# The Impact of Curing Temperatures on Physical, Mechanical and Thermal Properties of CAC-Based Refractory Castables

Andrius Kudžma<sup>a\*</sup>, Valentin Antonovič<sup>a</sup>, Rimvydas Stonys<sup>a</sup> and Viktor Gribniak<sup>b</sup>

<sup>a</sup> Laboratory of Composite Materials, Vilnius Gediminas Technical University, Vilnius,

Lithuania

<sup>b</sup> Laboratory of Innovative Building Structures, Vilnius Gediminas Technical University,

Vilnius, Lithuania

\* Corresponding author: andrius.kudzma@vilniustech.lt

#### Abstract:

This investigation delves into the intricate relationship between curing temperatures and the physical properties of calcium aluminate cement (CAC)-based refractory castables, including conventional castables (CC), medium cement castables (MCC), and low cement castables (LCC). Crucially employed in industries with extreme temperature demands-such as biofuel boilers, oil, steel, and chemical sectors-these castables must endure thermal shocks while upholding robust physical and mechanical characteristics and minimizing temperature deformations. The study focuses on castables with varying cement content—CC (25% of CAC), MCC (12%), and LCC (7%)—scrutinizing their mechanical strength after high-temperature treatment, resistance to thermal cycling, and shrinkage, with evaluations conducted with samples cured at different temperatures, specifically 10 °C, 20 °C, and 35 °C. The test results indicate that higher CAC content (i.e., CC materials) makes castables less sensitive to variations in curing temperature, resulting in minimal changes in cold crushing strength (CCS), maintaining it at approximately 95 MPa. In contrast, MCC castables exhibit high sensitivity to the curing temperature, with the CCS increasing from 96 to 103 MPa as the curing temperature rises. To mitigate sensitivity and stabilize mechanical performance, accelerator and retarder additives were employed to control the curing of castables at both low and high temperatures. The study showed that additives used for this purpose, such as lithium carbonate for acceleration at temperatures above 10 °C and citric acid for retarding at temperatures above 30 °C, positively impact the thermal properties of castables after heat treatment. These additives effectively mitigate undesirable variations in characteristics.

**Keywords**: refractory castables; curing temperature; thermal shock resistance; calcium aluminate cement; medium cement castable.

## **1** Introduction

Refractory castables are specialized materials that withstand high temperatures, substantially outperforming conventional Portland cement-based concretes [1]. Unlike standard concrete, refractory castables use specialized aggregates, binders, and additives that can endure extreme heat without significant loss of strength or structural integrity [2]. These castables are commonly used in industrial settings such as furnaces, kilns, and reactors, where exposure to intense heat is routine. Unlike Portland cement-based concretes, refractory castables often contain high alumina or silica content and other additives to enhance their resistance to thermal shock and abrasion [3]. Calcium aluminate cement (CAC) is used in the composition of refractory castables, and these castables can be classified according to their content. Conventional castables (CC) usually have 25% of CAC and have good mechanical properties, but these properties decrease significantly at high temperatures [4]. Medium cement castables (MCC) have lower CAC content, which reaches ~12%, and this reduction in cement content helps improve the refractoriness and thermal shock resistance while maintaining adequate strength [5]. Low cement castables (LCC) further reduce the

cement content (7% of CAC), typically using specialized binders and additives to achieve desired properties. This type of concrete exhibits excellent high-temperature performance (up to 1600 °C), including superior strength, abrasion resistance, and thermal shock resistance [6]. Ultra-low cement castables (ULCC) contain minimal cement content, often less than 3-4% by weight, and no cement castables (NCC) rely on advanced bonding systems, such as colloidal silica or alumina, to achieve high strength and thermal stability [7].

