PHOSPHATE BONDING IN REFRACTORIES

by

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FOREWARD

The prosecution of this research was undertaken since almost no fundamental data has been available in connection with mechanism or properties of phosphate bonds for refractories. This state of affairs has existed even though a considerable number of bonding compositions containing phosphate materials have been described in the patent literature. Readers interested in this literature are referred to section III.

The research reported here falls into three main divisions. The mechanism by which phosphate materials form air setting bonds, and a theory of the development of optimum strength in these bonds is considered in sections II and IV. Properties of phosphate bonding materials which are of basic importance to this class of materials are considered in sections V and VI. Finally, the testing and properties of certain air-setting mortars containing phosphate bonds are reported in section VII. Readers interested in immediate applications are referred to this section, although a better appreciation of these materials may be gained by the study of the more fundamental portions of this work.

The author desires to express his appreciation for the guidance and advice of Professor F. H. Norton, who supervised this work. In addition, the author is grateful for the financial assistance of the American Refractories Institute Fellowship, which supported a considerable portion of this work. A large number of the phosphate materials employed were kindly supplied by the Monsanto Chemical Company.

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I. INTRODUCTION

A. Refractory Bonding Materials.

In various refractory applications, bonding materials are of great importance. These may be divided into the major applications of refractory mortars, castables, plastics and unfired brick. Mortars are used for bonding refractory brick work and may be either heat-setting or air setting. The air setting type contain some bonding material. Castable materials are used for forming monolithic sections or units. Plastics are used for ramming refractory shops or monolithic structures. Unfired brick are formed by combining an air-setting bond material with a volume constant aggregate. Various types of these materials, and their uses are well described by Norton[1] and will not be described in detail here.

The types of bonding materials employed are of interest however. Air setting mortars are generally formed with a bond of sodium silicate. Either "wet" or "dry" mortars are available. In commercial mortars tested by Heindl and Pendergast[2,3] it was found that the majority of wet mortars are satisfactory but that none of the commercial mortars of the dry type was completely satisfactory. The advantages in shipping weight, convenience, and the avoidance of settling, hardening in storage, etc., would make the development of a satisfactory dry-type mortar desirable.

Air-setting plastics are also generally formed with sodium-silicate as a bond material, while castables are usually composed of a hydraulic high-alumina cement, or for more refractory applications pure tricalcium penta-aluminate.

Chemically bonded unfired brick may be made with a number of bond materials. About half the magnesite brick now being made are chemically bonded.[4] Bonds used for this purpose include magnesium-oxychloride, organic material such as resins or bakelite, sulfite waste liquors, sodium silicate, phosphoric acid and others.

B. Phosphate Bonding Materials.

It is somewhat difficult to ascertain the extent of present use of phosphate bonding materials since most bonded compositions are considered trade secrets. Although a considerable patent literature is available with regard to these materials (see section IV), it is probable that few of these are being employed at present.

No mortars are known to be commercially available utilizing phosphate bonds, and no castables are known to be used with phosphate bonds, although small amounts of these materials may contain phosphate bonds for special very high temperature applications. The Monsanto Chemical Co. is attempting at the present time to evaluate certain aluminum phosphate mortar bond compositions.

Plastics bonded with phosphate materials are commercially available (Quigly Co., Philadelphia) and are reported to give good service for burner ports, fire-doors, etc.[6] Chemically bonded refractories have employed phosphate bonds for alumina and zircon brick, and perhaps others.

In addition to these refractory applications, phosphate bonds have long been used for dental cements and other applications.

Phosphate materials are of particular interest for refractories since a number of phosphate materials are stable at elevated temperatures. For this reason, bonds can be formed which remain at high temperatures as an integral part of the structure without becoming fluid or friable. With the increasing importance of the attainment of very high temperatures, the use of such materials becomes more and more necessary. This need makes desirable a fundamental understanding of the mechanism and basic properties of these materials.

C. Research Program.

The research reported here covers three major divisions in addition to the general discussion of bonding theory and a review of the literature.

A considerable portion of this research is relative to the reactions and mechanism of air-setting phosphate bonds. In addition to determining the probable setting mechanism, a theory is developed of the formation of high strength bonds.

A second portion of the experimental research is concerned with the basic properties of a phosphate bond. In addition to the setting of a liquid bond, this work includes the effect of temperature on bond structure and strength, the adsorption of phosphates by clay and bond migration.

Finally, tests have been made of several mortar compositions prepared with phosphate bonds. These tests demonstrate that satisfactory mortars of both the wet-type and the dry-type can be prepared with phosphate bonds.

II. PRINCIPLES OF ADHESION

A. Mechanical Adhesion.

The earliest theories of adhesion explained that bonding was caused by solidification of the bonding material around fibere and in pores of the materials being bonded.[7] Twenty years ago, an authority was able to say, "It may be safely concluded that adhesion is a mechanical solidification of gel around and upon minute fibers".[8] Later work[9,10] modified this to the view that mechanical adhesion is operative with porous surfaces, while "specific" adhesion, due to chemical forces, is operative with smooth dense surfaces. This view is often held at present.[11]

These views are derived from the fact that gelatin glue, gum arabic, shellac, etc., are adhesive to wood but that adhesion to silver can only be obtained by welding silver gauze to the metal. In addition, ebony stain renders hard wood joints very weak but has little effect on soft wood joints. This was thought due to the stain filling the pores of hard wood but not the soft. In addition, no orientation of the molecules was found by x-ray patterns of thin glue layers.

Reinterpretation of these data and other data have led to the view that in ordinary cases at least some chemical forces of attraction are necessary for adhesion. Lipowitz alloy having a melting point of 60° does not wet wood and shows no adherence to it. The effect of stains may be due to the adsorption of soft wood, which leaves the cellulose surface unaffected. When paraffin wax or collodion is used and the material sanded, good joints are obtained with greatly reduced penetration. The determination that attractive forces in lubricants act through monomolecular layers,[14] which is in agreement with calculations of the force fields of ionic materials,[15] makes the difficulty in determining the presence of orientation understandable.

From these results, the fact that even in pores, adhesion requires contraction on drying to leave the glue cylindrically attached to the cell walls,[16] the determination of specifcity with smooth surfaces,[17] and the findings of numerous investigators for other specific cases it seems well established that adhesion, even between porous surfaces, is not primarily a mechanical phenomenom.[18] This is not to say that porosity is of no importance. It does affect the area of contact and provide additional strength.

B. Specific Adhesion.

In contrast to mechanical adhesion, "specific" adhesion refers to adhesion primarily due to forces of chemical attraction. These forces consist of the well known electrostatic, covalent, metallic and van der Waals' or residual bonding forces. In perfect crystals these forces are exactly satisfied except on the surfaces. However, in amorphous materials, some of these attractive forces may not be directly satisfied because of randomness of distribution of the atoms. At surfaces these forces are not directly satisfied because of the unsymetrical arrangement of atoms about the surface. These forces are available for bonding both in adhesives and in bonding of separate crystals into a coherent mass. Adhesion and cohesion are not fundamentally different.

Most organic adhesions are carbohydrates, protiens or resins. All these are polymeric high molecular weight compounds having active polar groups which are capable of extended hydrogen bonding. (Probably many of the effects often loosly characterized as being due to polarity catalysis, etc., are the effects of hydrogen bonds.[19]) These structures first provide the internal strength required for a good adhesive, and secondly are capable of chemical attraction to similar materials. Good bonds are formed with paper or wood, but only weak bonds can be formed with paraffin or metal surfaces. However, a good bond can be formed with metal by polymerizing a small amount of maleic acid with the resin. This gives free carboxyl groups which are responsible for the adhesion.[20] Similarly, rubber can be easily vulcanized to brass due to the ease of sulfide formation of copper and zinc, but only difficultly to iron.

These few examples indicate the importance of the chemical nature of adhesion phenomena. Many other examples are available in the literature which fully confirm the view prevalent today that adhesion is primarily due to forces of chemical attraction at the interface. The types of these forces are well known and can be calculated for the simplest cases.[22]

III. LITERATURE REVIEW

A. Dental Cements.

The oldest and perhaps widest use of phosphate bonding has been in the preparation of dental cements. Two major types have been used. Zinc oxide and phosphoric acid for forming a cement for fillings, caps, inserts, etc., and a silica frit-phosphoric acid mixture for "porcelain" fillings.

The first type of cement is prepared by mixing a calcined zinc oxide powder with phosphoric acid that has been partially neutralized with zinc and/or aluminum hydroxide. The reaction proceeds to form a hard, dense product which, by analogy with Sorel cement, was originally and erroniously believed to consist of zinc oxyphosphate.[23] Although the complete reaction products are not definitely known,[24] they are crystalline and probably consist mainly of dibasic zinc phosphate, $ZnHPO_4 \cdot 3H_2O$.[25] Di-zinc phosphate has been found to be the equilibrium phase in cement compositions.[26] Suggestions that hydroxyapatite is formed is based on reactions in neutral solutions which is expected to lead to different products. Suggestions that the normal phosphate is formed[28] are based on the presence of only one x-ray diffraction line.

A large number of modifications of the basic zinc oxide phosphoric acid mixture have been suggested. These include the addition of beryllium,[29] magnesium,[30] acetate,[31] tin,[32] bismuth, copper, manganese,[33] etc., compounds to alter the setting characteristics or the cement properties. In addition materials such as silver[34] and mercury[35] compounds are added for their antiseptic value.

The so-called "porcelain" dental cements consist of powdered alumina-lime-silica glass mixed with phosphoric acid to form a hard white translucent product.[35] The mixture sets by solution of about 30% of the powder with the formation of a silica gel. X-ray diffraction patterns show no evidence of a crystalline structure.[36] Various auxilliary materials may be added to alter the properties of this cement, but the basic setting mechanism remains the formation of a silica gel structure somewhat like that formed on the solidification of soluble silicate bonds.

B. Silicate Cements.

Although the low melting silicate frit employed in dental cements is unsuitable for refractory applications, various processes have been suggested for the refractory use of siliceous materials with phosphoric acid. These also depend on the solution of silica by phosphoric acid and the formation of a silica gel structure. If heat-setting processes are used, the formation of silicyl metaphosphate, $SiO(PO_3)_2$, is to be expected at temperatures greater than 260°C.[37]

Phosphoric acid has been added to a refractory patching cement composed of ground silica brick, silica flour and ball clay.[38] The addition of 1/2 gal. per 100 lb. dry weight serves as a bonding medium.

Various patents have been issued for zircon refractories bonded with phosphoric acid. One such process consists of a zircon refractory composition bonded with an alkali, alkaline earth or magnesium zirconium silicate and its reaction product with hydrochloric, nitric, sulfuric or phosphoric acid.[39] Phosphoric acid gives the best results, presumably because of its greater attack on the silicate components. Another patent calls for zircon together with a zirconate, zirconium spinel or oxide, and an acid, preferably phosphoric.[40] The phosphoric acid attack on the silicate portion is probably of considerable importance to the bonding action.

It has been claimed that the high shrinkage of zirconia can be somewhat counteracted by use of silica in conjunction with it.[41] Although ordinary sodium silicate can be used, it was found that a better bond was obtained by fixing the precipitated silicate with phosphoric acid. The preferred method consists of adding the silica as zircon, treating with phosphoric acid, shaping and firing at 1800°F. A silicon phosphate compound is formed as one of the bonding materials and was found not to volatilize or soften at temperatures up to 3000°F.

A refractory having high electrical resistance, high thermal conductivity and a small coefficient of expansion can be prepared from silicon or ferrosilicon, zircon and phosphoric acid.[42] These materials can be mixed together and formed, or a zirconia, zircon and phosphoric acid mixture having a creamy consistency may be digested for several hours at 200 - 350°F to allow bonding reactions to proceed prior to forming with a ferro-silicon aggregate and firing.[43]

Other silicates such as those of aluminum, chromium and magnesium also react with phosphoric acid to form a bond at about 200°C.[44] Mica[45] and asbestos,[46] have also been found to form a bonded material on mixing with phosphoric acid and given suitable heat treatment.

The addition of chromic acid is reported to increase the activity of phosphoric acid, as might be expected from its powerful chemical action. A mixture of clays with phosphoric and chromic acid forms a bond product on heating at 250 - 600°F, but 1200°F is required if water resistance is desired. The product can be greatly improved by adding 3 - 15% zircon. The addition of chromic acid also improves the product formed entirely from zircon and phosphoric acid or from ferro-silicon and aluminum silicates with phosphoric acid.[47]

C. Oxide-Phosphoric Acid Bonds.

Phosphoric acid forms bonds through reaction with the cation as well as with the silicate group. Thus, the silicates previously considered usually have two bonding reactions. Zircon, for example, appears to form zirconium phosphates as well as silicon phosphates, and may form double phosphates of silicon and zirconium as well.[48]

Aluminum, chromium, magnesium and zirconium oxides react chemically with phosphoric acid at 200°C to form a bonded material.[49] The metal phosphate reaction products are refractory and stable. Rather than using the oxides, the halides of magnesium, tin, thorium, calcium, barium, aluminum, zirconium or titanium may be used with phosphoric acid to form a bonded refractory.[50] After mixing the constituents to a pasty consistency, the plastic mass is formed and heated to approximately 1000°C to effect the bonding reactions and form the final product. Using aluminous refractory materials, phosphoric acid reacts to form a film of aluminum phosphate around each particle,[51] which acts as a bond. The bonded material hardens with drying at elevated temperature, while it will remain plastic for a considerable length of time if kept at low temperatures. A cementing material may also be prepared from beryllium compounds with phosphoric acid.[52]

Aluminum hydrate may be used with refractory clay, filler and phosphoric acid to form a bond which becomes permanent when heated to 100 - 300°C.[53] The addition of aluminum hydrate to refractory compositions of zircon, silicon, etc., and phosphoric acid is also advantageous. Use of this material allows final heat hardening at temperatures of about 600°F rather than the 1200°F which must otherwise be applied.[54]

D. Acid Phosphate Bonds.

Refractory bonds may be formed by the direct addition or formation <u>in situ</u> of mono- or di basic phosphates. With aluminous materials, alkaline earth acid phosphates or ammonium acid phosphates may be used in place of phosphoric acid.[55] On heating to 200 - 300°C bonding action is obtained to give good strength by reaction of the phosphate with the aluminous material. The alkaline earth phosphates are reported to have too low a melting point, and while ammonium acid phosphates are satisfactory, their considerable solubility tends to cause the formation of a crystalline surface layer due to migration. It has been found preferable to use various organic derivatives such as hydrazine, hydroxylamine, aniline, methylamine or ethylamine acid phosphates.[56] A quick setting refractory composition for precision castings was prepared from an aggregate bonded with sodium, calcium, magnesium, zinc ammonia or organic acid phosphates which react on the addition of water with alkali or alkaline earth zirconium silicates, various zirconates or dead burned magnesia.[57] Fluo-silicates may be added to increase the setting time to the desired range.

Acid Phosphates may also be formed by the addition of triphosphate and an acid which readily reacts with it forming mono- or bi-phosphates. This process may be used with alkaline earth phosphates, preferably calcium which is less expensive than other materials.[58] Less than one per cent of such material gives temporary cohesion in the dry state, contributes to the gradual solidification during firing, can be used with acid or basic aggregates and acts as a mineralizing agent in some cases.[58,59] Similiarly, zirconia can be bonded with a solution of magnesium phosphate in phosphoric acid containing an ammonium compound.[60]

Solutions of mono- or di-aluminum phosphate prepared from aluminous material and phosphoric acid[61] form cold setting plastics and mortars with suitable aggregates.[62] Three to ten per cent of aluminum phosphate materials gives cold set strengths (Modulus of Rupture) from 400 to 2200 psi. These materials may be utilized as ordinary liquid bonds or by drying a thin layer of aluminum acid phosphate coating each particle of the aggregate used.[63] On forming, this film acts as a bonding agent.

E. Other Phosphate Bonds.

Additional types of phosphate bonds have been employed for refractory purposes. An inorganic colloid, $Na_4P_2O_7$ - $Na_6P_4O_{13}$, which can be used to disperse titanium dioxide for casting, improves green strength.[64] Also, the strength of alkali silicate binders is reported improved by the addition of about 10% alkali phosphate.[65]

A study of the use of metaphosphates in refractory mortars by Herold and Bust[66] indicated that rubber-like metaphosphate polymers form a clay-gel cement with clay. However, a large amount of the phosphate was required to form an adequately plastic mass. A systematic study of the effects of metaphosphates added to a standard fireclay mortar indicated that they increased strengths considerably and did not lower the fusion point or change shrinkage and porosity appreciably. These materials also increased mullite formation on firing.

Greaves-Walker and Amero[67] studied a zinc phosphate binder of the composition 12.3% ZnO, 68.5% H_3PO_4, 18.3% H_2O for use with an unfired pyrophyllite refractory. In amounts up to 1.50% this bond stood up well under thermal gradient and hot load tests, showed the best workability of any bond material tested, increased the compressive strength in approximately the same manner as sodium silicate, and showed unusually high impact resistance in the green state. However, a fluxing action was evidenced which lowered the PCE from 30 to 28 with an addition of 1.25% bond. This bond is thus unsuitable for high heat duty refractories, but posses excellent properties for low and intermediate heat duty applications.

IV. AIR-SETTING MECHANISM

A. Oxide-Phosphoric Acid Reactions.

In order to investigate reactions between phosphoric acid and oxides, a systematic study was made of a large number of oxide-phosphoric acid mixtures. An intimate mixture of the oxide and phosphoric acid (68.7%) was formed by spatulation. After mixing, a portion of the material was immediately transferred to a hard rubber calorimeter containing a 0.5 cc chamber. Temperatures were measured with a copper-constantan thermocouple. This was found to be a rapid and simple method of making semi-quantitative determinations of the heat effects of any reactions taking place. A second portion of the material was transferred to equipment for measuring setting time until no indentation was noted under a weighted needle (470 grams on 4.0 sq.mm.). When setting reactions occured, a third portion of material was formed in bar molds into 1/4" square specimens. The transverse strength (modulus of rupture) of these specimens was determined.

In all, the oxides and/or hydrates of thirty-four cations were tested. Detailed results of these experiments are recorded in Appendix A. These data show that at room temperature oxide-phosphoric acid reactions fall into three distinct classes. Oxides of an acidic or chemically inert nature do not react with phosphoric acid (SiO_2, H_2SiO_3, TiO_2, ZrO_2, CeO_2, WO_3xH_2O, CrO_3xH_2O, MoO_3, $Cr_2O_3xH_2O$, Co_2O_3, Al_2O_3(fused), PbO_2, NiO, SnO_2). Oxides of a highly basic nature react so violently with phosphoric acid that a porous friable structure results (MgO, ZnO, CaO, La_2O_3, BaO, SrO). It was attempted to reduce these reaction rates by, (a) calcining the oxide and (b) using partially neutralized acid. Calcined magnesia reacted to form a bonded product. Calcined calcia reached to form a bonded product with partially neutralized acid.

Strontia and baria still reacted violently even when calcined and used with partially neutralized acid. Calcined lanthana reacted to form a bonded product.

A large number of weakly basic and amphoteric oxides did react with phosphoric acid to form a bonded cement-like product. Included in this group are BeO, CuO, Cu_2O, CdO,Fe_2O_3, Fe_3O_4, SnO, Pb_3O_4, $Al(OH)_3$, $Ti(OH)_4$, $Zn(OH)_4$, ThO_2 and V_2O_5 in addition to calcined ZnO, MgO, La_2O_3 and CaO. These results show that the property of forming cements with phosphoric acid is not restricted to a few materials as is often supposed. A considerable number of materials react to form bonded products.

In addition to these results, it was found that mercuric and mercurous oxides and litharge reacted with phosphoric acid without disruption of the structure due to a violent reaction. However, these materials did not form bonded or cement-like products.

In order to investigate the reaction products formed by the reacting mixtures, a careful study was made of the chemical literature. It was found that in all cases where setting occurred the reaction products were mono- and di-basic phosphates. Compounds reported formed are shown in Appendix A.

X-ray diffraction patterns were also obtained for some of the reaction products. However, identification by x-ray diffraction is difficult since data is available in the literature for only a few phosphates. In addition, the complex nature and varying degrees of hydration makes analysis difficult. For example, there are more than thirty varieties of calcium phosphates reported in the literature. Of these only a few have known diffraction patterns. The x-ray data is included in Appendix A. Insofar as data is available, these results confirmed the products reported in the chemical literature.

