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Possibilities to Recycle Thermal Power Plant By-Products in Refractory Castables

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Abstract: The current research focuses on the analysis of fly ash cenospheres (FACs), a waste generated in coal-fired power plants, and the possibilities of using them in refractory castables. Cenospheres are micro-scale (~50–400 μm) spherical structures derived from fly ash, predominantly composed of silica and alumina oxides (86.7%). Their distinctive morphology and characteristics make them highly advantageous for a diverse array of applications, notably as lightweight fillers and nondegradable pore-forming agents. Furthermore, cenospheres have the potential to contribute significantly to the performance of refractory castables when incorporated into compositions with calcium aluminate cement (CAC). FAC XRD analysis revealed that FACs mainly consist of mullite along with cristobalite, which forms at higher temperatures. Furthermore, the study examined the impact of FACs on the properties of medium cement castable (MCC), especially durability, when 3%, 5%, and 7% of fine fireclay were replaced by FACs; 5% of FACs were found to reduce the density of refractory castables and decrease the cold crushing strength by approximately 6%, but it increased the resistance to thermal shock by approximately 75% and 43%, depending on the thermal treatment temperature, 950 °C and 1100 °C, respectively, and improved resistance to alkali corrosion. A higher FAC content (7%) does not have any positive effect on the MCC properties tested.

Keywords: fly ash cenospheres; power plant waste; aluminosilicate refractory castable; thermal shock resistance; alkali corrosion



Citation: Škamat, J.; Boris, R.; Malaiškienė, J.; Antonovič, V.; Stonys, R.; Kudžma, A. Possibilities to Recycle Thermal Power Plant By-Products in Refractory Castables. *Sustainability* **2024**, *16*, 6349. <https://doi.org/10.3390/su16156349>

Academic Editors: Jeongsoo Yu, Kazuaki Okubo and Xiaoyue Liu

Received: 15 May 2024

Revised: 19 July 2024

Accepted: 22 July 2024

Published: 24 July 2024



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1. Introduction

Coal- [1] and heavy fuel oils- [2,3] fired power plants generate large amounts of fly ash, a waste by-product that contains the so-called aluminosilicate microspheres (MSs). Depending on the morphology of the particles, two basic types of MSs are distinguished: fly ash cenospheres (FACs), which are hollow spherical microparticles filled with gas, and fly ash plerospheres (FAPs), which are filled with fine mineral particles or porous substances [4–6]. The International Energy Agency reports that today, coal remains the largest energy source for electricity generation [7]. According to recent estimations, the global production of fly ash is approx. 1000 tons a year [8], of which up to 15% [9] (or up to 150 tons) are the FACs. An overview of the performance of cenospheres [9] reports that FACs are primarily composed of SiO_2 and Al_2O_3 , with content varying between 52 and 73% and 17 and 38%, respectively. Therefore, FACs can be applied at high temperatures. The following ranges of minor compounds are given in the overview: 1–11% for Fe_2O_3 , 0–5% for CaO , 0–4% for K_2O , and 0–3% for Na_2O . The diameter of FACs varies between ~10 μm and ~600 μm , and the bulk density may be as low as 200 kg/m^3 due to the hollow structure of the cenospheres and as high as 1000 kg/m^3 . Due to their size, shape, composition, and properties, FACs are considered to be a useful fraction of fly ash [10] with potential application in several industry fields, such as construction, pharmaceutical, biomedical,

etc. [11], reducing in such a way the use of raw materials and energy consumption for their processing and contributing to the development of sustainable manufacture.

A review of recent publications in the construction field shows that, due to the specific morphology and properties, FACs are mainly considered a lightweight filler and a non-sacrificial pore-forming agent that reduces density and/or improves thermal insulation properties of lightweight concrete [12,13], MOC-based composites [14], fireclay-based ceramic composites [15,16], geopolymer composites [17], lightweight carbon–FACs composite foams [18], etc. Furthermore, cenospheres have the potential to contribute significantly to the performance of refractory castables when incorporated into compositions with calcium aluminate cement (CAC). CAC-based refractory castables have been widely applied for the lining of various types of furnaces operating at high temperatures [19]. The key requirement for refractory castables is the ability to withstand thermal stresses caused by the change in the temperature of the structure. Researchers found that porous refractory castables have enhanced thermal shock resistance, which, however, reduces with excessive porosity. For example, the number of thermal shock cycles that a porous refractory material can withstand decreases rapidly when porosity exceeds 40%. The porosity of about 20% creates the optimal combination of thermal shock cycles and the minimum safety factor, indicating that thermal shock resistance is maximized at this porosity level [20]. Small round pores in dense refractory materials of low porosity reduce stress concentration and act as crack-stoppers, thus improving the thermal shock resistance of the material [21,22]. These findings suggest that hollow microsphere-shaped FACs could improve the structure of the refractory castable and enhance its thermal shock resistance.

The effect of FAC additives on the alkali resistance of refractory castables is an interesting aspect that will be tested in this research work. Alkali exposure conditions are typical in biomass combustion boilers when aggressive alkaline compounds, such as potassium and sodium carbonates, chlorides, etc., are generated and produce low-melting ash and aggressive vapor, which over time penetrates the refractory material, react with it, and induce its spalling [23–26]. Ground quartz (SiO_2) sand added to fireclay refractory castables has the potential to mitigate alkali-induced damage by promoting the formation of a protective glassy layer on the castable surface when exposed to high temperatures and alkali salts [27]. However, the quantity of quartz sand added must be carefully considered, as polymorphic transformations of SiO_2 occur at specific temperature thresholds, accompanied by a volume change [28] and a considerable decrease of thermal shock resistance of refractory material with such additive [29]. Andalusite, after complete mullitization, was found [30] to have high resistance to alkali attack due to the mullite–high silica glass phase structure formed. At first, potassium vapor reacts with the silica-rich glass phase, forming the potassium silicate phase and preventing direct interaction with mullite. Mullite and quartz are the most often mentioned [9,31–34] crystalline phases of FACs, while the amorphous phase is represented mainly by aluminosilicate. The results reported in [35] show that FACs with a high amount of $\text{SiO}_2 + \text{Al}_2\text{O}_3$ (93.4–94.5 wt.%) and a low content of alkalis (K_2O) form cristobalite from the amorphous phase at 1100–1200 °C temperatures, indicating the presence of SiO_2 glass rather than amorphous aluminosilicate in raw FACs. The already determined positive effect of adding SiO_2 on the ability of aluminosilicates to withstand alkali attacks [27,29,30] suggests that the presence of free SiO_2 in the micro-scale dispersive FACs (crystalline or glassy) will also contribute to alkali resistance of CAC-FAC composites. The improvement of thermal stability and alkali resistance of CAC-based refractory castables is the main way to increase their durability. The use of power plant by-products for the modification of CAC-based refractory composite properties will potentially not only save the raw materials but also enhance the durability and lifespan of refractory composites, contributing to their sustainability increase by reducing the frequency of replacement and conserving resources.

This work aims to analyze the impact of FACs on the properties of CAC-based aluminosilicate refractory castable, such as density, cold crushing strength, shrinkage, etc., and most importantly, the durability by evaluating the thermal shock and alkali resistance.

