

Cements – Properties and Characteristics

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Cements – Properties and Characteristics

This new edition of this Technical Note supersedes the 1989 edition *Hydraulic Cements – Properties and Characteristics* (TN 59) published by the Cement and Concrete Association of Australia. The superseded document was based on the then-current Australian Standards AS 1315 *Portland Cement* and AS 1317 *Blended Cement* which have since been replaced by AS 3972—1997 *Portland and Blended Cements*¹. This Technical Note takes account of this new Standard.

1 INTRODUCTION

'Cement' is a generic term used to describe a wide variety of organic and inorganic binding agents. The most widely used binding agents are those known as hydraulic cements – finely ground inorganic materials which possess a strong hydraulic binding action, ie when mixed with water they harden to give a stable, durable product.

There are many types of hydraulic cement and this Technical Note discusses those available to the construction industry.

2 FIELDS OF APPLICATION

The main use for hydraulic cement is the manufacture of concrete. Some limits will be placed on the choice of concrete for a particular structure, eg by the construction techniques, the service conditions, the environment, and the structural behaviour of individual elements and the structure. Such constraints may make the use of a certain type or types of cement more appropriate than others.

3 PORTLAND AND BLENDED CEMENTS

3.1 General

Hydraulic cements produced in Australia fall broadly into two categories: portland cements and blended cements. The latter are mixtures of portland cement with other materials which either possess cementitious properties of their own, eg ground granulated iron blastfurnace slags, or which are pozzolanic in nature, ie they react with lime in the presence of water to form cementitious compounds, eg fly ash and silica fume. Portland and blended cements are manufactured in Australia to comply with the requirements of AS 3972 *Portland and Blended Cements*¹. A number of different types of cements are covered by this Standard. A summary of their physical and chemical properties specified in AS 3972 is given in **Table 1**.



Table 1 Summary of AS 3972 Requirements

AS 3972 Requirements*	Cement types					
	GP	GB	HE	LH	SL	SR
Chemical limitations						
Loss on ignition	reported if required – no limit is specified					
Sulfuric anhydride SO ₃ (max)%	3.5	3.5	3.5	3.5	3.5	3.5
MgO	Portland cement clinker shall contain less than 4.5%					
Physical properties						
Setting time						
Minimum (minutes)	45	45	45	45	45	45
Maximum (hours)	10	10	10	10	10	10
Soundness maximum (mm)	5	5	5	5	5	5
Compressive strength minimum (MPa)						
3 days	–	–	20	–	–	–
7 days	25	15	30	10	20	15
28 days	40	30	–	30	30	30
Peak temperature rise maximum °(C)	–	–	–	23	–	–
Drying shrinkage maximum (microstrain)						
28-day	–	–	–	–	750	–
Sulfate expansion maximum (microstrain)						
16-week	–	–	–	–	–	900

* Determined in accordance with the methods set out in AS 2350 *Methods of Testing Portland and Blended Cements*²

AS 3972 is a performance based specification in which portland and blended cements are defined in terms of their performance characteristics. As the raw materials used to produce portland and blended cements can vary widely from locality to locality, the chemical composition of cements can also vary quite widely. Nevertheless, with modern technology, from these diverse materials it is possible to produce cements which have similar physical characteristics. Hence, AS 3972 specifies only those restrictions on chemical composition which are necessary to ensure satisfactory performance, eg upper limits on the MgO and SO₃ contents to guard against excessive long-term volumetric expansion of the hydrated cement paste.

3.2 General Purpose Portland Cement – Type GP

In keeping with world-wide practice, portland cements complying with AS 3972 may contain up to 5% mineral additions. Mineral additions are defined as being selected fly ash, slag, limestone containing more than 80% calcium carbonate, or combinations of these materials. Fly ash and slag are to comply with the requirements of AS 3582.1 and AS 3582.2 respectively³.

Thus portland cement is defined in AS 3972 as a hydraulic cement which is manufactured as a homogenous product by grinding together portland cement clinker and calcium sulfate, and which at the discretion of the cement manufacturer may contain up to 5% of mineral additions.

General purpose portland cement is intended for use in most forms of concrete construction and should be specified where the special properties of the other types, such as low heat of hydration, are not required.

As the raw materials used to produce portland cements vary widely from location to location, Type GP cements may have a range of chemical compositions. The restrictions placed on the chemical and physical properties of Type GP cement by AS 3972 are those necessary to ensure satisfactory performance as a general purpose cement.

3.3 General Purpose Blended Cement – Type GB

Blended cement is defined in AS 3972 as a hydraulic cement containing portland cement and a quantity greater than 5% of fly ash or slag or both and/or up to 10% silica fume. Fly ash, slag and silica fume are to comply with the requirements of the relevant parts of AS 3582 *Supplementary Cementitious Materials for Use with Portland Cement*³.

