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Research on Resistance to Sulfate and Chloride of Reinforced Metakaolin-Based Geopolymers

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Abstract: This research aims to examine the sulfate and chloride durability behaviors of geopolymer composites synthesized by the alkali activation of metakaolin (MK), reinforced by boron waste colemanite (C), silica fume (SF), and slag (S). The resultant geopolymer composites were subjected to magnesium sulfate ($MgSO_4$) solution (concentration 10%), sodium sulfate (Na_2SO_4) solution (concentration 10%), and sodium chloride (NaCl) solution (concentration 10%) for up to 12 months. The compressive and flexural strengths, microstructure (X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM)), weight changes, and visual inspection of the geopolymer composites were investigated to evaluate their durability behavior. The conclusion proved that the mix of a metakaolin with the addition of 10% C, and 20% SF shows the highest compressive strength for the studied range of mixture design. In geopolymer mortar samples, compressive strength increase was observed due to sodium chloride and sodium and magnesium sulfate effects after three months, while a decrease was observed after six months. These fluctuations were due to the diffusion of solutions in the matrix, formed during the transition of alkali ions from the samples to the solution. The loss of strength after three months could be due to the presence of microcracks, as a consequence of ettringite and gypsum creation in the pores, as well as the transition of alkalis from the sample matrix to the solution.

Keywords: Geopolymer, metakaolin, colemanite waste, silica fume, magnesium sulfate, sodium sulfate, sodium chloride

1. Introduction

Rapid urbanization has significantly increased the demand for concrete as a construction material in recent years; this situation is expected to continue for the foreseeable future. The most important component in concrete is the ordinary Portland Cement (OPC), which has been used in construction for nearly 200 years. However, there are environmental problems caused by Portland Cement, on a global scale. The Portland Cement industry is reported to account for 5% of global CO_2 emissions. It is known that approximately 0.8 tons of CO_2 are released into the atmosphere during the production of 1 ton of cement. Also, it has been seen to cause greenhouse gasses and acid rain by emitting SO_3 and NO_x. The search for alternatives to provide a balance between an increase in construction and environmental protection has accelerated due to this situation (Liu et al., 2020; Rivera et al., 2020). Geopolymer is an important alternative and has low CO_2 emissions and many excellent properties. Geopolymer has shown significant potential in building materials, fire-resistant ceramics, composites, and other applications (Bouna et al., 2020; Medri et al., 2020).

The most widely tested aluminosilicate precursor materials in geopolymer production are metakaolin, followed by fly ash, slag, and various secondary or waste materials (Clausi et al., 2016). Silica fume and colemanite are important alternatives for waste materials. Uysal et al. (2018) used up to 40% silica fume and colemanite together with metakaolin.

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Due to the porous structure of the metakaolin, colemanite and silica were found to act as fillers during geopolymerization and to improve mechanical properties up to certain proportions.

Sulfate attack from the external environment is observed in infrastructure where wastewater is treated in seawater, contaminated soil, or groundwater and this has various effects on materials that come into contact with these environments (Kwasny et al., 2018). The impacts of the attack depend on the factors directly relating to the concrete itself, such as the type of cement preferred in that region and the overall quality of the concrete, as well as the current, ambient aggressivity conditions. Aggressive environmental conditions depend on the concentration and mobility of the sulfate ions, the type of cations it has (Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}), and pH (Komnitsas et al., 2013; Ren et al., 2017). As a result of the sulfate attack, compounds such as calcium hydroxide (CH), monosulfate (AFm), and tricalcium aluminate (C_3A) react with sulfate ions, causing expansive salt crystals such as gypsum and ettringite (ettringite is more harmful than gypsum) to form in the hardened cement paste (Tiburzi et al., 2020; Nosouhian et al., 2019). Consequently, the expansion and cracking caused by the sulfate effect, adversely affect the structural integrity of the concrete. Furthermore, the increase in cracking increases the effect of the attack. An alternative solution to this situation is to improve the composition of the concrete by making changes. Cement with reduced C_3A content (sulfate resistant) or reduced CH content can be used in concrete instead of using blended cement to increase sulfate resistance (Irassar, 2009). Recently, due to its ceramic-like microstructure, geopolymer binders have been a promising solution to the sulfate effect.

Albitar et al. (2017) produced concrete samples with fly ash (class F) and slag and the samples were tested in 5% Na_2SO_4, 5% NaCl, 5% Na_2SO_4 + 5% $MgSO_4$ and 5% H_2SO_4 solutions for up to 9 months. Kwasny et al. (2018) investigated the durability performance of lithomarge-based geopolymer mortars. Geopolymer samples were cured at normal room temperature and then exposed to magnesium and sodium sulfate, hydrochloric acid, and sulphuric acid solutions. Portland cement mortars were prepared as reference samples. Rashidian-Dezfouli & Rangaraju (2017) studied the performance of geopolymers using three main materials: glass fiber, glass powder, and fly ash. Alkali activators were used in different proportions of sodium silicate and sodium hydroxide mixtures. Changes in the strength and weight of the samples were investigated for 120 days under the influence of a 5% sodium sulfate solution. When all of the studies were examined, it was seen that geopolymers provide high performance against durability effects. In the tests examined, it was observed that, in general, low concentrations of sulfate and chloride solutions were used.

Many studies have been performed on the behavior of Portland concrete and geopolymer composites under the effects of sulfate and sodium chloride. Although there are a significant number of studies on the behavior of geopolymers, which are produced by using materials such as slag, fly ash, against sulfate and chloride, there is a limited number of studies on metakaolin-based geopolymers. Besides, in this study, not only the effect of metakaolin is investigated, but also the effect of silica fume and colemanite. This study tested the behavior of a metakaolin-based geopolymer containing up to 20% colemanite and silica fume, under the influence of sulfate and chloride at a high concentration of 10% (instead of low concentration studies), which enable researchers and industry to design promising mixes for a variety of applications. The geopolymer samples were tested for up to twelve months (3, 6, and 12 months). Flexural and compressive strengths, weight changes, and visual inspection of the samples were investigated as a result of the solution effect. Besides, XRD and SEM analyzes were performed before and after the sulfate and chloride test.

2. Methodology

2.1 Materials

In this study, metakaolin was used as the main material and was supplied by the Kaolin EAD Company. The value of specific gravity for metakaolin is 2.52. The total ratio of alumina + silica + iron oxide is 97.18% in metakaolin and it has high pozzolanic activity. The remaining amount of metakaolin is 0.70% on the 45 µm sieve, so it is a fine-grained raw material. Having smaller particles creates a higher surface area and, due to this effect, they are very reactive. Slag was provided by the Bolu Cement Company (specific gravity is 2.91). Colemanite was supplied by the Eti Maden Boron Company (specific gravity is 2.42). Silica fume was provided by Antalya Inc. (Antalya/Turkey) and it has a specific gravity value of 2.20. The Blaine-specific surface areas of the slag and silica fume are 450 m^2/kg and 20,000 m^2/kg, respectively. Table 1 shows the chemical compositions of the raw materials.

