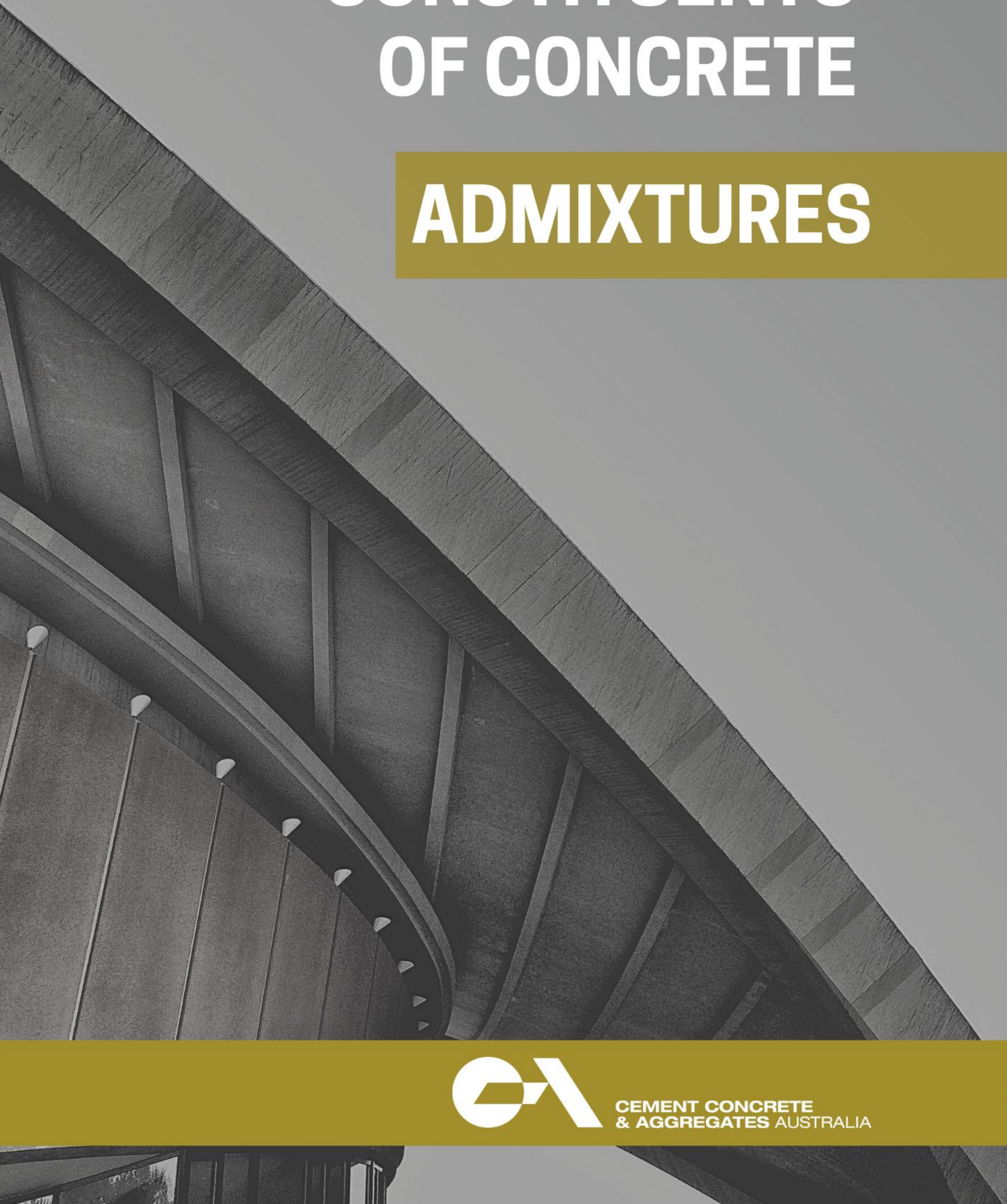
PART II. CONSTITUENTS OF CONCRETE

ADMIXTURES



CEMENT CONCRETE
& AGGREGATES AUSTRALIA

This section provides general information on admixtures used to modify the properties of concrete – in both the plastic and hardened states. Comment is included on their purpose and effects, including the influence of the other constituents of the concrete. In addition, it provides some general guidance on the use of admixtures.

CONTENTS

1 INTRODUCTION

Many materials have been used over the centuries to modify the properties of ancient and modern binders and concrete mixes. The Roman's use of blood as an admixture was an early (and effective) means of producing air entrainment. The Romans also used lard and milk for this purpose.

The increased use of modern chemical admixtures was closely aligned with the growth in ready mixed concrete production that occurred in the middle of the 20th Century.

While early admixture use was primarily in the USA, Australia was quick to realise the advantages offered to the construction industry, and by about 1970 the prevalence of admixture use in Australia was probably the highest in the world. Britain and Europe were somewhat slower to adopt this approach and ultimate acceptance was probably linked to Australian involvement in promoting the use of ready-mixed concrete as an alternative to site-mixed concrete.

The introduction of modern dispensing equipment provided a major advance in gaining consistent concrete properties when using chemical admixtures.

Until the mid-1960's, the only recognised standard for the use of chemical admixtures was that issued by the ASTM. Work on an Australian Standard commenced around 1965 with the first Australian Standard being published in 1969.

The Australian Standard (AS 1478.1) defines an admixture as *'a material, other than water, aggregate and cementitious materials, used as an ingredient of concrete, and added to the batch in controlled amounts immediately before or during its mixing to produce some desired modification to the properties of the concrete'.*

In general terms, concrete admixture use involves using relatively small quantities of (powerful) chemicals which must be used in controlled doses. Their actions can be quite complex, and one admixture may impact on the performance of another in a concrete mix. It is always advisable to (a) check history of using particular admixture combinations, or (b) test the proposed combination in a trial mix before embarking on concrete production on a large scale. Admixture suppliers are generally able to provide historical usage information.

Some admixtures have a specific role and only affect one property (e.g. water reduction) but many admixtures affect more than one property of the concrete. Most work with the other materials in the concrete, including the cement and SCM's, to determine their ultimate effect. Their effectiveness is usually temperature dependent, generally improving with increasing temperature and slowing down as temperatures fall. This potential for multiple effects emphasises the need to carry out trial mixing with all concrete mix components to fully assess admixture effectiveness.

2 TYPES OF ADMIXTURES

2.1 CLASSIFICATIONS AND MECHANISMS

Chemical admixtures for concrete can be classified in general terms as General Use and Special Purpose Admixtures. The former group is used in most concrete, while the latter provide specific performance characteristics such as providing anti-washout, hydration control and corrosion inhibiting actions.

Table 5.1 describes the types of admixtures available for both General Use and Special Purpose applications, and the **Summary** table (pages 20-21) describes their application and general effects on concrete performance.

There are several mechanisms that are fundamental and form the basis of (most) admixture use:

- Dispersion of cement in the aqueous phase of concrete;
- Alteration of the rate of cement hydration – particularly of the C_3S mineral;
- Reaction with by-products from hydration e.g. alkalis and free lime;
- Pore filling.

Table 5.1 – Types of Admixtures

Air entraining	(Type AEA)
Set-controlling	Set-accelerating (Type Ac); Set-retarding (Type Re).
Water-reducing	Normal (Type WR); Medium-range water-reducing – Superplasticisers (Type MWR); High-range water-reducing – Superplasticisers (Type HWR).
Water-reducing/ set-controlling	Water-reducing/ set-accelerating (Type WRAc); Water-reducing/set-retarding (Type WRRe); High-range water-reducing/set-retarding – superplasticisers (Type HWRRe).
Thickening agents	‘Pumpability’ aids
Shrinkage-reducing/ shrinkage-compensating	
Permeability reducing	
Special purpose	Special purpose/normal setting (Type SN); Special purpose/accelerating (Type SAc); Special purpose/retarding (Type SRe).

