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Metakaolin and Red-Mud Based Geopolymer: Resistance to Sodium and Magnesium Sulfate Attack

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Abstract

This paper aims to study strength properties, UPV, and weight changes exposed to sulfate attack, and microstructural properties of geopolymer mortar prepared using metakaolin and red-mud as binder materials by mixing with river sand replaced partially by limestone, marble and basalt powder with different ratios (25%, 50%, and 75%) as filler materials, the mix proposed were activated by sodium silicate and sodium hydroxide solutions (12mol). The proposed samples were exposed to 10% of magnesium and sodium sulfate solutions for various periods of 60, 120, and 180 days to investigate the durability properties of the manufactured geopolymer mortar. The experimentally obtained results uncover that the prepared geopolymer mortar's strength properties increase at 60 days for all the proposed mixes, while at 180 days; the geopolymer mortar suffers a significant loss. Change in weight increase obviously between 10.83% and 13.65% for 60 days and decrease gradually for 120 days between 9.22% and 10.19% to reach a stable value between 120 and 180 days. Furthermore, to evaluate this work, the Scanning Electron Microscopy and X-ray Diffraction methods were investigated.

Keywords: Geopolymer, binder, metakaolin, red-mud, SEM, XRD.

2. Introduction

Regarding the durability of concrete structures, the sulfate attack is one of the factors causing deterioration cement paste due to the expansion, spalling, and softening. According to some previous research, the OPC (ordinary portland cement) showed severe damage when exposed to the sulfate attack [1]. Under the effect of sulfate attack on OPC concrete the chemical reaction between the aluminate component of cement paste and C–S–H[2], help out the formation of ettringite and gypsum which is the leading cause of the concerts' expansion and cracking, furthermore the destruction of C–S–H cause the disintegration and softening for the concerts' sample[3, 4]. The geopolymer mortars, known as known, have very low emission of CO_2[5, 6]. Moreover, the geopolymer mortars using waste materials, MK (metakaolin), Fly-ash, and ferrochrome slag supply sustainable development under the effects of sulfate attack. Recently, the geopolymers' term has been viewed as the future cement, and their evolution emerged and fostered by way of Davidovits [7], due to its good mechanical properties, low permeability, and excellent durability properties [8]. The geopolymers must be considered a new material, a new binder, and a new cement of concrete, which has no dangerous alkali-aggregate reaction reported by Davidovits. Previous researches indicated the development of strength properties and hydration products throw the effects of curing, the composition of the alkaline solution, and the ratio of water and binder, the alkaline solution generally comprise sodium silicate, sodium hydroxide. The geopolymer binder materials have lower costs and a higher reduction in CO_2emissions than Portland cement (PC).

Moreover, the compressive strength of geopolymer samples Range is 40-70MPa [9], due to the curing Hydrothermal, which accelerates the chemical reaction between binder and alkali solution. In the case of an acid attack, some previous researches study the durability of geopolymer materials to present its processing and characterization [10], and due to the absence of high-calcium phases, the geopolymer materials have excellent resistance under the sulfate solutions effects. Nowadays, the durability and maintenance of concrete structures become a critical issue [11] because they start to deteriorate after 20–30 years while their design life was at least 50 years [12]. The constructions in contact with seawater, sewages, tunnels, and deep foundations are exposed to external chemical attacks [13]. When subjected to sulfate attack in the environment, the ordinary Portland cement showed cases of concrete deterioration due to the involved reactions of C–H, C–S–H and the aluminate component of cement [14]; thus for the geopolymer waste materials, the sulfate attack is a vital durability concern. Several additives are used to increase the strength properties of the manufactured geopolymer concrete, such as slag. When exposed to sulfate solutions effects, the geopolymer samples with low calcium base have shown excellent durability and strength properties [15]. Besides the OPC' durability problems are associated with its main phases; calcium content, when C_3a exposed to the sulfate ions ettringite and gypsum will be formed in the presence of Ca$(OH)_2$; thus the concrete's disruptive expansion and degradation occur due to the non-cohesive particles mass [16].

The geopolymers present a high durability and strength properties resistance under the effects of sulfate attack due to its strength, low creep, and low shrinkage [17], and low phase of calcium. Furthermore, the geopolymer activating solution, especially NaOH, accelerates chemical dissolution, which inhibits the formation of ettringite and carbon-hydrogen during binder formation and promotes higher strengths at early ages of reaction, which improved excellent stability in aggressive environments due to the development of higher crystallinity [18]. However, high concentrations of NaOH caused undesirable morphology and non-uniformity of the manufactured geopolymer samples due to the excessively OH– in solution.
This work presents a geopolymer mortar manufactured by MK and RM (red-mud) as binder materials activated with (NaOH and Na_2SiO_3) chemical materials, and as filler materials limestone, marble and basalt powder were used replaced river sand with different ratio (25%, 50%, and 75%). The performance of the manufactured geopolymer samples was conducted under the effect of 10% magnesium sulfate and 10% sodium sulfate solutions. Visual appearance, the strength properties, weight changes, XRD, and SEM of these samples were obtained experimentally.

