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Use of slurry fluorogypsum (FG) with controlled pH-adjustment in FG-based blends

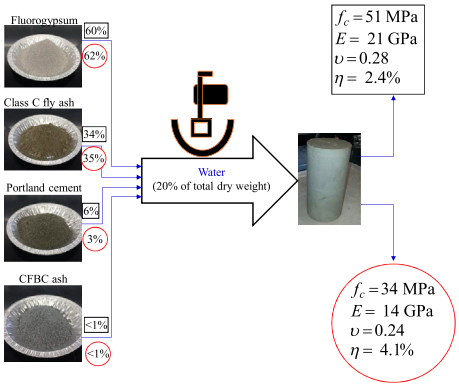
Yasser Bigdeli, Michele Barbato *, Maria Teresa Gutierrez-Wing, Charles D. Lofton

Department of Civil and Environmental Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

HIGHLIGHTS

- Novel material developed using slurry fluorogypsum and controlled pH-adjustment.
- Determined effects of alkali materials' addition to slurry fluorogypsum.
- Achieved high compressive strength after 28-day curing.
- Better mechanical properties than FG-based blends with uncontrolled pH-adjustment.
- Material can be used as a low-cost green substitute for ordinary concrete.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the mechanical and durability properties of blends made of fluorogypsum (FG) with the pH adjusted by using controlled amounts of circulating fluidized bed combustion ash (CFBCA) and denoted as C-FG, class C fly ash (FA), and type II Portland cement (PC). A series of pH tests was conducted on samples of C-FG to develop an analytical relationship between acidity and CFBCA content, which can be used to determine the optimal amount of CFBCA needed to obtain a specified pH value. Two compositions of C-FG-based blends were investigated in detail to identify the effects of CFBCA content on compressive strength, modulus of elasticity, Poisson's ratio, relative volumetric expansion, unit weight, and setting times. The obtained properties were compared with those of FG-based blends having the same composition and made using FG with the pH adjusted by using uncontrolled amounts of CFBCA (U-FG). Results suggest that the amount of CFBCA can have significant effects on the properties of C-FG-based blends, depending on the composition. In addition, C-FG-based blends generally achieve a higher compressive strength and initial stiffness than the corresponding U-FG-based blends.

1. Introduction

Millions of tons of solid by-product materials are produced every year by chemical industries all over the world. The accumulation of these materials causes substantial societal costs for containment and disposal, including environmental pollution and related economic losses [1]. Therefore, finding new beneficial applications for these large reserves of unused and/or underutilized materials is of great interest and provides important opportunities for sustainable economic development. At the same time, the construction industry is always searching for alternative supplies of usable materials in order to curb its carbon footprint, reduce

* Corresponding author.
E-mail addresses: ybigde1@lsu.edu (Y. Bigdeli), mbarbato@lsu.edu (M. Barbato), mgutie5@lsu.edu (M.T. Gutierrez-Wing), clofto5@lsu.edu (C.D. Lofton).

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the cost of new projects, and ensure long term sustainability of the industry itself [2–6].

Among the different options that have been investigated in the last few decades, significant attention has been paid to the utilization of gypsum-based by-product materials in the construction industry [7–9]. One of these gypsum by-products is fluorogypsum (FG), which is an acidic by-product of the industrial production of hydrofluoric acid from fluorspar. FG is discharged in slurry form from the producer and placed in settlement ponds until the FG hardens [10–12]. The hardened FG has a very low pH and needs to be neutralized in order to avoid potentially harmful properties such as corrosiveness [12]. This neutralization is usually performed by adding a small amount (2%–6% of dry weight) of alkaline materials such as pure lime [13] or circulating fluidized bed combustion ash (CFBCA) [14], and obtaining a new material referred to as blended calcium sulfate [9] or pH-adjusted FG [16]. This material is then stockpiled in mounds, where it is exposed to weather and potential contaminants before it is removed for potential use. The composition of the natural fluorspar, the addition of alkaline materials, and the stockpiling of this material are generally not subjected to quality control. Thus, different batches of the resulting material can have very different chemical and physical properties even when produced by the same chemical plant. This material is referred to as uncontrolled pH-adjusted FG (U-FG) hereinafter.

Most of the research available in the literature regarding the use of FG in construction applications employed U-FG [7,15–18]. This selection is most likely due to the fact that: (1) U-FG is readily available, since it is stockpiled by the chemical plants producing hydrofluoric acid; and (2) pure FG cannot be used as is because it presents high levels of acidity and long setting times, which are considered undesirable properties for a construction material [16]. However, the usage of U-FG in both experimental research and real-world construction applications is often associated with a wide variability of the experimental results and performance of the materials [16], mainly due to the following issues: (1) the composition of the natural base fluorspar varies between different batches; (2) U-FG can present a high variability in the alkaline material content between different batches and even within the same batch due to the non-uniformity of the lime/CFBCA treatment (both in time and space) and the usage of alkaline materials with different levels of purity; and (3) the chemical, physical, and mechanical properties of U-FG can be influenced by the exposure to contaminants and environmental phenomena, such as temperature changes, precipitation, and freezing/thawing cycles, which depend both on the location and the duration of the stockpiling before use of this material. In order to mitigate these effects, Garg and Pundir [18] used pure FG mixed with a small (0.5% to 1.0% in weight) quantity of lime to investigate the feasibility of using a blend of pH-adjusted FG, granulated blast furnace slag, and Portland cement (PC) as a composite binder for outdoor construction applications. Yan and You [19] and Yan et al. [20] also used pure FG mixed with large amounts (i.e., greater than 50% of dry weight) of fly ash (FA) and activated with PC to obtain a cementitious binder of "high strength, good volume stability, and excellent water resistance" [19].

This study investigates the use of pH-adjusted FG obtained by adding controlled amounts of CFBCA to FG in slurry form, which is referred to as controlled pH-adjusted FG (C-FG) hereinafter, for the production of FG-blends containing PC and FA. CFBCA was considered instead of lime in this research because it is currently used in the neutralization of FG in Louisiana as a cheaper alternative to lime. The FG-based blends made by utilizing this C-FG material are referred to as C-FG-based blends, in order to distinguish them from FG-based blends made by using U-FG material, which are referred to as U-FG-based blends hereinafter and have been previously investigated for outdoor and underwater construction applications [16].

