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NEWSLETTER

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ASR prevention – common concepts and testing methods

Most test procedures evaluate aggregates, but valid performance tests are necessary

Over the last decades, several accelerated ASR testing methods were developed enabling investigators to achieve reliable results and thereby assess the alkali-reactivity of aggregates in acceptable periods of time. These methods have been examined internationally by many research groups to correlate them with conventional, but time consuming test procedures and verify their validity and precision. Today, researchers have many tools for aggregate assessment and ASR prevention at their disposal. Currently a performance test for the estimation of the ASR potential of particular concrete mixes is being enhanced by the Research Institute of the Cement Industry in Düsseldorf to incorporate the influence of alkali-containing deicing salts.

Since the alkali-silica reaction (ASR) was first described in the 1940s, a multitude of different test procedures has been developed for the assessment of the alkali reactivity of aggregates. From 2002 to 2006, the European research program PART-

NER investigated and compared a large number of different testing methods, among them widespread tests proposed by RILEM as well as regional tests, in order to develop an assessment scheme valid for all European aggregates. For this purpose, the different procedures were carried out on a large number of European aggregates known to be alkali-reactive. The results are currently being evaluated. Suitable procedures will be recommended to CEN.

RILEM recommendations

In 1988, a RILEM technical committee (TC) began to revise ASR-related testing methods and collated them into an assessment scheme capable of evaluating the ASR potential of all types of aggregates. In 2000, a second TC continued the work, which has just been followed by a third one. The RILEM recommendations and the assessment scheme (*Fig. 1*) are described here only in a condensed form, especially omitting parts describing testing methods regarding alkali-carbonate reaction.

Many national regulations comprise one or more of the testing methods

recommended by RILEM or at least resemble the RILEM testing concept. The evaluation of an aggregate is generally divided into several successive steps, assuring an assessment as fast and precise as possible. In terms of its alkali reactivity, an aggregate is then assigned to a category. RILEM proposes 3 different reactivity-classes: Class I (very unlikely to be alkali-reactive), Class II (potentially alkali-reactive or alkali reactivity uncertain) and Class III (very likely to be alkali-reactive). However, in many cases a degree of differentiation beyond the categories “not reactive – reactive” (Class I – Class III) is difficult. Depending on the classification of an aggregate, appropriate precautions can be taken to prevent a deleterious ASR.

Petrography

The foundation of most regulations is a petrographical classification (e.g. RILEM AAR-1) of the investigated aggregate. Certain aggregates or groups of aggregates are known to be not alkali-reactive and can be assigned to RILEM Class I (or a corresponding category) without further testing. In Germany, aggregates like basalt, which are not listed in the national ASR guideline, are automatically considered as non-reactive. Furthermore, a petrographic examination is necessary since not all testing methods are applicable to all types of aggregate. For example, aggregates containing certain alkali-reactive components like porous flint cannot be reliably evaluated with the RILEM AAR-2 testing method (accelerated mortar bar test). Aggregates which cannot be classified unambiguously can subsequently be investigated with suitable testing methods. Mostly test procedures following petrography are based on the measurement of expansion of mortar or concrete specimens.

Screening test

In the second step of the RILEM assessment scheme, an accelerated mortar bar test (RILEM AAR-2) can be performed as a screening test. This test provides results in a very short time (2 weeks), but seems to overestimate the alkali reactivity of different aggregates. The investigated aggregate is crushed to grain sizes ≤ 4 mm. Mortar bars are produced and stored at 80 °C in a sodium hydroxide solution. Aggregates passing this test can be assigned to RILEM Class I.

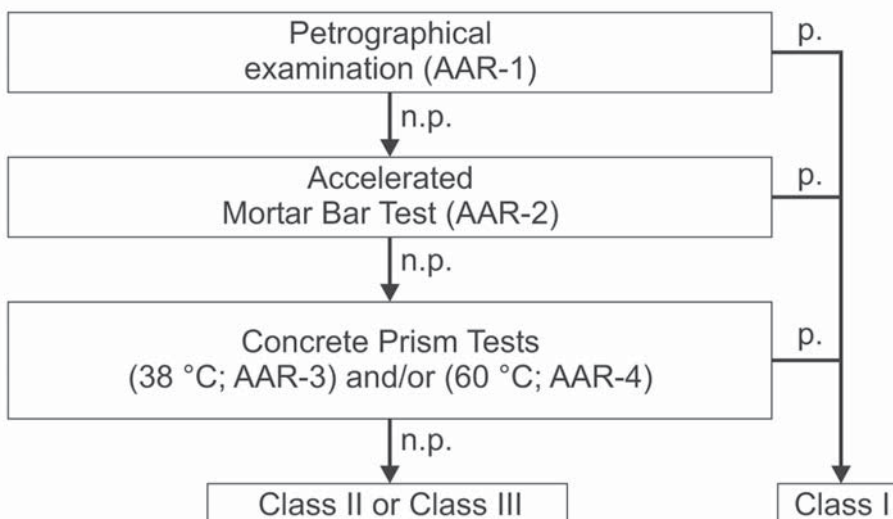


Fig. 1: Simplified flow chart for the assessment scheme for ASR potential as proposed by RILEM (p. = passed, n.p. = not passed)

Concrete tests

Aggregates that do not pass AAR-2 can be tested in a third step with more time consuming but more precise and often less rigorous concrete testing methods. In the concrete prism test AAR-3, concrete samples are stored at 38 °C above water, in the accelerated concrete prism test AAR-4 at 60 °C above water. AAR-4 was originally developed in France as a performance test.