3. Materials and Methods

In this purpose, metakaolin and red mud were used as a binder material while limestone, marble, and basalt powder were used as filler materials. Red mud was collected from Seydişehir Aluminum Plant (Konya/Turkey). The ground granulated blast furnace slag is manufactured by Bolu Cement Industry (Bolu/Turkey). The slag's specific weight is 2.91g/$cm^3$and the amount remaining on the 45-micron sieve is 1.4%, and it was used in 13% of the mixture. Kaolin was extracted from Industrial Minerals San.ve Tic. Inc. (Istanbul/Turkey), the specific gravity is 2.52 g /cm^3, The powder of this kaolin was once calcined at 700℃ for four hours at a heating rate of 1℃/min to get a surprisingly reactive metakaolin. Silica + alumina + iron oxide ratio = 97.18%>70%, Moreover metakaolin has fine grain which increase the reaction. Slag, metakaolin, and red mud were stated in S, MK, and RM abbreviations, respectively. Liquid sodium silicate (SiO_2/Na_2O = 3.29 M) ratio and analytical grade sodium hydroxide (12mol) were once used for alkaline activation taken from AS Kimya (Istanbul/Turkey). Sodium hydroxide and sodium silicate were expressed in SH and SS abbreviations, respectively. The sodium hydroxide was prepared by adding 1liter of distilled water to 480g of sodium hydroxide pellets to obtain 12mol. The obtained water glass has been stored at room temperature for 24 hours before being used with sodium silicate/sodium hydroxide in a 2:1 ratio. The mix was prepared using the mixer drill using the chemicals (SS and SH) with MK and mixed for 5mins. The RM was added to the bellow mix and also mixed for 5 mins to homogenate the mortar prepared, to enhance the tenacity of mix blast furnace slag was used and mixed for just 2 mins then immediately one the filler materials (limestone, basalt powder, and marble powder) with river sand using one of the different ratio approved for this work (25%, 50%, and 75%) were added. Filler materials used in this work has a very fine grain and convert large voids to small ones. Limestone, marble, and basalt powder used in this work as filler materials. Limestone powder was provided from Gebze Rock Quarry (Gebze/Turkey), basalt samples were homogenized, dried at 105℃for 24 hours. From INCI Group Company (Sakarya/Turkey) the basalt powder stone was extracted. Marble powder was dried the same as basalt powder, obtained from Turkan Company (Alibeykoy/Istanbul). All the filler materials used were less than 0,0063mm particle diameter. In this work as aggregate, the river sand with less than 0,25 mm particle diameter was used correspondent to TS 706 EN 12620 [19]. Limestone, marble, and basalt powder were expressed in LS, MR, and BS abbreviations, respectively. While the mixing procedure has been finished, the mortar was used to the molds 50x50x50 mm and 71x71x71 mm cubes, 40x40x160 prisms, and 300*150 mm cylinders and vibrated, and then the geopolymer samples were kept for 24h in the ambient temperature. All the specimens were held for 24 hours in the drying oven at 100℃. After the curing, the samples were preserved in room temperature conditions. After 28 days, durability tests were performed under the effect of sulfate solutions. Moreover, the mechanical tests, compressive strength test according to ASTM C 109 was executed after 60, 120, and 180 days utilizing the 50x50x50 mm cubes, the Flexural strength test quoted by ASTM C 348 utilizing the 40x40x160 prisms samples was carried also after 60, 120, and 180 days [20].When the results of the exposed samples to the effect of sulfate solutions, the SEM and XRD analysis was performed.

Table 1. The MK, RM, and S chemical properties.

Chemical Analysis(%)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	SO_3
MK	56,1	40,23	0,85	0,55	0,19	0,16	0,51	0,24	-
RM	17,38	24,52	35,25	-	3,22	0,42	0,43	8,45	-
S	40,55	12,83	1,1	-	32,58	5,87	-	0,79	0,18

Table 2. SH chemical properties.

Chemical Analysis (%)	NaOH	Na_2CO_3	CL	SO_4	Al	Fe
SH	99,1	0,3	≤0,01	≤0,01	≤0,002	≤0,002

Table 3. SS chemical properties

Chemical Analysis (%)	SiO_2	Na_2O	Fe (%)	Density (g/ml)	Heavymetals (%)
SS	27,0	8,2	≤0,005	1360	≤0,005

Table 4. Fine aggregate's chemical properties.

ChemicalAnalysis (%)	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	CaO_2	K_2O	Na_2O	SO_3
LS	3,3	0,82	0,58	-	-	92,9	-	-	1,18
MR	1,12	0,73	0,05	-	-	83,22	-	-	0,56
BS	56,9	17,6	8,1	0,9	7	-	1,9	3,8	-

Table 5. Mix of control sample geopolymer composites (g)

Metakaolin	Red-Mud	Slag	SS (Na_2SiO_3)	SH (NaOH (12 mol))	River Sand
500	500	133	667	333	2000

Table 6. The mix of the three different filler materials replacing river send with different ratios (g)

Metakaolin	Red-Mud	Slag	Na_2SiO_3	NaOH (12mol)	River Sand	Limestone or Marble or Basalt powder
500	500	133	667	333	1500 1000 500	500 1000 1500

4. Results and Discussions

Table 7. Compressive strength loss rates (%) due to magnesium and sodium sulfate effect.

	Magnesium sulfate			Sodium sulfate		
Mix ID	60 days	120 days	180 days	60 days	120 days	180 days
Control	-3,20	3,044	7,33	-3,87	2,28	3,98
25%LS	-3,08	3,215	7,59	-3,55	2,58	4,14
50%LS	-2,18	3,519	8,69	-2,50	2,98	5,43
75%LS	-1,79	4,634	9,82	-2,09	3,30	6,37
25%MR	-3,12	3,198	7,42	-3,62	2,47	4,06
50%MR	-2,31	3,407	8,42	-2,65	2,84	5,13
75%MR	-1,98	4,140	9,28	-2,16	3,20	6,21
25%BS	-3,25	2,960	7,22	-3,96	2,28	3,87
50%BS	-3,52	2,575	6,70	-4,03	2,19	3,52
75%BS	-4,19	2,176	5,67	-4,48	1,81	2,97

Geopolymer mortar specimens were exposed to 10% Sodium (N$\boldsymbol{a}_2$S$\boldsymbol{O}_4$) and 10% Magnesium (MgS$\mathbf{O}_4$) Sulfate solutions for 60 days, 120 days, and 180 days. The results for each sample were given in (Tables 7, 8) compared with 28 days'.

3.1. The Visual Appearance

The visual appearance of the test specimens at 60 and 120 after moistening in magnesium and sodium sulfate solutions (Figs. 1 and 2). Clearly it was seen that there were no changes as surface erosion, cracking in the surface appearance of the manufactured geopolymer samples. It was mean that geopolymer mortar had a good resistance to sulfates, agreement to values limit of the expansion suggested in the ASTM C1012-13. Moreover, at 180 days after the samples were immediately removed from both magnesium and sodium sulfate solutions and kept at room temperature 25°C, a wire brush was used to clean up the accumulated salt attack scaling behind the surface of the manufactured geopolymer mortar specimens, which did not affect the integrity of specimens mechanically. Furthermore, for both magnesium and sodium sulfate solutions there were no severe damages observed similar results were reported by other there is no severe deterioration was observed. Similar observations also have been reported by other studies' [16, 21-26]. Skvara et al. [27] stated that also more than one year there was not any significant sign of surface deterioration because of their lower susceptibility to form hydration byproducts, due to the cross-linked structure of the gels in the geopolymer samples.

