

# Mechanochemical Activation of Sodium Geopolymers Containing Carbon-Nano Powder

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## ABSTRACT

Two different sodium geopolymers including 9 or 18 moles carbon nano-powder were prepared for mechanochemical activation by using the well-known geopolymer route. While 9 moles carbon were incorporated into geopolymer resin during the geopolymer route, 18 moles carbon were mixed with produced geopolymer after the geopolymer route. Both geopolymer carbon precursors named as NaGP9C and NaGP18C were mechanochemically activated for 24 hours and, the NaGP18C was also activated for 48 hours. Activation processes were carried out in a planetary ball mill with a ball to powder wt % ratio of 25:1 at 250 rpm. Depending on the activation and carbon content, room and high temperature properties of resultant compositions were evaluated by making optical microscope, XRD, SEM and DSC analyses.

**Keywords: Geopolymer, Mechanochemical, Activation.**

## ÖZ

Mekanokimyasal aktivasyon için 9 veya 18 mol karbon nano-tozlar içeren iki farklı sodyum geopolymer iyi bilinen geopolymer yöntemi ile hazırlanmıştır. 9 mol karbon, geopolimer üretimi aşamasında geopolimer reçineye dahil edilirken, 18 mol karbon, geopolimer işleminden sonra üretilen geopolimer ile karıştırılmıştır. NaGP9C ve NaGP18C olarak adlandırılan her iki geopolimer karbon başlangıç malzemesi 24 saat mekanokimyasal olarak aktive edilmiş ve NaGP18C ayrıca 48 saat aktive edilmiştir. Aktivasyon işlemleri 250 dev/dak' da ağırlıkça bilye toz oranı 25:1 olacak şekilde bir gezegen bilyeli değirmende gerçekleştirilmiştir. Aktivasyon ve karbon içeriğine bağlı olarak, sonuç kompozisyonların oda ve yüksek sıcaklık özellikleri optik mikroskop, XRD, SEM ve DSC analizleri yapılarak değerlendirildi.

**Anahtar Kelimeler: Geopolimer, Mekanokimyasal, Aktivasyon.**

## 1. INTRODUCTION

Global warming is one of the most important problems continuing on the World due to its both environmental and social effect. In recent years, environmentally friendly materials are starting to draw attention to overcome the effect of global warming. Having geopolymers energy efficient and less environmental impact have increased its usage as Portland cement alternative materials. Namely, GP are made at ambient temperature and release less CO<sub>2</sub> emission (about 80%) to the atmosphere [1-4].

GPs are X-ray amorphous materials and can be produced by mixing an aluminosilicate source and silica in the presence of highly caustic aqueous alkaline (MOH) media. Although they can be made a large composition range, TEM studies revealed the typical composition of M<sub>2</sub>O•Al<sub>2</sub>O<sub>3</sub>•4SiO<sub>2</sub>•11H<sub>2</sub>O or [1:1:4:11]. Where, M is a charge balancing cations such as Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>. Thanks to their intrinsic properties, GPs have found a lot of application such as fire and corrosion resistance coating, porous insulators, refractories and concrete production [5].

However, low strength and brittle fracture nature of GPs limit their usage for the structural applications. GPs have

been reinforced with various continuous fibers and short fibers in order to improve their mechanical properties. By developing of GP composites with the introduction of these high strength fibers, even though the catastrophic brittle failure of the materials can be prevented, very weak GP matrix and matrix-reinforcement interface problems are still ongoing. In addition to being considered as matrices for GP composites, GPs can be considered as a precursor to ceramic fabrication. Pure GPs were crystallized into useful refractoriness ceramics, such as Na-based GPs crystallized into nepheline, K-based GPs crystallized into leucite, Cs-based GPs crystallized into pollucite on heating to high temperatures [6-8].

In our previous study, we systematically studied on the conversion of crystalline phase by a subsequent heat treatment of mixed GPs with carbon. In the present study, achieving of geopolymeric structures by using just mechanochemical activation at room temperature would be more energy efficient production. Additionally, this effect would be seen during heat treatment of the activated precursors. Mechanochemical activation of different silicon sources were made in literature [9-12], we used a sodium geopolymer in this study.

