1   Introduction

Acid–base (AB) cements have been known since the mid 19th century. They are formed by the interaction of an acid and a base, a reaction which yields a cementitious salt hydrogel (Wilson, 1978) and offers an alternative route to that of polymerization for the formation of macromolecular materials. They are quick-setting materials, some of which have unusual properties for cements, such as adhesion and translucency. They find diverse applications, ranging from the biomedical to the industrial.

Despite all this there has been a failure to recognize AB cements as constituting a single, well-defined class of material. Compared with organic polymers, Portland cement and metal alloys, they have been neglected and, except in specialized fields, awareness of them is minimal. In this book we attempt to remedy the situation by unifying the subject and treating this range of materials as a single class.

Human interest in materials stretches back into palaeolithic times when materials taken from nature, such as wood and stone, were fashioned into tools, weapons and other artifacts. Carving or grinding of a material is a slow and time-consuming process so the discovery of pottery, which does away with the need for these laborious processes, was of the greatest significance. Here, a soft plastic body, potter's clay, is moulded into the desired shape before being converted into a rigid substance by firing. Pottery is but one of a group of materials which are formed by the physical or chemical conversion of a liquid or plastic body, which can be easily shaped by casting or moulding, into a solid substance. Other examples of this common method of fabrication are the casting of metals and the injection moulding of plastics.

Into this category come the water-based plasters, mortars, cements and concretes which set at room temperature as the result of a chemical reaction between water and a powder. Some of these have been known

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since antiquity. The AB cements are related to these materials except that water is replaced by an acidic liquid.

The first AB cement, the zinc oxychloride cement, was reported by Sorel in 1855. It was prepared by mixing zinc oxide powder with a concentrated solution of zinc chloride. Its use in dentistry was recommended by Feichtinger in 1858 but it did not prove to be a success (Mellor, 1929). However, other AB cements have proved to be of the utmost value to dentistry, and their subsequent development has been closely associated with this art (Wilson, 1978). The AB cements, developed against the backcloth of the severe demands of dentistry, have interesting properties. Some possess aesthetic appeal and the ability to adhere to base metals and other reactive substrates. Most have superior properties to plasters, mortars, and Portland cements, being quick-setting, stronger and more resistant to erosion. These advantageous properties make them strong candidates for other applications. In fact, one of these cements, the magnesium oxychloride cement of Sorel (1867), is still used to surface walls and floors on account of its marble-like appearance (Chapter 7).

In the 1870s more effective liquid cement-formers were found: ortho-phosphoric acid and eugenol (Wilson, 1978). It was also found that an aluminosilicate glass could replace zinc oxide, a discovery which led to the first translucent cement. Thereafter the subject stagnated until the late 1960s when the polyelectrolyte cements were discovered by Smith (1968) and Wilson & Kent (1971).

In recent years Sharp and his colleagues have developed the magnesium phosphate cements – Sharp prefers the term magnesia phosphate cement – as a material for the rapid repair of concrete runways and motorways (Chapter 6). These applications exploit the rapid development of strength in AB cements. This cement can also be used for flooring in refrigerated stores where Portland cements do not set. Interestingly, this material appears to have started life as an investment for the casting of dental alloys.

The glass polyalkenoate, a polyelectrolyte cement, of Wilson & Kent (Chapter 5), was originally developed as a dental material but has since found other applications. First it was used as a splint bandage material possessing early high-strength and resistance to water. Currently, it is being used, as a biocompatible bone cement, with a low exothermicity on setting and the ability to adhere to bone, for the cementation of prostheses (Jonck, Grobbelaar & Strating, 1989).

Outside the field of biomaterials it has been patented for use as a cement for underwater pipelines, as a foundry sand and as a substitute for plaster

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in the slip casting of pottery. Quite often it appears as a substitute for plaster of Paris, for it is stronger, less brittle and more resistant to water. There are other possibilities. Its translucent nature suggests that it could be used for the production of porcelain-like ceramics at room temperature.

Phosphate and polyelectrolyte AB cements are resistant to attack by boiling water, steam and mild acids and this suggests that they could be employed in technologies where these properties are important.

The ability of the polyelectrolyte-based AB cements (Chapter 5) to bond to a variety of substrates, combined with their rapid development of strength – they can become load-bearing within minutes of preparation – suggests that they have applications as rapid-repair and handyman materials.

