Cement Type Influence on Alkali-Silica Reaction in Concrete with Crushed Gravel Aggregate

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Abstract. Alkali-silica reaction is one of the chemical reactions which have a significant influence for durability of concrete. During alkali and silica reaction, silicon located in aggregates of the concrete, reacts with high alkali content. This way in the micropores of concrete is forming hygroscopic gel, which at wet environment, expanding and slowly but strongly destroying concrete structures. The goal of this paper- to determine the influence of cement type on alkali-silica reaction of mortars with crushed gravel. In the study crushed gravel with fraction 4/16 mm was used and four types of cements tested: CEM I 42.5 R; CEM I 42.5 SR; CEM II/A-S 42.5; CEM II/A-V 52.5. This study showed that crushed gravel is low contaminated on reactive particles containing of amorphous silica dioxide. The expansion after 14 days exceed 0.054 %, by RILEM AAR-2 research methodology (testing specimen dimension 40×40×160 mm). Continuing the investigation to 56 days for all specimens occurred alkaline corrosion features: microcracking and the surface plaque of gel. The results showed that the best resistance to alkaline corrosion after 14 days was obtained with cement CEM I 42.5 SR containing ash additive, and after 56 days with cement CEM II/A-V 52.5 containing low alkali content. The highest expansion after 14 and 56 days was obtained with cement CEM I 42.5 R without active mineral additives.

1. Introduction

Today, concrete is the most popular building and construction material. Concrete is the prime ingredient in the world’s largest and most prominent structures and landmark edifices, including hydropower dams, coastal defense works, telecommunication, office skyscrapers, theatres, hotels and casinos, nuclear power plants, oil and gas drilling and productions rigs, sea ports and harbors, airports and runways, as well as in numerous but perhaps less glamorous motorway and railroad structures, industrial floors, utility structures and facilities, residential dwellings, even bath and shower tubs, kitchen sinks and flower pots, garden ornaments and home decorations [1].

Concrete is supposed to last for decades and/or centuries due to its excellent durability characteristics [2]. Nowadays, concrete deterioration has become a major problem throughout the world [3]. Environmental risks may involve weathering action, chemical attack, alkalinity, carbonation, freezing and thawing and abrasion. It is reported in literature that not only placement, curing and service environment influence the durability characteristics of concrete but proportioning and interaction between concrete ingredients significantly control the durability and life of the concrete. Different mineral admixtures are often added in concrete to improve the durability, rheology of fresh concrete, and mechanical properties of hardened concrete [2]. Admixtures are added in concrete to improve the quality of concrete. Mineral admixtures which possess certain characteristics through which they influence the properties of concrete differently [4].
It is well known that changes and deterioration in concrete limit service life of the concrete structures. Addition of mineral admixtures to concrete not only reduces the cement content thereby reducing heat of hydration, but also inhibits deterioration of concrete making it durable and better quality concrete by reducing pore size or permeability and improving resistance against sulfate attack, carbonation, chloride attack on reinforcement, freezing and thawing, abrasion, fire, acid and of course alkali-silica reaction (ASR) [5]. ASR, discovered in the 1940s, is a long-term chemical reaction and detrimental to a concrete structure. ASR is characterized by the breakdown of the siloxane bonds (Si–O) in poorly crystallized silica of aggregates, which is attacked by the hydroxyl ions OH\(^-\) from the pore solution in the hardened cement paste [6].

Concrete structures are often subject to degradation due to alkali silica reaction (ASR) [7]. Alkali-silica reaction has become one of the most challenging problems in concrete technology today [8].

ASR is a problem that has a well documented history, not just in the United States, but worldwide. Several countries and states in the U.S. have had problems with ASR. ASR is the reaction between alkali hydroxyl ions in portland cement and certain siliceous minerals found in the aggregate, such as opaline chert, and strained quartz [9].

Aggregate reactivity is evaluated by considering one or more of the following options [10]:

- field performance history;
- petrographic assessment;
- chemical composition.

