# PART II. CONSTITUENTS OF CONCRETE

## CEMENTS

CEMENT CONCRETE & AGGREGATES AUSTRALIA

This section provides general information on the types of cement available in Australia and their characteristics and their chemical and physical properties. In addition, it supplements the information on the influence of cement on the properties of concrete given in Part VIII, Section 25 *'Properties of Concrete'*.

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## 1. INTRODUCTION

Concrete is a generic term that refers to composite material in which aggregates are bound together by a binding agent to form a solid structural product. Typical examples are Portland cement concrete and asphaltic concrete where the binders are Portland cement (paste) and bitumen respectively.

This section describes 'Portland cement' as used in 'conventional' concrete – though the applications of 'Portland cement' concrete have grown remarkably in the last few decades. 'Portland cement', through the hydration reaction, is the fundamental component that determines the performance of conventional concrete and is usually the most expensive component. Its selection and proper use are important in obtaining the balance of properties required for a particular concrete application and in minimising the cost of the concrete.

An understanding of the properties of the available cementitious materials and their influence on the properties of the concrete is important for the proper selection and use of these materials. This understanding requires some familiarity with the chemical and physical characteristics of cement and cementitious materials and of their influence on cement and concrete performance.

## 2. TYPES OF CEMENT AND THEIR USES

### 2.1 GENERAL

Cement is a term used to describe a wide variety of organic and inorganic binding agents. The most widely used are those known as hydraulic cements – finely ground inorganic materials which possess a strong hydraulic binding action, i.e. when mixed with water they harden, in the absence of air, to give a strong, stable and durable product. (**NOTE**: *Hydraulic cements may also harden under water.)*

Hydraulic cements manufactured in Australia fall into two broad classes – general purpose cements and blended cements. The latter are mixtures of general purpose cement with other materials which either (a) possess inherent cementitious properties – e.g. ground granulated blast-furnace slags (hereinafter referred to as slag), or (b) which are pozzolanic in nature – i.e. they react with lime in the presence of water to form cementitious compounds. The most commonly used pozzolans are fly ash and silica fume.

Cements are manufactured in Australia to comply with the requirements of AS 3972. Seven different types of cements are covered by this Standard, three of which are designated as 'General Purpose' and four as 'Special Purpose' cements. The term 'Portland cement' as noted in AS 3972 refers to cement made using clinker and gypsum only and the descriptor is no longer relevant in most cases. For the remainder of this section, the term 'general purpose cement' will generally be used.

The table at the end of this section lists the common cements and their typical applications. In addition, it covers a number of other hydraulic cements, some of which are produced locally and some of which are imported. The use of these additional materials is limited but they provide valuable additions to the range of binding agents available.

### 2.2 GENERAL PURPOSE CEMENTS

General purpose cements were known originally as Portland cement. 'Portland cement' was patented in 1824 in England and has evolved since then. The term 'Portland' derives from the colour of the product which is similar to natural rocks found in the Portland region in England. 'Portland cement' is manufactured by carefully proportioning a mixture of calcium carbonate, alumina, silica and iron oxide which, when calcined and sintered at high temperatures (about 1,400°C), yields a new group of minerals which react with water to form cementitious compounds. The raw materials most commonly used in making cement are calcium carbonate (in the form of limestone, coral or chalk); silica, alumina and iron oxide (often from clay and shale). Sources of silica (such as sand), of alumina (such as bauxite), and iron oxide (such as iron ore) may also be used as supplements if the other materials are deficient. Effectively, cement manufacture involves a set of (stable) natural minerals being converted into a new set of (less stable) synthetic minerals. These new minerals are described (hypothetically) as:

- Tricalcium silicate: $C_3S$ – about 60% of clinker;
- Dicalcium silicate: $C_2S$ – about 20% of clinker;
- Tricalcium aluminate: $C_3A$ – about 10% of clinker;
- Tetracalcium aluminoferrite: $C_4AF$ – about 10% of clinker.

The properly proportioned raw materials are inter-ground to produce a finely divided 'raw meal' for transfer to the kilns. The 'raw meal' is heated in rotary kilns at temperatures from 1,300 to 1,500°C where the components react together and partially fuse to form 'clinker' – hard balls of ceramic-like material. The application of heat energy causes chemical reactions to take place which results in the conversion of the original minerals to new minerals. The relatively coarse clinker can be stored in sheds or silos as it is quite stable. It may also be shipped to distant destinations without any significant effect on the performance of the cement ultimately made from the clinker.

To manufacture cement suitable for use in concrete, the clinker plus a small amount (about 5%) of gypsum (calcium sulfate) is ground in a 'cement mill' to a fine powder. Mineral addition materials may also be added at this time – with AS 3972 allowing 'up to 7.5%' of a suitable mineral addition to be added. Typically, the mineral addition material used is limestone. These materials are milled together in either large ball mills (100-150 tonnes/hour capacity) or vertical roller mills (typically about 200 tonnes/hour capacity). The lower energy consumption of vertical roller mills is making them the 'mill of choice' in modern cement plants.

In addition to gypsum, small quantities of other materials may be inter-ground with the clinker – generally to improve mill throughput. These 'grinding aids' act in various ways – typically preventing the cement particles from adhering to one another. This has the added advantage of limiting or preventing an issue known as 'pack set' where cement powder stored in large quantities may form soft lumps over time. These lumps can cause blockages when transferring the powder from silos and/or ships.

Chemicals known as 'cement improvers' may also sometimes be added during milling. These often have limited benefit.

The previously mentioned 'mineral additions' are used primarily to lower the $CO_2$ intensity of cement – simply by diluting the clinker content. Note that fly ash and/or slag may also be considered as 'mineral additions' when used at 'up to 7.5%'.

The gypsum added during milling has a critical effect on cement performance. Cement can be made without gypsum, but such cement would suffer from a condition known as Flash Set when water was added to it. Flash Set occurs when one of the cement minerals ($C_3A$) reacts immediately with the water. The $C_3A$ hydration product causes the mix to immediately stiffen, making the concrete or mortar unable to be placed or compacted. The gypsum, which has been partially converted to 'Plaster of Paris' when heated during the milling process, partially dissolves releasing sulfate ions that coat the $C_3A$ mineral and prevents it hydrating

for about 12 hours, by which time the mortar or concrete has been placed and finished.

In the 2010 review of AS 3972, a new general purpose cement was included in the Standard. This cement, a General Purpose Limestone Cement (Type GL), 'may contain limestone alone or in combination with minor additional constituents (maximum 5%) of 8-20% by mass of the total cement.' This cement type was introduced to (a) allow producers to reduce the $CO_2$ intensity of cement substantially, and (b) to facilitate further research into higher (than 7.5%) levels of mineral addition in Type GP cement through making trial cements with >7.5% (and up to 20%) mineral addition compliant with AS 3972. Little or no commercial production of Type GL cement is currently occurring in Australia.

## 2.3 BLENDED CEMENTS

In AS 3972, blended cements are defined as hydraulic cements containing general purpose cement and a quantity, greater than 7.5%, of a supplementary cementitious material (SCM) – slag or fly ash (or both) and/or up to 10% silica fume. The SCM's approved in AS 3972 for blending with general purpose cement are fly ash, slag and silica fume conforming to the requirements of the relevant parts of AS 3582. By extension, mixtures of general purpose cement and other reactive ingredients can be considered to be blended cements also but are not presently included in AS 3972.

As might be expected, the range of properties which can be achieved with blended cements is quite wide, depending on the nature of the SCM and the proportions in which the constituents are mixed. In practice, however, the difference in properties between Type GP (general purpose cement) and Type GB (general purpose blended cement) is not necessarily huge as both are formulated to be used in general building construction. Indeed, there is very little concrete used in general building construction today which does not contain a proportion of fly ash and/or slag.

## 2.4 PRINCIPAL CEMENTS USED IN AUSTRALIA

*General* – The physical and chemical properties specified in AS 3972 are summarised in **Table 1.1**. As may be noted, there are few restrictions on the constituents of general purpose and blended cements. AS 3972 is largely a performance-based standard in which the cements are described in terms of required performance characteristics rather than just their chemical composition.

