

Proceeding Paper

# Effect of Low-Quality Calcined Clay on the Suppression of the Alkali–Silica Reaction †

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**Abstract:** This article presents the results of an experimental investigation into the mitigation of the alkali–silica reaction (ASR) resulting from using low-grade clay calcined at 850 °C. The clay used in the experiment was domestic clay with an Al<sub>2</sub>O<sub>3</sub> content equal to 26% and a SiO<sub>2</sub> content of 58%. The performance of calcined clay in ASR mitigation was evaluated according to ASTM C1567 using reactive aggregates. The control mortar mixture consisted of 100% Portland cement (Na<sub>2</sub>O<sub>eq</sub> = 1.12%) binder and reactive aggregate. The test mixtures used the same reactive aggregate and binders, in which part of the cement was replaced with either 10%, 20% or 30% calcined clay. The microstructure of specimens was examined on the polished sections using a scanning electron microscope (SEM) operated in the backscattered mode (BSE). The results of expansion obtained from the mortar bars made with the reactive aggregate showed that replacing cement by calcined clay reduced their expansion, with the level of expansion decreasing with the increase in the level of cement replacement.

**Keywords:** calcined clay; alkali–silica reaction; expansion; mitigation; microstructure



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## 1. Introduction

Nowadays, the continuous development of the cement-based materials industry, fueled by unflagging demand, is a cause for concern due to the large amount of CO<sub>2</sub> and NO<sub>x</sub> emitted during the production process. One of the most effective ways to reduce the negative environmental impact of the cement industry is the use of so-called supplementary cementitious materials (SCMs). The most commonly used SCMs are fly ash and ground-granulated blast furnace slag. However, their availability will continue to decline, thus increasing the need for alternative sources of SCMs. One of the most promising alternative sources are calcined clays, which are abundant and widely available [1–3]. Among the most well-known material to be used as a calcined clay in cement and concrete technology is metakaolin. Metakaolin is a pozzolanic material obtained by calcination of kaolinitic clay, and it has been shown to considerably enhance the mechanical and chemical properties of concrete [1]. Calcined clays other than metakaolin are rarely used as SCMs due to the complex composition of clay minerals, such as the calcite impurities in clays containing kaolinite and insufficient knowledge of the basic reaction mechanisms [2–4]. Additionally, although there is an increasing interest in demonstrating the effectiveness of various treatments that can lead to improvements in the reactivity of clays with respect to their usage as an SCM [3], issues such as the required quality control procedures and the acceptance criteria also need to be taken into account [1].

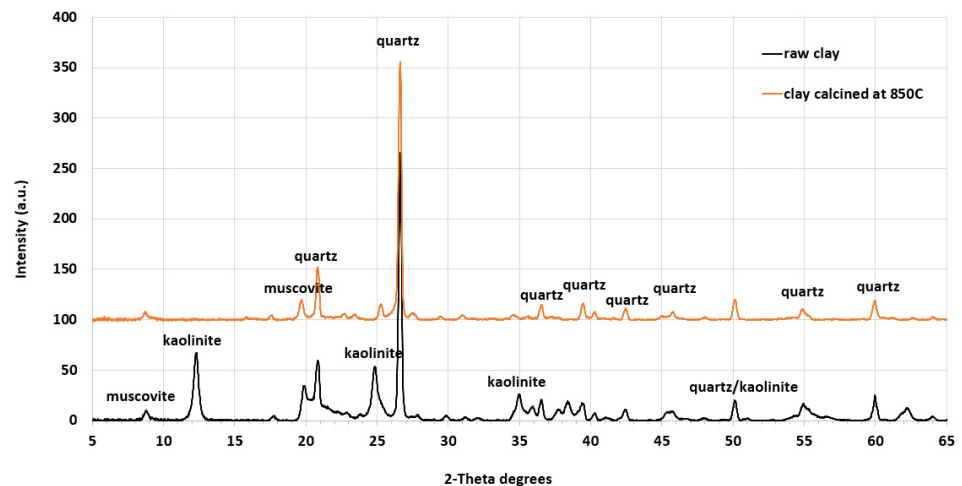
One of the possible applications of calcined clays, making use of their composition and pozzolanic properties, is as an additive to cement or concrete with the objective of

reducing the expansion induced by an alkali silica reaction [5,6]. However, previous studies have mostly focused on the application of metakaolin [7–9], thus overlooking the fact that the efficacy of calcined clays in mitigating ASR can vary significantly due to differences in quality and sources [5]. As a result, the information on the efficacy of ASR mitigation of calcined clays obtained from various sources and of different quality is still limited [6].