2. Materials and Methods

To investigate the effect of FACs addition on the thermal shock resistance and alkali-induced damage of refractory castables, medium cement refractory concrete (MCC) was chosen. MCC is increasingly preferred for biomass boiler installations due to its consistent quality, even under variable manufacturing conditions [36]. The following raw materials were used for the MCC compositions:

- Calcium aluminate cement Gorkal 70 (G70) (Gorka Cement Company; Trzebinia, Poland) with the chemical composition (wt.%) as follows: Al_2O_3 70.0–72.0; CaO 28.0–29.0; $\text{SiO}_2 < 0.5$; $\text{Fe}_2\text{O}_3 < 0.5$ and having a specific surface area of $450 \text{ m}^2/\text{kg}$;
- Reactive alumina (RA) (CTC 20; Almatix, Germany) containing 99.7% Al_2O_3 and having a specific surface area of $2100 \text{ m}^2/\text{kg}$;
- Microsilica (MS) (RW-Fuller; RW Silicon GmbH, Pocking, Germany) with the chemical composition (wt.%) as follows: SiO_2 96.1; Al_2O_3 0.2; Fe_2O_3 , 0.05; C 0.6; CaO 0.25; MgO 0.4; K_2O 1.2; Na_2O 0.1; SO_3 0.35 and having an average particle diameter of 150 nm;
- Fireclay aggregate (FA) 0–4 mm (Tabex-Ozmo, Ostrowiec Świętokrzyski, Poland) with the chemical composition (wt.%) as follows: SiO_2 53.7; Al_2O_3 36.6; Fe_2O_3 3.3; CaO 3.1; MgO 0.7; K_2O , 1.0; TiO_2 1.3. Fireclay was also used as a fine filler (FF) after milling FA for 1 h and sieving through a 0.14 mm sieve. The bulk density of FA was $1430 \text{ kg}/\text{m}^3$, FF was $1100 \text{ kg}/\text{m}^3$, and the refractoriness of FA was 1710°C ;
- Deflocculants Castament FS20 (FS20) (BASF Construction Solutions GmbH, Trotsberg, Germany) and technical sodium tripolyphosphate (NT) (BASF Construction Solutions GmbH, Trotsberg, Germany);
- Tap water (W);
- Fly ash cenospheres (FACs), which are lightweight, spherical, hollow, micro-sized particles consisting mainly of silica and alumina (86.7 wt.%) and having low alkali content (0.78 K_2O , 0.55 Na_2O) (Table 1). The bulk density of FACs is approximately $410 \text{ kg}/\text{m}^3$.

Table 1. Chemical composition of the raw FACs (wt.%).

C	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	Fe ₂ O ₃	Other
4.84	0.55	0.26	34.8	51.9	0.78	1.12	1.28	2.12	2.35

FAC size varied in quite a wide range, ~50–400 μm , with the prevailing particle size approximately ~140 μm (Figure 1a). FAC shells have a spherical shape (Figure 1b) with porous walls with thicknesses ranging from 1 to 2 μm up to 10 to 15 μm (Figure 1c).

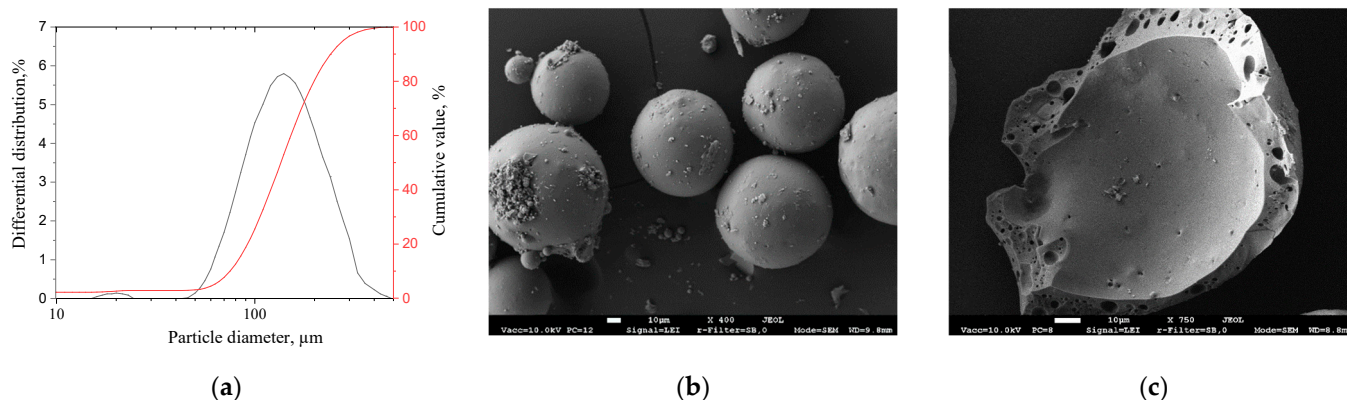


Figure 1. FAC particles' size (a) (red curve—cumulative value, black curve—differential distribution) and SEM images of FAC external morphology (b) and porous structure of the FAC shell (c).

According to XRD phase analysis (Figure 2), raw FACs consist mainly of crystalline mullite and at least one amorphous phase showing a “halo” in a 2θ angle range between

$\sim 15^\circ$ and $\sim 30^\circ$. Thermal treatment of FACs at 950°C for 10 h did not change the phase composition significantly; however, a weakly expressed peak at a 2θ angle of $\sim 21.5^\circ$ revealed a slow crystallization reaction in the amorphous phase at this temperature. Moreover, the reflections attributable to mullite were more intense, showing a high probability of crystallinity improvement and additional crystallization of a small quantity of mullite. FAC heating at 1100°C for 10 h resulted in the crystallization of a high amount of cristobalite, indicating the correspondence with the results presented in [35] and confirming the presence of the glassy phase of free SiO_2 in raw FACs studied in the present work. Moreover, a low quantity of anorthite formed due to CaO present in raw FACs and a high-temperature reaction in the $\text{SiO}_2\text{--Al}_2\text{O}_3\text{--CaO}$ system should be mentioned. The transition of the SiO_2 phase from the amorphous state into the crystalline may affect the high-temperature behavior of the FACs since the coefficient of thermal expansion, Young's moduli, Poisson ratio, strength, and brittleness differ for these SiO_2 modifications [37]. Therefore, studies of the properties of concrete with such additives at temperatures of 950°C and 1100°C were initiated.

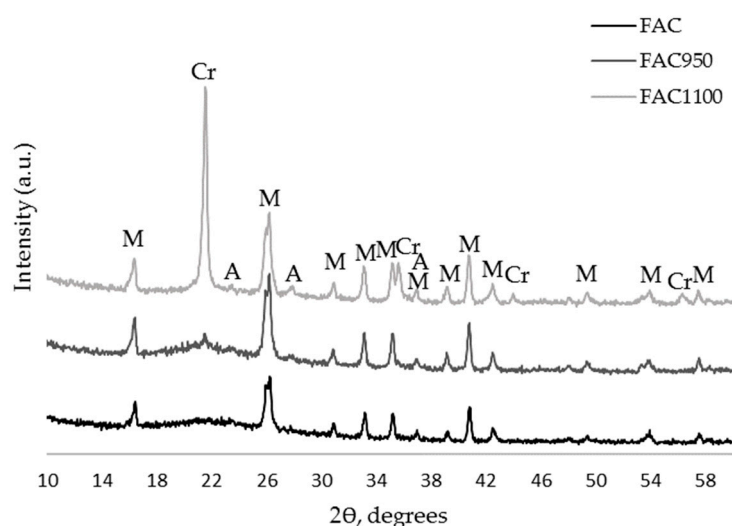


Figure 2. X-ray diffraction patterns of raw FACs and FACs after heat treatment at 950°C and 1100°C : M—mullite, Cr—cristobalite, A—anorthite.

MCC samples in the form of $70 \times 70 \times 70 \text{ mm}^3$ cubes were prepared from the raw materials listed above. Compositions of the samples are given in Table 2. The addition of a potentially weaker aggregate can result in a remarkable decrease in the strength properties of CAC-based refractory castables. As the earlier study of the effect of hollow corundum microspheres (HCMs) has shown [22], 2.5% and 5% of HCMs did not worsen the strength of the castable, while increasing the amount of HCMs up to 10% was accompanied by a compressive strength drop. Based on these previous results, it was expected that $\sim 3\text{--}7\%$ FACs could have a positive effect on the thermal stability of MCC without significant loss in strength. First, dry components were mixed in a Hobart planetary mixer for 5 min and then mixed with water for 3 min. The samples were kept at $20 \pm 1^\circ\text{C}$ for 72 h, then dried at $105 \pm 2^\circ\text{C}$ for 48 h, and sintered at 950°C and 1100°C for 5 h. The samples of refractory castables were prepared and treated (curing, drying, and thermal treatment) according to the requirements of LST EN ISO 1927-5:2013 [38]. The main physical and mechanical properties were determined according to LST EN ISO 1927-6:2013 [39]. Three samples from each composition were used for the testing. The alkali resistance of the refractory castable was determined according to ASTM C454-83(2007) [40]. The ultrasonic pulse velocity (UPV) was determined according to [41].