The product of this reaction is a gel that surrounds the aggregate in the concrete matrix. This gel can appear as a dark border around the aggregate or a white spot within the aggregate, sometimes the white area extending into the concrete matrix. With the introduction of moisture, the gel expands and causes the characteristic cracking of the concrete [9].

ASR damage is a result of a number of sequential reactions, including: (1) dissolution of metastable silica, (2) formation of nano-colloidal silica sol, (3) gelation of the sol, and (4) swelling of the gel:

\[
(SiO_2)_{\text{solid}} \rightarrow (SiO_2)_{\text{aqueous}} \rightarrow (SiO_2)_{\text{sol}} \rightarrow (SiO_2)_{\text{gel}} \rightarrow \text{swelling of gel} \quad (1)
\]

Alternatively, a highly degraded (SiO\(_2\))solid may transform directly into (SiO\(_2\))gel, as long as sufficient but not excessive cross-linking is maintained between silica chains. Among these reactions, silica dissolution is often the slowest, and as such, primarily controls the rate of ASR in concrete. In addition to silica dissolution, swelling of the gel depends on availability of moisture and mass transport properties of concrete, and could limit the rate of ASR damage in dry and dense concrete [11].

The alkali-silicate gel absorbs water from surroundings and increases in volume. Once the pressure is larger than the tensile strength of concrete, cracks occur and lead to additional water permeation through migration and gel swelling. Extensive expansion and severe cracking are caused by high-swelling gel. The rate of the expansion depends on the chemical composition and the available alkali content of the cement matrix [12]. The pressure induces microand, eventually, macro-cracking of the structure when the tensile strength of concrete is exceeded. Overall, three factors are indispensable for ASR [13]:

- alkali content in the pore solution;
- poorly crystallized silica in aggregates;
- moisture content.

Common symptoms of ASR-affected structures are map cracks, longitudinal cracks, exudation, pop out, buckling and spalling [14].

This paper reports the results of a systematic study on the effect of different mineral admixtures in the resistance of Alkali corrosion. In the mortar mixture was amended different cement types with mineral additives, to determine which cement are suitable in practice while operating the concrete constructions in unfavorable conditions.
2. Materials and test methods
Portland cements CEM I 42.5 R; CEM I 42.5 SR; CEM II/A-S 42.5; CEM II/A-V 52.5 were used for the test. Cements specifications are presented in Table 1.

### Table 1. Various types of cements and their characteristics.

| Cement characteristics | CEM I 42.5 R | CEM I 42.5 SR | CEM II/A-S 42.5 | CEM II/A-V 52.5 |
|------------------------|-------------|-------------|----------------|-----------------|
| **Mechanical and physical** |            |            |                |                 |
| Compressive strength, MPa | after 2 days | 28 ± 2 | 19 ± 3 | 22 ± 3 | 31 |
|                          | after 28 days | 54 ± 3 | 54 ± 4 | 52 ± 3 | 58 |
| Setting time – start, min | 160 | 170 | 160 | 150 |
| Specific surface, (cm²/g) | 3700 | 3200 | 3500 | 3000 |
| **Chemical** |            |            |                |                 |
| Loss on ignition, % | 1.4 | 0.4-1.0 | 1.4 | 1.1 |
| Insoluble residue, % | 0.4 | 0.2 | 0.4 | 0.3 |
| Sulphate content, % | 2.8 | 2.3-2.5 | 2.7 | 3.5 |
| Chloride content, % | 0.003 | 0.01-0.03 | 0.007 | 0.08 |
| Alkali content, % | < 0.8 | < 0.6 | < 0.8 | < 0.4 |

Gravel aggregate fraction 4/16 mm were used for the test. Gravel aggregate specifications are presented in Table 2.

