The Chemistry and Binding Properties of Aluminium Phosphates

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This review covers the chemistry of some aluminium phosphates and their application as systems which will bind together particulate or fibre materials to form structurally cohesive products. No comprehensive review of aluminium phosphates has appeared since the work of Kingery.[1]

1 Classification of Binders

A binder may be defined as[1] 'a bonding material formed by reaction which is capable of imparting strength and elasticity to a body of aggregate in which it is present in minor proportion, while retaining in part the properties of the aggregate'. Attempts have been made to systematize and classify the large variety of binders[1-3] on the basis of the type of 'bond formation', and a comprehensive classification which is in common usage has been suggested by Sychev (Figure 1).[2]

Mineral binders are divided broadly into two classes, adhesives and cements. Adhesives are considered to be those binders, such as water glass and metal acid phosphates, which are suitable for immediate use. The second class is by far the larger and so has been subdivided into those which harden by physicochemical processes, and those which harden by formation of a new insoluble or sparingly soluble phase as the result of a chemical reaction. The first sub-group includes hardeners such as highly concentrated, finely divided suspensions of clays, oxides, and carbides; here water is the binder. Evaporation of water from the system causes capillary forces to act in the pores. As a result, surface forces pull the particles together and a coagulation structure is formed. The second sub-group can be further divided into those cements which react with water, *i.e.*, the hydraulic cements, and those involving acid–base interaction. The latter include metal oxide and hydroxide reactions with phosphoric acid, cements made from oxides and water glass, *e.g.* $ZnO + Na_2SiO_3$, and silicate coatings, *e.g.*, $Ca(OH)_2 + Na_2SiO_3$.

With regard to phosphate binding, Sychev[2] differentiates between bonds formed from phosphate binders (adhesives) and bonds involving phosphates which are formed as a result of chemical reaction (cements), in which the phosphoric acid is the material which is added as the binder.

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[1] J. F. Wygant, in 'Ceramic Fabrication Processes', ed. W. D. Kingery, Chapman and Hall, London, 1958, p. 171.

[2] M. M. Sychev, *Zhur. priklad. Khim.*, 1970, **43**, 528; 1970, **43**, 758.

[3] I. Teoreanu, *Rev. Roumaine Chim.*, 1972, **17**, 1211.

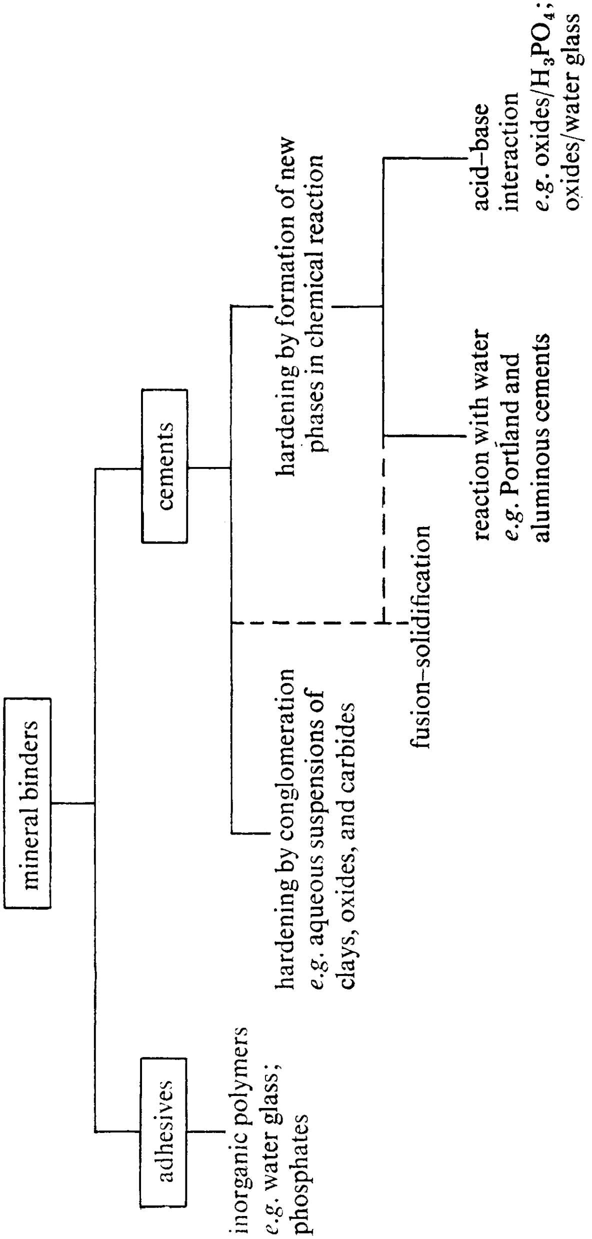

Figure 1 *Schematic classification of mineral binders (after Sychev[2])*

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2 General Binding Principles

The requirements for cementitious bonding have been studied,[1–4] and with particular regard to aluminium phosphate are as follows:

Two essential properties of binders are cohesion and adhesion. Cohesion of a binding material requires that a continuous structure be formed *in situ* from a large number of 'nuclei'. Crystalline materials always fulfill this requirement, although they generally do not show good bonding characteristics. For, although strength can arise from crystal interlocking, such crystalline structures tend to be rigid, and the lack of residual forces in a well-ordered crystal leads to poor adhesive properties. Amorphous structures may also possess three-dimensional continuity and, in contrast with crystalline phases: (i) they are more flexible and can accommodate internal stresses and strains more readily, (ii) the rate of their formation is not so critical, (iii) random structures incorporate residual forces which promote adhesion.

Kingery[5] has related the formation of disordered structures to the cationic size in a number of phosphate systems of potential binder interest. Large metal cations can form structures in which they have a high co-ordination number. The higher the co-ordination number, the greater the tendency towards ordered regular structures; conversely, the smaller the cation, the greater the tendency to form structures of low co-ordination number, thereby increasing the degree of randomness in polymers. Thus aluminium, with a relatively small cationic radius, increases the bonding power of a phosphoric acid binder, whereas with the large thorium cation, strength is correspondingly decreased. This is shown in the Table.

Table *The relation of cationic size to the strength of the phosphoric acid bond (Kingery*[5]*)*

Cation	*Basicity*	*Ionic radius*[6]/nm	*Phosphoric acid bond*
Be^{2+}	amphoteric	0.035	strength increased
Al^{3+}	amphoteric	0.051	strength increased
Fe^{3+}	weak base	0.064	strength increased
Th^{4+}	weak base	0.102	strength decreased

It has been noted that, in order for the binding phase to be cohesive, it must be capable of forming continuous structures throughout the bonded material. There are two essential requirements for this to happen. (i) Prior to the formation of the binding phase, the binder is in the form of a well-dispersed system which allows for mobility of ions. Phosphate binders are always added as aqueous solutions partly for this reason. (ii) The binder is required to have functional groups if continuous network structures are to be formed by condensation–

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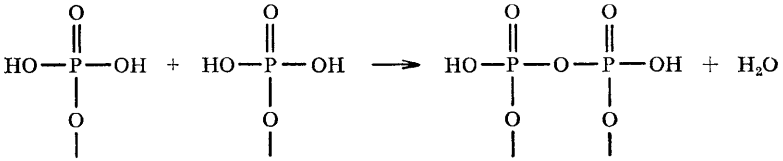
[4] M. M. Sychev, *Zhur. priklad. Khim.*, 1971, **44,** 1740.