The chemical analysis of FACs was performed with an X-ray fluorescence spectrometer (XRF) Rigaku ZSX Primus IV using the wavelength dispersion method. The generator used 60 kV voltage and 150 mA current. Rh X-ray tube anode and 4 kW X-ray tube power were

used. Powdered material was compressed with a hydraulic press Herzog TP20 by holding the load of 200 kN for 3 min to form the test samples with a diameter of approx. 40 mm and a height of 3 mm. The samples were tested in a vacuum (~6 Pa) at 36.5 °C temperature.

Table 2. Compositions of MCC samples (wt.%).

Sample Designation	G70	MS	RA	FA (0–4 mm)	FF (0–0.14 mm)	FAC	FS20	NT	Water ¹
FAC0	12	5	12	60.5	10.5	-	0.1	0.1	9.0
FAC3	12	5	12	60.5	7.5	3	0.1	0.1	9.0
FAC5	12	5	12	60.5	5.5	5	0.1	0.1	9.0
FAC7	12	5	12	60.5	3.5	7	0.1	0.1	9.5

¹ above 100% of the dry mix.

Microstructural analysis was performed using a JSM-7600F (JEOL, Tokyo, Japan) scanning electron microscope equipped with the energy dispersive spectrometer Inca Energy 350 SDD X-Max 20 mm² (Oxford Instruments, Oxford, UK) for X-ray microanalysis (EDS). The voltage of 10 kV was used for both SEM and EDS analyses, and the secondary electron mode was used for image formation. Before the test, the surface to be investigated was covered with a layer of electrically conducting material using a QUORUM Q150R ES device (Quorum Technologies Ltd., Lewes, UK). The samples with a fractured surface were used to evaluate the changes in the microstructure.

XRD analysis of the phase composition of the materials was carried out using a diffractometer DRON-7 at 30 kV voltage and 15 mA current, the diffraction angle ranging from 4° to 60°, the detector movement step of 0.02°, and the per-step duration of the intensity measurement of 2 s. The phases were identified by decoding the XRD patterns according to the ICDD diffraction database.

The samples for thermal shock resistance tests were fired at 950 °C and 1100 °C. The thermal shock resistance of refractory castables was determined according to DIN 51068 by keeping the samples at 950 °C for 40 min and cooling them in water for 5 min and then in air for 10 min (cycle 1).

The crucible method (ASTM C 454-83:2007 [40]) was chosen to assess the influence of alkali attack on the tested refractory castable at 1100 °C.

3. Results and Discussion

Microstructural analysis of the cleavage surface of MCC samples revealed quite a uniform distribution and good incorporation of FACs in the cement matrix when 3% or 5% FACs were added by weight. The image (Figure 3a) shows that each microsphere is densely surrounded by the cement matrix with good contact and no significant gaps. At higher FAC amounts (7%), the agglomeration of microspheres was observed more often, resulting in the formation of gaps and cavities between them (Figure 3b), as tight packing for cenospheres having a natural spherical shape is challenging [11,12]. Local spot reactions between the cement matrix and FACs surface were observed at both 950 °C and 1100 °C temperatures, resulting in the development of well-connected common crystals (Figure 3c,d).

According to the results of the XRD phase analysis (Figure 4), the main reflections that appeared in the XRD patterns of the concrete after drying belong to the phases of the fireclay aggregate, which are mullite, cristoballite, quartz, and corundum. The reflections attributable to calcium monoaluminate CaO·Al₂O₃ (CAC cement mineral) were observed as well. The main phase changes occurring in concrete samples at firing are associated with the formation of anorthite and gehlenite, whose peaks were not observed after drying, appeared at 950 °C, and increased in intensity at 1100 °C. Anorthite and gehlenite are the products of high-temperature reactions between CaO from cement, SiO₂ from fireclay, and Al₂O₃ present in both cement and fireclay. As was expected, a similar reaction takes place between the cement matrix and FAC particles, mainly consisting of SiO₂ and Al₂O₃. EDS analysis of the crystals formed at the interface between the cement matrix and FACs

showed their elemental composition very similar to that of anorthite: ~7.90% Ca, ~17.63% Si, ~20.55% Al, ~53.92% O (in wt.%). Similar results were obtained when studying fluidized bed cracking catalysts waste, a material chemically close to FACs, when the formation of anorthite in compositions with calcium aluminate cement was found at 1200 °C [42].

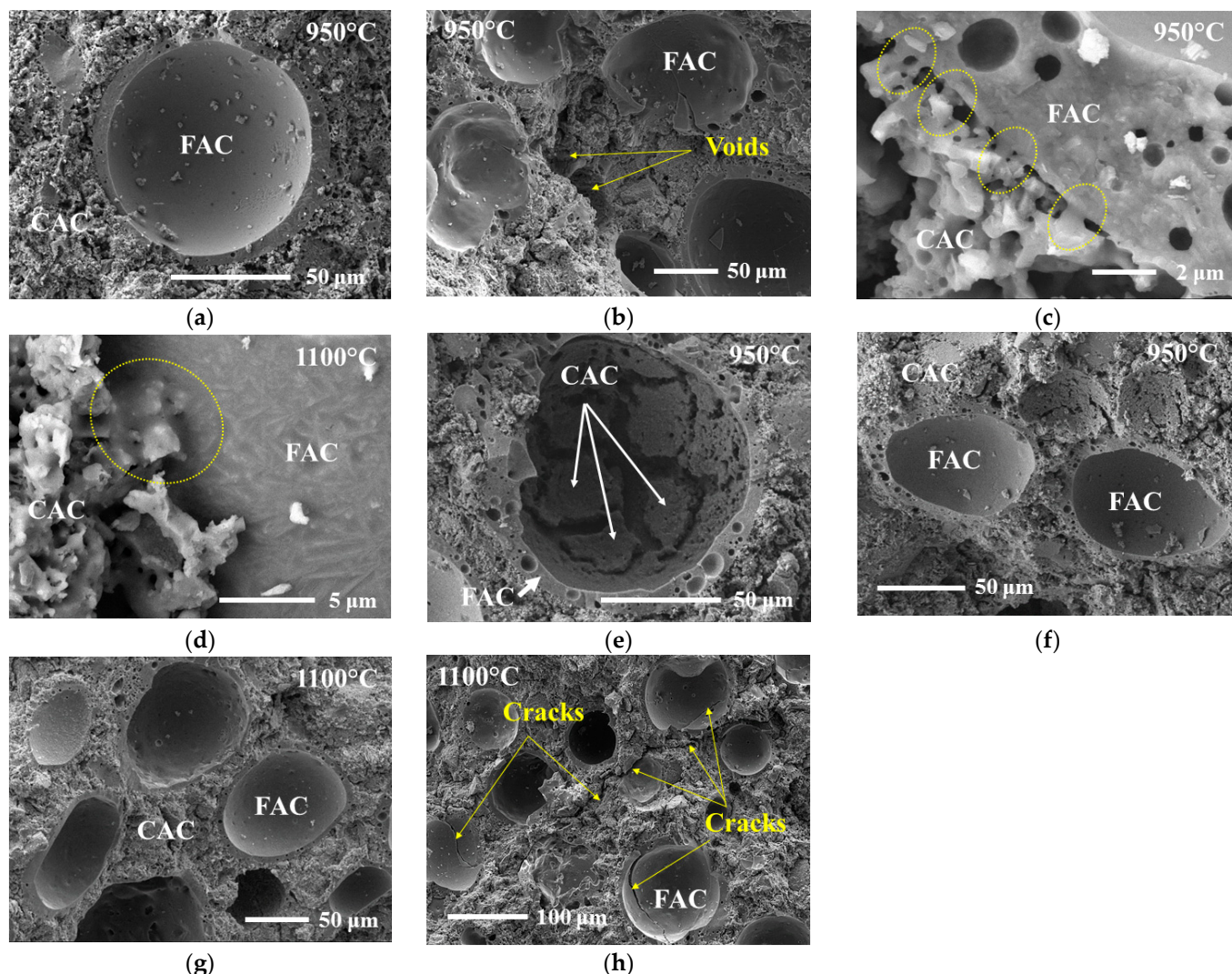


Figure 3. SEM micrographs of MCC containing 5 and 7 wt.% FACs and fired at 950 °C and 1100 °C.

