface


10μ
a.
4
3
5μ
b.
c.
1
d.
e.
2
1μ
f.

apparently resting on the surface of the brick. EDXA shows particle 3 in b to be a paste particle, probably a calcium silicate hydrate. Particle 4, however, is shown to be brick with a higher calcium content than for plain brick indicating some type of surface coating or absorption of calcium on the brick.

The brick surface in d appears to have some material growing from it. This is confirmed in f, which shows small finger-like growths on the brick. Particle No. 2 in f is a brick particle, high in calcium, as determined by EDXA. Small finger-like growths can be seen on that particle as well as nearby surfaces. These growths are presumed to be C-S-H gel similar to those seen in Figure 16. It appears that prewetting the chip promotes the hydration of the cement at the interface region and promotes the growth of the C-S-H on the brick surface.

d. Micrographs of untreated chips, cement and $Ca(OH)_2$ paste The paste droplets placed on the brick chips in Figure 21 consisted of a blend of cement and $Ca(OH)_2$, 50/50 by weight proportions. The chip shown at a and b was not prewetted before applying the paste droplet, whereas the chip shown at c and d was prewetted. The latter chip is the same as 7A-2 in Figure 18.

In Figure 21, the paste particles appear to be smaller, and the degree of penetration of the paste into the brick pores is greater than that for the plain cement paste shown in Figure 16. The small particles in Figure 21 are probably a mixture of cement and lime particles at various stages of hydration.

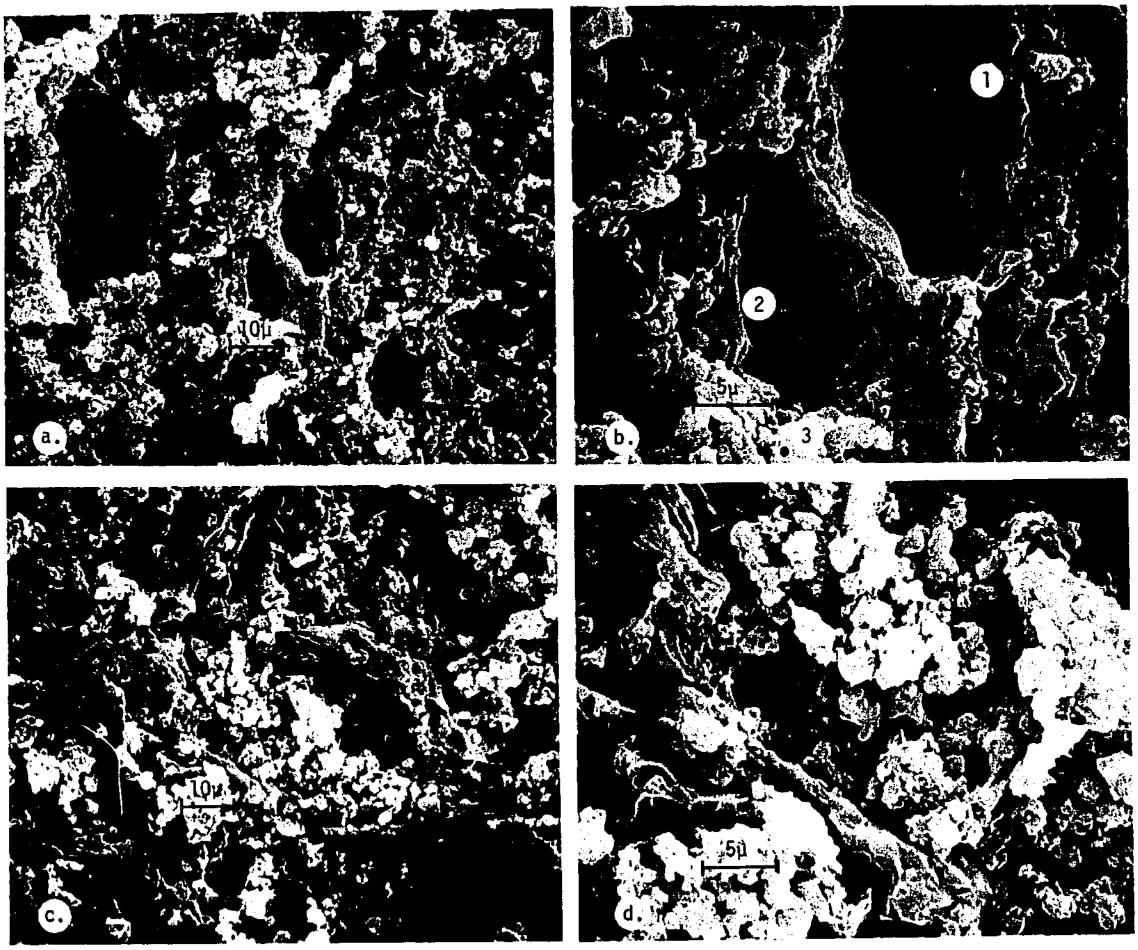
Figure 21. Micrographs of chip surfaces with no chemical treatment, after removal of cement and $Ca(OH)_2$ paste, 28 days

a - Residual mortar, placed on dry chip

b - Magnified view of a

c - Residual mortar, placed on wetted chip

d - Magnified view of c


a.
10μ
①
②
3
5μ
b.
10μ
c.
5μ
d.

The effect of lime in the paste appears to be a more complete filling of the brick pores and a more intimate contact between the paste and brick. This does not necessarily mean that the bond will be better, but to the extent that the lime assists in the transport of cementitious products into the pores, and the possible interaction of lime with the brick, and its eventual change to $Ca(CO_3)$ within the brick pores, this visible increase in intimate contact could result in better bond than with cement alone.

In comparing a to c, Figure 21, there does not appear to be any difference in the degree of filling the brick pores. Thus, the pre-wetting of the brick in c does not appear to have a significant effect on the degree of mortar penetration. However, an examination of b and d shows the particles in b to be more blocky and angular than those in d. The particles in d appear more irregular, with rounded edges, and some evidence of growing together into an integral mass. The wetting of the chip appears to have had a beneficial effect in enhancing the degree of hydration of the paste in this region.

Particles 1 and 2 in b are brick with either a calcium coating or absorbed calcium. The excess calcium shows up in EDXA examination. Particle 3 in b is probably calcium silicate hydrate.

e. Micrographs of limewater treated brick chips These micrographs are shown at Figure 22. All surfaces were wetted prior to placing the paste. Micrographs a and b are of the surface after the removal of a cement paste droplet at seven days. This is chip 7B-1 in Figure 18. The brick and paste structure show no apparent difference from

Figure 22. Micrographs of chip surfaces, with limewater treatment, after removal of the paste droplet, 7 and 28 days

a - Cement paste, 7 days

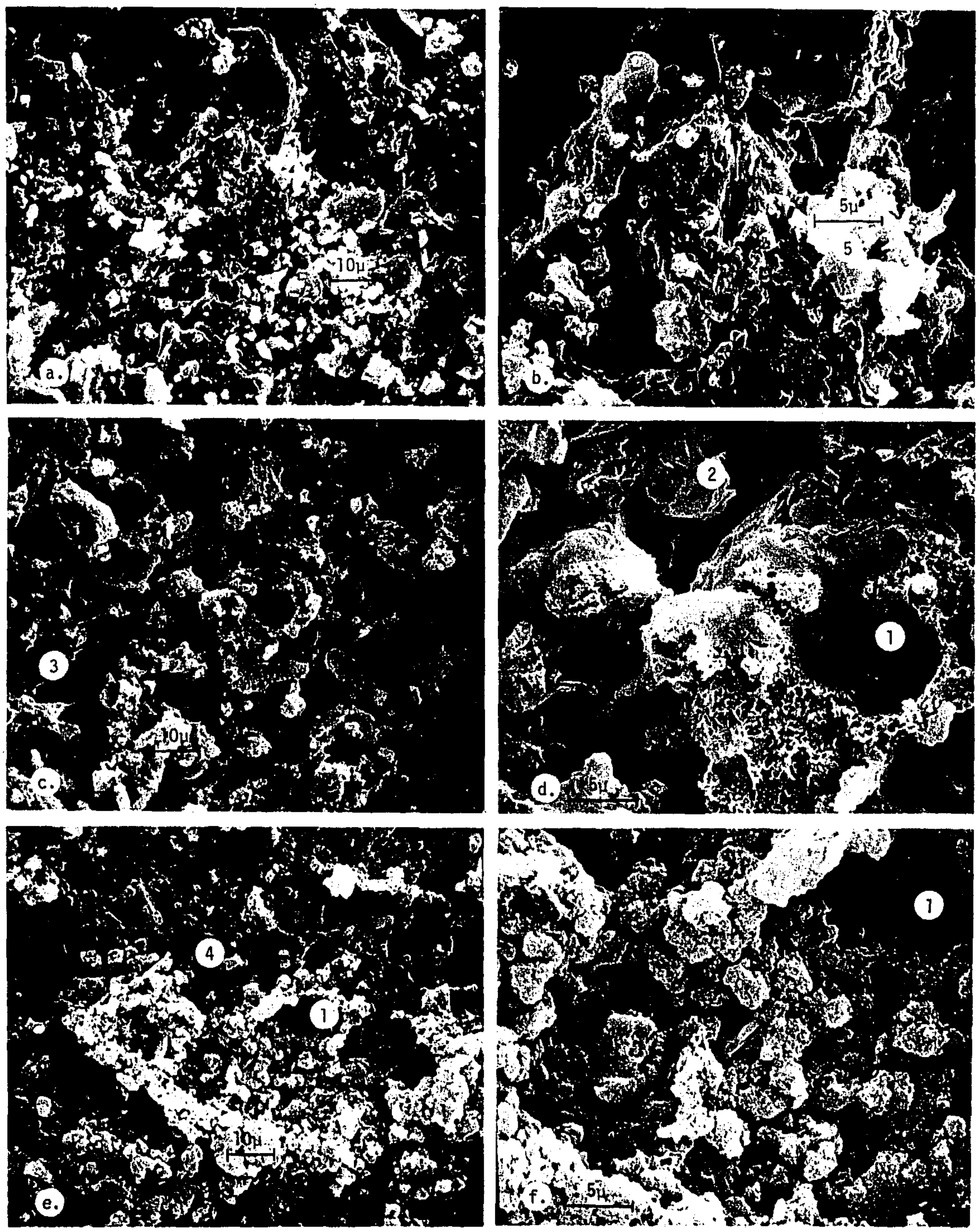
b - Magnified view of a

c - Cement paste, 28 days

d - Magnified view of c

e - Cement plus $Ca(OH)_2$ paste, 28 days

f - Magnified view of e


a.
10μ
b.
5μ
5
c.
3
10μ
d.
5μ
2
1
e.
4
1
10μ
f.
5μ
1

cement on untreated brick, Figure 20. EDXA shows that the paste particle at 5 in b is a calcium silicate, probably hydrated. Micrographs c and d are views of a chip surface at the end of 28 days. This is chip 28B-1 in Figure 19. The growth of hydration products is more evident at 28 days. The brick surfaces show the growth of a hydration product. Particle 1 in d shows a high calcium and silicon content, but little iron. It is probably a calcium silicate hydrate particle, showing hydration product around its edges. Particle 2 in d shows a much higher iron content, and is probably calcium coated brick. In general, there appears to be more evidence of hydration and coating of the brick in c and d than in a and b. This is to be expected with the hydration having been permitted to progress for 28 days versus 7 days.