The results of the testing procedures recommended by RILEM show good correlations with each other and with the results of other established concrete testing methods like the German "fog chamber" method (Fig. 2), which prescribes storage conditions similar to AAR-3 (concrete prisms and a concrete cube stored at 40 °C / 100 % RH).

These concrete based testing procedures enable the final categorization of aggregates with regard to their alkali reactivity.

Performance test

A new RILEM technical committee is beginning its work in autumn this year. One of its main objectives is the development of a performance testing procedure. This performance test is supposed to be added

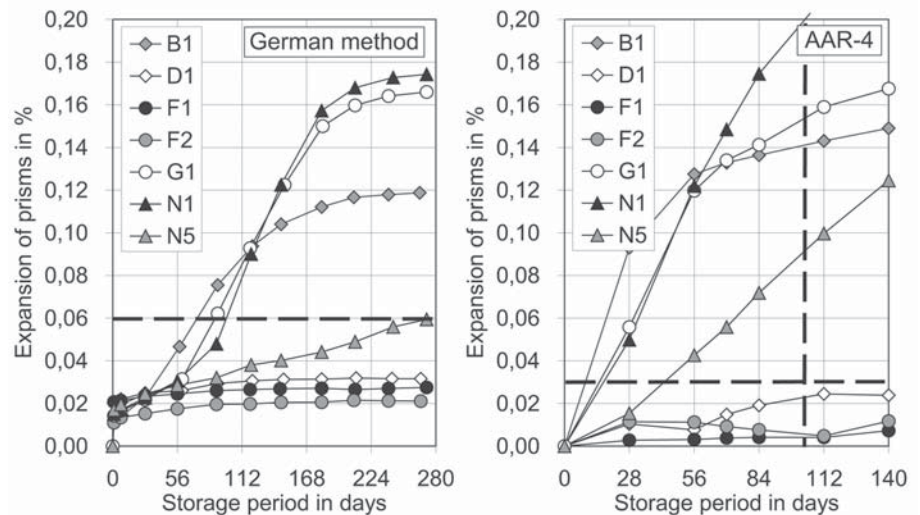


Fig. 2: Results from the PARTNER project for different European aggregates in the AAR-4 and the German concrete testing methods, giving corresponding classifications (limit values: 0.03 % expansion after 15 weeks for AAR-4, 0.06 % expansion after 9 months for the German method)

to the RILEM assessment scheme as a fourth step and shall enable the evaluation of the ASR-potential of particular concrete mixes for use in concrete structures. In this way even potentially alkali reactive aggregates could be used, e. g. in combination with cements with low effective alkali content or with portions of certain supplementary cementitious materials like fly ash, to produce concrete mixes with a minimized potential for a deleterious ASR.

At the Research institute of the Cement Industry in Düsseldorf a performance test especially aiming at the evaluation of concrete mixes for highway structures is currently being developed. This testing procedure has to simulate the exposure of concretes to de-icing salts and hence an external supply of alkali ions. Recent results imply that a deleterious ASR could be worsened under these conditions.

Chromate reduction is still a challenge for the cement industry

The diversity of reducers is the basis for different chromate reducing strategies

It is well known that handling of wet cement and wet cement-containing preparations may, without proper precautionary measures, lead to dermatitis amongst workers in the construction industry. This is due to the irritant and alkaline nature of wet cement paste and due to the allergic reaction due to water-soluble chromium(VI). As a consequence, the cement producers have been committing themselves together with the cement consuming industries for a long time to mini-

mize the risk of dermatitis amongst construction workers by appropriate information, education and promotion of the use of individual protection in case of manual application of cement-preparations.

Although existing statistical evidence about cement dermatitis does not provide an unambiguous link between chromium(VI) reduction and the incidence of related cases of dermatitis, the chromate content in cement has been limited according to recent European legislation.

According to the European Directive 2003/53/EC cements and cement-containing preparations may not be used or placed on the market if they contain more than 2 ppm of water-soluble chromium(VI). This does, however, not apply, when the cement or the preparations are handled in controlled, closed and totally automated processes, where the possibility of skin contact is not given. The aim of the Directive on market restrictions for cements is to decrease skin diseases due to chromium(VI). However, the future success of these measures is questionable: It is well known that irritating allergies can not be reduced by lowering the chromium content of cement and cement containing preparations.

