Polycarboxylate Based Admixture’s Trend in Europe

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Abstract The benefit of polycarboxylate based superplasticizers spreads the widely application of it in Europe and it is occupying about 20% of a market share in concrete admixture. Meanwhile a study and development of the new molecular structure of it has been continued. Recently a unique adaptation combined with SCC especially for the European precast industry has been achieved by a new molecular designing.

Keywords : Polycarboxylate, admixture, adsorption, hydration, SCC, precast

1. The use of superplasticizers in Europe

Concrete admixtures are widely used to enhance the properties of fresh and hardened concrete. With the use of an admixture, the fluidization and lowering of the water-to-cement ratio improves the workability and durability of the concrete. Superplasticizers, such as sulphonated naphthalene formaldehyde condensates (NS) and sulphonated melamine formaldehyde condensates (MS), are well known and are used as high-range water reducers. In addition to these, polycarboxylate (PC)-based admixtures have also been used as high-range water reducers.

These substances have various applications. Fig. 1 shows the admixture channel segmentation in Europe. There are three key business segments: the first is “ready-mixed”, the second is “precast (including drycast),” and the third is “underground” use. The admixture market in Europe is around 570 million Euro, thereof 340 million Euro belongs to the ready-mix concrete segment. The precast industry has developed into the second position in the European admixture market, and also plays an important role in the market.

PC admixtures occupy approximately 20% of the entire chemical admixture market in Europe and have grown to take 20% of the market in the ready-mix segment. PC-based admixtures exhibit better slump retention, less set retardation, and higher early strength development compared with NS- and MS-based superplasticizers. Furthermore, PC-based superplasticizers offer the flexibility of permitting molecular design so that the desirable performance can be obtained. PC-based admixtures are strengthening their market position in the ready-mixed concrete segment. In addition, recent molecular designs in Europe have led to the development of new admixtures for the precast industry.

2. New designed PC application

2.1 PC designing on demand

The precast industry has offered quality, economical constructions elements over decades. More recently, precast concrete producers have been challenged to maintain their profitability while facing such issues as improved quality of the element, more expensive and scarce skilled labor and rising materials and equipment costs. Precast production processes vary throughout the industry and throughout the world. In almost all the cases the goal is the efficient, cost effective use of the labor, power or energy, materials, equipment and other resources. Production output and formwork turnaround are universally critical economical factors for the precast industry. Typically,
A precast process includes designing and producing a concrete mixture to achieve specific properties such as high early strengths, placing the concrete in the forms, heat or ambient curing (depending on the climatic conditions) of the concrete elements, transferring the prestress of the tendons to the concrete, removal from the forms and handling of the elements during transport and erection. In a state of the art plant the placing and consolidation of concrete is facilitated by utilizing high workability concrete and efficient vibration. Heat curing is normally applied to obtain the required strengths at the desired early age. A system, based on a rational use of new superplasticizer specifically developed for the precast industry, is proposed. It combines the use of self compacting concrete (SCC) and rapid development of strength with the new designed PC superplasticizer and utilizing the heat developed by the hydration process of the cement. This system, combining the effective use of SCC and the rapid development of strength is based on newly advanced polycarboxylic ether polymers (ACE) and a particular type of a viscosity-modifying admixture. This combination provides the concrete an optimum yield stress and plastic viscosity imparting not only the self-compacting ability but, also, superior flow speed distance and filling ability through better exploitation of the energy derived from the force of gravity.

2.2 Mechanism of ACE

The polycarboxylate ether polymers (CE) are designed according to a specific balance between the negative electric charges (carboxylic groups) and the hydrophilic side chains. These polymers act as dispersing agents through both electrostatic and steric repulsion CE superplasticizers are very effective in concrete mixes with a large amount of fine particles (500–600 kg/m³). They impart very high fluidity at low water to binder ratio, without any risk of bleeding or segregation. The innovation of the combined system of SCC and ACE is the minimization of the energy required for the rapid strength development in the concrete. This is provided by the new CE polymers where the negative charges and the hydrophilic chains are placed along the molecule backbone in specific configuration which imparts a different adsorption behavior onto the cement particles, as compared to CE superplasticizers. The hypothesis of the mechanism of action is that the new ACE polymers adsorbed onto the cement particles leave greater free surface exposed to water for hydration, maintaining, if not increasing, the dispersion effect (Fig. 2 and Fig. 3).