Table 1 - The raw materials' chemical analysis

Chemical analysis, %	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O	B_2O_3	L.O.I.
MK	56.10	40.25	0.85	0.55	0.19	0.16	0.55	0.24	-	1.11
S	40.60	12.83	1.37	0.75	36.08	6.87	0.68	0.79	-	0.03
SF	90.58	1.37	0.15	-	0.35	4.02	2.55	0.58	-	0.40
C	5.00	0.40	0.08	-	26.02	3,00	-	0.50	40.00	25.00

Standard sand has a specific gravity value of 2.6 and a unit weight value of 1.35 kg/m^3. Standard sand was utilized for geopolymer preparation. Besides, the water absorption rate of the sand is 1.276. Standard sand was provided from the Limak Cement Factory (according to BS EN 196-1). Sodium hydroxide and sodium silicate were utilized as alkali activators. Alkali activators were provided by Merck. A blend of sodium silicate (SiO_2 / Na_2O = 3.29) and sodium hydroxide (12M) was used.

2.2 Mix Design and Specimen Preparation

In this study, the geopolymer mortars were manufactured using colemanite, standard sand, silica fume, metakaolin, slag, sodium hydroxide, and sodium silicate. While preparing the mixtures, the sodium hydroxide/sodium silicate ratio of 1:2, alkali activator/binding material ratio of 1:1, and binding material/sand ratio of 1:2.5 were kept constant. Water was used while preparing the sodium hydroxide solution, and no additional water was used. For this reason, sodium silicate/binder ratio and sodium hydroxide/binder ratio were used when describing the mixture instead of the water/binder ratio. 5 series were used for the mixture. Fig. 1 shows the mixture quantities required for 450 g of binder material. A detailed mix description was made for 100% metakaolin from these series. In the other series, there was only a change in the amount of binders.

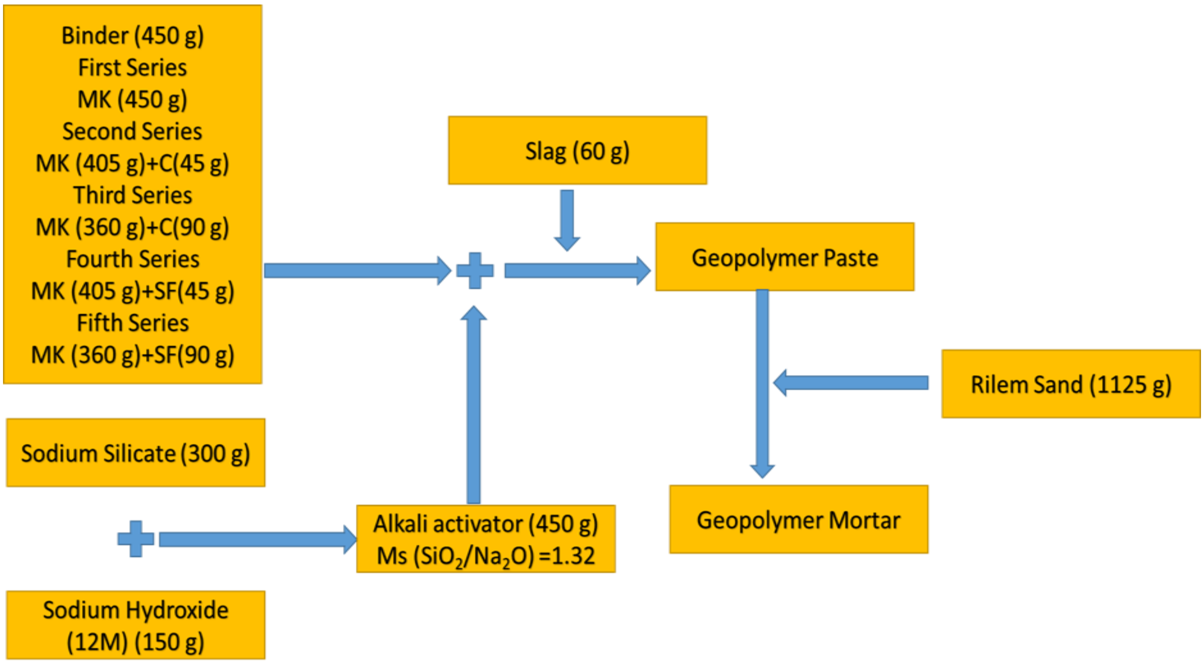

Fig. 1 - Mixing method of samples (g).

The preparation of the control mixture (100% MK) is as follows: 450 g of metakaolin was mixed with a pre-prepared mixture of sodium silicate and sodium hydroxide (12M), using a mixer drill. The activator/binder ratio was considered as being 1:1. Later, 60 g (13% of the binder) slag (as a calcium source) was added and utilized for a shorter setting time. Slag with a composition of 36% Ca and a high content of alumina and silica was not used as a binder for this mixture. The reason for using the slag was that it was useful in curing the geopolymer. Accordingly, slag was added to the mixture after mixing activator and binder materials. Thus, it also had an impact on early and late age strength characteristics.

Finally, the standard sand was added and the sand/binder ratio was taken as 2.5:1. The vibration was applied to the samples after placement in the molds (50 mm side cubes and 40 x 40 x 160 mm prisms). Samples were kept in the mold for 2 hours after vibration and then removed, due to the early setting, with the effect of the slag used. Samples were kept at a relative humidity (50 ± 4%) and room temperature for 24 hours after being removed from the mold. Then, the samples were placed in a fireproof oven bag and kept at 60°C in the oven for 72 hours. Before heat curing, the samples were placed in a fireproof oven bag which aimed to reduce the evaporation of the water in it. After the oven process, the samples were then stored in plastic boxes until the durability tests were carried out after 28 days. Details of the 5 series are shown in Table 2. The first series is 100% MK series and the other four mixtures were obtained by mixing colemanite and silica fume with up to 20% of metakaolin, respectively.

Table 2 - Geopolymer mixtures

Mix ID	Binder
MK	100% MK
10SF	90% MK+10% SF
20SF	80% MK+20% SF
10C	90% MK+10% C
20C	80% MK+20% C

2.3 Test Procedure

The geopolymer samples were exposed to 10% sodium sulfate (Na_2SO_4), 10% magnesium sulfate ($MgSO_4$), and 10% sodium chloride (NaCl) solutions in plastic storage boxes for up to 12 months at room temperature, after 28 days. The samples were placed in the oven at 105ºC for 24 hours, prior to the test for better absorption and effectiveness of the solution. The solution was renewed in the 1st, 2nd, 3rd, and 6th months to maintain the concentration and pH of the solution and, thus, to ensure homogeneity of the test. After the samples and solutions were stored in a plastic box (1 unit volume of sample for 4 units of solution), the test was started. After 3 months, 6 months, and 12 months' duration, samples were removed from the plastic box and left to dry at room temperature (23± 2°C). The surfaces were then cleaned using a wire brush. After the test, the compressive and flexural strengths, and weight change results of the samples were compared with the 28-day results. Also, microstructural analyses and visual inspections were carried out. While 50 mm cube samples were used for compressive strength results, prism samples (40x40x160 mm) were used for flexural strength.

3. Results and Discussion

3.1 Strength Results

In this study, the compressive strength results obtained from exposure to the sulfate and chloride solutions were checked with the results after 28 days (Figs. 2-4). If the results are examined in general, two conclusions can be drawn: 1) The replacement of up to 20% of SF increased the compressive strength. When the silica fume was substituted into the geopolymer matrix, the creation of both C-S-H gel and aluminosilicate in the samples was accelerated since the Si and Al ratio increased and the reactivity increased with this process. Also, the fact that the silica fume was very finely grained allowed the voids in the matrices to shrink. This situation caused progress in geopolymer matrices. Using it at a higher rate reduced the workability, causing a negative effect on mechanical properties. Higher specific surfaces in the silica fume resulted in reduced workability (Wu et al., 2019; Ardalan et al., 2017).

