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The Use of Chemical Admixtures to Prevent Delayed Ettringite Formation in Concrete

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Abstract: This paper reviews the chemical admixtures preventing delayed ettringite formation (DEF) and can be used for researchers to (i) identify potential chemicals alternative to the conventional methods using supplementary cementing materials (SCMs) and evaluate these chemical solutions to prevent DEF via reported mechanisms, (ii) understand the effects of these chemicals on the concrete properties, and (iii) develop guidelines and/or implementation plan for future research.

Keywords: Delayed ettringite formation, Chemical admixture, Fly ash, Concrete durability

Introduction

One of the concrete durability problems, delayed ettringite formation (DEF), has been observed over the years. DEF is a chemical attack by the source of sulfate ions within the concrete (e.g., a gypsum-contaminated aggregate, high sulfate content cement) with ettringite associated with the heat curing at temperatures greater than 70°C (Pavoine et al. 2012). Many studies have investigated the effect of supplementary cementing materials (SCMs) on the expansion of concrete caused by DEF and the use of fly ash (primarily class F fly ash) is the common effective remedial practice to prevent this concrete durability problem (Amine et al. 2017, Leklou et al. 2017). However, there is a major concern that class F fly ash with required quality and quantity will not be available to prevent DEF in the long term as both class F fly ash quality and quantity is changing due to the controls imposed by the new emission standards (Shahzad Baig and Yousaf 2017). Therefore, identifying chemical admixtures alternatives to class F fly ash through detailed and effective research is highly needed in order to address the above concern and ensure long lasting durable concrete in the future. The primary goals of this paper are to (i) summarize the use of chemical admixtures (alternative to class F fly ash) to prevent DEF, and (ii) identify the potential research gaps on the use of chemicals for future investigations.

Summary and Discussion

Some control measures have been used widely to prevent DEF (Thomas 2001) such as (i) lowing the maximum curing temperature less than70°C, (ii) selecting the use of cement types and contents. It has been reported that the use of high-early-strength cement and high cement contents in concrete lead to high DEF susceptibility (Fu and Beaudoin 1996, Fu et al. 1997, Lawrence et al. 1999), and (iii) using SCMs (such as fly ash, slag, silica fume, etc.) (Ghorab et al. 1980, Heinz et al. 1989). Among the use of SCMs, class F fly ash was found to be the common effective practice to prevent DEF (Leklou et al. 2017). However, the change of coal composition along with applying control measures by thermal power plants to reduce environmental pollution is gradually leading to a situation of limited or no production of good quality class F ash in the future (Shahzad Baig and Yousaf 2017). Therefore, identifying chemicals alternative to class F fly ash is highly needed and presented in this study. Table 1 summarizes the effects of chemicals inhibiting the DEF along with the most commonly used test methods for assessing DEF in mortar bars or concretes presented in Table 2.

Table1. *Dosage, Effects and Mechanisms of Different Chemical Admixtures to Prevent DEF by Different Researchers*

Chemicals	Observations on dosage and effects	Mechanisms
Lithium-based (e.g., lithium nitrate)	Molar ratio of Li and Na+K = 0.74 controlled DEF up to 2 years (Ekolu et al. 2007)	In order to ensure the effectiveness of lithium salts delivering the interaction and mechanism for certain combination of lithium salt and aggregate is necessary since reactions might be varied by different combinations.
Acid-based (e.g., phosphoric acid, acrylic acid)	A reduction of 17% expansion can be reached by applying phosphoric acid and acrylic acid polymer (Shaikh 2007).	• Reduce precipitation or modify the precipitation morphology • Prevent the growth of ettringite crystallite at the nuclei stage so that ettringites is unable to fully develop into crystals • The crystals dissolve and never fully precipitate (Cody 1991, Cody et al. 2001)
Silicone-based (e.g., siloxane)	A reduction of 30% expansion can be reached by applying siloxane (Shaikh 2007).	React chemically with minerals within the concrete to create a hydrophobic zone to shield against water penetration and deicing chemicals

Table2. *Test Methods to Assess the Susceptibility of Concrete to DEF*

Method	Test condition	Note
Kelham's test (Kelham 1996) (mortar bar or concrete prism)	• 100% RH at 23°C for 4hrs. • Heat up from 23°C to 95°C in 4hrs in 100% RH and hold for 12hrs. • Cool down from 95°C to 23°C in 4hrs • Demold and store in lime water at 23°C	• Mimic the precast concrete operation • Fu's test (Fu 1996) is more severe than Kelham's test (Kelham 1996) due to (i) short procuring time, (ii) rapid ramping period which change chemical composition other than breakdown ettringite to form monosulfate, and (iii) drying at high temperatures which might change chemical composition of cements.
Fu's test (Fu 1996) (mortar bar)	• 100% RH at 23°C for 1hr • Heat up from 23°C to 95°C in 1hr in 100% RH and hold for 12hrs • Cool down from 95°C to 23°C in 4hrs • Demold and store in lime water at 23°C for 6hrs • Dry at 85°C for 24hrs	

Based on Tables 1 and 2, the following summary can be drawn.