2.2 AIR-ENTRAINING ADMIXTURES (AEA)

Air entrainment is different to air entrapment. Air will be entrapped in the plastic concrete during mixing; and should be removed by compaction during placing. It is uncontrolled – and can create large voids in the hardened concrete which is very detrimental to concrete performance. It is <u>critical</u> that this entrapped air be removed during the compaction of concrete.

Air entrainment is <u>purposefully entrained air</u> comprising very small-sized bubbles that are evenly distributed through the concrete paste and which remain (quite) stable during handling and compaction. These finely dispersed air bubbles have a minor impact on strength that can be compensated for in mix design. The air bubbles are spherical and may vary in size from 10 microns to 1 mm (**Figure 5.1**).

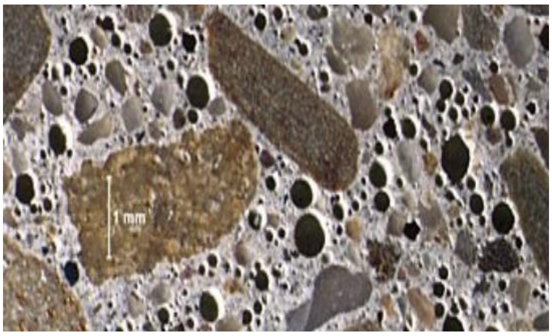


Figure 5.1 – Air Entrained in Concrete Paste

Air entrainment was developed primarily to improve the resistance of concrete to destructive cycles of freezing and thawing (**Figure 5.2**). Freeze-thaw protection is of major importance in any region where snow and ice are common weather features. It is therefore almost mandatory in much of the northern hemisphere.

Figure 5.2 – Pavement Damage due to Freeze Thaw Cycles

There are only a few regions in Australia where such protection is needed. These include any areas where there are repeatedly low overnight temperatures capable of causing freezing of the water in concrete.

The use of air entrainment has extended beyond its primary purpose and it is also used to enhance plastic performance in concrete mixes with (a) a low cementitious content, and (b) where workability of mixes is compromised by poor sand grading(s). Higher air contents will increase the cohesiveness of concrete mixes and can also lead to a reduction in bleed volume and rate.

Benefits of Air Entrainment

- Protection against freeze-thaw damage;
- Cohesiveness improved = less segregation;
- Control of bleed;
- Improved workability – enables a reduction in water content and therefore a decreased W/C ratio;
- Improved durability in cold climates.

Negative Aspects of Air Entrainment

Increasing air content reduces strength. This effect can be offset by changing mix proportions and is assisted by the reduction in the W/C ratio that may occur.

Regardless of the form it takes, a 1% increase in air content in the concrete can reduce the compressive strength by about 5%. In favourable conditions, the water reduction obtained from air entrainment can be sufficient to offset the strength loss.

AS 1478.1 indicates that the compressive strength of concrete with air entrainment should not be less than 90% of the compressive strength of the concrete without the admixture.

Air entrainment in Normal Class concrete not subject to freeze-thaw conditions is typically 2-4% but is increased to 5-6% for freeze-thaw conditions. The reduction in compressive strength and the durability benefit are shown in **Figure 5.3**.

Air entrainment at levels in the order of 5% is also used for low slump concretes (20-40 mm slump) that are supplied to paving machines for concrete road construction and for other slip-forming applications.

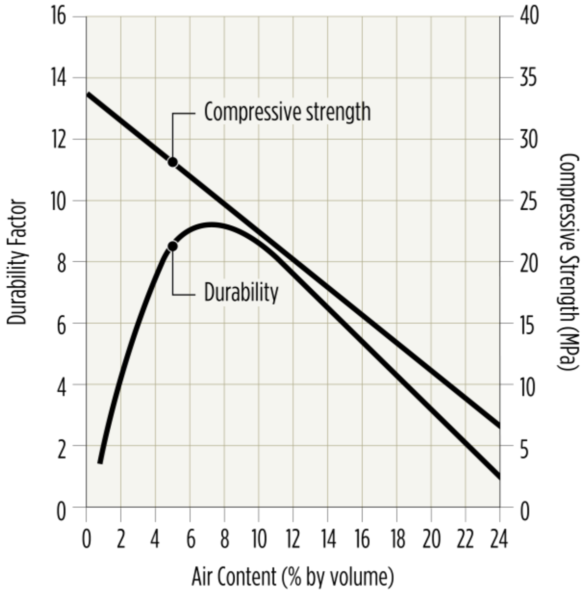


Figure 5.3 – Effect of Air Entrainment on Compressive Strength and Durability

Materials

Air-Entraining Agents (AEA's) are derivatives of:

- Salts of wood resins;
- Sulfated or sulfonated petroleum hydrocarbons;
- Salts of petroleum acids;
- Fatty and resinous acids and their salts.

Air-Entraining Action

Air entrainment creates a void system with a large number of minute air bubbles dispersed evenly through the concrete paste. The size and spacing of the bubbles are very important.

The air-entraining action is affected by:

- Type and concentration of admixture;
- Type and composition of cement:
  - – Increasing alkali increases air content but improves the stability of the entrained air;
  - – Increases in cement fineness tend to reduce the air content.
- Cement content:
  - – Effect is greater with lower cement contents.
- Use of SCM:
  - – May require higher dose for particular air content – particularly with some (high LOI) fly ashes.
- Mix proportions;
- Grading of fine aggregate – increase in fine sand may reduce air content:
  - – It may be possible to reduce sand by 1% for every 1% of air while water may be reduced from about 4% for rich mixes to about 15% for lower grade mixes.
- Type and condition of mixing equipment;
- Presence of other admixtures:
  - – Admixture interactions may increase air entrainment.
- Temperature of the concrete as mixed:
  - – Lower temperature permits more air entrainment.

2.3 SET CONTROLLING ADMIXTURES

'Set controlling' refers to those admixtures that either accelerate or retard the setting and hardening of concrete.

Accelerators (Type Ac)

Accelerators are used to reduce the setting time of a concrete mix and/or accelerate the strength gain of concrete. Some will do both tasks while others will predominantly perform one of the tasks. This is accomplished by accelerating the initial rate of the hydration reaction between the cement and the water.

In the plastic state, accelerators affect both the initial and final set of the concrete providing positive benefits relating to finishing time, particularly in colder weather. Total bleed may also be reduced due to the faster setting time.

In the hardened state accelerators may increase the strength at early ages but may reduce the long-term strength of concrete. Their use can also impact on drying shrinkage and creep and generally results in increases in both properties. Heat of hydration development will typically increase due to the accelerated hydration reaction.

History

Historically, calcium chloride was used as an accelerator as its use results in a significant reduction in setting time as well as increased early strength development.

However, due to its chloride content, calcium chloride has an adverse effect on the durability of the concrete through the promotion of corrosion of any embedded reinforcement. Calcium chloride may also have negative effects on concrete durability by enhancing the degree of attack where (a) the concrete is exposed to high levels of sulfates, and (b) where ASR is being experienced.

Non chloride-based accelerators are now available and are widely used. They have similar effects on setting time and strength development, but without increasing the risk of corrosion of embedded reinforcement.

Compounds which have been used as accelerators include calcium formate, calcium nitrate, calcium nitrite and thiocyanate salts.

