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Chemical technologies for modern concrete production

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Abstract

Modern era is linked with global issues in limited energy resources and ecological degradation as hurdles for sustainable industrialization and urbanization. In these contexts, concretes are the most widely adopted construction materials to build supporting civil structural systems. However, massive productions of concretes significantly consume global energy resources and induce negative impacts to ecology which should be paid with serious attentions. Modern concrete productions are strived for not only producing highly performing materials but also being continuously more ecological and energy efficient. The uses of chemicals as additives and admixtures are recognized to be relatively more obvious approaches to answer the needs of modern concrete production for more energy efficiencies and carbon footprint reductions. Chemical additives are added to the cement and it is usually during the comminution stage. Chemical admixtures are intermixed together with other concrete constituents. In the current situation, the momentum of increasing concrete consumption contributes the energy requirement and creates negative ecological impacts massively spreading all over the world. The present study aims to identify the transformations and outlooks in additive and admixture chemical technologies used for modern and future concrete productions. The perspective discussed in this study can assist to formulate research needs for future developments of additive and admixture chemicals.

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1. Introduction

Concretes are the most used and viable construction materials that their production processes need to be improved adapting modern global issues in energy and ecological conservations. Concrete productions are regarded as one of the most significant contributors to the global issues in energy demand and ecological degradations. The discussion in these circumstances cannot be separated from the context of cement production as main binder component in concrete. Indeed, the main issues lie on the productions of cements which the main component is clinker. Its production releases approximately equal amount carbon dioxide equivalent CO_{2e} of clinker produced and requires high amount of energy during sintering process. Approximately 5 – 7 % of global CO_{2e} come from cement productions [1,2]. In later stage, the comminution processes of clinker together with other constituents (e.g. gypsum and supplementary cementitious materials) to form cement powder requires high amount of energy as well. This cement comminution process consumes about one-third of the energy requirement to produce a ton of cement [3]. At this time and the foreseen future no option of construction materials is more viable than concretes and this is the main reason that the efforts are needed to improve the eco-aspects [2] and energy efficiency in concrete productions with particular intentions on clinker consumption and cement production energy.

The efforts have included such as advancements in the equipment for cement productions as well as optimizations of cement and concrete mixture compositions by the adjustments of particle size distributions (PSD) and the uses of supplementary cementitious materials (SCM). The outcomes of these efforts are found can be intensified significantly by further relatively easier manner of complementing chemicals. In modern practices chemicals are used as additives and admixtures. Small dosages of chemical additives commonly within the magnitude of hundreds ppm by weight of cements are added during the comminution process that act as cement grinding aids (CGA) in order to decrease the unnecessary energy consumption. Additionally, the uses of CGA can improve the performances of hydrated cements either due to better PSD, chemical influences or these combinations. In these cases, the portion of clinker as the most chemically active element in cement can be substituted with SCM. In majorities of countries, the performances requirements of cements are nationally standardized and the innovations are commonly put upon production processes to accord the standard such as by the reductions in clinker consumption and energy which are also cost benefit. A relatively higher dosage of chemical admixtures but still within a few percent of cement weight is admixed during concrete productions. Commonly used chemical admixture noticed to have relatively significant impacts on clinker and cement reductions are water reducer agents. These allow concrete production with low water to cement ratio (w/c). Low w/c allows production of concretes with better performance, higher strength and durability, with relatively lower cement content hence clinker content. Dispersions of cement particle agglomerations are the main features used in both CGA and water reducers. Agglomerated particles in cement comminution process are detected as a big particle by size based separator causing over milling and decreasing the process efficiency. During concrete productions, water trapped within agglomerated particles causing less water available to fluidize concrete. In this case, unnecessary excess water put to achieve workability negatively impacts hydrated concrete performances.

The objective of present study is to have the appreciations on the roles of chemicals in past, present and future concrete productions. The scopes of discussions are CGA and water reducers. Here, the history in technological transformations of CGA and water reducers are literarily reviewed with more emphasis on polycarboxylate ethers (PCE). Successively, the outlook upon chemical systems for future concrete productions is drawn and realistic recommendation for immediate future research is proposed.