[5] W. D. Kingery, *J. Amer. Ceram. Soc.*, 1950, **33,** 242.

[6] 'Handbook of Chemistry and Physics', ed. R. C. Weast, Chemical Rubber Company, Ohio, 1972/3, 53rd. edn., p. F-177.

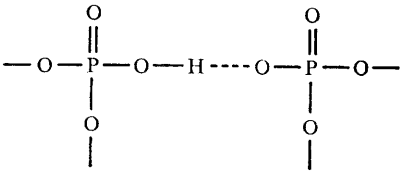
polymerization reactions; *e.g.* phosphate binders contain hydroxy-groups and undergo the following condensation–polymerization reaction on dehydration:



$$\mathrm{HO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle |}{\displaystyle O}}{P}}{-}OH + HO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle |}{\displaystyle O}}{P}}{-}OH \longrightarrow HO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle |}{\displaystyle O}}{P}}{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle |}{\displaystyle O}}{P}}{-}OH + H_2O}$$

The binding phase must also possess adhesive properties which are either inherent in the binder or are formed during the binding process. Adhesion results from the development of molecular attractive forces acting between the binding phase and the surface of the aggregate or filler. Mechanical adhesion due to surface roughness is also possible, and this can be increased by external pressure. The first requirement for adhesion is close contact between the interacting surfaces. The presence of an efficient wetting liquid increases the contact surface and allows Brownian motion to contribute to contact establishment.[4] Filler materials with ionic lattices are readily wetted by polar liquids such as water or aqueous solutions. In the case of phosphate reaction cements, the function of the phosphoric acid is three-fold: first to provide the phosphate linkages, secondly to act as a dispersing medium to promote cohesion, and thirdly to serve as a wetting liquid to increase adhesion.

A further requirement for adhesion is that the binding phase incorporates residual polar force fields.[5] Not only are acid phosphate binders capable of forming amorphous glass phases, the polar forces in which promote adhesion, but they also contain hydrogen bonds, formed through their functional groups (1). These probably serve to increase adhesion by bonding to oxygen atoms on the surface of a filler.



$$\mathrm{{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle |}{\displaystyle O}}{P}}{-}O{-}H\cdots O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle |}{\displaystyle O}}{P}}{-}O{-}}$$

(1)

In reaction cements the rate of the chemical reaction in which the binding phase is formed is important. Fast reactions can produce a breakdown in cohesion or adhesion, resulting in a weak cement. A good example of this is the hydration of the tricalcium aluminate phase in portland cements. Unless a retarder is added to slow its reaction with water, a ‘flash set’ occurs which produces a weak structure.

With acid phosphate reaction cements, a close relationship has been shown to exist between the rate of reaction and the strength of the bond.[5,7] The rate of reaction of oxides with phosphoric acid depends on the basicity of the oxide. Because the reaction between 'amphoteric' aluminium oxide and phosphoric acid is slow, the phosphate bonds are gradually developed. Basic zinc oxide, on the other hand, reacts so violently with phosphoric acid that the structure is effectively destroyed and no cohesion results.

The reaction between metal oxides and phosphoric acid can be retarded in some cases by calcining the oxide to give a less reactive surface or by partially neutralizing the acid or both. Preliminary firing of the oxides of zinc and magnesium to temperatures of 1373—1473 K is sufficient to slow down the reaction to a rate which will allow adhesive bonding to occur. For especially basic oxides, such as calcium oxide, a better technique is to use partially neutralized phosphoric acid.

It is significant, from the results of Kingery,[5] that aluminium phosphate possesses the highest modulus of rupture of all the phosphates he studied. This is probably due to a fortuitous combination of factors, in that the binding phase which is formed is amorphous and the rate of formation of the product from uncalcined alumina is low.

3 Classification of Aluminium Phosphates

Phosphates of aluminium exist in many different forms with varying stoicheiometry, structure, and properties. A number exist in the natural mineral state and feature in early phosphate studies.[8,9] These minerals are widely distributed but most deposits are small and not commercially viable. However, the material is actively mined in North Africa and in the U.S.A., where aluminium phosphates are found in association with apatites in the Florida phosphate fields.[10] In Florida, wavelite, $Al_3(PO_4)_2(OH)_3,5H_2O$, crandallite (also known as pseudowavelite), $CaAl_3(PO_4)_2(OH)_5,H_2O$, and millisite, $(Na,K)CaAl_6(PO_4)_4(OH)_9,3H_2O$, have been identified.

Aluminium phosphate is a valuable mineral source of both alumina and phosphate; the latter is obtained by nitric or sulphuric acid leaching to produce mixed and superphosphate-type fertilizers, respectively.[10]

Studies of the Al_2O_3–P_2O_5–H_2O system have been carried out by several groups under a range of conditions.[11–15] Although a hydrate with an Al_2O_3:P_2O_5 molar ratio of 1:2 is known, it is apparent that the chemistry of aluminium

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[7] S. L. Golynko-Vol'fson and L. G. Sudkas, *Zhur. priklad. Khim.*, 1965, **38**, 1466.

[8] C. Ramelsberg, *Pogg. Ann.*, 1845, **64**, 251.

[9] G. C. Wittstein, *Pogg. Ann.*, 1856, **97**, 158.

[10] H. M. Stevens, in 'Phosphorus and its Compounds', ed. J. R. Van Wazer, Interscience, London, 1961, Vol. II, p. 1056.

[11] J. C. Brosheer, F. A. Lenfesty, and J. F. Anderson, jun., *J. Amer. Chem. Soc.*, 1954, **76**, 5951.

[12] R. F. Jameson and J. E. Salmon, *J. Chem. Soc.*, 1954, 4013.

[13] S. A. Sigov and G. Ya. Sadykova, *Uzbek. khim. Zhur.*, 1961, **2**, 7 (*Chem. Abs.*. 1965, **62**, 4671).

[14] H. Guerin and R. Martin, *Compt. rend.*, 1952, **234**, 1799.

[15] V. N. Sveshnikova, *Zhur. neorg. Khim.*, 1960, **5**, 477.

phosphates is based on compounds with Al_2O_3:P_2O_5 molar ratios of 1:1 ($AlPO_4$,$x$$H_2O$) and 1:3 [$Al(H_2PO_4)_3$]. Only these will be discussed in detail in this review.

Aluminium Phosphates of Ratio Al_2O_3:P_2O_5 = 1:1.—Phosphates with an Al_2O_3:P_2O_5 molar ratio of 1:1 are the most common and, to date, have been the most widely studied. This stems from (i) their being naturally occurring, (ii) their structural similarity to silica, and (iii) their commercial value.

Hydrates. Two methods have been reported for the preparation of the hydrates of aluminium phosphate.[16,17] Preliminary preparation of a solution of alumina in phosphoric acid, with an Al_2O_3:P_2O_5 molar ratio of 1:2.7, and subsequent refluxing, gave a precipitate of $AlPO_4$,$2H_2O$ the form of which was concentration dependent;[16] concentrated solutions produced metavariscite, and dilute solutions variscite. A number of metastable hydrates of $AlPO_4$, with between one and two molecules of water per atom of aluminium, were formed successively in small amounts before transforming to variscite or a mixture of variscite and metavariscite, depending on the initial concentration of the solution.

