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Geo-Polymerization of Marble Sludge: A Way Forward for its Eco-friendly Utilization

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***Abstract*—**Pakistan boasts abundant marble reserves, primarily concentrated in provinces like Khyber Pakhtunkhwa and Baluchistan. The extraction of marble blocks in these regions leads to the generation of marble sludge, comprising water and marble powder, which presents significant environmental challenges by contaminating water bodies, infiltrating groundwater, and posing health risks due to airborne particles. Given the pressing climate situation, it is imperative to address these concerns. To mitigate the environmental impact, we propose the application of a geo-polymerization technique. This method leverages marble powder, fly ash, and blast furnace slag to substitute cement in concrete production. Various mixtures were prepared, utilizing different proportions of these components and diverse liquid media. Particularly noteworthy was the use of a Na2SiO3-8M NaOH solution, which yielded concrete samples with significantly higher compressive strength compared to other media. Upon analyzing the results, it has been concluded that replacing 50% of cement with a combination of 25% marble powder and 25% fly ash, using this solution, resulted in an impressive 143% increase in strength compared to standard concrete (M20 grade) and other geo-polymer concretes. This innovative approach not only mitigates the environmental impact of marble sludge but also contributes to a circular economy by producing high-strength geo-polymer concrete suitable for a wide range of applications.

***Keywords*—**Geopolymerization, Marble Sludge, Fly Ash, Blast Furnace Slag, Alkaline activators, Compressive Strength.

I. INTRODUCTION

Pakistan has been bestowed with tremendous amount of marble and other dimension stones. The reserves of marble stone explored are 300 billion tones, but it could be more than this. More than 90% of dimension stone is present in Khyber Pakhtunkhwa (KP) and Baluchistan provinces [1]. However, outdated technologies in use contribute to waste production in marble processing. Marble is a metamorphic rock derived from limestone, and its processing results in marble sludge, causing environmental concerns [2].

The historical use of marble in construction has led to critical issues in its disposal. There is a need to recycle waste sludge by converting it into an environmentally friendly material [3]. Similarly solid and semi-solid marble processing wastes, indicating potential for their utilization in the mineral industry [4]. In its advantages the marble sludge could be used as a solution to minimize soil erosion, water contamination, and project costs associated with marble waste [5].

To recycle marble powder; geo-polymers, alternative materials to conventional concrete, show promise in reducing environmental impact. geo-polymer materials are economical, durable, and heat-resistant, presenting a greener option than ordinary Portland cement (OPC) [6]. It is also observed that marble effluents negatively affect soil pH, plant growth, and seed germination, necessitating proper waste water management [7].

Geopolymer materials can be used an eco-friendly alternative by utilizing mining by products. Also, it is confirmed that the durability and strength of geo-polymers compared to OPC is greater [8]. Similarly lower carbon footprint and high durability of geo-polymers utilizing marble sludge in geo-polymerization can be achieved [9].

Recycling marble waste has been explored to mitigate environmental issues, fly ash impacts on geopolymer eco-bricks and the carbon dioxide emission were studied and the Geopolymerization potentially reduced the environmental impacts of these wastes[10-11]. [12] Highlighted the waste generated from marble processing in KPK and proposed its utilization for eco-friendly materials. Similarly recycling marble can yield profit while solving environmental problems [12]

Geo-polymerization, a process central to the development of environmentally conscious construction materials, hinges on a careful orchestration of specific conditions to achieve optimal outcomes. A study underscored the significance of raw material selection and precise processing conditions as pivotal determinants of resulting material properties. Similarly the findings underscored the fact that the choice of inputs and the control of manufacturing variables play a crucial role in steering the characteristics of the final geo-polymer product [13]. Fly ash based geopolymer along with marble powder and filler materials were used for the enhancement of geopolymer materials, the results showed that the products formed offer comparable strength as well as more environmentally friendly [14-16].

Fly ash and blast furnace slag can be used as alternative to Ordinary Portland Cement (OPC) [17]. However varying properties of alkaline activators can change the engineering properties of the geopolymer concrete (Babu, Rahul, & Kumar, 2020). Geopolymer materials can be made by using different industrial wastes like a combination of fly ash and rice husk, a combination of fly ash and blast furnace slag and a combination of marble powder with other pozzolanic materials etc. These geopolymer materials enhance the strength and reduce environmental impact [18-21].

In conclusion, recycling marble waste for eco-friendly materials and exploring geo-polymerization offer promising solutions to minimize the environmental impact of marble processing. Utilizing alternative materials like fly ash, slag, and kaolin in geo-polymers presents a greener approach to construction.

II. Materials and Methods

Marble powder was sourced from Adil Marble Factory located in Sheikh Killay, Bajaur. Fly ash was supplied by a private fly ash brick factory. Blast furnace slag was obtained from KPK Steel Mill in Bara District, Khyber. The cement used in the experiments was from Kohat Cement Factory and the sand and crush were acquired from a plant in Peshawar. Alkaline activators were purchased from Boraq Scientific Trader. The laboratory tests (XRF) were carried out at the Centralized Resource Laboratory, University of Peshawar. The cylindrical concrete samples of dimensions 4×8 was prepared for the experiments [22] and were performed in the mineral processing laboratory of Mining Department University of Engineering and Technology Peshawar.

Various mix designs have been created by blending marble powder with two other industrial wastes, namely fly ash and blast furnace slag. The alkaline activator utilized is a solution with a concentration of 20% weight by volume of sodium silicate (Na_2SiO_3) and 8M sodium hydroxide (NaOH) in a ratio of 4:1. The water-to-cement ratio is fixed at 0.55, as per ACI standards in 2002 [23-24]. Four types of mix designs have been developed and tested, including the use of portable water, a solution of Na_2SiO_3 and NaOH, only NaOH, and a complete replacement of cement using a solution of NaOH and Na_2SiO_3.

Waste materials used were passed from 2.74mm sieve size and then mixed in various proportions to make different mix designs. The materials mixed were according to the ingredients used in M20 grade concrete. Sand and crushed stones used were of constant quantity throughout the research, the variation was applied only to the waste's quantities used. We replaced cement partially as well as completely by using three types of liquid media i.e. a solution of mixing 8 molar sodium hydroxide and 20 % weight by volume concentration of sodium silicate in a ratio of 1:4, only sodium hydroxide and other liquid media utilized is portable water. The water to cement ratio used is 0.55.

All materials were first dry mixed for 3 minutes and then liquid was introduced, the materials were then moist mixed thoroughly for another 5 minutes and a final uniform paste was obtained. The paste is poured into 4 ×8-cylinder molds and tamped 25 times with a tamping rod. After tamping molds were kept in open air at room temperature for 24 hours and then they were demolished. All cylindrical core samples were then moist cured for 21 days in the ambient temperature and then after the mentioned curing time they were subjected to compressive strength tests through UTM in the civil department of UET, Peshawar. We prepared 43 samples and then its compressive strength is compared with standard M20 grade concrete.

Figure 1. A) Marble Sludge Effluent from Adil Marble Industry Sheikh Killay Bajaur, B) Entering of Marble Sludge into a Nearby Stream.

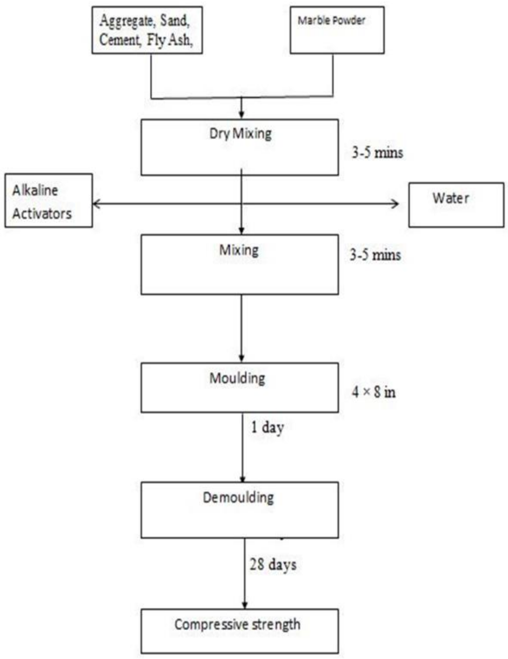

Figure 2. Flow Chart for the Geo-polymerization of Marble Sludge.

2.1 Mixing of Marble Sludge and raw Materials

We prepared total of 43 Samples in which the quantities of industrial wastes i.e. marble powder, fly ash and blast furnace slag is varied while the quantities of sand and aggregates are remain the same. Different samples prepared are shown in tables 1-5.

Three samples of M20 Grade Concrete were prepared for this study. The proportions of Sand, Aggregate, and Cement was maintained at a ratio of 1:1.5:3. Additionally, the water-to-cement ratio was set at 0.55, following the guidelines provided by ACI 211 (2002) [23].

Three samples were prepared to obtain a uniform and an average Compressive strength for the M20 Grade concrete. Its compressive strength will be compared with Geo-polymer concrete having partial and completely replaced cement. The purpose of preparing three samples is to ensure consistency and obtain an average compressive strength measurement for the M20 Grade concrete. By testing multiple samples, any variations in the material or the casting process can be accounted for, providing a more accurate representation of the concrete's strength.

In order to evaluate the performance of the Geo-polymer concrete, its compressive strength will be compared to that of M20 Grade concrete. The Geo-polymer concrete is created by partially replacing or completely replacing the cement with alternative materials. This comparison will help determine the effectiveness and potential advantages of using Geo-polymer concrete in construction applications.

2.2 Samples preparation using portable water

Following table shows geo-polymer samples of different composition and different liquid media in which the cement is replaced partially with marble powder alone and also in combination with fly ash and blast furnace slag. The liquid media applied here is portable water which is used in 0.55 water to cement ratio. The calculated quantity of each material is given below in the Table 2.

