Changes crushing resistance (CR) of granulated aggregate obtained from fluidized bed fly ash (FBFA) processed in a CO_2 atmosphere and seasoned in an of high humidity air

Zmiana odporności na miażdżenie kruszywa granulowanego otrzymanego z popiołów lotnych z kotłów fluidalnych przetworzonych w atmosferze CO_2 i sezonowanych w warunkach podwyższonej wilgotności

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The aim of the research presented in the article was to investigate how the high-humidity air environment changes the crushing resistance (CR) of granulated carbonated fluidized bed fly ash (CGFBFA). It was assumed that CR influences the way it is used in geoengineering as a substitute for natural aggregates. The results of testing the granulate obtained in the three-phase carbonation reaction with carbon dioxide and granulation process in a multifunctional rotary granulator (MRG) are presented. The obtained product was exposed for a period of time three years in the conditions of the atmosphere of the mine gallery of the experimental mine. The air humidity ranged from 76% to 98% and the temperature ranged from approx. 6°C to approx. 14°C. The crushing resistance tests (CRT) of the samples were carried out using a SCHIMADZU AGX-300kN VINSTON hydraulic press (USA). Mineralogical studies were performed using the powder diffractometric method (DSH), using Bragg-Brentano geometry. The Bruker D8 Discover diffractometer, CuKα radiation, Ni filter and LYNXEYE_XE detector were used. Has been demonstrated, that the 3-year exposure of in the mine air atmosphere had a positive effect on the increase CR of CGFBFA, causing its increase from 5 MPa to 7.4 MPa, i.e. by approx. 32.4%. The increase of CR was interpreted as the result of the formation of relatively large amounts of gypsum in the composition in CGFBFA after the exposed period. Mineralogical research also leads to the preliminary conclusion that calcite and ettringite also play a role in this process. It was hypothesized that calcite is a binding factor at the stage of the carbonation process. We assumed that later, this too phase participating in the crystallization process of ettringite by replacing some of the sulfate ions (SO_3^{2-}) with $CO_3{}^2$ – ions. As a result of this process, the conditions of thermodynamic equilibrium in ettringite may change, which favours the crystallization of gypsum. This issue will be the subject of further research.
Research carried out and analyses showed that granulation of LPF in an atmosphere of carbon dioxide may be a prospective method of their management in combination with CO_2 utilization. This idea is consistent with the EU strategy regarding the circular economy (CE) and carbon dioxide sequestration and utilisation(CCS/CCSU).
Keywords: fluidized bed fly ash, carbonated fluidized bed fly ash, granules, crushing resistance, mineralogical tests.

Celem badań przedstawionych w artykule było zbadanie, jak środowisko powietrza o dużej wilgotności zmienia odporność na miażdżenie granulowanego karbonizowanego popiołu lotnego z kotła fluidalnego. Założono, że odporność na miażdżenie wpływa na sposób jego wykorzystania w geoinżynierii jako substytut kruszywa naturalnego. W artykule przedstawiono wyniki badań granulatu otrzymanego w wyniku trójfazowej reakcji karbonatacji dwutlenkiem węgla oraz procesu granulacji w wielofunkcyjnym granulatorze obrotowym. Otrzymany produkt poddano ekspozycji przez okres trzech lat w warunkach atmosfery chodnika kopalni doświadczalnej. Wilgotność powietrza wahała się od 76% do 98%, a temperatura od ok. 6°C do ok. 14°C. Badania odporności na miażdżenie próbek przeprowadzono przy użyciu prasy hydraulicznej SCHIMADZU AGX-300kN VINSTON (USA). Badania mineralogiczne przeprowadzono metodą dyfraktometrii proszkowej (DSH) z wykorzystaniem geometrii Bragga-Brentano. Zastosowano dyfraktometr Bruker D8 Discover, promieniowanie CuKα, filtr Ni i detektor LYNXEYE_XE.

