Sulfuric acid effect and application of freezing-thawing curing on long fiber reinforced metabentonite and slag-based geopolymer composites

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Abstract. In this study, different types of metaboronite (MB) and slag (S)-based geopolymer were produced based on origin, polyvinyl alcohol (PVA) and basalt (B) fiber at different percentages of 0.2%, 0.4%, and 0.6%. A total of 7 series were produced. Two steps of curing method were applied for the samples, the first step was at room temperature from day 1-7, and the second step freezing-thawing from 8-28 days. Thus, the applicability of a curing method that used less energy instead of heat curing was investigated. Due to the freezing-thawing curing, the continuation of geopolymization reactions was ensured and a compact structure was created. The produced samples were subjected to 10% sulfuric acid effect for 3 months after the 28th day. Compressive strength, flexural strength, ultrasonic pulse velocity (UPV), and weight losses due to acid effects were found. Despite the decrease in mechanical properties after the acid effect, the geopolymer products didn’t experience easy dispersal because they had strong aluminosilicate bonds, crystalline phase formation, morphology, and lower calcium content that provided high stability. Also, SEM, XRD, FT-IR, and TGA-DTA analyzes and visual inspection resulting from the acid effect were examined.

Keywords: basalt fiber; freezing-thawing; geopolymer; metaboronite; PVA fiber; slag; sulfuric acid

1. Introduction

Due to rapid urbanization today, concrete demand has an important place in the construction industry and this situation is expected to continue in the future. Traditional Portland Cement, which has an important place in this sense, has been used for more than 200 years (McGuire et al. 2011). Cement production is thought to cause 5% of the current carbon dioxide absorption in the world (Flower and Sanjayan 2007). Traditional Portland Cement production also leads to the greenhouse effect and acid rain-inducing gases such as SO$_2$ and NO$_x$ (Rashad 2013). To prevent environmental damages caused by these effects and to meet the demand for construction increase, the search for an alternative product to Portland Cement concrete has an important place. Geopolymer product is a new generation material that is an alternative to Portland Cement in this sense and can cover the disadvantages of Portland Cement products. It is possible to use large numbers of aluminosilicate solids produced in nature by natural sources or industrially as binders in the production of geopolymers. Aluminosilicate materials are easily dissolved in alkaline solutions due to their amorphous silica and alumina content and can play a role in geopolymer synthesis (Xu and Van Deventer 2000, Kurtoglu et al. 2018, Wang et al. 2005, Duxson et al. 2007). Such aluminosilicate materials include feldspar and albite obtained by natural means, metakaolin produced by calcining kaolin, fly ash and slag produced as waste material (Álvarez-Ayuso et al. 2008).

Bentonite is a natural clay with different minerals such as cristobalite, montmorillonite and feldspar, volcanic glass, and crystal quartz, which are available in many countries in the world (Ahmad et al. 2011, Sakizci et al. 2009). According to its structural examination, montmorillonite is of the 2:1 layered aluminosilicate class and consists of two silica tetrahedra versus one alumina octahedral layer (Ahmad et al. 2011, Sakizci et al. 2009, Paluszkiwicz et al. 2008). Bentonite was used in the production of Portland Cement by natural method and calcination. Ahmet et al. (2011) investigated the strength activity index using natural bentonite, bentonite calcined at 500°C and 900°C in concrete and mortars. According to the results, the highest value was obtained with 500°C calcination. Mirza et al. (2009) substituted bentonite calcined at different temperatures (150°C, 250°C, 500°C, 750°C, and 950°C) and showed that mortars containing 25% calcined (at 150°C) bentonite and 20% natural bentonite would be a sustainable material. Bentonite is a clay mineral with an Al$_2$O$_3$:SiO$_2$ ratio of approximately 1:4. Studies have shown that calcined bentonite can also be used in the production of geopolymers (Hamdi et al. 2019, Xu et al. 2016). But these studies are limited. Due to this situation, durability properties need to be studied in detail.

