Chloride-Enhanced Delayed Ettringite Formation (CLDEF): An Obscure Process

S. O. Ekolu(✉)

Department of Civil Engineering Science, University of Johannesburg,
Auckland Park, South Africa
sekolu@uj.ac.za

Keywords: Chloride ingress · Delayed ettringite formation · Monosulphates · Friedel's salt

1 Introduction

From the historical perspective Delayed Ettringite Gormation (DEF) is known to occur usually in cementitious systems made at high cement contents with rapid hardening Portland cements (RHPC) such as Type III cements. Elevated curing temperatures exceeding 70 °C are necessary for DEF to occur. However, there have been controversies, leading to speculations that DEF could occur outside these generally recognized conditions [1–9]. For example, large pours of concretes under hot weather concreting could increase concrete temperature levels to DEF critical temperatures. Johansen and Thaulow [10] found that a concrete beam of 1 m × 1 m cross-section developed a peak temperature of 84 °C at ambient temperatures of 35 °C, without heat treatment. Hobbs [11] also suggested that large sections of field concretes made with high cement contents of about 500 kg/m^3, could attain maximum temperatures in the range of 85 °C. So in hot or tropical climates, concreting conditions similar to those found under heat curing, could arise as a combined effect of the following factors:- use of RHPC/Type III cement, mix designs of high cement contents such as 500 kg/m^3, large concrete pours or casting of large sections, and ambient temperatures exceeding 30 °C. In laboratory studies, however, there are no reports of DEF occurrence in the absence of heat curing.

2 The Controversies of Chloride-Sulphate Interactions in Concrete

Chlorides commonly migrate or are incorporated into concrete, leading to two categories comprising:

- *Admixed* chlorides, that are added or incorporated during mixing of concrete, and may be considered as 'internal chlorides' or
- *Ingressed* chlorides, which migrate into hardened concrete from external sources and may be regarded as 'external chlorides'.

K. Kovler et al. (Eds.): ConcreteLife 2020, RILEM Bookseries 26, pp. 67–73, 2020.
https://doi.org/10.1007/978-3-030-43332-1_14

In the early ages of concrete technology development during the first half of the 20th century, chloride-based chemical admixtures were extensively used as accelerators, to promote hydration of concrete especially for casting under cold weather conditions. Various researches were devoted to understanding of the effects of admixed chlorides on cement hydration [12–14]. The understanding that emerged showed that the admixed chlorides compete with internal sulphate ions to react with C_3A in a Cl-C_3A interaction, to form Friedel's salt as the end reaction product. The interactions involving ingressed chlorides are quite different from those of admixed or internal chlorides, since most of the C_3A will have reacted by the time external chlorides migrate into concrete. Accordingly, the unstable product that chlorides may find available in the hardened concrete system is monosulphate (AFm), which sets up the Cl-AFm interaction. The different interaction processes for admixed or ingressed chlorides, eventually determine their effects on volume stability of the material system.

The Cl-AFm interactions of ingressed chlorides in concrete, has resulted in controversies regarding their effects on sulphate attack, for which each of the following observations have been reported in the literatures:

- No effect [15]
- Suppressive [16–18]
- Increase [19–21]

A close look at the experimental set-ups of the various researches lead to two important deductions that:

(i) *The effect of ingressed chlorides is a function of chloride concentration*. There is agreement on the experimental observations showing that high chloride concentrations suppress sulphate attack, as reported in the literatures [16–21]. Further evidence is also available from field investigations done at the Arabian Gulf, which showed sulphate attack to have been majorly suppressed owing to exposure of the concrete structures to high chloride concentrations in the environments [22].

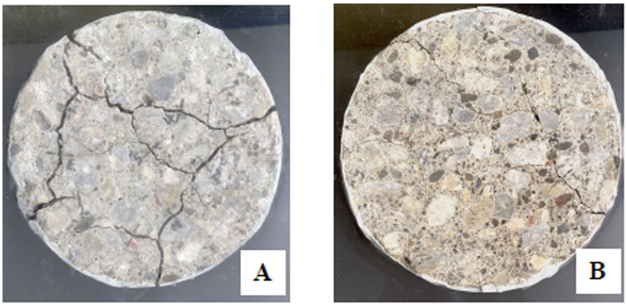
(ii) *Only heat-treated systems appear to exhibit the DEF expansion enhancing effect of ingressed chlorides*. To the best knowledge of the author, no chloride – induced expansions have been reported in moist-cured cementitious systems. The author's researches [20, 21, 23] have consistently found chlorides to enhance DEF expansions in heat-treated cementitious systems. It is also possible that non – expansive systems of low SO_3 can become DEF expansive as a consequence of exposure to chlorides. The second important consideration is that only low chloride concentrations produce the chloride-enhanced DEF expansion (CLDEF). The researches done so far indicate 0.5 M chloride concentration to give the most severe CLDEF expansion.

