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Foreword

This document (CEN/TR 15697:2008) has been prepared by Technical Committee CEN/TC 51 "Cement and building limes", the secretariat of which is held by NBN.

This CEN/TR is a state of the art review of the international research literature dealing with testing/assessing the sulfate resistance performance of cements and related binders. It outlines the difficulties faced by CEN/TC 51 in applying a prescriptive approach to the specification of sulfate resistant cements and identifies the different mechanisms and forms of deterioration that occur during sulfate attack. This report compares the advantages and disadvantages of different test specimen types (paste, mortar or concrete), different exposure conditions and different techniques used to assess specimen deterioration. The importance of test method reproducibility is reviewed with reference to the experimental work carried out by CEN/TC 51 during the 1990s. The report lists the key parameters that must be controlled in any robust standardised method and makes suggestions for the main features of a pan-European performance test.

Introduction

Under the terms of EU Mandate 114, committee CEN/TC 51, cement, building limes and other hydraulic binders, is required to develop standards for 'common cements' and also for cements with special properties such as low heat cements, calcium aluminate cements and sulfate resisting cements.

EN 197-1: Composition, specifications and conformity criteria for common cements was adopted in 2000 and was the first harmonised European Standard to be adopted for a construction product.

Since 2000, European Standards for masonry, low heat, and low early strength blastfurnace cements, very low heat special cements and calcium aluminate cements have been published. The development of a prescriptive EN for sulfate resisting cements has been complicated by national differences in the types of cement that are recognised to have sulfate resisting properties. Note, however, that all nationally standardised sulfate resisting cements meet the requirements of EN 197-1:2000 and that the absence of a specific standard for sulfate resisting cement has not constituted a barrier to trade.

In order to overcome these national difficulties, and also to permit new types of cement to be recognised in the future, work was directed towards the development of a performance test for sulfate resistance. Work commenced in 1991 and following a preliminary assessment of the French NF-P-18-837 procedure and the German, so called flat prism method, a decision was taken to concentrate on developing the French procedure. The method measures the expansion of 20 mm x 20 mm x 160 mm prisms in a sodium sulfate solution containing 16 g/l SO_4^{2-}.

During five co-operative testing exercises involving up to thirteen laboratories, the method was refined with the objective of improving reproducibility and also discrimination between sulfate resisting and non-sulfate resisting cements. In 1998 it was concluded that further development would require a more fundamental approach and efforts were directed towards obtaining EU funding for 'pre-normative' research. These applications were not successful.

In early 2004 a meeting was arranged with representatives of the NANOCEM programme to explore a more fundamental approach to the problem of sulfate resistance and sulfate resistance testing. The aspects of particular interest to CEN/TC 51 were:

a) understanding sulfate attack mechanisms in relation to the type of cement and the concentration/temperature conditions;

b) establishing a relationship between laboratory tests and field performance;

c) methods to accelerate the test;

d) using parameters other than deformation measurement to monitor the progress of the sulfate attack;

e) understanding the role of thaumasite in sulfate attack.

The NANOCEM group has formulated a research programme that addresses the above aspects and work on this programme commenced in 2006 within the framework of a larger programme funded by the Marie Curie Training Network. In parallel with this programme, CEN/TC 51 asked committee WG 12 (Additional Performance Criteria) to prepare a CEN Technical Report outlining the current state of the art concerning sulfate resistance testing.

A literature search identified over 250 relevant papers and reports published during the period 1970 to 2006. To assess the different sulfate resistance techniques employed and their possible influence on the performance of different cement/binder types, the testing details from 129 papers were entered into an Access Database. The papers selected for entry into the database were those which contained original research data and detailed information concerning test conditions.

This report draws on the information contained in these 129 papers plus a further 50 papers and reports not selected for entry into the database. In the interests of brevity the current report only includes references to selected references that are either key papers or contain specific information. It is intended that a statistical analysis of the database and a full listing of the papers studied will be made available as a supplementary document of CEN/TC 51 / WG 12.

1 Sulfate resistant cements

Portland cement concrete can undergo attack by sulfate bearing solutions such as natural groundwater or those contaminated by industrial activity. Attack can result in expansion, strength loss, surface spalling and ultimately disintegration.

The resistance that a cement matrix provides to sulfate attack depends on a number of factors which include:

- nature of the reaction products formed with the sulfate solution and in particular, whether their formation results in disruptive expansion;
- impermeability of the matrix (including the important paste-aggregate interfacial zone) which provides a barrier against penetration by sulfate ions;
- concentration of sulfate ions (in this report expressed as g/l SO_4^{2-});
- mobility of the sulfate containing groundwater;
- nature of the accompanying cation e.g. Na^+, Mg^{2+}, Ca^{2+} etc;
- pH of the sulfate bearing ground water/solution;
- presence of other dissolved salts such as chlorides;
- temperature of the exposure;
- degree of pre-curing before exposure, although in the field this is only likely to affect the performance of the concrete surface;
- presence of finely divided limestone (calcium carbonate) in the aggregate, or carbonate ions dissolved in the groundwater, which may promote the formation of thaumasite under low temperature conditions.