2. Transformation on chemical technology

History of water reducing chemical admixtures was started from the efforts to remedy the issue of carbon bleeding in concrete dates back in mid-1930s [4]. Dewey and Almy proposed to disperse the carbon in concrete using dispersing agent which has been found also acting as dispersant for cement resulting in improved concrete strength [4]. Later, called TDATM, the product has been patented and regarded as the pioneer for water reducing chemical admixtures [4]. Following this inventions numerous water reducer products have been introduced with the well-known and widely used chemicals in such classes of lignin, naphthalene and melamine [5,6]. PCE was introduced in 1981 [7] and have been successfully gaining wide acceptance. In general, PCE are reported to have

superior performance over traditional superplasticizer [8]. Further main advantage of PCE are the potentials that their molecular architectures can be modified [5] to adjust their effects on concrete and adapt incompatibility issues.

In July 1933, the patented TDATM was first tested as cement chemical additive at Universal Atlas plant in Hudson New York [4]. This test shows clear benefits of TDATM on improvements in cement production rate and quality [4]. Since then numerous of chemical additives named as CGA for the uses in cement production have been introduced. Well known chemicals used as CGA are alkylene, glycols, amines or amino alcohols [9,10]. Recently PCE technology are introduced in cement additive systems. Complements of PCE into the aforementioned chemicals, alkylene, glycols, amines or amino alcohols, are found enhancing the performances of the combined chemical systems [9,11-13].

The terms classical, traditional or conventional chemicals are very often being used in the discussion of PCE chemicals to differentiate non PCE with PCE chemicals [12, 14]. In this study the terms conventional chemicals are used. PCE themselves are differentiated into conventional and non-conventional PCE based on molecular elements.

3. Polycarboxylate ether (PCE)

3.1. Conventional molecular structure

Conventional PCE are typically composed of comb-like copolymer structure with an adsorbing linear anionic backbone (typically a polyacrylate or polymethacrylate) holding carboxylate groups as trunk chain linked with ether group to non-adsorbing side chains (typically polyethylene oxides) holding methoxy chain [12,15]. Fig 1. illustrates the typical structure of conventional PCE. The notations used in Fig 1 and the present study follow the one introduced by Gay and Raphaël's model [16] for comb-homopolymers and extended by Flatt et al. [17] for comb copolymers [12]. In this notation, n is the number of side chains in the polymer, P is the number of monomers in a side chain, and N is the number of backbone monomers per side [12]. Other types of PCE can be derived by molecular architecture modification.

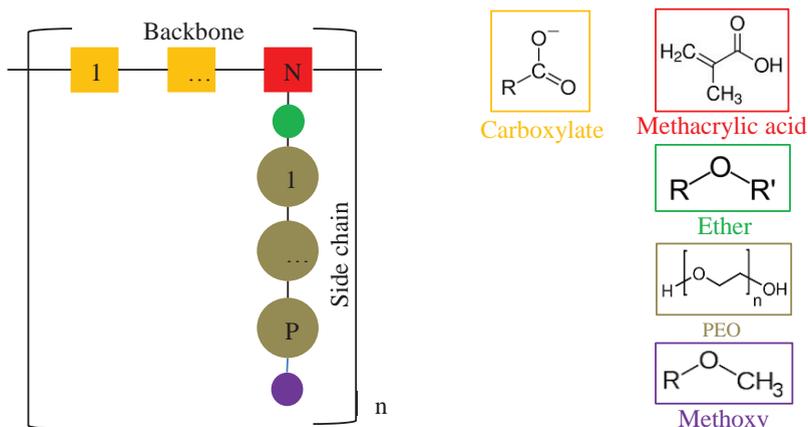


Fig. 1. Illustration of typical structure PCE molecule.

The backbone of PCE in cement – water system is adsorbing to the cement surfaces mainly through electrostatic interactions while the side chains are non-adsorbing which induce steric hindrance [18]. At high pH of hydrated cement environment, the deprotonated carboxylate groups dissociates in water providing a negative charge along the PCE backbone whereas the PEO side chains are neutral [8]. Negatively charged carboxylic groups are coupled with Ca^{2+} ions on the surface of cement particles or hydrated products [8]. The polyethylene oxide (PEO) group affords a not uniform distribution of electron cloud, which gives a chemical polarity to the side chains. The increased performance of PCE superplasticizers is generally explained by the exerted steric hindrances from side chains

repelling apart cement particles [19]. The superplasticizers are adsorbed on the cement particles and act as dispersants by electrostatic and/or steric repulsion effects [6].

