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Research Article

One-Part Geopolymer Binder Based on Boron Wastes: Effects of Calcination Temperature and NaOH Dosage on Strength and Microstructure

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Abstract

Boron Enterprise Facilities are located in Kütahya-Emet, Eskişehir- Kırka and Balıkesir-Bigadiç regions in Türkiye. Waste materials containing a sum of boron (15-20%) occur during boron beneficiation with different mining procedures. Boron mine wastes are not evaluated completely in any sector. In the scope of this study, boron mine wastes from Kırka Boron Enterprise Facility were used as raw material in the production of one-part geopolymer binder by alkali fusion method. The effect of sodium hydroxide dosage (%4, %6, %8 and %10) and calcination temperature (600 °C, 650 °C and 700 °C for 4h) on compressive strength and microstructure was investigated. Test results showed that one-part geopolymer binder can be produced from boron wastes by using alkali fusion method. The highest compressive strength of 29,1 MPa was obtained by using 4% NH and calcination at 650 C for 4h. Furthermore, the formation of new crystalline phases in geopolymer binders at higher calcination temperature caused a decrease in compressive strength values. The main reaction product of the one-part geopolymer based on boron wastes is Mg and Na incorporated C-(Mg, Na)S-H structure.

Keywords: Boron mine waste, Calcination, One-part geopolymer binder

1. Introduction

Türkiye has 74% of world proven boron reserves [1]. The boron reserves in our country are located in Kütahya-Emet, Bigadiç-Balıkesir and Kırka-Eskişehir. The number of different boron minerals is around 230.The most important boron minerals in terms of commercial value and availability in Türkiye are tincal, colemanite and ulexite. While the tincal mineral is just in Kırka, the colemanite and ulexite minerals are in Emet, Bigadiç and Kestelek. Boron is a strategic mine that has been commonly used in a lot of different industrial areas such as nuclear, construction, ceramic and etc.

The boron mine wastes having %15-20 B_2O_3 are created during the enriching process of boron mine via different mining methods to produce various boron compounds such as boric acid, hydrated borax, and sodium perborates [2-4]. These wastes cannot be used at any sector and have to be stored at waste dams by boron enterprises. Furthermore, the storage of these wastes as open to atmosphere results in several enviromental problems such as water, air and soil pollutions because the boron minerals in these wastes dissolve by the rain water [5,6]. This situation may generate a risk in terms of people who live near the Boron Enterprise Facilities. In literature, there are several investigations as to the use of boron waste especially to produce concrete [7], Portland cement [8] or based mortar [9,10] and brick [4,6,11].

Portland cement is the most extensively used binder in the world to produce construction materials such as concrete, mortar, etc. However, the raw materials (limestone and clay) used in the production of Portland cement bring about the devastation of the natural habitat and the production of the Portland cement leads to emissions of hazardous gases such as CO_2, SO_2, NO_X, etc. considerably damage to natural habitat. The complex compounds in Portland cement such as C_2S, C_3S, C_3A and C_4AF occur at 1300 °C-1400 °C, so the energy comsumption rises to high level during production of Portland cement. Therfore, the production of greener binders alternative to Portland cement has been one of the significant research studies in recent years. These studies have genereally focused on the production of two-part geopolymer binders. Nevertheless, the alkali activators used in two-part systems are corosive which, is risky for human health. Moreover, the feasibility of two-part geopolymer binders is difficult for concreting in-situ [12,13].

Researchers have focused on the production of one-part geopymer binders (just add water) in recent years due to the above mentioned reasons. One- part geopolymer binder can be produced three different methods, mixing solid raw material and solid activator, grinding solid raw material and solid activator together and alkali fusion. Alkali fusion is a method which is used to synthesise one-part geopoymer binders. Raw materials together with alkalis are calcined at high-temperatures. A limited number of studies on the geopolymer binders produced by alkali fusion method have been published up to now.

