# A REVIEW ON USING CALCINED CLAYS TO MITIGATE ALKALI-SILICA REACTION

Chang Li[1*], Jason H. Ideker[1], Thano Drimalas[2], Matthew P. Adams[3]

[1] Oregon State University, Corvallis, OR, USA

[2] The University of Texas at Austin, Austin, TX, USA

[3] New Jersey Institute of Technology, Newark, NY, USA

**Abstract**

Metakaolin, a commonly used calcined clay, has been investigated extensively for its role to mitigate alkali-silica reaction (ASR) in concrete. It has been proven to be a useful supplementary cementitious material (SCM) that is capable of effectively mitigating ASR by reducing the alkalinity in the pore solution of paste, mortar and concrete as well as binding available alkalis in the mixture. However, previous research indicated that the efficacy of calcined clays in mitigating ASR can vary significantly due to differences in quality and source. This paper reviews current studies on the factors that could influence the pozzolanic reactivity of calcined clays from different sources as well as their efficacy in mitigating ASR. In addition, test results from accelerated mortar bar tests (AMBT), concrete prism test (CPT) were evaluated for their accuracy by comparing to the results of the field exposure block test. The review was focused on: the impact of the manufacturing process - specifically calcination temperature, the mineral phase composition of calcined clays, and the pozzolanic reactivity of these minerals. The effect of the composition of calcined clays, especially alumina and alkalis, on the efficacy of alkali binding ability and ASR mitigation as well as suggested replacement levels for ASR mitigation based on composition and mineral phases of calcined clays are also presented along with the correlation of lab tests to the exposure concrete block test.

**Keywords**: calcined clay, ASR, aluminium, pozzolanic reactivity,

## 1 INTRODUCTION

Calcined clay is manufactured by heating raw material under high temperatures ranging from 600 to 800°C. Kaolin-containing clays are the primary raw materials for manufacturing calcined clay. The annual output of kaolin worldwide was about 250 million tonnes in 2002 [1]. Another source of raw material is the clay wastes produced during the paper manufacturing process [2, 3]. As a high purity calcined clay, metakaolin made from high-quality kaolin, containing a high content of kaolinite, has been extensively investigated. Through the calcination, dehydroxylation of the raw material occurs, which leads to the transition of the raw material from crystalline phases to amorphous phases [4]. During dehydroxylation, the raw material was reported to lose nearly 14% of its original weight; the structure of kaolin is reorganised; and the alumina and silica layers in the crystal structure break down to form $Al_2O_3\cdot 2SiO_2$ [5, 6]. Due to its particular structure, metakaolin showed high pozzolanic reactivity, therefore it can be used as a helpful supplemental cementitious material (SCM) in concrete.

The use of metakaolin in concrete can address the concerns of carbon emission by partially replacing cement. Metakaolin can also benefit concrete microstructure as well as concrete durability. However, the production and sources of high purity kaolin are limited. Calcined clays of different sources and qualities are of great interest as an effective pozzolan for use in concrete. Recently, more research has focused on using calcined clays of lower qualities. Compared with commercial high purity metakaolin, these calcined clays usually contain varying chemical and mineralogical compositions. Low quality calcined clays often contain impurities such as quartz, calcite, feldspar, mica, anatase and sulphides [7, 8]. The existence of these impurities can influence the pozzolanic reactivity of calcined clays. Research by Badoginnis et al. [9, 10] showed that calcined clay made of poor Greek kaolins showed similar effects as a

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[*] Correspondence: licha@oregonstate.edu

commercial metakaolin on cement strength development, consumption in $Ca(OH)_2$ as well as the resistance of chloride permeability. In addition, Krajči et al. [11] revealed that burnt kaolin sands, which were heated from original kaolin sand containing 4.10 to 14.48 wt% of metakaolin, showed the pozzolanic reaction when being used to partially replace cement. Besides, calcined clay produced from the paper sludge or wastes showed pozzolanic reactivity. Pera et al. [3] produced calcined clays by using paper sludge, and the calcined clays were compared to a commercial metakaolin by using a lime consumption test. Results indicated that calcined clay made from paper sludge showed a better pozzolanic reactivity than commercial metakaolin (especially at early ages), despite a lower content in metakaolinite (formed when kaolinite dehydroxylated). Frías et al. [2] reported that by heating clay wastes at 700°C for 2 hours, the calcined clay showed a great pozzolanic reactivity.