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Wykazano, że 3-letnia ekspozycja atmosfery powietrza kopalnianego pozytywnie wpłynęła na wzrost odporności na miażdżenie badanych próbek, powodując jego wzrost z 5 MPa do 7,4 MPa, tj. o ok. 32,4%. Wzrost odporności na miażdżenie interpretowano jako skutek wytworzenia się po okresie naświetlania stosunkowo dużych ilości gipsu w składzie granulatu. Badania mineralogiczne prowadzą także do wstępnego wniosku, że rolę w tym procesie odgrywają także kalcyt i ettringit. Postawiono hipotezę, że kalcyt jest czynnikiem wiążącym na etapie procesu karbonatyzacji. Założyliśmy, że później także ta faza bierze udział w procesie krystalizacji ettringitu poprzez zastąpienie części jonów siarczanowych (SO32-) jonami CO32-. W wyniku tego procesu warunki równowagi termodynamicznej w ettringicie mogą ulec zmianie, co sprzyja krystalizacji gipsu. Zagadnienie to będzie przedmiotem dalszych badań.
Przeprowadzone badania i analizy wykazały, że granulacja popiołów lotnych z kotłów fluidalnych w atmosferze dwutlenku węgla może być perspektywiczną metodą ich zagospodarowania w połączeniu z utylizacją CO_2. Idea ta jest spójna ze strategią UE dotyczącą gospodarki o obiegu zamkniętym (CE) oraz sekwestracji i utylizacji dwutlenku węgla (CCS/CCSU).
Słowa kluczowe: popiół lotny z kotła fluidalnego, karbonizowany popiół lotny z kotła fluidalnego, granulaty, odporność na miażdżenie, badania mineralogiczne.

Introduction

One of the directions of CO_2 utilization is the use of a reversible reaction between CaO and CO_2. i.e.

$$CaO + CO_2 \leftrightarrow CaCO_3$$

This reaction enables processing of fly ash (FA) into products used in industry, geoengineering and environmental protection [1, 2]. The publication [3] indicates that this reaction may be the basis for the idea of reducing emissions in the context of synergy: a power plant and a cement plant. The process of processing fluidized bed fly ash (FBFA) from hard coal with CO_2, leading to obtaining carbonated fluidized bed fly ash (CFBFA) as a non-clinkerite component of concrete [4], fulfils this postulate. It gives possibilities to partially reduce CO_2 emissions for both power and cement plants.

The FBFA carbonation technology is still a developing technology that requires further research. In particular of the possibility of economic use of this product as a substitute for natural raw materials in the industry and in geoengineering for the reclamation of degraded post-industrial, especially areas after the closure of the mine. The potential possibilities of using carbonated fluidized bed fly ash in underground mining are described in the article [5]. The technology of granulating FBFA in a carbon dioxide atmosphere seems to be particularly promising, allowing for obtaining a product as a substitute for natural aggregates [2].

This article presents the results of research how atmospheric conditions of high humidity and relatively stable temperature affect crushing resistance (CR), adopted as a measure of the mechanical strength of this product. An additional goal was to investigate the direction of changes in the mineral composition of granulated, carbonated fluidized bed fly ash (GCFBFA).

The appropriate conditions for sample exposure for the experiment were provided in one of the galleries of the GIG experimental mine "Barbara" located at a depth of 30 m. The exposure time in the atmosphere of an underground mining tunnel was three years. It was assumed that on this basis it would be possible to make an approximate prediction of the behaviour of GCFBFA if it be used for geoengineering works related to the reclamation of post-industrial areas, including the closure of mines.

Experiment conditions

The basic test material used was fluidized bed fly ash originating from hard coal combustion in a circulating fluidised bed. The chemical composition of the ash used for the tests is presented in Table 1 below.

Table 1. Chemical analysis of fluidized bed fly ash used for research
Tabela 1. Analiza chemiczna popiołów lotnych z kotła fluidalnego wykorzystywanych w badaniach

Component	%
SiO_2	36.79
Al_2O_3	20.98
Fe_2O_3	6.02
CaO	16.71
MgO	2.22
Na_2O	1.16
K_2O	1.83
SO_3	8.80
TiO_2	0.95
P_2O_5	0.26
Mn_3O_4	0.03
Ignition losses	3.91
Sum	99.66

Source: Own study.

The simultaneous triphase granulation process was conducted in an intensive counter-rotary mixer made to order Department of Mechanical Testing and Material Engineering of the Central Mining Institute, in a solid-fluid-gas system, yielding granulated, carbonated fluidized bed fly ash (GCFBFA).