Ye et al. [14] prepared various dry mixes of red mud and sodium hydroxide at certain ratios. The prepared dry mixes were calcined at 800°C for 1h. Red mud based geopolymer binders produced via alkali fusion method was replaced with silica fume at certain ratios to prepare geopolymer pastes. Ye et al. [14] reported that the compressive strength values of paste specimens improved significantly with the increasing silica fume and decreasing water/binder ratio. Abdel-Gawwad and Khalil [15] prepared a dry mix consisting of 60% cement kiln dust and 40% feldspar. The dry mix was calcined via alkali-fusion method to obtain one-part geopolymer binder. The effects of calcination temperatures (1200 °C and 1300 °C) and the calcination durations (2h and 3h) and the amount of sodium hydroxide (10% and %20) were investigated on geopolymer pastes. A compressive strength value of 52 MPa was obtained at 28d. Peng et al. [16] produced the geopolymer clinker by calcining bentonite with both sodium carbonate and sodium hydroxide. The calcination temperatures were 700 °C, 850 °C and 1000 °C and the calcination duration was 3h. Peng et al. [16] reported that the compressive strength of geopolymer paste obtained with geopolymer clinker that was produced by calcining the mixture of bentonite + sodium hydroxide (25%) at 1000 °C was 45 MPa while bentonite + sodium carbonate (33%) at 850 °C was 55 MPa at 210d. Ke et al. [17] calcined the blend of red mud and sodium hydroxide at 800 °C for 1h. Sodium hydroxide ratios were adjusted as 5%,10% and 15% Na_2O of red mud. Ke et al. [17] reported that the geopolymer paste specimens prepared with red mud based geopolymer binder having 5% sodium hydroxide gained the strength after 14d. Notwithstanding, the geopolymer paste specimens which were prepared with red mud based geopolymer binder having 10% and %15 sodium hydroxide gained 10 MPa and 8 MPa compressive strength in 7 days, respectively.

In the scope of this study, the use of boron mine wastes procured from Kırka Boron Enterprise Facility as a raw material was investigated to produce one-part geopolymer binder via alkali fusion method. The effects of different calcination temperatures (600 °C, 650 °C and 700 °C) and Na_2O ratios (4%, 6%, 8% and 10%) were investigated on compressive strength and microstructure.

2. Materials and Methods

2.1. Materials

The XRF analysis of raw and calcined boron mine wastes were given in Table 1. The XRF result of calcined boron mine was obtained from powder specimen calcined at 600 °C for 1h without using alkali fusion method. Furthermore, pellet sodium hydroxide with 97%-purity (TEKKIM®) was used as an alkali activator during the calcination process. Standard silica sand (LIMAK®) was used to produce mortar mixtures.

Table 1. The chemical compositions of raw and calcined boron mine waste

Waste Type	Oxides, by weight (%)										
	SiO_2	**CaO**	**Al_2O_3**	**B_2O_3**	**MgO**	**K_2O**	**Fe_2O_3**	**Na_2O**	**SO_3**	**TiO_2**	**LOI**
Raw	19,20	16,12	1,47	6,40	18,60	0,68	0,31	4,81	0,24	-	32,17
Calcined	25,21	22,03	1,59	7,34	24,55	0,93	0,40	5,55	0,38	-	12,03

2.2. Methods

Boron mine wastes were dried in an oven at 100 °C for 24h before they were calcined via alkali fusion method. After the drying process, boron mine wastes were grinded in a ball mill at 400 rpm and for 2 minutes. Sodium hydroxide solutions having different Na_2O ratios (4%, 6%, 8% and 10%) were prepared one day before the calcination process. Then, grinded boron mine wastes and sodium hydroxide solutions with a water/binder ratio of 0.37 were mixed together. The obtained paste mixtures were firstly shaped as a ball-bearing form to avoid the negations, such as melting and bonding to vessel, during the calcination process. Then, the paste mixtures were calcined at different calcination temperatures (600 °C, 650°C and 700 °C) for 4h at a high-temperature oven. The calcination temperatures used in this study were determined according to the TG/DT analysis of raw boron waste given in Figure 1.