The objectives of the present paper are: (1) developing an analytical model to describe the relation between the pH of C-FG and the CFBCA content; (2) studying the effects of using controlled amounts of CFBCA to neutralize FG in slurry form (as produced by the chemical plants before any neutralization or weather exposure) on the mechanical and physical properties of C-FG-based blends (namely compressive strength, modulus of elasticity, Poisson's ratio, unit weight, volumetric expansion, and setting times); and (3) comparing the properties of C-FG-based blends to U-FG-based blends that were previously investigated by the authors [16]. This research is a step toward the development of a FG-based material that can be used as a substitute of ordinary concrete. Therefore, the experimental methods used to investigate the physical and mechanical properties of the developed FG-based blends correspond to those used to investigate the same properties in ordinary concrete specimens.

2. Research contributions and significance

To the authors' knowledge, this is the first paper that investigates the use of slurry FG with controlled quantities of alkali materials as a direct substitute of ordinary unreinforced concrete (i.e., not as a binder) for construction applications. This paper rigorously evaluates the effects of alkali materials' addition to slurry FG separated from the effects of weather exposure and other contaminations during stockpiling. The significance of this research derives from the following advantages of using C-FG-based blends versus U-FG-based blends: (1) the sources of variability for the mechanical and physical properties of C-FG are reduced to the natural variability of the base fluorspar only, which can allow the production of construction materials with more easily reproducible properties; (2) the quality control for construction materials made using C-FG is significantly simpler and easier to implement than that for materials made using U-FG; and (3) the production costs of C-FG-based blends can be reduced when compared to that of U-FG-based blends because the costs associated with pH neutralization, stockpiling, and maintenance can be minimized or avoided. Thus, the results presented in this paper provide the basis toward the development of an economical and sustainable substitute of ordinary concrete using industrial by-product FG.

3. Characterization of raw materials

The FG in slurry form was obtained from the Honeywell chemical plant located in Geismar, LA (USA). Experimental tests showed that the provided slurry FG had a water content of 20% by weight and a pH of 2.28. All the slurry FG used in this research was left to air dry and solidify for four days and then was ground and sieved by using a US standard sieve #10 (corresponding to a maximum particle size of 2 mm). A sample of FG was analyzed using X-ray Diffraction (XRD) to identify its crystallographic composition, as shown in Fig. 1. The Rietveld analysis [21] of the XRD pattern indicated that the material quantitatively contains 74.6% of anhydrite (A), 24.2% of gypsum (G), 1.0% of fluorite (F), and smaller amounts of other materials, as reported in Table 1.

The CFBCA used in this research was produced by burning petroleum coke, tree bark, and limestone in a boiler used for power generation [14]. The provided material had a water content of 20% by weight and a pH of 12.6. The material was air dried and sieved by using the US standard sieve #10 prior to its use in the experiments. A sample of CFBCA was analyzed using XRD to identify its crystallographic composition, as shown in Fig. 2. The Rietveld analysis of the XRD pattern indicated that the CFBCA

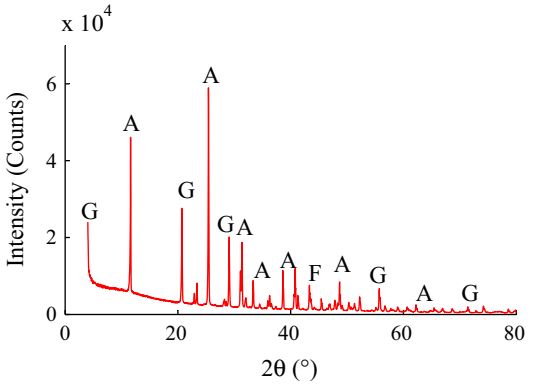

Fig. 1. X-ray diffractogram of an FG sample (G: gypsum, A: anhydrate, F: fluorite).

Table 1
Crystallographic compositions of FG, CFBCA, FA, and PC by weight percentage (%).

Components	FG (%)	CFBCA (%)	FA (%)	PC (%)
Akermanite: $Ca_2Mg(Si_2O_7)$	–	–	32.6	–
Alite: $3CaO.SiO_2$	–	–	–	70.4
Anhydrite: $CaSO_4$	74.6	–	6.8	–
Brownmillerite: $Ca_2(Al,Fe)_2O_5$	–	–	29.4	23.3
Calcite: $CaCO_3$	–	17.6	–	–
Ettringite: $Ca_6Al_2(SO4)_3(OH)_{12}{\cdot}26H_2O$	–	6.8	–	–
Fluorite: CaF_2	1.0	–	–	–
Gypsum: $CaSO_4{\cdot}2H_2O$	24.2	64.9	–	1.4
Periclase: MgO	–	–	5.9	–
Perovskite: $CaTiO_3$	–	–	3.9	–
Portlandite: $Ca(OH)_2$	–	4.1	–	–
Quartz: SiO_2	0.1	5.9	20.3	–
Tricalcium Aluminate: $3CaO.Al_2O_3$	–	–	–	4.9

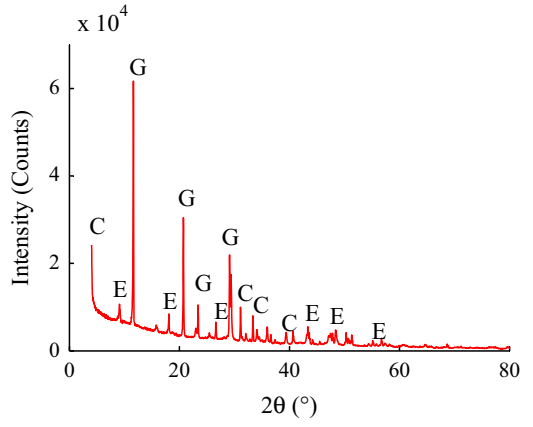

Fig. 2. X-ray diffractogram of a CFBCA sample (G: gypsum, C: calcite, E: ettringite).

contains about 64.9% of gypsum, 17.6% of calcite (C), 6.8% of ettringite (E), and 10.7% of other materials, such as quartz and portlandite, as reported in Table 1. Table 1 also reports the results of the Rietveld XRD analyses for representative samples of FA, and PC.

For the purpose of comparison with the results presented in Bigdeli et al. [16], it is noted here that: (1) the FA and PC used for this research and in Bigdeli et al. [16] were the same; (2) the FG used here was slurry FG which was dried and ground before the addition of CFBCA, whereas the FG used in Bigdeli et al. [16] was U-FG; and (3) the main difference in crystallographic compositions between the dried slurry FG and the U-FG is that the former has a predominance of anhydrite, whereas the latter has a predominance of gypsum. This change in crystallographic composition appears to be due to the weather exposure rather than to addition of CFBCA.