The research presented in this paper is focused on the effectiveness of locally available low-quality calcined clay with respect to its ability to control the expansion due to the alkali–silica reaction. The scope of experimental work includes a characterization of the raw and calcined clay, an assessment of the effectiveness of the calcined clay in mitigation according to ASTM C1567 [10] and a microstructural analysis. Although a different clay was tested than that used in [6], similar assumptions were made. One calcination temperature (850 °C) was used because the highest pozzolanic reactivity was reached when the clay was calcined at 800 °C [11,12], and the strength performance was maximized for raw clays calcined at temperatures up to 850 °C [3]. In the conducted research, the main factor, which is the replacement level, was taken into consideration.

## 2. Materials

The material used in the research was a domestic clay calcined at 850 °C with the loss on ignition equal to 9.20%. The material was classified as a low-quality clay due to the fact that it only contains 26%  $\text{Al}_2\text{O}_3$  [2]. The main associated mineral, except for kaolinite and muscovite, found in the raw clay by XRD was quartz, Figure 1. A previously analyzed aggregate from igneous rocks with medium reactivity (aggregate reactivity class R1 according to [13,14]) was selected for the reference aggregate. Ordinary Portland cement (CEM I 42.5R) with a high alkali content ( $\text{Na}_2\text{O}_{\text{eq}} = 1.12\%$ ) was used in this research. A detailed chemical composition of the raw clay and cement determined by XRF is shown in Table 1.



**Figure 1.** Mineral composition of the raw and calcined clay.

**Table 1.** Chemical composition of raw clay and Portland cement CEM I [15] by XRF (wt%).

Constituent	Raw Clay	CEM I
	Content %	
SiO <sub>2</sub>	58.23	19.43
TiO <sub>2</sub>	2.04	0.27
Al <sub>2</sub> O <sub>3</sub>	26.18	4.84
Fe <sub>2</sub> O <sub>3</sub>	1.53	3.18
Mn <sub>2</sub> O <sub>3</sub>	0.03	0.06
MgO	0.27	2.56
CaO	0.22	61.81
Na <sub>2</sub> O	0.13	0.41
K <sub>2</sub> O	1.86	1.08
P <sub>2</sub> O <sub>5</sub>	0.06	0.11
SO <sub>3</sub>	<0.01	3.93
Cl	0.01	0.03
F	0.03	-

### 3. Methods

Clay calcination was carried out in a laboratory chamber furnace with a heating capacity of 8.8 kW. Prior to loading into the furnace, the clay was dried to a constant weight at 110 °C, then ground and sieved through a 0.125 mm mesh. The heating ramp was 4 °C/min until a temperature of about 150 °C was reached, and 12 °C/min after this threshold was exceeded. After a temperature 850 °C was reached, it was maintained for 60 min, after which the material was allowed to cool in the oven to a temperature below 50 °C.

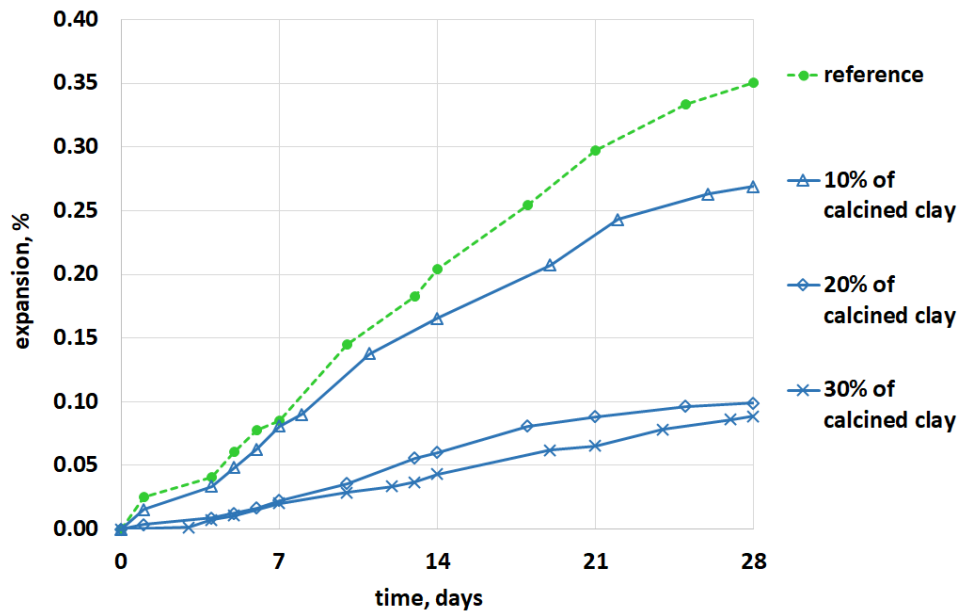
X-ray diffraction was used to estimate the main minerals in the investigated clays. XRD diffractograms were obtained with a diffractometer (Cu K $\alpha$  radiation source) equipped with a Göbel mirror and a GADDS 2D detector system. The operation parameters of the equipment were 40 kV and 40 mA. Diffraction patterns were collected over a 2 $\theta$  range from 5° to 65° with a 1°/min step using flat plane geometry.