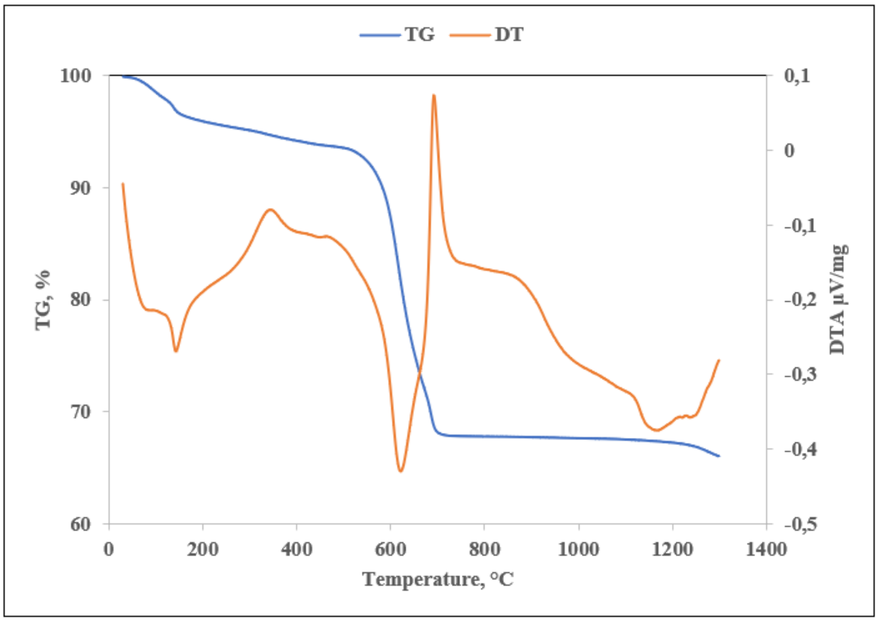

Figure 1. TG/DT analysis of boron waste

It is shown from Figure 1 that new exothermic peak has occurred at higher temperatures (at about 700 °C), which means that the cristalinity of calcined boron waste has increased and the reactivity of calcined boron wastes decreased. Calcined boron mine wastes were suddenly cooled to room temperature at the end of calcination process, and they were grinded again in a ball mill at 400 rpm and for 3 minutes. After the ball mill process, the d90 value of calcined boron mine wastes was about 30µ.

Geopolymer mortar mixtures were produced by using laboratory type mixer. The aggregate/binder ratio of all geopolymer mortar mixtures were constant as 2.5. Initially, the geopolymer binders and standard sand were mixed in a dry state together to obtain homogen mixtures during 1 minute. Then, tap water was slowly added, and the mixing process continued during 3 min. Fresh geopolymer mortars were cast into steel molds (in size 50x50x50 mm) and compacted for 30 sec. The water/binder ratio of prepared geopolymer mortar mixtures was 0.52. After casting, the surface of geopolymer specimens open to atmosphere was covered with a nylon bag to avoid evaporation. The geopolymer specimens were left in laboratory conditions for 16h and then cured at 100 °C for 24h. After curing, the compressive strength values of geopoymer mortar specimens were determined in accordance with ASTM C109/C109M [18]. Finally, the SEM/EDS and XRD analyses were performed on the selected geopolymer paste specimens.

3. Results and Discussion

3.1. Compressive Strength Results of Geopolymer Mortars

Twelve geopoymer binders were produced at different calcination temperatures, Na_2O ratios and constant calcination duration via alkali fusion method along this study. It is importantly noticed that the mixtures codes were shortened as SH(A)-(B). SH is the abbreviation of sodium hydroxide. The A represents the Na_2O ratio while the B represents the calcination temperature. The water/binder ratio and calcination duration that were kept constant for all geopolymer binders were 0.52 and 4h, respectively.

The compressive strength results of geopolymer mortar specimens were presented in Figure 2. The increase in calcination temperatures from 600 °C to 650 °C, without taking into account Na_2O ratios, resulted in improving the compressive strength values of geopolymer mortars between 32% and 67%. While the minimum compressive strength value was 16.3 MPa at 600 °C for geopolymer mortars having 10% Na_2O, the maximum increase rate (67%) between geopolymer mortars at 650 °C was obtained from mortars with 10%Na_2O. The compressive strength values of geopolymer mortars at 700 °C decreased as compared to 650 °C. The decrease in the strength was more pronounced for 4% and 6% Na_2O. This situation may be associated with the formation of new crystalline phase in geopolymer binders at higher calcination temperature.