The beryllia and alumina cements showed a reaction product amorphous to x-rays. For the alumina cement, a determination of the product as mono-aluminum phosphate was made by comparison of the rate of weight loss of the cement and a sample of this material (Appendix B). The rate of weight loss was determined on laboratory equipment previously described.[68]

B. Setting Mechanism.

The experimental data for oxide-phosphoric acid reactions (Appendix A) showed that the acid reacts with many oxides of weakly basic or amphoteric nature, but that not all of these form bonded products. However, similar products are formed in all the cases where bonding results. All these products are mono- and di-basic phosphates. In contrast, these materials which react with phosphoric acid to form a non-cohesive product do not form acid phosphates. This leads to the conclusion that acid phosphates act as the bonding media in cold-setting phosphate cements. The considerable number of oxides reacting to form bonded phosphates indicates that this is a general property of the hydrogen phosphates rather than of any one particular compound.

Two experiments tended to confirm these conclusions. If phosphoric acid is added to normal phosphates, the opportunity exists for reaction to form mono- and di-basic phosphates. Normal phosphates of magnesium, zinc, calcium, aluminum and lead were investigated (Appendix C). All of these materials reacted with phosphoric acid to form bonded products. In addition, it is known that litharge reacts with phosphoric acid to form the normal phosphate, but if excess phosphoric acid is present, this salt reacts further to form acid phosphates.[69] It was found, experimentally, that only with an excess of phosphoric acid were cement-like products formed. Further evidence of this view is inferred from the fact that phosphoric acid itself acts as a bonding material. (See Fig. 1).

The mechanism of cold-setting by the formation of mono- and diphosphate is in complete agreement with the general theories of adhesion considered in Section II. Many of the adhesive effects described there are due to hydrogen bonding and many of the effects often loosely described as being due to "polarity" are believed to be actually the effect of hydrogen bonds.[70] The acid phosphates are capable of and known to possess considerable hydrogen bonding. The strongest O-H-O hydrogen bonds measured up to this time occur in an acid phosphate, KH_2PO_4.[71]

The extended hydrogen bonding of which the acid phosphates are capable provides a surface on each crystallite capable of extended chemical bonding with other crystals in its vicinity as well as a strong internal structure. In addition, the hydrogen phosphates have a flexible structure as indicated by the large number of polymeric modifications possible and reported and the strong tendency of these compounds to form with many varying degrees of hydration.[72] This tends to increase the number of residual fields of force at crystal surfaces, and increase mutual attraction. The tendency toward amorphic or non-ordered, arrangement of atoms increases the effects of residual forces and contributes to bonding the structure. Phosphoric acid is known to form completely amorphous hydrogen-bond glasses.[73]

The bond-forming reactions of oxides with phosphoric acid are quite general, but require certain definite properties from the cation involved. Oxides of an acidic nature and chemically inert oxides of a very stable nature show no reaction with phosphoric acid at room temperature. In addition to this general requirement of reactivity or solubility, the reaction must proceed at a rate compatible with organization of the reaction products to form a cohesive mass. Zinc oxide, lanthanum

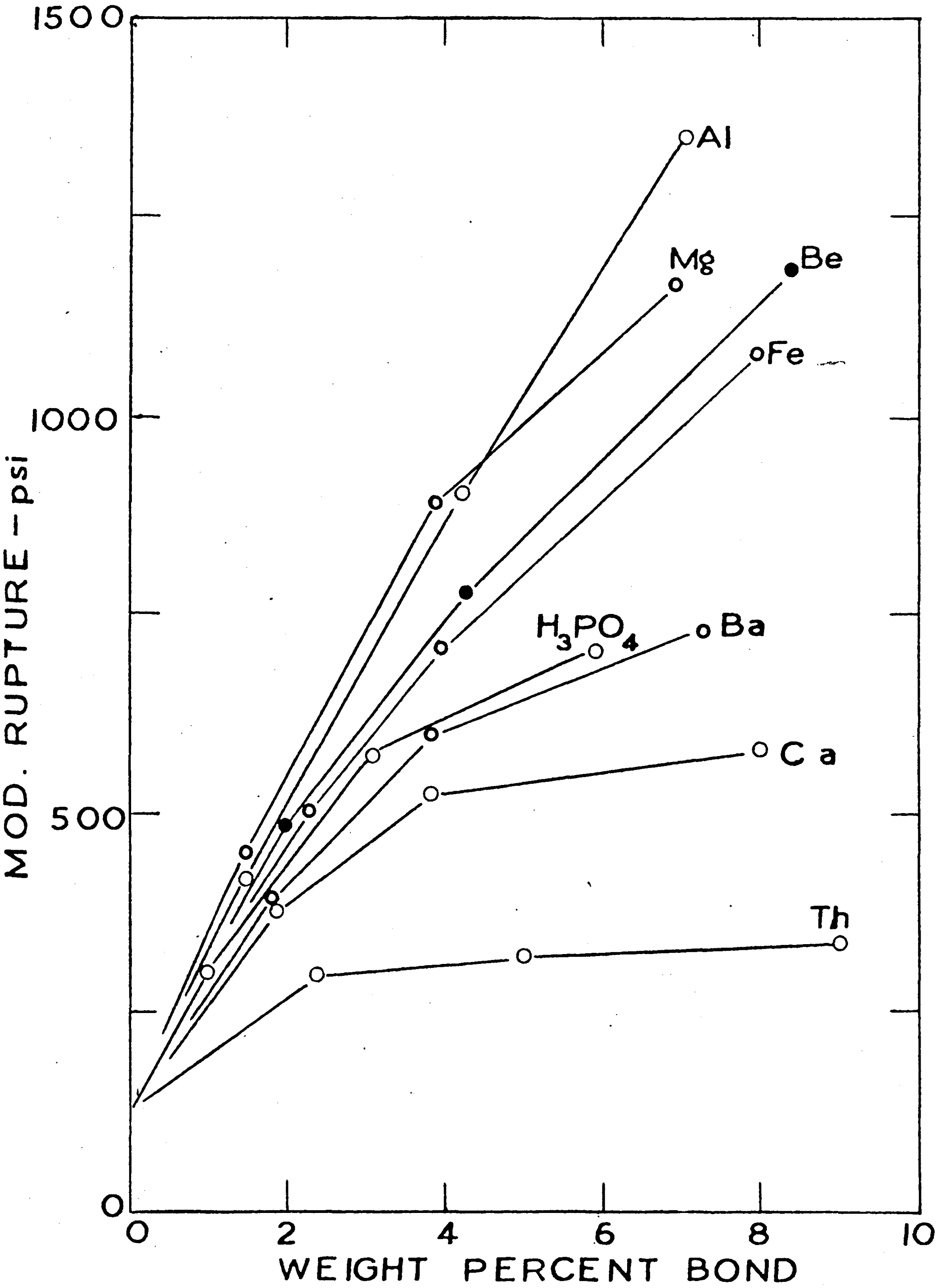


Fig. 1. - Effect of cation additions on bond strength. Transverse strengths of 90% fused alumina, 10% Florida kaolin bonded with liquid acid phosphate bonds.

oxide and the alkaline earths react so violently that the structure is effectively torn apart, and no cohesion is possible. As previously reported, this effect can sometimes be eliminated by calcining the oxide or using partially neutralized phosphoric acid. This effect is caused by the strongly basic nature of these oxides; the alkaline earths are the most basic divalent ions, while lanthanum is much more basic than any other trivalent ion.[74] Thus lanthana reacts violently while yttria, a much less basic rare earth, reacts to form a bonded product. In group II of the periodic table the progressive effect of basicity can be noted. While the least basic beryllia reacts directly with phosphoric acid to form a cement, magnesia must be calcined, calcia must be calcined and used with a partially neutralized acid, and the most basic strontia and baria still react violently even when calcined and used with a partially neutralized acid.

Inasmuch as phosphate bonding is due to the presence of acid phosphates, it should be possible to form bonds from solutions of the acid phosphates. Such was found to be the case (Fig. 1).

C. Bond Strength.

In order to examine the effect of the cation used on the strength of the phosphate bond, a number of compositions were prepared using solutions of different materials. A base mixture of 90% fused alumina (220F, Norton Co. Grade 38X) and 10% Florida kaolin (Edgar Plastic Kaolin Co.) was bonded with varying amounts of phosphate solutions of aluminum, magnesium, beryllium, iron, (ic.), barium, calcium and thorium. In addition samples bonded with phosphoric acid were prepared. Specimens were formed in small bar molds, and after drying at room temperature for twenty four hours and at 105°C for twenty four hours, transverse strength was determined. Results are shown in Fig. 1. It may be observed that phosphoric acid itself acts as a bonding material. Calcium, barium and thorium additions to phosphoric acid decrease its effectiveness. However, additions of aluminum, magnesium, iron and beryllium greatly increase the bonding power of phosphoric acid.

It may be recalled that x-ray diffraction patterns of alumina and beryllia products indicated an amorphous product while magnesia showed only very weak lines due to the mono-basic phosphate. The calcium, barium and thorium products are crystalline. The formation of amorphous or glassy structures is believed to be the cause of the increased strength of the alumina, beryllia, magnesia and iron phosphate cements. The formation of these variable and flexible structures is in accord with the glass forming properties of phosphoric acid. The residual fields present and the flexible nature of the structures which allows adjustment of the structure for maximum bonding would lead to greater adhesive power for bonding action.

The cause of varying cationic bonding action lies in two complimentary factors - cationic size and basicity. Basicity is considered here as equivalent to weak cation oxygen bonds which allow that bond to be broken with greater ease than a hydrogen-oxygen bond. This is due to lack of covalent bond character, a low positive charge, large ionic radius and low electronegativity.[75] These conditions are present in the first group and higher atomic number elements of the second and third groups in the periodic table. For highly basic cations, crystalline structures tend to result. For less basic materials a more amorphous or glassy structure can result since strongly bonded polyhedra are held together with considerably weaker forces.

Cationic size is important in the formation of this non-ordered arrangement which promotes additional bond strength even though the structure is not completely amorphous. This is due to the fact that large ions, even if highly charged and weakly basic, form

TABLE I

Effect of Cations on Phosphoric Acid Bond

Cation	Basicity*	Ionic Radius (A^o)**	Effect on Bond
Be^{++}	amphoteric	0.31	increases strength
Al^{+++}	amphoteric	0.50	increases strength
Fe^{+++}	weak base	0.60	increases strength
Mg^{++}	weak base	0.65	increases strength
Ca^{++}	strong base	0.99	decreases strength
Th^{++++}	weak base	1.1*	decreases strength
Ba^{++}	strong base	1.35	decreases strength

* W. M. Latimer and J. H. Hildebrand, Reference Book of Inorganic Chemistry, 2nd Ed., The Macmillan Co. (1940)

** L. Pauling, The Nature of the Chemical Bond, 2nd Ed., p346, Cornell Univ. Press (1945) structures having a high oxygen coordination number. With a high coordination number (greater than six, at least) it is difficult to form a variable structure of coordinated polyhedra having mobility and flexibility. Smaller cations which form structures having a lower coordination number are able to form a variable structure of connected polyhedra much as occurs in glass formation.

The pertinent data for cations referred to in Fig. 1 are tabulated in Table I. From the above discussion it seems apparent that for optimum bonding a weakly basic or amphoteric cation of relatively small ionic radius is required.

V. BOND PROPERTIES

A. Setting.

The process of setting of a liquid phosphate bond was determined for solutions of mono-aluminum phosphate - selected as typical of high strength bonds and of the potentially greatest very high temperature usefullness. These solutions were found to form highly viscous solutions as concentration increases, finally solidifying into a glassy solid. Solutions having a concentration of greater than about 50 weight per cent were found to precipitate a "sticky" solid phase on long standing.

Measurements of viscosity as a function of composition and temperature were made with a modified McMichael viscosimeter previously described in the literature.[76]

As shown in Fig. 2, as the concentration of mono-aluminum phosphate is increased, the viscosity increases until a solid material is formed. Up to a concentration of about 50 weight per cent, the viscosity increases slowly. At 50% concentration, the viscosity begins to increase rapidly and reaches 500 centipoise at 67.5%. In the high viscosity range, these values pertain to freshly prepared solutions measured prior to any evidence of precipitation.

The viscosity was measured as a function of temperature over the range from 20°C to 60°C (Fig. 3). As is to be expected, viscosity decreases considerably with an increase in temperature. The value of viscosity at 50°C is only about half the value at 20°C.

These data show that the setting process for phosphate material with the loss of water is substantially the same as for other adhesive materials. That is, the formation of an amorphous or glassy solid of increasing viscosity as the solvent material is lost.

Fig. 2. - Effect of concentration on bond viscosity.

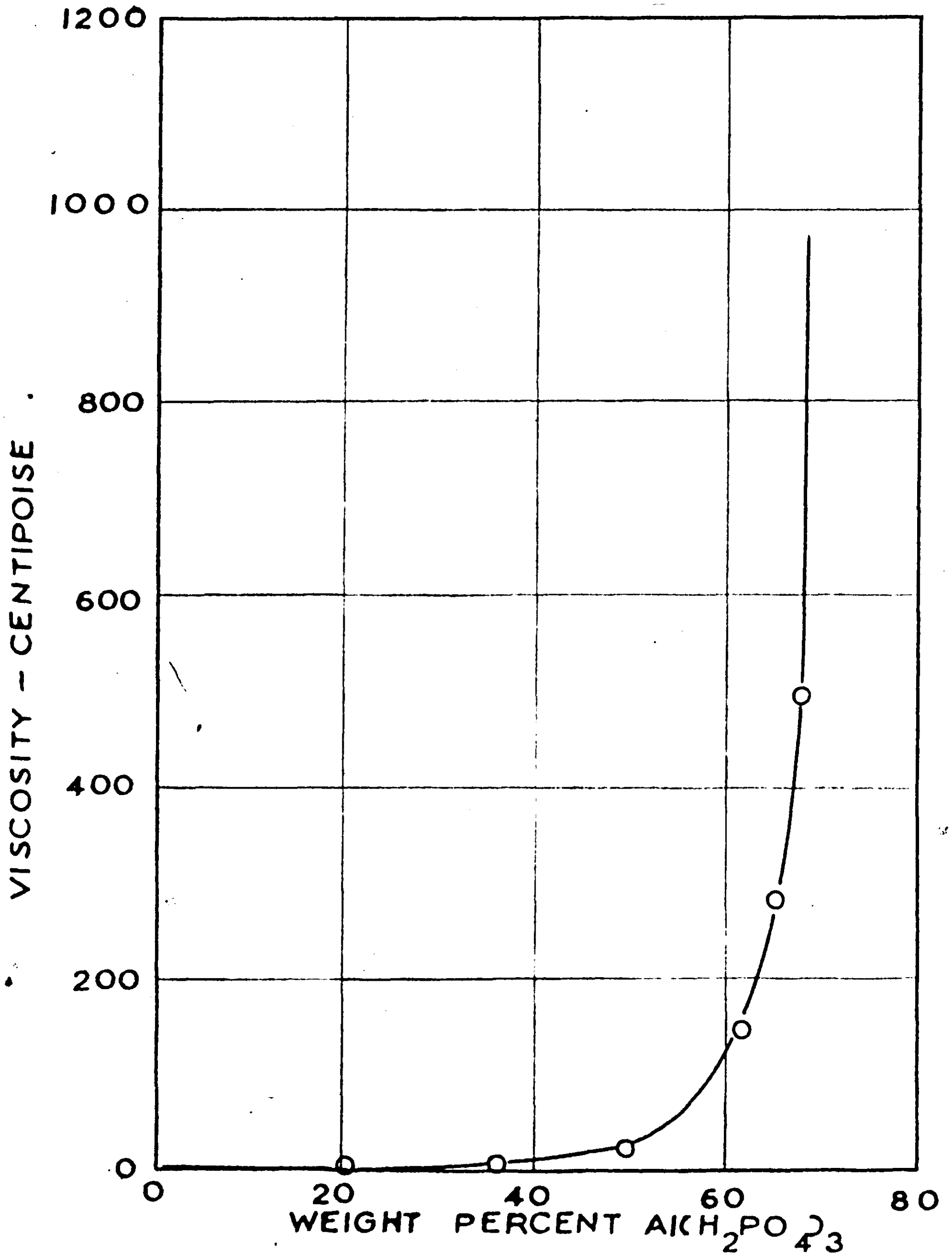
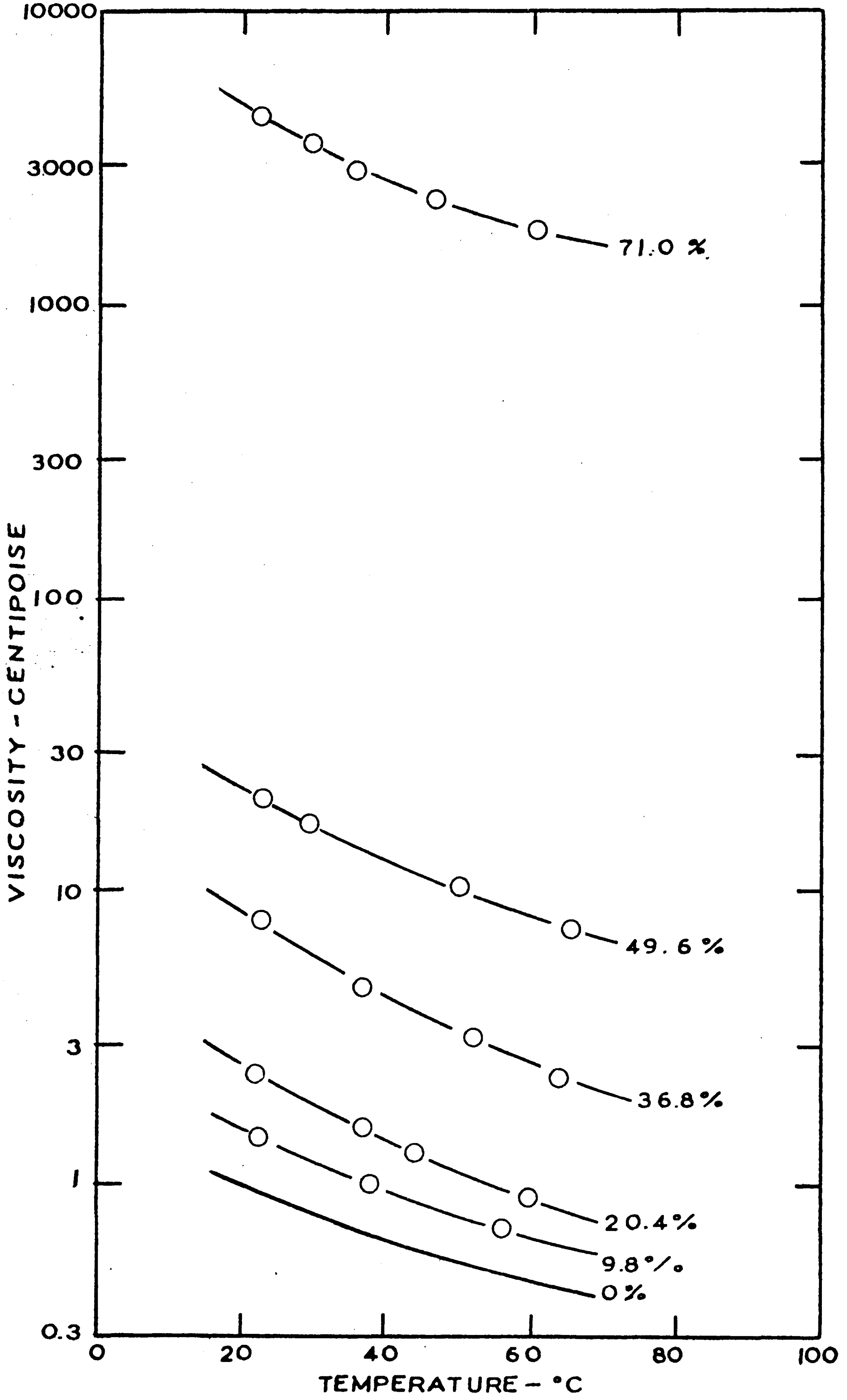


Fig. 3. - Effect of temperature on bond viscosity.



