ADVANCES IN CHEMICAL ADMIXTURE TECHNOLOGY AND ITS ROLES IN DEVELOPMENT OF HIGH PERFORMANCE CONCRETE

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ADVANCES IN CHEMICAL ADMIXTURE TECHNOLOGY AND ITS ROLES IN DEVELOPMENT OF HIGH PERFORMANCE CONCRETE

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Abstract

Chemical admixture technology has significantly grown over the past 5 decades resulting in various products used by construction, ready mix and precsast concrete industries. The advent of such technology is reviewed in herein and in particular, is related to usages and roles of admixture for developing high performance concrete. Concrete products such as self compacting concrete is found to benefit the most from advances in admixture technology. Guidelines for applying and specifying admixtures are also discussed at some length. In addition, applications describing usages of recently developed admixtures are also described in this paper.

Keywords: Chemical admixture, Concrete

1. INTRODUCTION

ACI 116R-00 [1] definition of admixture is a material other than water, aggregates, hydraulic cement, and fiber reinforcement, used as an ingredient of a cementitious mixture to modify its freshly mixed, setting, or hardened properties and that is added to the batch before or during the mixing (see also Fig. 1 for description).

Figure 1. Schematic description of concrete ingredients and their interactions

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Admixtures interact chemically with the ingredients of the concrete and affect its performance in the fresh and hardened state. They can exhibit special beneficial effects to concrete and enhance workability of the fresh mixture, and strength or durability of the hardened concrete.

Depending on the enhanced property, chemical admixtures can be classified as water reducers, superplasticizers, accelerators, retarders, air-entraining agents, corrosion inhibitors, alkali- aggregate expansion inhibitors, shrinkage reducing admixtures, etc.

a. Overview of Admixtures

Within the last 30 years admixtures have evolved significantly (see in Fig. 2), where the second millennium marks the development of next generations viscosity modifier and high range water reducer (HRWR) products.

Figure 2. Evolution of chemical admixtures

Admixtures are diosed according to function. There are five distinct classes of chemical admixtures [2]: air-entraining, water-reducing, retarding, accelerating, and plasticizers (superplasticizers). All other varieties of admixtures fall into the specialty category whose functions include corrosion inhibition, shrinkage reduction, alkali-silica reactivity reduction, workability enhancement, bonding, damp proofing, and coloring.

Water-reducing admixtures usually reduce the required water content for a concrete mixture by about 5 to 10 percent. Consequently, concrete containing a water-reducing admixture needs less water to reach a required slump than untreated concrete. The treated concrete can have a lower water-cement ratio. This usually indicates that a higher strength concrete can be produced without increasing the amount $\sqrt{\ }$ cement. Recent advancements in admixture technology have led to the development of mid -range τ ater reducers. These admixtures reduce water content by at least 8 percent and tend to be more stable over a wider range of temperatures. Mid-range water reducers provide more consistent setting times than standard water reducers.

Retarding admixtures, which slow the setting rate of concrete, are used to counteract the accelerating effect of hot weather on concrete setting. High temperatures often cause an increased rate of hardening which makes placing and finishing difficult. Retarders keep

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Ponder to Exercise System and delay the initial set of concrete. Most retarders also function as water reducers and may entrain some air in concrete.

 $|8|$

 $20[°]$

Accelerating admixtures increase the rate of early strength development, reduce the time required for proper curing and protection, and speed up the start of finishing operations. Accelerating admixtures are especially useful for modifying the properties of concrete in cold weather.

Superplasticizers, also known as plasticizers or high ange water reducers (HRWR), reduce water content by 12 to 30 percent and can be added to concrete with a low-tonormal slump and water-cement ratio to make high-slump flowing concrete. Flowing concrete is a highly fluid but workable concrete that can be placed with little or no vibration or compaction. The effect of appropriational lasts only 30 to 60 minutes, depending on the brand and dosage rate, and is followed by a rapid loss in workability. As a result of the slump loss, superplasticizers are usually added to concrete at the jobsite.