Incorporating calcined clays to mitigate alkali-silica reaction (ASR) was initiated a few decades ago. Walters et al. [12] showed that by incorporating metakaolin in concrete, ASR can be entirely mitigated if 10% or more metakaolin were used. Research by Ramlochan [13] indicated the efficacy of ASR mitigation was increased with the increase of the amount of metakaolin incorporated. In addition, for highly reactive metakaolin, 10% to 15% could be sufficient in controlling expansion caused by ASR [13]. Research done by Gruber et al. [14] showed similar results that by replacing 15%, expansion caused by reactive aggregates-Spratt was entirely controlled.

Since this time, more calcined clays of low quality with varying minerals and impurities have been investigated, including research on using low quality calcined clays to mitigate ASR was also done. This paper aims to review current research on pozzolanic reactivity of calcined clays from different sources, including metakaolin, and the use of calcined clays to mitigate ASR. Calcined clays of different qualities and sources investigated in previous research were reviewed and categorized as shown in Table 1. This information will be used to lead the discussion of possible parameters determining the efficacy of ASR mitigation using calcined clays as a replacement for cement in concrete.

## 2 POZZOLANIC REACTIVITY AND ASR MITIGATION

As a material of high pozzolanic reactivity, the metakaolin typically been used to replace cement by 10% to 20%. Compared with other commonly used SCMs, metakaolin contains a high content of alumina and silica, which reacts with $Ca(OH)_2$ in cement to form C-S-H. Asbridge et al. [15] showed that by comparing fly ash, silica fume, and metakaolin at the same replacement levels, metakaolin consumed more $Ca(OH)_2$, which indicated its high pozzolanic activity. As an effective pozzolan, its high reactivity indicates the ability of metakaolin to consume hydroxyl ions in the pore solution, and thus mitigate ASR. Coleman and Page [16] found that the pH of pore solution was reduced from 13.7 to 13.4 and 13.2 respectively when 10% and 20% metakaolin were incorporated in cement paste. Ramlochan [17] reported that by incorporating highly reactive metakaolin, the hydroxyl ion concentration in pore solution was significantly reduced. Therefore, due to the ability to react with hydroxyl ions in pore solution, the available alkalis in concrete were largely consumed by metakaolin, which reduces the risk of occurrence of ASR. Therefore, the ability of ASR mitigation can be related to the pozzolanic reactivity of the investigated calcined clays.

Thomas [18] compared ASR with the pozzolanic reaction and noted that the nature of ASR was similar to the pozzolanic reaction. Both reactions involve the reaction between reactive silica and alkalis. Due to the small particle size of pozzolans, the pozzolanic reaction usually occurs before ASR [18]. However, if finely-divided pozzolan particles agglomerated, ASR is likely to occur [18]. In addition, the research found that the amount of calcium in SCMs can influence the alkali binding capacity of the C-S-H and expansive properties of ASR gel [19-21]. Bhatty and Greening [18, 22] revealed that C-S-H with low Ca/Si ratio showed higher capacity in binding sodium and potassium in the pore solution. Calcined clays usually contained a low content of calcium (0~2%). Therefore, the Ca/Si ratio is generally not a concern when calcined clays are used to control ASR.

Previous research showed that SCMs without aluminium, such as silica fume, showed an increase in hydroxyl ion concentration in pore solution and more expansion in concrete or mortar at the later age [18, 23-25]. This observation indicated that the existence of aluminium in SCMs can influence the alkali binding ability. Different with other SCMs, calcined clays contain a high content of aluminium (20~50%), which contributes to ASR mitigation. He [26] pointed that due to the efficacy on ASR mitigation is largely determined by the alkalis bound when the pozzolanic reaction occurs, C-S-H and $C_4AH_x$ were detected as the reaction products when portlandite in cement reacts with Si and Al in calcined clays. Hong and Glasser

[27] showed that the existence of aluminium led to the formation of C-A-S-H, besides C-S-H. The alkali binding ability of C-A-S-H was reported to be higher than that of C-S-H [27].

Therefore, the pozzolanic reactivity of a calcined clay can largely determine its ASR mitigation efficacy. However, to effectively use calcined clays for ASR mitigation, a few factors should be taken into consideration: calcination temperature, raw material mineralogy, the content of aluminium, replacement level, and fineness of calcined clays.

# 3 FACTORS INFLUENCING POZZOLANIC REACTIVITY AND ASR MITIGATION

## *Calcination temperature*

Calcination temperature can significantly influence mineral formation in calcined clays. Therefore, an optimum calcination temperature is preferred to achieve a high pozzolanic reactivity. He et al. [26] showed that after dehydroxylation the amount of crystalline phase increased when calcination temperature increased. Seiffarth et al. [28] investigated both illite-based clay and smectite clay samples at different temperatures; results indicated that when calcination temperatures went above 850 °C, the maximum amount of reactive amorphous substances were obtained due to the formation of a spinel phase. In addition, the favourable temperature for kaolinite dehydroxylated was 550°C according to He et al. [26]. He et al. [26] also pointed out that kaolinite had the highest compressive strength when heated to 650°C. Shavarzman [4] showed kaolinite was fully dehydroxylated at 570°C to 700°C. For calcined clays containing alunite ($KAl_3(SO_4)_2(OH)_6$), the content of alunite was observed to be a good indicator for the optimum calcination temperature for kaolins. Badogiannis [29] also showed that for kaolins with low content of alunite, the optimum calcination temperature was 650°C, and for kaolins with a high content of alunite, the optimum calcination temperature was 850°C.