2.3 Mix design by using Alkaline Activators (Solution of Sodium Silicate and Sodium Hydroxide)

The Table 3 presented illustrates various geo-polymer samples containing different compositions and utilizing diverse liquid mediums. In these samples, a partial replacement of cement with marble powder has been carried out, both individually and in conjunction with fly ash and blast furnace slag. The chosen liquid medium for experimentation is a solution of sodium silicate at 20% weight by volume concentration and 8 molar sodium hydroxides, utilized at a solution-to-cement ratio of 0.55. The table further provides the specified quantities of each component for reference. Similarly, the following table consists of complete replacement of cement with a liquid media of a solution of sodium silicate a 20% weight by volume concentration and 8 molar sodium hydroxide. The liquid to solid ratio applied was the same as that of the partial replacement.

2.4 Samples Preparation by using Alkaline Activator (8M Sodium Hydroxide)

In this particular scenario, the liquid medium initially specified has been substituted with a solution containing sodium hydroxide at a concentration of 8 molar. It's important to note that the ratio of liquid to solid materials has been consistently maintained across all phases of the research study, ensuring uniformity in this aspect of the experimental design.

Table 1. Mix design for Standard (M_{20} grade) concrete.

	Sample ID	Sand (g)	Aggregate (g)	Cement (g)	Water/Cement Ratio	Sample Weight (g)
Standard Concrete	MI 01	1146	2150	664	0.55	3960
	MI 02	1146	2150	664		3960
	MI 03	1146	2150	664		3960

Table 2. Samples preparation by using Portable water and replacing 50 % of cement with varying quantities of wastes.

Sample ID	Sand (g)	Aggregate (g)	Cement (g)	Marble Powder (g)	Blast Furnace Slag (g)	Fly Ash (g)	Water/(Cement + Marble) ratio	Sample Weight (g)
MI 04	1146	2150	332	332				3960
MI 05	1146	2150	332	332				3960
MI 06	1146	2150	332	332			0.55	3960
							Water/(Cement+Marble+BFS) ratio	
MI 07	1146	2150	332	166	166			3960
MI 08	1146	2150	332	166	166		0.55	3960
MI 09	1146	2150	332	166	166			3960
							Water/(Cement + Marble + Fly Ash)	
MI 10	1146	2150	332	166		166		3960
MI 11	1146	2150	332	166		166	0.55	3960
MI 12	1146	2150	332	166		166		3960

							Water/(Cement + Marble + Fly Ash + BFS)	
MI 13	1146	2150	332	110.6	110.6	110.6		3960
MI 14	1146	2150	332	110.6	110.6	110.6		3960
MI 15	1146	2150	332	110.6	110.6	110.6	0.55	3960

Table 5, which is presented as part of the research findings, a range of diverse combinations that have been explored and examined within this altered experimental framework. The table serves as a visual representation of the various amalgamations and configurations that have been studied under these specific conditions involving the sodium hydroxide solution.

Table 3. Samples preparation by using alkaline activators and replacing 50 % of cement with varying quantities of wastes used.

Sample ID	Sand (g)	Aggregate (g)	Cement (g)	Marble Powder (g)	Blast Furnace Slag (g)	Fly Ash (g)	Na_2SiO_3/NaOH	Alkaline activator /(Cement+ Marble)
MI 16	1146	2150	332	332			4:1	0.55
MI 17	1146	2150	332	332				3960
MI 18	1146	2150	332	332				3960
							Alkaline Activator /(Cement+Marble+BFS)	
MI 19	1146	2150	332	166	166			0.55
MI 20	1146	2150	332	166	166		4:1	3960
MI 21	1146	2150	332	166	166			3960
	Alkaline Activator /(Cement+Marble+Fly Ash)						**Water/(Cement + Marble + Fly Ash)**	
MI 22	1146	2150	332	166		166		0.55
MI 23	1146	2150	332	166		166	4:1	3960
MI 24	1146	2150	332	166		166		3960
							Alkaline Activator /(Cement+Marble+Fly Ash +BFS)	
MI 25	1146	2150	332	110.6	110.6	110.6	4:1	0.55
MI 26	1146	2150	332	110.6	110.6	110.6	**Na_2SiO_3/NaOH**	3960
MI 27	1146	2150	332	110.6	110.6	110.6		3960

Table 4. Samples preparation by using alkaline activators and replacing 100 % of cement with varying quantities of waste used.

Sample ID	Sand (g)	Aggregate (g)	Cement (g)	Marble Powder (g)	Blast Furnace Slag (g)	Fly Ash (g)	Na_2SiO_3 /NaOH	Alkaline Activator/(Cement + Marble)
MI 28	1146	2150	0	664			4:1	0.55
MI 29	1146	2150	0	664				3960
MI 30	1146	2150	0	664				3960
							Alkaline Activator /(Cement + Marble +BFS)	
MI 31	1146	2150	0	332	332		4:1	0.55
MI 32	1146	2150	0	332	332			3960
MI 33	1146	2150	0	332	332			3960
	Alkaline Activator /(Cement + Marble + Fly Ash)						**Water/(Cement + Marble + Fly Ash)**	
MI 34	1146	2150	0	332		332	4:1	0.55
MI 35	1146	2150	0	332		332		3960
MI 36	1146	2150	0	332		332		3960
							Alkaline Activator /(Cement + Marble + Fly Ash +BFS)	
MI 37	1146	2150	0	221.3	221.3	221.3	4:1	0.55
MI 38	1146	2150	0	221.3	221.3	221.3		3960

MI 39	1146	2150	0	221.3	221.3	221.3		3960

Table 5. Samples preparation by using 8M Sodium Hydroxide and replacing 50 % of cement with varying quantities of wastes used.

Sample ID	Sand (g)	Aggregate (g)	Cement (g)	Marble Powder (g)	Blast Furnace Slag (g)	Fly Ash(g)	NaOH Molarity	NaOH/(Cement + Marble)	Sample Weight (g)
MI 40	1146	2150	332	332			8	0.55	3960
MI 29	1146	2150	332	332					3960
MI 30	1146	2150	332	332					3960
								NaOH/(Cement + Marble +BFS)	
MI 41	1146	2150	332	166	166		8	0.55	3960
MI 32	1146	2150	332	166	166				3960
MI 33	1146	2150	332	166	166				3960
								NaOH/(Cement + Marble + Fly Ash)	
MI 42	1146	2150	332	166		166	8	0.55	3960
MI 35	1146	2150	332	166		166			3960
MI 36	1146	2150	332	166		166			3960
								NaOH/(Cement + Marble + Fly Ash +BFS)	
MI 43	1146	2150	332	110.6	110.6	110.6	8	0.55	3960
MI 38	1146	2150	332	110.6	110.6	110.6			3960
MI 39	1146	2150	332	110.6	110.6	110.6			3960

2.5 Mix Designs

In Figure 3 the process of experimentation involves a careful and detailed approach where precise measurements play a crucial role. Based on the calculated quantities assigned to each material, meticulous measurements are taken using a digital precision balance. This ensures a high level of accuracy in determining the exact weight of each material required for the geo-polymer mixture. This method is vital to maintaining uniformity and dependability throughout the entire experimental procedure.

Following the accurate measurement of the materials, the subsequent step involves their deliberate combination according to equation (Proportion of material for M20 grade Concrete =1: 1.5: 3). This formula embodies the optimal proportions and ratios needed to achieve the desired composition of the geo-polymer. By adhering to this formula, the researchers aim to establish a comprehensive and systematic method for blending the materials. This guarantees that the resulting geo-polymer samples are consistent and aligned with the objectives of the study. This thorough process of weighing and mixing not only enhances the precision of the experimental outcomes but also creates a strong basis for drawing meaningful conclusions from the research.

Likewise, all the ingredients were blended to create a variety of geo-polymer materials with different compositions. The first step was to mix the dry components for about five minutes, ensuring that they were evenly combined. Following this dry mixing, water was introduced, and the process of moist mixing was carried out for the subsequent three minutes. This moist mixing led to the formation of a paste-like substance, which was now prepared to be poured into molds.

In simpler terms, the different materials were combined to create various types of geo-polymer mixtures. Initially, the dry ingredients were mixed together for a short while to ensure they were evenly distributed. Then, water was added, and the mixture was mixed again, but this time with a bit of moisture. This made the mixture turn into a paste, which was now ready to be poured into molds for shaping.

Every aspect of the experimental work was meticulously conducted in strict accordance with the established mix designs, ensuring consistency and accuracy in the research process.

2.6 Molding of Samples

In the process of conducting geo-polymer concrete testing, a uniform paste was meticulously created, and this paste was then poured into molds measuring 4 × 8 inches in dimensions. The pouring was carried out in a precise manner, ensuring that the paste was distributed evenly in three distinct layers within each mold. To achieve the desired density and consistency, each layer was subjected to compaction by gently tamping the mixture exactly 25 times, adhering to the guidelines outlined in (ACI 211, 2002) [23]. Following this procedure, a total of 43 samples were prepared, with three samples assigned for each composition. The mold was left undisturbed at room temperature for a period of 24 hours. After this duration, the molds were carefully removed, resulting in the de molding of the samples. After 24 hours the samples were de molded from the molds and assigned specific ID to all the samples according to their respective composition. The ID mark was done through permanent marker started from MI 01 to MI 43 as shown in the following figure.

With the objective of conducting comprehensive experiments and obtaining reliable results, a total of 43 samples were prepared. The samples were carefully assigned to different compositions, with each composition having three corresponding samples. This systematic approach was implemented to ensure a thorough analysis of various concrete compositions and their properties. After the molds were filled with the paste, they were left undisturbed at room temperature for a specific period, precisely 24 hours. During this curing duration, the chemical processes within the concrete took place, contributing to its setting and strength development. At the end of the 24-hour period, the molds were cautiously removed, leading to the de-molding of the samples. The de-molding process was carried out with utmost care to prevent any damage to the freshly prepared concrete specimens. In order to distinguish and identify each sample uniquely, a specific ID was assigned to all of them based on their respective compositions. The identification process was performed using a permanent marker, and the samples were consecutively marked from MI 01 to MI 43.