Despite the potential of geopolymers, there are some limitations to implement marketable large-scale solutions as they are not yet adequately developed in terms of logistics. There is no exact and clear standard for geopolymer materials yet. On the contrary, standards for Portland Cement are clear. If this situation is explained in more detail, there is no standard curing method for preparing the geopolymer mixture. Different curing methods such as heat
curing, room temperature curing, sunlight curing, and steam curing are tried. A clear method has not yet been determined on this subject. However, the water curing method for Portland Cement is the most used today and is now accepted as standard curing (Van Deventer et al. 2012). Heat curing is an important requirement for strength development in geopolymer production. High compressive strength and flexural strength results have been obtained in numerous studies on the application of heat curing for geopolymerization. Temperatures generally between 40°C and 90°C were applied for the geopolymerization reaction (Palomo et al. 1999, Aygörmez et al. 2020a, Almashhadani et al. 2018, Uysal et al. 2018, Perera et al. 2007, Kani and Allahverdi 2009). After the geopolymer pastes produced using fly ash were cured at room temperature, it was shown that the reaction occurred slowly (Vijai et al. 2010). Results below 20 MPa were obtained in 28 days. Also, it was observed that the initial setting time took longer than 24 hours for the geopolymer paste in case of curing in room conditions (Shinde and Kadam 2016). In the case of long-term heat curing for geopolymers, the thermolysis of the -Si - O - Al - O- bond has been determined, so residence declines have been observed in older ages (Heah et al. 2011). In other words, in the case of curing at high temperatures (40-80°C), deterioration in mechanical properties was observed in older ages (Rovnanik 2010). The high-temperature effect facilitates the dissolution of the binder solid material and supports the formation of reaction products while causing negative effects on the quality and microstructure of the reaction products at later ages (Aygörmez et al. (2020b), Puertas et al. 2000). Although geopolymer composites have important mechanical and durability properties, the most important disadvantage is the high energy requirement by curing with this method. This situation prevents geopolymer products from becoming more involved in the market. It is important to investigate different methods to reduce this energy requirement. Although freezing-thawing is a durability test, it has been observed that it has a positive effect on geopolymer composites at low cycles. Aygörmez et al. (2020a) found improvement in mechanical properties when they performed 56 cycles of the freezing-thawing test. Based on this situation, it has been shown that this method can be used as a curing method (Aygörmez 2021a).

Sulfuric acid affects many different sectors such as sewer pipes, the food industry, nuclear power plants, mining. For example, it is known that nuclear power plants are used for uranium enrichment. Uranium salts are obtained by dissolving uranium metal with sulfuric acid. Sulfuric acid is very effective in a short time even at low concentrations. Also, acid resistance is an important and sought-after feature especially for concrete material produced in aggressive environments such as chemical factories (Frost and Armstrong 1994). Detailed investigation of the effects of sulfuric acid on geopolymer composites and Portland Cement-based composites has been done in previous studies. Geopolymers provide more structural integrity with alumina-silicate type binder than Portland Cement with calcium silicate hydrate binder, which has been reported to be more acid-resistant. Different studies on this subject mostly focused on other waste products such as slag and fly ash, however, it was seen that the lower concentrations were mostly examined (Thokchom et al. 2009, Izzat et al. 2013). Also, it has been found that there is no in-depth acid attack information about the met Bentonite-based geopolymer. In this regard, it is necessary to investigate the resistance of different materials such as met Bentonite against sulfuric acid. However, it is necessary to look for a longer time and at a higher concentration to determine the boundary condition of the material. Davidovits (1994) found that the weight loss was slow after exposing metakaolin-based geopolymer mortars to 5% sulfuric acid for 4 weeks. Bakharev (2005) found that geopolymer materials produced using fly ash exhibited better resistance than conventional cementitious materials after exposing them to 5% sulfuric acid for 5 months. Song et al. (2005) applied the effect of 10% sulfuric acid to the fly ash-based geopolymer for 56 days with the accelerated test and showed that the durability was good. Allahverdi and Skavara (2001) investigated the corrosion mechanism of geopolymer cement with low and high sulfuric acid concentrations. According to the literature, it is seen that there is no standard method for performance against acid and the results obtained in different acid action procedures make it difficult to correlate.