Almost all developed countries have product specification standards for sulfate resisting cement(s). With a few exceptions these are prescriptive standards that specify cement composition. The permitted compositions are based upon long-standing laboratory test results and also satisfactory performance in the field. National differences reflect different exposure conditions and also differences in the nature of the available cement constituents.

Poor performance under sulfate exposure conditions is normally associated either directly or indirectly, with the formation of ettringite. In the hydrated matrix of a CEM I cement, the source of reactive alumina is normally the monosulfate phase according to the reaction:

$$\underset{\text{(monosulfate)}}{C_4Al_2(OH)_{12}.SO_4.6H_2O} + 2Ca^{2+} + 2SO_4^{2-} + 20H_2O \Rightarrow \underset{\text{(ettringite)}}{C_6Al_2(OH)_{12}(SO_4)_3.26H_2O}$$

Any unreacted C_3A is also a potential source of ettringite.

Monosulfate will normally also be present in composite cements containing blastfurnace slag, fly ash or natural pozzolana but in the hydrated matrix of these cements, alumina is also present in phases such as hydrotalcite or hydrogarnet or substituted in C-S-H in which latter forms. It does not appear to be available to form an expansive reaction product [1].

Strength loss and disintegration are also associated with decalcification of C-S-H, which is an important mechanism during attack by $MgSO_4$ solutions but which also occurs to a lesser extent in Na_2SO_4 solutions [2].

Current sulfate resisting cements standardised in CEN member countries can be divided into two categories:

1) Portland (CEM I) cements with a maximum permitted C_3A content.

2) Portland composite cements containing appropriate levels of glassy blastfurnace slag, fly ash or natural pozzolana.

Low C_3A sulfate resistant cements provide a chemical resistance to sulfate attack. The products that reaction with sulfates is not expansive and consequently the matrix is not disrupted facilitating further attack. The unreactive nature of the hydration products of low C_3A cements is attributed to a low level of monosulfate and/or the formation of an iron-rich form which is slow reacting and produces a 'non-expansive' form of ettringite [3].

Portland composite cements (i.e. CEM II, III, IV and V types) provide resistance to sulfate attack which is predominantly micro-structural in nature [4 to 8]. This is derived from the significantly lower permeability of the hydrated matrix. Additional positive factors are:

- reduced level of free calcium hydroxide in the matrix which reduces calcium availability for ettringite formation and also the formation of gypsum when the matrix is exposed to concentrated sulfate solutions;

- formation of hydrates containing alumina which are non-reactive to sulfate solutions.

The reduced availability of calcium may also result in the formation of ettringite with a morphology and distribution throughout the hydrated matrix which is not expansive [9].

One factor that is often overlooked is that resistance to external sulfates is normally positively influenced by the level of SO_3 in the binder; the higher the level in a range between ~ 1 % to ~ 4 %, the greater the resistance. This applies to concrete produced from CEM I cements [10] and also particularly to slag and fly ash containing concretes. Where the ash or slag is added to the mixer [2], [11, 12] the SO_3 level is lowered by dilution and the hydrated matrix is more vulnerable to attack by penetrating sulfates in comparison with a binder with an optimised SO_3 level. The improved resistance can be attributed to the increased level of sulfated phases, such as ettringite, formed during initial hydration, which are stable in the presence of an elevated sulfate level.

2 Sulfate resistance test procedures

2.1 General review

The sulfate resistance properties of cement can be assessed by preparing realistic concretes specimens and placing them in conditions which are representative of field conditions. Unfortunately, unless the concretes are of low quality (high w/c, poorly compacted) several years exposure will be required to provide any meaningful discrimination between sulfate resistant and non-sulfate resistant cements [13, 14]. Consequently, there is a need for accelerated test procedures that provide discrimination within a timescale of weeks or months.

The first laboratory test procedure to determine the sulfate resistance properties of a cement was the Le Chatelier - Anstett procedure, [15] in which cement paste is hydrated, crushed and dried and then interground with 50 % (by mass) of gypsum. The expansion of a moist cylinder, formed from the interground mixture is determined at 1 day, 28 days and 90 days. The method is severe and cements with a low potential to form expansive products such as calcium aluminate cement and supersulfated cement perform well, while low C_3A sulfate resisting Portland cements perform poorly.

The first test procedure to attain the status of a national standard was the ASTM C 452 procedure, which was adopted in 1964. In this test, cement is blended with finely divided gypsum to bring the SO_3 level to 7,0 % and the expansion of 25 mm x 25 mm x 285 mm mortar bars (1:2,75, w/c 0,485) placed in water at 23 ^{0}C is