## *Raw material mineralogy*

Kakali et al. [30] found that kaolin with a high degree of crystallization showed less pozzolanic reactivity after calcination. The minerals in calcined clay have a significant influence on the pozzolanic reactivity. Research by Fernandez et al. [31] indicated that among kaolinite, illite and montmorillonite, kaolinite showed that best pozzolanic reactivity after calcination due to its high content of hydroxyl groups and the crystal structure that provided more aluminium to the system. Shvarzman [4] also revealed that kaolin with more than 50% of amorphous phase content can be regarded as chemically reactive. Tironi [7] indicated that materials with a medium to high content of kaolinite and disordered structures showed high pozzolanic reactivity. Research done by Li et al. [32] showed that mineral content in calcined clays impacted its efficacy of mitigating ASR in mortar samples. Further, calcined clays with the most amorphous structures showed better efficacy in controlling expansion caused by ASR [32]. Besides the major minerals in calcined clays, the impurities in calcined clays should be paid attention as well. Frías et al. [2] reported that the initial setting time of cement were shortened when calcined clays made from clay wastes were incorporated. Another study by Frías et al. [33] showed cellulose can still be observed in calcined clay made from paper sludge waste at 600°C; indicating that the use of low quality calcined clays made from industrial wastes (especially the raw material was the mix of organic matters or inorganic minerals) may have a negative influence on the properties hardened cement paste.

## *The role of aluminium*

As mentioned above, Thomas [34] showed that the presence of aluminium in SCMs has a significant impact on ASR mitigation efficacy. It was also revealed that SCMs with additional aluminate could be effective in reducing the expansion caused by ASR. Li [32] found that among four different types of calcined clays, the one with the lowest amount of alumina showed the least efficacy in controlling expansion caused by ASR (Figure 1 and Table 2). Meanwhile, it was found that ASR-related expansion was well correlated with the additional $Al_2O_3$ from calcined clays. When $Al_2O_3$ content was more than 4.5%, the expansion was controlled [32]. Therefore, the research indicated aluminium can be beneficial in controlling ASR by being introduced to the system in the form of either alumina or aluminium. Warner [35] also indicated that with artificially increased alumina in SCMs, ASR-related expansion was controlled. The content of aluminium is key to the ASR expansion. [18, 36]. Chappex et al. [37] found that the presence of aluminium could influence the dissolution of silica in simulated pore solution and 3.9 mM of aluminium in the simulated pore solution can substantially reduce the deterioration of aggregates.

*Replacement level of calcined clays*

Typically, the replacement level of calcined clay was mainly determined by its purity, chemicals and composition. When calcined clays were used to partially replace cement in concrete, the investigated concrete showed a reduction in workability [38]. Therefore, there is the need to balance between the benefits provided by the pozzolanic reaction and the reduction in workability. To effectively control the expansion caused by ASR, a 10% to 15% replacement of highly pozzolanic reactive metakaolin for cement was reported to be sufficient (as seen in Figure 2) [14]. Research by Moser et al. [39] showed 15% to 20% metakaolin is sufficient to mitigate ASR in two years in the concrete prism test (CPT). Li et al. [40] found that by incorporating 10% metakaolin, expansion caused by ASR in accelerated mortar bar test (AMBT) can be controlled, however, for lower quality calcined clays, up to 20% was needed to reduce the ASR-related expansion to within acceptable limits.

*The fineness of clays*

As mentioned above, the fineness of calcined clays can influence their pozzolanic reactivity. Typically, the fineness of commercial metakaolin powder is about 12,000-15,000 $m^2/kg$. The major grain size of metakaolin particle is smaller than 5 μm [11, 26, 41]. This indicates that the particle size of metakaolin is smaller compared to that of cement. Curcio et al. showed that the fineness of calcined clays can have an influence on its pozzolanic reactivity (see Table 3); it was highlighted that the finer metakaolin was more pozzolanically reactive than the coarser ones [42]. Tironi reported that surface area was correlated well with pozzolanic reactivity of the investigated metakaolins (see Figure 3) by showing that the consumption of $Ca(OH)_2$ increased when the specific surface of the investigated metakaolins increased [43].

