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PHOSPHATE-BONDED GLASS CEMENTS FOR GEOTHERMAL WELLS

FINAL REPORT

September 1979

Prepared by the
DEPARTMENT OF MATERIALS AND CHEMICAL ENGINEERING
UNIVERSITY OF RHODE ISLAND
KINGSTON, RHODE ISLAND 02881
Under Contract No. 418691-S
For the
PROCESS SCIENCES DIVISION

MASTER

DEPARTMENT OF ENERGY AND ENVIRONMENT

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK 11973

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ABSTRACT

Calcium aluminosilicate glasses were found to react with phosphoric acid in three ways depending upon silica content. Above 55% SiO_2 they are insoluble while below 50% they dissolve readily. The transition compositions release calcium and aluminum ions and a silica gel phase replaces the glass. Activation energies in the order of 10 kcal/mole are associated with the dissolution.

Equilibrium studies in the systems $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$, $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ and $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ were made to determine the phases which are stable at 200°C in excess water. The CaO system shows hydroxylapatite, monetite and monocalcium orthophosphate are the stable phases. The Al_2O_3 system contains augelite, berlinite and a high phosphate aluminum hydrate. The quaternary system shows the above phase plus a lime alumina hydrogarnet and crandallite.

Cement made from a glass frit of the composition 45% SiO_2 : 24% CaO : 24% Al_2O_3 has a compressive strength of 500 psi after several days in steam at 200°C and 800 psi after months in steam. Bonding of cements to mild steel are discussed.

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SUMMARY

Phosphate cements have been studied to determine if they have potential as a material for the construction of geothermal wells. The results show that there is potential for the development of a cement which would be stable to at least 400°C and which could be mixed and emplaced in the field. Cost estimates indicate that the cost of materials for the set cement will be about 43 cents per pound.

Phosphate cements are formed by mixing a glass with phosphoric acid. The glass supplies calcium and aluminum ions which react with phosphate groups to form a cement. Corrosion of glasses in phosphoric acid was studied to determine the compositional variables which could cause glass to form phosphate cements. The effect of temperature on corrosion rates was determined, as was the effect of phosphate concentration in the acids. Glasses with more than 55% SiO₂ were insoluble under all conditions and those with less than 50% silica were extremely soluble. At the transition compositions a silica gel phase forms on the glass surface. The corrosion behavior suggests that the glasses undergo phase separation on cooling with an inversion from a soluble to an insoluble matrix taking place near 50 wt% silica.

Equilibrium studies were completed to determine which phases form and are stable under geothermal conditions. With such knowledge a cement could be designed which would have such a phase as the cementing phase. The system CaO-P₂O₅-H₂O shows portlandite, hydroxylapatite, monetite, and monocalcium orthophosphate monohydrate as the stable phases. Under geothermal conditions, i.e. 200°C in water and steam, the system Al₂O₃-P₂O₅-H₂O has as stable phases boehmite, angelite, berlinite, and a high phosphate aluminum hydrate. The quaternary system CaO-Al₂O₃-P₂O₅-H₂O has the above phase crandallite.

A phosphate cement was examined for compressive strength after exposure to geothermal environments. This cement was made by mixing a glass powder of the composition 45 SiO₂: 7Na₂O: 24CaO: 24Al₂O₃ with various phosphoric acids. While the strength of one cement only about 500 psi, there was no loss in strength after exposure to geothermal environments. Tests on samples held for 72 days show continued improvement of strength (898 psi) indicating that long-term stability is possible. The same cement mixed differently shows strength of 1600 psi. Cement coatings were applied to steel to test compatibility. The major problem associated with adhesion is hydrogen evolution produced by corrosion of the steel at the cement interface. Proper surface treatments can overcome this problem. Filler can be added to the cement without serious degradation of properties, and this will have important implications for the economics of the cement.

The goals of this project were to develop a cement which would have a compressive strength in excess of 1000 psi 24 hours after emplacement, a permeability of 0.1 millidarcy, a bond strength to steel of at least 10 psi, prolonged stability at 400°C, a 3 to 4 hour setting retardation, pumpability

and compatibility with drilling muds and casing steel. While the research was directed at finding a composition which would give the above properties, most of the time was spent in developing the composition necessary to give an acceptable compressive strength. While some data was obtained on the cement steel bond and on the long term geothermal stability time did not permit the work necessary to address many of the area listed above. No data was obtained on pumpability or on permeability. While the data could have been obtained on some of the cement, it did not seem like a wise expenditure of time to obtain that data on cements shown to be unacceptable on the basis of setting time and compressive strength data.

PHOSPHATE-BONDED GLASS CEMENTS
FOR
GEOTHERMAL WELLS

Final Report

July, 1977 to August, 1979

I. INTRODUCTION

The results reported here are from research carried out at the University of Rhode Island under the direction of the Process Sciences Division of Brookhaven National Laboratory for the Geothermal Energy Division of the Department of Energy. The goal of the program was to obtain basic information regarding phosphate cements to determine if they have potential as a cementing material for use in geothermal wells where the cement must be emplaced in severe environments where the normally used well cements might deteriorate. The properties needed in such a cement are compressive strengths of 1000 psi, permeability of 0.1 milli Darcy, some bond strength to steel, long term stability in geothermal environment, and compatibility with steel drilling muds.¹

There are two types of phosphate cements: (1) the refractory ceramic cements and ramming mixes²; and (2) the dental phosphate cements (often referred to as silicate cements) which are used as restorative materials and cap cements.³ Both cements form as the result of the reaction of a phosphoric acid liquid when it is mixed with a solid powder. The refractory cement results from the formation of an aluminum phosphate hydrate (which is water soluble) but hardens further on heating by the formation of $AlPO_4$. The dental cements harden by extraction of ions from a glass phase by the phosphate liquid which react to form complex phosphates that are not water soluble.

The study reported upon here was aimed at obtaining the information necessary to design a cement which could be pumped into a geothermal well, set after 3 to 4 hours, and then develop further strength by reacting in the geothermal environment to form stable high temperature cementing phases. The final cement would resist degradation by steam and brine, be impervious to fluids, and adhere to the steel casing and wall rock.

From information available on high temperature phase stability,^{4,5} a decision was made to prepare a glass containing ions which would be leached by the phosphoric acid (thereby neutralizing the acid during setting) and react with the phosphate ions to form stable cementing phases. These phases would undergo further reaction at elevated temperatures in superheated steam and hot water to form high temperature stable cements.

To obtain the information needed to design a geothermal phosphate cement, the study and this report were divided into four major areas. The first, grouped under the section on glass corrosion, concerns the type of interactions that take place between a glass and phosphoric acid. These interactions will determine if a cement will form, if the cementing phase is soluble in water, and the setting time of the cement.

The second group of studies is concerned with the stability at geothermal conditions of the possible cement phases. If it is known which phases are stable at elevated temperatures and pressures, a glass can be selected which will react with phosphoric acid to yield phases with high temperature and pressure stability. These results are included in the section on phase relations.

The third group includes work done on the properties of experimental cements to determine the relationship between cement liquids and glass compositions and the properties of resultant cements. The results reported for this section are encouraging but by no means conclusive. More information must be obtained before a cement can be made for final testing preliminary to field use. Included in this section are a series of experiments designed to evaluate the compatibility of the cement with mild steel.

The final stage of this study will involve the selection and production of large-scale amounts of cement of the composition selected from the property tests. This material should be mixed and set and engineering data gathered on admixtures, aggregate design, and performance under a wide range of conditions. This phase was not begun during the reporting period but its completion is highly recommended. Also, data on the effect of scaleup would also be obtained. For instance, some heat of reaction is known to be evolved on setting. This is no problem with laboratory samples but could significantly change temperatures and therefore setting time if hundreds of pounds of material is being set.

II. CORROSION OF GLASS

A. Introduction and Summary

The glass phase which is mixed with the phosphoric acid liquid to form the cement performs two functions. First, it controls the setting time of the cement, and second, it determines the phase which will cement the undissolved grains and aggregate together. A wide variety of different cements can be made by altering the glass composition. The glass is a silicate network which contains dissolved cations. These cations are leached from the network (replaced by H^+ ions from the acid), and once in the liquid they react with the phosphate ions to form the cement matrix. The rate at which the acid dissolves the glass determines reaction rates for cement phase formation.

The results of this study have proved that the setting time is a function of the corrosion rate of the glass. Only when the corrosion rate is appreciable is there any cement formation and as the corrosion rate increases, the setting time decreases. The corrosion rate is basically related to the percent of silica in the glass network. Therefore, by designing

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glasses with varying silica contents, the setting time of the cements can be fixed.

The cementing phase which forms depends on the type and amount of cations present in the phosphate liquid when the solubility limits are reached. Since these ions come from the glass phase, the cementing phase is determined by controlling the cation composition of the glass. Just as the silica content can be controlled when the glass is formulated so also can the cation concentration. This study has examined only the glasses containing calcium, aluminum, and sodium ions. Further, these ions have been present only in a narrow composition range. The equilibrium studies reported below suggest other ranges of promise, and zinc ion should also be tried as a cement glass constituent. All of the studies have been made on glasses containing equal amounts of CaO and Al_2O_3 . More stable cements would result from glass containing twice as much Al_2O_3 than CaO .

The corrosion rates of a series of calcium aluminosilicate and sodium calcium aluminosilicate glasses were determined in three phosphoric acids at 40°C . The effect of temperature on the rate was determined for one of the glasses in 30 wt% H_3PO_4 acid and an activation energy was obtained. The glasses are virtually insoluble at silica concentrations >55 wt% SiO_2 and show extreme solubility at silica concentrations <50 wt%. At the transition composition, a silica gel film is formed on the surface. The corrosion behavior suggests that the glasses undergo phase separation on cooling and the inversion from a soluble to an insoluble matrix phase takes place near 50 wt% silica.

B. Literature Review

From the work of Lavoisier in 1770 and Faraday in 1830⁶ to the present many studies have been made on glass corrosion. ⁷Excellent reviews of the research literature have been presented by Morey,⁷ Holland,⁸ Weyl and Marboe,⁹ and Filbert and Hair.¹⁰ The formation and nature of silica-rich films on glass surfaces caused by proton exchange with glass alkali ions have been the subject of many investigations in recent years. These studies have increased our understanding of the energetics and time dependence of the extraction process and the subsequent corrosion behavior of the silica-rich surface film. Recent developments in analytical techniques have led to a better understanding of ion-depleted surface films on glasses.^{11,12} El-Shamy and co-workers have defined the effects of various acids on soda-lime glasses,¹³ and Wood and Blachere recently reported work on the corrosion of lead glasses.¹⁴ The effects of phase separation on the corrosion behavior of borosilicate glass have been investigated by Tomazawa and Takamori who showed that microstructure size has little influence on corrosion rate and is determined by the composition of the more soluble phase.^{15,16} No studies were found reporting the effects of phosphoric acid on glass.

C. Experimental Procedure

All of the corrosion studies were made by measuring the weight loss

with time of single glass fibers immersed in various phosphoric acids. The glasses were made by melting silica and alumina with calcium carbonate or calcium and sodium carbonate.* Melting was done in platinum crucibles. The melts were held above the liquidus temperature for several hours; they were stirred with an alumina rod and checked microscopically for homogeneity. Fibers were drawn by dipping an alumina rod in the melt and withdrawing it as slowly as possible to obtain the thickest possible fibers (.5 to 2mm). Devitrification was observed in only one melt and this was overcome by drawing from a higher melt temperature. Two series of glasses were made. The calcium aluminosilicate had the formula $(X)\text{CaO}:(X)\text{Al}_2\text{O}_3:(100-2X)\text{SiO}_2$ wt%, where the silica content varied from 65 to 40 wt%. These glasses contained almost equal numbers of calcium and aluminum ions. The second series with quaternary sodium calcium aluminosilicates having the formula $7\text{Na}_2\text{O}:(X)\text{CaO}:(X)\text{Al}_2\text{O}_3:(93-2X)\text{SiO}_2$. In these glasses, the silica content varied from 60 to 40 wt%.