2.7 Curing of Samples

Following the de-molding process, the samples were assigned unique identification numbers and then carefully placed in PVC tubs, which were filled with portable water. These tubs were then stored in an ambient temperature environment for a period of 28 days. This 28-day duration is crucial as it allows the concrete to undergo the initial curing process, which significantly impacts its strength and durability. After the completion of the 21-day curing period, the samples were taken out of the water-filled PVC tubs. At this point, they underwent an additional step to further enhance their properties. The samples were soaked in open air for a continuous period of 24 hours. This air soaking process helps in further improving the concrete's strength and overall performance. By subjecting the de-molded samples to this post-curing procedure, the research ensured that the concrete reached its optimal level of hydration and maturity. This meticulous approach is critical in producing concrete specimens with consistent and reliable characteristics. The combination of the initial 21-day curing period in water and the subsequent 24-hour air soaking allowed for a comprehensive evaluation of the concrete's long-term behavior and performance.

2.8 Compressive Strength of Samples

After the completion of the 28-day curing period, the wet concrete samples underwent a drying process in open air for 24 hours. The drying stage is essential as it allows the excess moisture to evaporate, bringing the samples to their dry state for testing. Once the samples were sufficiently dry, they were subjected to a strength test to determine their compressive strength. This crucial evaluation aimed to measure the samples' ability to withstand squeezing forces. To conduct the compressive strength test, a specialized machine called a universal testing machine (Shimadzu's) was employed. This high-precision equipment is widely recognized for its accuracy and reliability in material testing. The tests were meticulously carried out by experts at the Civil Department of UET Peshawar, ensuring that all procedures were executed with precision and attention to detail to obtain accurate and consistent results as shown in Figure 4.

During the testing process, a loading rate of 0.06 ton-force was applied to the samples. This loading rate was selected to ensure a controlled and steady application of force. The steady application helps in obtaining reliable data, and the controlled nature of the process prevents any sudden or erratic loading that could affect the accuracy of the results. The compressive strength tests provided valuable insights into the samples' ability to bear pressure and resist deformation when subjected to squeezing forces. These results play a significant role in assessing the overall quality and structural integrity of the concrete used in the experiment. All concrete samples were tested using the same universal testing machine (UTM) and under identical environmental conditions to ensure consistency and reliable results. Each sample was placed between circular plates of the UTM, designed for even load distribution, minimizing variations in the testing process. Following the 28-day curing period, the samples were allowed to dry for 24 hours before being carefully positioned in the UTM. A controlled and steady load was applied, and the UTM recorded the data throughout the process to evaluate the compressive strength of each sample accurately.

Formula used for the calculation of compressive strength is given below:

Compressive Strength = Load at failure / Cross sectional area of the sample

$C = P/A$ 1

Where;

C is the compressive strength in mega pascal, P is the maximum load or load until failure in newton and A is the cross section of the material in m2 resisting the load.

All the samples were passed from the same universal testing machine at the same environmental conditions. Each sample was put between circular plates of the UTM and the load was applied; the whole process can be shown in the figures below.

Figure 3. Different mix designs and making of final geopolymer concrete; A) Dry mixing of raw materials, B) Different mix designs, C) Mixing Chemicals, D) Paste prepared, E) Molding of concrete, F) Final Samples prepared.

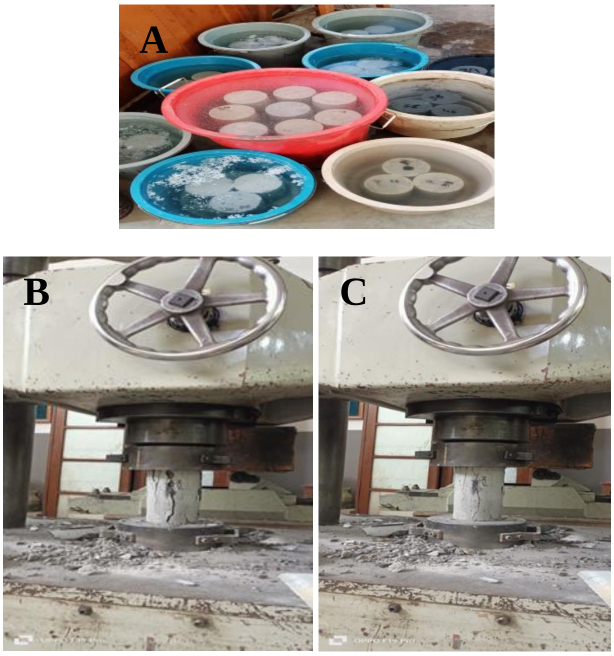

Figure 4. Curing of samples and load application through universal testing machine; A) Curing of samples, B and C) Failure of Samples.

III. Results and Discussions

Marble sludge, a waste product from marble processing factories, poses a significant environmental threat by contaminating nearby streams and affecting both surface and groundwater. This waste material also has adverse effects on both terrestrial and aquatic plants and animals. To mitigate its environmental impacts and promote sustainability, we devised a solution by incorporating it into the production of geo-polymer concrete, a novel alternative to conventional concrete that not only recycles the waste but also serves as a substitute for cement. In our approach, we utilized the geo-polymerization technique, where marble powder, fly ash, and blast furnace slag were mixed in varying proportions with other raw materials like sand and aggregate. Prior to the mixing process, thorough chemical analysis of the waste materials and other raw materials was conducted using an XRF spectrometer to ensure their suitability for the geo-polymerization process.

Different mix designs were prepared by combining the waste materials with the liquid media, which consisted of portable water, a combined solution of sodium silicate of 20% by weight concentration, and 8 molar sodium hydroxides, and a set with only 8M NaOH solution. These mix designs were transformed into pastes and shaped into cylinders using 4x8 molds. After 21 days of moist curing in water, their compressive strength was measured. Among the mixes, those with 25% marble powder and 25% fly ash, combined with sodium silicate and sodium hydroxide, showed the highest strength. However, completely replacing cement with marble powder resulted in no strength, highlighting the need for careful component proportioning for successful geo-polymer concrete production. By incorporating marble sludge and other waste materials into the geo-polymer concrete production process, we not only contribute to waste recycling but also open new avenues for sustainable construction practices that are environmentally friendly and economically viable.

3.1 XRF Spectrometer Analysis of Marble Sludge and Materials Used

By carefully examining the raw materials using XRF tests, researchers looked closely at the composition and uses of marble powder. From Table 1it is clear that the major ingredients of the wastes used are silica, alumina and lime which contributes to be used as pozzolanic materials. These materials take part in pozzolanic reaction and makes strong geo-polymer material. To examine the pozzolanic properties of the waste used and the strength of the final product we used different proportions of these wastes and made geo-polymer concrete.

From Table 6 it is evident that marble sludge contains 99% lime and minor traces of other ingredients. Similarly fly ash and blast furnace slag consist of sufficient amount of silica and alumina along with lime that can be used to be mixed with marble powder to make a geopolymer concrete.

From the XRF analysis marble powder contains 99.79% lime. Similarly fly ash consist of 54.452% silicon dioxide (SiO_2), 33.913% aluminum oxide (Al_2O_3), and 3.962% lime (CaO) and blasat furnace slag consist of 37.871% Silicon dioxide (SiO_2), 15.546% Aluminum Oxide (Al_2O_3), and 11.138% Lime (CaO). From this analysis these wastes can be efficiently used to be utilized in formation of an eco-friendly geopolymer material.

Table 6. XRF (Oxide Analysis) of materials used in the research.

Analyte	Aggregate (%)	Sand (%)	Marble Powder (%)	Fly ash (%)	Blast furnace slag (%)	Cement (%)
SiO_2	9.222	62.717		54.452	37.871	21.085
Al_2O_3		21.381		33.913	15.546	5.028
Fe_2O_3	3.478	5.122	0.075	4.120	18.776	3.283
CaO	86.065	7.348	99.790	3.962	11.138	64.473
TiO_2	0.323	0.592		1.600	3.130	0.336
K_2O	0.388	2.582		0.931	0.305	1.143
MnO	0106	0.090		0.050	9.244	0.045
SrO	0.074	0.064		0.150	0.225	0.111
V_2O_5	0.016	0.028	0.061	0.073	0.295	0.018
Cr_2O_3	0.274	0.021		0.029	2.532	0.018
NiO	0.009	…		0.011		
CuO	0.038	0.015	0.034		0.078	0.018
ZnO		0.007	0.040	0.008	0.445	
ZrO_2	0.006	0.014		0.052	0.038	0.014
Y_2O_3		0.002		0.013		
PbO				0.007		
Ga_2O_3				0.007		
NbO		0.005		0.004	0.030	
Rb_2O				0.000		0.006
SO_3				0.499	0.515	4.422
ThO_2		0.013		0.004		
Tm_2O_3				0.116		
As_2O_3					0.013	

3.2 Compressive strength of samples prepared

All samples were subjected to compression in universal testing machine and the loads applied were noted down. The load applied was in ton-force which was then converted into newton and the compressive strength was calculated according to equation 1. The following Table 7 and Table 8 show the compressive strengths of all core samples.

Table 7. Compressive strength of standard (M20) concrete.