General purpose blended cement is intended for use in most forms of concrete construction where the special properties of other cement types are not required.

By varying the proportions of portland cement and fly ash, slag, and silica fume in blended cement it is possible to produce cements with a fairly wide range of characteristics. In practice, however, the difference in properties between Types GP and GB

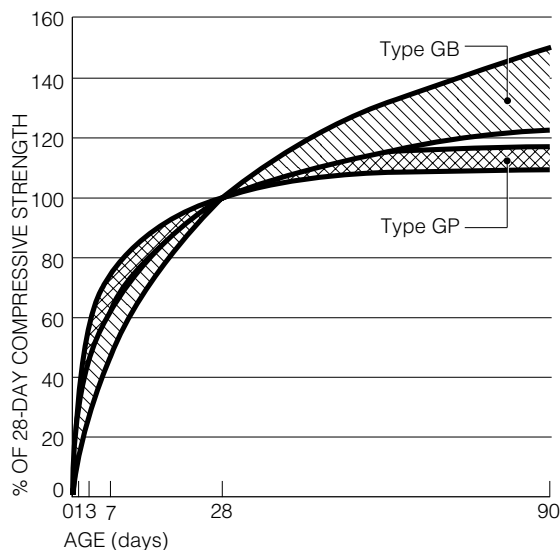


Figure 1: Typical development of concrete strength with age

may not be great, as both are formulated to be used in general building construction.

A possible exception to this are those Type GB cements containing silica fume, which are often intended to be used for particular applications where high early strengths or specific durability requirements are sought.

Whilst the minimum strengths specified for Type GB cement in AS 3972 are lower than those for Type GP (in recognition of their generally lower rate of strength gain), it is not uncommon for their ultimate strengths to equal or exceed those of Type GP cement, provided moisture is available (eg through curing) for a sufficient length of time **Figure 1**.

It should be noted that Type GB cements containing up to 10% silica fume would be expected to have a different strength development curve to that of other Type GB cements shown in **Figure 1**.

3.4 High Early Strength Cement – Type HE

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 development.

High early strength cement lends itself to applications where rapid strength development is required, eg when formwork is to be removed early for reuse, or where early strength is required so that further construction can proceed. Rapid strength development is usually accompanied by a higher rate of heat evolution. Hence, Type HE cement should not be used in thick concrete sections or in mass construction. On the other hand, its use for construction under cold weather conditions is beneficial.

The typical strength development of concrete made with Type HE cement is shown in **Figure 2**.

3.5 Low Heat Cement – Type LH

Type LH cement is intended for use where limitation of the heat of hydration (and hence the temperature rise in the concrete) is necessary to avoid unacceptable thermal stresses, such as in massive structures or in thick structural elements. Low heat cement may be a portland or a blended cement provided it meets the requirements for temperature rise specified in AS 3972 Table 1.

Low heat characteristics are achieved by reducing the content of the more rapidly hydrating compounds in cement or by blending with supplementary cementitious materials. This, generally, will result in a slower rate of strength development. Blended cements can have some inherent advantages in minimising heat evolution because of their generally lower rates of strength gain.

However, the ultimate strength of Type LH cement may be equivalent to, or higher than, that for other types of cement **Figure 2**.

3.6 Shrinkage Limited Cement – Type SL

For many years, some major specifications in Australia have recommended chemical composition of cement as a means of controlling the shrinkage of cements to be used in concrete structures. Within the scope of AS 3972, a cement characterised in terms of its shrinkage performance was required to reflect/cover the existing practice in some areas and applications.

Type SL cement is intended for use where emphasis is placed on drying shrinkage and crack control in concrete structures (eg road pavements and bridge structures). Type SL cement may be a portland or a blended cement provided it meets the drying shrinkage limit specified in AS 3972 Table 1.

3.7 Sulfate Resisting Cement – Type SR

The relationship between the sulfate resistance of portland 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 world-wide, including Australia until recently.