The CAC present in refractory castables is formed from various minerals, including active CA (mono calcium aluminate – CaO·Al<sub>2</sub>O<sub>3</sub>), CA<sub>2</sub> (grossite – CaO·2Al<sub>2</sub>O<sub>3</sub>), CA<sub>6</sub> (hibonite – CaO·Al<sub>2</sub>O<sub>3</sub>),  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and  $C_{12}A_7$  (mayenite – 12CaO·7Al<sub>2</sub>O<sub>3</sub>) [8, 9]. In contrast to the hydration process of Portland cement, where the types of minerals formed remain independent of the duration and temperature of curing, the hydration of CAC results in the formation of various crystalline and amorphous hydrates, primarily influenced by the curing temperature [10]. The hydration of CAC can generate four principal temperature-dependent hydrates: CAH<sub>10</sub> (CaO·Al<sub>2</sub>O<sub>3</sub>·10H<sub>2</sub>O), C<sub>2</sub>AH<sub>8</sub> (2CaO·Al<sub>2</sub>O<sub>3</sub>·8H<sub>2</sub>O), AH<sub>3</sub> (Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O), and C<sub>3</sub>AH<sub>6</sub> (3CaO·Al<sub>2</sub>O<sub>3</sub>·6H<sub>2</sub>O) [11]. The composition of hydration products varies depending on the hydration and curing conditions. At hydration temperatures below approximately 15 °C, the main hydration product is CAH<sub>10</sub>; between 15 and 30 °C, C<sub>2</sub>AH<sub>8</sub>, and AH<sub>3</sub> typically form, but small amounts of CAH<sub>10</sub> can also be formed; and at curing temperatures exceeding 30 °C, the main hydration products are C<sub>3</sub>AH<sub>6</sub> and AH<sub>3</sub> (gibbsite or gel) [10]. However, it is essential to note that these temperature thresholds may exhibit slight variations across different published research sources [12]. These hydrates, which are formed at different curing temperatures, differ not only in shape but also in density. The shape of CAH<sub>10</sub> hydrates is like hexagonal prisms,  $C_2AH_8$  has a plate shape, and  $C_3AH_6$  has a cubic shape [13], with densities of 1720 kg/m<sup>3</sup>, 1950 kg/m<sup>3</sup>, and 2520 kg/m<sup>3</sup>, respectively [14]. In producing advanced binders, micro-silica is employed to improve the mechanical performance of CAC [15]. Consequently, micro-silica plays a role in forming semi-amorphous sub-microcrystalline C<sub>2</sub>ASH<sub>8</sub> (2CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>·8H<sub>2</sub>O) phases (e.g., stratlingite) alongside those hydrates [16]. Hence, the temperature conditions during the formation of refractory castable, which occurs not in a controlled laboratory environment but on the construction site, may range from 10 °C to 30 °C. Consequently, varying hydrates may form, leading to differences in the properties of the final product. These differences alter the mechanical and physical characteristics of the concrete [13,17], including thermal shock resistance, and potentially affect the performance and lifespan of the end product. During service, wear in refractory castables primarily arises from chemical corrosion, abrasive particle flow, and thermal shock failure induced by thermal cycling or temperature disparities within the material. Unlike erosion and corrosion, which typically exhibit a relatively constant wear rate, thermal shock failure can lead to sudden refractory loss, resulting in premature refractory castable failure [18]. Therefore, the thermal shock resistance of refractories is a significant concern for researchers and users. Understanding the effect of thermal shock resistance on refractory castables necessitates evaluating how different curing temperatures can affect it. The hydration of CAC can vary with curing temperature [19], with higher temperatures accelerating the process and increasing the degree of hydration, thus resulting in more hydrated products [20]. As CAC hydration follows a dissolution-precipitation process [21], hydration products are expected to be more uniformly distributed in CAC-based refractory castables, and the presence of unreacted CAC particles should decrease with higher curing temperatures.

To regulate the hardening speed of CAC-based refractory castables under different hardening conditions, retarders such as citric acid [22] or accelerators like lithium carbonate ( $Li_2CO_3$ ) [23] are commonly added to the material. Citric acid has been observed to retard both the initial stiffening and final hydration of CA cement-bonded refractory castables. This retardation effect on hydration is likely due to the complexation of  $Ca^{2+}$  ions by citric acid, leading to the withdrawal of  $Ca^{2+}$  ions from the pore solution [24]. On the other hand, the presence of  $Li_2CO_3$  in CAC-based refractory castables has been found to induce the dissolution of CA and CA<sub>2</sub> and the precipitation of hydrate phases. This process is reported to be accelerated to varying degrees depending on the concentration of  $Li^+$  ions [25,26]. According to Niziurska et al. [27],  $Li_2CO_3$  has been observed to promote the formation of larger quantities of metastable  $C_2AH_8$  hydrates, which can enhance thermal shock resistance parameters.

