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CARBONATE AGGREGATE IN CONCRETE EXPOSED TO HIGH TEMPERATURES

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Abstract: The paper presents the experimental campaign on the problem of post-fire rehydration of carbonate aggregates, resulting in expansion and fall of the treated layer at high temperature. In the experimental campaign, three types of aggregates (2-8 and 8-16 mm grain size) are used for the production of concrete specimens: (1) the thermally stable representative of igneous rocks - basalt and two representatives of sedimentary carbonate rocks: (2) dolomite (with 1% calcium carbonate at 20 °C and 25% of calcium carbonate after heating > 500°C) and (3) limestone (with 98% calcium carbonate). The 150 mm cubic samples were heated in an electric furnace at 1 °C/min to the set temperature (200 °C, 600 °C, 1000 °C). After heating, the following measurements were compared: mass and density (directly after cooling), compressive strength (after 14 days), and crack development and height of the samples were monitored for 6 days, followed by heating (144 hours). As a result of heating to a temperature of 1000°C, a sharp decrease in concrete mass and an increase in the cross-sectional height of the specimen are observed in concrete with carbonate aggregate. This results in a large reduction in bulk density and compressive strength and in the disintegration of samples containing carbonate aggregate in the days following heating. This peculiarity of carbonate aggregate has already been studied in the literature. Carbonate aggregates have a convincing property as an aggregate used daily in construction. However, these properties deteriorate significantly in the event of fire and more effort needs to be made to disseminate this knowledge.

1 INTRODUCTION

The performance of concrete under high-temperature conditions greatly depends on the interaction between its primary components: the cement matrix and the aggregates. Aggregates, which constitute 65-80% of concrete by volume, play a crucial role in determining its overall properties. Among the various types of aggregates, carbonate aggregates such as limestone and dolomite are commonly used due to their availability, cost-effectiveness and distinctive properties of carbonate aggregates. As a result of the formation of carboaluminate in the contact zone, the strength and adhesion of matrix to

the carbonate aggregate are increased while the porosity and permeability are reduced [1–3]. However, these materials exhibit specific behaviors when exposed to elevated temperatures that can deteriorate concrete's performance.

This study focuses on monitoring the thermal stability of concrete with carbonate aggregates. It examines the deterioration of physical and mechanical properties of concrete resulted from chemical changes of these aggregates due to fire exposure.

Carbonate aggregates, such as limestone and dolomite, undergo distinct transformations when exposed to temperatures above 600°C.

These transformations are primarily driven by the decomposition of calcium carbonate (CaCO₃), which leads to the release of carbon dioxide (CO₂) and the formation of calcium oxide (CaO): CaCO₃ \rightarrow CaO + CO₂. This decomposition results in a significant loss of mass and shifts the microstructure of the aggregates. The newly formed calcium oxide, CaO, reacts with moisture during the cooling calcium produce hydroxide $(Ca(OH)_2)$: $CaO + H_2O \rightarrow Ca(OH)_2$. The hydration of CaO causes volumetric expansion within the aggregate particles, leading to internal stresses that manifest as cracking and sloughing in concrete structures. This process is particularly detrimental as it weakens the bond at the cement-aggregate interface, which is critical for the mechanical stability of the concrete. Figure 1 shows calcium hydroxide crystals formed during the cooling of calcium oxide. The grains increased in volume, causing their destruction [1].

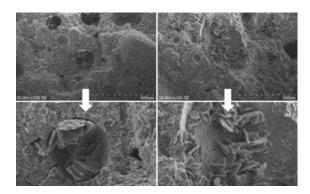


Figure 1: Calcium hydroxide formed by the hydration of calcium oxide after heating [1].

As temperatures increase up to 600°C, the mechanical integrity of carbonate aggregates continues to decline. Dolomite, a carbonate mineral containing both calcium and magnesium, undergoes a two-stage decomposition:

$$\begin{aligned} &(I)CaMg(CO_3)_2 \leftrightarrow CaCO_3 + MgO + CO_2 \\ &(II)CaCO_3 \rightarrow CaO + CO_2 \end{aligned}$$

The decomposition of dolomite results in the formation of magnesium oxide (MgO) and calcium oxide, further contributing to mass loss and structural instability. The presence of MgO, which does not rehydrate like CaO, keeps the aggregate with increased cohesion and strength, comparing to the limestone aggregate that transforms into calcium oxide only.

Netinger et al. [4] showed that dolomite-based concrete demonstrated higher compressive and tensile strength retention at 600–800°C than river gravel aggregates. However, dolomite's thermal stability deteriorated at higher temperatures (800–1000°C) due to further calcite decomposition.