Fig.1. a) Samples after exposed to (MgSO_4), b) Samples after exposed to (Na_2SO_4) c) Samples while exposed to (MgSO_4), d) Samples while exposed to (Na_2SO_4)

3.2. Strength Properties

3.2.1. Compressive strength of magnesium sulfate

According to the magnesium sulfate effect, fluctuations in the compressive strength were seen up to 120 days. The fluctuations occurred were due to the diffusion of Magnesium from the mixture of alkaline ions to the solution, resulting in diffusion to the matrix formed [16]. Furthermore, a decrease in strength was observed for up to 120 days. The microcracks presence and alkalis transition geopolymers to the solution caused the strength losses at 120 days [28]. The compressive strength increase rate of magnesium sulfate in geopolymer samples after 60 days compared to 28 days results at room temperature were between 1.79% and 4.19%. After 120 days, the compressive strength decrease was occurred between 2.17% and 4.63%, while after 180 days, the decrease was between 5.67% and 9.82%. The results are shown in table 7. The compressive strength ls and bs powder at 60 days were 58.94 MPa and 77.58 MPa respectively, while the control sample was 65.09 MPa. The results for 120 days were between 73.01 MPa and 50.25 MPa. The obtained results for 180 days were between 69.92MPa and 42.51 for bs and mr powder specimens, respectively. According to the results, it was seen that the geopolymer samples have better behavior under the magnesium sulfate attack effects. Microstructural changes occurring in the control, bs and ls samples at 6 months after the magnesium sulfate attack. The microstructure of the samples was preserved after exposure to magnesium sulfate. The excellent resistance of geopolymeric materials to sulfates was attributed to the source material having a lower Ca content and a more stable cross-linked alumino silicate polymer structure while for the material having a higher Ca content as limestone and marble powder exhibited a new phase of gypsum (Y: gypsum), throw the chemical reaction happened between Ca and ($MgSO_4$) occurring the decomposition of the C-A-S-H, the notion proposed was identified by XRD and SEM. Besides, the geopolymer materials are less susceptible to attack's sulfate than standard cement hydration products. Low Ca content was found to be a significant feature in the durability of metakaolin. In this case, the reaction manufacture is an alkali gel (aluminosilicate) with a three-dimensional structure, which was significantly different from the hydrated calcium silicate gel formed in GPC hydration [29].

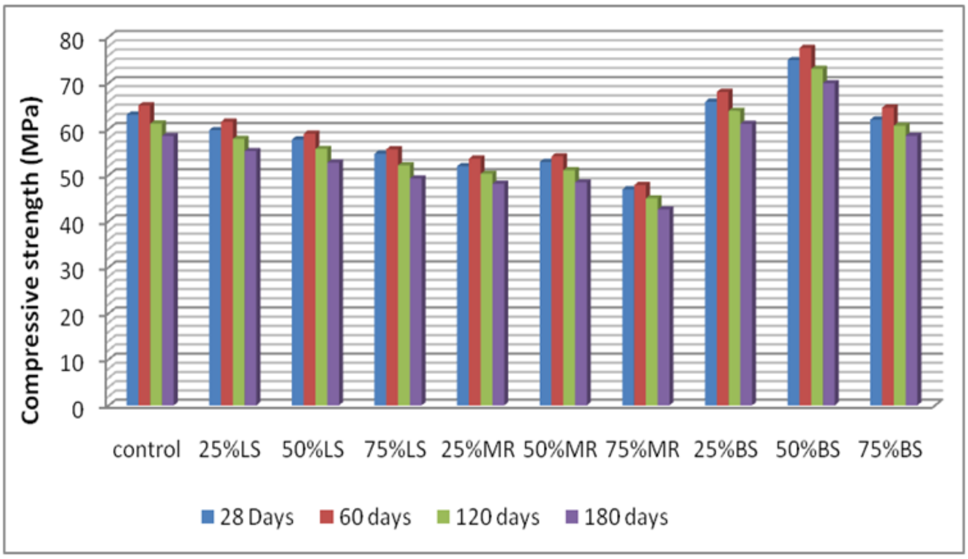


Fig. 2. Compressive strength results of geopolymers samples exposed to magnesium sulfate

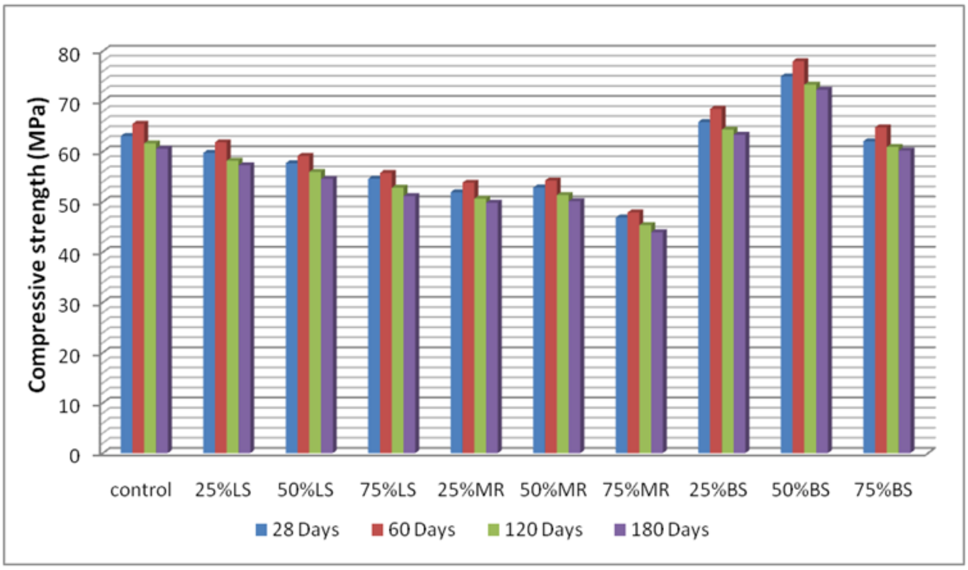


Fig. 3. Compressive strength results of geopolymers samples exposed to sodium sulfate.

3.2.2. Compressive strength of sodium sulfate

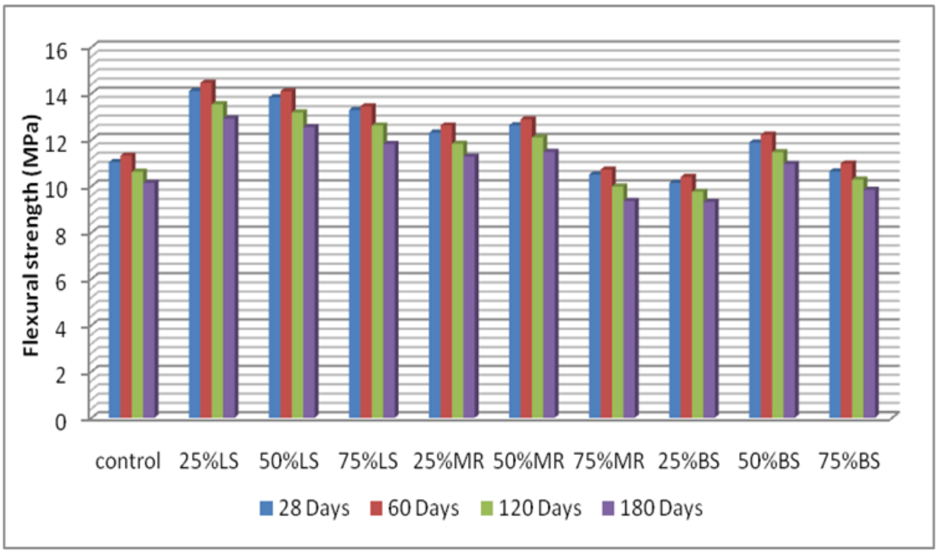


Fig. 4. Flexural strength results of geopolymers samples exposed to magnesium sulfate.