## 4 TEST METHOD EVALUATION

Currently, the AMBT and CPT are the most commonly used test procedures to evaluate the reactivity of aggregates and mitigation efficacy. Both tests methods measure the expansion of specimens under environmental conditions that favor the occurrence of ASR. AMBT is a quick test, which takes only 16 days to obtain results. However, the test conditions of AMBT have been regarded as too severe, which may lead to falsely rejecting qualifying aggregates [44, 45]. On the other hand, Thomas reported AMBT correlated well with CPT in determining the minimum level of SCMs required to control ASR-related expansion (see Figure 4) [44].

CPT is regarded as a more accurate test method when compared with AMBT. However, it sometimes produces inaccurate results due to leaching of alkalis [44, 46]. In addition, the CPT is a relatively long-term test; it takes one year for reactivity evaluation and two years for mitigation evaluation when SCMs were incorporated [47]. Thomas showed the CPT correlates well with exposure block test in determining the minimum SCMs (calcined clay not included) required for controlling expansion [44]. However, research by Li et al. showed that exposure blocks with 10% calcined clay (exposed at Austin, Texas, USA) expanded more than 0.04% (expansion limit in CPT) in the sixth year of exposure, while results of the CPT only showed 0.03% expansion at 2 years (see Figure 5 and Table 4) [40]. A possible explanation for this observation could be the leaching of alkalis from concrete prisms in CPT, resulting in an inaccurate prediction of the long-term performance of concrete [44, 48].

These findings indicate that although the AMBT and CPT are helpful in determining the replacement level of an SCM to mitigate ASR, these tests still have limitations. A short-term method that can better address alkali leaching issues and accurately predict long-term performance is in great need to be developed. In addition, block expansion data of concrete with different calcined clays is still limited, so more data on concrete exposure block with calcined clays of various sources will be more helpful to provide guidelines in new methods development. The long-term data is particularly important for determining if the current expansion limits set on the AMBT and CPT will accurately predict performance in the field.

## 5 CONCLUDING REMARKS

This paper reviewed up to date research on using calcined clays to mitigate ASR. Much of the current research focused on using high purity metakaolin to mitigate ASR in concrete. In addition, calcined clays of different sources were discussed regarding their pozzolanic reactivity. Prior research has revealed that calcined clays manufactured from low-quality raw materials can still exhibit pozzolanic reactivity.

However, the differences in the pozzolanic reactivity primarily influence the alkali binding ability of the systems including calcined clays; therefore, the efficacy of mitigation is impacted by the type of calcined clay used. Based on the review, the authors provided a few recommendations on using calcined clays to mitigate ASR in concrete:

- Quantify the amount of aluminium and amorphous phase in calcined clays prior to using them for ASR mitigation. The amount of aluminium can potentially "control" the dissolution of reactive silica and help to form hydrates having higher alkali-binding ability, therefore knowing the amount of aluminium can provide helpful information in its ASR mitigation ability.
- Quantify the impurities in calcined clays. The impurities in calcined clays are usually not pozzolanically reactive. Therefore, calcined clays with a high content of such impurities can have a reduced ability to mitigate ASR compared to higher purity calcined clays. In addition, the existence of these impurities can influence cement properties such as setting time.

Furthermore, despite a good understanding of the effectiveness of calcined clays when used as an SCM in concrete, further research is still needed to guide the use of calcined clays based on their sources and qualities to make them more effective for use in mitigating ASR. Future research needs include:

- Establish the link between the pozzolanic reactivity of calcined clays to its efficacy in ASR mitigation. As shown, the highly pozzolanic reactive material tends to be more efficient in consuming and binding hydroxyl ions, which helps to reduce the available alkalis in the pore solution. Therefore, tests on the pozzolanic reactivity of calcined clays should be investigated before using as a strategy to mitigate ASR. In addition, the results of pozzolanic reactivity should be used to determine the minimum replacement level.
- Establish the link between the results of AMBT and CPT to the results of exposure block data. A database of concrete blocks with varied calcined clays incorporated is in need.

## 6 REFERENCES

[1] Wilson, I (2003), Current world status of kaolin from south-west England. Geosicence in South West England, 10(4): 417-423.

[2] Frías, M, Rodríguez, O, Vegas, I, and Vigil, R (2008), Properties of calcined clay waste and its influence on blended cement behavior. Journal of the American Ceramic Society, 91(4): 1226-1230.

[3] Pera, J and Amrouz, A (1998), Development of highly reactive metakaolin from paper sludge. Advanced Cement Based Materials, 7(2): 49-56.

