Alkali Silica Reaction In The Presence Of Metakaolin - The Significant Role of Calcium Hydroxide

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Abstract. Reducing the internal corrosion, which is the result of reactions between alkalis and reactive aggregates is especially important in ensuring durability properties of concrete. One of the methods of inhibiting the reaction is using some mineral additives which have pozzolanic properties. This paper presents the efficacy of high-reactivity metakaolin in reducing expansion due to alkali-silica reaction. It was demonstrated that metakaolin in the amount from 5% to 20% by mass of Portland cement reduce linear expansion of mortar bars with opal aggregate. Nevertheless, the safe expansion level in the specimens, classified as non-destructive to concrete, was recorded for the mortars prepared with 20% addition of metakaolin. Depletion of free calcium hydroxide content was considered as one of the most beneficial effects of metakaolin in controlling alkali silica reaction. Based on thermogravimetric analysis (TGA) performed on mortar bars with and without metakaolin the differences in portlandite content were determined. Microstructural observation of the specimens containing metakaolin indicated the presence of a reaction products but fewer in number than those forming in the mortars without mineral additives.

1. Introduction

The alkali-silica reaction (ASR) is a type of an internal concrete corrosion which occurs within its entire volume. The negative effects of ASR were observed in elements such as concrete sidewalks, concrete pavements, bridges, dams and other structures exposed to humidity over an extended period of time [1,2]. The product resulting from these chemical reactions is sodium-potasium-calcium silica gel, able to absorb water, which in turn results in the increase of the volume of those products [3]. The gel causes pressure to occur that exceeds the concrete's tensile strength, therefore causing it to expand and crack. Mineral additives, i.e. silica fume, fly ash, granulated blast furnace slag, chalcedony dust, metakaolin or ground clay brick which are used in the form of partial substitutes of cement, show the ability to diminish the negative results of alkali corrosion [4-9]. In a pozzolanic reaction Ca(OH)2 is consumed and hydrated calcium silicates with a low C/S ratio is created. It is assumed that decreasing the alkalinity of a pore solution by taking advantage of the increased ability of the silicate phases to adsorb sodium and potassium ions and by decreasing the amount of portlandite is what determines the ability of the pozzolanic additives to decrease the expansion caused ASR [10,11]. Over recent years, reports have surfaced concerning the key role that aluminium ions play in ASR. Research and tests done by some scientists show an increased efficacy of the mineral additives which contain aluminium compared to the additives of pure silica e.g. silica fume [12]. This Supplementary Cementitious Materials (SCMs) may improve the ASR inhibition by forming calcium silicate hydrate gel containing aluminium which has more potential to bind alkalis [13]. Several papers also indicate a high potential
of lithium compounds, such as lithium nitrate or lithium hydroxide, in mitigating alkali-silica reaction in concrete [14-16].

The objective of this work was to study the effect of high reactivity metakaolin on mitigating ASR. A minimum quantity of the mineral additive was determined, which decreases the harmful expansion of mortars as a result of the alkali-silica reaction. The results of the expansion measurements were compared with the microstructures of mortars and the composition of the gels created. The content of free calcium hydroxide was quantified to investigate the differences and the trends in the content of Ca(OH)2 in mortars with and without metakaolin undergoing ASR.

2. Materials
The chemical composition of metakaolin, obtained as a result of the thermal activation of kaolin (T=750°C, t=2h) and the composition of Portland cement CEM I 42.5R used in the tests are presented in Table 1. The contents of alkali in Portland cement in the form of sodium equivalent Na2Oe was 0.79%.

Table 1. Chemical composition of cement and metakaolin

| Material   | SiO2  | Al2O3 | Fe2O3 | CaO | MgO | SO3 | SrO  | K2O | Na2O | TiO2 | LOI  | N.s.p |
|------------|-------|-------|-------|-----|-----|-----|------|-----|------|------|------|------|
| Cement     | 18.47 | 5.40  | 2.96  | 63.35 | 1.42 | 3.34 | -    | 0.93 | 0.18 | 0.45 | 3.00 | 1.00 |
| Metakaolin | 55.80 | 41.06 | 0.73  | 0.09 | 0.10 | -   | 0.11 | 0.92 | 0.00 | 0.69 | 0.31 | -    |

aLOI – loss of ignition,  
bN.s.p – parts non-soluble in HCl and Na2CO3

The aggregate used in the mortars was standard quartz sand with 6% opal aggregate with the fraction of 0.5-1 mm. The mineral composition of the aggregate was presented in table 2.