AS 3600 *'Concrete structures'* and AS 1379 *'Specification and supply of concrete'* impose limits on total chlorides in concrete which effectively prohibits the use of calcium chloride in reinforced and prestressed concrete. Calcium chloride can be used in concrete that does not contain any embedded material (including reinforcing steel) that requires protection from corrosion.

Benefits of Accelerators

- Faster setting; and/or
- More rapid strength gain.

Negative Aspects of Accelerators

- Possible lower long-term strengths;
- Increased shrinkage and creep.

Materials

Accelerators can be derived from inorganic or organic materials.

Inorganic

- Sodium silicates;
- Aluminates;
- Calcium chloride;
- Calcium nitrate.

Organic

- Triethanolamine;
- Calcium formate.

The degree of set acceleration depends on:

- Type and concentration of accelerator;
- Temperature of concrete;
- Type of cement;
- Use of SCM;
- Cementitious content.

In specialised concrete applications like shotcrete, high performing accelerators are used to cause concrete to set almost immediately it makes contact with the substrate it is being placed on (typically the roof or walls of a mine shaft). These shotcrete mixes are often 'put to sleep' to maximise the plastic stage to allow transport of the concrete to the job site. When the plastic concrete is sprayed onto the mine roof or wall a highly effective accelerator is added to the concrete at the spray nozzle. The effectiveness of these accelerators is such that the concrete almost immediately sets upon contact with the substrate. Typical of these accelerators are silicate and aluminate compounds.

Retarders (Type Re)

Retarders are designed to slow down the rate of setting of concrete which can provide advantages in certain situations. Retardation is accomplished by slowing down the rate of reaction between the cement and the water in the first few hours. Retarders have minor impacts on strength development. Retarders are used as follows:

In hot weather:

- To ensure concrete remains placeable after long hauls;
- To provide adequate time for compaction and finishing.

In large pours:

- To maintain a live face for concrete placement in mass concrete and large pours to avoid the creation of cold joints.

Benefits of Using Retarders

- Slows down setting time;
- Negligible impact on strength after 1 day;
- Maintains workability in hot conditions.

Negative Aspects of Retarders

- Strengths up to 1 day may be reduced slightly;
- Additional time prior to concrete setting. (For highly workable mixes this may increase the risk of plastic settlement cracking. In high evaporation environments this may increase the risk of plastic shrinkage cracking.)

Materials Used

- Sugars and carbohydrates;
- Soluble borates and phosphates;
- Hydroxy-carboxylic acids.

Retarders operate by attaching themselves to the hydrating cement particles and slowing the rate of hydration and hence slowing the progress towards setting (**Figure 5.4**).

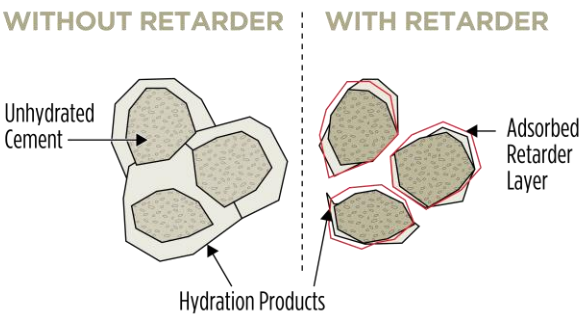


Figure 5.4 – Retarder Action on Hydrating Cement Particles

The degree of retardation is affected by:

- Type and concentration of admixture;
- Temperature of concrete;
- Chemical composition of cement:
  - Cement fineness, alkali content, C_3A and gypsum content all affect the reactivity;
  - Higher cement surface area requires greater dose for same effect;
  - Higher alkali and higher C_3A contents require greater dose for same effect.
- Cementitious content;
- SCM;
- Time of addition to mix:
  - Delaying addition until after water has been added to cement will give longer, more effective retardation.

2.4 WATER REDUCING ADMIXTURES

Water reducing admixtures are generally described as being either Normal Range, Mid-Range or High Range. As the names imply, these admixtures provide water reduction to various degrees, and without any detrimental effect on other concrete properties. The ability of certain chemicals to provide water reduction was first recognised in the early 1930's.

Normal-Range Water Reducers (Type WR)

Effects

Water reducers can be used in three main ways:

- To increase workability or slump without other changes and hence maintain the same strength;
- To maintain the workability (or slump) and cement content with less water and produce increased strength;
- To reduce the cement content and the water content whilst maintaining the workability, slump and strength, hence providing greater economy.

For most normal range water (Type WR) reducers, the level of water reduction is of the order of 4-10%.

Action of Water Reducers

These admixtures disperse cement particles that otherwise tend to clump together. This is achieved by applying the same electrical charge to all cement particle surfaces – which causes the particles to repel one another. Water trapped between the cement grains becomes available to the mix which improves the workability of the mix. As well as increasing the fluidity of the cement paste (and the concrete), it also provides a larger available cement surface area for hydration to occur (**Figure 5.5**).

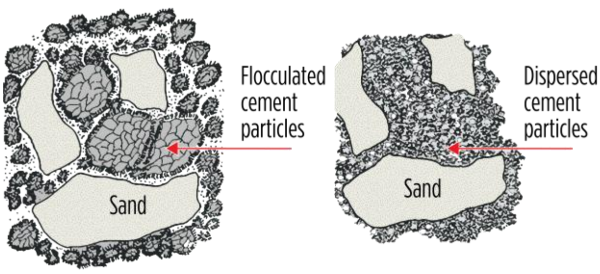


Figure 5.5 – (a) Flocculated Cement Particles and (b) Dispersed Cement Particles

Benefits of Using Water Reducers

- Same workability with less water;
- Better slump control;
- Improved pumpability;
- Greater cohesiveness;
- Reduced segregation;
- Reduced bleeding;
- Superior finishing;
- Higher ultimate strengths;
- Higher durability;
- Reduced permeability;
- Higher early strength.

Materials

Water reducers may contain a range of components including:

- Salts of ligno-sulfonic acids;
- Triethanolamine;
- Hydroxy-carboxylic acids;
- Biocides;
- Sugars – Polysaccharides – Carbohydrates.

Some of the water-reducing chemicals used may also have a natural retarding effect on the concrete and as a result Water Reducing Admixtures may contain a small amount of accelerator to offset any retardation. This effect enables a range of water reducing products to be produced – ranging from those with retarding capabilities; to those that are setting time-neutral; and through to those that have combined set accelerating and water reducing functions. This range of products is useful when changing from summer to winter conditions.

The degree of water reduction obtained is affected by:

- Type and concentration of admixture;
- Chemical composition of cement:
  - Water reduction is more noticeable in cements with lower alkali levels and lower C_3A;
  - Different cement brands or cement sourced from different manufacturing plants may be affected differently.
- Cementitious content;
- Temperature of concrete;
- Time of addition to the mix:
  - Delaying the addition until later in batching will increase the degree of water reduction.

The type of water reducer can be chosen to suit, amongst other things, the climatic or weather conditions.

Where set acceleration is required (in cold weather) then WRAc can be used.

Where set retardation is required (in hot weather) then WRRe can be used.

<u>Mid-Range Water Reducers (Type MWR)</u>

Mid-range water reducers act in the same way as Type WR water reducers but offer improved water reduction capability – in the order of 10-15%. Their similarity to the Type WR admixtures is such that no further elaboration is necessary.

