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13. ABSTRACT *(Maximum 200 words)*

The objectives of this program were to investigate the relationships among phase equilibria, kinetics, mechanisms and microstructural development in chemically bonded ceramics which exhibit cementing properties. This objective was based on the need to identify the above relationships if advanced cement-based materials are to be developed. Although cements are normally regarded as civil engineering materials, this view is unduly limited. Emphasis in this program was on the broader objectives of near net shape fabrication at low temperature. The use of the term "cement-based" is intended to imply that the reactions leading to microstructural development occur in an aqueous environment. Emphasis was on non-civil engineering materials, as such these materials are called chemically bonded ceramics.

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FINAL REPORT
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Principal Investigator:
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GENERAL SUMMARY OF ACCOMPLISHMENTS

The program has demonstrated that chemically bonded ceramics (CBC's) can be formed by reaction involving an aqueous phase regardless of whether the products formed contain water of crystallization (as do the hydrated calcium silicates), hydroxyl water (as does hydroxyapatite: $Ca_5(PO_4)_3OH$) or are completely anhydrous (as is $AlPO_4$). The general goals of the program were to establish generic relationships between phase equilibria, microstructure, and kinetics of reaction. These goals were met for each of the classes of compounds described above. Because it was a major goal to develop fundamental underpinnings in the general area of chemically bonded ceramics it was a concomitant goal to demonstrate the advantages associated with this class of ceramics. Several accomplishments from the program warrant specific mention:

The first has been to demonstrate the formation of hydroxyapatite under conditions of clinical relevance (38°C and near neutral pH). Because the reaction reaches a substantial degree of completion in a relatively short time, this reaction has evoked interest on the part of the medical community and it is likely that further work will go forward in this area. Thus, the results of the present program may be used in the formation of synthetic bone in vivo and in a period during which it is suitable to maintain an individual in an operating theatre.

Secondly, the mechanism of the so-called alkali-silica reaction in concrete was elucidated. This reaction results in damage to concrete which results in repair costs which probably exceed one hundred million dollar annually.

Thirdly, we demonstrated a low temperature route to $AlPO_4$. $AlPO_4$ in the cristobalite polymorph is stable to above 1800°C. In contrast to conventional ceramic processing which requires application high temperature, sometimes coupled with high pressure, we produced $AlPO_4$ at ambient pressure and at a temperature of less than 10% of its stability limit. This is believed to be significant in that it demonstrates that low temperature routes can be used to produce high temperature materials. In general, the more innocuous the processing conditions required to form the compounds of interest, the greater is the latitude with respect to combining materials to realize composites having advanced properties and to achieving complex geometries at net shape.

Twenty-five publications will result from this 3 year effort. Three awards have been received in association with the work done in this program.

OBJECTIVES

The objectives of this program were to investigate the relationships among phase equilibria, kinetics, mechanisms and microstructural development in chemically bonded ceramics which exhibit cementing properties. This objective was based on the need to identify the above relationships if advanced cement-based materials are to be developed. Although cements are normally regarded as civil engineering materials, this view is unduly limited. Emphasis in this program was on the broader objectives of near net shape fabrication at low temperature. The use of the term "cement-based" is intended to imply that the reactions leading to microstructural development occur in an aqueous environment. Emphasis was on non-civil engineering materials, as such these materials are called chemically bonded ceramics.

The rationale for the approach used in this program was two-fold:

1. to exploit the possibility of fabricating both individual materials and composite materials at near net shape
2. to carry out the fabrication under relatively innocuous processing conditions with respect to pressure and temperature.

WORK DONE

In contrast to conventional ceramics, it is not undesirable for the reactants in cement-based systems to have a range of particle size distributions. This is because the nature of the reactions that occur in these systems do not lead to difficulties with exaggerated grain growth. Thus it is desirable to fill space as efficiently as possible prior to the reactions. However, assessing the kinetics of reactions of polydisperse systems is made difficult by the fact that particles exhibiting a range of sizes are reacting. There is an important relationship between the rate of property development and particle size distribution. Because the products of cement-like reactions tend to form as barriers on the surfaces of the reactants, the rate-limiting step may change from one involving surface area control to one involving diffusion control. It is desirable within the constraints of effective space filling to avoid depending on a diffusionally controlled process of property development. It should be noted that the results of this analysis are quite general and apply to reactions involving polydisperse powders regardless of composition.

