

**NEW GENERATION GEOPOLYMER BINDERS
INCORPORATING CONSTRUCTION DEMOLITION
WASTES**

**İNŞAAT YIKINTI ATIKLARI İÇEREN YENİ NESİL
JEOPOLİMER BAĞLAYICILAR**

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This work titled “**NEW GENERATION GEOPOLYMER BINDERS INCORPORATING CONSTRUCTION DEMOLITION WASTES**” by Anıl KUL has been approved as a thesis for the Degree of **MASTER OF SCIENCE IN CIVIL ENGINEERING** by the Examining Committee Members mentioned below.

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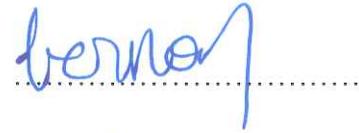
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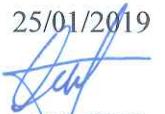
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ABSTRACT

NEW GENERATION GEOPOLYMER BINDERS INCORPORATING CONSTRUCTION DEMOLITION WASTES

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As a result of consistently expanding urban population, continuous development and industrialization of countries' economies around the world, construction and demolition industry gained prominence, despite the fact that it is also considered to be one of the largest producers of solid wastes on a global scale. At the root of substantially increased amounts of construction and demolition waste (CDW) around the world, there, for the most part, stand the new structural applications, repair/maintenance, renovation, demolition works and infrastructural development projects. If not controlled appropriately, these wastes, most of which are going to clean landfills and which are likely to incorporate toxic substances, can endanger the health of individuals and environments surrounding them. Therefore, it is crucial to deal with CDW in proper ways for environmental, social and economic benefits. From the material greenness point of view, geopolymers have been drawing the attention of numerous researchers as promising alternatives to Ordinary Portland Cement (OPC). Geopolymer is a class of aluminosilicate-based binding materials and relies on no cement. It can be made from industrial by-products such as fly ash and slag activated by an alkaline solution. Geopolymers are appealing due to engineering performances such as higher strength and resistance to acid, corrosion, fire/temperature and frost, in addition to

material greenness. The aim of this thesis is to evaluate the usability of construction demolition wastes in geopolymer production. Roof tile, red clay brick, hollow brick, concrete and glass wastes which are forming a large part of construction demolition wastes were classified, crushed and grounded right after demolition. These waste materials were used as aluminosilicate precursors individually for alkali activation without inclusion of any type of mainstream pozzolanic materials. Sodium hydroxide, sodium silicate, potassium hydroxide were used individually or combined at different ratios as alkaline activator for polymerization reactions at different molarity and concentrations. Geopolymer pastes which are based on construction demolition wastes were tested under uniaxial compressive strength loading to determine implementability of using CDW as an aluminosilicate source for geopolymers. Besides, geopolymer pastes were characterized with respect to their morphology, chemical and crystallographic structure using methods of Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDX), X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF) and Thermogravimetric Analysis (TGA). Consequently, usability of the construction demolition wastes as aluminosilicate sources in the geopolymer production individually or combined at specific ratios has been proven. Results show that it is possible to obtain the desirable strength grades from geopolymer pastes by alkali activation of brick-based construction demolition waste. However, it seems necessary to place more focus on the improved usability of waste concrete and glass in the production of geopolymer pastes.

Keywords: Construction Demolition Wastes, Geopolymer Binders, Alkali Activation, Mechanical Properties, Microstructural Properties

ÖZET

İNŞAAT YIKINTI ATIKLARI İÇEREN YENİ NESİL JEOPOLİMER BAĞLAYICILAR

Anıl KUL

Yüksek Lisans, İnşaat Mühendisliği Bölümü

Tez Danışmanı: Prof. Dr. Mustafa ŞAHMARAN

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Tüm Dünya'daki ülkelerin sürekli artan kentsel nüfusları, gelişen sanayileri ve ekonomilerinin doğal bir sonucu olarak, inşaat ve yıkım endüstrisi önem kazanmış olsa da, halihazırda küresel ölçekte ortaya çıkan katı atıkların önemli bir bölümünden sorumlu tutulmaktadır. İnşaat ve yıkıntı atıklarının (İYA) dünya çapında göz ardı edilemeyecek seviyelere ulaşmasının temelinde yeni yapısal uygulamalar, kentsel dönüşüm, bakım/onarım, yenileme, yıkım uygulamaları ve altyapısal kalkınma projeleri bulunmaktadır. Uygun bir biçimde kontrol altına alınıp bertaraf edilmedikleri takdirde toksik malzemeler bulundurma ihtimali olan ve temiz toprağa karışacak bu atıklar bireylerin sağlığını ve buldukları çevreleri tehlikeye atabilir. Bu bağlamda, İYA'nın mümkün olan en uygun yöntemlerle çevresel, sosyal ve ekonomik kaygılar göz önünde bulundurularak kontrol altına alınması önem arz etmektedir. Çevre dostu malzemelerin geliştirilmesi bağlamında, jeopolimerler, geleneksel Portland çimentolu sistemlere kıyasla son yıllarda farklı araştırmacıların dikkatini çekmiştir. Jeopolimer çimentodan tamamen bağımsız, alüminosilikat esaslı bir bağlayıcı malzeme sınıfıdır. Uçucu kül, cüruf gibi endüstriyel yan/atık ürünlerin alkali çözeltileri içerisinde aktive edilmelerinin ardından elde edilmektedirler. Jeopolimerler çevre dostu olmalarına ek olarak, mühendislik özelliklerinin (yüksek dayanım, ve asit, paslanma, yangın/yüksek sıcaklık ve don etkisine karşı yüksek direnç) üstün olmaları bakımından da göz önündedirler. Bu tez çalışmasının amacı, inşaat

yıkıntı atıklarının jeopolimer üretiminde kullanılabilirliklerinin uygunluğunun değerlendirilmesidir. İnşaat yıkıntı atıklarının önemli bir bölümünü oluşturan çatı kiremiti, harman tuğla, delikli tuğla, beton atığı ve cam atığı yıkım, onarım işlerinden sonra toplanıp tasniflenmiş, kırıcı yardımı ile kırılmış ve bilyalı değirmen yardımı ile öğütülmüştür. Bu atık malzemeler, tek başlarına ve belirli oranlarda karıştırılarak yaygın olarak kullanılan herhangi bir puzolanik malzeme ilavesi olmaksızın alkali aktivasyon sırasında alüminosilik esaslı öncül malzemeler olarak kullanılmıştır. Polimerizasyon tepkimelerini gerçekleştirebilmek adına sodyum hidroksit, sodyum silikat ve potasyum hidroksit tek başına veya farklı molarite ve konsantrasyonlarda oranlarda karıştırılarak alkali aktivatör olarak kullanılmıştır. İYA'nın jeopolimer üretiminde alüminosilikat kaynağı olarak kullanılabilirliğinin tespit edilebilmesi amacıyla İYA esaslı jeopolimer hamurlar aksenel basınç yüklemesi altında test edilmiştir. Buna ek olarak, jeopolimer hamurlarının morfolojik, kimyasal ve kristalografik yapılarının karakterizasyonu için Taramalı Elektron Mikroskobu (SEM), Enerji Dağılımlı X-Işını Analizi, (EDX), X-Işını Kırınım Analizi (XRD), X-Işını Floresans Spektrometresi (XRF) ve Termogravimetrik Analiz (TGA) gerçekleştirilmiştir. Sonuç olarak, çeşitli İYA'ların jeopolimer üretiminde tekil veya belirli oranlarda karıştırılarak alüminosilikat kaynağı olarak kullanılabilirliği kanıtlanmıştır. Sonuçlar tamamen atık tuğla esaslı jeopolimer hamurların arzu edilen dayanım sınıflarına ulaşabildiğini göstermiştir. Ancak, atık beton ve atık tuğlanın jeopolymer hamur üretiminde daha etkin kullanılabilirliklerinin belirlenmesi için konunun daha detaylı bir şekilde ele alınması gerektiği görülmüştür.

Anahtar Kelimeler: İnşaat Yıkıntı Atıkları, Jeopolimer Bağlayıcılar, Alkali Aktivasyon, Mekanik Özellikler, Mikroyapısal Özellikler

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SYMBOLS AND ABBREVIATIONS

Abbreviations

CDW	Construction Demolition Wastes
CW	Concrete Waste
GW	Glass Waste
RCB	Red Clay Brick
RF	Roof Tile
HB	Hollow Brick
FA	Fly Ash
BA	Bottom Ash
BFS	Blast Furnace Slag
GBFS	Ground Granulated Blast Furnace Slag
RCBW	Red Clay Brick Waste
XRD	X-ray Diffraction Analysis
XRF	X-ray Fluorescence Analysis
MAS NMR	Magic-Angle Spinning Nuclear Magnetic Resonance
SEM	Scanning Electron Microscopy
EDX	Energy Dispersive X-Ray Analysis
TGA	Thermogravimetric Analysis
DTA	Differential Thermal Analysis
FTIR	Fourier Infrared Transformation Spectroscopy
ICC	Isothermal Conduction Calorimetry

1. INTRODUCTION

The concrete material used in a wide variety of infrastructural applications is historically designed in a way that it will have certain characteristics at the beginning of the service period and complete a predetermined lifetime. However, under the influence of mechanical and environmental loads, the structures ending up in a shorter time than planned require demolition or maintenance/repair operations. As can be expected, in addition to the demolition and rebuilding of existing structures, a considerable amount of waste material is produced as a result of maintenance, repair and/or renovation, and these wastes are generally referred as construction and demolition waste (CDW). Since the 1980s, as a result of construction, demolition, renovation and maintenance/repair applications, significant amounts of CDW have emerged and a continuous effort has been made to reduce the CDW involved in clean soil and to eliminate the problems related to CDW. In the open literature, there are many studies that clearly demonstrate that it is possible to reuse various CDW types in addition to providing the option of recycling through various innovative technologies. In the context of this thesis, CDW-based materials such as roof tile waste, red clay brick waste, hollow brick waste, concrete waste and glass waste were tried to be used in geopolymer production. These waste materials were used as aluminosilicate precursors individually and in combination for an alkali activation without the addition of any type of mainstream pozzolanic materials. Sodium hydroxide, sodium silicate, potassium hydroxide were used individually or together as an alkaline activator for polymerization reactions at different molarity and concentrations. The main purpose of current research was to come up with innovative ideas to recycle/reuse a significant portion of CDW to result in completely recycled, eco-friendly geopolymer binder systems. By this way, both the CDW-based damage on environment and the damage caused by the cement production were tried to be reduced. Moreover, on a societal level, the current research is believed to touch every individual's life by proposing ideas for truly sustainable construction materials that considerably lower the energy consumption and carbon emissions related with the construction and building industries. It is believed that proper utilization of CDW in producing geopolymer binders will multiply the benefits in terms of environmental/health issues, material cost and wide-spread usage of such materials at reasonable prices to that of their counterparts.

2. LITERATURE REVIEW

Concrete is the second mostly used material in the world after water (Aitcin, 2000). The carbon dioxide generated during the production of the cement required for concrete constitutes at least 5 to 8% of the worldwide emission of carbon dioxide (Scriviner and Kickpatrick, 2008). Many institutions and organizations around the world are working on developing and implementing alternative binder systems to reduce the environmental impacts of cement. Today, the use of cement as a binder in building materials has become indispensable. Production of alternative binders has become important in recent years, as cement production is not likely to be reduced in the near future. However, cement production has various negative features such as high production cost and environmental unfriendliness. These reasons, in general, have made the development of new binder systems a necessity. In recent years, to come up with ideas to result in new generation binding systems, geopolymers produced by alkali activation of various pozzolanic materials have begun to be a subject of very serious interest. Detailed information is given in the following sections related to such binding materials.

2.1. Geopolymer Binder Systems

As a result of the national and international environmental problems and policies, the cement industry has undergone a major change in terms of carbon dioxide emissions, energy consumption, sustainability and the use of natural raw materials in recent years. In addition to this change, studies on the development of alternative binder systems for cement are continuing rapidly. Systems with geopolymer binders are an important part of alternative binder systems. Geopolymer binders have the potential to reduce the environmental problems mentioned above by providing similar properties of cement-based binder systems. Geopolymer binders have an important role in alternative binder systems and are obtained by activating the amorphous aluminosilicate based powder materials with alkali-based solutions. Natural pozzolans (volcanic tuff, volcanic glass, and trass) that exist in nature at amorphous state, calcined aluminosilicates (metakaolin, calcined clay) and aluminosilicate materials emerging as industrial wastes (blast furnace slag, fly ash and silica fume) can be used as powder material in geopolymer binder production. Theoretically, all the materials in the aluminosilicate class can be activated by alkalis and show binding property. However, the physical, chemical and mineralogical properties of the powder materials directly affect the behavior of the geopolymer binder. Knowing the properties of the powder material to be

used in this respect is very important in terms of determining the performance of the geopolymer binder.

2.2. Historical Development of Geopolymer Binding Systems

The first use of geopolymer binder systems dates back to 1930. In those years, ground slag powder was activated with potassium hydroxide solution to examine setting time of the mixtures. The reactivity of slag which was activated with sodium and potassium hydroxide was investigated in 1937. In 1940, Purdon carried out his first laboratory work on the development of cement-free binder materials formed with slag-sodium hydroxide and slag-alkali salts (Shiet al., 2011). Later, Glukhovsky (1959) revealed that it is possible to producing of binder materials using low calcium or calcium-free aluminosilicate (clay) and alkaline solution. Glukhovsky used "soil cements" for such binders and the term "soil silicates" for concrete obtained from such binders. According to the composition of the initial materials, these binders were separated to two groups as alkali binder systems ($\text{Me}_2\text{O}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$) and alkaline-earth binder systems ($\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$; Me: alkaline metals such as Na, K). Studies and developments on alkaline activated binder systems have begun to gain momentum after this date. In the 1980s, studies have been made on alkaline-activated modified cements in Scandinavian countries with binders called "Trief cements" and "F-cements".

Davidovits developed a new binder in 1981 by alkali activating of the aluminosilicate-based material obtained from a mixture of burned kaolin, limestone and dolomite. By giving the name "geopolymer" to the product that has a polymer structure and creating a trademark like "Pyrament, Geopolycem and Geopolymite" for binders, he has patented this product (Davidovits, 1994). Such binders were similar to the alkali binder systems discovered by Glukhovsky. Malek et al. (1986), defined this type of binders as matrix alkaline activated binding material formed by solidification of some radioactive materials. Roy and Langton (1989) stated that very old (historical) concretes have some similarities with such materials. Krivenko (1994a) has determined that silicates, aluminates and aluminosilicates react with alkalis and alkali metal salts in alkaline aqueous medium if the alkali concentration is sufficient. Such interactions occur with non-calcium clay minerals and aluminosilicate glasses of natural or artificial origin. In addition, this interaction takes place in calcium-based binder systems under natural conditions and water-resistant alkaline or alkaline-earth hydroaluminosilicates are formed which are similar to mica with natural zeolite. From the late 1980s onwards, conferences were organized on alkali-activated binders. In 1988 and

1999, Davidovits organized two international conferences on geopolymers in France. In 1994 and 1999, Civil Engineering and Architecture Department of the National University of Kiev organized international conferences about alkaline activate binders and concretes (Krivenko, 1994b; 1999). In 2002, Van Deventer, an academician of University of Melbourne, held a conference on geopolymers and in 2005 a workshop about geopolymer binders was held in France and Australia, respectively.

The first technical committee on the development of binders with alkali activations was established by RILEM. RILEM Technical Committee on Alkali Activated Materials (TC224-AAM) completed its studies in 2012 and published a detailed report on the materials activated with alkalis in 2013 (Provis and van Deventer, 2014). As the discrepancies in the literature on the durability properties of alkaline activated materials continue, RILEM's next technical committee (247 HBA) has commenced its studies in 2012 and has carried out a five-year work plan focusing on the "Durability Tests on Alkali Activated Materials".

In accordance with the above mentioned; amorphous materials with silica and alumina are theoretically used as powder materials for the production of geopolymer binders. The most commonly used powder materials for geopolymer binder systems are slag (especially blast furnace slag), fly ash from coal-fired thermal plants and calcined clay (especially metakaolin). Apart from these, natural pozzolans, bottom ash coming from coal-fired thermal power plants, calcined clays other than metakaolin and double or triple binding powder material systems with all the materials mentioned above are used and laboratory studies are carried out on them (Kutti et al., 1982; Pacheco-Torgal et al., 2008; Chindaprasirt et al., 2007; Hardjito et al., 2004; Kovalchuk et al., 2007; Bondar et al., 2011a; Fernandez-Jiménez and Palomo, 2003). In addition to these studies, in recent years, studies focusing on the production of geopolymers from different types of waste materials such as brick dust and roof tile dust were carried out.

2.3. Geopolymer Mechanism

Geopolymer binders are a member of the inorganic polymer species and have a chain structure comprising Al and Si ions. The chemical composition of geopolymer binders is similar to the chemical composition of natural zeolitic materials. However, unlike zeolitic materials, it has an amorphous structure instead of a crystal structure. (Palomo et al., 1999; Xu and van Deventer, 2000). The geopolymerization process involves an extremely rapid chemical reaction of Si and Al minerals in a high alkaline environment. This alkaline

precipitate. Initially rich in Al, this product is called "Gel 1" and is known as a semi-balanced intermediate reaction product (Fernández-Jiménez et al., 2006). Since Al-O bonds are weaker than Si-O bonds, reactive aluminates dissolve more rapidly. Thus, the formation of the gel is due to the high Al^{+3} ion concentration in the alkaline medium at the early stage of the reaction. As the reaction proceeds, more Si-O groups in the aluminosilicate source are dissolved. Thus, the concentration of silica in the reaction medium and in the N-A-S-H gel (Gel 2) is increased. The binding property of the product as a result of the reaction is determined by the final composition of the polymer, the gap microstructure and the distribution of the cavity.

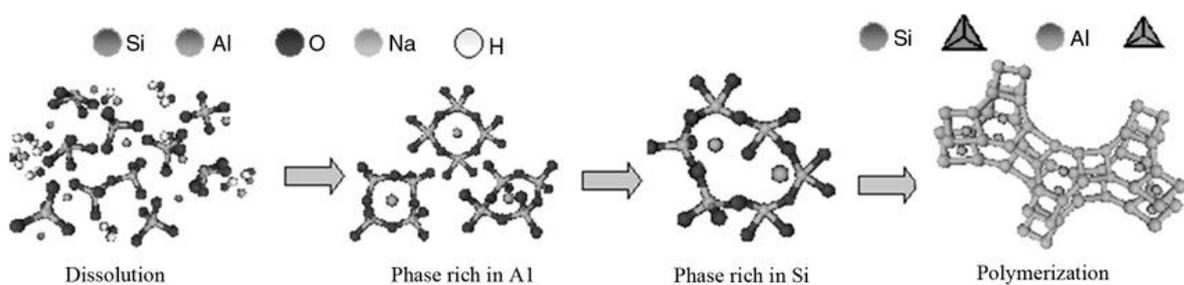


Figure 2.4 Recommended model for N-A-S-H gel formation (Fernández-Jiménez et al., 2005; Shi et al., 2011)

Geopolymers are combined with aluminum and silica atoms to form tetrahedral structures with alkalis such as K and Na. Oxygen atoms in the environment are used alternately by geopolymers. The structure of Al-O-Si forms the basis of geopolymer. Geopolymer reactions formed by dissolution of aluminates and silicates hydroxides with alkali salts. Figure 2.5 shows the formation of highly reactive structures by dissolving and polymerizing aluminates and silicates with alkali metals (Khale and Chaudhary, 2007). Davidovits, while defining the chemistry of geopolymer, proposed "Polysilicate", abbreviated form of alumina silicate oxide (Torgal et al., 2008).

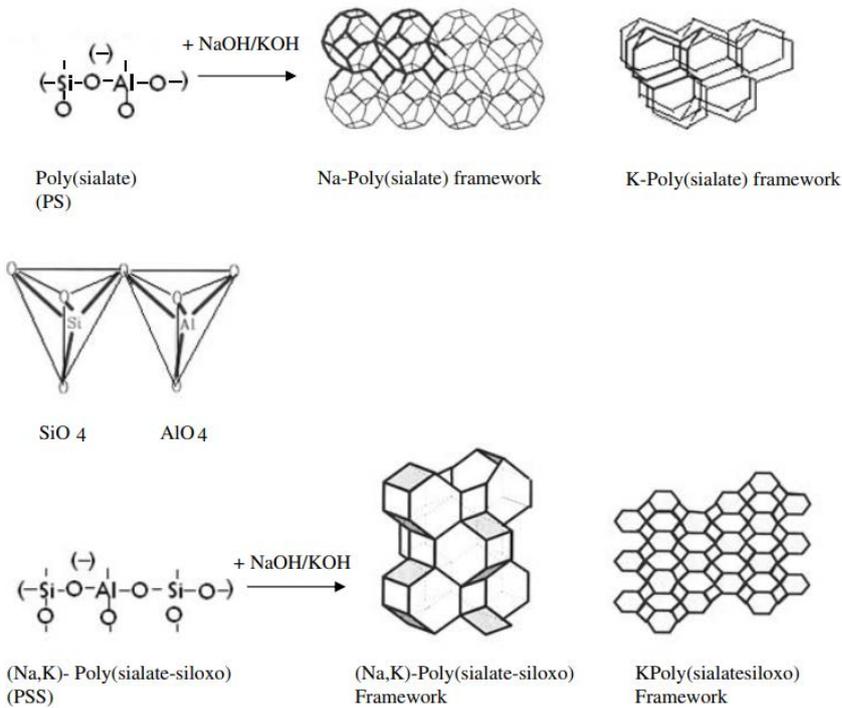


Figure 2.5 Geopolymer formation model with silicate and aluminates (*Khale and Chaudhary, 2007*)

2.4. Geopolymer Reaction Products

The main reaction product resulting from the alkaline activation of silica and aluminate-rich materials is the amorphous alkali aluminosilicate hydrate, also known as N-A-S-H (Pacheco-Torgal et al., 2015) (Figure 2.6). The silicium and aluminum in this product form a three-dimensional skeleton, which is randomly distributed in the form of a smooth four-sided structure (Palomo et al., 2004; Fernández-Jiménez et al., 2003; Provis and van Deventer, 2009).

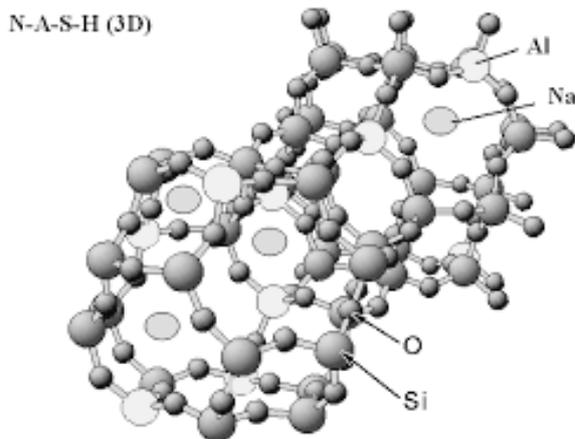


Figure 2.6 Three-dimensional view of the structure of the N-A-S-H gel (*Pacheco-Torgal et al., 2015*)

In such systems, as the second reaction product, hydroxysodalite ($\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$), “zeolite P” [$(\text{NaAlO}_2)_7(\text{SiO}_2)_9$], “Na-chabazite” ($\text{Na}_2[\text{Al}_2\text{Si}_4\text{O}_{12}] \cdot 6(\text{H}_2\text{O})$) and “zeolite” structures such as “faujasite” ($(\text{Na}_2,\text{Ca},\text{Mg})_{3.5}[\text{Al}_7\text{Si}_{17}\text{O}_{48}] \cdot 32(\text{H}_2\text{O})$) are formed (Palomo et al., 1999; Fernández-Jiménez et al., 2003, 2006; Duxson et al., 2007b).

Studies by some researchers (Palomo et al., 2005; Bakharev, 2005 a; Criado et al., 2005) showed that the curing temperature and activator type affected the reaction kinetics and the degree of reaction increased with the increase in cure temperature. In addition, the structure of aluminosilicate activation products (N-A-S-H gel and zeolite structure) varies with the curing time and temperature. Long curing times increase the formation of silica-rich products and contribute positively to the strength of the material.

The only source of silicon in the N-A-S-H gel is not powder aluminosilicate materials. Also part of the silicon in the main product is silicon dioxide from the activator (water glass) (Duxson et al., 2007b; Criado et al., 2007). Silicon dioxide in sodium silicate solution, the solution which is generally used as an alkali activator, is highly soluble and can easily be incorporated into the structure of the N-A-S-H gel. Depending on the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of sodium silicate, the degree of polymerization determines the gel structure that precipitates at various stages of the N-A-S-H gel formation.

Criado et al. (2007) studied the effect of different activator dosages (0.17, 0.60 and 1.90 $\text{SiO}_2/\text{Na}_2\text{O}$ ratio) on the reaction products resulting from alkaline activation of fly ash. As a result of the studies, it has been observed that this parameter plays an effective role in the kinetics, structure, and composition of the resulting product. In addition, it was concluded that the increase in sodium dioxide in the sodium silicate had no effect on the structure of the final reaction products. It was stated that the increase of Si/Al ratio did not affect the N-A-S-H gel structure alone. As a result of the study, it was stated that the optimum Si/Al ratio is 2. In addition, it was stated in the study that highly polymerized silica retards the ash reaction and zeolite crystallization on the formation kinetics of the N-A-S-H gel.

2.5. Geopolymers Produced by Fly Ash and Blast Furnace Slag

In their study, Sathonsaowaphak et al. (2009) used fly ash obtained from lignite to produce geopolymer. Sodium silicate and sodium hydroxide solutions were used in the activation. The effects of fly ash fineness, alkali concentration, sodium silicate/sodium hydroxide ratio on strength were investigated. The geopolymers obtained from lignite ash have been reported to have a compressive strength in the range of 20 to 60 MPa.

In the study of Komljenović et al. (2010), mechanical and microstructural properties of Class-F fly ash based geopolymer concrete were investigated. Fly ashes from six different thermal power plants were investigated. The fly ashes used were sieved from a sieve with an opening of 43 μ m and activated with NaOH+Na₂CO₃, KOH, Na₂O.nSiO₂ and NaOH solutions. 40x40x160 mm prismatic samples were produced, first cured at 20 °C room temperature for 1 day and then at 55 °C for 6 days. In terms of activation potential for equal concentration of different alkali solutions, they reached the conclusion of Na₂O.nSiO₂>NaOH>NaOH+Na₂CO₃>KOH. The highest compressive strength was 40 MPa with sodium silicate. They also determined that the increase of SiO₂/Na₂O ratio of sodium silicate solution caused the increase of Si/Al ratio of the product resulting from the reactions and the compressive strength values were directly related to the Si/Al ratio.

Vijai et al. (2010) obtained geopolymer from a fly ash containing high amounts of aluminum and silica. The density and compressive strength of geopolymer cement were studied. At the same time, the compressive strength of fly ash based geopolymer cements at different cures was investigated. Aggregates were used with fly ash, and geopolymer concrete was produced with sodium silicate and sodium hydroxide as activators and water. The samples were cured at room temperature and at 60 °C. Samples cured at 60 °C resulted in a higher compressive strength and 30 MPa compressive strength has been reached.

Criado et al. (2010) investigated the effect of small amounts of sulfate (SO₄) on N-A-S-H gel and zeolites resulting from the activation of Class-F fly ash. They prepared different solutions having a liquid/solid ratio of 0.4% with sodium oxide and sodium hydroxide with a sodium oxide ratio of about 20%. They cured the samples in an oven at 85 °C 8 hours and examined the compressive strength of 7, 28 and 180 days. Sodium sulfate was added 2.5%, by weight of fly ash. According to the results, sodium sulfate decreased the reactions and compressive strength. They observed that when sodium hydroxide (NaOH) was used as the activator, the effect of sulfate was higher and the presence of sulfate did not cause the formation of new compounds. They observed that the presence of sulfate in the pores had a negative effect on the formation of N-A-S-H gel, delaying the formation of gel and this situation decreased the pH of the medium by decreasing the reaction density.

Al Bakri et al. (2011), scanned various studies to have a general look at the fly ash based geopolymer concrete and provided guiding information by compiling some of the results on activation studies. Accordingly, they stated that the geopolymer concretes showed better

strength and durability properties compared to Portland cement concretes. They stated that with increasing temperature, the polymerization took place more rapidly and about 70% of the compressive strength development of geopolymer concretes was gained in the first 3-4 hours of curing. They indicated that with the increase of water, porosity increases in geopolymer concrete as in other concrete types. They stated that with the increase in sodium hydroxide and sodium silicate amount, the mortar consistency decreased. It was registered that extra water or superplasticizer could be added to improve workability, but the use of superplasticizer lowered the compressive strength value, therefore they emphasized that the addition of water had less negative impact on compressive strength. Compressive strength was directly related to the curing temperature and curing time so that with 60-90 °C curing temperature and 24-72 hour curing time, values in the range of 40-50 MPa could be achieved. It has been reported that fly ash with a grain size of less than 43 μm gives better results in terms of compressive strength. It has been stated that the higher compressive strength is obtained when sodium silicate is used as the activator. As a result, it was stated that geopolymer concretes have more positive results compared to normal concretes in terms of compressive strength, resistance against adverse environmental effects, workability and high-temperature exposure.

Rashad and Zeedan (2011), used 3 different proportions of sodium silicate (water glass) which contains solutions by 20%, 30%, and 40% and fly ash as a binder in their study, and examined the changes in compressive strength of samples at different levels of high temperature. Performances of activated mortars exposed to high temperatures ranging from 200 °C to 1000 °C were compared with traditional Portland cement mixtures. For the study, Class-F fly ash with a specific gravity of 2.4 and CEM I 42.5N Portland cement were used, liquid sodium silicate solution with a liquid/solid ratio of 0.35 was chosen as an activator. Three 100% fly ash-activated mortar samples with a water glass contents of 20%, 30%, and 40% were prepared and cured at 60 °C for 2 days and compared to Portland cement based mortar samples in terms of compressive strength measurements. Some of the 28-day-old samples were dried in an oven and subjected to thermal shock from 200 °C to 1000 °C in 2 hours. In addition, information about the internal structure of the samples were obtained by looking at the pH measurements. As a result of the experiments, it was concluded that the alkali-activated fly ash mortars can resist higher temperatures than the mortars produced by traditional Portland cement. As the activator concentration increased, it was stated that the first day and ultimate strength also increased. However, relative strength after the fire

exposure decreased although the compressive strength increased as the alkaline concentration increased. Alkali activated samples subjected to thermal shock effect have given better results than those produced with traditional Portland cement at all concentrations. In addition, it was observed that the thermal shock resistance decreased as the activator concentration increased. The pH of the intrinsic structure decreased after the thermal shocking of Portland cement based samples but slightly decreased after 600 °C in the samples activated with fly ash. It is stated that the pH value increases as the activator concentration increases and this situation helps prevent reinforcement corrosion by forming a passive layer on the reinforcement.

Olivia and Nikraz (2012) investigated the optimization of mechanical and durability properties of geopolymer concrete with fly ash by using Taguchi method. Nine types of the mixtures were selected for the determination of the aggregate content, fly ash/alkaline solution ratio, sodium hydroxide/sodium silicate ratio, and curing conditions. At the end of 28 days with the geopolymer concrete, they have reached up to 55 MPa compressive strength. They have used Class-F fly ash, three types of aggregates as materials, and sodium hydroxide and sodium silicate combination as activators. They used Taguchi method to select the most suitable mixture in order to reach maximum strength levels of geopolymer based concrete and applied steam curing to geopolymeric concrete. Increases in compressive strength levels have been observed in the mixtures and the highest and lowest compressive strength values were recorded as 54.89 MPa and 29.71 MPa at the end of 28 days, respectively. They found the tensile strength to be 8-12% higher and the modulus of elasticity to be 14.9-28.8% lower than the control samples. In general, the mechanical properties of geopolymeric concretes were better than conventional Portland cement concretes and they also indicated that geopolymeric concretes were more resistant to wetting and drying cycles in seawater.

Ryu et al. (2013) investigated the mechanical properties of alkali activated fly ash concrete. They used sodium hydroxide and sodium silicate as an activator in the activation of Class-F fly ash. The samples were cured at 60 °C for 24 hours before curing at 23±2 °C for 24 hours. Compressive strength tests were performed on 50x50x50 mm cubic samples and it was observed that high sodium hydroxide concentration increased the compressive strength results at an early age. They also found that chemical alterations of the alkali activators in high molarity were effective on the strength and that the optimum activator solution was the solution with 9 molars.

Ariffin et al. (2013) investigated the durability properties of fly ash and palm oil ash based geopolymers by exposing the concretes to 2% sulfuric acid for 18 months. In order to make a comparison, they produced control samples with Portland cement. In this study, compressive strength, mass change, and microstructural disturbances were evaluated. They used the fly ash and palm oil ash obtained in Malaysia to have a grain size below 45 microns. They used sodium hydroxide and sodium silicate as activators. They also added a superplasticizer additive to promote the workability. They produced 100x100x100 mm cubic samples and kept them at 28 °C room temperature for 28 days. Control samples obtained by Portland cement were cured in water for 28 days. As a result, the mass loss of Portland cement samples exposed to sulfuric acid at the end of 18 months was 20%, while the mass loss of geopolymer concrete with ashes was 8%. The loss of compressive strength was 35% in geopolymer concrete, while this rate was recorded as 68% in control sample.

Oh et al. (2014), activated two different types of Class-F fly ash which were obtained from the a thermal power plant in Korea with NaOH. The solution/fly ash ratio was selected as 0.6 and samples were cured at 60 °C. X-ray diffraction (XRD) analysis, compressive strength tests, particle size distribution analysis, X-ray fluorescence (XRF) analysis, magic-angle spinning nuclear magnetic resonance (MAS NMR) tests were performed on the samples activated with alkalis. The Si/Al and Ca/Si ratios of the first group samples (FA1) were selected as 3 and 0.1, respectively while the Si/Al and Ca/Si ratios of the second group samples (FA2) were selected as 2.6 and 0.4, respectively. The 24-hour average compressive strength of the FA1 group was 1.3 MPa and the results for the FA2 group were obtained as 6.6 MPa. The 28-day average compressive strength of FA1 group was 8.7 MPa, while the same results for the FA2 group were 41.6 MPa. In the second group, the increase in the activation level was shown by increasing the compressive strength as a result of decreasing the grain size. It was stated that the high first day strength of FA2 group was caused by high CaO ratio.

Zhu et al. (2014) focused on the changes in porosity depending on the mass liquid/solid ratio used in geopolymer concrete and the determination of the changes in chloride permeability depending on this situation, and the effect of alkali activation on the durability of the final products in the case of substitution of fly ash and slag at changing rates of up to 40%. The geopolymer concrete mixtures were cured at 20 °C temperature and 95% humidity for 1 day, in a closed environment at 65 °C temperature for 2 days and at 20 °C temperature and 95% humidity for 14 days. Control specimens prepared with cement were cured at 20 °C

temperature and 95% humidity for 1 day, then were cured in water at 50 °C for 14 days. For the compressive strength tests, 20 x20x20 mm cube specimens and for the chloride penetration Ø20x80 mm cylinder samples were prepared and also water absorption tests and SEM analyses were performed. In order to determine the proper ratio for workability of mortars, the liquid/solid ratio was chosen 0.6%, by mass. For the investigation of chloride permeability, the liquid/solid ratio was chosen between 0.7 -0.8% by mass, and the liquid/solid ratio was chosen 0.7, by mass for the mortars which are with 20-40% substitution of fly ash with slag. As a result of experiments, the chloride permeability of mortars with alkali activated fly ash have been observed to be higher than traditional Portland cement based mortars. The reduction of the liquid/solid ratio from 0.8 to 0.6 reduced chloride permeability by 40-60%. It was stated that the change of fly ash slag substitution at a constant liquid/solid ratio (0.7) did not change porosity much but decreased the tortuosity by reducing the diameter of pores. Specifically, it was indicated that it was a feature to take into consideration for durability since it will cause chloride permeability to the reinforcement in concrete made with the alkali activated fly ash based samples. They also suggested the use of superplasticizers to reduce the amount of water to reduce porosity and the addition of an effective amount of slag to improve the pore properties. It was stated that if the fly ash is coarse, the amount of activator increases and porosity is adversely affected, which may lead to the corrosion by causing movement of the chloride ions towards the reinforcement. In cases where blast furnace slag is replaced with fly ash, it was stated that a high amount of calcium source was provided for the system.