<u>High Range Water Reducers (Type HWR and HWRRe)</u>

Major advances in concrete technology have been made following the development of high range water reducers. These admixtures are often called super-plasticisers and have exceptional water-reducing capability – usually between 15% and 25%. Their use has allowed concrete to be produced and used in a range of specialised applications including high strength concrete, high durability concrete and flowing (super-workable) concrete.

Benefits of Using High Range Water Reducers / Superplasticisers

- High level of water reduction;
- Superior workability;
- Improved concrete strength and durability;
- Very high workability for a short period.

The high water-reduction capabilities of super-plasticisers enables the production of concrete with very low water content – very close to the minimum required for hydration of cement.

Concrete meeting high strength/ high durability requirements, which cannot always be produced using normal ingredients, mixing, placing and curing practices, is generally referred to as High Performance Concrete (HPC).

The common denominator in all HPC is a low water/cementitious ratio (<0.35) from which follows high early strength, high durability, low shrinkage and long service life. However, these properties in the hardened state can only be achieved if the low W/C ratio concrete is fluid enough to allow proper placing and compaction, particularly in areas of congested reinforcement.

The use of super-plasticiser in high dosages in HPC mix designs can generate the twin characteristics of flowability and acceptable cohesiveness in the plastic state.

Super-plasticisers permit the production of ‘self-compacting’, ‘self-levelling’ or ‘flowing’ concrete (see Part VI, Section 22 of this Guide). These terms are prone to being misleading or misinterpreted and it may be inferred that these concretes ‘place themselves’. Care is still required in placing these concrete products. Australian literature suggests the term ‘Super-Workable Concrete’ (SWC) should be used for these products.

SWC can best be described as a fluid concrete with a ‘slump’ in excess of 250 mm that is able to slump or ‘flow’ without segregation. It may have the same W/C ratio as that of a low slump concrete, but it can be (almost) self-levelling and will require only minimal compaction (**Figure 5.6**).

(a)

(b)

Figure 5.6 – (a) SWC Flowing Out of Slump Cone and (b) ‘Slumped’ SWC Showing No Segregation

Very low W/C ratio concrete produces high durability performance if proper placing and compaction techniques are followed. The use of super-plasticisers enables lower W/C ratios which in turn give lower concrete permeability that inhibits the flow of fluids (liquids or gases) through the concrete and which consequently should provide concrete with high durability performance.

Action

Very high workability (‘slumps’ >250 mm) can be produced to enable easy placement due to the almost ‘flowing’ concrete consistency. With the older superplasticisers this property was only maintained for a short period after which the flow characteristic reversed allowing normal finishing procedures to be used.

Current versions of these admixtures provide extended working times at the very high workability levels (**Figure 5.7**). Mix designs require special attention to avoid segregation and bleed problems and greater control over batching and mixing and good supervision at the building site is necessary to ensure expected outcomes with these flowing concretes.

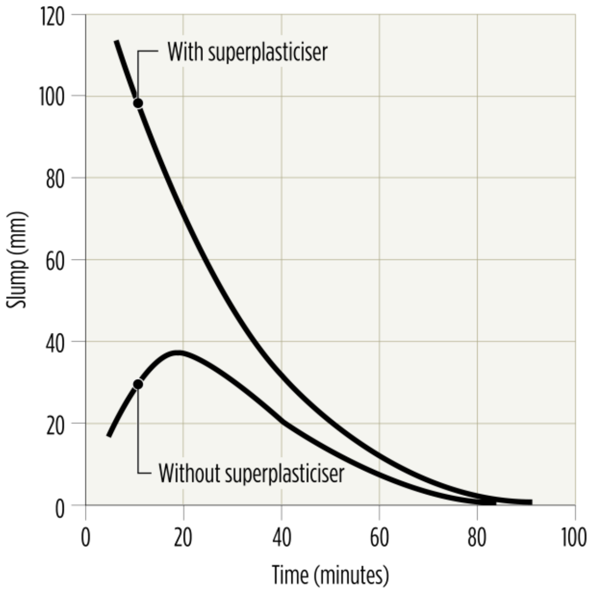


Figure 5.7 – Concrete Workability with and without Superplasticiser

Use of HWR

The admixtures are used in two main ways (**Figures 5.8** and **5.9**):

- To increase concrete workability greatly without changing other plastic properties;
- To increase the strength of concrete of a specified workability through large water reduction.

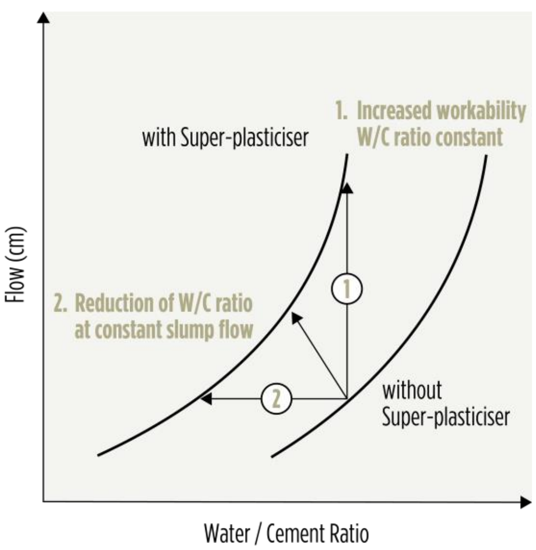


Figure 5.8 – Use of HWR to (1) Increase Workability or (2) Lower W/C Ratio (= Increased Strength)

There are many possibilities with these two types of applications that can be of benefit in concrete construction, including:

- Placing concrete in elements with congested reinforcing;
- Placing thin sections;
- Achieving high quality surface finishes;
- Increased pumping distances and heights;
- 'Flowing' concrete for large pours;
- Low noise situations – resulting from a reduced need for mechanical vibration.

When used specifically for SWC they are able to provide:

- Flow consistency;
- Low W/C ratio;
- High fines content;
- Good pumping;
- Segregation-free;
- Minimal bleed;
- Almost self-compacting and self-levelling.

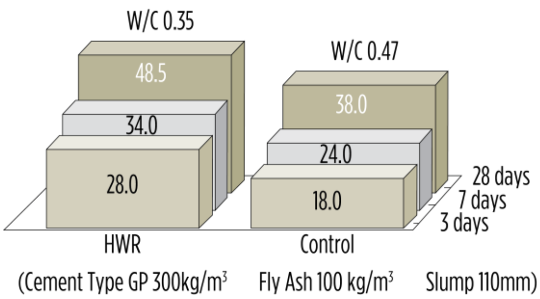


Figure 5.9 – Strength Improvement When Using HWR Through Reduced W/C Ratio

Superplasticisers used in high performance concrete are able to provide:

- Low W/C ratio to meet tough durability specifications;
- High workability;
- High early strength;
- High durability performance and long service life;
- Lower drying shrinkage in some circumstances.

While the very high workability concrete appears to self-compact, there may be a need for some compaction to achieve the required performance properties.

*(**NOTE:** Due to the very fluid nature of the concrete, the formwork will need to be sealed more tightly to prevent the flowing concrete flowing out of leakage points. Re-assessment of formwork pressures must also be made as the flowing concrete is not self-supporting and may require greater strengthening of the formwork (see Part IX, Section 27 of this Guide).)*

Materials

There are a range of materials used as High Range Water Reducers, including:

- Sulfonated Melamine (SMFC) or Sulfonated Napthalene (SNFC) Formaldehyde Condensates;
- Polycarboxylate polymers (PCE);
- Modified Lignosulfonates;
- Hydroxylated polymers.

The first two are the most common in use. They should not be used together as such a combination can result in severe slump loss. The SMFC and SNFC products were first introduced into the Australian market in about 1974.