2) Colemanite waste provided a favorable influence up to a replacement of 10%. So colemanite waste acted as a filler during geopolymerization. It was also found that it formed a protective layer. These two conditions improved the permeability properties of the geopolymer and improved the mechanical properties. After 10%, it was guessed that the anions and cations, formed by unstable compounds in the system, interfered with the activation mechanism of cement. The effect of this situation was that the deterioration of mechanical properties began to appear (Uysal et al., 2018; Celik et al., 2018; Aygörmez et al., 2020). This condition showed that, although the loss of durability after a certain period was seen in the geopolymer samples due to sulfate and chloride effects, the replacement of two raw materials developed the durability properties in the geopolymer composites (Ren et al., 2017).

When examined in Figs. 2-4, it was observed that geopolymer samples were slightly strengthened, up to 3 months after exposure to sulfate and chloride solutions, but then the strength generally entered a decreasing trend regardless of the initial state. Geopolymerization continued with solution effects up to 3 months and this created a strength increase. The calcium expansion products combined with chloride or sulfate crystals to replenish the pore structure, making the geopolymer sample compact and resistant (Duan et al., 2016). After 3 months, sulfate and chloride attacks caused significant cracks in geopolymer samples and high porosity. This led to a loss of strength due to erosion.

The case of magnesium sulfate can be specifically considered. According to the effect of magnesium sulfate, fluctuations in compressive strength results were observed for up to 12 weeks. These fluctuations were due to the diffusion of Mg to the matrix formed during the transition of alkali ions from the samples to the solution (Elyamany et al., 2018; Bakharev, 2005). After this period, a strength reduction was observed for up to 48 weeks. Also, the pre-test samples were placed in the drying oven at 105°C for 24 hours and this situation provided more effective absorption of sulfate solutions. This trend could be related to the fact that temperature had a favorable effect on the voids ratio. The loss of strength after 3 months could be due to the presence of microcracks as a consequence of ettringite and gypsum being created in the pores, as well as the transition of alkalis from the sample matrix to the solution (Bakharev, 2005; Thokchom et al., 2010).

The results of the magnesium sulfate, sodium sulfate, and sodium chloride effects could be compared. Magnesium sulfate was a more aggressive solution than sodium sulfate (Zhang et al., 2016; Škvára et al., 2005). After 3 months, the loss of strength was less due to sodium sulfate than the loss of strength due to the effects of magnesium sulfate. The penetration of chloride ions was greater than that of sulfates and this was due to the smaller size of the chloride ions (Zhang et al., 2016; Škvára et al., 2005). Because of this, increases in the compressive strength were greater for sodium chloride than those exposed to sulfate.