As the raw materials used to produce general purpose and blended cements can vary from locality to locality, the chemical compositions of cements may also be variable. Nevertheless, with modern technology, it is possible to produce cements from these materials which have very similar physical and performance characteristics. AS 3972 specifies only aspects of chemical composition which are necessary to ensure satisfactory performance – e.g. upper limits on the MgO (in clinker) and $SO_3$ contents to guard against excessive long-term volumetric expansion of the hydrated cement paste, plus a limit on chloride ion content to assist in managing corrosion in concrete structures containing embedded steel.

*Type GP-General Purpose Portland Cement* – Type GP cement is intended for use in most forms of concrete construction and should be specified where the special properties of other types (such as high early strength, low heat of hydration, or resistance to sulfates) are not required.

*Table 1.1 – Physical and Chemical Properties for Different Cement Types (AS 3972)*

| AS 3972 requirements | Type of cement | | | | | | |
|---|---|---|---|---|---|---|---|
| | GP | GB | GL | HE | SL | SR | LH |
| Physical properties[a] | | | | | | | |
| Setting time | | | | | | | |
| *Max.(h)* | *6* | *10* | *10* | *6* | *10* | *10* | *10* |
| *Min. (minutes)* | *45* | *45* | *45* | *45* | *45* | *45* | *45* |
| Soundness | | | | | | | |
| *Max. expansion (mm)* | *5* | *5* | *5* | *5* | *5* | *5* | *5* |
| Compressive strength (MPa) | | | | | | | |
| *Min. at 3 days* | *-* | *-* | *-* | *25* | *-* | *-* | *-* |
| *Min. at 7 days* | *35* | *20* | *20* | *40* | *(b)* | *(b)* | *10* |
| *Min. at 28 days* | *45* | *35* | *35* | *-* | *(b)* | *(b)* | *30* |
| Peak temperature rise | | | | | | | |
| *Max.(°C)* | *-* | *-* | *-* | *-* | *-* | *-* | *23* |
| Drying shrinkage | | | | | | | |
| *Max.(microstrain) 28 days* | *-* | *-* | *-* | *-* | *750* | *-* | *-* |
| Sulfate expansion | | | | | | | |
| *Max.(microstrain) 16 weeks* | *-* | *-* | *-* | *-* | *-* | *750* | *-* |
| Chemical limitations[a] | | | | | | | |
| MgO in clinker | | | | | | | |
| *Less than (%)* | *4.5* | *4.5* | *4.5* | *4.5* | *4.5* | *4.5* | *4.5* |
| $SO_3$ content | | | | | | | |
| *Max.(%)* | *3.5* | *3.5* | *3.5* | *3.5* | *3.5* | *3.5* | *3.5* |
| Chloride ion | | | | | | | |
| *Max.(%)* | *0.1* | *0.1* | *0.1* | *0.1* | *0.1* | *0.1* | *0.1* |

**NOTE:** *(a) When determined in accordance with the methods set out in AS 2350;*
*(b) Strengths shall comply with the Type GP or Type GB requirements depending on the cement composition.*

Type GP cement may contain up to 7.5% of approved mineral additions. Acceptable mineral additions in AS 3972 include limestone containing not less than 80% by weight of $CaCO_3$ and fly ash and slag complying with the requirements of AS 3582. Such additions, in the proportions specified, assist the cement manufacturer in the production of a more economical and more uniform product and lower the $CO_2$ intensity of the final product. Mineral additions are inter-ground with clinker and cannot be added as a separate component.

The performance requirements for Type GP cement are those necessary to ensure satisfactory performance with concrete used in general applications. Thus, for example, its minimum strengths at 7 and 28 days are higher than those for the Special Purpose cements (except Type HE), but it is not required to have the special properties associated with the Special Purpose cements e.g. low heat of hydration or improved sulfate resistance.

***Type GB-General Purpose Blended Cement*** – Type GB cement may be seen as a companion to Type GP cement, being intended for use in most forms of general concrete construction.

By varying the proportions of general purpose cement and fly ash, slag and silica fume in blended cements, it is possible to produce cements with a wide range of performance characteristics. Whilst the minimum strengths specified for Type GB cements are lower than those for Type GP (in recognition of their generally lower rates of strength gain), it is not uncommon for their ultimate strengths to equal or exceed those with Type GP cement, provided moisture (e.g. through proper curing) is available for a sufficient length of time.

Type GB cement containing silica fume, which is often intended for use in applications where high strengths are sought, will generally achieve relatively high early-age and 28-day strengths, but the later age strengths are typically not much higher than those achieved at 28 days. The allowable silica fume content is limited to 10% maximum as higher levels may lead to concrete with poor workability properties.

***Type HE-High Early Strength Cement*** – As the name implies, Type HE cement develops strength more rapidly than Type GP or Type GB cements. Rapid strength development should not be confused with rapid setting, the latter being the rate at which the cement paste loses its plasticity. Most cements have somewhat similar setting times but may have significantly different rates of strength gain.

High early strength performance is achieved through grinding the cement finer which promotes more rapid hydration. It lends itself to applications where rapid strength development is required; for example, where formwork has to be removed as soon as possible (precast concrete), or where early strength is required so that further construction can proceed (post-tension concrete). The rapid strength development is usually accompanied by a higher rate of heat evolution. Type HE cement should not generally be used in thick concrete sections or in mass construction. On the other hand, its use in construction under cold weather conditions may be beneficial.

***Type LH-Low Heat Cement*** – Type LH cement is designed for use where limitation of the heat of hydration (and hence the temperature rise in concrete) is necessary to avoid unacceptable thermal stresses. These situations may occur in mass concrete structures or in thick structural elements. Low-heat cement may be a general purpose cement or a blended cement provided it meets the requirements for temperature rise specified in AS 3972.

Low heat characteristics are achieved by reducing the content of the more rapidly hydrating compounds in cement ($C_3S$ and $C_3A$) or by blending with supplementary cementitious materials. These, generally, will result in a lower rate of strength development. Blended cements have inherent advantages in minimising heat evolution because of their lower rates of strength gain, and act by diluting the general purpose cement. Typically, 40% fly ash and 65% GGBFS are used to make a Type LH cement.

***Type SL-Shrinkage Limited Cement*** – Some major specifications in Australia require the use of Type SL cement as a means of controlling the shrinkage of concrete used in significant

concrete structures. Within the scope of AS 3972, a cement characterised in terms of its shrinkage performance was required to reflect/cover these industry requirements.

Type SL cement is intended for use where emphasis is placed on drying shrinkage and crack control in concrete structures (e.g. road pavements and bridge structures). Type SL cement may be a general purpose or a blended cement provided it meets the drying shrinkage limit specified in AS 3972 (see **Table 1.1**). With general purpose Type SL cements, a coarser grind than that used for Type GP is typically used.

*Type SR-Sulfate Resisting Cement* – Type SR cement is intended primarily for use where resistance to ground waters and other external water sources containing sulfates in solution is required. The relationship between the sulfate resistance of general purpose cement and its tricalcium aluminate ($C_3A$) content is well established. Portland cement containing less than 5% $C_3A$ is classified as sulfate resisting cement in many codes and standards for cement worldwide, including Australia until recently.

Studies have shown that cements potentially containing less calcium hydroxide on hydration perform well with sulfate exposure, e.g. certain blended cements. A limit on $C_3A$ content for these cements is neither appropriate nor applicable. Therefore, as a performance-based specification, AS 3972 replaced the limit on $C_3A$ for sulfate resisting general purpose cement with a performance test involving the measurement of expansion of mortar bars after exposure in a sulfate solution. A performance limit (maximum expansion) suitable for a compliant Type SR cement is noted in **Table 1.1**. This limit was developed by benchmarking the performance of Australian Type SR cements with recognised and accepted sulfate resisting cements from other countries.

Type SR cement may be a general purpose cement or a blended cement provided it meets the sulfate expansion limit specified in AS 3972. The minimum strength requirements in AS 3972 for Type SR cements (as noted in **Table 1.1**) are required to be equivalent to

those for either general purpose or blended cements – depending on the composition chosen for the particular Type SR cement.