Evaluation of the calcined clay efficiency in ASR mitigation was performed following the ASTM C1576 standard specification [10]. The test involved exposing standard mortar bars to a 1 M NaOH solution at a temperature of 80 °C. The test was carried out on reference mortar and on mortars with 10%, 20% and 30% of cement replacement by calcined clay. One set of test specimens consisted of three mortar bars of 25 × 25 × 285 mm. After 24 h, the specimens were disassembled and stored in distilled water at 80 ± 2 °C for the next 24 h. Then, the initial length reading was taken for each of the bars and then specimens were placed in 1 M NaOH at 80 ± 2 °C. Systematic measurements of the expansion of the mortar bars were carried out at least 4 times within 14 days. An expansion of less than 0.10% after 14 days of testing in 1 M NaOH at 80 °C indicated acceptable ASR performance behavior; however, the test was extended to 28 days for expansion curve analysis.

A post-mortem evaluation of the microstructure of the mortars was conducted using a scanning electron microscope (SEM) operated in the backscattered electrons (BES) mode and equipped with an energy dispersion X-ray (EDX) detector. The beam specimens, previously used for monitoring the expansion, were cut to the dimensions of 45 × 30 × 15 mm, dried at 50 °C for 3 days, vacuum-impregnated with a low-viscosity epoxy resin and lapped and polished using a special procedure for SEM specimens. The specimens were coated with a carbon layer (~20 nm) and a strip of conductive tape was attached to each specimen to improve the conduction properties. Each of the specimens was examined using a JEOL JSM-6380 LA SEM-EDX with an acceleration voltage of 20 kV and a working distance of 8–10 mm. More than 50 EDX point analyses were collected to assess the composition of the ASR products in the mortar during post-mortem analysis.