The aim of this study was to investigate low and high temperature properties of mechanochemically activated NaGPs with carbon addition. Tailored geopolymeric structures as well as above crystallize structures would be

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expected to depend on the carbon amount, activation duration and heating temperature.

## 2. EXPERIMENTAL

### 2.1. Materials

Laboratory grade NaGPs were made with alkaline of sodium hydroxide (99.0 wt% trace metal basis), supplied from Fisher Scientific. Amorphous fumed silica having a fine particle size was used as a silica source. Metakaolin ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) used as aluminosilicate source had an average particle size of 1.2  $\mu\text{m}$ , a specific surface area of 13  $\text{m}^2/\text{g}$ , and was of ~97% purity.

### 2.2. Geopolymer Processing (Geopolimer İşlemleri)

Geopolymer carbon composition deemed NaGP9C and NaGP18C were made in-situ and ex-situ routes, respectively. The composition of both geopolymers were  $\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4.5\text{SiO}_2 \cdot 12\text{H}_2\text{O}$ . We added 0.5 mole excess silica in geopolymer to improve any possible reaction between silica and carbon during mechanochemical activation and to dissolve the excess silica and carbon, 1 mole water was also added the composition.

In the in-situ route, alkali sodium silicate solution (waterglass) was prepared by dissolving the fumed silica in a pre-prepared NaOH alkaline solution in a stainless steel container on a magnetic plate. In order to dissolve the silica properly, a total of 2.5 moles silica was added in small batches, before adding the next batch, each time allowing for complete dissolution of the silica. Additionally, the temperature of magnetic plate was kept at about 45-50 °C and the container sealed with a plastic film to contribute fully dissolving of silica for overnight. Although this process, any water content lost due to the exothermic reactions in solution was replaced to maintain the proper chemical compositions. After preparing the clear sodium silicate solution having low viscosity, the metakaolin ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) was added the sodium silicate solution and then mixed in a high shear mixer for 5 min. Following, 9 moles carbon was incorporated in to the viscous and homogenous NaGP slurry and the slurry was mixed for 5 min again to obtain NaGP9C. The NaGP9C slurry was poured into the poliasetal mold, sealed with a plastic film and then kept in an open air furnace, at a constant temperature of 45 °C for 1 day.

In the case of ex-situ route, due to rapid solidification effect of carbon into the GP resin, the pre-prepared and powdered pure NaGP were ball milled with 18 moles carbon to obtain NaGP18C. So, after the pure NaGP prepared by following the typical GP route as mentioned above, the NaGP sample were then additionally dried in an open air furnace at 300 °C for 1 h at a heating rate of 5 °C/min and then powdered in a ceramic crucible. 18 moles of carbon were added to the dried and powdered geopolymer samples to make NaGP18C precursors. Table 1 shows the molar compositions of both GP carbon samples.

**Table 1.** The molar compositions of both GP carbon samples

Sample	$\text{Na}_2\text{O}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{H}_2\text{O}$	C
NaGP9C	1	1	4.5	12	9
NaGP18C	1	1	4.5	12	18

NaGP9C and NaGP18C precursors were planetary milled in a zirconia bowl (45 ml) with cylindrical zirconia balls at room temperature. Table 2 shows the mechanochemical activation conditions of GP samples. Along with ball to powder ratio and rotation speed can be selected within a wide range, a greater ball to powder ratio and rotation speed could contribute to the reaction between reactant particles [12-14]. Rotation speed was selected relatively lower due to high milling duration and dry milling media.

**Table 2.** Mechanochemical activation conditions of GP samples

Sample	Rotation speed (rpm)	Ball to powder wt % ratio	Duration (Hour)
NaGP9C	250	25:1	24
NaGP18C	250	25:1	24
NaGP18C	250	25:1	48

### 2.3. Characterization

Differential scanning calorimetry (DSC) was conducted on all mechanochemically activated GP carbon samples using a **SEIKO - EXSTAR 6300**. Each of the GP carbon samples was placed in Pt/Rh pans fitted with a lid. The DSC signal was acquired while heating in a high purity (99.99%) nitrogen atmosphere under dynamic conditions, between 900 °C -1500 °C at a rate of 5 °C/min.