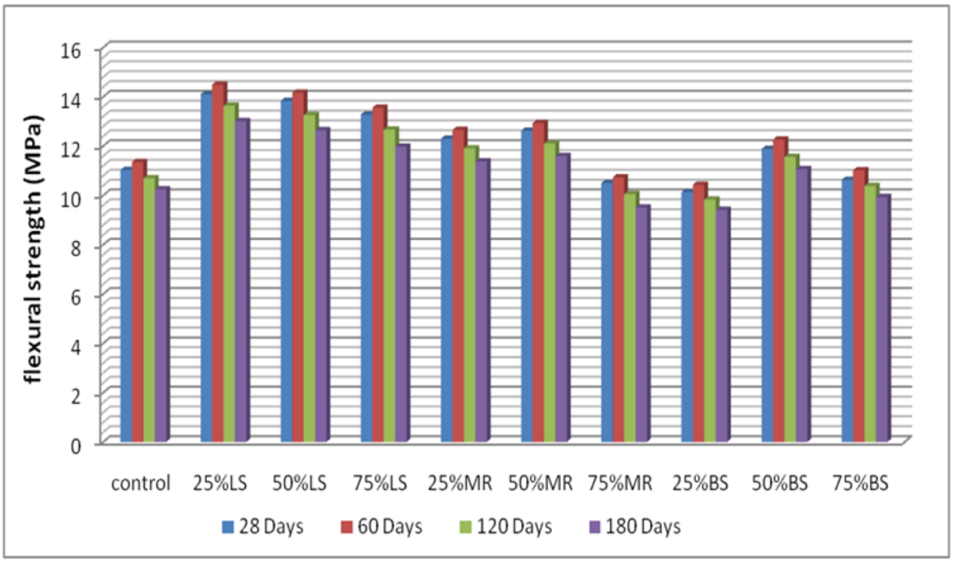


Fig. 5. Flexural strength results of geopolymers samples exposed to sodium sulfate.

Table 8. Flexural strength loss rates (%) due to magnesium and sodium sulfate effect

	Magnesium sulfate			Sodium sulfate		
Mix ID	60 Days	120 Days	180 Days	60 days	120 Days	180 Days
Control	-2,54	3,81	8,16	-2,90	3,08	7,16
25%LS	-2,48	4,04	8,44	-2,77	3,33	7,73
50%LS	-1,88	4,70	9,33	-2,39	4,19	8,60
75%LS	-1,20	5,05	11,07	-2,03	4,59	9,79
25%MR	-2,52	3,90	8,37	-2,85	3,17	7,56
50%MR	-2,06	4,12	9,11	-2,46	4,12	8,16
75%MR	-2,00	4,95	10,95	-2,19	4,29	9,43
25%BS	-2,57	3,75	8,09	-2,96	2,96	7,11
50%BS	-2,78	3,54	7,83	-3,20	2,69	6,90
75%BS	-3,20	3,29	7,53	-3,67	2,35	6,59

The geopolymer samples showed fluctuations in compressive strength of up to 120 days in the results with sodium sulfate. The geopolymerization reaction continued with exposure time to the sulfate, resulting in increased compressive strength [24] since sodium sulfate has the ability to act as an activation factor. Calcium (Ca) expansion products combined with sulfate continuously fill the pore structure for up to 120 days. After this period, a decrease in resistance was observed for up to 180 days. Remarkable cracks and high porosity ratio after 120 days resulted in decreased strength. Magnesium sulfate is a more aggressive solution than sodium sulfate [30]. After 120 days, the loss of strength was lower in sodium sulfate effect than in magnesium sulfate effect. After 60 days, the increase in the compressive strength of geopolymer samples was 2.09% and 4.48%. At 120 days, there was a decrease in strength between 1.81% and 3.30 %, and after 180 days, the decrease was between 2.87% and 6.37%. The compressive strength of 61.84 MPa, 58.18 MPa, and 57.25 MPa was obtained in 25LS in 60 days, 120 days, and 180 days, respectively. In the 50BS sample, the compressive strength 77.96 MPa, 73.36 MPa, and 72.31MPa were obtained in 60 days, 120 days, and 180 days, respectively. Besides, the compressive strength results of 50MR were 54.23 MPa, 51.33 MPa, and 50.12 MPa in 60 days, 120 days, and 180 days, respectively. The compressive strength results were shown in fig. 2. According to the results, it has been observed that the geopolymer samples have excellent behavior under sodium sulfate better magnesium sulfate.

3.2.3. Flexural strength of magnesium and sodium sulfate

The flexural strength results of the geopolymer specimen's exposure to the solution were obtained and compared with 28-day results (Figure 4 and 5), the maximum deterioration of the manufactured samples was observed in the 180 days exposure time. Decreases in bending strengths were observed with the effect of magnesium sulfate and sodium sulfate and [28]. As known, the magnesium sulfate is a more aggressive solution than sodium sulfate [29]. Thus, the flexural strength decrease rate is formed in the lowest sodium sulfate and then magnesium sulfate, respectively. According to the results, it has been observed that the geopolymer samples have a better behavior under sodium sulfate than magnesium sulfate due to its aggressive. After 60 days, the flexural strength geopolymer samples increases under magnesium sulfate effect were between 1.20% and 3.21% and decrease between 3.29% and 5.05% after 120 days and between 7.53% and 11.07% after 180 days (table. 8). Theflexural strength of 14.45 MPa, 13.53 MPa, and 12.91 MPa was obtained in 25LS in 60, 120, 180 days, respectively.