Table 1 lists the runs made in this study. A data point for a given run was obtained in the following manner: the drawn fibers were sectioned into 1-to 2-inch segments; each fiber was weighed and its surface area calculated from diameter and length measurements; each fiber (having a volume of 0.02 to 0.04 cc) was placed in a polypropylene bottle which was then filled with 60 ml of the required phosphoric acid preheated to the proper temperature; the bottles were held at 40°, 65°, or 90°C for the required time; the fibers were then removed, rinsed in distilled water, dried, and reweighed; the weight difference divided by the original surface area was plotted and finally the fiber was examined for the presence of surface films. Ten to thirty such runs were made to obtain the weight loss curves from which the corrosion rates were obtained. The phosphoric acids were prepared by diluting $85\text{H}_3\text{PO}_4:15\text{H}_2\text{O}$ (commercial concentrated phosphoric acid) with distilled water.

Some compositions which showed no surface film were examined by following the continuous weight loss of a single suspended fiber. As described by Kilroy,¹⁷ the fiber was suspended in the liquid inside an oven by a platinum wire attached to a gravimetric balance above the oven. To obtain the weight loss, a buoyancy correction was made and the loss was divided by the initial surface area to keep all data in the same units. These experiments are designated as "suspended fiber" runs in Table 1.

The balance used for the weight determinations could be read to 0.0001 grams. Repeated weighings on a standard weight suggest that the data are accurate to ± 0.0002 grams. The corrosion rates were determined by the slope of the best fitting line to the time data as determined by least squares analysis using the computer program, Statpack.**

*Reagents obtained from J. T. Baker Co., N.J.

**"Call/360: Statistical Package (STATPACK) Version 2," International Business Machines Corp. (1970).

Table 1
Glass Compositions Studied

Run	Glass composition wt%				H ₃ PO ₄ concentration	Temperature	Type of run	
	Na ₂ O	CaO	Al ₂ O ₃	SiO ₂	wt%	°C		
1	0	17.5	17.5	65	30	40	Individual fiber	
2	0	17.5	17.5	65	30	90	"	"
3	0	21.5	21.5	57	30	40	"	"
4	0	21.5	21.5	57	30	90	"	"
5	0	22.5	22.5	55	30	40	"	"
6	0	22.5	22.5	55	30	90	"	"
7	0	23.5	23.5	53	30	40	"	"
8	0	23.5	23.5	53	30	90	"	"
9	0	25	25	50	30	40	"	"
10	0	25	25	50	30	90	"	"
11	0	30	30	40	30	40	"	"
12	0	30	30	40	30	90	"	"
13	0	30	30	40	30	65	Suspended fiber	
14	0	30	30	40	10	40	"	"
15	0	30	30	40	10	90	"	"
16	0	30	30	40	50	40	"	"
17	0	30	30	40	50	90	"	"
18	7	16.5	16.5	60	30	40	"	"
19	7	19.0	19.0	55	30	40	"	"
20	7	21.5	21.5	50	30	40	"	"
21	7	24.0	24.0	45	30	40	"	"
22	7	26.5	26.5	40	30	40	"	"
23	7	26.5	26.5	40	10	40	"	"
24	7	26.5	26.5	40	50	40	"	"

D. Results

The data obtained on the weight loss of the various glass fibers in phosphoric acids of different compositions at the experimental temperatures are given in Table 1 of the appendix. Approximately 230 weight loss determinations were made on fibers of 12 different glass compositions at four temperatures.

Examples of the types of data obtained from the experiments are shown in Figures 1 and 2. Figure 1 gives the weight loss curves for the calcium aluminosilicates at 40°C in 30 wt% H_3PO_4 acid. Even after 128 hours, no weight loss was detected for the 57, 60, or 65 wt% SiO_2 glass fibers. As the silica content decreases, the solubility rises sharply between 53 and 50 wt% SiO_2 . Figure 2 shows the same type of behavior at much higher weight losses for the same glasses at 90°C. Again, no weight loss was detected after 128 hours for the 57, 60, or 65 wt% SiO_2 fibers. Other runs with these glasses were made at 140°C in pressurized cells, but no weight loss was detected at these temperatures.

Most of the data are best fitted by a straight line. These lines pass through the origin. A notable exception is the 53% silica glass at 40°C in 30% acid. This glass shows linear behavior for the first ten hours of corrosion and approaches $t^{1/2}$ parabolic behavior from 10 to 100 hours. This same glass shows linear behavior at 90°C. The corrosion rate reported below is obtained by taking the slope of the initial part of the curve.

Figures 3, 4, and 5 show the corrosion rates of the glasses studied as a function of silica content. In all three cases, the solubility of the glass containing 55 Wt% silica is reported as zero since no weight loss was observed in 100 hours. The transition from insoluble to highly soluble occurs at about the same composition and takes place over a very small composition range. The corrosion rates for the sodium-containing glasses were higher than for the soda-free counterpart.

Some fibers of each composition were studied under the scanning electron microscope after immersion in phosphoric acid. The 53% SiO_2 and 55% silica glasses showed a film forming on the glass. This was not observed on the fibers of other compositions. Chemical analysis showed the film to be almost pure silica with 1% CaO or Al_2O_3 . No phosphate was detected in the fiber. Upon removal from the acid the film was not obvious, but upon drying it crazed and turned white. The index of refraction of the dried film, measured by the Becke line technique, was 1.415. The volume change produced by drying indicates that the film was a hydrated silica gel. Photographs of the film are shown in Figure 6. After drying, the film can easily be scraped from the unaffected bulk glass. The curve shown in Figure 7 represents the diameter of the unattached glass fiber. No film is seen on the dried fiber after 30 minutes even though some weight loss has occurred. This clearly indicates that in addition to a visible silica-rich surface film there must be a layer of ion-leached material. No efforts were made to establish the thickness or chemical gradient in this layer.

Figure 1. Weight loss data for the calcium aluminosilicate glasses in 30 wt% H_3PO_4 at 40°C.

Figure 2. Weight loss data for the calcium aluminosilicate glasses in 30 wt% H_3PO_4 at 90°C.

Figure 3. Corrosion rate of the calcium aluminosilicate glasses as a function of silica content at 40°C in 30 wt% H_3PO_4 acid.

Figure 4. Corrosion rate of the calcium aluminosilicate glasses as a function of silica content at 90°C in the 30 wt% H_3PO_4 acid.

Figure 5. Corrosion rate of 7 wt% sodium calcium aluminosilicate glasses as a function of silica content at 40°C in the 30 wt% H_3PO_4 acid.

Figure 6. Calcium aluminosilicate glass fibers containing 53% silica. Top is SEM photo fiber after drawing (100x). Bottom is transmitted light photo after leaching in 30% phosphoric acid at 90°C for 2 hours. Central core of unaffected glass is surrounded by silica gel layer (100x).

Figure 7. Decrease in the diameter of the bulk glass in the 53% SiO_2 fibers in the 30 wt% H_3PO_4 acid 90°C as a function of time. These fibers show a surface film of silica gel which causes the outside diameter of the fiber to increase by as much as 30 percent during this time.

Figure 8 shows the relationship between temperature and corrosion rate for the 40 wt% silica, sodium-free glass. The rates were determined at 40°, 65° and 90°C. From the slope of this curve, an activation energy of 10.08 kcal/mole can be established. The same value was obtained for the 50% glass. The value for the 53% glass was 13.86 kcal/mole.

The effect of acid concentration on corrosion rates is given in Table 2. Maximum rates are obtained for 30% acid. The pH and ionic conductivity of the 10, 30, and 50% acids were measured, and both values show considerable increase from 10 to 30 and a slight increase from 30 to 50. The viscosity of the 50% acid is much higher than that of the 30%.

E. Discussion

Since the soda-free glasses appear to be members of a continuous solution within the primary field of anorthite, the sudden break in solubility at 53 wt% silica suggests that a phase separation phenomenon controls the corrosion behavior. A transformation of the glass structure upon cooling into a silica-rich glass phase and a silica-poor phase could explain the sudden change in solubility. The fibers richer in silica than 53% would contain a virtually insoluble matrix phase with a dispersed silica-poor phase. Since the latter phase is isolated and protected from corrosion by the matrix phase, no solubility would be seen. The low-silica glasses would phase separate into a very soluble matrix phase with dispersed units of silica-rich material. Upon corrosion of the glass, the silica-rich units would be released to form a colloidal suspension in the phosphoric acid. The compositions near 53% silica would contain roughly equal amounts of the two phases existing in an interconnected structure. Corrosion would remove the lime-alumina-rich phase leaving the porous hydrated silica-rich surface film which was observed. Attempts were made to observe phase separation in the fibers. In spite of repeated attempts with different heat treatments and etchants, no two phase structure was seen using a scanning electron microscope with a maximum magnification 20,000 times.

The calculated activation energy of 10.08 kcal/mole, low compared with literature values for other glasses, was obtained on the very soluble low-silica glass. The corrosion mechanism is assumed to be proton exchange for calcium and aluminum in the glass with subsequent hydrolysis of the soluble silicate groups. Just what is activated is now known. It is probably some combination of Ca-O and Al-O bond breaking.

Another unanswered question is the cause of the drop in corrosion rate in going from 30 to 50 wt% acid. If phosphate complexes are formed at the fiber surface, this could account for the decrease in rate. While this is possible, there is no direct evidence for such a reaction.

These studies not only show the behavior of calcium aluminosilicate glasses in phosphoric acid, but they also suggest ways of checking other glasses for cementing properties. Determination of the corrosion rate

Figure 8. Natural log-inverse temperature plot used to determine activation energy for the 40% SiO₂ calcium aluminosilicate glass dissolution.

Table 2

Effects of Acid Concentration on Corrosion Rate of Glass

Glass composition, wt%	Acid concentration wt% H ₃ PO ₄			Temp °C
	10	30	50	
40SiO ₂ :30CaO:30Al ₂ O ₃	30.23 x 10 ⁻⁴ gm/cm ² ·hr	127.7 x 10 ⁻⁴ gm/cm ² ·hr	97.36 x 10 ⁻⁴ gm/cm ² ·hr	40
40SiO ₂ :30CaO:30Al ₂ O ₃	439.6 x 10 ⁻⁴ gm/cm ² ·hr	1188 x 10 ⁻⁴ gm/cm ² ·hr	276.69 x 10 ⁻⁴ gm/cm ² ·hr	90
40SiO ₂ :7Na ₂ O:26.5CaO: 26.5Al ₂ O ₃	483 x 10 ⁻⁴ gm/cm ² ·hr	692.4 x 10 ⁻⁴ gm/cm ² ·hr	551.68 x 10 ⁻⁴ gm/cm ² ·hr	40

of other glasses can be determined in phosphoric acid. If the rate at 40°C is about 1×10^{-2} gm/cm²hour, the glass will form a cement if the proper ions are contained in the glass. Just which ions should be in the glass is determined by the equilibrium studies discussed in the next section.

III. EQUILIBRIUM STUDIES

A. Introduction

In designing a glass to mix with a liquid to yield a cement, it is critical to know the composition of the cementing phase and whether that phase will maintain its stability at geothermal conditions. For example, referring to Figure 9, if one knows that a stable cementing phase exists at point "P," a liquid of composition A can be mixed with a solid at point "X" to yield a cement. On the other hand, a solid at point "Y" made up of the same components B and C could exist in equilibrium with the liquid A until A vaporized leaving a dried uncemented powder of composition "Y." Furthermore, a powder of the composition "W" could react with "A" to form a cement compound of composition "Q." If that phase is not stable at elevated temperatures, the cement would decompose on heating. For high temperature use, a cement which yielded phase "P" would be selected over the phase "Q" cement.

Just which phases can form within a given system and their ranges of stability are the subject of phase-equilibrium studies. The geothermal cement of interest in this study is one that can be formed by mixing phosphoric acid with a glass which will release calcium and aluminum ions. In order to select the best glass for the cement it was necessary to determine the phase relations at geothermal temperatures for the systems CaO-P₂O₅-H₂O, Al₂O₃-P₂O₅-H₂O, and CaO-Al₂O₃-P₂O₅-H₂O.