4. Effects of CFBCA on pH of C-FG

Several mixtures with different proportions of FG and CFBCA (as described in Table 2) were prepared to investigate the effects of CFBCA content on the acidity of C-FG. In particular, 11 compositions were selected as fitting points to develop a mathematical relation between CFBCA content and pH of the C-FG material. For these 11 compositions, the specific proportions of the two base materials were selected to accurately describe the range in which the pH of the mixture is highly sensitive to the change in CFBCA content. Thus, the mixtures considered included amounts of CFBCA going from 0.0% to 2.0% with increments of 0.5%, to 10.0% with increments of 2.0%, to 20% and 100%. Two additional compositions were selected as control points to validate the developed model.

In order to determine the pH of the selected C-FG mixtures, 20 samples of 20 g of material were prepared for each mixture. The pH of each sample was measured according to the procedure described in ASTM D4972 [22]. The sample mean, μ_{pH}, and the coefficients of variation, COV_{pH}, of the pH for each composition are reported in Table 2 together with the mean's 95% confidence intervals (CI). Slurry FG samples showed very acidic properties with $\mu_{pH} = 2.28$. Conversely, CFBCA showed alkali properties with $\mu_{pH} = 12.60$. In general, the variability of the results is small, with $COV_{pH} \leq 5.03\%$ for all compositions. A functional regression model was fitted to the sample mean of the fitting data points to obtain a relation between CBCA content and pH. This model consists of two polynomial equations: (1) a third degree polynomial in the range $0\% \leqslant w_{CFBCA} \leqslant 2\%$, and (2) a second degree polynomial in the range $2\% < w_{CFBCA} \leqslant 20\%$, and is given by:

$$pH = \begin{cases} 0.927w_{CFBCA}^3 - 1.710w_{CFBCA}^2 \\ \quad +1.720w_{CFBCA} + 2.257 & 0\% \leqslant w_{CFBCA} \leqslant 2\% \\ -0.016w_{CFBCA}^2 + 0.696w_{CFBCA} \\ \quad +4.924 & 2\% < w_{CFBCA} \leqslant 20\% \end{cases} \quad (1)$$

in which pH represents the acidity of the C-FG mixture in pH unit and w_{CFBCA} denotes the content of CFBCA in percentage of total dry weight. The relation has a coefficient of determination $R^2 = 0.997$ and its fitting to the experimental data is represented graphically in Fig. 3, where the individual experimental results and the 95% CI for the fitting curve are also reported. The developed model was validated through comparison of the numerical estimates of the pH and experimental results at two control data points, namely with $w_{CFBCA} = 4.8\%$ and $w_{CFBCA} = 7.4\%$, which are also represented in Fig. 3. The relative errors (obtained as the difference between the predicted and average measured pH divided by the average measured pH) are very small, i.e., 0.05% and –0.13%, respectively, which indicate that the model is very accurate in predicting the pH based on w_{CFBCA}. According to this model, pH = 7 is obtained for $w_{CFBCA} = 3.2\%$. This result is consistent with the fact that the amount of CFBCA currently used to neutralize the FG material is contained in the range $2\% \leqslant w_{CFBCA} \leqslant 6\%$ (G. Mitchell, Brown Industries, personal communication).

It is noted here that other functional expressions were also investigated in the development of the regression model (e.g., sigmoid functions to impose continuity of the first derivative); however, the model presented provided the best compromise between prediction capabilities and number of fitting parameters. Based on the previously reported results, it is concluded that the pH- w_{CFBCA} model developed in this study can be used to determine the optimal amount of CFBCA needed to neutralize the FG material or, more in general, to obtain a desired pH.

Table 2
Effects of CFBCA on pH of C-FG: compositions of C-FG mixtures and sample mean, coefficient of variation, and 95% confidence intervals of measured pH.

Data point classification	Sample	FG (%)	CFBCA (%)	μ_{pH} (-)	COV_{pH} (%)	95% CI (-)
Fitting data points	1	100.0	0.0	2.28	0.58	2.27–2.29
	2	99.5	0.5	2.70	1.84	2.68–2.72
	3	99.0	1.0	3.36	4.81	3.28–3.44
	4	98.5	1.5	4.01	5.03	3.92–4.10
	5	98.0	2.0	6.30	2.19	6.24–6.36
	6	96.0	4.0	7.45	1.78	7.39–7.51
	7	94.0	6.0	8.41	3.02	8.29–8.53
	8	92.0	8.0	9.54	2.52	9.43–9.65
	9	90.0	10.0	10.35	1.98	10.25–10.45
	10	80.0	20.0	12.54	0.17	12.53–12.55
	11	0.0	100.0	12.60	0.25	12.59–12.61
Control points	12	95.2	4.8	7.90	0.97	7.86–7.94
	13	92.6	7.4	9.21	0.27	9.20–9.22

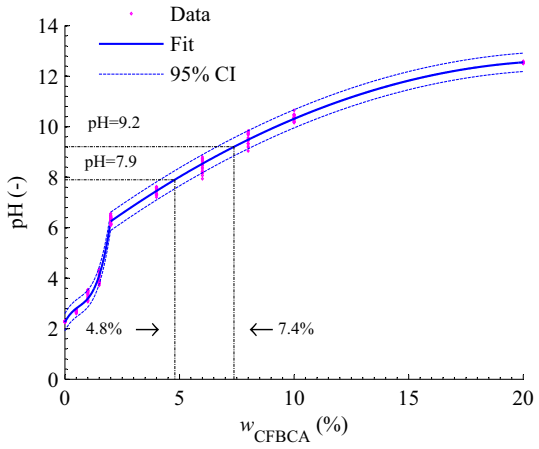

Fig. 3. Relation between w_{CFBCA} and pH of C-FG: comparison between proposed functional model and experimentally measured pH.

A steep change in pH is observed between $w_{CFBCA} = 1.5\%$ and 2.0%, which is consistent with an acid-base chemical reaction and is similar to the shape of a titration curve [23]. Most of the pH increase is observed for C-FG with w_{CFBCA} contained between 1.0% and 4.0%, with the average pH rapidly increasing from $\mu_{pH} = 3.36$ to $\mu_{pH} = 7.45$. According to the model given in Eq. (1), neutrality is achieved for $w_{CFBCA} = 3.2\%$. When w_{CFBCA} increases from 4.0% to 20.0%, the average pH increases from $\mu_{pH} = 7.45$ to $\mu_{pH} = 12.54$. For $w_{CFBCA} > 20.0\%$, the concentration of hydroxide ions (OH^-) in the C-FG solution becomes predominant over that of hydrogen ions (H^+) and the average pH increases slowly to $\mu_{pH} = 12.60$, which is the average pH for CFBCA.