Jun and Oh (2014) produced geopolymer concrete mixtures by using 6 different Class-F fly ashes originating from Korea and compared the mechanical and microstructural properties. XRF analyses on fly ashes, compressive strength tests, XRD and SEM/EDX analyses on geopolymeric concrete samples were performed. Sodium hydroxide was used as the alkali activator for the production of samples. After curing of geopolymer mortars at room temperature for 5 minutes, they were kept at temperature of 60 °C for 24 hours and then at an environment of 23 ± 2 °C and 99% humidity until the implementation of uniaxial compressive strength tests on 7 and 28 days. 28-day-old samples were used for XRD and SEM/EDX analyses. As a result, they obtained 9.93 MPa as the highest compressive strength from samples produced with fly ash having the lowest percentage of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$. Although there were differences in the compressive strength results, it was observed that

there were few differences in the microstructures of the alkali activated samples and it was stated that there were gaps due to non-activated alkali particles.

Sarker et al. (2014) carried out studies on fire resistance and cracking/spalling properties of Class-F fly ash based geopolymeric concrete. In the study, the amount of fly ash passing through 45-micron sieve was determined as 25% and sodium hydroxide and sodium silicate were used as the alkali activators. Steam curing was applied to geopolymeric concretes at 60 °C and 80 °C. They exposed traditional Portland cement and geopolymer based concrete to high temperatures above 1000 °C. The compressive strength of geopolymeric concrete mixtures was found to be between 39-58 MPa. After exposure to high temperatures, geopolymeric concretes with fly ash, compared to Portland cement based control concretes, were found to be less damaged. In addition, at the temperature of 800-1000 °C, while traditional Portland cement based concretes showed severe spalling, geopolymeric concrete was not swollen. In general, geopolymeric concretes have maintained their strength compared to the control samples. It was stated that the increases in microstructural damage with increased temperature was due to the damage caused by the expansion of aggregates and geopolymeric paste with different levels.

Görhan and Kürklü (2014) produced geopolymeric concrete mixtures by using Class-F fly ash from Kütahya Seyitömer Thermal Power Plant and by making changes in curing temperatures and times. In their study, they investigated the relation between different time periods and curing temperatures with alkaline concentration. Therefore, they used 3M, 6M and 9M sodium hydroxide and sodium silicate solutions. As different curing temperatures, 65 and 85 °C were chosen. After 7 days of curing time, physical properties such as unit weight, apparent density, porosity and water absorption and mechanical properties such as bending and compressive strength were evaluated. As a result of the experiments, they concluded that when curing time and activator concentration increased, porosity decreased. They observed the highest compressive strength in geopolymeric concrete samples produced with 6M sodium hydroxide and reached to a maximum of 22 MPa compressive strength after 24 hours at curing temperature of 85 °C. It was stated that the increase in curing temperature generally increased the compressive strength but did not affect the physical properties significantly.

In their study, Ma and Ye (2015) investigated the autogenous and drying shrinkage behaviors of Class-F fly ash based geopolymer pastes prepared by different proportions of sodium

silicate solution and cured at 40 °C for 7 days. In addition, the paste samples which were produced by CEM I 42.5 cement having a water/binding material ratio of 0.4 and cured for 7 days, were used for control purposes. In the study, three mixtures with water/fly ash ratio of 0.35 were prepared by changing the SiO₂ and Na₂O molar values of geopolymer mixtures. As the molar values of SiO₂ and Na₂O increased from 1 to 1.5, an increase in compressive strength values was observed. At high SiO₂ and Na₂O ratios, autogenous and drying shrinkage values increased. Autogenous shrinkage occurred between 1-3 days in the alkaline activated samples and no crack formation was observed due to autogenous shrinkage at early ages. Cement-based and alkali-activated pastes reacted differently in terms of autogenous shrinkage. In terms of 180-day drying shrinkage, the results of alkali activated samples with SiO₂ and Na₂O molar values of 1.0-1.5 and 1.0-1.0, respectively, were lower than paste samples produced with cement. Alkali activated specimens with molar values of 1.5-1.5 had close drying shrinkage results. As the SiO₂ and Na₂O ratio of the alkaline activated samples increased, the drying shrinkage increased, but the losses in the weights were not proportional. The values of the capillary pressure formed in different pores of the samples activated by alkalis were shown as the reason of the formation of different weight loss/drying shrinkage rates.

Kumar et al. (2015) examined the effects of different particle size distributions on the properties of mortar samples activated with fly ash. The fly ash with a maximum particle size of 40.37, 23.64, 10.33 and 2.98 μm was collected by electrostatic method, activated with 6M NaOH and cured at 60 °C. In all physical tests, the liquid/solid ratio was used as 0.35. Samples were first cured at 60 °C for 24 hours, then stored at 27±2 °C for 3, 7, 14 and 28 days and subjected to compressive strength tests. Isothermal conduction calorimetry (ICC), XRD, SEM, EDX and Fourier infrared transformation spectroscopy (FTIR) tests were used to evaluate geopolymerization and microstructural properties. As a result, it was stated that, fly ashes in different grain sizes had a different chemical and mineralogical structure, with the increase in fineness the ratio of SiO₂/Al₂O₃ have increased and, there was a specific relevance between formation of geopolymer reaction and the ratio of silica. It was concluded that more reaction products were obtained in the fly fine ash (10.33 and 2.98 μm) and higher early strength development was noted. Compressive strength, geopolymerization reactions and microstructure were directly related to the SiO₂/Al₂O₃ ratio. Electron microscope images showed that the best grain distribution occurred in the samples incorporated fine-grained ash and non-reacted particles remained in the samples incorporated coarse-grained ash.

Atış et al. (2015) have activated Class-F fly-ash by NaOH and formed an alkaline medium providing high pH. They investigated the effect of heat curing temperature, curing time and Na concentration on compressive and flexural strength of mortar samples. The sand/binder ratio in the mixtures was selected as 3 and the water/binder ratio was selected as 1/3. The Na concentration was kept between 4% and 20% while the curing temperature was maintained at levels ranging from 45 °C to 105 °C. As the duration of thermal curing 24, 48 and 72 hours were chosen. In order to investigate the effect of each parameter, three 40x40x160 mm samples were produced and cured, then were kept in ambient temperature and their flexural and compressive strength were determined. For Na ratio of 14%, temperature of 115 °C and curing time of 24 hours, flexural strength of 15 MPa and compressive strength of 120 MPa were achieved. As the alkali activator concentration and heat curing temperature increased in geopolymer mortar mixtures, the flexural and compressive strengths increased to the optimum levels, but the excess Na ratio and curing temperatures decreased the strength results. It has been thus stated that the increase in curing time increases flexural and compressive strength up to a certain point. For strength development, 72 hours of curing was enough at low temperatures while 24 hours of curing was enough at high temperatures. When the Na concentration was lowered below 8%, the strength development was not observed even at high-temperature levels.

Kaya (2016) have used Class-F fly ash obtained from the Tunçbilek Thermal Power Plant and Class-C fly ash obtained from the Kangal Thermal Power Plant to produce geopolymeric mortars in the presence of sodium hydroxide (NaOH) and sodium silicate ($n\text{SiO}_2 \cdot \text{Na}_2\text{O}$). Compressive strength tests were carried out on the samples which were kept in the ambient medium for 28 days after subjected to thermal curing. Durability tests were carried out on the specimen group which gave the highest compressive strength. The highest compressive strength was found to be 50.64 MPa in the presence of Class-F fly ash. In the presence of Class-C fly ash, the highest compressive strength that could be obtained was 13.88 MPa.

In his doctoral thesis, Görür (2015) activated Sugözü Class-F fly ash using sodium hydroxide (NaOH). By preparing the mortars in different sodium ratios, the optimum mixing parameters for strength tests were determined as 14% Na concentration rate and 115 °C curing temperature levels. With these parameters, the maximum compressive strength reached to 118.8 MPa level. He also stated that the samples did not gain any strength under a temperature of 55 °C.

Castel and Foster (2015) carried out pull-out tests to determine reinforcement adherence of geopolymer concrete obtained under different curing conditions. Using the mixture of NaOH and Na₂SiO₃ as activator, they activated the source materials composed of Class-F fly ash and slag mixture and applied two different curing methods on the samples. The samples in the first group were cured in the oven at 80 °C for 1 day, in a water bath at 80 °C for 1 day and then at room temperature until 28 days while the samples in the second group were cured at 80 °C for 1 day, in a water bath at 80 °C for 6 days and then at room temperature until 28 days. The water/binder ratio of the mixtures was 0.35, NaOH molarity was 12M, Na₂SiO₃/NaOH ratio was 2.5. They stated that the mechanical properties of geopolymers are increasing depending on the curing conditions. The samples which were cured at high temperature for 2 days gave similar adhesion strength results with traditional Portland cement samples, while the samples which were cured at high temperature for 7 days reached the highest values.

Hamidi et al. (2016) investigated the effect of NaOH concentration on the mechanical performance and internal structure of geopolymers. For this purpose, they activated the fly ash with NaOH concentrations having Na ranging from 4% to 18%. Curing time and temperature were chosen as 24 hours and 60 °C, respectively. In order to evaluate the structure of geopolymers, to examine the internal structure, and to evaluate the mechanical properties FTIR, SEM and flexural strength tests were performed, respectively. They determined the Si-O-Si and Al-O-Si bonds at low frequencies with FTIR and the presence of water molecules at high frequencies. In addition, they observed the formation of sodium carbonate. They also showed that the flexural strength results showed a steady increase at NaOH concentrations of 4, 6, 8, 10 and 12%, but started to decrease at 14, 16, and 18% levels. They stated that the optimum Na concentration was 12% for the 24-hour curing time and 60 °C thermal curing temperature.

Okoye et al. (2016) investigated the durability characteristics of fly ash based geopolymer concretes in the case of fly ash and silica fume substitutions. For this purpose, a group of cement based control samples, a group of 10% silica fume-substituted samples, a group of 20% silica fume-substituted samples and 100% fly ash based geopolymer concrete were produced. The geopolymer samples were prepared using NaOH and Na₂SiO₃ mixture as alkali activator and cured at 100 °C for 72 hours. The water/binder ratio of the mixtures was 0.20, the molar ratio of NaOH was 14M, the alkali/fly ash ratio was determined as 0.40 and the superplasticizer was used for achieving a proper workability. After exposing all samples

to 2% sulfuric acid solution and 5% sodium chloride solution, changes in physical appearance, weight loss and compressive strength results were examined. As a result of the sulfuric acid exposure of the sample group in which fly ash was replaced with silica fume by 20%, no acid erosion and deterioration were observed in the concrete. Although each sample lost weight, the minimum loss was observed in samples produced with 20% silica fume substitution and the maximum loss was observed in control samples. The maximum loss in terms of compressive strength was observed in the control samples, the minimum strength loss was observed in fly ash based geopolymer concrete produced with 20% silica fume substitution. Although the loss of strength was higher in 100% fly ash based samples, it was less than the control samples. The maximum loss in terms of compressive strength was observed from the control samples, the minimum loss was observed in fly ash based geopolymer concrete produced with 20% silica fume substitution. In the control samples, the loss of compressive strength increased due to time and the increase was the highest in this group. The lowest strength loss was again observed in geopolymer samples produced with 20% silica fume substitution. Consequently, it was reported that 20% silica fume substitution had a positive effect on the long-term durability properties and suggestion has been made to try different silica fume substitution ratios.

Assi et al. (2016), has investigated the relation between the mechanical properties of fly ash based geopolymer concrete and the parameters such as the type of alkali activation solution, curing conditions and fly ash source in their study. The microstructure, density, water absorption and void ratio of geopolymer mortars were investigated. Sodium hydroxide, silica fume and water in the first activator mixture; sodium hydroxide, sodium silicate and water in the second activator mixture were used. The first mixture was kept for two days under ambient conditions then heated at a temperature of 75 °C for two days. The second mixture group was kept under ambient conditions for one day then subjected to thermal curing at a temperature of 75 °C for two days. The compressive strength tests were carried out after 7 days. Early-age compressive strength of the mixture obtained by silica fume reached to 105.1 MPa. The silica fume mixture gave higher results than the mixture obtained with sodium silicate. In addition, it was stated that the compressive strength of the mixtures with different fly ashes was affected at the same rate, as the microstructure and grain size changed.

Noushini and Castel (2016) investigated the various transportation properties of geopolymer concretes obtained under various curing conditions depending on the pore structure. For this, a total of 12 different curing conditions were chosen at 60, 75, 90 °C and 8, 12, 18 and 24

hours of thermal curing periods. Cement based control samples were kept in water at 23 °C for 28 days and geopolymer samples were kept at room temperature for 28 days after thermal curing. A mixture of sodium silicate and sodium hydroxide was used as the alkali activator. The compressive strength, elasticity modulus, ultrasonic sound wave propagation speed, water absorption, permeable void volume, void size distribution and electrical resistance measurements were performed on the produced samples. It has been stated that the compressive strength ranged between 27.4-62.3 MPa and the modulus of elasticity ranged between 13.5-25.9 GPa when thermal curing temperature was 75 °C and curing time exceeded 24 hours. The compressive strength values of the geopolymers cured under ambient conditions were insufficient. It was stated that there was an increase in the permeable pores of samples cured below 75 °C and less than 18 hours. Optimum permeable pore formation occurred at 75-90 °C and after 18-24 hours of curing. High capillary water absorption was observed in the samples cured under 60 °C, and the values decreased with increasing heat curing time and temperature. Electrical resistance increased with increased humidity. The electrical conductivity of the control group samples was higher. While the humidity rate was below 40%, the rate of increase in electrical conductivity decreased. The compressive strength of geopolymer concretes decreased from 60 MPa to 40 MPa and electrical resistance decreased by 50%. According to these results, it was stated that the quality of geopolymers, similar to conventional Portland cementitious concretes, can be considered in terms of compressive strength results.

Leong et al. (2016) activated fly ash by mixing alkali hydroxides (NaOH, KOH or Ca(OH)₂) and sodium silicate and investigated the changes in compressive strength results. Samples were prepared with various Na₂SiO₃/NaOH (KOH or Ca(OH)₂) and alkali activator/ash ratios by selecting fly ash/sand ratio as 1/2. All samples were covered with a plastic cover to avoid the loss of pore water and subjected to thermal curing for 24 hours at 60 °C. High Na₂SiO₃/NaOH (KOH) ratio did not provide high compressive strength, the most suitable strength was obtained when the alkali activator/ash ratio was 0.4, and the use of NaOH or KOH as an alkali activator with a Na₂SiO₃/NaOH ratio of 2 and Na₂SiO₃/KOH ratio of 1. It was stated that high oxide molar values did not give high compressive strength results. CaO/Al₂O₃, SiO₂/Al₂O₃, CaO/SiO₂ oxides had similar results with NaOH and KOH type activators. When the Ca(OH)₂ alkali activator was used, it was observed that the compressive strength values were significantly lower than those obtained with NaOH and KOH. It was observed that samples produced with Ca(OH)₂ hardened quickly than NaOH and KOH based

geopolymers. When $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio was 0.5 and 1, KOH based geopolymers had higher compressive strength results but when $\text{Na}_2\text{SiO}_3/\text{NaOH}$ ratio was greater than 1.5, NaOH-based geopolymers were found to have higher compressive strength.

Helmy (2016) evaluated the compressive strength values by applying intermittent curing in the presence of Class-F fly ash. As an alkali activator, NaOH and Na_2SiO_3 were used in different ratios. In the intermittent curing method, the samples were cured 6 hours at 70°C , then kept under ambient conditions for 18 hours. This 24-hour process was considered as a cycle and the samples were cured in four cycles. It was indicated that there was an increase in compressive strength results at each step of the intermittent curing cycle. It was stated that the increase in compressive strength was directly proportional to the high specific gravity of sodium silicate, the molar ratio of NaOH used, the ratio of alkali/fly ash and the ratio of $\text{H}_2\text{O}/\text{Na}_2\text{O}$.

2.6. Geopolymers Produced by Construction Demolition Wastes

2.6.1. Use of Construction Demolition Wastes in Cement Based Materials

CDW production has increased significantly as a result of the ever-growing construction sector. This increase in the production of CDW has caused to a significant increase in the construction management related problems. This situation has also made concerns about the disposal of CDW more and more dominant. Therefore, in order to promote sustainable development, increasing the use of CDW as alternative raw materials appears to be an issue to be emphasized (Rodrigues et al., 2013). There are many studies in the literature evaluating the usability of CDW as alternative aggregates. These studies have mostly focused on the substitution of CDW as coarse aggregates in sustainable concretes which can show the desired properties in terms of durability and mechanical performance. However, although the results obtained are numerous and varied, in some cases there are discrepancies between them. These discrepancies are generally associated with the differences in the interface transition zone (ITZ) characteristics between the coarse aggregates and new binders. According to Pereira-de-Oliveira et al. (2014), the hydrated cement paste on the CDW is adhered to the surface of the aggregates. This hydrated portion has several unknown properties and consequently affects the intended ultimate performance of the concrete in both fresh and hardened form. Therefore, in order to overcome such problems, a large number of researchers have begun to investigate the use of recycled fine aggregates from CDW. For instance, Khatib (2004) carried out research on the feasibility of using fine CDW

aggregate instead of natural fine aggregate with ratios ranging from 0% to 100% in concrete. The results showed that using of 25% and 100% fine CDW aggregates instead of the natural fine aggregates are the causes of losses in compressive strength by 15% and 30%, respectively. In addition, Fan et al. (2015; 2016) studied the effects using fine CDW aggregates instead of natural aggregates which were obtained by different crushing methods, on the properties of concrete and determined that important concrete properties (i.e. mechanical properties) were significantly associated with the amount of CDW aggregates. In the literature, it is also stated that it is beneficial to use mineral additives in concrete mixtures which are produced with recycled fine aggregates. For instance, Sim and Park (2011) evaluated the compressive strength of samples prepared by substituting different amounts of fly ash with recycled fine aggregates. They stated that the increase in the amount of recycled fine aggregates continuously increases the strength of the produced mortar samples until the end of the 28 days total curing time. Khoshkenari et al. (2014) stated that they observed decreases in the compressive strength results in their work where CDW-based fine aggregates were used together with silica fume; however, the addition of silica fume with the reduction of water-to-cement ratio resulted in significant increases in the compressive strength of the CDW-based concretes compared to the control group.

Regardless of the size, the properties of recycled aggregates used in concrete were tried to be developed and different recycling applications were investigated in various studies. Song and Ryou (2014) proposed a washing process which could improve the physical properties of the final product to obtain appropriate fine recycled aggregates. Koshiro and Ichise (2014) introduced a new method of recycling by using a thermal grinder system to produce higher quality fine recycled aggregates. Florea and Brouwers (2013) used three different crushing-sieving techniques to obtain CDW-based aggregates with different properties such as various particle size distribution, density, heat treatment reaction and mineralogical composition. They concluded that the crushing-sieving method used had a significant effect on the quality of the final aggregates and that an optimized crushing method could lead to obtain better properties from the recycled fine aggregates. The process consists of the following steps in sequence: after a single crushing process, the mashing of the raw material is applied then fine aggregates are obtained by sieving the CDW-based materials. Fan et al. (2016; 2017) observed that the fine CDW-based aggregates obtained by repeated crushing show better results than those made by sieving after the first crushing process, but that the first recycling method resulted in higher energy consumption.

2.6.2. Use of Construction Demolition Wastes in Geopolymer Mortars

In recent years, the use of CDW in geopolymerization methods has emerged as a subject of interest to researchers worldwide. The fact that CDW has high silica and alumina content similar to various industrial by-products makes it possible to reuse these materials in the construction sector. Recently, in the literature, CDWs such as silt, brick, concrete, ceramic products; sludge from water treatment plants, marine sediments have been used successfully in sustainable geopolymer based products but their performance has been different. Figure 2.7 shows the position of each CDW and mineral additive in the triangular chart for chemical compounds. Data for mineral admixtures were obtained from the average values of the chemical compositions presented in Table 2.1. Data for various CDW materials such as concrete, red clay brick waste (RCBW) and tile waste were reported by Ahmari et al. (2012), Rakhimova and Rakhimov (2015), Zaharaki et al. (2016). This chapter mainly focuses on the mechanical properties of CDW-based geopolymers.

Table 2.1 Chemical compositions of various mineral additives used for geopolymer production

%	Class-F fly ash	Metakaolin	GGBS	Silica fume	Palm oil fuel ash
SiO₂	38-65	43-53	26-36	88-96	46-54
Al₂O₃	25-50	40-52	5-17	0.1-1.2	1.9-3.1
Fe₂O₃	2-13	0.4-2.6	0.6-1.9	0.3-1.6	1.1-2.4
MgO	0.3-1.8	0.03-0.4	4-9.5	0.4-1.8	4.0-4.5
CaO	0.7-8	0.02-0.1	34-54	0.2-1.8	8.0-8.5
K₂O	0.1-3	0.2-1.3	0.05-0.9	0.2-1.2	4.0-6.5
Na₂O	0.05-0.9	0.15-0.25	0.03-0.5	0.1-1.2	0.1-1.3
LOI	0.03-7.7	0.5-2.4	0.02-2.05	0.4-3.5	18-22

In the previous sections, it is stated that the performances of geopolymer based binders and concretes vary depending on the factors such as chemical properties of the source materials, molarity, ratio of alkaline activators, curing conditions. Table 2.2 details the research activities carried out since 2009, emphasizing the feasibility of using CDW in geopolymer technology, considering the important factors in geopolymerization technology.

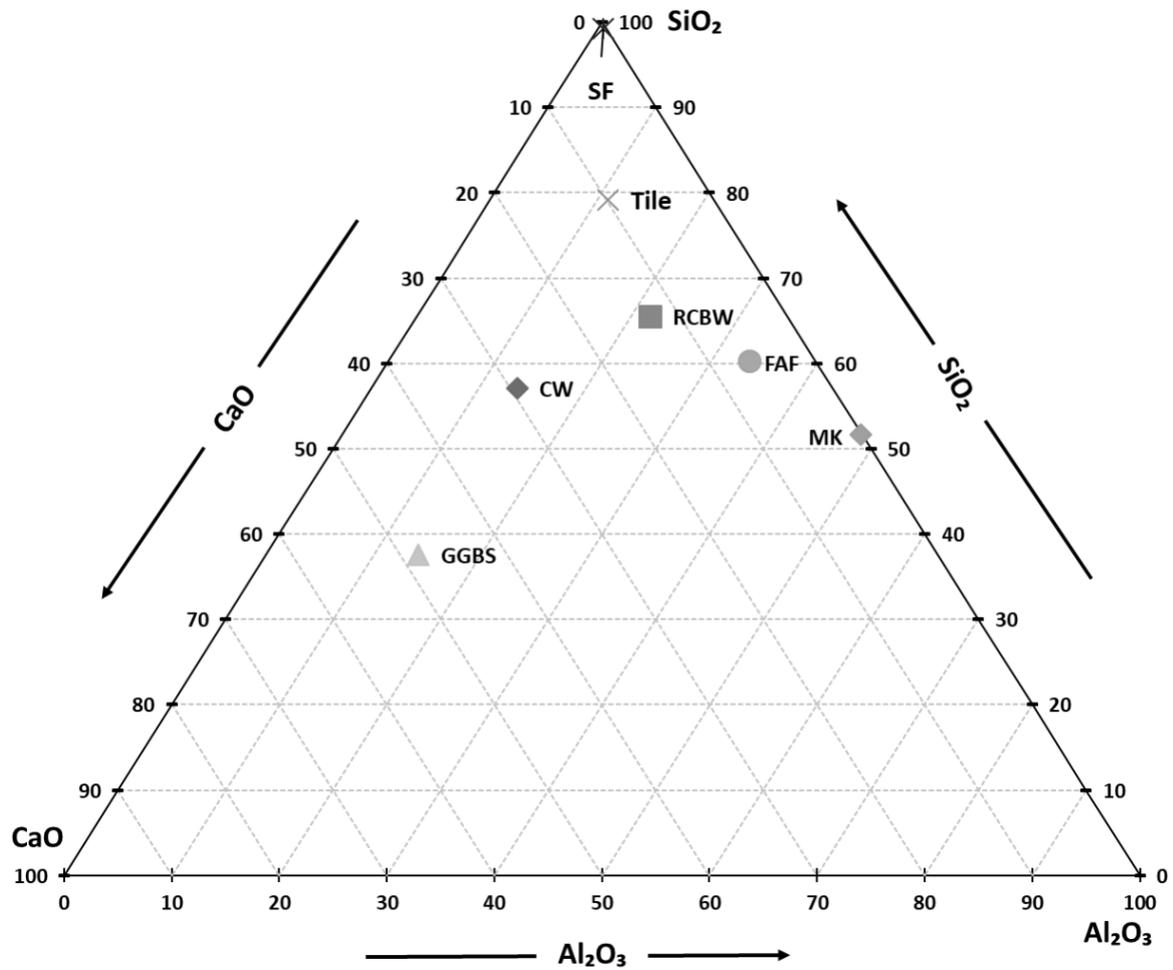


Figure 2.7 The position of CDW and mineral additives on the triangular chemical compound chart (CW: Concrete waste, RCBW: Red clay brick waste, FAF: F-class fly ash GGBS: Ground granulated blast furnace slag SF: Silica Fume, MK: Metakaolin) (*Saha et al., 2017; Adak et al., 2014; Ahmari et al., 2012; Zaharaki et al., 2016*)

Table 2.2 Research activities since 2009 on the feasibility of using CDW in geopolymer technology

Reference	CDW geopolymers constituents	Curing conditions	Studied parameters	Compressive strength range	Major conclusions
Lampris et al. (2009)	Fly Ash, Metakaolin, Silt, NaOH solution, liquid sodium silicate	1. Room temperature, 2. 3 days at 60 °C and 4 days at room temperature (RT) 3. 24 hours at 105 °C	Compressive strength, Scanning electron microscopy (SEM) analysis	8-40 MPa Binder	The mechanical properties of the final products are related on the composition and curing conditions. In addition, metakaolin may improve the geopolymerization process by increasing the solid-liquid ratio and adjusting the Si/Al ratio, while treatment of silt is required to high initial water demand.
Allahverdi and Najafi Kani (2009)	Waste brick, waste concrete, NaOH solution, liquid sodium silicate	24 hours at room temperature with relative humidity 95% Then soaked in the water bath	Compressive strength, Setting time, Infrared spectroscopy, SEM analysis	10-40 MPa Binder	In the geopolymerization process, the waste brick reacted better than the waste concrete. Na ₂ O concentrations were significantly effective on final setting times.

Yang et al. (2009)	Concrete sludge, metakaolin, silica fume, 10M NaOH solution, liquid sodium silicate	24 hours room temperature	Compressive strength, Flexural strength, XRD and SEM analyses	7-27 MPa Mortar	Fine aggregates in concrete mud-based paste and mortar exhibited low interface quality. However, due to the better polymerization of the raw materials, metakaolin and silica fume showed higher performance.
Ahmari et al. (2012)	Waste concrete, Class F Fly ash, NaOH solution (98% purity), liquid sodium silicate	24 hours room temperature and 6 days in plastic bags	Compressive strength, XRD, SEM and EDX analyses, Infrared spectroscopy	6-34 MPa Binder	The use of waste concrete has a threshold in increasing the compressive strength in terms of chemical composition. At higher NaOH concentrations, higher compressive strengths were obtained.
Khater (2012)	Waste concrete, demolished wall with cementing binders, calcium hydroxide (hydrated lime), metakaolin, NaOH solution (99% purity), liquid sodium silicate	1. Soak in tap water at RT, 2. 40 °C with 100% relative humidity, 3. water cured at RT and 24 hours at 80 °C	Compressive strength, XRD and SEM analyses, Infrared spectroscopy	1.5-27 MPa Binder	For SiO ₂ /Al ₂ O ₃ ratios, better mechanical properties were reported in the range 3.0-3.8. Calcium hydroxide increases the solubility of aluminosilicate-based materials in the alkaline solution. Different curing conditions showed different performances. The curing condition (i) performed better than the curing condition (ii). Development achieved in terms of mechanical and microstructural properties in curing condition (iii).

Sun et al. (2013)	Waste ceramic, liquid sodium silicate, NaOH solution, KOH solution	60 °C with 100% relative humidity	Compressive strength, TGA, XRD and SEM analyses, Infrared spectroscopy	26-71 MPa Binder	The initial reaction system and alkaline solutions have the highest effect in the geopolymerization process. Waste ceramic based geopolymers have shown increased strength results with proper heat treatment after calcination at 1000 °C.
Reig et al. (2013a)	Red clay brick waste, NaOH solution (98% purity), liquid sodium silicate	65°C with 90-95% relative humidity	Compressive strength, Porosimetry, TGA, XRD and SEM analyses, Infrared spectroscopy	4-50 MPa Mortar	Both NaOH and sodium silicate can be used to activate red clay brick zeolitic with better results at high alkaline solution concentration. Strengths can be improved by optimizing SiO ₂ /Na ₂ O, water/binder and binder/sand ratios.
Reig et al. (2013b)	Red clay brick waste, Porcelain stoneware, NaOH solution (98% purity), liquid sodium silicate	7 days at 65°C with 100% relative humidity	Compressive strength, TGA, XRD, SEM and EDX analyses	21-42 MPa Mortar	Red clay brick wastes required higher water content and lower sodium concentration compared to porcelain stoneware. Optimum results were obtained for low water/binder ratio and constant Na ⁺ /binder and SiO ₂ /binder ratios.

Rakhimov a and Rakhimov (2015)	Granulated blast furnace slag, four different types of red clay brick waste, liquid sodium silicate, sodium carbonate solution.	16 hours at steam curing (ascending and descending program). Then keep at RT with 95% relative humidity.	Compressive strength, Setting time, Water requirement, Water absorption, Density, Flexural strength	2-140 MPa Binder	The type of alkaline activator, concentration of red clay brick waste, milling methods, curing conditions and source of red clay brick waste have the highest and lowest effect on the properties of the final product.
Komnitsas et al. (2015a)	Waste concrete, brick, tile, marine sediments, KOH solution, liquid sodium silicate	N/A	Compressive strength, Infrared spectroscopy, SEM analysis	3-55 MPa Binder	The partial use of marine sediments with bricks/tiles can be used for the formation of a strong geopolymeric bond, in consequence of the sufficient Si/Al in the raw materials.
Komnitsas et al. (2015b)	Waste concrete, brick, tile, NaOH solution, liquid sodium silicate.	24 hours at RT with plastic bags, then curing at 60, 80 and 90°C.	Compressive strength, Infrared spectroscopy, XRD and SEM analyses, thermal stability	3-57.8 MPa Binder	The activation of bricks and tiles was showed better performance than waste concrete due to the high content of SiO ₂ and Al ₂ O ₃ . For better properties, it was recommended to cure in a temperature range of 80-90 °C with 7 moles of NaOH in the range 8-10 M for up to 7 days.

Zawrah et al. (2016)	Waste fired clay bricks, granulated blast-furnace slag, liquid sodium silicate, NaOH solution (99% purity)	24 hours with polythene sheet, then 90 days at RT	Compressive strength, Apparent porosity, Bulk density, Water absorption, XRD, SEM and EDX analysis, Infrared spectroscopy, Elemental mapping	3-83 MPa Binder	Curing at environmental conditions was not found suitable a complete geopolymerization. The addition of granulated blast furnace slag to clay brick-based geopolymer results in better physico-mechanical properties.
Rovnaník et al. (2016)	Fly ash, brick powder, NaOH solution, liquid sodium silicate	21±2 °C with 50±5% relative humidity	Compressive strength, Flexural strength, Bulk density, SEM analysis	5-65 MPa Binder	50%-50% fly ash-brick powder exhibited optimum compressive strength for blended geopolymers. In addition, the geopolymer based on bricks powder showed a less compact structure than that of fly ash (one component) geopolymers.
Khater et al. (2016)	Ceramic waste, clay brick waste, NaOH solution (99% purity)	24 hours at RT, then 40°C with 100% relative humidity	Compressive strength, Water absorption, Infrared spectroscopy, XRD analysis	19-48 MPa Mortar	Due to the stronger/good shape and matrix bonding properties of the particles, the ceramic particles showed better mechanical properties than the clay brick particles.

Zaharaki et al. (2016)	Electric arc furnace slag, tile, brick, waste concrete, red mud, NaOH solution, liquid sodium silicate	4 hours at RT, keep in plastic bags with 80°C for 24 hours and then 7 days at RT	Compressive strength, TGA, XRD and SEM analyses, Infrared spectroscopy, Thermal stability	2.5-76.1 MPa Binder	Suitable SiO ₂ /Al ₂ O ₃ and SiO ₂ /CaO ratios and sufficient NaOH concentration are important to obtain the desired properties for the final product. In addition, the presence of sufficient water in the system is a necessity in the early activation process.
Vásquez et al. (2016)	Waste concrete, metakaolin, Portland cement, NaOH solution, liquid sodium silicate	Keeps in polyethylene film at: 1. RT 2. 24 hours at 70°C, then environmental chamber with 90% relative humidity	Compressive strength, XRD and SEM analyses, Infrared spectroscopy	3-55 MPa Binder	The percentage of Na ₂ O significantly affected the results of compressive strength. The authors noted that the addition of metakaolin and Portland cement to the system could lead to the better dissolving of the crystalline phases in the concrete wastes, resulting in improved geopolymerization.

Robayo-Salazar et al. (2017)	Red clay brick waste, waste concrete, waste glass, NaOH solution, liquid sodium silicate	Keeps in polyethylene film at: 1. RT 2. 24 hours at 70°C, then environmental chamber with 90% relative humidity	Compressive strength, Laser granulometry, XRF, XRD and SEM analyses	2-102 MPa Binder	The use of red clay brick waste or waste concrete as the main components of the high mechanical geopolymer binder was made possible by the regulation of the synthesis of alkali activators by curing at room temperature.
Goncalves Rapazote et al. (2017)	Different ceramic products, waste concrete, sludge from water treatment plant, NaOH solution (99% purity), liquid sodium silicate	65 °C with 98% relative humidity for 48 hours.	Compressive strength, Flexural strength, Thermal stability	20-44 MPa Binder	The geopolymer based materials have a better performance in terms of mechanical properties and higher temperature resistance than conventional concrete.