Similarly, Xing et al. [5] presented highstrength concrete with limestone aggregates that exhibited superior thermal resistance up to 600°C compared to siliceous and siliceous limestone aggregates while the limestone aggregate concretes disintegrated in cooling phase due to the rehydration of quicklime, leading to expansive portlandite formation.

These chemical changes in carbonate aggregates influence the thermal expansion characteristics of the concrete. While the initial heating may cause a modest increase in volume due to thermal expansion, the subsequent chemical reactions and material loss lead to shrinkage and the formation of microcracks. This complex interplay of thermal and chemical effects makes carbonate aggregates less reliable in high-temperature applications compared to more thermally stable alternatives such as basalt.

2 MATERIALS AND METHODS

To investigate the thermal behavior of concrete with carbonate aggregates, three types of fine and coarse aggregates were selected: basalt (magmatic origin), dolomite, and limestone (carbonate origin), Table 1. These aggregates were chosen to represent a range of thermal stability and mineral compositions.

Concrete samples were prepared using a standardized mix design, maintaining a water-to-cement (w/c) ratio of 0.3. This low w/c ratio was chosen to ensure high compressive strength and minimize excess porosity in the samples. By obtaining high performance of mortar, the observed degradation in concrete due to aggregate impact can be more pronounced. Aggregates were graded into two

size fractions: 2-8 mm and 8-16 mm, ensuring uniform distribution within the mix. Cement used was Portland cement (CEM I 42.5 R) with high early strength properties.

Table 1: Characteristics of aggregates used

Origin	Basalt (Gracze, Poland)	Devonian Dolomite (Brudzowice, Poland)	Devonian Limestone (Trzuskawica, Poland)
8/16 mm			
2/8 mm			
$CaCO_3$	none	1% at T = 20°C; 25% at T > 500°C	98% by mass

Table 2: Concrete mixes composition (kg per 1 m³)

CEM I 42.5 R (Małogoszcz, Poland)	482
Water	145
Quartz Sand 0/2 mm (Dwudniaki, Poland)	660
Fine aggregate 2/8 mm (Basalt / Dolomite / Limestone)	641
Coarse aggregate 8/16 mm (Basalt / Dolomite / Limestone)	587
Superplasticizer Sika ViscoCrete-6 RS	4.34

Concrete mixtures were poured into molds to produce standardized specimens, including 8 cubes (150 mm x 150 mm x 150 mm) for each of 3 mixes. The samples were demolded after 24 hours and cured under controlled conditions (20°C, 95% relative humidity) with ensuring the free ventilation around the sample for 28 days to achieve full hydration and strength development.

After curing period, the specimens were subjected to controlled heating in a high-temperature furnace. The heating protocol included target temperatures of 200°C, 600°C, and 1000°C. Heating was applied at a uniform rate of 1°C per minute to minimize thermal shock, followed by stabilization at the target temperature for three hours. After the heating cycle, samples were allowed to cool naturally to room temperature within the furnace. 2 samples for each set temperature were tested.

Physical changes, including mass loss and dimensional stability, were recorded before after thermal exposure. Density and measurements were taken to assess changes in porosity and internal structure. Compressive strength tests were conducted using a hydraulic testing machine, and visual inspections as photographic inventory and measurement of samples' height changes in time were performed to document cracking, extent of delamination, and surface changes.

3 RESULTS AND OBSERVATIONS

Samples with carbonate aggregates showed significant mass loss due to the decomposition of CaCO₃ at temperatures above 600°C. The loss was most pronounced in limestone aggregates, which have higher CaCO₃ content dolomite. compared to Bulk density measurements revealed an inverse relationship between temperature and density, as the decomposition of carbonate minerals increased porosity within the concrete matrix. Limestone samples exhibited up to 27% reduction in bulk density at 1000°C. Figure 2 shows the residual bulk density changes in heated up to 200°C. 600°C and 1000°C.

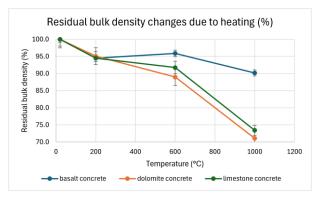


Figure 2: Changes of residual bulk density due to heating up to 200°C, 600°C and 1000°C.

While comparing the residual compressive strength drop due to heating, Figure 3, it is observed that concrete with basalt aggregates (basal concrete) retained higher compressive strength across all temperature range (from 200°C to 1000 °C), demonstrating good thermal stability. The compressive strength reduction in basalt samples at 1000°C was

limited to 10%. In the opposite, dolomite and limestone aggregates showed significant losses, with compressive strength reductions exceeding 50% and 60%, respectively, at 600°C. At 1000 °C the compressive strength was not able to measure as the samples had been destroying "in hands". This decline was attributed to structural degradation caused by thermal decomposition. It shall be highlighted that initial compressive strength of all concretes was classified as HSC, reaching 99 MPa, 91 MPa and 79 MPa for basalt, dolomite and limestone concrete, respectively.