Most of the cenospheres were empty; however, part of the FACs incorporated in MCC contained cement hydration products (dehydrated phases after firing at high temperature) inside (Figure 3e), which means that part of the FACs may entrap cement paste during the mixing of refractory castable.

SEM analysis revealed that a lot of cenospheres had irregular or elongated shapes rather different from the regular spherical shape (Figure 3e–g). This observation suggests that FAC particles undergo deformation during MCC firing. This deformation is caused by the expansion of the cement matrix and aggregates while heating and their shrinkage while cooling. Moreover, it was found that a part of the cenospheres had cracks (Figure 3h), which were most likely caused by the pressure of expansion and shrinkage of the matrix and the aggregates. Figure 3h also shows that cracks tend to propagate between the agglomerated cenospheres, indicating that a thin interlayer of the cement matrix between closely packed FAC particles is not strong enough to withstand crack propagation. It should also be noted that more deformed and cracked cenospheres were observed after firing at 1100 °C than at 950 °C. This is influenced by the more significant expansion and shrinkage of the structural

components of the concrete and, possibly, a more intensive process of formation of new phases at a temperature of 1100 °C: cristobalite in the FACs (Figure 2) and anorthite in the concrete cement matrix (Figure 4).

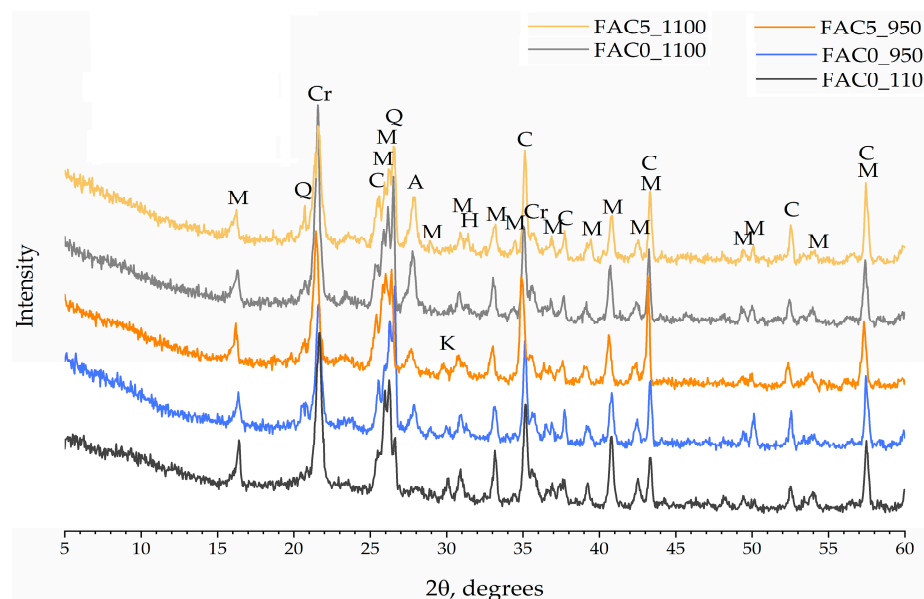


Figure 4. XRD patterns of MCC after drying (110) and firing (950, 1100): M—mullite; Cr—cristobalite; Q—quartz; C—corundum; K—calcium monoaluminate $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (CA); H—gehlenite; A—anorthite.

The addition of FACs reduces the density of modified concrete due to the form and structure, low density, and high porosity of cenospheres [43–45]. We observed a 3–5% and 3–6% drop in density at 3 days of curing when ground fireclay was replaced by FACs at 3% and 5% (Figure 5a); 7% of FACs resulted in a 12–14% density drop, which cannot be explained only by the replacement of ground fireclay with FACs. Another reason confirmed by the microscopic examination is the accumulation of cenospheres and voids not filled with cement between them (Figure 3h). The reduction of density in dried and fired samples as compared to the cured samples is, first of all, related to the removal of unbound water and further dissociation of hydrates. The density of the samples fired at 950 °C and 1100 °C was 1805–1990 kg/m³ and 1800–1970 kg/m³, respectively. The difference is insignificant and depends mainly on the FAC content, indicating that the phase transformations ongoing in the material in this temperature range did not remarkably affect the final density of the samples.

The variation of UPV, which shows the changes in the microstructure of a material, was the same for all the compositions tested in the treatment temperature range (Figure 5b). Additional hydration of CAC minerals ($\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{CaO} \cdot 2\text{Al}_2\text{O}_3$), which occurs during the drying process [46], contributes to the filling of pores and compaction of the structure and is the possible reason for increased UPV after the drying (110 °C) compared with UPV after 3 days of normal hardening. After the firing of MCC at high temperatures, UPV drops due to the dehydration process and the formation and propagation of microcracks, which hinder the propagation of ultrasonic waves. It should be noted that UPV in MCC compositions containing 3% and 5% of FACs (FAC3 and FAC5) measured after hardening (3 days), drying (110 °C), and firing (950 °C and 1100 °C) did not differ significantly from the control composition (FAC0) and among each other. However, the addition of 7% FACs resulted in the UPV decrease by 4.5–7.5%, indicating that (i) ultrasonic pulse velocity is mainly predetermined by the integrity of the cement matrix, and (ii) the addition of FACs created more discontinuities. These findings were confirmed by the microstructure analysis.

