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Enhancing the Durability of Pre-Cracked Concrete: The Crucial Role of Metakaolin and Ground Granulated Blast Furnace Slag

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Abstract
This study conducted a rigorous experiment to assess the strength and durability of pre-cracked concrete modified with metakaolin (MK) and ground granulated blast furnace slag (GBFS). Three categories of hardened concrete were compared to conventional concrete, focusing on key parameters such as compressive strength, mass loss, open porosity, water penetration, capillary water absorption, and drying shrinkage. The assessments were performed under two levels of compression damage and exposure to sulfuric acid (5% concentration). The results demonstrated a significant long-term improvement in compressive strength by incorporating MK and GBFS, despite a reduction of up to 80% in the presence of sulfuric acid. The F10 formulation exhibited the best performance, highlighting the positive impact of additives on concrete durability. Replacing cement with MK and GBFS at a 10% level was identified as the optimal design for sewer structures due to minimal shrinkage compared to other formulations.
Keywords: Concrete durability; Metakaolin (MK); Ground granulated blast furnace slag (GBFS); Compressive strength; Sulfuric acid exposure.

1. Introduction

The deterioration of concrete sewer pipes and wastewater treatment plants involves several chemical and microbiological processes. This deterioration reduces the service life of concrete sewer structures and increases maintenance operation costs (M. O'Connell, et al, 2010; Linping Wu, et al, 2021). Concrete corrosion is the main pathology present in aeration tanks, septic tanks, pumping stations, and the underside of concrete slabs and walls (M. O'Connell, et al, 2010). Excessive localized corrosion of concrete surface is developed after less than a decade in service (Martin O'Connell, et al, 2012), and the service life of sewer structures could be drastically reduced to less than 20 years (L. Wu, et al, 2018). The durability threat of wastewater structures is caused by sulfuric acid and sulfate attacks involving several other corrosion mechanisms (Torres ALT, et al, https://doi.org/10.1680/jmacr.18.00194). This corrosion depends on the contribution of various factors, among which the most important are the wastewater pH, biological oxygen demand, amount of dissolved oxygen, gaseous H2S concentration, wastewater flow velocity and turbulence, air temperature and relative humidity inside sewer/tank, concrete permeability and composition, and cyclic wetting-drying due to the fluctuation of wastewater levels (Piotr Woyciechowski, et al, 2021).

The corrosion process can be divided into four stages (L. Wu, et al, 2018). First, the H2S gas is generated by converting sulfur present in wastewater. After, the concrete surface is neutralized by the accumulation of H2S gas and its reaction with CO2 of air. Then, the concrete surface is colonized by sulfide oxidation bacteria and converts H2S into sulfuric acid. Finally, the concrete is deteriorated by sulfuric acid (H2SO4), which attacks the cement matrix, causing corrosion. During the corrosion process, sulfuric acid reacts with calcium hydroxide (CaOH), forming calcium sulfate (CaSO4) (Alexander M, et al, Dordrecht, pp 177–218; M. O'Connell, et al, 2010; Torres ALT, et al, https://doi.org/10.1680/jmacr.18.00194). The latter is subsequently hydrated to form gypsum (CaSO4 2H2O), the appearance of which on the surface of the concrete takes the form of a white, mushy substance that has no cohesive properties (M. O'Connell, et al, 2010 ; Alexander M, et al, Dordrecht, pp 177–218). The next process that can occur is the reaction of gypsum with the calcium aluminate hydrate (C3A), leading to the formation of ettringite, which is an expansive product (M. O'Connell, et al, 2010; Torres ALT, et al, https://doi.org/10.1680/jmacr.18.00194 ; Alexander M, et al, Dordrecht, pp 177–218). The cement matrix's deterioration by sulfuric acid leads to a loss of strength and cohesion in cementitious calcium compounds (M. O'Connell, et al, 2010). The degradation process occurs very slowly and may take years before corrosion is observed (Hasan MS, et al,2013; Alexander MG,et al 2011).