### Table 2. Gravel aggregate characteristics.

| Characteristics (fraction d/D) mm | Value |
|----------------------------------|-------|
| Particle size | 4/16 |
| Particle form: | |
| Flatness indicator | < 15 of mass % |
| Form indicator | < 15 of mass % |
| Bulk density | < 1.39 Mg/ m³ |
| Particle density | < 2.70 Mg/ m³ |
| Splitting indicator MSK | < 12 of mass % |
| Water absorption WA24 | < 2.0 of mass % |
| Resistance to freezing and thawing | < 1.0 of mass % |
| Alkaline reactivity Rfrac. | < 2.0 of mass % |

The reactivity of aggregates was tested according to RILEM RECOMMENDED TEST METHOD: AAR-2 (the ultra-accelerated mortar-bar test). This method is used to assess the level of reactivity of the aggregates. According to AAR-2 method procedure mortar bars (40×40×160 mm) hardened in water of 80 °C are kept in 1M NaOH solution for 14 days at 80 °C and their expansion is measured. Changes in the specimen dimensions are determined in the test. Test criteria determines the linear expansion limit 0.054 % from the initial length of 40×40×160 mm prisms, which is related to the cracking of material structure and can have negative impact on the concrete durability [15].When the aggregates contain slowly reacting rocks, the hardening time should be longer (21 or 28 days).

The ultra-accelerated AAR-2 can be used for testing aggregate mixes, however the aggregate particle size shall be from 125 μm to 4 mm. Coarse aggregate is crushed by jaw crusher according to specific requirements presented in Table 3 and washed.
Table 3. Aggregate sifting requirements [16].

| Sieve size when the aggregate fraction goes through | Sieve size when the aggregate fraction remains on the sieve | Sieve size when the aggregate fraction goes through |
|---------------------------------------------------|----------------------------------------------------------|---------------------------------------------------|
| 4 mm                                              | 2 mm                                                     | 10%                                               |
| 2 mm                                              | 1 mm                                                     | 25%                                               |
| 1 mm                                              | 500 µm                                                    | 25%                                               |
| 500 µm                                            | 250 µm                                                    | 25%                                               |
| 250 µm                                            | 125 µm                                                    | 15%                                               |

Washed samples are dried at 100–110 °C for 16 hours. The mortar was made of 1 part cement and 2.25 parts aggregate. 600 g of cement and 1350 g of dry aggregate is required for three prisms (40 × 40 × 160 mm). 6 prisms with each aggregate were moulded. The water/cement ratio was 0.47. The mortar flow diameter must be from 205 to 220 mm. Polycarboxylate-based superplasticizer was used to obtain the required mortar flow.

Mix compositions per one test specimen are presented in Table 4. The mortar was made in accordance with cement class requirements as per EN 196-1 [18].

Table 4. Amount of materials per specimen.

| Mix     | Cement, g | Aggregate, g | Water, ml | Plasticizer, g | W/C | Flow diameter, mm |
|---------|-----------|--------------|-----------|----------------|-----|-------------------|
| A- CEM I 42.5 R | 1200     | 2700         | 564       | 3.6            | 0.47 | 205               |
| B- CEM I 42.5 SR | 1200     | 2700         | 564       | 2.4            | 0.47 | 205               |
| C- CEM II/A-S 42.5 | 1200    | 2700         | 564       | 3.6            | 0.47 | 208               |
| D- CEM II/A-V 52.5 | 1200     | 2700         | 564       | 2.4            | 0.47 | 210               |

The elongation of specimens is measured by a digital dial indicator with the scale interval of 0.001 mm. The indicator is fixed in the frame (Figure 1a) where the prisms are placed. The frame and indicator axles are inserted into the moulded holes at the ends of the specimen.

Figure 1. Used equipment: a- Digital dial indicator and frame; b- Stainless steel container; c- Climatic chamber

Four prisms with each aggregate were selected for the test. The prisms are immersed into water at 80 °C. After 24 hours the distance between the inner ends of the metal pins are measured and the specimens are placed into stainless steel containers (Figure 1b) with 1 M NaOH alkali solution at 80 °C.