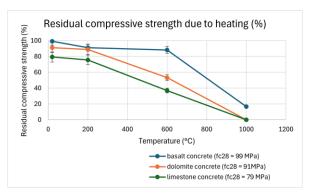


Figure 3: Changes of residual compressive strength due to heating up to 200°C, 600°C and 1000°C.

To present the abovementioned degradation of the concretes with carbonate aggregate, the dimensional stability as increasing of the cubic sample's height was monitored for 6 days (144h) following the end of heating-cooling procedure. The photographic inventory of the samples changes during next 144h after heating to 200°C, 400°C and 1000°C for basalt, dolomite and limestone aggregate concretes are presented in Figure 4, 5, 6, respectively, while the increase in sample's height is depicted in Figure 7.

Basalt concrete exhibited minor cracking and retained their structural integrity, even at Dolomite temperatures. samples showed moderate cracking and extensive damage at 1000°C, while limestone samples experienced severe cracking, surface delamination, and visible disintegration with catastrophic failure observed at 1000°C. The sources of degradation were concentrated around aggregate, particularly in the interfacial transition zones. The increased cracking was linked to the thermal decomposition and subsequent hydration of CaO, leading to expansion and internal stresses.

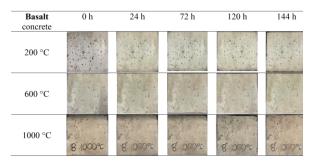


Figure 4: Visual changes in basalt concrete during next 144h after heating to 200°C, 400°C and 1000°C.

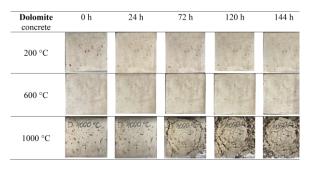


Figure 5: Visual changes in dolomite concrete during next 144h after heating to 200°C, 400°C and 1000°C.

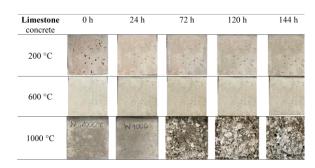


Figure 6: Visual changes in limestone concrete during next 144h after heating to 200°C, 400°C and 1000°C.

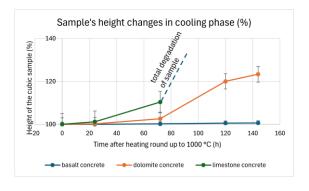


Figure 7: Changes in samples' heights during next 144h after heating to 1000°C.

These findings underscore the critical influence of aggregate type on the thermal performance of concrete, emphasizing the need for material optimization in high-temperature applications.

4 DISCUSSIONS

The findings indicate limitations in the performance of carbonate aggregates when exposed to elevated temperatures. The thermal decomposition of calcium carbonate within these aggregates is a crucial factor contributing to their instability, occurring at above 600°C. This decomposition results in the release of carbon dioxide and the formation of calcium oxide. The chemical changes reduce the aggregates' mass and damage their structural integrity, triggering secondary reactions during the cooling phase. The hydration of CaO to Ca(OH)₂ introduces volumetric expansion, generating internal stresses that induce cracking and extensive delamination within the concrete. These effects are particularly severe in limestone-based concretes, where the higher calcium carbonate content intensifies degradation.

The findings demonstrate the superior performance of basalt aggregates in thermally demanding environments. Concrete samples made with basalt aggregates retained a strength even compressive at 1000°C. exhibiting only minor structural and dimensional changes. In contrast, dolomite concrete, despite retaining some compressive strength at intermediate temperatures (600-800°C), experienced substantial degradation at 1000°C. Limestone concrete demonstrated the poorest performance, exhibiting catastrophic disintegration at the highest temperature.

Observations of the physical changes over time further confirm post-heating dimensional instability, measured as an increase in the height of concrete specimens, being more pronounced in carbonate aggregates. The photographic documentation revealed extensive cracking, surface delamination, and structural breakdown in dolomite and particularly limestone concretes, after exposure to 1000°C. In contrast, basalt-based concrete demonstrated superior resilience,

retaining their structural integrity and exhibiting only minor cracking.

5 CONCLUSIONS

This study highlights the challenges and implications of using carbonate aggregates in concrete exposed to high temperatures. While these materials are suitable for standard conditions, their performance degrades significantly under thermal stress. The findings emphasize the need for careful selection of aggregates based on the anticipated thermal exposure of the structure.

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