This study assesses the mechanical properties of CC, MCC, and LCC refractory materials curried at 10 °C, 20 °C, and 35 °C, followed by high-temperature treatment. Furthermore, their resistance to thermal shock

and shrinkage, as well as structure formation, are evaluated. Additionally, this study examines the effects of an accelerator on low-temperature curing castables and a retarder on high-temperature curing castables to assess their impact on structure formation and mechanical properties.

### 2 Methods and Materials

Three refractory castables with different compositions are utilized in this study: CC, representing a conventional castable made with calcium aluminate cement Istra 40 (alumina oxide  $Al_2O_3 \le 40$  wt%); MCC and LCC, representing medium cement castable and low cement castable, respectively, made with calcium aluminate cement Gorkal 70 (alumina oxide  $Al_2O_3 \le 70$  wt%). Additionally, two MCC mixtures containing 0.1 wt% citric acid (MCC CA) and 0.1 wt% lithium carbonate (MCC LC) were also prepared to assess the impact of these additives on the hardening of the castables. **Table.1** outlines the mix proportions.

The dry components were mixed with deflocculants for 5 minutes in a Hobart mixer, after which water was added and mixed for another 5 minutes. The amount of water was determined using the ball-in-hand method (ASTM C0860-15R19). The freshly prepared refractory mixture was poured into molds measuring 160x40x40 mm and cured in an environmental chamber (RUMED RUBARTH APPARATE GmbH, Germany) at temperatures of 10 °C, 20 °C, and 35 °C for 72 hours. Subsequently, these specimens were transferred to a dryer and dried for 72 hours at 110±5 °C.

The CC, MCC, and LCC concretes underwent testing after curing temperatures of 10 °C, 20 °C, and 35 °C, resulting in the preparation of 36 specimens for each composition (12 specimens for each curing temperature). MCC AC, treated with a retarder, was exclusively tested at a curing temperature of 35 °C, yielding 12 specimens. Similarly, MCC LC, subject to the effects of an accelerator, was cured at a temperature of 10 °C, resulting in 12 specimens. From each composition and at each curing temperature, 3 specimens for assessing the material's thermal shock resistance, 8 specimens for evaluating its flexural and cold crushing strength (CCS) after heat treatment at 950±5 °C, and one specimen reserved as a precautionary measure in case of discrepancies requiring the repetition of experiments. Physical properties were evaluated for all 12 specimens after drying at 110 °C and heat treatment at 950 °C.

The refractory specimens were prepared and processed (stored, dried, and heat treated) following the LST EN ISO 1927-5:2013 standard requirements. The physical and mechanical characteristics were determined according to LST EN ISO 1927-6:2013 and LST EN 196-10:2016. The CCS, which indicates a refractory specimen's capacity to resist failure under compressive load at room temperature, was determined after 72 hours of hardening, drying at 110±5 °C and after heat treatment for 5 hours at 950±5 °C temperature. The CCS was measured via hydraulic press ALPHA3-3000S (RIEDLINGEN, Germany).

Ta	able. 1 Composition of the re	efracto	ry casta	bles (wt <sup>e</sup>	%).	
Μ	ixture	CC	MCC	LCC	MCC LC	MCC CA
CAC	Istra 40	25	-	-	-	-
CAC	Gorkal 70	-	12	7	12	12
Chamatta POS145	Miled	10	12	-	12	12
	Crushed	60	65.5	60.5	65.5	65.5
Mic	prosilica	2.5	3	5	3	3
Reactiv	ve alumina	-	5	25	5	5
Milled	quartz sand	2.5	2.5	2.5	2.5	2.5
	Castament FS30	0.1	-	-	-	-
Deflocculant*	Castament FS20	-	0.1	0.1	0.1	0.1
	Sodium tripolyphosphate	-	0.1	0.1	0.1	0.1
Datandan/agaalanatan*	Citric acid	-	-	-	-	0.1
Relarder/accelerator*	Lithium carbonate	-	-	-	0.1	-
W	/ater*	7.5	7.5	6.5	7.5	7.5

\*Content exceeding the 100% dry castable weight.