1. Only lithium-based chemicals (e.g., lithium nitrate) have been investigated recently for long-term observations (e.g., over 6 years) in migrating DEF in concrete (Ekolu et al. 2017). The results show that lithium nitrate significantly diminished ettringite infilling, exhibiting less intense microcracking and internal stress. Identification of the effective and widely used chemicals with proven records as well as formulation of new chemical admixtures to prevent DEF are needed.

2. Table 2 shows the most commonly used test method to assess the risk of swelling due to DEF. Although many tests and specifications have been published in the past (Escadeillas et al. 2007, Grabowski et al. 1992, Pavoine et al. 2006a, b), the test procedures were either modified from the tests listed in Table 2 or used small specimens of mortar (Aubert et al. 2009, Brunetaud et al. 2008, Escadeillas et al. 2007, Famy et al. 2001, Pavoine et al. 2006a, b, Tosun 2006, Zhang et al. 2002a, b). Moreover, unlike other durability problems [e.g., ASR, for which a rapid test has been developed to access aggregate reactivity (Liu and Mukhopadhyay 2014a, Liu and Mukhopadhyay 2014b, Liu and Mukhopadhyay 2015, Mukhopadhyay and Liu 2014)], no rapid method was developed for accessing DEF potential in concrete specimens (Pavoine et al. 2012) and determining optimum dosage of available chemicals. A rapid but reliable test to determine the optimum dosage of chemical admixtures is needed.

Recommendations for Future Research

This paper reviews chemical admixtures (alternative to SCMs) to solve DEF concrete durability problems. The effort to identify chemicals compounds both at the national and international level shall continue and research in the following aspects shall be investigated.

- Identification of the effective and widely used chemicals with proven records as well as some promising chemicals to prevent DEF
- Identification of areas of upgradation of existing chemicals as well as potential of formulation of new multifunctional chemical admixtures
- The procedure to determine optimum dosage of available chemicals as well as other products needs to be developed. From Table 2, the effectiveness of a test/approach to determine the optimum dosage of chemicals listed in Table 1 needs to be verified. For example, Fu's test is rapid but drying at high temperature might change chemical composition of the cement. The demand of a rapid but reliable test to determine the optimum dosage of chemical admixtures is growing.
- Mixing procedure - Practice to add the compound in a batch plant as well as time in a mixing sequence needs to be developed.
- Fresh/harden properties to be measured in order to detect any changes of the fresh/harden concrete properties due to any kind of cement-admixes incompatibility - Based on the available literatures, it seems that different admixtures do not interfere with each other's action in a negative way; however cement-admixes interaction might sometimes lead to incompatibilities which affect the fresh/harden properties.
- Control mechanisms for the concrete durability aspect including, but not limited to DEF for the available chemical admixture products need more research. A clear understanding of controlling mechanisms based on agreed upon facts is yet to be established for some compounds. For example, in order to ensure the effectiveness of lithium salt, more research on the factors to determine effective dosages for controlling DEF, such as lithium salt type, aggregate type (e.g., use of an alkali-silica reaction (ASR) non-reactive aggregate), cement type (e.g., a cement with high C_3A, C_3S, Na_20_e and fineness and having a high SO_3 content will be used for DEF testing as this kind of cement have the greatest susceptibility to DEF expansion when heat cured), the chemical interactions and mechanism are needed. Therefore, a clear understanding of mechanisms is highly needed in order to ensure an effective utilization of a product.
- Development of approach of combined use of chemicals to obtain the benefits of controlling multiple durability aspects (e.g., DEF, corrosion, ASR, etc.).
- Development of guidelines on proper utilization of chemical admixtures to improve DEF concrete durability - Guidelines shall aid engineers in making a cost-based decision on the use of chemical admixtures

considering factors related to materials, construction, fresh and hardened concrete properties, and ensuring effective DEF durability performance. The guidelines shall include, but not limited to:

- Best mix design practices - the permissible and optimum levels of replacement of potential chemicals to obtain optimum durability performance,
- Selecting effective chemicals, individually or combined, to control DEF,
- Selecting the optimum dosage of the selected potential chemicals to control DEF,
- Recommendation on the use of effective and innovative approach and methods to evaluate performance of the potential chemicals,
- Guidelines to check the effect on fresh and hardened concrete properties and planning to avoid those issues. Possible criteria of acceptance based on mechanical properties and durability testing,
- Best construction practices to ensure successful project using concrete made of appropriate chemicals to control DEF,
- A cost and benefits analysis to determine if the use of chemicals is cost effective,
- Developing an implementation plan - Based on the results obtained from lab experimental studies and results from exposure blocks/beams plus some limited construction of structural element, an effective implementation plan needs to be developed and proposed as a future implementation project, and
- Specification development - The guidelines and specification for use of chemical alternatives to fly ash need to be developed. The guidelines should be incorporated in the construction specifications in different transportation agencies.

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