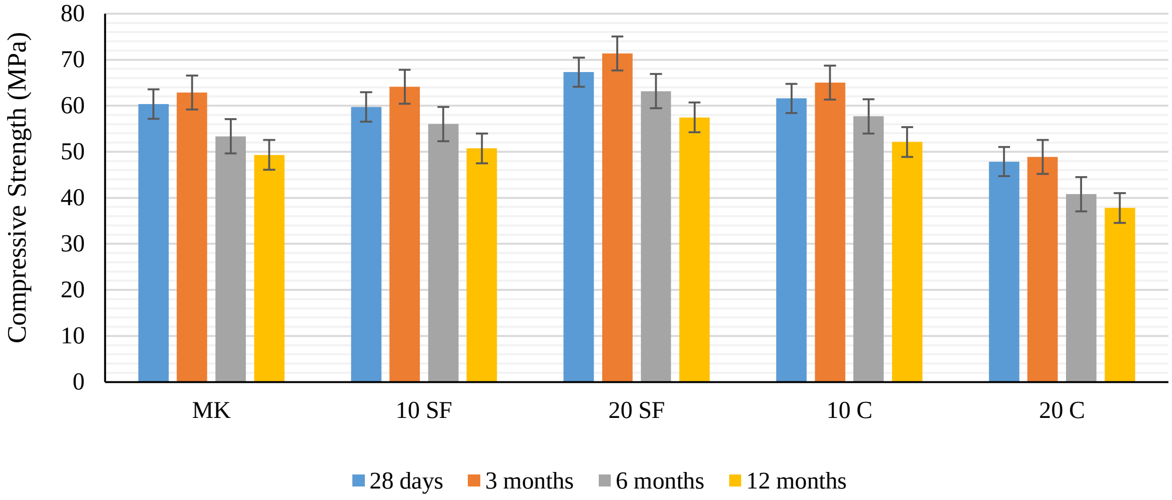

Fig. 2 - Residual compressive strengths after the magnesium sulfate effect

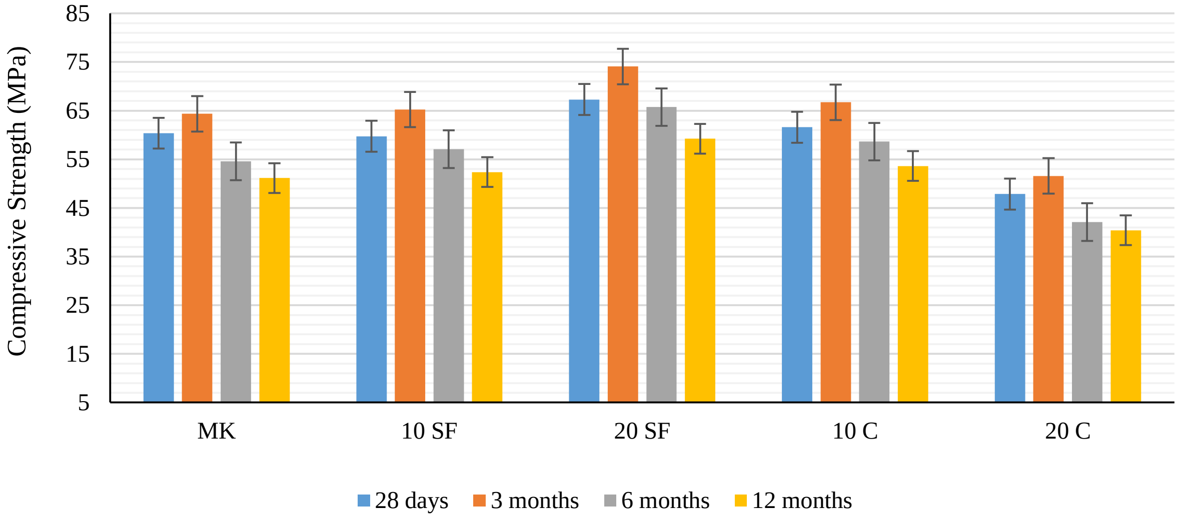

Fig. 3 - Residual compressive strengths after the sodium sulfate effect

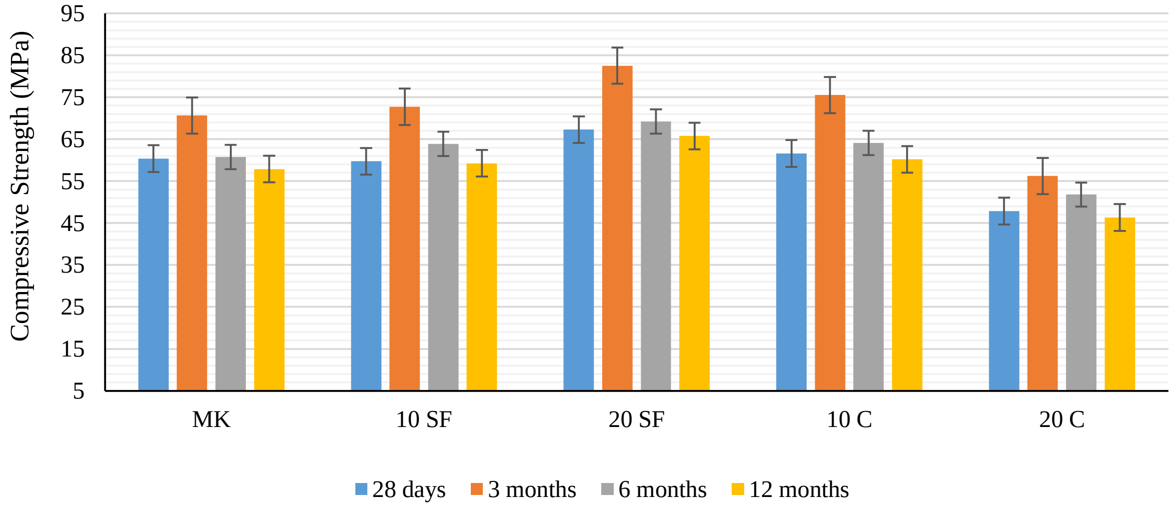

Fig. 4 - Residual compressive strengths after the sodium chloride effect

According to the magnesium sulfate effect, 71.36 MPa, 63.17 MPa, and 57.45 MPa of the residual compressive strengths were obtained for sample 20SF after 3, 6, and 12 months, respectively. For sample 10C, the results were 65.02 MPa, 57.71 MPa, and 52.12 MPa after 3, 6, and 12 months, respectively. According to the sodium sulfate effect, 74.08 MPa, 65.74 MPa, and 59.22 MPa of the residual compressive strengths were obtained for sample 20SF after 3, 6, and 12 months, respectively. For sample 10C, the results were 66.71 MPa, 58.63 MPa, and 53.63 MPa after 3, 6, and 12 months, respectively. According to the sodium chloride effect, 82.51 MPa, 69.23 MPa, and 65.76 MPa of the residual compressive strengths were obtained for sample 20SF after 3, 6, and 12 months, respectively. For sample 10C, the results were 75.52 MPa, 64.12 MPa, and 60.19 MPa after 3, 6, and 12 months, respectively.

The flexural strength results obtained from exposure to the chloride and sulfate solution effects were checked with the results after 28 days (Figs. 5-7). When the flexural strength results were investigated for the geopolymer mixtures, a decrease was seen instead of an increase according to the compressive strength results due to the effects of magnesium sulfate, sodium sulfate, and sodium chloride (Thokchom et al., 2010). When compressive and flexural strength reduction ratios were compared, flexural strength results were found to be more sensitive. There was a decreasing tendency in flexural strength caused by the growth and propagation of microcracks in porous structures (Zhang et al., 2016). In terms of the flexural strength of the three solutions, the sequencing was similar to the compressive strength results (Zhang et al., 2016; Škvára et al., 2005). For these reasons, the rate of decrease in flexural strength was lowest in sodium chloride, then sodium sulfate, and magnesium sulfate, respectively.

According to the magnesium sulfate effect, 10.32 MPa, 9.96 MPa, and 9.44 MPa of the residual flexural strengths were obtained for sample 20SF after 3, 6, and 12 months, respectively. For sample 10C, the results were 9.05 MPa, 8.27 MPa, and 7.64 MPa after 3, 6, and 12 months, respectively. According to the sodium sulfate effect, 11.83 MPa, 10.74 MPa, and 9.82 MPa of the residual flexural strengths were obtained for sample 20SF after 3, 6, and 12 months, respectively. For sample 10C, the results were 10.49 MPa, 9.45 MPa ve 8.56 MPa after 3, 6, and 12 months, respectively. According to the sodium chloride effect, 12.28 MPa, 11.08 MPa, and 9.93 MPa of the residual flexural strengths were obtained for sample 20SF after 3, 6, and 12 months, respectively. For sample 10C, the results were 10.88 MPa, 9.83 MPa, and 8.75 MPa after 3, 6, and 12 months, respectively.