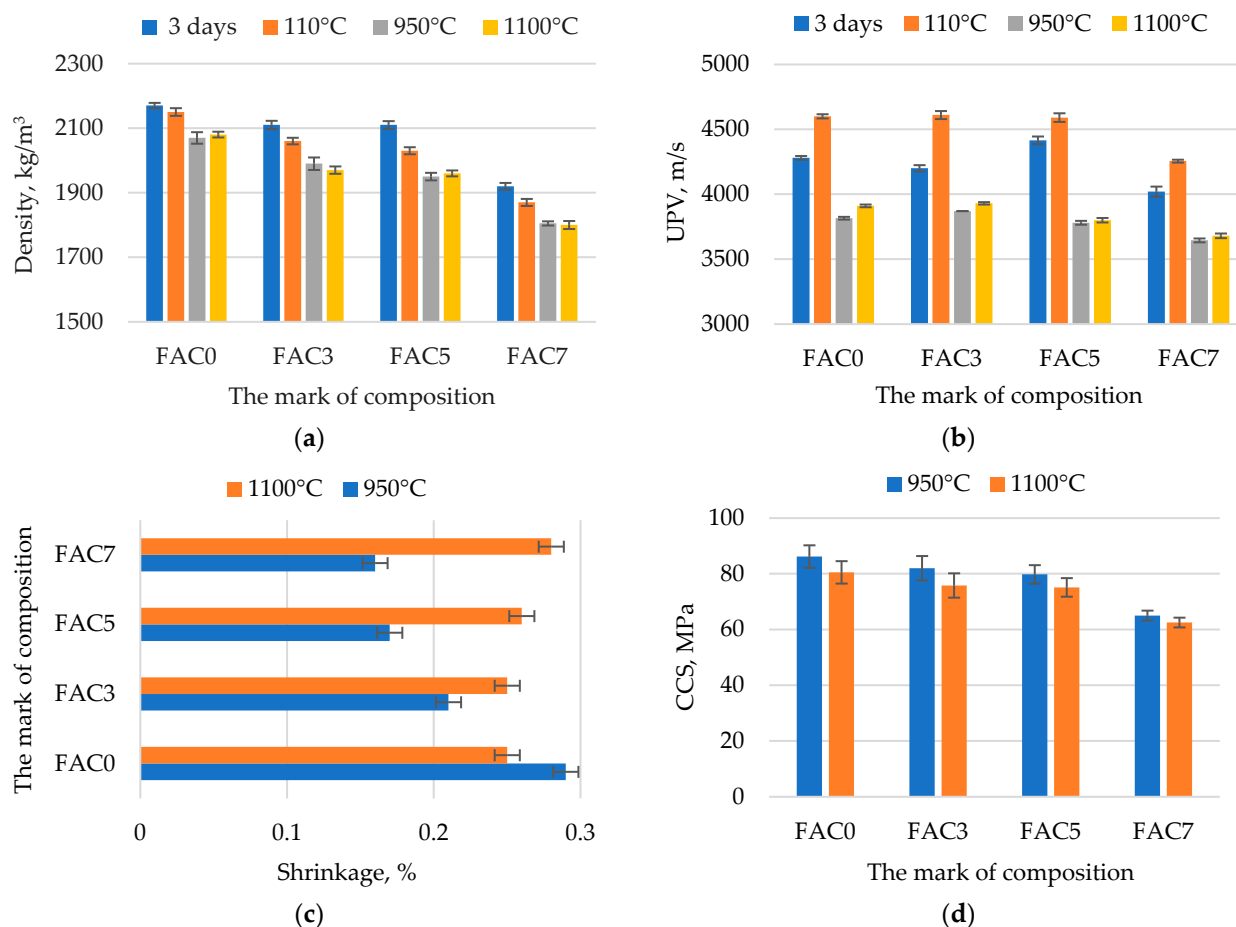


Figure 5. The impact of FAC content and treatment temperature on the density (a), UPV (b), shrinkage (c), and CCS (d) of MCC.

The analysis of shrinkage results (Figure 5c) showed that FACs reduce the shrinkage of MCC concrete by about 45% at the firing temperature of 950 °C. Lower shrinkage is attributed to the sufficient FAC strength at this temperature. At 1100 °C, the shrinkage of the samples with 3% FACs remained unchanged, while the shrinkage of the samples containing 5% and 7% FACs increased 4.0% and 12.0%, respectively. These results agree with the results of microscopy tests, which showed that at 950 °C, only a small fraction of FAC particles deformed and/or split, whereas at 1100 °C, the number of deformed and split particles was much higher. Similar results were reported by Pundiene et al., 2018 [47] in the study of refractory concrete. Researchers found that at 1000 °C, FACs reduce the shrinkage of refractory concrete up to 50%, but at 1200 °C, the shrinkage of FAC-modified samples was higher than that of the reference sample.

The analysis of the mechanical characteristics of concrete showed that CCS reduced with the addition of FACs (Figure 5d). The replacement of ground fireclay with 3%, 5%, and 7% FACs caused the CCS to reduce by 5.8%, 6.7%, and 22.4%, respectively. The lower density of the samples is the first reason for the CCS decrease [48,49]. Another reason is the low-quality interaction zone between FACs and the cement matrix, which deteriorates further at 1100 °C temperature [50]. The third reason is the lower strength of the FAC shell, which tends to fracture under higher loads [11,51]. Most often, the compressive strength of FACs is below 25 MPa [52]. Refractory concrete with the highest FAC content (7%) had the lowest CCS. Multiple FAC and cement matrix defects were visible in the structure after firing at 1100 °C (Figure 3h).

The addition of 5% FACs significantly improves thermal shock resistance (TSR) (Figure 6); a 75% improvement was observed after firing the samples at 950 °C and 43% at 1100 °C. The

increased temperature gradient explains the lower effect of improvement at a higher temperature. The improvement was not so stable in the sample containing 3% FACs, and the effect was related to the initial firing temperature. A higher FAC content can have a negative impact on TSR. Compared to the reference, TSR decreased by 35.7% in the samples containing 7% FACs. A more visible positive effect of FACs may be noted when MCC is fired at 950 °C. There are two possible reasons for that. First, as the XRD results revealed (Figure 2), the major part of the amorphous phase remained in the FACs after firing at 950 °C, while at 1100 °C, more brittle cristobalite is formed. Second, the initial firing at a higher temperature (1100 °C) induces greater damage to the material (both FACs and concrete).

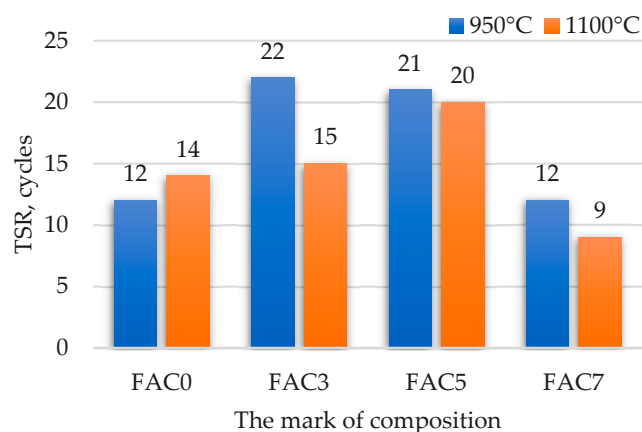


Figure 6. The impact of FACs on the TSR of MCC.

Authors found [53] that FACs have low thermal expansion, considerable thermal stability, and high crack resistance. Additionally, the presence of an amorphous phase significantly impacts the creep behavior of the material, particularly when there are large quantities of the amorphous phase, and it is distributed evenly [54]. The effect of the vitreous phase can be advantageous in terms of thermal shock resistance for two main reasons: (1) it helps to alleviate residual thermal stresses, and (2) it strengthens the material by facilitating the crack-bridging mechanism. Consequently, it enhances the material's ability to withstand sudden temperature changes [55,56]. Conversely, pores within the material can absorb thermal stress and hinder crack propagation under thermal shock conditions [57]. One more probable mechanism for increasing the TSR of refractory castable is the reduction of stress concentration in the material due to the regular spherical shape of cenospheres [22].

Thermal quenching can cause the formation of new cracks or propagation of the existing ones, leading to strength reduction. The formation of cracks significantly affects the velocity of ultrasonic wave propagation (UPV) through the material. UPV measuring helps to effectively track the extent of damage caused by the thermal shock [56]. Table 3 and Figure 7 show the change in UPV when the samples are subjected to thermal cycles. After three TSR cycles, the UPV decreased by about 20–30% in all samples due to the cracks formed. The lowest change in UPV was observed in composition FAC7, with the highest content of FACs. SEM analysis (Figure 3h) showed that at high FAC content, the particles agglomerate, and the cracks in the cement matrix between the cenospheres become wider and deeper.

Irrespective of the fact that after 9 TSR cycles, FAC7 samples show the lowest decrease in UPV, deep cracks cause the samples to break up into large fragments and lose more than 30% of their weight (Figure 8c). The degradation pattern of reference samples without FACs was similar to that of samples FAC7 (Figure 8a). Samples FAC3 and FAC5 showed a higher decrease in UPV; however, the fragmentation of the material into smaller pieces was observed in sample FAC5 (Figure 8b). According to [58], the material with a high concentration of short microcracks will have high resistance to the propagation of long cracks and improved resistance to thermal shock. It is likely that at 3% and 5% FACs, the

sufficiently even distribution of particles in the cement matrix inhibits the propagation of long cracks, thus forming a network of microcracks and leading to heterogenization and fragmentation of the structure, which helps the specimens to retain their shape for a longer time and to avoid degradation when exposed to TSR cycles.

Table 3. UPV decrease after thermal shock cycles, %.