The ultrasonic pulse device PUNDIT 7 (SCHLEIBINGER GERÄTE, Germany), equipped with two 54 kHz cylindrical transducers (transmitter and receiver), was utilized to measure the ultrasonic pulse velocity (UPV) changes of the fresh castables cured at 10 °C, 20 °C and 35 °C temperatures. A single specimen for each castable was poured into a cylindrical container measuring  $Ø70 \times 40$  mm and had transducers affixed to opposite sides.

Additionally, the PUNDIT 7 instrument was employed to measure the propagation time of ultrasound waves in the refractory castable specimens (160x40x40 mm) after different curing temperatures and heat treatment, enabling the calculation of UPV (m/s) using the formula:

$$UPV = \frac{l}{\tau} \tag{1}$$

where UPV is ultrasound pulse velocity (m/s), l represents the length of the specimen (m), and  $\tau$  is the signal propagation time (s).

The resistance to thermal shock was assessed by monitoring the variations in UPV [28] during cyclic heating at 950 °C, followed by cooling between two metal plates filled with cold water. Before testing, the UPV was measured after heat treatment at 950 °C and subsequently measured after 3 and 7 heating and cooling cycles. The relative thermal shock resistance R was then calculated using the formula:

$$R = \frac{\sqrt{UPV3 \times UPV7}}{UPV} \tag{2}$$

where *R* is relative thermal shock resistance, UPV3 and UPV7 are ultrasound pulse velocities after 3 and 7 heating and cooling cycles.

### **3 Discussion**

Ultrasonic pulse velocity (UPV) was utilized to monitor changes in structure formation during the cement hydration process in freshly prepared castable specimens. **Fig.1** illustrates the UPV test results of the CC, MCC, and LCC castable specimens, which underwent curing at 10 °C, 20 °C, and 35 °C (Section 2).

**Fig.1** depicts the tendencies of structure formation in the refractory castables during the hardening process. **Fig.1a** showcases explicitly the formation of hydrate structures in the conventional castable CC. Irrespective of the curing temperature, the curing process of the CC specimens commenced almost simultaneously (after ~6 hours). By the 24-hour mark of curing, the final structure had already formed across all three curing temperatures. Refractory castables possess a unique characteristic that allows them to attain their final structure within 24 hours. Notably, only the final UPV value varies with the curing temperature. The specimen cured at 10 °C exhibited the highest velocity, reaching 5000 m/s. The CC specimen cured at 20 °C achieved a velocity of 4700 m/s, while the specimen cured at 35 °C recorded the lowest velocity at 4440 m/s. However, as the proportion of calcium aluminate cement in the refractory castable decreases significantly from 25 wt% (CC) to 7 wt% (LCC), the castable hardening properties also change. Notably, the LCC (**Fig.1b**) specimen cured at 10 °C exhibited the latest onset of curing, with the final structure forming after approximately 48 hours. Despite this delayed hardening, the UPV of the final structure was the highest, reaching a maximum velocity of 4440 m/s after 72 hours.

Similarly, the LCC specimen cured at 20 °C did not conform to the 24-hour curing time observed in CC specimens. The formation of the final structure occurred after approximately 30 hours of curing. Conversely, the specimen cured at 35 °C formed its final structure after approximately 8 hours of curing, aligning with the 24-hour mark observed in CC specimens. The UPV tendencies of LCC specimens hardened at 20 °C and 35 °C were 4250 m/s and 3960 m/s, respectively. This UPV trend in LCC specimens remained consistent with that observed in CC specimens – UPV<sub>10</sub>>UPV<sub>20</sub>>UPV<sub>35</sub>.

The MCC (**Fig.1c**) specimens cured at 10°C exhibited a longer curing time than the CC and LCC specimens, taking approximately 54 hours for structure formation. On the other hand, the MCC specimen cured at 20 °C underwent structure formation in about 30 hours. At 10 °C, the curing process was intermittent, with a 24-hour curing period interspersed with a 6-hour duration of structure formation. After 72 hours of curing, the UPVs of the MCC specimens were measured at 4700 m/s, 4500 m/s, and 4600 m/s, respectively.