The carbonation process was carried out in a manner described in detail in the patent PL No 431864: "Method of obtaining carbonatizated granulate on the basis of fly ash" and granulated, carbonated fluidized bed fly ash (GCFBFA) was obtained. The process consisted in filling the working space of the granulator with 100% carbon dioxide and maintaining a constant supply of carbon dioxide in the amount of about 2 l/min during the entire process. Then, the obtained material was homogenized with the addition of water and subjected to the pelletizing process to obtain GCFBFA. Water is necessary both for the initiation of the carbonation process, enabling the reaction of free calcium oxide present in the ashes with gaseous carbon dioxide, as well as for the granulation process, in which it activates the surface bonds of the granules, causing their gradual growth [2].

The granulator's method of operation as an multifunctional rotary granulator consists in the mixing of a mass by a rapid rotor moving in the direction opposite to the rotations of the mixer pan [6]. Granulation in such a granulator makes it possible to obtain compact granules containing a condensed material with the desired shape and dimensions [7]. Furthermore, the device enables the conduction of carbonation and granulation processes with simultaneous homogenisation as part of a single operation. For these processes, water is necessary, which activates the surface bonds of the granules, causing their gradual growth.

The tests were carried out in the Experimental Mine "Barbara" belonging to the Central Mining Institute in Katowice. It is a research and development facility where research is carried out in the field of new technologies for underground mining and safe conduct of mining works. The granulate samples were placed in three litter containers of 5 kg each. Fig. 1 shows the arrangement of the containers in the gallery of the experimental mine and the appearance of the samples after the end of the exposure. Sample No. 2 is located closer to the wet wall of the mine gallery. These primitive exposure conditions perfectly reflect the natural conditions in the mine gallery. The underground working ventilation system ensured the constant airing of the exposure area. During the entire testing period, to conduct an analysis of the local conditions, the underground working was equipped with a mine atmosphere parameter monitoring system for measuring temperature and air humidity. The utilised measuring equipment encompassed a fragment of the dispatch system used in hard coal mines. The temperature in the described underground working was about 6°C in the winter and about 14°C in the summer. The air humidity, dependent on the gallery ventilation requirements and the atmosphere on the surface, ranged within 76 to 98%.

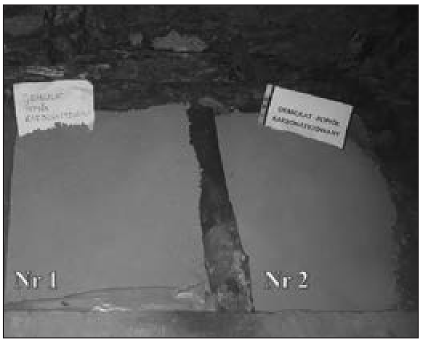


Fig. 1.
Distribution of containers and view of samples no. 1 and 2 after exposure conclusion
Fig. 1. Rozmieszczenie próbek nr 1 i 2 po zakończeniu ekspozycji

Test methods

The sample crushing resistance tests were conducted by means of the SHIMADZU AGX-300kN VINSTON (USA) hydraulic press. The test consisted in the uniaxial compression of a granulate portion inserted into a steel cylinder. The crushing resistance values, denoted as *C*, were calculated from the following formula:

$$C = \frac{L+F}{A} \frac{N}{mm^2},$$

where:

C – crushing resistance in N/mm^2 (MPa),
L – initial force exerted by the piston,
F – force required to insert the piston into the tested material,
A – piston surface area in mm^2.

The crushing resistance tests thus performed were conducted according to the requirements of standard PN-EN 13055:2016-07 "Lightweight aggregates", and deemed as sufficient to assess the quality of GCFBFA as an aggregate [8, 9].

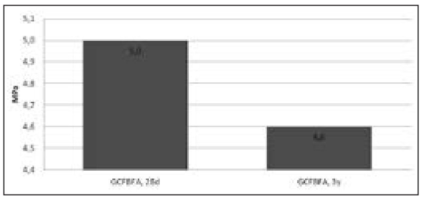
The mineralogical tests were performed by powder diffraction (DSH) in Bragg-Brentano geometry. The tests involved a Bruker D8 Discover diffractometer, CuK radiation, a Ni filter and a LYNXEYE_XE detector. The mineral composition was determined and calculated based on licensed references in ICDD PDF-4+ 2022 RDB (International Centre for Diffraction Data) and the following databases: ICSD (Inorganic Crystal Structure Database) and NIST (National Institute of Standard and Technology). Recording and diagnostics was carried out by means of Bruker AXS DIFFRAC v.4.2 and TOPAS v.4.2 software. Quantitative crystalline phase calculations were performed based on Rietveld's methodology [10, 11, 12, 13, 14] while the amorphous substance content was determined using the ZnO substance as an internal reference.