B. Temperature Effects.

The effects of temperature on the properties and constitution of a bond material are of special interest in the field of refractories. Most refractory bonding materials show a zone of weak strength in the range from 500 - 1000°C where original air-set properties disappear and prior to the formation of strength due to incipiant fusion. This effect is noted in silicate bonds and is especially important in hydraulic cements.

A determination of the effect of temperature on strength was made by preparing mortar bars composed of 85.7% fused alumina (Norton Co., 220F, grade 38X), 7.15% light English ball clay (Enfield) and 7.15% mono-aluminum phosphate. These samples were heated for two hours at 105°, 300°, 500°, 800°, 1100° and 1300°C and the transverse strength was determined after cooling. The results found (Fig. 4) are notable in that the strength was greater than the original strength at all temperatures. No zone of weakness was encountered. These results led to an investigation of the changes taking place on heating.

Changes in bond structure were investigated by determining the rate of weight loss vs. temperature, equilibrium compositions and x-ray diffraction patterns at various temperatures, and by differential thermal analysis.

On heating mono-aluminum phosphate at a constant rate of temperature increase, the rate of weight loss vs. temperature (Fig. 5) was determined. Maxima occur in the rate curve at 250°C and 490°C. The two peaks in the rate curve suggest the transitory formation of an intermediate product. The composition of the material at the minimum between the two peaks is approximately $Al_2O_3 \cdot 3P_2O_5 \cdot 3H_2O$. At a temperature rise of about 10°C per minute, the weight loss is complete at 800°C with the formation of aluminum meta-phosphate, $Al(PO_3)_3$.

Fig. 4. - Effect of temperature on bond strength. Transverse strength of fused alumina, 7.15% light English ball clay and 7.15% mono-aluminum phosphate after heating.

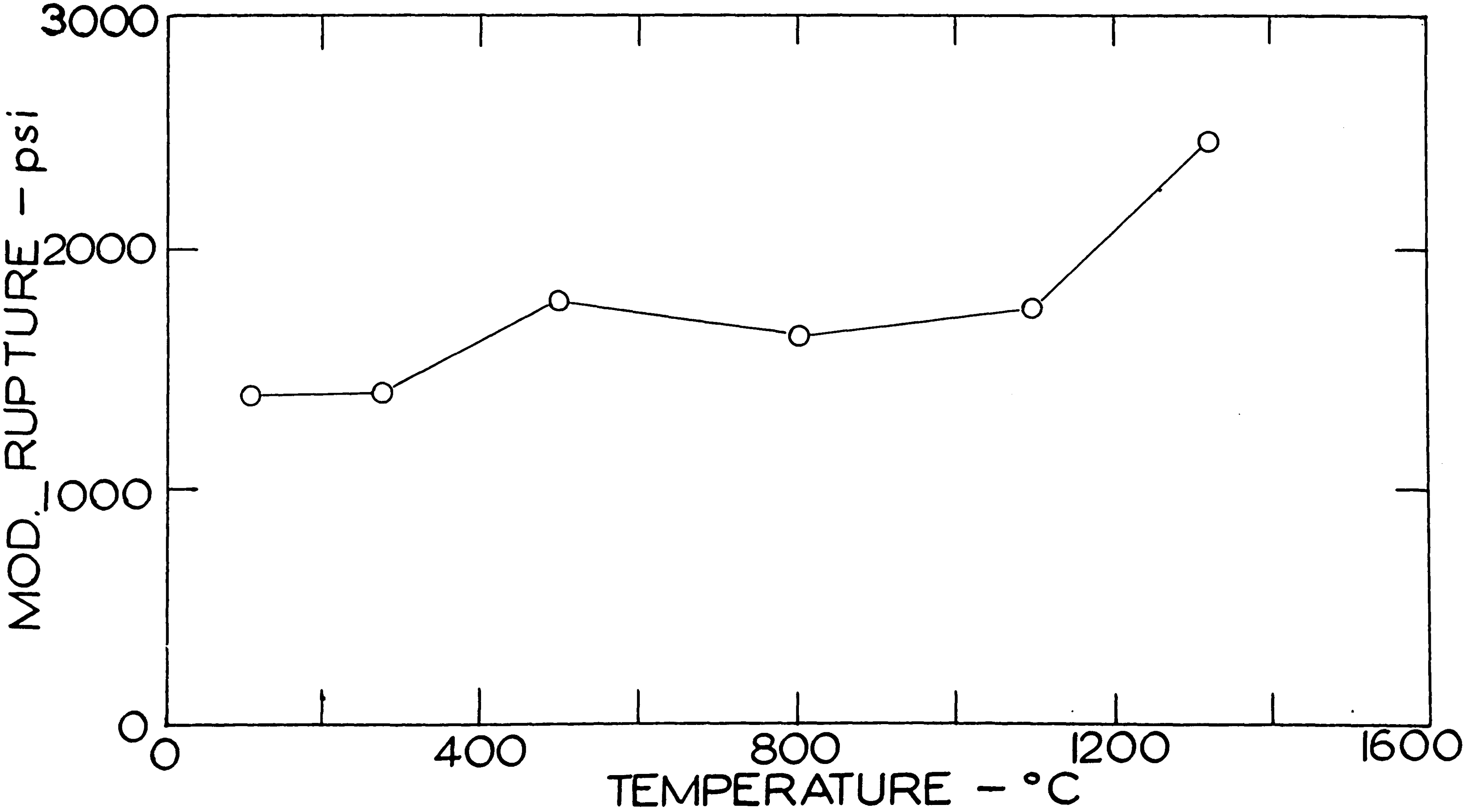
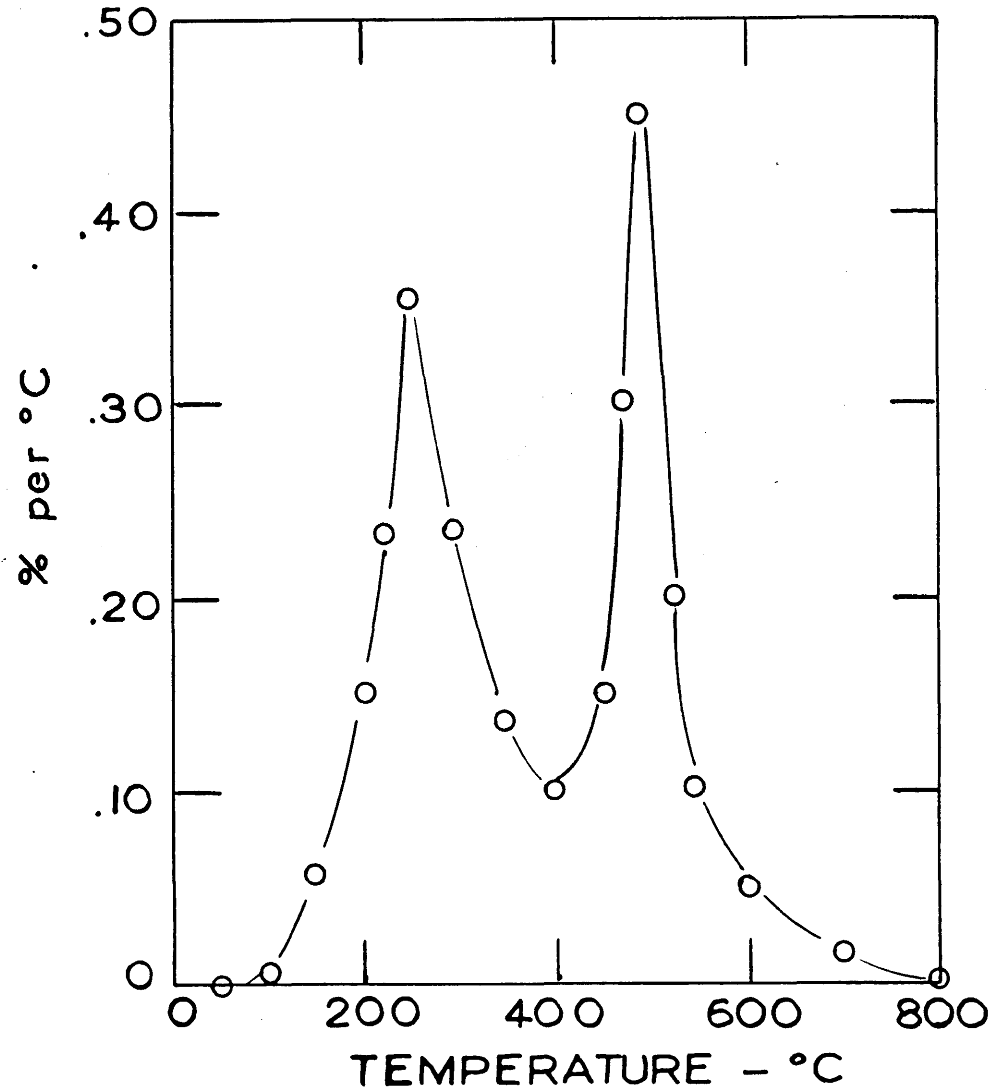


Fig. 5. - Continuous rate of weight loss of mono-aluminum phosphate. Percent of total weight lost per °C plotted against temperature.



The loss of "combined" water of mono-aluminum phosphate was also studied by measuring the weight loss of heating specimens to constant weight at various temperatures. The equilibrium compositions at various temperatures are plotted in Fig. 6 as mols of water present for each mol of alumina. The composition varies from mono-aluminum phosphate, $Al_2O_3 \cdot 3P_2O_5 \cdot 6H_2O$ to the metaphosphate, $Al_2O_3 \cdot 3P_2O_5$, and steps are indicated for various phases. A sharp break occurs at a water content of about three mols, $Al_2O_3 \cdot 3P_2O_5 \cdot 3H_2O$. The curve is typical of a hydrous-hydrate material. That is, the change from one hydrated material is not absolutely sharp, but is partially continuous.

X-ray diffraction data for the equilibrium products at various temperatures (Fig. 7) show that an essentially amorphous material is formed by the original loss of "combined" water. This material partially crystallizes and then form aluminum metaphosphate by a temperature of 500°C.

Differential thermal analysis (Fig. 8) showed a large endothermic peak at 265°C which developed into a slightly exothermic reaction which continued until about 900°C. An endothermic effect was noted at about 450°C.

The lack of any weak temperature zone on heating mono-aluminum phosphate is probably due to the process of decomposition. There is no sharp break or change in structure as occurs with other types of cements. In addition to the gradual loss of "combined" water, the crystallization of the dehydration products is gradual and continues over a long temperature range with no sharp rupturing effects. At higher temperatures the reaction product forms a bond with the aggregate which gives continuous bonding action. Other workers have found that the presence of metaphosphate in itself acts to increase bond strength.[77]

Fig. 6. - Equilibrium water content of mono-aluminum phosphate.

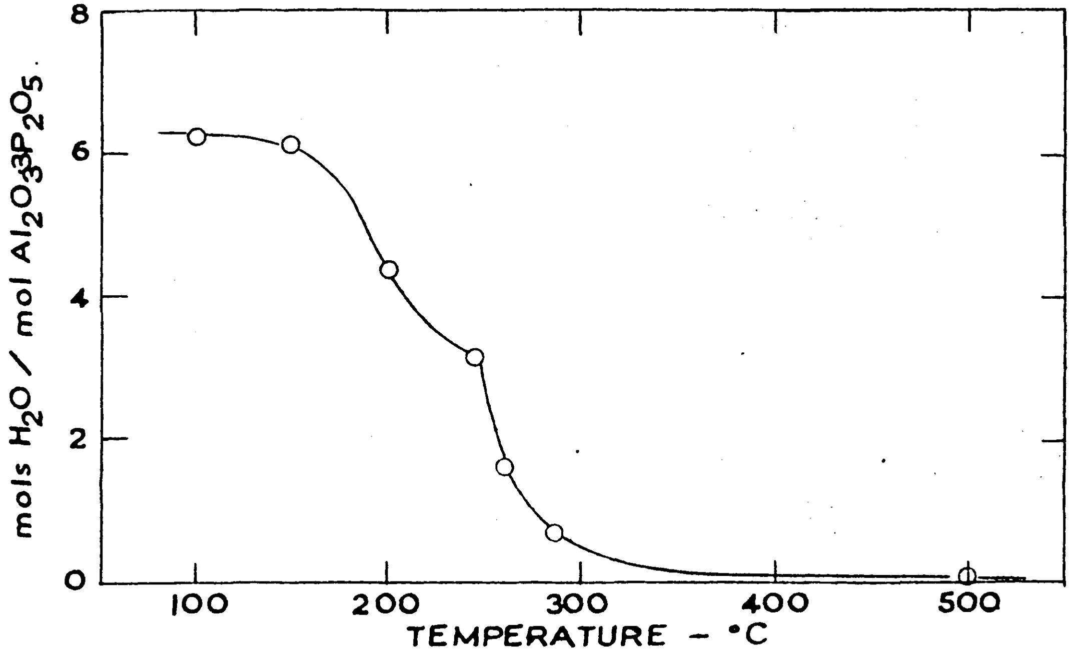
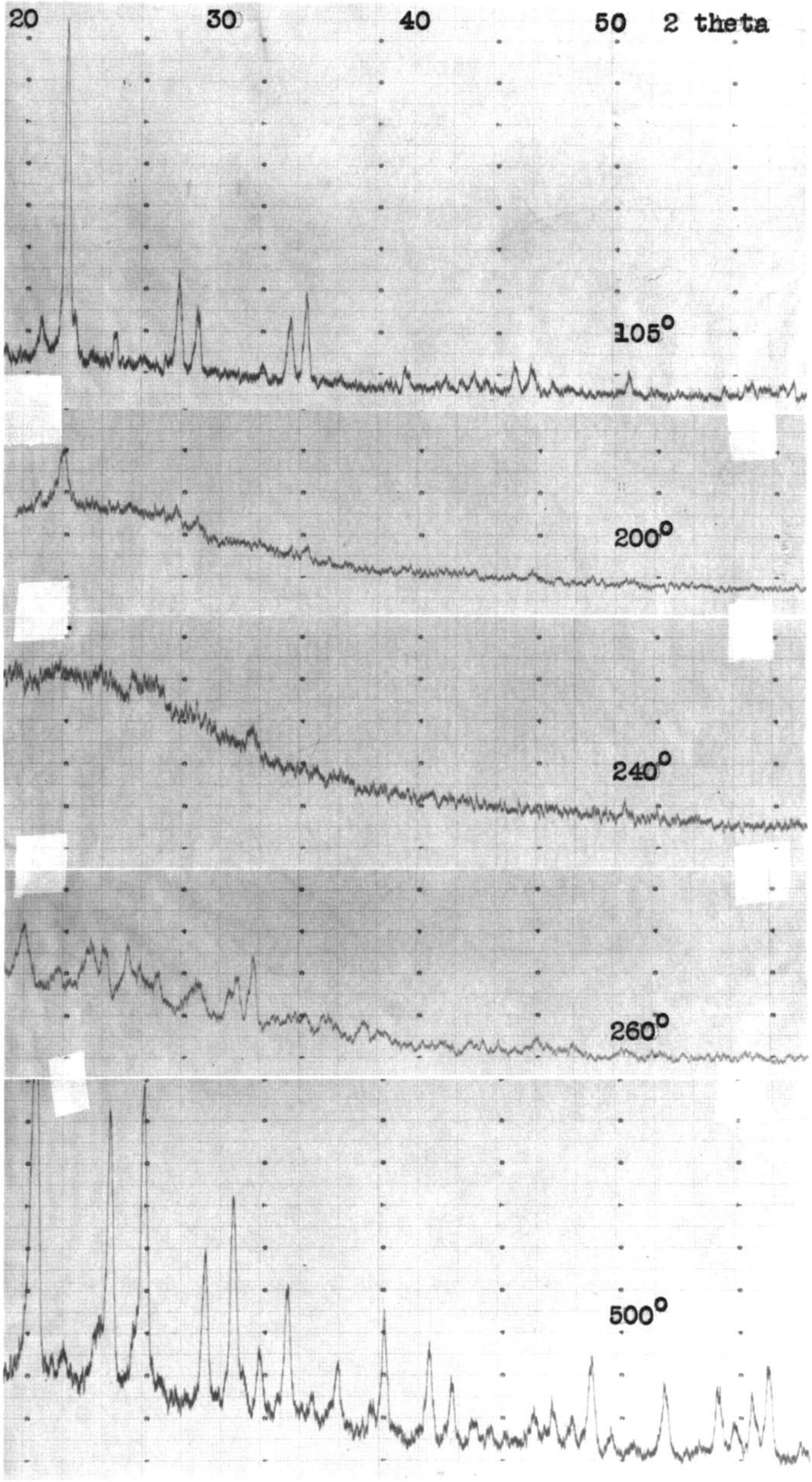


Fig. 7. - X-ray diffraction patterns of equilibrium products of mono-aluminum phosphate at various temperatures.



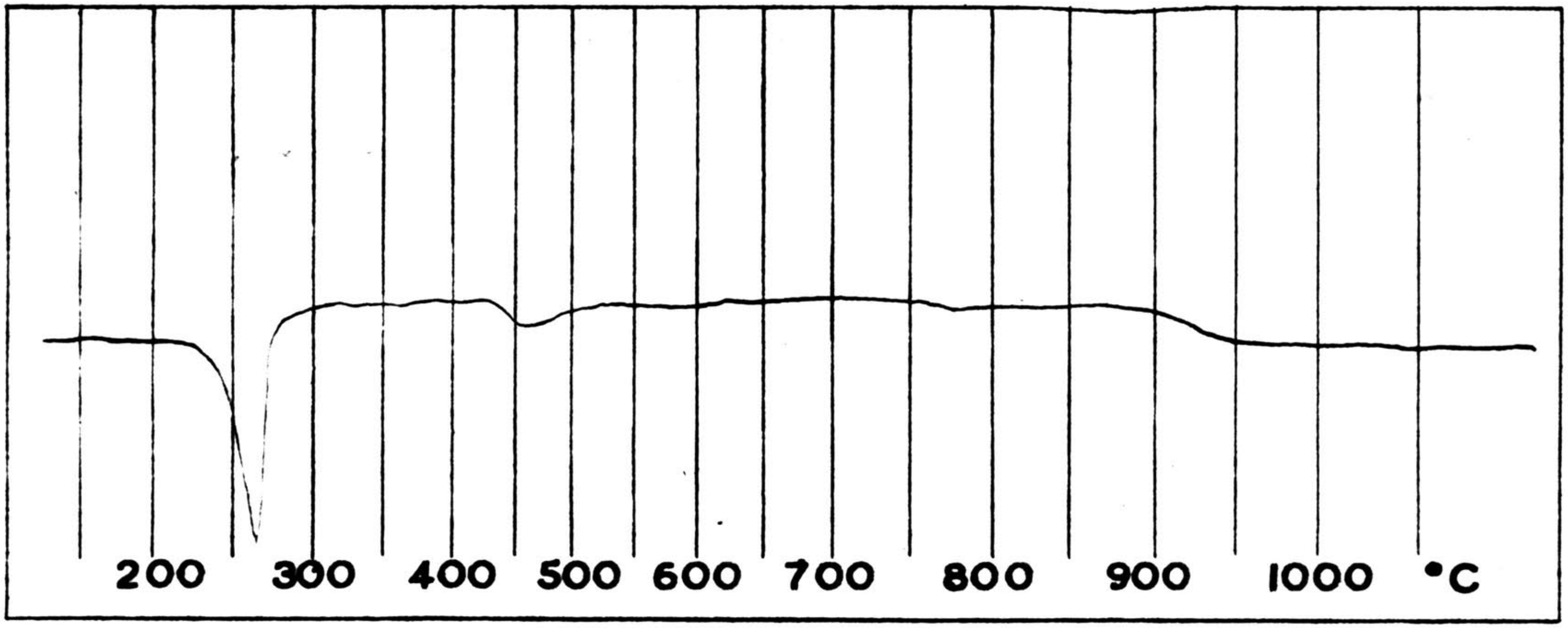


Fig. 8. - Differential thermal curve of mono-aluminum phosphate.