The micrographs at e and f are of a chip surface where the paste was cement and lime, removed at 28 days. This is chip 28B-2 in Figure 19. The filling of the pores appears to be more extensive than with the cement paste alone. At 28 days, the hydration is quite evident as shown at f. The smaller, white and gray particles shown in e and f are high in calcium content, but also show significant amounts of iron, aluminum and silicon. The preponderant element not present in brick is calcium. Thus, the particles may be $Ca(OH)_2$ or C-S-H. EXDA shows particle 1 to probably be calcium coated brick.

f. Micrographs of NaOH treated brick chips Figures 23 through 25 contain a representative sampling of micrographs which show the effects of treating the brick with NaOH. All of the micrographs are from one chip, *i.e.*, 7C-1 of Figure 18, which showed the greatest degree of adherence between paste and brick. Figures 23a and b show the residual paste inside the residual paste ring. Micrograph b reveals a crystalline formation in the bottom of the void which is not present in the residual paste of other chips. The material around the periphery of the void has the appearance of hydrated cement. The crystalline material in the bottom of the void is apparently associated with the interface region. The area shown in c is at the outside toe of the slope of the residual paste ring, at the point where it meets the brick. The crystal shapes appear similar to those in b. The area in d is a blow-up of the central part of c. EDXA analysis of particle 1 shows it to consist of calcium and silicon only in the molar ratio of 7 Ca:1 Si. This may be calcium carbonate mixed with a calcium silicate hydrate. No sodium is present in particle 1. Particle 2 contains a large amount of calcium, along with some silicon, iron and potassium in the molar ratios of 12 Ca:2 Si:.33 K:1 Fe. Particle 3 contains calcium, silicon and iron in the molar ratios of 56 Ca:14 Si:1 Fe. It is probably predominantly a calcium silicate hydrate. Particle 4,5 in e contains a large amount of potassium, sulfur and calcium, plus lesser amounts of sodium, silicon, and iron, in the approximate molar ratios of 42 K:36 Ca:24 S:8 Si:1 Na:1 Fe. Particle 6 in d and e contains a large amount of calcium and lesser quantities of silicon, sodium, iron and potassium in the approximate molar ratios of 15 Ca:4.3 Si:0.5 K:1 Fe:0.25 Na. Particles 2 and 6 are probably the same material. Particle 7 in d has approximately the same composition. Particle 8 in e has a large quantity of calcium and some silicon, potassium and iron in the approximate molar ratios of 30 Ca:4.5 Si:2.5 K:1 Fe. Although it appears to grow from particle 3, it is richer in calcium. Micrograph f shows the brick outside the paste ring. A comparison with the brick shown in Figures 20-22 shows the brick surface at f to have a rougher, etched appearance. It is likely that the NaOH treatment has etched away some of the material in the brick. EDXA of the brick surface outside the paste ring shows no presence of sodium, suggesting that any brick-sodium compounds present may be water soluble and may have migrated to the paste when the paste was applied.

Figure 24a shows the path of a traverse up the exterior slope of the residual paste ring. The composite micrograph shows the lower end of the traverse at a higher magnification. The treated brick is on the right. The crystal structure at the interface is composed of a needle-like growth on the brick. EDXA of particle 10 shows the particle composed of calcium, iron, aluminum and silicon in the proportions 33 Ca:3.6 Si:1 Fe:0.33 Al, suggesting that the particle is a calcium-iron-aluminum-silicate hydrate mixed with $CaCO_3$. Carbonation cannot be ruled out, and a significant part of the calcium is likely in the carbonate form.

Proceeding up the slope of the paste ring, the morphology becomes more densely packed and the crystal needles become pyramidal in shape and more fully developed.

Figure 25 shows the morphology as the traverse continues up the slope to about one-third of the way toward the top. The crystal structure becomes very massive, dense and foliated. This type of morphology was not found within the paste ring, except at the bottom of the void shown in Figure 23. The reason the crystals may not be visible inside the paste

Figure 23. Micrographs of chip surfaces and residual paste, NaOH treatment, 7 days hydration

a - Residual paste inside residual paste ring

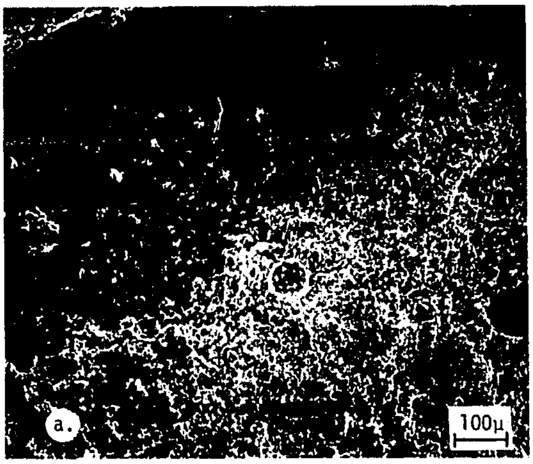
b - Magnified view of void shown in a, showing formation of crystals in bottom of void

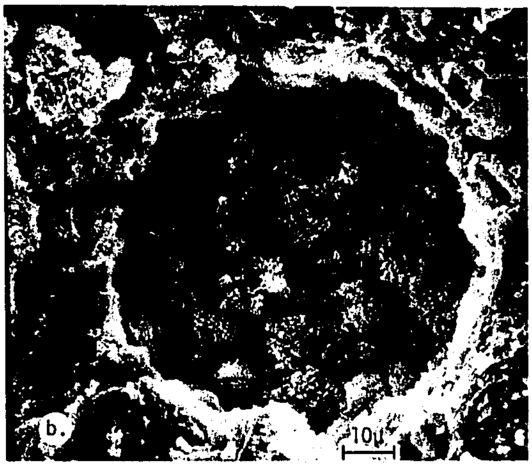
c - Crystal formation at the brick-paste interface at exterior toe of residual paste ring

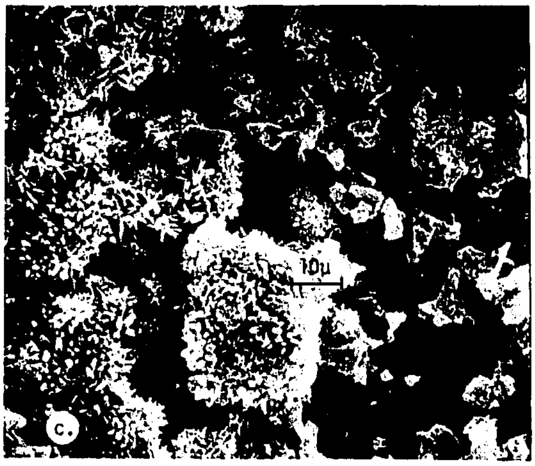
d - Magnified view of c

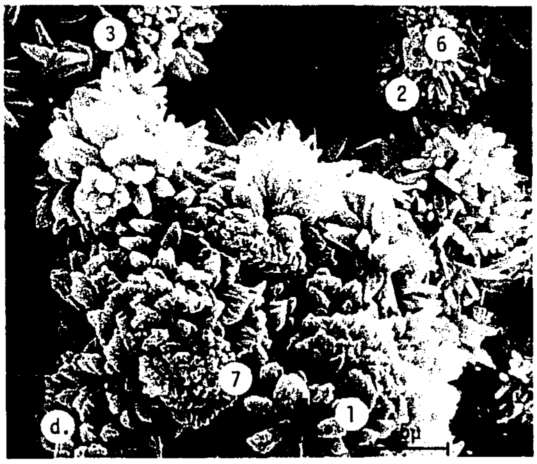
e - Magnified view of upper center of c

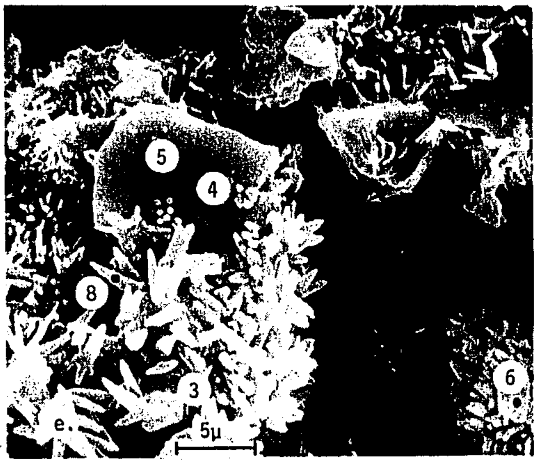
f - Treated brick surface outside of paste ring


a.
100μ


b.
10μ


c.
10μ


3
6
2
7
1
d.
5μ


5
4
8
3
6
e.
5μ

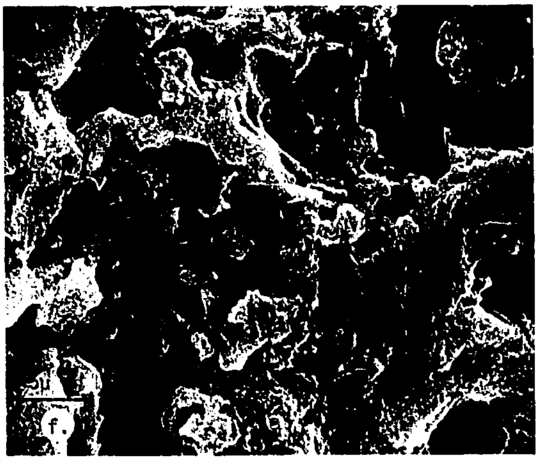

μ
f.

Figure 24. Morphology on exterior slope of residual paste ring, cement paste on NaOH treated chip, 7 days hydration

a - Path of traverse, Figures 29 and 30

b - Mosaic showing morphology at the toe of the residual paste ring, brick on the right, paste on the left

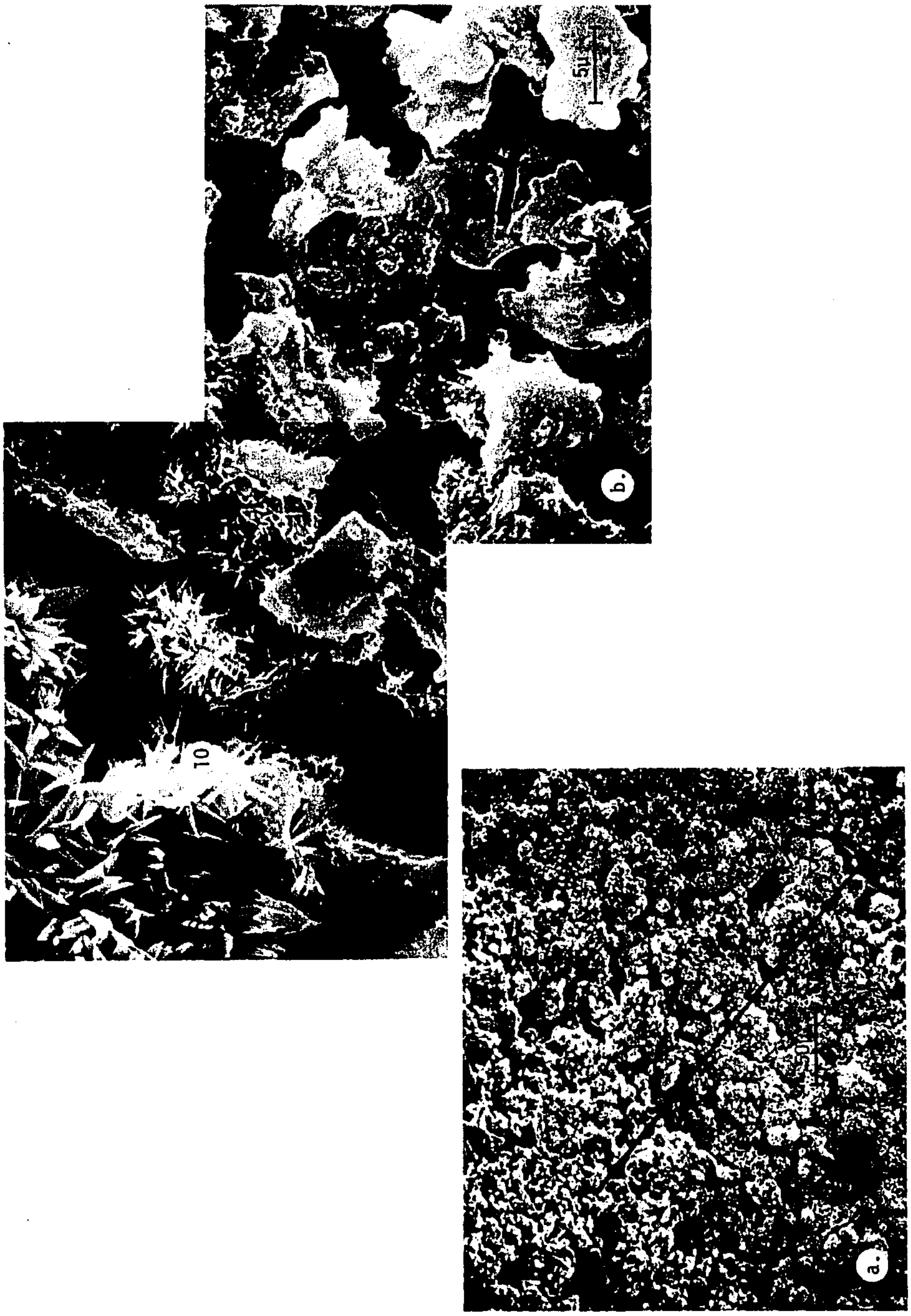
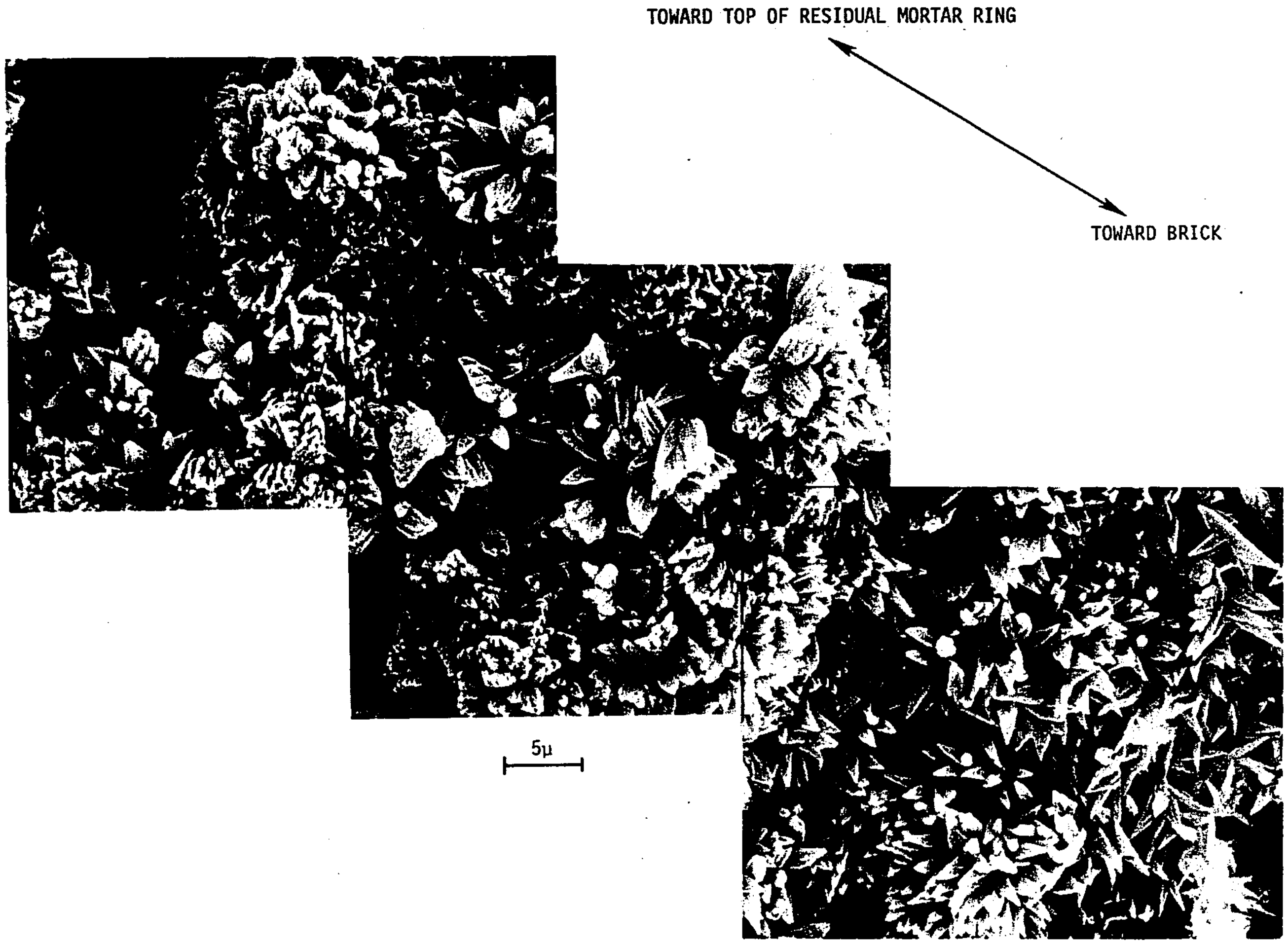