One of the attributes to cement-based systems is that chemistry can be used to specifically control microstructural development. In the system CaO-Al_2O_3-$CaSO_4$-H_2O, a fibrous phase, ettringite, can form. If this is the first-formed phase, then it is possible to form an <u>in-situ</u> composite material. However, the formation of such a composite relies both on the proper sequence of reactions occurring and of the formation of the fibrous phase reaching completion prior to the formation of a matrix phase. As a basis for controlling the sequence of reactions, an analysis of the kinetics of ettringite formation was carried out.

In civil engineering materials, the reacting species are commonly in the same molecule. For example, in tricalcium aluminate, $3CaO \cdot Al_2O_3$, basic calcium oxide and acidic (in this context) aluminum oxide are present in the same molecule. When placed in water the molecule hydrolyzes and calcium aluminate hydrates form. This diminishes the latitude for controlling the chemistry of such a reaction. However, in other systems, such as the aluminum phosphate and calcium phosphate systems, it is possible to specifically control the conditions under which product formation occurs. This can be done by mixing acidic and basic phosphates whose solubility curves form a ternary invariant point which is unstable with respect to a product phase. The benefits to this in terms of controlling the microstructure of the product phases has not been appreciated. In because the formation of the product phase occurs in a solution of constant composition, it is possible to manipulate the nature of the solution speciation in a manner that may allow direct microstructural control. Another benefit to this approach is that the pH conditions under which such reaction occur can be controlled to some degree. This is important when fibers that may lose desirable properties when exposed to strongly acidic or strongly basic solutions are present. These considerations, along with those related to the effects of porosity have been discussed in a number of published outputs.

The stabilities of many of the phases of importance in cement-based systems remain poorly understood. This is because they frequently involve quaternary or higher order systems. For example, the stabilities of alkali substituted calcium silicate hydrates and calcium substituted sodium silicate hydrates require consideration of quaternary equilibria. Representation of the stability regions by a method developed by the author allows phase relationships in quaternary systems to be more effectively illustrated. An analysis of the equilibria in the system: CaO-SiO_2-Na_2O-H_2O has been carried out. This analysis was based on an innovative representation technique developed in this program and was used to demonstrate the principle that mechanistic paths in quaternary systems can be carried out. This specific quaternary system was selected for study because the establishment of mechanisms by which a phenomenon called the alkali-silica reaction occurs has been the objective of continued research interest since about 1940 because this reaction is a major cause of deterioration in concrete.

The approach taken in the fabrication of hydroxyapatite, $Ca_5(PO_4)_3OH$, monoliths by the method that has used provides a generic model for the fabrication of a broad class of chemically bonded ceramics (CBC's). The term CBC is used in his regard to denote materials that may be fabricated using cement-type reactions but that do not contain free water of hydration. Thus, CBC's are not, therefore, intrinsically limited to low temperature applications. Hydroxyapatite, for example, is stable to 1450°C or more, while $AlPO_4$ is stable to about 1800°C.

As mentioned above, there are distinct advantages associated with the formation of a chemically bonded ceramic at an invariant point. In this instance, the invariant point involving $CaHPO_4$ and $Ca_4(PO_4)_2O$ and solution is metastable with respect to hydroxyapatite, $Ca_5(PO_4)_3OH$. Thus, hydroxyapatite is formed at a nearly constant condition in solution. It is also formed from a solution that is much closer to a neutral pH than if hydroxyapatite were being precipitated by reaction of neutral salts or by an acid-base reaction of the type: $Ca(OH)_2 + H_3PO_4$. Because the conditions in solution are not strongly acidic nor strongly basic in the present instance, should such a reaction occur in the presence of fibers, whether ceramic, metallic or polymeric, the introduction of strength-limiting flaws in the fiber surfaces becomes much less of a problem. Thus, the strategy summarized here may provide a means to the fabrication of net shape composites at low temperature and pressure.