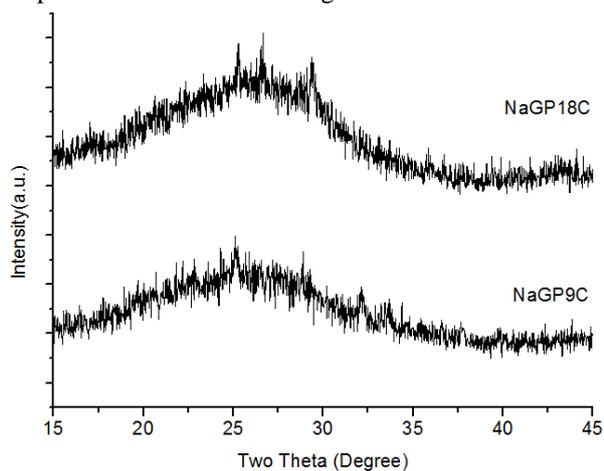
Raw GP carbon and mechanochemically activated GP carbon samples were characterized by X-ray diffraction in **PANalytical- EMPYREAN** diffractometer equipped with a  $\text{CuK}\alpha$  source ( $\lambda = 15406 \text{ nm}$ ). Tests were carried out at 40 kV, 30 mA, and the Bragg angle ( $2\theta$ ) varied from 5° to 80° with a step size of 0.02, and at a scan rate of 1°/min. The reaction products were finely ground to powders before X-ray analysis. Whole pattern fitting and manual matching was carried out and the phases were determined using Jade 9 software.

Carbon added NaGP9C and NaGP18C precursors were examined by the optical microscope (Nikon ECLIPSE LV150N). All the mechanochemically activated GP carbon samples were microstructurally investigated by SEM (Scanning Electron Microscopy). SEM studies were performed at 25k magnification using an accelerating voltage of 20 kV with SEI in high vacuum mode.

### 3. RESULT AND DISCUSSION

XRD patterns of NaGP9C and NaGP18C compositions before mechanochemical activation were shown in Fig. 1. A broad  $2\theta$  peak at about  $28^\circ$  shows the well-known amorphous geopolymer formation. We can also see from the XRD pattern that the two GP compositions revealed similar trends in the XRD patterns. This meant that the carbon couldn't seriously affect the geopolymerisation in the case of NaGP9C, which the carbon was added the GP slurry during the preparation of GP. In the case of NaGP18C which the carbon was added the final GP, it can also be seen that the pattern was very close to the typical XRD pattern of pure GP [15].

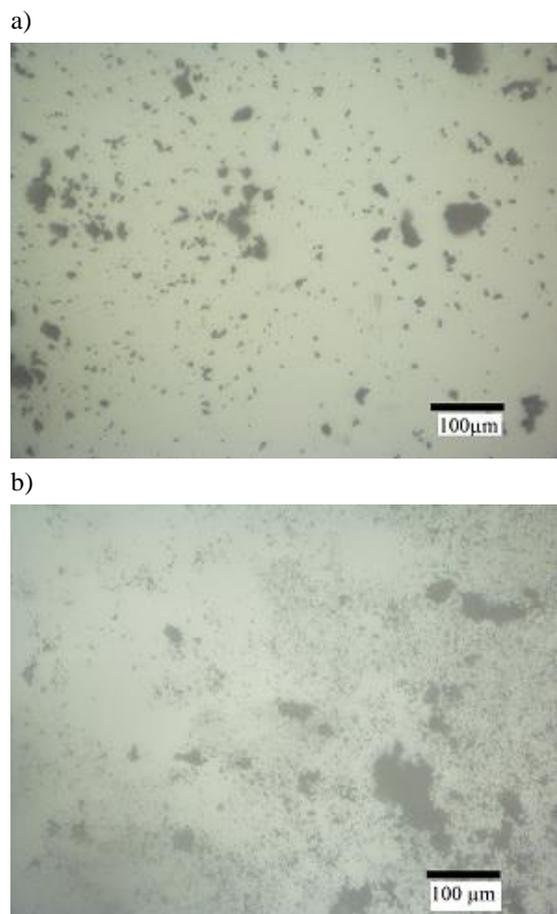
Recently, we have studied in our previous work that it is mostly related to composition optimization by making and analyzing one series of GP carbon samples [10]. So, excess carbon could prevent the fully reaction between GP components by playing a barrier role. Therefore, excess silica could be present in the form of unreacted silica in the final GP. Before mechanochemical activation, proper preparation of GP and achieving of homogeneous carbon distribution in GP were so important in terms of reaching the end.