Studies have shown that cements potentially containing less calcium hydroxide on hydration perform well in sulfate exposure, eg 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 portland cement by a performance test and a performance limit (expansion limit) suitable

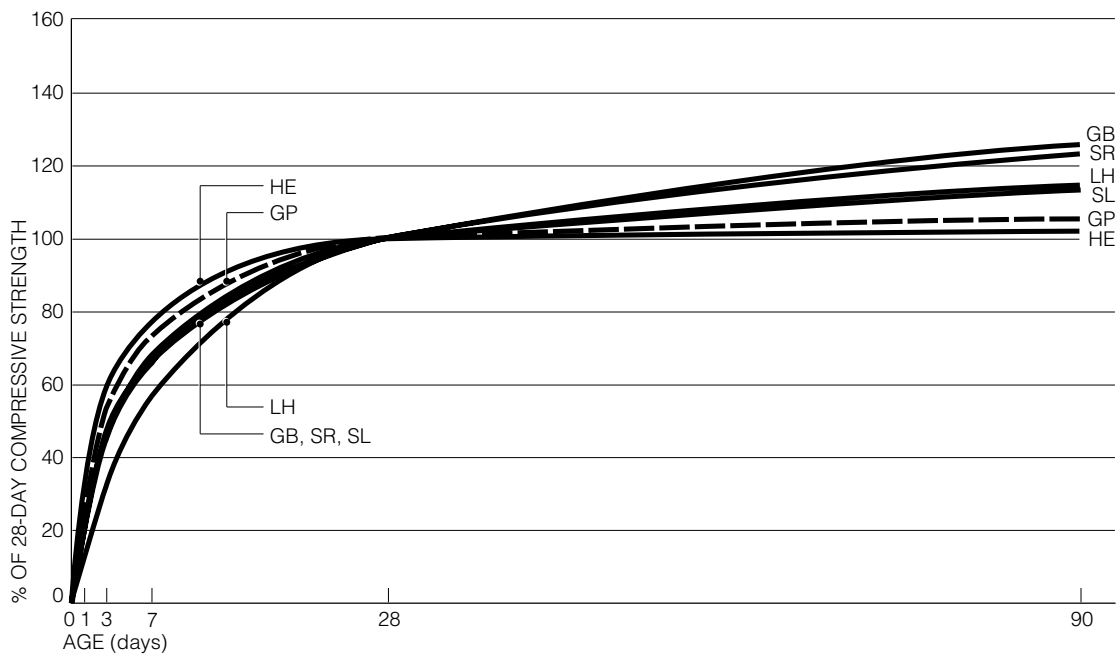


Figure 2: Typical concrete strength development with age for various cements. *Note: Types SR and SL cements may be portland or blended cements. If required, specific strength development data should be sought from the manufacturer.*

for Type SR cement, being portland or blended cement **Table 1**.

The formulation of Type SR, as a blended cement, or as a portland cement with a low C_3A content, may produce a cement having a lower rate of strength development at early age than, say, Type GP cement **Figure 2**. Hence, the minimum strength requirements in AS 3972 for Type SR cement are lower than those for Type GP cement **Table 1**.

Type SR cement is intended primarily for use where resistance to sulfates in solution is required. Type SR cement may be a portland or a blended cement provided it meets the sulfate expansion limit specified in AS 3972 Table 1.

4 OTHER TYPES OF CEMENT

4.1 General

There is a continual growth in the types of cement available to the construction industry. Most of these cements have limited uses and the output of them is very small.

The following is a brief description of other types of cement available in Australia (manufactured or imported) and their applications.

4.2 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 portland 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, etc may also be incorporated.

Masonry cement is produced to meet the requirements of Australian Standard AS 1316 *Masonry Cement*.

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

4.3 Off-white and White Portland Cement

The grey colour of portland cement is due mainly to the ferrite phase – tetracalcium aluminoferrite, C_4AF .

By lowering the iron content, off-white and white 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 portland cements.

The composition of off-white and white cements is characterised by relatively high C_3A contents (9 to 15%) and low C_4AF contents (1.5 to 2% for off-white and 0.3 to 0.4% for pure white cements).

Off-white and white cements are used for aesthetic reasons. Since relatively high cement contents are normal in this application, dense concrete of low water-cement ratio, which are required properties for durability, can be obtained. However, due to 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, GB or HE cements in AS 3972. Off-white and white cements imported into Australia are generally required to comply with AS 3972 also.

4.4 Coloured Cements

Most coloured cements consist of cement and inorganic pigments interground 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 (for dark colours) or the more costly off-white or white cement (for light 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 which may cause efflorescence.

4.5 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 portland cements that are designed to serve this need. They consist of coarsely ground portland cement of low C₃A content, with or without a retarder.

The properties required of oil-well cements are set out in the American Petroleum Institute Standard STD 10A *API 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*.

4.6 High Alumina Cement (HAC)

HAC is entirely different from portland 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 (Al₂O₃) content and a low lime (CaO) content as compared with portland cement. In some literature, HAC is called 'calcium aluminate cement', but it is more commonly known as high alumina cement. It is 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 restricts HAC's 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 application 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 this process, some of the hydrated compounds of the hardened cement paste convert to other compounds of smaller volume. This results in a cement paste with reduced strength. The rate at which conversion occurs depends on the moisture condition and temperature of the concrete. Where moisture is present and 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.