Past studies show PVA and basalt fiber addition in concrete increased the mechanical properties (Celik et al. 2018, Özkan and Demir 2020). PVA fibers are in an important fiber category due to the high stability that they provide in the alkaline environment and the strong bond that they form with the geopolymer matrix (Almashhadani et al. 2018). Li et al. (2005) reported that the ductility of the matrix increased and an improvement in flexural strength and toughness was achieved with the addition of PVA fiber in the geopolymer composites. Dias and Thamaturgo showed that their properties improved in terms of deformation and energy absorption with the use of basalt fiber in geopolymer concrete (Dias and Thamaturgo 2005). Arunagiri et al. (2017) achieved an increase in mechanical properties in geopolymer concretes produced with 2% basalt fiber.

Bentonite is natural and low-cost clay, and if calcined, it has an important potential in the production of geopolymers. In this study, a different curing method was applied in met Bentonite geopolymer samples, where heat curing was applied in general. The application of freezing-thawing and room temperature curing was tried as an alternative to heat curing. As a curing condition, met Bentonite-based geopolymer samples were kept under room conditions for up to 7 days and then the freezing-thawing test was applied for up to 28 days as a curing method. Slag was also substituted to provide hardening at room temperature curing. Evaluation of this advantage will give a new perspective on geopolymer production. Since 28 days have been a period applied for curing in many studies, it was also evaluated in this study. 7 series were produced. While the first series was the control sample, the other series used 0.2%, 0.4%, and 0.6% PVA and basalt fibers. The produced samples were subjected to 10% sulfuric acid effect for up to 3 months after 28 days. In order to
determine how metabentonite-based geopolymer materials behave while preserving their physical and mechanical integrity. 10% high concentration was preferred, while the variability in an equal period up to 3 months was desired to be investigated. The flexural strength, compressive strength, UPV, and weight losses resulting from the acid effect were examined. Also, TGA-DTA, XRD, SEM, and FT-IR analyses resulting from the acid effect were examined.

2. Experimental program

2.1 Materials

Metabentonite was used as a binder material in the production of geopolymer mortar in this study. The metabentonite used was obtained from Esan Eczacıbaşı Industrial Raw Materials Co. Al₂O₃ + Fe₂O₃ + SiO₂ content of the metabentonite constitutes 88.98% of the total content and this shows that it has high pozzolanic activity. The very thin material size of metabentonite facilitates the reaction and ensures stronger geopolymeric bonds. Slag was obtained from the Bolu cement company and was also used as a binder material. The important feature of the slag is to increase the calcium content of the mixture and shorten the setting time. The chemical properties of the materials are given in Table 1. As an alkali activator, a mixture of sodium silicate and hydroxide was prepared. While Rilem sand was used as an aggregate, it complies with BS EN 196-1 (BS EN 196-1 2016). In this study, two different fibers (polyvinyl alcohol and basalt) were used. The properties of the fibers are given in Table 2.