5μ
b.
10
5μ
a.

Figure 25. Continuation of traverse shown in Figure 24. Interface between paste and brick is in lower right corner. Upper left corner is approximately 1/3 of the distance up the outer slope of the residual paste ring


TOWARD TOP OF RESIDUAL MORTAR RING
TOWARD BRICK
5μ

ring could be because they are responsible for the bonding that takes place and may lie underneath the residual paste.

The proportion of sodium in the crystal structure is very low, compared to the other elements. Yet, it appears that this small quantity of sodium is sufficient to stimulate the intense crystal growth shown and that this dense crystal structure may be responsible for the increased bond of NaOH treated brick.

g. Micrographs of H_3PO_4 treated brick chips Figures 26 and 27 contain the micrographs of the H_3PO_4 treated chips. Representative micrographs are arranged in a manner which best show the crystalline structure that might account for the better bond of the H_3PO_4 treated brick chips. The micrographs in Figure 26 correspond to 7D-1 in Figure 18 which had cement paste applied and which was cured 7 days. Figure 26a and b show the residual paste inside the paste ring. In a, there does not appear to be any difference from untreated brick. However, in b, certain features can be noted. There appear to be small polyp-like growths on the surface of the brick. Some of these look more like separate particles; others appear to be small raised spots on the surface of the brick. EDXA of the white particles similar to 1 and 2 in b show 1 to contain primarily calcium and silicon, with lesser amounts of aluminum, potassium and iron. The molar ratios are 5.7 Si:4.3 Ca:1.5 K:1 Fe:0.8 Al. No phosphorus is present. This could be a particle which was near the top of the paste and fell to the bottom of the chip, hence no evidence of phosphorus. On the other hand, particles similar to 2 do contain phosphorus. The approximate ratios of the elements are 21 Si:10 Ca:6 P:3

K:1 Fe:1 Al:0.5 Ti. Thus, a reaction between the brick, phosphoric acid and paste is indicated. The brick surface does not show any marked amount of etching, but some cracks are evident which are not present in other chips. These cracks could be the result of some type of stress caused by chemical interaction.

Figure 26c is a view of the toe of the outside slope of the residual cement paste ring. The crystal structure, magnified in d, is common only to the H_3PO_4 treatment. EDXA of the crystals in d show them to be high in calcium and phosphorus, with lesser amounts of other elements in the following ratios: 44 Ca:24 P:1.5 K:1 Si:1 Al:1 Fe.

The crystals are rectangular in cross section. The individual elongated crystals appear to stem from a common base. Their thickness is approximately 0.7 microns, their width is approximately 1.67 microns, and their length varies, but can be as long as 20 microns. These crystals are probably a complex calcium-aluminum-iron-silicate phosphate. The interlocking of these crystals may be responsible in large measure for the increased bond with H_3PO_4 treated chips.

Figure 26e is a view of some crystals which appear over the brick surface, outside of the residual paste ring. Figure f shows a magnified view of these thin wafer-like crystals. EDXA shows the element ratios of these crystals to be approximately 11.4 Ca:5.4 Si:5.3 S:1.7 P:1.4 Al:1 Fe:0.9 K. The sulfur reading may be erroneous due to overlapping lines, because sulfur does not appear in other EDXA analyses of brick, or may be due to migration of sulfate ion from the paste. The wafer-like plates are approximately 0.5 microns thick by 4 microns wide, by 18 microns long.

Figure 26. Micrographs of chip surfaces and residual cement paste, H_3PO_4 treatment, 7 days hydration

a - Residual cement paste on chip surface inside outer residual ring

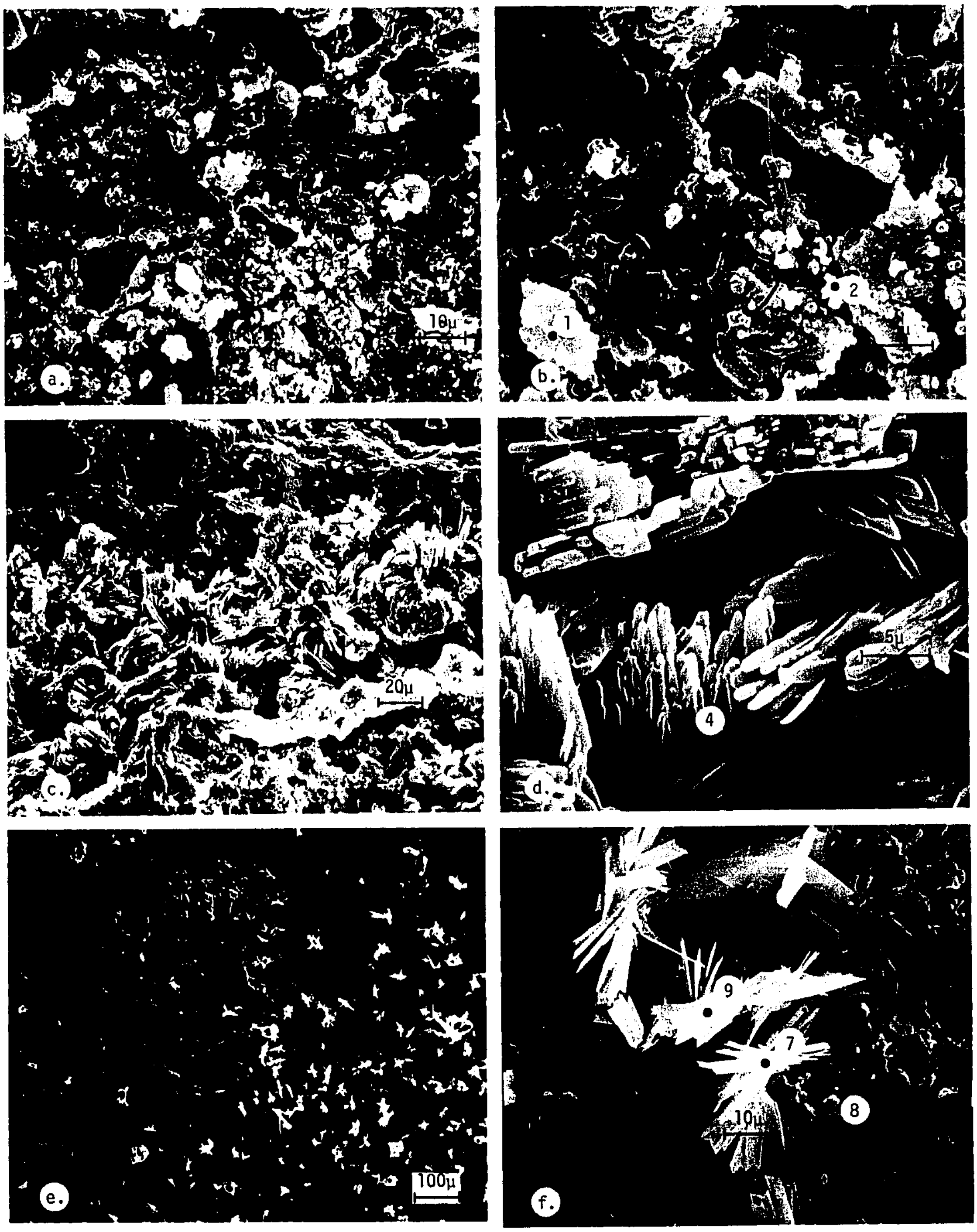
b - Magnified view of a

c - Interface region at outer toe of residual cement paste ring

d - Magnification of crystals in c

e - Brick surface outside paste ring

f - Magnification of crystals in e


10μ
1
2
a.
b.
20μ
c.
5μ
4
d.
100μ
e.
9
7
10μ
8
f.

The source of the calcium could be the brick itself since EDXA of this brick does show calcium to be present. These particles do not appear within the residual paste ring and probably do not play a role in bonding the paste to the brick.

Figure 27 shows the crystal structure inside and outside of the paste ring for two samples using cement and lime paste. Micrographs a and b are views inside the paste ring of a sample hydrated 28 days, corresponding to 28D-2 in Figure 19. The white, fibrous particles are represented by particle 1 in b. EDXA shows these particles to contain elements in the ratios 4.5 Si:1.4 Al:1.25 Ca:1 Fe:0.8 K:0.6 P:0.1 Ti. The white massive particle in a appears to be residual paste firmly attached to the brick. The crystals appear to be stacked platelets. EDXA of 3 shows it to be high in calcium and phosphorus. The elemental ratios are 14 Ca:8 P:5 Si:1.3 Al:1 Fe:0.5 K:0.3 S:0.1 Mg. Of particular note in b is the appearance of crystals growing from the brick surface, similar to those in d of Figure 26.