Fig. 1 UPV dependence on curing conditions: a) CC; b) LCC; c) MCC

The observation that the MCC specimen required the longest time to form the final structure among all refractory specimens at 10 °C and the shortest time at 35 °C highlights the sensitivity of this refractory castable to the hardening temperature. Consequently, two additional compositions were formulated: one supplemented with an accelerator (lithium carbonate – MCC LC) and cured at 10 °C to observe the accelerating effect of this additive, and another composition containing a retarder (citric acid – MCC CA) and cured at 35 °C, aiming to compare the impact of this retarder on structure formation.

Lithium carbonate proved effective in accelerating the reaction, reducing the time required for final structure formation at 10 °C by 38 hours to just 16 hours. Conversely, citric acid successfully slowed down the reaction, extending the curing time for final structure formation at 35 °C by 18 hours to approximately 24 hours compared to compositions cured under corresponding conditions. The UPV values for MCC supplemented with citric acid (MCC CA) and MCC with lithium carbonate (MCC LC) were measured at 4650 m/s and 4600 m/s, respectively.

Having identified the variations in the hardening process of the material, it becomes crucial to assess how these differences will impact the properties of the castable after undergoing heat treatment. A heat treatment temperature of 950 °C has been selected for the refractory castables under investigation.

The variations in hardening temperatures are clearly illustrated in the relative thermal shock (R) results (**Fig.2**). It is evident that the R-value of CC castables enhances as the initial curing temperature of these specimens rises. In particular, the R-value at a curing temperature of 10 °C was measured at 0.715, while at 20 °C, it increased to 0.722, and at 35 °C, it further improved to 0.734. A consistent trend was observed in the LCC class castable, with the highest R-value recorded for the specimens hardened at 35 °C, reaching

0.848. The *R*-value remained almost constant for other hardening temperatures, measuring 0.790 and 0.791. Still, the *R*-value of the LCC specimens was superior to other castables.

Meanwhile, the curing temperature significantly influenced the *R*-value of MCC castables, exhibiting the most notable differences within its castable class. At curing temperatures of 10 °C, 20 °C, and 35 °C, the R was measured at 0.741, 0.776, and 0.820, respectively. Incorporating the accelerator and retarder substances improved the *R*-value of this castable, bringing it closer to the optimal result observed when the specimen was cured at 35 °C. Specifically, MCC LC and MCC CA demonstrated an *R*-value of 0.810 and 0.817, respectively.

The density of the castable after drying and firing at 950 °C varied slightly within each class regardless of the temperature at which the specimens hardened (**Table.2**). After drying at 110 °C and firing at 950 °C, CC castable exhibited a density of 2300 kg/m<sup>3</sup> and 2210 kg/m<sup>3</sup>, MCC specimens 2290 kg/m<sup>3</sup> and 2230 kg/m<sup>3</sup>, and LCC 2400 kg/m<sup>3</sup> and 2360 kg/m<sup>3</sup>. Notably, further attention is warranted for MCC CA and MCC LC specimens, as the retarder and accelerator slightly reduced density to 2270 kg/m<sup>3</sup> after 110 °C and 2220 kg/m<sup>3</sup> after 950 °C.

**Table.2** illustrates the contractions of the specimens and indicates a strong correlation between shrinkage after firing at 950 °C and curing temperature: as the curing temperature increases, firing shrinkage decreases. This phenomenon aligns well with literature analysis, which suggests that when specimens cure at higher temperatures, stable cement hydrate  $C_3AH_6$  forms [13].