Table 2. Opal aggregate composition

| Constituent | opal | chalcedony | quartz | tale | goethite | pores |
|-------------|------|------------|--------|------|----------|-------|
| Content [% vol.] | 65   | 30         | 2      | 1.5  | 1        | 0.5   |

3. Experimental methods
Bars with diameter of 25x25x250 mm were formed from mortars with the aggregate cement ratio of 2.25 and the w/c=0.5 in accordance with the method determined in the ASTM C1260 standard [17]. The metakaolin was introduced in the amount of 5%-20% by mass of cement. Mortar bars without the mineral additive were also formed. After removing from the moulds the specimens were immersed in water, the temperature of which was 80±2°C, for 24h. Then, the mortars were stored for 28 days in the solution of 1M NaOH, T=80±2°C. Expansion measurements of linear changes were taken using Graf-Kaufman apparatus. The expansion of the mortars was determined relative to their initial length, measured after storing the mortars in water for 24h. The measurements were taken every day until the 14th immersion day in a normal sodium hydroxide, then after 21 days and 28 days. The mortars with the greatest content of a mineral additive were subject to observing their microstructure under a scanning electron microscope coupled with the X-ray microanalyser (EDS), subsequently after 2, 7, 14 and 28 days of immersion. The samples for the TGA analysis were obtained by breaking the mortar without additive and with the highest metakaolin content after 0, 2, 7, 14 and 28 days of storing it in
conditions identical to those used in the case of measuring the expansion of mortar bars. Additionally the content of Ca(OH)$_2$ was measured in the mortars in which the entire aggregate was composed of non-reactive quartz sand. The pieces of up to 5g in weight were taken from the middle of the broken mortar and crushed to pass the 0.063mm sieve [18]. The reaction was being stopped using an addition of acetone, then the material was broken and dried in a stream of cold air. The TGA measurement of Ca(OH)$_2$ content were performed with a SDT Q600 thermogravimetric analyzer. The thermal analysis was performed in a nitrogen gas atmosphere within a range of temperatures from 20 to 1050 °C with the heating rate of 10°C/min. The contents of portlandite were determined based on the TGA decomposition profile of Ca(OH)$_2$.

4. Results and discussion
4.1. Mortar expansion
Figure 1 presents the results of linear changes in bars of mortar with metakaolin (MK) and without a mineral additive (OPC) stored in the conditions determined by the ASTM C1260 standard. The expansion of reference mortars exceeded the expansion limit, according to ASTM C1260 standard, which amounts to 0.2% as early as after 2 days. After 14 days of immersion, the linear changes of mortars reached the level of approx. 0.73%, and after 28 days approx. 0.85%. Linear elongation of the mortars decreased after introducing metakaolin. Together with the increase in the contents of a mineral additive, expansion decreased. When 15% and 20% of the cement mass was replaced by metakaolin, the 14-day expansion was lower by 92% and 98% respectively relative to the reference sample. However, after 28 days only 20% of metakaolin successfully protected the mortar against the after effects of the ASR. The expansion of mortars was significantly lower than 0.1%, the expansion threshold established by the standard.

![Figure 1](image)

**Figure 1.** Expansion behaviour of mortar bars without and containing 5% to 20% metakaolin

4.2. Analysis of calcium hydroxide content
Figure 2 shows the percentage of portlandite content versus time as a percentage of the initial mass of mortar samples in the TGA pan. The content of free portlandite was calculated based on the mass loss correspond to the dehydroxylation of portlandite in accordance with equation 1

\[
CH_f = ML \times \frac{M_{Ca(OH)_2}}{M_{H_2O}}
\]

(1)
where:

- CH\(_f\) – portlandite content
- ML - mass loss corresponds to the dehydroxylation of portlandite,
- M\(_{Ca(OH)2}\) – portlandite molar mass
- M\(_{H2O}\) - water molar mass

\[ \text{where:} \]

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**Figure 2.** Comparison of Ca(OH)\(_2\) content in mortars with opal and 20% content of metakaolin

The amount of Ca(OH)\(_2\) in the mortars with opal aggregate increased in the initial periods, reaching the highest value after 2 days of the mortars’ immersion in 1M NaOH. Further on into the reaction, a decrease in the percentage of Ca(OH)\(_2\) was observed. Probably calcium hydroxide was gradually washed out, which was proven by a similar course of the curve, recorded for the mortars with non-reactive aggregate. However, smaller contents of Ca(OH)\(_2\) may result from the consumption of calcium hydroxide in the reaction of alkali with opal aggregate.