Figure 27c shows the exterior toe of the slope of the residual cement-lime paste ring. In Figure 27d the massive crystalline growth at the interface can be seen. At least three separate crystal shapes can be seen. Long slender crystals are in the upper right quadrant. EDXA shows these crystals to contain elements in the ratio 51 Ca:19 P:3.5 K:1 Si:1 Fe. Feather-like crystals appear at the left side of the micrograph. These were not analyzed. The lower right quadrant contains a blocky appearing material. EDXA of particle 5 shows the elemental ratios to be 47 Ca:31 P:6.6 K:3 Cl:1.6 Si:1 Fe. The appearance of the crystals in

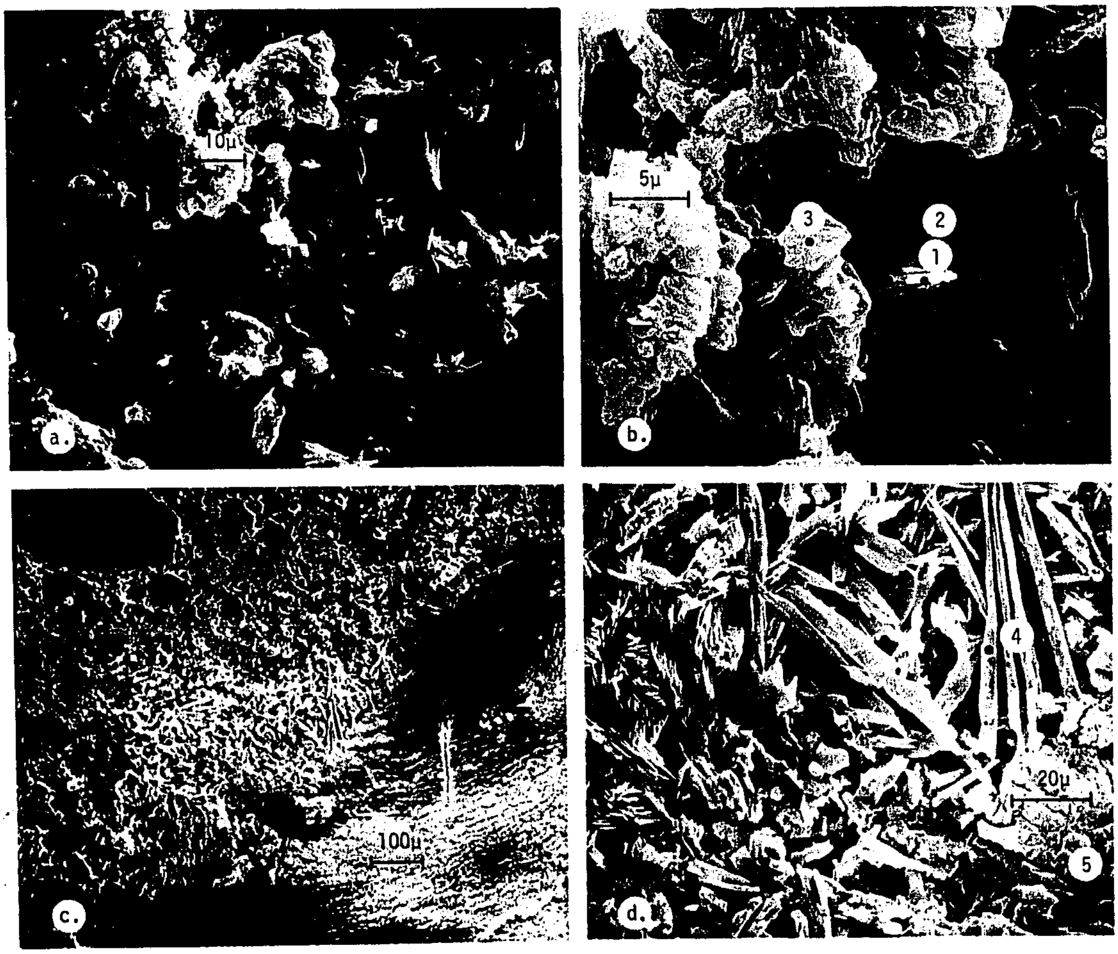
Figure 27. Micrographs of chip surfaces and residual cement and lime paste, H_3PO_4 treatment, 7 and 28 day hydration

a - Residual paste inside paste ring, 28 days, lime and cement paste

b - Magnified view of a

c - Interface region at outer toe of residual paste ring, lime and cement paste

d - Magnification of c


10μ
a.
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3
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1
b.
100μ
c.
4
20μ
5
d.

Figure 27d are quite different from those in Figure 26d. Both are views of the outer interface between brick and paste. The additional calcium in the paste of Figure 26d may account for the difference in structure; however, the calcium and phosphorus ratios do not differ markedly.

Figures 18 and 19 show that the H_3PO_4 treatment results in more residual paste than with untreated brick. The effort required to remove the paste droplets was also considerably greater. The answer to the improved bond may lie in the massive interlocking crystal structure shown here to occur at the interface.

5. Summary

This series of micrographs and photographs is but a small portion of many hundreds of micrographs taken of various combinations of brick and paste as a part of this investigation. The photos selected are representative. Figures 16 and 17 provide edge views of the interface region between cement paste and brick. At 7 days, the material is preponderately fibrous at the line of separation. It may provide a zone of weakness, causing the observed separation. At 42 days, the fibrous growth changes to what appears to be a Type III C-S-H gel, according to Diamond (40). There is no separation of brick and paste, indicating that the bond is stronger. It would be expected that bond would increase with hydration time.

Figures 18 and 19 show that pretreatment with NaOH and H_3PO_4 result in a better bond between both types of mortar paste and the brick.

Figures 20 and 21 show that a prewetted chip may enhance the degree of hydration of the paste at the interface. They also show that lime in the paste results in a more complete filling of the brick pores. There is probably an optimum lime content, and this could be the subject of additional investigations.

Figure 22 shows an increased amount of hydration product at the interface with limewater treated brick. This could account for the increased bond strength noticed in the couplet tests, and a slight increase in the residual paste shown in Figures 18 and 19.

Figures 23, 24, and 25 show a significant increase in crystalline material when brick is treated with NaOH. These crystals show, at the interface, the exterior face of the residual paste and selected locations near the brick, inside the residual paste ring. These crystals are preponderantly calcium-silicate-hydrate with minor amounts of Na, K, and Fe. The extensive, dense growth of these crystals may account for the increase in bonding for NaOH treated brick. The etched brick surface may also contribute to the increased bond.

Figures 26 and 27 also show extensive crystal growth at the interface of paste and brick treated with H_3PO_4. These crystals are apparently calcium silicate phosphate hydrates with minor amounts of Al, Fe, and K. This crystal growth is not common to untreated brick, and probably contributes to the increased bond observed with H_3PO_4 treated brick.

SEM and EDXA studies show that a variety of crystals, depending on the type of brick treatment, form at the brick and paste interface. Complete characterization of these crystals from elemental composition revealed by EDXA would not be possible for the following reasons:

(1) Influence of background composition on results of EDXA.

(2) Without reference standards and elaborate techniques, the results of EDXA are at best semi-quantitative.

(3) The presence of poly crystals and solid solutions cannot be differentiated by EDXA.

However, semi-quantitative results obtained from EDXA furnish valuable information to estimate the formation of possible catagories of compounds as done in the previous discussions. Most importantly, these results can be used to support the final interpretation of X-ray diffraction analysis.

D. X-Ray Diffraction Examinations

1. General

A major portion of this investigation involved the use of X-ray diffraction techniques to search for any crystalline compounds that might exist at the interface between brick and mortar.

The X-ray equipment used was a Siemans D500 X-ray Diffractometer, purchased in 1979. An X-ray tube using a copper target was used. Samples of the various mortar constituents, without sand, with and without brick powder, were examined at various times of hydration. Comparative strip charts showing the peaks that correspond to the constituent interplanar spacings are in Figures 28-31.

For comparison, it was decided to look at the following combinations:

a. Plain vs treated brick powder

1) Brick powder
2) Brick powder treated with limewater

3) Brick powder treated with NaOH
4) Brick powder treated with H_3PO_4

b. Individual and combined paste constituents

1) $Ca(OH)_2$ plus water, hydrated 7 days
2) Cement plus water, hydrated 7 days
3) Cement plus $Ca(OH)_2$ plus water, hydrated 7 days

c. Brick powder, and paste individually and combined

1) Brick powder
2) Cement plus $Ca(OH)_2$ plus water, hydrated 7 days
3) Cement plus $Ca(OH)_2$ plus brick powder plus water, hydrated 7 days

d. Paste and brick powder, treated and untreated

1) Cement plus $Ca(OH)_2$ plus brick powder plus water, hydrated 7 days
2) Cement plus $Ca(OH)_2)$ plus brick powder treated with NaOH, hydrated 7 days
3) Cement plus $Ca(OH)_2$ plus brick powder treated with H_3PO_4, hydrated 7 days

The objective of comparison "a" was to look for the formation of crystalline products when brick powder is treated with limewater, NaOH, and H_3PO_4. The objective of comparison "b" was to note the crystalline compounds formed by exposing lime, cement, and a mixture of the two, to water, allowing hydration to proceed for 7 days. The objective of comparison "c" was to search for possible crystalline reaction products that might be formed when brick and cementitious constituents are intermixed. This should show any crystalline reaction product at the interface between brick and the cementitious constituents in mortar. The objective of comparison "d" was to examine any new crystalline products that might form in a paste when the brick powder has been treated with NaOH and H_3PO_4.

2. Procedure

a. Preparation of samples

The specimens consisted of finely ground powder or paste, compacted and leveled by hand, into a flat, circular, Plexiglass mount. The Plexiglass mount, 5 cm outside diameter and 4 mm thick, contained a cylindrical well, open at the top, with an inside diameter of 3 cm and a depth of 1.7 mm, for placement of the sample.

The brick was initially crushed into small pieces using a hammer. When the pieces were approximately 0.5 cm in diameter, they were placed in the Spex 8000 mixer mill (shatter-box) and ground to a fine powder. This powder was then pulverized further, by hand, using a mortar and pestle.

In the case of the cement and $Ca(OH)_2$, the product was removed from the commercial paper bags as needed and ground by hand, using a mortar and pestle, until the product was uniformly small enough to stay in the holder. This resulted in the powder being sufficiently fine that it would pass a #200 sieve.

If the powders were to be mixed, the ingredients were carefully weighed, then mixed in a glass beaker with a stainless steel spatula until the mixture appeared homogeneous. The weight portions used were as follows:

Brick powder (BP) plus $Ca(OH)_2(L)$; 1 part BP, one part L.

Brick powder (BP) plus $Ca(OH)_2(L)$ plus cement (C); 2 parts BP, 1 part L, one part C.

$Ca(OH)_2(L)$ plus cement (C); one part of each

The lime and cement portions were the same as those used for the scanning electron microscope series, discussed earlier.

The treated brick powders were prepared in the following manner. For the limewater treatment, the solution of limewater prepared for the couplet tests was used. The limewater was poured out and mixed with approximately 4 grams of brick powder in a glass beaker. The two were allowed to stay in contact for ten minutes, then the mixture was filtered. The treated brick powder residue was dried in laboratory air for two days before placing in a foil covered beaker for storage. For the NaOH treated brick powder, the one molar solution of NaOH used for couplet testing was used. The procedure was the same as above. For the H_3PO_4 treatment, the solution prepared for the couplets was also used, and the same procedure was followed as above.

Brick powder and treated brick powder specimens were prepared by pressing the powders into Plexiglass sample holders with a metal spatula. The powder was compacted and leveled to be even with the top surface of the sample holder, using a glass microscope slide.

The pastes were prepared by adding de-ionized water to the mixed powders. Sufficient water was added to make a paste of approximately toothpaste consistency. No attempt was made to measure the quantity of water added or the water/cement ratio. These pastes were placed in the

Plexiglass sample holders and leveled using a glass slide. Every effort was made to insure a smooth top surface. The Plexiglass holders containing pastes were placed in a glass desiccator jar over water, with 20% NaOH, by weight, added, to retard formation of $CaCO_3$. The relative humidity in the jar was approximately 75%, and was measured using a humidistat. The paste samples were allowed to hydrate for seven days at room temperature, then they were removed and examined by X-ray diffraction.

b. Examination Samples were examined in the Siemans D500 diffractometer. Monochromatic copper K_α radiation was used for all studies. Monochromatization was provided by a graphite crystal in front of the detector. The accelerating voltage and filament current used were 25 kV and 10 ma, respectively. Three apertures of 1° each and two collimating slits of 0.05° and 0.15° were used to collimate the incident and diffracted beams prior to striking the graphite monochromater. The detector voltage was 910 volts. The time constant, τ, was one second. The linear range was 400 counts per second, which corresponds to the distance from the bottom to the top of the strip chart paper. Scanning speed was 2 degrees per minute. Chart speed was 2 cm per minute, resulting in a scale of $2\theta = 1$ degree per cm on the strip chart. Samples were observed from $2\theta = 2$ degrees, to $2\theta = 80$ degrees.