**Fig. 1.** XRD patterns of geopolymer carbon compositions before mechanochemical activation

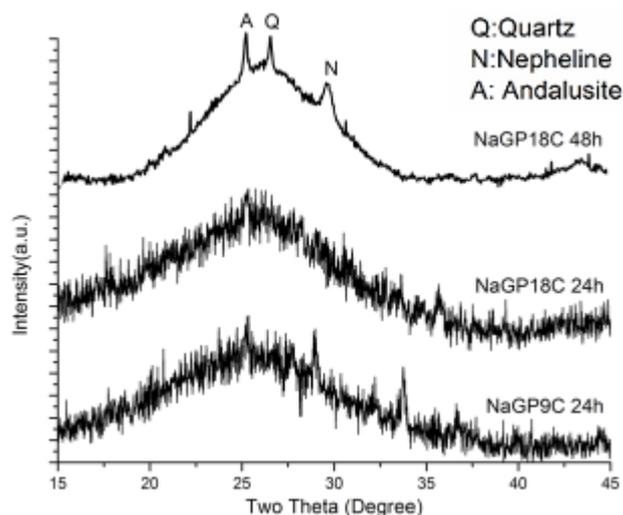
Fig. 2 reveals that optical micrographs of two different starting geopolymer carbon compositions after powdering the samples in a mortar and pestle. It is clearly seen that the microstructure of NaGP9C (Fig. 3a) mainly consisted of coarse particles, whilst excessive carbon in the case of (Fig. 3b) promoted the formation of fine particles [16, 17]. In NaGP9C, nano particles of the carbon nearly diffused into the porous geopolymeric structure and dispersed homogeneously [18]. Moreover, being the addition of 9 moles carbon during the geopolymer production route resulted in geopolymerization of more reactive GP resin with carbon [19]. Being powdered of GP9C compact following the drying GP9C resin gave rise to coarse particles. Any individual carbon could not be seen on the optical micrograph.

NaGP18C samples were prepared by the addition of 18 moles carbon in GP compact after completing of the geopolymerization. This resulted in fine particles due to brittle nature of pure GP and also excess carbon which did not incorporate into the solid GP structure by mixing the constituent in a mortar and pestle yet [5, 6]. Particle agglomeration was seen due to increasing surface area of the smaller particles.



**Fig. 2.** Optical micrographs of (a) NaGP9C and (b) NaGP18C precursors.

Fig. 3 presents XRD patterns of NaGP9C after 24 h and NaGP18C compositions after 24 h and 48 h mechanochemical activation, respectively. The broad  $2\theta$  peak at about  $28^\circ$  seen from Fig. 1 began slightly to be narrow in the case of NaGP9C sample. Some sharp peaks showing crystallization was also observed in the amorphous section of this sample. These peaks were assigned to quartz ( $\text{SiO}_2$ ). As for NaGP18C, we can see a similar pattern after 24 h mechanochemical activation. When compared to the XRD pattern before mechanochemical activation, amorphous structure retained after 24 h. Even the mixing was carried out in high reactivity GP, due to less carbon content, little crystallite phase occurred in the NaGP9C for 24 h activation.



**Fig. 3.** XRD patterns of (a) NaGP9C for 24 h, (b) NaGP18C for 24 h and (c) NaGP18C for 48 h mechanochemical activation.