	Sample ID	Load Applied (Ton-force)	Compressive Strength (MPa)	Avg. Compressive Strength (MPa)
Standard Concrete	MI 01	11.14	13.48	13.26
	MI 02	12.7	15.36	
	MI 03	9.04	10.94	

Table 8. Compressive strength of geo-polymer concrete samples

Sample ID	Load Applied (Ton-force)	Compressive Strength (MPa)	Avg. Compressive Strength (MPa)
MI 04	3.62	4.38	5.11
MI 05	5.38	6.51	
MI 06	3.68	4.45	
MI 07	4.78	5.76	5.79
MI 08	4.54	5.49	
MI 09	5.08	6.14	
MI 10	9.20	11.13	10.38
MI 11	8.10	9.80	
MI 12	8.46	10.23	
MI 13	6.92	8.37	8.37
MI 14	7.30	8.83	

MI 15	6.54	7.91	
MI 16	18.14	21.95	21.11
MI 17	18.52	22.41	
MI 18	15.68	18.97	
MI 19	15.18	18.37	16.16
MI 20	15.32	18.50	
MI 21	9.64	11.66	
MI 22	26.48	32.04	32.22
MI 23	24.36	29.48	
MI 24	29.04	35.14	
MI 25	25.80	31.22	30.06
MI 26	22.60	27.35	
MI 27	26.12	31.61	
MI 28	0	0	0
MI 29			
MI 30			
MI 31	0	0	0
MI 32			
MI 33			
MI 34	0.49	0.59	0.58
MI 35	0.40	0.56	
MI 36	0.48	0.58	
MI 37	0.22	0.26	0.26
MI 38	0.25	0.30	
MI 39	0.20	0.24	
MI 40	2.1	2.51	2.51
MI 41	1.52	1.83	1.83
MI 42	5.04	6.09	6.09
MI 43	3.74	4.52	4.52

3.3 Effect of Marble Powder on Compressive Strength of Geo-polymer Concrete

Cement in the standard concrete is partially and completely replaced with varying quantities of a mixture of marble powder, blast furnace slag and fly ash by applying different liquid. The various mix designs and their resultant compressive strengths are discussed below.

3.4 Using Portable Water

i. Replacing 50% Cement with Marble Powder

Samples from ID MI04 to MI06 from Table 8 were subjected to compression in a universal testing machine and then there compressive strengths were compared with compressive strength of standard concrete of Table 7. The graph presented in Figure 3 underscores a significant reduction in compressive strength when 50% of cement is replaced with marble powder, coupled with the use of portable water. This reduction, from 13.26 to 5.11 MPa, underscores the adverse impact of this combination on the mechanical performance of the concrete. The observed decrease in strength can be attributed to the absence of two key constituents, silica (SiO2) and alumina (Al2O3), within the chemical composition of marble powder. Silica and alumina play pivotal roles in the formation of the calcium-silicate-hydrate (C-S-H) gel, a critical binder in concrete that contributes significantly to its strength and durability.

The C-S-H gel, being the fundamental building block of concrete's mechanical properties, is formed through the reaction between calcium hydroxide (Ca(OH)2) and the silica and alumina-rich components in the cementitious mix. In the case of marble powder, the lack of these essential components in its composition limits the extent of C-S-H gel formation. This reduction in C-S-H gel content directly correlates with the observed decrease in compressive strength. In contrast, the higher compressive strength observed in concrete (standard concrete) without marble powder can be attributed to the greater availability of silica and alumina in traditional cement. This enables more substantial C-S-H gel formation, thereby enhancing the overall strength of the concrete. These results highlight the importance of silica and alumina in the chemistry of cementitious materials and their direct influence on the mechanical performance of concrete.

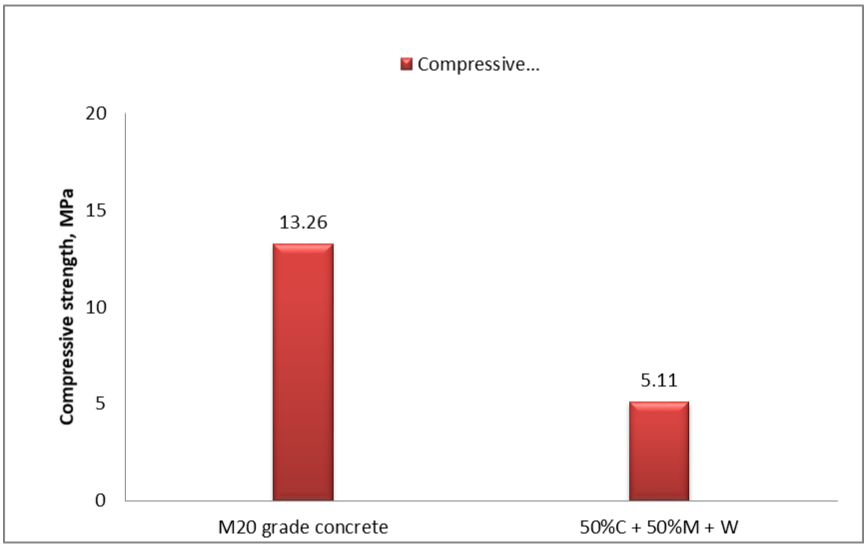

Figure 5. Comparing Compressive strength of standard concrete and 50% marble based geo-polymer concrete. C = Cement, M = Marble powder, W = Water.

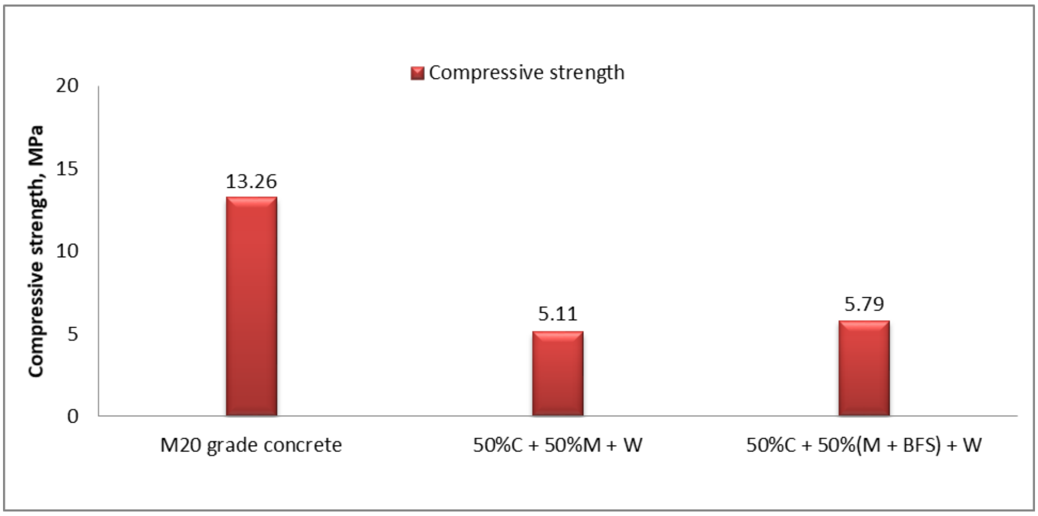

Figure 6. Comparing compressive strength of samples made of replacing 50% of cement with marble powder + Blast furnace slag with standard concrete. C = Cement, M = Marble Powder, BFS = Blast furnace slag and W = water.

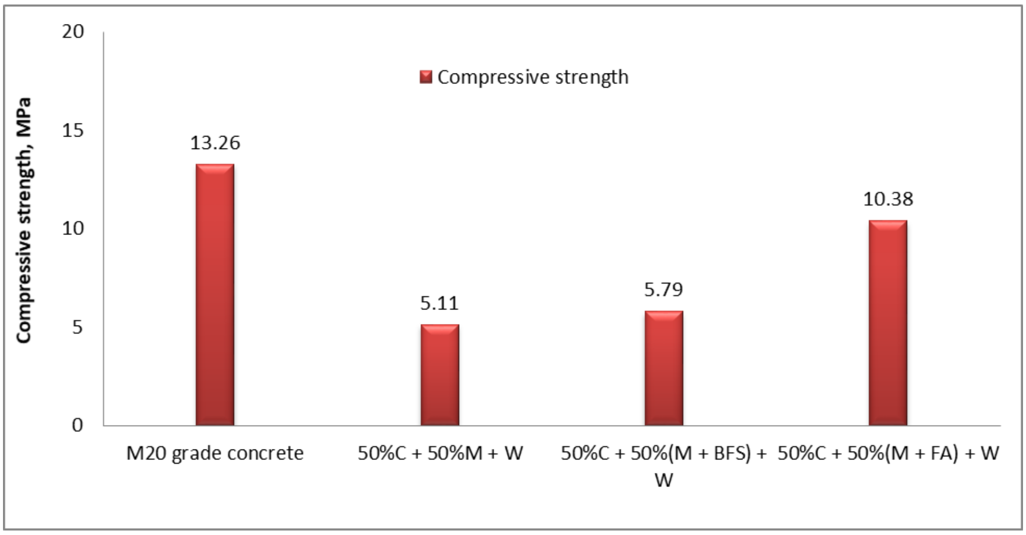

Figure 7. Compressive strength of geo-polymer material containing marble powder and fly ash, C= cement; M= marble powder; BFS= Blast furnace slag; FA= Fly ash; W= water.