To establish the viability of this approach the kinetics of the reaction to hydroxyapatite discussed above have been investigated. It was established that the rate of reaction shows a strong temperature dependence over the range of temperatures between 5° and 60°C. Reaction approaches substantial degree of completion after relatively short times. Microstructural development could be directly correlated with phase equilibria, with rate-limiting kinetic mechanisms, and with solution chemical parameters.

It is worthy of note that this work is of significance in that it demonstrates the ability to form ceramic matrix phases at low temperature and pressure. These conditions are compatible with composite formation almost regardless of the composition of the fibers involved. This is because the reaction to hydroxyapatite approaches completion in several hours. and occurs in solution pH conditions that are innocuous. Work to establish whether high-temperature aluminum phosphates can be fabricated as described above, was also carried out. This work demonstrated that the cristobalite and berlinite polymorphs of $AlPO_4$ could be formed at temperatures below 140°C.

AWARDS

Three awards were given based on the results obtained in this investigation. These are listed below.

PUBLICATIONS

Twenty-five publications will result from this program. Of these 14 have been published or accepted, three have been submitted, and the remainder are in preparation.

AWARDS:

Paper: "The Approach of Cement-Based Materials to Phase Equilibria." Nominated for Best Paper Award, Nuclear Division American Ceramic Society.

Paper: "The Influence of Particle Size Distribution on the Kinetics of Tricalcium Silicate Hydration," P. W. Brown, J. Am. Ceram. Soc., 72, 1829 (1989)." Awarded best paper award, Cements Division American Ceramic Society.

Xerox Award: "The Kinetics of Hydroxyapatite Formation at Low Temperature," M. Fulmer and P. W. Brown, J. Am. Ceram. Soc. 74, 934-40 (1991).

OUTPUTS ACKNOWLEDGING AFOSR

1. P.W. Brown, "Hydration Reactions in Non-Civil Engineering Systems," in Advances in The Manufacture and Use of Cement, E. Gartner, Ed., Engr. Foundation (1989).
2. "Kinetics and Solution Chemistry of Hydroxyapatite Formation," Materials Synthesis Utilizing Biological Processes, M. Fulmer and P.W. Brown, 39, MRS, P. Rieke, P. Calvert, and M. Alper, Eds. (1990).
3. "Low Temperature Synthesis of $AlPO_4$," Advances in Cementitious Materials, J.V. Bothe and P.W. Brown, Ceramic Trans. 16, 689-700 (1991).
4. Cements Research Progress-1987, P. W. Brown, Ed., American Ceramic Society (1989).
5. Cements Research Progress-1988, P. W. Brown, Ed., American Ceramic Society (1990).
6. "The Kinetics of Ettringite Formation," P.W. Brown and P. LaCroix, Cement and Concrete Res. 19, 879 (1989).
7. "The Influence of Particle Size Distribution on the Kinetics of Tricalcium Silicate Hydration," P.W. Brown, J. Am. Ceram. Soc., 72, 1829 (1989).
8. "The System Na_2O-CaO-SiO_2-H_2O," P.W. Brown, J. Am. Ceram. Soc. 73(11) 3457 (1990).

9. "Early Age Cement Hydration Reactions," P.W. Brown, Trans. Res. Rec., No. 1284, 53-59 (1991).

10. "The Kinetics of Hydroxyapatite Formation at Low Temperature," M. Fulmer and P.W. Brown, J. Am. Ceram. Soc. 74, 934-40 (1991).

11. "The Solution Chemistry of Hydroxyapatite Formation at Low Temperature," P.W. Brown, N. Hocker, and S. Hoyle, J. Am. Ceram. Soc. 74, 1855 (1991).

ACCEPTED

12. "Formation of Hydroxyapatite at Near-Physiological Temperature," M.T. Fulmer, R.I. Martin, and P.W. Brown, J. Mat. Sci. Materials in Medicine,

13. "A Model for the Variations in the Aqueous Phase During the Hydration of Tricalcium Silicate," P.W. Brown and D. Shi, Advances in Cement Research.