Fig. 2 Relative thermal shock resistance dependence on curing conditions and castable type

		v 1		<i>.</i>		
Sorios		Density	y, kg/m <sup>3</sup>		- Shrin	kaga %
Series	11	0 °C	95	50 °C	51111	kage, 70
CC10	2311	±10.92	2215	$\pm 14.79$	0.09	$\pm 0.02$
CC20	2296	$\pm 20.38$	2208	±12.85	0.08	$\pm 0.01$
CC35	2300	$\pm 11.87$	2208	±12.57	0.08	$\pm 0.05$
MCC10	2272	±15.09	2233	±16.28	0.26	±0.03
MCC20	2296	$\pm 10.28$	2230	$\pm 17.38$	0.25	$\pm 0.02$
MCC35	2287	$\pm 23.80$	2210	$\pm 19.98$	0.20	$\pm 0.03$
LCC10	2383	±15.26	2364	±15.59	0.33	$\pm 0.04$
LCC20	2395	$\pm 14.17$	2368	$\pm 10.44$	0.30	$\pm 0.05$
LCC35	2398	±10.62	2350	±9.43	0.15	$\pm 0.04$
MCC LC	2266	±11.49	2220	±12.16	0.34	$\pm 0.05$
MCC CA	2273	±9.77	2222	±5.59	0.26	$\pm 0.05$

rubic. 2 r nysicar properties of the refractory custables
---

Additionally, in MCC samples, it is evident that citric acid does not impact shrinkage compared to MCC samples cured at 35 °C. However, introducing lithium carbonate increases shrinkage from 0.20% to 0.34% when samples are cured at 10 °C. This could be attributed to the effect of lithium carbonate at low curing temperatures, which promotes hydration according to reference [25,26]. This hydration process leads to the formation of hydrates, resulting in a higher degree of hydration. Consequently, this increased hydration level may contribute to more significant shrinkage when the substrate is subjected to high temperatures.

**Fig.3** illustrates the flexural and CCS results of castables hardened at various temperatures. We observe that the CCS of the LCC samples reaches 125 MPa after curing at 10 °C and 35 °C, while it reaches 139 MPa after curing at 20 °C. This suggests that the curing temperature does not exhibit a consistent effect on the sample, and the strength largely depends on the formation of the structure; CCS remains relatively constant, reaching about 95 MPa at different curing temperatures.

MCC samples exhibit the highest sensitivity to changes in curing temperature. When cured at 10 °C, 20 °C, and 35 °C, the CCS measures were 96 MPa, 100 MPa, and 105 MPa, respectively. The curing temperature does not affect the flexural strength, which varies from 11.2 MPa to 11.8 MPa.

After incorporating the retarder, citric acid, the CCS remains relatively unchanged at ~105 MPa compared to the MCC specimen cured at 35 °C. However, the flexural strength increases from 11.8 MPa to 13.4 MPa. Conversely, adding the lithium carbonate accelerator improves the CCS from 96 MPa to 103 MPa compared to the MCC sample cured at 10 °C. It also enhances the flexural strength from 11.2 MPa to 14.7 MPa.



Fig. 3 Strength dependence on the curing temperature and mix proportions

## **4** Conclusions

The mechanical and physical properties of refractory conventional, medium cement, and low cement castables, formulated with 25 wt%, 12 wt%, and 7 wt% of calcium aluminate cement, respectively, change when these castables are hardened at 10 °C, 20 °C, and 35 °C:

- The structure formation process and its evolution duration vary depending on the curing temperature. In MCC cured at 10 °C, the structure typically forms after approximately 54 hours, whereas at 35 °C, it forms within 6 hours. Similarly, in LCC, the most prolonged duration for structure formation is observed at 10 °C, taking 48 hours, while at 35 °C, it occurs within 8 hours. However, CC samples containing the highest amount of calcium aluminate cement show less sensitivity to differences in curing temperatures.
- 2) Temperature shock resistance studied at 950 °C across all castable classes is best when the samples are hardened at 35 °C. After undergoing 7 heating and cooling cycles, the relative thermal shock resistance of CC, MCC, and LCC castables reached 0.734, 0.820, and 0.848, respectively. Lower calcium aluminate cement content also contributes to better relative thermal shock resistance results.

- 3) The thermal treatment at a temperature of 950 °C also affects the shrinkage of the samples. Across all cases, specimens cured at 35 °C exhibited the lowest shrinkage.
- 4) In the MCC samples, when hardened at 35 °C, the mechanical properties of samples fired at high temperatures notably improve. The cold crushing strength is 9% higher than samples of the same composition cured at 10 °C. In CC samples, the hardening temperature appears to have no significant effect. Across different hardening temperatures, the cold crushing strength remained consistent at 95 MPa.