5. Effects on CFBCA on the properties of C-FG-based blends

Two particular compositions of the C-FG-based blends were selected to investigate the effects of CFBCA amounts on the mechanical and physical properties of interest. Hereinafter, each composition is identified by a letter indicating the type of pH-adjusted FG employed (namely, C denotes C-FG and U denotes U-FG), and by three numbers in parentheses separated by hyphens and indicating the weight percentages of C-FG/U-FG, FA, and PC, respectively. The two compositions considered in this study are C (60-34-6) and C(62-35-3), which were selected because comparable experimental results are available in the literature for compositions U(60-34-6) and U(62-35-3) [16], and because previous studies on mechanical and physical properties of U-FG-based blends indicated that these two compositions were promising in terms of strength and durability for outdoor and underwater construction applications [16]. In particular, composition U(60-34-6) had the highest compressive strength among all compositions tested in Bigdeli et al. [16]. It is noted here that, for composition U(62-35-3), experimental data are available for all properties considered in this study (i.e., compressive strength, initial stiffness, Poisson's ratio, relative volumetric expansion, unit weight, and initial and final setting times), whereas experimental data for composition U(60-34-6) are available only for compressive strength and relative volumetric expansion [16].

In order to investigate the effects of the CFBCA content on the properties of the C-FG-based blends, seven mixtures of FG and CFBCA were prepared, with w_{CFBCA} varying between 0% and 12% with intervals of 2% (see Table 3). For the U-FG-based blends, the specific amount of CFBCA could not be determined; however, the amount of CFBCA was contained between 2% and 6% (G. Mitchell, Brown Industries, personal communication).

5.1. Specimen preparation and testing procedures

The C-FG mixtures listed in Table 3 were prepared by carefully proportioning the dried slurry FG and CFBCA passing a US standard sieve #10 with a nominal opening of 2 mm. Before sieving, the hardened slurry FG was ground and the CFBCA was air dried. The dry C-FG mixtures were then blended with FA and PC to obtain C (62-35-3) and C(60-34-6) compositions. Finally, the material was mixed with water amount equal to 20% of the total weight of the dry mix (i.e., with a water-cement ratio equal to 20/3 and 10/3 for the two compositions) until a uniform paste was obtained, according to the ASTM C305-14 standard [24]. It is highlighted here that no aggregate or any other admixtures were added to the C-FG-based blends. Specimen preparation and testing procedures followed standard methods used for ordinary concrete because the objective of this study was to investigate the mechanical and physical properties of FG-based blends when used as a substitute for

Table 3
C-FG mixtures used to study the effects of CFBCA content on the properties of C-FG-based blends.

Mixture	FG (%)	w_{CFBCA} (%)
$C\text{-}FG_1$	100	0
$C\text{-}FG_2$	98	2
$C\text{-}FG_3$	96	4
$C\text{-}FG_4$	94	6
$C\text{-}FG_5$	92	8
$C\text{-}FG_6$	90	10
$C\text{-}FG_7$	88	12

ordinary concrete. All specimens were tested after 28 days of curing at room temperature (20 ± 2 °C) and 100% humidity condition.

Sets of five cylindrical specimens of 10.15 cm × 20.3 cm (4 in × 8 in) size were prepared following the ASTM C192/C192M-16a standard [25] using different C-FG-based blends for all tests of mechanical and durability properties, with the exception of the setting time tests, for which three samples of fresh mix were tested per ASTM C403/C403M-08 standard [26]. The water content of each blend at the curing condition was determined by following the ASTM D2216 standard [27]. Compressive strength, f_c, was tested following ASTM C39/C39M-16b [28]; chord modulus of elasticity, E, and Poisson's ratio, ν, were tested by following the procedures described in ASTM C469/C469M-14 [29]; relative volumetric expansion, η, was calculated as the ratio between the change in volume and the initial volume, i.e., $\eta = (V_2 - V_1)/V_1$, where V_1 and V_2 denote the volume of each specimen immediately after demolding and after 28 days of curing, respectively. This method was followed because ASTM does not provide a standard for volumetric expansion of the material considered in this study and the ASTM standards for expansion measurement of cement mortars (i.e., ASTM C806 [30]) and shrinkage-compensating concretes (ASTM C878 [31]) cannot be directly used for these FG-based blends. Unit weight was obtained according to ASTM C642-13 [32]; and initial and final setting times were measured according to ASTM C403/C403M-08 [26].

Tables 4 and 5 report the experimental result statistics for compositions C(62-35-3) and C(60-34-6), respectively, in terms of sample means and standard deviations. All results are reported as functions of the CFBCA content in the C-FG mix. Tables 4 and 5 also report the statistics available in Bigdeli et al. [16] for compositions U(62-35-3) and U(60-34-6), respectively. The following subsections provide a discussion of these experimental results.

5.2. Compressive strength

Fig. 4 plots the sample mean of the compressive strength, μ_{f_c}, together with its 95% CI as a function of w_{CFBCA} for compositions C(62-35-3) and C(60-34-6). The same figure reports also the compressive strength sample means, as well as their 95% CI, for compositions U(62-35-3) and U(60-34-6), which are reported over the range $2\% \leqslant w_{CFBCA} \leqslant 6\%$ because the exact CFBCA content is unknown. It is observed that: (1) the average compressive strength of composition C(62-35-3) slowly increases from 22.5 MPa to 33.9 MPa for w_{CFBCA} increasing from 0% to 10% and then slightly decreases to 31.5 MPa for w_{CFBCA} = 12%; (2) the average compressive strength of composition C(60-34-6) is almost constant for $w_{CFBCA} \leqslant 4\%$, reaches a maximum value of 52.7 MPa at $w_{CFBCA} = 4\%$ and then decreases dramatically, reaching the value of 7.5 MPa for $w_{CFBCA} = 12\%$; (3) the average compressive strengths of both compositions U(62-35-3) and U(60-34-6) are equal to 8.9 MPa and 13.8 MPa, respectively, and thus are significantly lower (i.e., smaller by a factor larger than 3) than those of the corresponding C-FG compositions in the range $2\% \leqslant w_{CFBCA} \leqslant 6\%$; and (4) the lengths of the 95% CI for all compositions are small (i.e., less than 4 MPa), which indicates that the estimates of the average compressive strengths are highly reliable.