14. "Ettringite Formation," P.W. Brown, Cem. Concr. Res. 21(5), 958 (1991).

SUBMITTED

15. "The Kinetics of Tricalcium Aluminate and Tetracalcium Aluminoferrite Hydration in the Presence of Calcium Sulfate," P.W. Brown, J. Am. Ceram. Soc.

16. "The Hydration of Tricalcium Germanate-Tricalcium Silicate Solid Solutions," D. Sample and P.W. Brown, J. Am. Cer. Soc.

17. "Hydration in the System Ca_2SiO_4-$Ca_3(PO_4)_2$ at 90°C," M. Barnes, M. Klimkiewicz, and P.W. Brown, J. Am. Ceram. Soc.

DRAFTS COMPLETED BUT NOT YET SUBMITTED

18. "Effects of the Common Ion Buffers Na_2HPO_4 and NaH_2PO_4 on Hydroxyapatite Formation," M. Fulmer and P.W. Brown, J. Mat. Res.

19. "Invariance Among Acidic Calcium Phosphates," M. Fulmer and P.W. Brown, J. Cryst. Growth

20. "The Effect of Fluoride on the Kinetics and Solution Chemistry of Hydroxyapatite Formation at 25°C, M. Fulmer and P.W. Brown, J. Mat. Sci.

IN PROGRESS

21. "Microstructural Development During the Low-Temperature Formation of $AlPO_4$," planned submission, J.V. Bothe and P.W. Brown, J. Am. Ceram. Soc.

22. "Kinetics of Reaction of Alumina and Hydrated Alumina with Phosphoric Acid," J.V. Bothe and P.W. Brown, planned submission, J. Am. Ceram. Soc.

23. "Hydrolysis of Brushite," M. Fulmer and P.W. Brown, planned submission, J. Cryst. Growth

24. "Effects of Temperature on the Low-Temperature Formation of Hydroxyapatite," M. Fulmer and P.W. Brown, planned submission, J. Mat. Res.

25. "Interrelationships Among Reactant Particle Size Distribution, and Common Ion Effects on the Low-Temperature Formation of Hydroxyapatite," M. Fulmer and P.W. Brown, planned submission, J. Mat. Sci.

SELECTED ABSTRACTS FROM PUBLISHED AND SUBMITTED PAPERS:

Low Temperature Synthesis of $AlPO_4$

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ABSTRACT

A reactive alumina was utilized to form aluminum orthophosphate, $AlPO_4$, at temperatures below 150°C. Well crystallized berlinite was the predominant phase at 110°C, whereas poorly crystallized cristobalite predominated at 80°C. The crystallization process takes place primarily in solution with the degree of crystallization increasing as the amount of time the reactants are allowed to soak at room temperature increases.

VARIATIONS IN SOLUTION CHEMISTRY DURING THE LOW-TEMPERATURE FORMATION OF HYDROXYAPATITE

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ABSTRACT

Both the kinetics and the microstructure of monolithic hydroxyapatite formed by a low-temperature dissolution and precipitation reaction strongly depend on the conditions in solution during the reaction. The relationships between the molar ratio of the particulate reactants, dicalcium phosphate and tetracalcium phosphate, the solution chemistry, and the rates of formation of hydroxyapatite are examined. During reaction steady-state solution conditions are rapidly achieved. However, the steady states attained are not those associated with the metastable invariant point involving the reactants. Rather, the steady state condition vary depending on the molar ratio of the reactants. The ultimate product of the reactions investigated is calcium deficient hydroxyapatite. Hydroxyapatite formation occurs in two stages: initial formation of nearly stoichiometric hydroxyapatite followed by its conversion to calcium deficient material. Microstructural evidence indicates the formation of hydroxyapatite occurs in association with dicalcium phosphate eventually causing the dissolution of this reactant to become diffusionally controlled. Effects of common ions, NaCl and $MgCl_2$ on the chemistry of the aqueous phase and on microstructural development were investigated.