The formation of gypsum and ettringite resulting from sulfuric attack leads to expansion and cracking of concrete and can cause serious damage to concrete structures (M.W. Kiliswa, et al 2019; M. Zhang,et al, 2013).and Scalny et al. (J.P. Skalny, J. Marchand, I. 2003) reported that the formation of ettringite as microcrystal compounds dispersed in C-S-H gel causes the expansion of the gel structure and the appearance of cracks. Bulatović et al. (Vesna Bulatovic´, et al, 2017) showed that cracks' development is also associated with the contact surface between the gypsum layer and the cement matrix. (L. Wu, et al, 2018) reported that the generated gypsum is swelling and expansive with a volume increase of 124% compared with the cement hydration products causing microcracks in concrete. (V. Marcos-Meson, et al, 2019;) and M. Koushkbaghi, et al, 2019). concluded that the accumulation of ettringite could cause significant inner cracks, thus promoting acid penetration. Wetting-drying cycling also contributes to the micro-cracking of concrete. Wu et al. (Linping Wu, et al, 2021) noted that the drying process causes sulfate crystallization, resulting in samples' micro-cracking. In addition, the wetting of samples causes capillary suction of acid, which can cause interior corrosion of concrete (Matiwos Tsegaye, Dinku Abebe, 2018).

Several researchers have studied the improvement of the durability of concrete under sulfuric acid attack (Naraindas Bheel, et al 2020). The main purpose of these studies is to meet the growing demand for sewer structures to have a long service life with minimal maintenance. This field's main research is the development of innovative construction techniques and various binder combinations in concrete. Reducing the amount of clinker in the cement mix by replacing it with mineral additives also reduces the environmental impact (CO2 footprint, consumption of natural resources, waste recycling). Previous studies have reported that the binary substitution of cement with ground granulated blast furnace slag (GBFS) and metakaolin (MK) enhances the mechanical proprieties of the concrete after 28 days (Naraindas Bheel, et al 2020).

This study focuses on the effect of pre-cracked hardened concrete on mechanical behavior and durability proprieties of mixes incorporating blast furnace slag and metakaolin. Different percentages of GGBF and MK were used as cement substitution to evaluate their effect on compressive strength, for two damage levels of concrete under chemical attack. The sulfuric acid was used as a corrosive agent to provide faster results tests (Hocine Boudjehm,et al, 2022) .

2. Material and Methods

2.1. Materials

2.1.1. Aggregates

A combination of three aggregates acquired from a local quarry was used: natural dune sand (S) 0/5 mm, medium gravel (G1) 5/15 mm, and coarse gravel (G2) 10/25 mm. Table 1 lists all aggregates' physical properties (specific gravity, sand equivalent, fineness modulus, Los Angeles abrasive). Fig.1 shows the grading curves of the three aggregates.

Table 1. Proprieties of aggregates

Properties	Sand	Medium gravel	Coarse gravel
Specific gravity	2.54	2.62	2.62
Sand equivalent	81	/	/
Fineness modulus	1.94	/	/
Los Angeles value (LA)	/	24 (< 30)	26 (< 30)

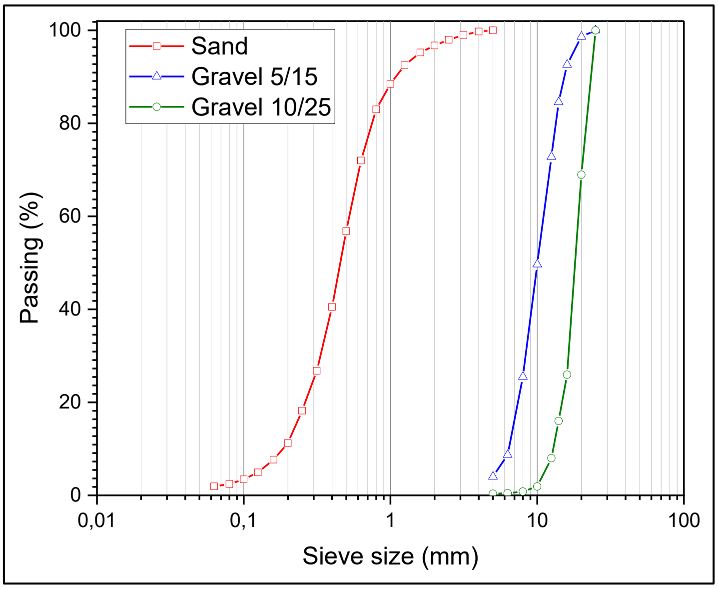

Figure 1. Grading curves of aggregates (Hocine Boudjehm,et al, 2022)