For observation, paste samples were removed from the glass jar environment, and were examined immediately. No period for drying was provided.

c. Method of analysis The resulting strip charts for the comparisons chosen are shown in Figures 28-31. Determination of the crystalline compounds present involved several approaches.

For the cement pastes, Lea (70) and Bogue (24) provide tables which list X-ray data for probable cement constituents and hydrated cement compounds. In addition, Midgley (73) and Diamond (40) provide sample X-ray strip charts of hydrated cement pastes.

Data from Lea and Bogue, as well as the Powder Diffraction Data File (62), were used to prepare strip charts. These strips, which are the same scale as the diffraction charts, are then compared with the peaks on the diffraction charts to help determine if a particular compound is present. Strip charts were prepared for all of the crystalline unhydrated and hydrated cement compounds, as well as commonly encountered crystalline phases in fired brick.

Hedges (53) discusses and provides a listing of the crystalline and glassy phases present in fired brick. His paper, along with data from Plummer (83) were used to help determine the crystalline compounds present in brick powder.

When instances arose in which peaks could not be identified using one of the sources above, the Fink method (61) of peak search was used to help identify the unknown compound.

1) LC500 and IDENT programs During the course of this investigation, the Materials Laboratory at Iowa State University obtained several software programs from the Siemans Corporation, two of which are entitled LC500 and IDENT (88). The LC500 program provides for count data

to be stored for future recall. The user must specify the starting and ending 2θ angles, the step size in degrees, and the counting time in seconds. This program was used to obtain data on brick powder, treated and untreated. The starting 2θ angle was specified as 2°, and the ending 2θ angle as 80°. The step size of 0.1 degree, and a counting interval of three seconds at each step required 40 minutes to complete the examination of one sample. This compares with 40 minutes required to obtain each of the diffraction diagrams shown in Figures 30-33. It was felt that the step size and counting time selected were adequate in that they would provide quantitative data similar to that shown in the diffraction charts, yet would not require an inordinate amount of time to perform.

The IDENT program is used to examine the stored data and determine the location, height and integrated intensity of the peaks. A representative output for brick powder treated with H_3PO_4 is shown in Figure 28. It shows that there are forty distinct peaks identified. For each, a value of 2θ, the corresponding d spacing in Angstroms (based on copper K_α radiation) integrated intensity in percent, integrated intensity in terms of total count, and a maximum peak intensity, is given. This information can then be used to interface with the Data Base and Search Program (60), described in the next section.

Considerable caution must be exercised in using this computer generated data. It should be compared to the actual diffraction chart. In some cases, two peaks on the diffraction diagram will be merged into one peak in the computer generated data. In other cases, a smaller, yet apparently significant peak on the diffraction chart will not be

Figure 28. Representative output from IDENT program showing 2θ, d, integrated intensity, and maximum intensity for 40 identified peaks from a sample of brick powder treated with H_3PO_4

PEAK SEARCH FOR BRK PWDR+H_3PO_4

```
SEARCH PARAMETER:
2 POINTS ARE AVERAGED
MAXIMUM BACKGROUND SLOPE OVER ONE DEGREE = 0.10
THE SMALLEST PEAK RELATIVE TO THE STRONGEST = 1.0

NO.     2 THETA       D       INTEG.I (%)     INTEG.I       MAX.I

 1      12.616      7.0105        2.7          239.          82.
 2      15.693      5.6422        1.3          114.          46.
 3      16.609      5.3329        1.3          115.          56.
 4      21.050      4.2167       21.5         1880.        1047.
 5      24.385      3.6471        4.3          379.         115.
 6      25.910      3.4359        1.5          129.          66.
 7      26.841      3.3187      100.0         8759.        4817.
 8      27.645      3.2240        5.1          451.         168.
 9      29.296      3.0460        2.5          223.         111.
10      31.192      2.8650        1.9          168.          66.
11      31.523      2.8356        2.1          187.          80.
12      33.484      2.6739        8.6          757.         301.
13      35.946      2.4962        3.8          329.         157.
14      36.730      2.4447       13.6         1188.         333.
15      39.656      2.2708        5.9          517.         262.
16      40.464      2.2273        3.1          275.         163.
17      41.123      2.1931        3.1          271.          85.
18      42.632      2.1189        6.1          535.         223.
19      43.264      2.0894        1.2          101.          44.
20      45.958      1.9730        4.9          429.         152.
21      47.260      1.9216        1.4          121.          42.
22      50.305      1.8122       14.9         1306.         417.
23      54.555      1.6807        6.1          534.         130.
24      55.065      1.6663        5.2          453.         191.
25      55.530      1.6534        2.9          257.          87.
26      57.527      1.6007        3.8          332.          48.
27      60.145      1.5371       11.5         1004.         302.
28      60.700      1.5244        2.4          208.          62.
29      62.954      1.4751        3.0          260.          58.
30      64.370      1.4461        4.8          419.          95.
31      65.997      1.4143        4.3          373.          81.
32      66.278      1.4090        2.1          181.          87.
33      68.290      1.3723       15.7         1377.         304.
34      73.629      1.2854        1.8          155.          59.
35      75.814      1.2537        4.1          361.         108.
36      77.804      1.2265        2.4          208.          62.
37      79.624      1.2030        1.6          139.          38.
38      81.395      1.1812        6.2          545.         132.
39      81.601      1.1788        2.0          175.         153.
40      83.960      1.1516        3.4          298.          88.
```

recognized as a separate peak in the computer generated data. Two parameters which can be selected and which seemed to influence the degree of match between the diffraction chart and the computer generated data were the number of points to be averaged and the smallest peak relative to the strongest. Through trial and error, it appeared that selecting two points to be averaged and a ratio of smallest to largest peak of 1% gave the best comparison between the chart and computer data.

2) Data base and SEARCH program The data base and SEARCH program (60) is a program prepared by the Joint Committee on powder diffraction standards. It takes the output data of the IDENT program and searches the data base of approximately 27,000 powder patterns, of which 19,000 are inorganic and about 8,000 are organic. Based on the degree of match between the data base patterns and the peak data provided from the IDENT program, the SEARCH program will provide a listing of compounds that may be present in the sample.

Certain chemistry is provided by the user when the SEARCH program is being used. For example, in providing input data for brick powder treated with H_3PO_4, the positive elements listed were Fe, Si, Al, O, H, Ti, K, Ca, S, and P as identified in EDXA studies. These can be further subdivided into major and minor elements. In this case, the major elements were listed as Fe, Si, Al, O, and H, and the minor elements were listed as Ti, K, Ca, S, and P.

The user can also specify an error window, which can vary from 1 to 10, and which is a measure of the accuracy of the input data. The lower the number, the better the data, and fewer possible compounds will be listed. The higher the number, the poorer the data, and a large number of possible compounds are listed. By trial and error, for the data used, it was found that an error window of 5 appeared to provide reasonable output in terms of numbers of possibilities that made sense, based on elements known to be present.

The most useful output of the SEARCH program is the first of three listings of possible compounds. This listing is entitled, "Chemically Correct - Matches Positive Input Chemistry." An example of the listing for brick powder treated with H_3PO_4, using an error window of 5, is shown in Figure 29. Two other listings provided are a list of the top 50 candidates which are chemically incorrect, based on the data provided, and a listing of the top ten candidates based on the original data provided, but computer modified. The first listing, chemically correct, proved to be the most useful and appeared to have the best listing of possible candidates. Using this list, it was then possible to go to the Powder Diffraction File Search Manual (63) and, using the X-ray data listed for each compound, verify the presence or absence of the compound, using the diffraction chart. The utility of the SEARCH program lies not in its ability to provide answers, but instead on its ability to narrow the choices from 19,000 to a more reasonable fifty or less. The user must then determine which of these candidates are actually present. This involves using the PDF data file to eliminate the unlikely candidates, and verify the possible presence of others.

```
  PDF   FORMULA                                                  REL
NUMBER                                                         FACTOR


CHEMICALLY CORRECT - MATCHES POSITIVE INPUT CHEMISTRY

 50490  SI 02                                                   *4 47
190926  K AL SI3 08                                             *4 29
220675  K AL S13 08                                             C4 28
190932  K AL S13 08                                             *4 25
290713  FE 0 ( 0 H )                                            *4 25
130534  FE2 03                                                  *4 24
130430  AL (P 03 ) 3                                            *  22
200199  CA2 AL2 SI 07                                           *4 22
140617  K FE SI3 08                                             *  21
300256  CA FE3 05                                               I  21
251402  FE2 03                                                  I4 20
310966  K AL SI3 08                                             *4 19
220687  K AL SI3 08                                             C4 18
150776  AL6 SI2 013                                             *4 17
190629  FE3 04                                                  *4 17
220632  FE SI                                                   I4 17
 10588  CA ( H2 P 02 )2                                            16
120483  K2 S2 08                                                *  16
220018  AL2 SI 05                                               *4 15
100423  AL P 04                                                 *4 14
230767  K AL ( S 04 )2                                          *  14
250177  CA TI SI 05                                             *4 14
160335  CA4 AL6 012 04                                             11
210816  CA S 04 . 2 H2 0                                        *4 11
211276  TI 02                                                   *4 11
 60226  CA S 04                                                 *4  9
200921  K3 P 04                                                     9
230493  K2 0                                                    C   7
210428  2 FE ( 0 H ) S 04                                       *   5
210676  K4 P2 07                                                    5
 10864  K H S 03                                                    4
 50682  ( TI )                                                2H*   4
160730  CA3 P2                                                      4
211272  TI 02                                                  *4   3
```

Figure 29. Representative partial output of the SEARCH program, showing the chemically correct possible crystalline compounds based on IDENT input

3. Results and discussion

a. Brick powder The diffraction trace of brick powder only is shown in Figure 30a. The primary crystalline compounds present are quartz (SiO_2), hematite (Fe_2O_3), mullite ($Al_6Si_2O_{13}$) and microcline ($KAlSi_3O_8$). $CaSO_4$ (d, 100% intensity = 3.5 Å ≡ 25.4° 2θ) also appears to be present in minor amounts. There are some unidentified peaks at 3.86 Å ≡ 23.2° 2θ, 3.71 Å ≡ 24° 2θ, 2.97 Å ≡ 30.1° 2θ, and several peaks between 2θ = 37° and 37.7°. Use of the JCPDS Fink Search Method (61) and the SEARCH program yields no clue as to their identity. Plausible candidates listed as possibilities by the SEARCH program, but which do not appear to be present, include Cristobolite (SiO_2), and calcium oxide (CaO). Microcline maximum, $KAlSi_3O_8$, PDF #19-926, may be present, but its major peaks at 21.05°, 27.3° and 27.4° are all masked by larger peaks.

The rounded hump between 2θ = 5° and 2θ = 12° is caused by amorphous material in the brick powder. Such a hump is referred to as an amorphous halo. Such halos are characteristic of amorphous materials (68). Glass is considered an amorphous material. Alkali-silica glass can be expected to form in fired clay products, according to Hedges (53).

b. Brick powder treated with limewater The diffraction chart for brick powder treated with limewater is shown in Figure 30b. There are no major apparent changes in crystalline structure. There does appear to be a new peak at 2θ = 29.3°, which corresponds to the 100% peak of $CaCO_3$. This is understandable since some of the dissolved $Ca(OH)_2$ in the limewater would carbonate upon exposure to moisture and CO_2, even though an effort was made to reduce the CO_2 present in the sealed curing jar.