B. The System CaO-P₂O₅-H₂O

1. Introduction. In addition to its importance for geothermal cements, knowledge of this system will be helpful for the manufacture of commercial fertilizers. The equilibrium in this system has been studied by Elmore and Fair¹⁸ at 25°, 40°, 50.7°, 75°, and 100°C. They reported five solid phases in equilibrium with the phosphate solutions: hydroxylapatite Ca₅(PO₄)₃OH, brushite CaHPO₄·2H₂O, and monetite CaHPO₄; monocalcium orthophosphate monohydrate (MCPM) Ca(H₂PO₄)₂·H₂O which is in equilibrium with the liquid of intermediate phosphoric acid concentration; and monocalcium orthophosphate Ca(H₂PO₄)₂ in the high P₂O₅ region. The first three phases exist in equilibrium with solutions at the H₂O corner.

Three ternary invariant points have been located in this system.¹⁹⁻²⁰ The first one has been estimated to occur at 160°C with a liquid composition of 5.2% CaO and 54.5% P₂O₅. At this point this liquid coexists with CaHPO₄, Ca(H₂PO₄)₂·H₂O, and Ca(H₂PO₄)₂. Above this temperature, Ca₂(H₂PO₄)₂·H₂O no longer exists in the system. The second invariant point corresponds to the equilibrium among CaHPO₄, CaHPO₄·2H₂O, Ca₅(PO₄)₃OH, and the saturated solution of 0.05% CaO and 0.14% P₂O₅ at about 36°C. Above this temperature, CaHPO₄·2H₂O

Figure 9. Hypothetical cementing system.

disappears from the phase diagram. The third invariant point corresponds to the equilibrium among $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, CaHPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, and the saturated solution at 20°C which is virtually pure water. Below this temperature CaHPO_4 no longer exists in equilibrium with a liquid phase.

2. Experimental Procedure. The aqueous phosphate solutions with concentrations of 2, 5, 10, 20, 30, 40, 50, 60, and 61.6% P_2O_5 were prepared from concentrated orthophosphoric acid (61.6% P_2O_5) by dilution with distilled water. Mixtures at different compositions of $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ were prepared by mixing CaO or $\text{Ca}_3(\text{PO}_4)_2$ powder with the prepared phosphate solutions. The mixtures were charged into heavy wall pyrex glass tubes (8 mm o.d., 5 mm i.d., 20 cm long) to about three-fifths capacity. Both ends of the glass tubes were sealed to secure a completely closed system. In all tubes a vapor composed of water-saturated air exists after firing. The pressure in the tube is calculated to be 250 psi (1700 kPa).

An oven set at 200°C was used for the isothermal chamber. The time required for the mixtures to reach equilibrium varies. A maximum of 26 days was given to certain compositions. Literature studies¹ suggested that equilibrium would be achieved in several days. After the system reached equilibrium, the glass tube was removed from the oven. An observation was made before the tube began to cool down to determine whether the glass tube contained a clear solution or solutions and crystalline phases. The solid phase in the sample was separated from the liquid immediately and was ground and analyzed by the x-ray diffraction technique. High temperature microscopy was used to identify some of the phases. Calcium concentration in some of the solutions was made by atomic absorption spectroscopy to check the liquidus isotherm determined by direct observation.

3. Results and Discussion. Table 2 of the appendix shows the results of 56 runs made to determine the 200°C solubility isotherm in the ternary system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$. Three solid phases show stability at this temperature: hydroxylapatite $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, dicalcium orthophosphate or monetite CaHPO_4 , and monocalcium orthophosphate monohydrate $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. The solubility isotherm and the phase relations, as determined by these runs, are shown in Figure 10. Figure 11 shows a schematic location of the isotherm in the very high H_2O region of the system drawn on rectangular coordinates.

Hydroxylapatite is found as the solid phase in samples 20, 21, 22, and 23. No runs yielded hydroxylapatite, portlandite, and a liquid. Therefore, the maximum solubility of CaO at the H_2O apex was not determined. At least 9 wt% CaO can be dissolved and small amounts of phosphate ion increase the solubility of lime.

Two solid phases, monetite and hydroxylapatite, were found coexisting in samples 17 and 29. These two compositions must, therefore, lie in the three-phase region where monetite and hydroxylapatite are two stable phases in equilibrium with a saturated liquid. All other samples shown in Figure 11 have the one solid phase, monetite, except 48 which is all liquid and therefore below the solubility limit.

Figure 10. The system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ at 200°C and 250 psia.

Figure 11. Diagram of the high water region of the system $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ at 200°C showing a schematic location of the solubility isotherm.

Dicalcium orthophosphate, which is the mineral monetite, CaHPO_4 , is the solid phase in equilibrium with the liquids over the range from H_2O to about 50% P_2O_5 . This compound crystallized as triclinic tablets. The best region for the monetite crystallization is between 2 and 20% P_2O_5 . In this region, the triclinic single crystal can grow to 0.8 mm in several days. The crystal size becomes small in the area where P_2O_5 is greater than 20%. In the high P_2O_5 region only a very fine powder of CaHPO_4 was obtained. The invariant liquid at high phosphate compositions which can coexist with monetite and monocalcium orthophosphate monohydrate (MCPM) falls at 6.5 CaO :50 P_2O_5 :43.5 H_2O .

It is difficult to analyze accurately the solid phases and to locate the compatibility joins at 200°C in the high P_2O_5 region because of the fast reactions between monetite, MCPM, and liquid phase when the sample is cooled down to room temperature. Monetite has a negative temperature coefficient of solubility, that is, the higher the temperature, the lower the solubility, and will dissolve as the temperature goes down. It was found that the rate of dissolution of monetite increases with the P_2O_5 concentration. Also, the smaller the monetite crystals, the higher the dissolution rate. Since the monetite crystals are large in the low P_2O_5 region, they do not dissolve when the sample is taken out of the oven, cooled down to room temperature, and separated from the liquid phase. In sample 38, where the solid phase at 200°C is a very fine powder, all solid phases dissolved on cooling and the sample became a clear liquid in 10 minutes. This phenomenon was also observed in samples 39, 31, 32, 42, and 4. X-ray diffraction analysis showed the presence of MCPM in these samples; this phase formed during cooling. The stable phase at 200°C observed by high temperature microscopy was monetite.

At temperatures above 160°C, MCPM has been reported to be unstable.¹⁹ These observations were made in open systems which could lose water. In this research, MCPM was observed in samples 53, 54, 55, and 56 at 200°C. Because of difficulties in handling solutions and analyzing phases, no runs were made in the system at P_2O_5 compositions greater than 61 wt%. The liquidus isotherm must drop to the H_2O join at about 80 wt% P_2O_5 and will have to change direction drastically. This suggests that monocalcium orthophosphate (1·1·2) is stable at 200°C and would account for this change in the isotherm direction.

4. Conclusions. The liquidus isotherm for the calcium phosphates extends from the H_2O corner to 6.5 CaO :50 P_2O_5 :43.5 H_2O and over this range monetite is the primary phase. At higher P_2O_5 concentrations, $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ is encountered. A range of liquidus compositions from virtually pure water to at least 9% CaO with very low phosphate concentration are in equilibrium with hydroxylapatite.

C. The System Al_2O_3 - P_2O_5 - H_2O at 200°C

1. Introduction. This system will not only yield information for geothermal cements but is also of interest because of phosphate-bonded re-

fractories, crystal growth of the piezoelectric, berlinite, and for its mineralogic significance. The literature on the aluminum phosphates and their hydrates is extensive,²¹⁻²⁵ but little is reported at temperatures above 90°C. Table 3 lists the phases which have been observed in the system and while agreement between various authors is not perfect, the major relationships are well understood. Retrograde solubility is observed for the liquidus surfaces from 25° to 90°C in the low P₂O₅ region,²⁶ and increasing solubility with increasing temperature is observed for acids 30 wt% P₂O₅. At temperatures above 300°C, Wise and Loh report the stable phases to be corundum, diaspore AlOOH, berlinite AlPO₄, augelite Al₂PO₄(OH)₃, and trolleite Al₄(PO₄)₃(OH)₃.²⁴ Aluminum metaphosphate Al(PO₃)₃ is also a stable phase.²⁷

2. Experimental Procedure. Sixty compositions were studied after firing at 200°C. The compositions are given in Table 3 of the appendix. Slurries were made by mixing phosphoric acids, ranging in composition from 2% P₂O₅ (2.8% H₃PO₄) to 62% P₂O₅ (85% H₃PO₄), with either α-Al₂O₃,* or Al(PO₃)₃.* The Al₂O₃ content ranged from 1 to 10 wt%. These slurries were placed in Pyrex glass tubes (20 cm x 8 mm o.d.-5 mm i.d.) so that the tubes were half filled and both ends were sealed. The procedure for study was identical to that used for the CaO-P₂O₅-H₂O system. The glass tubes were placed in capped steel pipes to contain fragments in the event of an explosion. Of several hundred runs, two explosions took place, both in runs containing alumina hydroxide and water. Firing times ranged from 1 to 590 hr. After each run a vapor phase was present with a liquid phase and, depending upon the equilibrium, one or more crystalline phases were also present in some of the reaction tubes. The vapor phase was saturated air and the internal pressure was calculated to be 250 psi (1,700 kPa). Measurement of the Pyrex wall thickness, before and after firing, showed no detectable change. The solubility isotherm was determined by direct observation. Clear liquids were examined by microscopy to be certain no crystalline phase was present. The identity of crystalline phases in the liquid was determined by x-ray diffraction analysis.

3. Results and Discussion. The firings made in the system are listed in Table 3. The compositions, times of firing at 200°C, and phases identified are given. Figure 12 is the phase diagram constructed from the data, and Figure 13 shows the phases coexisting with the solutions at the H₂O apex of the diagram.

Two solid phases were found in equilibrium with the acidic solutions. The hexagonal quartz isomorph of AlPO₄, berlinite, precipitates from almost all phosphoric acids saturated with Al₂O₃. Over the range of pure water to 35 wt% P₂O₅ phosphoric acid, less than 1 wt% Al₂O₃ is soluble.

*Linde 0.05 micron alumina; aluminum phosphates supplied by Pfaltz and Bauer, Inc.

Table 3

Solid Phases Reported in the Literature for the System $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 25°, 50°, 60°, 75°, and 90°C (the Aluminophosphate Hydrates Are Represented by the Number of Moles of Al_2O_3 , P_2O_5 , and H_2O in Each Compound)

Temperature °C	Solid phases present	Reference
25	1.1.4, 1.1.7, 2.3.10, 1.3.6	(25)
25	1.1.6, 1.2.9	(22)
50	1.1.4, 1.2.9, 1.3.6	(22)
60	1.1.4, 1.2.5, 1.2.9, 1.3.6	(21)
75	1.1.2, 1.2.9, 1.3.6	(22)
90	1.1.4, 2.3.8	(23)

Figure 12. Phase diagram of the system Al_2O_3 - P_2O_5 - H_2O at 200°C and 250 psi. Dashed lines on this isothermal isobaric section represent possible equilibrium relationships.

Figure 13. Phase relations at 200°C in the high H_2O region of the system Al_2O_3 - P_2O_5 - H_2O . The exact location of the isotherm at the corner was not determined and approaches pure water.

As the temperature is lowered, the solubility increases. The 35 wt% P_2O_5 phosphoric acid will dissolve up to 6 wt% Al_2O_3 . Maximum solubility occurs at the isothermal-isobaric invariant point located at 7.5 Al_2O_3 :65 P_2O_5 :27.5 H_2O at which that liquid coexists with berlinite and third-phase aluminum metaphosphate hexahydrate. Along the berlinite isotherm, single crystals 1 mm in length were observed.

In the high phosphate region, the primary crystal encountered is the hexagonal phase of aluminum metaphosphate hexahydrate, which can be written as either $Al(H_2PO_4)_3$ or $AlH_2P_3O_{10} \cdot 2H_2O$. The liquids are extremely viscous and hygroscopic and difficult to separate from the crystal phase which reacts with atmospheric water. Acicular single crystals up to an inch in length grow in radiating clusters in the Pyrex tubes. The x-ray diffraction pattern is identical to the one reported by Lehr et al.²⁸ The literature suggests that the 1·3·6 and the 1·3·3 phases are both stable at 200°C, but the 1·3·3 compound was not observed in any of the firings made.