Number of TSR Cycles	After Firing at 950 °C				After Firing at 1100 °C			
	FAC0	FAC3	FAC5	FAC7	FAC0	FAC3	FAC5	FAC7
3	31.3	22.5	21.2	16.6	29.7	34.5	26.8	26.4
6	35.8	27.4	23.3	29.4	32.2	43.3	28.2	28.8
9	44.4	37.2	37.0	33.3	37.3	50.6	33.4	37.6
12	48.1	38.2	44.4	36.9	39.9	51.9	39.7	
15		41.9	47.9		41.2	53.7	43.9	
18		45.5	48.1				47.1	
21		49.4	56.6					

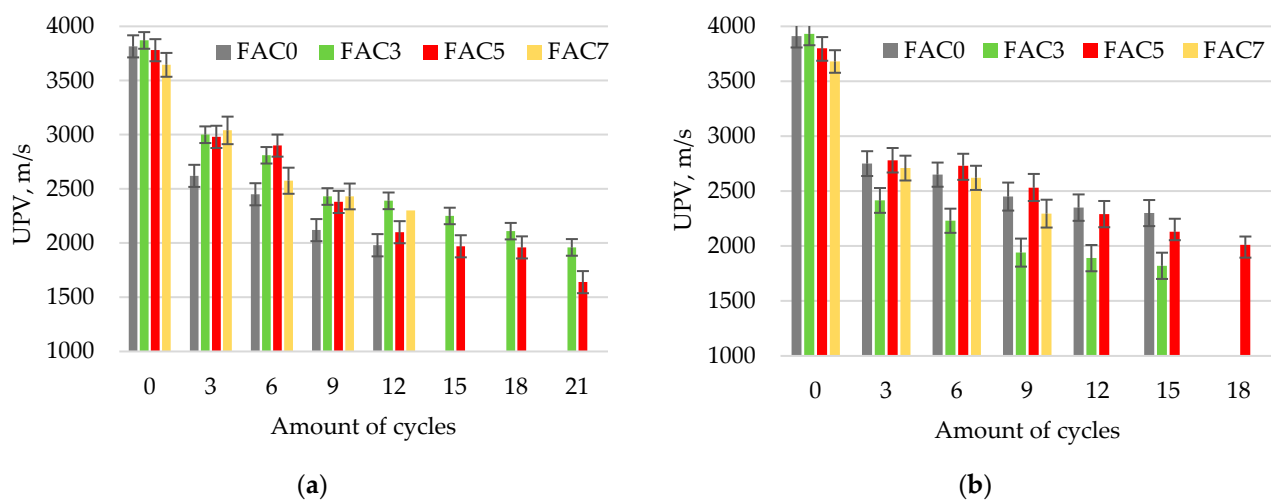


Figure 7. UPV changes after thermal shock cycles in the samples fired at 950 °C (a) and 1100 °C (b).

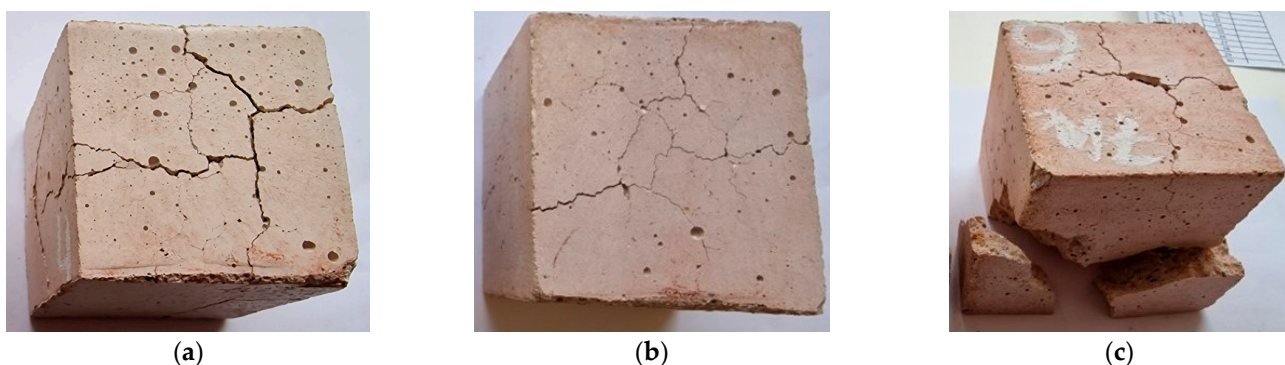


Figure 8. Images of FAC0 (a), FAC5 (b), and FAC7 (c) samples fired at 1100 °C after 9 TSR cycles.

The fracture of refractory materials is a two-stage process involving the crack's initiation and its further propagation. Before exploitation, refractory castable materials undergo hardening, drying, and firing stages, which are accompanied by the conversion of hydration products, evaporation of physically and chemically bound water, and expansion and shrinkage of the cement matrix and fillers. Due to the volume changes occurring at these stages and the mismatch in thermal expansion coefficients of the matrix and aggregates, the microcracks and gaps are formed both in a matrix and at the interface with aggregates.

Together with pores, sharp edges/corners of the aggregates act as stress concentrators and other possible pre-existing flaws, facilitating crack initiation. In Figure 9a, the initiation of a crack from the gap formed at the matrix and aggregate interface and from the sharp corner of the fireclay aggregate may be observed. Crack propagation in CAC-based refractory concrete with fireclay aggregates can occur through the matrix, the aggregates, or along the interfaces, depending on their relative properties and structure. SEM observation of the control samples (fired both at 950 °C and 1100 °C) after their exposure to thermal cycling revealed propagation of cracks mainly in the matrix, partially at the interface between the cement matrix and fireclay particles, and at the much lower degree through the fireclay particles.