3.2. Compatibility

The performances of PCE based water reducers can be severely affected by the individual cement elements [20] as well as other. The type of surface which provides the best steric match with the molecular configuration of the PCE molecule will attract more PCE than others [21] and such adsorbing preferences is the main explanation of incompatibility PCE – cement/concrete systems. Numbers of elements that have more competitive preferences of PCE adsorption over cements have been investigated. PCE have preferential absorption to silica fume [21]. High volume blast-furnace slag decrease fluidity retention and strength enhancement [22]. PCEs are known to easily incorporate into the layer structure of clay by means of their pendant PEO side chains, hence their dispersing ability in concrete is much impeded by clay impurities [23]. Free sulfate anions compete over PCE occupying the positively charged anchoring sites on cement [24]. PCE have been reported to have adsorption competitiveness with viscosity modifying agents (VMA) such as polyvinyl acetate (PVA) onto bentonite competitively with PCE [25] and *N,N*-dimethyl acrylamide (NNDMA) [24]. In general concrete productions, PCE prolong setting time [26] and entrain more air [6].

3.3. Design

Modifications on molecular architectures of conventional PCE based water reducers have been reported for improved compatibilities, performances and functionalities. Modified vinyl ether-based PCEs synthesized from maleic anhydride and 4-hydroxy butyl vinyl ether are reported to give concrete more clay possessing tolerance [15]. PCE with higher contents of β -CD pendants synthesized via partially replacing PEO monomer by MA- β -CD is more tolerant toward kaolin [27]. PCEs grafted with MA hydrolyzed to carboxylic and hydroxyl groups, are found to restrain the hydration of cement paste [28]. Hydrophilic–lipophilic balance (HLB) value, the balance between the hydrophilic and lipophilic parts in PCE molecules determines their effect on the plastic viscosity (stickiness) of a concrete, higher HLB values, impart lower plastic viscosity [29]. Allyl ether—maleic acid based PCEs with higher HLB than methacrylate-ester and vinyl ether PCEs give lower viscosities of concrete [29]. PCE with a star-shaped structure was prepared through copolymerization of acrylic acid, isobutenyl polyethylene glycol, and star-shaped polymerizable active center by an esterification between polyol and AA shows better fluidity effect adsorption behavior [30]. PCE effect on flowability is closely related to adsorption amount [31]. PCE of much larger molecular weight leads to larger adsorption amounts from the view of both kinetics and thermodynamics [31]. PCE - graphene oxide nanosheets (GON) composite prepared by copolymerization of GONs with PC's monomers such as methacrylic acid, sodium allyl sulfonate, and methacrylate polyoxyethylene ether give evenly disperse GONs in cement paste [32].

3.4. CGA application

The dispersion and adsorption of PCE molecules to the surfaces of cement particles are considered dominantly occurring via surface contact instead of gas phase transfer based on PCE low vitality and its decomposition temperature is over 150 °C above the temperature in cement comminution environment [12, 14]. Table 1 shows the influence of PCE physical structure adsorption energy on C₃S surface based on the molecular simulation study by Mishra et al., [12].

Table 1. Influence of PCE physical structure on adsorption.

| Adsorption | Number of side chain (n) | Number of backbone (N) | Number of monomer in side chain (P) | Length of the backbone (n x N) |
|------------|-----------------------------------|------------------------|---|--------------------------------|
| Energy | - | + | - | + |
| | Higher anionic charge of backbone | | Steric hindrance effect, caused by the extension of graft chains of PEO | |

Molecular simulation study of C_3S as representation of cement shows that main chains of PCE containing carboxylate groups and the polyether side chains adsorbed on dry C_3S surface [14]. The branching prevents flat adsorption of the entire PCE molecule but linear molecules consisted of polyethylene oxide chain are possible for complete flat adsorption [14]. A specific steric effect occurs if branching makes flat adsorption impossible or if very long polymer chain overlap [14]. Adsorption of PCE on C_3S surface happens mainly due to electrostatic interactions and negligible contributions from van der Waals interactions [12]. Calcium ions of C_3S tend attached to PCE (into some extent it gets repelled from the surface of C_3S) and the top of C_3S surface is slightly reconstructed due to the adsorption of PCE [12]. Another observation is silicate ions comes out from C_3S surface [12]. In short explaining mechanism, polar sides of adsorbed PCE molecules partially compensate polar surface of surfaces and reduce it by shielding effect of their nonpolar alkylene groups [14]. Therefore, the attractive force between particles fall with decreasing surface polarity hence the tendency to agglomeration formations are minimized due steric effects [14]. PCE molecules are substantially remain intact during grinding as the water reducing effect of PCE is observed during water – cement mixing such as in concrete [14, 33].