In the 50MR samples, the flexural strength results of 12.88 MPa, 12.1 MPa, and 11.47 MPa were obtained in 60, 120, 180 days, respectively. The results of magnesium sulfate flexural strength were shown in fig. 4. The flexural strength of geopolymer samples increases with sodium sulfate effect at 60 days; the obtained results were between 2.03% and 3.67%. After 120 days, the geopolymer samples' results decrease significantly between 2.35% and 4.59%, while after 180 days, the decrease was between 6.59% and 9.79% (table.8). The flexural strength results obtained of 25LS geopolymer samples were 14.49 MPa, 13.63 MPa, and 13.01 MPa in 60, 120, 180 days, respectively. Besides the 50MR samples, the flexural strength results obtained were 12.93 MPa, 12.1 MPa, and 11.59 MPa in 60, 120, 180 days, respectively. The results of sodium sulfate flexural strength were shown in fig. 5.

3.3 Ultrasonic Pulse Velocity (UPV) Results

Table 9. UVP loss rates (%) due to magnesium and sodium sulfate effect.

	Magnesium sulfate			Sodium sulfate		
Mix ID	60 Days	120 Days	180 Days	60 days	120 Days	180 Days
Control	-2,00	3,92	7,63	-2,33	3,98	7,34
25%LS	2,04	7,89	11,15	1,87	8,04	11,09
50%LS	3,17	9,39	12,47	3,22	9,36	12,42
75%LS	-0,73	5,36	8,44	-0,79	5,30	8,53
25%MR	-3,17	3,65	6,59	-3,20	3,56	6,53
50%MR	-2,87	3,32	6,64	-2,81	3,29	6,52
75%MR	-1,22	4,55	7,55	-1,28	4,58	7,67
25%BS	0,99	7,12	10,87	1,28	7,29	10,75
50%BS	2,26	8,29	11,97	2,01	8,20	11,89
75%BS	2,82	8,14	11,77	2,48	8,20	11,83

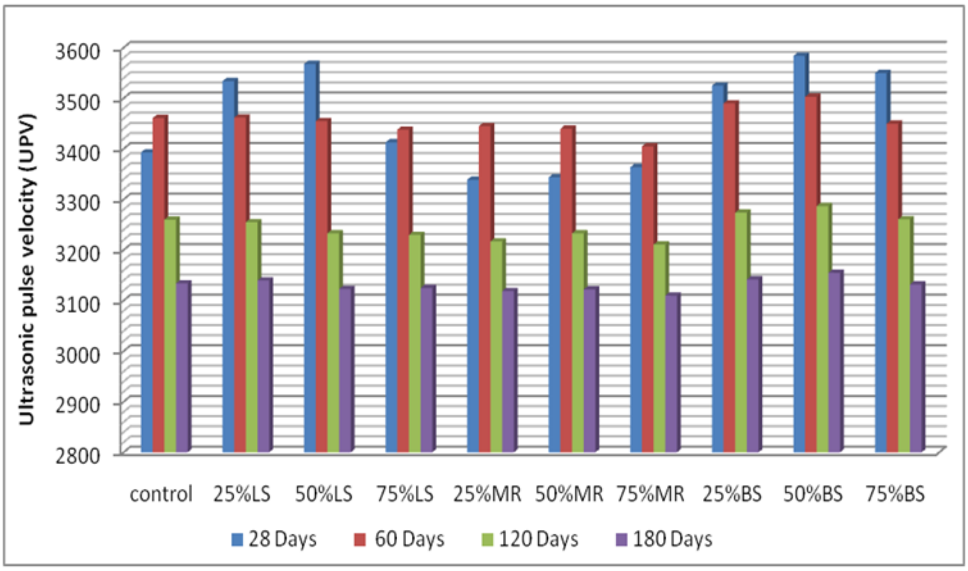


Fig. 6. UPV results of magnesium sulfate.

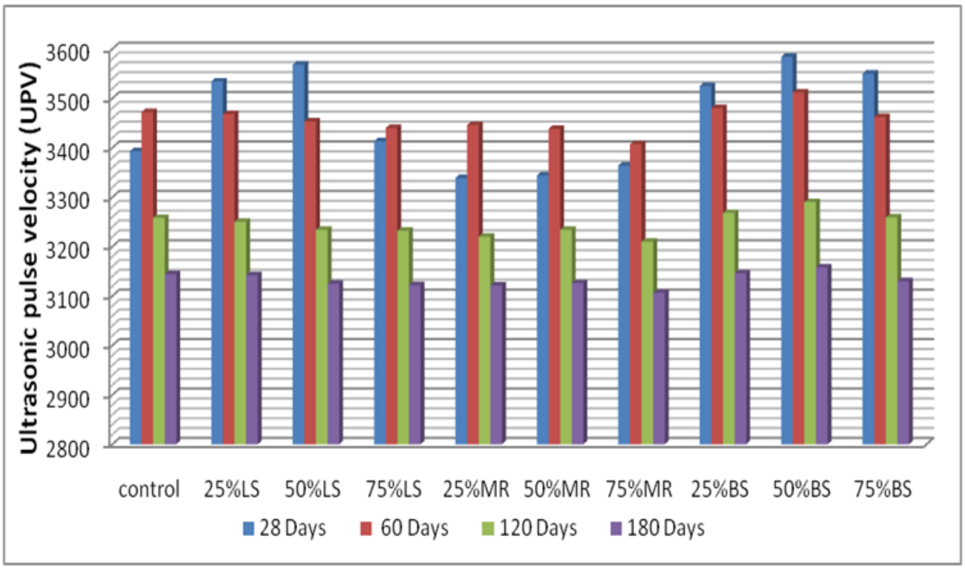


Fig. 7. UPV results of sodium sulfate.

The UPV results obtained under exposure to the solution effects were compared with the results of 28 days (Figure 6 and 7). The UPV test's change was obtained from the UPV results of the samples after exposure to the solution effects (Table. 9) With the effect of magnesium sulfate and sodium sulfate, there was an increase in the UPV test results up to 60 days, due to the filling of voids with sulfate salts and hydration products under the action of solution [16]. The results were reduced with the effect of the microcracks formed later [27]. Magnesium sulfate is a more aggressive solution than sodium sulfate [26]. Thus, the UPV test increase rate was formed in the highest sodium sulfate and magnesium sulfate. According to the results, it has been observed that the geopolymer samples have better behavior under the effect of sulfate solutions. After 60 days, UPV results increase rates were between 0.99% and 3.17% with the effect of magnesium sulfate in geopolymer samples. At the end of 120 days, there was a decrease between 3.32% and 9.39%; moreover, after 180 days was between 6.59% and 10.87%. The geopolymer manufactured 25LS specimens, UPV results of 3462 m / s, 3255 m / s, and 3140 m / s were obtained in 60 days, 120 days, and 180 days, respectively. Furthermore, for 50BS specimens, UPV results were 3503 m / s, 3287 m / s, and 3155 m / s obtained in 60 days, 120 days, and 180 days, respectively. The geopolymer samples' UPV results that increase at 60 days under the sodium sulfate effect were between 0.79% and 3.22%. At 120 days, there was a decrease of between 3.29% and 9.36%; thus, after 180 days, the decrease was between 6.53% and

10.75%. The geopolymer 25LS sample, UPV results of 3468 m / s, 3250 m / s, and 3142 m / s were obtained in 60 days, 120 days, and 180 days, respectively.60 days, 120 days, and 180 days, respectively. Moreover, for the. 50BS sample, UPV results were 3512 m / s, 3290 m / s, and 3158 m / s obtained in 60 days, 120 days, and 180 days, respectively.