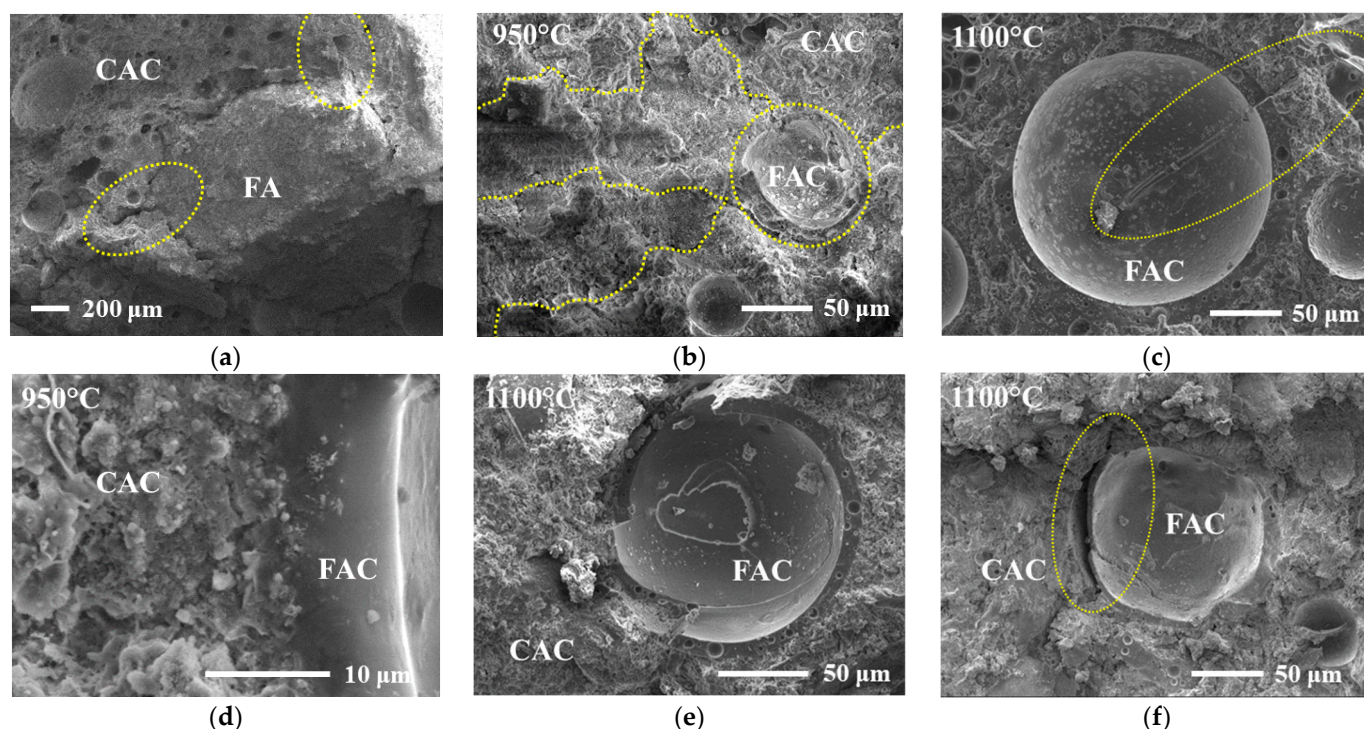


Figure 9. Microstructure of studied composites fired at 950 °C and 1100 °C after TSR cycles: (a) crack initiation at the sharp corner of the FA aggregate; (b) crack reflection from the FAC particle or its stopping and formation of fragmentary structure; (c) crack propagation stopping when falling inside the FAC; (d) interface between CAC matrix and FAC after exposure for TSR cycles; (e) fracture of FAC particle (in sample fired at 1100 °C) without signs of plastic deformation; (f) the same, but with the signs of plastic deformation; FA—fireclay aggregate; CAC—cement matrix; FAC—cenosphere. (marks in yellow—crack propagation).

In the samples containing FACs, the role of the FAC particles in crack propagation in the cement matrix can be explained by analyzing the SEM images in Figure 9b,c; the crack reflects from the surface of the FACs, changing the direction of propagation (Figure 9b), which contributes to the formation of a fragmentary structure or, the crack stops, falling inside the FAC particles (Figure 9c). Such crack propagation modes could be observed in samples fired both at 950 °C and at 1100 °C.

In general, most of the FAC particles retained their good contact with the CAC matrix (Figure 9d). The plane of fracture of the particles coincides with the plane of fracture of the matrix, indicating that the FAC particles are sufficiently firmly bound to the matrix and work as a whole. However, for samples fired at 1100 °C temperature, the more expressed FACs trend to crack without (Figure 9e) or with (Figure 9f) previous plastic deformation may be pointed out. When fired at 950 °C, FAC particles are more prone to plastic deformation without fracture. It can be observed from Figure 9f also the formation

of a visible gap between the CAC matrix and the FAC, which can be attributed to the increased thermal expansion coefficient of FACs after the formation of cristobalite, which firstly causes more significant plastic deformation, when CAC matrix constrains free FAC expansion and then leads to a more significant shrinkage. The gap formed may act as a defect for crack initiation; on the other hand, it may stop or reflect propagating cracks as well.

A 5% FAC concentration is favorable to the alkali resistance of MCC (Figure 10). The first cracks appeared in the samples with 5% FACs after six cycles of alkali attack, whereas in the reference and other compositions with higher or lower FAC content, the first cracks appeared after three cycles. After 15 cycles of alkali attack (Figure 11), all cut samples had a potassium barrier (blurred white line) formed in the contact zone with the reactant (K_2CO_3).

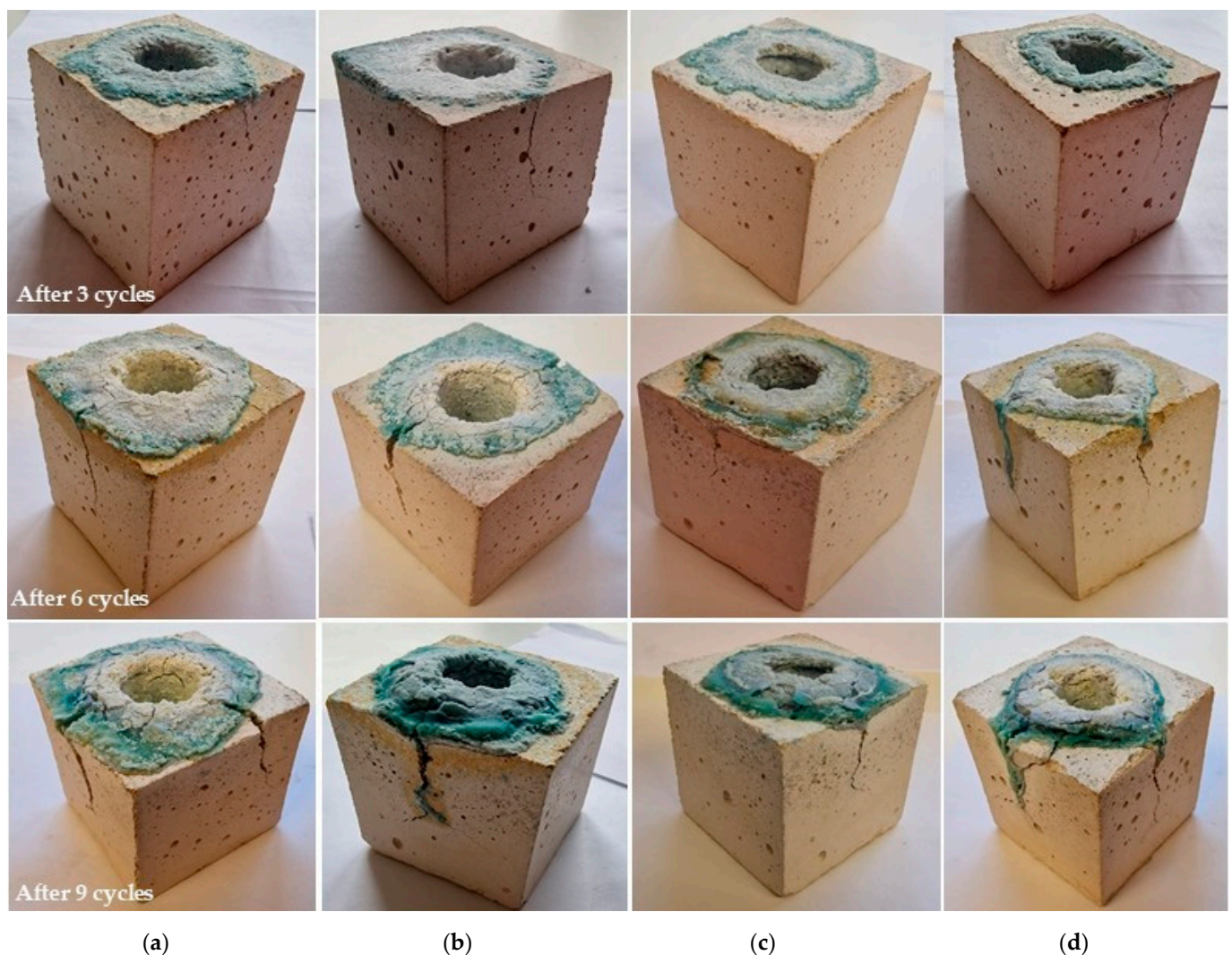


Figure 10. Images of the samples after 3, 6, and 9 cycles of alkali attack: (a) reference sample, (b) sample with 3% FACs, (c) sample with 5% FACs, (d) sample with 7% FACs.

The corrosion mechanism of refractories operates on two main premises: K_2CO_3 undergoes reduction to form K vapor, which then permeates into the sample via open pores. The K vapor subsequently reacts with SiO_2 and alumina, resulting in the formation of $KAlSi_2O_6$ and $KAlSiO_4$ [59]. When alkali attacks mullite, it transforms into leucite and forms a transient liquid phase. Subsequently, the liquid phase formed induces erosion and dissolution of the mullite phase, thereby inhibiting the direct erosive reaction of alkali vapor on mullite [30]. Therefore, the transient liquid phase effectively blocks alkali penetration by

confining the attack solely to the surface layer. Consequently, mullite demonstrates superior resistance to alkali attack. However, the larger volume of corrosion products formed and the pressure generated by increasing the number of cycles result in uneven deformation of the samples and the opening of cracks (Figure 9), which facilitate further diffusion of potassium compounds. Previous studies [29] on the alkali resistance of refractory castables indicate that incorporating 2.5% finely ground quartz sand into fireclay castable enhances the development of a protective glassy layer on the refractory surface. The reaction between potassium and quartz sand leads to the formation of potassium silicate and an additional amorphous phase. The resulting viscous glass fills the pores and capillaries of the material, creating a protective layer. This layer hinders the potassium penetration into deeper layers of the material. In our study, this could have been caused by the presence of a SiO_2 phase in a composition of dispersive FACs (cristobalite formed from FACs after firing the samples at 1100 °C temperature) uniformly distributed in a cement matrix of the concrete.