VI. PHOSPHATE ADSORPTION BY CLAY AND BOND MIGRATION.

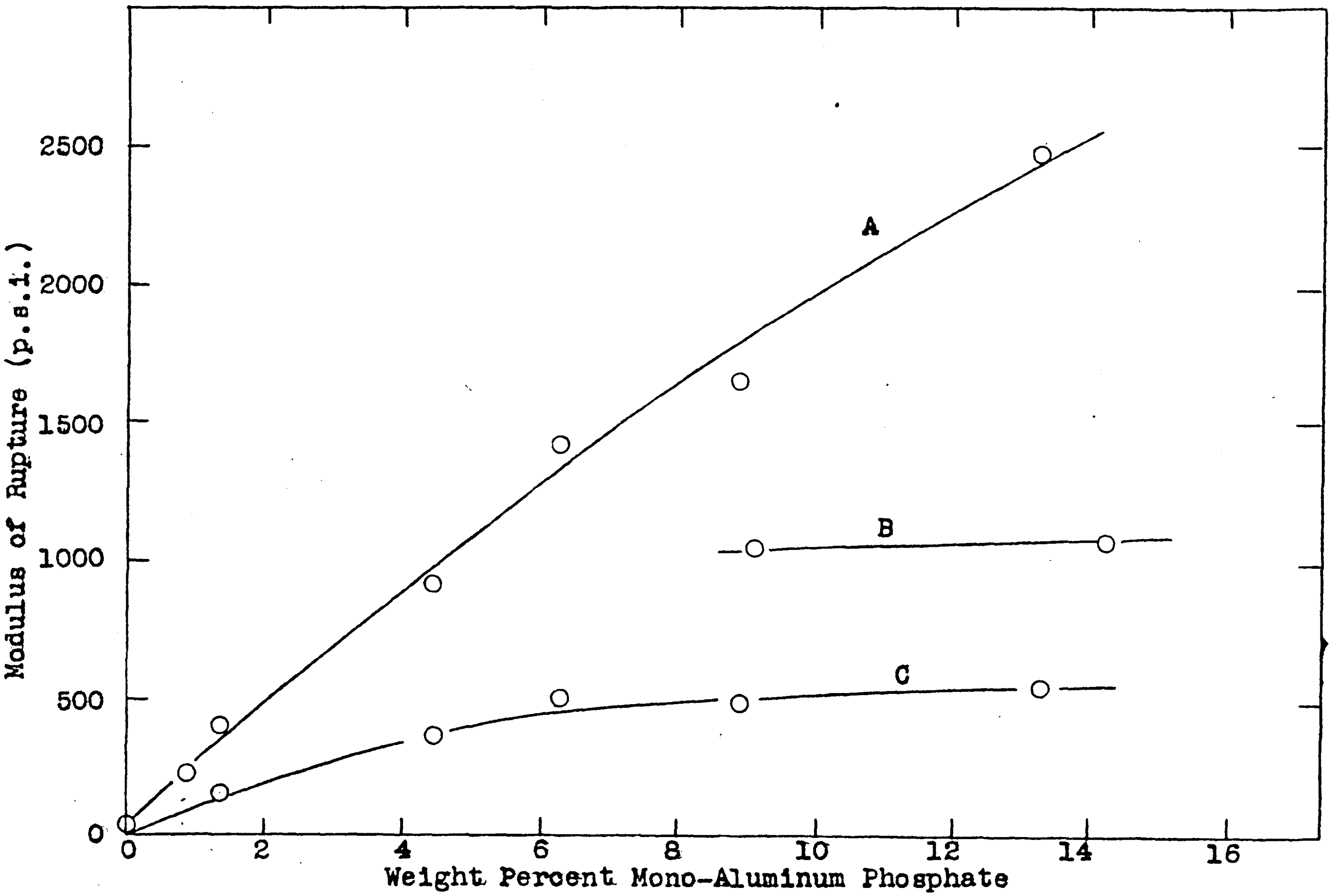
A. Migration Effects.

The migration of bonding materials has presented a limitation on the usefulness and application of cold setting bonds. Bond migration causes variation in mortar and unfired refractory properties due to variations in bond content through the structure. Excessive bond must be used to provide adequate strength throughout the structure. If excessive migration occurs, the surface may be composed completely of bond material.

In the formation of mortar bars, migration effects have been noted by this author and others[78] in that mortar bars are strongest when the uppermost or drying surface is broken in tension. This is due to the tendency of the mortar to migrate to the drying areas, forming a channel section (⊓) of increased mortar concentration. In addition, it has been found that with fused alumina-phosphate mortars, those prepared with a dry bond have higher strengths than those prepared with a liquid bond. The addition of a few percent clay increases the strength by a much larger amount, and was qualitatively observed to decrease migration. (Fig. 9.)

These effects may be due to the increased area available for bonding between particles - the increased particle contact area present. This would tend to give a more homogeneous and stronger structure. Another factor which might be of importance is the absorption of the phosphate material by the clay. The general phenomena of migration and absorption are so little understood that an investigation of these factors in bonding was undertaken.

Fig. 9
STRENGTH OF MONO*ALUMINUM PHOSPHATE MORTARS



A - 90% Alumina(220F), 10% Florida Kaolin, liquid bond
B - Alumina(220F), dry mix
C - Alumina(220F), liquid bond

B. Phosphate Adsorption.

Phosphate adsorption by clay minerals is a well known phenomenom[79] that has generally been ascribed to the replacement of surface hydroxyl ions by phosphate ions. In some cases iron and aluminum ions are believed to precipitate phosphates as well. Extraordinarily large values of adsorption have been reported by Stout for kaolin and halloysite ground in rubber-lined ball mills.[80] In the present work the effects of pH, concentration, time of adsorption, particle size and ball milling of the clay material were investigated.

The adsorption of mono-aluminum phosphate was determined by mechanically shaking a weighed amount of absorbant with a known amount of phosphate solution. After separating the solid material with a centrifuge, an aliquot of the solution was withdrawn and the phosphate determined. From the decrease in concentration, the phosphate adsorbed could be determined. A typical calculation is shown in Appendix D.

Florida plastic kaolin was found to adsorb 13.3 meq. per 100 gm. This value was adsorbed after twenty minutes of mechanical shaking with no further adsorption in twenty six hours. This value was constant for solutions containing as little as 23.0 meq. (2.40 gm.) per 100 cc and as much as 200 meq. per 100 cc.

Due to hydrolysis, mono-aluminum phosphate solutions precipitate at pH values greater than about 2.8. Phosphate adsorption was found to increase slightly at lower pH values - from 13.2 meq. / 100 gm. at pH 2.7 to 13.7 meq./ 100 gm. at pH 1.0 (Fig. 10).

Compared to this adsorption by clay, fused alumina (220F, Norton Co., grade 38X) was found to adsorb less than 0.1 meq. per 100 gm.

Wet grinding in a porcelain ball mill was found to be an effective method of reducing the particle size of a natural clay. Samples of

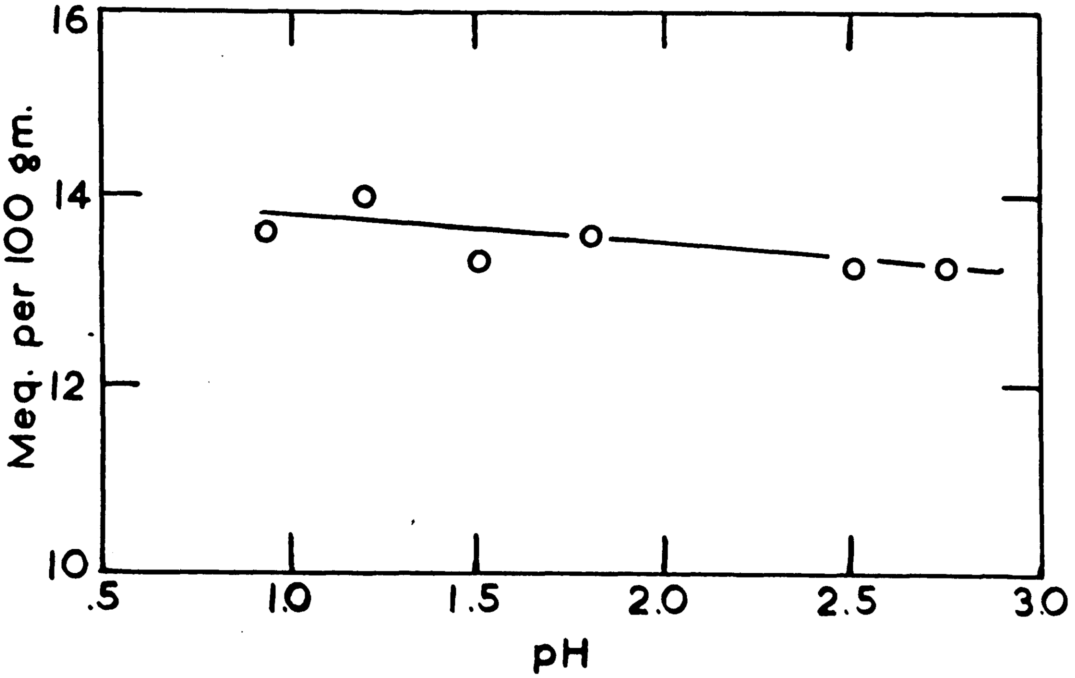


Fig. 10. - Effect of pH on phosphate adsorption by clay.

North Carolina kaolin were ball milled for 16, 44 1/2 and 98 hours after which they were examined for particle size distribution (hydrometer method[81]) and adsorption of mono-aluminum phosphate. The size distribution of the unground material and the material ground for 98 hours is shown in Fig. 11. While the unground material has only 28 weight percent finer than one micron, the ground material has 66 weight percent finer than one micron. Adsorption of mono-aluminum phosphate is increased greatly by grinding. While the adsorption of the unground material is only 9.6 meq. per 100 gm., the adsorption of the material ground 98 hours is 92.5 meq. per 100 gm. (Fig. 12.)

In order to quantitatively determine the effect of particle size in phosphate adsorption, monodisperse fractions of the ground material were separated with a Sharples super-centrifuge.[82] Size fractions having equivalent spherical diameters of 0.6 - 0.7, 0.37 - 0.42, and 0.12 - 0.15 microns were separated. The equivalent spherical diameters were determined by means of a nomograph calculated for the centrifuge used.[83] The nomograph is included in Appendix E. The adsorption of mono-aluminum phosphate by these fractions and by a mono disperse fraction of unground clay were determined (Fig. 13).

The straight-line logarithmic relation found indicates that the data follow an equation having the form,

$$a = k(d)^{-n}$$

a = meq. adsorbed/100 gm.
d = equiv. spherical diameter
k,n = constants

This indicates that the phenomenom is a surface adsorption rather than any chemical precipitation type of reaction. However, the effect of grinding cannot be due entirely to the reduction in particle size. Although the surface area of the material ground 98 hours is about doubled, phosphate

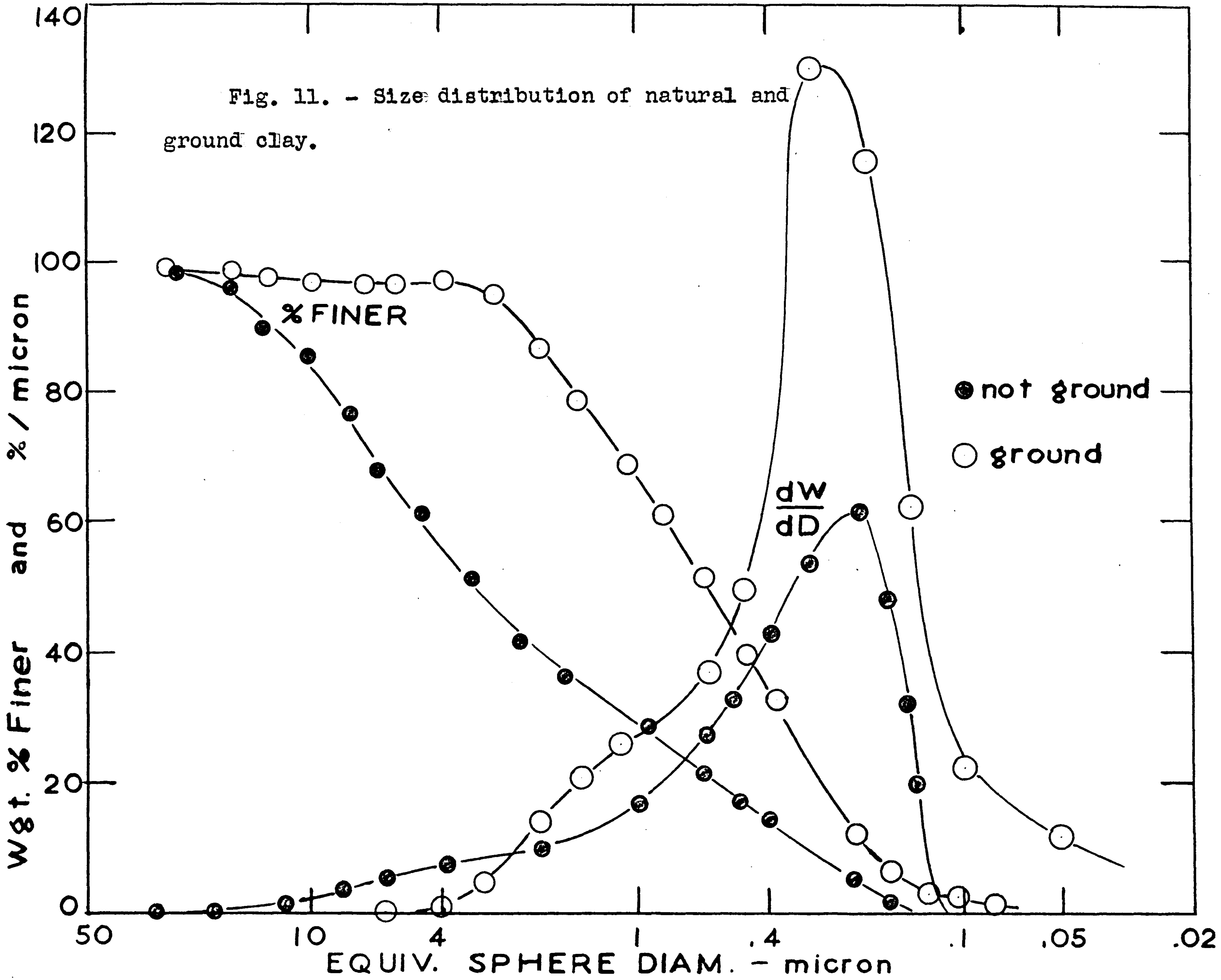
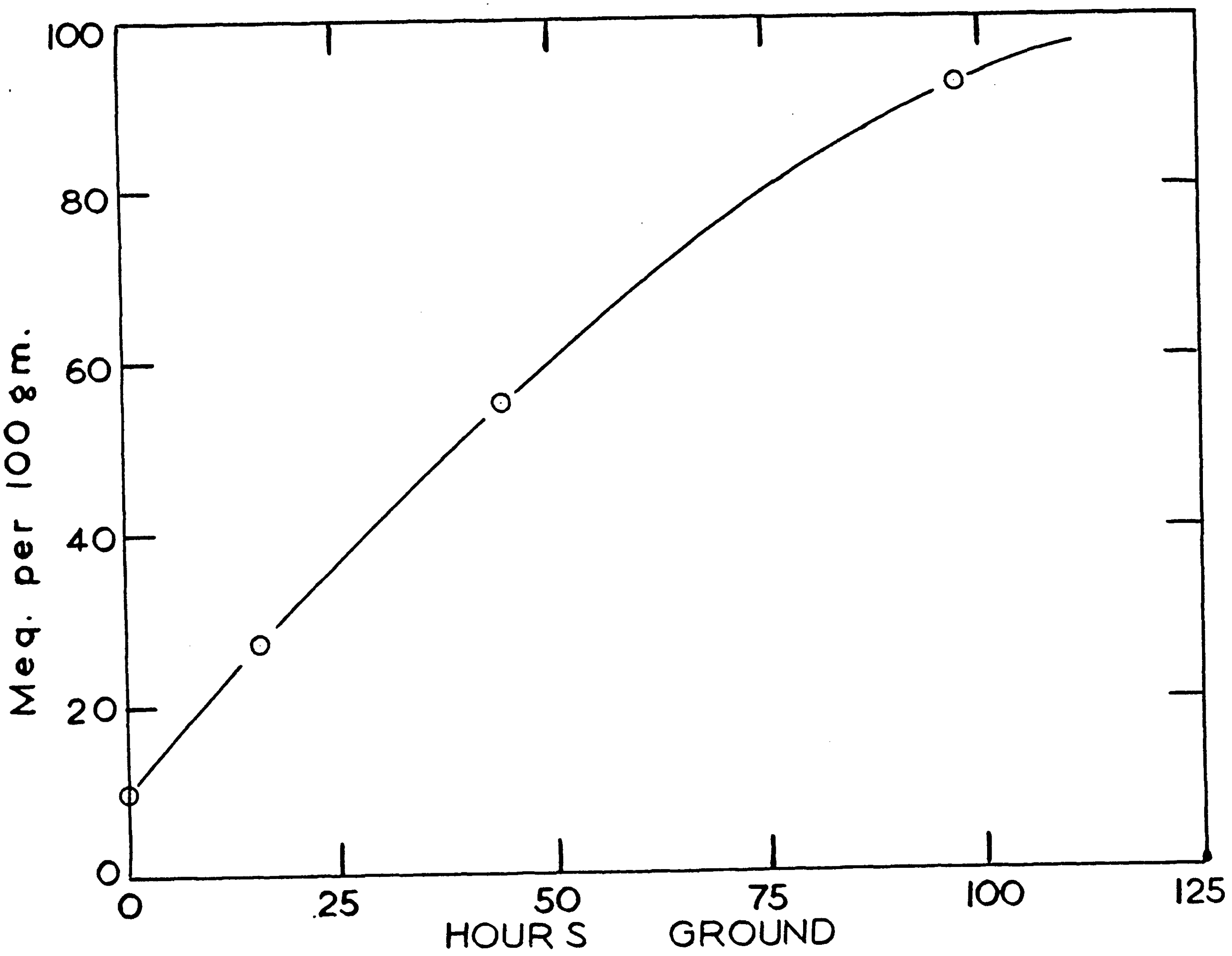


Fig. 11. - Size distribution of natural and ground clay.

Fig. 12. - Effect of grinding time on phosphate adsorption by clay.



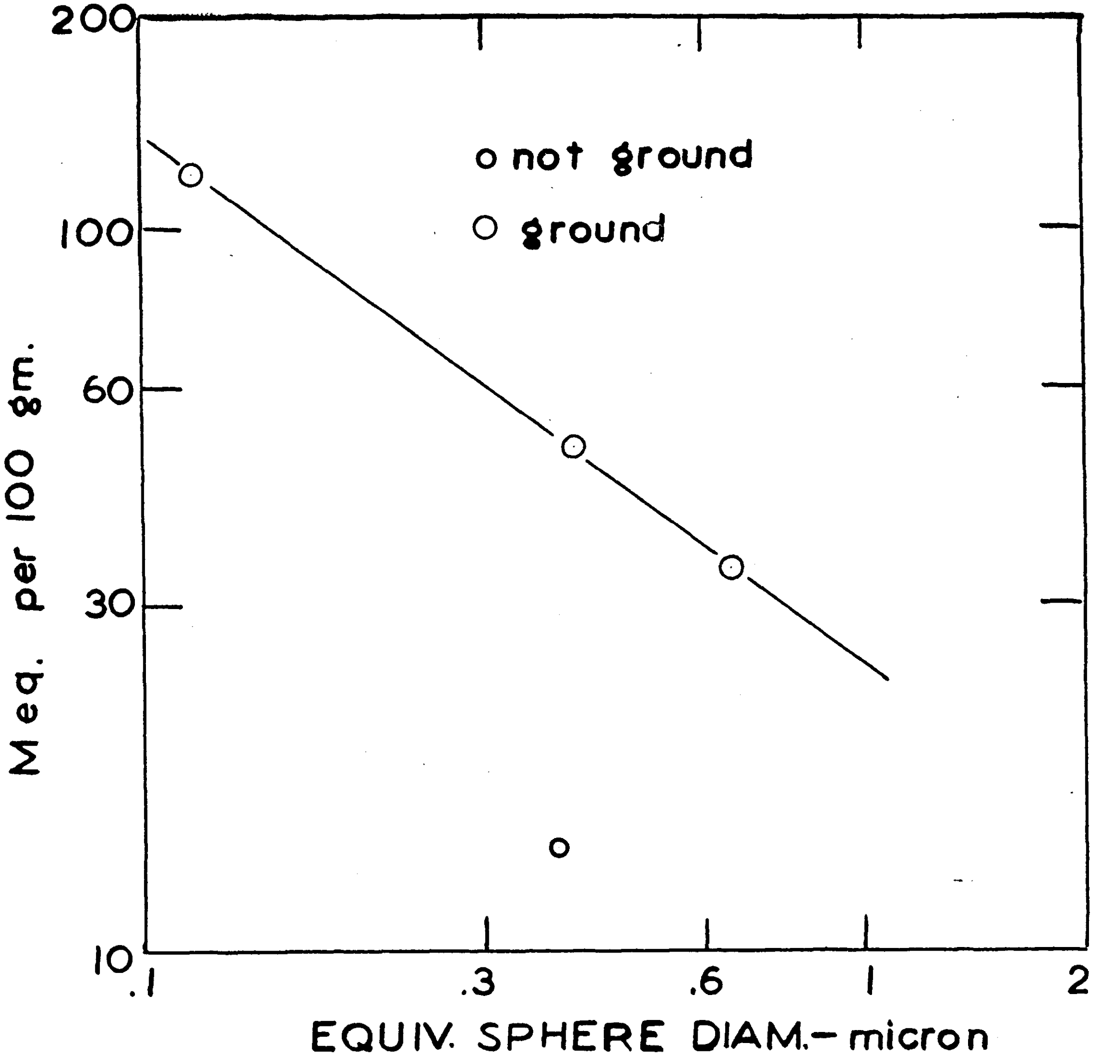


Fig. 13. - Phosphate adsorption of monodisperse fractions of clay.