*Off-White and White Cements* – The grey colour of cements is due mainly to the presence of iron in the cement (in the ferrite phase — tetracalcium aluminoferrite, $C_4AF$). By lowering the iron content, light-coloured cements can be produced. This is achieved by using raw materials low in iron and manganese oxides. Because of more costly raw materials and special requirements in manufacturing, Off-White and White cements are more expensive than the more widely used grey cements.

The composition of Off-White and White cements is characterised by relatively high $C_3A$ contents (9 to 14%) and low $C_4AF$ contents (3% for Off-White and 0.3 to 0.4% for White cements).

Off-White and White cements are used principally for architectural purposes. Since relatively high cement contents are normal in this application, dense concretes of low water/cement ratio, which are required properties for durability, can be obtained. However, because of the high $C_3A$ content of this type of cement it should not be used in low heat or sulfate resisting applications.

There is no specific Australian Standard for these types of cement, but Off-White cement is manufactured in Australia to meet the requirements for Type GP or Type HE in AS 3972. Off-White and White cements imported into Australia are typically required to comply with AS 3972.

*Coloured Cements* – Most coloured cements consist of cement and inorganic pigments inter-ground or mixed together, although some are produced from clinkers having a characteristic colour derived from the raw materials or the manufacturing process.

In the production of coloured cements with pigments, the base is either grey cement or the more costly Off- White or White cement. Grey cement is normally used to produce dark colours.

To be suitable for use with cements, pigments are required to be colour-fast under exposure to

light and weather and of a chemical composition such that the pigment is neither affected by the cement, nor detrimental to its setting, hardening, and durability characteristics. Pigments should not contain salts that may cause efflorescence. Black, red and yellow pigments are usually finely-ground iron oxides of different composition, while white pigments are usually titanium dioxide.

***Masonry Cement*** – Masonry cement is intended mainly for use in mortar for brick, stone and concrete block construction. It is a finely ground mixture of general purpose cement clinker, gypsum (calcium sulfate) and suitable inorganic materials such as hydrated lime, limestone and pozzolans. Air-entraining agents, water-reducers (plasticisers) and water-repellent substances may also be incorporated. Masonry cement is produced in Australia to meet the requirements of AS 1316.

It is characterised by producing mortars of high workability and high water retentivity, but which have a lower rate of strength development than those made from only general purpose cement. These characteristics make masonry cement especially suitable for masonry work, but it is entirely unsuitable for any form of structural concrete (plain, reinforced or prestressed).

***Oil-Well Cement*** – Oil-well cement is used in the petroleum industry to grout oil and gas wells. In these applications, the cement slurry must remain sufficiently fluid (at temperatures ranging from normal to about 200°C and under pressures ranging from atmospheric to about 125 MPa) for the several hours needed to pump it into position. It should then harden fairly rapidly. It may also have to resist corrosive conditions resulting from sulfur gases or waters containing dissolved salts.

Oil-well cements are modified general purpose cements that are designed to serve this need. They consist of coarsely ground cement of low $C_3A$ content, with or without a retarder.

The properties required of oil-well cements are set out in the American Petroleum Institute Standard API STD-10A *'Specification for Oil-well Cements and Cement Additives'*. They are subdivided into six classes each applicable to a specified range of well depths, temperature and corrosion conditions.

Special methods of testing oil-well cements for thickening times and strength under conditions of high temperature and pressure have been developed and are covered by the American Petroleum Institute Standard API-RP 10B *'Recommended Practice for Testing Oil-Well Cements and Cement Additives'*.

***High Alumina Cement (HAC)*** – HAC is very different from general purpose cement in its chemical composition and in its characteristics. The difference is derived from the raw materials from which it is made – principally bauxite and limestone. The product resulting from the chemical combination of these two materials is a cement having a high alumina ($Al_2O_3$) content and a low lime (CaO) content as compared with general purpose cement. In some literature, HAC is called 'calcium aluminate cement' or 'Ciment Fondue', but it is more commonly known as high alumina cement. It is all imported into Australia.

HAC is characterised by a very rapid rate of strength gain which results in very high early strengths and high rates of heat evolution. The latter characteristic allows hardening to take place at relatively low temperatures but prevents its use in mass concrete or in other applications where high rates of heat evolution may cause problems. HAC is resistant to attack by sulfates and sulfate solutions, a property which, combined with its high early strength, has led to its use in factory floors and similar applications. It also finds applications in refractory concrete because of its resistance to very high temperatures.

However, HAC may suffer a substantial loss of strength in conditions which are both warm (above, say, 25°C) and humid. Under these conditions, a chemical process known as 'conversion' takes place during which some of the hydrated compounds of the hardened cement paste convert to other compounds of smaller volume. This results in a cement paste with significantly reduced strength.

The rate at which 'conversion' occurs depends on the moisture condition and temperature of the concrete. Where moisture is present and

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temperatures are above 25°C, the rate is fairly high. Water/cement ratio also affects the rate of 'conversion' – the greater the original water/cement ratio, the faster the rate of 'conversion' and the lower the converted strength. External chemical agents may also affect the rate of 'conversion'.

The use of HAC in warm humid environments should therefore be approached with great caution because of the possibility of 'conversion' and loss in concrete strength.

If general purpose cement is added to HAC, the setting time of the mixture is significantly less than that of either product used alone. The exact proportion at which the most rapid setting is obtained varies with particular batches of HAC and general purpose cement.

Mixtures of the two cements are used in pastes, mortars and concretes, for applications requiring quick setting and the development of reasonable strength at a very early age, e.g. for sealing leaks or stabilising rock. However, in general, the faster the setting time the lower the ultimate strength obtained. Caution should therefore be exercised in applications where the strength of the concrete is an important element of its performance.

## 3. CHEMICAL PROPERTIES

### 3.1 GENERAL

The chemical composition of Portland cements, high alumina cements, slags and pozzolans is dominated by three elements – namely calcium, silicon and aluminium. The proportions of these elements, expressed as oxides, are shown in the ternary diagram in **Figure 1.1**.
(**NOTE**: *Each axis of the diagram represents 0-100% of the respective oxides.*)

### 3.2 GENERAL PURPOSE CEMENT

***Chemical Composition*** – The chemical composition of most modern general purpose cements falls within the ranges given in **Table 1.2**. The composition for individual cements depends on the type of cement being manufactured and the composition of the raw materials being used. Given the wide range of
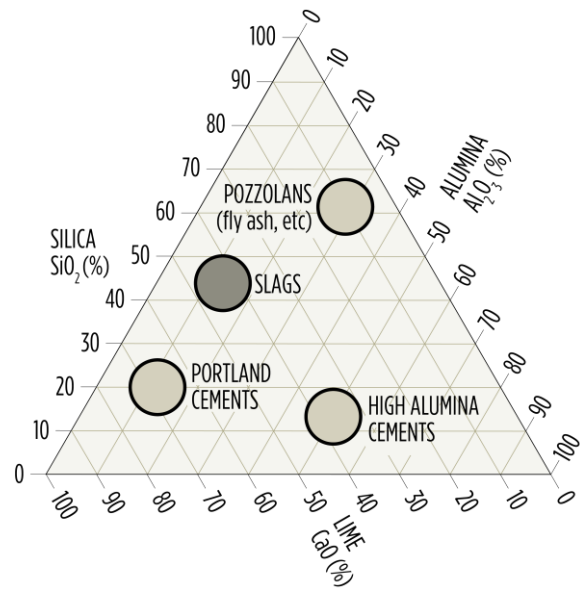


*Figure 1.1 – Relative Chemical Compositions of Cementitious Products*

raw materials found in Australia, it is not usual for all cements, even of the same type, to have exactly the same chemical composition.

*Table 1.2 – Typical Oxide Content Ranges for General Purpose Cements*

| Oxide | Content (mass %) |
|---|---|
| Lime (CaO) | 60 – 67 |
| Silica ($SiO_2$) | 17 – 25 |
| Alumina ($Al_2O_3$) | 3 – 8 |
| Iron Oxide ($Fe_2O_3$) | 0.5 – 6.0 |
| Magnesia (MgO) | 0.1 – 4.5 |
| Alkalies ($Na_2O + K_2O$) | 0.5 –1.3 |
| Titania ($TiO_2$) | 0.1 – 0.4 |
| Phosphorus ($P_2O_5$) | 0.1 – 0.2 |
| Sulfate (expressed as $SO_3$) | 1 – 3 |

'Portland cement' includes four major (hypothetical) minerals which are formed during the clinkering process. These are identified as: tricalcium silicate ($C_3S$), which exists in clinker in the impure form (and is also known as alite); dicalcium silicate ($C_2S$) (which is also known as belite); tricalcium aluminate ($C_3A$); and the ferrite phase which exists as a compound close

in composition to tetracalcium aluminoferrite ($C_4AF$).