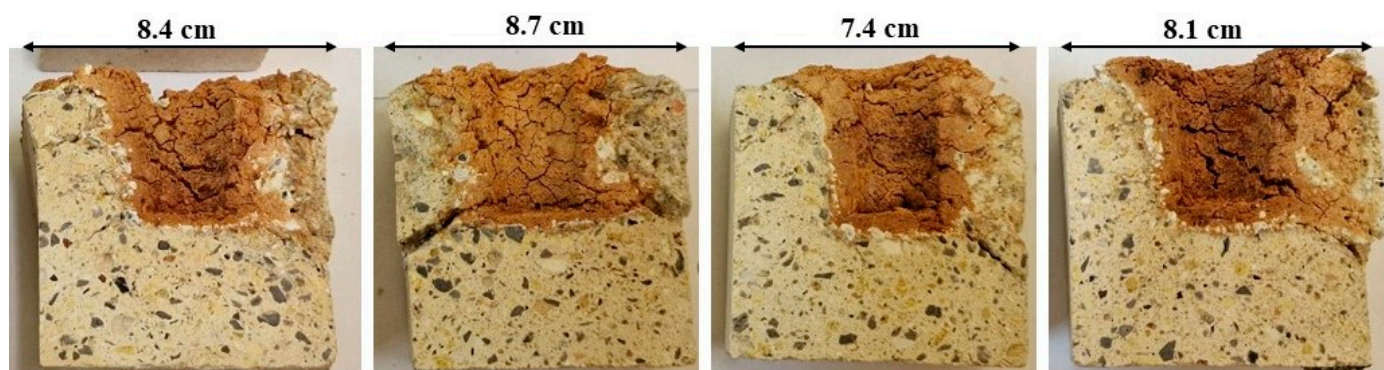


Figure 11. Images of cut samples after 15 cycles of alkali attack: FAC0, FAC3, FAC5, and FAC7 from left to right.

No positive effect on alkali resistance was observed in the samples containing 3% FACs compared to the reference composition, indicating that the addition of 3% FACs is not enough to form a sufficient protective layer. There was no positive effect at 7% FACs either, presumably due to the agglomeration of cenospheres accompanied by the formation of voids and cracks between them, which facilitate K vapor diffusion inside the material. A 5% FAC concentration (or 2–3% if converted to the entire mix content) was shown to be optimal as the number of particles was enough to form a protective layer, and the distribution of particles in the material was quite uniform to avoid their accumulation. A 5% FAC concentration had the least negative effect caused by alkali compounds as the change in the sample surface dimensions was the least (increased approx. 6%) compared to 20% of the reference sample FAC0 (Figure 9).

Summarizing the research results, it is necessary to note the effect of firing temperature on the properties of MCC concrete with FAC admixture. At a temperature of 950 °C, a pronounced positive effect of FACs on concrete shrinkage and thermal shock resistance is observed. When at a temperature of 1100 °C, concrete and FACs themselves undergo pronounced mineral changes; increasing the amount of FACs increases the shrinkage of concrete, and resistance to thermal shock is clearly noticeable only in compositions with 5% FACs.

A possible mechanism for improving the thermal shock resistance of FACs in dense refractory concrete is based on the effect of stopping or reflecting propagating cracks, thus inhibiting the formation of long microcracks and promoting the formation of smaller ones. In this way, a fragmentary concrete structure is formed, in which individual fragments can displace relative to each other under thermal loading, withstanding a greater number of thermal shocks without fatal collapse. Moreover, when concrete is exposed to high temperatures, part of FACs, as a weak component in the structure of dense concrete, deforms and cracks, taking over and reducing the stresses in the material. The regular spherical shape

of the FAC particles may also contribute to the reduction of stress concentration levels in the composite.

4. Conclusions

Fly ash cenospheres are a suitable component for the medium cement refractory castable mix due to their porous structure, spherical shape, and appropriate chemical and mineral composition. These properties of fly ash cenospheres improve the resistance of medium cement refractory castable to thermal shock: refractory concrete modified with 5% fly ash cenospheres had 75% higher resistance to thermal shock than the reference after firing at 950 °C temperature and 43% higher resistance after firing at 1100 °C temperature.

FACs containing 86.7 wt.% $\text{SiO}_2 + \text{Al}_2\text{O}_3$ at an SiO_2 to Al_2O_3 ratio of ~1.49 has mullite and amorphous SiO_2 as the major phase constituents and undergoes SiO_2 transformation to cristobalite at temperatures range from 950 °C to 1100 °C. The effect of this phase transition on the structural transformations of concrete containing FACs is mainly associated with a greater FAC tendency to crack than to plastically deform due to higher cristobalite brittleness compared with amorphous SiO_2 . However, both FACs containing amorphous and crystalline SiO_2 act as weaker components in terms of the compression strength of the MCC concrete and act as crack propagation stoppers or reflectors, improving the resistance to thermal cycles.

A concentration of 5% of fly ash cenospheres improved the alkali resistance of medium cement refractory castable: the first cracks appeared after six cycles of alkali attack, whereas in the reference sample, the first cracks appeared after three cycles.

Fly ash cenospheres have a hollow spherical shape, gaps between the particles, and low strength, reducing the density and cold crushing strength of medium cement refractory castable. When 3%, 5%, and 7% ground fireclay was replaced with FACs, the density of refractory concrete decreased by 3–5%, 3–6%, and 12–14%, and the cold crushing strength decreased by 5.8%, 6.7%, and 22.4%, respectively.

Fly ash cenospheres reduce the shrinkage of medium cement refractory castable fired at 950 °C approx. by 45%. However, the shrinkage of the samples fired at 1100 °C containing 3% and 5% FACs was similar to the shrinkage of the reference sample and increased by 12% in the samples containing 7% FACs because FACs start softening and lose their shape at 1100 °C temperature.

Considering the effect of FACs on all the MCC properties studied, it can be concluded that the addition of FACs at 7% is too high because it deteriorates all properties of refractory castable. The addition of FACs at 5% can be considered to be appropriate because it improves resistance to thermal shock (after the initial firing of the samples at both 950 °C and 1100 °C) and has a positive effect on the resistance to alkali attack.

It is clear that FACs, as a light and weak component, reduce the strength characteristics of heavy and dense MCC concrete. However, the reduction in strength to 6% in concrete with 5% FACs is not critical (decrease from about 80 MPa to about 75 MPa), considering the remarkable increase in sustainability indicators (thermal shock resistance and alkali resistance at 1100 °C) of such refractory concrete. We believe that this admixture can also be used in other types of refractory concrete to increase sustainability.

Author Contributions: Conceptualization, J.Š. and V.A.; methodology, R.B. and J.Š.; formal analysis, A.K. and R.B.; investigation, J.Š., R.B., J.M. and R.S.; resources, R.S.; data curation, J.Š., J.M. and A.K.; writing—original draft preparation, J.M., R.B., J.Š. and A.K.; writing—review and editing, J.Š. and V.A.; supervision, J.Š. and V.A.; project administration, V.A.; funding acquisition, R.S. All authors have read and agreed to the published version of the manuscript.

Funding: The equipment and infrastructure of the Civil Engineering Scientific Research Center of Vilnius Gediminas Technical University were employed for investigations. This research was supported by the Center of Excellence project “Civil Engineering Research Centre” (Grant No. S-A-UEI-23-5).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All results are presented in the article.

Conflicts of Interest: The authors declare no conflicts of interest.

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