Based on the mechanical and thermal properties assessment, it was concluded that MCC is the most sensitive to variations in curing temperatures. Moreover, the incorporation of lithium carbonate and citric acid into the composition proves beneficial in adjusting the properties of this castable fired at high temperatures, presumably enhancing its performance across different curing conditions:

- 5) Lithium carbonate serves as an accelerator, expediting the structure formation by 36 hours at a curing temperature of 10 °C, thus reducing the duration to only 16 hours compared to the composition without the accelerator additive. Conversely, citric acid is a retarder, slowing the reaction at 35 °C. The structure formation is delayed by 18 hours, extending to 24 hours compared to the composition without citric acid.
- 6) Lithium carbonate significantly enhances the material's relative thermal shock resistance at 950 °C, improving it from 0.741 to 0.810. Conversely, citric acid does not worsen the result, with the relative thermal shock resistance remaining similar to the initial reading at 0.817, whereas it was 0.820 for the specimen without citric acid.
- 7) The incorporation of lithium carbonate and citric acid proves beneficial in enhancing the mechanical properties of the material fired at 950 °C. The flexural strength improves by 30% with lithium carbonate and by 13% with citric acid. Similarly, the cold crushing strength shows improvement, with a 7% increase with lithium carbonate and approximately 1% higher with citric acid.

## 5 Acknowledgment

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

### References

- [1]. Sarkar, R. (2016). Refractory technology: fundamentals and applications. CRC Press.
- [2]. Kumar, S., & Sarkar, R. (2023). Alumina-spinel castable for steel ladles: An overview. International Journal of Applied Ceramic Technology, 20(1), 410-423.
- [3]. Wen, L., Nie, J., Dong, H., Ju, M., Liang, Y., & Cai, M. (2023). Enhancing the thermal shock resistance of Al2O3-SiC-C castables via the generation of in-situ SiC whiskers. Journal of Asian Ceramic Societies, 11(1), 208-214.
- [4]. Plioplys, L., Kudžma, A., Sokolov, A., Antonovič, V., & Gribniak, V. (2023). Bond behavior of stainless-steel and ordinary reinforcement bars in refractory castables under elevated temperatures. Journal of Composites Science, 7(12), 485.
- [5]. Kudžma, A., Antonovič, V., Škamat, J., Stonys, R., Malaiškienė, J., & Gribniak, V. (2023). Effect of low oxidation graphene oxide on physical and mechanical properties of MCC type refractory castable. In International Conference Modern Building Materials, Structures and Techniques (pp. 438-446). Cham: Springer Nature Switzerland.
- [6]. Xu, L., Liu, Y., Chen, M., & Wang, N. (2022). An accurate correlation between high-temperature performance and cement content of the high-alumina refractory castables. Ceramics International, 48(15), 22601-22607.