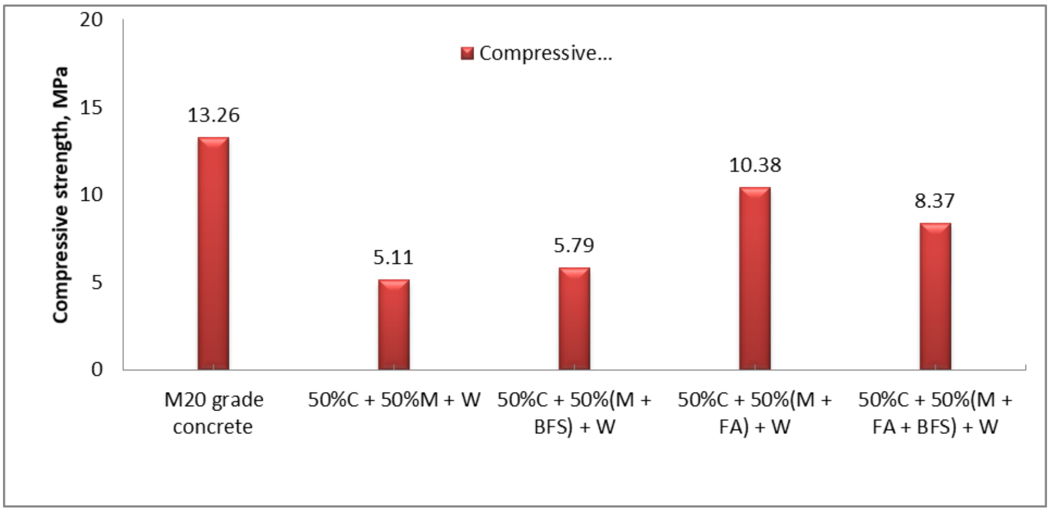

Figure 8. Compressive strength of geo-polymer material containing marble powder, blast furnace slag and fly ash, C= cement; M= marble powder; BFS= Blast furnace slag; FA= Fly ash; W= water.

ii. Replacing 50% Cement with a combination of Marble Powder and Blast Furnace Slag

Figure 6 presents valuable insights into the effects of replacing 50% of cement with a mixture of marble powder and blast furnace slag on compressive strength. The observed reduction in strength, from 13.26 MPa to 5.79 MPa, suggests that the substitution of cement led to a decrease, it outperforms the compressive strength of marble-based geo-polymer concrete, which is registered as 5.11 MPa. This reduction in strength compared to pure cement-based concrete can be attributed to the combination of marble powder and blast furnace slag resulting in a lower formation of calcium-silicate-hydrate (C-S-H) gel - the key constituent in hardened geo-polymer concrete. The presence of blast furnace slag in a 25% blend with marble powder generates a limited amount of C-S-H gel and a modest quantity of calcium-aluminate-hydrate (C-A-H) gel, contributing to the concrete's stability. Although this hybrid mixture demonstrates lower strength than conventional cement-based concrete due to the limited C-S-H gel formation, its strength surpasses that of marble-based geo-polymer concrete. This advantage can be attributed solely to the presence of cement, leading to the production of a smaller amount of C-S-H gel. The findings highlight the complex interplay of components in concrete compositions, impacting the resulting mechanical properties and demonstrating the potential benefits of utilizing blended materials for enhanced performance.

iii. Replacing 50% cement with a combination of marble powder and Fly Ash

Figure 7 offers valuable insights into the compressive strength of concrete samples utilizing a blend of marble powder and fly ash. Notably, the compressive strength of this mixture is lower compared to traditional cement concrete, decreasing from 13.26 MPa to 10.38 MPa. This decrement, however, is mitigated when contrasted with marble powder-based geo-polymer concrete, indicating a relative improvement. Furthermore, in comparison to a composite of marble powder and blast furnace slag, the mixture exhibits higher strength. This observed reduction in compressive strength, relative to cement concrete, is influenced by several factors. First, the varying pozzolanic activity of fly ash and marble powder can impact their effectiveness in reacting with calcium hydroxide, a byproduct of cement hydration, to generate supplementary cementitious compounds. If the pozzolanic activity is inadequate, limitations may arise in the creation of these secondary cementitious compounds, potentially leading to strength reduction.

Referring to data in Table – 6, the mixture's higher silica, alumina, and lime content, especially in fly ash, contributes to its superior strength compared to marble-based geo-polymer and blends with blast furnace slag. This heightened reactivity enhances strength. However, despite this, the blend falls short of traditional cement concrete's compressive strength due to cement's higher lime content and more robust formation of key calcium-silicate-hydrate (C-S-H) and calcium-aluminate-hydrate (C-A-H) gels during hydration, enhancing its mechanical properties.

iv. Replacing 50% Cement with a Combination of same quantities of Marble Powder, Fly Ash and Blast Furnace Slag

The information presented regarding the compressive strength depicted in Figure 8 offers valuable insights into the relative performance of different concrete compositions. The compressive strength of 8.37 MPa, as shown, is lower than that of traditional cement concrete and the combination of marble powder (MP) and fly ash (FA) geo-polymer concrete. However, it surpasses the compressive strength of both the MP-blast furnace slag (BFS) combination and the MP-based geo-polymer concrete. The observed decrease in compressive strength compared to certain combinations can be attributed to the limited formation of cementitious calcium-silicate-hydrate (C-S-H) and calcium-aluminate-hydrate (C-A-H) gel. These gels are essential for the mechanical integrity of concrete. This reduced gel formation is responsible for the comparatively lower strength when compared to the mentioned combinations.

The mixture in Figure 8 demonstrates greater C-S-H and C-A-H gel production than the other two mentioned combinations, leading to its higher strength. This higher gel formation compensates for the limited gel formation in this mixture, contributing to its improved performance relative to those combinations.

3.5 Using Solution of Mixed Sodium Silicate and Sodium Hydroxid

i. 50% Cement Replacement with Marble Powder Only

The analysis of Figure 9 provides valuable insights into the enhanced compressive strength of marble powder-based geo-polymer concrete. Replacing 50% of cement with marble powder and utilizing an 8M NaOH-Na2SiO3 solution (20% weight by volume) in a 1:4 ratio resulted in a notable strength increase from 13.26 to 21.11 MPa. This improvement can be attributed to the chemical reaction between the solution and the silica in the marble powder mixture, yielding a novel binding material, calcium silicate hydrate (C-S-H) gel.

This gel's resemblance to the C-S-H gel formed during cement hydration underscores its contribution to concrete's strength and durability. The C-S-H gel produced by the NaOH-Na2SiO3 solution and marble powder reaction is likely more robust than that resulting from cement hydration alone, explaining the rise in compressive strength. This stronger gel formation facilitates enhanced inter-particle bonding and a denser matrix, ultimately.

leading to heightened compressive strength values. The incorporation of the NaOH-Na2SiO3 solution introduces an alternative chemical reaction pathway, generating a more potent binding material. This innovation, bolstering the concrete's strength properties, showcases the potential to exceed the strength achieved through cement utilization alone.

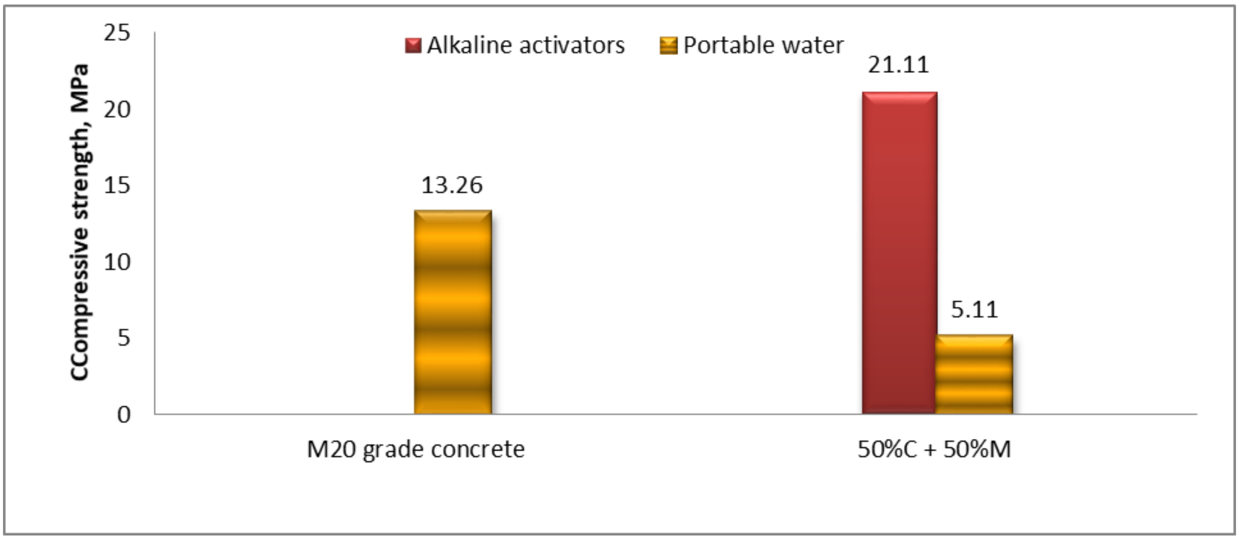

Figure 9. Compressive strength of NaOH-Na2SiO3 based geo-polymer samples containing marble powder. C= cement; M= marble powder.

ii. Partial Replacement of Cement with Marble Powder and Blast Furnace Slag

The analysis of Figure 10 provides insightful observations about the compressive strength of a mixture of marble and blast furnace slag-based geo-polymer concrete. The strength enhancement from 13.26 MPa to 16.17 MPa suggests the potential for utilizing this blend to replace 50% of the cement in traditional concrete, surpassing its strength. However, in comparison to marble-based geo-polymer concrete (21.11 MPa to 16.17 MPa), its strength falls short. Several key factors contribute to this strength enhancement: Blast furnace slag and marble powder react with calcium hydroxide and water, forming compounds that strengthen concrete over time. Fine particles of slag and marble powder fill spaces in concrete, increasing density and mechanical strength by improving particle interlocking. Slag and marble powder decrease heat generated during curing, minimizing thermal cracking risk and maintaining concrete strength. Adding 8M NaOH and Na2SiO3 boosts reactions among slag, marble powder, and calcium hydroxide, enhancing strength development and compressive strength.

However, despite these positive attributes, the mixture's strength is lower than that of marble-based geo-polymer. One contributing factor is the slightly larger particle size of blast furnace slag, impacting its reactivity and potentially reducing its ability to contribute to gel formation compared to finely ground marble powder.