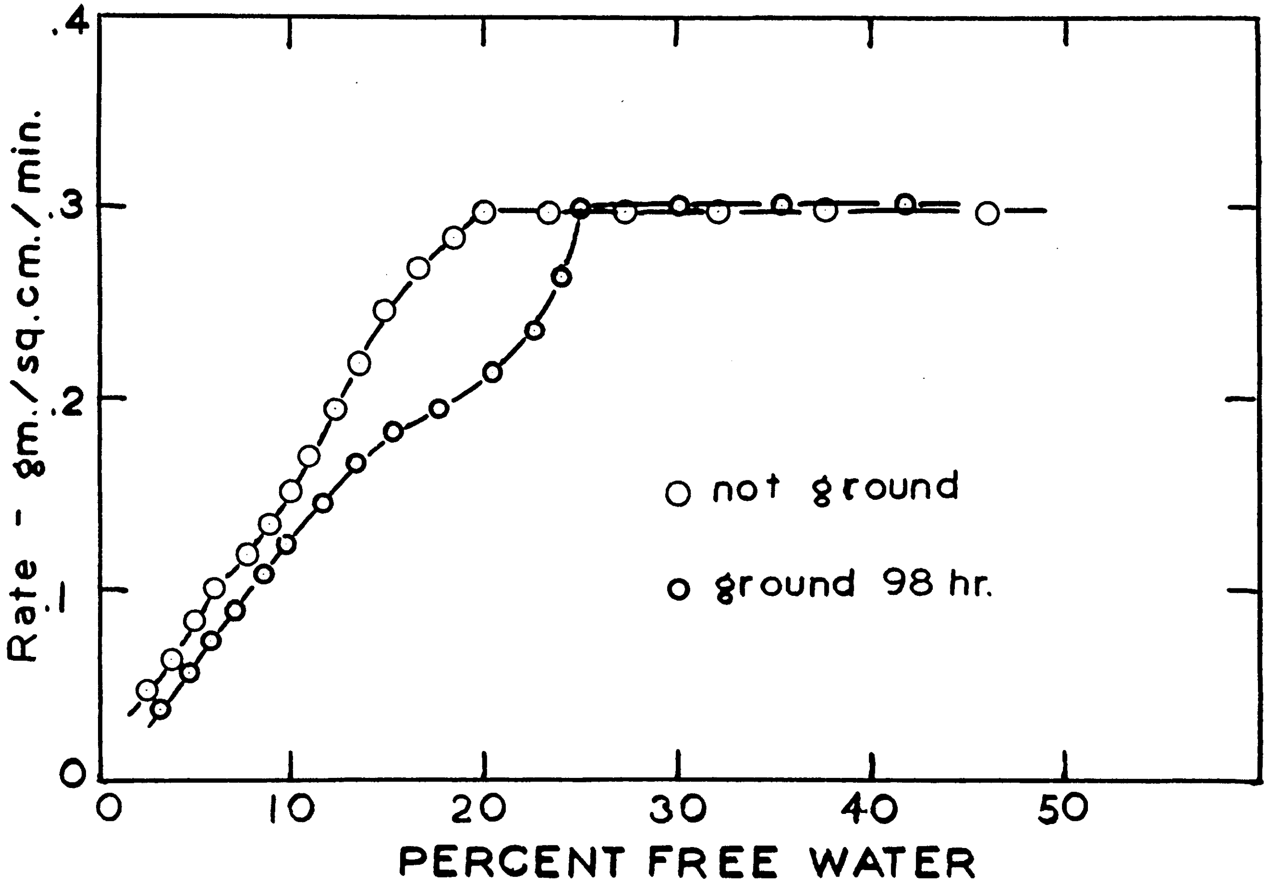
adsorption is increased by about ten times. Also, as shown in Fig. 13, the adsorption of ground kaolin is about four times the adsorption of unground material of the same particle size. It seems probable that the grinding action tends to open or loosen the bonding in kaolinite "books", providing additional spaces on which adsorption can take place.

C. Phosphate Migration.

The phosphate adsorption phenomena are of interest in phosphate bonding since they affect the migration tendencies of phosphate bonds. A study of the effect of adsorption on bond migration was made using unground North Carolina kaolin (adsorption capacity of 9.6 meq. per 100 gm.) and North Carolina kaolin ground 98 hours (adsorption capacity of 92.5 meq. per 100 gm.). These materials were blunged, screened and filtered with water, sodium chloride solutions and mono-aluminum phosphate solutions. Small slabs (5x4x1 cm.) were formed in a brass mold and dried from two parallel surfaces at constant temperature (60°C) while measuring the continuous rate of drying by methods previously described.[84] Drying was restricted to two parallel surfaces by covering the other sides of the sample with tin foil. After drying, the samples were sectioned and analyzed to determine the salt concentration across the slab.

The samples dried with water showed typical rate of drying curves (Fig. 14). The critical point for the unground material occurs at about 20% free water while the critical point for the ground material occurs at 24%. This indicating that the ground material contains a larger amount of pore water than the unground material. In the falling rate period, the rate of drying of the ground material decreases more rapidly than the unground, and the rate of drying is slower. This is to be expected since the interstices are smaller and offer a greater resistance to liquid diffusion.

Fig. 14. - Rate of drying of water from natural and ground clay.



The samples dried with sodium chloride solutions showed rate of drying curves in which the duration of the constant rate period depended on the amount of solution present. After a short period of drying a surface layer of crystalline material was observed. At the point where this layer formed, the start of the falling rate period was observed. It is thus apparent that the diffusion through this layer is comparatively slow, and for that reason the drying rate drops. Grinding had no major effect on the shape of the curve - as would be expected if the salt layer is the controlling factor. Rate of drying curves for two different original liquid contents are shown in Fig. 15.

The samples dried with mono-aluminum phosphate solutions showed significant differences between the ground and unground samples in Fig. 16. The unground material showed a drying curve much like that with the sodium chloride solution. The critical point occurred when a surface layer of mono-aluminum phosphate was observed to precipitate, and this point was a function of the salt content rather than the clay material. However, with the material that was ground 98 hours, the rate of drying was exactly similar to this material with water (Fig. 14). The critical point occurs at 24% free water as in the water sample, and no surface precipitate of mono aluminum phosphate was observed.

An analysis of the migration of soluble salts on drying gives information as to the processes occuring. The original and final concentrations of sodium chloride in the drying samples are shown in Fig. 17. These show that migration toward the surface occurs for both ground and unground material, and that the same type of final distribution occurs. The unground material shows a greater precipitation on the surface while the ground material tends to deposit at and below the surface due to the smaller interstices. However, the two cases are very similar. The ratio of the final minimum concentration (at center line) to the original

Fig. 15. - Rate of drying of sodium chloride solution from natural and ground clay.

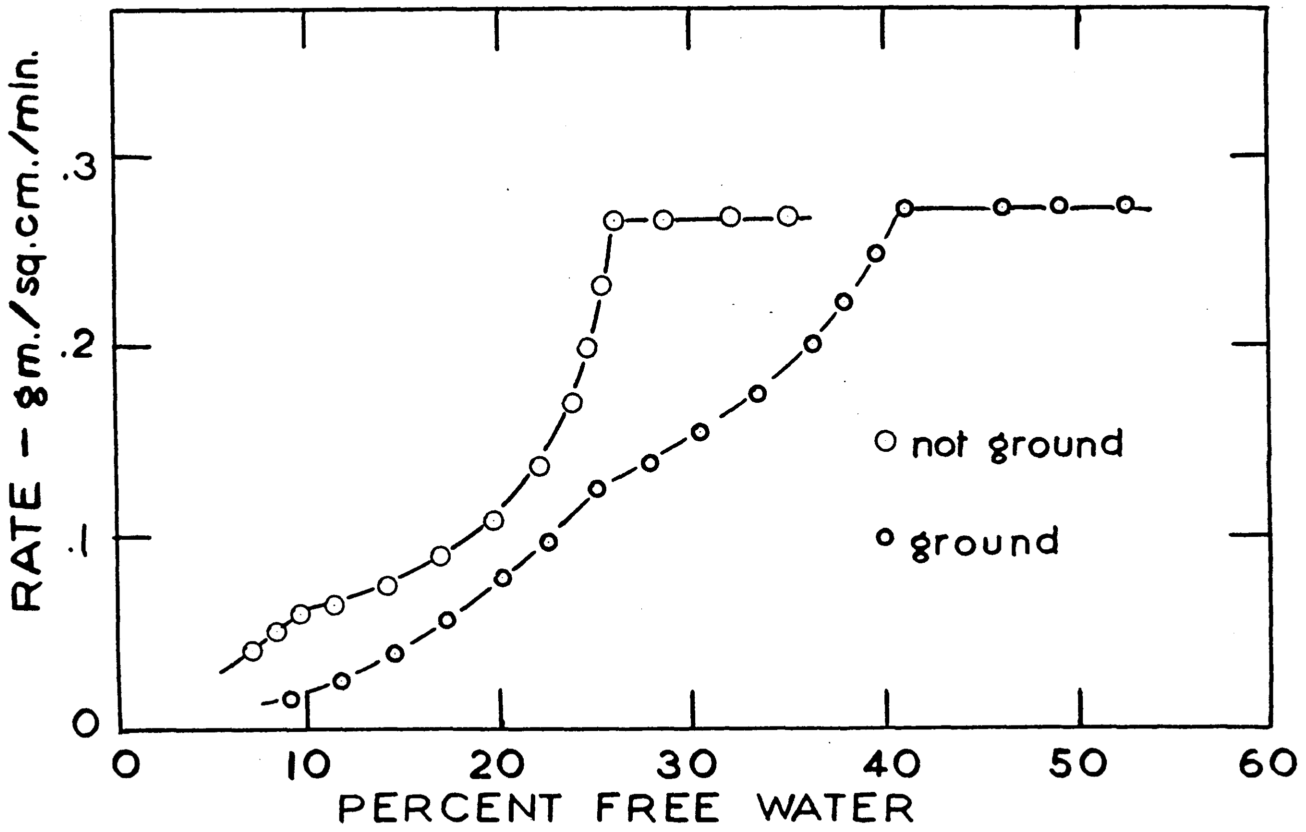


Fig. 16. - Rate of drying of mono-aluminum phosphate from natural and ground clay.

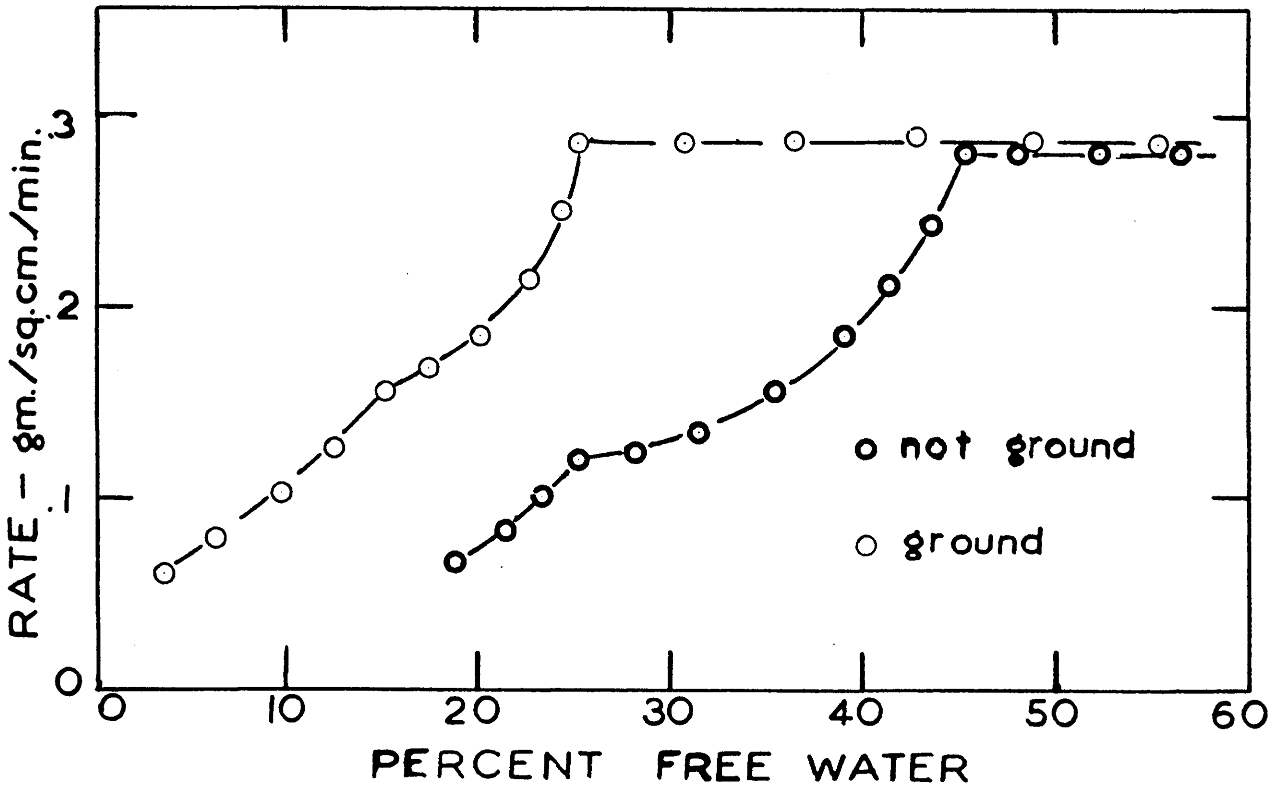
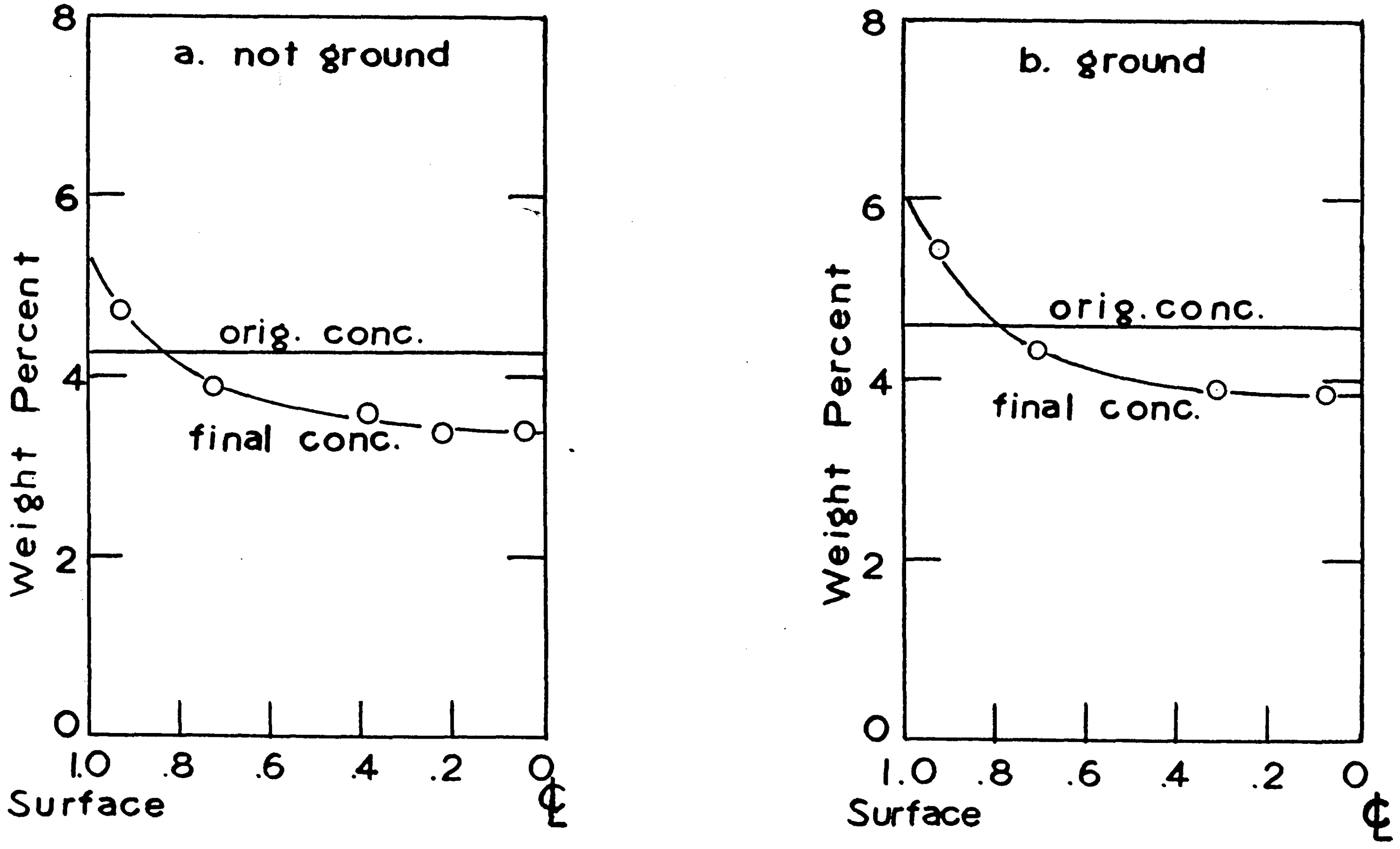


Fig. 17. - Migration of sodium chloride in matural and ground clay.