Because of the possibility of conversion and loss in concrete strength, the use of HAC in warm humid environments should be approached with great caution. It should not be used in combination with other types of cement without first checking on the effect of this on the properties and behaviour of the fresh and hardened concrete.

5 CHEMICAL AND PHYSICAL PROPERTIES OF CEMENTS

5.1 Portland Cements – General

Portland cements consist of carefully proportioned mixtures of calcium carbonate, alumina, silica, and iron oxide which, when calcined and sintered at high temperatures, give a new group of chemical compounds capable of reacting 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 (all in the form of clay and shale). Sources of silica (such as sand), of alumina (such as bauxite), and iron oxide (such as iron ore) are also used.

These materials are interground to produce the finely divided 'raw feed' for the kilns. This is then burnt in rotary kilns at temperatures from 1300 to 1500 °C when the components partially fuse to form 'clinker' – hard balls of ceramic-like material. During burning, chemical reactions take place which convert the raw materials to new chemical compounds capable of reacting with water. When cool, the clinker is mixed with a small amount of gypsum (calcium sulfate) and ground to a fine powder. The resultant product is known as portland cement.

In addition to gypsum, which is necessary to control the rate at which the cement hydrates when mixed with water, small quantities of other materials may be interground with the clinker in order to enhance the properties of the cement. They range from a minor quantity (less than 1%) of processing additions to aid the manufacture or improve the handling properties of cement, eg organic compounds which may be added to assist in grinding the clinker, to mineral additions such as limestone, slag or fly ash. AS 3972 limits the amount of mineral addition to portland cement to no more than 5%.

The oxide composition of most modern portland cement falls within the ranges given in **Table 2**.

Portland cement includes four major minerals which are formed during the clinkering process. These are identified as: tricalcium silicate (C_3S), which exists in clinker in the impure form – alite; dicalcium silicate (C_2S); tricalcium aluminate (C_3A); and the ferrite phase which exists as a compound close in composition to tetracalcium aluminoferrite (C_4AF).

In addition, some minor constituents will be present in relatively small amounts eg gypsum, alkali oxides and magnesia. Further details of these constituents are given in the **Appendix**. The properties of the four major compounds (phases) are summarised in **Table 3**^{4, 5}.

Table 2 Approximate oxide composition of portland cement

Oxide	Composition (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
Gypsum (expressed as SO_3)	1–3

Table 3 Properties of the major constituents of clinker

Mineral (phase)	Characteristics	Potential heat of hydration* (J/g)
C_3S	Light in colour. Hardens quickly with evolution of heat. Gives early strength.	500
C_2S	Light in colour. Hardens slowly. Gives late 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

* *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.*

The percentages of the hypothetical pure compounds in a portland cement without mineral addition can be calculated from the oxide analyses of a cement using the Bogue formulae in AS 2350.²² These formulae employ certain simplifying assumptions. Despite the fact that the actual compound composition might differ from the hypothetical calculation, these formulae have proven to be of great value to cement producers and users as an aid to understanding the performance of cements.

The Bogue formulae cannot be used for cements containing mineral additions. The hypothetical

composition of cement with mineral addition could theoretically be calculated from the cement oxide analysis by correcting for the oxide contribution from the mineral addition. However, in practice the exact composition of the mineral addition in the sample of cement would not be known and so it is not possible to properly calculate the Bogue composition of such cements.

5.2 Blended Cements – General

As noted earlier, blended cements contain, in addition to portland cement, either slag, fly ash, silica fume or a combination of these. These materials are referred to as supplementary cementitious materials and are covered by AS 3582³.

Slag is a non-metallic product, consisting essentially of silicates and aluminates, which is produced simultaneously with iron in a blast furnace and which is then granulated by rapid quenching. Finely ground granulated slag possesses the property of latent hydraulicity, ie it does not set when mixed with water alone, or does so only slowly, but will behave as an hydraulic cement in the presence of activators. Portland cement is an effective activator as it releases sufficient calcium hydroxide during hydration to activate the slag and enable it to form hydration products similar to those produced by portland cement.

Slag may be blended with portland cement to form a blended cement or it may be added to the ingredients of a concrete batch as a replacement for cement.

Pozzolans are defined as siliceous, or siliceous and aluminous, materials which in themselves possess little or no cementitious value but which will, in finely divided form and in the presence of moisture, react chemically with calcium hydroxide to form compounds possessing cementitious properties.

Pozzolanic materials include natural pozzolans, some fly ashes and silica fume (microsilica). Natural pozzolans occur as siliceous, or as siliceous and aluminous rocks or minerals such as volcanic ashes and diatomaceous earths. They are not common in Australia.