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Corrosion-inhibiting admixtures fall into the specialty admixture category and are used to slow corrosion of rein prcing steel in concrete. Corrosion inhibitors can be used as a defensive strategy for zoncrete structures, such as marine facilities, highway bridges, and parking garages, that will be exposed to high concentrations of chloride. Other specialty admixtures include shrinkage-reducing admixtures and alkali-silica reactivity inhibitors. The shrinkage reducers are used to control drying shrinkage and minimize cracking, while ASR inhibitors control durability problems associated with alkali-silica reactivity.

b. High Performance Concrete

In a broader sense high performance concrete (HPC) can be considered as concrete in which certain characteristics are developed for a particular application and environments including: ease of placement, compaction without segregation, early-age strength, good long term mechanical and transport properties (compressive strength, elastic moduli, tensile strength, fracture toughness, permeability, durability), low risk of cracking, good dimensional stability [3].

Key features of HPC include usages of low water to binder ratio (w/b) , optimal use of silica fume (and/or other mineral admixtures), smaller aggregates and fine sand, sufficient dosage of superplasticizers, occasional specialized treatments and application of pressure especially for ultra high strength concrete after mixing (at curing stage).

Performance measures and parameters that represent important aspects of HPC products can be studied by observing the macroscopic and microscopic behaviour including.

- Mechanical and physical properties (compressive and tensile strength, modulus of i. elasticity, fracture toughness, resistance to abrasion $\&$ wear, porosity, density)
- ii. Transport properties (permeability, sorptivity, chloride and sulphate penetration resistances)
- iii. Dimensional stability (thermal, shrinkage and creep)
- iv. Workability

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Table 1. Microstructural parameters and their roles [3]

Mechanical properties are responsible for high load bearing and mechanical resistance capabilities of RC or plain concrete members. Meanwhile, transport properties are tied closely to durability performance of concrete against penetrations of chloride and sulphate ions, leaching, etc. High stability against thermal, shrinkage and creep-induced deformations are desired for structural members to maintain their shapes and avoid additional stresses. In general, microstructure controls the macroscopic behavior of hardened concrete (points i, ii, and iii above). Therefore, observing HPC microstructure will lead to enhanced understanding on how characteristic behavior of HPC can be controlled. Workability is considered important as production and placement of well compacted and non-segregated fresh HPC require sufficient consistency and flow. Microstructural parameters and their roles are summarized in Table 1 above.

2. AM VANCES IN ADMIXTURE TECHNOLOGY

The effectiveness of an admixture depends upon factors such as type, brand, and amount of cementing materials; water content; aggregate shape, gradation, and proportions; mixing time; slump; and temperature of the concrete.

Admixtures being considered for use in concrete should meet applicable specifications as presented in Table 2 [2]. Trial mixtures should be made with the admixture and the job materials at temperatures and humidities anticipated on the job. In this way the compatibility of the admixture with other admixtures and job materials, as well as the effects of the admixture on the properties of the fresh and hardened concrete, can be observed. The amount of admixture recommended by the manufacturer or the optimum amount determined by laboratory tests should be used. Some types of admixtures will be discussed further in the following.

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Superplasticizers are also referred to as high-range water reducers or plasticizers. These admixtures often meet both ASTM C 494 (AASHTO M 194) and ASTM C 1017 specifications.

3 Superplasticizer

Superplasticizers cause dispersion into smaller cement particles of coarse agglomerates which predominate in the cement paste of the concrete mix [4]. Due to the dispersion effect, there is a fluidity increase in the cement mixture. In the past time the dispersion effect was ascribed only to the development of the same electrostatic (negative) charge on the cement particles [5]. The electrostatic attractive forces, existing among cement particles and causing agglomeration, would be neutralized by the adsorption of anionic polymers negatively charged, such as SNF or SMF, for the presence of SO₃ groups on the surface of cement particles. The dispersion of cement particles \uparrow puld be related with the electrical repulsion produced by the negatively charged groups $(SO₃)$ on the other side of the main polymer chain (Fig. 3).

Four major groups of superplasticizers are:

- i. Sulfonated naphthalene-formaldehyde condensate (SNF)
- ii. Sulfonated melamine-formaldehyde condensate (SMF)
- iii. Modified lignosulfonate (MLS)
- Polycarboxylates iv.