THE KINETICS OF HYDROXYAPATITE FORMATION AT LOW TEMPERATURE

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ABSTRACT

The influence of temperature on the kinetics of formation of calcium deficient hydroxyapatite by an acid-base reaction has been determined. Calcium deficient hydroxyapatite is compositionally similar to bone apatite. Reactants used in this study were tetracalcium phosphate, a calcium phosphate more basic than hydroxyapatite, and dicalcium phosphate, which is more acidic than hydroxyapatite. The kinetics of hydroxyapatite formation are initially controlled by the surface areas of the reactants; however, eventually the rate of hydroxyapatite formation becomes diffusionally controlled. The origin of diffusion control appears to be associated with the epitaxial formation of hydroxyapatite on the surface of the dicalcium phosphate reactant. The microstructures of hydroxyapatite formed at 5, 15, and 25∞C were generally similar and are characterized by the formation of a porous acicular product which covers the surfaces of the reactants. The microstructure of the hydroxyapatite formed at 38∞C, was distinct from this and exhibited a pseudomorphic relationships with the dicalcium phosphate reactant. Seeding with hydroxyapatite accelerated the initial reaction but did not appear to have major long-term effects on the fractional degree of reaction or on microstructural development. Reaction was also accelerated in a neutral salt solution of high ionic strength.

THE EFFECTS OF PARTICLE SIZE AND SOLUTION CHEMISTRY ON THE FORMATION OF HYDROXYAPATITE

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ABSTRACT

The effects of varying the particle sizes of particulate reactants which form hydroxyapatite by a dissolution-precipitation reaction is considered. The effect of Mg^{2+} ion, known to inhibit hydroxyapatite formation in vivo, on the reaction to form hydroxyapatite is discussed.

HYDRATION IN THE SYSTEM Ca_2SiO_4-$Ca_3(PO_4)_2$ AT 90°C

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ABSTRACT

Compositions along the Ca_2SiO_4-$Ca_3(PO_4)_2$ join were hydrated at 90∞C. Mixtures containing 15, 38, 50, 80, and 100% $Ca_3(PO_4)_2$ were fired at 1500°C, forming nagelschmidtite + a'-$CaSiO_4$, A-phase, and silicocarnotite and a-$Ca_3(PO_4)_2$, respectively. Hydration of these produced hydroxyapatite regardless of composition. Calcium silicate hydrate gel was produced when Ca_2SiO_4 π 0 and portlandite when Ca_2SiO_4 was > 50%. Relative hydration rates were a-$Ca_3(PO_4)_2$ > nagelschmidtite > a-Ca_2SiO_4 ~ A-phase > silicocarnotite. Hydration in the presence of silica or lime influenced the amount of portlandite produced. Hydration in NaOH solution produced 14Å-tobermorite rather than calcium silicate hydrate gel.

Hydration of Tricalcium Germanate-Tricalcium Silicate Solid Solutions

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Abstract

The hydration characteristics of solid solutions of composition $3CaO\cdot xGeO_2\cdot(1-x)SiO_2$ were investigated at 25∞C by isothermal calorimetry The compositions hydrated were for x = 0, 0.2, 0.4, 0.6, 0.8, and 1.0. Full hydration was achieved for compositions in which $x > 0.2$. Both the rate of hydration and the total heat evolved for complete hydration varied with composition. Hydrate compositions were determined, and these also showed a compositional dependence. The morphologies of the calcium germanate silicate hydrates are reminiscent of that of calcium silicate hydrate; however, they are far more fibrous.

Kinetics of Tricalcium Aluminate and Tetracalcium Aluminoferrite Hydration in the Presence of Calcium Sulfate.