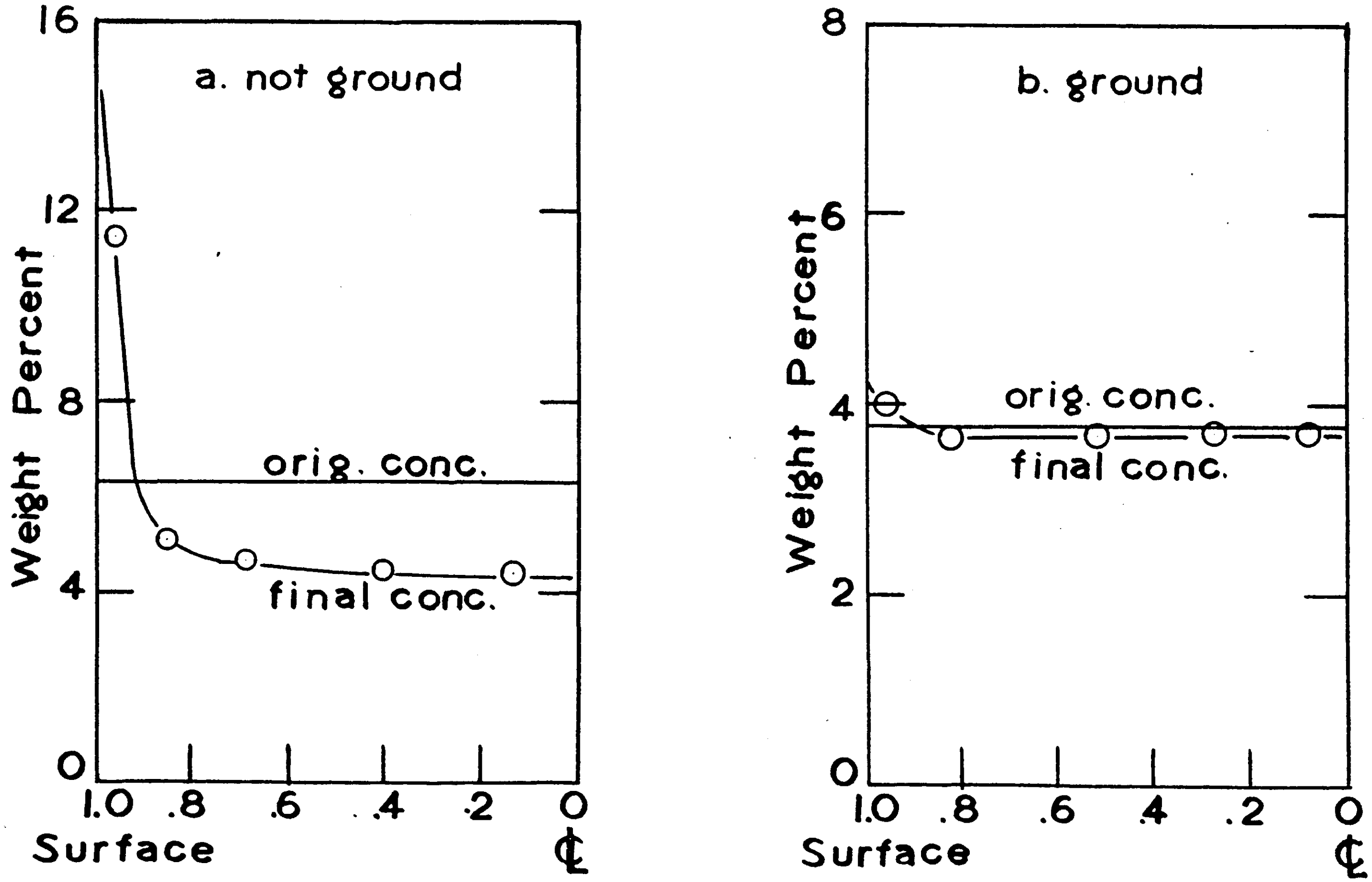


concentration is 0.79 for the unground material and 0.80 for the material ground 98 hours.

The original and final concentrations of mono-aluminum phosphate in the drying samples show significant differences between the ground and unground materials (Fig. 18). While the unground material shows considerable bond migration and surface deposition the material ground 98 hours shows very little migration and no appreciable surface deposition. The ratio of final minimum concentration to the original concentration was 0.72 for the unground material and 0.97 for the ground material.

The differences between the ground and unground material with mono-aluminum phosphate, and between sodium chloride and mono-aluminum phosphate are the result of phosphate adsorption by the clay material. With the unground material having an adsorption of 9.6 meq. per 100 gm. the ratio of phosphate added to phosphate adsorbed equals 6.2, and fraction of phosphate adsorbed is not high enough to significantly affect the migration tendencies. However, with ground material having an adsorption of 92.5 meq. per 100 gm., the ratio of phosphate added to that adsorbed is 0.39, and almost no migration takes place. The final minimum concentration is 97% of the original concentration, no surface deposition takes place, and the rate of drying is not greatly altered from that of water.

Fig. 18. - Migration of mono-aluminum phosphate in natural and ground clay.



VII. REFRACTORY MORTARS.

A. Mortar Tests.

Various tests for refractory mortars have been well thought out by previous investigators and applied to a number of commercial mortars. Tests on mortar prepared with phosphate bonds have closely followed this previous work.

In general, the best tests for mortars are simulative tests or tests which closely resemble actual operating conditions. For example, a P.C.E. determination on an air-dried mortar may vary for a given sample by as much as six or seven cones. Such variation occurs not only between laboratories but also in a given laboratory.[85] Tests employed are in general an attempt to measure strengths, shrinkage and cracking, workability and water retention, and fusion properties.

Two types of strength measurements have been made; either of neat mortar bars or of bonded joints. There is a reasonably good correlation between the strength of bars and bonded joints for dry-mix mortars.[86] There is poor correlation for wet mix mortars[87] (Fig. 19 and Fig. 20). For the variation with strength with temperature, neat mortar bars do not necessarily vary in the same manner as the bonded joints.[87] These results may be due to the fact that mortars may weaken or strengthen the portions of brick adjacent to the bond. In addition, the bond may separate rather than the mortar breaking. For this research, mortar bars have been prepared from varying compositions and the strength measured at room temperature. From these results, mortar compositions for more extended tests have been chosen. These were formed into 1/16" joints with a high heat duty stiff mud fire clay brick (Empire S.M., A.P. Green Co.). Transverse strengths of these bonded bricks were measured after heating at 105°, 750°, 1200° and 1500°C. The 1/16" bonds were formed

Fig. 19. - Bar and bonded brick strength of commercial dry type mortars.

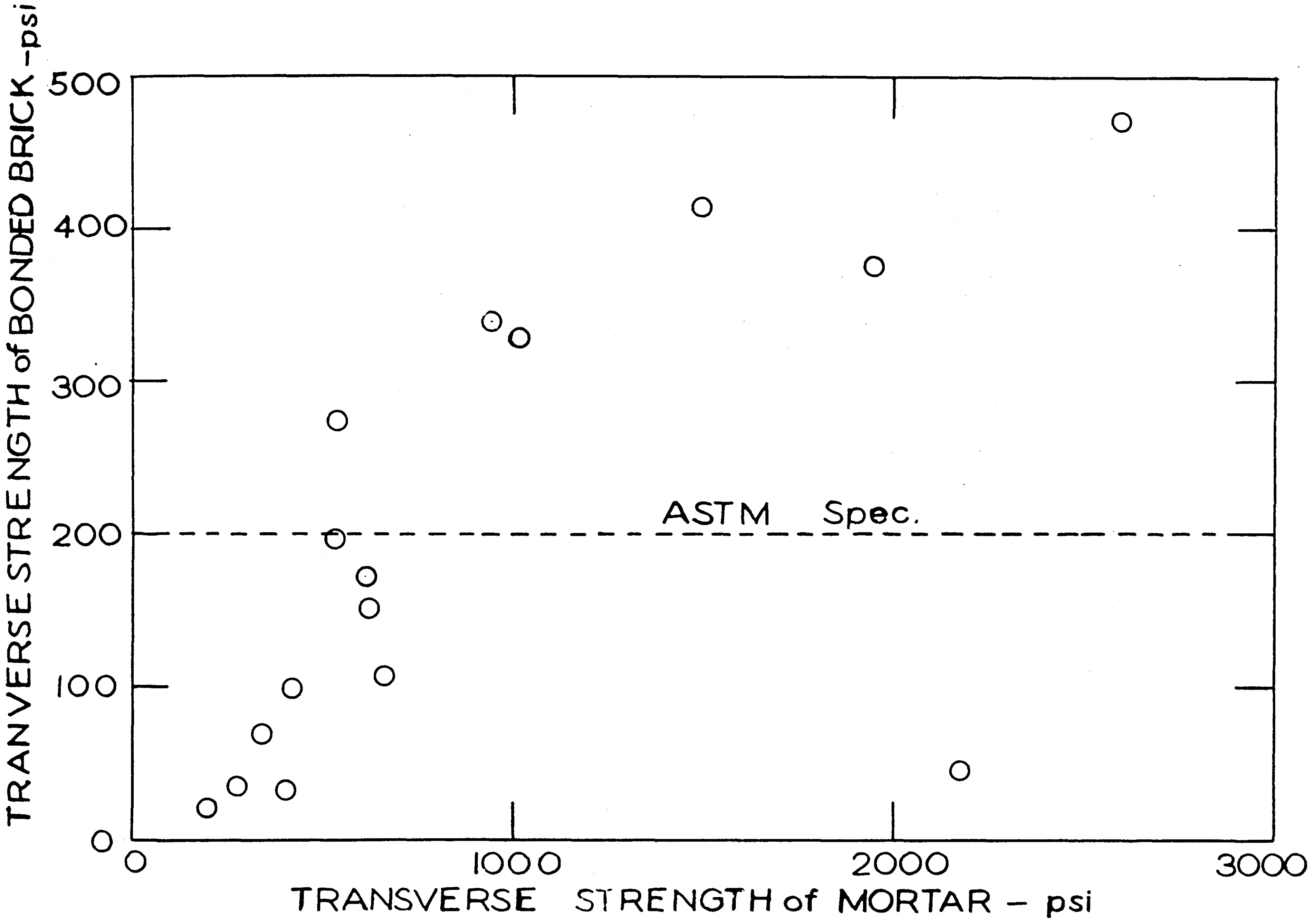
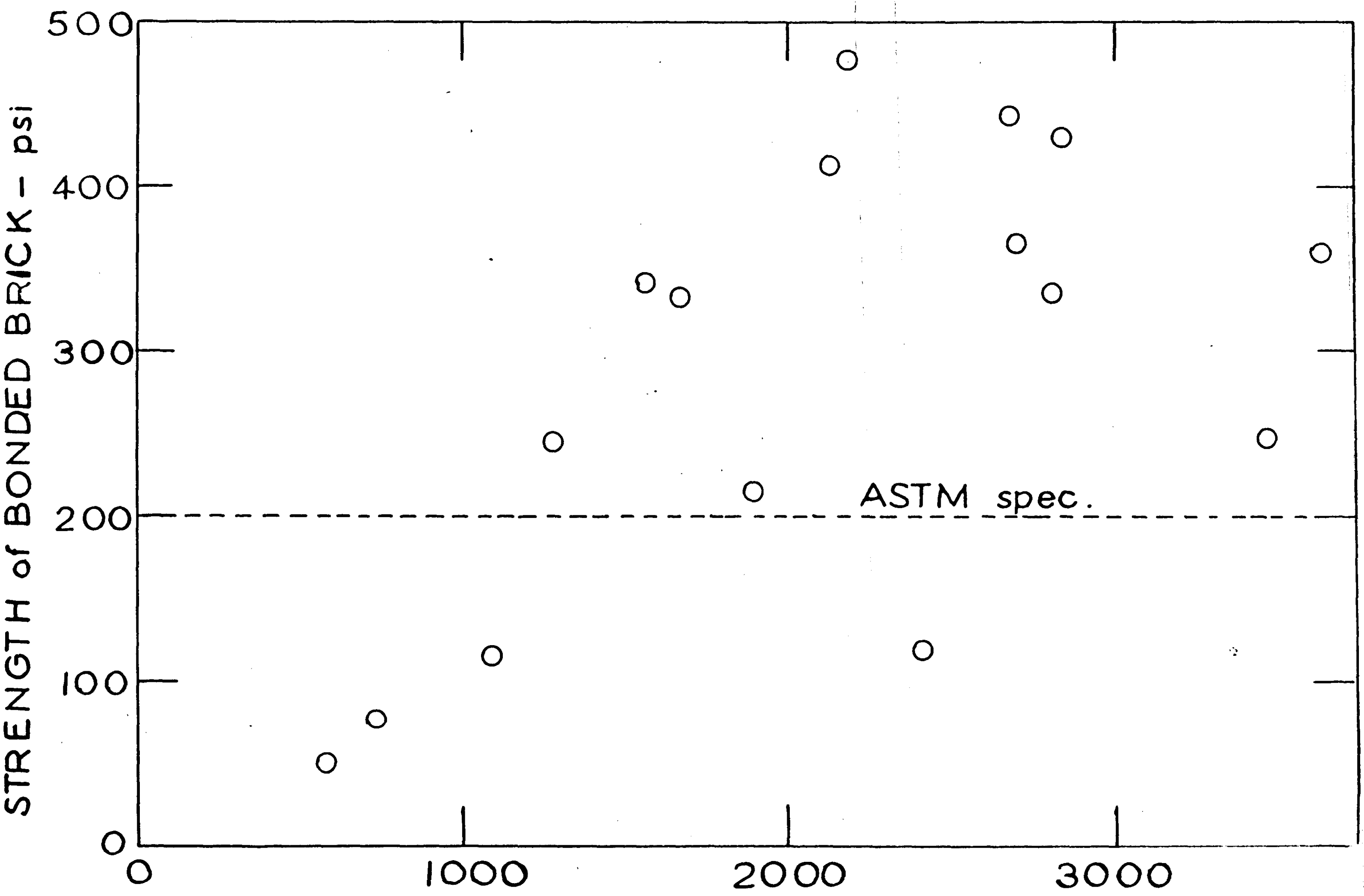


Fig. 20. - Bar and bonded brick strength of commercial wet type mortars.

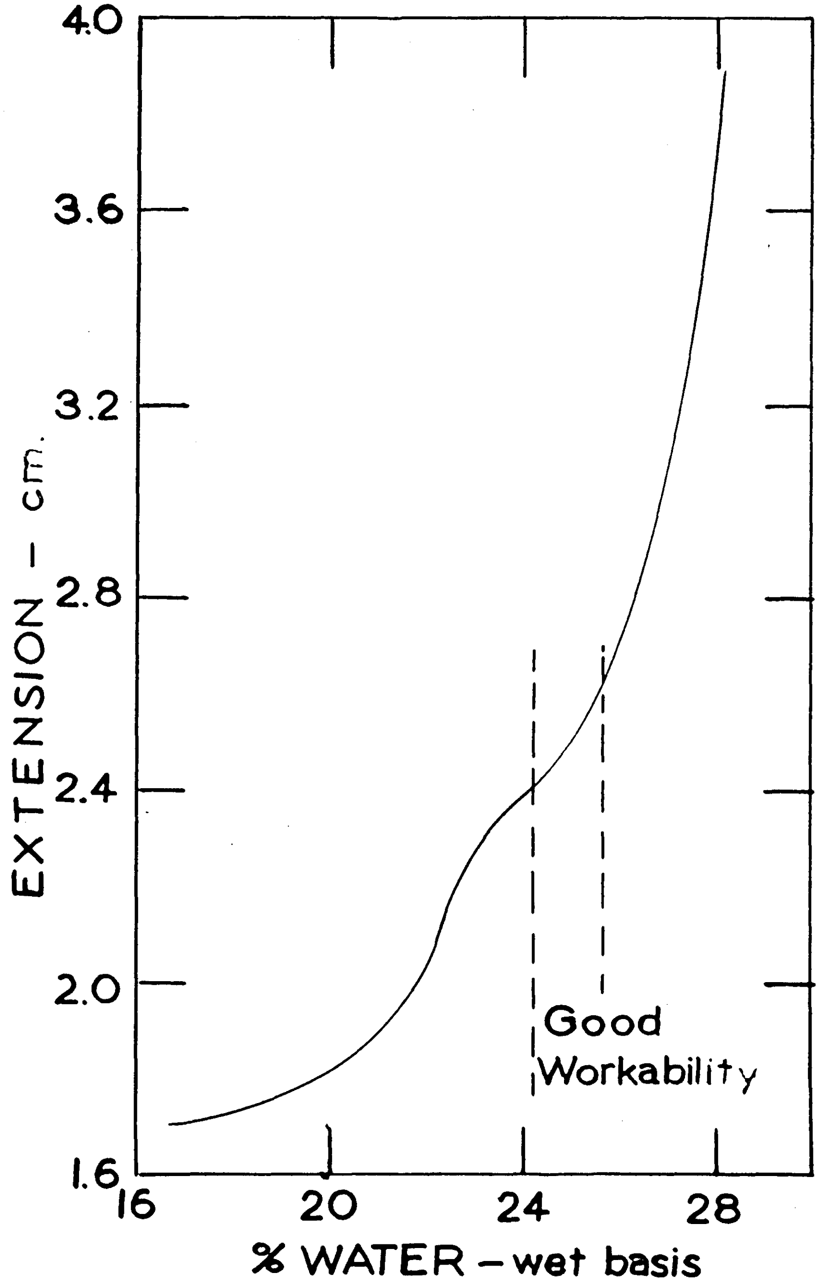


with 1/16" drill rod spacers in accordance with A.S.T.M. specification C198-47 and broken across a 7 inch span. After drying at 110° overnight, the assemblies were heated at the higher temperatures for five hours in each case.

Testing of shrinkage and cracking was made in neat mortar bars, bonded joints, mortar caps, and fusion blocks. The refractory fusion blocks (obtained from the Washington Porcelain Co.) having a cavity 1/2" deep was prepared with the mortar for testing. Length changes were made on neat mortar bars after drying at 105°C and heating to the higher temperatures. Bonded joints were observed for any signs of cracking. Mortar caps were prepared of about 1/16" thickness and observed for cracking or curling at various temperatures.

Workability is a singularly difficult property to define and measure quantitatively. Although the Bureau of Standards had developed a troweling machine,[87] this is not felt to be much of an advantage over qualitative estimation. The maximum diameter spread of two grams of the mortar (Fig. 21) under a 200 gm. load was found to be 2.5 cm. at the point of best workability. For consistency, all mortars were prepared to this consistency. The ability of remaining workable after being applied to the brick is important. Cements which become short, sandy and thick when applied to brick are difficult to trowel and often make it impossible to lay up the desired "thin joint". This is due to the adsorption of water from the mortar by the brick. The water retention test for this property[85] consists of preparing a 1/4" joint with two silica half brick by using 1/4" square metal rods parallel to the 2 1/2" edge. The spacers are removed and a load of 2 psi applied after a given time. The maximum time at which the mortar is squeezed out of the joint measures the water retention. Silica brick are used as they give more reproducible results than fire brick.[88]

Fig. 21. - Consistency evaluation of mortars. Extension of 2.0 grams under a load of 200 grams is plotted against the water content of the mortar.



Fusion tests of the neat mortar or PCE tests of the mortar are of little value since reproducible results are difficult to obtain and since reaction of the mortar-brick interface at high temperatures may alter the fusion point considerable. Consequently no PCE tests have been made. Mortar joints, mortar caps and fusion blocks were examined for flow and glassiness at 1500°C. This is the refractory specification suggested by Phelps.[85]

B. Mortar Compositions.

In order to choose suitable compositions with which to work, a series of mortars were prepared with k-80 grog, Florida kaolin and a mono-aluminum phosphate bond. As shown in Fig. 22 and Fig. 23, the bond strength is almost unaffected by clay additions between 10 and 30% while less than 10% clay decreases bond strength rapidly. Since the shrinkage of the 30% clay composition was only about 5%, which is satisfactory, and workability was good for the range 20-30% clay, it was decided to use about 25-30% clay. Variations of the amount of bond used increased strength about linearly to a value of 1000 psi at 12 1/2%. Data for commercial bonds indicated that a bar strength of about 750 psi would give satisfactory bonded strength.

Five different bonds were tested. These were bonded with mono-aluminum phosphate and mono-magnesium phosphate as indicated below:

Mortar	Bond
A	$Al(H_2PO_4)_3$ solution, wet mix
B	$Al(H_2PO_4)_3$ solid, dry mix
C	$MgO\ 1.1\ P_2O_5$ solution, wet mix
D	$Mg(H_2PO_4)_2$ solid, dry mix
E	$Al(H_2PO_4)_3$ solution, wet mix prepared with ground clay.

Fig. 22.- Effect of clay additions on mortar tranverse strength. Modulus of rupture determined on neat mortar bars of varying composition.