As shown in Figure 2, the effect of Na_2O ratio on compressive strength values was found limited at 600 °C and 650 °C. The compressive strength values of the mortars prepared with geopolymer clinker calcined at 600 °C increased up to 8% Na_2O ratio while the compressive strength value of geopolymer specimens with 10% Na_2O decreased. A similar trend was observed at 700 °C. Furthermore, the compressive strength values of geopolymer mortar specimens having 4% Na_2O and 6% Na_2O ratios at 650 °C were obtained equal as 29.1 MPa. However, the compressive strength values decreased at higher Na_2O ratios. According to the obtained compressive strength results, the calcination temperature is a more effective parameter than the Na_2O ratio. Consequently, the optimum calcination temperature regardless of Na_2O ratios was determined as 650 °C.

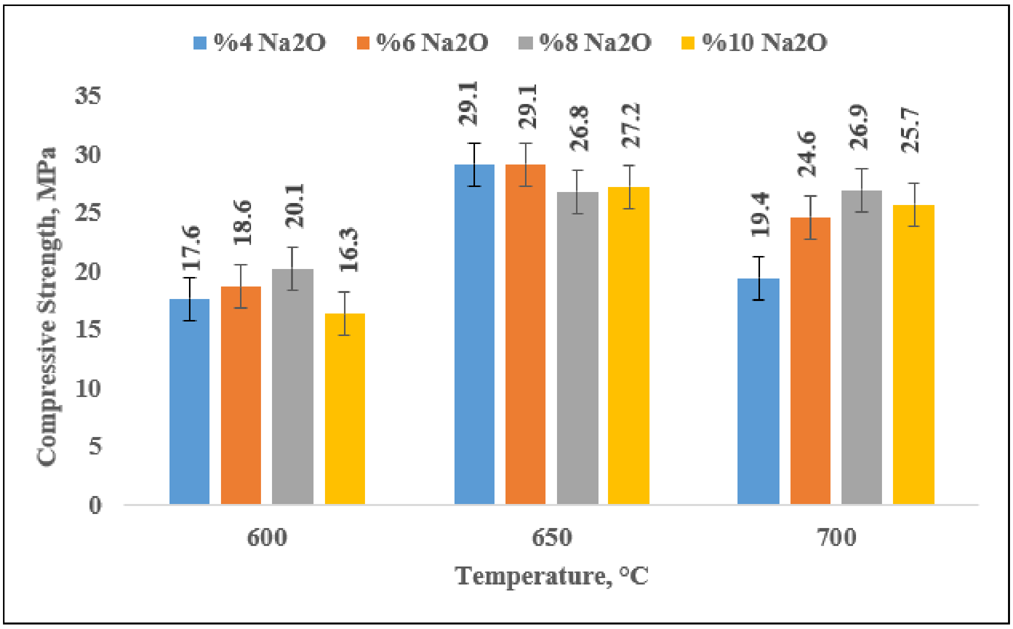

Figure 2. The compressive strength values of geopolymer mortars

3.2. Microstructure

In this section, four one-part geopolymer pastes (SH4-600, SH4-650, SH4-700 and SH10-700) were selected to determine the effect of different calcination temperatures and Na_2O ratios on the microstructures. Thus, XRD and SEM/EDX analyses were performed on the selected geopolymer pastes. Furthermore, XRD analysis of raw boron waste was performed to reveal the crystalline phases. XRD pattern of raw boron waste was illustrated in Figure 3. As shown in Figure 3, raw boron waste consisted of some crystalline phases such as dolomite, tincalconite and quartz. The most dominant phase in terms of intensity and count was dolomite.