Variscite and metavariscite have also been obtained[17] from a solution of sodium dihydrogen phosphate and aluminium chloride. Variscite was obtained after digestion of the solution at 333 K for 7 days and metavariscite after digestion at 363 K for 27 days. The preparation of the two compounds has been carried out also by the present Reviewers.[18]

Thermogravimetry[16] has shown that variscite and metavariscite[18] both have two moles of water per gm atom of aluminium and that both are capable of undergoing rehydration if dehydration is incomplete. The latter compound begins to lose weight at 358 K and weight loss is complete at 483 K. Furthermore, differential thermal analysis[18] of the materials shows an irreversible endothermic peak between 357 and 446 K, reaching a maximum at 428 K. I.r. measurements have revealed that both hydrates have the structure $AlPO_4$,$2H_2O$ rather than $Al(OH)_2$,H_2PO_4. Close similarity of the i.r. and X-ray powder diffraction patterns of the synthetic variscite and metavariscite with those of their naturally occurring counterparts was observed. The interplanar distances measured also agree with later work.[18]

The dihydrate formulation of variscite and metavariscite has been confirmed by ^1H n.m.r.[19] and by X-ray crystal determination of the structure of metavariscite.[20] Here PO_4 tetrahedra share vertices with four $AlO_4(H_2O)_2$ octahedra, and the two water molecules are *cis* to each other.

The surface and porosity properties of the Xerogel non-stoicheiometric

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[16] F. D'Yvoire, *Bull. Soc. chim. France*, 1962, 1762.

[17] E. Z. Arlidge, E. C. Farmer, B. D. Mitchell, and W. A. Mitchell, *J. Appl. Chem.*, 1963, **13,** 17.

[18] J. H. Morris, P. G. Perkins, A. Rose, and W. E. Smith, *J. Appl. Chem. Biotechnology*, 1976, **26,** 385; A. E. A. Rose, PhD Thesis, University of Strathclyde.

[19] C. Doremieux-Morin, M. Krahe, and F. D'Yvoire, *Bull. Soc. chim. France*, 1973, 409.

[20] R. Kniep and D. Mootz, *Acta Cryst.*, 1973, **B29,** 2292.

$AlPO_4$ have also been investigated,[21] and its exchange properties with Fe^{3+} have been studied using Mössbauer spectroscopy.[22] Polymorphic forms of the dihydrate have also been investigated by i.r. spectroscopy.[23]

Anhydrous Forms. Anhydrous aluminium phosphate has attracted the interest of many investigators since the observation that $AlPO_4$ is isostructural with silica; $AlPO_4$ exists in quartz (as berlinite), tridymite, and cristobalite forms.

Each of these forms can be prepared by several methods. The berlinite or quartz form of $AlPO_4$ is obtained[24] by heating precipitated, amorphous, aluminium phosphate to 823 K with lithium fluoride. Phosphotridymite and phosphocristobalite have been prepared by similar methods in the presence of sodium, potassium, or lithium chlorides[25] or sodium or potassium fluoride or carbonate[26] as promoters of crystallization.

Both the hydrates, variscite and metavariscite, are transformed into phosphotridymite on heating (variscite at 673 K and metavariscite at 723 K) and to phosphocristobalite at higher temperatures.[16]

The quartz, tridymite, and cristobalite forms of aluminium phosphate result when alumina reacts directly with phosphoric acid.[27,28]

The temperature–stability relationships of the aluminium phosphate polymorphs, studied by *X*-ray diffraction, thermal analysis, and thermal expansion, revealed[29] a close parallel of the system with earlier results for silica, and comparable results have been found by differential thermal analysis (Scheme 1).[30]

$$\mathrm{AlPO_4}$$

$$\text{berlinite} \xleftrightarrow{1088 \pm 4\ \mathrm{K}} \text{tridymite-form} \xleftrightarrow{1298 \pm 5\ \mathrm{K}} \text{cristobalite-form}$$

$$\beta \xleftrightarrow{446\ \mathrm{K}} \alpha \qquad \beta \xleftrightarrow{366\ 2 \times \mathrm{K}} \alpha_1 \xleftrightarrow{403\ \mathrm{K}} \alpha_2 \qquad \beta \xleftrightarrow{483\ 2 \times \mathrm{K}} \alpha$$

$$\mathrm{SiO_2}$$

$$\text{quartz} \xleftrightarrow{1140\ \mathrm{K}} \text{tridymite} \xleftrightarrow{1743\ \mathrm{K}} \text{cristobalite}$$

$$\beta \xleftrightarrow{446\ \mathrm{K}} \alpha \quad \beta \xleftrightarrow{390\ \mathrm{K}} \alpha_1 \xleftrightarrow{436\ \mathrm{K}} \alpha_2 \quad \beta \xleftrightarrow{493\text{—}543\ \mathrm{K}} \alpha$$

Scheme 1

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[21] V. M. Chertov, R. S. Tyutyunnik, and I. E. Niemark, *Adsorbtsiya Adsorbenti*, 1974, **2,** 109 (*Chem. Abs.*, 1974, **81,** 111721).

[22] A. S. Plachinda, V. M. Chertov, I. P. Suzdalev, E. F. Makarov, R. S. Tyutyunnik, and I. E. Niemark, *Teor. i eksp. Khim.*, 1974, **10,** 549 (*Chem. Abs.*, 1974, **81,** 159417).

[23] S. V. Gevorkyan, L. N. Egorova, and A. S. Povarennykh, *Geol. Zhur.* (*Russ. edn.*), 1974, **34,** 27 (*Chem. Abs.*, 1974, **81,** 127842).

[24] J. Papailhau, *Compt. rend.*, 1956, **242,** 1191 (*Chem. Abs.*, 1956, **50,** 12717).

[25] M. Orliac and J. Papailhau, *Compt. rend.*, 1963, **256,** 202 (*Chem. Abs.*, 1963, **58,** 7444).

[26] J. Papailhau, *Compt. rend.*, 1955, **240,** 2336 (*Chem. Abs.*, 1955, **49,** 15408).

[27] M. Tsuhako, I. Motooka, and M. Kobayashi, *Nippon Kagku Zasshi*, 1971, **92,** 318 (*Chem. Abs.*, 1971, **75,** 58098).

[28] A. S. Yutina, Z. D. Zhukova, and S. V. Lysak, *Izvest. Akad. Nauk S.S.S.R., neorg. Materialy*, 1966, **3,** 2020.

[29] W. R. Beck, *J. Amer. Ceram. Soc.*, 1949, **32,** 157.

[30] O. W. Floerke and H. Lachenmayr, *Ber. deut. keram. Ges.*, 1962, **39,** 55 (*Chem. Abs.*, 1962, **56,** 12387).

However, these must be regarded with caution, since the tridymite form of silica is probably not a true polymorph. Conversions from one form into another are much more rapid than for the corresponding transformations of silica and, with the exception of the berlinite inversion, take place at lower temperatures.

The temperature inversion of phosphocristobalite depends on its thermal history[31] and, although the cristobalite inversion temperature showed similar variation, the presence of a double endothermic peak during the low–high inversion of phosphocristobalite may indicate that the mechanism is different from that involved in the low–high cristobalite inversion.

The enthalpy of the berlinite–phosphotridymite transition, calculated[32] from the pressure–temperature curve up to 1000 atm, is 1096 J mol^{-1}, although this value is based on an observed transition temperature of 978 ± 7 K, which is about 110 K lower than that found by Beck[29] and Floerke.[30]

The $\alpha \rightleftharpoons \beta$ berlinite phase transition occurs[33] at 854 K, with a change in the heat capacity of 14.6×10^{-2} J g^{-1} K^{-1}. The enthalpy of the transition is 11.05 J g^{-1} and the gain in volume is 8.8×10^{-4} nm per unit cell. As in quartz, the transformation involved dilation in the *c*-direction of the unit cell. The latent heat of transformation and the increase in the length of the *c*-axis and cell volume are much greater for $AlPO_4$ than for SiO_2.