[4] Shvarzman, A, Kovler, K, Grader, G, and Shter, G (2003), The effect of dehydroxylation/amorphization degree on pozzolanic activity of kaolinite. Cement and Concrete Research, 33(3): 405-416.

[5] Rashad, AM (2013), Metakaolin as cementitious material: History, scours, production and composition–A comprehensive overview. Construction and building materials, 41: 303-318.

[6] Kostuch, J, Walters, V, and Jones, T (2000), High Performance Concretes Incorporating Metakaolin: A Review. Concrete, 2(1993): 1799-811.

[7] Tironi, A, Trezza, MA, Scian, AN, and Irassar, EF (2012), Kaolinitic calcined clays: Factors affecting its performance as pozzolans. Construction and Building Materials, 28(1): 276-281.

[8] Habert, G, Choupay, N, Montel, J-M, Guillaume, D, and Escadeillas, G (2008), Effects of the secondary minerals of the natural pozzolans on their pozzolanic activity. Cement and Concrete Research, 38(7): 963-975.

[9] Badogiannis, E, Kakali, G, Dimopoulou, G, Chaniotakis, E, and Tsivilis, S (2005), Metakaolin as a main cement constituent. Exploitation of poor Greek kaolins. Cement and Concrete Composites, 27(2): 197-203.

[10] Badogiannis, E and Tsivilis, S (2009), Exploitation of poor Greek kaolins: durability of metakaolin concrete. Cement and Concrete Composites, 31(2): 128-133.

[11] L'udovit Krajéi, I, Kraus, I, and Jamnicky, P (2007), Burnt kaolin sand as pozzolanic material for cement hydration. Ceramics− Silikáty, 51(4): 217-224.

[12] Walters, GV and Jones, TR (1991), Effect of Metakaolin on Alkali-Silica Reaction (ASR) in Concrete Manufactured with Reactive Aggregate. ACI Special Publication, 126.

[13] Ramlochan, T, Thomas, M, and Gruber, KA (2000), The Effect of Metakaolin on Alkali-silica Reaction in Concrete. Cement and Concrete Research, 30(3): 339-344.

[14] Gruber, K, Ramlochan, T, Boddy, A, Hooton, R, and Thomas, M (2001), Increasing concrete durability with high-reactivity metakaolin. Cement and concrete composites, 23(6): 479-484.

[15] Asbridge, A, Walters, G, and Jones, T (1994), Ternary blended concretes-OPC/GGBFS/metakaolin. Denmark: Concrete Across Borders: 547-557.

[16] Coleman, N and Page, C (1997), Aspects of the Pore Solution Chemistry of Hydrated Cement Pastes Containing Metakaolin. Cement and Concrete Research, 27(1): 147-154.

[17] Ramlochan, T, Thomas, M, and Gruber, KA (2000), The effect of metakaolin on alkali–silica reaction in concrete. Cement and Concrete Research, 30(3): 339-344.

[18] Thomas, M (2011), The effect of supplementary cementing materials on alkali-silica reaction: A review. Cement and Concrete Research, 41(12): 1224-1231.

[19] Thomas, M (2001), The role of calcium hydroxide in alkali recycling in concrete. Materials Science of Concrete Special: 225-236.

[20] Hou, X, Kirkpatrick, RJ, Struble, LJ, and Monteiro, PJ (2005), Structural investigations of alkali silicate gels. Journal of the American Ceramic Society, 88(4): 943-949.

[21] Hou, X, Struble, LJ, and Kirkpatrick, RJ (2004), Formation of ASR gel and the roles of C-S-H and portlandite. Cement and Concrete Research, 34(9): 1683-1696.

[22] Bhatty, M and Greening, N (1978). Interaction of alkalies with hydrating and hydrated calcium silicates. in Proceedings.

[23] Aquino, W, Lange, D, and Olek, J (2001), The influence of metakaolin and silica fume on the chemistry of alkali–silica reaction products. Cement and Concrete Composites, 23(6): 485-493.

[24] Shehata, MH, Thomas, MDA, and Bleszynski, RF (1999), The effects of fly ash composition on the chemistry of pore solution in hydrated cement pastes. Cement and Concrete Research, 29(12): 1915-1920.

[25] Shehata, MH and Thomas, MD (2002), Use of ternary blends containing silica fume and fly ash to suppress expansion due to alkali–silica reaction in concrete. Cement and Concrete Research, 32(3): 341-349.

[26] He, C, Osbaeck, B, and Makovicky, E (1995), Pozzolanic reactions of six principal clay minerals: activation, reactivity assessments and technological effects. Cement and concrete research, 25(8): 1691-1702.