3 Review and Discussion

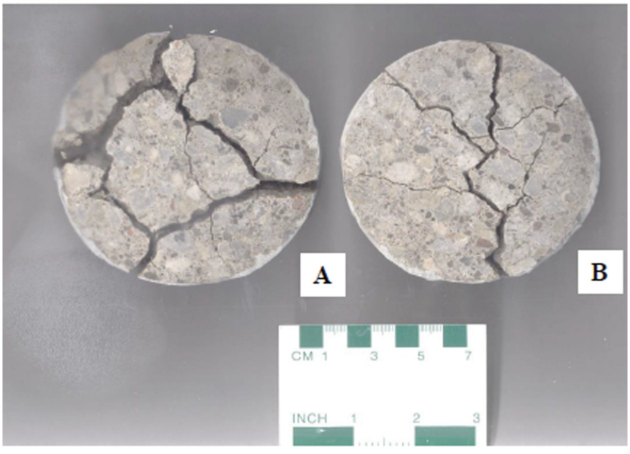
3.1 Incidental Observations

In this section, the DEF experiments that were conducted in Canada and in South Africa under completely different investigations, are reviewed. The early evidence of CLIDEF was first reported in [20, 21]. In the study, concrete cylinders 100 dia 200 mm height were made at 0.45 water/cement ratio (w/c) with 7% entrained air, then heat-cured at 95 °C in accordance with the 18-h conventional steam curing cycle [21]. The Type 30 Portland cement used in the study was known to be DEF expansive, as shown in Fig. 1 [21]. Its high $SO_3 > 4.0\%$ met the requirement for sulphate expansive cements [24, 25].

Following heat curing, the cylinder samples were exposed outdoors for 28 days. In preparation for the bulk diffusion test ASTM C1556 [26], cores of size 100 dia 50 mm thick were cut from the concrete cylinders then ponded in 2.8 M NaCl solution for 90 days. Prior to profile grinding of the cores for chloride analysis, the cores were



(a) Cracked cores after 22 months of storage in a freezer



(b) Severely cracked cores after 26 months of storage in a freezer

Fig. 1. DEF expansion of Type 30 Portland cement [20]

removed from the chloride solution then dry - stored in a freezer at −18 °C. It was during the frozen storage that strangely interesting observations appeared. It was found that after the dry-storage of the cores in the freezer for 9 months, cracks developed in some cores. These observed cracks were monitored and found to continue growing rapidly with age while under storage in the freezer.

Figure 1 shows photographs of crack growth in the Cores A and B. It can be seen that Core A showed rapid crack growth attaining average sizes 0.1, 0.32, 7.3 mm at 9, 22, and 26 months respectively. Similarly, Core B rapidly developed cracks from about 0.0 mm at 9 months to 0.07 mm and 3.0 mm at 22 and 26 months, respectively. Once the onset of cracking occurred, crack development progressed rapidly, increasing by 43% and by 17.6% for the Cores A and B respectively, over a duration of 17 months.

3.2 Experimental Investigations

In order to further investigate the incidental observations discussed in the foregoing section, two experiments were conducted at different times. One study was done in Canada [21] while the other was carried out in South Africa [22]. The experiment conducted in Canada was a detailed study done using 25 × 25 × 285 mm bars made at 1:2.25:0.47 cement to sand to water, and using 75 × 75 × 285 mm concrete prisms made at 0.45 w/c. Both sets of samples were steam-cured at 95 °C then stored in water (for the control), 0.5 M or 2.8 M NaCl as reported in [21].