There do appear to be several small peaks at 2θ = 43° and 65.3° which were not present in the untreated brick. These peaks are unidentified. Other than those peaks, there is no evidence of a new crystalline compound being formed. There does appear to be a change in the amorphous halo, however. It is broadened considerably after treatment with limewater, indicating a possible interaction between limewater and the glassy phase in brick. Kondo and Oshawa (69) report on the reactivity of various silicates with $Ca(OH)_2$. Silica glass is mildly reactive with $Ca(OH)_2$ at room temperature. The exact constitution of the glassy phase in the brick is unknown, but it may have reacted with the $Ca(OH)_2$. To the extent that this might etch the glass, this might result in a greater bond between the brick and mortar phases.

c. Brick treated with NaOH   The diffraction chart for brick powder treated with NaOH is shown in Figure 30c. As with the limewater treatment, no new crystalline compounds are apparent. There are no major unidentified peaks, and no significant changes in the peak heights except that there is a slight decrease in the height of the two unidentified peaks at 2θ = 18.2° and 19°. The SEARCH program indicates that there are eight plausible candidate compounds that contain sodium that could be present. Of these, six must be ruled out at the present time because of lack of corresponding peaks on the diffraction chart. These are $Na_4Al_2SiO_9$, $NaAlSiO_4$, $Na_6Al_4Si_4O_{17}$, $NaAlSiO_4$, $NaAl(SO_4)_2$, and $NaHSO_4 \cdot H_2O$. A possible compound is $(Na,K)AlSi_3O_8$, PDF file #19-1227, with major peaks at 2θ = 27.3°, 27.7°, 23.65° and 13.5. The first two peaks would be masked. The third, at 23.65°, may be present. The fourth, at

Figure 30. X-ray diffraction diagrams for brick powder

a - Plain brick powder

b - Brick powder treated with limewater

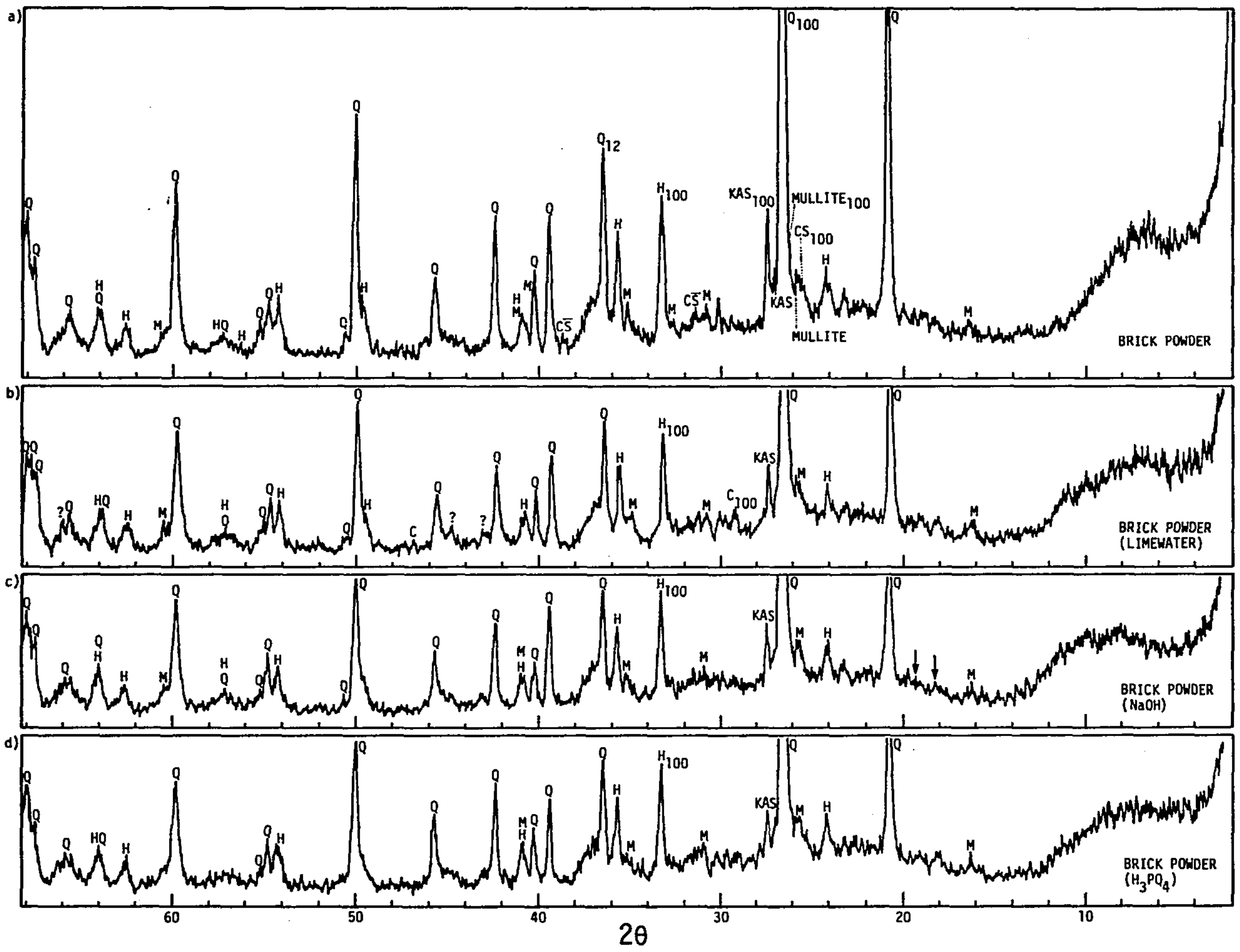
c - Brick powder treated with NaOH

d - Brick powder treated with H_3PO_4

Q = Quartz; H = Hematite, Fe_2O_3; KAS = $KAlSi_3O_8$;

M = Magnetite; $C\bar{S}$ = $CaSO_4$; Mullite = $Al_6Si_2O_{13}$

The 100 notation indicates the major peak for each compound


a)
b)
c)
d)
BRICK POWDER
BRICK POWDER (LIMEWATER)
BRICK POWDER (NaOH)
BRICK POWDER (H$_3$PO$_4$)
Q$_{100}$
Q$_{12}$
H$_{100}$
KAS$_{100}$
MULLITE$_{100}$
CS$_{100}$
KAS
MULLITE
C$\overline{S}$
C$_{100}$
Q
H
M
HQ
C
?
60
50
40
30
20
10
2θ

13.5°, shows no change. Another possible compound is $NaFeO_2$. There are very slight peaks at the major spacings corresponding to $2\theta = 40.6°$, 36.0°, and 61.3°.

The broadening effect on the amorphous halo is evident, indicating some effect of the NaOH on the glassy phase. Silica glass is easily attacked by NaOH, according to Holland (55). Oshawa and Kondo (77) also report the dissolution of silicate glass with NaOH. As with limewater, this etching action may account for the increased bond between brick treated with NaOH and the paste.

d. Brick treated with H_3PO_4 The diffraction chart for brick powder treated with H_3PO_4 is shown in Figure 30d. There are no major unidentified peaks and no significant changes in peak height. There does appear to be a new peak at $2\theta = 28°$, which corresponds to a d spacing of 3.18 Å. Possible candidate compounds that have a prominent peak at 3.18 Å include $CaH_2P_2O_7$, PDF #9-354, with prominent peaks at 3.35 Å = 26.6°(2θ), 3.19 Å = 27.95°(2θ), and 3.74 Å = 23.8°(2θ) and $KH_5(PO_4)_2$, PDF #20-890, with the first three peaks at 4.33 Å = 20.5°(2θ), 3.18 Å = 28.05°(2θ) and 3.39 Å = 27.3°(2θ). The SEARCH program provided a list of eight possible compounds resulting from phosphorus interaction with brick, based on the X-ray data. Of these, two were eliminated because there is no evidence on the diffraction chart of their presence. They are $K_4P_2O_7$, PDF #21-676, and $AlPO_4 \cdot 2H_2O$, PDF #25-0019. Possible candidates, where there is some match with the peaks are shown in Table 32 with their corresponding prominent peaks. About all that can be said is that these compounds may

Table 32. Possible interaction products between H_3PO_4 and brick powder

Compound	PDF No.	First three peak spacings					
		d,Å	2θ°	d,Å	2θ°	d,Å	2θ°
$AlPO_4$	10-423	3.37	26.4	4.28	20.8	1.84	49.5
$Ca_3(PO_4)_2$	9-348	2.91	30.7	2.62	34.2	3.91	22.7
$K_4P_2O_7 \cdot 4H_2O$	25-1351	2.84	31.5	2.95	30.3	7.06	12.5
$K_3H_3(PO_4)_2$	19-0964	3.07	29.1	2.97	30.1	3.02	29.6
$Ca_4P_4O_{11}$	21-839	6.07	14.6	3.82	23.3	4.4	20.2
$FePO_4$	29-0715	3.45	25.8	4.36	20.4	2.36	38.1

be present, but there is certainly no overwhelming evidence that they are there.

As with limewater and NaOH, there appears to be a broadening of the amorphous halo which would tend to indicate a reaction between the H_3PO_4 and the glassy phase in the brick. Holland (55) indicates that all silicate glasses are attacked by hot phosphoric acids, but does not indicate if they are attacked by cold phosphoric acid. Kingery _et al._ (66) discuss phosphoric reactions with a variety of oxides, and for SiO_2 they show no reaction. It would appear from the diffraction chart, however, that the glassy phase in brick is being attacked by the H_3PO_4. If it is, then the etched surface might promote better bonding with mortar.

e. Hydrated cement and lime The diffraction charts for the hydrated paste constituents are shown in Figure 31. Figure 31a shows the pattern for $Ca(OH)_2$, hydrated for 7 days. The peaks are readily identified as belonging to $Ca(OH)_2$ indicated as "L" on the diagram, or as $CaCO_3$, indicated as "C" on the diagram. Figure 31b shows the pattern for portland cement, hydrated for 7 days. Most of the peaks were identifiable as belonging to yet unhydrated cement compounds or $Ca(OH)_2$, $CaCO_3$, or the hydrated cement compounds ettringite (E), C_4AH_{13}, or CSHII. Figure 31c shows the pattern for lime and portland cement.

Surprisingly, there is a considerable increase in the expected $Ca(OH)_2$ peak intensities. The lime-cement paste consists of a 50/50 mixture of both $Ca(OH)_2$ and cement by weight. Lime ($Ca(OH)_2$) is a product of the hydration of cement and is represented in Figure 31b by a 100% peak at $2\theta = 33.7°$, a 74% peak at $2\theta = 18°$, and lesser peaks at other angles. Lime is also present as the primary crystalline compound in lime hydrated in water for 7 days (Figure 31a). One would expect the resulting peak intensities not to be the sum of the two constituents since the quantity of each has been halved in mixing them together. Yet, all of the lime peaks in the mixture are considerably larger than either of the constituents.

Another noticeable change is the disappearance of the C_3S peaks found at $2\theta = 51.8°$, 38.8° and 34.3° in Figure 31b. This would tend to indicate that mixing the lime and cement together may have had an accelerating effect on the hydration of the C_3S. Indeed, one of the hydration products of C_3S is $Ca(OH)_2$, and according to Bache, Idorn, Nepper-Christensen and

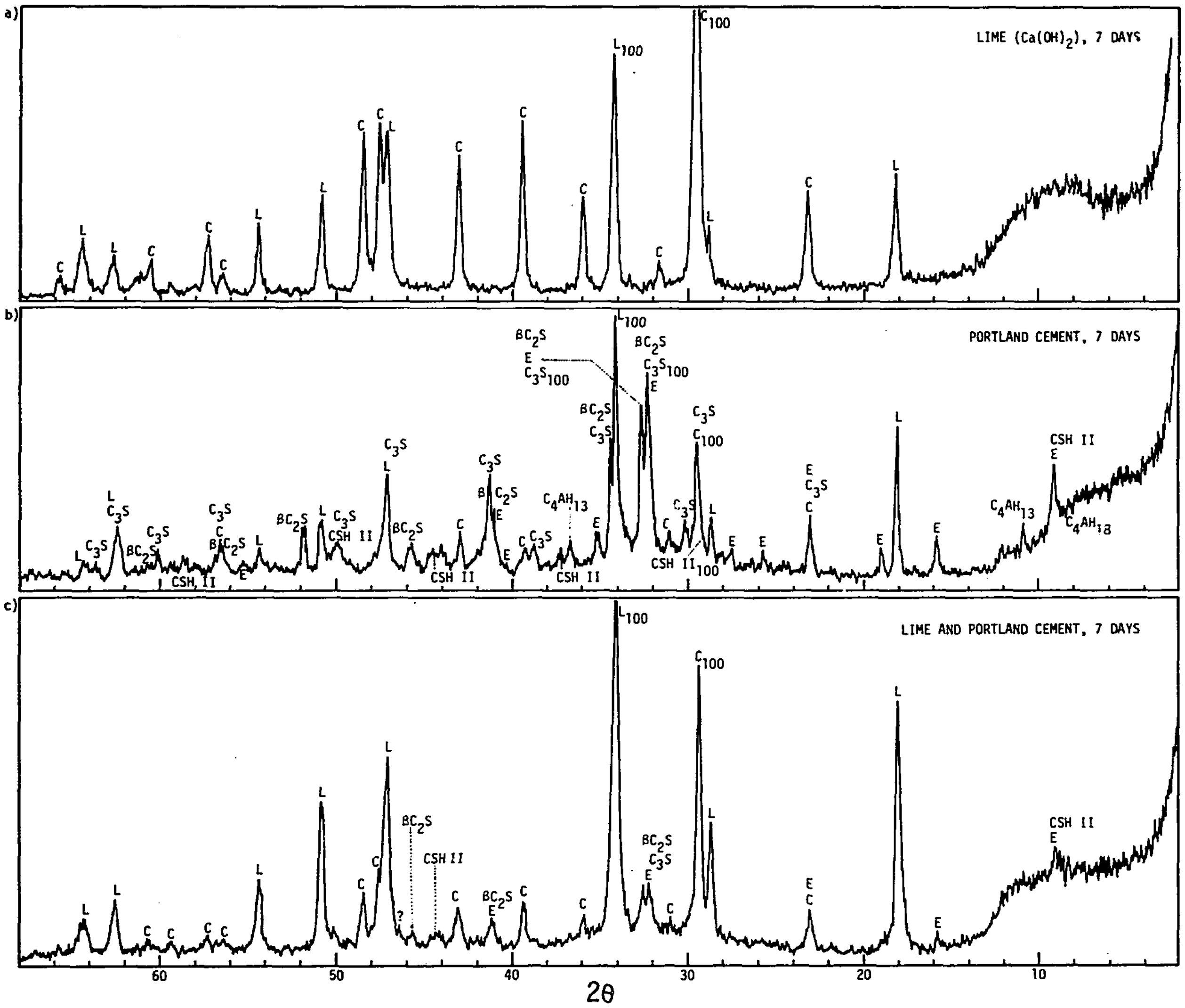
Figure 31. X-ray diffraction diagrams of paste constituents, hydrated 7 days