Figure 13 shows the solid phases in equilibrium with the solutions in the H_2O region of the diagram. The exact location of the isotherm is not known in this region. The invariant liquid in equilibrium with augelite and boehmite falls above 5% Al_2O_3 .

Run 54, the highest alumina run made in this region, was still within the two-phase region of augelite and solution (pH=3.5). Small amounts of phosphate ion increase the alumina solubility markedly. Radial crystal masses of an unidentified, probably metastable, aluminum hydrate were observed in runs 30 and 31 after 100 hours. Run 32 yielded boehmite.

The aluminum phosphate hydrate augelite $Al_2PO_4(OH)_3$ is found in several runs as the only crystal phase present and with a tridymite phase of $AlPO_4$. This phase could be the basis of a high temperature geothermal cement formed by mixing alumina with phosphoric acid. The final crystalline phase encountered is the tridymite phase of $AlPO_4$, which is observed in runs after 400 hours and is found just with solution, with augelite, and with berlinite. It occurs in the same composition range as trolleite $Al_4(PO_4)_3(OH)_3$, a phase which is stable above 300°C²⁴ but which was never observed in this study. In pure anhydrous $AlPO_4$, the tridymite phase does not form until 820°C. If our observations on this phase represent stability, then the substitution of excess aluminum ion and hydroxyl ion in the structure stabilizes the phase to the lower temperature of 200°C.

4. Conclusions. Boehmite, augelite, berlinite, and a high phosphate phase have been shown to crystallize from aluminophosphate solutions. The solubility isotherm is established at 200°C for most of the system. Further work is necessary to determine the limit of alumina solubility in very low phosphate solutions.

D. The System $CaO-Al_2O_3-P_2O_5-H_2O$

1. Introduction. Knowing the equilibrium for the systems $CaO-P_2O_5-H_2O$

and $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$, it is now possible to determine the behavior in the quaternary system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$. It is in this system that the reaction products of a phosphoric acid with a lime-alumina glass will be found. The previous studies^{29,30} on the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ showed that there are no ternary compounds in the system. M. S. Crowley³¹ reported that the hydrogarnet C_3AH_6 is the only stable phase in the system $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$ at relatively high pressure at 200°C . However, he also mentioned that if traces of foreign ions exist in the samples, C_2AH_6 will be formed.

D. Roy in her study of geothermal cement stability has reported the occurrence of the hydrogarnet C_3AH_6 at 380°C in some low silica hydrothermal runs. This is above the temperature that Crowley reports for the stability of C_3AH_6 , but the run is made at a lower pressure. Both authors report $\text{C}_4\text{A}_3\text{H}_3$ at temperatures of 400°C .³²

Because of the lack of available experimental information on the quaternary system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 200°C , this isothermal is being investigated. A literature review of the compounds which occur as minerals has indicated some quaternary compounds which may be encountered in this study. There are five related compounds which are listed in Dana's System of Mineralogy³³: tavistockite $\text{Ca}_3\text{Al}_2(\text{PO}_4)_3(\text{OH})_3$; montgomeryite $\text{Ca}_4\text{Al}_5(\text{PO}_4)_6(\text{OH})_5 \cdot 11\text{H}_2\text{O}$; overite $\text{Ca}_3\text{Al}_8(\text{PO}_4)_8(\text{OH})_6 \cdot 15\text{H}_2\text{O}$; davisonite $\text{Ca}_3\text{Al}(\text{PO}_4)_2(\text{OH})_3 \cdot \text{H}_2\text{O}$; and crandallite $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$. P. G. Embrey and E. E. Fejer³⁴ reported that tavistockite probably is an apatite or fluoro-apatite. The original analysis was made on a mixture of apatite and kaolinite. From their electron probe and laser microprobe analysis, Paul B. Moore³⁵ and Luca Fanfau et al.³⁶ found the presence of Mg in Montgomeryite crystal. Paul B. Moore³⁷ also pointed out that the formula of montgomeryite should be $\text{Ca}_4\text{Mg}(\text{H}_2\text{O})_{12}[\text{Al}_4(\text{OH})_4(\text{PO}_4)_6]$. Paul B. Moore and T. Araki³⁸ recommended that the chemical formula of overite be changed to $[\text{Mg}(\text{H}_2\text{O})_4]_2[\text{CaAl}_2(\text{OH})_2(\text{PO}_4)_4]$, replacing the erroneous original formula. Thus only davisonite ($\text{C}_6\text{AP}_2\text{H}_5$) and crandallite ($\text{C}_2\text{A}_3\text{P}_2\text{H}_6$) appear to be verified compounds of the quaternary system. In addition, Paul B. Moore³⁹ found a new calcium aluminophosphate hydrate $\text{Ca}(\text{H}_2\text{O})_2[\text{CaAl}_2(\text{OH})_4(\text{PO}_4)_2]$, discovered in rocks from North Groton, New Hampshire, which he named foggite.

2. Experimental Procedures. In order to establish the phase relation in the quaternary system, four planes were chosen for investigation: $25\text{CaO}:75\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$; $50\text{CaO}:50\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$; $75\text{CaO}:25\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$; and the 90% H_2O plane, chosen because of the characteristics of solid-liquid equilibria. All phases in the system which show equilibrium with water must have tie lines which pass through this plane. Therefore, we feel this is the best way to define the stable hydrate at 200°C in the system. A diagram representing the planes of investigation is shown in Figure 14.

The experimental procedures have been described above. The sealed Pyrex ampules are used for reactions. For the first three planes, $\text{CaO-Al}_2\text{O}_3$ mixtures of specific proportions were prepared by grinding to a powder

pellets consisting of exact amounts of CaO and Al_2O_3 which had been fired at 1200°C for at least 8 hours. The H_3PO_4 was diluted to make the solutions which are reported as P_2O_5 and H_2O . For the 90% water plane, the starting materials for all runs were Al_2O_3 , $\text{Al}(\text{PO}_3)_3$, CaO , $\text{Ca}_3(\text{PO}_4)_2$, $75\text{CaO}:25\text{Al}_2\text{O}_3$, $50\text{CaO}:50\text{Al}_2\text{O}_3$, and $25\text{CaO}:75\text{Al}_2\text{O}_3$, made up to exact composition of required points on the $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ plane after using a material balance to calculate the proportions accurately. These compositions are shown in Figure 15. Samples were made up of 10 wt% solid powder and 90 wt% distilled water, and then the above-mentioned procedure was followed.

3. Results and Discussions. The firings made in the $25\text{CaO}:75\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ are shown in Figure 16. Figures 17 and 18 show the firings made on the remaining two planes. The results of all firings are presented in Table 4 of the appendix. Firing time varied from 100 to 600 hours. From the available data, the phase relations at 200°C in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ can be deduced. For example, the compatibility join between monetite and berlinite has been established and a large part of the tetrahedron is dominated by the three-phase region monetite + berlinite + solution. The solutions are phosphoric acids in which Ca^{++} and Al^{+++} are dissolved up to several percent at higher phosphate compositions. At low phosphate compositions, calcium and aluminum are only sparingly soluble. The species in the solutions are not known. There are probably ion phosphate complexes present. These relationships are shown diagrammatically in Figure 19. The other relationships can not be shown in this manner because of the difficulty in three-dimensional representation. Therefore, the stable joins have been projected from the water apex onto the $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ triangle. These relations are shown in Figure 20.

The one quaternary compound, which is stable at 200°C , is crandallite, $\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5\cdot\text{H}_2\text{O}$. In one run there was some evidence for a second quaternary compound with a pattern close to woodhouseite, $\text{CaAl}_3(\text{PO}_4)(\text{SO}_4)(\text{OH})_6$. This compound is closely related to crandallite and while there is no sulfate ion present in this system a sulfate free woodhouseite may be stable.

At 200°C the following compatibility joins are stable: hydrogarnet and hydroxylapatite, hydroxylapatite and boehmite, boehmite and crandallite, crandallite and hydroxylapatite, crandallite and augelite, augelite and hydroxylapatite, hydroxylapatite and berlinite, berlinite and monetite, and finally monetite and the 1.3.6 compound.

While the compound protlandite $\text{Ca}(\text{OH})_2$ was never observed, it should be in equilibrium with hydroxylapatite and hydrogarnet under geothermal conditions. An examination of these results with reference to phosphate cements indicates that the two best regions for cement formation are the compositions near crandallite and those near hydrogarnet. Since the hydrogarnets fall in the realm of the calcium aluminate cements and are being studied elsewhere, the area of interest in phosphate cement studies is the crandallite region.

Figure 14. Planes under investigation in the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$.

Figure 15. Compositions of firings made in the 90% water plane.

Figure 16. Compositions of firings made in the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ on the 25% CaO : 75% Al_2O_3 plane.

Figure 17. Compositions of firings made in the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ on the 50% CaO : 50 Al_2O_3 plane

Figure 18. Compositions of firings made in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ on the 75% CaO : 25 Al_2O_3 plane.

Figure 19. Phase relations at 200°C in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$.

Figure 20. Projection of tentative compatibility joins in the system $\text{CaO}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{H}_2\text{O}$ at 200°C .

If a 1-to-1 glass is reacted with a phosphate liquid, it will form more crandallite as the phosphate content of the liquid increases. In the tests reported below, increased strengths were observed when acids richer in phosphate were used. A second method of getting a cement which would react to form crandallite is to add phosphate to the glass phase and react the glass with a low phosphate (10%) liquid. This has not been attempted but is recommended for further studies.

IV. CEMENT PROPERTIES

A. Introduction

An experimental cement frit was prepared in bulk to obtain some data on geothermal effects on the phosphate bond. The composition was by no means the optimum glass but was chosen because solubility data showed that some reaction with the phosphate would take place. Several pounds of the glass ($45\text{SiO}_2:7\text{Na}_2\text{O}:24\text{CaO}:24\% \text{Al}_2\text{O}_3$) was mixed, melted in platinum crucibles at 1400°C , fritted in water, ball milled, and sieved through 200-mesh (77-micron) screens.

B. Compressive Strengths

Initial tests showed the cement to set far too quickly to be considered for well cementing. The cements set in one hour. However, it was still usable for testing the stability of the phosphate cement bond under geothermal conditions and for determining whether a filler could be mixed with the cement. Subsequent tests on this cement have shown that an increased acid concentration will yield cements of 200-psi compressive strength, but the high temperature tests were made using the 30% acid. However, these cements also set very rapidly with a considerable exotherm during setting.

Compression tests were conducted to determine compression strength of the cement and also cement filler. Samples were cured at room temperature and also at high temperature and pressure for varying lengths of time before testing.

1. Cement Proportions and Mixing Procedure. The cement-acid mixture consisted of the cement ($45\text{SiO}_2:7\text{Na}_2\text{O}:24\text{CaO}:24\text{Al}_2\text{O}_3$) and a 30% solution of H_3PO_4 in the ratio of 2.0 ml acid per gram of cement. The cement-filler-acid mixture consisted of 50% cement and 50% filler (silica sand). One ml of H_3PO_4 was mixed with 1g of cement filler. The mixing was done in a glass container surrounded by ice to increase the setting time and permit the mixture to be placed in the molds.

The cement mixture was then poured into 1.0-cm-diam by 2.0-cm-long cylindrical split ring stainless steel molds which were held rigidly in a clamping device. The top surface of the mold was capped with a glass

slide to ensure parallel surfaces for testing. To allow easy removal of the hardened samples from the molds, the interior surfaces were wiped with a thin layer of WD-40 oil prior to casting.

2. Curing. All samples were left in the molds overnight (approximately 24 hours), and were then removed and placed in water at room temperature until the time of testing or in a hydrothermal chamber at a temperature of 200°C and a water pressure of 250 psi. Tests on the high temperature samples were conducted immediately after the samples cooled to room temperature. There were no tests made on cements which were cured in the autoclave. Any future work should include these tests.

3. Compression Tests. Because of the size of the samples the standard laboratory testing equipment for cements could not be used. All tests were conducted with a bench top compression testing unit. Load was applied slowly by means of a hand-operated hydraulic jack.

The top and bottom surfaces of the samples were generally parallel, but to ensure a more uniform load distribution on the small samples a stiff rubber cushion was placed between the sample and the testing machine at both the top and bottom surfaces.