2.6.3. Mechanical Properties of Construction Demolition Waste Based Geopolymers

2.6.3.1. Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio

The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio (or Si/Al mass ratio) is one of the most important factors affecting the properties of geopolymers. Several studies have been conducted to investigate the effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio on geopolymers. For instance, Cheng and Chiu (2003) reported that maximum compressive strength is obtained when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio in the range of 3.16-3.46. Stevenson and Sago-Crentsil (2005) and Silva et al. (2014) stated that the optimum range of $\text{SiO}_2/\text{Al}_2\text{O}_3$ for geopolymers was 3.4-3.8. However, differences in general molar ratios may be observed due to the chemical composition of the source materials and alkali activators. Figures 2.8 and 2.9 show the relationship between the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and compressive strength values of 7 and 28 days, respectively (Ahmari et al., 2012; Zaharaki et al., 2016; Komnitsas et al., 2015; Vásquez et al., 2016; Robayo-Salazar et al., 2017).

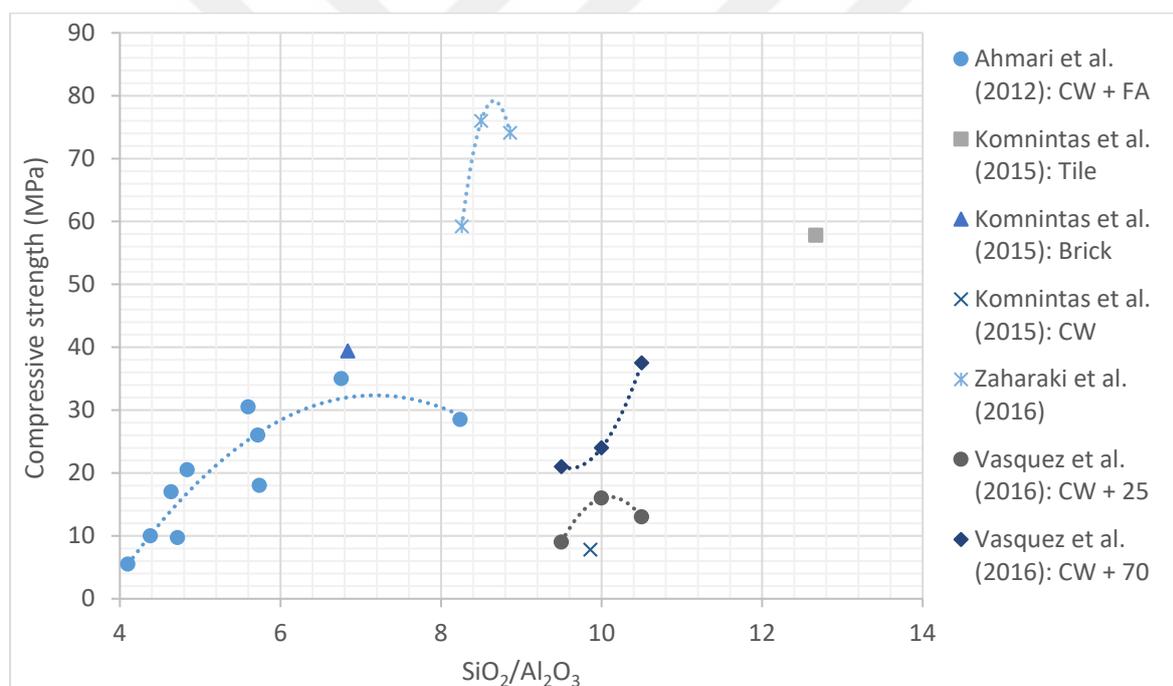


Figure 2.8 The relationship between molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ compressive strength (7 days) (CW 70: Concrete waste based geopolymer cured at 70 °C, FA: Fly Ash) (Ahmari et al., 2012; Zaharaki et al., 2016; Komnitsas et al., 2015; Vásquez et al., 2016)

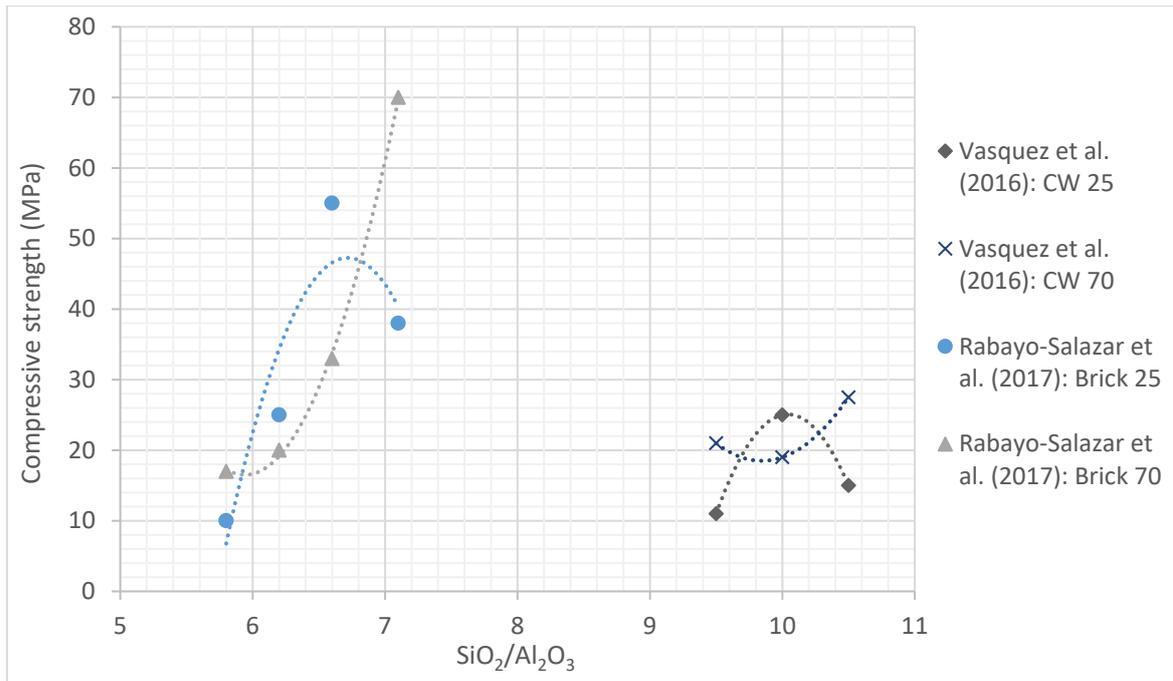


Figure 2.9 The relationship between molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ compressive strength (28 days) (Vásquez et al., 2016; Robayo-Salazar et al., 2017)

According to the reported data, the compressive strength at the end of 7 days in the geopolymers based on CDW varies depending on the different molar ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3$. As shown in Figure 2.8, Ahmari et al. (2012) reported that the increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ increased the compressive strength to a certain point (6.76 MPa) and then decreased. The same situation was reported by Zaharaki et al. (2016) and Vasquez et al. (2016). Zaharaki et al. worked on blended CDW (brick, concrete and tile wastes), Vasquez et al. worked on concrete waste (CW) and in these two studies, samples were cured at ambient conditions. These results show that, regardless of the source material, the range of an optimum $\text{SiO}_2/\text{Al}_2\text{O}_3$ (or Si/Al mass ratio) is present, where the final product reaches the highest compressive strength value. However, Vasquez et al. (2016) stated that the curing condition may affect the observed tendency and may reverse the relation between $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio and compressive strength. In addition, as noted in Figure 2.9, Robayo-Salazar et al. (2017) described a similar model for $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and compressive strength relation in conditions of ambient temperature and high temperatures. According to the results presented in the literature and in Figures 2.8 and 2.9, the CDW-based geopolymers produced from concrete waste have a lower compressive strength in all $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios compared to other CDW-based geopolymers derived from materials such as bricks and ceramics. In Figure 2.10, Komnitsas et al. (2015) and Robayo-Salazar et al. (2017) the SEM micrographs of geopolymers produced by concrete waste (CW) and waste bricks were shown. As seen in

the micrographs, geopolymers in the CW-based paste phase have a heterogeneous matrix, including unreacted CW particles. The main reason for the partial reaction of CW based geopolymers is the low amount of Si and Al in the concrete waste which is the main element in the geopolymerization process.

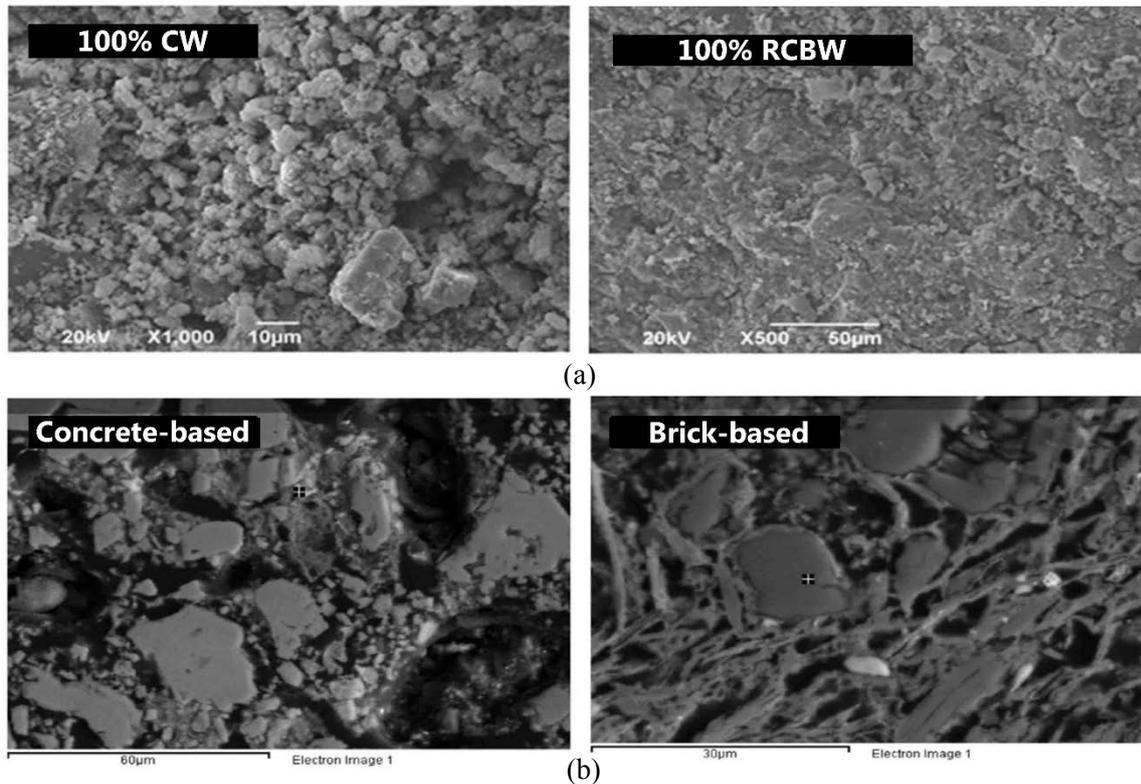


Figure 2.10 Scanning Electron Microscope (SEM) micrographs of CDW-based geopolymers: (a) images of CDW-based geopolymers by Robayo-Salazar et al. (2017) and (b) images of CDW-based geopolymers by Komnitsas et al. (2015)

2.6.3.2. Effect of NaOH Concentration

Although many studies in the literature have been used various combinations of different activators such as sodium hydroxide, sodium silicate, potassium hydroxide and potassium silicate, sodium hydroxide is currently the most prominent alkaline activator in geopolymer technology. Other activators such as sodium silicate or potassium silicate are more commonly used in commercial forms, while the NaOH solution can be used in a variety of molarities due to its low cost. Several studies have been conducted to investigate the effect of different molarities of sodium hydroxide on the properties of geopolymers.

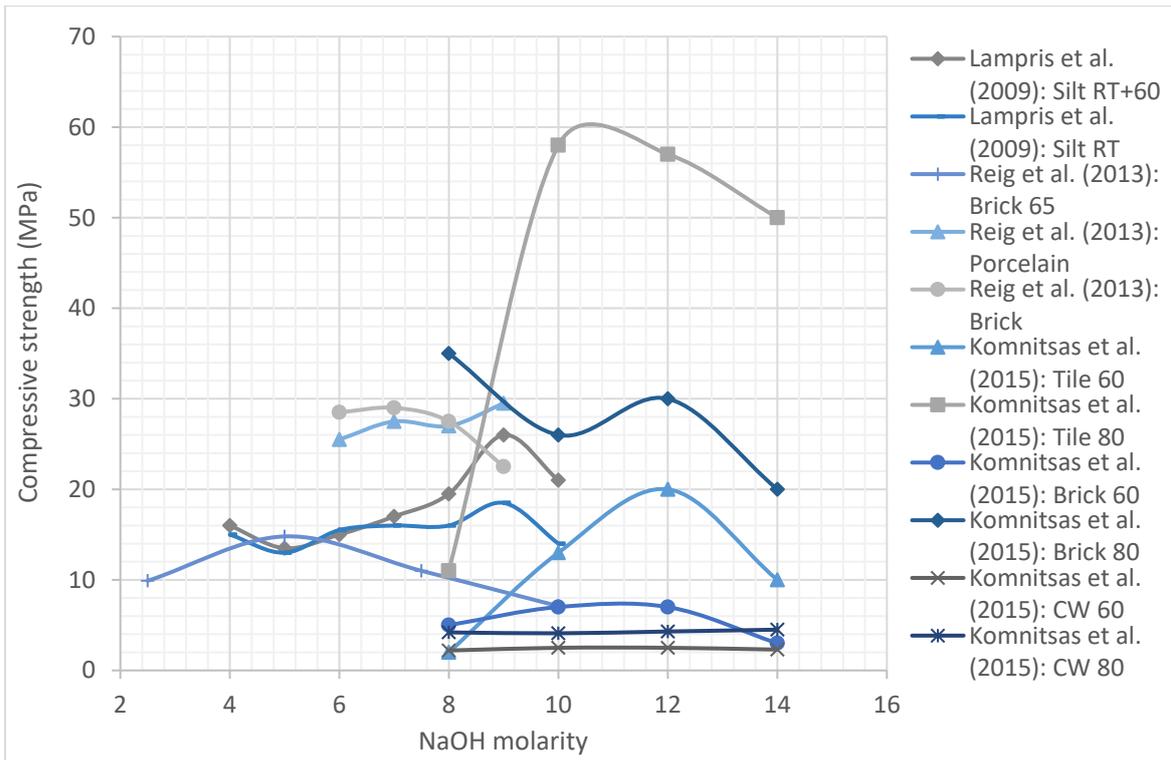


Figure 2.11 The relationship between NaOH molarity and compressive strength (7 days) (RT: Room temperature, CW 60: Concrete waste based geopolymer cured at 60 °C) (Lampris et al., 2009, 2013; Reig et al., 2013a; Komnitsas et al., 2015)

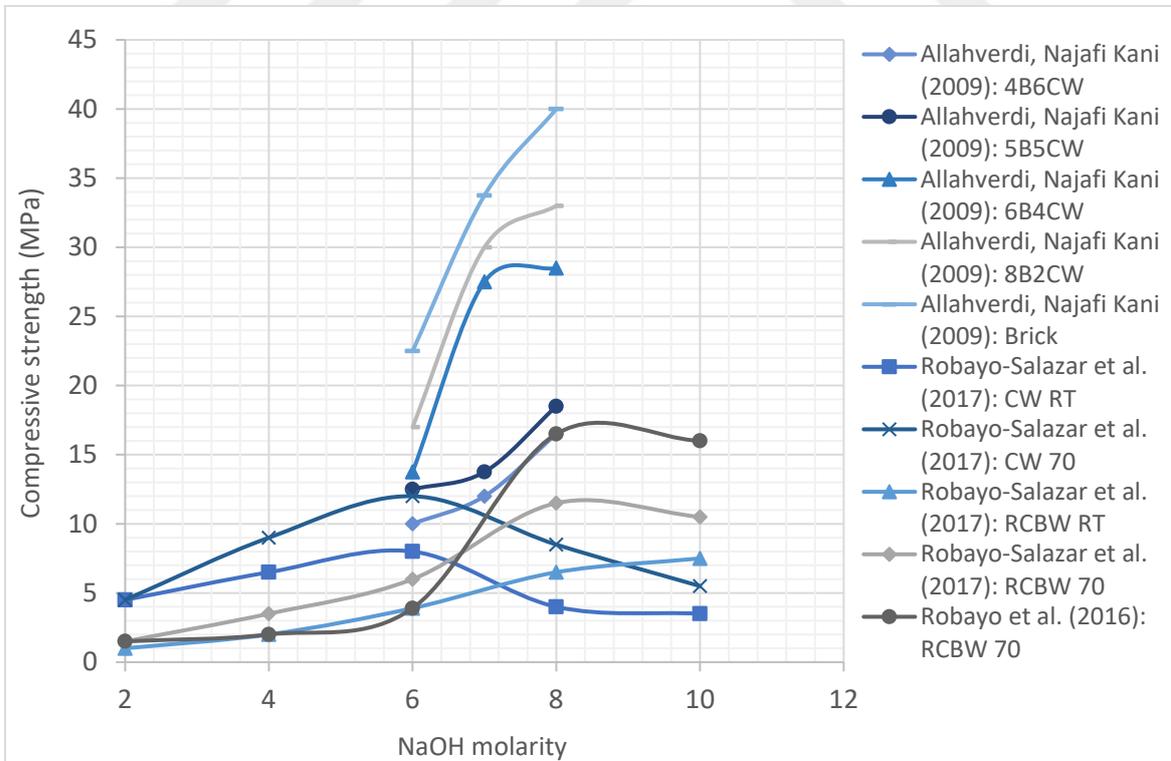


Figure 2.12 The relationship between NaOH molarity and compressive strength (28 days) (RCBW: Red clay brick waste, 5B5CW: 50% Brick + 50% Concrete waste) (Allahverdi and Najafi Kani, 2009; Robayo-Salazar et al., 2017; Robayo et al., 2016)

Figures 2.11 and 2.12 show the relationship between different NaOH molarities and compressive strengths at the end of 7 and 28 days, respectively, and the data of the graphs were obtained from the following studies (Lampris et al., 2009; Allahverdi and Najafi Kani, 2009; Reig et al., 2013a; Komnitsas et al., 2015; Robayo-Salazar et al., 2017; Robayo et al., 2016). For example, Lampris et al. (2009) investigated the effects of 4 to 10 different NaOH molarities in different curing conditions to activate the silt obtained from CDW washing plants. As can be seen from Figure 2.11, the high curing temperature (60 °C) for 8 to 10M accelerates the geopolymerization process and ensures high strength after 7 days. In addition, as it can be seen from the curve of Figure 2.11, Lampris et al. (2009) in their study, they obtained the results of optimum compressive strength from the samples in which 9M sodium concentration had been used. Reig et al. (2013b) showed that for the activation of red clay brick waste (RCBW), the optimum NaOH molarity was 5M and the curing temperature was 65 °C. Reig et al. (2013a) in another study reported that at 65 °C curing temperature, the most appropriate NaOH solution concentration for alkaline activation of both porcelain tile material and RCBW was 7M. Komnitsas et al. (2015) examined the effect of different NaOH concentrations on CDW-based geopolymers at different curing temperatures. As a result of the studies, it was determined that different NaOH molarities had no effect on activation at 2 different cure temperatures (60 and 80 °C). In addition, the brick and tile were showing the highest compressive strength from different construction and demolition wastes after 7 days at a temperature of 80 °C, with the 10M for the tile and 8M for the brick with optimum NaOH concentration. According to Figure 2.12, from the results presented by Robayo-Salazar et al. (2017) and Robayo et al. (2016), it can be observed that the optimum NaOH concentrations are determined as 6, 8 and 10M. Allahverdi and Najafi Kani (2009) stated that the highest compressive strength can be achieved by increasing the NaOH molarity to 8M at both curing temperatures of 60 °C and 80 °C when CDW-based brick and concrete waste were used together. Figure 2.13, shows the micrographs of SEM of geopolymers based on CDW of produced by Reig et al. (2013a). Micrographs summarizing the microstructure of brick and porcelain based geopolymers with two different NaOH molarity (7M and 9M) coinciding with the data in Figure 2.11 clearly demonstrated that the higher NaOH concentration (9M) provides denser and more homogenous matrices under the same curing conditions for both materials. On the other hand, the bricks-based geopolymer showed lower compressive strength at a concentration of 9M NaOH compared to 7M. In this case, it can be stated that an excessive amount of sodium hydroxide may adversely affect the microstructure of the matrix and the mechanical properties of geopolymers (Reig et al.,

2013a; Kourti et al., 2010). In this direction, it has been stated that technically, based on the reactivity and binding properties of the particles, a specific NaOH molar threshold can be defined for each CDW material. This recommendation is consistent with the recommendation of Kourti et al. (2010).

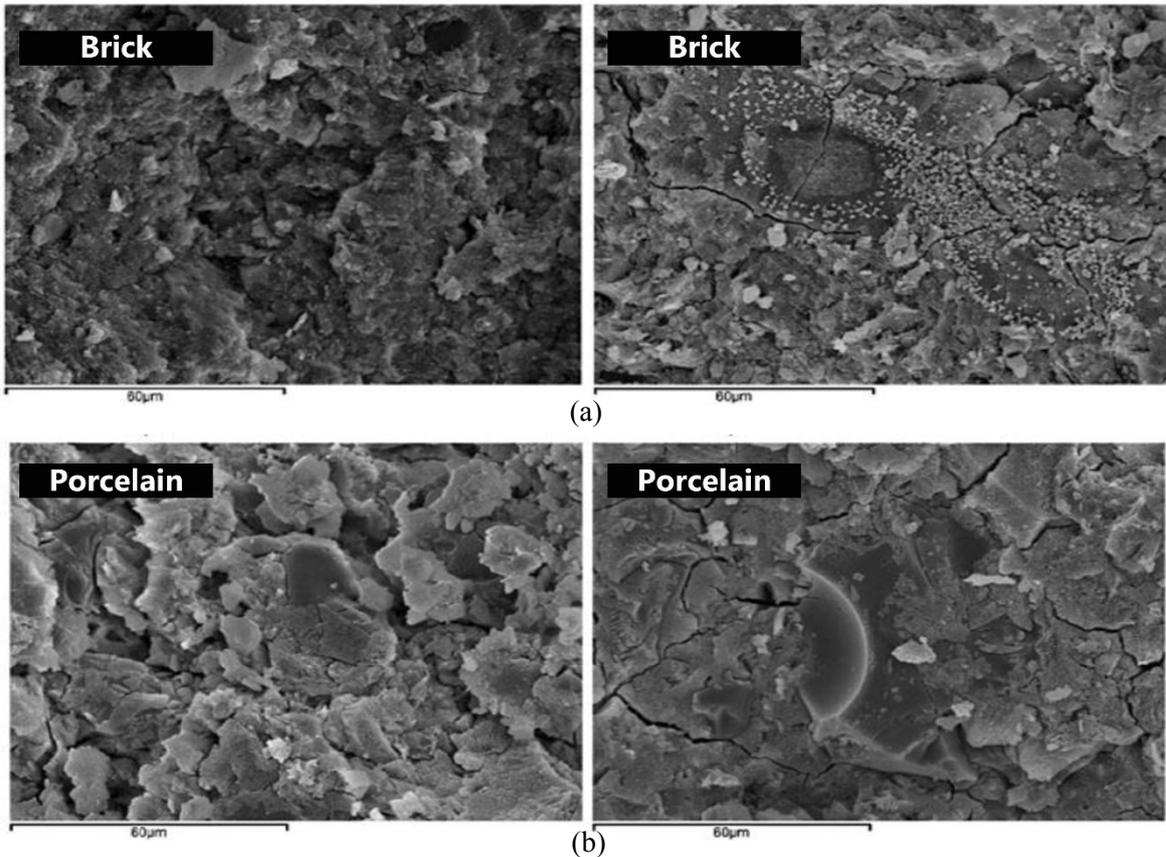


Figure 2.13 Scanning Electron Microscope (SEM) micrographs of CDW-based geopolymers with different NaOH concentrations: (a) Brick-based geopolymer, left: 7M, right: 9M, (b) Porcelain-based geopolymer, left: 7M, right: 9M (Reig et al., 2013a)

2.6.3.3. Effect of R_2O/SiO_2 Ratio

The R_2O/SiO_2 molar ratio (R , represents Na^+ and/or K^+) is considered to be one of the factors affecting the geopolymerization process, which is calculated based on chemical activators such as sodium hydroxide, sodium silicate and potassium hydroxide. This ratio represents the amount of soluble sodium and silicate in alkali activators. The relationship between R_2O/SiO_2 ratio and compressive strength is shown in Figure 2.14 in the context of the data obtained from a limited number of studies on the effect of R_2O/SiO_2 on CDW-based geopolymers.

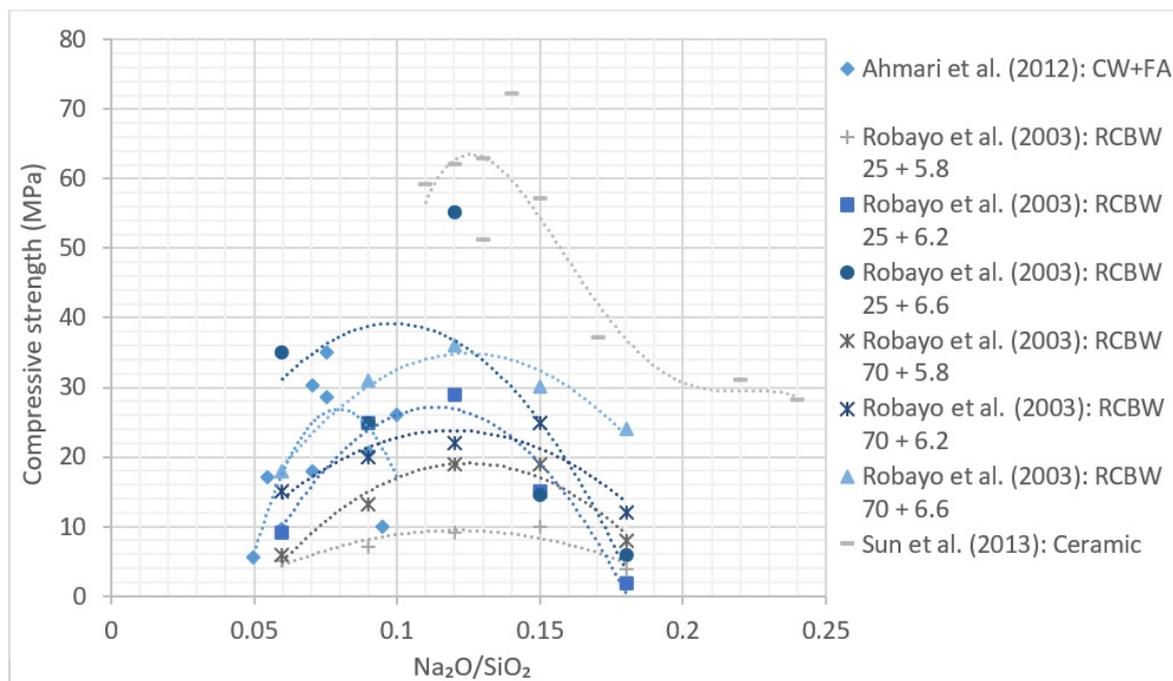
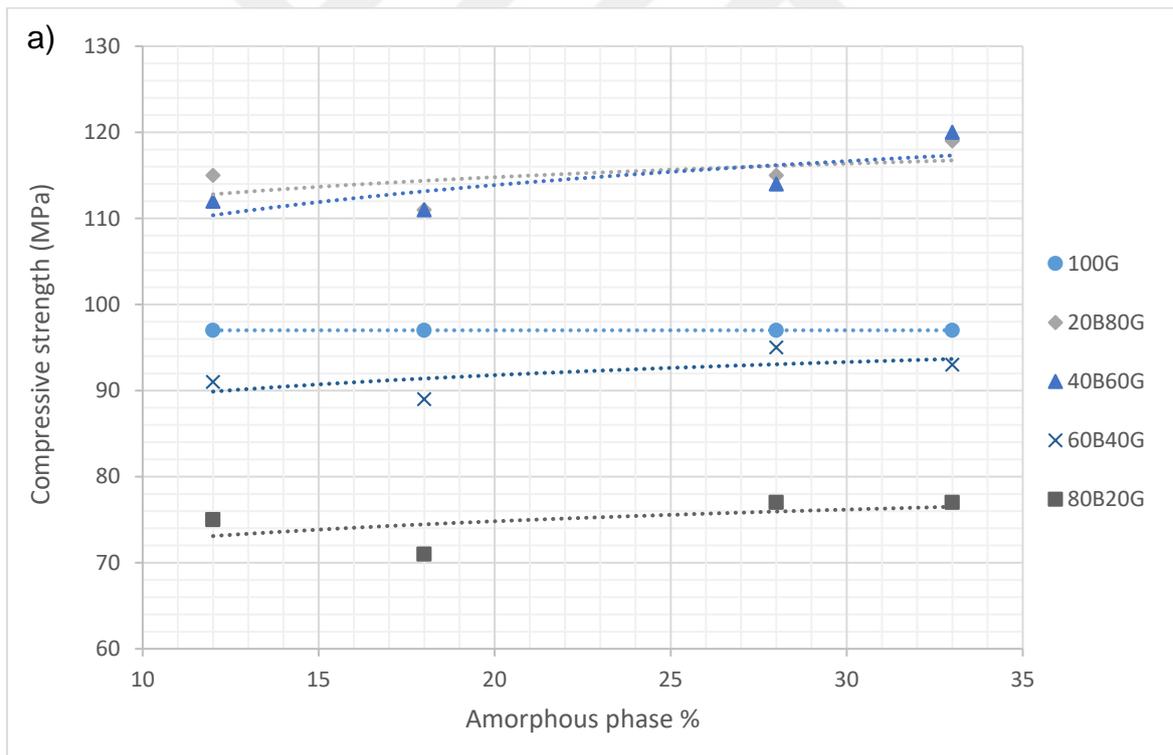


Figure 2.14 The relationship between R_2O/SiO_2 and compressive strength (R: Na^+ and/or K^+ , CW: Concrete waste, RCBW 25 + 6.2: SiO_2/Al_2O_3 : Red clay brick waste cured at 25 °C with a molar ratio of 6.2) (Ahmari et al., 2012; Sun et al., 2013; Robayo et al., 2016)

The data were compiled from the single study of Robayo et al. (2016) in the literature considering the effect of R_2O/SiO_2 on the compressive strength of red clay brick waste (RCBW) based geopolymers. Other data were compiled from studies of Ahmari et al. (2012) and Sun et al. (2013). As shown in Figure 2.14, all trend lines represent the most appropriate point R_2O/SiO_2 for maximum strength. Depending on the composition of CDW, the optimum point may vary. According to Ahmari et al. (2012), the main solvent elements that perform the activation of Si and Al in the system are Na^+ and/or K^+ . However, due to the effect of other factors that cut geopolymeric networks such as calcium (Ca^{2+}), lower strengths were obtained in the highest Na^+ content. On the other hand, Robayo et al. (2016) stated that the amount of sodium silicates caused differences in compressive strength and, Pacheco-Torgal et al. (2008), as previously stated, have argued that the amount of soluble silica in the alkali activator provides better conditions for higher compressive strengths due to geopolymerization. However, they stated that the properties of the activators led to the presence of optimum points (Robayo et al., 2016). Further research is needed to provide a better understanding of the effects of R_2O/SiO_2 , Al_2O_3/R_2O and liquid/solid ratios in the geopolymerization process of CDW.

2.6.3.4. Effect of Other Properties

Although it is expected that the activation properties of the source materials will change the properties of the final geopolymer product, a limited number of studies have been performed to evaluate the effect of amorphous phases on geopolymer binders and mortars. Rakhimova and Rakhimov (2014) proposed a new approach in order to classify CDW in its use for alkaline active slag cement. Within the scope of this approach, three different groups have been defined: 1-chemically activated amorphous phases, 2-physically activated materials classified according to their crystalline phases, 3-physically active and reactive materials containing the previous categories. In another study by Rakhimova and Rakhimov (2015), the effects of the amorphous phase content of four different red clay brick wastes (RCBW) on the RCBW and ground granulated blast furnace slag (GBFS) based geopolymer binders were evaluated. Figures 2.15-a and b show the relation between amorphous contents and compressive strengths of geopolymer binders which are activated separately with NaOH and sodium silicate at the end of 28 days.



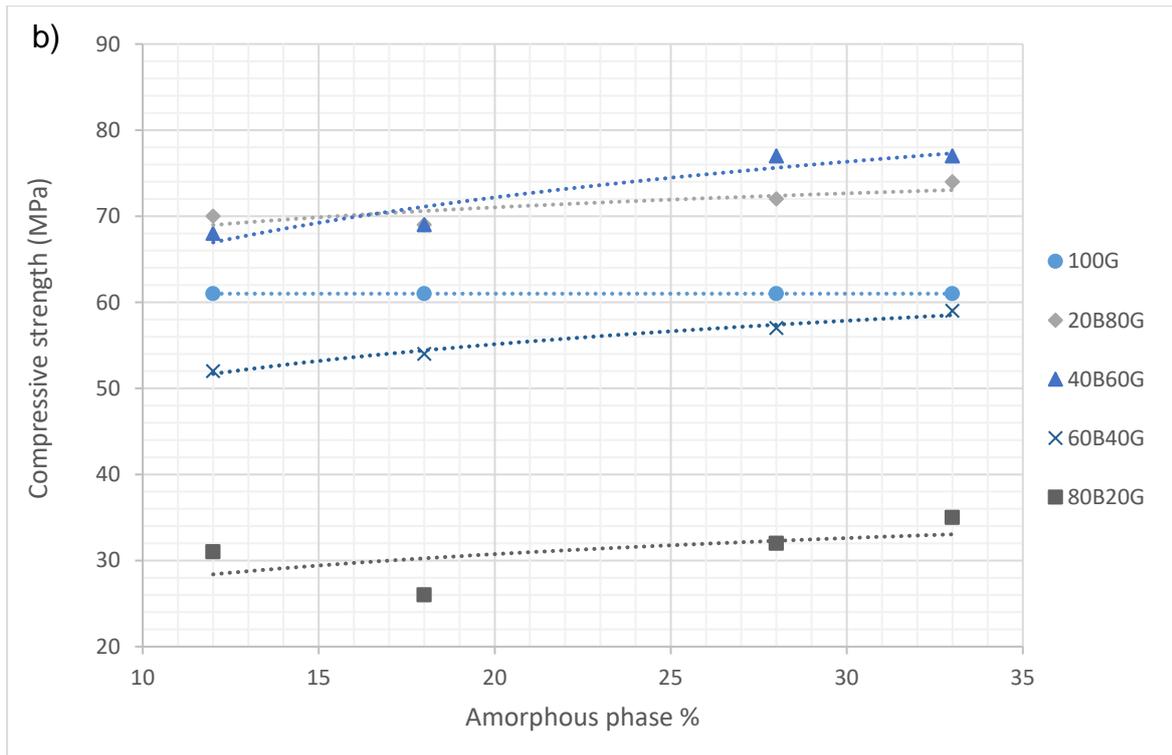


Figure 2.15 The effect of amorphous content on the compressive strength of RCBW-GGBS based geopolymers (28 days) (a) Activated by sodium hydroxide, (b) Activated by sodium silicate (40B60S: 40% RCBW + 60% GGBS) (*Rakhimova and Rakhimov, 2015*)

According to this figure, it can be seen obviously that the increase of the amorphous phase in RCBW content causes an increase in compressive strength of geopolymer binders containing RCBW. However, due to the lack of adequate studies in this subject, further research is needed to make further explanations and discussions.