2.1.2. Binders

a) Cement

Sulfate-resisting Portland cement (CRS), named Mokaouem Plus, was used to produce all concrete mixtures (Fig.2). It was supplied by the LAFARGE Cement Group of Algeria (region of M'Sila). It has a strength class of 42.5

N-SR3 in accordance with NF EN 197-1 and a C3A content of less than 3%. The main hydration products of this cement are CH and C-S-H. Table 2 summarizes the physical and chemical composition of the cement used.

Figure 2. Sulfate-resisting Portland cement (CRS)

b) Metakaolin

Local natural kaolin extracted from Djebel Debbagh near Guelma (North-East of Algeria) by ETER ceramic factory was used to produce metakaolin (MK). The kaolin noted DD3 is greyish colored, containing impurities (% MnO between 2 – 5%). First, the kaolin was milled into fine dust using Micro-Deval apparatus containing steel balls. Then, it was sieved through 80 µm to remove large particles. Finally, it was thermally calcined by furnace under a controlled temperature at 750°C for 5 h to produce MK (Fig.3). Table 2 lists the physical properties and chemical composition of MK.

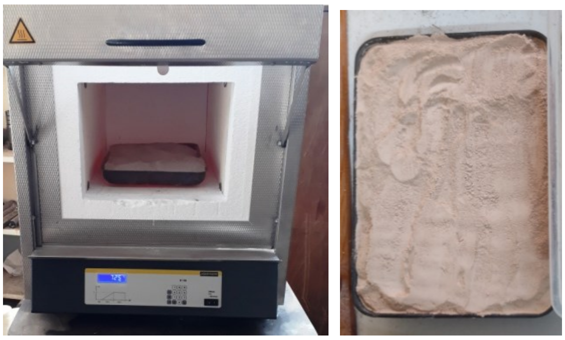

Figure 3. Thermal calcination of kaolin (Metakaolin)

c) Granulated blast furnace slag

The Granulated Blast Furnace Slag (GBFS) was collected from the metallurgic factory of El Hadjar of Annaba (North-East of Algeria). The GBFS was dried in the oven and crushed with the Micro Deval machine (Fig.4). Two kilograms of GBFS with four kilograms of steel balls were used for the grinding operation, which lasted 12 h. Table 2 summarizes the chemical composition and physical properties of GBFS.

Figure 4. Crushed Granulated blast furnace slag (GBFS)

2.1.3. Superplasticizer and water

MasterGlenium 114 superplasticizer was employed for the production of all concrete mixes. It is a superplasticizer based on polycarboxylic ether polymers and provides flowable concrete with greatly reduced water demand. Its normal recommended dosage rate is 0.8 - 2.5 L/100 kg of total cementitious material. It was used at very low percentages according to the results obtained for the slump test. Tap water was used for casting and curing all concrete specimens.

Figure 5. MasterGlenium superplasticizer and tap water

Table 2. Physical and chemical composition of CRS cement, MK and GBFS

Properties	Blaine (cm/g^2)	Chemical analysis (%)							
		SiO_2	Al_2O_3	Fe_2O_3	Cao	MgO	Na_2O	K_2O	Fire loss
Cement (CRS) [29]	3200 – 3800	21.33	3.63	4.31	-	2.29	0.25	0.09	-
MK (DD3) [30]	~ 3500	43	39.9	1.9	0.20	0	0.06	0.10	15
GBFS [31]	~ 4000	41.07	9.06	3.31	42.71	2.25	0.25	0.83	0.32