#### 4. Results and Discussion

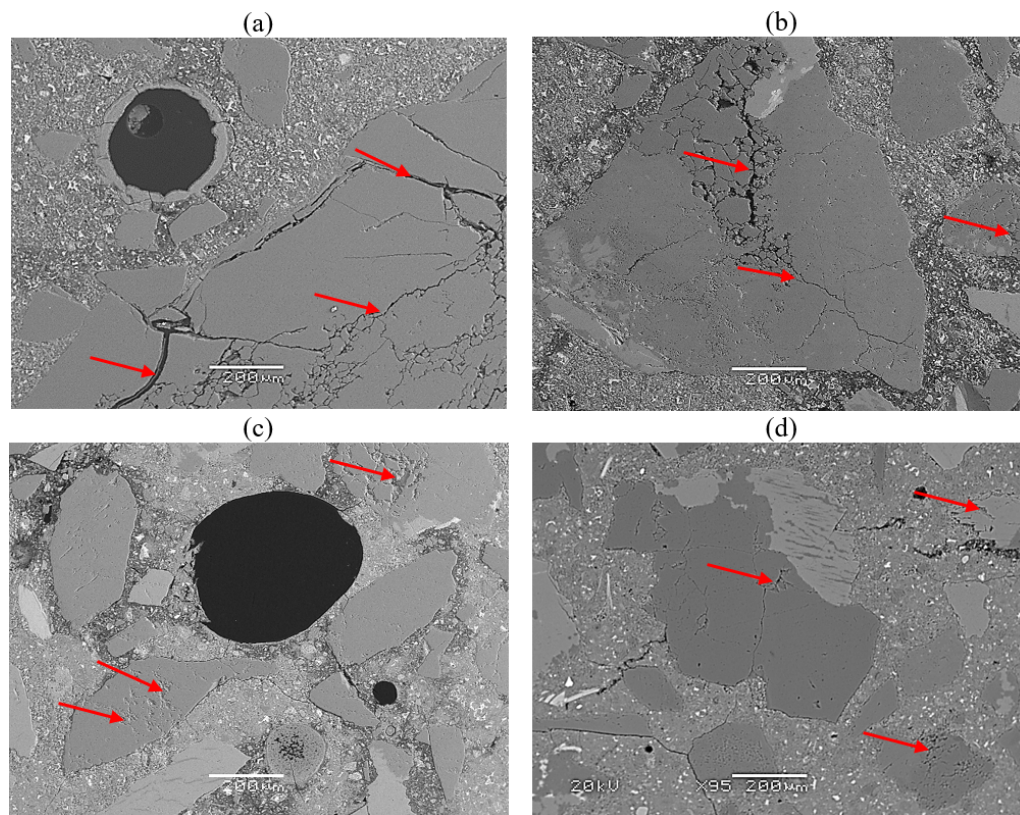
The accelerated mortar bar test results are presented in Figure 2. For the first 14 days, for all specimens the mortar bar expansion increased with the test duration. The fastest and the most extensive expansion development was found for the reference mortar and for the mortar containing 10% calcined clay. The expansion of specimens with 10% calcined clay exceeded the 0.1% limit after just 9 days of exposure and reached values higher than 0.15% after 14 days. Mortar bars with 20% and 30% calcined clay showed significantly lower expansions. The elongations were similar (below 0.06%) after 14 days of testing. It is worth noting that even after 28 days of testing, specimens with 20% and 30% calcined clay showed an expansion of less than 0.1%. Moreover, the slowing of the expansion is clearly visible in the expansion curve. The slowing phenomenon is more pronounced for 20% calcined clay specimens when compared to the specimens with 30% clay replacement. It is also worth noting that this effect is weaker for the 30% calcined clay content, suggesting that a 20% replacement rate is a slightly better solution.



**Figure 2.** Expansion of mortar specimens with various content of calcined clay as a function of exposure time to 1 M of NaOH solution and a temperature of 80 °C.

A microscopic analysis confirmed the results of the mortar bar expansion test according to ASTM C1567 [10]. The observed cracks in the aggregate and in the cement matrix were caused by an alkali–silica reaction, Figures 3 and 4. The degree of damage and the size and content of cracks in the aggregate decreased with an increase in the content of calcined clay. The same trend was also observed in the amount of ASR of the gel in the air voids, Figure 4. The ASR gel layer in the air voids in the reference mortar was approx. 35 µm, while in the mortar with 20% calcined clay it was half of that. There were also differences in the morphology and composition of the ASR gel. Based on the SEM observations, it was found that in the reference specimens, the ASR gel was largely amorphous and was characterized by a homogeneous composition of Si-Ca-Na-K (Figure 4a), typical for this kind of product [16]. Regardless of the location, the contents of Si, Ca and alkali ions in the gel were similar, while the ASR gel visible in the specimens containing calcined clay seemed to consist of two layers, outer and inner, Figure 4b. The inner (thinner) part of the ASR gel was composed of Si, Ca, Na and K, i.e., a typical composition. However, the outer part of the ASR gel, apart from being significantly cracked, also contained Mg and Al in

its composition, Figure 4b. Additionally, the content of K ions was lower compared to the composition of the gel in the inner part.



**Figure 3.** Dependency of the degree of cracking of the aggregate on the replacement level of cement with calcined clay: (a) 0%, (b) 10%, (c) 20% and (d) 30%; SEM-BES, scale bar = 200 μm.

The dependence of the expansion of the mortar bars on the content of calcined clay as a substitute for mass cement is presented in Figure 5. The obtained results are in line with expectations, assuming that the calcined clay exhibits pozzolanic properties as a supplementary cementitious material [2,4]. A similar dependence was demonstrated when using high-quality calcined clay, i.e., metakaolin [5,6].