2.6.3.5. High Temperature Resistance

The effect of high temperature on CDW-based geopolymers (thermal stability) is one of the parameters, not comprehensively evaluated by researchers. There are very few studies that refer to the mechanical properties of high temperature exposed CDW-based geopolymers. Figure 2.16 shows the stability of different CDW-based geopolymers exposed to high temperature. Data were obtained from studies which were conducted by Zaharaki et al. (2016) and Komnitsas et al. (2015). In these studies, geopolymer binders were subjected to high temperatures of 400 °C to 800 °C. As can be seen from Figure 2.16, the compressive strength of all CDW-based geopolymers decreases with increasing temperature. According to Zaharaki et al. (2016), CDW-based geopolymers, when exposed to high temperatures that affect the porosity of the matrix and consequently reduce the mechanical properties, have caused problems such as mass loss and volumetric shrinkage as well as the appearance of

visible microcracks on their surfaces. In addition, the partial decomposition of aluminosilicate networks when exposed to high temperatures of CDW-based geopolymers, previously discussed by Zaharaki et al. (2016), Chuah et al. (2015) and Ren et al. (2016).

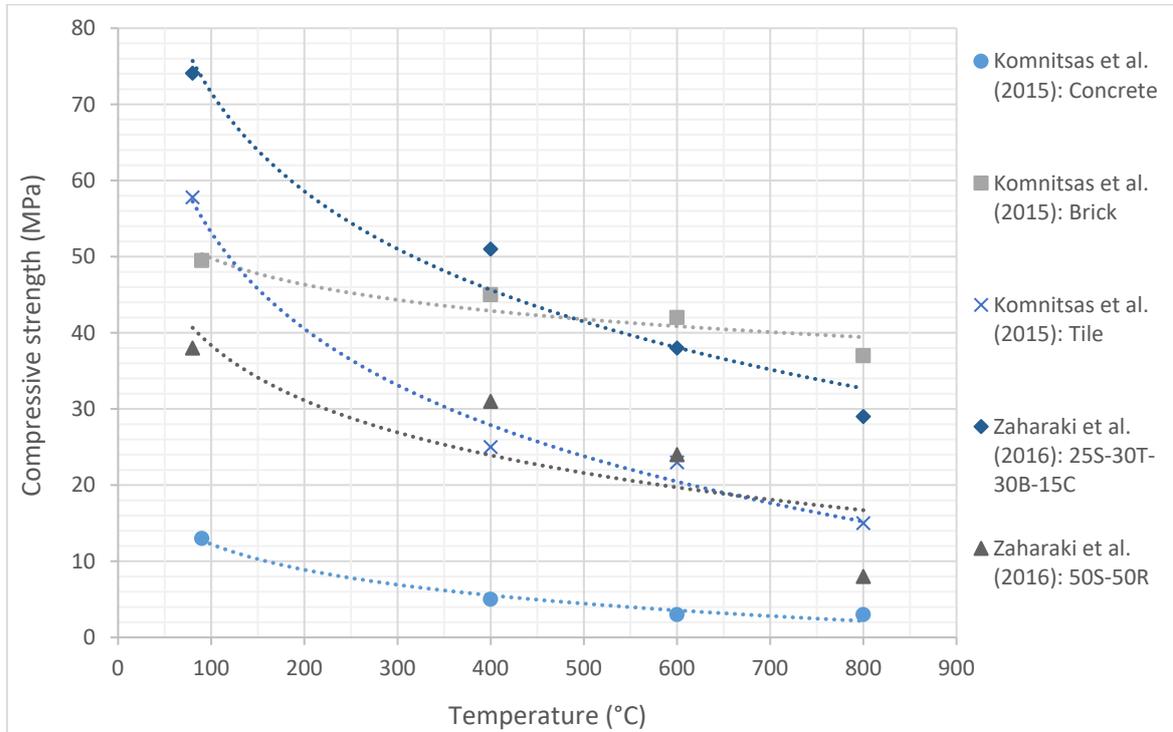


Figure 2.16 High temperature resistance of CDW-based geopolymer binders (25S-30T-30B-15C: 25% Slag+30% Tile+30% Brick+15% Concrete) (Komnitsas et al., 2015; Zaharaki et al., 2016)

2.6.3.6. Rheology and Durability

In literature, very few studies were conducted about the rheological properties and durability parameters of the CDW-based geopolymers. (Zawrah et al., 2016; Khater et al., 2016). In the study conducted by Zawrah et al. (2016) about the effect of GBFS on brick-based geopolymers, the water absorption rate from the parameters related to durability was evaluated as the main parameter. Figure 2.17 shows water absorption rates of brick-based geopolymers containing different amounts of GBFS and bricks. As is evident from the figure, the increase in the level of substitution of GBFS leads to a reduction in the water absorption rates of the geopolymer binders. GBFS has led to the formation of new phases (calcium-silicate-hydrate) with aluminosilicate networks in geopolymeric matrices which have a significant effect on the hardened properties of geopolymer binders (Zawrah et al., 2016).

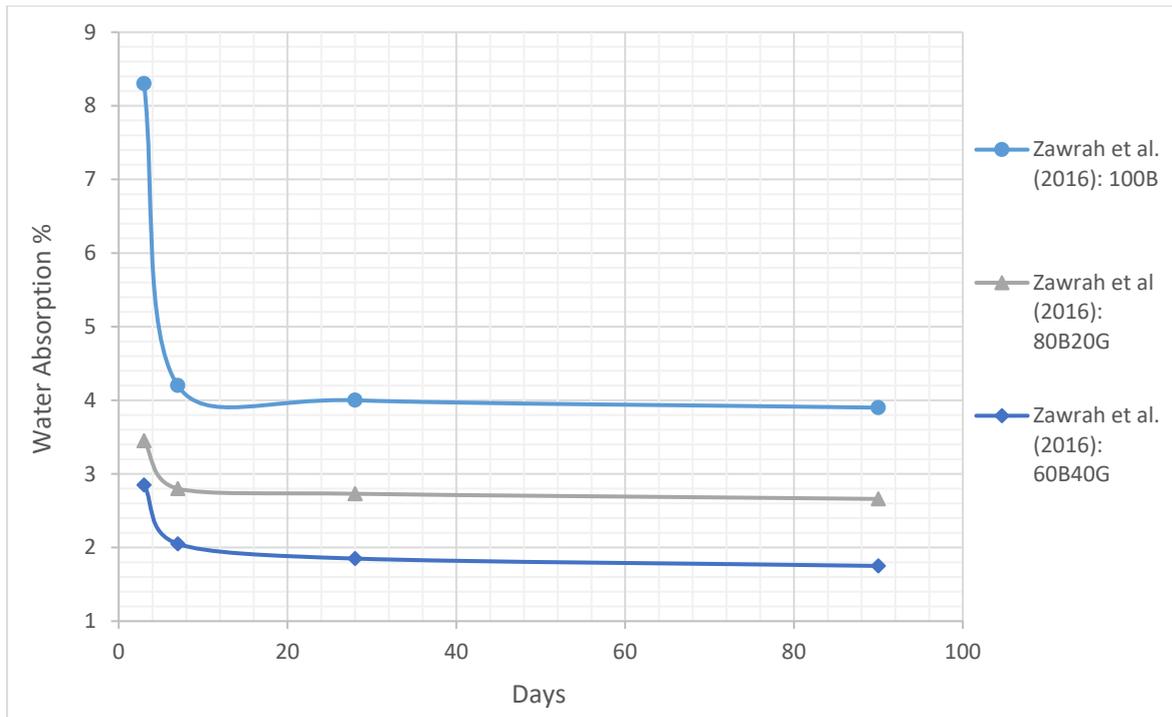


Figure 2.17 The water absorption results for different replacement levels of GGBS in brick-based geopolymer binders (80B20G: 80% Brick+20% GGBS) (Zawrah et al., 2016)

In addition, the water absorption rates of ceramic-based geopolymers with the substitution of different levels of brick are shown in Figure 2.18. The results show that water absorption is gradually decreasing until 90 days of curing time (Khater et al., 2016). However, ceramic-based geopolymers appear to have a threshold value for brick substitution. As can be seen from Figure 2.18, water absorption was reduced in mixtures with only 20% brick substitution compared to non-brick ceramic-based mixtures. The water absorption rate increased when the brick amount that substituted was above 40%. This can be explained by the need for higher water and the resultant zeolite formation in the geopolymer matrix. Further studies are needed to provide a detailed explanation and assessment for other durability parameters such as chloride permeability, electrical resistance, freeze-thaw, and alkali-silica reaction.

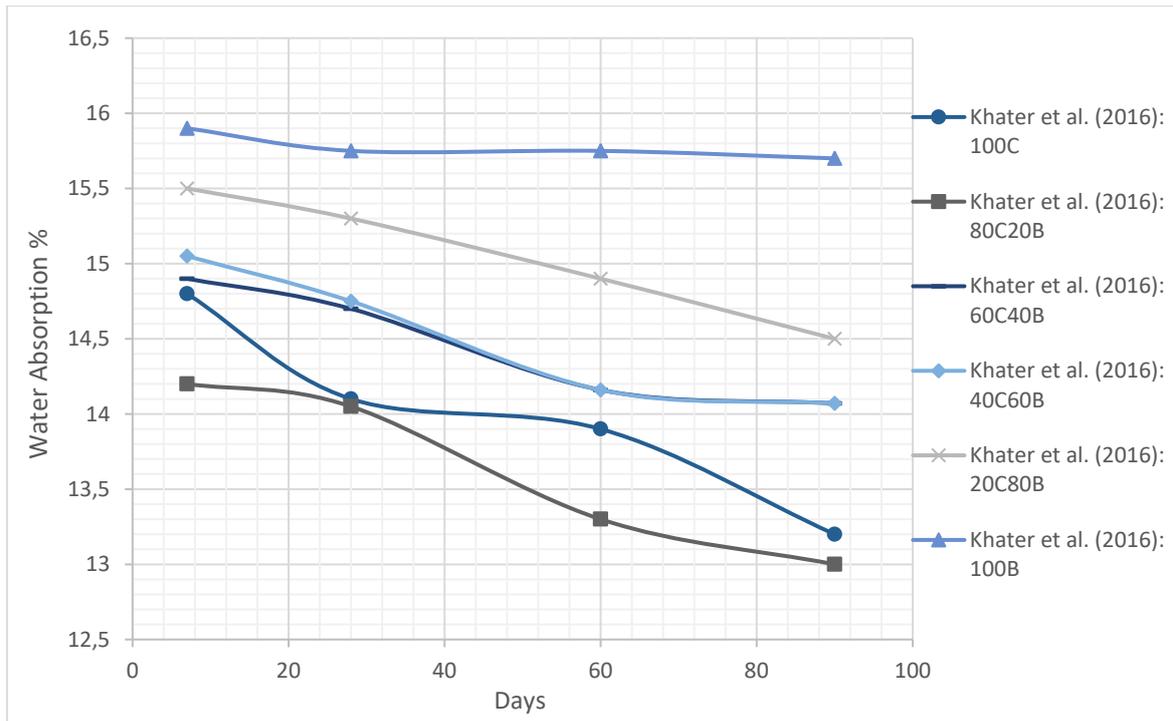


Figure 2.18 The water absorption results for different replacement levels of brick in ceramic-based geopolymer mortars (60C40B: 60% Ceramic+40% Brick) (Khater et al., 2016)

Rheological properties (shear stress, yield stress, viscosity etc.) of geopolymers based on CDW, have not been studied extensively. Only two studies conducted by Allahverdi and Najafi Kani (2009) and Rakhimova and Rakhimov (2015) made evaluations about the setting time of geopolymer products. In the context of the data obtained from these studies, Figure 2.19 shows the relation between the concentration of Na_2O and final setting time of the geopolymers (brick and concrete waste). As can be seen from Figure 2.19, all geopolymer binders have been set longer with a lower Na_2O concentration (6%). The setting time of the geopolymer binders is comparable to that of the normal cemented binders. In addition, the researchers reported that, due to the high thixotropic properties of the fresh binders, there was initially a false setting issue at all geopolymeric binders. Therefore, they concluded that the increase in Na_2O concentration for the constant $\text{Na}_2\text{O}/\text{SiO}_2$ value accelerated the process of geopolymerization; however, this may reduce the final setting time. In another study by Rakhimova and Rakhimov (2015), the effect of ground powder (waste brick and GBFS) with specific surface area and two different activators (sodium silicate and sodium carbonate) on the initial and final setting time of the geopolymer binders were investigated. The results showed that with the increase in the specific surface areas of the source materials (from 300 to 900 m^2/kg) both the initial and final setting times of the geopolymer decreased. However, sodium carbonate was able to increase the setting time (both initial and final) compared to

sodium silicate with a constant specific surface area (Rakhimova and Rakhimov, 2015). As a result, more studies are needed to make detailed evaluations and discussions on the setting time and rheological characteristics.

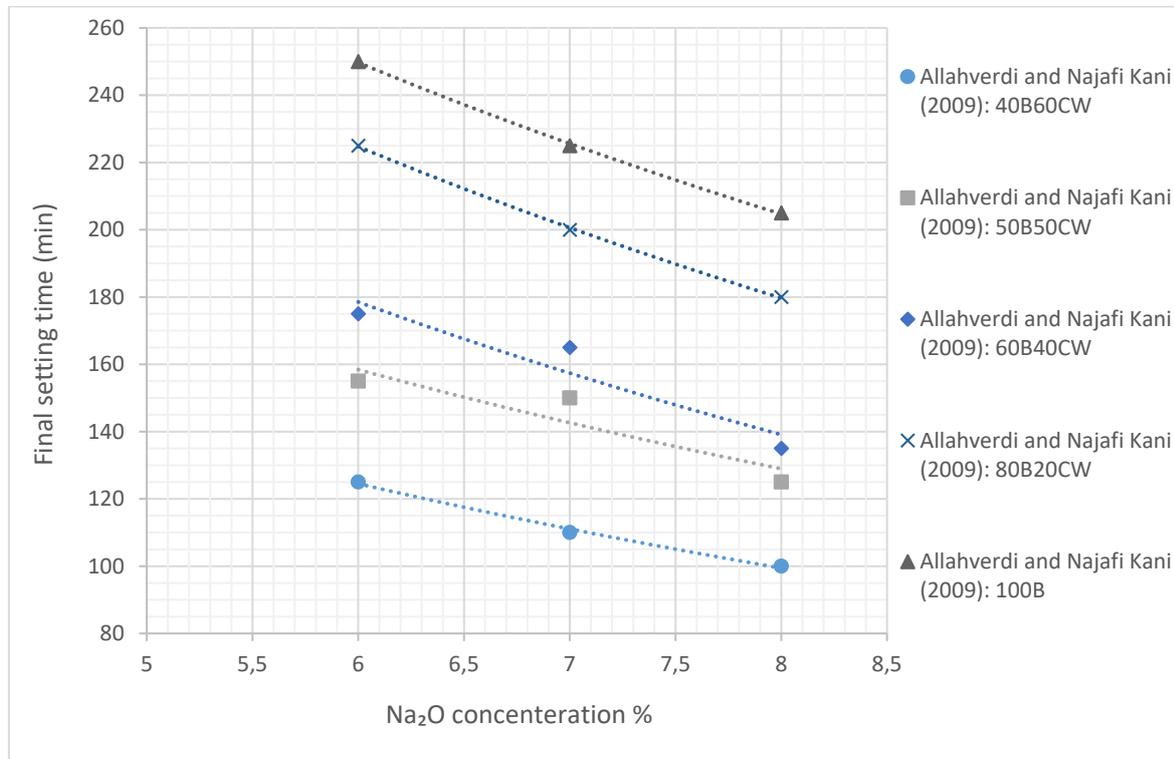


Figure 2.19 The relationship between Na₂O concentration and final setting time in CDW-based geopolymers (50B50CW: 50% Brick+50% Concrete Waste) (Allahverdi and Najafi Kani 2017)

2.6.3.7. Current Challenges Regarding to Industrial Applications of Construction and Demolition Wastes

Over the last two decades, action plans for climate change in the world have greatly increased the demand for mineral additives in the cement and concrete industry. For example, Bouzoubaa and Fournier (2005) have collected data from mineral additives used in the Canadian market and have clearly stated that mineral additives producers are unable to meet market demand and therefore Canada imports high amounts of mineral additives (especially silica fume) from the US and Norway. Today, due to insufficient action plans designed to reduce carbon dioxide emissions into the atmosphere, it can be clearly stated that mineral additives are being consumed more effectively. In this context, in order to reduce the market demand, investigation of the using of various CDW-based waste materials individually or in combination with different mineral admixtures is an issue that needs to be carefully considered. However, there are serious challenges to the effective use of CDW in the

geopolymer industry in particular. As it can be deduced from the literature review detailed above, it has been observed that, although several studies have been carried out on geopolymerization of CDW-based materials, very limited progress has been made in terms of industrial applications. The main reason for inadequate development of the industry-oriented advances is the complexity of the geopolymerization processes and the complicated activation of CDW which has various chemical constituents. Therefore, in different applications, a number of arrangements are required for parameters such as $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, activator types, concentrations, curing conditions. According to the literature studies summarized above, it can be stated that the properties of CDW-based geopolymers are greatly influenced by the changes in the chemical composition of the source materials and this situation made more complicated the process of making a specific mixture design. It is also thought that future research and development studies should focus on acceptable threshold levels, rather than focusing on achieving the best possible mixture designs that are not likely to be obtained simultaneously all over the world. In addition, the current activation methods, such as alkali chemical activators and high-temperature curing should be improved and the number of well-trained personnel in the field needs to be increased in order to raise awareness in the production of such products and the desire for industrial applications. Therefore, emphasis should be placed on the simplification of production processes depending on the availability and functionality of the source materials, activators, and curing conditions.

3. MATERIALS AND TESTING METHODS USED IN EXPERIMENTAL STUDIES

In the first phase of the study, the optimum temperature and alkali activator utilization rates in the production of paste mixtures were determined and it was aimed to obtain the appropriate compressive strength values which were important for reaching the targets in the following stages. Within this context, parametrical optimum design studies have been performed by using aluminosilicate based source materials which were obtained entirely from CDW (powders of waste concrete, brick, tile and glass) and different alkaline activators (sodium hydroxide, potassium hydroxide, sodium silicate and sodium metasilicate). The experiments/tests carried out for the purposes of current thesis were grouped under a general title by taking into account the solutions obtained by mixing of the alkaline activators and the solutions prepared with the use of different alkali activators alone. For each type of solution, the aluminosilicate based source waste materials were used either alone or in combination with certain proportions. 50 mm cubic samples were produced with the designed mixtures and the compressive strength assessments were made.

Chemical compositions of the raw materials used for alkaline activation, crystallographic structures, particle size distributions and chemical compositions of activators (silica module etc.) and molarity values affect the mechanical properties and durability performance of the binders produced by alkali activation. To determine the suitability of the milled materials for use in the production of geopolymer as raw material and then to estimate the rate at which they will be used with which activators and their molarity values, as well as graded construction and decay for comparison with XRF analyzes were performed to determine the chemical composition and crystallographic structure of CDW-based mineral additives. In addition, grain size distribution analysis was performed with equipment having Br and Mastersizer 2000.

3.1. Construction Demolition Wastes as a Source of Aluminosilicate

The waste materials to be used in the study were obtained from the buildings which were demolished due to the urban transformation within the province of Ankara. These materials are divided into five different groups: hollow brick, red clay brick, roof tile, glass and concrete waste (Figure 3.1).



Hollow brick waste



Red clay brick waste



Roof tile waste



Glass waste



Concrete waste

Figure 3.1 Samples of various construction and demolition wastes

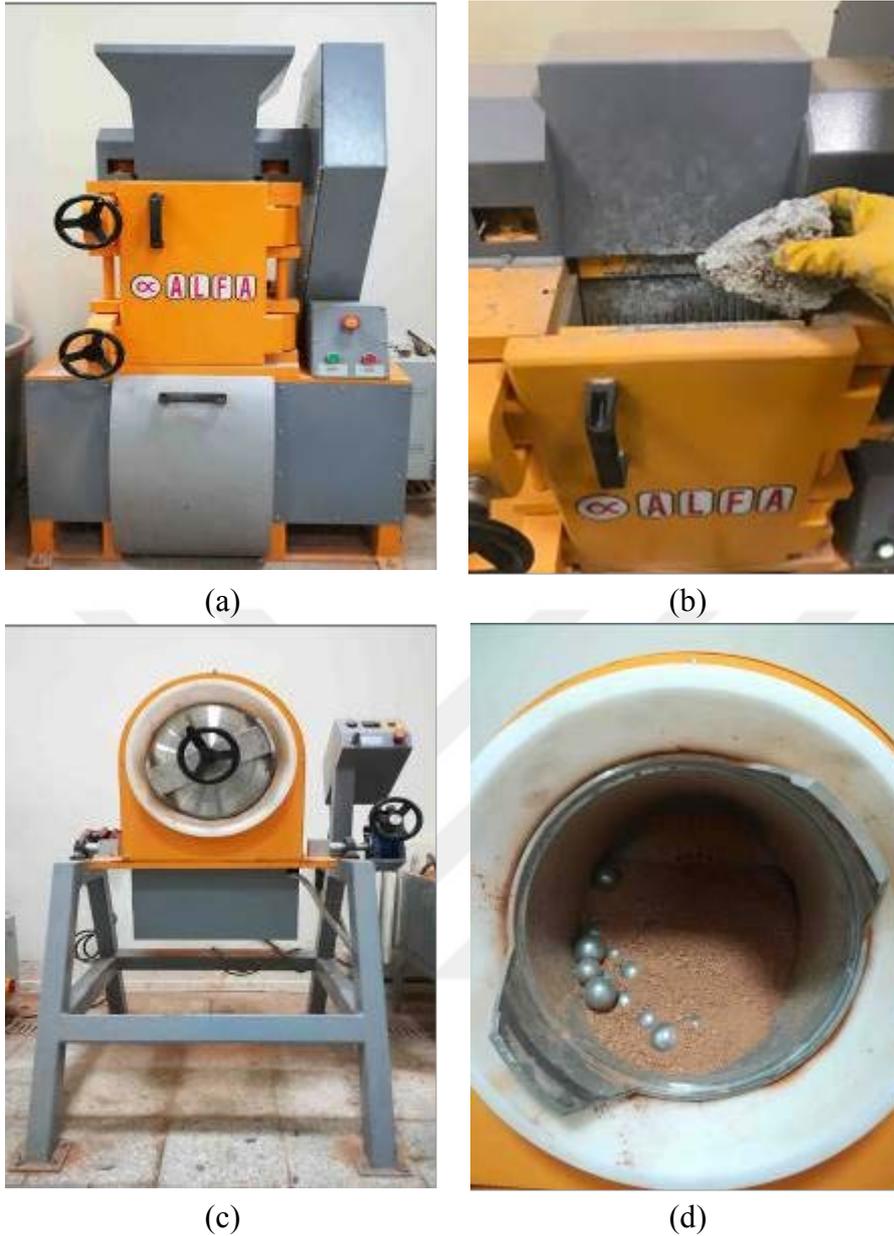


Figure 3.2 Jaw crusher (a, b) and ball mill (c, d)

The materials were each milled in a jaw crusher at a size of about 0.5 cm (Figure 3.2) and milled at a time in the ball mill (Figure 3.2) until reaching cement fineness approximately. Particularly for concrete waste, milling and sieving processes were carried out at different breaker openings in order to obtain more unhydrated products. However, it was found that the strength results for milled concrete wastes were similar after they were broken at different openings. Therefore, in order to make the milling process more efficient, the concrete waste was milled together with the aggregate without any different treatment. The crushed and ground forms of the CDW-based materials are shown in Figure 3.3.



Crushed hollow brick



Ground hollow brick



Crushed red clay brick



Ground red clay brick



Crushed roof tile



Ground roof tile



Crushed glass waste



Ground glass waste



Crushed concrete waste



Ground concrete waste

Figure 3.3 Crushed and ground forms of construction demolition waste

3.1.1. Chemical Compositions of Construction Demolition Wastes

The chemical content of CDW and fly ash for reference are shown in Table 3.1. When examined in terms of SiO₂ amounts, brick wastes are similar to fly ash and the closest values can be obtained from hollow bricks. It is estimated that lost on ignition around 16% of the concrete waste is caused by carbonated parts in concrete. Al₂O₃ amounts indicate that the brick waste resembles fly ash, the closest value is the red clay brick. In terms of CaO content, as expected, the concrete waste has a high amount of CaO. Na₂O content of glass waste is around 13% and it requires the use of reactive silica-free aggregates in case of geopolymer binder production. The positions of CDW-based materials and fly ash used in the study are shown in SiO₂-Al₂O₃-CaO triple diagram in Figure 3.4.

Table 3.1 Chemical composition of construction and demolition wastes and fly ash

Chemical Composition, %	Hollow brick	Red clay brick	Roof tile	Glass waste	Concrete waste	Fly ash
Loss of Ignition	1.99	2.18	2.11	0.29	15.77	2.61
SiO ₂	61.61	53.39	54.02	73.42	43.10	60.07
Al ₂ O ₃	17.27	20.50	15.98	1.27	7.60	21.35
Fe ₂ O ₃	6.70	7.77	8.93	0.18	3.63	7.41
CaO	3.31	4.75	7.42	10.96	24.00	0.99
MgO	2.66	3.70	4.84	0.18	1.54	1.82
SO ₃	0.38	1.16	0.68	0.10	0.43	0.22
Na ₂ O	1.61	1.53	1.41	12.77	1.39	0.99
K ₂ O	2.80	3.42	2.30	0.08	1.34	2.91
TiO ₂	0.81	1.02	1.19	0.07	0.41	0.94
P ₂ O ₅	0.18	0.18	0.23	0.00	0.14	0.15
Cr ₂ O ₃	0.03	0.04	0.04	0.02	0.07	0.03
Mn ₂ O ₃	0.11	0.13	0.16	0.01	0.09	0.08

Although it was thought that glass waste would not provide sufficient performance when used alone as a raw material due to its low Al_2O_3 content, the SiO_2 content was largely amorphous, indicating a good source of SiO_2 and performance. According to the chemical contents of the CDW-based materials, it was concluded that materials could be used alone or in double/triple combinations.

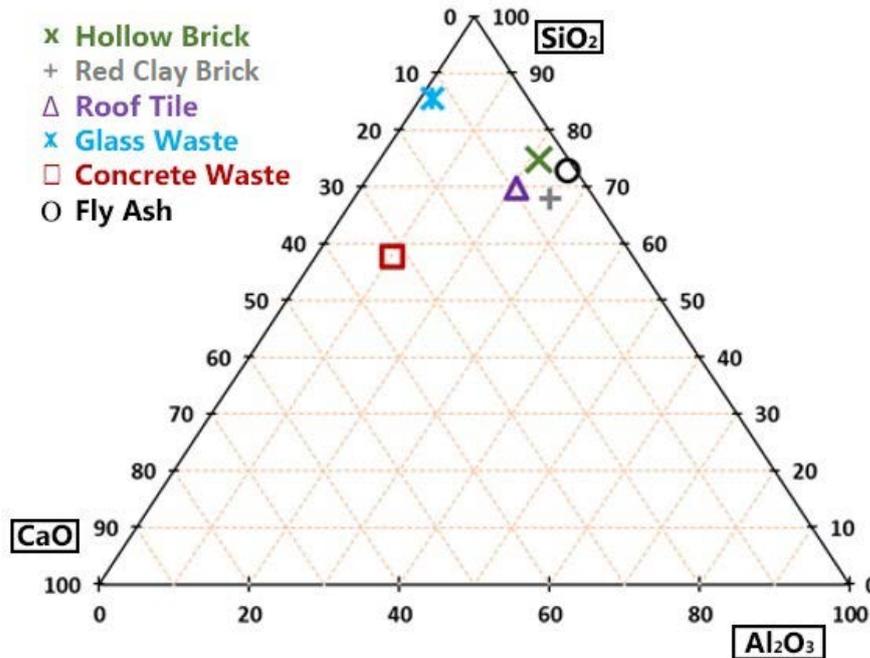


Figure 3.4 Positions of wastes used in the study on SiO_2 - Al_2O_3 - CaO triple diagram

3.1.2. Crystallographic Structures and SEM Micrographs of Construction Demolition Wastes

Figure 3.5 shows the X-ray diffraction (XRD) phase diagrams of the waste materials and the fly ash in Figure 3.6. In these diagrams, Q, A, M and H represent quartz, albite, montmorillonite and hematite respectively. Glass waste and roof tile are the most amorphous materials. It can be seen that the waste material which possesses the densest crystalline phase is the waste concrete which contains elements such as different hydration products and unhydrated cementitious particles. Additionally, montmorillonite phase exists in hollow brick and red clay brick and hematite exists in red clay brick.

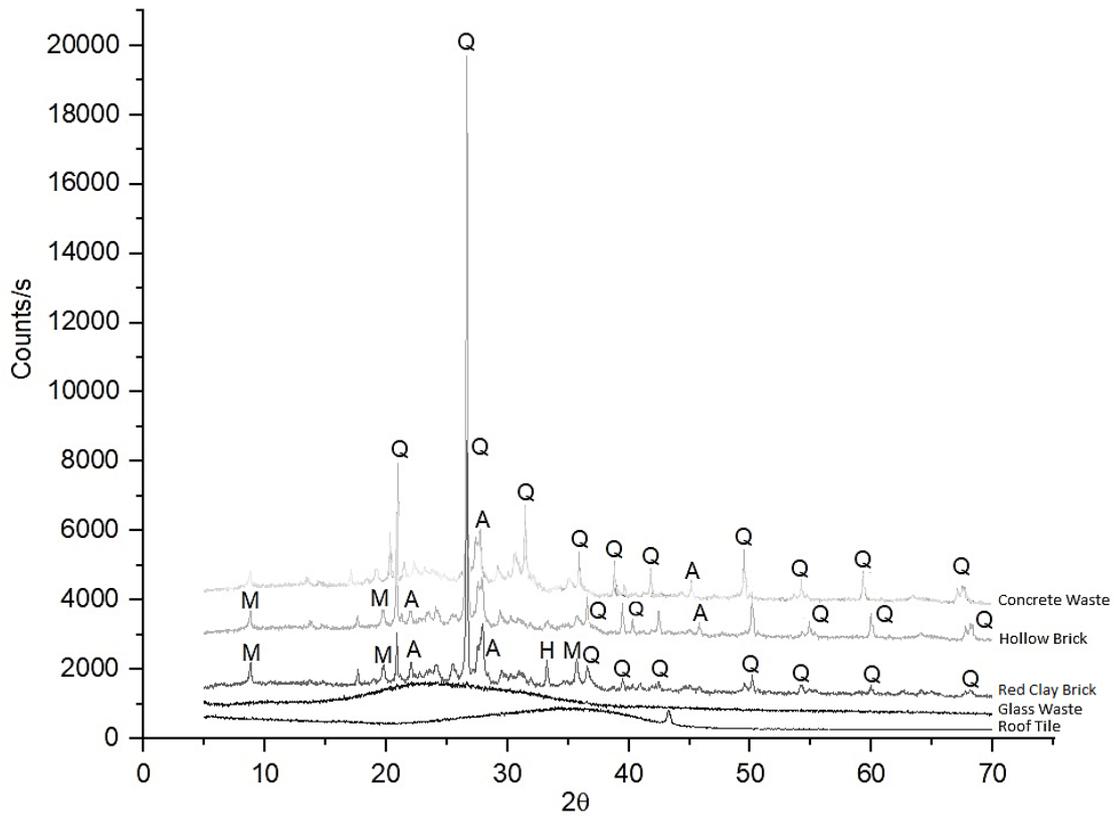


Figure 3.5 XRD phase diagrams of concrete waste, red clay brick, hollow brick, roof tile and glass waste (*Q=Quartz, A=Albite, M=Montmorillonite, H=Hematite*)

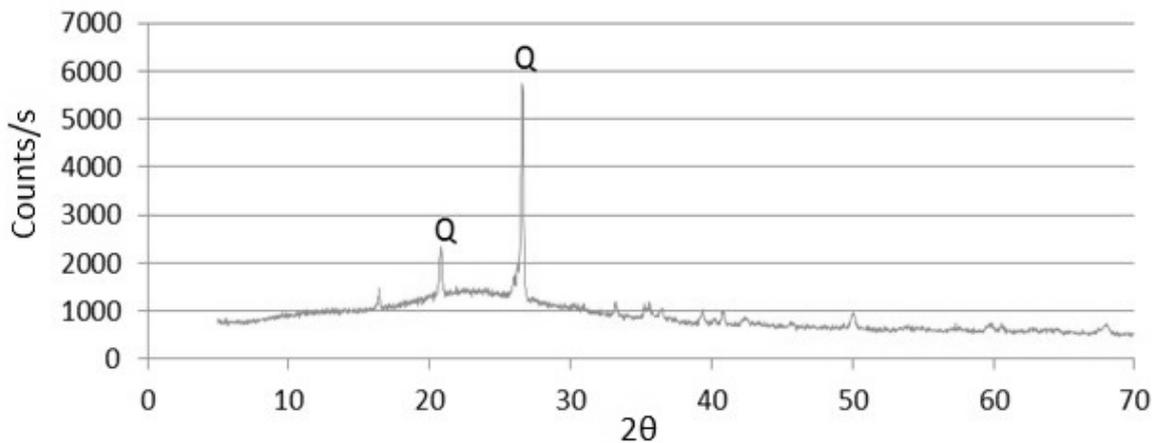
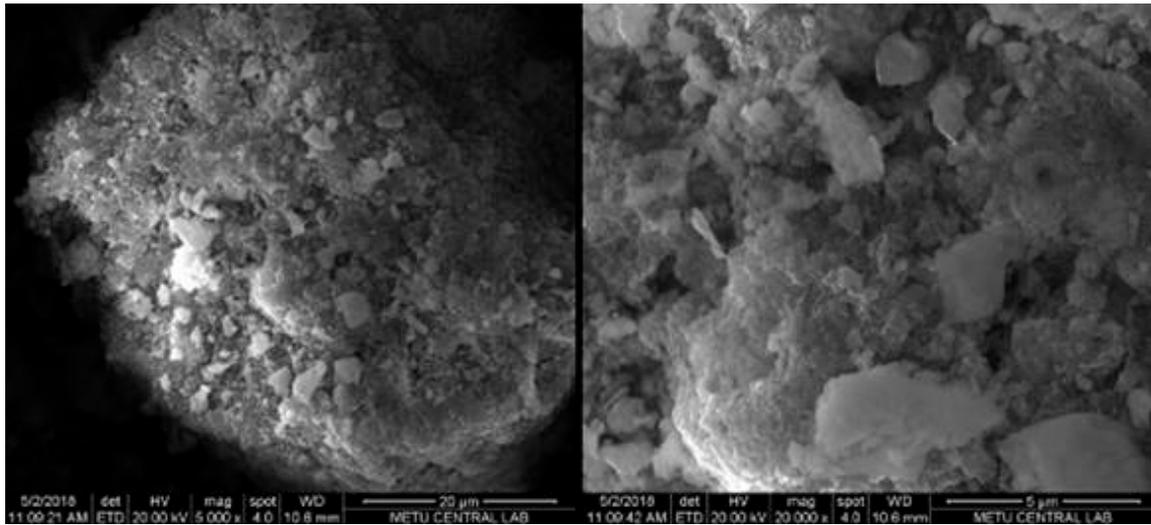
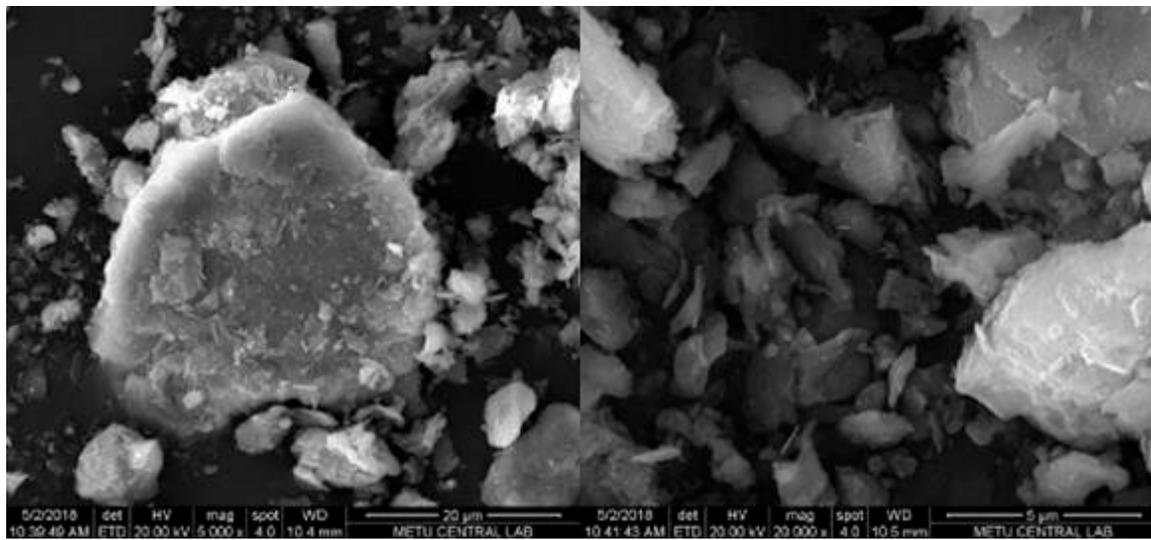


Figure 3.6 XRD phase diagram of fly ash

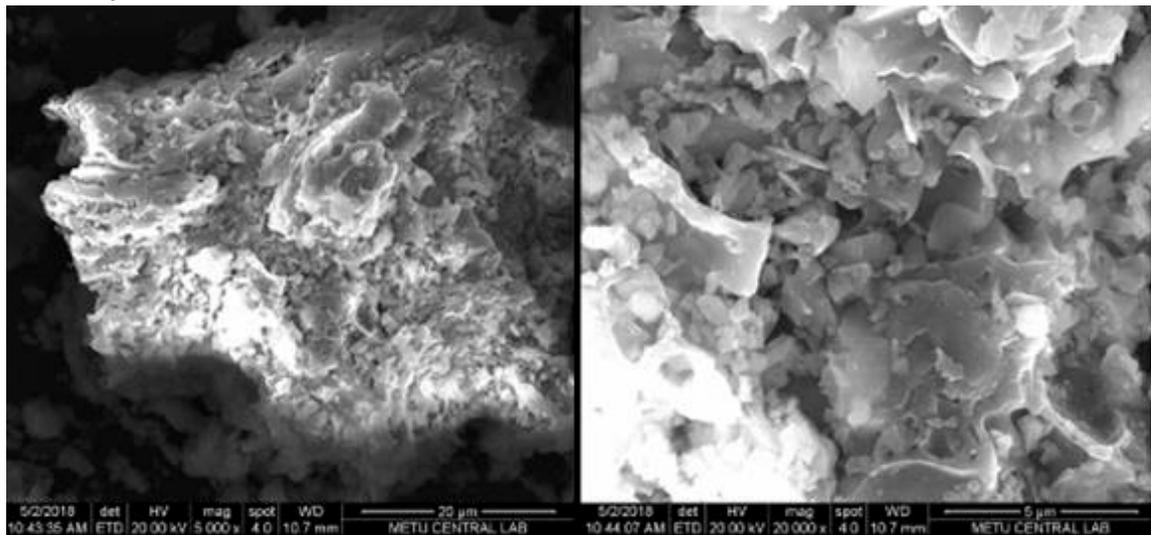
It is clearly seen from the XRD phase diagrams that among different waste materials, the crystallographic structures of red clay brick and hollow brick wastes are closest to that of fly ash. The SEM micrographs of various CDW-based materials taken at different magnification levels after milling are shown in detail in Figure 3.7 below.