2.2. Test methods

2.2.1. Specimen preparation and curing

For the experimental step, four concrete mixes were prepared with different content of Sulfate-resisting cement replacement by MK and GBFS. One was the control mix (F0), and the remaining three mixes (F5, F10, and F15) were produced by partial replacement of cement at gradually higher percentage levels (5%, 10%, and 15% by mass of binder), respectively. An equal quantity of MK and GBFS was used as binary binder material for substituting cement. All above mixes were designed according to NF EN 206-1 . The mix design was chosen to represent the minimum acceptable specified under chemical exposure class XA3. The selected concrete mix involved a binder content of 366 kg/m^3 and a water-binder ratio of 0.45. The mass of coarse aggregate was fixed at 630 kg/m^3. The medium aggregate was fixed at 575 $kg/m^{3,}$ and the fine aggregate (sand) used was 629 kg/m^3. Table 3 reports the details of mix proportions with mix notations for one cubic meter of concrete.

The concrete production was carried out in a mobile cylindrical mixer of 50 L capacity, and the same mixing procedure was carefully followed for all mixes. Concrete specimens were prepared as follows; first, aggregates and binders (cement and MK+GBFS) were dry mixed for 1 min. Subsequently, water and superplasticizer were added to the homogeneous dry mixture, swirling continuously for 3 min. Then, the mixed concrete slurry was poured into steel molds, and the casting of concrete specimens was conducted in two layers. Each layer was compacted with a concrete vibrator needle to ensure good compaction and reduce the air voids. After casting, the concrete specimens were cured under laboratory conditions. After 24 h, they were demolded, and all samples were stored in a curing tank in tap water at 20 ± 2 °C until testing age. Eighteen standard cubes, i.e., nine 150 mm and nine 100 mm edge cubes, were cast per mixture in one lift. Four concrete prisms measuring 280 x 70 x 7 mm were also cast to monitor shrinkage. A total of 288 concrete specimens (cubes) were cast. For each mix, 72 specimens were cast, which consisted of 36 cubes of size 150 mm and 36 of size 100 mm.

Table 3. *Mix proportions (kg/m^3)*

Description	Symbol	M0	M5	M10	M15
Cement	c	366	347.7	329.4	311.1
Metakaolin	MK	0	9.15	18.3	27.45
Blast furnace slag	GBFS	0	9.15	18.3	27.45
Sand (0/5)	s	629	629	629	629
Medium gravel (8/15)	g1	575	575	575	575
Coarse gravel (15/25)	g2	630	630	630	630
Water	w	172	172	172	172
Superplasticizer (1%)	spe	3.7	3.66	3.66	3.66
Total weight	W	2375.7	2375.7	2375.7	2375.7

2.2.2. Pre-cracking protocol and sulfuric attack

Concrete specimens with two different damage levels were produced to study the effect of pre-cracking on the degradation of concrete under sulfuric attack. First, the compressive strength at 28 days of all concrete mixes (F0, F5, F10, and F15) was measured for three prismatic specimens. The average value was taken as the axial compressive strength for each mixture. The initial sonic time wave velocity T0 was measured for each specimen by the Ultrasonic Pulse Velocity (UPV) before loading by placing the transducers on opposite faces of cubes. A commercial Ultrasonic Pulse Analyzer manufactured by CONTROLS was used (Fig.6). Then, mechanical damages were imposed on the concrete specimens. The loading rate was 0.5 MPa/s, and the loading levels were 40% and 60% of the ultimate compressive strength at 28 days. After reaching each loading level, the loading was maintained for 1 min, and the samples were unloaded (Fig.6). Using UPV, the sonic time wave velocity with applied loading Ti was measured to quantify the induced mechanical damage. Fig.6 shows the applied loading test and sonic time wave velocity measurement. The damage degree D of concrete specimens was calculated using Eq. (1):

$$D = 1 - \left(\frac{T_0}{T_i}\right)^2 \qquad (1)$$

where, T0 and Ti are the sonic time without and with applied loading, respectively .