Disputably, the parallel between $AlPO_4$ and SiO_2 continues into the melt and Al_2O_3,P_2O_5 glasses can be made.[34–36]

The addition of small amounts of silica to aluminium phosphate inhibits the formation of well-ordered crystal structures.[30] Silica also lowers the inversion temperature of phosphocristobalite,[37] owing to the formation of molten surface layers of SiO_2–P_2O_5, whereas all phosphates have a retarding effect on the conversion of quartz to cristobalite, with aluminium phosphate the least effective.[38]

There are 15 compounds related by crystalline structures[39] to silica polymorphs. They have been classified[40] into two categories (i) 'half-breed' derivatives, (ii) 'stuffed' derivatives. $AlPO_4$ occurs among the 'half-breed' derivatives, in which half of the silicon positions are occupied by aluminium atoms and half by phosphorus atoms. In addition to an AlP pair of atoms being isoelectronic with two Si atoms, the combined radii are also comparable[6] (Al^{3+}, 0.051 nm;

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[31] F. A. Hümmel, *J. Amer. Ceram. Soc.*, 1949, **32**, 320.

[32] E. C. Shafer and R. Roy, *Z. phys. Chem.* (*Frankfurt*), 1957, **11**, 30 (*Chem. Abs.*, 1957, **51** 11023).

[33] M. Trocaaz, C. Berger, M. Richard, and L. Eyraud, *Bull. Soc. chim. France*, 1967, 4256 (*Chem. Abs.*, 1968, **68**, 73102).

[34] F. Drexler and W. Schutz, *Glastech. Ber.*, 1951, **24**, 172.

[35] P. Beyersdorfer, *Silikat. Tech.*, 1962, **13**, 346 (*Chem. Abs.*, 1963, **58**, 11075).

[36] A. Dietzel and H. J. Poegel, *Naturwiss.*, 1953, **40**, 604.

[37] O. W. Floerke, *Monatsh.*, 1972, **103**, 81 (*Chem. Abs.*, 1972, **76**, 130966).

[38] T. Chvatal, *Sprechsaal Keram., Glas. Email. Silikate*, 1972, **105**, 537 (*Chem. Abs.*, 1972, **77**, 155788).

[39] M. J. Buerger, *J. Chem. Phys.*, 1947, **15**, 1.

[40] M. J. Buerger, *Amer. Min.*, 1948, **33**, 751.

Si^{4+}, 0.042 nm; P^{5+}, 0.035 nm) and it is required that Al and P alternate in the structure.[41]

π-Bonding between aluminium and oxygen may also occur, although this is likely to be less effective than that involving phosphorus.[42]

A consequence of similar radii is that corresponding phases of $AlPO_4$ and SiO_2 have cell dimensions which are similar or simple multiples. The cell constants are as follows. Berlinite (trigonal, space group $P3_121$: $z = 3$);[33,34–48] $a_0 = 0.494$ nm (0.493—0.497_5 nm); $c_0 = 1.095$ nm (1.084—1.097 nm) (*cf.* quartz:[49] $a_0 = 0.490_3$ nm; $c_0 = \frac{1}{2} \times 1.078$ nm). β-Cristobalite form of $AlPO_4$ at room temperature (orthorhombic or pseudotetragonal, space group $C222_1$);[46,50] $a_0 = b_0 = 0.7099$ nm; $c_0 = 0.7006$ nm (*cf.* β-cristobalite $a_0 = 0.7003$ nm; $c_0 = 0.6950$ nm). At 523 K, the β-cristobalite form is cubic with $a_0 = 0.711$ nm.[51]

Related Studies. The formation of insoluble iron and aluminium phosphates helps to cause soluble phosphate fertilizers to become unavailable to plants and crops. The nature of these phosphates, their availability to plants, and other precipitation properties of aluminium phosphate, have received attention. Digestion[52] of precipitated aluminium or iron phosphate in solutions containing alkali and alkaline earth cations leads to a wide range of crystalline species, many of which correspond to natural minerals, *e.g.*, variscite, strengite, taranakite, leucophosphate, and minyulite. The removal of soluble orthophosphates from aqueous solutions using activated alumina[53] may be useful for controlling phosphate in rivers and lakes.

Early work suggested that aluminium is strongly complexed by orthophosphoric acid,[54,55] and the dissociation constants of assumed aluminium complexes with orthophosphoric acid have been reported.[56] When *ca.* 1.0—1.5 mol Al_2O_3 per mol P_2O_5 is dissolved in phosphoric acid, an extremely viscous solution is formed which can be dried, yielding an amorphous solid.[57,58]

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[41] R. Brill and A. P. De Bretteville, jun., *Acta Cryst.*, 1955, **8**, 567.

[42] J. R. Van Wazer, 'Phosphorus and its Compounds', Interscience, London, 1961, Vol. 1, p. 553.

[43] B. Sharan and B. N. Dutta, *Acta Cryst.*, 1964, **17**, 82.

[44] B. N. Dutta, *Indian J. Pure Appl. Phys.*, 1964, **2**, 362 (*Chem. Abs.*, 1965, **62**, 4720).

[45] D. Schwarzenbach, *Naturwiss.*, 1965, **52**, 343.

[46] R. W. G. Wyckoff, 'Crystal Structures', Interscience, London, 1965, Vol. 3, p. 28.

[47] H. F. Huttenlocher, *Z. Krist.*, 1935, **90A**, 508.

[48] H. Strunz, *Z. Krist.*, 1941, **103**, 228; A. N. Winchell and H. Winchell, 'The Microscopic Characters of Artificial Inorganic Solid Substances', Academic Press, New York and London, 1964.

[49] R. Brill and A. P. De Bretteville, jun., *Amer. Min.*, 1948, **33**, 750.

[50] R. C. L. Mooney, *Acta Cryst.*, 1956, **9**, 728.

[51] G. Trömel and B. Winkhouse, *Fortschr. Min.*, 1949, **28**, 82 (*Chem. Abs.*, 1951, **45**, 9980).

[52] J. F. Haseman, J. R. Lehr, and J. P. Smith, *Proc. Soil Sci. Soc. Amer.*, 1951, **15**, 76.

[53] R. D. Neufield and G. Thodos, *Environ. Sci. Technol.*, 1963, **3**, 661 (*Chem. Abs.*, 1969, **71**, 51717).

[54] L. Dede, *Z. anorg. Chem.*, 1923, **125**, 28.

[55] S. R. Carter and H. F. Clews, *J. Chem. Soc.*, 1924, **125**, 1880.

[56] N. Bjerrum and C. R. Dahn, *Z. Phys. Chem.*, 1931, 627.

[57] H. H. Greger, *Brick and Clay Record*, 1950, **117**, 63.

[58] H. H. Greger, U.S.P. 2460344; B. P. 597169.