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Hamada et al. [6] developed a new family of acrylic polymers based on the following changes with respect to the PC-based superplasticizer:

- A polyether (PE) based superplasticizer with nuch longer side chains of ethylene i. oxide (EO): 130 moles of EO instead of 10-25 moles as in traditional PC-based superplasticizer (Fig. 4); this change produces a lower adsorption speed and reduces the typical retarding effect related to the early adsorption;
- ii. A modified PE-based superplasticizer where a great number of carboxylic groups are replaced by a slump- loss controlling agent (SLCA) to achieve a still higher slump retention with minimal setting retardation: indeed, due to the relatively low number of carboxylic groups in SLCA (Fig. 4) the initial adsorption and the dispersing effect are negligible as well as the setting retardation; however, subsequently to the hydrolytic effect related with the OH⁻ presence in the aqueous phase of the cement paste, the number of carboxylic units increases (Fig. 4) and the slump can still increase by prolonging the mixing time due to the increasing adsorption of the polymer on the surface of the cement particles.

Figure 4. The schematic molecular structure of polycarboxylate type (PC), polyether type and slump-loss-controlling agent superplasticizer (SLCA) [4]

b. Viscosity Modifying Admixtures

Viscosity modifying admixtures (VMA) is a material added to concrete that changes its viscosity and improves the stability of the mixture [7]. Types of VMA include:

- Cellulose i.
- ii. **PEG**
- iii. Glycol derivative Natural Gums (Welan, Diutan, Guar)

Figure key function of VMA is to modify the rheological properties of the cement paste. The rheology of fresh concrete can be mainly described by its yield point and plastic viscosity $(see also Fi(18))$:

- The yield point describes the force needed to start the concrete moving. Yield point i. is related to the workability of the concrete and may be assessed by tests such as the slun¹⁸ value (EN 12350-2).
- Plastic Viscosity describes the resistance of a concrete to flow under external ii.

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stress. Viscosity is caused by internal friction. The speed of flow of concrete is related to its plastic viscosity as shown in the diagram below and may be assessed by the T_{500} time during a slump flow test (prEN 12350-8) or by the time to flow through a V Funnel (prEN 12350-9).

Figure 5. Illustration of effect of VMA [7]

The balance between the yield point and the plastic viscosity is key to obtaining the appropriate concrete rheology. VMA's change the rheological properties of concrete by increasing the plastic viscosity but usually cause only a small increase in the yield point. Admixtures which decrease the yield point are called plasticizers and are often used in conjunction with a VMA to optimize the yield point.

VMA also provides cushion to aggregate particles, adds more "body" or "cream" to concrete, keeps particles/aggregates suspended, and reduces segregation, as illustrated by the following figure.

Figure 6. Example illustrating effect of VMA

c. Rheology Controlling Admixtures

Rheology: the study of the deformation and flow of matter under the influence of an applied stress, which might be shear stress or extensional stress. A rheology controlling admixture shall be used to facilitate the extrusion and consolidation of low-slump concrete (< 75 mm) and placement and consolidation of normal slump concrete (\geq 75 mm). The rheology-controlling admixture may also be used in mortar and grout applications if desired. The admixture effects include:

- i. Lowers force required to initiate flow, without affecting the viscosity
- ii. Improves response to vibration

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Lubrication effect iii.

iv. Enhances consolidation

The rheology-controlling admixture shall not adversely affect the setting characteristics, air content or hardened properties of the concrete, mortar or grout mixture. Use of the rheology-controllipse admixture shall exhibit the following properties or provide the following benefits compared to untreated concrete of similar mixture proportions:

- Improve the workability or flow of bulk concrete, and improve the response to i. vibration without a significant change in slump. Low-slump concrete containing the rheology-controlling admixture shall show a minimum increase in relative volume flow of 30%, as measured by the Test Method for Volume Flow.
- ii. Lower the yield stress, or force required to initiate flow, of the bulk concrete mixture, without necessarily changing its viscosity.
- iii. Not disperse cement, but impart a lubricating effect to concrete that influences particle to particle interactions, thereby facilitating flow of the bulk concrete mixture during consolidation.
- iv. Concrete properties shall be within tolerances specified in ACI 117.