2.2 Specimens preparation

Sodium hydroxide solution (12M) was prepared one day before the geopolymer mixture was made and mixed with sodium silicate. For the activator mixture, the sodium silicate/sodium hydroxide mixture ratio was taken as 2:1. Then the activator was mixed with the binder materials. The activator/binder material ratio was taken as 1:2:1. Slag and metabentonite were used together as binder material. At this stage, slag was used to aid early hardening by increasing the calcium content. Finally, Rilem sand was added to the mixture in a ratio of 2.5:1 according to the binder material. The prepared mortar mixture was placed in the mold and exposed to vibration. As a curing condition, firstly room temperature was used in this study. Samples were kept at room conditions for 7 days after being removed from the mold. It was then kept in the freezing-thawing cabin for up to 28 days. The cabin was adjusted to be 12 hours at +4°C and 12 hours at -18°C. After 28 days, the samples were removed from the cabin. A total of 7 series were prepared. The first series was considered as a control mixture (MBS). Information about the mixture amounts for the control series is given in Table 3. Sample amounts are given for a standard 450 g binder. In other series, the polyvinyl alcohol and basalt fibers were added to the mixture at percentages of 0.2%, 0.4%, and 0.6%.

2.3 Testing procedures

After completing 7 and 28 days, compressive and flexural strengths and ultrasonic pulse velocity tests were applied to the samples. 7 series were then subjected to the sulfuric acid tests. The sulfuric acid solution was prepared as 10% by volume. To make the solution more effective, the samples were first kept at 105°C for 12 hours before the sulfuric acid test. The samples were then put in plastic storage boxes. For one unit sample volume, four units of acid solution were prepared and poured into plastic storage boxes. The solution was renewed every 30 days to maintain the concentration of the solution. Samples were kept in solution for up to 3 months. After each month, compressive and flexural strengths, UPV, and weight loss results were found and compared with the 28-day results. Flexural and compressive strength tests were conducted according to ASTM C 348 (ASTM C348-14 2014) and ASTM C 109 (ASTM C109 2016), respectively. Three geopolymer samples were utilized for each test, and the final results were calculated by finding the average of the samples. Also, TGA-DTA, XRD, SEM, and FT-IR analyses and visual inspection resulting from the acid effect were examined.

3. Results and discussion

3.1 Strength properties

The compressive and flexural strength results of the produced series at 7 and 28 days and after the sulfuric acid effect are shown in Figs. 1-2. Due to the crystal structure of the clay mineral, clay and shales didn’t have pozzolanic properties in the form of raw materials. However, a plate-like particle shape caused an increase in water demand and created high porosity (Duxson and Provis 2008). Due to the low pozzolanic reactivity of natural bentonite, calcination of 700 to 900°C was required. Disruption of the crystal structure of clays and shales created an aluminosilicate structure with an amorphous shape. In this way, a compact
structure was formed by geopolymerization with metabentonite (Calabria-Holley et al. 2017, Buchwald et al. 2009, Seiffarth et al. 2013). Heat curing also required high energy. In order to eliminate the negative effects of heat curing, room temperature and freezing-thawing curing were applied together and brought significant advantages. Since the application of room temperature curing prolonged the setting time, slag was used as a solution method for this situation. In another saying, slag was used to prevent the slow setting, which was the disadvantage of curing in room conditions. Slag has been found to create a more homogeneous microstructure by increasing the CaO ratio. Thus an increase in CSH/CASH gel formation was achieved. It was determined that this situation reflected positively on mechanical properties (Shinde and Kadam 2016). After 7 days, the freezing-thawing test was applied as a curing method. A geopolymer matrix has been found to have a more compact structure with freezing-thawing. Cycles have been shown to play a role in maintaining the reaction (Yunsheng et al. 2008). Thus, an increase in the results was

![Fig. 1 Compressive strength results before and after sulfuric acid effect](image1)