The Polycarboxylates (PCE's) offer the newest technology and have tended to displace the sulphonated naphthalene and melamine formaldehyde condensates. The PCE's provide earlier action and work primarily by the action of steric hindrance in which the PCE attaches to cement particles and effectively pushes them apart. There is a wide variety of PCE admixtures possible, and they may be 'tailored' to achieve specific results. PCE's have a tendency to entrain air in concrete and always contain a de-foamer to reduce this tendency. It has been found that in some circumstances, the PCE admixture tanks must be continuously stirred to ensure that the de-foamer remains active. If the concrete materials contain any significant amounts of clay, PCE's can be adsorbed resulting in reduced efficiency. While PCE's can be used in virtually all concretes, they have been found to be particularly effective in low W/C ratio mixes.

The efficiency and effectiveness of the super-plasticisers depends on:

- Type and dose rate of super-plasticiser (**Figure 5.10**);
- Temperature of concrete;
- Composition of cement – *they perform better with higher alkali cements*;
- Cementitious content;
- Time of addition (though less so for PCE's);
- Presence of other admixtures;
- SCM's – very effective at dispersing SCM's (e.g. silica fume with a high surface area of about 20,000 m^2/kg must be fully dispersed to achieve maximum efficiency);
- Mix design.

HWR additions may be made at the batch plant for those with longer action times, while on-site addition may be necessary for others.

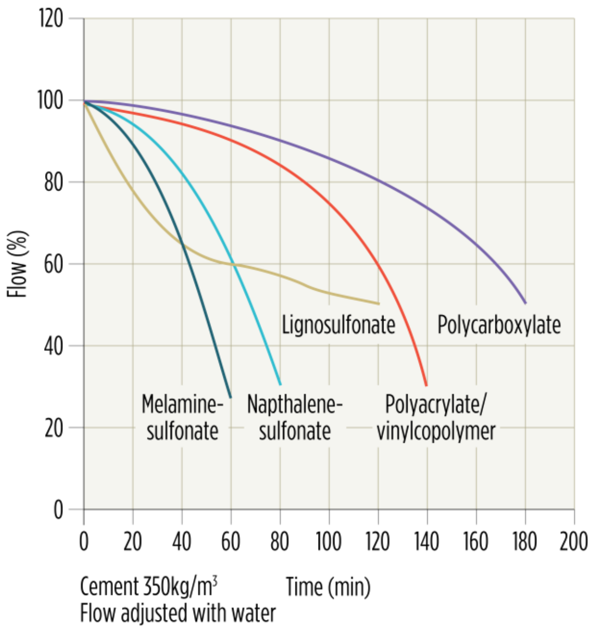


Figure 5.10 – Comparative Effectiveness of HWR Types

Testing Super-Plasticisers in Concrete

AS 1478.1 provides guidance on acceptability testing for all the chemical admixtures. The main test methods are listed in AS 1478.2.

Concrete Testing

Ideally, concrete trial mixes should use the cement, aggregate and other materials proposed for a project. Admixtures used must be added in the same dose and at same time in trial work as is proposed in practice.

Information provided with the trial mix test results must include the following test data for the cement:

- Name, type and source;
- SO_3 content;
- Type and quantity of mineral additions;
- Fineness;
- Sodium Oxide and Potassium oxide (i.e. alkali components).

Other Properties

Drying Shrinkage
High range water-reducing admixtures are expected to cause little or no increase in drying shrinkage. The reductions in total water and cement contents of concrete resulting from the use of these admixtures would be expected to lower drying shrinkage. **Figure 5.11** shows concrete samples with an initial slump of 45 mm and treated at different dose rates of super-plasticiser. All show minimal effect on drying shrinkage when compared to the Control sample.

DRYING SHRINKAGE (microstrain)

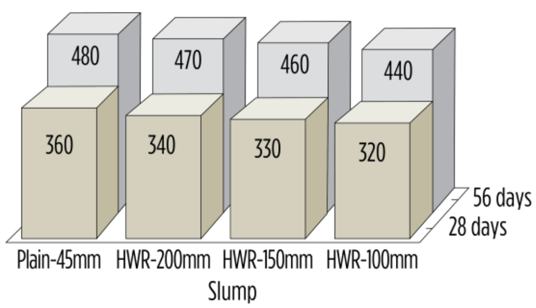


Figure 5.11 – Concrete Drying Shrinkage Minimally Affected by HWR Use

Slump Retention

Slump retention has been a major concern with super-plasticised concrete. With mixes designed as SWC or for high flow/spread, any significant loss of 'slump' can impact the intended application of the concrete. While when initially introduced PCE's did experience difficulties with slump loss, this property has been much better managed with newer versions of these products. Some PCE's now feature a 'time-release' function that provides slump control over (relatively) long periods. This outcome can be achieved in several ways, including by using blends of two or more PCE's to achieve the required properties at different times.

Super-plasticisers have been manufactured for hot weather applications with an in-built retarder to help provide slump retention. **Figure 5.12** shows the level of slump change of high range water reducers with and without retarders relative to a 'plain' concrete control.

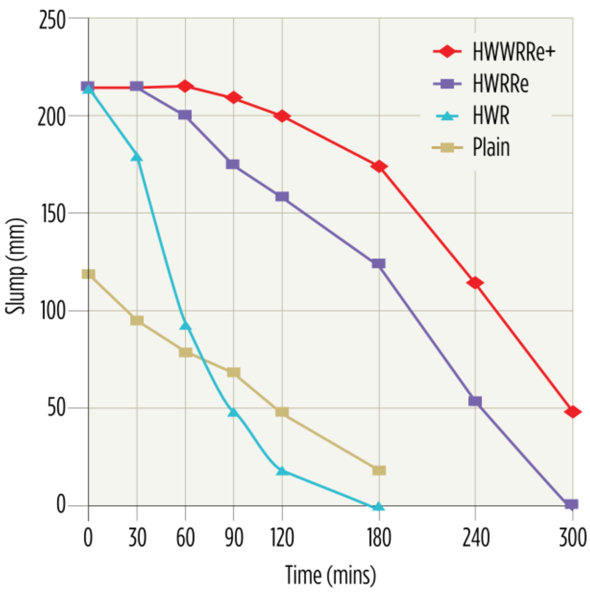


Figure 5.12 – Slump Retention When Using Several HWR Products

2.5 OTHER ADMIXTURES

There are a variety of highly specialised admixtures used in concrete projects. These admixtures are used much less frequently than the conventional admixtures previously described but are important in that they (a) increase the range of applicability of concrete as a construction material, and (b) improve concrete performance in (often) extreme conditions.

Shrinkage Reducing / Compensating Admixtures

Reducing the drying shrinkage of concrete has been an elusive goal for years and admixtures have now been developed to assist in achieving this.

Some shrinkage compensating admixtures make use of an expansion mechanism within the cement paste to counter any shrinkage that occurs. There are several methods of achieving this outcome including (a) rapid oxidation of iron particles deliberately added to the mix, and (b) hydrogen gas generated from fine aluminium powder particles (aluminium reacts with lime to produce hydrogen gas). These techniques have been mainly used in grouting applications.

More recent developments in Shrinkage Reducing Admixtures (SRA's) for concrete have included the use of ethylene and propylene glycol derivatives that act on fine capillaries in the concrete, reducing surface tension within the pore solution which helps prevent the collapse of capillary walls which leads to reduced shrinkage and cracking (**Figure 5.13**). These SRA's also affect air entrainment and compressive strength performance. Compressive strengths can be reduced by 10-15% by using these SRA's and mix designs need to be amended to compensate for this effect.