The mode of failure for most tests indicated that a uniform load was applied to the sample.

The results of the compression tests are shown in Table 4. The number of samples tested is indicated. There was relatively little scatter in the results for the tests.

4. Effects of Liquid Composition. Several experiments were performed using the $45\text{SiO}_2:7\text{Na}_2\text{O}:24\text{CaO}:24\text{Al}_2\text{O}_3$ glass with different liquids to determine if the liquid compositions affect the compressive strength. The data are shown in Table 5.. The 42% phosphate liquid yields the best strength, 1691 psi. Further optimization of the powder should yield strengths well in excess of 5000 psi.

5. Conclusions and Recommendations for Future Studies. The room temperature tests show a slight increase in strength with curing time for samples both with or without filler. No increase in strength was observed with the addition of the filler, but no decrease was observed either.

Curing at 200°C and 250 psi results in a substantial decrease in compression strength at 1 day, followed by an increase at 3 days and a second decrease at 7 days. The longest test of 72 days showed a continued increase of strength to 898 psi. These changes in strength reflect the changes in the cementing phases to the high temperature equilibrium compounds. The strength range for the five 72 day samples was from 600 psi to 1691 psi. This wide range is probably due to difference in sample preparation. In testing the samples, if the two ends of the cylinders are slightly out of

Table 4
Results of the Compression Tests

Series	Age at test (days)	Average compression stress in psi (No. of samples)
A	1	514 (2)
A	7	571 (5)
B	1	479 (10)
B	7	573 (5)
C	1	279 (5)
C	3	864 (5)
C	7	632 (7)
D	1	125 (3)
D	3	435 (6)
D	7	309 (4)
C	72	898 (5)
E	1	2,342 (5)

	<u>% Filler</u>	<u>Curing</u>
Series A	50	Room temperature
Series B	0	Room temperature
Series C	50	200°C and 250 psi
Series D	0	200°C and 250 psi
Series E	0	Room temperature, 40% acid.

Table 5
Effect of Liquid Concentration
on Compressive Strengths

Sample	Curing conditions	Liquid/powder	Strength (psi)
F-1	24 hr. @ room temp.	4 ml/3.4 g.	1397
F-2	"	"	1544
G-1	"	"	1691
G-2	"	"	1544
H-1	"	1.25 ml/1.0 g.	1434
H-2	"	"	1691
J-1	"	"	662
J-2	"	"	588
K-1	6 hr. @ room temp.	"	1030
K-2	"	"	1176

Acids

F:	42% H_3PO_4 , 4% ZnO, 1.5% Al_2O_3
G:	42% H_3PO_4 , 1.5% Al_2O_3
H:	42% H_3PO_4
J:	30% H_3PO_4
K:	50% H_3PO_4

*All samples were mixed under cold conditions. No samples contained filler.

parallel the measured strength will be significantly below the true strength. The cement-acid-filler mixture appears to withstand the temperature increase considerably better than the mixture without filler. In fact, the 3-day strengths are substantially higher than those of the samples cured continuously at room temperature.

The addition of a filler which appears to increase the high temperature strength would also reduce the total cost of the cementing mixture. Therefore, it would be desirable to determine the effect of cement filler ratio on compression strength at high temperatures and whether an optimum ratio exists.

The reason for the increase and the decrease in strength under high temperature curing conditions is not apparent from the limited tests completed. Additional tests should show whether the changes were caused by the curing procedure that was used or by an inherent property of this cementing mixture. The effects of liquid composition must also be defined before the optimum cement can be obtained.

C. Compatibility of Phosphate Cement With Mild Steel

Any cement used to complete a geothermal well must be compatible with the steel used for the well casings. A number of reviews are available on the interactions of "rebar" steel and portland cement-based concrete.⁴⁰⁻⁴² No such information is available for phosphate cements. Ideally, any cement emplaced around a drill casing should adhere to the steel and should not promote corrosion of the steel even in the presence of chloride solutions.

A series of experiments were carried out to determine if (1) phosphate cements adhere to steel and if (2) the unset cement reacts with the steel. 1020 mild steel in 1-in. x $\frac{1}{2}$ -in. x $\frac{1}{4}$ -in. domino-shaped tabs were used for the tests. Various treatments were performed on the steel surfaces, and phosphate cements were mixed and applied to the surface with a stainless steel spatula. The coatings were allowed to set in a humidity chamber at room temperature for 24 hours. The coatings were then examined under a "dissecting" microscope and tested for adhesion, qualitatively, by scraping with a probe.

Figure 21 shows two of the tabs with phosphate coatings. Table 6 lists the experiments performed and the results obtained. With proper treatment of the steel, an adhesive layer of cement can be obtained on steel. The major problem associated with adhesion of phosphate cement to steel is hydrogen evolution produced by corrosion of the steel at the cement interface by the phosphoric acid before setting. With proper surface treatment of a steel, such as formation of a surface phosphoric film, this problem can be overcome.

Figure 22 shows a scanning electron micrograph of the adhering section of a phosphate coating on a steel. The smooth areas are the bottom of gas bubbles. Shrinkage cracks are caused by volume changes associated with the vacuum dehydration of the cement. They form when the cement is placed in the vacuum evaporator used to coat the samples with gold-palladium before viewing under the SEM.

The bubbles are caused by corrosion of the steel by phosphoric acid prior to setting of the cement. The corrosion results from the following oxidation/reduction reaction.⁴³

In spite of this reaction, a layer of phosphate cement stayed on the steel surface. The bulk of the coating broke off at low stress because of the presence of the bubble layer near the base of the cement.

The corrosion reaction listed above could cause some corrosion to the steel casing during emplacement. As the cement sets, the acid is neutralized and long term problems are not expected. Some gas and oil wells are acidified in the field and cause no severe problems with the casing. In this procedure, hydrochloric acid, a more corrosive acid than phosphoric, is pumped down the casing into the wall rock to increase formation yield. If this acid can be tolerated, phosphoric should be more problem for field operation. It may be possible to circumvent the entire problem of using phosphoric acid in the field by putting the phosphate necessary to form a cement into the glass phase. A glass powder could then be mixed with water, pumped, and set by extraction of phosphate to form phosphoric acid "in situ" which would react with the other glass constituents to form a cement.

As shown in Table 6, several attempts were made to prevent the cathodic reaction and eliminate the bubbles. The most effective method is to use a stainless steel such as 316 which is not affected by the acid, but such an alternative is extremely expensive. Coating by a metal that is more "noble" than steel is also a possibility. Phosphatization of the steel was ineffective. The steel was pretreated with warm phosphoric acid in an attempt to form a passivating layer of iron phosphate on the surface. The surface was washed to remove excess acid and the cement was coated on the surface. Hydrogen evolution was observed which indicates that the phosphates formed must have been soluble and removed during washing.

Much of the experimentation done on the steel compatibility has been preliminary in nature. Continued work on the phosphatization using more complex solutions should be conducted. Van Wazer reports passivation by tertiary phosphates of iron, zinc, or manganese.⁴⁴ The effects of other metal coatings on steel applied by solution methods should be investigated and the effects of primers and passivators should also be examined.

Figure 21. Mild steel (1020) tabs coated with phosphate cement.
White region is cement coating.

Figure 22. Scanning Electron Micrograph of phosphate cement layer adhering to mild steel. (Mag = 200x). A sketch of the cross-section is shown to the right.

D. Cost Estimates

Using conservative figures, based on current prices, the price of cement was estimated. By far the most expensive item will be the cost of the frit. Frit producers quote prices of from \$1.00 to \$2.50 per pound for frits which include starting materials, melting, crushing, and sizing costs. Since many of these contain rare elements and melt at high temperatures, a cost estimate for a phosphate cement glass frit of \$2.00 per pound seems reasonable. Phosphoric acid can be purchased in quantity for 20 cents per pound.

The above figures indicate that the filler-to-cement ratio is critical to the economics of a phosphate cement. The data reported above show that 50% filler produces an excellent cement. At this filler ratio, the cement cost per pound is \$1.02. The phosphoric acid must be diluted at least 1 to 1 with water; the cement liquid will cost 10 cents per pound. In the final cement there are 2 parts by weight solids to 3 parts by weight liquid which gives a cost of set cement of 0.47 cents per pound. One conclusion of the above is that more work must be done to establish the maximum filler-to-cement ratio that can be used in the cement.

V. CONCLUSIONS

The major conclusions regarding the use of phosphate cements for cementing geothermal well is that the potential is there but at least 2 more years of research and development activity would be necessary to obtain a usable product.

Improvement of strength has continued at a great enough rate that strength in excess of 1000 psi is a virtual certainty. The strengths after 72 days suggest that instead of degrading, the materials are increasing in strength as equilibrium conditions are being reached. For geothermal applications, this is both a significant and encouraging finding.

Many of the tests on the cements which were proposed were not carried out. The reason for this is that more time was required in developing glass compositions than was anticipated. Also, many of the early cements did not meet the strength criteria and collecting data on the pumpability and permeability of a cement known to be unacceptable would have been a poor expenditure of effort. Instead the effort was put into learning how to design a cement which would be acceptable. Adequate strength cements were developed at the end of this contract.

From the glass corrosion work, it was learned that glasses which would react with phosphoric acid to yield cements fell into three categories depending upon their silica content. The first group, high silica glasses (greater than 55% SiO_2) were insoluble in phosphoric acid and therefore would not interact to form a cement. Those glasses with SiO_2 less than 50% silica react too rapidly. They yield cements but the setting time is

Table 6
Results of Coating Experiments
on 1020 Steel

Solutions	Cement w/45%SiO ₂	Surface Treatment	Comments
30% H ₃ PO ₄	"	None	Some adhesion
42% Buffered H ₃ PO ₄ (Zinc)	"	100°C-30%H ₃ PO ₄ -0°C	No adhesion
42% Buffered H ₃ PO ₄	"	" "	No adhesion
30% Buffered H ₃ PO ₄	"	" "	Some adhesion
42% Buffered H ₃ PO ₄	"	100°C-40%H ₃ PO ₄ -0°C	No adhesion
30% Buffered H ₃ PO ₄	"	" "	Some adhesion
42% Buffered H ₃ PO ₄	"	100°C-42% Buffered H ₃ PO ₄ -0°C	No adhesion
30% Buffered H ₃ PO ₄	"	" "	No adhesion
30% Buffered H ₃ PO ₄	"	HCl-Zinc coated	Slight adhesion
30% Buffered H ₃ PO ₄	"	HCl-Copper coated	Good adhesion- not consistent
30% H ₃ PO ₄	"	100°C-40%H ₃ PO ₄ -0°C 42% Buffered H ₃ PO ₄ (recoated)	Good adhesion
30% H ₃ PO ₄	"	30%H ₃ PO ₄ -45%SiO ₂ glass (recoated)	Good adhesion
30% H ₃ PO ₄	"	100°C-40%H ₃ PO ₄ -0°C 30% Buffered H ₃ PO ₄	Some adhesion

too rapid and the heat of reaction produced is too high. Between these two extremes, the glasses containing 50 to 55% silica react slowly and will for cements with a setting time acceptable for well completion. It is the glasses of the transition zone that deserve further investigation.

The equilibrium studies have shown that crandallite and perhaps woodhouseite are quaternary compounds which are stable in water at 200°C and can act as cementing phases. Design of glasses which contain leachable calcium and aluminum ions in the same ratio as exist in crandallite should be made to determine their cementing properties. All of the cement frits studied thus far contained calcium and aluminum ions in a 1 to 1 ratio. Higher aluminum is indicated.

Finally, there is indication that the phosphate cement will adhere to steel. It is also time that the phosphoric acid can corrode the steel. As the cementing reaction proceeds the acid is neutralized. To avoid any complications which might arise using the acid in the field, a glass frit should be investigated which could be mixed with water. Such a glass would contain the necessary phosphate. On mixing with water a cement would form by the following reactions: the water leaches phosphate ion from the glass forming phosphoric acid "in situ"; this acid then reacts with the remaining glass constituents (calcium, aluminum and silica) to form a cement matrix. This phosphate cement could reduce the cost of the cement by lowering the energy requirement to make the frit and by avoiding the handling, shipping and mixing of phosphoric acid.