While the earlier study [21] was done in Canada, the later study [23] was conducted in South Africa using CEM I 42.5R supplied by Afrisam (pty) Ltd. The cement contained clinker SO_3 of 2.0% which is very low and non-expansive. In the experiment, the sulphate content of the cement was increased to a total of 5.0% SO_3, by adding Na_2SO_3 of technical grade supplied by Merck (pty) Ltd. The CEM I 42.5R cement was used to prepare mortar prisms of 25 × 25 × 285 mm at 1.0:2.25:0.5 cement to sand to water. The mortars were heat-cured at 95 °C then stored in water (0 M), 0.5 M, 1.0 M, 1.5 M, 2.0 M NaCl solutions. Both of the studies conducted in Canada and in South Africa, confirmed that indeed ingressed chlorides of low concentrations 0.25 M to 1.5 M enhance DEF, as seen in Fig. 2a,b [21, 23]. The mechanism by which chlorides enhance DEF expansion was proposed in [21]. This process was attributed to instability of monosulphate upon exposure to low chloride concentrations leading to CLDEF. At high chloride concentrations, the instability of both monosulphate and ettringite occurred, leading to suppression of DEF expansion. The proposed mechanism was also found to be consistent with kinetic theory that was employed for mathematical modelling of the chloride-DEF interation [27].

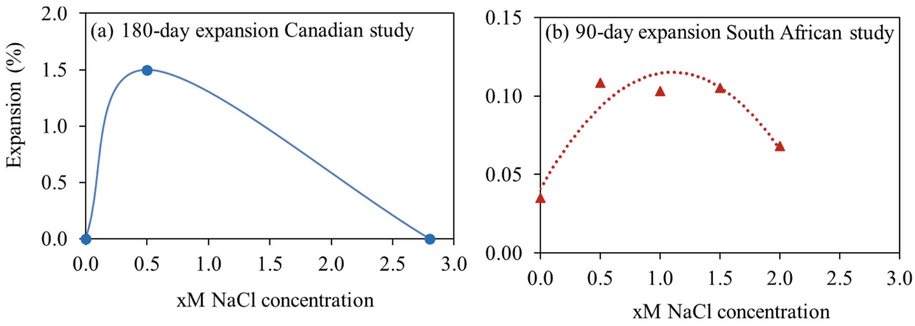


Fig. 2. Mortar expansions showing the pessimum effect of ingressed chlorides on DEF at (a) 180 days [21] (b) 90 – days [23]

4 Conclusions

This paper has provided additional insights on a less known mechanism by which externally applied chlorides can enhance delayed ettringite formation, to form a process that may be referred to as *chloride – enhanced delayed ettringite formation* (CLDEF), which was first reported in [21]. The present study has affirmed the following findings:

- Externally applied chlorides indeed exhibit pessimum effect on DEF expansion
- Low concentrations of about 0.25 to 1.5 M NaCl give the most severe enhancement of DEF
- Only expansive cements with SO_3 exceeding 4.0% can develop CLDEF
- Low expansive cementitious systems can develop expansive behaviour exceeding 0.10% threshold due to CLDEF

References

1. Heinz, D., Ludwig, U.: Mechanism of subsequent ettringite formation in mortars and concretes after heat treatment. In: Proceedings of the 8th International Congress on the Chemistry of Cement, Rio de Janeiro, Brasil, vol. V, Theme 4, pp. 189–194, 22–27 September 1986
2. Heinz, D., Ludwig, U.: Mechanism of secondary ettringite formation in mortars and concretes subjected to heat treatment. In: Scanlon, J.M. (ed.) Concrete Durability, Katharine and Bryant Mather International Conference, SP-100, vol. 2, pp. 2059–2071. American Concrete Institute, Detroit (1987)
3. Heinz, D., Kalde, M., Ludwig, U., Ruediger, I.: Present state of investigation on damaging late ettringite formation(DLEF) in mortars and concretes. In: Erlin, B. (ed.) Ettringite-The Sometimes Host of Destruction, SP-177. ACI Spring Convention, Seattle (1999)
4. Ekolu, S.O.: Heat curing practice in concrete precasting technology - problems and filture directions. J. Concr. Soc. South. Afr. **114**, 5–10 (2006)
5. Ekolu, S.O., Thomas, M.D.A., Hooton, R.D.: Dual effectiveness of lithium salt in controlling both delayedettringite fonnation and ASR in concretes. Cem. Concr. Res. **37**(6), 942–947 (2007)