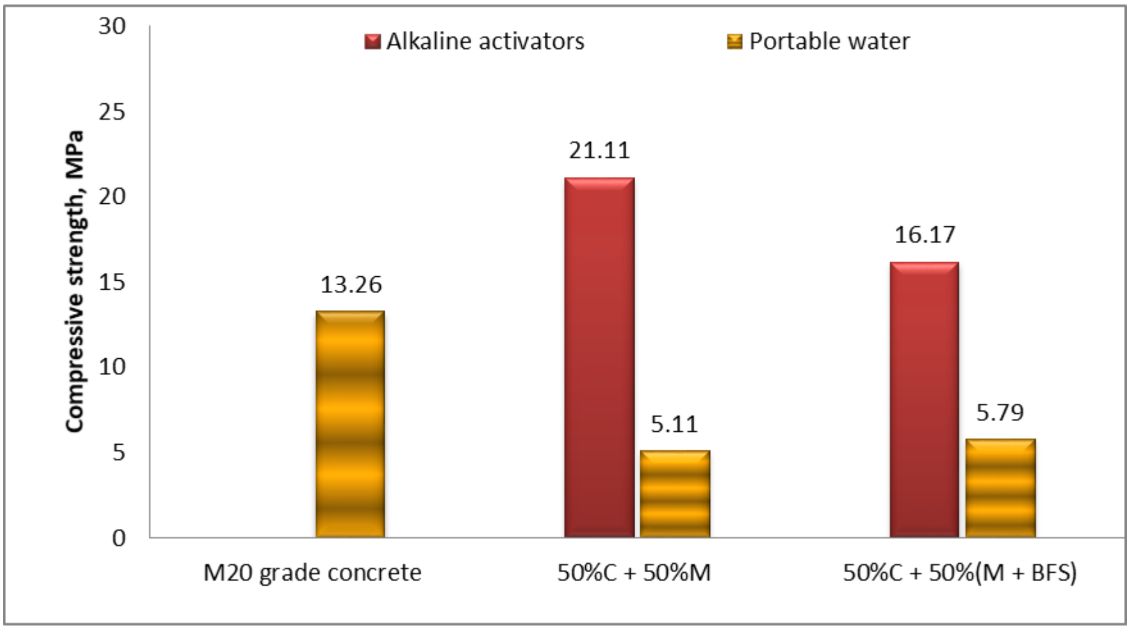

Figure 10. Compressive strength of NaOH-Na2SiO3 based geo-polymer samples containing marble powder and blast furnace slag. C= cement; M= marble powder; BFS=Blast furnace slag.

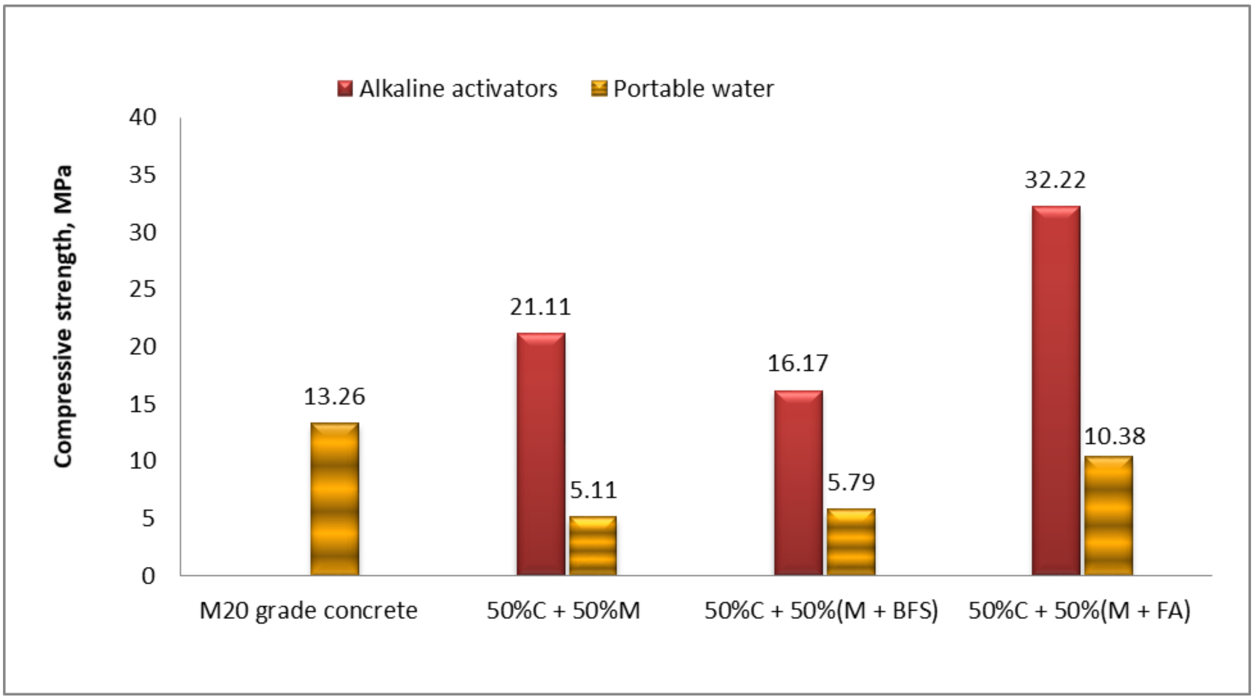

Figure 11. Compressive strength of NaOH-Na2SiO3 based geo-polymer samples containing marble powder and fly ash. C= cement; M= marble powder; BFS= Blast furnace slag; FA= Fly ash.

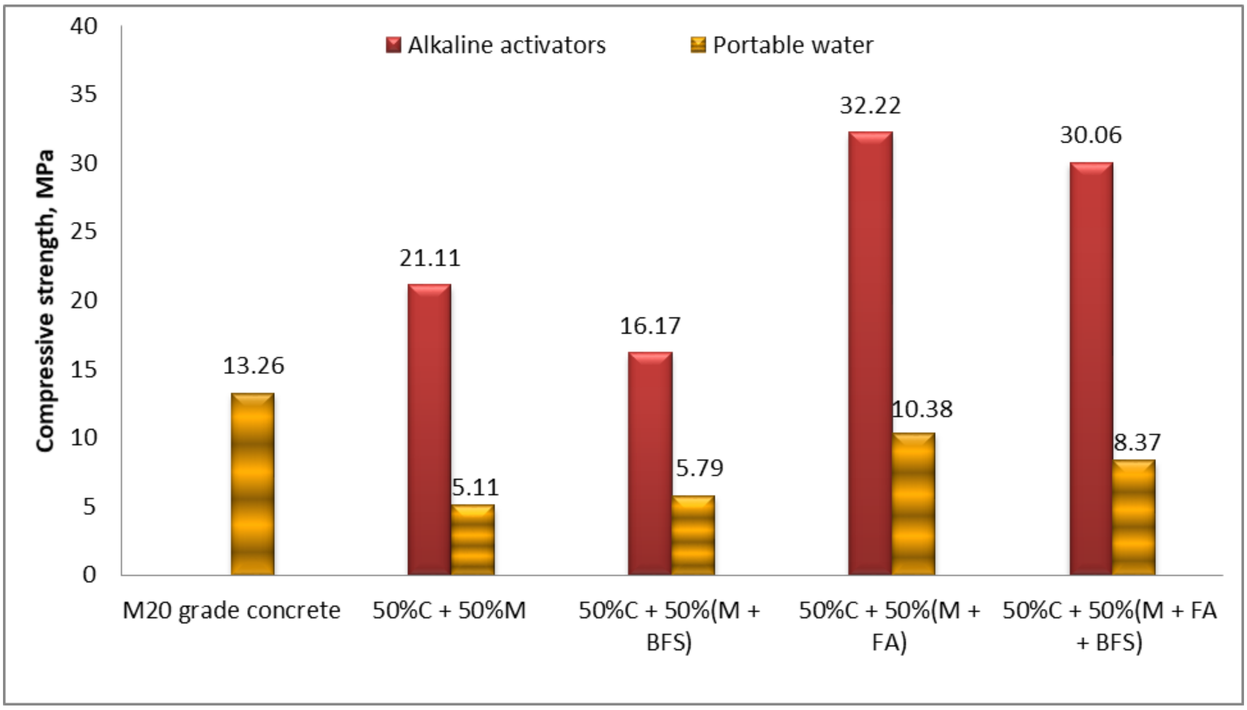

Figure 12. Compressive strength of NaOH-Na2SiO3 based geo-polymer samples containing marble powder, fly ash and blast furnace slag. C= cement; M= marble powder; BFS= Blast furnace slag; FA= Fly ash.

iii. Partial Replacement of Cement with Marble Powder and Fly Ash

The data shown in Figure 11 highlights a significant enhancement in compressive strength by using a sodium silicate and sodium hydroxide solution while replacing 50% of cement with a mixture of marble powder and fly ash. The resulting compressive strength of 32.22MPa greatly surpasses the 13.26MPa of conventional cement concrete. The key factor contributing to this remarkable strength increase is attributed to the chemical composition of fly ash and marble powder. The interaction of the sodium silicate and sodium hydroxide solution with the marble powder and fly ash mixture leads to the formation of more robust C-S-H and C-A-H gels, crucial components driving the solidification of geo-polymer concrete. Additionally, the comparative assessment could benefit from a broader context. While the improvement relative to conventional cement concrete is clear, a comparison with alternative mixtures, including pure fly ash or exclusively marble-based geo-polymer, would offer a more comprehensive understanding of the method's effectiveness.

iv. Partial Replacement of Cement with Marble Powder, Fly Ash and Blast Furnace Slag.

The data presented in Figure 12 highlights a reactions among blast furnace slag (BFS), fly ash (FA), and marble powder (MP), along with their interactions with calcium hydroxide, culminating in the creation of a stable and durable geo-polymer concrete. However, the exact mechanisms behind the observed gel formations and the interplay of these components need further elucidation to solidify the understanding of this strength enhancement. Additionally, a deeper analysis of the MP-FA combination's performance in relation to this mixture would enhance the context and overall interpretation of the results compressive strength of 30.06MPa for the specific combination involving a sodium silicate and sodium hydroxide solution. This strength surpasses most other combinations, with the exception of the MP-FA combination. The strength improvement is attributed to enhanced C-S-H and C-A-H gel formation, which can be credited to the influence of the sodium silicate solution. Furthermore, the activation by 8M NaOH and Na2SiO3 is identified as a driving factor, fostering.