It is concluded that the compressive strength of C-FG-based blends can experience significant variations for varying amounts of CFBCA and different compositions. It is also concluded that using U-FG has a negative effect on the compressive strength of FG-based blends. Since the chemical analysis of the U-FG used for compositions U(62-35-3) and U(60-34-6) did not identify significant amount of impurities [16], the results presented in this paper seem to indicate that prolonged weather actions produce this negative effect independently on the amount of CFBCA used to neutralize the FG. It is also observed that, for appropriate values of w_{CFBCA}, the C-FG-based blends considered in this study achieve compressive strengths that are compatible with their use as structural construction materials.

5.3. Modulus of elasticity and Poisson's ratio

Figs. 5 and 6 plot the sample means of the modulus of elasticity, μ_E, and Poisson's ratio, μ_ν, respectively, as functions of w_{CFBCA} for compositions C(62-35-3) and C(60-34-6), as well as for composition U(62-35-3). The corresponding 95% CI are also reported.

For composition C(62-35-3), the modulus of elasticity slightly increases from 11.9 GPa to 14.6 GPa for w_{CFBCA} increasing from 0% to 12%; whereas the Poisson's ratio slightly increases from 0.21 to 0.26 when w_{CFBCA} increases from 0% to 6%, and then remains almost constant for $6\% \leqslant w_{CFBCA} \leqslant 12\%$. One-way ANOVA analysis [33] confirms that the changes in Poisson's ratio for

Table 4
Statistics of the mechanical and physical properties for composition C(62-35-3) made with different C-FG mixes and for composition U(62-35-3).

w_{CFBCA} (%)	μ_{f_c} / σ_{f_c} (MPa)	μ_E / σ_E (GPa)	μ_ν / σ_ν (-)	μ_ρ / σ_ρ (kg/m^3)	μ_η / σ_η (%)	μ_{t_i} / σ_{t_i} (min)	μ_{t_f} / σ_{t_f} (min)
0	22.5/0.4	11.9/1.2	0.21/0.02	1987/1	0.9/0.9	207/19	694/14
2	28.1/0.8	12.6/0.3	0.23/0.02	2008/6	0.1/0.2	109/5	455/6
4	30.1/0.8	13.3/0.1	0.25/0.01	2049/5	0.8/0.5	99/7	411/40
6	32.0/1.1	14.1/0.9	0.26/0.02	2041/7	3.0/0.9	96/11	428/20
8	33.6/1.0	14.1/0.2	0.25/0.01	2048/30	2.2/0.2	122/9	458/4
10	33.9/1.5	13.8/0.1	0.24/0.01	1983/5	4.1/0.6	113/12	419/23
12	31.5/0.3	14.6/0.1	0.25/0.01	1978/27	7.7/0.5	120/6	415/12
U-FG	8.9/0.6	8.7/0.8	0.18/0.01	1750/7	4.1/0.6	131/8	325/7

Table 5
Statistics of the mechanical and physical properties for composition C(60-34-6) made with different C-FG mixes and for composition U(60-34-6).

w_{CFBCA} (%)	μ_{f_c} / σ_{f_c} (MPa)	μ_E / σ_E (GPa)	μ_ν / σ_ν (-)	μ_ρ / σ_ρ (kg/m^3)	μ_η / σ_η (%)	μ_{t_i} / σ_{t_i} (min)	μ_{t_f} / σ_{t_f} (min)
0	51.5/0.6	21.1/0.3	0.28/0.02	2080/15	2.4/0.9	167/22	626/26
2	49.8/0.9	20.1/0.3	0.28/0.01	2097/8	2.3/0.2	175/14	639/12
4	52.7/2.1	19.4/1.1	0.27/0.01	2048/9	2.4/0.5	192/29	611/52
6	45.8/1.9	18.8/1.5	0.25/0.01	2025/11	5.3/0.5	181/11	620/25
8	29.6/1.3	19.4/0.7	0.23/0.01	1998/17	6.9/0.5	172/13	567/17
10	11.7/0.9	6.8/0.8	0.23/0.01	1887/3	13.1/0.6	159/13	531/17
12	7.5/0.4	6.4/0.5	0.20/0.01	1844/7	14.2/0.3	142/19	510/19
U-FG	13.8/1.5	NA	NA	NA	2.7/0.9	NA	NA

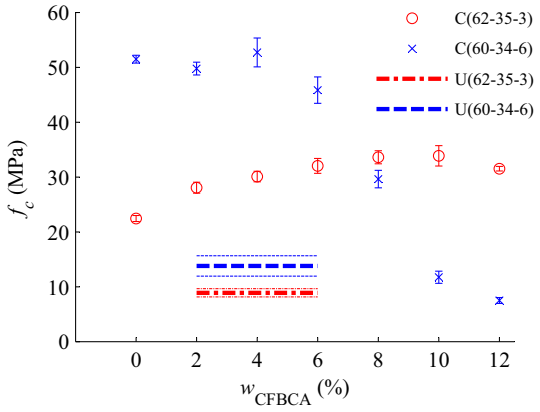

Fig. 4. Effects of CFBCA content on compressive strength of FG-based blends.

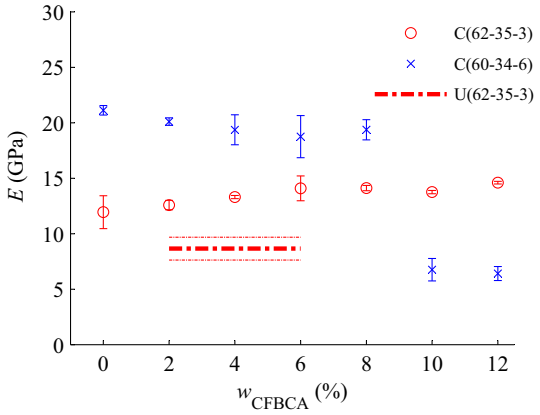

Fig. 5. Effects of CFBCA content on modulus of elasticity of FG-based blends.