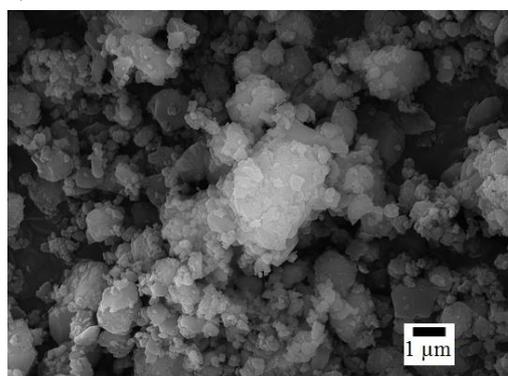
On the other hand, even we used high carbon content, due to low reactivity; little crystallization was carried out in NaGP18C sample after 24h activation as well. Moreover, low diffusion of solid particles in NaGP18C could not allow intensive crystallization. When NaGP18C samples mechanochemically activated for 48h, with the increase of activation time, peak broadening decreased and intensities of peaks increased. This was the result of crystallization of some refractory phases. These refractories were assigned to quartz ( $\text{SiO}_2$ ), nepheline ( $\text{NaAlSi}_3\text{O}_8$ ) and andalusite ( $\text{Al}_2\text{SiO}_5$ ) as seen in the XRD pattern (Fig. 3). Although there was no crystalline phase detected related to the carbon, excess carbon could serve to form the geopolymeric refractory phases by incorporating into microporous in amorphous GP and by allowing structural ordering [20-21].

The scanning electron micrographs studies of all the mechanochemically activated samples are shown in Fig. 4. The NaGP9C for 24 h sample has particles ranging from submicron-size to nano-size size distribution (Fig. 4a). It is clear that particle size decreased and particle shape became globular with narrow particle size distribution in the case NaGP18C for 24 h (Fig. 4b). This was the fact that the excess carbon could contribute to formation of finer particles by preventing the particles growth during activation [21]. In Fig. 4c, the increment of the activation duration to 48 h resulted in an agglomeration of the finer particles due to a greater surface area and energy. Higher milling duration doesn't mean finer particle size since finer particles could more readily adhere to each other in the bowl. On the other hand, compared with the classical solid state reaction methods, owing to the increase in the particle surface area where the reaction takes place and creation of valance electrons, it is expected from the particles that are produced with the mechanochemical activation method to have better reactivity [9-11]. This reactivity resulted in better crystallization seen in the

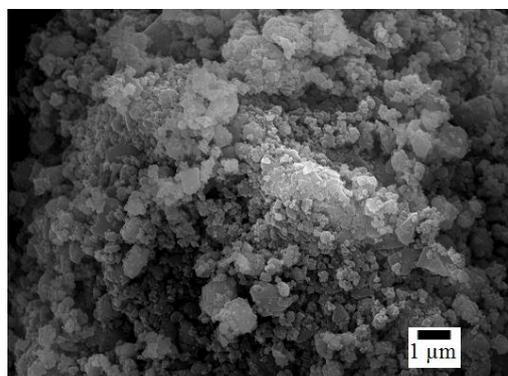
XRD analysis and this could also be confirmed by SEM analysis.

As well as surface reactivity, another advantage of mechanical activation is of improving bulk reactivity. Mechanical activation MA enables the possibility to alter the reactivity of solids through physicochemical changes in bulk without altering overall chemistry of the material. When, a fly ash that is used for aluminosilicate source for GP were mechanochemically activated before GP route, an increment of compressive strength of resultant GP [9]. Therefore, mechanically activated fly ash gives rise to nano-scale particles [11] and shows improved geopolymerisation rate [10]. If bulk materials make from the produced powders in this study, it would be expected that they show better mechanical properties.