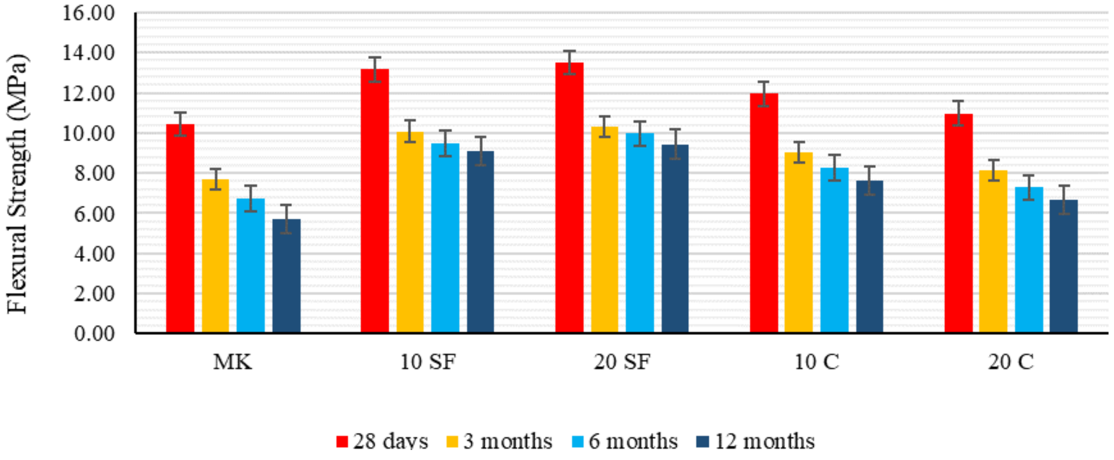

Fig. 5 - Residual compressive strengths after the magnesium sulfate effect

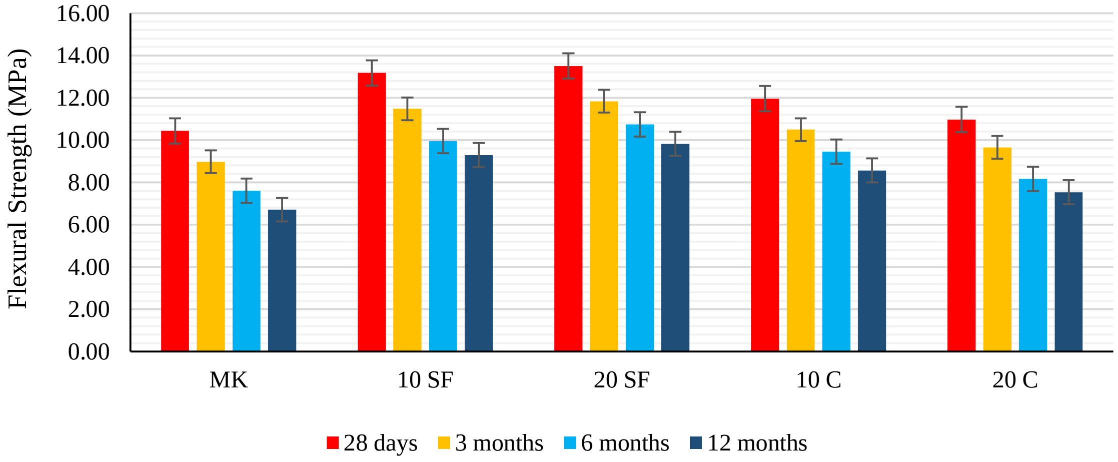

Fig. 6 - Residual compressive strengths after the magnesium sulfate effect

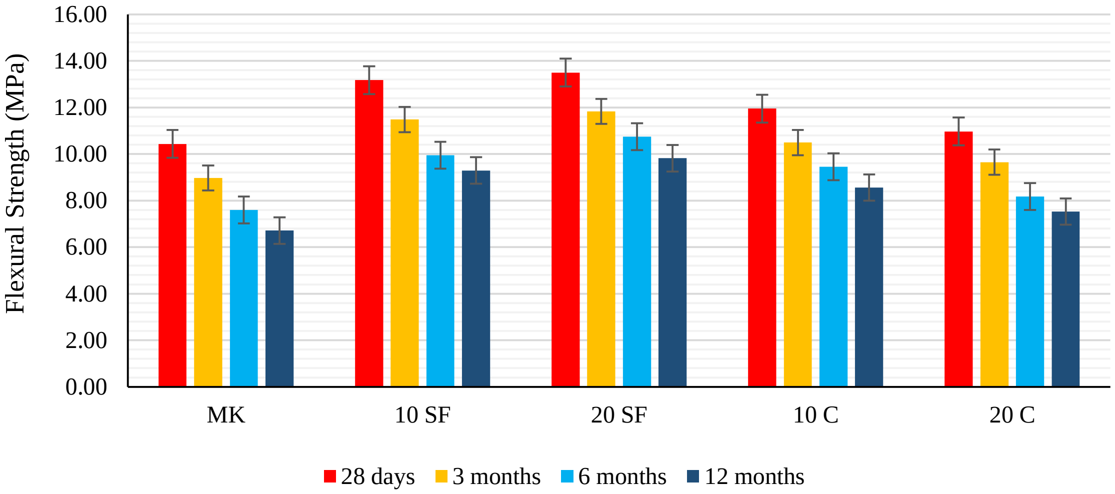

Fig. 7 - Residual compressive strengths after the magnesium sulfate effect

3.2 Weight Change Results

In the geopolymer samples, the weight changes in sulfate and chloride effects can be mainly due to two processes: 1) dissolving the paste in the solution (weight loss formation) and 2) absorption from the solution into the geopolymer structure (resulting in weight increase) (Rashidian-Dezfouli and Rangaraju, 2017). Magnesium sulfate, sodium sulfate, and sodium chloride effects resulted in increased weights for up to 3 months. The initial weight increase was thought to be due to the small absorption from the solution into the microstructure of the samples (Kwasny et al., 2018). In other words, this was due to the fact that the voids were filled with sulfate salts, sodium chloride salts, and hydration products (Bakharev, 2005). So weight gain was due to the voids ratio and the formation of reaction products, such as ettringite and gypsum, in the form of white deposits on the surface and pores exposed to the solution. The curing of all samples at 60°C explained that the voids and pores present in the samples were almost substantially anhydrous at the beginning. Also, the pre-test samples were placed in the drying oven at 105°C for 24 hours and this situation provided better, more effective absorption of sulfate and chloride solutions. Although the reasons for the loss of weight were not clear, alkali leakage from the samples was thought to be the most important cause due to the solution effects. In other words, the decrease in weight after exposure for 3 months was due to the migration of alkalis from the samples into the solution and, possibly, due to partial disintegration and dissolution of the geopolymer products (Elyamany et al., 2018). In general, the weight gain in mortar samples over 12 months was thought to be due to the partial filling and saturation of the voids and pores, despite the small weight loss amount over time caused by dissolution in the paste. Magnesium sulfate was a more aggressive solution than sodium sulfate (Škvára et al., 2005). The penetration of chloride ions was greater than that of sulfates; this was due to the smaller size of the chloride ions (Škvára et al., 2005). For these reasons, the highest rate of weight increase occurred in sodium chloride and then in sodium sulfate and magnesium sulfate, respectively.

Rates of weight increase in the geopolymer mortars with the magnesium sulfate effect were between 3.47% and 4.86% after 3 months, between 2.83% and 4.34% after 6 months, and between 2.47% and 3.88% after 12 months (Fig. 8). Rates of weight increase in the geopolymer mortars with the sodium sulfate effect were between 4.56% and 5.84% after 3 months, between 4.32% and 5.40% after 6 months, and between 3.26% and 4.47% after 12 months (Fig. 9). Rates of weight increase in the geopolymer mortars with the sodium chloride effect were between 5.89% and 6.76% after 3 months, between 5.25% and 5.96% after 6 months, and between 4.45% and 5.38% after 12 months (Fig. 10).