Containers with the specimens are placed into climatic chamber (Figure 1c) where 80 ± 2 °C temperature is maintained. The elongation of specimens is measured regularly. When the specimens are removed after 24 ± 2 hours hardening in water at 80 °C temperature, the length, i.e. The zero reading \( L_0 \) is recorded; this is a reference reading for further measuring of specimen expansion. After the specimens are placed into 1 M NaOH alkaline solution at 80 °C, the specimen dimensions \( L_n \) are recorded after 1, 3, 6, 9, 12, 14, 21, 28, 35, 42, 49, 56 days ± 2 hours.
The linear expansion of each specimen is obtained by calculating the difference between the length of the specimen at each period of measurement ($L_n$) and zero measurement ($L_0$), to the nearest 0.001% of the effective length, as follows [16]:

$$\text{Expansion,} \% = \frac{100 \cdot (L_n - L_0)}{l}$$

(2)

Where:

- $L_0$ - measurement of the specimen just before the immersion into sodium hydroxide solution (zero reading),
- $L_n$ - a reading taken at each period of soaking in sodium hydroxide solution, n being the number of days counted from the zero reading.
- $l$ - distance between the inner ends of the metal pins, measured to the nearest of 0.1 mm.

3. Test results and analysis

The test (AAR-2) of A, B, C and D mixes with gravel aggregate and different cements after 14 and 56 testing days gave the results presented in Figure 2 (after 14 testing days) and Figure 3 (after 56 testing days).

Expansion of A and C mixes specimens placed in 1 M NaOH alkaline solution at 80 °C after 14 testing days exceeded the linear expansion limit 0.054 % according to AAR-2. Therefore, we can state that used crushed gravel aggregate is reactive and classified as a potentially reactive aggregate. Expansion of B and D mixes did not seek to the linear expansion limit 0.054 %. According to data of Table 1 we can strongly indicate that these results were influenced by the smaller alkali content of cement: A and C mixes contains <0.8 % alkali content, B and D accordingly contains <0.6 % and <0.4 % alkali content.

![Figure 2](image)

**Figure 2.** Expansion of A, B, C and D mixes with crushed gravel aggregate and different cements after 14 testing days.

Continuing the investigation until 56 days tendencies remained the same. The expansion of A and C mixes were higher than B and D mixes. Reason is the same- alkali content of cement.
Figure 3. Expansion of A, B, C and D mixes with crushed gravel aggregate and different cements after 56 testing days.

Figure 4 presents the dependence of expansion on alkali content of cement. As we can see the tendency after 14 and 56 days remain the same, so it can be stated that expansion of mortar prisms directly depends on the alkali content of cement (chemical composition of cement).

Figure 4. Expansion dependence on alkali content of cement.
4. Conclusions
The test with gravel aggregate after 14 testing days gave the results that during the first 14 days alkaline corrosion most occurred in mixtures with cement without mineral additives (CEM I 42.5 R) and cement with slag additive (CEM II/A-S 42.5), whose average expansion attaining respectively 0.055% and 0.054%. The lowest average expansion after 14 testing days- 0.044 % fixed with cement containing ash additive (CEM I 42.5 SR). After 56 testing days alkaline corrosion most occurred in mixture with cement without mineral additives (CEM I 42.5 R)- 0.148 %, the lowest average expansion after 56 testing days fixed with cement containing low alkali content (CEM II/A-V 52.5)- 0.116%.

Alkali induced corrosion tests with gravel aggregate and four types of cements show visually microcracks, which spread in different directions on the surface and surface gel deposits were observed.

It was found that in accordance with AAR 2 methodology investigated gravel aggregate classified as potentially alkali-reactive aggregates. Mix A (CEM I 42.5 R) and mix C (CEM II/A-S 42.5) expansion after 14 days exceed 0.054%. This is related to the chemical composition of the cement. The A and C mix cements have the highest alkali content (<0.8 %) while cement CEM I 42.5 SR of mix B has <0.6% and cement CEM II/A-V 52.5 of mix D has <0.4% alkali content.