[27] Hong, S-Y and Glasser, F (2002), Alkali sorption by CSH and CASH gels: Part II. Role of alumina. Cement and Concrete Research, 32(7): 1101-1111.

[28] Seiffarth, T, Hohmann, M, Posern, K, and Kaps, C (2013), Effect of thermal pre-treatment conditions of common clays on the performance of clay-based geopolymeric binders. Applied Clay Science, 73: 35-41.

[29] Badogiannis, E, Kakali, G, and Tsivilis, S (2005), Metakaolin as supplementary cementitious material: optimization of kaolin to metakaolin conversion. Journal of Thermal Analysis and Calorimetry, 81(2): 457-462.

[30] Kakali, G, Perraki, T, Tsivilis, S, and Badogiannis, E (2001), Thermal treatment of kaolin: the effect of mineralogy on the pozzolanic activity. Applied Clay Science, 20(1): 73-80.

[31] Fernandez, R, Martirena, F, and Scrivener, KL (2011), The Origin of the Pozzolanic Activity of Calcined Clay Minerals: a Comparison between Kaolinite, Illite and Montmorillonite. Cement and Concrete Research, 41(1): 113-122.

[32] Li, C, Ideker, JH, and Drimalas, T (2015). The Efficacy of Calcined Clays on Mitigating Alakli-Silica Reaction (ASR) in Mortar and Its Influence on Microstructure. in Calcined Clays for Sustainable Concrete. Springer.

[33] Frías, M, García, R, Vigil, R, and Ferreiro, S (2008), Calcination of art paper sludge waste for the use as a supplementary cementing material. Applied Clay Science, 42(1): 189-193.

[34] 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(8): 1049-1054.

[35] Warner, SJ (2012), The role of alumina in the mitigation of alkali-silica reaction.

[36] Lindgård, J, Andiç-Çakır, Ö, Fernandes, I, Rønning, TF, and Thomas, MD (2012), Alkali–silica reactions (ASR): Literature review on parameters influencing laboratory performance testing. Cement and Concrete research, 42(2): 223-243.

[37] Chappex, T and Scrivener, KL (2012), The influence of aluminium on the dissolution of amorphous silica and its relation to alkali silica reaction. Cement and Concrete Research, 42(12): 1645-1649.

[38] Sabir, BB, Wild, S, and Bai, J (2001), Metakaolin and Calcined Clays as Pozzolans for Concrete: A Review. Cement and Concrete Composites, 23: 441-454.

[39] Moser, RD, Jayapalan, AR, Garas, VY, and Kurtis, KE (2010), Assessment of binary and ternary blends of metakaolin and Class C fly ash for alkali-silica reaction mitigation in concrete. Cement and Concrete Research, 40(12): 1664-1672.

[40] Li, C, Ideker, JH, and Drimalas, T (2015). Calcined Clays for ASR Mitigation: Mechanisms and Long-term Performance. in 14th International Congress on the Chemistry of Cement. Beijing.

[41] Gleize, PJ, Cyr, M, and Escadeillas, G (2007), Effects of metakaolin on autogenous shrinkage of cement pastes. Cement and Concrete Composites, 29(2): 80-87.

[42] Curcio, F, DeAngelis, B, and Pagliolico, S (1998), Metakaolin as a pozzolanic microfiller for high-performance mortars. Cement and Concrete Research, 28(6): 803-809.

[43] Tironi, A, Trezza, MA, Scian, AN, and Irassar, EF (2013), Assessment of pozzolanic activity of different calcined clays. Cement and Concrete Composites, 37: 319-327.

[44] Thomas, M, Fournier, B, Folliard, K, Ideker, J, and Shehata, M (2006), Test methods for evaluating preventive measures for controlling expansion due to alkali-silica reaction in concrete. Cement and Concrete Research, 36: 1842-1856.

[45] ASTM Standard 1260, (2014), "ASTM C 1260 Standard test method for potential alkali reactivity of aggregates (mortar-bar method)," ASTM International, West Conshohocken, PA, 2003, www.astm.org.

[46] Ideker, JH, Bentivegna, AF, Folliard, KJ, and Juenger, MCG (2012), Do current laboratory test methods accurately predict alkali-silica reactivity. ACI Materials Journal, 109(4): 395-402.

[47] ASTM Standard 1293, (2008), "Standard Test Method for Determination of Length Change of Concrete Due to Alkali-Silica Reaction," ASTM International, West Conshohocken, PA, 2003, www.astm.org.

[48] Folliard, KJ, Barborak, R, Drimalas, T, Du, L, Garber, S, Ideker, J, Ley, T, Williams, S, Juenger, M, Fournier, B, and Thomas, MDA (2006), Preventing ASR/DEF in new concrete: final report FHWA/TX-06/0-4085-5.