As a consequence of the Chromate Directive, chromate reducing agents have to be added to most of the cements. Therefore the European cement industry has invested in



Fig. 1: Different solid reducing agents for chromium(VI) in cement. From left to right: Two iron(II) sulfate heptahydrates, two iron(II) sulfate monohydrates and two tin(II) sulfates

equipment to add reducing agents. The total annual costs for a typical cement plant are from 500 000 Euro to 1 000 000 Euro.

Reducing agents under practical conditions

Chromate reduction is a technical, financial and human resources consuming challenge for the cement industry. Very early it became obvious that a successful implementation of Directive 2003/53/EC requires detailed knowledge of the physical, chemical and analytical background of chromate reduction. This is because the chemical, thermal and mechanical stressing of the chromate reducers during addition to cement and cement-containing preparations influences their effectiveness. Even the test method for the determination of the water-soluble chromium(VI) during the use of cements or cement-containing preparations under practical conditions plays an important role. In the Research Institute of the Cement Industry these aspects of chromate reduction have been investigated at an early stage.

Increasing diversity of reducing agents

Most of the European cements contain more than 2 ppm of water-soluble chromium(VI). To fulfil the requirements of the European Directive 2003/53/EC this water-soluble chromium(VI) has to be reduced by means of a reducing agent. Ferrous sulfate and tin(II) sulfate were the most often used reducing agents for cement. Since the early stages of chromate reduction in cement mainly iron(II) sulfate heptahydrate has been used. In recent years iron(II) sulfates with lower crystal water content have also successfully been tested for this

purpose. Especially iron(II) sulfate monohydrates are promising reducing agents. Tin(II) sulfate is available in the form of fine-grained crystalline material or very fine powder and it is on offer as suspensions and solutions. According to investigations of the Research Institute of the Cement Industry the different reducing agents display differing advantages for the wide variety of addition conditions. This diversity of reducers is the basis for finding the most suitable reducing agent for a certain chromate reducing strategy (Fig. 1).

Principle aspects of the effectiveness of reducing agents

For the actinism of all reducing agents the chemical availability of the bivalent iron (Fe^{2+}) and bivalent tin (Sn^{2+}), respectively, is essential. The availability of these bivalent ions during the use of cement under practical conditions depends on the degree of dissolution of the reducing agents in the mixing water.

The dissolution of the reducing agents in the fresh cement/water suspension is affected by two contributing factors: their intrinsic passive solubility and the mechanical acceleration of the dissolution during the process of mixing cement, water and other constituents of the intended cement-based building material. Particularly the grinding effect of sand and gravel in fresh mortar and concrete increases the solubility of the reducing agent due to the enlargement of the chromate reducer particle surface. The passive solubility itself can be affected by different factors. The most significant one is the stressing of the reducers during addition to the cement and their aging in the course of storing the cement/reducer mixture.

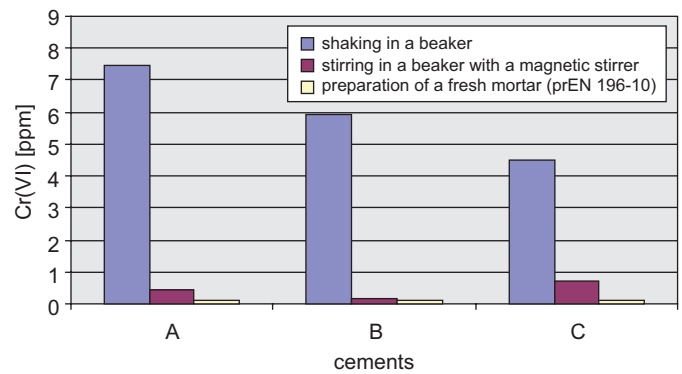


Fig. 2: The influence of increasing mechanical assistance of the dissolution on the effectiveness of the reducing agents during suspension of three different cements

Importance of the test method

However, the actual efficiency of the chromate reducing agent can only be correctly represented by a test method that realistically simulates the dissolving of the reducer particles under practical conditions. The dissolving even of passivated reducing agents, and therefore their effectiveness, is mechanically assisted during the practical application of cement in mortar and concrete by the pulverizing action of the aggregate (Fig. 2). This crucial circumstance was taken into account during the compilation of the new European test method for determining the content of water-soluble chromium(VI) in cements described in prEN 196-10. This eagerly awaited harmonized European standard EN 196-10 for verifying the successful implementation of European Directive 2003/53/EC for cements will be published shortly. However, from further current investigations it can be concluded that for cement-containing preparations possibly a different or a modified test method might be necessary.



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European Cement Research Academy

Tannenstr. 2 40476 Düsseldorf
P.O. Box 30 03 32 40403 Düsseldorf
Germany

Phone: +49 (0)211 2 39 83 8-0
Fax: +49 (0)211 2 39 83 8-500

info@ecra-online.org
www.ecra-online.org