Test results

Crushing resistance

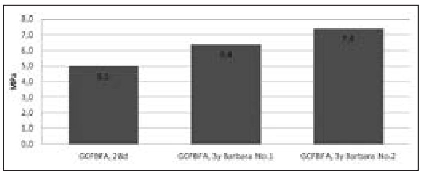
The crushing resistance test results are presented in Figures 2 and 3. Analysing the crushing resistance test results indicates that the granulate exposure time, depending on whether the granulates were seasoned under standard conditions or in the mine air atmosphere, has a significant influence on the variations in this parameter. That is, the GCFBFA granulate resistance decreased from 5.0 MPa after 28 days of seasoning under standard conditions to 4.6 MPa after three years of seasoning under the same conditions (Fig. 2).

On the other hand, under the atmospheric conditions of a mine gallery, which



Source: Own study.
Fig. 2.
Changes in crushing resistance during granules seasoned under normal humidity conditions
Fig. 2. Zmiany odporności na miażdżenie podczas sezonowania granulatu w normalnych warunkach wilgotnościowych

is characterized by high humidity, after three years of seasoning, compared to the initial sample (5.0 MPa), the crushing resistance of GCFBFA increases to 7.4 MPa (Fig. 3). The trend of increasing crushing resistance also seems to be related to the location of individual granulate exposure stations in the mine gallery, which suggests the influence of humidity on the increase in crushing resistance of GCFBFA. Macroscopically, it was found that the GCFBFA No. 2 sample, which showed greater resistance to crushing, was covered with a damp layer of softened surface on the granules. In sample No. 1, this phenomenon was noticed to a much lesser extent.



Source: Own study.
Fig. 3.
Changes in crushing resistance during granules seasoned in conditions of increased humidity
Fig. 3. Zmiany odporności na miażdżenie podczas sezonowania granulatu w warunkach podwyższonej wilgotności

There is a clear difference between the increase in crushing resistance between GCFBFA granules seasoned in room conditions and in an air atmosphere with high humidity. After three years of exposure in underground mining conditions, GCFBFA achieves much greater strength, which is important during application. The explanation for the differences found in crushing resistance both during and under exposure conditions of GCFBFA are mineral changes in this granulate. This is indicated by previously conducted mineralogical studies focusing on the identification of these crystalline phases, which, as shown by previous studies on fluidized bed fly ash (FBFA) and carbonated fluidized bed fly ash (CFBFA), may carry key significance to the understanding of the observed phenomenon [1, 2, 4].

Mineralogical testing

The conducted mineral composition tests and analysis for the investigated samples demonstrated the predominance of the amorphous substance in the mineral composition, and of anhydrite, quartz and feldspars in the crystalline phases. The differences between fluidized bed fly ash (FBFA) before and after carbonation (CFBFA) are primarily found in the quantities of free lime and calcite. The determined mineral phases present in the tested

Table 2. Mineralogical test results for FBFA, CFBFA, GCFBFA and seasoned for 3 years in the Barbara Mine No.1 (GCFBFA) and No.2 (GCFBFA)
Tabela 2. Wyniki badań mineralogicznych dla FBFA, CFBFA, GCFBFA i sezonowanych przez 3 lata w Kopalni Barbara nr 1 (GCFBFA) i nr 2 (GCFBFA)