These solutions probably[59] consist of aggregation polymers of aluminium and phosphate ions in randomized three-dimensional networks; their stability and degree of polymerization are strongly dependent on the pH of the medium.[42] The impurity complexes of PO_4^{3-} and Al^{3+} in a KBr lattice have been studied by i.r. spectroscopy.[60]

The mass spectra of $AlPO_4$ vapour in thermodynamic equilibrium with the condensed phase at various ionization energies show that thermal dissociation occurs into a complex mixture of oxides of phosphorus.[61]

The Chemistry of Aluminium Dihydrogen Phosphate.—The acid phosphate of aluminium is frequently represented in terms of the 1:3 stoicheiometry of its oxides as $Al_2O_3,3P_2O_5,6H_2O$. The chemistry of $Al(H_2PO_4)_3$ is complex, and many differing and often contradictory results are reported in the literature. Its chemical properties appear to vary according to the method of its preparation.

The first preparations of $Al(H_2PO_4)_3$ were reported in 1878[62] and 1888.[63] A solution of alumina was heated in concentrated phosphoric acid at 373 K, and partial evaporation of the solution produced $Al(H_2PO_4)_3$ as a crystalline solid.

Little work was done on the chemistry of $Al(H_2PO_4)_3$ until 1957, when D'Yvoire[64,65] studied the thermal and *X*-ray diffractive properties of powders of $Al(H_2PO_4)_3$ and showed that at least two species of $Al(H_2PO_4)_3$ (labelled A and B) and probably another (labelled D) existed, all of which produce *X*-ray line diffraction patterns different from that of the so-called classical (or C) form prepared by the original method.[62,63]

Clays may also be used as alumina sources for preparing aluminium phosphates,[18,66,67] although the composition of the final product depends on the Al:P ratio in the reaction mixture and aluminium extraction is rarely complete, even with excess phosphoric acid (1: > 6).

Because the basis of phosphate binding is the formation of polymers as a result of dehydration, the thermal properties of $Al(H_2PO_4)_3$ have been studied by a number of investigators.[18,65,68–72] Correlations of thermogravimetric analysis,

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[59] C. F. Callis, J. R. Van Wazer, and P. G. Arvan, *Chem. Rev.*, 1954, **54**, 777.

[60] Ya. P. Tsyackenko and V. M. Zaporozhets, *Fiz. Tverd. Tela. (Leningrad)*, 1974, **16**, 2444 (*Chem. Abs.*, 1974, **81**, 129282).

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differential thermal analysis, and *X*-ray diffraction studies reveal distinct stages of dehydration, represented by Scheme 2. The first product is essentially amorphous, and no evidence for the crystalline second product (acid tripolyphosphate) was obtained by some workers, who found direct crystallization of the aluminium metaphosphate $Al(PO_3)_3$ (B) from the amorphous phase.

$$2Al(H_2PO_4)_3 \xrightarrow{498\text{—}563\ K} Al_2O_3,3P_2O_5,3H_2O + 3H_2O\uparrow$$

$$Al_2O_3,3P_2O_5,3H_2O \xrightarrow{563\text{—}778\ K} 2AlH_2P_3O_{10} + H_2O\uparrow$$

$$2AlH_2P_3O_{10} \xrightarrow{778\text{—}898\ K} 2Al(PO_3)_3 + 2H_2O\uparrow$$

Scheme 2

More recently, it has been reported[73] that the dehydration of a solution of aluminium phosphate of ratio 1:3.7 proceeds *via* the formation of crystalline $Al(H_2PO_4)_3$. Subsequently, a mixture of the diphosphate $Al_8H_{12}(P_2O_7)_9$ and the triphosphate $H_2AlP_3O_{10},2H_2O$ is formed in the 293—573 K range. At 598 K, crystalline $Al(PO_3)_3$ is formed, which has a phase transition at 723—773 K. Other workers have reported the formation of $AlPO_4,Al_2(H_2P_2O_7)_3$, $H_2AlP_3O_{10}$, and $Al(PO_3)_3$ during the dehydration of $H_3Al(PO_4)_2,2H_2O$, $Al(H_2PO_4)_3$, and $Al_2(HPO_4)_3$.[74,75]

$Al(H_2PO_4)_3$ (B) is also formed from the decomposition of the disubstituted acid phosphate of aluminium, $AlH_3(PO_4)_2,3H_2O$.[76] Thus:

$$2AlH_3(PO_4)_2,3H_2O \xrightarrow[423\text{—}473\ K]{-6H_2O} Al(H_2PO_4)_3\ (B) + AlPO_4\ (\text{cristobalite})$$

Traces of $Al(H_2PO_4)_3$ (A) and of another phosphate, which may be $Al(H_2PO_4)_3$ (D), are also present. $Al(H_2PO_4)_3$ has also been observed to be formed from an aluminium phosphate solution in which the molar ratio is $Al_2O_3:P_2O_5$ = 1:2.2.[77,78] A disubstituted phosphate of aluminium was formed which thermally decomposed to equimolar quantities of $Al(H_2PO_4)_3$ and $AlPO_4$. It appears that thermal transformations of $Al(H_2PO_4)_3$ (B) exhibit a pattern similar to those of the classical form, $Al(H_2PO_4)_3$ (C), although opinions differ as to the mode of decomposition. Initial dehydration produces an amorphous phase[76-79] at a

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temperature about 30 K below that of the corresponding phase transition of $Al(H_2PO_4)_3$ (C), probably owing to differences in crystal size between the two forms, and some doubt exists as to whether $Al_2P_3O_{10}$ is formed as an intermediate in the transformation of $Al(H_2PO_4)_3$ (B).[76–80]

The formation of amorphous phases is considered to be important[1,5] for the cementing properties of a binder, because of their ability to adhere and cohere, and their ability to absorb strain. $Al(H_2PO_4)_3$ forms two amorphous phases: the first, partially dehydrated, is formed between 503 and 573 K and the second, an anhydrous phosphate, at temperatures greater than 1273 K. Between 523 and 573 K, binders containing $Al(H_2PO_4)_3$ [or disubstituted aluminium phosphates which produce $Al(H_2PO_4)_3$], acquire strength[78,81,82] and moisture resistance. The latter property arises because the amorphous phase which is formed is a vitreous substance insoluble in water,[77] whereas its precursor phase, $Al(H_2PO_4)_3$, is extremely hygroscopic. The formation of the amorphous phase is responsible for the cold-setting properties of aluminium phosphate binders.[5] However, not much is known about the properties of the low-temperature amorphous phase, although it has been described as 'possessing a randomized structure'.[78] Its binding action is due to a 'polymer shell of chains and rings of aluminium phosphate and alumina tetrahedra'.[83] Although its presence is readily identified by *X*-ray powder diffraction, it is somewhat metastable and slowly crystallizes,[77,80] yielding $AlH_2P_3O_{10},(2—3)H_2O$.[77] Its stoicheiometry is probably $Al_2O_3,3P_2O_5,3H_2O$[5,71,79] and, although its structure is unknown, a pyrophosphate formulation, $Al_2(H_2P_2O_7)_3$, has been proposed.[71,73,75]

The high-temperature amorphous phase formed at temperatures greater than 1273 K is a metastable glass of unknown composition and structure.[68,69] The thermal transitions in $Al(H_2PO_4)_3$ (B) are summarized in Figure 2.