Fly ash is finely-divided residue from the combustion of pulverised coal in power stations. It is removed from the flue gases by electrostatic precipitators. It consists mainly of aluminosilicate glassy material with inclusions of small amounts of sodium, potassium, calcium, magnesium, titanium and iron. Fly ash is used as a component of blended cement or as a separate material added to the concrete batch.

Silica fume is a by-product from the production of elemental silicon and ferro-silicon alloys. Although sometimes referred to as silica dust, silica

powder, silica flour or microsilica, the name most commonly used in Australia is silica fume.

It consists of extremely fine spherical particles of amorphous silicon dioxide and possesses an exceedingly high specific surface area which gives it an active pozzolanic characteristic.

Silica fume is used as a component of blended cement or as a separate material added to the concrete batch. The high surface area of silica fume can increase the water demand of the concrete mix and to optimise the benefits of silica fume, high range water reducers (superplasticisers) are used to maintain mixing water requirements at an acceptable level.

5.3 Setting Time

When mixed with water, portland 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 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 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 which determine 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 portland and blended cements is specified in AS 3972 Table 1.

Final set for cement is the point at which the paste may be regarded as a rigid solid and at which 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 therefore specified in AS 3972 Table 1.

The initial and final setting times are determined by the Vicat needle apparatus, details of which are given in AS 2350.⁴²

The setting times for cement paste are not, however, those which are applicable to concrete. The latter 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.

The setting times as measured in the laboratory on either paste or concrete specimens should not be confused with the concept of 'finishing time'. Finishing time is the time at which placed concrete is ready to be floated. At this stage the bleed water has disappeared and the concrete is firm enough to take the weight of an operator.

5.4 Heat of Hydration/Temperature Rise

The heat of hydration of cement is the heat liberated as the cement and water react. The amount and rate of heat liberation depends on the type of cement, water-cement ratio and the 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 with water and then subsides appreciably.

Liberation of heat during the hydration of the cement results in rise in temperature. Temperature-rise/age relationship of various cements is shown in **Figure 3**. In most concrete construction, heat is dissipated from the concrete and large rises in temperature do not occur. However, in structures such as massive foundations, dams, and thick structural elements the differential temperature, between the core and the outside surface, in the large concrete sections may lead to cracking. Thus, limiting the temperature rise in concrete is important to avoid thermal cracking. Cements of low heat characteristics are produced for use in these 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, eg Langavant method.

AS 3972 specifies/characterises low heat cement by the peak temperature rise, **Table 1**, measured on a standard cement mortar under semi-adiabatic conditions. **Figure 3** shows typical temperature-rise/age curves for various types of cement.

Peak temperature rise is determined in accordance with AS 2350.7². This test method is based on a French test known as the Langavant method, but modified to put the emphasis on measurement of temperature rise allowing, as an option, the calculation of heat of hydration, if required.

5.5 Strength Development

On addition of water, the cement constituents hydrate, giving mainly hydrates of calcium silicate and calcium aluminate, and calcium hydroxide. The hydration involves an increase in the volume of solids, bringing about stiffening of the cement paste (setting). Further hydration decreases the porosity of the set paste, thereby increasing its strength. The gain in strength of the set paste (strength

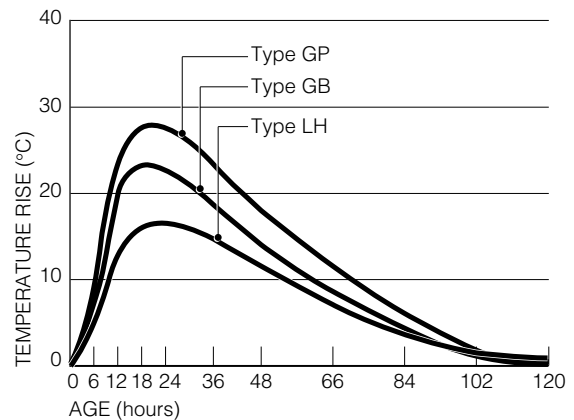


Figure 3: Typical temperature rise with age of cement mortars – semi adiabatic calorimeter (AS 2350.7)

development) is at its maximum rate at early ages, and gradually decreases with time **Figure 4**. Ultimate compressive strength may take several years to achieve, but for practical purposes 28-day strengths are used as indicators for the 'final' strength of most cements and are specified in cement Standards all over the world.

The rate of strength development of portland cement 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, ie the type and properties of portland cement, and the properties of the fly ash, slag and silica fume. As mentioned earlier, fly ash and slag blended cements gain strength more slowly than portland cements at early ages, but they exhibit more strength gain over a longer period, particularly if moisture is available for a sufficient time. On that basis, the ultimate strength of blended cements can be higher than that of the portland cement it incorporates **Figure 1**.