VI. RECOMMENDATIONS

While preliminary results from this study show there is potential for cements as a completion material for geothermal wells, there are many unanswered questions and unsolved problems that must be resolved before the material can be used in the field. The following tasks must be completed if the phosphate cements are to find a use in the geothermal area:

1. Stability data must be obtained for the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at higher temperatures. The data are now available to 200°C and should be extended to 400°C .
2. New glasses should be tested for cementing properties based upon the findings of this work. A glass of higher alumina/lime ratio, one containing zinc and one containing phosphate, should be made and tested.
3. The phosphate liquid must be optimized for maximum cement properties. The proper buffering agents and acid concentration must be determined for each cement.
4. The effects of surface treatments on the adhesion of phosphate cements to mild steel should be investigated. There is evidence to show that the cement might bond well to steel through an iron phosphate phase.
5. Engineering data on an optimum cement must be generated. Mechanical properties tests, high temperature stability, permeability, aggregate design, and better economic data should be obtained.

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VIII. APPENDIX
TABLES OF PRIMARY DATA

Table 1

Weight Loss Data for 30 wt% Glass Fibers

Fiber composition (wt%): 55 SiO₂, 22.5 CaO, 22.5 Al₂O₃

Temperature: 90°C

Acid composition (wt%): 30H₃PO₄

Fiber No.	Time of immersion (hr)	Weight loss (g) Surface area (cm ²)
G ⁹ ₆₁	-----	-----
G ⁹ ₆₂	-----	-----
G ⁹ ₆₃	1.0	0
G ⁹ ₆₄	2.0	1.42 x 10 ⁻⁴
G ⁹ ₆₅	4.0	0
G ⁹ ₆₆	8.0	0.72 x 10 ⁻⁴
G ⁹ ₆₇	16.0	0.7 x 10 ⁻⁴
G ⁹ ₆₈	32.0	2.96 x 10 ⁻⁴
G ⁹ ₆₉	64.0	4.94 x 10 ⁻⁴
G ¹⁰ ₆₁₀	128.0	9.2 x 10 ⁻⁴

Fiber composition (wt%): 55 SiO₂, 22.5 CaO, 22.5 Al₂O₃

Temperature: 40°C

Acid composition (wt%): 30H₃PO₄

G ₆₁	0.167	3.58 x 10 ⁻⁴
G ₆₂	0.5	4.62 x 10 ⁻⁴
G ₆₃	1.0	4.42 x 10 ⁻⁴

Table 1 (cont'd.)

Fiber composition (wt%): 55 SiO₂, 22.5 CaO, 22.5 Al₂O₃

Temperature: 40°C

Acid composition (wt%): 30H₃PO₄

Fiber No.	Time of immersion (hr)	Weight loss (g) Surface area (cm ²)
G ₆₄	2.0	3.7 x 10 ⁻⁴
G ₆₅	4.0	1.04 x 10 ⁻⁴
G ₆₆	8.0	1.1 x 10 ⁻⁴
G ₆₇	16.0	2.58 x 10 ⁻⁴
G ₆₈	32.0	0.82 x 10 ⁻⁴
G ₆₉	64.0	0.922x 10 ⁻⁴
G ₆₁₀	128.0	1.12 x 10 ⁻⁴

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 90°C

Acid composition (wt%): 30H₃PO₄

	Run Number 2	
2G ⁹ _{10,1}	2.5	120.68 x 10 ⁻⁴
2G ⁹ _{10,2}	5.0	104.08 x 10 ⁻⁴
2G ⁹ _{10,3}	7.5	135.66 x 10 ⁻⁴
2G ⁹ _{10,4}	10.0	243.18 x 10 ⁻⁴
2G ⁹ _{10,5}	12.5	233.72 x 10 ⁻⁴
2G ⁹ _{10,6}	15.0	264.70 x 10 ⁻⁴
2G ⁹ _{10,7}	17.5	335.80 x 10 ⁻⁴
2G ⁹ _{10,8}	20.0	407.66 x 10 ⁻⁴

Table 1 (cont'd.)

Fiber composition (wt%): 50 SiO₂, 25 CaO, 25 Al₂O₃

Temperature: 90°C

Acid composition (wt%): 30H₃PO₄

Time of immersion (hr)	Weight loss of the fiber (g)
0.25	0.0028
0.50	0.0066
0.75	0.0099
1.00	0.0126
1.25	0.0160
1.50	0.0199
1.75	0.0246
2.00	0.0251
2.50	0.0317
2.75	0.0367
3.00	0.0390
3.25	0.0456
3.50	0.0497
3.75	0.0504
4.25	0.0575
4.75	0.0634

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 90°C

Acid concentration (wt%): 50H₃PO₄

5.0	0.0034
10.0	0.0064
15.0	0.0086
20.0	0.0103
30.0	0.0139
40.0	0.0169
50.0	0.0203
60.0	0.0217
70.0	0.0233
95.0	0.0285
105.0	0.0299

Table 1 (cont'd)

Fiber composition (wt%): 65 SiO₂, 17.5 CaO, 17.5 Al₂O₃

Temperature: 90°C

Acid concentration (wt%): 30H₃PO₄

Fiber No.	Time of immersion (hr)	Weight loss (g) Surface area (cm ²)
G ₄₁ ⁹	0.167	0
G ₄₂ ⁹	0.5	0
G ₄₃ ⁹	1.0	2.38 x 10 ⁻⁴
G ₄₄ ⁹	2.0	1.568x 10 ⁻⁴
G ₄₅ ⁹	4.0	3.98 x 10 ⁻⁴
G ₄₆ ⁹	8.0	2.36 x 10 ⁻⁴
G ₄₇ ⁹	16.0	3.94 x 10 ⁻⁴
G ₄₈ ⁹	32.0	1.14 x 10 ⁻⁴
G ₄₉ ⁹	64.0	0
G ₄₁₀ ⁹	128.0	0

Fiber composition (wt%): 57 SiO₂, 21.5 CaO, 21.5 Al₂O₃

Temperature: 90°C

Acid concentration (wt%): 30H₃PO₄

G ₈₁ ⁹	0.167	0
G ₈₂ ⁹	0.5	4.26 x 10 ⁻⁴
G ₈₃ ⁹	1.0	0
G ₈₄ ⁹	2.0	5.66 x 10 ⁻⁴
G ₈₅ ⁹	4.0	0
G ₈₆ ⁹	8.0	2.58 x 10 ⁻⁴

Table 1 (cont'd)

Fiber composition (wt%): 57 SiO₂, 21.5 CaO, 21.5 Al₂O₃

Temperature: 90°C

Acid concentration (wt%): 30H₃PO₄

Fiber No.	Time of immersion (hr)	Weight loss (g) Surface area (cm ²)
G ⁹ ₈₇	16.0	4.4 x 10 ⁻⁴
G ⁹ ₈₈	32.0	4.74 x 10 ⁻⁴
G ⁹ ₈₉	64.0	2.06 x 10 ⁻⁴
G ⁹ ₈₁₀	128.0	0

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 40°C

Acid concentration (wt%): 30H₃PO₄

	Run Number 1	
1G ⁴ _{10,1}	0.5	54.68 x 10 ⁻⁴
1G ⁴ _{10,2}	1.0	132.04 x 10 ⁻⁴
1G ⁴ _{10,3}	1.5	210.90 x 10 ⁻⁴
1G ⁴ _{10,4}	2.0	274.24 x 10 ⁻⁴
1G ⁴ _{10,5}	2.5	369.60 x 10 ⁻⁴
1G ⁴ _{10,6}	3.0	419.84 x 10 ⁻⁴
1G ⁴ _{10,7}	3.5	dissolved completely
1G ⁴ _{10,8}	4.0	454.90 x 10 ⁻⁴

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 90°C

Acid concentration (wt%): 30H₃PO₄

	Run Number 1	
1G ⁹ _{10,1}	10.0	220.80 x 10 ⁻⁴

Table 1 (cont'd)

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 90°C

Acid concentration (wt%): 30H₃PO₄

Run Number 1

Fiber No.	Time of immersion (hr)	Weight loss (g)
		Surface area (cm ²)
1G ⁹ _{10,2}	20.0	467.56 x 10 ⁻⁴
1G ⁹ _{10,5}	5.0	118.12 x 10 ⁻⁴
1G ⁹ _{10,6}	15.0	342.42 x 10 ⁻⁴
1G ⁹ _{10,7}	2.5	63.66 x 10 ⁻⁴
1G ⁹ _{10,8}	7.5	143.73 x 10 ⁻⁴
1G ⁹ _{10,9}	12.5	206.66 x 10 ⁻⁴
1G ⁹ _{10,10}	17.5	270.62 x 10 ⁻⁴

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 90°C

Acid concentration (wt%): 30H₃PO₄

Run Number 3

3G ⁹ _{10,1}	2.5	79.64 x 10 ⁻⁴
3G ⁹ _{10,2}	5.0	128.90 x 10 ⁻⁴
3G ⁹ _{10,3}	7.5	163.24 x 10 ⁻⁴
3G ⁹ _{10,4}	10.0	212.10 x 10 ⁻⁴
3G ⁹ _{10,5}	12.5	301.64 x 10 ⁻⁴
3G ⁹ _{10,6}	15.0	347.86 x 10 ⁻⁴
3G ⁹ _{10,7}	17.5	397.68 x 10 ⁻⁴
3G ⁹ _{10,8}	20.0	449.50 x 10 ⁻⁴

Table 1 (cont'd)

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 40°C

Acid concentration (wt%): 50H₃PO₄

Time of immersion (hr)	Weight loss of the fiber (g)
0.50	0.0008
0.75	0.0018
1.00	0.0032
1.25	0.0046
1.50	0.0054
1.75	0.0064
2.00	0.0080
2.25	0.0084
25.75	0.0471
28.00	0.0503
28.50	0.0506
44.75	0.0677
46.00	0.0692
47.00	0.0697

Fiber composition(wt%): 65 SiO₂, 17.5 CaO, 17.5 Al₂O₃

Temperature: 40°C

Acid concentration (wt%): 30H₃PO₄

Fiber No.	Time of immersion (hr)	Weight loss (g) Surface area (cm ²)
G ₄₁	0.167	7.04 x 10 ⁻⁴
G ₄₂	0.5	0
G ₄₃	1.0	1.58 x 10 ⁻⁴
G ₄₄	2.0	0
G ₄₅	4.0	4.9 x 10 ⁻⁴
G ₄₆	8.0	4.94 x 10 ⁻⁴
G ₄₇	16.0	7.16 x 10 ⁻⁴

Table 1 (cont'd)

Fiber composition (wt%): 65 SiO₂, 17.5 CaO, 17.5 Al₂O₃

Temperature: 40°C

Acid concentration (wt%): 30H₃PO₄

Fiber No.	Time of immersion (hr)	Weight loss (g) Surface area (cm ²)
G ₄₈	32.0	3.70 x 10 ⁻⁴
G ₄₉	64.0	0.62 x 10 ⁻⁴
G ₄₁₀	128.0	15.2 x 10 ⁻⁴

Fiber composition (wt%): 57 SiO₂, 21.5 CaO, 21.5 Al₂O₃

Temperature: 40°C

Acid concentration (wt%): 30H₃PO₄

G ₈₁	0.167	0
G ₈₂	0.5	1.605 x 10 ⁻⁴
G ₈₃	1.0	0
G ₈₄	2.0	2.38 x 10 ⁻⁴
G ₈₅	4.0	2.38 x 10 ⁻⁴
G ₈₆	8.0	1.98 x 10 ⁻⁴
G ₈₇	16.0	2.42 x 10 ⁻⁴
G ₈₈	32.0	10.2 x 10 ⁻⁴
G ₈₉	64.0	6.14 x 10 ⁻⁴
G ₈₁₀	128.0	0

Table 1 (cont'd)