Recently, series of PCE based CGA developed from waste materials derived from petro-chemical and palm oil waste are reported to be effective CGA and the hydrated cements ground incorporating these PCE show improved strengths [34].

3.5. Remarks

The developments in PCE based CGA and water reducers have been intended to address the identified compatibilities, improve PCE performances and give more functionalities of CGA and water reducers. Furthermore, the development of PCE themselves start to include the attention on ecological aspects such as incorporating industrial by products. All these directions may be expected to provide more performing concretes with less ecological impacts in the future.

4. Outlook upon chemical system

Concrete industries worldwide are being faced to more complexity in the requirements of construction materials for performances and costs. Meanwhile more challenges are also arising from limited material and energy resources as well as from ecological constraints. Optimizations in production process are needed for the harmony between delivery of high performing product and limited resources as well as ecological conservations. As discussed by Damtoft et al. [35], the significant actions over these challenges may include introduction of low-energy clinker and clinker content reduction of cements substituted by SCM, optimization in concrete composition toward the quality in question with lower cement content, exploitation for concrete recycling and multi-functional construction materials of concrete. Reductions in clinker portion in cement and concrete have been identified to be effective approaches and will remain a key priority [36]. Major multinational cement industries, members of WBCSD Cement Sustainability Initiative, commit for global average 73% clinker portion in cement as one of main paths towards year 2050 ambition for half CO_2e emission of year 2006 per unit weight quantity of cement [37]. In 2006, the global average clinker portion in cements is 79 % with major SCM used are ground blast furnace slag, fly ash, natural pozzolans, rice husk ash, silica fume, artificial pozzolans and limestone [37]. In concrete production, uses of SCM are also the common approaches for cement (clinker) reductions [38-41]. In the constraints of resources, the growing concrete demands and cement productions along with the ambitions for clinker portion reductions will result in highly varied types and inconsistent characteristics of used SCM due to limited options in resources. These

also should be aware that in the limited resource of SCM, limestone is the promising source of SCM as they are readily available in most of cement plant. However, limestone is considered to be relatively inert in cement hydrations as compared to pozzolanic materials making the additional portion of limestone will be the substantial challenges for the performances.

In all the circumstances upon the efforts for clinker portion reductions, CGA and water reducers are continue to be the focal chemicals due to these respectively main advantages for finer grinding of cements and lower w/c of concrete which both of these effects benefit higher portion of SCM in concrete. Therefore, as the anticipation for highly varied types and inconsistent characteristics of used SCM, we may start exploring the more advance rapid systems of chemicals - cements matching processes over the current practices which involve tremendous time in laborious trials of material – chemical – performance matching processes. The shortly described steps of such rapid processes include the initial stages in examination of cement or concrete chemical compositions which in the later stages are matched with highly customizable CGA and water reducers. While rapid examinations in chemical compositions have been possible [42,43], the technologies in customizable CGA and water reducers as well as chemicals – cement matching processes are still insufficiently adequate. However, the development of such rapid matching processes are feasible with further development in the studies that have been started for customizable PCE based CGA and water reducers coupled with computational molecular simulation that recently have been introduced in the study on cement technology [44-50] including the cement – chemical interactions [12,14].

5. Conclusion

The requirements of modern concretes are becoming more complex not just merely from the viewpoints of performances and costs but also from the concerns of ecology and energy conservations. The technologies of concrete and cement productions have evolved in adapting the modern concrete requirements. In this study, we identify the essential chemicals in modern concrete productions are CGA and water reducers. Their technologies have evolved from conventional chemicals to PCE that offer superior performances and relatively more customizable molecular architectures to adapt different requirements and raw materials in cement and concrete productions. However, the incompatibility with certain components and impurities in cements and concretes are still being the issues, commonly solved with lengthy material – chemical – performance matching processes. These timely concerns are projected to grow in the future as more highly varied and inconsistent SCM characteristics. The more speedy matching processes are possible through advancement in customizable CGA and water reducers and computational techniques. Though, the realistic action in the near future may be started with the identifications upon the potential combinations of sciences and computational methods for quick designs of PCE molecular architecture and rapid compatibility analysis. These developed methods can be integrated with existing and future computational methods for advancement in concrete design and production processes.

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