A current area of interest is the use of AB cements as devices for the controlled release of biologically active species (Allen *et al.*, 1984). AB cements can be formulated to be degradable and to release bioactive elements when placed in appropriate environments. These elements can be incorporated into the cement matrix as either the cation or the anion cement former. Special copper/cobalt phosphates/selenates have been prepared which, when placed as boluses in the rumens of cattle and sheep, have the ability to decompose and release the essential trace elements copper, cobalt and selenium in a sustained fashion over many months (Chapter 6). Although practical examples are confined to phosphate cements, others are known which are based on a variety of anions: polyacrylate (Chapter 5), oxychlorides and oxysulphates (Chapter 7) and a variety of organic chelating anions (Chapter 9). The number of cements available for this purpose is very great.

A recent development has been the incorporation of a bioactive organic component into the AB cement during preparation. Since AB cements are prepared at room temperature, this can be done without causing degradation of the organic compound. In this case, the AB cement may merely act as a carrier for the sustained release of the added bioactive compound.

Another development has been the advent of the dual-cure resin cements. These are hybrids of glass polyalkenoate cements and methacrylates that set both by an acid–base cementation reaction and by vinyl polymerization (which may be initiated by light-curing). In these materials, the solvent is not water but a mixture of water and hydroxyethylmethacrylate which is capable of taking dimethacrylates and poly(acrylic acid)-containing vinyl groups into solution. In the absence of light these materials set slowly and

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have extended working times, but they set in seconds when illuminated with an intense beam of visible light. These hybrids are in their infancy but have created great interest.

From this account we are to expect diversification of these AB cements both for biomedical and for industrial usages. There should be further developments of the glass polyalkenoate cements both as bone substitutes and as bioadhesives. We also expect more types of AB cements to be formulated as devices for the sustained release of bioactive species. These materials would have applications in agriculture, horticulture, animal husbandry and human health care. In industrial fields we expect that there will be continued interest in developing AB cements as materials for the rapid repair of constructural concrete, as materials for the surfacing of floors and walls, and as adhesives and lutes for cementation in aqueous environments. The hybrid light-cured cements also appear to be a promising new line of development which may give us entirely novel classes of materials.
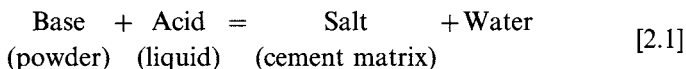
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2   Theory of acid–base cements

2.1   General

From the chemical point of view **AB** cements occupy a place in the vast range of acid–base phenomena which occur throughout both inorganic and organic chemistry. Like Portland cement they are prepared by mixing a powder with a liquid. However, this liquid is not water but an acid, while the powder, a metal oxide or silicate, is a base. Not surprisingly, the cement-forming reaction between them is extremely rapid and a hardened mass is formed within minutes of mixing.

AB cements may be represented by the defining equation

$$\begin{array}{cccccc} \text{Base} & + & \text{Acid} & = & \text{Salt} & + \text{Water} \\ \text{(powder)} & & \text{(liquid)} & & \text{(cement matrix)} & \end{array}$$
[2.1]

The product of the reaction, the binding agent, is a complex salt, and powder in excess of that required for the reaction acts as the filler. Each cement system is a particular combination of acid and base. The number of potential cement systems is considerable since it is a permutation of all possible combinations of suitable acids and bases.

Cement-forming liquids are strongly hydrogen-bonded and viscous. According to Wilson (1968), they must (1) have sufficient acidity to decompose the basic powder and liberate cement-forming cations, (2) contain an acid anion which forms stable complexes with these cations and (3) act as a medium for the reaction and (4) solvate the reaction products.

Generally, cement-forming liquids are aqueous solutions of inorganic or organic acids. These acids include phosphoric acid, multifunctional carboxylic acids, phenolic bodies and certain metal halides and sulphates (Table 2.1). There are also non-aqueous cement-forming liquids which are multidentate acids with the ability to form complexes.

Potential cement-forming bases are oxides and hydroxides of di- and

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Table 2.1. *Examples of acids used for cement formation*

Protonic acids (used in aqueous solution)	Aprotic acids (used in aqueous solution)
Phosphoric acid	Magnesium chloride
Poly(acrylic acid)	Zinc chloride
Malic acid	Copper(II) chloride
Tricarballylic acid	Cobalt(II) chloride
Pyruvic acid	Magnesium sulphate
Tartaric acid	Zinc sulphate
Mellitic acid	Copper(II) sulphate
Gallic acid	Cobalt(II) sulphate
Tannic acid	Magnesium selenate
	Zinc selenate
Protonic acids (liquid non-aqueous)	Copper(II) selenate
	Cobalt(II) selenate
Eugenol	
2-ethoxybenzoic acid	