The significantly different composition of the ASR gel in the mortar containing calcined clay is a new finding. In previous studies [6], no significant differences were found in the composition of the ASR gel between the two mixtures, with or without calcined clay. In the conducted test, a relationship between the Si/Al ratio in the ASR gel localized in air voids and the content of calcined clay, as well as a relationship between the mortar bars expansion and the Si/Al ratio in the ASR gel, were found, Figures 5 and 6.

An analysis was performed on the ASR gel in the air voids to determine the effect of the calcined clay and avoid the effect of aggregates. The differences in the ASR gel may be due to the presence of aluminum in calcined clay, which can influence the alkali binding ability. Although it is not presented in the article, the effectiveness of suppressing the alkali-silica reaction by low-quality calcined clay may be influenced by its pozzolanic reactivity, which may primarily affect the alkali binding capacity.

The next step of the research will be focused on the detailed characterization of domestic calcined clay and the properties of the obtained ASR gel.

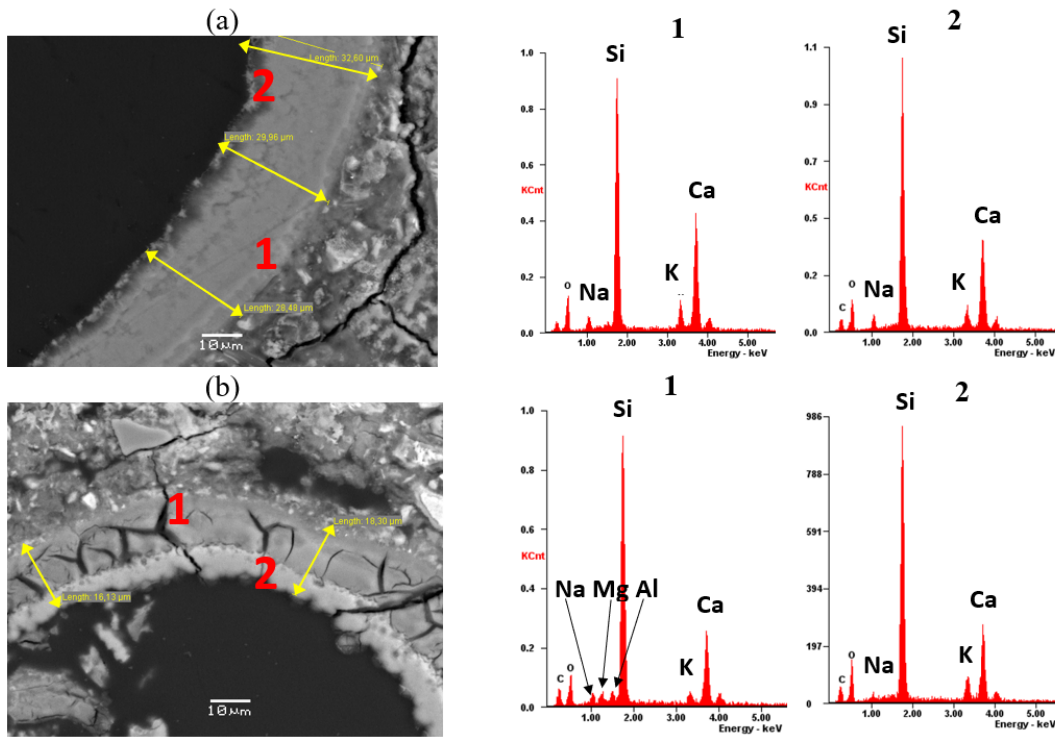


Figure 4. Microstructure and chemical composition of the ASR gel in air voids in specimens: (a) reference, 0% calcined clay and (b) 20% calcined clay, SEM-EDS, scale bar = 10 μm.