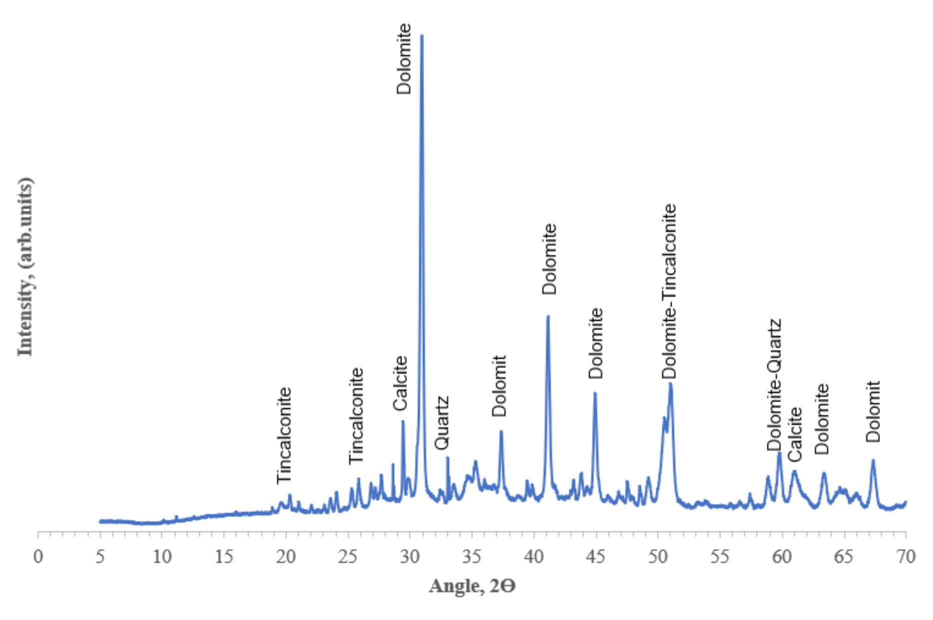

Figure 3. XRD analysis of raw boron waste

XRD patterns of selected geopolymer pastes were shown in Figure 4. After alkali fusion process, the crystalline phases in raw boron waste disappeared and was converted to the new crystalline phases. According to Figure 4, all geopolymer pastes consisted of brucite ($Mg(OH)_2$, PDF Card Nr:01-073-8391), merwinite (PDF Card Nr: 04-011-6738), monticellite (PDF Card Nr: 00-035-0590), sodium oxide (PDF Card Nr: 00-001-1105), riversideite ($Ca_5Si_6O_{16}(OH)_2$, PDF Card Nr:00-029-0329) and magnesium oxide (PDF Card Nr: 01-080-4184) crystal phases. However, the intensities of phases were different from each other. Merwinite ($Ca_3Mg(SiO_4)_2$) and monticellite ($CaMgSiO_4$) are a member of group of magnesium silicate. There is a peak for all geopolymer pastes about 29-30 °C (2Θ) belonging to riversideite phase. Riversidiete is a member of the group of tobermorite gel (C-S-H), which has binding property that improves the compressive strength of geopolymer pastes. Thus, the improvement in compressive strength values for all geopolymer pastes can be explained with the formation of this phase.

If the intensities and counts of peaks has increased, the crystallinity degree of geopolymer paste has increased. This situation induces decrease in the compressive strength values of geopolymer paste. For example, the peak intensities of SH4-600 paste was found higher than that of SH4-650 paste such as SO, MO and MH. Therefore, the compressive strength value of SH4-650 (29.1 MPa) was obtained higher than the compressive strength value of SH4-600 (17.6 MPa). There was a similar situation between SH4-700 and SH10-700. The crystallinity degree of SH4-700 was higher than SH10-700 and so the compressive strength value of SH10-700 (25.7 MPa) was obtained higher than SH4-700 (19.4 MPa). Finally, it can be seen from the test results that the XRD results and the compressive strength results were compatible with each other.