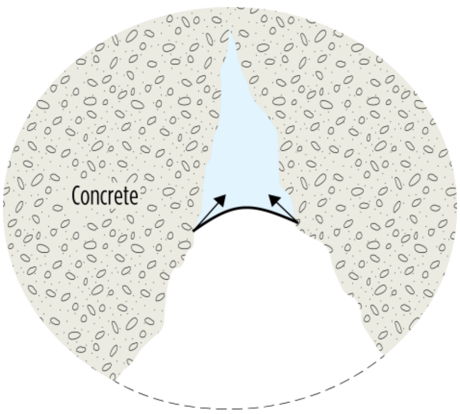


Figure 5.13 – SRA's act by Reducing Surface Tension of the Menisci in the Capillary Pore System

SRA Effectiveness is impacted by:

- Cement content – High cement contents result in greater expansion;
- SCM type and proportion;
- Aggregate type and grading;
- Curing method – Water curing gives greater expansion;
- Mix temperature – Higher temperatures reduce expansion;
- Interaction with other admixtures:
  - Using SRA's and AEA's may cause excessive air entrainment;
  - Accelerators offset some of the benefits as they may increase shrinkage.
- Combinations with other admixtures:
  - Super-plasticisers plus accelerator give greater expansion;
  - Retarders give greater expansion.
- High levels of reinforcement restrain expansion.

Corrosion Inhibitors

In certain environments, concrete requires high durability performance to withstand the intrusion of chloride ions which may corrode embedded reinforcing steel. Structures such as wharves and other buildings in marine environments, including bridges, are particularly at risk. The factors needed for corrosion to be propagated are:

- Moisture;
- Oxygen;
- Electrochemical reaction (creation of a galvanic cell).

Chlorides can initiate and accelerate the corrosion process. High quality concrete and good concreting practices are needed to ensure high durability and these fundamentals should be met before considering corrosion inhibitors as an adjunct protective measure. It is imperative that concrete placed in or adjacent to a marine (or other chloride-rich) environment has very low permeability to slow down chloride ion penetration.

Steel embedded in concrete is naturally 'passivated' because of the pH of the concrete paste. ('Passivation' means the creation of a thin, stable iron oxide layer that prevents steel from corroding.)

Corrosion occurs when electrochemical (galvanic) cells are created on the surface of the embedded steel when the protective passivating layer has been disrupted. Loss of passivation can occur if the pH of the concrete paste is reduced significantly (to about a pH of 10), or if the layer is breached or disrupted by some ions, including chloride ions.

During corrosion, steel is consumed at the anode of the cell(s) and 'rust' is created at the cathode. The 'rust' occupies a much larger volume than the original steel and the pressure from this greater volume of material creates tensile stresses in the concrete, leading to cracking. Once cracking occurs, the corrosion reaction can be accelerated by intrusion of greater quantities of aggressive agents through the cracks.

Some corrosion inhibitors promote and reinforce the passivating layer that naturally forms on steel in its alkaline environment, while others act as a surface coating to limit the cathodic reaction. Some of these corrosion inhibitors may also chemically 'fix' the chloride ions to prevent them from reaching the steel in the first place.

Materials
Corrosion-inhibiting admixtures are usually in liquid form and added to the concrete at the batching stage, though some are applied as surface coatings.

Types
Corrosion inhibitor types are described in terms of their mode of action, namely:

- Anodic;
- Cathodic;
- Mixed.

Anodic inhibitors enhance steel passivation and help prevent the anodic reaction. Cathodic inhibitors coat the steel surface to prevent the cathodic reaction occurring. Mixed inhibitors contain compounds that act on both anodic and cathodic sites on embedded steel.

Inhibitors may be inorganic materials, organic materials or combinations of both. Typical compounds used are:

Anodic Inhibitors – Nitrates, Nitrites, Chromates, Phosphates, Tungstates and Molybdates.

Anodic Inhibitors may be oxidising agents or non-oxidising agents and act by strengthening the passivating oxide layer on the surface of the steel reinforcement – a layer that can otherwise be broken down by the action of chloride ions. These agents may also alter the electrical potential at the steel surface to decrease the corrosion rate. The oxidising agents (chromates, nitrites etc.) act directly on the steel, while the non-oxidising agents (phosphates etc.) require the presence of oxygen to passivate the steel. Calcium nitrite is a well-tried inhibitor and considerable history of its use exists. Calcium nitrate can also be used though it tends to have reasonably significant impacts on plastic concrete properties. If the levels of these oxidising inhibitors drop below a critical limit, this can initiate pitting corrosion.

Cathodic Inhibitors – Zinc and Magnesium salts, Phosphates and Silicates

Cathodic inhibitors act by coating the surface of the steel – usually by precipitation of insoluble compounds on the steel surface – and when working properly, form a barrier film that prevents cathodic reactions from occurring. These agents are not as effective as anodic inhibitors but will not initiate pitting attack.

Mixed (Organic) Inhibitors – Amines and Amino-Alcohols

These chemicals inhibit both anodic and cathodic reactions and do so by forming adsorbed, hydrophobic coatings on the steel surface.

The various inhibitor types are generally added to the concrete mix at the time of batching. As they are required in quite large quantities (20 litres per cubic metre is common) they can have some impacts on workability and setting time.

Some of these inhibitors (particularly Cathodic and Mixed types) can also be applied to the surface of the concrete from where they gradually penetrate into the concrete until they reach the surface of the reinforcing steel.

Hydration Control Admixtures (Type HCA)
Hydration control admixtures are designed to control the rate of hydration of the cement. They differ from retarding admixtures in that they also affect the C_3A hydration.

Components
HCA systems have two components:

- A stabiliser which allows freshly batched concrete to remain plastic for extended periods of time;

- An activator which restarts the hydration process when desired.

The stabiliser suspends the hydration reaction through being readily adsorbed onto the cement particles and interacting with the cement hydration products, effectively suspending hydration. It can deactivate the concrete for hours or even days.

The activator is then used to reactivate the cement hydration reaction so that the concrete can be handled and finished in the normal manner.

The products are very useful for long hauls and where delays occur, and their use results in little adverse effect on the plastic or hardened properties of the placed concrete. If the activator is used to accelerate setting time, then some small strength loss may occur, and mix designs may require alterations to offset this effect.

HCA systems are used extensively in shotcrete applications (**Figure 5.14**) particularly in mining projects where batching operations, shift work, equipment breakdowns are all important economic considerations for concrete (and mine) production. HCA systems allow shotcrete to be 'put to sleep' from 3-72 hours depending on dosage and to be 're-awakened' at any stage.

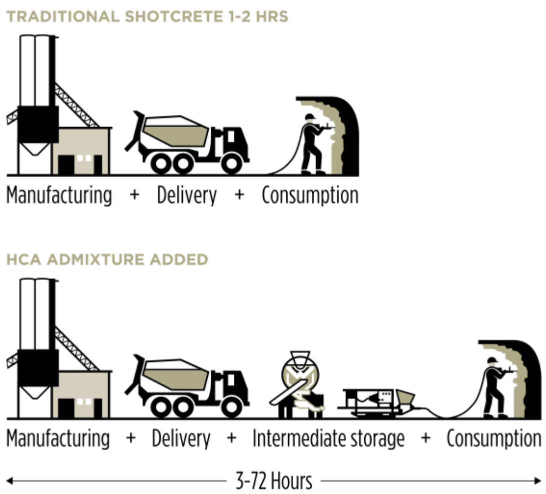


Figure 5.14 – HCA Used to Extend Working Time

Once activated by dosing the activator at the nozzle prior to spraying onto the vertical surface, the shotcrete begins setting by the time it hits the surface and may achieve initial set in about one minute and final set in 6-8 minutes.