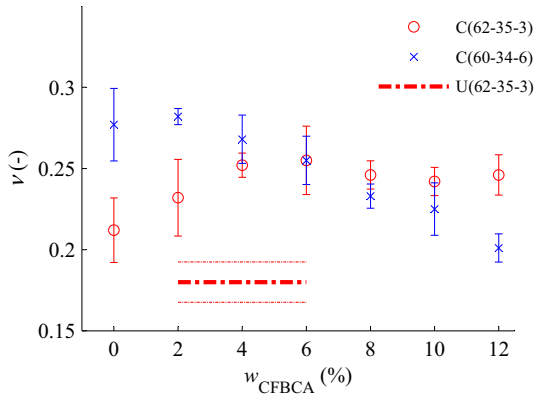

Fig. 6. Effects of CFBCA content on Poisson's ratio of FG-based blends.

$6\% \leqslant w_{CFBCA} \leqslant 12\%$ are not statistically significant considering a significance level $\alpha = 5\%$. Conversely, for composition C(60-34-6), the modulus of elasticity slightly decreases from 21.1 GPa to 19.4 GPa for w_{CFBCA} increasing from 0% to 8% and then dramatically decreases to 6.8 GPa and 6.4 GPa for $w_{CFBCA} = 10\%$ and 12%, respectively; whereas the Poisson's ratio monotonically decreases from 0.28 to 0.20 when w_{CFBCA} increases from 2% to 12%, with the difference between the Poisson's ratio for $w_{CFBCA} = 0\%$ and 2% that is not statistically significant ($\alpha = 5\%$). Finally, the modulus of elasticity and the Poisson's ratio for composition U(62-35-3) are 38.3% and 21.7%, lower, respectively, than their corresponding minimum values in the range $2\% \leqslant w_{CFBCA} \leqslant 6\%$ for composition C(62-35-3). It is observed that the modulus of elasticity for different CFBCA amounts is highly correlated with the corresponding average compressive strength, with correlation coefficients equal to 0.87 for composition C(62-35-3) and to 0.93 for composition C(60-34-6).

5.4. Relative volumetric expansion

Fig. 7 plots the sample mean of the relative volumetric expansion, μ_η, as a function of w_{CFBCA} for compositions C(62-35-3) and C(60-34-6), as well as for compositions U(62-35-3) and U(60-34-6). The corresponding 95% CI are also reported.

For composition C(62-35-3), the relative volumetric expansion is always less than 1% for $w_{CFBCA} \leqslant 4\%$, with differences that are not statistically significant ($\alpha = 5\%$). However, by further increasing w_{CFBCA} from 4% to 12%, μ_η increases up to 7.7%. For composition C(60-34-6), μ_η is almost constant in the range 2.3%-2.4% for $w_{CFBCA} \leqslant 4\%$, with differences that are not statistically significant ($\alpha = 5\%$), and then monotonically increases up to a value 14.2% for $w_{CFBCA} = 12\%$. In the range $2\% \leqslant w_{CFBCA} \leqslant 6\%$, the relative volumetric expansion for composition U(60-34-6) is similar to that of composition C(60-34-6) for $w_{CFBCA} \leqslant 4\%$ (in fact, the differences are not statistically significant for $\alpha = 5\%$), whereas μ_η for composition U(62-35-3) is higher than that of composition C(62-35-3).

For cases with $\mu_\eta \geqslant 6.5\%$, cracks visible to the unaided eye were detected on the surface of the specimens, as shown in Fig. 8. These cracks corresponded to a significant decrease in com-

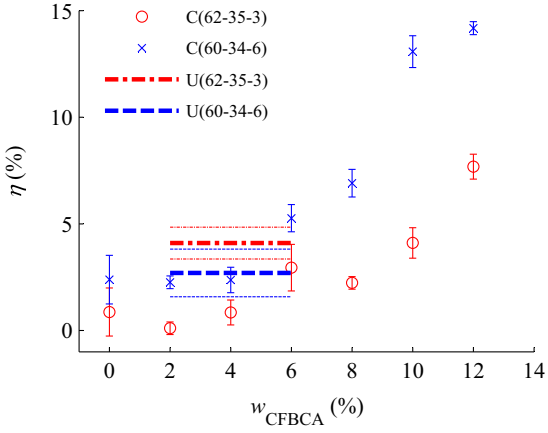

Fig. 7. Effects of CFBCA content on relative volumetric expansion of FG-based blends.

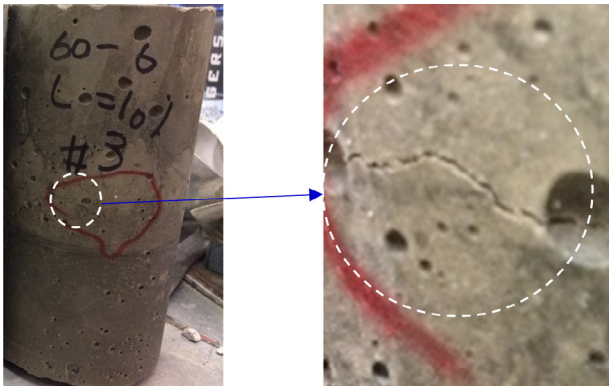

Fig. 8. Formation of surface cracks for specimens of composition C(60-34-6) with $w_{CFBCA} = 10\%$.

pressive strength for the C-FG-based blends. This result is consistent with observations made by Bigdeli et al. [16] for U-FG-based blends and indicates a strong negative correlation between material strength and relative volumetric expansion.

5.5. Unit weight

Fig. 9 plots the sample mean of the unit weight, μ_ρ, as a function of w_{CFBCA} for compositions C(62-35-3) and C(60-34-6), as well as for composition U(62-35-3). The corresponding 95% CI are also reported.

For composition C(62-35-3), μ_ρ slightly increases from 1987 kg/m^3 to 2049 kg/m^3 for w_{CFBCA} increasing from 0% to 4%, it remains almost constant for $4\% \leqslant w_{CFBCA} \leqslant 8\%$ (in fact, the differences are not statistically significant for $\alpha = 5\%$), and decreases to 1978 kg/m^3 for $w_{CFBCA} = 12\%$. For composition C(60-34-6), μ_ρ slightly increases from 2080 kg/m^3 to 2097 kg/m^3 for $w_{CFBCA} = 0\%$ and 2%, respectively, even though this change is not statistically significant with a significance level $\alpha = 5\%$, and then decreases monotonically to 1844 kg/m^3 for $w_{CFBCA} = 12\%$. The average unit weight of the U-FG-based blend made with composition U(62-35-3) is 1750 kg/m^3, which is significantly lower than that of C-FG-based blends. This difference is mainly due to the higher amount of gypsum (and the corresponding lower amount of anhydrite) contained by U-FG when compared to C-FG.