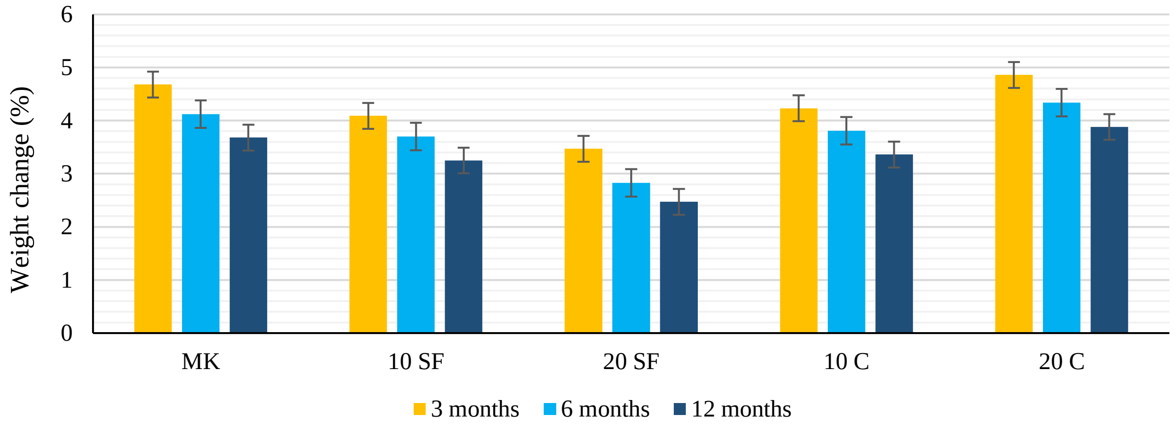

Fig. 8 - Results of weight change due to magnesium sulfate effect

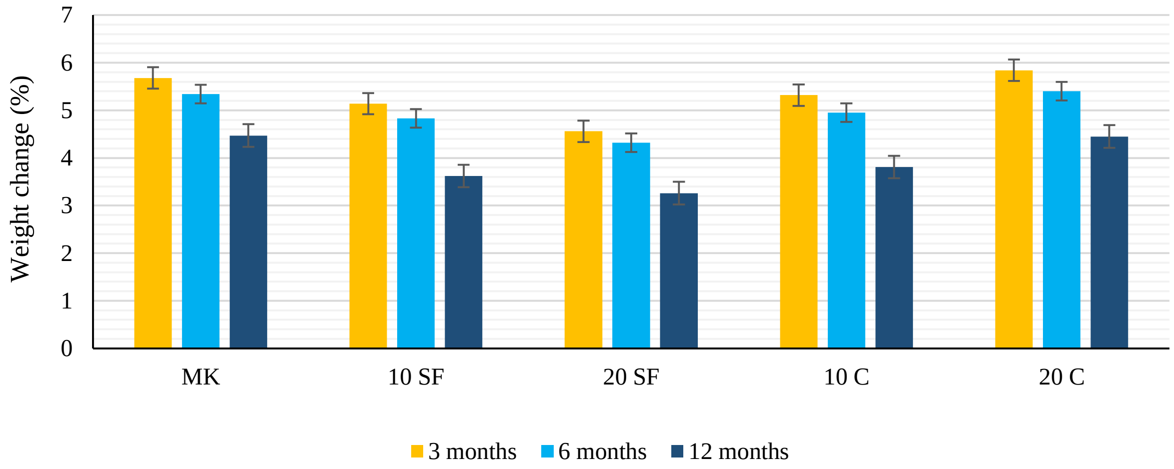

Fig. 9 - Results of weight change due to sodium sulfate effect

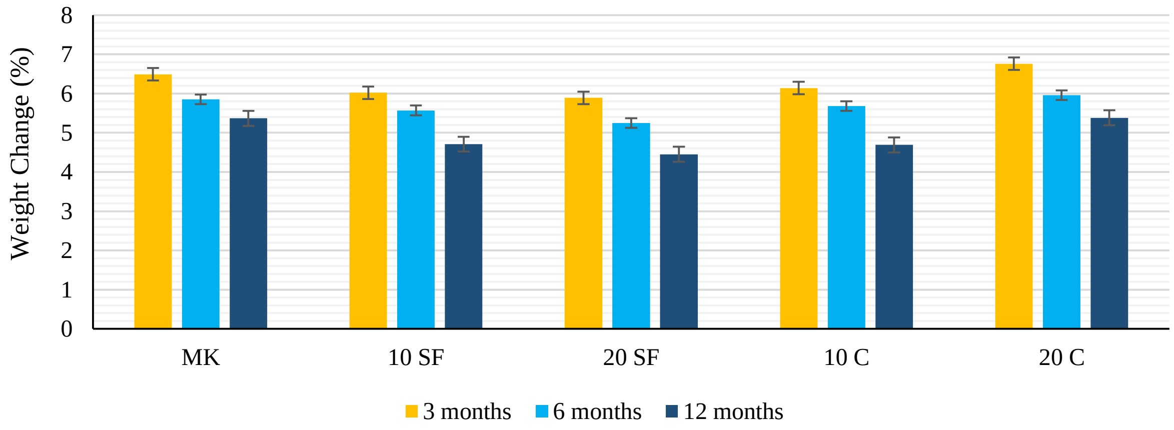

Fig. 10 - Results of weight change due to sodium chloride effect

3.3 Visual Inspection and Analyzes

Geopolymer samples were compared to the previous case before exposure to magnesium and sodium sulfate and sodium chloride. It was noticed that there was no change in the appearance of geopolymer mortars and there were no visible cracks, but the surfaces were whitened. Soft and dust-like sediments on the samples (due to sulfate exposure) became even more hardened over time. Also, few needles were seen on the specimen surfaces. Therefore, it could be thought that geopolymer specimen weight increased due to the penetration of the solution into these samples' voids and pores (Chen et al., 2017; Zhou et al., 2016; Atahan & Arslan, 2016). Corrosion products were not observed on the surface of geopolymer samples held in a NaCl solution. Magnesium sulfate, sodium sulfate, and sodium chloride effects are shown in Fig. 11 for 12-month samples.

Fig. 11 - Visual inspection in all samples over 12 months a) with magnesium sulfate effect b) with sodium sulfate effect c) with sodium chloride effect

Within the scope of this study, SEM analyzes were conducted to investigate the conditions of samples MK, 10C, and 20SF before and after the magnesium sulfate effect. When SEM micrographs were examined before exposure to the solution, it was determined that a good homogeneity was observed in the geopolymer gel. It was observed that the matrix had continuity in samples 20SF and 10C. In this way, a good bond structure was observed in the presence of colemanite and silica fume (Uysal et al., 2018). In this way, a compact and consistent structure was obtained. SEM micrographs of samples before and after the solution are shown in Fig. 12.

Magnesium sulfate attack affected the expansion stress in the geopolymer matrix due to gypsum and ettringite formation in cemented materials (Bakharev, 2005; Müllauer et al., 2013; Maes & Belie, 2014). As before described, the superb resistance of geopolymers to sulfate action was attributed to its low Ca content and higher stable and crosslinked aluminosilicate geopolymer structure (Sata et al., 2012; Karakoç et al., 2016). Also, the main products in the geopolymerization were less sensitive to sulfate effects than normal cement hydration products (Chindaprasirt et al., 2007). Previous studies suggested that low Ca content was a significant parameter that determined and affected the fly ash-based geopolymers' strength (Karakoç et al., 2016).

Therefore, the main product was an alkali aluminosilicate gel having a 3D framework (a zeolite product) which was importantly unlike the hydrated calcium silicate gel occurring in the Portland cement hydration (Karakoç et al., 2016). It can be explained that geopolymer composites had higher compressive strength due to the silica fume and colemanite having fine particles and the effect of filling the voids. When these analyzes were examined, it was found that metakaolin-based geopolymer samples were resistant to chemical attacks. The microstructures of the samples were preserved after exposure to magnesium sulfate. When the surface microstructures of geopolymer samples were examined, it was observed that no expansive product or crystals were present. However, a large number of large products or crystals were seen in the internal microstructure of the samples. It was found that the chloride and sulfate ions presented in the solution entered the interior of the samples, followed by the formation of expansive products and crystals and, thus, high porosity and cracking. This agreed with the compressive strength results found (Ren et al., 2017).