Składnik	FBFA	CFBFA	GCFBFA	GCFBFA No.1	GCFBFA No.2
Anhydrite ($CaSO_4$)	23.0	22.0	20.0	1.0	1.0
Quartz (SiO_2)	21.5	17.5	17.5	9.5	11.5
Feldspars (potassium* + plagioclase**)	2.0	2.0	3.0	4.0	2.0
Mullite ($3Al_2O_3 \cdot 2SiO_2$)	2.0	2.0	2.0	2.0	1.0
Hematite (Fe_2O_3)	2.0	2.0	2.0	2.0	2.0
Illite+muscovite ($KAl_2[AlSi_3O_{10}(OH)_2]$)	2.0	2.0	2.0	-	-
Substance CaO	2.0	-	-	-	-
Magnetite ($FeFe_2O_4$)	1.0	1.0	1.0	1.0	1.0
Substance $CaSO_3$	1.0	-	-	-	-
Calcite ($CaCO_3$)	0.5	5.5	6.5	6.5	6.5
Portlandite ($Ca(OH)_2$)	-	2.0	-	-	-
Bassanite ($CaSO_4 \cdot 0{,}5H_2O$)	-	-	2.0	-	-
Substance $Ca_6Fe_2(SO_4)_3(OH)_{12} \cdot nH_2O$	-	-	2.0	-	-
Gypsum ($CaSO_4 \cdot 2H_2O$)	-	-	1.0	41.0	42.0
Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$)	-	-	-	2.0	2.0
Amorphous substance	42.5	43.5	40.5	30.5	30.5

Source: Own study.
* potassium feldspars – $K[AlSi_3O_8]$,
** plagioclases – $Na[AlSi_3O_8]$ (albite) – $Ca[Al_2Si_2O_8]$ (anorthite)

samples of fluidized bed fly ash (FBFA), carbonated fluidized bed fly ash (CFBFA), and granulated, carbonated fluidized bed fly ash (GCFBFA) are compiled in Table 2.

The table also includes the mineralogical test results for the granulated material after three years of seasoning under the conditions of an underground mine working. The determined mineral compositions of FBFA, CFBFA and G-CFFA exhibit differences in the quantities of such components as the CaO substance, calcite ($CaCO_3$) and quartz (SiO_2). However, the quantities of minerals such as illite and muscovite, hematite and magnetite are nearly the same. The granulated, carbonated fluidized bed fly ash includes phases such as gypsum, bassanite and the $Ca_6Fe_2(SO_4)_3(OH)_{12} \cdot nH_2O$ substance, which are most likely generated as a result of pressure at the stage of granule formation. The mineral composition of all the tested fluidised fly ash, regardless of character or binding, was dominated by the amorphous substance, within a range of 30.5% to 43.5%. The quantity of the amorphous substance decreases slightly at the stage of fluidised ash hydration and granulation, whereas in the case of samples seasoned for three years in an underground mine working, it decreases from over 40% to 31%.

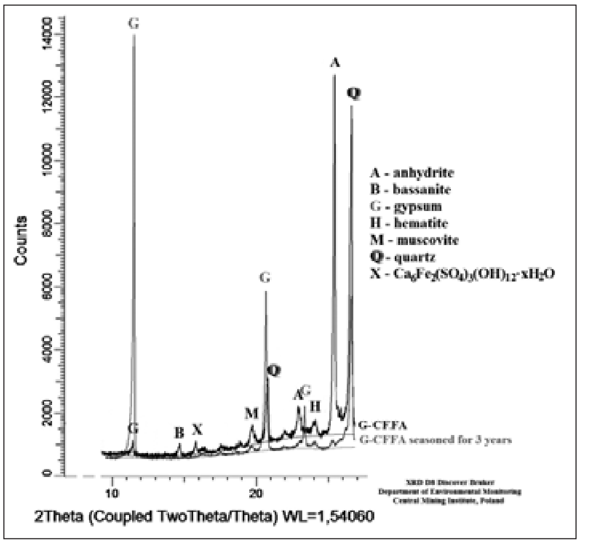
Comparing the mineral composition of the GCFBFA seasoned for 28 days under standard conditions with the one seasoned for 3 years under the conditions of an underground mine working that from the anhydrite (about 20%), bassanite (about 2%), the $Ca_6Fe_2(SO_4)_3(OH)_{12} \cdot nH_2O$ substance (about 2%) and a part of the amorphous substance in

GCFFA during hydration, 41% – 42% of gypsum content is produced. These changes are presented in diffractogram fragments Fig. 4.