The compressive strength of portland and blended cements is determined by crushing tests on prisms made from the standard mortar (1:3 cement-sand mixture of 0.5 water-cement ratio). The specimens are made in accordance with AS 2350.12² and the test is conducted in accordance with AS 2350.11².

5.6 Shrinkage

Variations in moisture content of the cement paste are accompanied by volume changes. Drying causes volume decrease, ie drying shrinkage or simply shrinkage, while wetting causes volume increase, ie swelling or expansion. A schematic description of volume changes in cement paste due to alternate cycles of drying and wetting is given in **Figure 5**. 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; ie part of the volume decrease is not recovered on subsequent

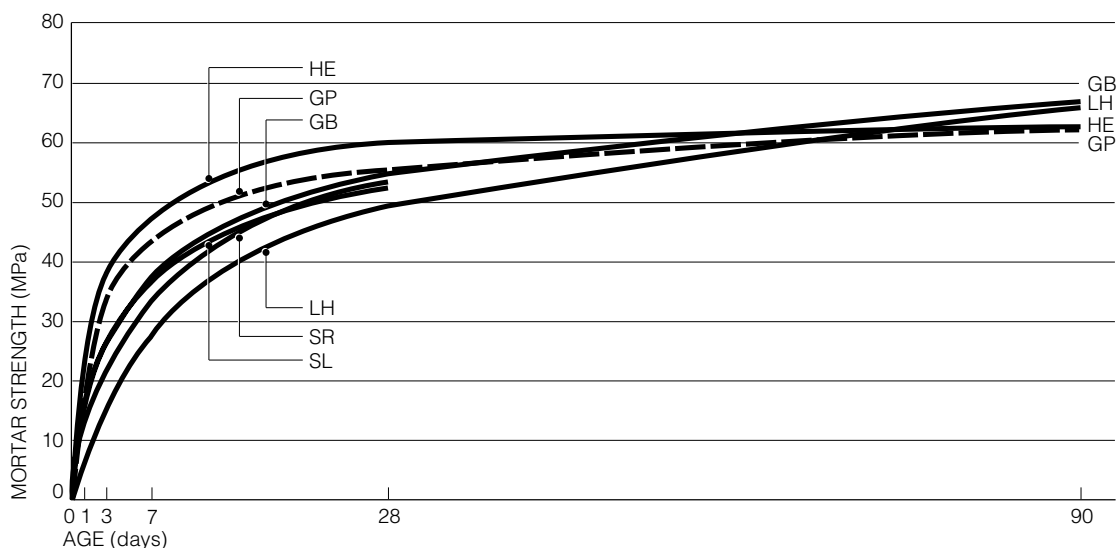


Figure 4: Typical cement mortar strength development with age (AS 2350.11)

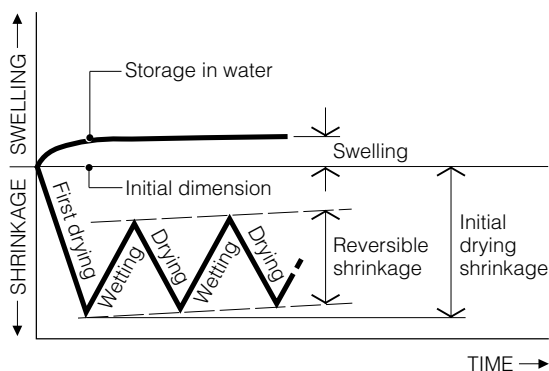


Figure 5: Schematic description of volume changes in cement paste due to alternate cycles of drying and wetting.

rewetting. On successive repetitions of dry/wet cycles the process becomes reversible, depending on the structure of the paste and on the relative duration of the wetting and drying periods. Since shrinkage is related to water loss it is affected by external factors that affect drying, such as temperature, humidity and air movement. Shrinkage is also affected by the properties of the cement.

Although it is generally concluded that the composition of cement can affect drying shrinkage, the effect is not completely determined. The C_3A and alkali content have been observed to have a dominant effect⁶. In turn, the effect of C_3A and alkali content on shrinkage is influenced by the gypsum content of the cement, ie shrinkage of cements of the same C_3A content differs for different gypsum contents⁷.

As a result, for many years, some major project specifications in Australia have specified the chemical composition of cement as a means of controlling shrinkage of concretes to be used in structures, such as road pavements and bridges. It was recognised, however, that there are other

cements outside these specifications which have performed well in low shrinkage concrete applications. This has led to the development of a cement characterised in terms of its shrinkage performance – Shrinkage Limited Cement, Type SL.