In the mortars with the addition of metakaolin, the content of Ca(OH)\(_2\) was smaller compared to the mortars without a mineral additive. When comparing the percentage of free calcium hydroxide, approx.70% less of Ca(OH)\(_2\) was found in the mortars containing metakaolin. This arised from the pozzolanic properties of metakaolinite. Active silica react with calcium hydroxide, which is a product of the hydration cement phases. The content of calcium hydroxide in the mortar with metakaolin increased up to the 7th day of storing in a solution of sodium hydroxide, and then decreased insignificantly. It needs to be noted, that the differences in the content of calcium hydroxide in the mortars that occur as the reaction progresses were very small, they practically remained steady. However, it needs to be indicated, that the consumption of portlandite in the ASR can be so low compared to the total amount of Ca(OH)\(_2\) produce by the cement hydration that it is not detectable by the TGA [19]. However, critically, in both cases small changes in the amount of portlandite were found, which additionally indicates that the tightness of the mortars with metakaolin is greater.

**4.3 Microstructure**

The microstructures of the mortars with reactive aggregate, without and with 20% metakaolin were tested after 2-28 days of being immersed in 1M NaOH. A significant number of cracks of both the aggregate and the cement paste were observed in the mortars without additive. The cracks appeared as a result of the swelling properties of the alkali silica gels created. The products were observed on the aggregates particle surfaces and in the interface between reactive aggregate and the paste (Figure 3).
The morphological and composition of reaction products were characteristic of alkali silica reaction occurring at elevated temperatures [20]. It was observed, that with the reaction progressing, the number of corrosion centres increased significantly (Figure 3a-b, d-e) and the products of the reaction were showing great alkali contents (Figure 3c, 3f).

The microstructural observations showed differences in the amount of reaction products between the mortars containing 20% of metakaolin and those with no mineral addition. The result of observation confirm the compact microstructure of mortar (Figure 4a-c). Small amount of micro-cracks were probably a result of specimen preparation for SEM observation.

![Image](image1.png)

Figure 3. The microstructure of the mortars without the addition of metakaolin after (a) 2 days, (b) 7 days, (d) 14 days, (e) 28 days; EDS spectrum at (c) location 1, (f) location 2
Figure 4. The microstructure of the mortars with metakaolin after (a) 2 days, (b) 7 days, (d) 14 days, (e) 28 days; EDS spectrum at (c) region 1, (f) region 2.

However, small amounts of the reaction products created, filled the area of the reactive aggregate, crystallised as lamellar shapes (Figure 4e). Some micro-cracks were observed in interfacial zone after 14 and 28 days (Figure 4d, 4e). In terms of morphology, the gels observed in the mortars with metakaolin showed no significant difference compared to those created in reference mortars, however, they were characterized by a smaller amount of sodium and potassium ions (Figure 4c, 4f). Less alkali content in reaction products were attributed to the high potential of alkali binding by C-S-H and C-A-S-H gels [13]. The smaller amount of the alkaline gel created is probably what influences the observed smaller expansion values in the mortars with metakaolin [21].

5. Conclusions
- Adding metakaolin to mortars as partial replacement of cement reduces the expansion of the mortars, which is a result of the reactivity of opal aggregate. Introducing 15% to 20% of a mineral additive into mortars is sufficient to control deterioration expansion. Moreover, the greater the contents of metakaolin, the later the expansion of mortars is observed. Only for the greatest amount of metakaolin, the linear expansion of mortars does not exceed the potential
aggregate reactivity threshold of 0.1% (according the ASTM C1260) even after measurements performed to 28 days.

- Significant differences between the contents of free calcium hydroxide in the mortars with a mineral additive and in the mortars without metakaolin prove that calcium hydroxide is consume in pozzolanic reaction. No evident dependences were found between the contents of Ca(OH)₂ in the mortars undergoing ASR and the changes in the linear expansion of mortars with metakaolin versus time. This can indicate that the consumption of Ca(OH)₂ is low enough not to be easily detectable.

- In the presence of metakaolin, aggregate reactivity products are created similar in terms of morphology to traditional ASR gels, however, the amount of swelling products is small, which is indicated by the compact microstructure, negligible number of micro-cracks and corrosion centres, while the gels that occurred in place of the reactive aggregate are hydrated calcium silicates with low sodium contents. It is well understood, that binding alkali and calcium hydroxide in the pozzolanic reaction decreases the concentration of hydroxyl ions aggressive towards the aggregate.