Each of these four minerals (phases) exists in several different crystal forms exhibiting some variation in properties. The main properties of the four phases are summarised in **Table 1.3**. In addition, some 'minor' constituents will be present in relatively small amounts – e.g. gypsum, alkali oxides and magnesia. Further details of these constituents are provided in the Appendix to this section.

*Table 1.3 – Properties of the Mineral Constituents of General Purpose Cement*

| Mineral Phase | Characteristics | Potential Heat of Hydration* (J/g) |
|---|---|---|
| $C_3S$ | Light in colour; Hardens quickly with evolution of heat; Gives early age strength. | 500 |
| $C_2S$ | Light in colour; Hardens slowly; Gives later age strength. | 250 |
| $C_3A$ | Light in colour; Sets quickly with evolution of heat; Enhances strength of the silicates. | 850 |
| $C_4AF$ | Dark in colour with little cementing value. | 400 |

**NOTE:** *This potential is not reached in cement hydration. The heat developed by a cement at any particular age is governed by the rate of hydration.*

***Reaction with Water*** – When cement is mixed with water, a series of chemical reactions – hydration reactions – take place which result in the formation of new compounds and the progressive hardening of the cement paste. Evolution of heat and the development of compressive and tensile strength within the paste occur with the passage of time. The strength development is a consequence of the formation of calcium silicate hydrates and calcium aluminate hydrates which become the 'glue' that binds the aggregate materials to form concrete. There are two by-products to these hydration reactions, namely heat (as noted above) and lime (calcium hydroxide). Calcium hydroxide is present in significant quantities ($50\text{-}100$ kg/m$^3$) in most concrete mixes.

When water is added, the resulting hydration of the tricalcium aluminate ($C_3A$) is moderated by the gypsum which is added to the cement to control its setting behaviour. The immediate reaction between the $C_3A$ and gypsum produces needle-like crystals of the mineral 'ettringite'. It is this ettringite layer on the surface of the $C_3A$ grains which retards the hydration of this mineral giving a 'dormant period' in which the concrete remains plastic and in which the silicate minerals begin to react.

After some hours, further hydration of the $C_3A$ results in the conversion of the ettringite into a monosulphate and a solid reaction product, approximated by the formula $C_4AH_{13}$.

**Figure 1.2** provides a schematic representation of the relevant chemical reactions with a typical time scale demonstrating the formation of the paste structure that develops over time. Note also the graphical representation of the reduction in paste porosity as the setting and hardening progress.
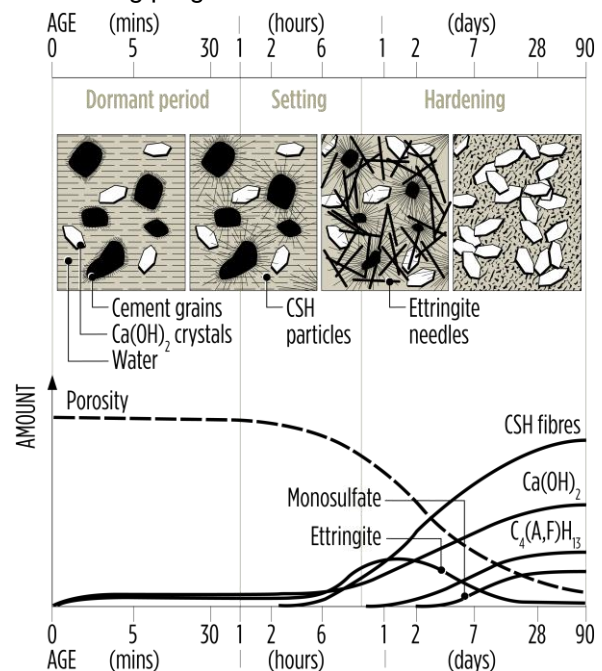


*Figure 1.2 – Schematic Representation of the Hydration Reaction – Timing and Reactions Products[1.1]*

The rates of the reactions and the nature and amounts of the products formed depend on (1) the chemical composition of the cement, (2) the temperatures at which the reactions take place, and (3) whether or not chemical admixtures are present in the mixture.

After setting has taken place, the hydration reaction continues. To facilitate this reaction, water is taken from the capillary pores to hydrate the previously unreacted cement. This loss of water causes shrinkage known as autogenous shrinkage. Autogenous shrinkage occurs in the paste and its effect on overall concrete shrinkage is limited by restraint by the aggregate. Typically, the autogenous shrinkage value in concrete is about 50 microstrain.

## 3.3 BLENDED CEMENTS

*Chemical Composition* – As noted earlier, blended cements contain, in addition to general purpose cement, either slag, fly ash, silica fume or a combination of these SCM's. The nature of these SCM's will be discussed in detail in Section 2 of this Guide.

When SCM's are used to manufacture blended cements, the final cement product may be obtained either by (1) inter-grinding the SCM(s) with the clinker and gypsum, or (2) (post) blending the SCM(s) with general purpose cement. For a blended cement to meet the requirements of AS 3972, this manufacturing process needs to be carried out in a 'cement plant'. Typically, slag blends are more likely to be manufactured using inter-grinding while fly ash blends are more likely to be manufactured by post-blending.

*(NOTE: In Australia, most concrete plants have separate silos of general purpose cement and SCM(s) and the concrete producer can make a large range of mixes with varying SCM types and proportions. When blending is done in a concrete plant the resultant 'blended cement' does not meet the requirements of AS 3972. However, the resultant concrete would be expected to have the same performance as if a blended cement with the same proportions was used.)*

For fly ash blended cements, the usual proportion of fly ash used is in the range 20-30%. For Type LH applications, 40% fly ash may be used.

With slag blended cements, Normal Class concrete mixes would typically use a blend containing about 30% slag. For some Special Class mixes and for Type LH and high durability requirements, a blend containing about 65% slag is typically used.

Silica fume is rarely used in the manufacture of Type GB cements in Australia. In countries where it is used, the blend would typically contain 8-10% silica fume.

*Reaction with Water* – When mixed with water, the cement component of blended cements hydrates to produce calcium silicates and calcium aluminates in a manner analogous to that of hydrating general purpose cement. However, there are some important differences. Firstly, with pozzolanic materials such as fly ash and silica fume, it is the calcium hydroxide produced during the hydration of the general purpose cement which reacts with the silica in the pozzolan to form additional calcium silicate hydrates. These reaction products are similar in structure to those produced by hydrating cement. The lime-silica hydration reaction is much slower than the hydration of cement and blended cements containing pozzolans tend to have lower strengths at early ages than cement-only mixes. They also have lower heat of hydration.

Secondly, with slags, the calcium hydroxide acts as an activator as well as participating in the hydration reactions. In this case also, calcium silicate hydrates and calcium aluminate hydrates are formed. Since slags are themselves weakly cementitious, the reactions will be somewhat faster than the lime-pozzolan mixes but are still slower than cement-only mixes. Blended cements made with slag can be expected to have lower rates of early-age strength gain. However, allowance for this can be made in the manufacture of the blended cement (e.g. by finer grinding) and in the curing of the concrete to ensure suitable strength development so that required 28-day strengths are achieved. At later ages, the strengths of blended cement mixes will generally exceed those of cement-only mixes.

# 4. PHYSICAL PROPERTIES

## 4.1 SETTING TIME

When mixed with water, general purpose and blended cements form a plastic workable paste which progresses through setting to eventual hardening. Setting time is the period during which the cement paste stiffens and loses its mobility. Arbitrarily defined initial and final setting times are used as a practical basis for ascertaining the end of the workability period and the onset of hardening.