An upper limit for drying shrinkage at 28 days of the standard cement mortar is set in AS 3972 for Type SL cement Table 1. The maximum limit of 750 microstrain takes into account not only the performance of the cement but also the precision of the test method. The precision of the test method is such that the difference between two test results for 28-day drying shrinkage obtained in two different but experienced laboratories, under conditions of reproducibility, is expected to be up to 150 microstrain. So, for a cement to comply with the maximum limit of 750 microstrain, a typical average result should be around 600 microstrain. For more discussion on interpretation of precision data see Guirguis⁸.

It should be pointed out that the use of Type SL cement alone will not guarantee the production of low shrinkage concrete. Concrete shrinkage is greatly influenced by factors other than cement properties. The type and amount of aggregate, the water content, and the use of admixtures are some of the important factors. A detailed discussion of all the factors influencing concrete shrinkage can be found elsewhere⁹. These factors need to be considered as they may outweigh the effect of cement on the drying shrinkage of concrete.

5.7 Thermal Expansion

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

5.8 Resistance to Chemical Attack

5.8.1 General Hardened paste may be attacked by chemical or physical aggressive agents. The intensity of the attack depends on the specific properties of the agent, its intensity or concentration, the duration and the nature of the contact with the paste (ie continuous or periodic). Regardless of the nature of the aggressive agent, the resistance of the paste to attack is related not only to its composition but also to its permeability.

Permeability of the paste depends not only on the porosity but also on other properties of the pore system, such as continuity and pore size distribution. These properties are affected by the water-cement ratio and the degree of hydration which in turn is affected by the amount of curing given to the paste. **Figure 6** shows the effect of water-cement ratio on the permeability of well-cured cement paste after Powers¹⁰.

5.8.2 Acids The action of acids on the hardened cement is the conversion of the calcium compounds to the calcium salts of the acid. The solubility of the resulting calcium salt determines to a large degree the aggressive-ness of the acid attack. If the calcium salt is soluble, then it is readily removed by dissolution and leaching. As a result, the structure of the hardened cement is ultimately destroyed. Hydrochloric acid and nitric acid give calcium salts which are readily soluble. Acids which result in insoluble salts, such as oxalic and hydrofluoric acid, are not expected to cause any damage.

In general, damage due to acid attack may be expected if the pH of the acidic solution is less than 6.5. Pastes of low permeability, and pastes containing blended cements can withstand weak and dilute acids. Severe conditions may be dealt with only by isolating the acid from contact with the hardened cement.

5.8.3 Sulfates All soluble sulfates attack 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 attack the aluminates in the cement. The reaction, in the presence of moisture, causes expansion 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 silicates. Attack is progressive and the hardened cement can be reduced to a soft mass. A further discussion of various mechanisms of sulfate attack can be found elsewhere^{11, 12}.

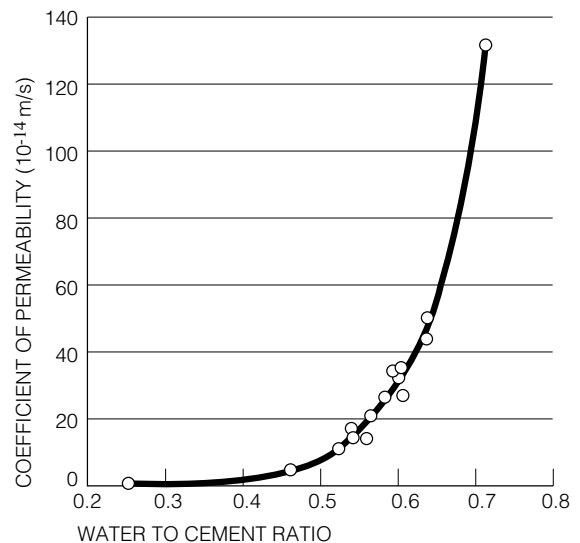


Figure 6: Effect of water-cement ratio on permeability of portland cement paste

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.

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. A detailed discussion of these factors is given by Idorn¹². Recommendations for concrete exposed to sulfates can be found elsewhere¹³⁻¹⁶.

5.8.4 Seawater The resistance of concrete to seawater is dependent mainly on its density and permeability and to a lesser degree on the particular type of cement involved.

Generally, seawater contains 3.6 to 4.0% salt by mass, of which chlorides make up 90% and sulfates the remaining 10%. The major influence of chlorides is to increase the risk of corrosion of reinforcing steel because, 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.

The role of the C_3A content of cement in resisting seawater corrosion is uncertain. Some researchers maintain that C_3A binds chloride ions and hence has a beneficial role in delaying the initiation of corrosion. Other researchers maintain that the chloride binding effects of C_3A are exaggerated and point out that the presence of sulfate ions reduces the chloride-binding capacity owing to the preferential formation of calcium sulfoaluminate hydrates with C_3A .