5.6. Initial and final setting times

The sample means of the initial setting time, μ_{t_i}, and final setting time, μ_{t_f}, are plotted as functions of w_{CFBCA} in Figs. 10 and 11, respectively, for compositions C(62-35-3) and C(60-34-6), as well as for composition U(62-35-3). The corresponding 95% CI are also reported.

For composition C(62-35-3), μ_{t_i} decreases from 207 to 109 min when w_{CFBCA} increases from 0% to 2%, changes very little (between 96 and 109 min) for $2\% \leqslant w_{CFBCA} \leqslant 6\%$ (with changes that are not statistically significant for $\alpha = 5\%$), increases to 122 min for $w_{CFBCA} = 8\%$ and then changes very little for higher values of w_{CFBCA} (with changes that are not statistically significant for $\alpha = 5\%$). The average final setting time of composition C(62-35-3) is 694 min for $w_{CFBCA} = 0\%$ and then oscillates in the range 411–458 min for higher values of w_{CFBCA}. One-way ANOVA results indicate that the changes in final setting times for composition C(62-35-3) are not statistically significant for $2\% \leqslant w_{CFBCA} \leqslant 12\%$ with a significance level $\alpha = 5\%$. Composition U(62-35-3) has an initial setting time equal to 131 min, i.e., 20% higher than the initial setting time of composition C (62-35-3) for $2\% \leqslant w_{CFBCA} \leqslant 6\%$, and a final setting time equal to 325 min, i.e., more than 20% lower than the final setting time of composition C(62-35-3) for $2\% \leqslant w_{CFBCA} \leqslant 6\%$.

For composition C(60-34-6), μ_{t_i} slightly increases from 167 to 192 min for w_{CFBCA} increasing from 0% to 4% (with changes that are not statistically significant for $\alpha = 5\%$), then monotonically decreases down to 142 min for w_{CFBCA} increasing from 4% to 12%. The average final setting time fluctuates in the range 611–639 min for $w_{CFBCA} \leqslant 6\%$ (with changes that are not statistically significant for $\alpha = 5\%$), then monotonically decreases down to 510 min for w_{CFBCA} increasing from 6% to 12%.

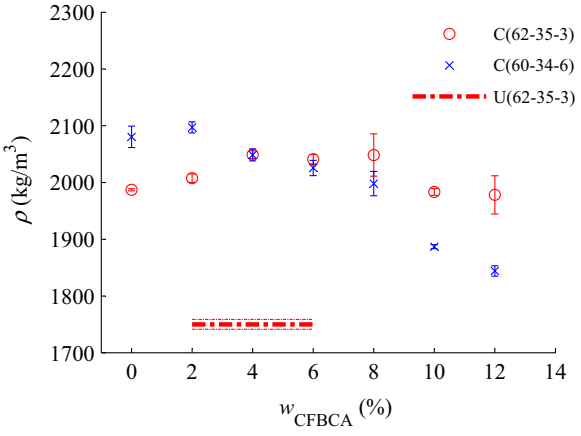

Fig. 9. Effects of CFBCA content on unit weight of FG-based blends.

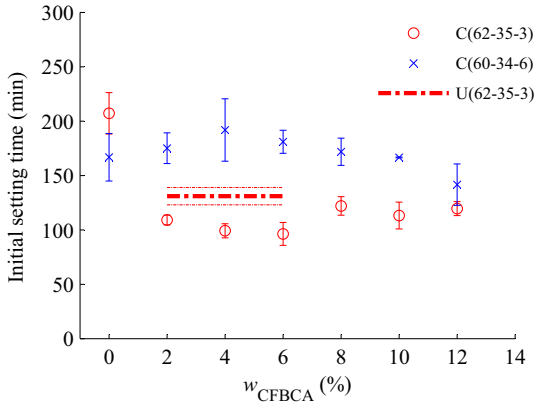

Fig. 10. Effects of CFBCA content on initial setting time of FG-based blends.

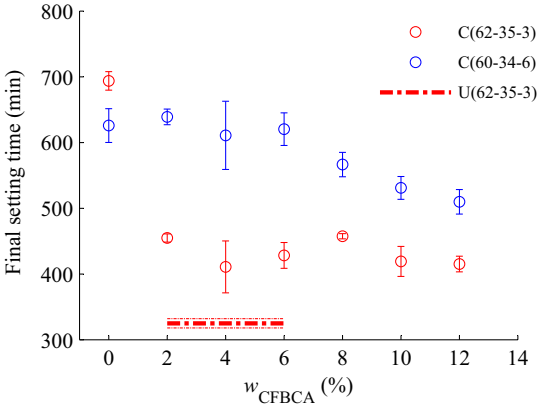

Fig. 11. Effects of CFBCA content on final setting time of FG-based blends.

5.7. Synoptic considerations and comparison with ordinary concrete properties

The experimental results presented in this research show that the content of CFBCA used to neutralize the FG material has a significant effect on the mechanical and physical properties of C-FG-based blends. The importance of this effect is different from composition to composition and could be explained by an increase in the hydration and crystallization processes induced by increasing amounts of CFBCA. The increasing amounts of hydration products, such as ettringite, for low amounts of CFBCA tend to increase strength and stiffness of the C-FG-based blends up to a point, after which the hydration process produces expansion within the hardened matrix, cracking, and reduction of strength and stiffness. This explanation is consistent also with the experimental results obtained for relative volumetric expansion and unit weight. However, further investigations and additional detailed chemical anal-

yses are required to fully demonstrate the hypothesized explanation.

It is observed that the maximum compressive strength is achieved for an optimal amount of CFBCA, which depends on the C-FG-based composition and is in the range $8\% \leqslant w_{CFBCA} \leqslant 10\%$ for composition C(62-35-3) and $2\% \leqslant w_{CFBCA} \leqslant 4\%$ for composition C(60-34-6). The chord modulus of elasticity follows a trend similar to that of the compressive strength. Considering the range $2\% \leqslant w_{CFBCA} \leqslant 6\%$ that is currently used in the neutralization of FG (G. Mitchell, Brown Industries, personal communication), composition C(60-34-6) achieves higher compressive strength and elastic modulus than composition C(62-35-3). Within the same range, it is observed that the mechanical and physical properties investigated in this study experience only relatively small changes (i.e., $\leqslant 13.1\%$ for all parameters with the exception of μ_η) for both compositions. These observations, in combination with the developed pH- w_{CFBCA} model, suggest that a good compromise between mechanical properties and production cost can be obtained using small amounts of CFBCA (i.e., $w_{CFBCA} \leqslant 4\%$). For composition C (60-34-6), it may even be advantageous to avoid neutralization of the FG (i.e., to use $w_{CFBCA} = 0\%$), as long as the low pH is not harmful to the equipment used to grind the dried slurry FG. The results of this investigation also indicate that composition C(60-34-6) with $w_{CFBCA} \leqslant 4\%$ is a promising material to substitute ordinary concrete in construction applications.