d. Shrinkage-reducing admixtures

Shrinkage-reducing admixtures, introduced in the 1980s, have potential uses in bridge decks, critical floor slabs, and buildings where cracks and curling must be minimized for durability or aesthetic reasons. Propylene glycol and polyoxyalkylene alkyl ether have been used as shrinkage reducers. Drying shrinkage reductions of between 25% and 50% have been demonstrated in laboratory tests. These admixtures have negligible effects on slump and air loss, but can delay setting. They are generally compatible with other admixtures.

e. Hydration Controlling Admixtures

Hydration controlling admixtures became available in the late 1980s. They consist of a two-part chemical system: (1) a stabilizer or retarder that essentially stops the hydra-tion of cementing materials, and (2) an activator that reestablishes normal hydration and setting when added to the stabilized concrete. The stabilizer can suspend hydra-tion for 72 hours and the activator is added to the mixture just before the concrete is used. These admixtures make it possible to reuse concrete returned in a ready-mix truck by suspending setting overnight. The admixture is also useful in maintaining concrete in a stabilized non-hardened state during long hauls. The concrete is reactivated when it arrives at the project. This admixture presently does not have a standard specification.

3. ROLES OF ADMIXTURE IN DEVELOPMENT OF HPC

a. Role of Superplasticizer

We will begin this chapter by discussing the role of superplasticizers. The reasons that superplasticizers are much more important than any other chemical admixture is the number of improvements which can be achieved by its use. Fig. 7 summarizes these schematically [4].

When a superplasticizer is used as a water reducer at a given workability (I in Fig. 7), it improves the properties of hardened concrete and, in particular, increases strength and durability due to the reduction in capillary porosity and permeability, both related to a lower water-cement ratio (w/c) .

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Another mode of use of superplasticizers involves reduction of both water and cement, so that workability and strength of the concrete with superplasticizer are the same as those of the control concrete with a admixture (II in Fig. 7). Since superplasticizers in this case act as cement reducers, they are capable of reducing the heat of hydration, a property that is useful for concreting in hot climates or massive structures. There is a so a beneficial effect on the reduction in shrinkage and creep due to the higher aggregate/cement ratio related to the reduction in cement content and the increase of aggregate compensating the volume decrease of cement and water.

Finally, if superplasticizers are added without modifying water and cement content, concrete workability improves (III in Fig. 7). This is perhaps the most useful effect of superplasticizers for placing concrete in areas of high steel content that require a more workable mixture.

The changes (I) and (II) in the presence of superplasticizers can be carried out without admixture by increasing the cement-content (IV) or both cement and water at a given w/c (V) respectively. Both changes (IV) and (V) occur with higher shrinkage, creep and heat of hydration for the increase of the cement content.

Figure 7. Roles of superplasticizers

b. Guidelines to Usage of Admixtures for HPC

The following guidelines are derived based on requirements provided by British Standard (BS) [8]. Except in special cases such as high-strength concrete, the maximum dosage of concrete admixtures is limited, by 5.2.6 of BS EN 206-1, to 50 g/kg cement. For low dosages of less than 2 g/kg cement, the admixture has to be dispersed in part of the mixing water.

The performance of concrete admixtures is controlled in BS EN 934–2 by requirements related to the main function for single-function admixtures and to the main function and secondary functions for dual- or multi-function admixtures. These performance requirements are shown in Table 2.

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In addition there are general performance requirements applying to all admixtures; these include:

- i. Effect on setting time;
- ii. Effect on compressive strength;
- Effect on air content in fresh concrete; iii.

to state the maximum alkali content of each admixture.