[49] Rabehi, B, Boumchedda, K, and Ghernouti, Y (2012), Study of calcined halloysite clay as pozzolanic material and its potential use in mortars.

TABLE 1: Commonly investigated calcined clays.

| | Source | Notes |
|---|---|---|
| High quality calcined clays | Kaolinite | Commercially use; low content of impurities; kaolinite is the major content in raw material; Highly pozzolanically reactive |
| Low quality calcined clays | Kaolinite with impurities | Impurities such as quartz, calcite, feldspar, mica, anatase and sulphides; the existence of the minerals can affect the pozzolanic reactivity of calcined clays[7, 8] |
| | Other Clay minerals | Such as illite, montmorillonite, alunite, halloysite etc.; may have lower pozzolanic reactivity than kaolinite due to the crystal structure of the mineral [31, 49] |
| | Paper sludge | Contains high quantity of impurities, including organic substances; can be pozzolanically reactive after calcination; the impurities and organic substances may affect properties of hardened cement/concrete/mortar [3, 33] |

TABLE 2: Chemical composition of calcined clays (%) [32].

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ | $K_2O$ | $TiO_2$ | $MnO_2$ | $P_2O_5$ | SrO | BaO | $SO_3$ | LOI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| CC1 | 51.93 | 42.18 | 1.43 | 0.40 | 0.12 | 0.05 | 0.23 | 1.99 | - | 0.17 | 0.04 | 0.11 | 0.05 | 1.32 |
| CC2 | 54.11 | 39.94 | 1.26 | 0.25 | 0.20 | 0.15 | 1.38 | 0.63 | 0.01 | 0.12 | 0.02 | 0.04 | 0.05 | 1.87 |
| CC3 | 60.17 | 27.00 | 3.05 | 0.40 | 0.53 | 0.90 | 3.22 | 0.39 | 0.02 | 0.16 | 0.02 | 0.04 | 0.35 | 3.73 |
| CC4 | 50.12 | 43.62 | 0.69 | 0.05 | 0.02 | 0.00 | 0.10 | 1.76 | 0.01 | 0.02 | 0.01 | 0.02 | 0.02 | 3.57 |

TABLE 3: Fineness of calcined clays investigated [42].

| Calcined clays | BET $m^2/g$ | Bulk density ($kg/m^3$) | Pozzolanic activity |
|---|---|---|---|
| M1 | 19.8 | 245 | 0.23 |
| M2 | 13.9 | 365 | 0.21 |
| M3 | 14.7 | 417 | 0.24 |
| M4 | 12.7 | 512 | 0.47 |

TABLE 4: AMBT results at 14 days and CPT results at years (10% calcined clay)[40].

| **AMBT** | | **CPT** | |
|---|---|---|---|
| | **14-day** | **1-year** | **2-year** |
| **Control (%)** | 0.21 | 0.29 | - |
| **10% CC5 (%)** | 0.02 | - | 0.03 |

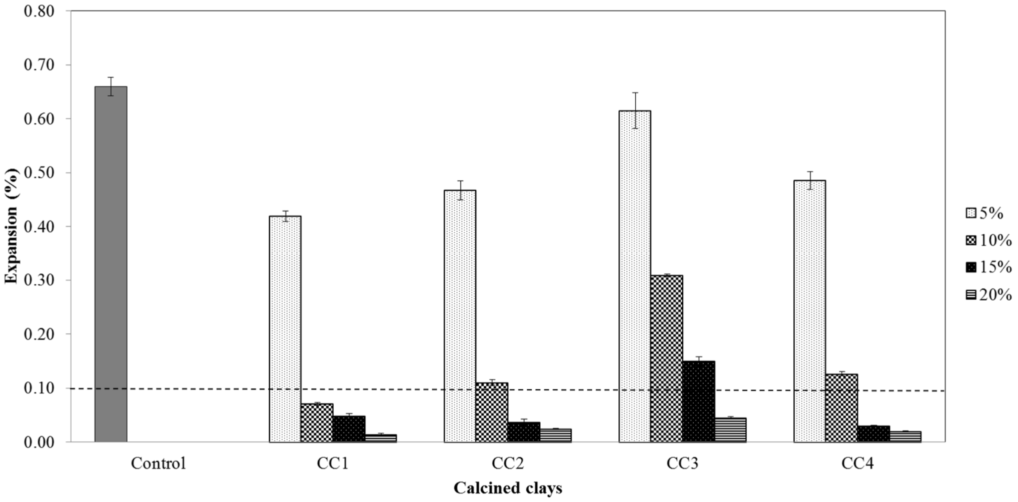

FIGURE 1: The efficacy of ASR mitigation by using calcined clays from different sources [32].