a - Lime paste

b - Portland cement paste

c - Lime and portland cement paste, 50/50 by weight

L = $Ca(OH)_2$, C = $CaCO_3$, C_3S = Tricalcium silicate, $3CaO \cdot SiO_2$, βC_2S = β Di-calcium silicate = 2 $CaO \cdot SiO_2$, E = Ettringite, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$, C_4AH_{13} = Tetracalcium aluminum hydrate, $4CaO \cdot Al_2O_3 \cdot 13H_2O$, CSHII = Calcium silicate hydrate II


a)
LIME (Ca(OH)2), 7 DAYS
C100
L100
b)
PORTLAND CEMENT, 7 DAYS
L100
βC2S
E
C3S100
CSH II
C4AH13
C4AH18
C100
c)
LIME AND PORTLAND CEMENT, 7 DAYS
L100
C100
CSH II
βC2S
C3S
E
C
L
60
50
40
30
20
10
2θ

Nielson (17), the concentration of the calcium hydroxide solution increases up to a certain critical value, at which crystal nuclei are formed. Crystalline calcium hydroxide begins to form after four hours reaction, then proceeds rapidly depending on the concentration of $Ca(OH)_2$ in the solution (17). The other hydration product of C_3S would be C-S-H, and should show a peak at $2\theta = 29.2°$. This peak, if present, cannot be detected because of the strong calcite, $CaCO_3$, (C) peak at that point.

It does appear that the most significant change caused by the addition of lime ($Ca(OH)_2$) to cement is an increase in the level of crystalline $Ca(OH)_2$ to a level greater than that which would be found in either constituent alone. To the extent that this crystalline $Ca(OH)_2$ could form calcite, $CaCO_3$, the effect on bond strength may be beneficial.

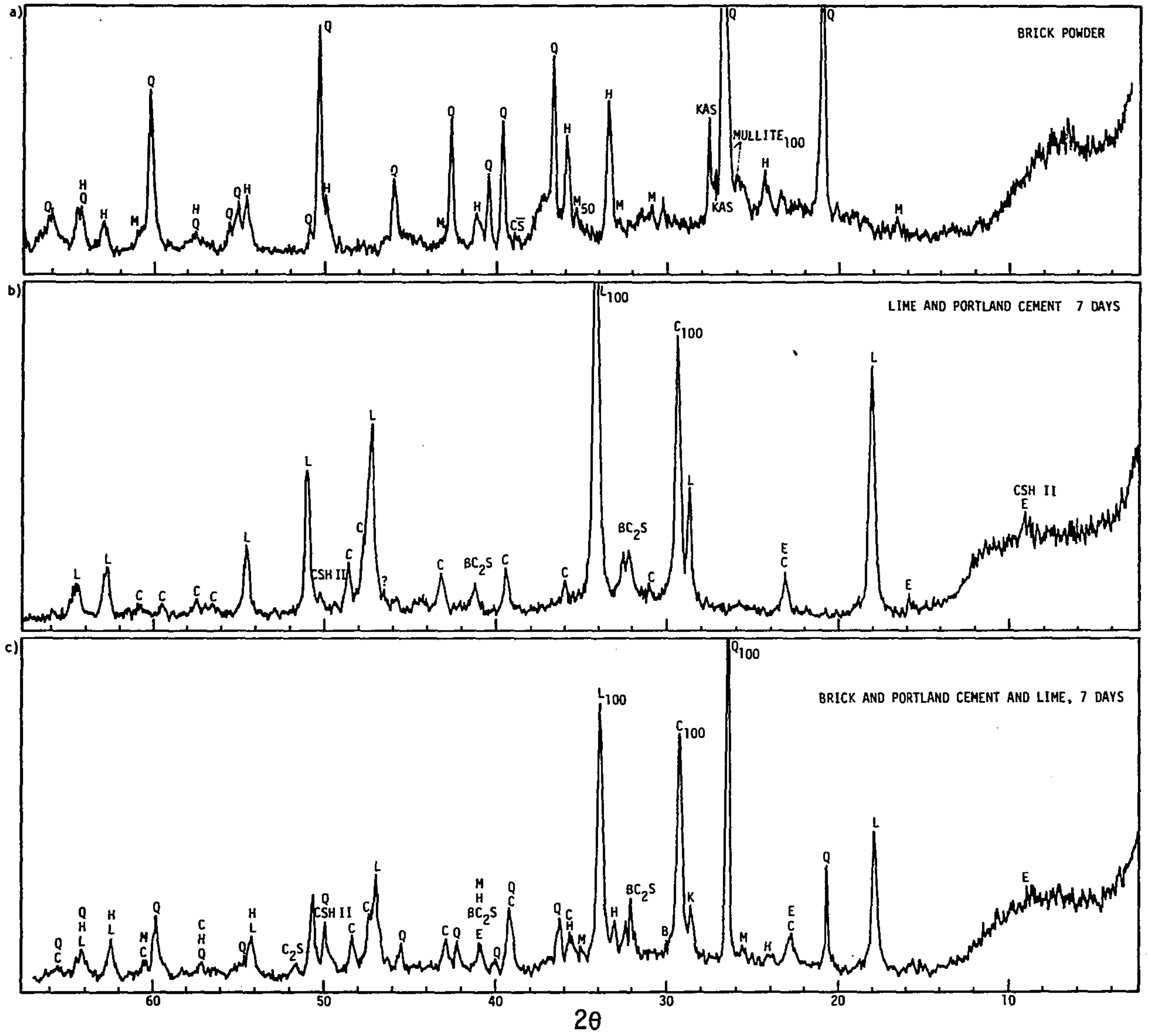
f. Brick, paste and a paste of brick plus cementitious ingredients The diffraction charts for the brick, hydrated paste, and a paste of brick and cementitious ingredients are shown in Figure 32. Figure 32a is the same untreated brick diagram shown in Figure 30a. Figure 32b is the same diagram of cement plus lime, hydrated for seven days, as shown at Figure 31c. Figure 32c shows the resulting diffraction chart when untreated brick powder is mixed with lime $(CaOH)_2$ and portland cement and water and allowed to hydrate for seven days. All of the resultant peaks are those of the constituents. There appear to be no new crystalline compounds forming. The $KAlSi_3O_8$ peaks at $2\theta = 27.5°$ and 27° have disappeared. This would indicate a reaction between the cement-lime constituents and the $KAlSi_3O_8$. However, no new peaks appear to be forming, and the reaction product remains unidentified. The relative proportion and size of the

Figure 32. X-ray diffraction charts for brick, paste, and a paste of brick and cementitious ingredients

a - Brick powder

b - Lime and portland cement paste, hydrated 7 days

c - Brick powder mixed with lime and portland cement, hydrated 7 days


a)
BRICK POWDER
Q
H
KAS
MULLITE100
M
M50
CS̄
b)
LIME AND PORTLAND CEMENT 7 DAYS
L100
C100
L
C
BC2S
CSH II
E
?
c)
BRICK AND PORTLAND CEMENT AND LIME, 7 DAYS
Q100
L100
C100
BC2S
C2S
CSH II
K
B
60
50
40
30
20
10
2θ

remaining peaks appear appropriate for the mixture. Accordingly, there does not appear to be any evidence that there is a crystalline reaction product obtained by mixing cement, lime, and brick powder with water and curing for 7 days.

There does, however, appear to be a broadening of the amorphous halo common to the brick. This may be the effect of the calcium hydroxide on the glassy phase of the brick.

g. Treated and untreated brick plus paste The diffraction charts for plain brick powder and treated brick powders mixed with lime, cement and water and allowed to hydrate for seven days are at Figure 33. No diffraction chart was made for brick treated with lime, because it was believed that it would not show any crystalline products not already present in the cement plus lime plus plain brick powder. The diffraction chart for the NaOH treated brick mixed with cement and lime is shown at Figure 33b. Several small peaks appear to be developing at 2θ = 23.5°, 41.4°, 44.1°, 51.8°, and 56.5°. An attempt to determine the products using the Fink search method proved fruitless. No attempt was made to use the SEARCH program because of the very small size of the peaks involved. Some additional means may be necessary to enchance the reaction so that the reaction products would be more evident in comparison to the other peaks. This might involve a more prolonged exposure of the brick to the NaOH or using a more concentrated solution of NaOH or raising the temperature.

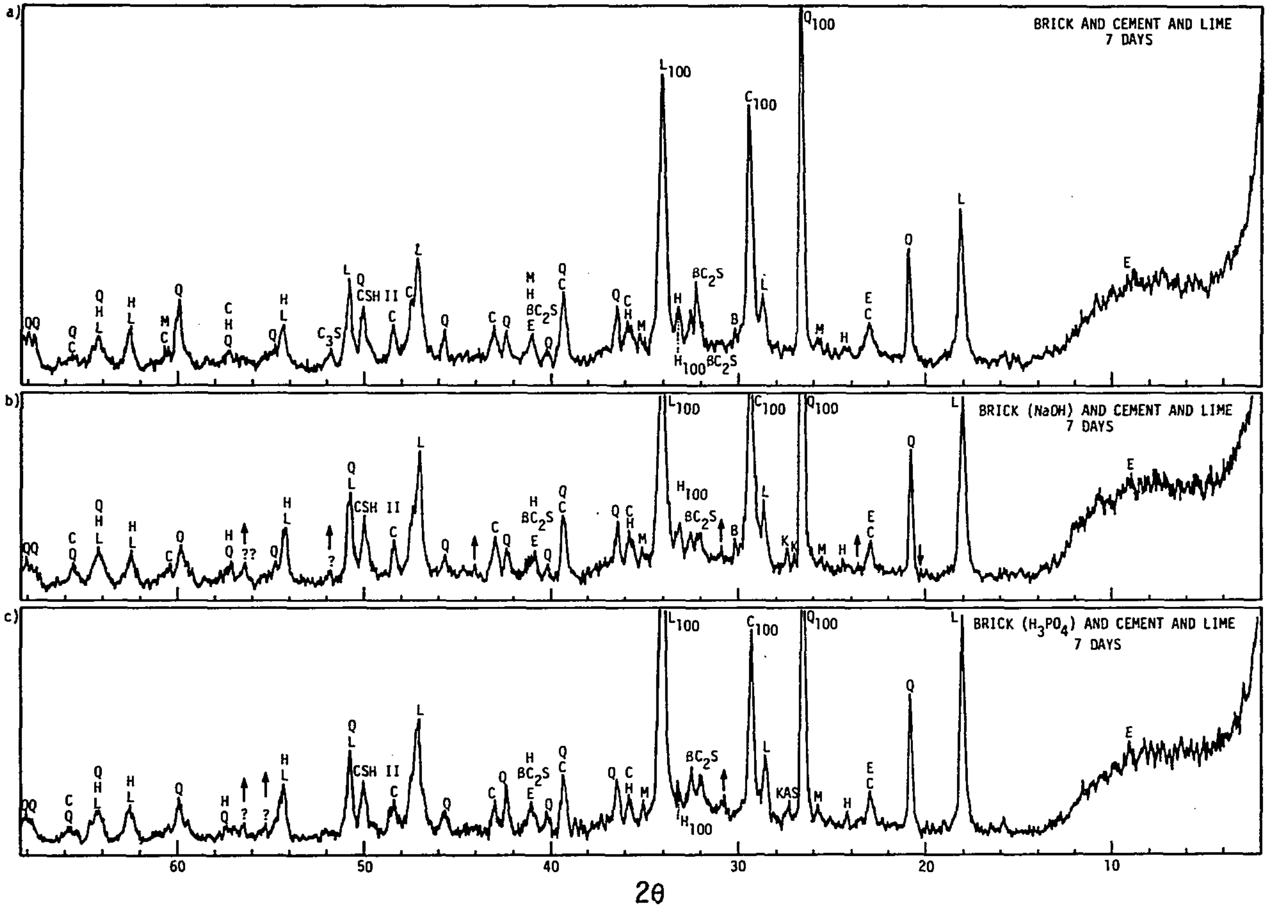
The diffraction chart for the H_3PO_4 treated brick mixed with cement and lime is shown at Figure 33c. Only two small new peaks appear to be