The liquid activator admixture is provided through a separate injector at the nozzle and mixes in with the concrete materials in the sprayed concrete stream.

In addition to providing rapid set times the admixture also increases the cohesiveness of the concrete and permits thicker layers to be sprayed with minimal rebound and slumping.

Through using these admixtures, strength development at early ages is improved, and comparable 28-day strengths are also obtained.

Anti-Washout Admixtures (Type AWA)

Anti washout admixtures are used for placing concrete underwater – a situation where part of the cement paste is normally washed away during the placing process. These admixtures reduce the quantity of the paste that is lost and also create a flowing concrete product. Their use can result in lower concrete compressive strengths.

The concrete produced with AWA is very cohesive and has a high flow characteristic. The admixture enables the concrete to resist segregation and sagging but enables it to be readily pumped – albeit with higher pump pressures.

These products are sometimes referred to as Viscosity Enhancing Admixtures.

Materials

The admixtures generally contain polymers, flocculants, organic emulsions and fine inorganic materials. They may be made from cellulose, synthetic polymers and organic gums such as Whelan, Guar and Eanthate gum.

Benefits

- Greater cohesiveness;
- Less segregation;
- Minimal bleed;
- Extended setting times.

Negative Aspects of AWA Use

- Some reduction in compressive strength.

Their effectiveness is affected by:

- Cement content;
- Concrete temperature:
  - High temperatures give slump loss and the mix requires retardation.
- Fine aggregate:
  - If it is too fine, it may impair workability.
- Other admixtures:
  - Not used with retarders;
  - Not used with water reducer-retarders;
  - May result in excessive air entrainment.

Permeability Reducing Admixtures (PRA's)

These materials are designed to decrease the permeability of concrete. They are sometimes loosely termed damp-proofers or water-proofers. Names such as these are misleading, and most products simply slow down the rate at which moisture penetrates the concrete by absorption or diffusion rather than stopping its movement entirely.

There is a wide variety of materials on the market and individual assessments are required for each material and each project. These admixtures reduce the migration and diffusion of moisture through the capillary pores of concrete using either a pore blocking or hydrophobic layer process.

Pore Blockers

SCM's and other high fineness materials can act as pore blockers.

Some permeability-reducing admixtures form crystalline, fibrous structures by reacting with products (typically lime) from the cement hydration reaction and these fibres/crystals form in the pores in the paste and block moisture movement.

Hydrophobic Agents

These agents coat the inside of capillary pores and effectively push water out of the pores. The hydrophobic agents are typically compounds based on stearic acid and other fatty acids or are derived from vegetable and animal fats and waxes.

Benefits

While PRA's will slow the rate of moisture movement in the concrete, they may also have other effects that need to be assessed using trial mixes. Impacts on strength and strength variability should always be checked prior to using these materials.

It is important to note that PRA's will not overcome issues due to poor quality concrete, poor concrete placing processes or design flaws. Voids from poor compaction, plastic shrinkage cracking or other cracks and lack of curing are all factors that facilitate water movement and create conditions that cannot be overcome simply by using PRA's.

Internal Curing Admixtures

Internal curing admixtures are intended to assist with the hydration of concrete in a manner similar to that of a curing compound – that is, by retaining water from within the concrete that might otherwise be lost by evaporation. It is claimed that they provide similar benefits to a good curing compound.

The admixtures are typically water-soluble polymers that reduce the rate of evaporation of water from the concrete by 'binding' the water through the formation of hydrogen bonds between the water and polymer molecules.

NOTE*: Another version of internal curing comes from the use of pre-moistened lightweight porous aggregate in concrete manufacture. These aggregates release water slowly into the hardened concrete and provide additional water for hydration as the concrete ages.*

Anti-Freeze Admixtures

These are not in great demand in Australia but are essential in areas where concreting must occur at temperatures at or below zero degrees Celsius.

They are intended to ensure the concrete will not freeze while in the plastic state and do this by depressing the freezing point of the mix water.

They may contain water reducing agents and/or accelerating agents and generally very good concrete strengths can be obtained when these admixtures are being used.

Foaming Admixtures

Foamed concrete may be used where lightweight materials are required or where concrete is required to have acoustic or thermal insulation characteristics.

The admixtures are supplied in powder, liquid or a stable foam form and can be designed to promote stable air contents at levels as high as 15-30%.

Other uses for foamed concrete include cavity filling of disused tunnels, tanks and mines and the encasement of in-ground pipelines with low strength fill.

3 GUIDANCE ON THE USE OF ADMIXTURES

Admixtures are not considered to be a substitute for good concrete materials, correct mix design and good concreting practice. However, they can offer more economical ways of adapting concrete than using continual changes in mix designs and can offer performance not possible using basic concrete technology.

It is important to recognise that reactions between admixtures, and with different types of cement, can change the effectiveness of a given admixture.

Incompatibility

There are two areas requiring caution, namely:

- Admixture – admixture interaction;
- Cement – admixture interaction.

There may be chemical reactions between cement hydrates and admixtures and there may be situations when changes in the physical nature of the cement (e.g. fineness) will impact on the effectiveness of an admixture.

Admixture – Cement Reactions

Most admixtures can be affected by the physical properties of a cement as their mode of action is via reaction between the admixture and the cement hydrates.

It is important to understand these effects to get the best results (or optimum use) and to assist in analysing problems in the field. Trial mixes provide one way of pre-determining the nature and extent of admixture – cement interactions.

Examples of Admixture – Cement Reactions

- Water Reducers – WR are most effective with low C_3A and low-alkali cements. An increase in C_3A from 6% to 12% can reduce the effectiveness of a WR by up to one-third. An increase in (total) alkali content from 0.55% to 0.8% can see a similar reduction;
- AEA's – The effectiveness of AEA's can be impacted by both cement fineness and cement alkali content. Neither property normally varies greatly for a constant cement supply, but changes in cement supplier may require a review of admixture dose rates;
- Blended cements may impact admixture dose rates. Some SCM's may adsorb WR's or AEA's, and variable LOI in fly ash used for Type GB (Fly Ash) products may affect levels of air entrainment.

General Precautions

Concrete manufacture involves management of a wide range of variables in terms of materials and batching systems as well as weather conditions. Admixture use can provide higher levels of consistency in many cases but may also contribute to increased variability if uncontrolled changes occur.

Always be aware of:

- Change in type, source, composition and amount of cement;
- Change in SCM properties;
- Changes in aggregate and sand grading;
- Modifications to mix proportions;
- Combinations of admixtures that may adversely affect other properties;
- Temperature conditions;
- Previous use-history for admixture combinations.

NOTE*: Always check what 'Chloride-Free' means – not many materials are absolutely chloride-free (e.g. water).*

Using trial mixes is the best way of determining what effects various combinations of materials may yield.

Once material combinations and mix designs have been determined, monitor uniformity for all materials being used.

This approach also applies to admixtures where the solids contents, specific gravity and active ingredient proportions should be regularly checked.

NOTE*: Never assume that a category of product from one supplier will perform in the same way as a 'similar' product from another supplier as they may use different source materials or have different manufacturing processes.*

4 AUSTRALIAN STANDARDS AS 1478 – PARTS 1 AND 2

AS 1478.1 provides the general standard covering the types of admixtures and their use. It provides performance limits for chemical admixtures and stipulates what must be disclosed about the ingredients used in the admixtures.