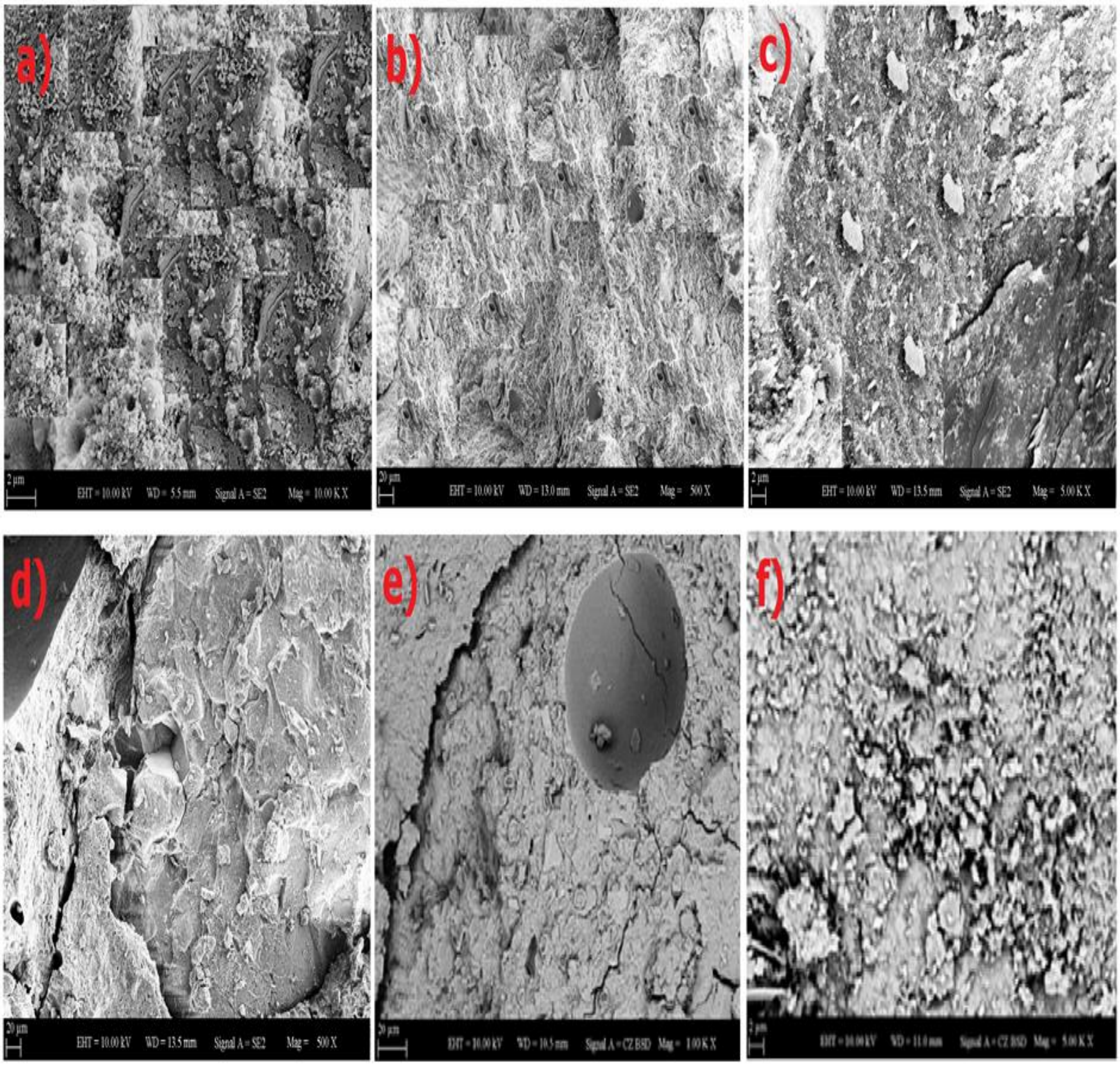

Fig. 12 - SEM images of samples a)MK, b)10C; c)20SF before the magnesium sulfate effect and samples d)MK, e)10C and f)20SF after the magnesium sulfate effect

XRD analyzes were performed before and after the magnesium sulfate effect in samples MK, 10C, and 20SF. XRD analyzes of samples after and before the magnesium sulfate effect are shown in Figs. 13-14. According to XRD analysis before the sulfate effect, quartz crystal peaks were determined. Mullite was detected in XRD analysis with quartz. While broadband was detected at 2Ө between 20° and 30°, this showed that the geopolymer properties were satisfactory. No difference was found in sample 10C except for the slippage in the peaks. In the sample 20SF, the amount of silicon oxide increased and quartz peaks were predominant (Uysal et al., 2018).

XRD analyzes of samples MK, 10C, and 20SF, under the influence of magnesium sulfate, were examined and instead of a large hump between 18^o and 36^o 2Ө (reflecting amorphous geopolymer characteristics (He et al., 2013)), a hump between 18^o and 50^o 2Ө was formed in these samples. This hump indicated that geopolymerization happened, while a pure geopolymer binder and a low rate of raw materials had a role as inactive fillers (He et al., 2012). SiO_2 and Al_2O_3 in the metakaolin material emerged as an amorphous phase involved in the geopolymerization. This showed that the amorphous phases present in the main materials were reactive and involved in the geopolymerization, which was consistent with the literature (He et al., 2013). Thereby, geopolymers were amorphous to semi-crystalline aluminosilicates (He et al., 2012). In the event of the exposed specimen, quartz was known as the main crystalline phase. In contrast to the sulfuric acid effect, quartz peak intensity increased with magnesium sulfate. This was related to the fact that sulfate ions in the solution entered the inside of the geopolymer sample and produced crystals in the geopolymerization reaction. These results could be utilized to determine why geopolymer samples had a higher strength over 3 months under the influence of magnesium sulfate (Salami et al., 2017). Although gypsum and ettringite formations were recognized to be the main reason for degradation in Portland cement-based samples subjected to the sulfate effect, no clear ettringite or gypsum signs were visible in XRD patterns of all samples. The results were agreeable with the studies in (Ismail et al., 2013; Bakharev et al., 2002), in which ettringite and gypsum formation were not affirmed in the geopolymer samples exposed to sulfate effects.