3.4. Weight Changes after Magnesium and Sodium Solution Effects

Under the effect of magnesium sulfate and sodium sulfate, there has been an increase in weight up to 60 days. Thus, to the filled voids with sulfate salts and hydration products under the action of a solution [16]. The results were reduced with the effect of the microcracks formed later [27]. Magnesium sulfate is a more aggressive solution than sodium sulfate [26]. For these reasons, the rate of weight increase occurs in the highest in sodium sulfate and magnesium sulfate, respectively. Moreover, placing the samples before the experiment in the oven for 24 hours at 105 ° C provided better sulfate solutions to be absorbed and more effective. The effect of magnesium sulfate in geopolymer mortars, the weight increase rates in 60 days were between 10.83% and 13.65%, the weight increase rates in 120 days were between 9.22% and 10.19%, and in the 180 days weight increase rates were between 7.19% and 8.16% (Figure. 8) according to the 28 days sample. The sodium sulfate effect in the weight of geopolymer mortars increases in 60 days, 120 days, 180 days, the results obtained were between 12.64% and 15.05%, 11.59%, and 14.23%, 8.43%, and 11.23% at 60 days, 120 days, 180 days, respectively.

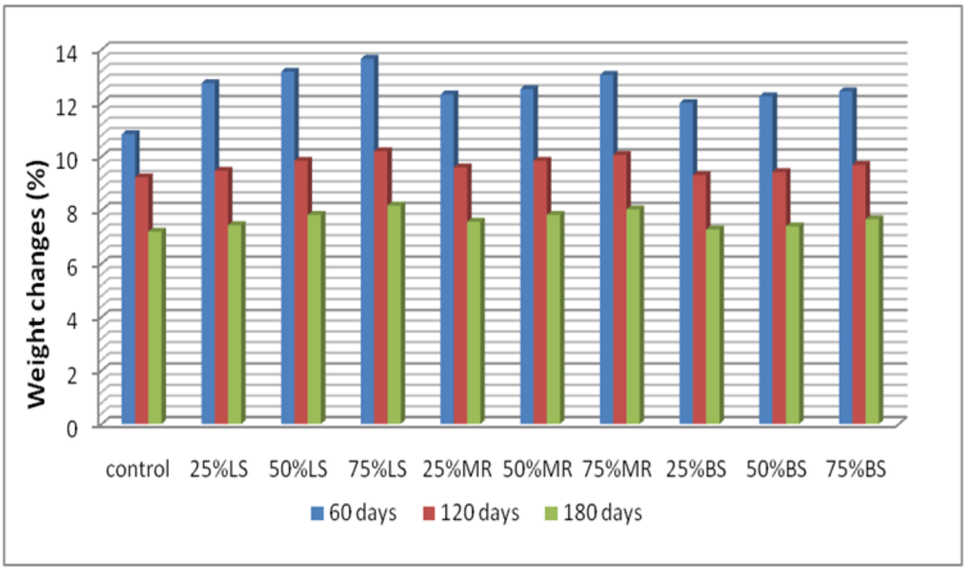


Fig. 8. Weight changes of magnesium sulfate.

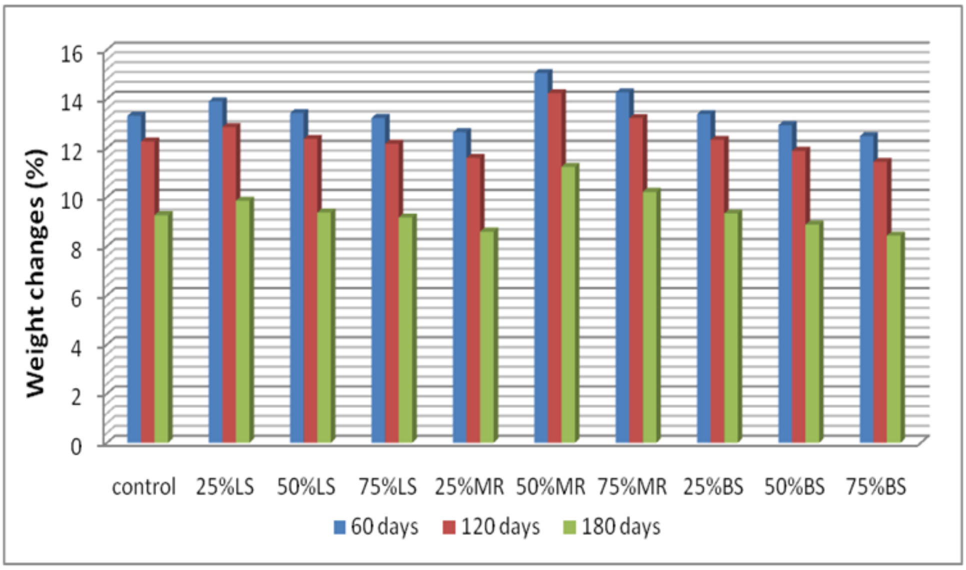


Fig. 9. Weight changes of sodium sulfate.

3.4. XRD Analysis

The XRD analysis of geopolymer samples after exposure to $Na_2SO_4$and $MgSO_4$over 180 days. The geopolymer samples XRD analysis uncover the crystalline phases of the raw materials.

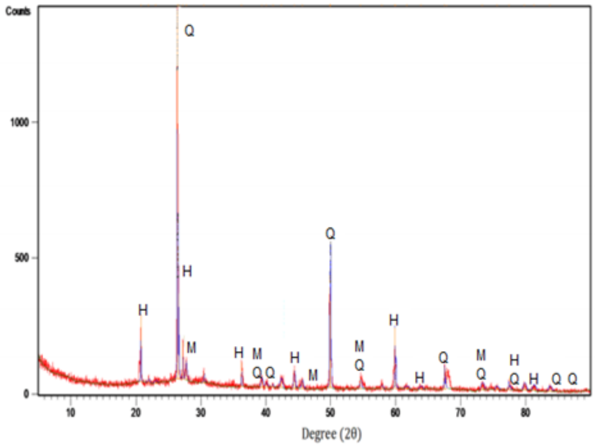


Fig. 10. X-ray diffractograms of control sample after 180days exposed to sodium sulfate exposure.