Fiber composition (wt%): 53 SiO₂, 23.5 CaO, 23.5 Al₂O₃

Temperature: 90°C

Acid concentration (wt%): 30H₃PO₄

Fiber No.	Time of immersion (hr)	$\frac{\text{Weight loss (g)}}{\text{Surface area (cm}^2\text{)}}$
G ⁹ ₉₁	0.167	8.32 x 10 ⁻⁴
G ⁹ ₉₂	0.5	18.74 x 10 ⁻⁴
G ⁹ ₉₃	1.0	39.09 x 10 ⁻⁴
G ⁹ ₉₄	2.0	91.00 x 10 ⁻⁴
G ⁹ ₉₅	3.0	139.14 x 10 ⁻⁴
G ⁹ ₉₆	4.0	244.00 x 10 ⁻⁴
G ⁹ ₉₇	5.0	252.60 x 10 ⁻⁴
G ⁹ ₉₈	6.0	241.60 x 10 ⁻⁴
G ⁹ ₉₉	8.0	278.00 x 10 ⁻⁴
G ⁹ ₉₁₀	10.0	340.00 x 10 ⁻⁴
G ⁹ ₉₁₁	12.0	304.75 x 10 ⁻⁴
G ⁹ ₉₁₃	32.0	240.16 x 10 ⁻⁴
G ⁹ ₉₁₄	40.0	451.60 x 10 ⁻⁴
G ⁹ ₉₁₅	128.0	307.40 x 10 ⁻⁴

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 40°C

Acid concentration: 30H₃PO₄

	Run Number 2	
2G ⁴ _{10,1}	0.5	78.24 x 10 ⁻⁴
2G ⁴ _{10,2}	1.0	162.60 x 10 ⁻⁴

Table 1 (cont'd)

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 40°C

Acid concentration (wt%): 30H₃PO₄

Run Number 2

Fiber No.	Time of immersion (hr)	$\frac{\text{Weight loss (g)}}{\text{Surface area (cm}^2\text{)}}$
2G ⁴ _{10,3}	1.5	193.00 x 10 ⁻⁴
2G ⁴ _{10,4}	2.0	306.30 x 10 ⁻⁴
2G ⁴ _{10,5}	2.5	322.00 x 10 ⁻⁴
2G ⁴ _{10,6}	3.0	362.00 x 10 ⁻⁴
2G ⁴ _{10,7}	3.5	470.90 x 10 ⁻⁴
2G ⁴ _{10,8}	4.0	554.00 x 10 ⁻⁴

Fiber composition (wt%): 50 SiO₂, 25 CaO, 25 Al₂O₃

Temperature: 40°C

Acid concentration (wt%): 30 H₃PO₄

	Time of immersion (hr)	Weight loss of the fiber (g)
	1.00	0.0041
	2.00	0.0048
	2.50	0.0052
	2.75	0.0059
	3.00	0.0064
	3.25	0.0066
	3.50	0.0070
	3.75	0.0071
	4.00	0.0077
	4.25	0.0082
	4.50	0.0100
	4.75	0.0111
	5.00	0.0114
	5.25	0.0127
	7.50	0.0177
	8.25	0.0187
	8.50	0.0203

Table 1 (cont'd)

Fiber composition (wt%): 50 SiO₂, 25 CaO, 25 Al₂O₃

Temperature: 40°C

Acid concentration (wt%): 30 H₃PO₄

Time of immersion (hr)	Weight loss of the fiber (g)
---------------------------	---------------------------------

8.75	0.0210
9.00	0.0214
22.50	0.0415
23.00	0.0430
24.00	0.0444
24.50	0.0453

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 40°C

Acid concentration (wt%): 10H₃PO₄

0.25	0.0015
0.50	0.0026
0.75	0.0038
1.00	0.0059
1.25	0.0068
1.75	0.0082
2.00	0.0096
2.25	0.0105
2.50	0.0122
3.75	0.0163
4.00	0.0178
4.50	0.0191

Table 1 (cont'd)

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 90°C

Acid concentration (wt%): 10H₃PO₄

Time of immersion (mins)	Weight loss of the fiber (g)
10.0	0.0068
20.0	0.0120
25.0	0.0142
30.0	0.0163
40.0	0.0208
45.0	0.0216
50.0	0.0232
55.0	0.0247
60.0	0.0259
65.0	0.0274

Fiber composition (wt%): 53 SiO₂, 23.5 CaO, 23.5 Al₂O₃

Temperature: 40°C

Acid concentration (wt%): 30H₃PO₄

Fiber No.	Time of immersion (hr)	Weight loss (g) Surface area (cm ²)
G ₉₁	0.167	0
G ₉₂	0.5	2.24 x 10 ⁻⁴
G ₉₃	1.0	6.06 x 10 ⁻⁴
G ₉₄	2.0	4.92 x 10 ⁻⁴
G ₉₅	4.0	16.14 x 10 ⁻⁴
G ₉₆	8.0	39.16 x 10 ⁻⁴
G ₉₇	16.0	65.62 x 10 ⁻⁴
G ₉₈	32.0	107.44 x 10 ⁻⁴
G ₉₉	64.0	196.64 x 10 ⁻⁴
G ₉₁₀	128.0	305.42 x 10 ⁻⁴

Table 1 (cont'd)

Fiber composition (wt%): 40 SiO₂, 30 CaO, 30 Al₂O₃

Temperature: 65°C

Acid concentration (wt%): 30H₃PO₄

Time of immersion (mins)	Weight loss of the fiber (g)
10	0.00178
15	0.0032
20	0.0050
30	0.0110
35	0.0130
45	0.0176
55	0.0201
65	0.0216
75	0.0246

Table 2

Results of Experiments Made in The System

 $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$ at 200°C

No.	Composition, wt%			Time	Phases present
	CaO	P_2O_5	H_2O	days, hr	
C1	5.0	38.0	57.0	14d	L + V
C3	5.0	47.5	47.5	9d, 5h	L + V
C4	10.0	45.0	45.0	9d, 5h	$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{L} + \text{V}$
C5	5.0	28.5	66.5	9d, 3h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C6	10.0	27.0	63.0	6d, 18h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C7	5.0	19.0	76.0	13d, 23h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C8	5.0	9.5	85.5	15d, 23h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C9	5.42	31.58	63.0	7d, 20h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C10	4.99	22.37	72.64	11d	$\text{CaHPO}_4 + \text{L} + \text{V}$
C11	4.77	13.15	82.08	9d, 3h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C12	2.87	7.16	89.97	13d, 23h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C13	1.0	4.95	94.05	20d, 9h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C14	2.0	4.9	93.1	20d, 9h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C15	3.0	4.85	92.15	20d, 9h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C16	4.0	4.8	91.2	20d, 9h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C17	5.0	4.75	90.25	19d, 10h	$\text{CaHPO}_4 + \text{Ca}_5(\text{PO}_4)_3\text{OH}$ + L + V
C18	1.0	1.98	97.02	11d, 4h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C19	2.0	1.96	96.04	15d, 4h	$\text{CaHPO}_4 + \text{L} + \text{V}$
C20	3.0	1.94	95.06	16d, 20h	$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{L} + \text{V}$
C21	4.0	1.92	94.08	16d, 20h	$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{L} + \text{V}$

Table 2 (cont..)

No.	Composition, wt%			Time days, hr	Phases present
	CaO	P ₂ O ₅	H ₂ O		
C22	5.0	1.9	93.1	16d, 22h	Ca ₅ (PO ₄) ₃ OH+L+V
C23	10.0	1.8	88.2	12d, 19h	Ca ₅ (PO ₄) ₃ OH+L+V
C24	0.81	2.66	96.53	9d, 21h	CaHPO ₄ + L + V
C25	1.95	3.58	94.47	13d, 22h	CaHPO ₄ + L + V
C26	2.71	4.19	93.1	15d, 16h	CaHPO ₄ + L + V
C27	3.8	5.06	91.14	15d, 9h	CaHPO ₄ + L + V
C28	4.88	5.94	89.18	15d, 10h	CaHPO ₄ + L + V
C29	8.14	8.56	83.3	15d, 11h	CaHPO ₄ +Ca ₅ (PO ₄) ₃ OH + L + V
C30	4.88	40.52	54.6	5d	L + V
C31	5.97	40.63	53.4	13d, 5h	CaHPO ₄ +Ca(H ₂ PO ₄) ₂ · H ₂ O+L+V
C32	7.05	40.75	52.2	13d, 20h	CaHPO ₄ +Ca(H ₂ PO ₄) ₂ · H ₂ O+L+V
C34	1.0	29.7	69.3	9d, 12h	L + V
C35	2.0	29.4	68.6	9d, 12h	L + V
C36	3.0	29.1	67.9	9d, 12h	L + V
C37	4.0	28.8	67.2	9d, 12h	CaHPO ₄ + L + V
C38	6.0	37.6	56.4	26d, 2h	CaHPO ₄ +Ca(H ₂ PO ₄) ₂ · H ₂ O+L+V
C39	7.0	37.2	55.8	26d, 2h	CaHPO ₄ +Ca(H ₂ PO ₄) ₂ · H ₂ O+L+V

Table 2 (cont.)

No.	Composition, wt%			Time		Phases present
	CaO	P ₂ O ₅	H ₂ O	days, hr		
C40	8.0	36.8	55.2	26d, 2h		CaHPO ₄ + L + V
C41	6.0	47.0	47.0	26d, 2h		L + V
C42	7.0	46.5	46.5	20d, 10h		CaHPO ₄ +Ca(H ₂ PO ₄) ₂ · H ₂ O+L+V
C44	1.0	19.8	79.2	8d		L + V
C45	2.0	19.6	78.4	8d		L + V
C46	3.0	19.4	77.6	7d, 22h		CaHPO ₄ + L + V
C47	4.0	19.2	76.8	7d, 23h		CaHPO ₄ + L + V
C48	1.0	9.9	89.1	10d		L + V
C49	2.0	9.8	88.2	10d		CaHPO ₄ + L + V
C50	3.0	9.7	87.3	10d		CaHPO ₄ + L + V
C51	4.0	9.6	86.4	10d, 1h		CaHPO ₄ + L + V
C52	5.0	58.52	36.48	20d, 10h		L + V
C53	6.0	57.9	36.1	20d, 10h		Ca(H ₂ PO ₄) ₂ ·H ₂ O+L+V
C54	7.0	57.29	35.71	26d		Ca(H ₂ PO ₄) ₂ ·H ₂ O+L+V
C55	8.0	56.67	35.33	26d, 1h		Ca(H ₂ PO ₄) ₂ ·H ₂ O+L+V
C56	9.0	56.06	34.94	26d, 2h		Ca(H ₂ PO ₄) ₂ ·H ₂ O+L+V
C57	2.87	60.77	36.36	17d, 10h		L + V
C58	3.85	60.48	35.67	17d, 10h		L + V
C59	4.83	60.19	34.98	17d, 10h		L + V

Table 3
Results of Experiments Made for the System
 $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$

No.	Composition, wt%			Time, hr	Phases present
	Al_2O_3	P_2O_5	H_2O		
A1	5.0	38.0	57.0	220	$\text{AlPO}_4 + \text{L} + \text{V}$
A2	10.0	36.0	54.0	220	$\text{AlPO}_4 + \text{L} + \text{V}$
A3	5.0	47.5	47.5	220	$\text{AlPO}_4 + \text{L} + \text{V}$
A4	10.0	45.0	45.0	220	$\text{AlPO}_4 + \text{L} + \text{V}$
A5	1.0	49.5	49.5	1.5	$\text{L} + \text{V}$
A6	2.0	58.8	39.2	1.5	$\text{L} + \text{V}$
A7	3.0	58.2	38.8	4	$\text{L} + \text{V}$
A8	4.0	57.6	38.4	9	$\text{L} + \text{V}$
A9	5.0	57.0	38.0	48	$\text{L} + \text{V}$
A10	6.0	56.4	37.6	121	$\text{AlPO}_4 + \text{L} + \text{V}$
A11	4.0	59.14	36.86	46	$\text{L} + \text{V}$
A12	5.0	58.52	36.84	19	$\text{L} + \text{V}$
A13	6.0	57.9	36.1	75	$\text{AlPO}_4 + \text{L} + \text{V}$
A14	7.0	57.29	35.71	75	$\text{AlPO}_4 + \text{L} + \text{V}$
A15	8.0	56.67	35.33	71	$\text{AlPO}_4 + \text{L} + \text{V}$
A16	2.0	49.0	49.0	17	$\text{L} + \text{V}$
A17	3.0	48.5	48.5	22	$\text{L} + \text{V}$
A18	4.0	48.0	48.0	41	$\text{AlPO}_4 + \text{L} + \text{V}$
A19	1.0	39.6	59.4	1	$\text{L} + \text{V}$
A20	2.0	39.2	58.8	50	$\text{AlPO}_4 + \text{L} + \text{V}$
A21	3.0	38.8	58.2	50	$\text{AlPO}_4 + \text{L} + \text{V}$
A22	1.0	19.8	79.2	82	$\text{AlPO}_4 + \text{L} + \text{V}$

Table 3 (cont.)