The optical indices of refraction of both amorphous phases are 513—573 K, $\eta = 1.512$; 1373—1573 K, $\eta = 1.510$.[68]

Aluminium tripolyphosphate, $AlH_2P_3O_{10}$, has been reported[77] to have the chain structure (2). The low-temperature form of aluminium trimetaphosphate, $Al(PO_3)_3$ (B), has a chain structure (3) in which the PO_4 tetrahedra are linked together to form infinite $(PO_3^-)_n$ chains. The high-temperature form, aluminium tetrametaphosphate, $Al(PO_3)_3$ (A), has the ring structure (4).[84] Evidence for cyclic character is the presence of bands at 1311 and 1028 cm^{-1} in the i.r. spectrum.[85] Both these bands are present in all metaphosphates containing the

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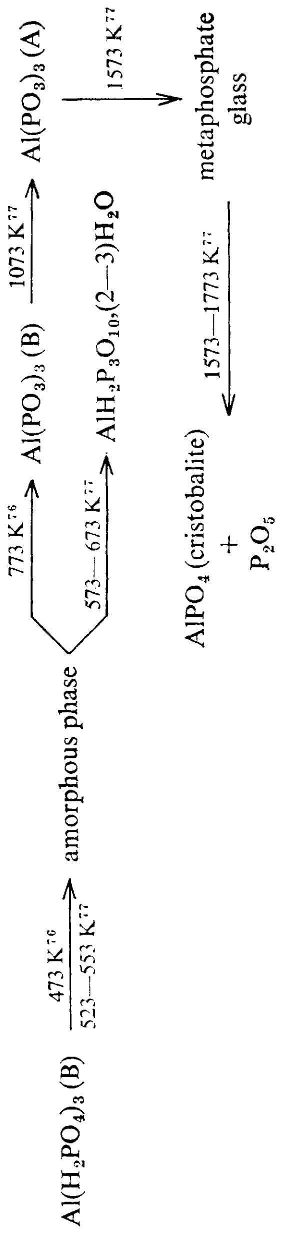
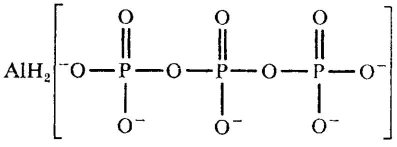


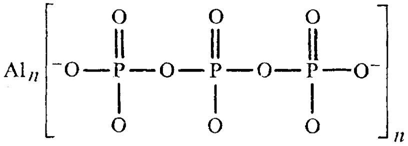
Figure 2 *Thermal transformations of* $Al(H_2PO_4)_3$ (B)

phosphorus–oxygen ring, but are absent in the spectra of the polyphosphates.[86–89]



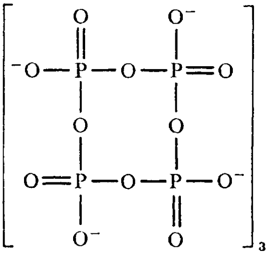
$\mathrm{AlH_2}\left[{}^{-}\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\underset{\underset{\mathrm{O^-}}{|}}{\mathrm{P}}}}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\underset{\underset{\mathrm{O^-}}{|}}{\mathrm{P}}}}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\underset{\underset{\mathrm{O^-}}{|}}{\mathrm{P}}}}-\mathrm{O}^{-}\right]$

(2)



$\mathrm{Al}_n\left[{}^{-}\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\underset{\underset{\mathrm{O}}{|}}{\mathrm{P}}}}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\underset{\underset{\mathrm{O}}{|}}{\mathrm{P}}}}-\mathrm{O}-\overset{\mathrm{O}}{\overset{\|}{\underset{\underset{\mathrm{O}}{|}}{\mathrm{P}}}}-\mathrm{O}^{-}\right]_n$

(3)



(4)

At higher temperatures (1073—1273 K), $Al(PO_3)_3$ (**B**) is non-reversibly converted into $Al(PO_3)_3$ (A),[65,68,72,77] although the latter has been observed at lower temperatures[76,80,90] apparently where traces of phosphoric acid have catalysed its formation. Relatively few studies have been made on the physical and chemical properties of aluminium metaphosphate.[91,92]

Potentiometric titration of base against $Al(H_2PO_4)_3$ between pH 2 to 12 reveals three end-points[18,93] similar to H_3PO_4, and the similarity of the behaviour of $Al(H_2PO_4)_3$ with that of H_3PO_4 is suggested to be due to the liberation of H_3PO_4 before the first end-point. The first end-point at pH 4.5 is strong, the next at pH 8.5 is less strong, and that at pH 11 is weak but observation can be facilitated by adding a precipitating agent. When $AgNO_3$ is added at pH 2.8, a precipitate of amorphous $AlPO_4$ is formed,[18] producing free H_3PO_4, which

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[87] D. E. C. Corbridge and E. Y. Lowe, *J. Chem. Soc.*, 1954, 493.

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[91] R. Arstanova, A. B. Bekturov, V. V. Tikhonov, and V. K. Esik, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1972, **22**, 1 (*Chem. Abs.*, 1972, **76**, 148317).

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is then partially neutralized in two steps by base. Finally, $AlPO_4$ redissolves in NaOH, giving $NaAlO_2$ and Na_3PO_4 at the third end-point.[18]

The effectiveness of $Al(H_3PO_4)_2$ as a binding agent may be due to chemical interaction with fillers such as silica. A study of the cross-breaking strength of a series of samples containing the phosphate with a varying proportion of silica as filler (Figure 3) is consistent with the existence of a silica-phosphate interaction. Studies of the interaction by analysis, thermal, and *X*-ray methods, rule out a bulk chemical reaction between the two components. Further studies[18] show that both aluminium and phosphate ions are absorbed on a quartz silica surface, but that aluminium is successively replaced by phosphate as more aluminium phosphate is added. When precipitated amorphous silica is employed, it is found that only aluminium ions are absorbed on its surface.

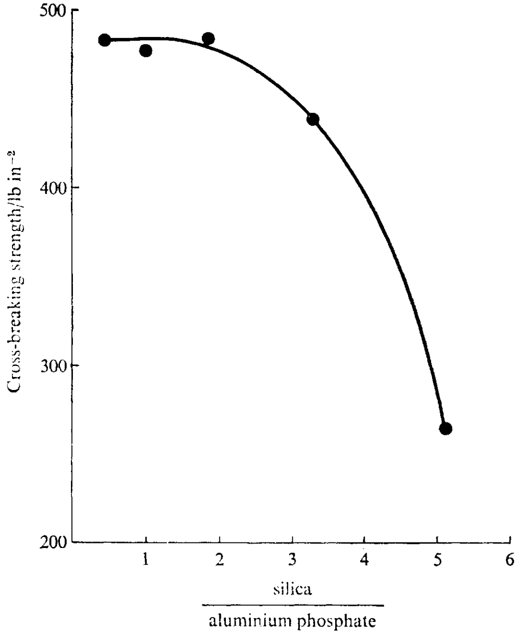

Figure 3 *Plot of the relation between silica content and cross-breaking strength of test boards using an aluminium phosphate binder*

The mechanism of this absorption process appears to be complex, and at least three stages can be postulated: (i) primary absorption of Al^{3+}, H^+, and $PO_4{}^{3-}$ ions on the surface; (ii) H^+ ions are then displaced by $PO_4{}^{3-}$ and Al^{3+} until all active sites are occupied; (iii) replacement of Al^{3+} by $PO_4{}^{3-}$ up to an ill-defined limit. The aluminium displaced possibly ends up as hydroxylated polymers, such as those described by Hsu.[94] The interaction on the interfaces between silica and aluminium phosphate is probably due to hydrogen bonding, as has also been suggested[95] for the interaction of phosphoric acid and talc.

The bulk binding properties of a crystalline compound may be influenced by the crystal habit.[96] In the $Al(H_2PO_4)_3$ series both needle and plate forms of crystal, which are crystallographically identical, can be formed. The needle and plate crystals, grown under a variety of conditions, have the same chemical composition, are both of C-form, and appear to be merely different crystal habits.