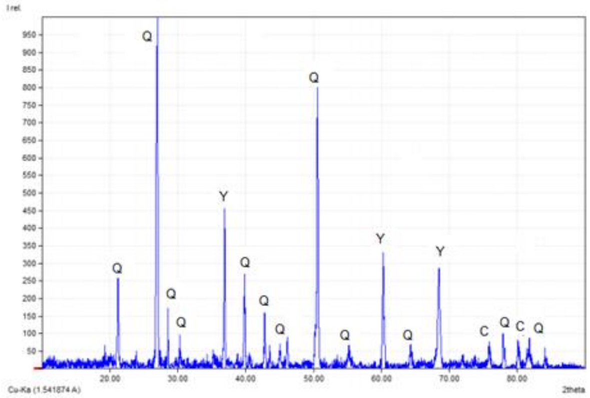


Fig. 11. X-ray diffractograms of 50%LS sample after 180 days of magnesium sulfate exposure.

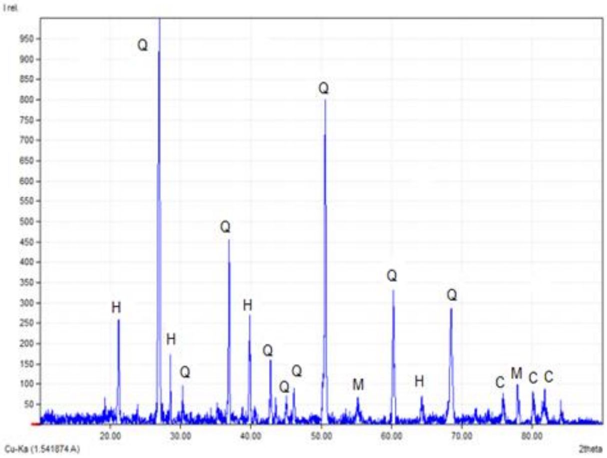


Fig. 12. X-ray diffractograms of 50%BS sample after 180 days of magnesium sulfate exposure.

The limestone and marble powder specimens exposed to $MgSO_4$ exhibited a new phase of gypsum with elevated intensity, produced by atomization of the C─(A)─S─H phase by the interfere of calcite with (CSH) of low crystallinity [30]. C─(A)─S─H phase peak were location at(30° 2Θ) indicating the low [36]. besides there was no sever damages seen in the control and basalt powder samples due to the lower Ca content which is almost insignificant and the existence of SiO_2 glass content obstructing the chemical reaction with $MgSO_4$. Regarding to the geopolymer sample's exposure to Na_2SO_4solution there was no different crystalline phases from the any immersed samples for this a small almost insignificant mechanical losses were observed similar to those previously mentioned by other researchers [8].The $MgSO_4$ solution attack were more aggressive than Na_2SO_4, especially for the limestone and marble powder samples due to the reaction of $MgSO_4$and Ca producing gypsum and magnesium hydroxide (brucite) which reduce the stability of CSH and poorly alkaline insoluble phase. Furthermore, at long term the sulfate attack progresses, and decalcification occurs due to the calcium extracted of CSH.

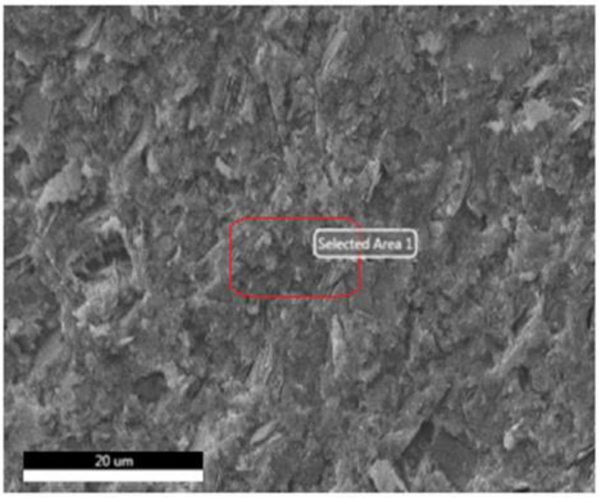
C: calcite ($CaCO_3$), Q: quartz (SiO_2), M : mullite, H : hermatite

3.4. The SEM Micrographs

The SEM micrographs of the geopolymer specimens that were exposed to Na_2SO_4 and $MgSO_4$ solutions for 180 days. The limestone and marble powder samples immersed in$MgSO_4$ exhibited the establishment of gypsum crystals in the geopolymer phase (Fig. 17), XRD analysis confirmed the presence of gypsum in the specimen, as shown in (Fig. 11).

While for the control and basalt specimens there was no significant changes occurred. Besides the manufactured geopolymer samples of this work immersed in Na_2SO_4 solutions, it was impossible to recognize the new phases formed because any XRD analysis changes were found, the results founded were in accordance with the research described by [28].

In addition to SEM analysis, EDS analysis was performed for control sample to examine the distribution of the elements within the matrices (Fig. 14). In general, spectra showed an expected distribution of elements. The main elements in the spectrum are Si, Fe and Al, which show a particular geopolymerization reaction and provide a good correlation with the relevant results.



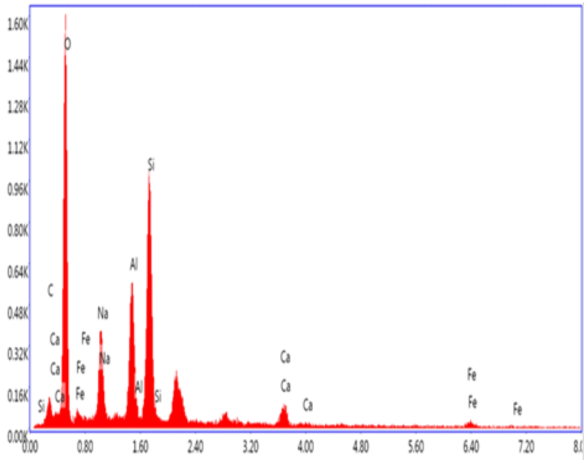


Fig. 13. EDS spectroscopy of the control sample before exposing to sulfate solution

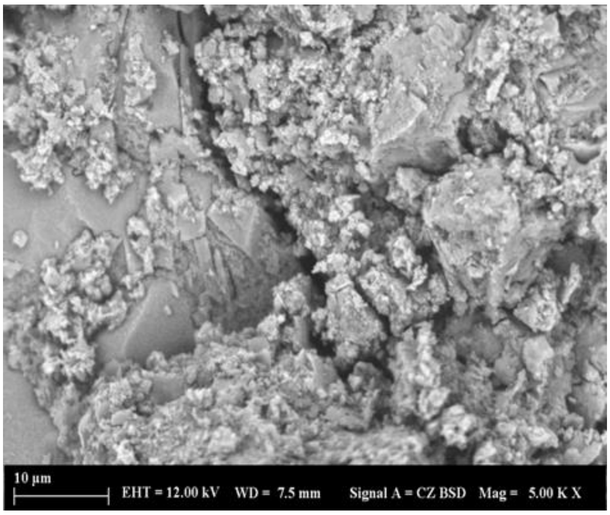


Fig. 14. The control sample after exposing to magnesium sulfate solution.