*Initial Set* – For cement, it is the point at which the paste reaches a certain degree of stiffness. The time required for the paste to reach 'initial set' is known as the 'initial setting time'. It is one of the major influences determining the length of time for which mortar and concrete remain plastic and workable. To ensure that mortars and concretes do not stiffen or set too early, a minimum initial setting time for general purpose and blended cements is specified in AS 3972.

*Final Set* – For cement, it is the point at which the paste may be regarded as a rigid solid, is no longer workable and after which time it begins to develop measurable strength. The time required for the paste to reach 'final set' is known as the 'final setting time'. A maximum value is specified in AS 3972.

The initial and final setting times are determined using the test procedure set out in AS 2350.4 which measures the penetration of a needle into a (cement and water) paste of specified consistency. When the needle fails to penetrate the paste to a specified depth within the specified time, the cement is said to have achieved its 'initial set'. Final set is said to have taken place when the needle fails to penetrate the paste to a depth of 0.5 mm.

The setting times for cement paste are not directly applicable to concrete. They are determined on a cement paste and under controlled conditions (including temperature). Concrete setting times are affected by the water content of the concrete mix, the temperature, whether or not the concrete incorporates admixtures and, if so, their type and dosage.

## 4.2 HEAT OF HYDRATION/ TEMPERATURE RISE

The heat of hydration of cement is the heat liberated as the cement and water react. The amount of heat liberated over time, and the rate at which this occurs is dependent on the cement quantity and type, water/cement ratio and temperature. In general, the rate of heat liberation parallels the rate of strength increase. This rate is usually high during the first two to three days after mixing and then subsides appreciably.

Heat is liberated during the hydration of the cement as the cement minerals adopt a lower-energy condition – resulting in a rise in temperature. Temperature-rise/ age relationships of various cements are shown in **Figure 1.3**. In most concrete construction, heat is dissipated from the concrete and large rises in temperature do not occur. However, in (low surface area) structures such as massive foundations, dams, and thick structural elements too great a temperature differential between the core and the surface may lead to thermal cracking. (*NOTE: The core is hot and expanding while the surface is cooling and contracting leading to the development of tensile stresses within the element.*)

Limiting the temperature rise in concrete is important to avoid thermal cracking. It is generally required that the temperature differential be limited to a maximum of 20°C.
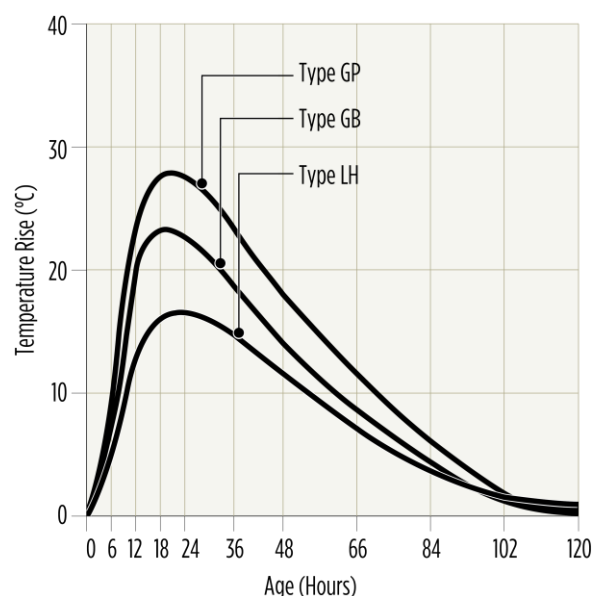


*Figure 1.3 – Typical Temperature Rise with Age of Cement Mortars – Semi Adiabatic Calorimeter (AS 2350.7)*

Cements with 'low heat' characteristics are produced for use in 'low heat' applications.

Measurement of heat of hydration using the heat of solution method has been used to characterise cements by many countries. While this method determines with good accuracy the total heat of hydration at seven days and longer, it gives no indication of the actual temperature rise under practical conditions or, more importantly, at early age when the maximum temperature rise is likely to occur. Further, the method is not suitable for blended cements for which other methods are now available, e.g. Langavant method.

AS 3972 specifies/characterises low heat cement by the peak temperature rise (**Table 1.1**) measured on a standard cement mortar under semi-adiabatic conditions. **Figure 1.3** shows typical temperature- rise/age curves for various types of cement.

Peak temperature rise is determined in accordance with AS 2350.7. This test method is based on a French test known as the Langavant method. It is modified to put the emphasis on measurement of temperature rise allowing, as an option, the calculation of heat of hydration, if required.

## 4.3 STRENGTH DEVELOPMENT

On addition of water, the cement minerals hydrate forming mainly hydrates of calcium silicate and calcium aluminate and calcium hydroxide as a by-product. The hydration involves an increase in the volume of the solids in the mix and growth of the gel binds particles, bringing about stiffening of the cement paste (i.e. setting). Further hydration decreases the porosity of the set paste, thereby increasing its strength. The rate of gain in strength of the set paste (strength development) is at its maximum rate at early ages, and gradually decreases with time (**Figure 1.4**). Ultimate compressive strength may take several years to achieve, but for practical purposes 28-day strengths are used as indicators of the 'final' strength – an approach taken and specified in cement and concrete Standards all over the world.
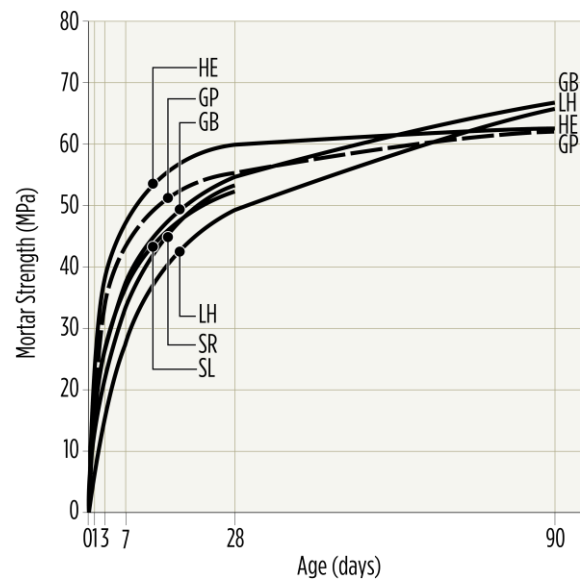


*Figure 1.4 – Typical Cement Mortar Strength Development with Age (AS 2350.11)*

The rate of strength development as cement hydrates is influenced by both the chemical composition and fineness of the cement. The rate of strength development of blended cements is dependent on the nature and proportion of the component materials, i.e. the amount, type and properties of the cement and the properties of the fly ash, slag or silica fume. As mentioned earlier, fly ash and slag blended cements gain strength more slowly than cement-only mixes at early ages, but they exhibit more strength gain over a longer period, particularly if moisture is available to support curing for a sufficient time. On that basis, the ultimate strength of blended cement mixes is generally higher than that obtained if the same general purpose cement was used alone (**Figure 1.5**).

The compressive strength of general purpose and blended cements as required in AS 3972 is determined by compressive strength tests on mortar prisms using a standard mortar (1:3 cement-sand mixture with a 0.5 water/cement ratio) as defined in AS 2350.12. The actual strength testing is conducted in accordance with AS 2350.11.
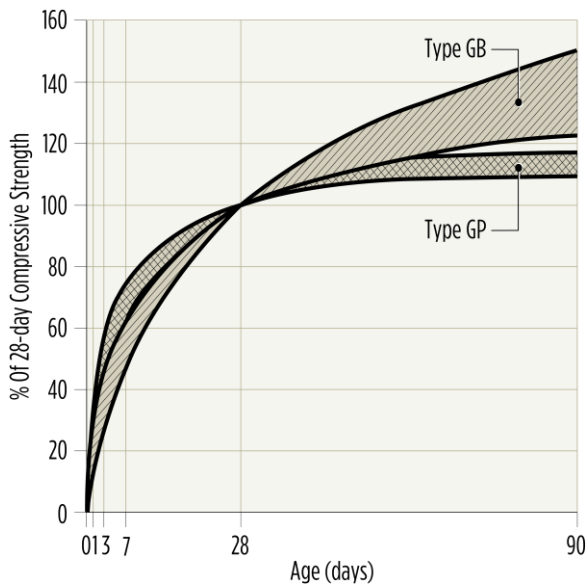
Figure 1.5 – Development of Concrete Strength with Age – Type GP versus Type GB

## 4.4 VOLUME CHANGE

*General* – A change in the volume of the hardened paste may be caused by chemical reactions, following for example, attack by aggressive solutions (see 4.7); or by physical factors, such as changes in the moisture content or in the temperature of the paste.