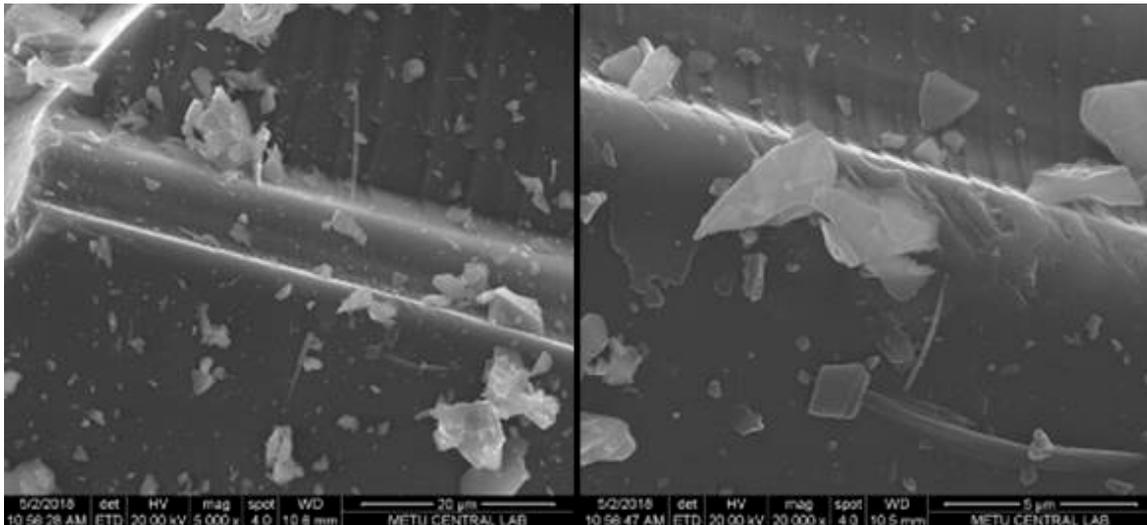
Hollow Brick



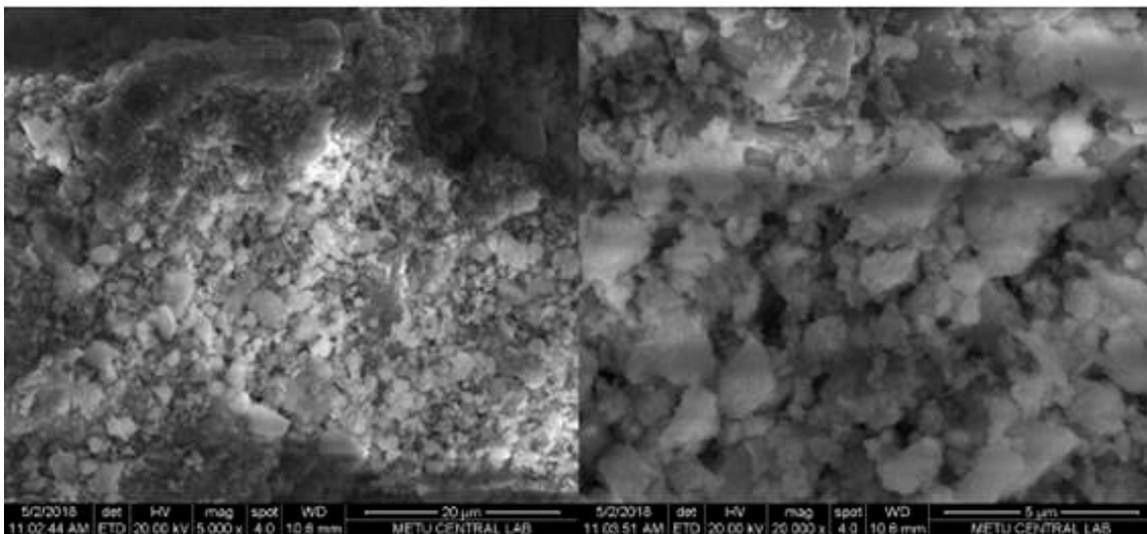
Red Clay Brick



Roof Tile



Glass waste



Concrete waste

Figure 3.7 SEM micrographs of various construction and demolition waste

3.1.3. Particle Size Distributions of Construction Demolition Wastes

According to the apparent surface weighed average grain size and volume weighed average grain size shown in Table 3.2, the red clay brick has the smallest average grain size among different CDW-based materials which was milled for an equal period of time. This value, which is smaller than the average grain size of fly ash, suggests the possibility that it may cause difficulties regarding with the workability of mixtures incorporating red clay brick waste. In addition, it is important to state that red clay brick waste has become finer than other waste materials during the same milling time which shows that it can reach the appropriate thickness in less time with less energy.

Table 3.2 Average grain size of CDW and fly ash

Material	Surface weighted average size	Volume weighted average size	D(0,1)	D(0,5)	D(0,9)
	D[3,2] (μm)	D[4,3] (μm)			
Hollow brick	4.7	82	1.8	27.5	246.7
Red clay brick	2.9	16.4	1.2	7.6	46.9
Roof tile	3.9	44.4	1.5	18.3	94.6
Glass waste	16.9	111.9	7.5	81.3	263.6
Concrete waste	4.3	51.2	1.7	24.2	142.1

As can be seen from Figure 3.8, the roof tile, red clay brick, hollow brick, and waste concrete show very close particle size distributions to that of fly ash, while the waste concrete and especially the hollow brick show a more continuous distribution than fly ash. This situation therefore implies that the use of waste hollow bricks and concrete will make things easier for the production of geopolymer paste.

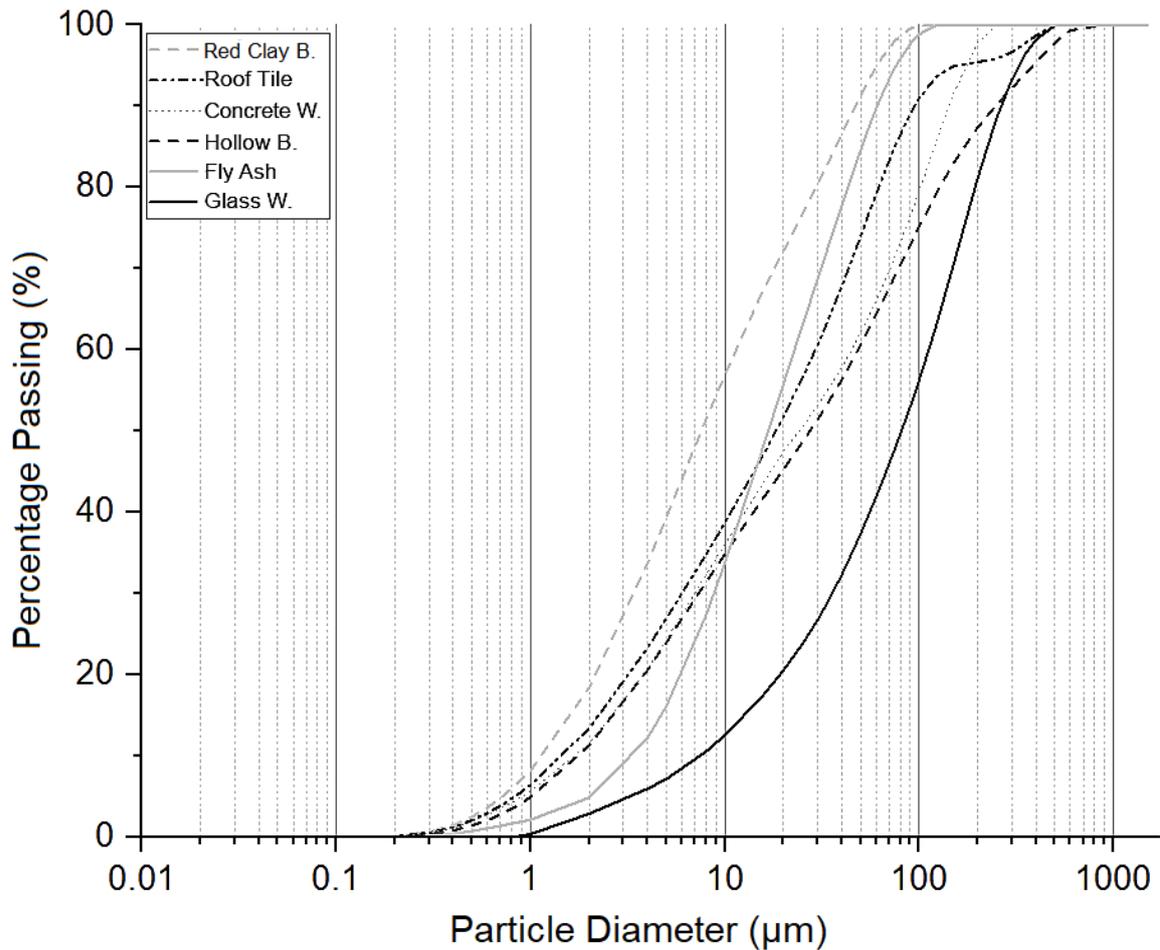


Figure 3.8 Particle size distribution of CDW and fly ash

3.2. Alkali Activators

Within the scope of the study, as a result of comprehensive literature review and preliminary investigations, sodium hydroxide (NaOH), sodium silicate ($\text{Na}_2\text{SiO}_3/\text{Na}_2\text{O}_7\text{Si}_3$), potassium hydroxide (KOH), solid sodium meta-silicate and were selected to be utilized as alkaline activators. As a result of experimental studies, NaOH, which is also known as caustic soda, provided better results and became more prominent among other activators because of cost and easier production. In the form of white flakes or beads, NaOH, dissolves in water by releasing heat and can be affected by moisture. NaOH shows similar properties to KOH. $\text{Na}_2\text{Si}_n\text{O}_n$, which was used as another activator, is a type of alkaline activator which is also known as water glass and dissolves in water. The sodium metasilicate is available in solid form but the liquid forms are also referred to as sodium silicate or water glass. The most common use is the ceramic industry.

3.2.1. Sodium Hydroxide (NaOH)

Sodium hydroxide, also known as caustic soda, is produced by electrolysis of sodium chloride water in a membrane or diaphragm electrolytic cell. Largest caustic soda users are paper industry and manufacturers which are in need of an alkaline based material. Sodium hydroxide generally exists in three forms. These are beads, straws and liquid forms. The chemical composition of these forms is the same (Occidental Chemical Corporation, 2000). The OH^- ions present in the sodium hydroxide solution not only catalyze the hydrolytic reactions at various stages of alkali activation. Sodium hydroxide also promotes the dissolution and condensation reactions of Si and Al minerals in the powder material by raising the pH of the medium to the required values (Duxson et al., 2005). In studies investigating the effect of sodium hydroxide concentration on the alkaline activation of fly ash based geopolymer binders, it was concluded that the optimum concentration of sodium hydroxide was 8M (Duxson et al., 2005; 2007a; Fernández-Jiménez and Palomo, 2005). Lower sodium hydroxide concentrations adversely affect the mechanical properties of the resulting binder. This is because the ion concentration resulting from alkaline activation is not high enough to hydrolyse the appropriate amount of silicon and aluminum contained in the powder materials. Palomo et al. (2004) analyzed the resulting matrices when Class-F fly ash was activated with hydroxyl solutions at different concentrations (from 8 to 18M). Findings revealed the intense effect of concentration on microstructure. If the alkaline activator concentration is high, the matrix becomes more intense and contributes to the formation of material which has a glassy structure.



Figure 3.9 Sodium Hydroxide

Table 3.3 Analysis results of sodium hydroxide

Sodium hydroxide (NaOH)			
Analyzes	Specifications	Unit	Results
Appearance	White flake		White flake
Sodium hydroxide	Min., 98	%	98.27
Sodium carbonate	Max., 0.40	%	0.35
Sodium chloride	Max., 0.10	%	0.020
Iron (Fe)	Max., 15	ppm	13.17

3.2.2. Sodium Silicate

Sodium silicate solutions which are also called as "water glass", can be produced by dissolving the alkali silicate pellets in hot water or by hydrothermally dissolving a reactive source of silica such as silica sand in the related alkali hydroxide solution (PQ Europe, 2004). Sodium silicate is used as a raw material or additive in sectors such as detergents, soap, ceramics, textiles, timber, paper and automotive. Their use as an alkaline activator for the development of geopolymeric binders is also quite common. Sodium silicates with different modulus ($\text{SiO}_2/\text{Na}_2\text{O}$ ratio) can be used in the production of geopolymeric binders. Sodium silicate is the second (mostly used material after sodium hydroxide for the alkaline activation of aluminosilicate based materials. The presence of soluble silica influences the workability of the mixture, the time of setting and the development of mechanical properties. It also changes the microstructure and composition of the inorganic product formed.

In the activation of aluminosilicates with sodium silicate, soluble silica causes the formation of a microstructure similar to the glassy structure (less porous, regular and denser). Furthermore, the highly soluble silica content of the aluminosilicate based powder material and activator solution results in an increase in the silicium content of these binders (Palomo et al., 2004). Similarly, in systems with a high silica content, the formation of zeolite-like products (minority products) is reported to be slower (Fernández-Jiménez and Palomo, 2005; Criado et al., 2007, 2008). However, having a very high concentration of silica of the activator solution reduces the pH of the binder and reduces the degree of reaction of the powder material with the activator solution by increasing the viscosity of the solution (Duxson et al., 2005).

In geopolymer binders obtained with sodium silicate solution, the presence of monomeric and dimeric (i.e. small amount of polymerized structure exist) silica shortens the time needed for the gel to begin precipitation. Furthermore, the increase in the amount of dimeric silica accelerates the precipitation of more gels, but the gel formed under these conditions has a lower stability. Finally, the presence of cyclic trimers initially leads to the formation of more stable gels, but they later delay the progression of reactions. As a result of the researches, it was stated that the optimum value of silicate modulus (M_s : $\text{SiO}_2/\text{Na}_2\text{O}$) for the activation of aluminosilicates with alkalis is between 1 and 1.5 (Duxson et al., 2005; Criado et al., 2008; van Deventer et al., 2007).

Na_2SiO_3 , which was used in experimental studies, is the product of "Koruma Klor Alkali Sanayi ve Ticaret A.Ş." and it was supplied with 5 lt cans in liquid form (Figure 3.10). Table 3.4 shows the results of the chemical analyses of sodium silicate.



Figure 3.10 Liquid sodium silicate

Table 3.4 Analysis results of sodium silicate

Sodium Silicate (Na₂SiO₃)			
Analyzes	Specifications	Unit	Results
Appearance	No-color Clear	-	No-color
Sodium Oxide, Na₂O	12.0-13.5	%	13.14
Silica, SiO₂	23.5-27.0	%	25.75
Bome (20 °C)	Max. 43	⁰ B	43.00
Module	Min. 2	-	2.02
Density (20 °C)	1.39-1.42	g/cm ³	1.40

3.2.3. Potassium Hydroxide

Potassium hydroxide, an alkaline base, has a wide range of uses. It is used in the production of soap in industry, the electrolyte in batteries and in fertilizer production. Potassium hydroxide is often used in agriculture to make alkaline to balance the pH of acidic soils. It is also used in medicine, industrial chemistry. Potassium hydroxide is used in the construction of recycled papers, liquid soap making, and many other cleaning products.

**Figure 3.11** Potassium hydroxide**Table 3.5** Analysis results of potassium hydroxide

Potassium Hydroxide (KOH)			
Analyzes	Specifications	Unit	Results
Appearance	White flake		White flake
Density	2.044-2.12	gr/cm ³	2.12
Solubility	Soluble	-	1120 g/L
Molecular Weigth	55.30-56.71	g/mol	56.11

3.2.4. pH Values of Alkali Activator Solutions

The pH values of the activators in different water/binder, Na%, K%, and Ms ratios were measured with the help of pH meter (Figure 3.11) and indicated in the following tables (Table 3.5-3.8).



Figure 3.12 Measuring pH values of various alkali activator solutions

Table 3.6 pH values of NaOH solutions

Water/Binder Ratio	6%	8%	10%	12%	15%	18%
	pH					
0.30	11.83	12.45	12.77	13.14	13.48	14.65
0.35	12.92	13.07	13.35	13.65	14.28	14.48
0.40	13.12	13.3	13.76	14.10	14.33	14.62
0.45	13.15	13.43	13.90	14.32	14.48	14.70
0.50	13.25	13.81	14.10	14.34	14.55	14.75

Table 3.7 pH values of Na₂SiO₃ solutions

Water/Binder Ratio	6%	8%	10%	12%	15%	18%
	pH					
0.30	12.23	12.3	12.33	12.36	12.38	12.35
0.35	12.17	12.22	12.24	12.26	12.29	12.31
0.40	12.14	12.18	12.20	12.21	12.24	12.25
0.45	12.08	12.12	12.15	12.16	12.22	12.24
0.50	12.04	12.08	12.11	12.12	12.16	12.18

Table 3.8 pH values of Na₂O₇Si₃ solutions

Water/Binder Ratio	6%	8%	10%	12%	15%	18%
	pH					
0.30	13.23	13.30	13.33	13.38	13.48	13.51
0.35	13.20	13.23	13.28	13.33	13.46	13.41
0.40	13.11	13.20	13.23	13.24	13.37	13.38
0.45	13.00	13.14	13.19	13.22	13.36	13.34
0.50	13.01	13.12	13.17	13.19	13.36	13.30

Table 3.9 pH values of KOH solutions

Water/Binder Ratio	6%	8%	10%	12%	15%	18%
	pH					
0.30	15.22	15.4	15.60	15.78	15.95	-
0.35	15.13	15.32	15.55	15.75	15.79	15.88
0.40	15.12	15.22	15.33	15.34	15.55	15.69
0.45	15.06	15.15	15.20	15.24	15.39	15.50
0.50	14.99	15.05	15.16	15.19	15.32	15.41

3.2.5. Water

In the production of samples of different mixtures, tap water from the city network was used. The utilized water was compliant with TS EN 1008 standard to be used as mixing water.

3.3. Compressive Strength Test

Compressive strength testing was performed with a 150-ton-capacity hydraulic concrete press. The compressive strength of the paste samples was tested on cubic samples measuring 50 mm in accordance with ASTM C 109 (2016) standard. During testing, the loading rate was set at 0.9 kN/s for paste samples.

3.4. Internal Structure Analysis with Scanning Electron Microscope (SEM)

Samples were prepared from geopolymer paste mixtures to perform internal structure analysis with scanning electron microscopy (SEM). The samples were examined by FEI QUANTA 250 FEG model (environmental) scanning electron microscope equipped with EDX system for semi-quantitative element analysis. 3-7 kV acceleration voltage, spot size 3 and appropriate pressure values were studied.

3.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was performed with TA Instruments SDT Q600 testing device. In the experiments, powdered geopolymer paste samples were used. The experiments were carried out at temperatures between 25 °C and 1000 °C and with an increased rate of 10 °C per minute.

3.6. X-Ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis was performed on the powdered geopolymer paste samples by Philips X'Pert Pro X-ray diffraction device. In the experiments, $5^\circ \leq 2\theta \leq 80^\circ$ scan range, 0.033° 2θ step length, 30.48 second scanning step time and $K\alpha_1$ wavelength copper ($\lambda = 1.5406 \text{ \AA}$) were used.

3.7. Strength Activity Index

The degree of reaction with calcium hydroxide from cement hydration and binding capacity that pozzolanic materials can have in the presence of water are defined as pozzolanic activity. Pozzolanic materials must have sufficient fineness, amorphous structure and sufficient amount of silica, alumina and iron oxide in order to show sufficient activity. Although the strength index is a preferred method for determining the usability of pozzolans in cement substitution, the strength activity index values have been examined to evaluate the effectiveness of CDW to be used for various purposes within the scope of the current thesis.

Pozzolanic activity depends mainly on the characteristics of the pozzolan and the quality and quantity of the active phases contained therein. Due to the heterogeneous nature of the pozzolans and the complex nature of the hydration reactions, a model has not been developed currently explain the pozzolanic activity. Additionally, the pozzolanic activity may vary depending on the amount of slaked lime bonded to the pozzolan, the specific surface, chemical and mineralogical properties, the amount of SiO_2 , the source of the pozzolan and the curing conditions. The ASTM C618 (1998) standard specifies that the strength activity index for both Class-F and Class-C fly ashes should be at least 75% for 7 and 28 days. Tests for the determination of pozzolanic activity index was carried out according to the ASTM C618 standard as follows: First, a control mortar was prepared using 500 g of Portland cement, 1375 g of sand and 242 ml of water. Then 400 g of Portland cement + 100 g of pozzolanic material was mixed with sufficient water so as to ensure the same consistency level like the control mixture. 5 cm cubic samples were prepared from these two mortars. After 7 and 28 days, compressive strength measurements were performed.

According to TS EN 450-1: 2015, compressive strength tests were carried out on standard mortar specimens prepared with reference cement (75%, by weight) and pozzolan (25%, by weight). Pozzolanic activity was expressed by calculating a value called "Strength Activity Index". This value calculated as given below:

$$\text{Strength Activity Index} = (A/B) \times 100,$$

where, A expresses the average compressive strength of mortar samples with a certain type of pozzolan and B expresses the average compressive strength of control mortar samples. Strength activity indices of the CDW-based materials and fly ash which was used for the comparison were determined according to TS EN 450-1 standard with completely Portland cement-based reference mixture and the results were given in Table 3.9.

Table 3.10 Strength activity index of CDW and fly ash

Material	Compressive Strength (MPa)			Activity Index (%)		
	7 days	28 days	90 days	7 days	28 days	90 days
Portland cement (CEM I 42.5R)	39.3	48.3	55.7	–	–	–
Hollow brick	30.7	40.3	47.1	78.1	83.4	84.6
Red clay brick	31.9	41.1	47.3	81.2	85.1	84.9
Roof tile	29.4	38.7	45.6	74.8	80.1	81.9
Glass waste	27.1	35.0	42.6	69.0	72.5	76.5
Concrete waste	28.9	37.1	42.5	73.5	76.8	76.3
Fly ash	29.5	40.1	51.5	75.1	83.0	92.5

4. EXPERIMENTAL STUDIES

Alkali activator solutions were prepared by using different alkalis at the desired molarity and sodium concentrations in order to prepare the alkaline activated mortars (Figure 4.1) . Alkaline activator solutions prepared with NaOH release excessive heat as a result of the reactions between NaOH and water, thus, before casting of samples which were activated by solutions containing NaOH, prepared solutions were kept in glass bottles at room temperature until the heat of the solution reaches to room temperature.



Figure 4.1 Process of cooling the solutions of various alkaline activators in glass bottles

In the case of sodium hydroxide and sodium silicate combination first, sodium hydroxide was placed in glass bottles, then the sodium silicate and the mixing water were added sequentially, and the whole liquid mixture was mixed thoroughly to dissolve the sodium hydroxide. While preparing the mixtures, firstly, with a consideration of the chemical compositions which showed good performances in accordance with the literature, different CDWs that were used single or red clay in certain ratios were placed in the mortar mixer and the dry content was stirred for 60 seconds. Then, when the alkaline solution at room temperature was poured into the CDW powder, the mixer was operated at a low speed (140 rpm) for 90 seconds. In the second stage, the mixer was operated for 90 seconds and mixing process was completed at a medium speed of 210 rpm. Then, the material was mixed at high speed (285 rpm) for 30 seconds. After this step, the mixture was allowed to rest for 15 seconds. At the final stage, the material was mixed at high speed for 60 seconds, and the completion of mixing, the paste was poured and compressed into the molds in two stages. 50-mm cubic samples were prepared for use in compressive strength tests. After surface

leveling of the samples, they were put into the oven and then cured. As a result of these processes, when the mixing time was increased, the alkali activator was determined to be more effective on all kinds CDW-based materials with different particle size and thus the mixing time was increased to 10 minutes with reference to TS EN 196-1 standard. Hence, it was observed that the compressive strength of geopolymer paste mixtures increased with mixing time.

While identifying the appropriate activator, the samples were heat-treated at room temperature for 24 hours at different temperatures and kept in room temperature for 24 hours. Afterwards, the effect of curing time at different temperatures was investigated and it was observed that the optimum curing period was between 48-72 hours. After determining the appropriate activator type, the samples were kept in the oven at different temperatures for 48-72 hours and then kept at room temperature (Figure 4.2). Various experimental studies were performed before decision making of the above-mentioned steps.



Figure 4.2 Geopolymer paste samples of various CDW

Within the scope of the experimental program, a number of studies were conducted in order to reach high strength classes. In this context, the water/binder ratio and the Na% ratio were changed for the mixtures prepared with sodium hydroxide and potassium hydroxide and for the mixtures prepared with sodium silicate, the water/binder ratio and Ms ($\text{SiO}_2/\text{Na}_2\text{O}$) values were changed. According to the compressive strength results of these mixtures, the optimum mixing ratios were determined. Molarity and Na% ratios were also changed in these mixing ratios. During the trial tests, samples were cured at temperatures of 50, 65, 75,

85, 95, 105, 115, 125 °C and different curing times based on these temperatures were chosen in accordance with the literature review.

4.1. Determination of Experimental Mixtures

A number of test mixtures were prepared to obtain the alkali activated pastes at the beginning of the experiments. The main objectives in the preparation of test mixtures were:

- Investigation of the effects of the alkali activators which were used alone or in combination on the fresh and hardened properties of geopolymer mixtures,
- Investigation of the optimum mixture design of CDW-based alkali activated geopolymers,
- Determination of the effect of water/binder ratio,
- Determination of the optimum activator concentrations and the activator mixing ratios based on different CDW types,
- Specification of the mixing time, suitable alkali activator addition time of the prepared alkali activator mixtures and observation of the effects on the mechanical properties of alkali activated samples,
- Investigation of the effects of alkali activator/binder and water/binder ratios on the geopolymers and the relationships between these ratios,
- Determination of the temperature ranges required for alkali activation reactions to take place.

In experimental testing, various mixtures were produced taking sodium concentration (Na%) by the weight and the silicate module $M_s = \text{SiO}_2/\text{Na}_2\text{O}$ ratio into consideration. Test studies were made considering the conditions such as the consistency of the produced pastes, workability, hardening as a result of the thermal curing time, ease of demolding, effect of waiting period after the activator preparation. An example regarding with the sample encodings and their contents are described in Table 4.1.

Table 4.1 Examples on the coding of the test mixtures

Sodium silicate ve Sodium hydroxide	Sodium/Potassium hydroxide
For the RCB10M0.2-105-48 coded sample;	For the HB15-75-24 coded sample;
▪ RCB: Red clay brick,	▪ HB: Hollow brick,
▪ 10: 10% Na content by weight,	▪ 15: 15% Na or K content by weight,
▪ M0.2: Silicate module is 0.2,	▪ 75: Curing temperature in °C,
▪ 105: Curing temperature in °C,	▪ 24: Curing time in hour,
▪ 48: Curing time in hour,	

Different CDW-based materials were encoded as follow: Concrete waste as (CW), red clay brick as (RCB), hollow brick as (HB), roof tile as (RT) and glass waste as (GW). For the blends which incorporated different CDWs in combination, coding was done by adding the mass usage percentages of each material in front of the material codes. For example, the sample which was encoded as "75HB25RT10M0.3-100-24" contains following properties: 75% hollow brick and 25% roof tile were used as a aluminosilicate source, sodium concentration was %10, silicate modulus was 0.3, and curing conditions were 100 °C for 24 hours.

4.1.1. Experimental Studies Using Sodium Metasilicate (Na_2SiO_3) and Sodium Hydroxide (NaOH)

In the experimental studies in which sodium metasilicate (Na_2SiO_3) and sodium hydroxide (NaOH) were chosen as alkaline activators, the solutions which have four different silicate modules (Ms: 0.75, 1.00, 1.25, 1.50) and three different percentages of sodium concentration (4%, 6%, 8%) were prepared by dissolving the sodium hydroxide and solid phase of sodium metasilicate with the help of a hand mixer in certain proportions of water content. As a source of aluminosilicate, waste concrete powder, waste brick powder (roof tile, red clay brick, hollow brick) and waste glass powder were used singly to determine the ability of the materials to react in the presence of solution. In this part of the study, the water/binder ratio was chosen as 0.5 although desired compressive strength could not be obtained at the end of 7 days from the samples which were cured at laboratory environment. The samples incorporated with the waste concrete powder as a source of aluminosilicate were able to break even by applying manual force without being subjected to compressive strength testing. The samples incorporated with the waste brick dusts (hollow brick, red clay brick, roof tile) were still soft even after 7 days. Based on these findings, it was understood that there is the necessity of presence of high-temperature curing for making alkali activation

reactions possible. Therefore, the mixtures were produced without changing the amount of alkali solution, binder and the water/binder ratio and cured at 75 °C for 24 hours, then cured in the laboratory environment for 6 days. However, as a result of the uniaxial compressive strength tests, the desired compressive strength levels could not be obtained and similar behaviors with previous castings were observed.

4.1.2. Experimental Studies Using Sodium Silicate ($\text{Na}_2\text{O}_7\text{Si}_3$) and Sodium Hydroxide (NaOH)

Based on the data obtained from the experimental studies using sodium metasilicate (Na_2SiO_3) and sodium hydroxide (NaOH) as an alkaline activator, the solutions obtained by dissolving the chemicals in certain proportions of water with the help of the hand mixer may not fully provide the required activator chemistry. Therefore, solutions were prepared with the liquid phase of ready-made silicate solution as considered in the literature previously. In this context, activator solutions were prepared with the commercially available sodium silicate solution ($\text{Na}_2\text{O}_7\text{Si}_3$) and the sodium hydroxide in solid phase, by stirring with a glass rod in a certain amount of water. In the studies where sodium silicate solution was used as alkaline activator and the waste concrete powder was used as binder, two different silicate modules (0.2 and 0.3) and three different percentages of sodium concentration (9%, 12%, 15%) were decided. Solutions were used for the purpose of determining the effect of silicate module and sodium percentage of the solution on the compressive strength results. Compressive strength test results of the samples obtained from these castings which were with water/binder ratio of 0.35, thermal curing temperature of 100 °C and curing time of 24 hours are detailed in Table 4.2.

Table 4.2 The compressive strength results of geopolymer pastes containing concrete waste activated by $\text{Na}_2\text{O}_7\text{Si}_3$ and NaOH in different Na concentrations and Ms ratios

Sample Name	Activator Type	Ms	Na%	W/B	Curing Temperature (°C)	Curing Time (hour)	Compressive Strength (MPa)
CW9M0.2-100-24	Water glass ($\text{Na}_2\text{O}_7\text{Si}_3$)	0.2	9	0.35	100	24	0.0
CW12M0.2-100-24			12				4.2
CW15M0.2-100-24			15				5.4
CW9M0.3-100-24	Sodium hydroxide (NaOH)	0.3	9	0.35	100	24	0.0
CW12M0.3-100-24			12				3.8
CW15M0.3-100-24			15				5.9

(Ms: Silicate Modulus, Na%: Sodium Concentration, W/B: Water/Binder)

In these castings which were with water/binder ratio of 0.35, desired consistencies were not achieved, thus, the same castings were repeated by increasing the ratio of water/binder to 0.40. Although the desired consistency was obtained with water/binder ratio of 0.4, the samples were easily broken by hand force without being subjected to the uniaxial compressive test. Castings utilizing waste concrete powder were repeated using waste brick powder at the same silicate modulus, sodium percentage, water/binder ratio and curing conditions. Because the chemical contents of the roof tile, red clay brick and hollow brick were very similar, only roof tiles were used as waste brick dust in the casting and the obtained compressive strength results from the samples were given in Table 4.3.