![Fig. 2 Flexural strength results before and after sulfuric acid effect](image2)
determined in 28 days compared to 7 days. The humid environment of the freezing-thawing improved this situation. With this method, while bonding reaction products were formed, it also contributed to geopolymerization. The curing process continued with this method. Interestingly, the freezing-thawing test was expected to decrease the strength results in hardened mortars but increased them here. Having a compact structure, the geopolymer prevented the ingress of water between dense plates compressed at low cycles, preventing the effects of deterioration. Also, the freezing temperature of alkali metal solutions such as slag between -15°C and -20°C increased the negative temperature resistance. This feature affected the start of the freezing-thawing test of materials with slag raw materials. At high cycles, the situation was reversed and strength losses occurred. Thus, the advantage of low cycles was utilized. This situation paves the way for the geopolymers products to be used in places where heat changes are intensive with a good adhesion degree (Aygörmez et al. 2020a, Aygörmez 2021a, Aygörmez 2021b, Puertas et al. 2003, Yunsheng et al. 2008). To support these results, an SEM micrograph of sample MBS+0.6PVA is shown in Fig. 3 after freezing-thawing curing. The compact structure image proved the positive effect of freezing-thawing at low cycles. Compare to the control sample, it was observed that the use of fibers increased the results. PVA and basalt fibers strengthened the bonds between the geopolymer matrices, leading them to exhibit more systematic behavior. PVA fiber formed stronger bonds than basalt fiber. Therefore, it increased the results more (Celik et al. 2018). In addition, the long PVA and basalt fibers contributed to the ductility by holding the particles securely with a long anchor system (Ali et al. 2020). After the results of 7 and 28 days flexural and compressive strength were examined, it was found that they were compatible with these conditions. After the 7-day compressive strength results were examined, 18.5 MPa, 26.45 MPa, and 26.12 MPa results were obtained in samples MBS, MBS+0.6PVA, and MBS+0.6B, respectively. After the 28-day compressive strength results were examined, 30.75 MPa, 37.12 MPa, and 36.56 MPa results were obtained in samples MBS, MBS+0.6PVA, and MBS+0.6B, respectively. After the 7-day flexural strength results were examined, 4.55 MPa, 6.56 MPa, and 6.34 MPa results were obtained in samples MBS, MBS+0.6PVA, and MBS+0.6B, respectively. After the flexural strength results of 28 days were examined, 5.52 MPa, 7.13 MPa, and 6.85 MPa results were obtained in samples MBS, MBS+0.6PVA, and MBS+0.6B, respectively.

Decreases in compressive and flexural strengths were observed as a result of 3 months of sulfuric acid effect. After the reasons for strength loss were investigated, it was known that acid attacks broke down the oxy-aluminum bridge (Si-O-Al) presented in the geopolymeric gel. The oxy-aluminum bridge played a role in strengthening the bond formed between matrix compositions (Chang et al. 2005). In this case, depolymerization instead of geopolymerization with acid effect began to occur. To explain this situation in more detail, it was necessary to examine the term poly(sialate). This term can be used to describe the chemistry of the geopolymer. While the concept of poly(sialate) was used as an abbreviation of silicon-oxo-aluminate, they were ring and chain polymers containing Si⁴⁺ and Al³⁺ in 4-fold coordination with oxygen. The chains and rings were cross-linked in the formation of a sialate Si-O-Al bridge. The alumino-silicate bridge in the geopolymer structure was attacked by hydrogen ions (H⁺) in the H₂SO₄ acid ionization, resulting in the fragmentation of the alumino-silicate network (−Al - O - Si - O-) in the aluminum regions. As a result of this decomposition, aluminum ions (Al³⁺) and silicic acid (Si(OH)₄) were released. Thus, the effects of acid increased with the effect of breaks in the oxy-aluminum bridge (−Al-O-Si-O) (Chindapasrit et al. 2013). However, geopolymer products didn’t experience easy dispersal because they contained strong aluminosilicate bonds, unlike Portland cement products. Also, the formation of the crystalline phase was another important factor that provided high stability (Bakharev 2005). The other factor that provided resistance to the acid effect was the sample morphology. Lower pore size and lower porosity prevented acid entry into the microstructure (Bakharev et al. 2003). The amount of pore decreased due to the condensation in the transition zone of the interface and the aggregate-paste interface was formed in an impermeable state. In this way, the transition of aggressive fluids to capillary action was limited. The layer formed of good quality lowered the degree of degradation (Afridi et al. 2019, Mobili et al. 2016). The other important factor that tested the acid effect was that it had a lower calcium content than Portland cement. Thus, the formation of gypsum and ettringite, which was formed by the harmful ions in the acid solution by entering the internal structure of the sample and reacting with calcium oxide, was prevented. These situations prevented problems such as cracking, expansion, and spreading in Portland cement from forming in geopolymer samples (Bassuoni and Nehdi 2007). Also, a parallel behavior was observed in the samples to the conditions that occurred before the sulfuric acid effect. The compact structure formed by the influence of polyvinyl alcohol and basalt increased acid resistance. The addition of fibers had a positive effect on the formability and stability of the shape in fiber-reinforced geopolymer mortars after the sulfuric acid effect. The homogeneous structure and fine distribution of the crystalline phases in fibrous materials provided higher mechanical properties. The microstructure was strengthened with the addition of nucleating agents such as TiO₂, P₂O₅, or ZrO₂. Basalt fibers also contributed to the resistance to sulfuric acid impact by naturally producing natural nucleators such as Fe₂O₃ during the melting of basaltic rocks. The high modulus of elasticity of the fibers provided ductile behavior after cracks formed by the effect of acid. These results are consistent with previous studies (Al-mashhadani et al. 2018, Aygörmez et al. 2020c). After 3 months of sulfuric acid effect, the compressive strength results were examined and 9.27 MPa, 12.25 MPa, and 12.02 MPa results were obtained in samples MBS, MBS+0.6PVA, and MBS+0.6B, respectively. After 3 months of sulfuric acid effect, the flexural strength results were analyzed and 1.78 MPa, 2.56 MPa, and 2.33 MPa results were obtained in samples MBS, MBS+0.6PVA, and MBS+0.6B, respectively. After both flexural strength and
compressive strength results were examined, it was observed that geopolymer stability was preserved under the effect of sulfuric acid, which was a very strong acid type, despite the decrease in strength.