Three different damage degrees were adopted: no initial damage D0, D40 (damage degree is 0.1± 0.02), and D60 (damage degree is 0.2± 0.02). The damage degree was produced by repeating the loading cycle on specimens until it reached the predetermined value. For example, the number of repeated loading cycles was about 3 times for the specimen with a damage degree of 0.2. These damage degrees are based on the work of [34].

Figure 6. Pre-cracking protocol and sonic time wave velocity measurements

After pre-cracking damage prefabrication, a sulfuric attack test was carried out to investigate the durability under chemical conditions similar to those found in wastewater treatment plant tanks, i.e., high acidity associated with wastewater. The concrete specimens were submerged in a 5% sulfuric acid solution (H_2SO_4) bath. This concentration is based on the work of [3], in which the degradation process was to field conditions where bacterial growth can take several years to produce. The remaining cubes were divided into two sets to compare samples and accurately quantify the binary effect of pre-cracking damage and sulfuric acid solution. One set was cured in a tap water tank, while the other was immersed in sulfuric acid solution (Fig.7). The mass of cubes was recorded at different intervals. The samples were slightly brushed at 7, 21, 42, and 63 days under running water, which resulted in a milky white runoff. Brushing ceased when the runoff color reverted to clear water. All cubes were drained and immediately weighed to record any mass changes (loss or gain), and the acid solution was replenished.

Figure 7. Sulfuric attack testing

After 63 days of acid attack, specimens were tested to quantify the impact of combined pre-cracking and sulfuric acid degradation in terms of mass loss and changes in compressive strength, water penetration, open porosity, and capillary water absorption. Table 4 presents the overall outline of the testing program, while a detailed description of each test method is provided in the following subsections.

2.2.3. Compressive strength

First, not damaged concrete cubes of 150x150x150 mm dimension were tested for compressive strength after 28, 56, and 90 days of water curing in accordance with standard NF P 18-406 [35]. The average compressive strength was determined by testing three specimens for each age (Fig.8). Second, similar (not damaged) concrete cubes were tested for each mix after 63 days of exposure to sulfuric acid. This test aimed to show the effect of chemical attack alone on compressive strength. Third, the compressive strength was determined for both damaged (D40 and D60), and sulfuric acid exposed concrete samples to quantify their binary effect.

Figure 8. Compressive strength measurements

3. Results and analysis

3.1. Compressive strength

Fig.11 shows an improvement in compressive strength (Rc) as a function of curing time (28, 56, and 90 days); this finding is valid for all formulations [19]. The F10 formulation provided the highest medium- and long-term strength (56, 90 days) compared to the other formulations. Comparing the compressive strength of uncracked concrete (0% cracking) before and after exposure to acid (Fig.12) shows that the F0 formulation is slightly more resistant to chemical attack than the other three formulations. Moreover, the replacement of cement by MK and GBFS in the three formulations F5, F10, and F15 indicates a resistance almost similar to the formulation F0, with a decrease of Rc between 45 and 50%. These same remarks are valid for the concrete cracked at 40% and 60%. A decrease in Rc is also observed as a function of the increase in the percentage of cracking (damage) for all the formulations, except for F5, where the strengths remained almost stable (Fig.13). This result is explained, a priori, by the deeper penetration of the acid inside the cement matrix of the cracked concrete (40%, 60%).