Composition U(62-35-3) provides an average compressive strength equal to 8.9 MPa, i.e., a reduction in compressive strength $\geqslant 68.3\%$ when compared to that of composition C(62-35-3) in the range $2\% \leqslant w_{CFBCA} \leqslant 6\%$. Similarly, composition U(60-34-6) has an average compressive strength equal to 13.8 MPa, with a reduction in compressive strength $\geqslant 69.9\%$ when compared to that of composition C(60-34-6) in the range $2\% \leqslant w_{CFBCA} \leqslant 6\%$. Based also on the other experimental results presented in this research, it is concluded that a prolonged exposure to environmental actions of the U-FG material has a negative effect on the mechanical and durability properties of U-FG-based blends. This effect appears to be significantly larger than that of different amounts of CFBCA. Therefore, the usage of C-FG should be preferred to the usage of U-FG in the preparation of FG-based blends. In addition, the production of C-FG from slurry FG with small amounts of CFBCA can potentially be done at lower costs than the current procedure of FG neutralization and stockpiling, due to the following advantages: (1) lower amounts of CFBCA than those needed for neutralization of the slurry FG can be used to produce C-FG-based blends, (2) the manufacture process can be streamlined by using directly the dried slurry FG (i.e., avoiding transportation to the stockpile and multiple grinding phases), and (3) the land use for stockpiling can be significantly reduced.

The experimental results presented in this research suggest that the C-FG-based blend made using composition C(60-34-6) with $w_{CFBCA} \leqslant 4\%$ is a promising sustainable substitute of ordinary concrete. This composition achieves a compressive strength between 49.8 MPa and 52.7 MPa, which is higher than the typical range of compressive strength for ordinary concrete, i.e., 20–40 MPa [34]. The modulus of elasticity is in the range 19.4–21.1 GPa, which is within the range that is typical for ordinary concrete, i.e., 14–40 GPa [34]. The Poisson's ratio varies between 0.27 and 0.28, which is higher than the typical Poisson's ratio for ordinary concrete, i.e., 0.15–0.20 [34]. The observed values of both strength and modulus of elasticity indicate that the mechanical properties of the proposed material are appropriate for structural applications.

The proposed composition has a unit weight contained in the range 2048–2080 kg/m^3, which is lower than that of normal weight concrete, i.e., about 2400 kg/m^3 [34], but higher than that of lightweight concrete, i.e., $\leq$1800 kg/m^3 [34]. The low unit weight of C-FG-based blends is an advantageous property for construction applications, because it can reduce the self-weight loads. It is also noted here that lightweight concrete is commonly obtained by using lightweight aggregates [34], whereas no coarse aggregates were employed for the C-FG-based blends investigated in this research. Therefore, the addition of normal weight and/or normal weight coarse aggregates to C-FG-based blends, albeit outside the scope of this study, could represent an interesting topic for future investigations. The average initial and final setting times of the proposed C-FG-based blend are in the ranges 167–192 min and 611–639 min, respectively. The initial setting time of this C-FG-based blend is comparable to the lower bound of the initial setting time range for ordinary concrete, i.e., typically 180–300 min in laboratory conditions; whereas the final setting time of the proposed material is slightly higher than the upper range of the final setting time for ordinary concrete, i.e., typically 360–600 min in laboratory conditions. This property may be less than desirable for structural applications. However, the final setting time of the proposed material should be also investigated in field conditions to determine if any modification to the composition could be needed.

Utilization of PC in the proposed compositions, i.e., 6%, is significantly lower than in ordinary concrete, i.e., 10%–15% [35]. This property is extremely advantageous, because it indicates that the material can be produced at a lower cost and with a lower CO_2 gas release than ordinary concrete, making this material even more promising as a green substitute of ordinary concrete.

6. Conclusions

In this paper, a series of pH tests was performed to identify the acidity of pH-adjusted fluorogypsum (FG) neutralized using controlled amounts of circulating fluidized bed combustion ash (CFBCA) and denoted here as C-FG to distinguish it from stockpiled pH-adjusted FG with uncontrolled amounts of CFBCA, which is referred to as U-FG. Using the obtained results, a functional model was developed to determine the acidity of C-FG as a function of its CFBCA content. This model was shown to be very accurate in predicting the pH for given CFBCA content and, thus, can be employed to determine the amount of CFBCA required to achieve a specified pH.

The effects of using different controlled amounts of CFBCA to neutralize FG were experimentally investigated with regard to the compressive strength, modulus of elasticity, Poisson's ratio, relative volumetric expansion, unit weight, and setting times of two C-FG-based blends made with (1) 62% C-FG, 35% fly ash, and 3% cement; and (2) 60% C-FG, 34% fly ash, and 6% cement.

The results of these experimental investigations show that the CFBCA content has significant effects on the compressive strength of the C-FG-based blend. A maximum value of compressive strength is achieved for an optimal content of CFBCA, which depends on the specific composition. It is also shown that employing U-FG negatively impacts the compressive strength and the modulus of elasticity of the blend. Additionally, the use of C-FG in C-FG-based blends provides the following economic and environmental advantages over U-FG: (1) lower amounts of CFBCA, (2) a streamlined production process, and (3) a reduction in the land use needed for stockpiling the FG.

This research suggests that a C-FG-based blend made with 60% C-FG, 34% fly ash, and 6% Portland cement in which the C-FG is obtained using a CFBCA content lower than or equal to 4% is a promising material to be used as a sustainable alternative to ordinary concrete in construction applications. In fact, this C-FG-based blend achieves values of compressive strength (49.8–52.7 MPa) and elastic modulus (19.4–21.1 GPa) that are comparable with those of ordinary concrete, whereas it has lower unit weight (2048–2080 kg/m^3) and lower Portland cement content.

Finally, it is noted that this study investigated the use of C-FG-based blends as a direct substitute of ordinary concrete in applications that do not require reinforcement. However, the behavior of these blends with the addition of coarse aggregates and/or their interaction with steel reinforcement bars represent attractive research topics for future investigations.

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