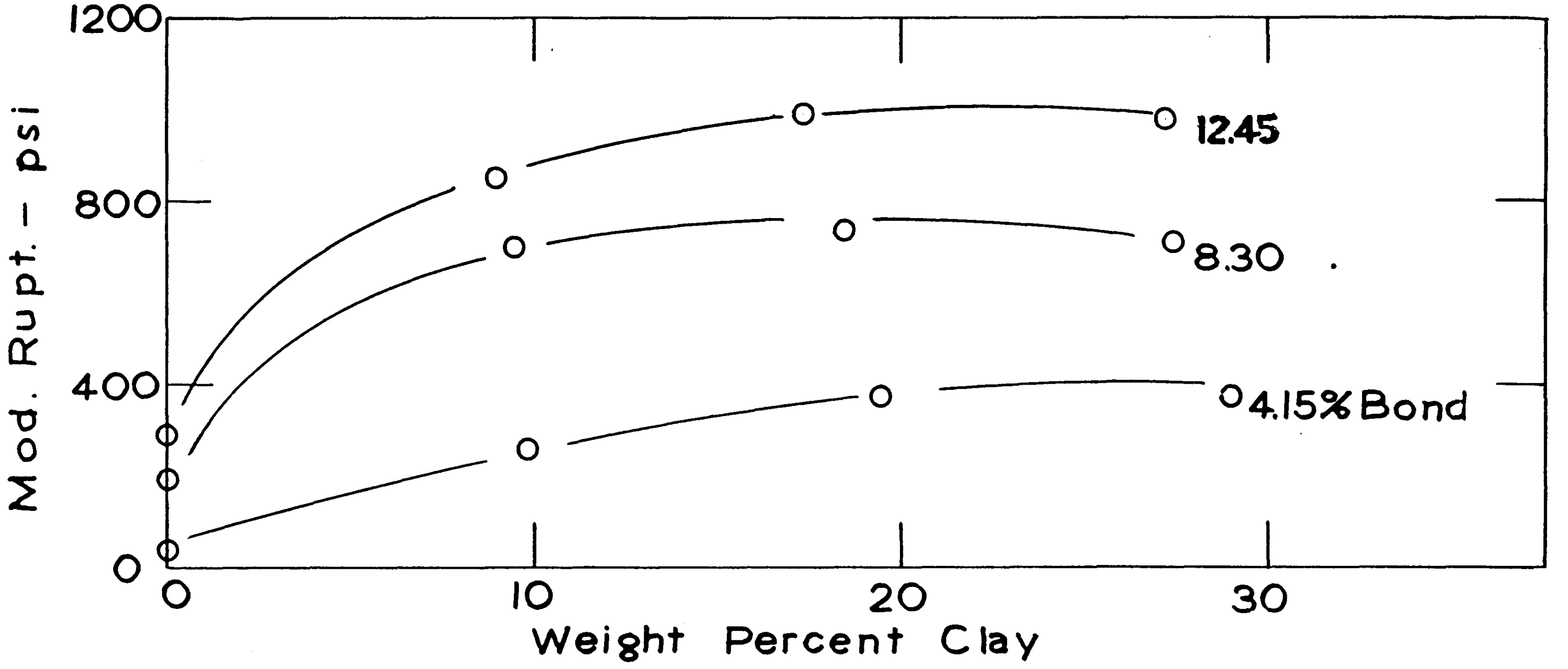
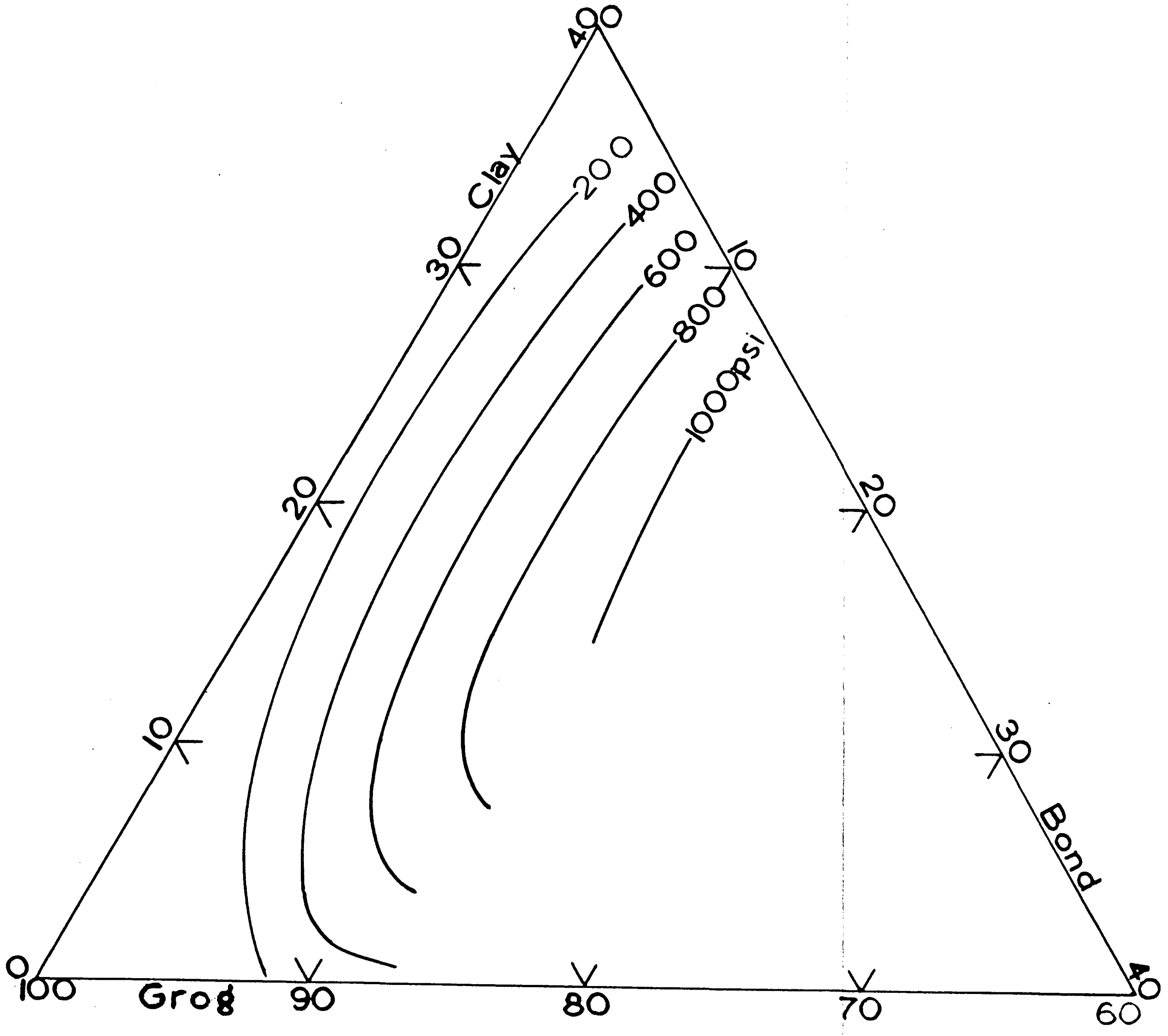


Fig. 23. - Effect of composition on bond strength. Modulus of rupture determined for neat mortar bars as a function of composition.



Mixtures of the grog with 20% clay were prepared with various percentages of each mortar bond. Bars were prepared and the mortar strength determined (modulus of rupture). Results obtained are shown in Fig. 24. From these results it was decided that 8% of each bond would give satisfactory and comparable results.

The grog used in these mortars was B & W K-80 ground to pass a 40 mesh screen. The grog size distribution is shown below:

Screen	Weight Percent Retained
40	0
65	36.8
100	61.4
150	65.3
200	84.3

From the tests just described, compositions were prepared for testing as mortars. Mortar compositions used are indicated in Table II. Tests employed included working properties, water retention, appearance of mortars in joints, as caps and in fusion blocks at various temperatures and strength and shrinkage of mortar bars and bonded assemblies at various temperatures.

The workability of all mortars was qualitatively judged to be satisfactory and all mixed easily to a homogeneous mortar. Dipping consistency was obtained easily and no settling was observed at dipping consistencies. The water retention was tested with three bricks of varying porosity. A high heat duty fire clay brick having an apparent porosity of 8.6%, a silica brick having an apparent porosity of 23%, and an insulating brick (K-28) having an apparent porosity of 59% were used. All mortars were satisfactory in each test. However, the mortar prepared with ground clay was found to have lower water retention than the others.

Fig. 24. - Effect of bond additions on mortar strength. Transverse strength of neat mortar bars containing various amounts of the bonds tested.

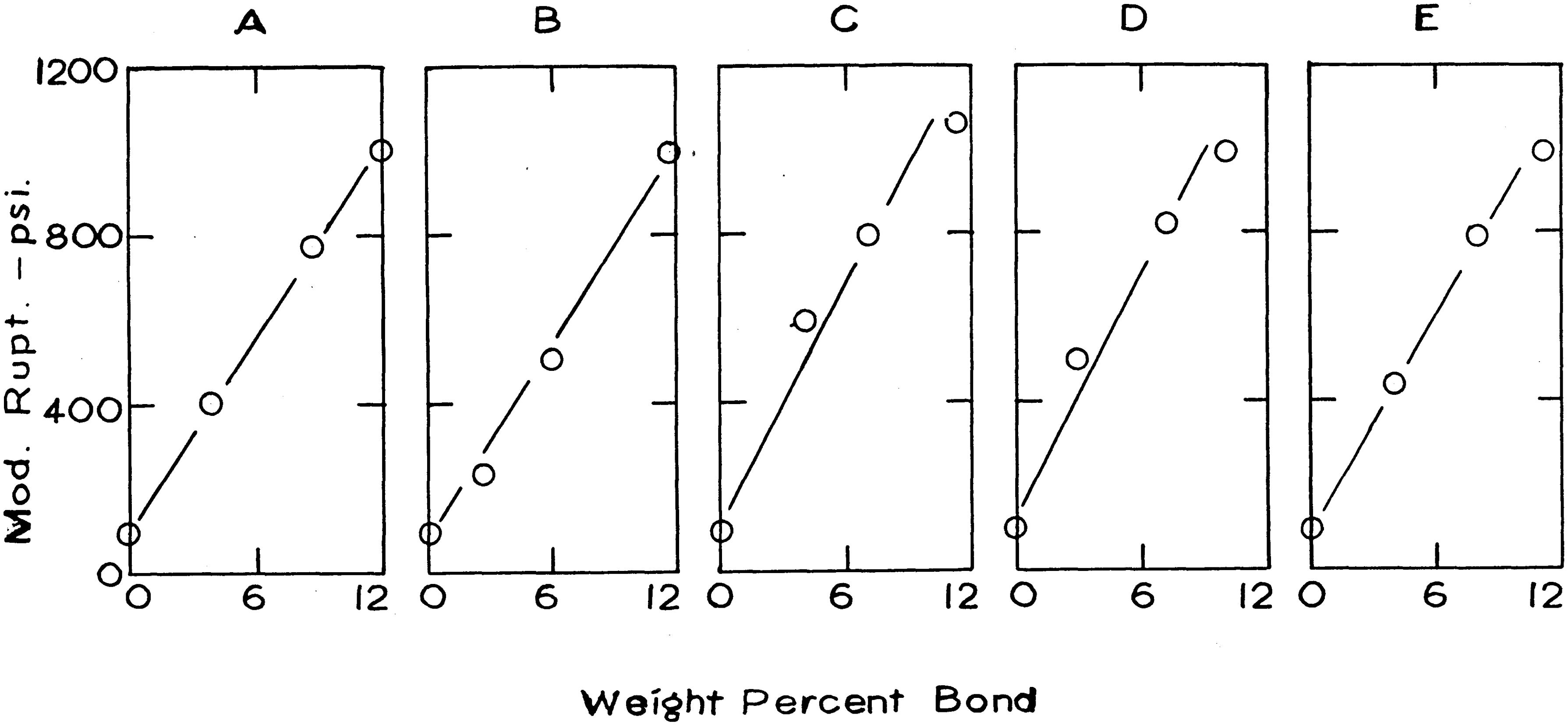


TABLE II

Mortar Compositions Tested

Mortar	Weight Percent		
	Grog	Flor. Kaolin	Bond
A	65	27	8 $Al(H_2PO_4)_3$ solution, wet type
B	65	27	8 $Al(H_2PO_4)_3$, dry type
C	65	27	8 $MgO.1.1P_2O_5$ solution, wet type
D	65	27	8 $Mg(H_2PO_4)_2$, dry type
E	65	27#	8 $Al(H_2PO_4)_3$ solution, wet type

Ground 100 hours.

A value of only two minutes was found with the K-28 test. Results of these tests are shown in Table III.

The appearance of the mortars in joints, as caps and in a fusion block are listed in Table IV. All results were good except that the mortar prepared with ground clay showed cracking and warpage in the cap and non-adherence in the fusion block. This is due to the larger shrinkage of this mortar and the lack of bonding due to decreased phosphate migration. These results would indicate that a certain amount of bond migration is desirable in order to bond firmly the brick and mortar.

Results of shrinkage measurements and transverse strength measurements are shown in Table V. The setting shrinkage of compositions A, B, C and D is about 5% or within the limit felt desirable. Due to the use of ground clay, the shrinkage of mortar E is about 8% which is high and results in the warpage and cracking found in the mortar cap, and shrinkage in the 1/2" fusion block. The shrinkage however, resulted in no visible cracks in the 1/16" mortar joints. Shrinkage and expansion on heating is low except for the magnesium bonds at 1500°C and the ground clay mortar at 1500°C. In the magnesium bond incipient fusion occurs at this temperature as shown by a slight slumping of the mortar bar. The joint however, shows no flow at this temperature, and for mortar purposes the bond is satisfactory.

Mortar bar strengths at room temperature are low compared to satisfactory commercial mortars; bonded joint strengths are high. At higher temperatures strengths remain high in contrast to the majority of commercial mortars. The magnesium phosphate bonds begin to fuse at temperatures of about 1500°C and therefore high strengths are achieved. Since the aluminum phosphate is higher melting, strengths remain moderate at 1500°C.

The samples prepared with ground clay show lower strengths for

TABLE III

Working Properties of Phosphate Mortars

Mortar	Troweling Consistency				Dipping Consistency	
	Workability	Water Retention (minutes)				
		Silica Brick*	K-28**	Stiff Mud***	Obtained Easily	Settl.
A	good	11	7	19	yes	no
B	good	9	6	18	yes	no
C	good	10	6	17	yes	no
D	good	9	6	20	yes	no
E	good	5	2	10	yes	no

* 23% apparent porosity

** 59% apparent porosity

*** 8.6% apparent porosity

TABLE IV

Appearance of Mortar on Heating

Mortar	1/8" Mortar Cap		1/16" Joint		Fusion Block	
	105°	750°, 1200°, 1500°	105°	750,1200,1500°	105°	750°,1200
A	good, no cracks adherent	same as 105°	good, no cracks	same as 105°	good,mod. shrinkage	same as 105°
B	"	"	"	"	"	"
C	good, few small cracks, adherent	"	"	"	"	"
D	good, no cracks adherent	"	"	"	"	"
E	cracks and warpage, 35% not adherent	"	"	"	no adherence	"

TABLE V

Strength and Shrinkage on Heating

Mortar	Transverse Strength of Bar , 105°C p.s.i.	Transverse Strength of Bonded Half Brick*, p.s.i.				Length Changes of Mortar Bar**, percent.			
		105°***	750°	1200°	1500°	105°	750°	1200°	1500°
A	705	240	225	285	540	4.3	+1.4	+1.4	-1.7
B	685	260	210	380	755	4.9	+1.4	+1.2	-1.2
C	805	285	265	375	1150	4.9	-0.5	-0.8	-3.5
D	875	250	190	300	690	5.1	-0.3	-0.6	-3.0
E	760	185	100	50	410	8.0	+0.3	-1.1	-4.8

* Strength of brick used was 1200 p.s.i.

** 105° value is drying shrinkage; other temperatures are length changes after heating, "+" = expansion.

*** A.S.T.M. specification for cold set strength is 200 p.s.i.

the bonded brick at all temperatures due to the lack of any bond migration. While bars of this mortar are strong it forms a poor bond due to lack of adhesion between bond and brick.

VIII. DISCUSSION OF RESULTS

A. Results.

A study of the literature indicated that phosphate bonding materials have been utilized by three methods. Siliceous material forms a bond with phosphoric acid. (For refractory applications, heat treatment is generally necessary for the development of any considerable strength.) Certain oxides have been reported to react with phosphoric acid to form bonds - usually at somewhat elevated temperatures. And certain acid phosphates have been utilized as refractory bonds. Except for dental cements, no data regarding bonding reactions and bond mechanism are available. References in the literature to the bonding mechanism in refractory phosphate bonds are universally vague. The properties of refractory bonds employing phosphates have not been systematically studied and the only data available is for the addition of metaphosphates to fire clay mortars. In addition, many of the claims in patent literature with regard to phosphate bonds are misleading. The only work reported in the general literature is either uninformative or misinforming.

From a systematic study of a large number of cold-setting phosphate reactions, a considerable group of data has been determined. It was found that cold-setting bonds may be formed by many cations by oxide-phosphoric acid reactions, by phosphate-phosphoric acid reactions, or by the direct use of liquid phosphate bonds. For oxide-phosphoric acid reactions to form bonding materials a weakly basic or amphoteric cation is required since excess basicity causes violent reactions and acidic or inert materials show no reaction. In all cases, bond formation was found to be due to the formation of acid phosphates. For optimum bond strength a weakly basic cation having a moderately small ionic radius is requird so that a non-ordered structure can be formed.

The setting process of a liquid phosphate bond on drying was determined by measuring the viscosity as a function of concentration. The effect of temperature on viscosity was also determined. On heating a phosphate bond, the effect of temperature on strength was determined. In contrast with most other bond materials no weak zone was found. A study of rate of weight loss, equilibrium compositions, x-ray diffraction patterns and differential thermol analysis data indicated that this is probably due to the gradual loss of "combined" water and the gradual crystallization of the dehydration products which also act as bonds.

An investigation of the adsorption of a phosphate bond material by clay indicated that Florida plastic kaolin adsorbed 13.3 meq. per 100 grams and North Carolina kaolin adsorbed 9.6 meq. per 100 gm. Time, solution concentration and pH were found to have little effect on phosphate adsorption in the ranges investigated. Ball milling reduced the particle size of clay and increased the phosphate adsorption. Phosphate adsorption of ground clay is greater than that of unground clay of the same particle size. Phosphate adsorption was found to follow an equation of the type: $(\text{adsorption}) = k\ (\text{particle size})^{-n}$, indicating that phosphate adsorption is a phenomenom of surface adsorption.

The rates of drying and migration of water, sodium chloride solutions and mono-aluminum phosphate solutions were determined for unground clay and for clay ground 98 hours. The final salt concentration and rate of drying of sodium chloride is similar for ground and unground material. Mono-aluminum phosphate with unground clay showed drying and migration properties similar to sodium chloride. However, mono-aluminum phosphate with ground clay having high adsorption capacity showed almost no salt migration, a rate of drying like that of water, and no surface deposition of mono-aluminum phosphate.

On the basis of bonding mechanism, bond properties and some preliminary tests of strength and workability five mortar compositions were prepared. Two of these were prepared with magnesium phosphate bonds and three with aluminum phosphate bonds. Three were the wet-type and two were the dry-type. One was prepared with ground clay. Standard mortar tests indicated that these bonding materials form mortars superior to those in general commercial use, and having fully satisfactory properties. The use of ground clay, however, was found to be detrimental since the prevented migration decreases bonding between brick and mortar.

B. Future Work.

Results of this investigation suggest some possibilities for future study. Those that seem probable of leading to useful information are:

(1) Study of properties of refractory plastics bonded with phosphate materials.

(2) Study of properties of refractory unfired brick bonded with phosphate materials.

(3) Detailed study of salt migration in ceramic materials along the lines of the work reported here for phosphate bonds, except that a detailed investigation of the complete process and an application of diffusion and precipitation factors in the process should be undertaken.

(4) A study of the exact effects taking place on grinding or milling of ceramic materials would be useful. This should include the effects of both wet and dry grinding and a study of the resulting particle shape and size distribution. The application of the election microscope to this problem would be enlightening.

IX APPENDIX

A. Oxide - Phosphoric acid Reactions.

Data obtained for reactions of oxides with phosphoric acid included time of setting, temperature rise on setting, transverse strength (modulus of rupture) of the reaction product, the reaction product reported in the chemical literature, and other observations such as the nature of the product, the nature of the reaction and x-ray diffraction results. These data are tabulated in the following pages (Table VI).