Volume changes due to variations in moisture content (shrinkage) and to variations in temperature (thermal expansion and contraction) are discussed below.

*Shrinkage* – Variations in the moisture content of cement paste are accompanied by volume changes: drying causes volume decrease, i.e. drying shrinkage; while wetting causes volume increase, i.e. swelling or expansion. A schematic description of volume changes in cement paste due to alternate cycles of drying and wetting is given in **Figure 1.6**. It can be noted that maximum shrinkage occurs on the first drying of the paste and that a considerable part of this shrinkage is irreversible; part of the reduction in volume is not recovered on subsequent rewetting. During successive repetitions of wetting and drying, the process becomes reversible, depending on the structure of the paste and on the relative durations of the wetting and drying periods. Since shrinkage is caused by water loss, it is affected by external factors that affect drying, such as temperature,

humidity and air movement. Shrinkage is also affected by some properties of the cement.

Although it is generally accepted that the composition of cement can affect drying shrinkage, the effect is not completely apparent. The $C_3A$ and alkali content have been observed to have a measurable effect. In addition, the effects of $C_3A$ and alkali content on shrinkage are influenced by the sulfate content of the cement, i.e. shrinkage of cements of the same $C_3A$ content differs for different sulfate contents.

*(**NOTE**: When determining the optimum gypsum/sulfate content for a cement, the cement manufacturer measures the effect of varying gypsum/sulfate levels on strength, setting time and shrinkage and sets the final gypsum/sulfate level at the point where the best performance is obtained.)*

For many years, major project specifications in NSW in particular have specified cement composition and/or performance as a means of managing shrinkage of concretes to be used in certain structures – such as road pavements and bridges. It was recognised, however, that there are other cements that have performed well in low shrinkage concrete applications. This led to the development of a cement characterised in terms of its shrinkage performance – Shrinkage Limited Cement (Type SL) and development of a test method to measure the 'shrinkage performance' of cements. This mortar test determines shrinkage at 28 days under standardised conditions. An upper limit for drying shrinkage has been set for a compliant Type SL cement in AS 3972 (see **Table 1.1**). These cements may be cement-only or blended cements.
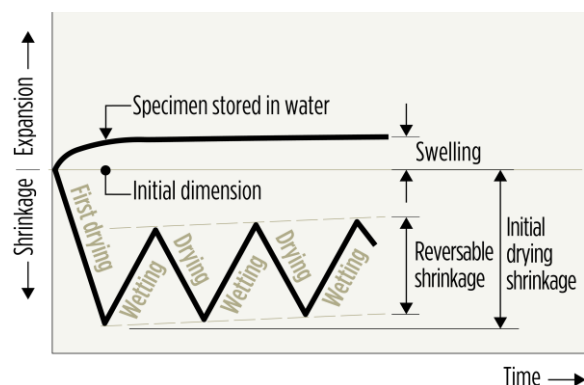


Figure 1.6 – Schematic Representation of Volume Changes in Cement Paste due to Alternate Cycles of Drying and Wetting

*Relationship Between 'Cement' Shrinkage and Shrinkage of Concrete* – The drying shrinkage values for a cement (mortar) cannot be applied directly to the shrinkage of concrete since the latter is greatly influenced by significant factors other than just cement properties. These factors include (a) the concrete components, and (b) the ambient conditions – temperature and humidity. Aggregates restrain the drying shrinkage of the cement paste. The restraining effect of the aggregate, illustrated in **Figure 1.7**, is determined by (a) the volume fraction of aggregate in the concrete, (b) its modulus of elasticity, (c) its absorption characteristics and (d) the maximum aggregate size. Aggregates that lack volumetric stability (such as certain volcanic breccias) will cause significantly higher drying shrinkage than those that are stable. The water content of the concrete influences its shrinkage – the higher the water content, the higher the shrinkage.
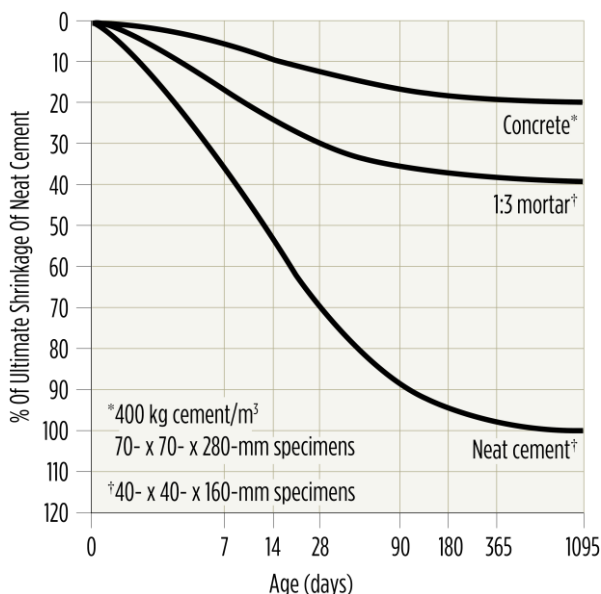


*Figure 1.7 – Comparative Drying Shrinkage of Concrete, Mortar and Cement Paste at 50% Relative*

Admixtures may also affect the shrinkage of concrete in a number of ways. For example, some set- accelerating admixtures (e.g. those containing triethanolamine) cause substantial increases in drying shrinkage. Also, when lignosulphonate-based water-reducing admixtures are added to a concrete mix without adjusting the mix proportions, an increase in the early drying shrinkage may occur.

The use of an admixture which enables a net reduction in the water content of the concrete will often result in reduced shrinkage. The complexity of modern admixtures is such that it is dangerous to generalise as to their likely effect.

The use of pozzolanic materials may result in either an increase or a decrease in drying shrinkage depending, in part, on their effect on the water demand of the concrete.

Therefore, using Type SL cement alone will not guarantee the production of low shrinkage concrete. The many other factors discussed need to be considered as they may outweigh the effect of the cement on the concrete drying shrinkage. This is stated clearly in the notes for Table 2 of AS 3972.

*Thermal Volume Changes* – The coefficient of thermal expansion of cement paste varies between $10\times10^{-6}$ and $20\times10^{-6}$ /°C depending, mainly, on the moisture content of the paste. The coefficient increases with increases in the relative humidity, reaching a maximum at about 70% relative humidity.

## 4.5 PERMEABILITY

Permeability of the cement paste depends not only on the paste porosity but also on other properties of the pore system, such as pore continuity and pore size distribution. These properties are affected by the water/cement ratio (and hence cement content) and the extent of hydration – which in turn is affected by the amount of curing given to the paste. The effect of the water/cement ratio is illustrated in **Figure 1.8** and the effect of moist curing in **Table 1.4**.

## 4.6 ALKALINITY

Hydrated cement paste is inherently an alkaline material having a pH of approximately 12.5. It is this high pH which allows concrete to protect steel from corrosion by assisting in the formation of a thin, passive iron oxide layer on the steel that prevents corrosion.
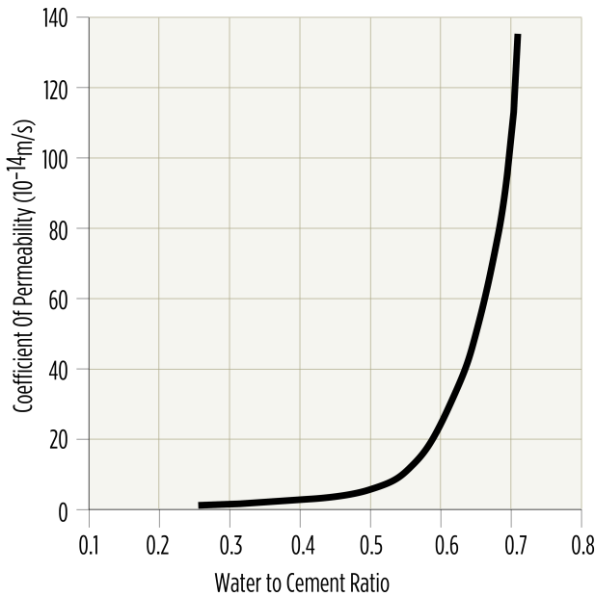
*Figure 1.8 – Effect of Water/Cement Ratio on Permeability[1.2]*

The composition of cement has little or no influence on the level of alkalinity of freshly hydrated cement paste, but a reduction in alkalinity may take place as a result of the leaching of alkalis from the paste and/or the carbonation of the hydrated cement. Field and laboratory investigations have shown that the rate and extent of carbonation with blended cements tends to be higher than that with general purpose cements, but the permeability of the paste is likely to be a much more important factor in determining the risk of corrosion. Impermeable pastes carbonate only very slowly, no matter what type of cement is used.