3.2 Ultrasonic pulse velocity properties

UPV test was carried out to determine the homogeneity and certain other properties of composite samples in a non-destructive way. According to Fig. 4, it was seen that ultrasonic pulse velocity results were compatible with compressive strength values. It was observed that curing at room temperature caused the binding material to dissolve at a low ratio, causing UPV values to be lower than cured at high temperatures (Vijai et al. 2010). The freezing-thawing curing method applied after 7 days helped the moisture in the environment where the test was carried out to fill the

![Fig. 3 SEM micrographs of sample MBS+0.6PVA after freezing-thawing curing](image)

![Fig. 4 UPV results before and after sulfuric acid effect](image)

![Fig. 5 Weight loss results after sulfuric acid effect](image)
sample voids. In this way, it led to an increase in UPV values (Yunsheng et al. 2008). It was observed that the results seemed to be close to each other after the fibers were added, resulting in a slight improvement in the results (Almaashhadani et al. 2018). After the 7-day UPV results were examined, 2454 m/s, 2591 m/s, and 2573 m/s results were obtained in samples MBS, MBS+0.6 PVA, and MBS+0.6B, respectively. After the 28-day UPV results were examined, 2713 m/s, 2816 m/s, and 2794 m/s results were obtained in samples MBS, MBS+0.6PVA, and MBS+0.6B, respectively.

UPV value in 1 month till 3 months was found decrease as the gaps in the crack such in SEM micrograph at Fig. 7 was formed. According to Amusaalum et al. (2003), the crack was initiate by the influence of sulfuric acid. It was determined that the increase in the duration of the acid effect led to an increase in this decrease. According to the results, it was seen that the non-destructive method offered an idea of the internal structure of the mortar and the deterioration caused by the acid effect (Yaman et al. 2001). If this situation was explained in more detail, the calcium hydrate products reacted with the effect of sulfuric acid and formed calcium sulfate and sulfoaluminate products due to the slag content in the samples. The forming gypsum was observed on the sample surface and caused a weak layer. The effect on the surface caused micro-cracks and air voids as time progressed. Since the use of fibers would increase the ductile behavior, increasing fiber percentages increased acid resistance. Because PVA fiber behaved more systematically, it increased UPV results. In other words, the cracks were observed to prolong the transition process of the ultrasound waves from the inner structure of the sample and thus led to a decrease (Rajamane et al. 2012). The results formed by the sulfuric acid effect were in line with the pre-acid results. After 3 months of sulfuric acid effect, the UPV results were investigated and 1393 m/s, 1545 m/s, and 1521 m/s results were obtained in samples MBS, MBS+0.6PVA, and MBS+0.6B, respectively.