Furthermore, the adsorption of this new polymer affects mainly on the unhydrated cement and very slightly the hydration products. For this reason, the crystallization reaction is activated in advance and not delayed by further adsorption of the superplasticizer molecules. The early development of the heat of hydration can further activate or accelerate the hydration of the cement. Therefore, the energy usually furnished from an external source (steam or electric heating) is internally activated by this revolutionary molecule. The viscosity-modifying admixture used is a blend of two different chemical species (Fig. 4). The first one generates molecular networks which are thickened further by the formation of molecular bridges by the second chemical species.

3. The combined precast system—Field applications

The combined system of SCC and ACE can be tailored to meet the individual needs of the precast producer. It can be used for optimizing the heat curing cycle, increase production by reducing the curing time, elimination of heat curing, elimination of vibration or a combination of any of these parameters. To
verify these applications, field tests were carried out in several European countries. Results of tests for the total implementation of the system, that is no external energy is provided for placing, compacting and curing of concrete, are presented below.

3.1 Italian experience

In this plant reinforced concrete beams, columns and prestressed TT beams are produced using 400 kg of cement CEM I 52.5 and a CE type superplasticizer. The W/C = 0.42 and the consistence class is S 5. The concrete is steam cured at 60°C and the required strength of 40 MPa for the prestress transfer is achieved at 18 hours. A self-compacting concrete mix with 400 kg of cement CEM I 52.5, 100 kg of limestone filler and 0.8% of ACE superplasticizer is now being used. The slump flow is 680 to 700 mm and the V-Funnel time is 8 to 10 seconds. The concrete is cured at the ambient temperature and covered with insulating mats just after placing. The required strength of 40 MPa is obtained after 16 hours. The surface appearance is excellent without any significant voids.

3.2 Spanish experience

In this plant prestressed concrete beams of up to 1.7 m height and 25 m span are produced. The cement content is normally 420 kg/m³ of type CEM I 52.5 and the consistence of the concrete is S 5 (slump>200 mm) using a CE superplasticizer. The concrete is steam cured at 70°C for 17 hours to obtain 43 MPa on cylinder specimens.

Now, using the following SCC mix made with 400 kg of the same cement, 850 kg of sand 0-2 mm size, 460 kg each of coarse aggregate 4-10 mm and 12-18 mm, 0.9% of ACE superplasticizer, 0.15% of a viscosity modifying admixture and 170 Liters of water, is used. The slump flow value is 650 to 700 mm and the V-Funnel time is 10-12 seconds. The cast elements are covered after placing and the strengths obtained, without any external heat being supplied are 15 MPa at 6 hours, 42 MPa at 16 hours and 62 MPa after 7 days. Also in this case the surface appearance is greatly improved.

3.3 Swiss experience

This plant produces shafts for elevators with lightweight concrete having a density of 1750 kg/m³. The cement content is 350 kg of type CEM I 52.5 and the concrete, manufactured at a ready mix plant with a CE superplasticizer is poured at a consistence of class S 4. It is then vibrated and cured at 40°C by electrical heating of the insulated forms for 17 hours when strength of 12 MPa is obtained. Often, on demoulding, unfilled sections are encountered and have to be patched (Fig. 5). A self-compacting concrete mix with 365 kg of cement, 100 kg of fly ash 330 kg of Liapor F 5 and 870 kg of sand was developed for this application. ACE superplasticizer, viscosity modifying admixture and an air entrainer are incorporated into the mix.
mix. The water powder ratio is 0.98 and the slump flow is 740 mm (Fig. 6). The concrete flows easily into the forms without any segregation and completely fills it. After demoulding the surface is blemish free and the strength at 17 hours is more than 25 MPa (Fig. 7).

3.4 U.K. experience

This plant produces prestressed concrete beams using the traditional technology with 375 kg of CEM 1 52.5 type of cement and a CE superplasticizer. The consistence class of the concrete is S3 and it is vibrated and then cured by heating the forms to obtain 40 MPa after 18 hours. In a trial application a self-compacting concrete mix with 400 kg of cement type CEM I 52.5 and 100 kg of limestone dust was developed and two beds of 100 m length were cast using CE and ACE superplasticizers. Both beds were covered after placing and only the bed with CE superplasticizer was heat cured. The temperature development is shown in Fig. 8. The strength after 18 hours of the heat cured bed with CE was 71 MPa and that of the normal cured bed with ACE was 65 MPa, both well above the required strength of 40 MP. The surface appearance was excellent (Fig. 9).