No.	Composition, wt%			Time, hr	Phases present
	Al ₂ O ₃	P ₂ O ₅	H ₂ O		
A23	2.0	19.6	78.4	93	AlPO ₄ + L + V
A24	1.0	29.7	69.3	93	AlPO ₄ + L + V
A25	2.0	29.4	68.6	93	AlPO ₄ + L + V
A26	1.0	4.95	94.05	312	AlPO ₄ + L + V
A27	2.0	4.9	93.1	312	AlPO ₄ + L + V
A28	1.0	9.9	89.1	312	AlPO ₄ + L + V
A29	2.0	9.8	88.2	312	AlPO ₄ + L + V
A30	2.0	0	98.0	116	Al ₂ O ₃ ·xH ₂ O + L + V
A31	5.0	0	95.0	116	Al ₂ O ₃ ·xH ₂ O + L + V
A32	10.0	0	90.0	116	γ-AlOOH + Al ₂ O ₃ ·xH ₂ O + L + V
A33	5.0	4.75	90.25	113	AlPO ₄ + AlPO ₄ (T) + L + V
A34	10.0	4.5	85.5	113	Angelite + L + V
A35	1.93	63.51	34.56	24	L + V
A36	3.86	65.42	30.72	57	L + V
A37	5.8	67.32	26.88	177	AP ₃ H ₆ + L + V
A38	7.73	69.23	23.04	177	AP ₃ H ₆ + L + V
A39	9.66	71.14	19.2	177	AP ₃ H ₆ + L + V
A45	1.0	1.98	97.02	394	AlPO ₄ + L + V
A46	2.0	1.96	96.04	399	AlPO ₄ (T) + L + V
A49	5.0	1.9	93.1	404	Angelite + L + V

Table 3 (cont.)

No.	Composition, wt%			Time, hr	Phases present
	Al ₂ O ₃	P ₂ O ₅	H ₂ O		
A51	3.0	4.85	92.15	413	AlPO ₄ + L + V
A52	4.0	4.8	91.2	413	AlPO ₄ + L + V
A53	5.0	4.75	90.25	424	AlPO ₄ + AlPO ₄ (T) + L + V
A54	10.0	4.5	85.5	424	Augelite + L + V
A55	5.0	9.5	85.5	424	AlPO ₄ + L + V
A56	6.0	9.4	84.6	428	AlPO ₄ + L + V
A57	7.0	9.3	83.7	428	AlPO ₄ + L + V
A58	10.0	9.0	81.0	428	Augelite + AlPO ₄ (T) + L + V
A59	5.8	67.32	26.88	471	AP ₃ H ₆ + L + V
A60	6.18	67.71	26.11	590	AP ₃ H ₆ + L + V
A61	6.76	68.28	24.96	492	AP ₃ H ₆ + L + V
A62	7.73	69.23	23.04	590	AP ₃ H ₆ + L + V
A63	6.91	63.14	29.95	586	AlPO ₄ + L + V
A64	7.85	63.35	28.8	586	AlPO ₄ + L + V
A65	8.8	63.55	27.65	588	AlPO ₄ + L + V
A66	9.74	63.76	26.5	590	AlPO ₄ + L + V
A67	10.68	63.98	25.34	591	AlPO ₄ + L + V

Table 4

Results of experiment made in the system $\text{CaO-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-H}_2\text{O}$ at 200°C

No.	Composition, wt%				Time (hr)	Phases present
	CaO	Al_2O_3	P_2O_5	H_2O		
75-1	1.5	0.5	9.8	88.2	92	$\text{AlPO}_4 + \text{CaHPO}_4 + \text{Liq.}$
75-2	3.0	1.0	9.6	86.4	92	$\text{AlPO}_4 + \text{CaHPO}_4 + \text{Liq.}$
75-3	4.5	1.5	9.4	84.6	138	$\text{AlPO}_4 + \text{CaHPO}_4 + \text{Liq.}$
75-4	6.0	2.0	9.2	82.8	98	$\text{AlPO}_4 + \text{CaHPO}_4 + \text{Liq.}$
75-5	7.5	2.5	9.0	81.0	98	$\text{AlPO}_4 + \text{CaHPO}_4 + \text{Liq.}$
75-6	1.5	0.5	29.4	68.6	138	Liq.
75-7	3.0	1.0	28.8	67.2	69	$\text{AlPO}_4 + \text{Liq.}$
75-8	4.5	1.5	28.2	65.8	138	$\text{AlPO}_4 + \text{CaHPO}_4 + \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}^* + \text{Liq.}$
75-9	6.0	2.0	27.6	64.4	142	$\text{AlPO}_4 + \text{CaHPO}_4 + \text{Liq.}$
75-10	7.5	2.5	27.0	63.0		Loss of Sample
75-11	1.5	0.5	49.0	49.0	48	Liq.
75-12	3.0	1.0	48.0	48.0	48	Liq.
75-13	4.5	1.5	47.0	47.0	120	$\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}^* + \text{Liq.}$
75-14	6.0	2.0	46.0	46.0	144	$\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}^* + \text{Liq.}$
75-15	7.5	2.5	45.0	45.0	120	$\text{CaAl}_3(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O} + \text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}^* + \text{Liq.}$
50-1	1.0	1.0	9.8	88.2	70	$\text{AlPO}_4 + \text{Liq.}$
50-2	2.0	2.0	9.6	86.4	96	$\text{AlPO}_4 + \text{Liq.}$
50-3	3.0	3.0	9.4	84.6	120	$\text{AlPO}_4 + \text{Liq.}$
50-4	4.0	4.0	9.2	82.8	120	$\text{AlPO}_4 + \text{Liq.}$
50-5	5.0	5.0	9.0	81.0	120	$\text{AlPO}_4 + \text{Liq.}$
50-6	1.0	1.0	29.4	68.6	72	$\text{AlPO}_4 + \text{Liq.}$

Table 4 (cont'd.)

No.	Composition, wt%				Time (hr)	Phases present
	CaO	Al ₂ O ₃	P ₂ O ₅	H ₂ O		
50-7	2.0	2.0	28.8	67.2	72	AlPO ₄ + Liq.
50-8	3.0	3.0	28.2	65.8	66	AlPO ₄ + Liq.
50-9	4.0	4.0	27.6	64.4	72	AlPO ₄ + CaHPO ₄ + Liq.
50-10	5.0	5.0	27.0	63.0	66	AlPO ₄ + CaHPO ₄ + Liq.
50-11	1.0	1.0	49.0	49.0	18	Liq.
50-12	2.0	2.0	48.0	48.0	95	Liq.
50-13	3.0	3.0	47.0	47.0	72	AlPO ₄ + Liq.
50-14	4.0	4.0	46.0	46.0	95	AlPO ₄ + Liq.
50-15	5.0	5.0	45.0	45.0	95	AlPO ₄ + Liq.
25-1	0.5	1.5	9.8	88.2	500	AlPO ₄ + Liq.
25-2	1.0	3.0	9.6	86.4	453	AlPO ₄ + Liq.
25-3	1.5	4.5	9.4	84.6	500	AlPO ₄ + Liq.
25-4	2.0	6.0	9.2	82.8	523	AlPO ₄ + CaHPO ₄ + Liq.
25-5	2.5	7.5	9.0	81.0	453	AlPO ₄ + Liq.
25-6	0.5	1.5	29.4	68.6	453	AlPO ₄ + Liq.
25-7	1.0	3.0	28.8	67.2	453	AlPO ₄ + Liq.
25-8	1.5	4.5	28.2	65.8	523	AlPO ₄ + Liq.
25-9	2.0	6.0	27.6	64.4	453	AlPO ₄ + Liq.
25-10	2.5	7.5	27.0	63.0	478	AlPO ₄ + Liq.
25-11	0.5	1.5	49.0	49.0	478	Liq.
25-12	1.0	3.0	48.0	48.0	478	Liq + Tiny Amount of Solid
25-13	1.5	4.5	47.0	47.0	478	AlPO ₄ + Liq.

Table 4 (cont'd.)

No.	Composition, wt%			H ₂ O	Time (hr)	Phases present
	CaO	Al ₂ O ₃	P ₂ O ₅			
25-14	2.0	6.0	46.0	46.0	478	AlPO ₄ + Liq.
25-15	2.5	7.5	45.0	45.0	478	AlPO ₄ + Liq.
W-1	8.0	1.0	1.0	90.0	788	Ca ₅ (PO ₄) ₃ (OH) + Liq.
W-2	5.9	1.0	3.1	90.0	1412	Ca ₅ (PO ₄) ₃ (OH) + Liq.
W-3	5.9	3.0	1.1	90.0	600	Ca ₃ Al ₂ (OH) ₁₂ + Ca ₅ (PO ₄) ₃ (OH) + Liq.
W-4	3.5	1.5	5.0	90.0	808	AlPO ₄ + Ca ₅ (PO ₄) ₃ (OH) + Liq.
W-5	4.0	4.0	2.0	90.0	763	γ-AlOOH + Ca ₅ (PO ₄) ₃ (OH) + Liq.
W-6	4.0	5.0	1.0	90.0	642	γ-AlOOH + Ca ₅ (PO ₄) ₃ (OH) + Ca ₃ Al ₂ (OH) ₁₂ + Liq.
W-7	2.0	1.2	6.8	90.0	1388	AlPO ₄ + CaHPO ₄ + Liq.
W-8	3.0	2.0	5.0	90.0	1388	AlPO ₄ + CaHPO ₄ + Liq.
W-9	2.0	5.0	3.0	90.0	861	Ca ₅ (PO ₄) ₃ (OH) + CaHPO ₄ + X-phase** + Liq.
W-10	2.0	7.0	1.0	90.0	1388	γ-AlOOH + Ca ₅ (PO ₄) ₃ (OH) + Liq.
W-11	6.9	1.0	2.0	90.1		Loss of Sample
W-12	4.9	1.0	4.1	90.0	811	Ca ₅ (PO ₄) ₃ (OH) + Liq.
W-13	4.9	3.0	2.1	90.0	811	Ca ₅ (PO ₄) ₃ (OH) + γ-AlOOH + Liq.
W-14	3.5	5.0	1.5	90.0	811	Ca ₅ (PO ₄) ₃ (OH) + γ-AlOOH + Liq.
W-15	2.9	0.9	6.2	90.0	788	AlPO ₄ + CaHPO ₄ + Liq.
W-16	3.0	2.9	4.1	90.0	739	Ca ₅ (PO ₄) ₃ (OH) + Al ₂ PO ₄ (OH) ₃ + CaAl ₃ (PO ₄) ₂ (OH) ₅ H ₂ O + Liq.

Table 4 (cont'd.)

No.	Composition, wt%			H ₂ O	Time (hr)	Phases present
	CaO	Al ₂ O ₃	P ₂ O ₅			
W-17	3.0	5.1	1.9	90.0	1244	Ca ₅ (PO ₄) ₃ OH + Al ₂ PO ₄ (OH) ₃ + Liq.
W-18	2.7	5.0	2.3	90.0	642	Ca ₅ (PO ₄) ₃ OH + Liq.
W-19	2.0	4.0	4.0	90.0	600	Ca ₅ (PO ₄) ₃ OH + Al ₂ PO ₄ (OH) ₃ + Liq.
W-20	4.1	2.3	3.6	90.0	788	Ca ₅ (PO ₄) ₃ OH + AlPO ₄ + Liq.

* Probably formed on cooling.

** Has crystalline structure similar to that of Woodhouseite, CaAl₃(PO₄)(SO₄)(OH)₆, which is like crandallite, CaAl₃(PO₄)₂(OH)₅ H₂O, with some water loss if (PO₄) group replaces (SO₄) group.