As the time elapsed in the acid effect increased, weight loss increased. Especially sulfuric acid, which entered the sample structure, reacted with calcium hydrated products, leading to the formation of gypsum and ettringite. With the progression of the reaction, a weak layer was formed, which triggered dissolution and caused weight loss (Rajamane et al. 2012). However, geopolymer samples were more resistant to acid effects due to their Na-rich gel content. This Na-rich gel content neutralized sulfuric acid with an acid-base reaction and reduced its destructive effects. Since the average pore diameter in the geopolymcer structure was small, it led to a decrease in acid intake and reducing weight loss (Değirmenci 2017). The weight-loss percentages of samples MBS, MBS+0.6PVA, and MBS+0.6B after 1-month sulfuric acid effect were 0.66%, 0.28%, and 0.41%, respectively. The weight-loss percentages of samples MBS, MBS+0.6PVA, and MBS+0.6B after 2 months sulfuric acid effect were 1.05%, 0.69%, and 0.77%, respectively. The weight-loss percentages of samples MBS, MBS+0.6PVA, and MBS+0.6B after 3 months sulfuric acid effect were 1.49%, 1.08%, and 1.14%, respectively. The weight loss results after sulfuric acid effects are shown in Fig. 5.

3.3 Visual inspection and analyses

Samples were kept for 3 months under the sulfuric acid effect. After 3 months, a visual inspection of the outer surfaces of the samples was made (Fig. 6). After the test was completed, some deformation was observed on the surfaces. The high concentration of sulfuric acid increased the resulting damage. Although the surface of the samples was softened a little, it didn’t become easily scratched with the nail. Some erosion was observed in the parts of the samples close to the corners and edges. Also, white scaly grains were seen on very small amounts of surfaces. The formation of gypsum and ettringite also increased disruption in the surface layers. However, it was observed that stability was maintained against all these situations and the changes remained low (Vafaei et al. 2018, Aygörmez et al. 2020c).

SEM analysis was performed on sample MBS+0.6PVA after 3 months under the effect of sulfuric acid (Fig. 7). Geopolymer samples had a dense microstructure. This structure became porous due to the microcracks formed by the fact that the Si-O-Al bonds underwent some breakdown under the influence of acid (Bakharev 2005). Air voids were also seen, although not to a significant extent. It was observed that voids and cracks formed together with the acid effect period. Shrinkage in the gel layer was also involved in the formation of cracks. With the effect of this situation, the transition of the acid to the internal structure became easier. It was observed that these effects, in which broken surfaces and pores were formed, caused air voids and cracks by forming needles or similar particles. Also, it was observed that the needle-like structures began to disappear in the pores by dissolving in acid. Calcium ions in the sample reacted with sulfate ions in solution and accelerated the formation of gypsum. Also, the reaction between sulfuric acid and gel led to the formation of sulfsur. Gypsum formation in the microstructure of the samples formed a crystalline structure (Sata et al. 2012). The reaction of gypsum with sulfuric acid also caused the formation of a whitish layer. In addition, according to the microstructure, it was seen that new crystals with a structure similar to the gypsum were formed. Gypsum crystals also increased cracks, triggering loss of strength. Despite these situations, the Na-rich gel contributed to the preservation of the classical geopolymer gel structure by playing a role in...
the improvement against acid effects. Another important reason was the low permeability. Also, geopolymers’ Si/Al ratio played an important role in resistance to acid effect (Djobo et al. 2016, Aygörmez et al. 2020c).