Table 4.3 The compressive strength results of geopolymers containing roof tile activated by $\text{Na}_2\text{O}_7\text{Si}_3$ and NaOH at different Na concentrations and Ms ratios

Sample Name	Activator Type	Ms	Na%	W/B	Curing Temperature (°C)	Curing Time (hour)	Compressive Strength (MPa)
RT9M0.2-100-24	Water glass ($\text{Na}_2\text{O}_7\text{Si}_3$)	0.2	9	0.35	100	24	15.3
RT12M0.2-100-24			12				30.8
RT15M0.2-100-24			15				20.9
RT9M0.3-100-24	Sodium hydroxide (NaOH)	0.3	9	0.35	100	24	13.4
RT12M0.3-100-24			12				19.9
RT15M0.3-100-24			15				20.3

(Ms: Silicate Modulus, Na%: Sodium Concentration, W/B: Water/Binder)

Based on the data obtained, it was determined that the increase in the sodium concentration of solution had positive effects on strength. However, in cases where the sodium concentration was higher than 12%, as the sodium concentration increased, the diffusion rate of sodium ions in the solution became more difficult and the reactions were disrupted. Therefore, sodium concentration of 12% was determined as the optimum value and in this direction, solutions were prepared at the ratio of silicate modulus (Ms: 0.2) with which higher compressive strengths were obtained, and new paste phases were produced by selecting the water/binder ratio as 0.35 with all binder types. The obtained paste phases were subjected to thermal curing at 100 °C. Strength results are given in Table 4.4.

Table 4.4 The compressive strength results of geopolymer pastes containing roof tile, red clay brick, hollow brick and glass waste, activated by $\text{Na}_2\text{O}_7\text{Si}_3$ and NaOH at 12% Na concentration and 0.2 Ms ratio

Sample Name	Activator Type	Ms	Na%	W/B	Curing Temperature (°C)	Curing Time (hour)	Compressive Strength (MPa)
RT12M0.2-100-24	Water glass ($\text{Na}_2\text{O}_7\text{Si}_3$) + Sodium hydroxide (NaOH)	0.2	12	0.35	100	24	29.8
RCB12M0.2-100-24							33.5
HB12M0.2-100-24							19.3
GW12M0.2-100-24							25.8

(Ms: Silicate Modulus, Na%: Sodium Concentration, W/B: Water/Binder)

In order to investigate the effect of the silicate module on the compressive strength, four different silicate modules were prepared for the same material types and mixing ratios and the castings were repeated considering the results obtained from the castings where the silicate module was 0.2 and the sodium concentration was 12%. As the silicate ratio of the solutions increased during casting, the consistency of the paste phase densified, regardless of the type of material used as the binder, and the problem of early setting was experienced during pouring of fresh mixtures into the mold. As can be seen from the results shown in Table 4.5, the increase in the silicate module ($\text{SiO}_2/\text{Na}_2\text{O}$) of solution, in other words, the increase in the amount of SiO_2 to be contained by the solution, has a positive effect on the strength gain up to a certain point. However it was determined that the compressive strength decreases unexpectedly, when the silicate module exceeds 0.2.

Table 4.5 Geopolymer pastes containing roof tile, red clay brick, hollow brick and glass waste, activated by $\text{Na}_2\text{O}_7\text{Si}_3$ and NaOH at Na concentration of 12% and different Ms ratios

Sample Name	Activator Type	Na%	W/B	Curing Temperature (°C)	Curing Time (hour)	Silicate Modulus (Ms)			
						0.1	0.2	0.3	0.4
RT12M0.2-100-24	Water glass ($\text{Na}_2\text{O}_7\text{Si}_3$)	12	0.35	100	24	18.8	29.8	20.2	16.3
RCB12M0.2-100-24	+					9.6	33.5	25.3	19.2
HB12M0.2-100-24	Sodium hydroxide					17.5	19.3	12.4	11.9
GW12M0.2-100-24	(NaOH)					18.4	25.8	20.6	18.5

(Ms: Silicate Modulus, Na%: Sodium Concentration, W/B: Water/Binder)

4.1.3. Experimental Studies Using Sodium Silicate (Na_2SiO_3) and Sodium Hydroxide (NaOH)

For a comparison of the results obtained from the studies in which the sodium metasilicate and glass water ($\text{Na}_2\text{O}_7\text{Si}_3$) were used as the alkali activators with sodium hydroxide in the previous stages, and to obtain all the required data for silicate source activator selection, another source of commercially available sodium silicate (Na_2SiO_3) with silicate modulus of 2.02 was used in certain castings. In these castings, solutions were prepared using sodium hydroxide and water in certain proportions by selecting the silicate module as above-mentioned and the previously tested values (Ms: 0.5). In order to overcome the problem of early setting and excessively dense consistency, the water/binder ratio was increased. Two series of castings were carried out in this direction. In the first series, solutions having a silicate modulus of 0.5 and three different sodium concentrations (8%, 10%, 12%) were selected and the water/binder ratio was determined to be 0.4. 75% hollow brick, 10% roof tile and 15% waste concrete were chosen as the binder. Compressive strength test results of samples cured at 105 °C for 24, 48 and 72 hours were shown in Table 4.6.

Table 4.6 The compressive strength results of geopolymer pastes containing hollow brick, roof tile and concrete waste activated by Na_2SiO_3 and NaOH at water/binder ratio of 0.4 and Ms ratio of 0.5 with various Na concentrations

Sample Name	Activator Type	Ms	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)
75HB10RT15CW8M0.5-105-24	Sodium Silicate (Na_2SiO_3) + Sodium hydroxide (NaOH)	0.5	8	0.4	105	24	12.9
75HB10RT15CW8M0.5-105-24			8			48	13.0
75HB10RT15CW8M0.5-105-24			8			72	13.2
75HB10RT15CW10M0.5-105-48			10			48	11.6
75HB10RT15CW10M0.5-105-48			10			48	11.2
75HB10RT15CW10M0.5-105-48			10			48	11.3
75HB10RT15CW12M0.5-105-72			12			72	7.4
75HB10RT15CW12M0.5-105-72			12			72	0.0
75HB10RT15CW12M0.5-105-72			12			72	0.0

(Ms: Silicate Modulus, Na%: Sodium Concentration, W/B: Water/Binder)

Due to the continuation of the placement problem of geopolymer pastes, in the 2nd series (Table 4.7) the water/binder ratio was increased to 0.5 by keeping the silicate module constant. As the binder, 75% hollow brick, 10% roof tile and 15% waste concrete were selected and the samples were cured at 105 °C for 24, 48 and 72 hours. Increasing the water/binder ratio to 0.5 decreased the thickness of the paste and helped overcome the problems related with the mold placement. Sodium concentrations of 6%, 8%, 10% were selected for these castings. As shown in the following compressive strength results, the samples with 8% and 10% sodium concentration achieved sufficient workability and compressive strength, however; these positive effects were not obtained when sodium silicate and sodium hydroxide were used together.

Table 4.7 The compressive strength results of geopolymer pastes containing hollow brick, roof tile and concrete waste activated by Na_2SiO_3 and NaOH at water/binder ratio of 0.5 and Ms ratio of 0.5 with various Na concentrations

Sample Name	Activator Type	Ms	Na%	W/B	Curing Temp (°C)	Curing Time (hour)	Compressive Strength (MPa)
75HB10RT15CW6M0.5-105-24	Sodium Silicate (Na_2SiO_3) + Sodium hydroxide (NaOH)	0.5	6	0.5	105	24	0.0
75HB10RT15CW6M0.5-105-24			6			24	8.6
75HB10RT15CW6M0.5-105-24			6			24	8.0
75HB10RT15CW8M0.5-105-48			8			48	0.0
75HB10RT15CW8M0.5-105-48			8			48	10.9
75HB10RT15CW8M0.5-105-48			8			48	9.7
75HB10RT15CW10M0.5-105-72			10			72	0
75HB10RT15CW10M0.5-105-72			10			72	21.8
75HB10RT15CW10M0.5-105-72			10			72	22.1

(Ms: Silicate Modulus, Na%: Sodium Concentration, W/B: Water/Binder)

In addition, with different ratios on the basis of the binder material (1st casting; 70% red clay brick, 15% roof tile, 10% waste concrete powder and 5% waste glass powder), silicate module of 0.2 and water/binder ratio of 0.4, two casting were carried out with sodium concentration of 8% and subjected to thermal curing at 105 °C for 24, 48 and 72 hours but no compressive strength results were recorded.

Another series produced by this sodium silicate solution was produced for the determination of the changes in strength as a result of the gradual substitution of the glass powder instead of waste concrete powder. For these series, two different sodium concentrations of 8% and 12%, silicate module of 0.3 and water/binder ratio of 0.35 were selected and subjected to 105 °C for 24, 48, 72 hours. The obtained compressive strength test results were as indicated in Table 4.8.

Table 4.8 The compressive strength results of geopolymer pastes containing glass waste and concrete waste activated by Na_2SiO_3 and NaOH at Ms ratio of 0.3 and Na concentrations of 8% and 12%

Sample Name	Activator Type	Ms	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)				
100CW8M0.3-105-24	Sodium Silicate (Na_2SiO_3) + Sodium hydroxide (NaOH)	0.3	8	0.35	105	24	4.1				
100CW8M0.3-105-48						48	4.2				
100CW8M0.3-105-72						72	4.1				
75CW25GW8M0.3-105-24						24	18.0				
75CW25GW8M0.3-105-48						48	23.5				
75CW25GW8M0.3-105-72						72	23.5				
50CW50GW8M0.3-105-24						24	20.2				
50CW50GW8M0.3-105-48						48	28.1				
50CW50GW8M0.3-105-72						72	25.7				
25CW75GW8M0.3-105-24						24	21.6				
25CW75GW8M0.3-105-48						48	17.2				
25CW75GW8M0.3-105-72						72	15.9				
100CW12M0.3-105-24			12			0.3	12	0.35	105	24	7.5
100CW12M0.3-105-48										48	4.8
100CW12M0.3-105-72										72	0.0
75CW25GW12M0.3-105-24										24	18.1
75CW25GW12M0.3-105-48										48	0.0
75CW25GW12M0.3-105-72										72	0.0
50CW50GW12M0.3-105-24										24	26.9
50CW50GW12M0.3-105-48										48	25.6
50CW50GW12M0.3-105-72										72	18.1
25CW75GW12M0.3-105-24										24	24.1
25CW75GW12M0.3-105-48										48	36.6
25CW75GW12M0.3-105-72										72	20.8

(Ms: Silicate Modulus, Na%: Sodium Concentration, W/B: Water/Binder)

4.1.4. Experimental Studies Using Sodium Silicate ($\text{Na}_2\text{O}_7\text{Si}_3$)

In previous studies included in the current thesis, solutions containing sodium hydroxide and different types of sodium silicate were prepared after dissolved in certain amounts of water. At this stage of the experimental studies using sodium silicate as a solution, the effects of different silicate modules and sodium concentrations obtained by the changes in the molarity of the solution were investigated. In this context, a constant silicate module (Ms: 0.3) was

used to determine the effects of different sodium concentrations (12%, 15%, 18%) on the compressive strengths of pastes. Water/binder ratio was chosen as 0.35 and two series of casting were performed. Due to difficulties related with the dense consistency and placement into the molds, the water/binder ratio was increased to 0.4. Then, one of these series cured at 100 °C for 24 hours and the other one cured at the same temperature for 48 hours. As can be seen from the compressive strength results given in Table 4.9, the increments in sodium concentration promoted the compressive strength proportionally. The increase in thermal curing time did not show remarkable effects on samples, except for those with sodium concentration of 12%.

Table 4.9 The compressive strength results of geopolymers containing 0.3 of tile activated by $\text{Na}_2\text{O}_7\text{Si}_3$ at Ms ratio of 0.3 with various Na concentrations

Sample Name	Activator Type	Ms	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)
RT12M0.3-100-24	Water glass ($\text{Na}_2\text{O}_7\text{Si}_3$)	0.3	12	0.4	100	24	0.0
RT12M0.3-100-48						48	8.4
RT15M0.3-100-24			15			24	11.3
RT15M0.3-100-48						48	10.9
RT18M0.3-100-24			18			24	16.7
RT18M0.3-100-48						48	16.0

(Ms: Silicate Modulus, Na%: Sodium Concentration, W/B: Water/Binder)

To determine the effects of increased sodium concentrations on the compressive strength development five different sodium concentrations of 12%, 15%, 18%, 20%, 22% with silicate module of 0.3 and water/binder ratio of 0.4 were tried. Samples were cured at 100 °C as in the case of previous castings and curing time was selected as 24 hours. As shown in Table 4.10, the increments in the sodium concentrations at a constant silicate module tended to increase the compressive strength of samples prepared by using glass water only.

Table 4.10 The compressive strength results of geopolymer pastes containing roof tile activated by $\text{Na}_2\text{O}_7\text{Si}_3$ at Ms ratio of 0.3 with various Na concentrations

Sample Name	Activator Type	Ms	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)
RT12M0.3-100-24	Water glass ($\text{Na}_2\text{O}_7\text{Si}_3$)	0.3	12	0.4	100	24	0.0
RT15M0.3-100-24			15				11.3
RT18M0.3-100-24			18				16.7
RT20M0.3-100-24			20				18.0
RT22M0.3-100-24			22				19.7

(Ms: Silicate Modulus, Na%: Sodium Concentration, W/B: Water/Binder)

Based on these results, a similar series was prepared using waste glass powder as the binder. Considering the positive effects of increased sodium concentrations on strength, for this series, silicate modulus was selected as 0.3, water/binder ratio as 0.4 and the sodium concentrations as 18%, 20%, 22%. This series, like others, was subjected to thermal curing for 24 hours at 100 °C. As a result, it was observed that the increments in sodium concentrations decreased the strength of samples of this series which utilized waste glass powder as the main binder (Table 4.11).

Table 4.11 The compressive strength results of geopolymer pastes containing glass waste activated by $\text{Na}_2\text{O}_7\text{Si}_3$ at Ms ratio of 0.3 with various Na concentrations

Sample Name	Activator Type	Ms	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)
GW18M0.3-100-24	Water glass ($\text{Na}_2\text{O}_7\text{Si}_3$)	0.3	18	0.4	100	24	11.4
GW20M0.3-100-24			20				10.0
GW22M0.3-100-24			22				0.0

(Ms: Silicate Modulus, Na%: Sodium Concentration, W/B: Water/Binder)

In another series in which the waste glass powder was used as a binder together with the roof tile, the silicate modulus was selected as 0.3, water/binder ratio as 0.4 and sodium concentrations as 18%, 20%, 22%. The samples of the mixtures were subjected to thermal curing at 100 °C for 24 hours. The results obtained from this series are given in Table 4.12.

Table 4.12 The compressive strength results of geopolymer pastes containing roof tile and glass waste activated by $\text{Na}_2\text{O}_7\text{Si}_3$ at Ms ratio of 0.3 with various Na concentrations

Sample Name	Activator Type	Ms	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)
50RT50GW18M0.3-100-24	Water glass ($\text{Na}_2\text{O}_7\text{Si}_3$)	0.3	18	0.4	100	24	14.4
50RT50GW20M0.3-100-24			20				13.9
50RT50GW22M0.3-100-24			22				13.7

(Ms: Silicate Modulus, Na%: Sodium Concentration, W/B: Water/Binder)

4.1.5. Experimental Studies Using Potassium Hydroxide (KOH)

In the studies using potassium hydroxide as the alkaline activator, aluminosilicate sources were allowed to react by mixing each one of waste materials singly at different molarities. For this purpose, various paste phases were obtained by using alkaline activator solutions prepared in four different molar concentrations (5M, 7M, 9M, 11M) with waste concrete powder, waste brick powder (roof tile, red clay brick, hollow brick) and waste glass powder. The water/binder ratio for the prepared paste phases was 0.4, and the compressive strength test results of samples after cured for 24 hours at 90 °C were presented in Table 4.13.

When the compressive strength results were evaluated, it was seen that the increase in molar concentrations of potassium hydroxide solution had negative effects on the compressive strength results. In order to investigate the effect of fineness of the binder materials on the degree of reaction and hence on the compressive strength results, samples were produced by using only roof tile in the presence of potassium hydroxide solution prepared at 5M concentration. Results showed that increased fineness of the binder has positive effects on the compressive strength development thanks to increased surface area.

Table 4.13 The compressive strength results of geopolymer pastes containing various CDW activated by KOH with various molar concentrations

Sample Name	Activator Type	M	W/B	Curing Temp.(°C)	Curing Time (hour)	Compressive Strength (MPa)
CW5-90-24	Potassium hydroxide (KOH)	5	0.4	90	24	0.0
CW7-90-24		7				0.0
CW9-90-24		9				0.0
CW11-90-24		11				0.0
RT5-90-24		5				7.4
RT7-90-24		7				6.6
RT9-90-24		9				5.4
RT11-90-24		11				4.2
RCB5-90-24		5				8.1
RCB7-90-24		7				9.0
RCB9-90-24		9				7.2
RCB11-90-24		11				5.0
HB5-90-24		5				8.5
HB7-90-24		7				6.8
HB9-90-24		9				7.7
HB11-90-24		11				6.1
AC5-90-24		5				21.2
GW7-90-24		7				19.1
GW9-90-24		9				16.9
GW11-90-24		11				10.6

(M: Molarity, Na%: Sodium Concentration, W/B: Water/Binder)

4.1.6. Experimental Studies Using Sodium Hydroxide (NaOH)

In the experimental studies in which sodium hydroxide was used as an alkaline activator, different CDW-based materials were activated singly with solutions having different sodium percentages. Within this context, various paste phases were developed using waste concrete powder and waste brick dusts (roof tile, red clay brick, hollow brick) as a aluminosilicate source together with alkaline activator solutions prepared with four different sodium concentrations 6%, 8%, 10% and 12%. The water/binder ratio for the prepared paste samples was 0.5 and the samples were cured for 7 days at 70 °C before the implementation of uniaxial compressive strength tests. Compressive strength tests carried out on samples showed that none of the samples were with considerable results. Therefore, at the second stage, in line with the studies in the literature, curing temperature of the samples was increased to 100 °C considering the possibility that the curing temperature of 70 °C was not sufficient for the activation of the aluminosilicate source materials. In addition, the sodium percentage of the solution was increased to 10%, 12%, 15% to investigate whether the increases in sodium

percentage of the activator solution would have positive effects on strength development or not. The results obtained after 24 hours of thermal curing at 100 °C are listed in Table 4.14.

Table 4.14 The compressive strength results of geopolymer pastes containing different CDW activated by NaOH with various sodium concentrations

Sample Name	Activator Type	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)
CW10-100-24	Sodium hydroxide (NaOH)	10	0.4	100	24	0.0
CW12-100-24		12				0.0
CW15-100-24		15				0.0
RT10-100-24		10				13.4
RT12-100-24		12				15.6
RT15-100-24		15				9.1
RCB10-100-24		10				8.5
RCB12-100-24		12				12.9
RCB15-100-24		15				10.2
HB10-100-24		10				7.0
HB12-100-24		12				11.5
HB15-100-24		15				7.1
GW10-100-24		10				32.8
GW12-100-24		12				43.0
GW15-100-24		15				41.6

(Na%: Sodium Concentration, W/B: Water/Binder)

When the obtained compressive strength results were evaluated, it was monitored that the increments in the sodium percentages of the sodium hydroxide solution had a positive effect on the compressive strength results up to a concentration level of 12%. Increasing the thermal curing temperature from 70 °C to 100 °C resulted in increments in compressive strength. It has been also observed that the increased curing temperatures did not have any effect on compressive strength developments of pastes cast only with waste concrete powder.

To confirm the positive effects of increased curing temperatures, to determine the effects of curing period and to evaluate the effects of increased sodium percentages in activator solutions on the compressive strength, paste samples were produced only by using hollow bricks at water/binder ratio of 0.35, with sodium percentages of 12%, 15%, 18%, curing periods of 24 and 48 hours and curing temperatures of 100 and 110 °C. As a result of the compressive strength testing of proposed samples results of which were shown in Table 4.15, it was determined that the increments in the sodium percentage of solution negatively affected the strength attainment and that increased curing time and temperature positively contributed to the strength.

Table 4.15 The compressive strength results of geopolymer pastes containing hollow brick activated by NaOH with various sodium concentrations

Sample Name	Activator Type	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)
HB12-100-24	Sodium hydroxide (NaOH)	12	0.4	100	24	7.2
HB12-100-48					48	26.5
HB12-110-24				110	24	27.0
HB12-110-48					48	28.1
HB15-100-24		15		100	24	6.4
HB15-100-48					48	11.2
HB15-110-24				110	24	16.0
HB15-110-48					48	22.5
HB18-100-24		18		100	24	2.9
HB18-100-48					48	9.4
HB18-110-24				110	24	10.3
HB18-110-48					48	15.6

(Na%: Sodium Concentration, W/B: Water/Binder)

In continuation of studies using sodium hydroxide as the alkaline activator, based on the data obtained from the previous studies, three different sodium percentages (10, 12, 15%) were selected and solutions with a water/binder ratio of 0.35 were prepared. The curing periods for the samples were selected as 24, 48 and 72 hours and samples were subjected to seven different curing temperatures (50, 65, 75, 85, 95, 105, 115 °C). In addition, the curing time was updated to be 24, 48, 72, 96, 120 hours since the targeted compressive strength increments were not noted for samples cured at 50, 65 and 75 °C. The results from compressive strength tests were shown in Tables 4.16, 4.17 and 4.18..

Table 4.16 The effect of curing temperature, curing time and sodium concentration on the compressive strength of samples with roof tile

Curing Time (hour)	Sodium Concentration (%)																							
	10								12								15							
	Curing Temperature (°C)								Curing Temperature (°C)								Curing Temperature (°C)							
	50	65	75	85	95	105	115	125	50	65	75	85	95	105	115	125	50	65	75	85	95	105	115	125
24	0	4.5	6.2	10.2	18.1	29.6	35.5	28.7	0	5.6	8	9.6	20.6	30.3	42.3	32.5	0	4.2	5.3	7.4	20.3	21.5	31.4	25.8
48	0	6.5	14.5	22.9	23.7	23.4	31.1	23.8	0	5.7	8.7	30	24.7	31.8	32.6	27.5	0	4.7	6.6	17.2	23.7	21.6	29.8	27.6
72	0	6.9	15.5	28.2	23.9	23.5	41.1	28.6	0	7.4	9.7	30.5	23.6	31.5	35.7	30.5	0	5.1	7.7	21.6	21.2	18.2	30.5	28.9
120	0	7.4	26.4	-	-	-	-	-	0	9.3	33.6	-	-	-	-	-	0	6.1	15.3	-	-	-	-	-

Table 4.17 The effect of curing temperature, curing time and sodium concentration on the compressive strength of samples with red clay brick

Curing Time (hour)	Sodium Concentration (%)																							
	10								12								15							
	Curing Temperature (°C)								Curing Temperature (°C)								Curing Temperature (°C)							
	50	65	75	85	95	105	115	125	50	65	75	85	95	105	115	125	50	65	75	85	95	105	115	125
24	0	4.2	5.4	9.7	17.4	30.6	19.8	23.5	0	4.3	4.7	6.7	8.0	21.6	34.8	13.6	0.0	4.4	5.1	5.7	6.5	9.6	27.3	20.1
48	0	6.2	11.2	22.5	41.8	23.4	22.4	19.9	0	5.5	6.3	13.1	19.1	19.5	33.9	18.3	0.0	5.5	5.6	7.2	10.8	27.3	42.5	23.4
72	0	7.1	12.4	35.3	40.2	23.5	21.6	21.1	0	6.6	7.1	14.2	33.9	45.0	33.5	17.1	0.0	5.7	6.8	9.7	16.0	39.0	38.0	27.0
120	0	8.3	18.6	-	-	-	-	-	0	9.6	21.2	-	-	-	-	-	0.0	6.3	16.1	-	-	-	-	-

Table 4.18 The effect of curing temperature, curing time and sodium concentration on the compressive strength of samples with hollow brick

Curing Time (hour)	Sodium Concentration (%)																							
	10								12								15							
	Curing Temperature (°C)								Curing Temperature (°C)								Curing Temperature (°C)							
	50	65	75	85	95	105	115	125	50	65	75	85	95	105	115	125	50	65	75	85	95	105	115	125
24	0	4.2	4.1	7.8	26.1	18.6	19.8	43.7	0	5.3	6.6	5.1	9.4	12.6	45.7	45.8	0	7.2	8.6	4.2	8.6	12.2	38.9	26.7
48	0	4.3	15.3	26.6	27.9	19.7	22.4	38.3	0	4.1	7.6	10.4	22.7	20.9	40.0	37.1	0	9.0	8.8	6.2	30.1	32.5	33.4	25.3
72	0	5.1	17.1	30.8	25.7	19.5	21.6	35.5	0	6.1	8.1	30.9	18.4	18.6	37.7	39.3	0	9.5	11.2	10.8	18.5	28.2	33.3	24.9
120	0	5.7	24.9	-	-	-	-	-	0	8.5	10.6	-	-	-	-	-	0	9.8	16.8	-	-	-	-	-

At the stage where the waste concrete powder was activated using alkali activator solutions prepared with sodium hydroxide, no strength gain could be observed in the previous trials performed at three different sodium concentrations and at two different water/binder ratios (0.4 and 0.5), thus, the water/binder ratio was reduced to 0.35 to obtain strength development. The specimens were subjected to thermal curing for 24, 48 and 72 hours in this repeated tests by increasing the heat curing temperature to 105 °C. As can be seen from compressive strength results presented in Table 4.19, the required strength levels could not be reached.

Table 4.19 The compressive strength results of geopolymer pastes containing waste concrete powder activated by NaOH with various sodium concentrations

Sample Name	Activator Type	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)
CW8-105-24	Sodium hydroxide (NaOH)	8	0.35	105	24	5.8
CW8-105-48					48	7.3
CW8-105-72					72	5.7
CW10-105-24		10			24	7.3
CW10-105-48					48	6.9
CW10-105-72					72	7.2
CW12-105-24		12			24	5.4
CW12-105-48					48	8.0
CW12-105-72					72	9.8

(Na%: Sodium Concentration, W/B: Water/Binder)

Since it was not possible to reach the desired results with the alkaline activation of waste concrete powder, waste concrete powder was used in combination with waste glass powder which had high amounts of SiO₂ in the following tests. As aluminosilicate source, waste concrete powder (75%, by weight) and waste glass powder (25%, by weight) were used and four different sodium concentrations (8, 10, 12, 15%) and water/binder ratio of 0.35 were selected for further testing. The samples produced were subjected to thermal curing at 105 °C for 24, 48 and 72 hours and the results of compressive strength tests were presented in Table 4.20.

Table 4.20 The compressive strength of geopolymer pastes containing mixture of waste concrete and waste glass powder activated by NaOH at different sodium concentrations

Sample Name	Activator Type	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)
50CW50GW8-105-24	Sodium hydroxide (NaOH)	8	0.35	105	24	23.1
50CW50GW8-105-48					48	19.9
50CW50GW8-105-72					72	19.2
50CW50GW10-105-24		10			24	31.0
50CW50GW10-105-48					48	26.7
50CW50GW10-105-72					72	24.8
50CW50GW12-105-24		12			24	31.0
50CW50GW12-105-48					48	23.9
50CW50GW12-105-72					72	23.5
50CW50GW15-105-24		15			24	23.1
50CW50GW15-105-48					48	24.8
50CW50GW15-105-72					72	24.4

(Na%: Sodium Concentration, W/B: Water/Binder)

It was decided to blend the various CDW-based materials obtained from a demolished building at certain proportions by using selective demolition method and to activate these blended materials with the solutions which were prepared by using sodium hydroxide as an alkaline activator. Along these lines, the binder mixture containing 70% red clay brick, 15% roof tile, 10% waste concrete powder and 5% waste glass powder was first activated with solutions having sodium concentration of 12% which resulted in the best performance in previous tests. For this casting where two different heat curing temperatures were selected, the water/binder ratio was chosen to be 0.35 and the samples were subjected to thermal curing for 24, 48 and 72 hours. As can be seen from the compressive strength results indicated in Table 4.21, values increased with the extension of the thermal curing time.

Table 4.21 The compressive strength of geopolymer pastes containing mixture of red clay brick, roof tile, waste concrete and waste glass activated by NaOH and cured at different temperatures

Sample Name	Activator Type	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)
70RCB15RT10CW5GW12-105-24	Sodium hydroxide (NaOH)	12	0.35	105	24	13.9
70RCB15RT10CW5GW12-105-48					48	31.7
70RCB15RT10CW5GW12-105-72					72	24.8
70RCB15RT10CW5GW12-115-24				115	24	19.4
70RCB15RT10CW5GW12-115-48					48	27.5
70RCB15RT10CW5GW12-115-72					72	26.7

(Na%: Sodium Concentration, W/B: Water/Binder)

For castings in which higher amounts of hollow brick were used in the binder mixture, solutions with a water/binder ratio of 0.35 were prepared with three different sodium concentrations. Samples were cured at 105 °C for 24, 48, 72 hours. Depending on the compressive strength results presented in Table 4.22, the castings were repeated with sodium hydroxide solutions which had concentrations of 8%, 10%, 12% since compressive strength results decreased when sodium concentration was selected as 15%. As shown in Table 4.23, it was observed that the early-age strength development at curing temperature of 115 °C was high although 3-day strength obtained at 105 °C was higher than the strength of the samples cured at 115 °C.

Table 4.22 The compressive strength of geopolymer pastes containing mixture of hollow brick, roof tile and waste concrete activated by NaOH and cured at 105 °C

Sample Name	Activator Type	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)	
75HB10RT15CW10-105-24	Sodium hydroxide (NaOH)	10	0.35	105	24	20.7	
75HB10RT15CW10-105-48					48	40.2	
75HB10RT15CW10-105-72					72	41.4	
75HB10RT15CW12-105-24		12			15	24	20.7
75HB10RT15CW12-105-48						48	53.7
75HB10RT15CW12-105-72						72	59.8
75HB10RT15CW15-105-24		15			15	24	8.9
75HB10RT15CW15-105-48						48	22.4
75HB10RT15CW15-105-72						72	28.1

(Na%: Sodium Concentration, W/B: Water/Binder)

Table 4.23 The compressive strength of geopolymer pastes containing mixture of hollow brick, roof tile and waste concrete activated by NaOH and cured at 115 °C

Sample Name	Activator Type	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)	
75HB10RT15CW8-115-24	Sodium hydroxide (NaOH)	8	0.35	115	24	39.6	
75HB10RT15CW8-115-48					48	42.6	
75HB10RT15CW8-115-72					72	35.9	
75HB10RT15CW10-115-24		10			12	24	38.5
75HB10RT15CW10-115-48						48	43.6
75HB10RT15CW10-115-72						72	40.2
75HB10RT15CW12-115-24		12			12	24	38.2
75HB10RT15CW12-115-48						48	46.2
75HB10RT15CW12-115-72						72	48.7

(Na%: Sodium Concentration, W/B: Water/Binder)

As a result of the positive outcomes obtained by mixing of CDW-based materials as aluminosilicate source, the amount of waste concrete powder was increased in the mixtures of binding material considering that the amount of concrete waste in a certain building demolished by selective demolition method is around 80-90%. In the formerly performed tests, activator solutions prepared with sodium concentration of 12% and castings that were made at different binder percentages with a water/binder ratio of 0.35 gave the best results. Therefore, a series of CDW-based binders at different percentages were blended, reproduced and subjected to 24, 48, 72 hours of heat curing at 105 °C for further compressive strength testing. Obtained compressive strength results were shown in Table 4.24.

Table 4.24 The compressive strength of geopolymer pastes containing mixture of hollow brick, roof tile and waste concrete activated by selected certain mixture parameters

Sample Name	Activator Type	Na%	W/B	Curing Temp. (°C)	Curing Time (hour)	Compressive Strength (MPa)
65HB10RT20CW5GW12-105-24	Sodium hydroxide (NaOH)	12	0.35	105	24	18.0
65HB10RT20CW5GW12-105-48					48	42.0
65HB10RT20CW5GW12-105-72					72	55.2
60HB10RT25CW5GW12-105-24					24	18.5
60HB10RT25CW5GW12-105-48					48	43.3
60HB10RT25CW5GW12-105-72					72	57.0

(Na%: Sodium Concentration, W/B: Water/Binder)

5. RESULTS AND DISCUSSION

As a result of the data obtained from experimental studies, significant compressive strength results were obtained from samples using sodium hydroxide and different types of sodium silicates as alkaline activators. However, compressive strength results which were obtained from the samples utilizing sodium hydroxide as the only alkali activator could not be reached when different types of alkali activators were used in combination. Also, the samples which were activated with glass water alone did not achieve the same performance of samples which were activated only with sodium hydroxide as the alkali activator. The reason for the observed situation was that the amount of sodium required for the tetrahedral structure formed by alkali and aluminum atoms of geopolymers such as potassium and sodium could not be achieved. In addition, the high pH value of sodium hydroxide is believed to be the main reason for the high activation performance obtained.

For the tests which used potassium hydroxide as the only alkaline activator, the desired compressive strength values could not be reached and therefore, further studies were continued by focusing mainly on the utilization of sodium hydroxide as the alkaline activator in the mixtures.

As a result of the use of sodium hydroxide as the only alkaline activator, for all different types of CDW-based materials, best results (i.e. highest compressive strength results) were acquired. Moreover, this was valid for geopolymer mixtures incorporating mixtures of different types of CDW-based aluminosilicate sources. Among other mixture parameters tried throughout the experimental studies, highest compressive strength results were recorded for samples activated by sodium hydroxide solution having sodium concentration of 12%, water/binder ratio of 0.35 and heat cured at 105 °C. Moreover, increased curing periods further enhanced the results.

Consequently, it can be clearly stated that different types of CDW-based materials can safely be used as aluminosilicate sources in the production of geopolymers individually or in combination with specific ratios. Although it was possible to obtain the desired strength grades by means of alkaline activation of samples with brick-based construction demolition waste, it is also necessary to focus on and improve the utilization of waste glass and waste concrete in geopolymer production. The results of these achievements during the thesis study are discussed in more detail in the following sections.

5.1. Mineralogical & microstructural characterization

Based on the results obtained from extensively performed XRD, XRF and TGA analyzes on selected geopolymer samples to interpret the effects of factors such as curing temperature, curing time, sodium concentration and binding material type on the microstructural changes of samples were investigated. In order to compare geopolymerization capabilities of different CDW-based materials, geopolymers from hollow bricks, red clay bricks, roof tiles and glass waste were prepared with alkali solutions having sodium concentration of 12% and samples were subjected to heat curing at 115 °C for 24 and 72 hours for determining the effects of curing time for the same samples. In order to assess the effects of sodium concentration, samples were chosen in which the hollow brick was used as the binder and had sodium concentrations of 10%, 12%, 15% and cured at 115 °C for 24 and 72 hours. Specimens selected to determine the effects of curing temperature on geopolymerization reactions were geopolymer paste samples based on hollow bricks which were prepared with sodium concentration of 12% and cured at 75 °C, 105 °C, 115 °C, 125 °C, respectively. Moreover, the effects of curing temperature and curing time on red clay brick-based geopolymer samples which were activated with alkaline activator solution having sodium concentration of 12% and cured at 105 °C and 115 °C for 24 hours and 72 hours were investigated. Furthermore, in order to observe the formation of geopolymeric structure at low curing temperatures, another paste sample which utilized red clay brick as the binder and was cured for 24 and 72 hours at a curing temperature of 85 °C was chosen.