Crystal growth was observed under polarized light on a Reichert hot-stage microscope. Viscous solutions favour the formation of needle crystals and the rate of growth is important. The plates are converted into a shapeless mass on heating to 573 K, whereas the needle crystals retain their shape. Since the material is amorphous after this treatment, the retention of form by the needles is clearly important. The effect on the strength characteristics of test boards containing the different crystal habits showed that those containing needle crystals had an approximate five-fold increase in cross-breaking strength over those containing platelets.

Aluminium Phosphates of Ratio Al_2O_3:P_2O_5 = 1:2.—Aluminium phosphate solutions with a molar ratio range of $Al_2O_3:P_2O_5$ = 1:2—4 form the basis of commercial thermostable binders and coatings, the exact molar ratio depending on the use.[80] The literature data concerning these solutions are extensive, although contradictory. It has been proposed that aluminium phosphate solutions contain chiefly the anionic triphosphatoaluminate complex $[Al(HPO_4)_3]^{3-}$, but other authors[59,97] have suggested that the viscous aluminium phosphate system contains polymeric molecules with a branched three-dimensional structure. The curve of the dependence of the reduced viscosity on concentration for aluminium phosphate solutions[97] has a shape characteristic of polyelectrolytes; the change in the conductivity also corresponds to that for polyelectrolytes. No evidence for condensed polyphosphate ions with P—O—P bonds was found using chromatographic techniques,[94] and the high viscosities of such solutions are suggested to be due to the formation of a polymer structure with a complex system of hydrogen bonds.

The composition and thermal transformations of the precipitates which form from these solutions have been widely studied.[76,79] From solutions of molar ratios of $Al_2O_3:P_2O_5$ = 1:2.7—4, D'Yvoire isolated the disubstituted phosphate, $AlH_3(PO_4)_2,3H_2O$ at room temperature. This compound dehydrated between 373 and 423 K to form equimolar quantities of $AlPO_4$ (cristobalite) and $Al(H_2PO_4)_3$ (B), with trace amounts of both $Al(H_2PO_4)_3$ (A) and another phosphate, probably $Al(H_2PO_4)_3$ (D). Dehydration under varying conditions of

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[95] R. Robinson and E. R. Segnit, *Austral. Ceram. Soc.*, 1967, **3**, 9.

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[97] V. N. Sveshnikova and S. N. Zaitseva, *Zhur. neorg. Khim.*, 1964, **9**, 1232.

humidity produced differing crystal forms: heating $AlH_3(PO_4)_2,3H_2O$ under vacuum (low humidity) produced appreciable amounts of $Al(H_2PO_4)_3$ (D) as well as $Al(H_2PO_4)_3$ (B) and $AlPO_4$ (cristobalite); under extremely moist conditions, $AlH_3(PO_4)_2,H_2O$ was first formed before rapidly decomposing to a mixture of the A-, B-, and C-forms of $Al(H_2PO_4)_3$ and $AlPO_4$ (quartz).

Evaporation of the binder solution, $Al_2O_3:P_2O_5$ (molar ratios = 1:2.7—4) at 388 K produces $AlH_3(PO_4)_2,H_2O$.[76] This disubstituted phosphate has been reported to lose two moles of water between 408 and 473 K to form a mixture of the B- and C-forms of $Al(H_2PO_4)_3$ and the quartz- and cristobalite-forms of $AlPO_4$. It is interesting to note that, if solutions having the molar composition of Al_2O_3 = 1:2.7—3 are refluxed for some days, hydrates of the trisubstituted phosphate, $AlPO_4$, are formed.[16] If, however, the reflux is stopped after some minutes, an amorphous compound of variable stoicheiometry forms.[76] This undergoes initial dehydration at temperatures between 293—323 K and 388—423 K, the range depending on the value of x, as follows:

$$2AlH_3(x-1)(PO_4)_x,yH_2O \xrightarrow{2yH_2O} (3-x)AlPO_4\ (\text{cristobalite}) + (x-1)\,Al(H_2PO_4)_3$$

The form of $Al(H_2PO_4)_3$ which is obtained depends on the value of x: for $x = 2.07$, form C is obtained; for the majority of other values of x (*i.e.*, $x \leqslant 1.5$), the B form of $Al(H_2PO_4)_3$ is produced, with traces of another phosphate which may be the D form of $Al(H_2PO_4)_3$. The results of D'Yvoire[76] also appear to suggest that, if a freshly prepared binder solution is cured, it will give rise to a crystalline phase composition at 473 K different from one which has been allowed to stand for some time, as shown in Scheme 3.

freshly prepared binder solution → $AlH_3(PO_4)_2,H_2O$ → $Al(H_2PO_4)_3$ (B) + $Al(H_2PO_4)_3$ (C) + $AlPO_4$ (quartz) + $AlPO_4$ (cristobalite)

$$\text{aged binder solution} \rightarrow AlH_3(PO_4)_2,3H_2O$$
$$\downarrow$$
$$Al(H_2PO_4)_3\ (\text{B}) + AlPO_4\ (\text{cristobalite})$$

Scheme 3

D'Yvoire's[76,79] results have been quoted in some detail here for they serve, not only to show the complexity of the chemistry of these solutions and of aluminium phosphate chemistry in general, but also to show how apparent contradictions between the work of various researchers can arise.

Thermal transformations of individual phases are not always identical with changes undergone when the aluminium phosphate solutions used in technology are heated. However, despite the wide variation in the results of the thermal transformations of the aluminium phosphates obtained from binder solutions having $Al_2O_3:P_2O_5$ molar ratios of between 1:2 and 1:4, it is apparent that formation of the disubstituted phosphate of aluminium, $AlH_3(PO_4)_2,3H_2O$, occurs. Moreover, subsequent dehydration produces equimolar amounts of trisubstituted $AlPO_4$ and monosubstituted $Al(H_2PO_4)_3$.[75]

The effect of phosphoric acid on the nature of the thermal transformations on a 1:2 aluminium phosphate have been studied[98] and found to lead to formation of $Al(H_2PO_4)_3$, which subsequently promotes the formation of pyrophosphates at lower temperatures. The presence of H_3PO_4 catalyses the decomposition of $H_3[Al(PO_4)_2]$ into primary and secondary phosphates. A summary of the low-temperature thermal transformations of aluminium phosphate binder solutions is given in Figure 4.

Commercial Aluminium Phosphate Binders.—The physical and mechanical properties of compositions containing aluminium phosphate binders result from a combination of factors, such as the method of preparation, the amount and concentration of the phosphoric acid, the amount of binder present, the degree of compression, the temperature of curing, the type of aggregate or filler, and the presence of a catalyst.