Fig. 8 shows the XRD spectrum of sample MBS+0.6PVA after 3 months of sulfuric acid effect. The geopolymer sample was examined and it was seen that quartz and mullite were included. The peaks were found to be intensely between 26° and 28° (Bouguermouh et al. 2017). According to the XRD analysis, it was understood to be a semi-crystalline structure. If the peaks were examined, it was observed that although the sulfuric acid effect was observed, it was protected significantly. After these results were examined, according to XRD analysis, it was seen that it was a resistant structure despite the acid effect formed in the matrix. The classical geopolymer structure had quartz peaks between 26° and 28°. As the strong Si-O-Al bond structure ensured the protection of this quartz peak in the XRD pattern after the effect of sulfuric acid, the mechanism was shown to retain its overall structure despite acid degradation and depolymerization (Aygörmez et al. 2020a). In previous studies, it was seen that better results were obtained than Traditional Portland Cement (Thokchom 2014). The FT-IR spectrum of sample MBS+0.6PVA exposed to sulfuric acid effect after 3 months is shown in Fig. 9. After the test, the wavelength was detected as 1055.35 cm⁻¹. It was determined that Si-O-Al bonds showed asymmetric stretching vibrations, while wavelengths reflected this situation. Also, at the end of the test, the band intensity was between 3376.18 and 1623.25 cm⁻¹ (Louati et al. 2017). After DTA and TGA curves of sample MBS+0.6PVA were examined, it was determined that blue curves showed weight loss after 3 months of sulfuric acid effect (Fig. 10). It was observed that the weight loss was 5.8%
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after 3 months, and this situation was also compatible with the limited weight loss in the sulfuric acid effect. However, endothermic peaks were also shown in DTA curves. It was determined that evaporation of free and bound water in the matrix in weight loss was mostly between 0 and 800°C. Both TGA-DTA and FT-IR analyses supported that the stability of the geopolymer matrix was maintained (Arslan et al. 2019, Değirmenci 2018).

4. Conclusions

For this paper, the sulfuric acid effects on the metabentonite-based geopolymer mortars were examined for up to 3 months and PVA and basalt fibers were used at different percentages of 0.2%, 0.4%, and 0.6%. Also, the freezing-thawing test was applied as a curing method and the following conclusions were obtained.

- Metabentonite, which was obtained by calcining bentonite, provided an important advantage when it was used in the production of geopolymer, while it was obtained naturally and cheaply and this situation also supported this advantage. Its use with slag also helped to achieve hardening at room conditions.
- In this study, less energy was used with room temperature and freezing-thawing curing instead of heat curing. The low-activation slag contributed to the continuation of the binder products and thus to the geopolymerization by taking advantage of the moisture created by the freeze-thaw test effect. With this method, the geopolymer samples became more compact. Thus, an improvement in mechanical properties was achieved.
- While long PVA and basalt fibers strengthened the bonds between geopolymer matrices, they contributed to...
ductility and showed a systematic behavior by holding the particles more securely with the long anchor system. The homogeneity of the fibers and the presence of fine crystalline phases contributed to the improvement of the mechanical results. While the results were higher with increasing fiber percentage, PVA fiber increased the results more than basalt fiber.

- The sulfuric acid effect formed flexural and compressive strengths and UPV reductions after 3 months. The geopolymer products didn’t experience easy dispersal because they had strong aluminosilicate bonds, crystalline phase formation, morphology, and lower calcium content that provided high stability. Visual inspection of the samples after the sulfuric acid effect showed that the damage to the sample surfaces remained minimal. According to SEM, FT-IR, XRD, and TGA-DTA analysis, the stability of the geopolymer matrix was preserved after 3 months in the sulfuric acid effect.

References


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