- iv. Water soluble chloride content:
- Alkali content as Na₂O_{eq}. $\mathbf{V}.$

The performance of admixtures is determined by using reference concrete. The test mix (with admixture) is compared with the control mix (without admixture). The chloride and alkali contents also have to be 23 asured and declared. Test procedures for admixtures are given in the BS EN 480 series, Admixtures for concrete, mortar and grout - Test methods. The chloride content of all concrete is limited by Table 10 of BS EN 206-1 and the contribution of admixtures to the chloride content can be calculated. BS EN 934–2 limits admixture chloride content to a maximum of 0.10% or the manufacturer's stated value. Where the alkali content is limited in accordance with 5.2.2.2 of BS 8500-2, the contribution from admixtures can be calculated. BS EN 934-2 requires the manufacturer

Type of admixture	Performance requirement	Value in BS EN 934-2
Water reducing/plasticizing	Water reduction at equal consistence	Reduction \geq 5%
High-range water reducing/ superplasticizing	Water reduction at equal consistence	Reduction $\geq 12\%$
	Increase in consistence at equal w/c ratio	Slump increase ≥ 120 mm
Water retaining	Reduction in bleeding	Reduction > 50%
Water resisting	Reduction in capillary absorption	Reduction \geq 50% by mass
Air entraining	Air void characteristics in hardened concrete	Spacing factor $\leq 0.200 \text{ }\mu\text{m}$
Set accelerating	Reduction in initial setting time	Reduction $\geq 40\%$ at 5°C
Hardening accelerating	Compressive strength at 1 day	Increase \geq 20% at 20°C
	Compressive strength at 2 days	Increase \geq 30% at 5°C.
Set retarding	Increase in initial and final setting times	Initial increase ≥ 90 min. Final increase \leq 360 min.
Set retarding/water reducing/ plasticizing	Water reduction at equal consistence	Reduction \geq 5%
	Increase in initial and final setting times	Initial increase ≥ 90 min. Final increase \leq 360 min.
Set retarding/high-range water reducing/super plasticizing	Water reduction at equal consistence	Reduction $\geq 12\%$
	Increase in consistence at equal w/c ratio	Slump increase ≥ 120 mm
	Increase in initial and final setting times at equal consistence	Initial increase ≥ 90 min. Final increase \leq 360 min.
Set accelerating/water reducing/plasticizing	Water reduction at equal consistence	Reduction $>$ 5%
	Reduction in initial setting time	Reduction ≥ 30 min. at 20°C. and \geq 40% at 5°C

Tabel 2. Performance requirement for admixtures

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c. Specifying Admixtures

Admixtures will normally be used in designed and designated concrete. The concrete producer should be left to select the most appropriate admixture to contribute to achieving the specified concrete properties. For ready-mixed concrete, the type of admixture used is stated on the delivery ticket.

There is no reason to prohibit the use of admixtures. For designed concrete, admixtures are frequently used to help achieve the following properties:

- *i.* Compressive strength:
- ii. consistence:
- iii. Density:
- iv. Air content;
- v. Strength development;
- vi. Retarded stiffening:
- vii. Resistance to water penetration.

viii. Other special properties (e.g. accelerated stiffening, high early strength development).

Clause 3.1.3 of BS EN 934-2 advises that "trial tests should be carried out with the materials to be used on site to find the dosage necessary to achieve the desired result". The concrete producer may well have the results of such tests, which should be obtained before specifying the type and dose of admixture for a specific concrete mix.

The specifier should take into account the following:

- i. Admixtures of the same type from different manufacturers may well require different doses to achieve the desired effect;
- ii. The effect of admixtures is dependent on the particular cement, additions and aggregates used in the concrete.

The specified dose should be within the recommended range of dosage for the particular type and brand of admixture. This information is provided by the manufacturer.

When a combination of admixtures is used it is important to obtain data for the performance of mixes incorporating the particular combination of admixtures.

4. APPLICATIONS

2 Self compacting HPC

Self-compacting concrete is a concrete that is able to flow and consolidate under its own weight, completely fill the formwork even in the presence of dense reinforcement, whilst **a** aintaining homogeneity and without the need for any additional compaction.

Self-compacting concrete may be classified in three types: the powder type, viscosity agent type and the combination type,

- i. The powder type SCC is characterised by the large amounts of powder (all material < 0.15 mm) which is usually in the range of 550 to 650 kg/m³. This provides the plastic viscosity and hence the segregation resistance. The yield point is determined by the addition of superplasticizer.
- ii. In the viscosity type SCC the powder content is lower $(350 \text{ to } 450 \text{ kg/m}^3)$. The segregation resistance is mainly controlled by a VMA and the yield point by the addition of superplasticizer.
- iii. In the combination type of SCC the powder content is between 450 to 550 kg/m³ but in addition the rheology is also controlled by a VMA as well as an appropriate dosage of the superplasticizer.