TABLE VI

OXIDE REACTIONS WITH PHOSPHORIC ACID

Oxide	Time of Setting	Reaction Temp. Rise °C for 0.5 cc	Mod. of Rupt. (psi)	Product Reported in Chemical Literature	Other Data and Observations
BeO	2 min	15	750	$Be(H_2PO_4)_2$[89] $Be(H_2PO_4)_2.BeHPO_4$[89]	x-ray data shows amorphous product
$Be(OH)_2$	2 min	18	570	"	---
MgO	not set	30	---	$MgHPO_4;Mg(H_2PO_4)_2$[90]	violent reaction
$Mg(OH)_2$	not set	--	---	"	"
MgO calcined 1280°C	2 min	25	500	"	x-ray data shows MgO and weak $Mg(H_2PO_4)_2$
CaO calcined 1100°C	not set	--	---	$Ca(H_2PO_4)_2.xH_2O$[91]	violent reaction
CaO calcined 1100°C; liq. 9.6% CaO	12 hr	24	520	"	x-ray data shows crystalline product
SrO calcined 1400°C; liq. 9% SrO	not set	--	---	---	violent reaction
BaO calcined 1400°C; liq. 9% BaO	not set	--	---	---	violent reaction
CuO	3 hr	6	570	$CuHPO_4.H_2O$[92]	---
Cu_2O	3 min	8	510	---	---

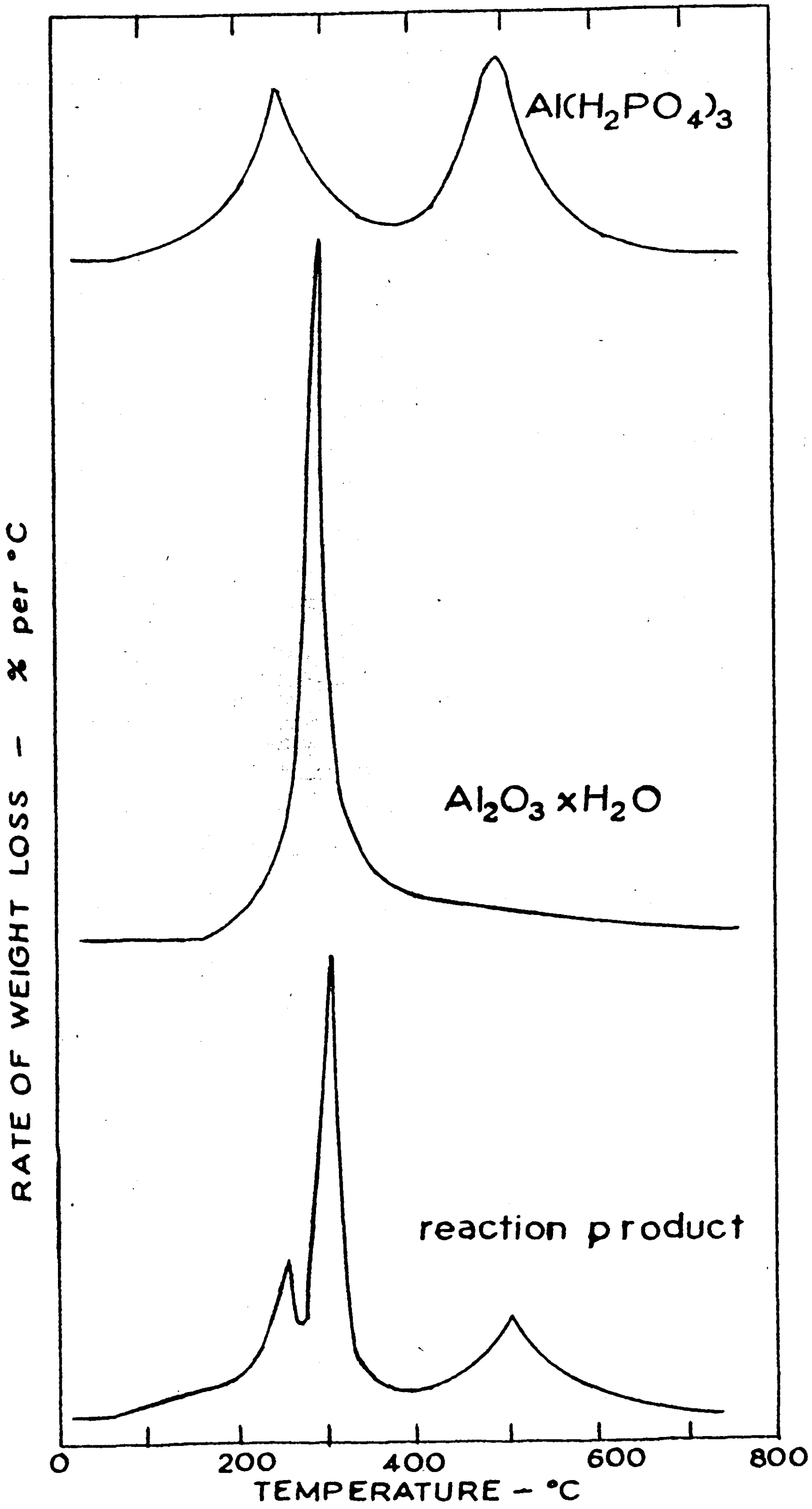
Oxide	Time of Setting	Reaction Temp. Rise °C for 0.5 cc	Mod. of Rupt. (psi)	Product Reported in Chemical Literature	Other Data and observations
CdO	30 min	15	700	$Cd(H_2PO_4)_2$[93]	x-ray data shows crystalline product; absence $Cd_3(PO_4)_2$
ZnO calcined 1100°C	3 min	27	850	$ZnHPO_4.3H_2O$[94]	x-ray data shows crystalline product; absence $Zn_3(PO_4)_2.0,2,4$ H_2O
SnO	3 hr	3	100	$SnHPO_4$[95]	---
SnO_2	no reaction	0	---	---	---
HgO	not set	23	---	$Hg_3(PO_4)_2$[96]	x-ray data shows $Hg_3(PO_4)_2$
Hg_2O	not set	24	---	Hg_3PO_4[96]	x-ray data shows Hg_3PO_4
NiO	no reaction	0	---	---	---
PbO	not set	7	---	$Pb_3(PO_4)_2$[97]	x-ray data shows $Pb_3(PO_4)_2$
PbO_2	no reaction	0	---	---	---
Pb_3O_4	1 min	38	---	$Pb(H_2PO_4)_4$[98]	cracked on setting; x-ray data shows crystalline product containing $Pb_3(PO_4)_2$, PbO_2 absent
B_2O_3	not set	5	---	H_2BO_3[99]	---

Oxide	Time of Setting	Reaction Temp. Rise °C for 0.5 cc	Mod, of Rupt. (psi)	Product Reported in Chemical Literature	Other Data and Observations
Al_2O_3	no reaction	0	---	---	---
$Al_2O_3.xH_2O$	24 hr.	1	1260	$Al(H_2PO_4)_3$[100]	x-ray data shows amorphous product.
Co_2O_3	no reaction	0	---	---	---
$Cr_2O_3.xH_2O$	no reaction	0	---	---	---
Fe_2O_3	72 hr	2	---	$FeH_3(PO_4)_2.2\frac{1}{2}H_2O$[101] $Fe(H_2PO_4)_3$	tacky product
Fe_3O_4	1 min	36	300	---	---
La_2O_3	1 min	--	---	$La_2(HPO_4)_3$[102]	violent reaction
La_2O_3 calcined at 1400°C	10 min	18	400	"	---
SiO_2	no reaction	0	---	---	---
H_2SiO_3	no reaction	0	---	---	---
TiO_2	no reaction	0	---	---	---
$Ti(OH)_4$	12 hr	2	200	$TiOHPO_4$[103]	---
ZrO_2	no reaction	0	---	---	---
$Zr(OH)_4$	18 hr	5	250	$Zr(HPO_4)_2$[104]	---
ThO_2 from $Th(NO_3)_4$ at 300°C	48 hr	2	---	$Th(HPO_4)_2.H_2O$[105]	tacky product

Oxide	Time of Setting	Reaction Temp. Rise °C for 0.5 cc	Mod. of Rupt. (psi)	Product Reported in Chemical Literature	Other Data and Observations
CeO_2	no reaction	0	---	---	---
V_2O_5	10 min	30	180	$VO_2H_2PO_4 \cdot 4\frac{1}{2}H_2O$	---
$CrO_3 \cdot xH_2O$, MoO_3 $WO_3 \cdot xH_2O$	no reaction	0	---	---	---

Appendix B:

Fig. 25. - Continuous rate of weight loss on heating momo-aluminum phosphate, hydrous alumina and the product of reaction between hydrous alumina and phosphoric acid.



C. Phosphate - Phosphoric Acid Reactions.

TABLE VII

Phosphate	Reaction Temp. Rise (°C for 0.5cc)	Nature of Product
$Mg_3(PO_4)_2$	7	Glue-like, set hard overnight.
$Zn_3(PO_4)_2$	5	"
$Ca_3(PO_4)_2$	12	hard, tacky.
$CaHPO_4$	10	"
$AlPO_4$	4	"
$Pb_3(PO_4)_2$	3	hard, brittle.

D. Typical Phosphate Adsorption Calculation:

Adsorption of $Al(H_2PO_4)_3$ by Florida kaolin:

To 10.00 grams of clay added 40.0 ml. of approximately 2% solution of mono-aluminum phosphate. After shaking mechanically, separate solid in centrifuge. Take 5.00 ml. and dilute to 100.0 ml.; then take 10.0 ml. of diluted aliquot (equivalent to 0.50 ml. of sample) and also take a similar sample of the original solution. Analyse for phosphorous content by precipitation of ammonium phosphomolybdate and titration with sodium hydroxide.

Dilute sample to 100 cc, add 5% HNO_3 and 5% NH_4NO_3. Heat to 30 - 40°C, add molybdate reagent, shake vigorously for 5 minutes and let stand 30 minutes. Filter on S&S blue line paper and wash thoroughly with potassium nitrate solution. Dissolve ppt. in 0.1 N NaOH, add 2 ml. excess and dilute with water. Add phenolphthalien indicator, discharge color with HCl and finish titration to endpoint with NaOH. (W. F. Hillebrand and G. E. F. Lundell, "Applied Inorganic Analysis", p 560, John Wiley & Sons, N. Y.,1946).

Phosphorous content is determined by the reaction:

$$(NH_4)_3PO_4.12MoO_3 + 23\ NaOH =$$

$$11\ Na_2MoO_4 + (NH_4)_2MoO_4 + NaNH_4HPO_4 + H_2O$$

Data:

		Original	Sample
Meq. NaOH		2.63	2.26
		2.65	2.24
		2.64	2.24
	mean =	2.64	2.25

Calculation:

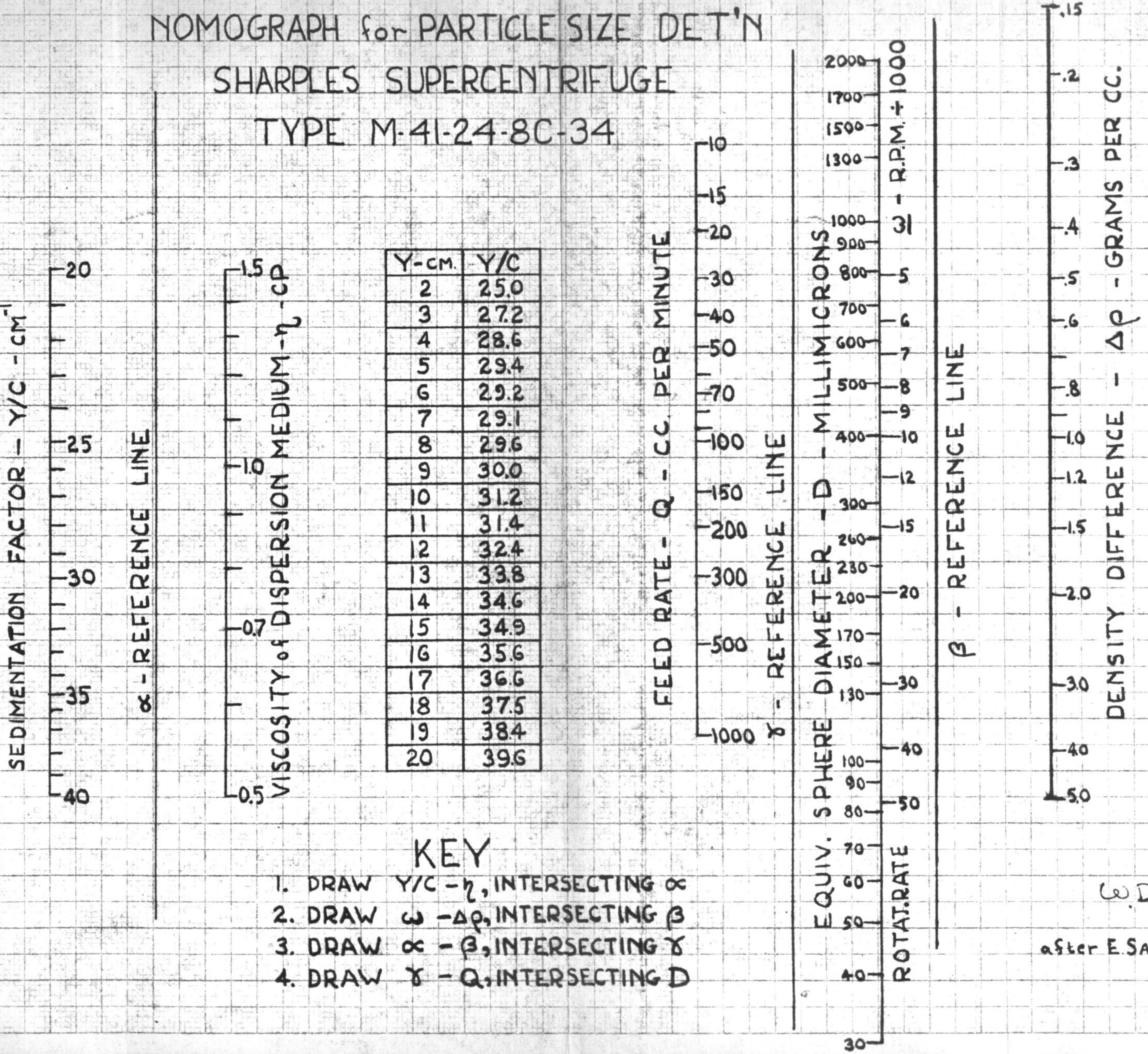
	Original	Adsorption Sample
Meq. NaOH	2.64	2.25
x 1/23 = meq. $(H_2PO_4)^-$ in 0.50 ml.	0.1150	0.0978
x 200 = meq. in 100 ml.	23.0	19.6
Difference = meq. ads. on (10 x 100/40) or 25 gm. clay		3.4
x 4 = meq. ads./ 100 gm.		= 13.6 meq./100gm.

Meq. wgt. of $Al(H_2PO_4)_3$ = 0.106

13.6 x 0.106 = 1.44 gm./100gm.

Fig. 26

NOMOGRAPH for PARTICLE SIZE DET'N
SHARPLES SUPERCENTRIFUGE
TYPE M-41-24-8C-34



Y-CM.	Y/C
2	25.0
3	27.2
4	28.6
5	29.4
6	29.2
7	29.1
8	29.6
9	30.0
10	31.2
11	31.4
12	32.4
13	33.8
14	34.6
15	34.9
16	35.6
17	36.6
18	37.5
19	38.4
20	39.6

KEY

1. DRAW Y/C – η, INTERSECTING α
2. DRAW ω – Δρ, INTERSECTING β
3. DRAW α – β, INTERSECTING γ
4. DRAW γ – Q, INTERSECTING D

W.D.K.

after E. Saunders, Anal. Chem. 20, 379 (1948)

F. Details of Mortar Testing.

Neat mortar bars were prepared in brass molds ½ x ¼ x 6 inches in length. The mold was set on paper, mortar inserted and smoothed with a spatula. After a few minutes the mortar set enough so that the mold could be removed with the aid of a razor blade. After a few hours the mortar was hard enough so that the paper could be stripped off the bottom. Bars were dried at room temperature for 24 hours and at 105°C for 24 hours. After drying the modulus of rupture was determined across a 3 inch span.

Mortar consistency was determined by measuring the spread of 2 grams of the wet mortar after one minute under a weight of 200 grams. A spread of 2.5 cm. was found to be satisfactory. Mortars for other tests were prepared to this consistency. All mortars were mixed for ½ hour in a Lancaster mixer prior to use.

Water retention was determined by forming a ¼ inch bond between the 4½ x2½ in. faces of two half brick. The spacing was set by laying ¼" square metal rods along each 2½" edge. After adding the mortar, the top half brick was immediately set, excess mortar was removed and timing commenced. After the test time had elapsed, the spacers were removed and a twenty pound weight was placed on the assembly (2psi). The time of water retention is the least time found for the mortar not to flow from the joint when the weight is applied. Three types of brick were used. A high heat duty stiff mud fireclay brick - A. P. Green Co. Empire SM; a Silica brick - Harbison Walker Co. Star Silica; and an insulating brick - B&W K-28.

Fusion blocks were prepared with the regular mortar mix, dried and heated. The samples were then examined for shrinkage, cracks, glassiness, flow, etc. Mortar caps and the mortar in joints were similarly examined.

Mortar joints of 1/16 " thickness were formed with a high heat duty stiff mud fireclay brick by the standard ASTM method C 198 - 47 which consists of using 1/16 " drill rod as spacers. After heating to various temperatures these assemblies of two half brick and mortar were broken across a 7 inch span to determine modulus of rupture.

G. Cost Data.

It may be of interest to report costs of various mortar bonding materials. These are listed below. It may be seen that the phosphate materials are reasonably expensive, but not prohibitively so.

Material	Cost / 100 lb.*
$2Na_2O.SiO_2$ (anhydrous)	5.25
Sodium Silicate (40°)	1.10
Lumnite cement	3.40
$Mg(OH)_2$	29.00
$MgCl_2$	2.00
HCl (18°)	2.15
H_3PO_4 (85%)	5.50
$Al(H_2PO_4)_3$	17.00**
$Mg(H_2PO_4)_2$	32.00**

* June,1950, Ind. Eng. Chem.

** June,1950, Monsanto Chemical Co.

H. Biographical Sketch.

Wm David Kingery was born July 7, 1926 in New York City, the third son of Dr. and Mrs. L. B. Kingery. After attending and graduating from White Plains High School, White Plains, N. Y., in 1942 he attended the Taft School, Watertown, Conn. and graduated cum laude in 1943.

He entered M. I. T. in 1943, the recipient of a Freshman Regional Scholarship. After completing two years of study he entered the United States Naval Reserve. Subsequent to service as electronics technician aboard a radar test ship, E-LSM 445, he re-entered M. I. T. and received the degree Bachelor of Science in Chemistry in 1948.

Following completion of his undergraduate work he was accepted in the graduate division of ceramics at M. I. T. and awarded the American Refractories Institute Fellowship.

He is a member of the American Ceramic Society, the American Chemical Society and the Society of the Sigma Xi. Publications include a paper on a spectrophotometric study of bismuth thiocyanate complexes published jointly with D. N. Hume. (W. D. Kingery and D. N. Hume, Jour. Amer. Chem. Soc., 71, 2393 (1949)).

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XI ABSTRACT

The literature regarding phosphate bonding in refractories is reviewed. Except for dental cements, no data regarding the basic properties or setting mechanism of phosphate bonds are available.

Experimental data indicate that cold setting bonds may be formed from oxide- phosphoric acid reactions, phosphate- phosphoric acid reactions or by the direct addition of liquid phosphate bonds. In all cases acid phosphates are responsible for the bonding action. For optimum bonding a weakly basic or amphoteric cation having a moderately small ionic radius is required so that a non-ordered structure can be formed. The solidification process for a liquid phosphate bond has been determined. No weak temperature zone appears on heating because of the gradual loss of "combined" water and the gradual crystallization of the dehydration products.

The adsorption of momo-aluminum phosphate by clay and the slight effects of time, concentration and pH were determined. Ball milling was found to decrease particle size and increase adsorption. Mono-disperse fractions of ground clay adsorbed more phosphate than the same particle sizes of unground clay. Adsorption was found to be a surface adsorption. The rate of migration of mono-aluminum phosphate was profoundly affected by

the phosphate adsorption of clay.

Actual refractory mortars were prepared using phosphate bonds. Tests of these mortars indicated that they posess properties superior to most refractory bonding materials.