The pore structure (permeability) of the hardened cement matrix is an important factor in restricting the mobility of the chloride ions. Blended cements have been shown to have some advantages. The

dense pore structure which results reduces the mobility of the chloride ions, thus reducing the risk of high chloride concentration near the steel.

The sulfate concentration of seawater is equivalent to an SO_4 concentration greater than 2400 mg/litre. Such concentration of sulfates can cause appreciable damage to the hardened paste. However, experience has shown that damage of cement-products in seawater is much lower than would be expected from the SO_4 concentration in the water. This reduced aggressiveness of the sulfate in seawater has been attributed, in part, to the greater solubility of gypsum and ettringite (formed by reaction with sulfates) in the presence of chlorides⁵.

Hardened paste may also be damaged by crystallisation of salts inside its pores in areas subject to alternate wetting and drying. Hence, a dense impermeable paste suffers less deterioration.

5.9 Resistance to Freezing and Thawing

The formation of ice involves an increase of about 9% in the volume of the water frozen. In saturated, or nearly saturated cement pastes, such volume increases will produce internal pressures which, in turn, cause dilation and cracking of the paste. Repeated cycles of freezing and thawing therefore damage cement pastes (and hence mortars and concretes) by causing internal stresses which crack the paste and eventually cause it to disintegrate. 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 system.

In the case of concrete containing fly ash, the carbon content may be important in determining the use of air-entraining agents. Otherwise, the type of cement has no inherent effect on the resistance of cement paste to freezing and thawing. In other words, for the same strength and air content the cement type has no significant effect on the resistance to cycles of freezing and thawing.

5.10 Resistance to High Temperature

The effect of high temperatures on the hardened 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 bursting the matrix.

At temperatures between 300 and 600°C, 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. In such conditions, high-alumina cements combined with selected refractory aggregates should be used to produce a refractory concrete.

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APPENDIX Minor Constituents of Cement

Gypsum Gypsum is added during grinding of the clinker in order to prevent flash setting of the cement.

The retarding action of gypsum is due mainly to the formation of coatings of ettringite (calcium sulfoaluminate) on the surface of the aluminate (C_3A) in the cement. The gypsum content must therefore be limited as an excess may cause the formation of increased amounts of ettringite leading to cracking and deterioration in the set cement. Consequently, cement standards specify a maximum gypsum content expressed as maximum SO_3 content. AS 3972 limits SO_3 content of cements to 3.5%.

Gypsum also has an influence on the strength and drying shrinkage properties of cement. A cement manufacturer optimises the percentage of gypsum to ensure the best combination of these properties to meet the needs of the market.

Free Lime (CaO) The presence of free (uncombined) lime in the 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 with the oxides is not completed during the clinkering process. When the amount of free lime exceeds certain limits, depending on the fineness of the cement, the cement shows unsoundness. The mechanism is as follows: the free lime is intercrystallised with other minerals and is therefore not readily accessible to water. It hydrates after the cement has set and because the hydration product occupies a larger volume than the free lime it may cause expansion. This consequence is termed 'unsoundness'.

It is evident that free lime in the cement should be limited. It is, however, difficult to specify a quantitative limit because its adverse effect depends on many factors. Consequently, cement standards do not specify a maximum free lime content but rather specify tests to be passed to consider a cement to be sound. The relevant test prescribed in AS 2350.5² is the Le Chatelier test. This test method is an accelerated test involving boiling a small cylinder of neat cement paste and measuring its expansion.

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 exists in cement as periclase, a material which can exhibit long-term expansion. Hence, most cement specifications have placed a limit on the amount of MgO. AS 3972 limits the magnesia content of clinker to 4.5%.

Alkali Oxides (K_2O , Na_2O) The alkali oxides, potash and soda, are introduced into cement through the raw materials. The total content of potash and soda in cement is small **Table 2**. A reaction may occur between these alkalies and some types of aggregates which contain reactive silica. This reaction involves expansion which may cause cracking and disruption of the concrete. Although the reaction will always occur in the presence of reactive silica, harm to the concrete may be avoided where the amount of alkali in the concrete is low. Thus, some specifications limit the amount of alkali in the cement to 0.6%, expressed as equivalent Na_2O ($Na_2O + 0.658 K_2O$). This approach is not adopted in Australia¹⁷, particularly as it is by no means fail-safe. In the presence of potentially reactive aggregate, a number of measures could be taken to minimise the risk of damage which are discussed in detail in the guidelines on AAR¹⁷.

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 sample to 900–1000°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.

No limit is specified in AS 3972 for loss on ignition but is reported if required.

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