Figure 33. X-ray diffraction charts of pastes made from untreated and treated brick powder mixed with cementitious ingredients

a - Untreated brick plus lime and portland cement, hydrated 7 days

b - Same as a, using NaOH treated brick powder

c - Same as a, using H_3PO_4 treated brick powder


a)
BRICK AND CEMENT AND LIME
7 DAYS
b)
BRICK (NaOH) AND CEMENT AND LIME
7 DAYS
c)
BRICK (H_3PO_4) AND CEMENT AND LIME
7 DAYS
L_{100}
C_{100}
Q_{100}
H_{100}
BC_2S
C_3S
CSH II
KAS
60
50
40
30
20
10
2θ

developing. These are at $2\theta = 56.4°$, $55.2°$, and 30.7. As with the NaOH treated brick, there is no clue as to their identity, and the SEARCH program was not utilized. There does appear to be a slight decrease in the minor peak at $2\theta = 22°$, and in the peak at $2\theta = 32°$ marked as B in Figures 33a and b. The B indicates that the peak was present in brick, but was unidentified.

4. Summary of X-ray results

The X-ray results were both revealing, yet disappointing. It was anticipated that the diffraction diagrams would clearly indicate the formation of reaction products in the treated brick and it was hoped that the mixture of brick and cementitious ingredients would reveal a new crystalline interfacial compound. Neither of these happened. However, the information provided is useful. Specifically, there is an indication that lime mixed with cement may increase the rate of hydration of C_3S, and that crystalline $Ca(OH)_2$ forms to a greater extent in a mixture of lime and cement than would be anticipated. There is a very slight indication of some crystalline reaction product as a result of the three treatments, but more work is needed to determine if they really exist, and their identity. Finally, it appears that all three treatments may change some of the glassy phase in brick, and this may account for some of the increased bonding using treated brick.

VII. CONCLUSIONS

As a result of these investigations, the following conclusions can be made:

1. The primary mechanism of bonding between untreated brick and mortar appears to be the growth of C-S-H on the surface of the brick.

2. Tensile bond strength between brick and mortar is promoted by prewetting the brick surface even when the brick initial rate of absorption (IRA) is only 12 grams per minute. This may be because prewetting brick aids in the hydration of the paste near the brick, as evidenced by the SEM micrographs.

3. Type M mortar exhibits a higher 28 day tensile bond strength than type S mortar at flows between 115 and 135.

4. For type S mortar, the tensile bond strength is higher in the range of flow of 115-124 than it is for higher or lower ranges of flow for all treatments observed.

5. For the entire range of flows, the effect of the chemical pretreatments on the brick is significant when compared to dry or water only treatment.

6. The treatments where the bricks were soaked for one minute in either limewater or NaOH or H_3PO_4, then dried for 48 hrs, then re-wetted at the time of assembly, provide a better bond strength at 28 days at an initial flow of 125-135, using type S mortar, than do bricks assembled wet or dry with no pretreatments, at the same flow. The better adherence of mortar to NaOH, and H_3PO_4 treated brick than with limewater or water

treated or dry brick was evident from the increased effort necessary to remove pastes from the treated brick chips, and the resulting 4X photographs of the residual paste left on the brick surfaces. This is probably due to the formation of dense crystalline structure at the interface, and some etching of the brick, as evidenced by the SEM micrographs.

7. There is no indication that the limewater, NaOH, H_3PO_4 treatments are more beneficial than water, using type M mortar. More data are needed.

8. X-ray studies on samples prepared from brick powder and the cementitious constituents of mortar show that all major identifiable diffraction peaks are those already present either in brick or paste. However, minor unidentifiable peaks do appear, indicating a chemical reaction may take place in the interfacial region between mortar and brick. Characterization of this reaction requires some means of enhancement such as autoclaving or increasing chemical concentration.

9. X-ray studies on samples of brick powder treated with $Ca(OH)_2$, NaOH and H_3PO_4 do not indicate new major peaks corresponding to products of chemical reactions between the components of the sample. However, amorphous halo alterations and appearance of unidentifiable minor peaks support the observations made with SEM, indicating the occurrence of surface chemical reactions. Characterization of these reactions, again, requires enhancement by such means as increasing the concentration of treating chemicals, elevating the reaction temperature and allowing longer times for reactions to proceed to detectable levels.

10. Based on x-ray diffraction studies, it appears that there is a higher proportion of crystalline $Ca(OH)_2$ in a paste of $Ca(OH)_2$ and portland cement than would be expected by summing the amount of $Ca(OH)_2$ in each of the constituents. Excess $Ca(OH)_2$ may accelerate the crystallization process.

11. Lime and cement paste results in a finer particle structure and more complete filling of the brick pores at the interface than cement only paste. This is shown by SEM micrographs. However, the effect of this on bond is not known. The long term effect, if these smaller lime particles carbonate, may be beneficial.

In summary, these investigations have provided a closer look at the brick-mortar interface, and the nature of the products formed, and the effect of certain pretreatments on bond strength. There does appear to be a potential for improving bond strength by using selected pretreatments such as NaOH, H_3PO_4 and limewater.

VIII. RECOMMENDATIONS

These investigations have just scratched the surface of an area that could profit from a sizeable amount of additional research. There does appear to be a potential here to improve bond strength between mortar and brick. This could affect both masonry strength and resistance to moisture. There are many unanswered questions. For example, what is the long range effect of using masonry in which the brick have been pretreated with one of the chemical treatments used here? What is the resistance of such masonry to prolonged cold, heat and moisture? What would be the economics and practicality of commercially pretreating brick if the treatments are shown to have a long range benefit to masonry strength and moisture resistance? What methods might enhance the reactions which have been seen in these investigations?

As a start, some short range investigations are in order. It is recommended that more detailed studies be made to identify and determine the properties of the interfacial products formed between mortar and NaOH, H_3PO_4 and limewater treated brick. The scope could initially be limited to X-ray diffraction, SEM, and differential thermal analysis (DTA) studies of a paste of cement and brick powder only. Increasing quantities of lime could be added to the paste, and any change in interfacial products could be determined. Moisture content of the cement and cement plus lime pastes should be measured and controlled. Various means to enhance the reaction could be tried, to include heat, increased concentration of the chemicals, or prolonged exposure. If proven beneficial, these treatments could be applied to bricks at some point in the manufacturing process; perhaps during cooling.

SEM examination could consist of sample pastes spread on a carbon stub and hydrated under the same conditions as the X-ray samples. Samples could be examined in a CO_2 free atmosphere and one with CO_2 to determine the effect of carbonation.

Differential thermal analysis, DTA, is a powerful tool in helping to identify compounds. DTA tests on the powders should also be performed, if practicable.

Some type of tensile bond test using the most promising treatments would be beneficial as a follow-on. If smaller bond test specimens were used, the samples, after separation, could be used for X-ray and SEM examination. These small bond specimens could be used to determine the durability of specimens when subjected to freeze-thaw, as well as the effect of a variety of curing times and curing conditions.

At some point in time, permeability tests should be made to determine the resistance of the best combinations of mortar and treated brick to water. Eventually, full scale, prototype walls should be constructed and tested for flexure, shear, durability, and permeability, and these results compared to the results of such tests using untreated brick.

A continuaton of the couplet tests is also warranted. More couplet tests to fill in the blank areas of Tables 29 and 30 are needed. Beyond that, couplet tests at 60 days and 180 days are required to investigate the longer range effects of all treatments.

In summary, much work remains to be done in this area, not only to increase the understanding of the basic phenomena involved, but also to confirm the potential practicability of applying pretreatments to brick.

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XI. APPENDIX

There were 113 observations made of bond strength. For these 113 observations, the flow varied from a low of 100.8 to a high of 133. There were eight treatments considered, including the control, which was brick assembled dry. The treatments and their means, determined across all flows is shown below along with their Duncan's multiple range test grouping:

Treatment	N Observations	Mean Bond Strength (psi)	Duncan Groupings			
NaOH (Dried)	8	76.6	A			
H_3PO_4 (Dried)	8	74.8	A	B		
Limewater (Dried)	8	72.4	A	B	C	
NaOH (Wet)	13	67.0	A	B	C	
Limewater (Wet)	9	60.3	A	B	C	D
H_3PO_4 (Wet)	13	59.1		B	C	D
Water	36	55.5			C	D
Dry	18	48.4				D

Means with the same letter are not significantly different, using an alpha = 0.05. The indications here are that the chemical pretreatments are more effective than plain water or no treatment, and that the chemical treatments which were dried after treatment appear to be most effective.

In developing a model for evaluation of the strength of the relationship between bond strength, flow and the various treatments, it was decided to treat flow as a quantitative independent variable and the treatments as qualitative variables. The first linear regression model developed included an interaction term between flow and treatments, *i.e.*,

$$y_{ij} = (\mu + \tau_i) + (\beta_0 + \beta_i)F_{ij} + \varepsilon_{ij},$$

where $\mu + \tau_i$ is the *y* intercept for treatment i, $\beta_0 + \beta_i$ is the slope of the regression line caused by flow on treatment i, and ε_{ij} is the unexplained error term. The general linear models procedure of the Statistical Analysis System (SAS) was used to evaluate the model. The null hypothesis used was H_0: $y_{ij} = (\mu + \tau_i) + \beta_0 F_{ij} + \varepsilon_{ij}$, *i.e.*, $\beta_i = 0$, which implies that there is no interaction between flow and treatment. The alternative hypothesis was that the model was correct, *i.e.*, at least one $\beta_i \neq 0$, which implies that there was an interaction between flow and treatment. The probability of obtaining an F greater than the F calculated (p value) for this data, given that H_0 is true, was 0.2776, indicating that there is insufficient evidence to reject H_0. Hence, the interaction term was dropped from the model. Next, an evaluation of a possible quadratic relationship between flow squared and bond strength was examined, using the model $y_{ij} = (\mu + \tau_{ij}) + \beta_0 F_{ij} + \beta_1 F_{ij}^2 + \varepsilon_{ij}$, where F_{ij} is the independent variable flow. Using a null hypothesis that $\beta_1 = 0$, *i.e.*, that no quadratic relationship exists between bond strength and flow, the p value is 0.0591. Thus, bond strength is marginally dependent on a quadratic term for flow and the null hypothesis could be rejected. However, a quadratic term was not used in the final model for two reasons. First, the data does not show a strong quadratic relationship. Second, the quadratic model did not show sufficient improvement over the linear model to warrant using it instead of the linear model.

The final model selected was:

$$y_{ij} = (\mu + \tau_i) + \beta F_{ij} + \varepsilon_{ij}$$

where $(\mu + \tau_i)$ is the intercept due to treatment and β is the slope of the regression line showing the effect of flow on bond strength. An F test on the model shows that the p value is 0.0001. This indicates that the effect of the treatments and flow taken together is highly significant. For the seven treatments the p value is 0.0012 and for flow, the p value is 0.004, indicating that the treatments as a group and the flow are each significant.

A set of orthogonal contrasts was established also to examine the effect of the various treatments. The contrasts, and their respective F values and p values, are as follows:

Contrast	F Value	PR > F (p value)
Control (Dry) vs. others	13.05	0.0005
Water vs. all others (less control)	11.02	0.0012
Wet vs. Dry for NaOH, H_3PO_4 and Limewater	7.15	0.0087
Lime vs. H_3PO_4 and NaOH	0.15	0.6961
H_3PO_4 vs. NaOH	0.71	0.4008

Based on the above, one can conclude that all treatments as a group have more effect on bond strength than no treatment, that there is a significant difference between water-only treatment and the chemical treatments, that there is a significant difference between the wet vs dried after treatment procedures for the chemical treatments, that the limewater treatment is not significantly different than the other two chemical treatments, and that there is no significant difference between the NaOH and the H_3PO_4 treatments.