*Table 1.4 – Duration of Moist Curing Required to Achieve Capillary Discontinuity*

| Water/cement ratio | Duration of moist curing |
| --- | --- |
| 0.4 | 3 days |
| 0.45 | 7 days |
| 0.5 | 14 days |
| 0.6 | 6 months |
| 0.7 | 1 year |
| >0.7 | Impossible |

## 4.7 RESISTANCE TO CHEMICAL ATTACK

***General*** – Hardened cement paste may be attacked by aggressive chemical agents. The intensity of the attack depends on the specific properties of the agent, its concentration, and on the duration and the nature of the contact with the paste, i.e. whether it is continuous or periodic. Regardless of the nature of the aggressive agent, the chemical resistance of the paste is related to its permeability – less permeable pastes are more resistant to all forms of chemical attack.

***Acids*** – The action of acids on the hardened cement results in the conversion of the calcium compounds in the paste to the calcium salts of the acid. The solubility of the resulting calcium salt determines to a large degree the extent of the acid attack. If the calcium salt is soluble it is readily removed by dissolution and leaching. As a result, the structure of the hardened cement is effectively destroyed. Hydrochloric acid and nitric acid give low pH solutions and calcium salts which are readily soluble. Acids which result in insoluble salts, such as oxalic and hydrofluoric acid, cause less significant damage.

***Sulfates*** – All soluble sulfates react with hardened cement pastes causing the formulation of expansive products which, in severe cases, can result in complete disintegration of the paste, mortar or concrete.

Calcium, sodium and potassium sulfates can attack the aluminates in the cement paste. The reaction, in the presence of moisture, creates an expansive reaction product which may lead to cracking. Magnesium sulfate and ammonium sulfate are potentially more severe in their action since they attack not only the aluminates but also the silicate hydrates. Attack is progressive, and the hardened cement can be reduced to a soft mass. The severity of the sulfate attack on cement paste, mortar and concrete depends on the type of the sulfate, its concentration, whether the sulfate solution is stagnant or flowing, and temperature.

The use of sulfate-resisting cements is recommended where the risk of sulfate attack is present.

It should be noted that resistance of concrete to sulfate attack is influenced not only by the factors affecting the chemical reactions but also, and more importantly, by the factors influencing the permeability and the overall quality of the concrete – as noted in Table 2 of AS 3972. Generally, sulfate resisting concretes should be at least 40 MPa (or higher), and ideally the cementitious materials should include an SCM.

*Chlorides* – The major influence of chlorides in concrete is to increase the risk of corrosion of reinforcing steel. If present in sufficient concentration in the vicinity of the steel, they cause a breakdown in the passive layer which normally protects steel from corrosion in alkaline conditions. Corrosion can then occur, particularly if the alkalinity of the cement paste is simultaneously reduced by carbonation.

The use of a cement relatively high in $C_3A$ may assist in reducing the influence of chlorides by 'binding' a portion of them. Chlorides will react with calcium aluminates to form calcium chloro-aluminates. However, this measure should not be relied upon to prevent corrosion of steel by chlorides, partly because calcium aluminates combine preferentially with sulfates (to form sulfo-aluminates) before chlorides, and partly because subsequent carbonation of the paste causes breakdown of the chloro-aluminates and the release of chloride ions into the system.

Blended cements have been shown to be advantageous. The dense pore structure which results from their use reduces the mobility of the chloride ions, extending the time to onset of corrosion.

## 4.8 RESISTANCE TO FREEZING AND THAWING

The freezing of ice involves an increase in the volume of the water frozen by about 9%. In saturated, or nearly saturated cement pastes, freezing of free water and the consequent volume increase will produce internal pressures which, in turn, cause dilation and cracking of the paste. Repeated cycles of freezing and thawing therefore damage cement pastes (mortars and concretes) by causing internal stresses which crack the paste and eventually cause it to disintegrate – most particularly at the exposed surface.

The damaging effect of frost depends primarily, therefore, on the amount of free moisture within the pores of the paste, and this in turn depends on the permeability and/or porosity of the paste. Pastes of low water/cement ratio and, hence, low permeability, are inherently more resistant to frost action. The resistance of cement pastes to freezing and thawing may be improved dramatically by the purposeful entrainment of air within the concrete.

Certain types of blended cements, notably those containing fly ash with high carbon content, tend to depress the effects of air-entraining agents and to produce a less uniform and a less stable air-void system. Otherwise, the type of cement has no specific effect on the resistance of cement paste to freezing and thawing resistance.

## 4.9 RESISTANCE TO HIGH TEMPERATURE

The effect of high temperature on the hydrated cement paste will vary with the following factors:

- Rate of temperature rise;
- Length of exposure;
- The final temperature reached;
- Age of the hardened paste;
- Degree of saturation.

With a slow rise in temperature, the hardened paste progressively dries out, but its properties are substantially unaffected up to about 200°C. Where the rise in temperature is rapid and the concrete is saturated – for example where it has not had the time to dry out thoroughly – significant damage may occur due to moisture trapped in the pores of the concrete turning into steam and it bursting through the surface. It has also been found that the decomposition of ettringite above 100°C, in conditions where temperature rise is rapid, can lead to the creation of water vapour that may 'pool' in cooler sections of the concrete and be later released resulting in spalling.

At temperatures between 300°C and 600°C, (chemically) combined water is driven off and dehydration begins to take place, resulting in a progressive loss in strength and a material which will be severely damaged by rewetting. Exposure to temperatures above 600°C will lead to complete loss of strength and, eventually, to failure. If such conditions are expected, high-alumina cements combined with selected refractory aggregates should be used to produce a refractory concrete.

# 5. STORAGE, SAMPLING AND TESTING OF CEMENT

## 5.1 STORAGE

The principle underlying the proper storage of cement is that, as far as possible, moisture (or air which may contain moisture) should be excluded from contact with the cement. If completely protected from moisture, cement may be stored for an indefinite period of time.

Bulk cement is stored at cement plants and terminals, and at concrete batching and products plants, in steel or concrete silos. Provided moisture is excluded from the interior of such silos, cement may be stored in them for quite long periods. Satisfactory storage for several months is not unusual. Often, conveying air used to load cement into silos from tankers is not moisture free and this can lead to lump formation if the cement is not regularly used.

Cement packed in multi-layer paper sacks has a more limited storage life as moisture will be absorbed from the atmosphere and cause progressive deterioration of the cement over time. In damp weather, such deterioration may be quite rapid and will be evidenced by the development of crusting or even hard lumps in the cement. Such cement is likely to have reduced strength and extended setting times, even if the hard lumps are screened out.

Soft lumps such as those which may occur in the lower bags in a high stack from the pressure of the bags above, and which can be broken up by rolling the bag a few times, is not a sign of deterioration.

(**NOTE**: This soft lump formation is known as 'pack set'.)

Bagged cement storage areas must be kept dry and, as far as practical, air movement restricted. Storing bags on pallets above ground, covering stacks with tarpaulins or plastic sheeting, and ensuring that the stock is used in the order in which it is received are all measures which will assist in preventing deterioration of bagged cement.

It should be noted that Off-White cements are more prone to lump formation and can have a considerably lower shelf life than general purpose (grey) cement.

## 5.2 SAMPLING AND TESTING

Sampling and testing of cement for compliance with specifications is normally carried out in accordance with the requirements described in AS/NZS 2350.1 and AS 3972. The test methods for cement are described in the AS 2350 series of Australian Standards.