Table 2.2. *Examples of bases used for cement formation*

Copper(II) oxide
Zinc(II) oxide
Magnesium oxide
Cobalt(II) hydroxide
Cobalt(II) carbonate
Calcium aluminosilicate glasses
Gelatinizing minerals

trivalent metals, silicate minerals and aluminosilicate glasses (Table 2.2). All cement-forming bases must be capable of releasing cations into acid solution. The best oxides for cement formation are amphoteric (Kingery, 1950a,b) and the most versatile cement former is zinc oxide, which can react with a wide range of aqueous solutions of acids, both inorganic and organic, and liquid organic chelating agents. Gelatinizing minerals, that is minerals that are decomposed by acids, can act as cement formers, as can the acid-decomposable aluminosilicate glasses.

In this chapter the nature of the cementitious bond and the acid–base reaction will be discussed.

2.2   *The formation of cements*

2.2.1   *Classification*

Before proceeding further it is well to consider the term *cement*, for its definition can be the source of some confusion. Both the Oxford English Dictionary and Webster give two alternative definitions. One defines a cement as a paste, prepared by mixing a powder with water, that sets to a hard mass. In the other a cement is described as a bonding agent. These two definitions are quite different. The first leads to a classification of cements in terms of the setting process, while the second lays emphasis on a property. In this book the term *cement* follows the sense of the first of these definitions.

Cements can be classified into three broad categories:

(1) Hydraulic cements. These cements are formed from two constituents one of which is water. Setting comprises a hydration and precipitation process. Into this category fall Portland cement and plaster of Paris.

(2) Condensation cements. Here, cement formation involves a loss of water and the condensation of two hydroxyl groups to form a bridging oxygen:

$$R-OH + HO-R = R-O-R + H_2O$$
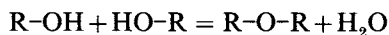
One example is silicate cement where orthosilicic acid, chemically generated in solution, condenses to form a silicic acid gel. Another is refractory cement where a cementitious product is formed by the heat treatment of an acid orthophosphate, a process which again involves condensation to form a polyphosphate.

(3) Acid–base cements. Cement formation involves both acid–base and hydration reactions (Wilson, Paddon & Crisp, 1979). These cements form the subject of this book.

This classification differs from that given by Wygant (1958), who subdivides cements into hydraulic, precipitation and reaction cements. The advantage of the present classification is that it clearly differentiates phosphate cements formed by condensation from those formed by an acid–base reaction (Kingery, 1950a). Wygant includes these in the same category, which can be confusing. Moreover, he puts silicate cements and the heat-treated acid phosphate cements into separate categories, although both are condensation cements.

Theory of acid–base cements

2.2.2   *Requirements for cementitious bonding*

The essential property of a cementitious material is that it is cohesive. Cohesion is characteristic of a continuous structure, which in the case of a cement implies an isotropic three-dimensional network. Moreover, the network bonds must be attributed to attractions on the molecular level. Increasingly, recent research tends to show that cements are not bonded by interlocking crystallites and that the formation of crystallites is incidental (Steinke *et al.*, 1988; Crisp *et al.*, 1978). The reason is that it is difficult to form rapidly a mass which is both cohesive and highly ordered.

Cement formation requires a continuous structure to be formed *in situ* from a large number of nuclei. Moreover, this structure must be maintained despite changes in the character of the bonds. These criteria are, obviously, more easily satisfied by a flexible random structure than by one which is highly-ordered and rigid. Crystallinity implies well-satisfied and rigidly-directed chemical bonds, exact stoichiometry and a highly ordered structure. So unless crystal growth is very slow a continuous molecular structure cannot be formed.

In random structures, stoichiometry need not be exact and adventitious ions can be incorporated without causing disruption. Bonds are not highly directed, and neighbouring regions of precipitation, formed around different nuclei, can be accommodated within the structure. Continuous networks can be formed rapidly. Thus, random structures are conducive to cement formation and, in fact, most AB cements are essentially amorphous. Indeed, it often appears that the development of crystallinity is detrimental to cement formation.

The matrices of AB cements are gel-like, but these gels differ from the tobermorite gel of Portland cement. In AB cements, setting is the result of gelation by salt formation, and the cations, which cause gelation, are extracted from an oxide or silicate by a polyacid solution. The conversion of the sol to a gel is rapid and the cements set in 3 to 5 minutes. Two basic processes are involved in cement formation: the release of cations from the oxide or silicate and their interaction with polyacid. This interaction involves ion binding and changes in the hydration state which are associated with gelation and structure formation (Section 4.3). Thus, there are two reaction rates to be considered: the rate of release of cations and the rate of structure formation. These two reaction rates must be balanced. If the rate of release of cations is too fast a non-coherent precipitate of crystallites is formed. If too slow the gel formed will lack strength.