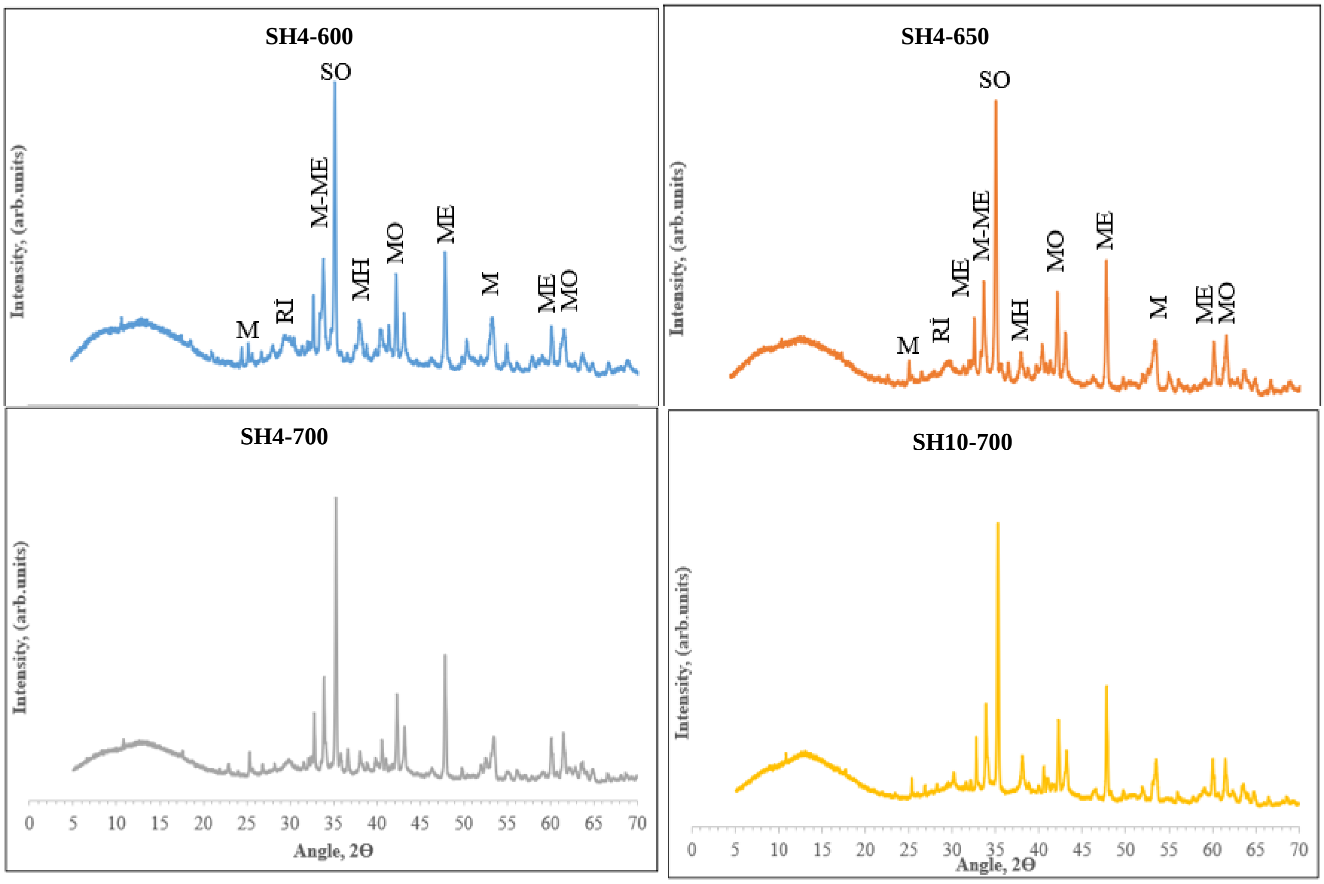

Figure 4. XRD patterns of geopoymer pastes (ME: Merwinite; M: Monticellite; SO: Sodium Oxide; MO: Magnesium Oxide; MH: magnesium hydroxide; RI: riversideite)

SEM images of geopolymer pastes were illustrated in Figure 5. The morphology of SH4-650 paste is denser than SH4-600 and SH4-700 pastes. The reaction products of SH4-650 has uniformly filled the voids with respect to SH4-600 and SH4-700. It explains the higher compressive strength value of SH4-650 as compared to SH4-600 and SH4-700 (Figure 2). The morphology of SH4-600 and SH4-700 was similar to each other like the compressive strength values. Furthermore, the matrix phase SH10-700 is denser with fewer voids than SH4-700 paste, which results in an increase in the compressive strength values. According to EDX analysis on SH4-600 paste having the lowest compressive strength, the reaction product marked with a circle on the SEM image in Figure 5, consists of Ca, Si, Mg and Na. The atomic ratios of Ca, Si, Mg and Na have been about 10%, 7%, 2% and %41, respectively. Ca/Si ratio was determined as 1.44 in this region. Therefore, it can be concluded that Mg and Na incorporated C-(Mg, Na)-S-H gel occurred as a binding phase in the light of EDX and XRD results. Furthermore, the excess of Na in this region derives from sodium oxide which was determined as crystalline phase as shown in Figure 4.