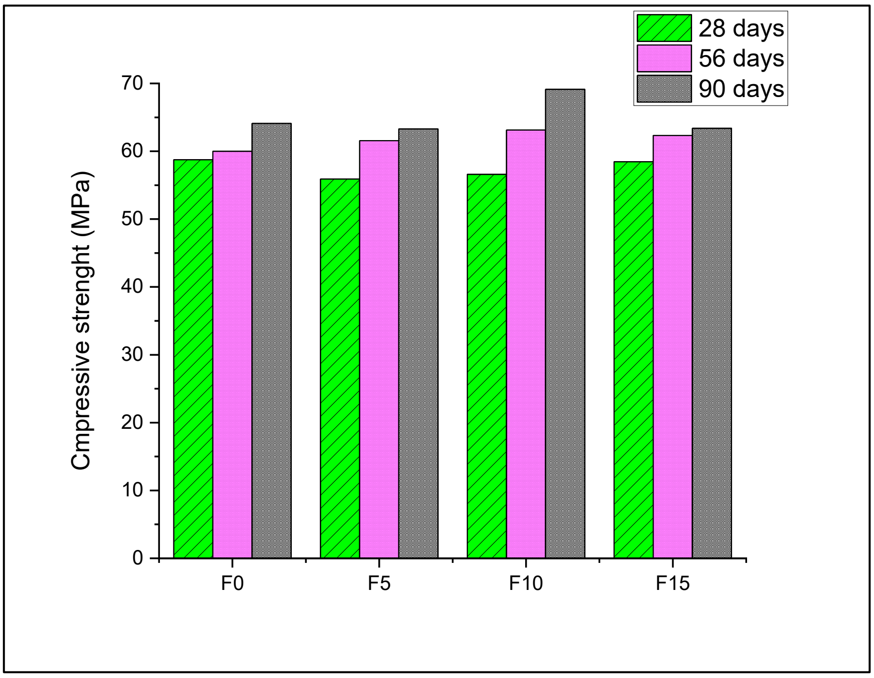

Figure 9. Compressive strength results before exposition to sulfuric acid

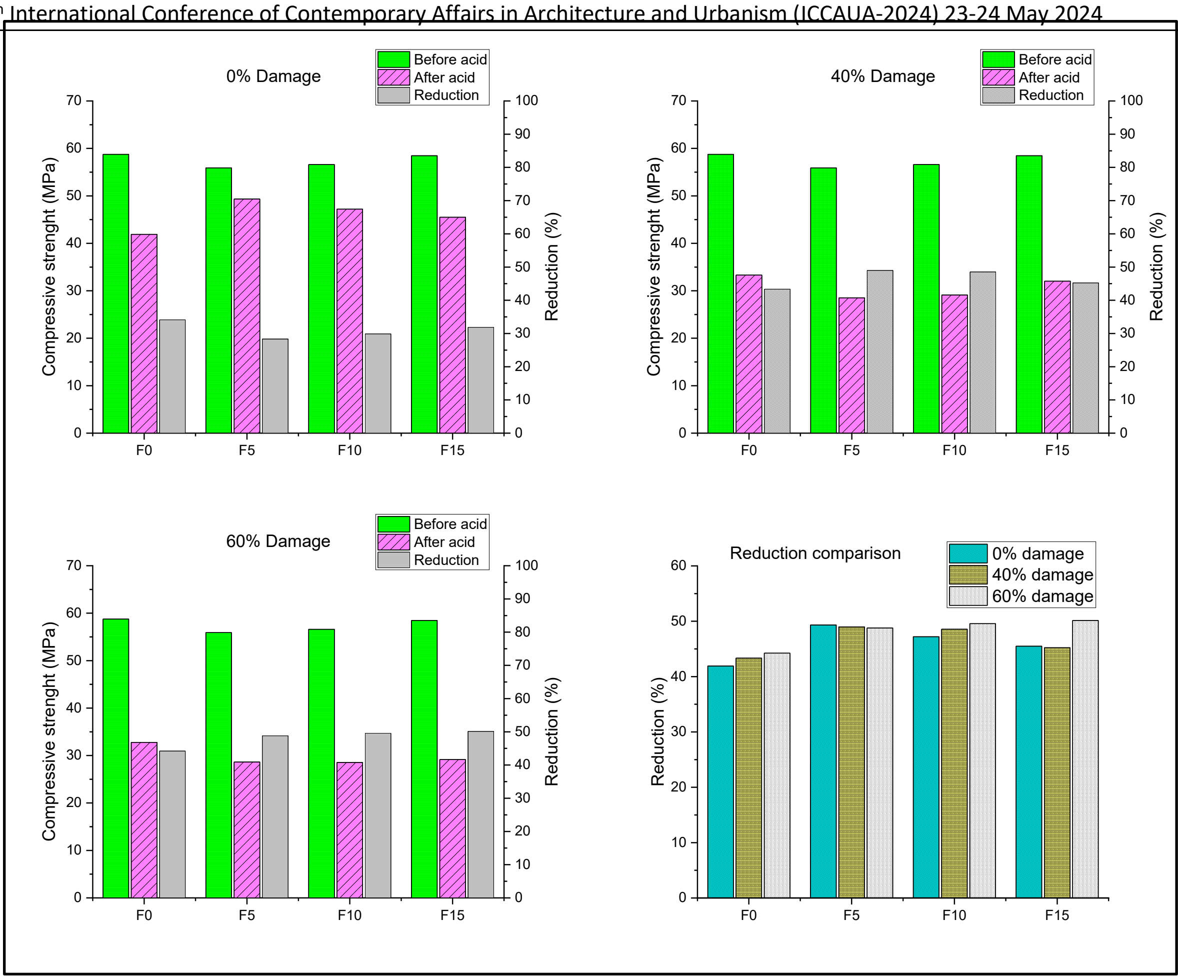

Figure 10. Evolution of compressive strength before and after exposure to acid for different formulations

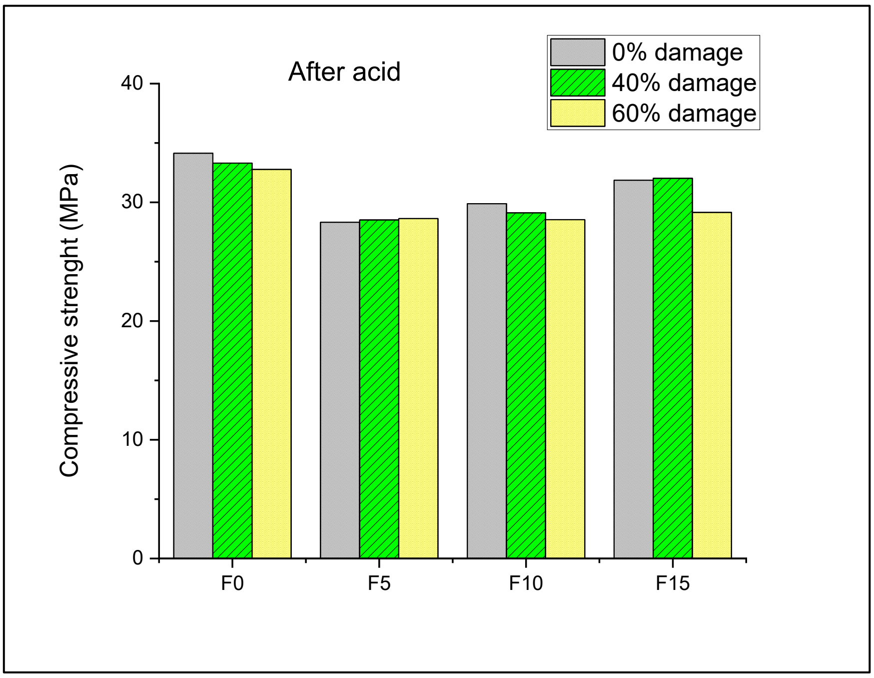

Figure 11. Comparison of compressive strengths after acid exposure for different formulations

5. Conclusions

This work investigated the coupling effects of pre-cracking and the use of MK and GBFS as binary cementitious materials on hardened concrete's mechanical and durability properties. From the test results, the following conclusions can be drawn:

- The concrete incorporating 10% of MK and GBFS (F10) gave higher compressive strength at 56 and 90 days than the reference concrete F0 and all other formulations (F5 and F15). The strength level continued to develop with time, attributed to the pozzolanic reaction provided by MK and GBFS.
- Comparing compressive strength at 28 days of uncracked concrete before and after acid exposure shows that replacing cement with MK and GBFS for the three formulations F5, F10, and F15 resulted in strengths almost similar to the reference formulation (F0). The percentages of strength decrease for different formulations after acid exposure varied between 45 and 50% (more than half).
- The increase in the degree of concrete cracking for all formulations reduced the overall compressive strength of the concrete after acid exposure.

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Conflict of Interests
The Author(s) declare(s) that there is no conflict of interest.

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