4. Conclusions

The chemical admixture field in the European market tends to polycarboxylate based admixture because of its advantages and developments of the admixture have been taken day by day. The new-engineered polymer developed shows superior performances in water reduction and strength development. The innovative aspect of this new polymer is that it acts essentially on the kinetics of hydration of the cement which is accelerated at the very early stage, releasing large amount of heat that is then able to self accelerate the crystal growth and consequently, the strength development. The laboratory tests and field applications validate this aspect. This system can be tailored to meet the individual needs of the precast producer to achieve very specific benefits. It may be used to decrease the duration of the heat curing cycle or to eliminate it all together, to obtain energy savings. It can be implemented in combination with self-compacting concrete to eliminate also the vibration of the concrete during placement, leading to effective filling of the forms, reduced noise and related health hazards, increased service life of the forms, reduced maintenance costs and labour savings. The combined system of SCC and ACE is a breakthrough innovation.
ヨーロッパにおけるポリカルボン酸系混和剤の動向

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ヨーロッパにおけるコンクリート混和剤の市場調査では、近年ポリカルボン酸系ポリマーを使用した混和剤が占める割合が増えてきており、ヨーロッパの混和剤市場全体の20％を占めるようになって来た。一方、ポリカルボン酸系ポリマーの研究開発も活発であり、分子設計による新規なポリマー、特にSCCと組み合わせたプレキャスト用の混和剤の開発に成功した。この新しいポリマーのヨーロッパ各国における応用例を取り上げる。

ヨーロッパではコンクリート用化学混和剤として、従来からβ-ナフタレンスルホン酸（NS）やメラミンスルホン酸（MS）系化合物が高性能減水剤として使用されていた。しかし、近年では日本と同じようにポリカルボン酸（PC）系が広く利用されるようになってきた。ヨーロッパの混和剤市場において使用比率が最も高いのは生コンクリートで60％以上を占めている。その後に大きく市場としてコンクリート二次製品分野が約20％を占めている。さらにUGC（地下建造物）部門が続き、約15％を占める。近年使用比率が高まったPC系混和剤は、現在ヨーロッパ市場で全混和剤中約20％を占めるようになってきており、また生コンクリート分野でも約20％利用されるようになってきている。PC系混和剤が利用されるようになったのはNSおよびMSと比較してPCはスランプ保持性や早期強度発現性等の優れた性能を有しているためである。さらにPCの利点としては、分子設計の自由さが挙げられる。最近ヨーロッパでは、この分子設計の自由さからコンクリート二次製品用に特化した混和剤が開発され、この混和剤と自己充填コンクリート（self compacting concrete：SCC）とを組み合わせた新しいシステムが利用されるようになってきた。

この新しいシステムでは、コンクリート製品の養生時間を短くすることで生産能力の向上を期待することができる。これは、セメントの水和反応を促進するように新規なPCポリマー（advanced polycarboxylic ether：ACE）が設計されたことによる。従来のPCポリマー（polycarboxylic ether：CE）のセメント粒子の吸着形態がセメント粒子を覆いつくすことになるが、ACEはセメント粒子に水と接触できる自由表面を多く残すように吸着する。この結果、CEと比べてACEは水和反応を促進し、この水和反応による発熱が更なるセメントの水和反応の促進をもたらす。この発熱は、今までの外部（スチームあるいは電気的に）から供給されていなかった熱源に匹敵するものである。さらにこのシステムではSCCを製造するための増粘剤が使用されている。増粘剤として二種類の水溶性高分子が組み合わされており、互いが網目構造をとるように設計されている。

この新しいシステムを使用した応用例の一つとしてイタリアにおける製造例を紹介する。セメント比＝42.0％、粉体量＝500 kg/m³（100 kg/m³：石灰石微粉末、400 kg/m³：CEM Iセメント）の配合で、フレッシュコンクリートの性状は、スランプフロー＝680～700 mm、V模倣通過時間＝8～10秒。コンクリートは常温で養生し、要求性能である圧縮強度40 MPaを16時間で得ることができた。硬化コンクリートの表面性状は痘痘も無く非常に良好であった。その他、ヨーロッパ諸国の一例を国別にスペイン、スイス、イギリスについて紹介している。

References