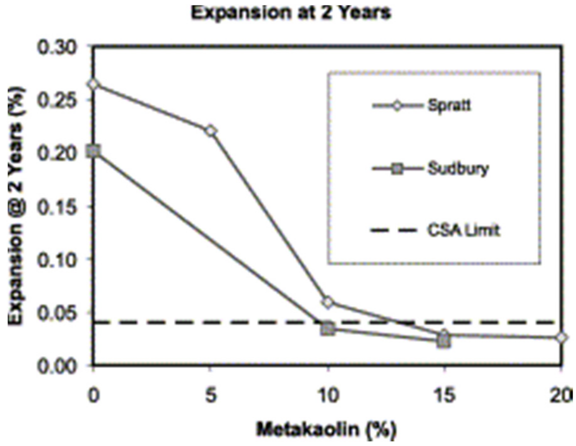

FIGURE 2: Control of expansions due to ASR using high-reactivity metakaolin [14].

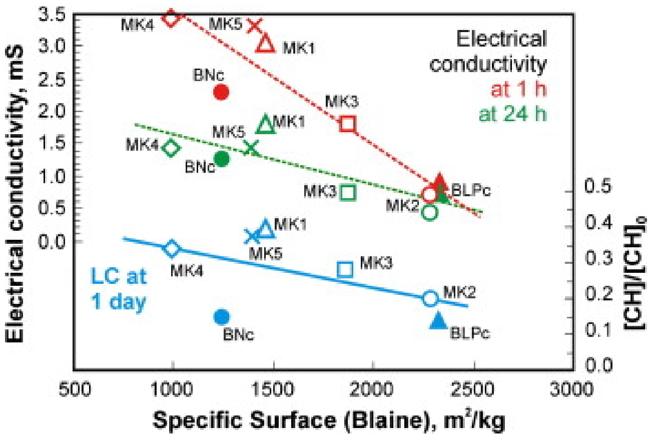

FIGURE 3: Correlation between pozzolanic activity using the saturated lime test (1 day) or the electric conductivity (1 and 24 h) and the (Blaine) specific surface of calcined clays [43].

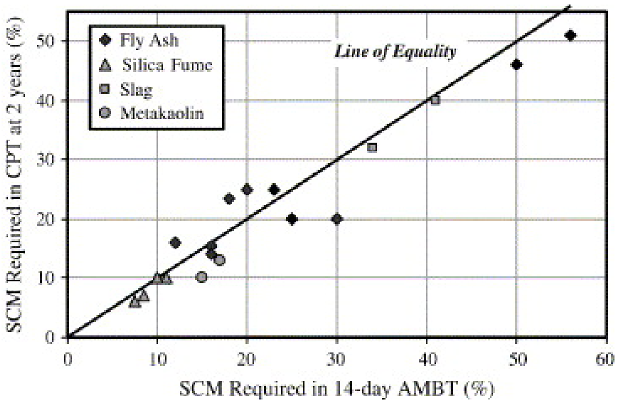

FIGURE 4: Comparison between the minimum level of SCMs required to control expansion in the CPT and AMBT [44].

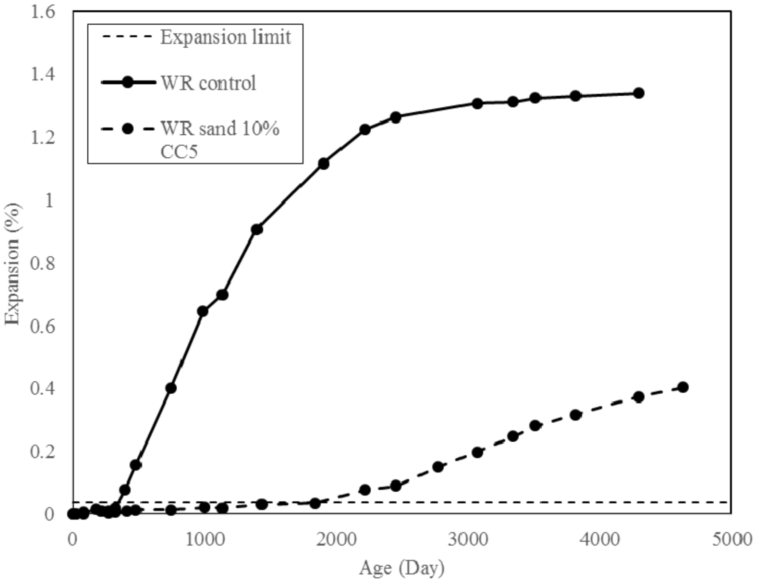

FIGURE 5: Exposure block results on concrete with 10% calcined clay [40].