Performance limits are set for:

- Water content of the concrete as a percentage of the Control;
- Time of setting as an allowable deviation from the Control;
- Compressive strength at 1, 3, 7, 28, 90 days as percentage of Control results;
- Measurement of drying shrinkage.

AS 1478.2 provides the methods for sampling and testing admixtures for concrete mortar and grout to determine compliance with performance stipulated in AS 1478.1.

AS 1478.1 includes:

- Sampling procedures;
- General information on admixtures;
- Guide to determining the chloride ion content;
- Information to be supplied on admixture:
  – Name and type.
- Compliance dose rate;
- Recommended dose rate;
- Chemical composition:
  – Chloride ion content;
  – Triethanolamine content.
- Compatibility with other admixtures;
- Sequence of addition;
- Use by date;
- Test procedures;
- Acceptability limits;
- Frequency of testing.

Acceptance Testing for Admixtures

These tests are generally done before introduction of the product into the concrete market.

Testing should include preparation of concrete mixes and assessment of:

- Water content;
- Strength;
- Drying shrinkage;
- Air content;
- Bleed testing may be done with selected products e.g. AEA;
- Time of setting may be done on selected products e.g. accelerators and retarders.

The Standards indicate the degree of variation from control samples permitted in these tests.

Certain product and test parameters must always be noted, including product type, source and properties of the cement with which the admixture is tested (including information on SO_3 content, fineness, total alkali contents and the presence of any mineral additions).

Similar requirements apply for other materials e.g. SCM's, aggregate and sand.

Uniformity tests are performed on the admixture, for properties including:

- pH;
- Relative density;
- Non-volatile content;
- Chloride ion content.

5 CHOOSING AN ADMIXTURE

Before using an admixture, it is important to understand:

- The intended purpose;
- The ingredients in the admixtures;
- The likely compatibility with other admixtures being used;

- The history of the use of the admixtures with the cement and SCM(s) being used;
- The likely need for mix changes;
- The timing of admixture addition to the mix;
- The need for any additional supervision.

Where there is no historical evidence about performance or where some conditions are unknown, trial mixes should be carried out to assess the product performance in the proposed concrete prior to commencing the project.

6 ADMIXTURE DOSE

Admixtures other than the Superplasticisers are dosed in very small quantities and proper dispensing equipment is important to maintain that level of dosage accurately. The dosing systems are normally set up in the batch plant.

The dose rate will vary with a range of parameters including:

- Properties sought;
- Seasonal temperatures;
- Concrete grade;
- Combinations of admixtures in use;
- Cement chemistry;
- SCM use – type and proportion.

Overdose Effects

Overdosing of an admixture will obviously produce an exaggerated effect of the property it is designed to modify. Some of the impacts of overdose are shown in **Table 5.2**.

The extent of actual effects will depend on:

- Type of concrete;
- Type of admixture;
- Overdose factor;
- Ambient conditions.

Table 5.2 – Effects from Admixture Overdose

Admixture Type	Some Typical / Possible Effects
Retarders	Long setting times | Increased plastic cracking risk | Surface crusting
Accelerators	Rapid setting | Finishing issues likely | Lower long-term strength
Water Reducers	Variable set times | Excessive air entrainment | Lower strengths
Water Reducer – Retarders	Long setting times | Excessive air entrainment | Lower early-age strength
Water Reducer – Accelerators	Erratic setting | Excessive air entrainment | Lower later-age strength
High-Range Water Reducers	Severe segregation | Retardation of set times

Example

Overdosing with a Water Reducer – Retarder (Type WRRe) may create the following effects:

Plastic Concrete:

- Excessive retardation;
- Copious bleed;
- Crusting of surface;
- Plastic shrinkage cracking.

Hardened Concrete:

- Surface dusting / poor finish;
- Loss or increase in strength.

7 SUMMARY – ADMIXTURES FOR CONCRETE

Type	Application	Effect	Comment
Air-Entraining (AEA)	To enhance freeze/thaw resistance; To increase workability.	Produces a large number of small air bubbles in the concrete paste.	Efficiency is reduced by increases in temperature, high cement content and by the presence of fly ash with high LOI.
Set-Accelerating (Ac)	For cold-weather concreting; To permit early finishing; To permit early formwork removal; To expedite completion of structure or repair.	Shortens setting time; May increase early strength of concrete; May reduce long-term strength.	Overdosing may lead to the very rapid set of concrete and to reduced ultimate strength. Products containing chloride ions (e.g. calcium chloride) have the tendency to promote corrosion of any embedded metals.
Set-Retarding (Re)	For hot-weather concreting; To facilitate the use of delayed finishes; For mass concrete; To eliminate cold joints.	Delays setting of concrete; Reduces early strength of concrete (up to 7 days).	Overdosing may lead to excessive retardation and delays in the development of concrete strength (in severe cases up to several days). Generally, later-age strengths are not affected.
Water-Reducing (WR, WRRe and WRAc) *[**NOTE**: Mid-range water-reducing (Type MWR) offer greater water reduction than Type WR.]*	To increase workability; To increase strength at same workability; A combination of the above two applications; To improve properties of concrete incorporating poorly graded aggregates.	Disperses cement particles and increases the fluidity of the concrete; Reduces the water demand of the mix; May affect setting time (retard or accelerate) depending on the formulation of the admixture.	Overdoses of lignosulphonates may cause excessive retardation and excessive air entrainment with subsequent effect on strength. The chloride content should be ascertained. PCE's need de-foamers to prevent high air levels.
High-Range Water-Reducing – Superplasticisers (HWR and HWRRe)	To facilitate placing and compacting (e.g. in heavily reinforced members); To increase strength; For the provision of high-quality formed surfaces; To facilitate pumping.	Increases the fluidity of the concrete and can be used to produce concretes with very low water/cement ratios.	Compatibility with other admixtures in the mix should be checked. Re-tempering of the concrete more than once to restore slump is not recommended.

Type	Application	Effect	Comment
Thickening	To facilitate pumping over greater distances at lower pressure; To improve lubrication and reduce segregation.	Increases the viscosity of the cement paste.	Will not convert unpumpable concrete into pumpable concrete – the mix must be designed specifically for pumping.
Shrinkage-Reducing	To offset volume change (in concrete, mortar and grout); For grouting of anchor bolts, prestressing ducts and prepacked-aggregate concrete; For bedding of machines and columns; For underpinning; To produce self-stressed concrete.	Some SRA's work in the plastic state and others in the hardened state.	Excessive dosage of the admixture, or the presence of unsuitable combinations of admixtures (or of admixture and cement) could generate excessive expansive forces that disrupt the concrete, mortar or grout. High doses of liquid SRA's may affect compressive strengths and consideration should be given to the combined use with a superplasticiser.
Permeability-Reducing	To reduce transmission of fluids.	Fills the capillary pores with reactive, inert or water-repellent materials.	Will not convert poor-quality concrete into water-tight concrete.

8 RELEVANT AUSTRALIAN STANDARDS

1) AS 1478 – *Chemical admixtures for concrete, mortar and grout*
2) AS 1478.1 – *Admixtures for concrete*
3) AS 1478.2 – *Methods of sampling and testing admixtures for concrete, mortar and grout*
4) AS 2072 – *Methods for the sampling of expanding admixtures for concrete, mortar and grout*
5) AS 2073 – *Methods for the testing of expanding admixtures for concrete, mortar and grout*
6) AS 1379 – *Specification and supply of concrete*
7) AS 3600 – *Concrete Structures*

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