In the presented case of GCFBFA seasoned in an of high humidity air hydration of anhydrite into gypsum takes place. Such a change is possible in a $CaSO_4 – H_2O$ system, at a temperature of 0-42°C, with the following transition: unstable hemihydrate ($CaSO_4 \cdot 0.5H_2O$) → metastable anhydrite II → dihydrate (gypsum) in the stable phase [15]. On the other hand, in the case of GCFBFA seasoning, the significant factor is the decomposition of the $Ca_6Fe_2(SO_4)_3(OH)_{12}$ substance, which contains major quantities of calcium and sulphates. The decomposition can have the following course:

$$Ca_6Fe_2(SO_4)_3(OH)_{12} + 3SO_4^{2-} + 10H_2O \rightarrow 6CaSO_4 \cdot 2H_2O + 2FeO(OH) + 6(OH)^-$$

This reaction demonstrates that the presence of sulphates in the water found in underground hard coal mine workings results in an increased quantity of gypsum, outside anhydrite hydration, also through the decomposition of substances such as $Ca_6Fe_2(SO_4)_3(OH)_{12} \cdot nH_2O$ or similar to ettringite (Fig. 4).The process of increasing the amount of gypsum at the expense of other hydrolyzed ingredients, GCFBFA, binds sulphates, which is a beneficial phenomenon in terms of protection of groundwater in places of application in mining workings.



Source: Own study.
Fig. 4.
GCFBFA mineral changes under various seasoning time and conditions
Fig. 4. Zmiany mineralne GCFBFA pod wpływem różnych czasów i warunków sezonowania

Discussion

Carbonation of fluidized bed fly ash using carbon dioxide seems to be a promising method of processing it in order to obtain a full-value substitute for natural aggregate for use in geoengineering. The favorable ratio of calcium carbonate to sulphates ions and the low content of calcium hydroxide prevents the formation of the so-called “secondary ettringite”, [16]. GCFBFA achieves increased crushing resistance due to an increased amount of gypsum as the basic binder and a reaction leading to the formation of an equivalent amount of natural ettringite. It is very likely that amorphous silica as a product of FA hydration takes an active part in these phase reactions, which is a known process. FBFA also contains small amounts of dehydrated aluminosilicates. Compounds of this type actively participate in the formation of ettringite [1]. Its amount is regulated by the availability of calcium aluminate. Research indicates this possibility, because perhaps due to the crystallization of gypsum, a calcium deficit appears (probably bound in the form of anhydrite), which prevents the formation of the so-called "secondary ettringite" causing a decrease in the mechanical strength of products with the addition of unprocessed FBFA.

The increase in CR observed in the presented research seems to confirm the significant participation of gypsum and ettringite in this process. It can be hypothesized that the presence of calcite also has a beneficial effect on their formation. Its content in the tested samples increased during seasoning, which can be attributed to further carbonation. In GCFBFA, despite carbonation, there is a residual content of portlandite. We observed in the tested solidified samples lack of bassanite, which is a precursor in the gypsum crystallization process [17]. Perhaps this is related to the influence of strong compaction of FBFA grains in the granulation process on the rate of the gypsum crystallization reaction. Research has also shown that the amount of amorphous substance changes significantly. This is probably due to its recrystallization. This fact, however, was not possible to confirm using the methods used in this study. However, magnetite, hematite or mullite do not undergo any transformations.

Conclusions

The following conclusions can be drawn from the conducted research:

1. The mine air atmosphere during the three-year period exhibited of GFBFA had a positive effect on the increase in crushing resistance. CR increased by approximately 32.4%.
2. The increase in crushing resistance can be explained by formation of large amounts of gypsum that crystallized after the seasoning period. It can be assumed that this is the basic binder of carbonated granules.
3. A thesis can be put forward that the increase in CR is also related to the presence of calcite and ettringite. Calcite is a binding factor for GCLPF granules at the stage of the three-phase carbonation reaction. Later, it is a phase participating in the process of ettringite formation.
4. It is also possible that the replacement of some SO_4^{2-} ions in ettringite with CO_3^{2-} ions changes the conditions of thermodynamic equilibrium, which over time favours the crystallization of gypsum. This issue will be the subject of further research.
5. The quality of the aggregate obtained as a result of the FBFA processing process in a carbon dioxide atmosphere, and in particular its high resistance to crushing, may constitute the basis for developing technical conditions for their use in geoengineering, and in particular for the reclamation of degraded areas.
6. The possibility of replacing natural aggregates with GCFBFA is consistent with the demands and guidelines of the circular economy.
7. Granulating FBFA in a carbon dioxide atmosphere may be a prospective method of their management, combined with CO_2 sequestration and utilization.

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