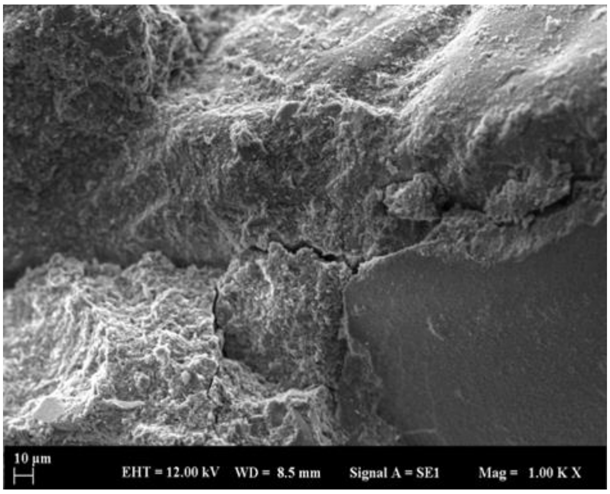


Fig. 15. The 50% BS sample after exposing to magnesium sulfate solution.

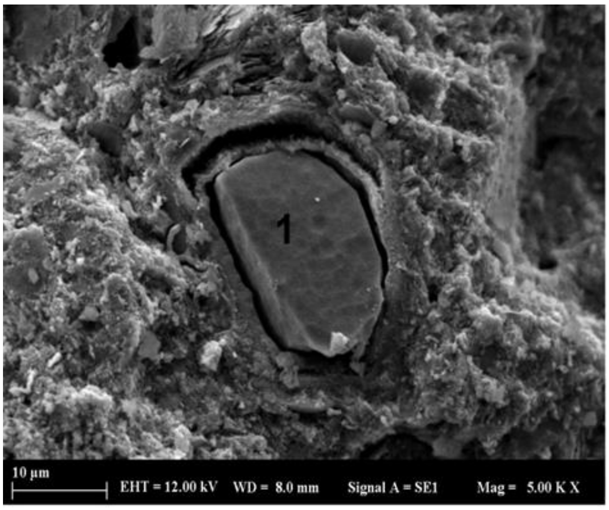


Fig. 16. The 50% LS sample after exposing to magnesium sulfate solution (1: gypsum).

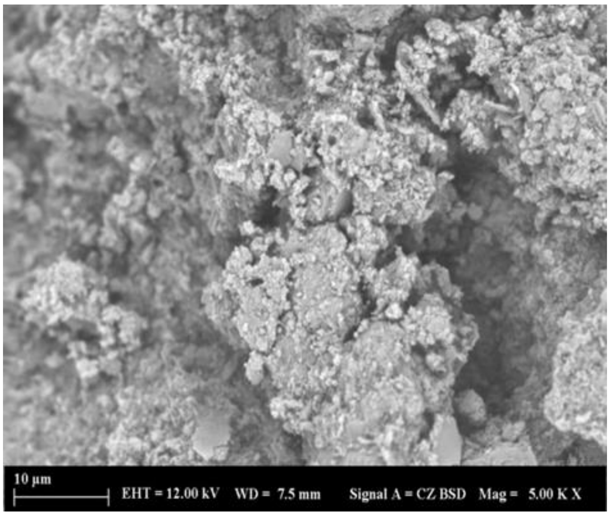


Fig. 17. The 50% LS sample after exposing to sodium sulfate solution.

5. Conclusion

The purpose of this work was to look into the durability, mechanical properties and microstructural composition impact of adding three different types of filler materials limestone, marble, and basalt powder, with the primary binder materials of this study Red-Mud and Metakaolin, based on geopolymer composites under the effect of magnesium and sodium sulfate solutions:

- After exposure to magnesium sulfate the compressive and flexural strengths of samples increase at 60 days then decrease after 120 days, especially limestone and marble powder due to the establishment of gypsum crystals in the geopolymer structure.
- There was no sever damages seen in the control and basalt powder samples due to the lower Ca content which is almost insignificant and the existence of SiO_2 glass content obstructing the chemical reaction with $MgSO_4$.
- The replacement of waste filler materials increased the strength properties, especially the basalt powder, with a 75% ratio.
- The $MgSO_4$ solution attack was more aggressive than Na_2SO_4, especially for the limestone and marble powder samples due to the reaction of $MgSO_4$and Ca which reduce the stability of CSH and poorly alkaline insoluble phase.
- The weight changes increase due to the filled voids with sulfate salts and hydration products under the action of a solution
- About the mechanical properties, there was a considerable increase estimate observing compressive and flexural strength was obtained at 60days, then a decrease after 120 days. For instance, the 60 days, compressive and flexural strength of basalt powder and control samples, were higher when compared to the marble and limestone powder geopolymer samples.
- About the manufactured geopolymer samples immersed in Na_2SO_4solutions, it was impossible to recognize the new phases formed because any XRD analysis changes were found.
-

As an established conclusion growing waste materials, as filler replacing river sand with different ratios, contributed the development of the durability and mechanical properties and microstructural behaviors of the composite, especially basalt powder concerning the control composites. Furthermore, the ratio (50%-50%) metakaolin and red-Mud as a binder material was given good results. Moreover, the mix of Metakaolin and Red-Mud is more durable and able to be used. Finally, the use of Red-Mud and the waste filler materials in manufacturing geopolymers are economical and environmentally friendly.

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Author’s Contributions

Ouiame Chakkor: Made literature search, prepared the samples used in the experimental work, and wrote the manuscript.

Mehmet Fatih Altan: Supervised the experiment work and analyze the results.

Orhan Canpolat: Edited the revisions, and helped in manuscript preparation.

Ethics

There are no ethical issues after the publication of this manuscript.

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