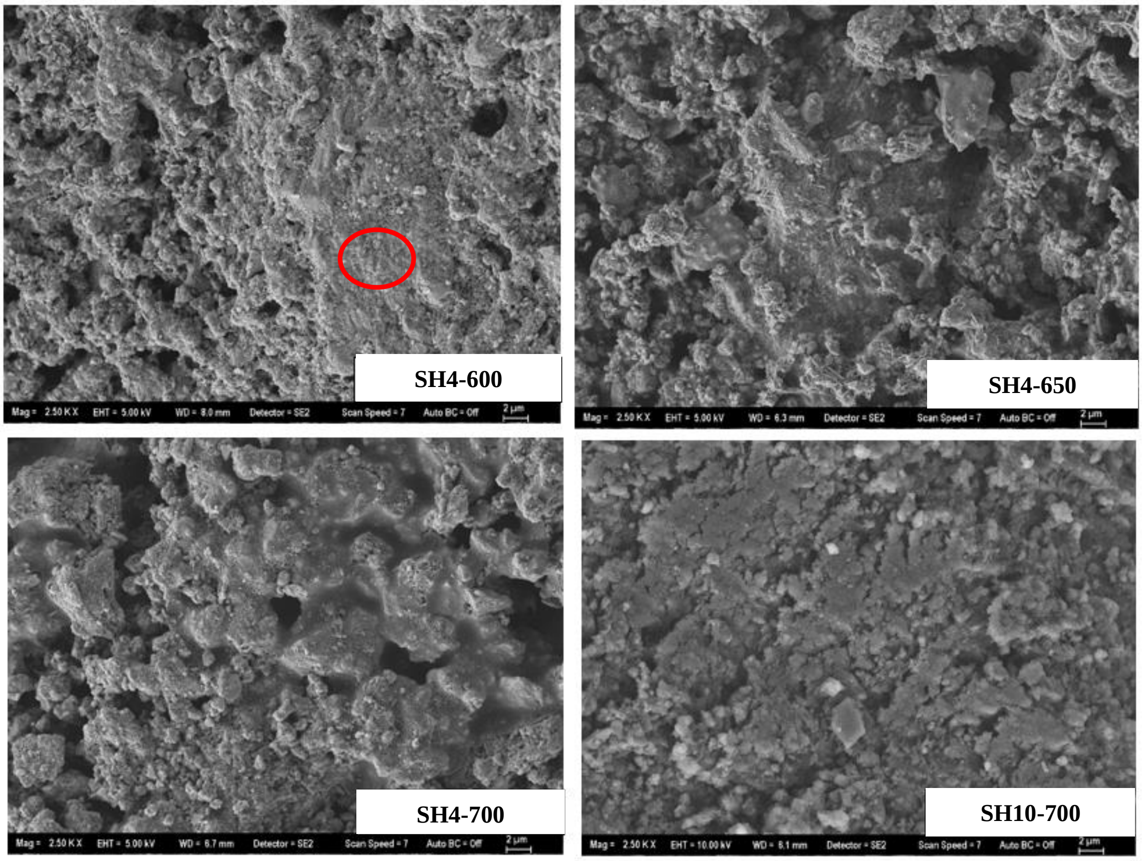

Figure 5. SEM images of geopolymer pastes

4. Conclusion

In the present study, boron mine waste discarded from Kırka Boron Enterprise Facility was used in the production of one-part geopolymer binder. The effects of calcination temperatures (600 °C, 650 °C and 700 °C) and Na_2O ratios (4%, 6%, 8% and 10%) of the geopolymer clinker on the compressive strength and microstructure of one-part geopolymer have been investigated. The obtained results in the scope of this study are as follows,

- The compressive strength values of geopolymer mortars increased by increasing the calcination temperature from 600 °C to 650 °C. On the other hand, with the increase in the calcination temperature from 650 °C to 700 °C, the compressive strength values of geopolymer mortars decreased. This situation is related to increase of the degree of crystallinity degree at higher calcination temperature. The more compressive strength values were obtained from geopolymer mortars which was calcined at 650 °C. The highest compressive strength value with 29,1 MPa was obtained from SH4-650 geopolymer mortar.
- The effect of Na_2O ratio of the geopolmer binders on compressive strength values was not as effective as calcination temperature.
- All geopolymer pastes have consisted of brucite merwinite, monticellite, sodium oxide, riversideite and magnesium oxide crystal phases.Mg-Na incorparated C-(Mg,Na)-S-H gel has occured as a reaction product which is responsible for high compressive strength.
- Test results showed that one-part geopolymer binder can be produced from boron wastes by using alkali fusion method. One-part geopolymer binder can be obtained at low activator dosage as compared to two-part geopolymer binder.

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