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 12 In a well proportioned SCC the major variation in the composition during production at the plant comes from normal changes in the moisture content of the sand and the coarse aggregates. Variations of 1.5 $\%$ moisture content are typical for aggregate will lead to a change of 10 to 15 liters/ $m³$ of free water in the concrete mix. This will lead to significant variations in the flow and cohesion properties of the concrete being observed from one **Isich** to another on the same day or from one day to another.

Viscosity Modifying Admixtures make the concrete more tolerant to variations in the water content of the mix so that plastic viscosity is maintained and segregation prevented. The concrete has become more robust to small but normal changes in the moisture of the aggregate. VMA's are a family of admixtures designed for specific applications [7]. They are used to:

- i. Reduce segregation in highly flowable/self compacting concrete
- ii. Reduce washout in underwater concrete
- iii. Reduce friction and pressure in pumped concrete
- iv. Compensating for poor aggregate grading, especially a lack of fines in the sand
- v. Reducing powder content in self compacting concrete
- vi. Reduce bleeding in concrete
- vii. Improve green strength in semi-dry concrete

Viscosity Modifying Admixtures are not a substitute for poor quality constituents or mix design. Aggregates with a good grading curve should always be used for SCC and for high workability concrete as a lack of fines in aggregates will affect the rheology and may contribute to segregation and settlement. However, where suitable aggregates are not economically available the required rheology of the mix can often be achieved by utilizing a VMA to provide a more homogenous and cohesive concrete.

Potential benefits of a VMA in SCC may be summarized as follows:

- i. Less sensitive to variations in the moisture content of the aggregate
- ii. The effects of small changes in the materials properties are minimized
- iii. Lower powder content
- iv. He duces the level of production control
- v. Allows more fluid mixes to be used without the risk of segregation
- vi. Improving placing rate
- vii. Reduced risk of segregation and bleeding
- viii. Reduced formwork pressure by thixotropic effect

12. Better surface appearance

An overdose of VMA could make the fresh concrete mix too cohesive and slow the placing rate. This effect can usually be overcome by increasing the superplasticizer content.

b. Benefits of Combining Admixtures

One can combine water reducer and HRWR and expect the following:

- i. Low water content of concrete, i.e. zero slump (initial water content is critical)
- ii. Add Type A (2.0 oz/cwt) to increase to 2 in slump
- iii. Add type F (9.0 oz/cwt) to increase to 11 in slump
- iv. Higher strengths, lower shrinkage High slump retention
- v. Good pumpability

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Combination of mid-range water reducer and retarder can be expected to:

- i. High temperatures, low humidity
- ii. Longer working time
- iii. Better control over set time
- iv. Typically 8.0 oz/cwt and 2.0 oz/cwt, respectively

Another effect is the combination of hydration stabilization admixture (HAS) and accelerator and HRWR, which can be expected to provide:

- i. Job Constraints/Specifications,
	- 3000 psi in 6 hrs, Type I/II cement
	- -2 yd³ bucket placement, 8 yd³ per truck
	- 45 min haul to job
	- No staging of trucks, tight jobsite
- ii. Admixture Sequencing:
	- Type F added to truck
	- Type C added after Type F
	- Type B added after Type F and C

5. CONCLUDING REMARKS

The following study has collected and gathered information on recent advances of admixture technology and present applications where high performance concrete can benefit from admixture usage. Desired effects of admixtures and their relations to performance requirement have also been presented.

Important application examples include usage of advanced types of admixtures such as viscosity modifying admixture (VMA), whether alone or as well as together with superplasticzer, for self compacting concrete (SCC). In addition, an example on combined use of two or more types of admixture to achieve some desired effects has also been provided.

In summary, admixture technology can contribute significantly to development of high performance concrete. Recent applications have also shown more advanced potentials for effective of use of more than one admixtures together and for reducing consumption of cement and therefore, leading to practices of sustainable construction.

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