Essentially, there are two methods of achieving the aluminium phosphate binding action. One method is to add phosphoric acid to an aluminous material, usually either alumina or aluminium hydroxide, which is contained in the composition to be cemented; binding is then obtained by heating directly. The second method is to preform the aluminium phosphate, which is then added as a solution to the composition to be cemented and binding obtained by heating. If the first method is used, there is generally a continuous increase in strength up to high temperatures.[99–101] Concentrated phosphoric acid (88%), however, was found[102] to impart a maximum crushing strength to alumina compacts at 873 K. Above 873 K, strength deteriorated rapidly with temperature. With aluminium phosphate as the binding agent, however, higher strengths are achieved at lower temperatures.[5,99,103] A maximum in shear,[104] transverse-breaking,[5] and crushing strengths[105] is reached at about 873 K. The maximum in transverse-breaking strengths occurred at 1473—1673 K in an aluminium phosphate–alumina composition.[5] The weaker compacts produced at lower temperatures by the phosphoric acid method may be due to polymerization reactions involving free phosphoric acid not being completed until a temperature greater than 673 K is reached.[103] Phosphoric acid added to corundum produced a bonded system that was not stable until the material had been treated to over 723 K.[69] Unpolymerized, free phosphoric acid is extremely hygroscopic and causes deterioration of the binding action through rehydration, and insufficient reaction occurs

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[98] A. N. Chivenkov, K. N. Lapko, A. K. Lobanok, A. N. Chivenkov, and A. A., Sokl'chik *Vesti Akad. Navuk Belarus. S.S.R. Ser. Khim. Navuk*, 1973, 124 (*Chem. Abs.*, 1973, **79**, 51084).

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[100] V. A. Bron, A. I. Uzberg, T. P. Karzhavina, and G. S. Krotova, *Ogneupory*, 1972, **1**, 37 (*Chem. Abs.*, 1972, **76**, 103245).

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[102] K. Fisher, *Proc. Brit. Ceram. Soc.*, 1969, **12**, 51.

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[104] F. Ya. Boradai and T. M. Evdokimova, *Izvest. Akad. Nauk S.S.S.R.*, *neorg. Materialy*, 1969, **5**, 1406.

[105] H. Bechtel and G. Ploss, *Ber. deut. keram. Ges.*, 1960, **37**, 362.

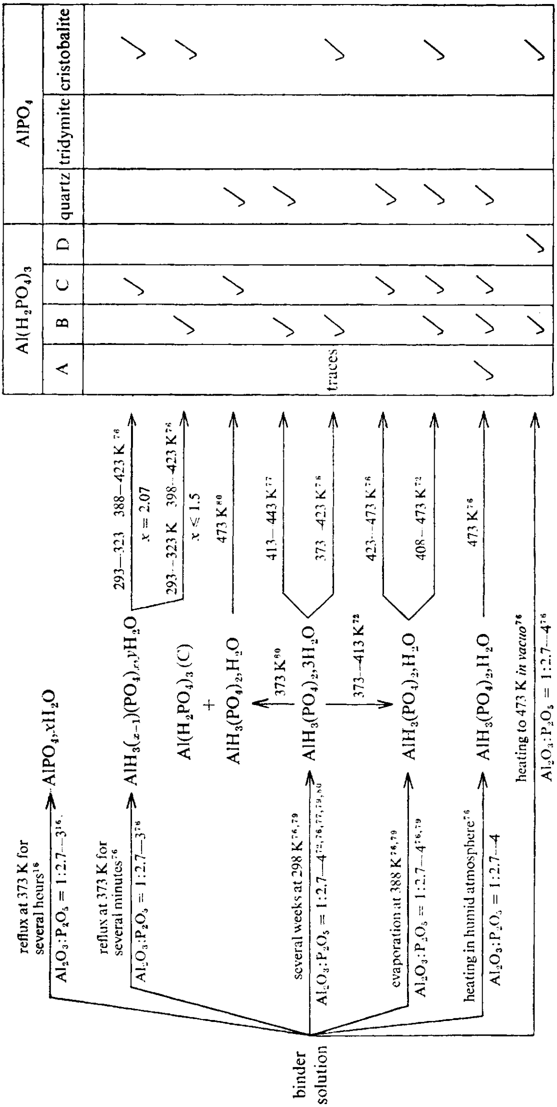

Figure 4 *Low-temperature thermal transformations of aluminium phosphate binder solutions*

if the phosphoric acid solution is too dilute.[106,107] The optimum concentration generally appears to be 60—70%.[69,103,108–112]

The filler and its proportion in the compact affects both strength and thermal expansion. Using alumina, with phosphoric acid as the binder, only 0.2% expansion at 573 K and 0.6% at 1073 K was observed.[113] An aluminium phosphate binder showed 0.8% at 1273 K,[102] although with vitreous silica the magnitude depended on the amount of silica present and on the temperature.[104] A considerable change in the coefficient of thermal expansion could be obtained by addition of alumina or titanium dioxide to the silica. This modification is useful because compositions can be tailored to match the thermal expansions of the material to be cemented and thus reduce thermal stresses.

For the preparation of suitable aluminium phosphate binder solutions, the optimum molar ratio of Al_2O_3:P_2O_5 is in the range 1:3 to 1:3.5.[103,109,114,115] If the ratio is greater than 1:4, strength decreases.[103] This is probably due to the presence of free phosphoric acid not involved in the reaction. A commercially available aluminium phosphate binder,[116] a process for the manufacture of condensed aluminium phosphates,[117] and the use of mortars with aluminium phosphate binders have been described.[118]

Aluminium phosphate gives strong binding with a variety of fillers, *e.g.* alumina[5,102,103,105,107,110,119,120] and silica.[99,104,121–126] In addition, other refractory materials such as zirconia,[103,109,110,127] silicon carbide,[110,128] and mullite[99] can be employed.

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[106] Unpublished data.

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The characteristics of aluminium phosphate binding may be altered by the addition of various catalysts. Ammonium fluoride accelerates the setting process,[110] whilst the following substances have been used as inhibitors: Rodine 78 (a complex amine),[110] 5-sulphosalicylic acid, acetylacetone, and dextrin.[71] Magnesium oxide can also be used to control the hardening process.[126] It is possible to reduce the curing temperature of the aluminium phosphate binder to room temperature by the addition of small amounts of curing catalysts such as aluminium powder[129] or magnesium oxide masked with either sodium hexametaphosphate or sodium tetrametaphosphate.[130] Addition of hydrated zirconia also has the effect of lowering the temperature of hardening and increasing water resistance.[131] The consistency of the viscous aqueous aluminium phosphate solution may be improved by addition of powdered iron or an iron oxide[132] or clay.[107,120]

Aluminium phosphate binding, produced directly or indirectly, has been used in a variety of applications in the field of refractories.[100,111,118,133–138] It has also found application as a binder for coatings,[139–144] thin films,[145] and furnace linings.[146] One of the most important advantages of aluminium phosphate binding in high-temperature furnace linings is its high resistance to attack by slag.[147–149] With suitable fillers or foaming agents, aluminium phosphate can be used to produce light-weight articles where a high strength/density ratio is

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required.[112,122,150–153] Dense materials from boron and aluminium nitride with a continuous skeleton derived from aluminium dihydrogen phosphate have been successfully used as slide bearings.[154] Aluminium phosphate binding is also used in catalytic bodies,[155] diamond abrasives,[156] electrically conducting cements,[157] porcelain compositions,[158] castable refractories,[159] foamed ceramics for building and insulating materials,[160] high-temperature nozzles,[161] lacquers for electrical sheets,[162] and vacuum[163] and dental cements.[66,164] Halogenated aluminium phosphates in solution can be used to coat glass fibres in order to increase their strength[165,166] or they can be crystallized to form resin-reinforcing fibres.[167]

The long-term action of high temperature on the mechanical properties and microstructure of glass fibre laminate in an aluminium phosphate binder has been found to result in some degradation of the protective film coating on the fibres, and then corrosion of the surface of the fibres.[168]

Other patents have been summarized,[18] and work on mixed aluminium—chromium phosphates has been reported.[132,169–176]

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