3.6 Utilizing 8Molar Sodium Hydroxide Solution

i. Replacing Half of the Cement with Marble Powder

In Figure 13 a noteworthy decline in compressive strength is observed when 50% cement is replaced with marble powder in geo-polymer concrete, i.e. the compressive strength as drop from 13.26MPa to 2.5MPa. The use of only 8M NaOH (sodium hydroxide) without Na2SiO3 (sodium silicate) can weaken cement's compressive strength due to the potential initiation of alkali-silica reaction (ASR). ASR occurs when NaOH reacts with reactive silica in certain cement mixtures, resulting in gel-like substance that can expand over time and cause cracking and deterioration, significantly reducing concrete strength. This weakening stems from the expansion and subsequent cracking triggered by the gel formation, compromising concrete integrity. However, the addition of Na2SiO3 alongside NaOH leads to a different outcome. Na2SiO3 reacts with cement silica to create a stable calcium silicate hydrate (C-S-H) gel. This unique gel enhances binding properties, bolstering compressive strength. Incorporating Na2SiO3 counteracts the negative impact of NaOH alone, fostering a stronger and more stable C-S-H gel and ultimately increasing compressive strength.

ii. Half of the cement replacement with Marble powder and Blast Furnace Slag

In Figure 14 the compressive strength of the marble powder and blast furnace slag-based geo-polymer concrete mixture is notably lower compared to both cement concrete and marble-based geo-polymer formed using 8M NaOH. The compressive strength dropped from 13.26MPa in cement concrete and 2.5MPa in marble-based geo-polymer to 1.83MPa in the marble powder and blast furnace slag-based mixture. This decrease could stem from various factors: Replacing 50% cement reduces available calcium oxide content, crucial for concrete strength development. This depletion may lead to lower strength. Blast furnace slag's aluminosilicate minerals react differently than cement's calcium silicates, potentially impacting strength development. Reactions among marble powder, blast furnace slag, and alkaline solution might differ from pure cement or marble-based geo-polymer reactions, possibly causing incomplete cementitious compound formation and weaker strength. Similarly reactive silica, coupled with the alkaline solution, could trigger ASR, leading to expansion and cracking, compromising both strength and durability. ASR might contribute to the observed strength reduction.

iii. Half of the Cement Replacement with Marble Powder and Fly Ash

In Figure 15, the use of 8M NaOH in geo-polymer concrete with 50% cement replacement by a combination of MP and FA demonstrates superior compressive strength compared to most other combinations, except for regular cement concrete. With a compressive strength of 6.09MPa, this combination falls below cement concrete but surpasses other mixtures utilizing 8M NaOH interaction between NaOH solution and active silica in the mixture, particularly from the high content of fly ash. Conversely, the combination's greater compressive strength than other mixtures can be attributed to the heightened formation of C-S-H and C-A-H gel solution. This reduction in strength, relative to cement concrete, is attributed to alkali-silica reaction (ASR), which occurs due to the This abundance of gels contributes to enhanced strength, setting this combination apart from the rest. However, while this approach demonstrates strengths that outperform certain mixtures, the observed ASR-caused reduction in strength compared to cement concrete signifies a trade-off between the benefits of enhanced gel formation and the potential drawbacks of ASR.

iv. Half of the Cement Replacement with Marble Powder, Fly Ash and Blast Furnace Slag

In Figure 16, the compressive strength of 4.52MPa is lower than cement concrete and the MP-FA based geo-polymer concrete. However, it surpasses other combinations utilizing the 8M NaOH activator. This decrease in strength is primarily attributed to the formation of alkali-silica reaction (ASR), a factor weakening the geo-polymer samples. Conversely, this combination exhibits a higher quantity of C-S-H and C-A-H gel formation compared to both MP- based and MP-BFS based geo-polymer concretes. This suggests a complex interplay between ASR-induced weakening and enhanced gel formation, influencing the overall compressive strength of the mixture. While this approach demonstrates strengths greater than certain mixtures, the impact of ASR on long-term durability and structural integrity should be carefully considered.

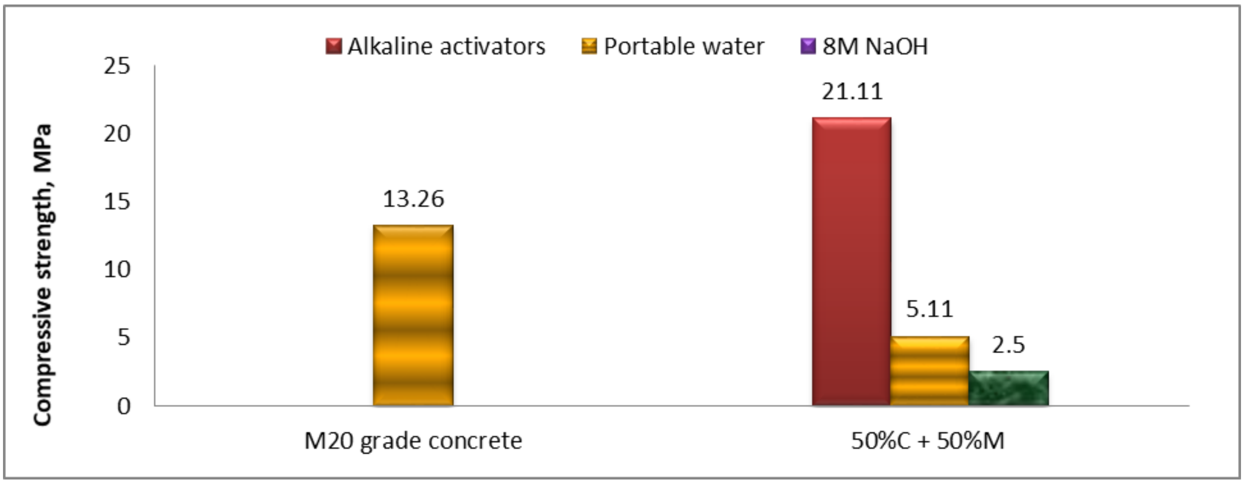

Figure 13. Compressive strength of geo-polymer samples containing marble powder using 8M NaOH, C= cement; M= marble powder

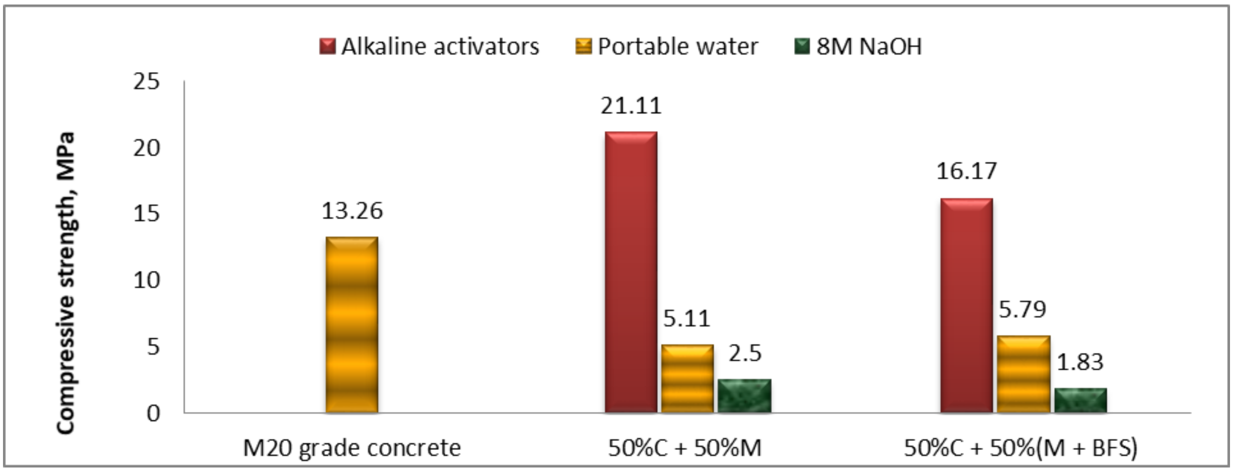

Figure 14. Compressive strength of geo-polymer samples containing marble powder and blast furnace slag using 8M NaOH. C= cement; M= marble powder; BFS= Blast furnace slag.

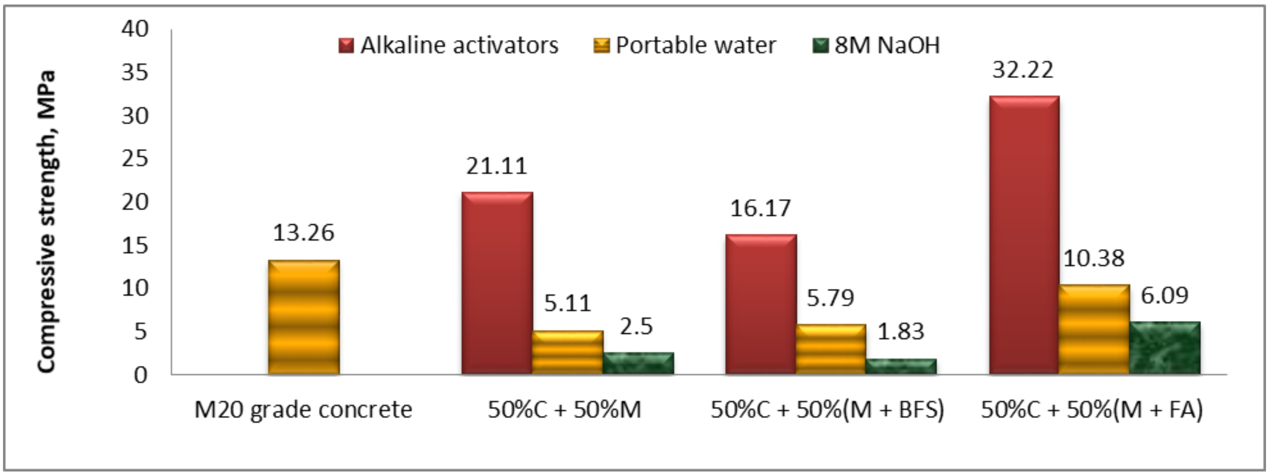

Figure 15. Compressive strength of geo-polymer samples containing marble powder and fly ash using 8M NaOH, C= cement; M= marble powder; BFS= Blast furnace slag; FA= Fly ash.