- [7]. Zemánek, D., Nevřivová, L., & Keršnerová, L. (2023). LCC, ULCC and NCC castables benchmarking. In AIP Conference Proceedings (Vol. 2780, No. 1). AIP Publishing.
- [8]. Goergens, J., Belli, R., Schulbert, C., & Goetz-Neunhoeffer, F. (2023). Influence of different CA2/CA-ratios on hydration degree, AH3 content and flexural strength investigated for a binder formulation of calcium aluminate cement with calcite. Cement and Concrete Research, 165, 107090.
- [9]. Taylor, H. F. (1997). Cement chemistry (Vol. 2, p. 459). London: Thomas Telford.
- [10]. Hewlett, P., & Liska, M. (Eds.). (2019). Lea's chemistry of cement and concrete. Butterworth-Heinemann.
- [11].Liao, Y., Wang, S., Wang, K., Al Qunaynah, S., Wan, S., Yuan, Z., ... & Tang, S. (2023). A study on the hydration of calcium aluminate cement pastes containing silica fume using non-contact electrical resistivity measurement. Journal of Materials Research and Technology, 24, 8135-8149.
- [12].Son, H. M., Park, S. M., Jang, J. G., & Lee, H. K. (2018). Effect of nano-silica on hydration and conversion of calcium aluminate cement. Construction and Building Materials, 169, 819-825.
- [13].Kudžma, A., Plioplys, L., Antonovič, V., Stonys, R., & Gribniak, V. (2022). Curing temperatures effect on explosive spalling in alumina cement-based concretes. In Proceedings of the fourth European and Mediterranean structural engineering and construction conference, Leipzig, Germany, June 20-June 25, 2022 (pp. 1-6). ISEC Press.
- [14].Adams, M. P., & Ideker, J. H. (2015). Pore solution chemistry of calcium aluminate cement systems undergoing accelerated conversion. In The 14th International Congress on the Chemistry of Cement, Beijing, China.
- [15].Barakat, A. J., Pel, L., Adan, O. C. G., Myhre, B., Peng, H., Wöhrmeyer, C., & Krause, O. (2020). The effect of permeability enhancement on dry-out behavior of CA-and microsilica gel-bonded castables as determined by NMR. Ceramics International, 46(9), 13556-13568.
- [16]. Šádková, K., Koňáková, D., Pommer, V., Černý, R., & Vejmelková, E. (2023). Application of secondary calcined shale in the design of low-cement binder for thermal-resistant composites. Ceramics International, 49(9), 13452-13468.
- [17].Cardoso, F., Innocentini, M. D., Akiyoshi, M. M., & Pandolfelli, V. C. (2004). Effect of curing conditions on the properties of ultra-low cement refractory castables. Refract. Appl. News, 9(2), 12-16.
- [18]. Yu, R., Zhang, L., Zhang, X., Liu, P., Qi, H., Wang, J., & Liu, X. (2020). Fracture behavior and thermal shock resistance of alumina-spinel castables-Effect of added fused zirconia-alumina. Ceramics International, 46(13), 20732-20741.
- [19].Li, Y., Zhu, L., Liu, K., Ding, D., Zhang, J., & Ye, G. (2019). Effect of curing temperature on volume stability of CAC-bonded alumina-based castables. Ceramics International, 45(9), 12066-12071.
- [20]. Antonovič, V., Kerienė, J., Boris, R., & Aleknevičius, M. (2013). The effect of temperature on the formation of the hydrated calcium aluminate cement structure. Procedia Engineering, 57, 99-106.
- [21].Zhang, Z. Z., Wang, X. Y., Chu, S. Z., Zeng, J. Y., Mu, Y. D., Li, Y. Q., ... & Ye, G. T. (2024). Effect of water loss during curing on hydration reaction and hydrates conversion in calcium aluminate cement-bonded castables. Journal of Iron and Steel Research International, 1-9.
- [22].Kasper, J., Bastian, M., & Dannert, C. (2023). Influence of the type of phosphate additive and its concentration on the setting kinetics of CA cement bonded refractory castables with special regard to the resulting pH value. Open Ceramics, 15, 100412.

- [23].Ponduru, S. A., Han, T., Huang, J., & Kumar, A. (2023). Predicting Compressive Strength and Hydration Products of Calcium Aluminate Cement Using Data-Driven Approach. Materials, 16(2), 654.
- [24].Luz, A. P., Braulio, M. A. L., & Pandolfelli, V. C. (2015). Refractory castable binders. Refractory Castable Engineering, 1st., Göller Verlag GmbH, Germany, 157-256.
- [25].Oliveira, I. R., Ortega, F. S., & Pandolfelli, V. C. (2009). Hydration of CAC cement in a castable refractory matrix containing processing additives. Ceramics International, 35(4), 1545-1552.
- [26].Duran, A., Sirera, R., Pérez-Nicolás, M., Navarro-Blasco, I., Fernández, J. M., & Alvarez, J. I. (2016). Study of the early hydration of calcium aluminates in the presence of different metallic salts. Cement and Concrete Research, 81, 1-15.
- [27].Niziurska, M., Małolepszy, J., & Malata, G. (2015). The influence of lithium carbonate on phase composition of calcium aluminate cement paste. Procedia Engineering, 108, 363-370.
- [28]. Antonovich, V., Shyukshta, M., Pundene, I., & Stonis, R. (2011). Procedural elements in estimation of the thermal shock resistance of different types of refractory concrete based on chamotte filler. Refractories and Industrial Ceramics, 52, 70-74.