Testing is carried out routinely by the cement manufacturer and the results of these tests are normally available on request on a formal test certificate. Industry laboratories are generally NATA accredited to carry out the specific testing required.

# 6. APPENDIX – MINOR CONSTITUENTS OF CEMENT

## 6.1 GYPSUM

Gypsum [calcium sulfate containing two molecules of water ($CaSO_4.2H_2O$)] is added during grinding of the clinker in order to prevent 'flash setting' of the cement when water is added. The heat from the milling operation (when using ball mills) partially converts the gypsum into 'Plaster of Paris' ($CaSO_4.0.5H_2O$) which is a more soluble material that is able to more readily provide the sulfate ions into solution necessary to prevent 'flash setting'.

The retarding action of gypsum/sulfate is due mainly to the formation of coatings of ettringite (calcium sulfo-aluminate) on the surface of the

aluminate ($C_3A$) in the cement which prevents its immediate hydration. The sulfate content of cement must be controlled as excess sulfate may cause the formation of increased amounts of ettringite, leading to expansion and cracking and deterioration of the hardened cement. Consequently, cement standards specify a maximum sulfate content (expressed usually as %$SO_3$). AS 3972 limits sulfate (as $SO_3$) content of cements to a maximum of 3.5%.

Gypsum/sulfate has an influence on the setting time, strength and drying shrinkage properties of cement. A cement manufacturer optimises the percentage of gypsum to ensure the best combination of these performance properties to meet the needs of the market.

## 6.2 FREE LIME (CaO)

The presence of free (uncombined) lime in cement may occur when the raw materials used in the manufacturing process contain more lime than can combine with the silica, alumina and iron oxides. Alternatively, free lime may occur when the amount of lime in the raw materials is not excessive, but its reaction is not completed during the burning process – i.e. the cement is underburnt. When the amount of free lime exceeds certain limits, depending on the fineness of the cement, the cement shows 'unsoundness'. The mechanism of 'unsoundness' is as follows: The free lime is inter-crystallised with other minerals and is therefore not readily accessible to water. It hydrates after the cement has hardened and because the hydration product occupies a larger volume than the free lime alone it may cause expansion and cracking. Thus, the hardened product is not 'sound'.

It is evident that free lime in the cement should be limited. It is difficult, however, to specify a quantitative limit for free lime in cement because its adverse effects depend not only on the amount present but also on other factors. Consequently, cement standards generally nominate a test for 'soundness' to ensure that the amount of free lime present does not have an adverse effect on the hardened cement products. The relevant test is prescribed in AS 2350.5. It is the Le Chatelier Test which involves making a cement paste, allowing it to harden and then boiling a small cylinder of the hardened paste to accelerate any latent hydration reactions and measuring any consequent expansion. An expansion limit for this test of 5 mm maximum is set in AS 3972.

## 6.3 MAGNESIA (MgO)

Magnesia is introduced into cement as a minor constituent of limestone. Except for a small amount held in the crystal lattice of the cement compounds, MgO normally exists in cement as the mineral periclase (MgO), a crystalline material which can exhibit long-term expansion due to later-age hydration. Most cement specifications place a limit on the amount of MgO that can be present in 'cement'. AS 3972 limits the magnesia content in clinker to 4.5% maximum.

## 6.4 ALKALI OXIDES ($K_2O$, $Na_2O$)

The alkali oxides (potash and soda) are introduced into cement through the raw materials. The total content of potassium and sodium oxides in cement is small (**Table 1.2**). A reaction may occur between these alkalis and some types of aggregates which contain reactive silica. This reaction, known as ASR or AAR, creates an expansive reaction product which, if it absorbs sufficient water, may expand and cause cracking and disruption of the concrete. Although the reaction will always occur in the presence of reactive silica, damage to the concrete may be avoided when the amount of alkali in the concrete is low. While AS 3972 does not impose any limit on alkali content, many specifications set limits on the alkali content of cement expressed as $Na_2O$ (or sodium) equivalent (%$Na_2O$+0.658%$K_2O$). The typical limit is 0.6% sodium equivalent maximum. In the presence of potentially reactive aggregate, a range of measures can be taken to minimise the risk of damage due to ASR/AAR. These are discussed in *'Alkali Aggregate Reaction – Guidelines on Minimising the Risk of Damage to Concrete Structures in Australia'*, Standards Australia HB-79:2015.

## 6.5 LOSS ON IGNITION

Loss on ignition (LOI) primarily measures the presence of moisture and carbon dioxide in the cement and is determined by heating a cement sample to 900-1,000°C. Whilst LOI can be used to indicate whether a cement has been impaired by exposure to undue levels of moisture and/or carbon dioxide, the presence of certain mineral additions such as limestone or relatively high levels of slag can affect the result, making interpretation difficult unless the general cement composition is known.

No limit is specified in AS 3972 for LOI but the value must be reported if requested.

## 7. SUMMARY

*Table 1.5 – Hydraulic Cements – Types and Applications*

| Type | Application |
|------|-------------|
| General Purpose (Type GP) | For general use in building and construction. |
| General Purpose Blended (Type GB) | For general use in building and construction. Early rates of strength gain may be lower than with Type GP, and curing may be more critical for full strength development. |
| High Early Strength (Type HE) | Where early strength is a critical requirement (e.g. for early stripping of formwork, precast concrete and pre-stressed concrete); In very cold weather; In repairs to concrete structures. |
| Low Heat (Type LH) | Where rise in concrete temperature must be limited to avoid thermal stresses (e.g. in mass concrete construction or in very hot weather); Where moderate resistance to some forms of chemical attack is required. |
| Shrinkage Limited (Type SL) | Where limiting the drying shrinkage of concrete is necessary for crack control (e.g. in road pavements and bridge structures). |
| Sulfate Resisting (Type SR) | Where high resistance to sulfate attack is required, e.g. with sulfate-bearing soils and ground waters, and in marine environments. |
| White and Off-White | In the production of architectural concrete and concrete products; Normally complies with the requirements of AS 3972 for Type GP or Type HE cement. |
| Coloured Cement | In the production of concrete products, decorative concrete paving and similar applications. |
| Masonry Cement | Mortar in brick, block and stone masonry construction. Unsuitable for use in structural concrete. |
| Oil-Well Cement | Grouting gas, oil and other deep bore holes and wells. Normally complies with the relevant specifications of the American Petroleum Institute (API). |
| High Alumina Cement (HAC) | Where high early strength and/or resistance to very high temperatures are required (e.g. refractory concrete and factory floors). |

CEMENT CONCRETE
& AGGREGATES AUSTRALIA

# 8. REFERENCES

1) AS 1316 – *Masonry cement*
2) AS 1379 – *The specification and supply of concrete*
3) AS 2350 – *Methods of testing Portland, blended cements and masonry cements*
4) AS 2350.1 – *Method 1: Sampling*
5) AS 2350.2 – *Method 2: Chemical composition*
6) AS 2350.4 – *Method 4: Setting time*
7) AS 2350.5 – *Method 5: Determination of soundness*
8) AS 2350.7 – *Method 7: Determination of temperature rise during hydration of Portland and blended cements*
9) AS 2350.11 – *Method 11: Compressive strength*
10) AS 2350.12 – *Method 12: Preparation of a standard mortar and moulding of specimens*
11) AS 3582 – *Supplementary cementitious materials*
12) AS 3582.1 – *Part 1: Fly ash*
13) AS 3582.2 – *Part 2: Slag – Ground granulated blast-furnace*
14) AS 3582.3 – *Part 3: Amorphous silica*
15) AS 3972 – *General purpose and blended cements*

# 9. FURTHER READING

1) Neville, A.M., '*Properties of Concrete*' (4th Edition), Longman Group Limited England, ISBN-0-582-23070-5 (1995), Chapters 1 and 2
2) Hewlett, P.C. (Editor), '*Lea's Chemistry of Cement and Concrete*' (4th Edition), Butterworth-Heinemann, ISBN-0-340-56589-6 (1998), Chapters 1-15

**End Notes**

1.1 Based on Figure 2.4 in *'Portland Cement Paste and Concrete 1'*, Soroka (1979)
1.2 Based on Figure 6 in Journal AC 51 (November 1954)