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### The formation of cements

During cement formation, domains are formed about numerous nuclei and there must be bonding between the domains as well as within them. In AB cements bonding within the domains is mainly ionic, with a degree of covalency. The attractive forces between domains are those of a colloidal type. In random structures, residual force fields exist which act in a similar fashion to polar forces and serve to bond domains. These forces must include hydrogen bonds, for the addition of fluoride ions always enhances cement strength and the fluoride–hydrogen bond is a strong one.

The structures of cement gels bear some relationship to the structure of glasses. Spatially, the O^{2-} ion is dominant. The matrices are based on a coordinated polyhedron of oxygen ions about a central glass-forming cation (Pauling, 1945). In effect, these are anionic complexes where the cations are small, highly charged, and capable of coordinating with oxygen or hydroxyl ions. Examples of these polyhedra are $[SiO_4]$, $[PO_4]$ and $[AlO_4]$. Thus, we find that there are silicate, phosphate and aluminosilicate glasses and gels.

There are, however, differences which are best illustrated by reference to the simple example of silica glass and silica gel. In silica glass, Si^{4+} is four-coordinate and the polymeric links are of the bridging type:
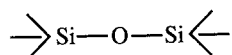
$$\diagdown\diagup Si - O - Si \diagup\diagdown$$

In aqueous solution, coordination increases to 6, Si–OH links are possible as well as Si–O–Si, and H_2O is a possible ligand. In silica cements the condensation of silicic acid, $Si(OH)_4$, to SiO_2 is only partial. Silica gel therefore contains both bridging oxygen and non-bridging hydroxyl linkages. Again, in contrast to the situation in glasses the possibility of hydrogen bond formation will also exist.

In AB cements the gel-forming cations are frequently Zn^{2+}, Mg^{2+}, Ca^{2+} or Al^{3+}. As Kingery (1950b) has pointed out, it is the amphoteric cations, for example Zn^{2+} and Al^{3+}, that possess the most favourable cement-forming properties. Their oxides are capable of glass formation, not by themselves, but in conjunction with other glass formers. Kingery also indicated that weakly basic cations, for example Mg^{2+}, are less effective, and more strongly basic cations, for example Ca^{2+}, even less effective.

The nature of the association between cement-forming cation and anion is important. As we shall see from theoretical considerations of the nature of acids and bases in section 2.3, these bonds are not completely ionic in character. Also while cement-forming cations are predominantly σ-

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Theory of acid–base cements

acceptors and the anions σ-donors, both have weak π-capabilities also. This topic is treated in more detail in the next section. Complex formation is clearly important and this view is supported by the anomaly that B_2O_3 forms cements with acids, not as a result of salt formation, but because of complex formation (Chapters 5 and 8).

A final point needs to be made. Theory has indicated that AB cements should be amorphous. However, a degree of crystallization does sometimes occur, its extent varying from cement to cement, and this often misled early workers in the field who used X-ray diffraction as a principal method of study. Although this technique readily identifies crystalline phases, it cannot by its nature detect amorphous material, which may form the bulk of the matrix. Thus, in early work too much emphasis was given to crystalline structures and too little to amorphous ones. As we shall see, the formation of crystallites, far from being evidence of cement formation, is often the reverse, complete crystallinity being associated with a non-cementitious product of an acid–base reaction.

2.2.3   Gelation

The formation of AB cements is an example of gelation, and the matrices may be regarded as salt-like hydrogels. They are rigid and glass-like. A gel has been defined by Bungenberg de Jong (1949) as 'a system of solid character, in which the colloidal particles somehow constitute a coherent structure'. A more exact definition is not possible, for gels are easier to recognize than define; they include a diversity of substances. Coherence of structure appears, however, to be a universal criterion for gels.

Flory (1974) classified gels into four types on the basis of their structures:

(1) Well-ordered lamellar structures. The lamellae are arranged in parallel, giving rise to long-range order. Examples are soaps, phospholipids and clays.
(2) Covalent polymeric networks which are completely disordered. Continuity of structure is provided by an irregular three-dimensional network of covalent links, some of which are crosslinks. The network is uninterrupted and has an infinite molecular weight. Examples are vulcanized rubbers, condensation polymers, vinyl–divinyl copolymers, alkyd and phenolic resins.

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