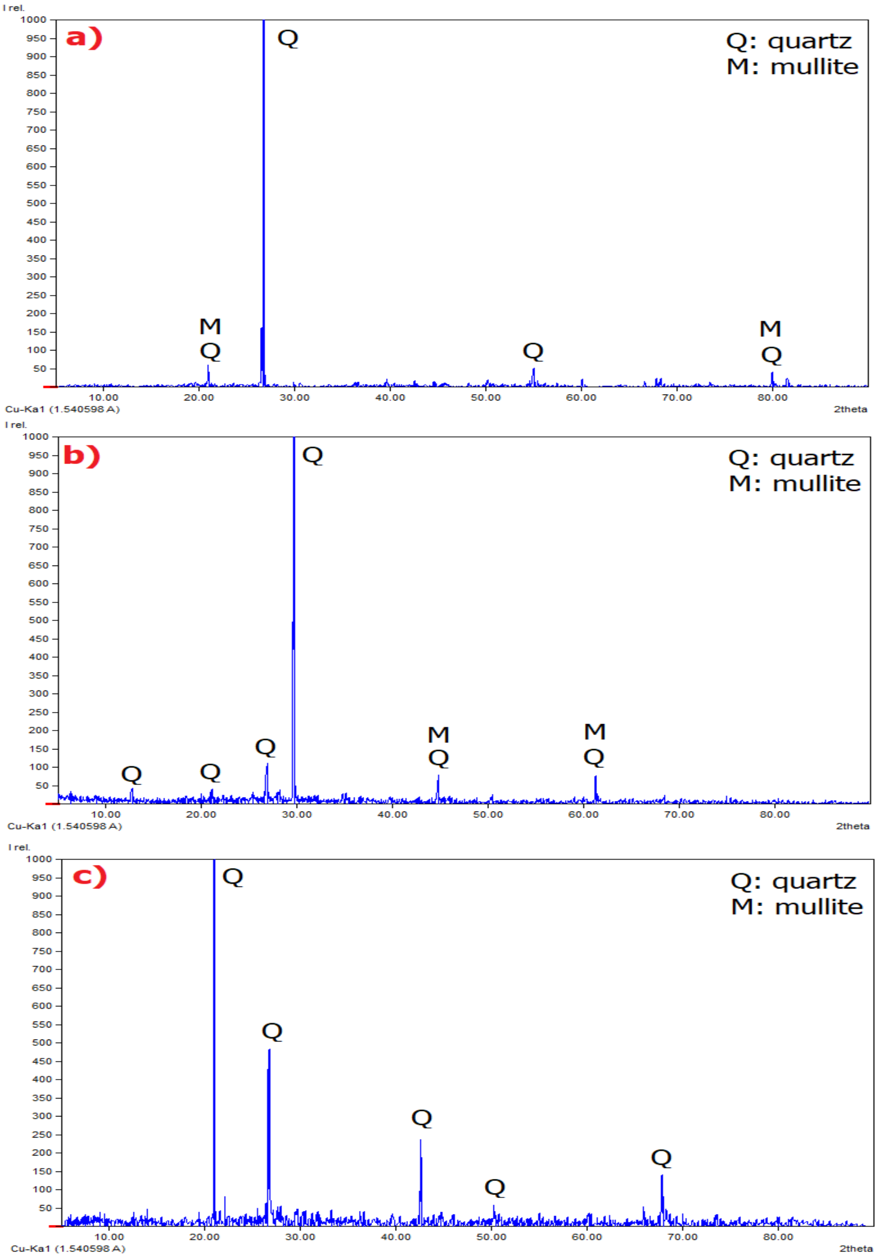

Fig. 13 - XRD patterns of samples a)MK, b)10C and c)20SF before magnesium sulfate effect

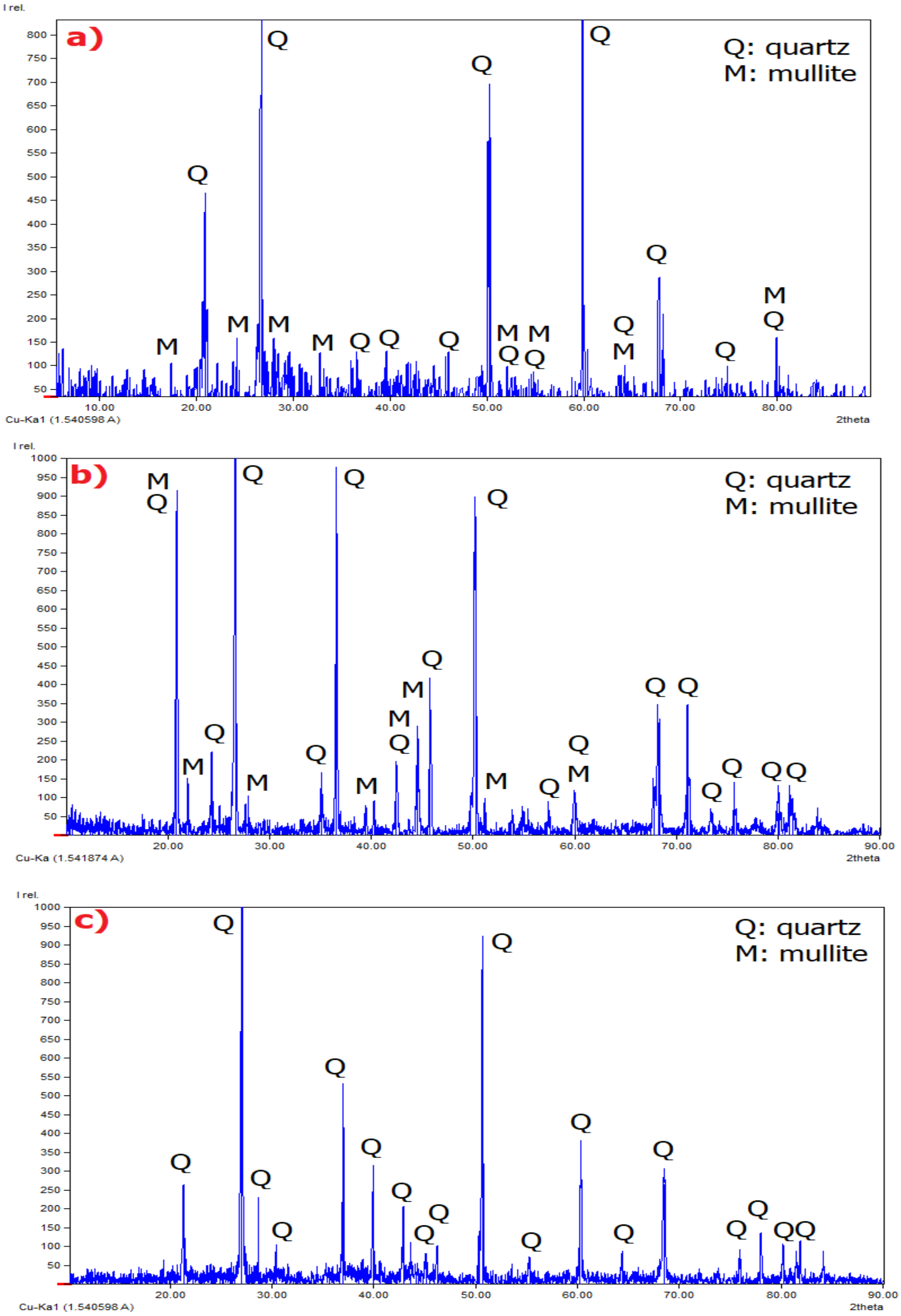

Fig. 14 - XRD patterns of samples a)MK, b)10C and c)20SF after magnesium sulfate effect

4. Conclusion

In this paper, an attempt was made to examine the feasibility of adding various materials to a geopolymeric matrix and to examine the influence of these additions on the strength, mechanics, and durability characteristics of the samples produced. When the results of the preliminary tests were examined, it was found that a 20% ratio of silica fume and colemanite substitution was critical to the mechanical properties. Higher utilization of silica fume reduced workability, while higher utilization of colemanite resulted in poor performance. When the geopolymer samples were under the influence of sulfate, compressive strength, and weight increases were observed after 3 months, and decreases were observed after 6 months. This showed that there were fluctuations in mechanical properties under the influence of sulfate. These fluctuations were caused by transitions between solutions and the geopolymer matrix. Also, keeping the test samples at 105°C for 24 hours, to absorb the solution, accelerated these transitions. After 3 months, in addition to the transition of alkalis from the sample matrix to the solution, reductions in the results were observed with the presence of micro-cracks in the pores, caused by the formation of ettringite and gypsum. Magnesium sulfate was a more aggressive solution than sodium sulfate. The penetration of chloride ions was greater than that of sulfates; this was due to the smaller size of chloride ions. In light of this fact, the rates of increase in the UPV, compressive strength, and weight were highest in sodium chloride and then in sodium sulfate and magnesium sulfate, respectively. The rates of decrease in flexural strength occurred lowest in sodium chloride and then in sodium sulfate and magnesium sulfate, respectively. The microstructures of the samples were preserved after exposure to magnesium sulfate, according to SEM analysis. According to XRD analysis, quartz peak intensity increased with magnesium sulfate. This was related to the fact that sulfate ions in the solution entered the inside of the geopolymer sample and produced crystals in the geopolymerization reaction.

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