5.1.1. XRD Analysis

Diffraction patterns of 24 hour-cured hollow brick-based geopolymers having sodium concentration of 12% can be seen in Figure 5.1. The figure indicates that main geopolymerization product was albite. As Provis and van Deventer (2009) mentioned, albite (NAS₆) is an aluminosilicate product of sodium activated feldspar containing clay. It seems that the amount of quartz minerals reduced after geopolymerization. Increased curing temperature initiated the formation of cancrinite which is a secondary phase of NaOH-activated fly ash according to Provis and Bernal (2014) and anorthite which is a mineral of plagioclase. Albite is another type of plagioclase, however amount of albite was more than anorthite. This was probably due to low calcium content of brick wastes.

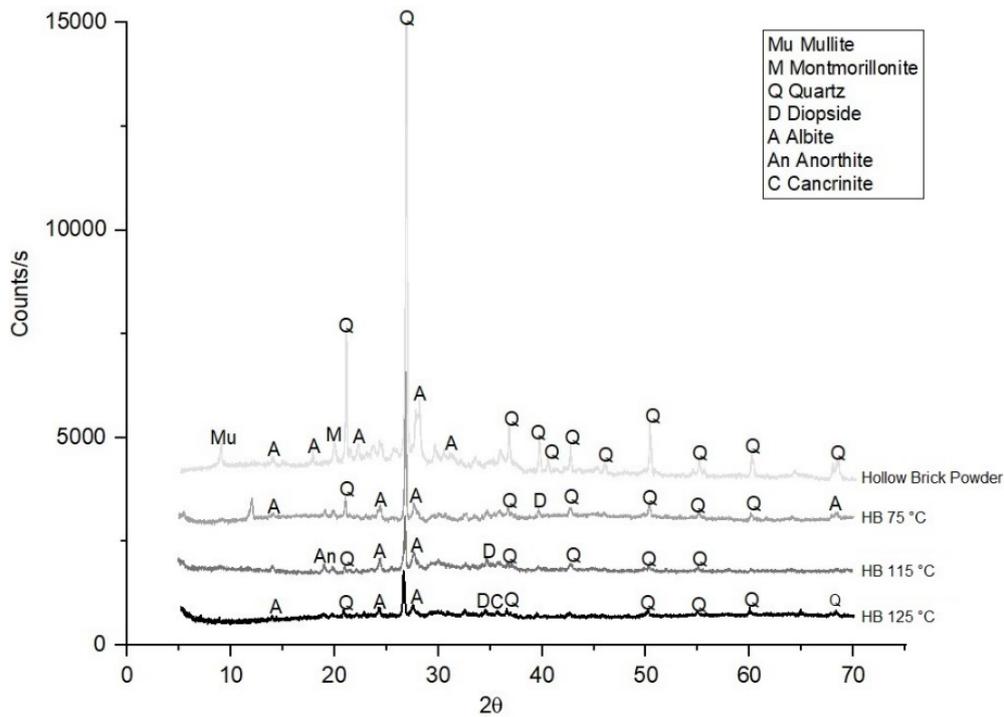


Figure 5.1 XRD comparison of hollow brick powder and alkali activated hollow brick binders for different curing temperatures

Evaluation of hollow brick-based geopolymers at the same curing temperature (115 °C) for 24 hours which were activated with alkaline activator solutions having different sodium concentrations indicated that an increase of sodium concentration supported the polymerization reactions. As shown in Figure 5.2, at increased sodium concentrations decreased amounts of quartz minerals are the evidence of polymerization that took place.

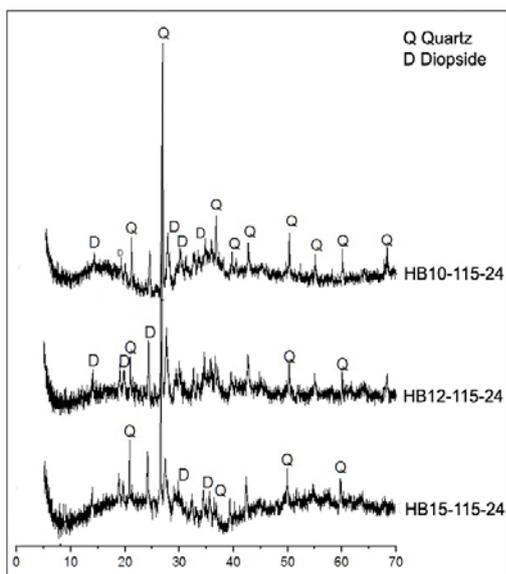


Figure 5.2 XRD comparison of hollow brick for different sodium concentrations (cured at 115 °C)

In Figure 5.3, XRD patterns for hollow brick-based geopolymers which were activated with alkali activator having sodium concentration of 10% and cured for 24 and 72 hours at 85 °C were shown. Although the albite phase decreased at 72 hours of curing compared to 24 hours, the compressive strength increased from 7.8 MPa to 30.8 MPa. This is the evidence of the formation of other geopolymer products. Comparison based on quartz minerals indicated the same trends, however, decreasing of quartz amount was not as high as samples cured at 115 °C. This situation was another evidence for the enhanced polymerization reactions due to the effect of curing time.

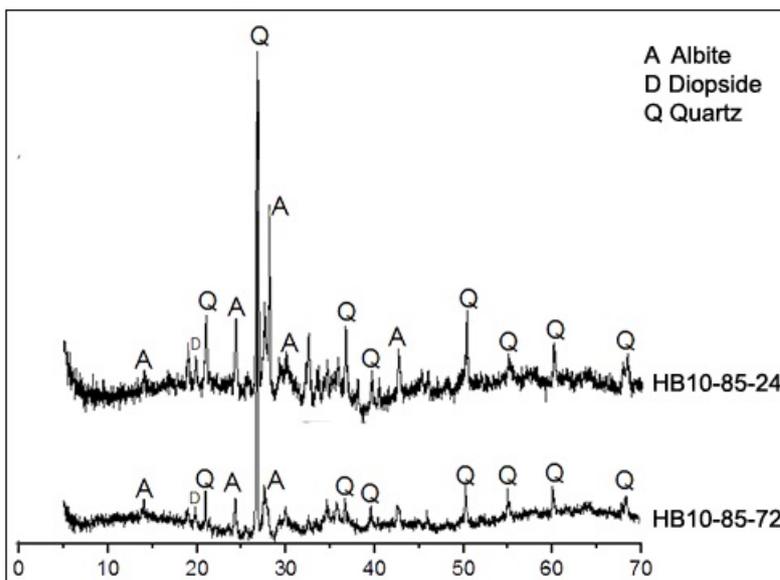


Figure 5.3 XRD comparison of hollow brick for different sodium concentrations (cured at 85 °C)

Compressive strength results of different types of geopolymers based on different CDW-based binders were shown in Figure 5.4 and XRD results were given in Figure 5.5 for different CDW-based geopolymer products that were cured at 115 °C for 24 hours. Glass waste-based geopolymer samples had lower compressive strength results compared to other CDW-based geopolymers and as shown in Figure 5.5, XRD analysis of glass waste-based geopolymers showed an amorphous structure and this did not change with the increased curing time. Depending on the increments in curing time, the quartz phases of all brick-based materials reduced and this was associated with the development of polymerization reactions. For roof tile-based sample, diopside phase formed after 72 hours of curing, but for hollow brick-based sample, existing diopside phase decreased and albite phase formed in the matrix. For both samples, losses in compressive strength were observed. In red clay brick-based samples, anorthite phase increased in amount, albite and quartz phases remain

approximately the same and compressive strength result did not show any significant change. Additionally, the SEM micrographs has represented in Figure 5.6.

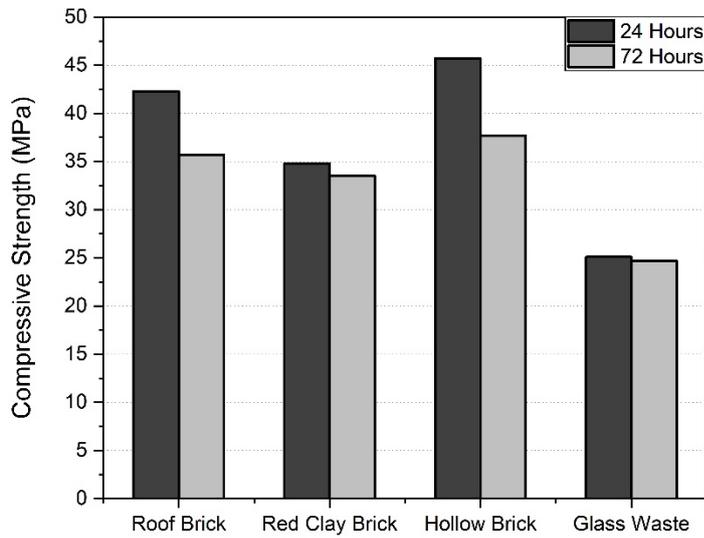


Figure 5.4 Compressive strength results of samples made by various construction demolition wastes

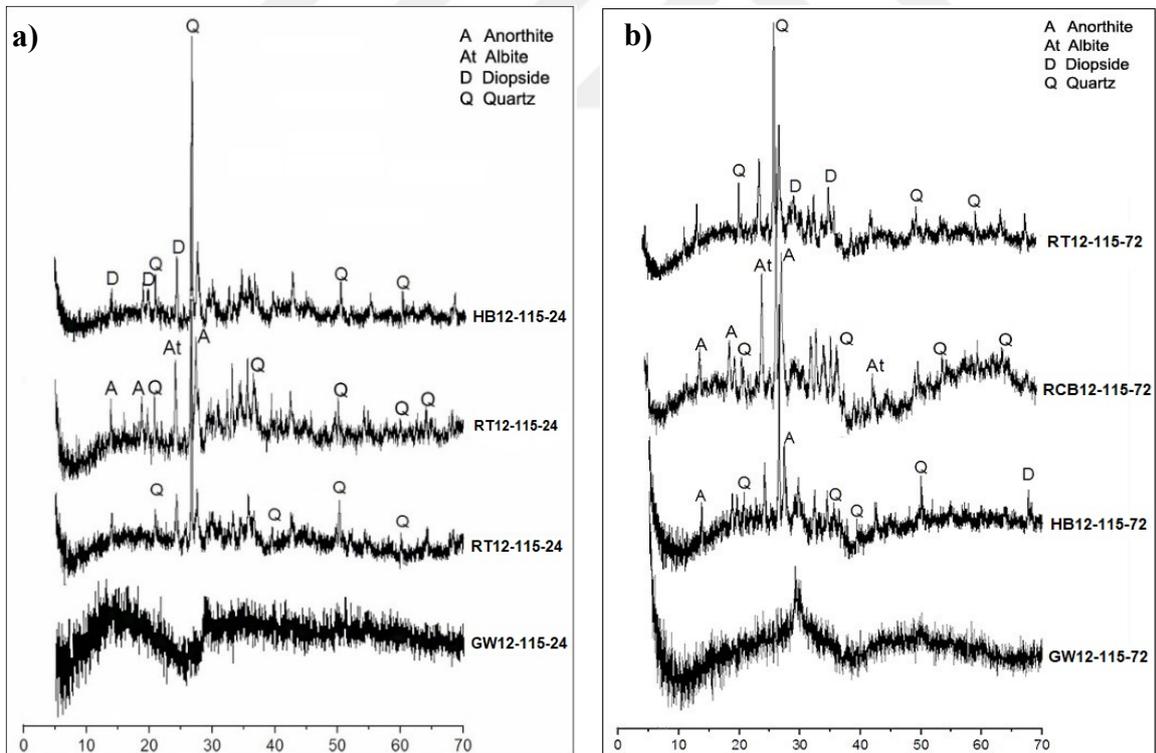
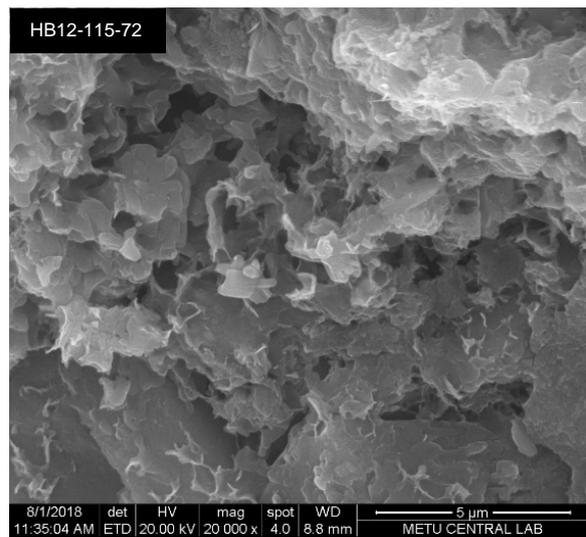
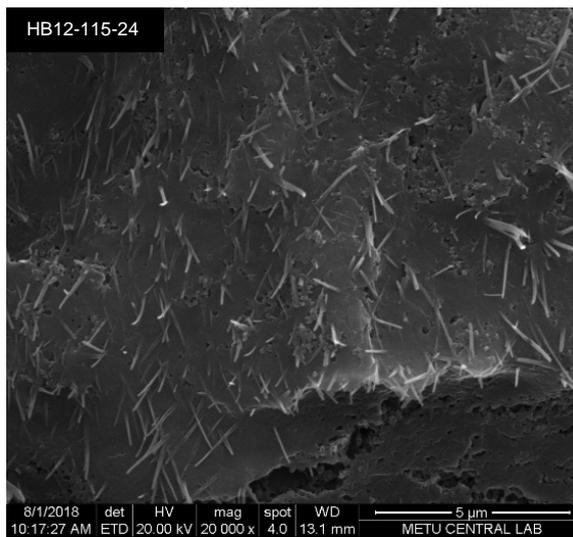
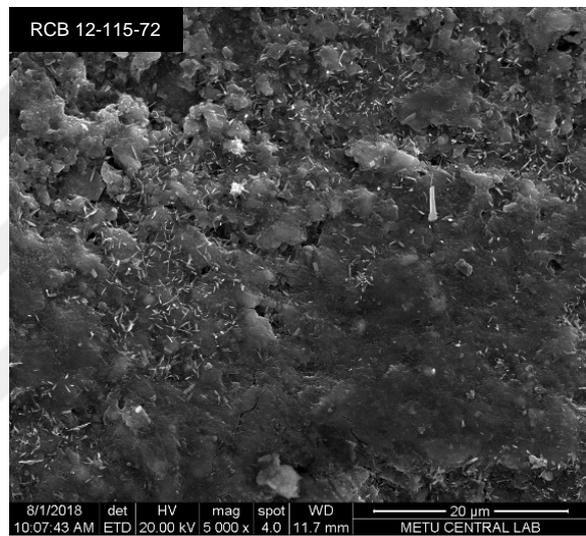
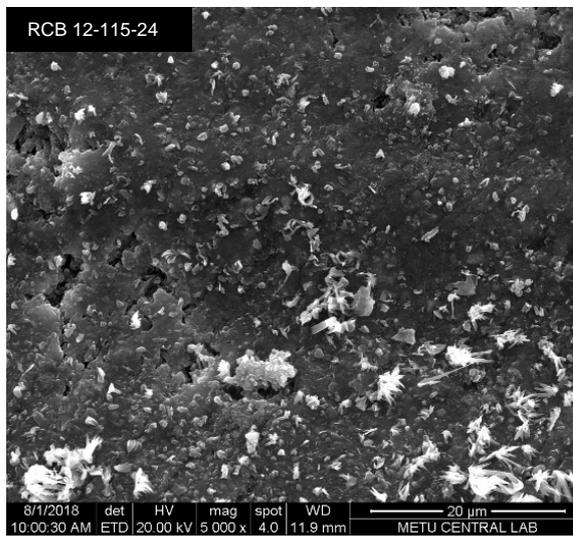
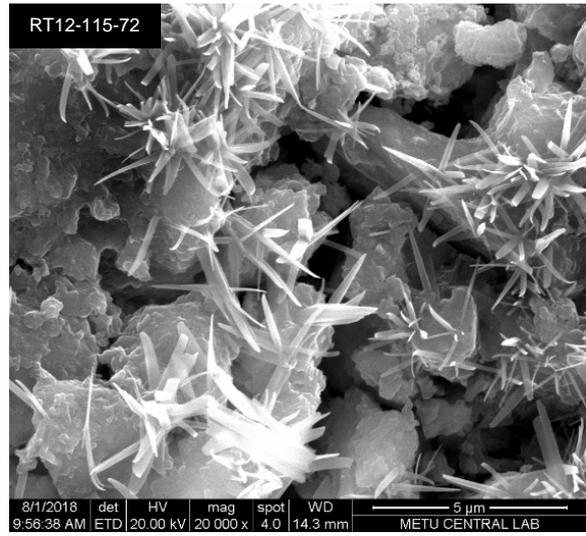
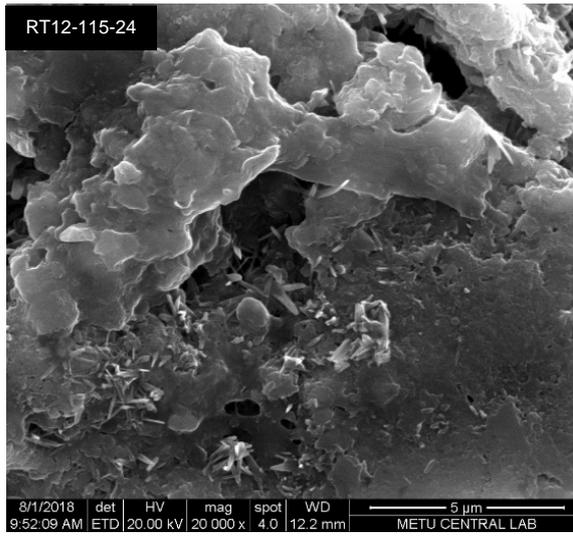
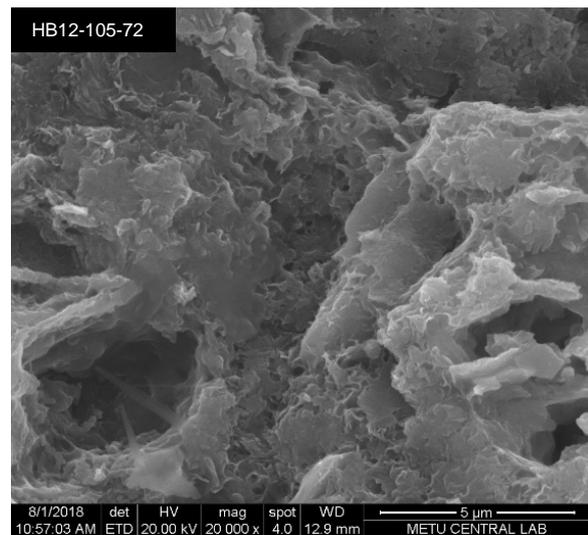
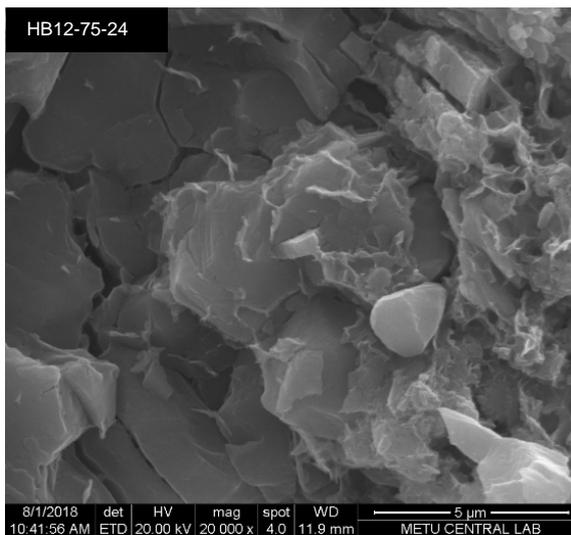
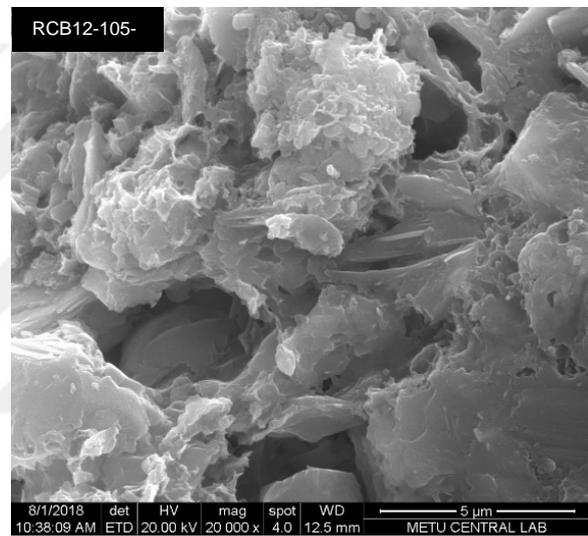
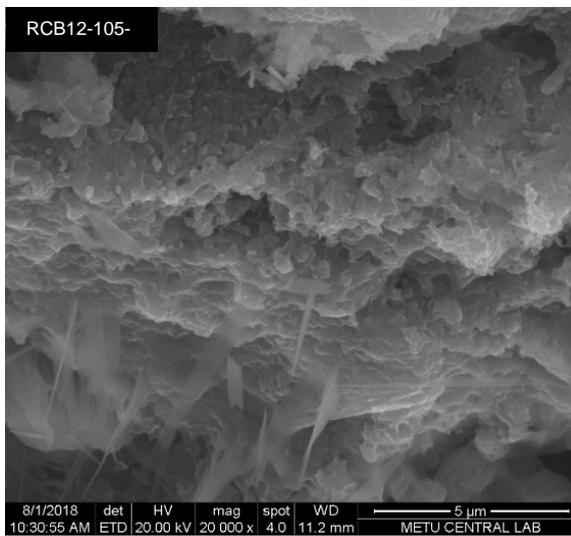
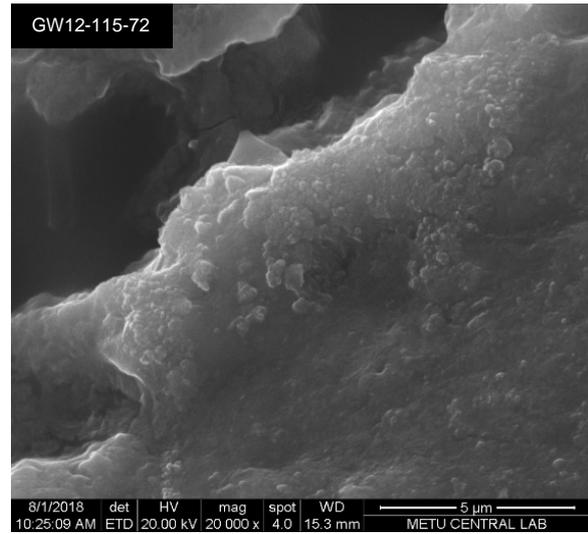
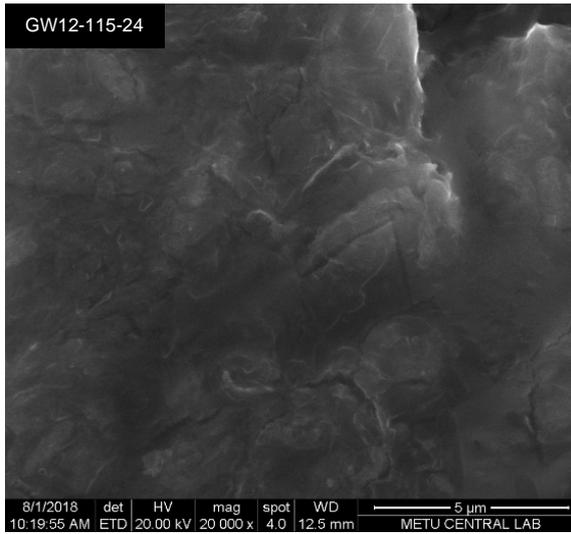
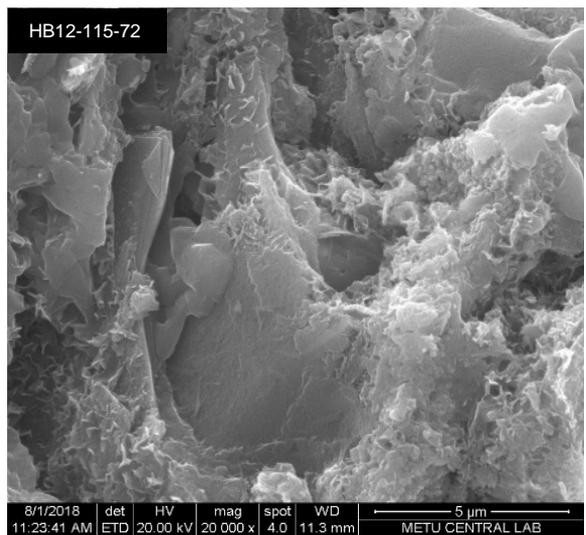
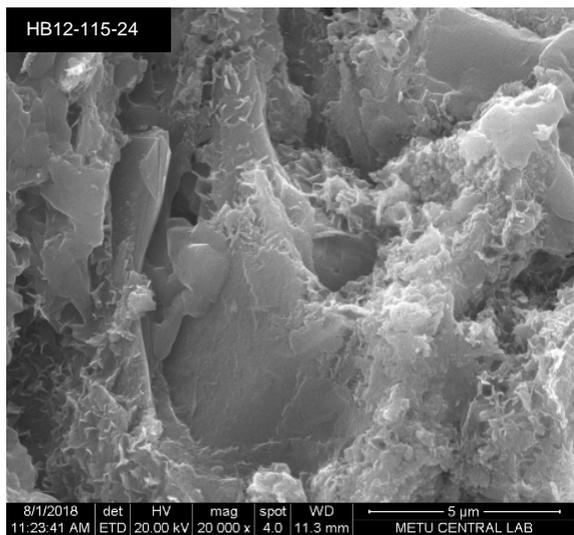
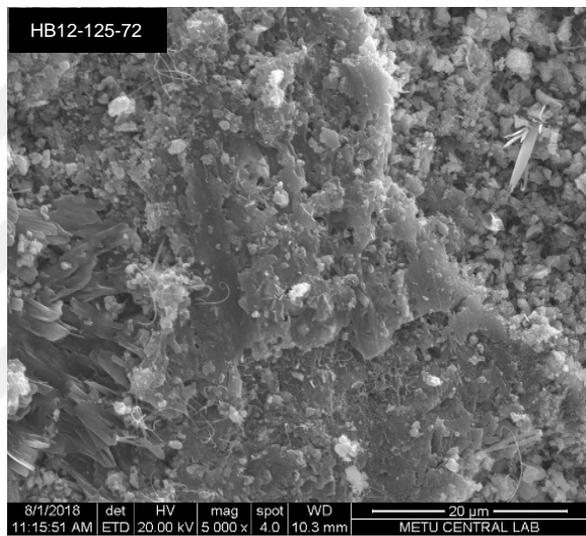
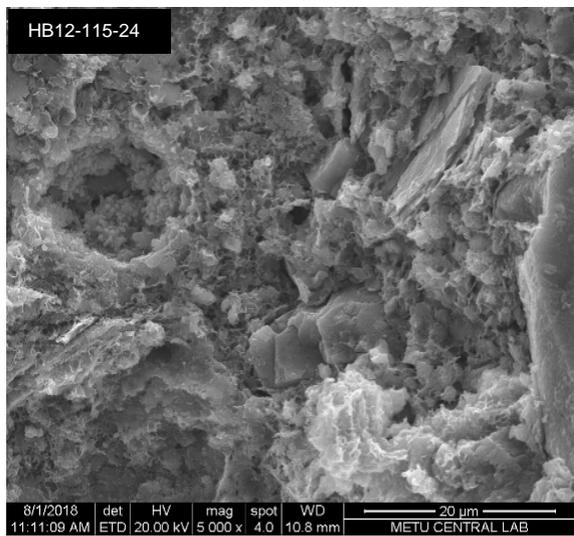
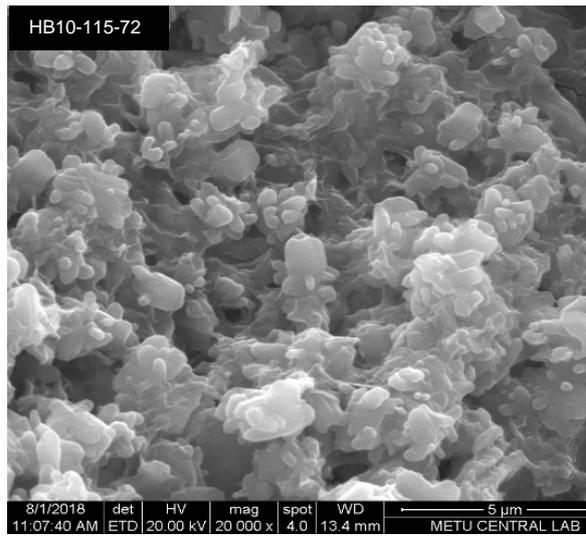
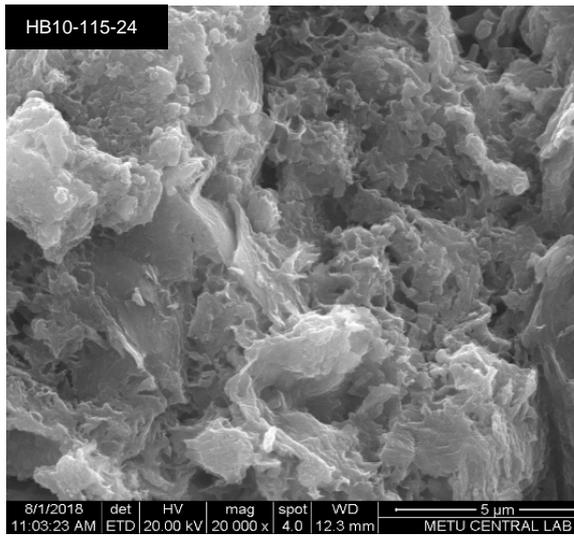


Figure 5.5 XRD comparison of various construction demolition waste a) Curing for 24 hours, b) Curing for 72 hours







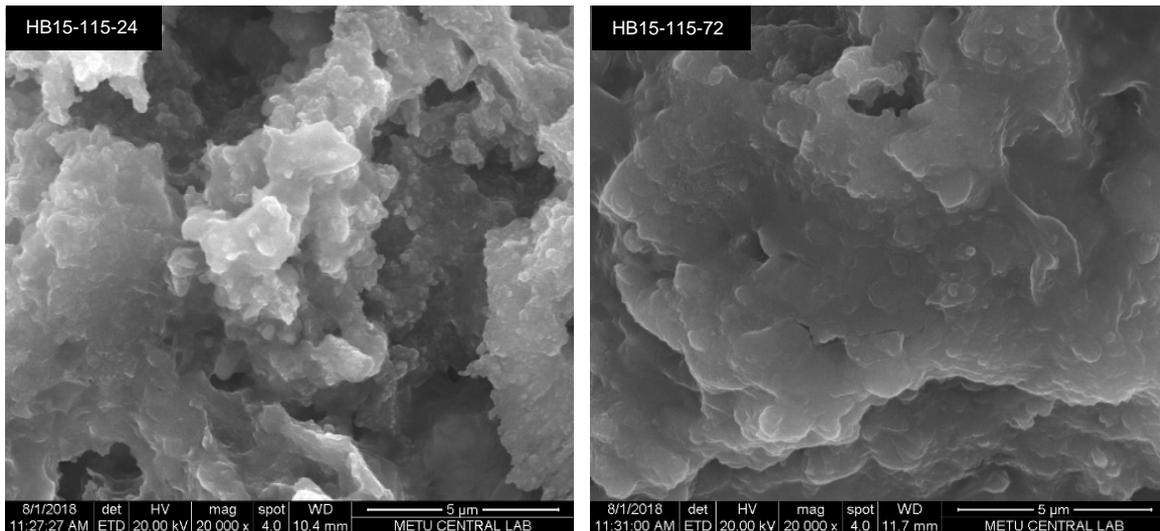
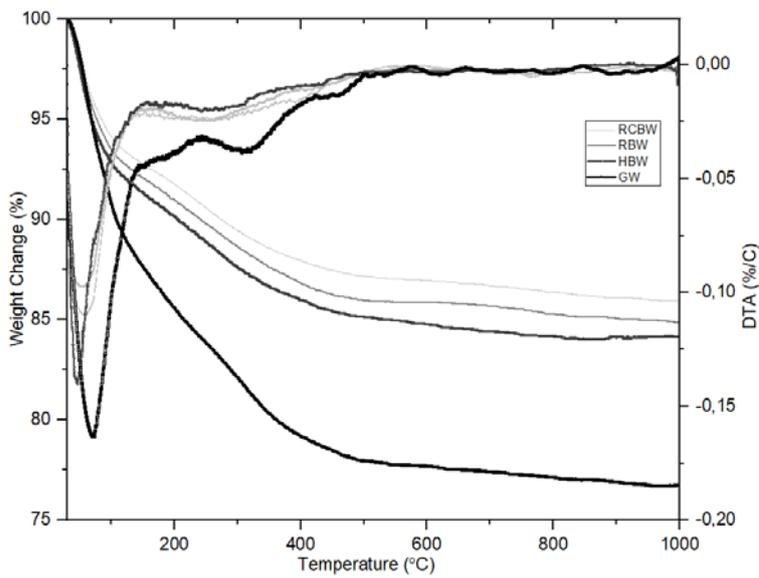


Figure 5.6 SEM micrographs of various CDW-based geopolymer pastes

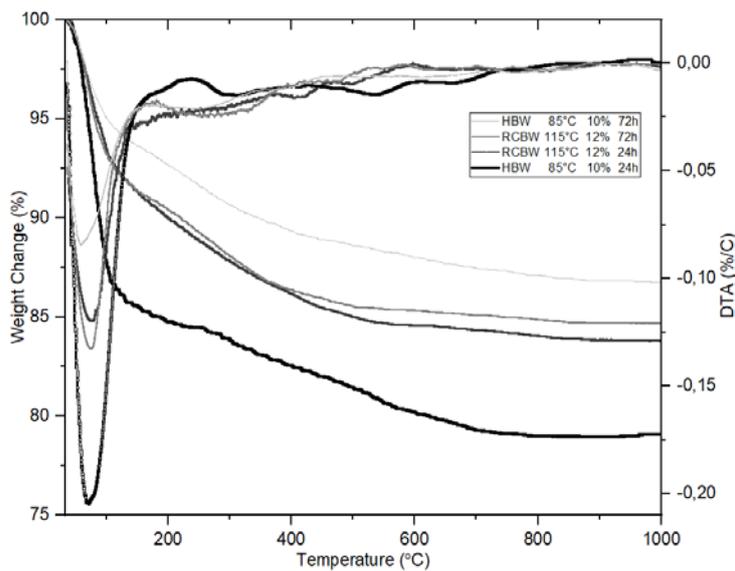
5.1.2. TGA & DTA Analysis

TGA/DTA plots can be seen in Figure 5.7. According to Kucharczyk et al. (2018), mass changes are mainly due to dehydration and dehydroxilation below 550 °C, and decarbonation above 550 °C. Free water is removed firstly then bound water in C-S-H or C-A-S-H is lost up to 550 °C. It can be seen from Figure 5.7a that glass waste has the highest amount of lost free water among others. Considering the same grinding effort for all wastes, it is expected that glass waste remained coarser than others and had highest free water content for the same w/b ratio. Weight loss above 300 °C is mainly due to loss of chemically bound water. Loss of chemically bound water were 3.5%, 3.7%, 3.6% and 5.5% for hollow brick, roof tile, red clay brick and glass waste, respectively. However the amount of chemically bound water of glass waste was higher than others, also its chemically bound water was the highest. Water first acts as a medium for dissolution, participates in geopolymerization reactions (Hajimohammadi et al., 2018) and after the geopolymerization, it is released back to the system (Provis and van Deventer, 2009). Main reaction product of geopolymerization is N-A-S-(H) which contains not structurally bound water and reaction product of alkali activated high-calcium systems is C-A-S-H which has a structure similar to C-S-H. Therefore, the presence of chemically bound water indicates the formation of C-S-H similar structures. Additionally, as it can be seen from Figure 3.8 and Figure 5.7a, fineness of wastes and amount of released free water are inversely proportional. Another point is that increased Si/Al ratio raises the water loss according to Figure 5.7a in step with Duxson et al. (2007c) results and it is attributed that low Si/Al geopolymers have water that is more tightly bound within gel (Duxson et al., 2007c).