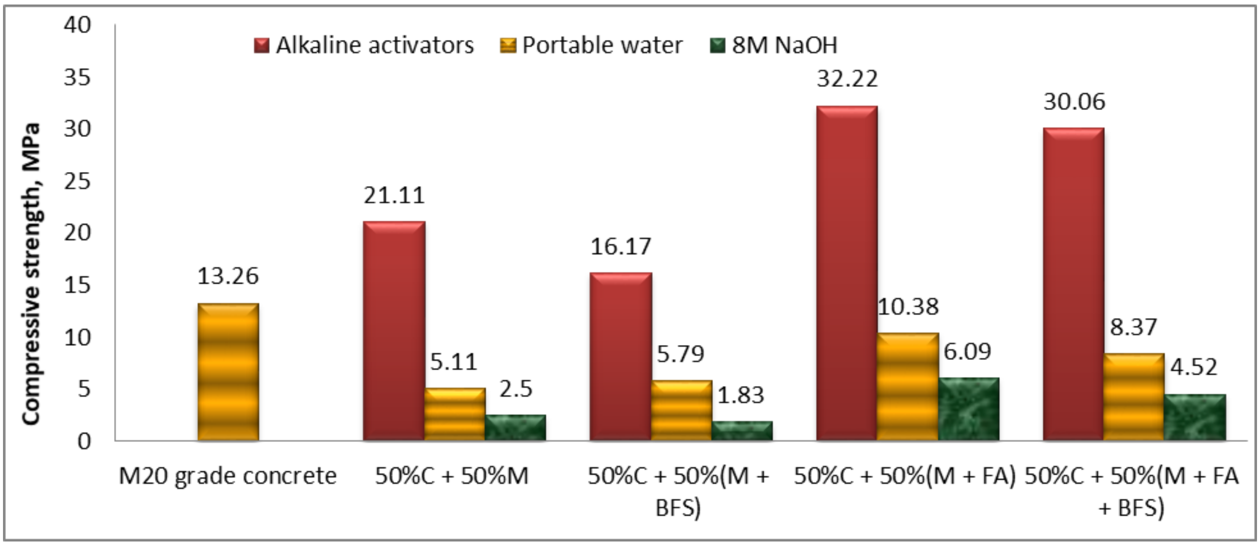

Figure 16. compressive strength of geo-polymer samples containing marble powder, fly ash and blast furnace slag using 8M NaOH, C= cement; M= marble powder; BFS= Blast furnace slag; FA= Fly ash.

3.7 100% Replacement of Cement with Marble Powder, Blast Furnace Slag and Fly Ash in the presence of 8M NaOH – Na2SiO3

In this experiment, we created a total of 12 samples, varying the replacement composition between every three samples. Samples ID MI28 to MI30 contained 50% cement and 50% marble powder, while samples ID MI31 to MI33 comprised 50% combination of marble powder and blast furnace slag (BFS) with 50% cement. Samples ID MI34 to MI36 included 50% marble powder and fly ash (FA) with 50% cement, and samples ID MI37 to MI39 contained a combination of 50% marble powder, BFS, and FA with 50% cement. A solution comprising 20% sodium silicate by volume and 8 molar sodium hydroxides in 4:1 was used as the liquid medium for all 12 samples. After determining compressive strengths for each composition, the graph in Figure – 17 was plotted to analyze strength relationships between the samples and standard concrete.

i. 100% Cement Replacement with Marble Powder

In Figure 17 full cement replacement with marble powder using alkaline activators (sodium hydroxide and sodium hydroxide in a 4:1 ratio) leads to decreased compressive strength. Samples exhibit poor hardening and structural integrity, easily breaking after 21 days in water.

Reduced compressive strength were caused due to marble powder lacks vital binding agents like calcium silicates and aluminates found in cement, crucial for concrete cohesion and strength. Also marble powder might lack reactive components necessary for chemical reactions that form stable compounds in concrete, hindering bonding and strength development. Similarly, alkali-silica reaction (ASR) might occur, causing gel formation, expansion, and cracking within the concrete, leading to reduced strength.

ii. 100% Cement Replacement with Marble Powder and Blast Furnace Slag

In Figure 17 complete cement replacement with a marble powder and blast furnace slag mixture results in zero compressive strength; samples break upon removal from water after 28 days. Likely reasons for this lack of strength include:

Alkali-silica reaction can occur between alkalis (e.g., sodium hydroxide) and reactive forms of silica in aggregates, forming gel-like substances that expand and weaken concrete. Similarly carbon dioxide reacting with calcium hydroxide from cement hydration forms calcium carbonate, reducing concrete alkalinity, corroding reinforcement, and weakening the structure.

iii. 100% Cement Replacement with Marble Powder and Fly Ash

Figure 17 reveals 0.58MPa compressive strength for the 100% cements replacement with a marble powder and fly ash combination. This strength is lower than cement concrete but higher than marble powder-based geo-polymer and marble powder and blast furnace slag-based geo-polymer. The likely cause is the limited production of C-S-H and C-A-H, which necessitate calcium hydroxide, a product of cement hydration. Complete cement replacement reduces calcium hydroxide production.

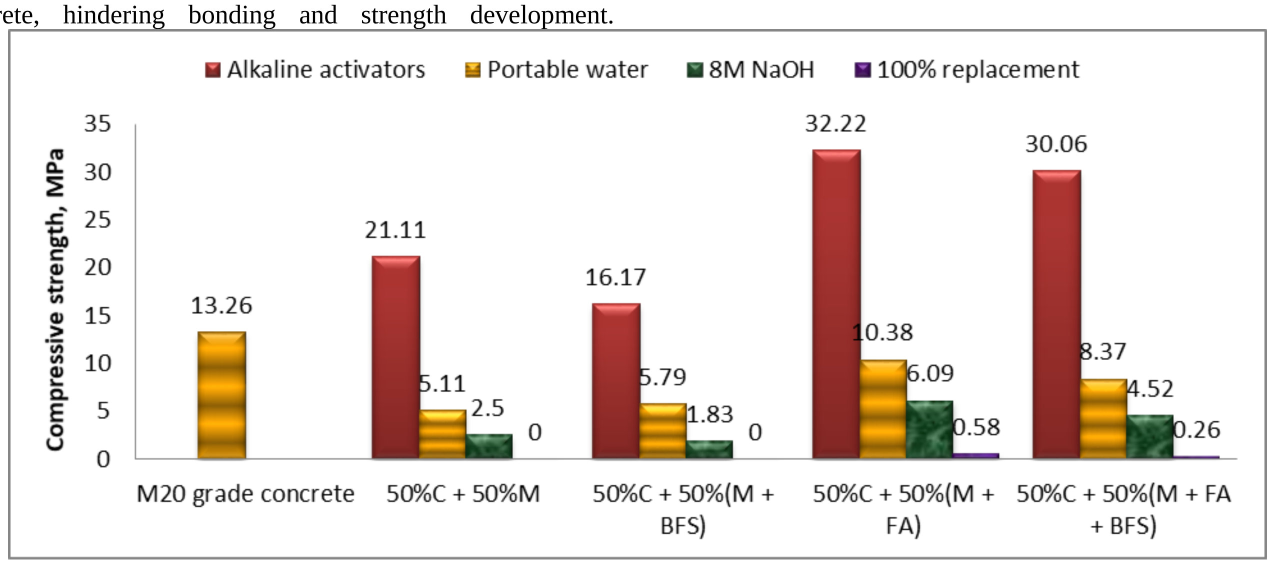

Figure 17. Compressive strength of geo-polymer samples of 100% replacement of cement with marble powder, fly ash and blast furnace slag using NaOH-Na2Si3 solution. C= cement; M= marble powder; BFS= Blast furnace slag; FA= Fly ash.

iv. 100% Cement Replacement with Marble Powder, Blast Furnace Slag and Fly Ash

In Figure 17, the given combination shows compressive strength of 0.026 MPa, surpassing all combinations except marble powder- Complete cement replacement results in negligible calcium based and marble powder-blast furnace slag-based ones. The negligible strength arises due to: hydroxide production, hampering the reaction of pozzolans silica and alumina and hindering C-S-H and C-A-S gel formation required for hardening. Similarly, alkali-silica reaction (ASR) between free silica in the mixture and alkali (NaOH) in the solution contributes to lower strength.

CONCLUSION

The effluents produced by the marble processing industry have a detrimental impact on the environment, causing harm to humans, aquatic and land plants, and various aquatic species. Additionally, they contaminate groundwater, rendering it unsuitable for drinking. To address these environmental issues, we employed a novel approach by incorporating marble sludge into the production of geo-polymer concrete. Based on the analysis of results it is concluded that:

1. Geo-polymer samples incorporating marble powder with a liquid medium of mixed solution of sodium silicate and 8 molar NaOH, exhibited higher compressive strength compared to standard concrete.

2. Among the two alkaline activators tested in this study, 8M NaOH-Na2SiO3 solution demonstrated superior compressive strength compared to 8M NaOH only.

3. Full replacement of cement with marble powder-fly ash combination (MP-FA) using 8M NaOH-Na2SiO3 solution yielded higher compressive strength compared to marble powder-blast furnace slag and fly ash combination (MP-BFS-FA) and other combinations.

4. Geo-polymer concrete with lower compressive strengths could be used in non-structural structures such as decorative purposes and sculptural or artistic elements in construction projects.

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