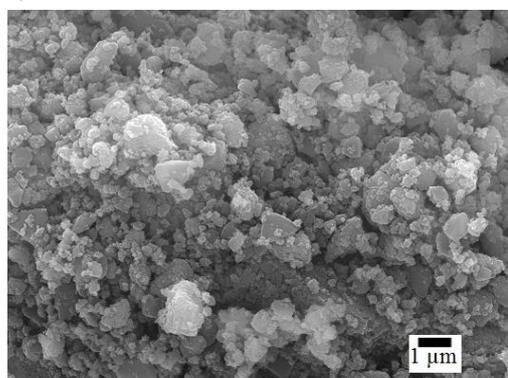
a)



b)



c)



**Fig. 4.** SEM micrographs of (a) NaGP9C for 24h, (b) NaGP18C for 24h and (c) NaGP18C for 48h mechanochemical activation.

To investigate possible conversion related to annealing temperature of samples, the DSC analyses of activated three samples was carried out and seen in Fig. 5. There was no sharp exothermic peak seen in three samples but a broad exotherm observed between 900 °C - 1000 °C indicated that the well-known nepheline crystallization [6]. Comparatively narrower exotherm showed a conversion of new crystalline phase after ~1300 °C. Consistent with our recent works [18], these result showed that initially, intensive nepheline formation was occurred and then Si in nepheline reacted with carbon nano-powder in all samples. Crystallization temperature between silicon and carbon increased with increasing carbon content and milling duration due to reamorphization of crystallized GP carbon structure [22].

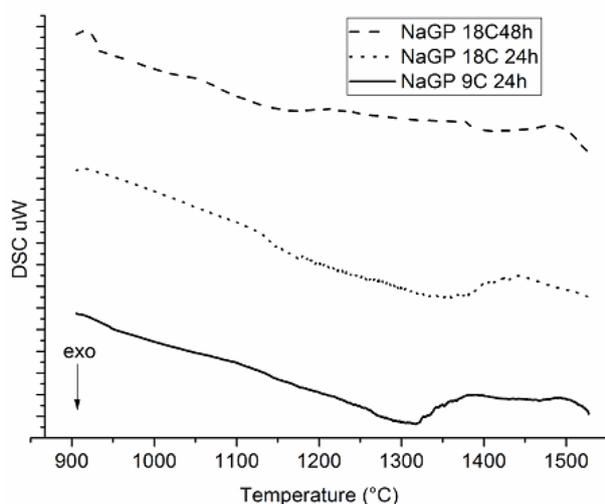


Fig. 5. DSC analysis of geopolymer carbon compositions after mechanochemical activation

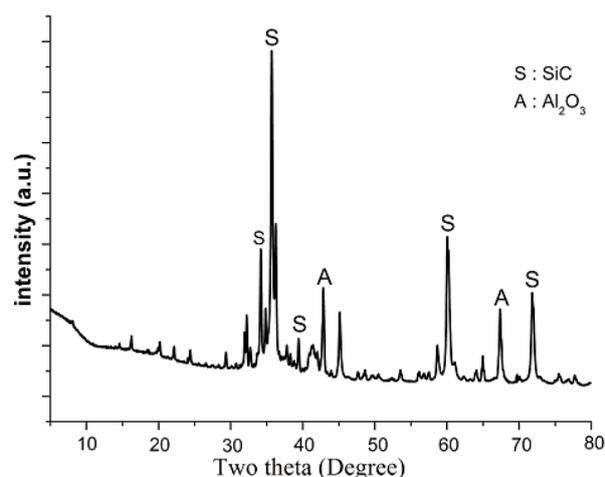


Fig. 6. XRD pattern of NaGP18C annealed at 1550°C for 2 h following mechanochemical activation for 24 h.

One of the DSC analyzed samples was also examined with XRD and Fig. 6 shows XRD pattern of NaGP18C annealed at 1550°C for 2 h following mechanochemical activation for 24 h. Sample mostly consisted of Silicon carbide (SiC) and a minor amount of alumina (Al<sub>2</sub>O<sub>3</sub>)

impurity. The details of conversion depending on heat treatment were previously reported by us [18].

#### 4. CONCLUSION

By mechanochemical activation of NaGP carbon precursors, tailored geopolymeric powders (nepheline/quartz/andalusite) can be produced at room temperature. Depended on the carbon amount, activation duration and heating temperature, the crystal phases (such as SiC) can be obtained by heating the mechanochemically activated GP carbon nano-powder precursor over 1300 °C.

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