6. Ekolu, S.O., Thomas, M.D.A., Hooton, R.D.: Implications of pre-formed microcracking in relation to theories ofDEF mechanism. Cem. Concr. Res. **37**, 161–165 (2007)
7. Ekolu, S., Rakgosi, G., Hooton, D.: Long-term mitigating effect of lithium nitrate on delayed ettringite fonnatiou andASR in concrete - microscopic analysis. Mater. Charact. **133**, 165–175 (2017)
8. ASTM C684-99: Standard test method for making, accelerated curing, and testing concrete compression testspecimens. ASTM International, West Conshohocken (1999). www.astm.org
9. BS 1881-112: Testing Concrete Part 112: Methods of accelerated curing of test cubes. British Standards Institution(BSI), London, UK (1983)
10. Johansen, V., Thaulow, N.: Heat curing and late formation of ettringite. In: Erlin, B. (ed.) Program on Ettringite-The Sometimes Host of Destruction, ACI SP-177, 1999, pp. 47–64. ACI, Seattle, April 1997
11. Hobbs, D.W.: Expansion and cracking in concrete attributed to delayed ettriugite formation. In: Erlin, B. (ed.) Program on Ettringite-The Sometimes Host of Destruction, AC1 SP-177, 1999, pp. 159–181. ACI Spring Convention,Seattle,April 1997
12. Skalny, J., Odler, I.: The effect of chlorides upon the hydration of Portland cement and upon some clinkerminerals. Mag. Concr. Res. **19**(61), 203–210 (1967)
13. Rosenberg, A.M.: Study of the mechanism through which calcium chloride accelerates the set of Portland cement. J.Am. Concr. Inst. Proc. **61**, 1261–1269 (1964)
14. Neville, A.M.: Properties of Concrete. 4th edn. Wiley, New York (1996). (also 3rd edition 1981)
15. Midgley, H.G., Illston, J.M.: The penetration of chlorides into hardened cement pastes. Cem. Concr.Res. **14**(4), 546–558 (1983)
16. Zuquan, J., Wei, S., Yunsheng, Z., Jinyang, J., Jianzhong, L.: Interaction between sulfate and chloride solution attackof concretes with and without fly ash. Cem. Concr. Res. **37**, 1223–1232 (2007)
17. Lee, S.T., Park, D.W., Ann, K.Y.: Mitigating effect of chloride ions on sulfate attack of cement mortars with or withoutsilica fume. Can. J. Civ. Eng. **35**, 1210–1220 (2008)
18. Sotiriadis, K., Nikolopoulou, E., Tsivilis, S., Pavlou, A., Chaniotakis, E., Swamy, R.N.: The effect of chlorides onthe thaumasite form of sulfate attack of limestone cement concrete containing mineral admixtures at low temperature.Constr. Build. Mater. **43**, 156–164 (2013)
19. Marks, V.J., Dubberke, W.G.: A different perspective for investigation of Portland cement concrete deterioration.Transp. Res. Rec. **1525**, 91–96 (1996)
20. Ekolu, S.O.: Role of heat curing in concrete durability: effects of lithium salts and chloride ingress on delayed ettringiteformation, Ph.D. thesis, Civil Engineering Department, University of Taroma, Canada (2004). 217p.
21. Ekolu, S.O., Thomas, M.D.A., Hooton, R.D.: Pessimum effect of externally applied chlorides on expansion due toDEF - proposed mechanism. Cem. Concr. Res. **36**, 688–696 (2006)
22. Matta, Z.G.: Deterioration of concrete structures in the Arabian Gulf. Concr. Int. 33–36 (1993)
23. Ekolu, S.O.: Influence of synthetic zeolite on delayed ettringite formation - preliminary investigation. In: 2nd InternationalWorkshop on Durability and Sustainability of Concrete Structures (DSCS), Moscow, Russia, 6–7 June 2018, SP 326-42, pp. 42.1–42.8 (2018)
24. Crammond, N.J.: Examination of mortars containing varying percentages of coarsely crystalline gypsum as aggregate.Cem. Concr. Res. **14**, 225–230 (1984)
25. Xu, A., Shayan, A., Baburamani, P.: Test methods for sulphate resistance of concrete and mechanism of sulphateattack: a state-of-the-art review. ARRB Transport Research Ltd., Review Report 5 (1998). 44 p.

26. ASTM C1556-11a(2016): Standard test method for determining the apparent chloride diffiJsion coefficient ofcementitious mixtures by bulk diffusion. ASTMIntematianal, West Conshohocken, PA (2016). www.astm.org
27. Mulongo, L., Ekolu, S.O.: Mathematical modelling of the pessimum action of chlorides on the extent of delayedettringite formation, Part 1: formulation. Key Eng. Mater. 400–402, 203–208 (2008)