References

[1] K. J. Folliard, M. D. Thomas, K. E. Kurtis, “Guidelines for the use of lithium to mitigate or prevent ASR,” FHWA Report: FHWA-RD-03-047, 2003.
[2] Z. Owsiak, “The internal corrosion of concrete,” Kielce, Poland, 2015.
[3] S. Diamond, R. S. Jr. Barneyback, L. J. Struble, “On the physics and chemistry of alkali-silica reactions,” Proceedings of the Fifth Conference on Alkali-Aggregate Reaction in Concrete, National Building Research Institute, Pretoria, South Africa, pp. 1-11, 1981.
[4] A. M. Boddy, R. D. Hooton, M. D. A. Thomas, “The effect of the silica content of silica fume on its ability to control alkali–silica reaction,” Cement and Concrete Research, vol. 33, pp. 1263-1268, 2003.
[5] M. H. Shehata, M. D. A. Thomas, “Use of ternary blends containing silica fume and fly ash to suppress expansion due to alkali-silica reaction in concrete,” Cement and Concrete Research, vol. 32 (3), pp. 341–349, 2002.
[6] P. R. Rangaraju, J. Desai, “Effectiveness of fly ash and slag in mitigating alkali–silica reaction induced by deicing chemicals,” ASCE Journal of Materials in Civil Engineering, vol. 21 (1), pp. 19–31, 2009.
[7] Z. Owsiak, A. Mazur, “Effect of Chalcedony Dust on ASR in Mortars of Reactive Aggregate,” Procedia Engineering, vol. 108, pp. 475 – 480, 2015.
[8] K. Afshinnia, A. Poursaei, “The potential of ground clay brick to mitigate Alkali–Silica Reaction in mortar prepared with highly reactive aggregate,” Construction and Building Materials, vol. 95, pp. 164–170, 2015.
[9] T. Ramlochan, M. Thomas, K. A. Gruber, “The effect of metakaolin on alkali-silica reaction in concrete,” Cement and Concrete Research, vol. 30, pp. 339-344, 2000.
[10] K. Zheng, “Pozzolanic reaction of glass powder and its role in controlling alkali-silica reaction,” Cement and Concrete Composites, vol. 67, pp. 30-38, 2016.
[11] M. Thomas, “The effect of supplementary cementing materials on alkali-silica reaction: a review,” Cement and Concrete Research, vol. 41, pp. 1224-1231, 2011.
[12] T. Chappex, K. Scrivener, “The influence of aluminium on the dissolution of amorphous silica and its relation to alkali silica reaction,” Cement and Concrete Research, vol. 42 (12), pp. 1645 -1649, 2012.
[13] S. Y. Hong, F. P. Glasser, “Alkali sorption by CSH and CASH gels: Part II. Role of alumina,” Cement and Concrete Research, vol. 32 (7), pp. 1101-1111, 2002.
[14] J. Zapala-Slaweta, Z. Owsiak, “The role of lithium compounds in mitigating alkali-gravel
aggregate reaction,” *Construction and Building Materials*, vol. 115, pp. 299-303, 2016.

[15] Z. Owsiak, J. Zapała-Slaweta, “The course of the alkali-aggregate reaction in the presence of lithium nitrate,” *Ceramic-Silikaty*, vol. 57(2), pp. 138-145, 2013.

[16] D. Bulteel, E. Garcia-Diaz, P. Dégrugilliers, “Influence of lithium hydroxide on alkali–silica reaction,” *Cement and Concrete Research*, vol. 40, pp. 526–530, 2010.

[17] ASTM C1260 – 07 Standard Test Method for Potential Reactivity of Aggregates (Mortar-Bar Method).

[18] S. Wild, J. M. Khatib, “Portlandite consumption in metakaolin cement pastes and mortars,” *Cement and Concrete Research*, vol. 27(1), pp. 137-146, 1997.

[19] T. Kim, J. Olek, H-G. Jeong, “Alkali–silica reaction: Kinetics of chemistry of pore solution and calcium hydroxide content in cementitious system,” *Cement and Concrete Research*, vol. 71 pp. 36-45, 2015.

[20] V. Oyan, M. Tapan, A. Ozvan, “Effectiveness of Pumice and Scoria Aggregates in Controlling Alkali Silica Reaction,” *Ninth International Concrete Conference and Exhibition for Sustainable Construction*, Kingdom of Bahrain, 2013.

[21] A. Leemann, G. L. Saout, F. Winnefeld, D. Rentsch, B. Lothenbach, “Alkali-silica reaction: the influence of calcium on silica dissolution and the formation of reaction products,” *Journal of the American Ceramic Society*, vol. 94 (4), pp. 1243-1249, 2011.