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ABSTRACT

Hydration reactions of C_3A and C_4AF with calcium sulfate were investigated and the kinetics of the reactions compared. The rates of C_3A and C_4AF hydration with calcium sulfate, as determined by heat evolution, vary depending on whether the sulfate-containing reactant is gypsum or calcium sulfate hemihydrate. The following sequence of reactions involving C_4AF occurs when hemihydrate is the reactant: gypsum formation during the first hour, formation over a period of 20 to 36 hours, and the conversion of ettringite to monosulfate over a period of about 12 hours. Monosulfate formation initiates prior to the complete consumption of gypsum. Compared to reaction with gypsum, the onset of this conversion occurs at a shorter hydration time when hemihydrate is an initial reactant and the total amount of heat evolved is lower. Reaction in saturated calcium sulfate solution occurs more slowly than reaction in water.

Ettringite formation occurs during the first 8 to 9 days of C_3A hydration. Once the gypsum is consumed, ettringite converts to monosulfate during two subsequent days. Based on the relative rates of heat liberation, C_4AF reacts at a much higher rate than C_3A. Compared to gypsum, the use of hemihydrate as the source of calcium sulfate decreases the rates of hydration of both C_3A and C_4AF. The effects on the hydration characteristics of C_4AF are significant.

The effects of varying the solution chemistry were compared by examining the hydration of C_3A with gypsum in water, in saturated $Ca(OH)_2$ solution, and in 0.3 M NaOH solution. Reaction in 0.3 M NaOH results in the onset of monosulfate formation prior to the complete reaction between gypsum and C_3A.

Formation of Hydroxyapatite at Near-Physiological Temperature

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Abstract

The formation of calcium deficient hydroxyapatite $Ca_9(HPO_4)(PO_4)_5OH$ (HAp) at 25°C by reaction of tetracalcium phosphate (TetCP), monocalcium phosphate monohydrate (MCPM), and calcium hydroxide was investigated. Phase pure, calcium deficient

hydroxyapatite was prepared in approximately 3.25 hours at 25°C by the reaction of dilute suspensions. Variations in the solution pH, calcium, and phosphorus concentration were determined during the reactions. The solution conditions for all reactions investigated show similar behavior. Isothermal calorimetry was carried out to determine the rates of heat evolution during reaction. Results indicate that significant reaction occurs in the first 15 minutes. During this period the solution pH ranges from 4.5 to 7.5 and three distinct stages of reaction occur. Early reaction occurs at low pH due to rapid MCPM dissolution. The presence of $Ca(OH)_2$ effects the pH in the first 2 minutes of reaction in association with the proportion of MCPM. Brushite ($CaHPO_4 \cdot 2H_2O$) is the predominant product formed until MCPM is consumed. X-ray diffraction analysis confirmed that brushite formed as an intermediate in the first few minutes. Brushite formed as thin plates of varying geometric shapes. The second stage is the reaction of brushite, tetracalcium phosphate, and $Ca(OH)_2$ (if present) as the solution adjusts to an invariant condition while forming hydroxyapatite. A rise in pH occurs during this period. A third stage of reaction proceeds at relatively constant near-physiological pH conditions for the remainder of the reaction as brushite is consumed along with tetracalcium phosphate in forming hydroxyapatite.

EARLY AGE CEMENT HYDRATION REACTIONS

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INTRODUCTION

At the time of mixing, fresh concrete contains cement, fine aggregate, coarse aggregate, and water. In addition, chemical admixtures and mineral admixtures may be present. Chemical admixtures include accelerating, retarding, water reducing or air entraining admixtures; mineral admixtures include pozzolans, such as fly ash and silica fume, and blast furnace-slag.

Concrete gains desirable mechanical properties principally as a result of the hydration of the cement present. However, if pozzolanic or latent hydraulic admixtures are present, additional hydration reactions will contribute to strength development.

The rate of cement hydration, the compositions of the products of hydration and the morphologies of these hydration products may be influenced by the presence of such mineral admixtures as well as by the presence of chemical admixtures.

The chemistry of the early reactions occurring during the hydration of the phases in portland cement concrete are considered. For the purpose of this article, early reactions are considered to be those which initiate within the first 28 days after mixing. Although emphasis is placed on portland cements, reactions in blended cements, regulated set cements, shrinkage compensating cements, and high alumina cements are briefly discussed.