The results showed that the best cement for alkaline corrosion conditions is cement (CEM II/A-V 52.5) containing low alkali content. Cement CEM I 42.5 R without mineral additives can be used, just only some precautions should be done (moisture, temperature etc.). Probably cement CEM I 42.5 R does not limit ASR.

References
[1] Broekmans M 2012 Deleterious Reactions of Aggregate With Alkalis in Concrete Reviews in Mineralogy & Geochemistry Vol. 74 pp. 279-364
[2] Ayub T, Shafiq N and Khan S U 2013 Durability of Concrete with Different Mineral Admixtures: A Review International Journal of Civil, Environmental, Structural, Construction and Architectural Engineering Vol:7 No:8
[3] Isneini M 2016 A Study on ASR Expansion Mitigation by Mineral Admixtures and LiOH·H2O A Dissertation Department of Civil and Structural Engineering Graduate School of Engineering Kyushu University
[4] Khan S U, Nuruddin M F, Ayub T and Shafiq N 2014 Effects of Different Mineral Admixtures on the Properties of Fresh Concrete The Scientific World Journal Vol. 2014 11 pages
[5] Thomas M, Hooton R D, Rogers C and Fournier B 2012 50 Years Old and Still Going Strong Concrete International vol. 34 pp. 35-40
[6] Wua T, Temizer I and Wriggers P 2014 Multiscale hydro-thermo-chemo-mechanical coupling: Application to alkali–silica reaction Computational Materials Science 84 381–395
[7] Chappex T and Scrivener K 2012 Alkali fixation of C–S–H in blended cement pastes and its relation to alkali silica reaction Cement and Concrete Research 42 1049–1054
[8] Aquino W, Lange D A and Olek J 2001 The influence of metakaolin and silica fume on the chemistry of alkali-silica reaction products Cement and Concrete Composites 23 485-493
[9] Ballard Z J, Caires W S and Peters S R 2008 Alternate mitigation materials for alkali-silica reaction (asr) in concrete Colorado department of transportation dtd applied research and innovation branch Report No. CDOT-2008-10
[10] Thomas M D A, Fournier B and Folliard K J 2012 Selecting Measures to Prevent Deleterious Alkali-Silica Reaction in Concrete: Rationale for the AASHTO PP65 Prescriptive Approach U.S. Department of Transportation Federal Highway Administration Report No. FHWA-HIF-13-002
[11] Rajabipour F Giannini E Dunant C Ideker J H and Thomas M D A 2015 Alkali–silica reaction: Current understanding of the reaction mechanisms and the knowledge gaps Cement and Concrete Research 76 130–146
[12] Islam M S and Akhtar S 2013 A Critical Assessment to the Performance of Alkali-Silica Reaction (ASR) in Concrete Canadian Chemical Transactions Vol. 1 Issue 4 Page 253-266
[13] Lemarchand E, Dormieux L and Ulm F J 2005 Micromechanics investigation of expansive reactions in chemoeelastic concrete *Philosophical Transactions of the Royal Society Mathematical Physical and Engineering Sciences* 363(1836): p. 2581-2602

[14] Thomas M D A, Fournier B, Folliard K, Ideker J and Resendez Y 2007 The use of lithium to prevent or mitigate alkali-silica reaction in concrete pavements and structures *Publication no. FHWA-HRT-06-133* The Transtec Group Inc. Austin, TX

[15] Bumanis G, Bajare D, Locs J, Korjakins A 2013 Alkali-silica reactivity of foam glass granules in structure of lightweight concrete *Construction and Building Materials* Volume 47, 2013, Pages 274-281

[16] RILEM recommended test method: AAR-2. Detection of potential alkali-reactivity. Accelerated mortar-bar test method for aggregates, pp. 1-15