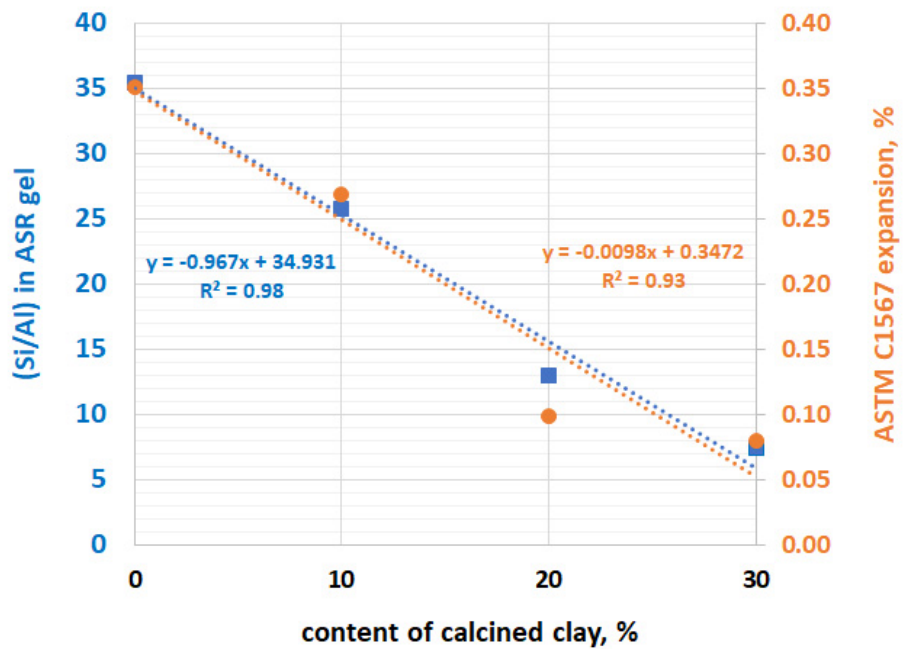
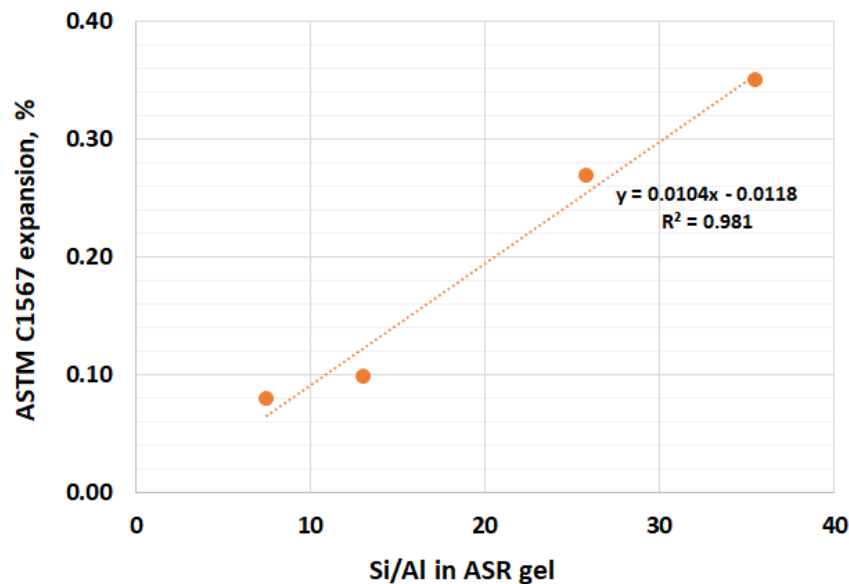


Figure 5. The relationship between the ASTM C1567 expansion and the Si/Al ratio in the ASR gel in relation to the content of the calcined clay cement substitute.



**Figure 6.** The relationship between the ASTM C1567 expansion and the Si/Al ratio in the ASR gel.

## 5. Conclusions

Based on the experimental analyses performed on mortars containing reactive aggregates and various contents of low-quality calcined clay, the following conclusions can be drawn:

- The effect of low-grade calcined clay on the ASR expansion was found.
- The results indicated a reduced alkali silica expansion in mortar containing low-grade calcined clay regardless of the percentage substitution with cement.
- At a lower percentage (10%) of calcined clay, the expansion results did not satisfy ASTM standard limits.
- Replacing 20% of the cement with calcined clay appeared to be sufficient to mitigate the alkali–silica reaction.
- The morphology and chemical composition, as well as the width of the ASR gel in air voids, was different depending on the calcined clay content.

The substitution method used in ASR-resistant composites results in less CO<sub>2</sub> being released into the atmosphere, making the material more sustainable. Future research will therefore focus on the study of eco-friendly concretes that use locally available aggregates as well as locally available, low-quality calcined clay as a partial substitute for Portland cement.

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