In Figure 5.7b, hollow brick-based samples cured for 72 hours had less free water content than hollow brick-based samples cured for 24 hours. It is attributed that hollow brick-based samples cured for 24 hours have not completed geopolymerization yet as it can be seen from compressive strength results of hollow brick-based samples cured at 85 °C for 24 and 72 hours were 7.8 and 30.8 MPa, respectively. However, red clay brick-based samples which were cured for 24 and 72 hours at 115 °C had approximately the same TGA graphs. Reason for this similarity is due to almost-complete geopolymerization reaction of red clay brick after 24 hours. This situation can be seen from compressive strength results of red clay brick specimens cured for 24 hours and 72 hours which were 34.8 MPa and 33.5 MPa, respectively.



a) Cured for 72 h, at 115°C with molarity of 12%



b) Cured for different conditions

Figure 5.7 TGA/DTA plots of alkali-activated wastes

TGA/DTA plots of glass waste-based samples cured for 24 hours at 115°C with different molarities can be seen in Figure 5.8. According to Tashima et al. (2012), NaOH-activated systems have a Na concentration gradient between partially reacted precursor particle surfaces and matrix, different from KOH-activated systems. Weight losses of glass waste-based pastes in Figure 5.8 have a trend to result in higher weight loss as Na concentration increases which is in agreement with Tashima et al. (2012).

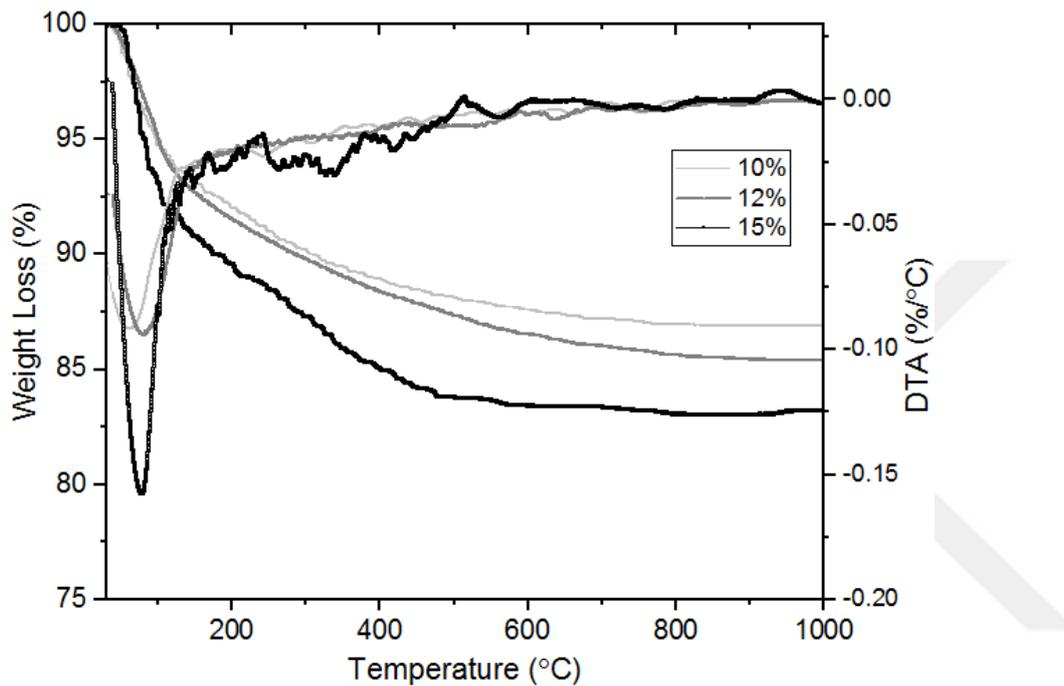


Figure 5.8 TGA/ DTA plots of specimens which are NaOH-activated with different sodium concentration

TGA/DTA plots of the other geopolymer specimens, which not represented in this section, are given in the appendix.

5.2. Influence of NaOH Content on Compressive Strength

One of the best ways to investigate the effect of alkaline activator solutions on the geopolymerization reactions of paste samples is to perform compressive strength tests. Therefore, compressive strength results of geopolymer samples produced with different sodium concentrations using hollow brick as the binder and was cured at a temperature of 115 °C were given in Figure 5.9. The increase in the sodium content increases the dissolution rate of the silica and alumina components required for geopolymerization and accelerates the reactions that produce the polymer (Singh et al., 2016). In other words, increasing the alkaline concentration increases the dissolution rate of silica and alumina and increases the

formation of N-A-S-H gel which gives strength property to geopolymer (Ahmari et al., 2012). However, an increase in the concentration of sodium in the alkaline solution gives a limit to the formation of polymers due to low mobility of the alkali ions and diffusion of them from the solution (Alonso and Plomo, 2001). If the increase in the sodium concentration of the activator in the bricks group is not exceeded the threshold, the positive effects on the strength can be clearly seen. In case of exceeding 12% sodium content, which is determined as a threshold according to the data obtained from the tests performed, the viscosity of the geopolymer paste increases, the mixing and casting processes become more difficult preventing the appropriate compaction of the geopolymer pastes. Na^+ ions are recharged as charge balancers in molecular structure formation (Ken, 2015). Hydroxide ions in excess of the limit with the increase in Na_2O content cause rapid precipitation of aluminosilicate gels (Tashima, 2013). Moreover, the increase in sodium concentration above the limit values makes the reaction process faster and impairs the homogeneity of the reaction products in the matrix (Provis, 2009). Due to the fact that the brick group materials are similar in terms of chemical content and the same processes were applied while obtaining the waste brick powders, these binders have shown the same characteristics, the different results of compressive strength tests could be related with particle size of binders, the crystallographic structure and the variation of surface loads. For the samples in which the glass waste was used as a silicate source, the compressive strength exhibited a behavior proportional to the sodium concentration. Although the high amorphous SiO_2 content of the bricks group (Table 3.1) supports the geopolymerization process, the low alumina (Al_2O_3) content limits the final strength achieved.

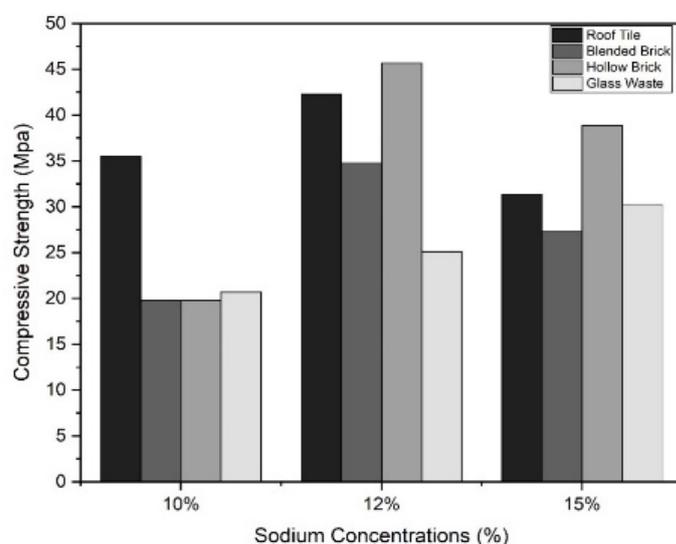
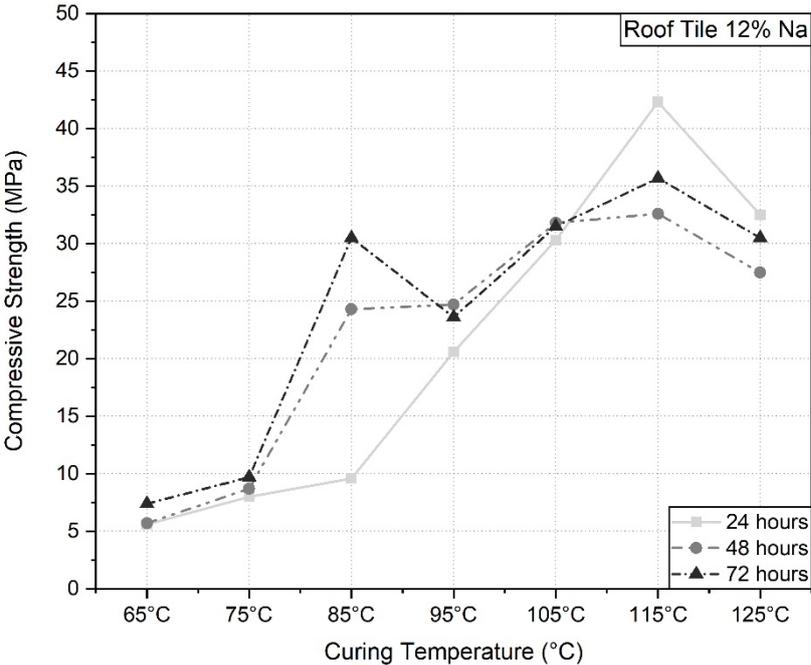
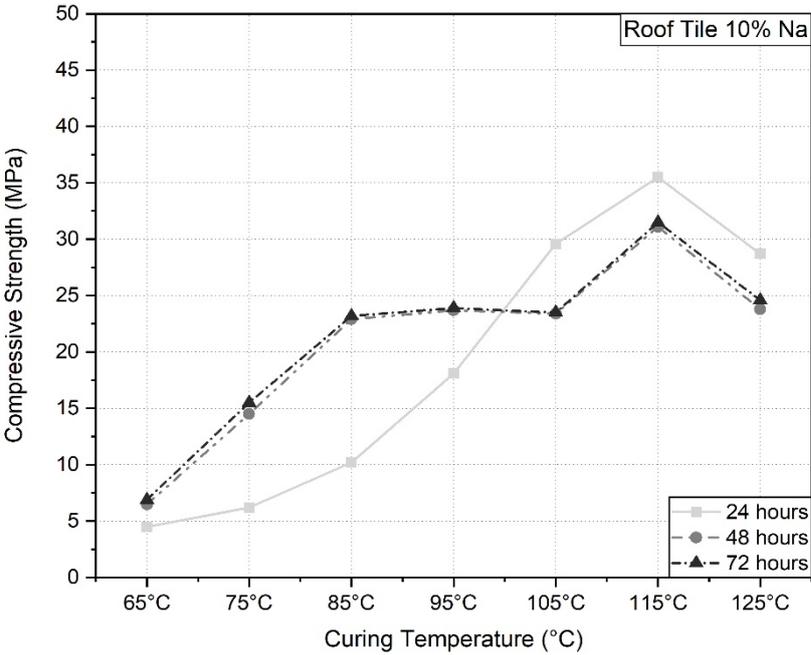


Figure 5.9 Effect of sodium concentration on compressive strength of construction demolition wastes

The compressive strength results of roof tile based samples are given in Figure 5.10. As a result of the 24-hour curing, it is clear that sample compressive strength results are proportional to the increase in sodium concentration, but strength losses occurred when the threshold for sodium concentration is exceeded. Although the samples tend to exhibit a strength change proportional to the increase in curing temperature, when the limit temperature and sodium concentration are exceeded, rapidly occurring reactions disrupt the strength increase. At 48 and 72 hours, the situation was unchanged and the samples reached the limit strengths at different optimum temperatures and loss of strength was observed at the points where the temperature had a negative effect on the matrix.



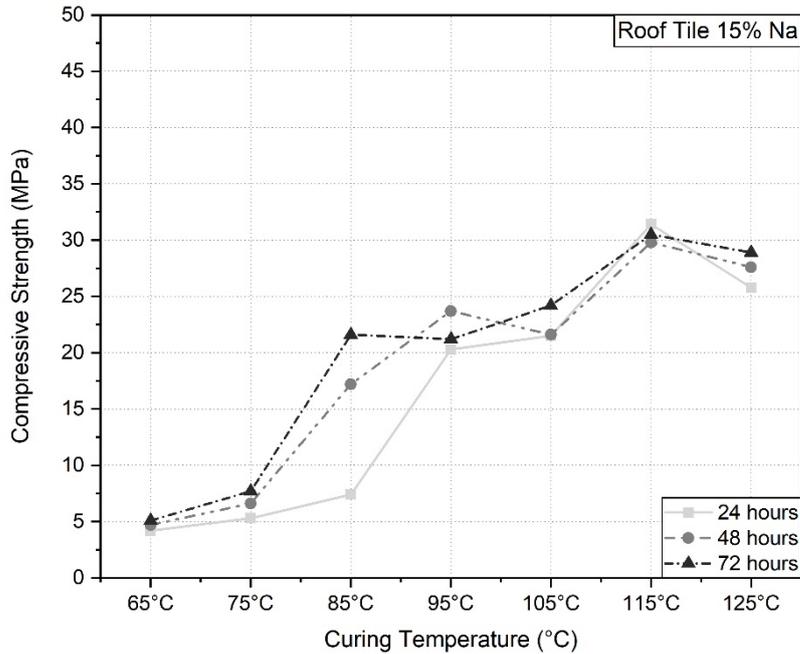
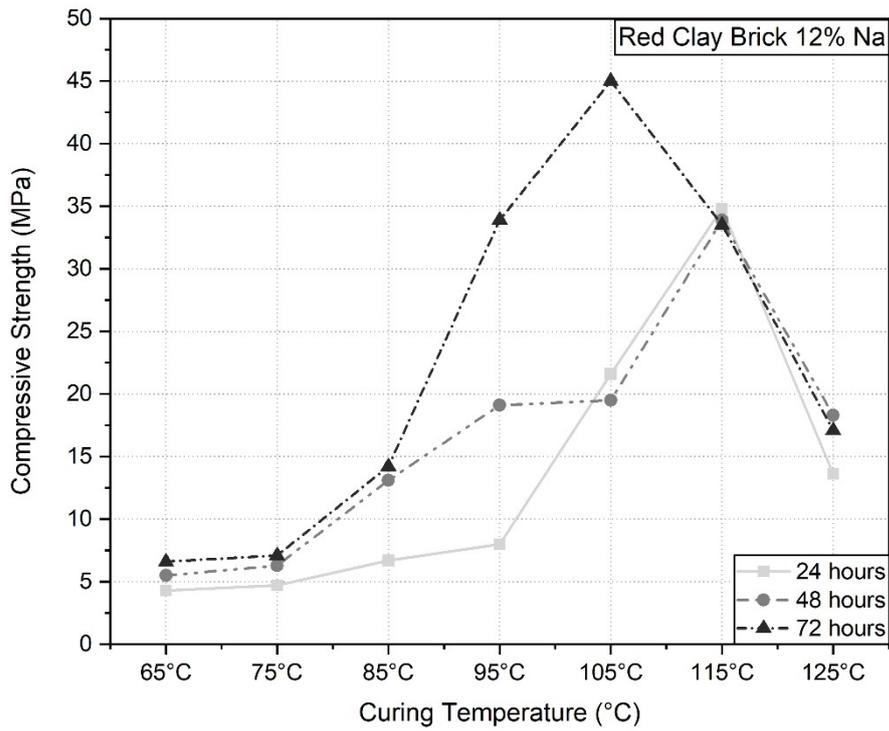
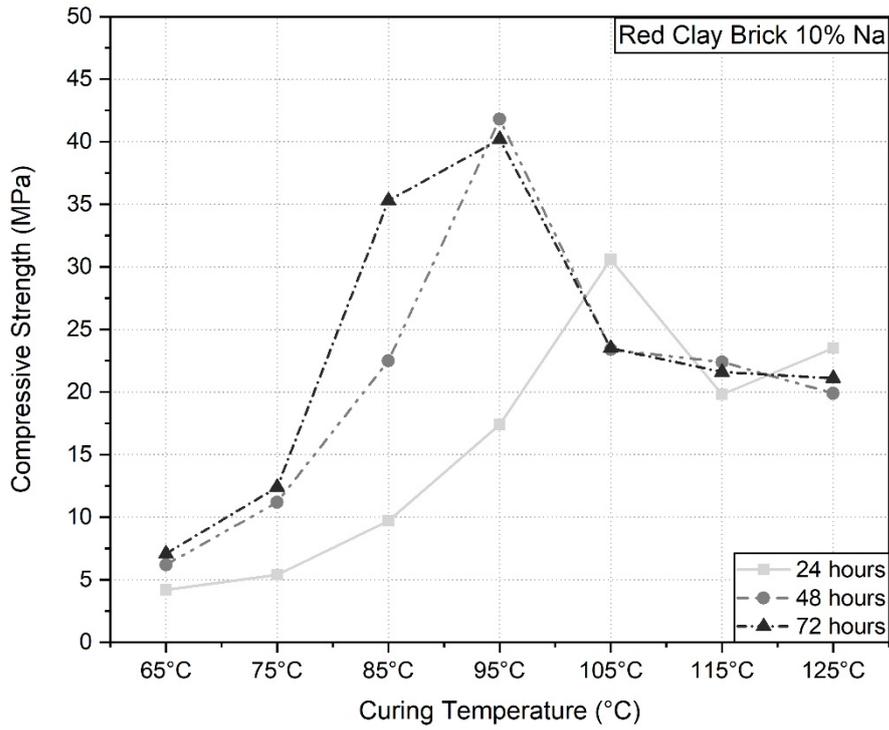


Figure 5.10 Effect of sodium concentration on roof tile waste

When the sodium concentration in the blend brick-based samples increased from 10% to 12%, an increase in compressive strength was observed, but when the sodium concentration exceeded 12%, loss in strength was observed (Figure 5.11). In addition, for these samples the curing time has a positive effect on compressive strength, for sodium concentration of 10%, compressive strength increased after 48 hours, at the end of 72 hours the compressive strength which was already obtained with a curing time of 48 hours was maintained. This can be explained by the stabilization of the polymerization reactions taking place. When the sodium concentration was 12%, the decrease in the mobility of the alkali ions due to increased viscosity concentration slowed down the speed of the process and the rate of ions diffusing to polymer formation (Alonso, 2001). This indicated the need for higher curing temperature or longer curing times to achieve high compressive strengths in samples with a sodium concentration of 12%. In the samples with a sodium concentration of 15%, at the end of the 24 and 72 hours curing period, lower strength values were obtained compared to the 12% concentration but at the end of 48 hours, high strength values were obtained.



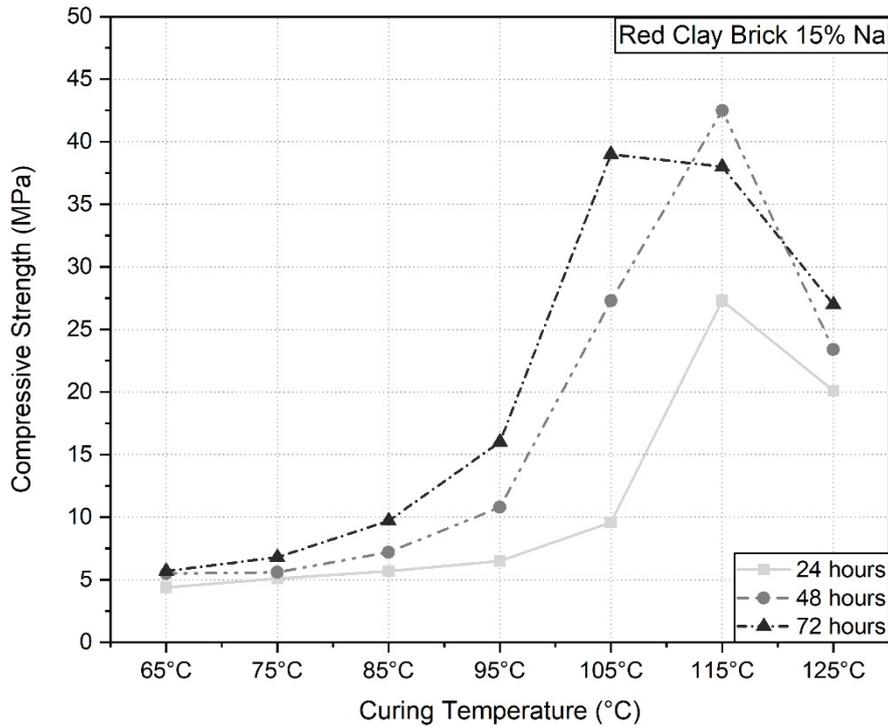
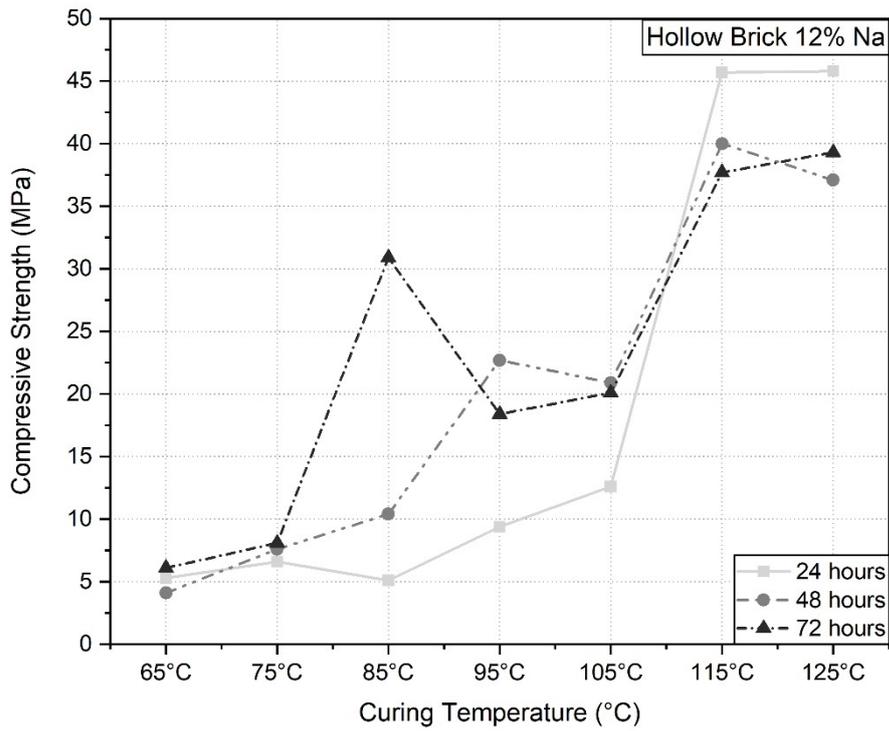
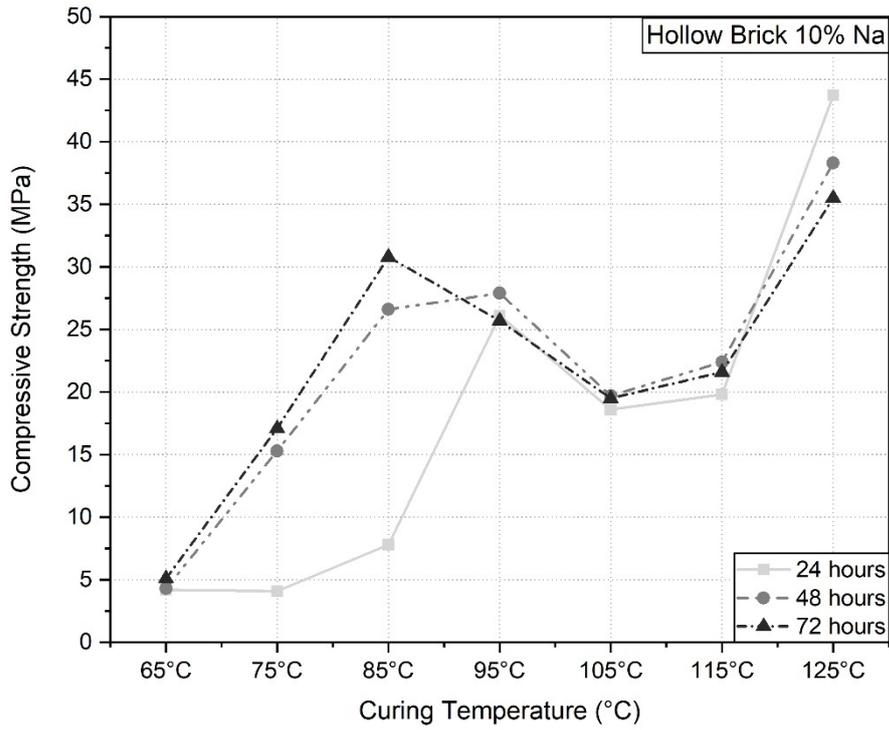


Figure 5.11 Effect of sodium concentration on red clay brick waste

The curing temperature had a significant effect on the hollow brick samples which were cured for 24 hours and had a sodium concentration of 10% (Figure 5.12). The same results were obtained for samples with sodium concentrations of 12% and 15%, and the sodium concentration of 12% remained as a threshold for compressive strength. In cases where the curing time was increased, the strength variation was similar, except for samples with a concentration of sodium concentration of 15% which were cured for 48 hours. In these samples, high compressive strengths were obtained at a temperature of 95 °C for a concentration of 15%, when 115 °C was exceeded, the loss of strength was observed for the samples. These strength values obtained as a result of longer curing time at lower temperatures in comparison with samples which had sodium concentration of 12% can be associated with variables such as the particle structure of the material, the water absorption capacity that needed for the continuity of polymerization reaction.



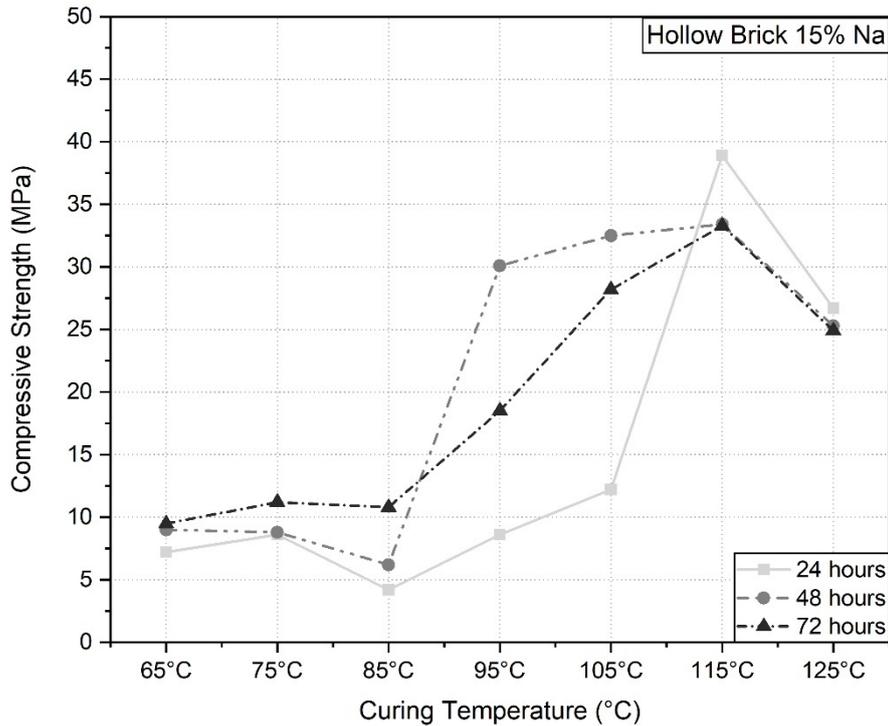
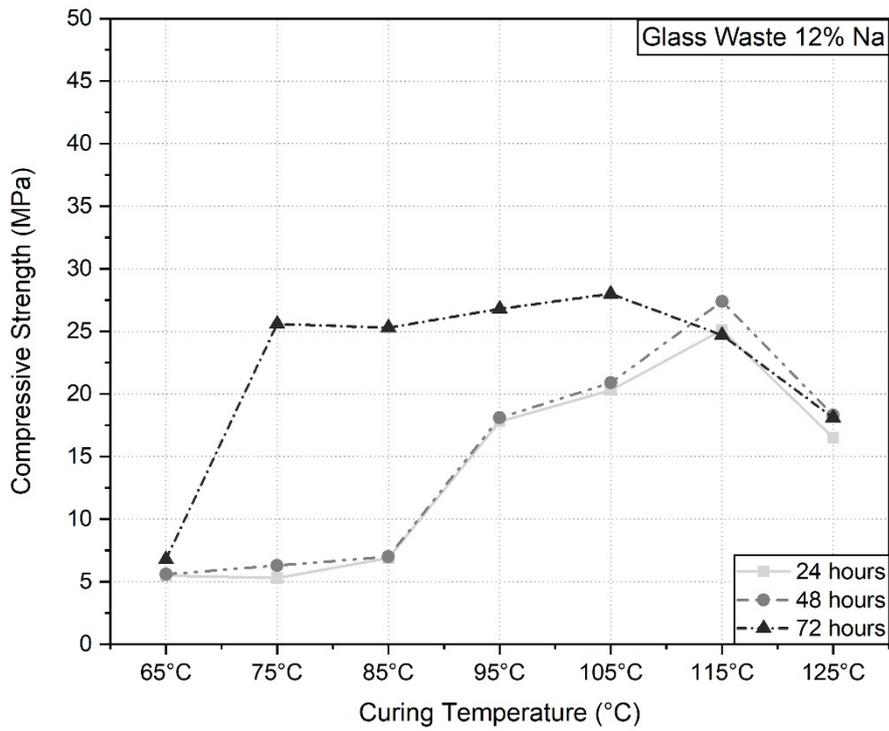
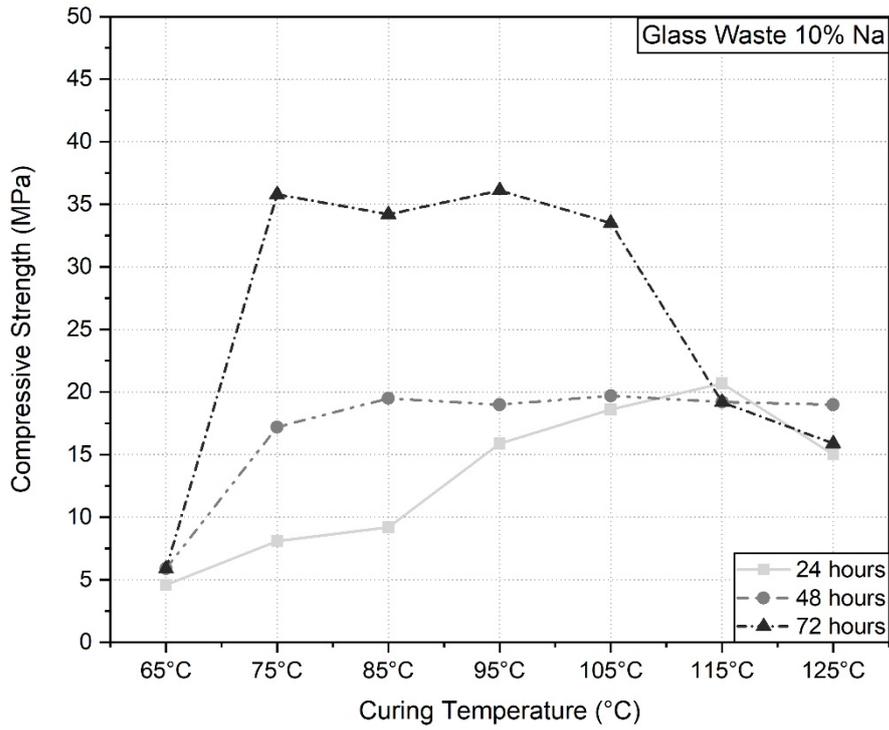


Figure 5.12 Effect of sodium concentration on hollow brick waste

As seen in Figure 5.13 for the samples in which glass waste was used as binder material exhibited approximately the same behavior at all concentrations, although the samples with sodium concentration of 10% which were cured for 24 and 48 hours showed different results. Samples with concentration of 10% reached maximum strength values at 72 hours at lower temperatures, samples with concentration of 12% showed similar behaviors. Samples with concentration of 15% reached their maximum compressive strength values at shorter curing periods. For 24 and 48 hours of curing, the compressive strength values increased in proportion to the sodium concentration. This situation became different for the curing time of 72 hours and the compressive strength results decreased inversely with the sodium concentration. Achieving the highest compressive strength after 72 hours of curing at sodium concentration of 10% indicates that glass waste may perform better with long curing times and temperatures at low sodium concentrations. Although glass waste is a very suitable material for the production of geopolymer due to its amorphous structure and high SiO_2 content, low Al_2O_3 content constitutes an obstacle to the proper propagation of the polymerization process.



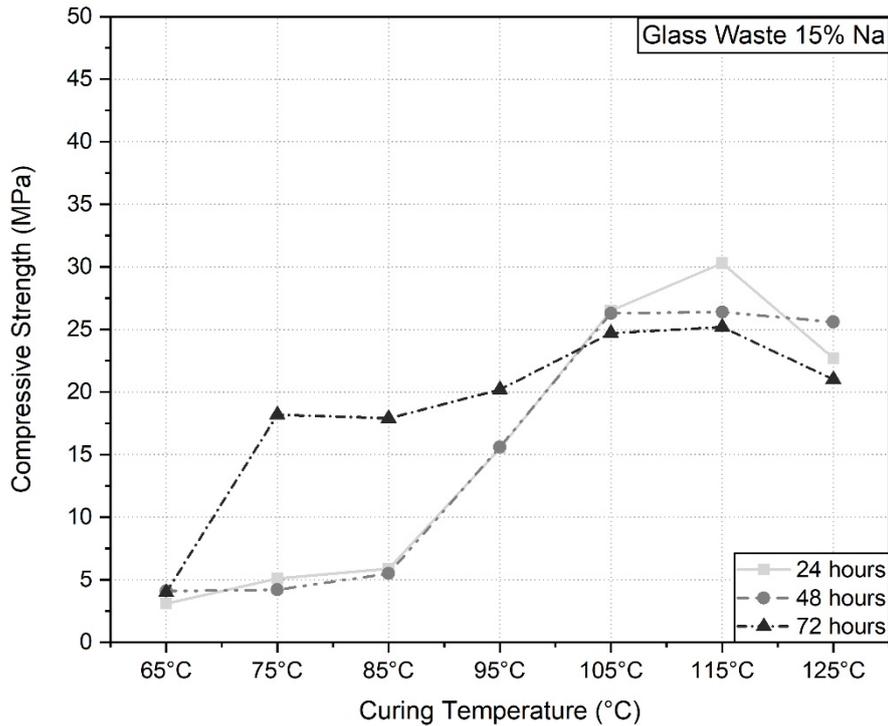


Figure 5.13 Effect of sodium concentration on glass waste

5.3. Influence of Curing Temperature and Curing Time on Compressive Strength

The compressive strength results of the samples with a sodium concentration of 10% were indicated in Figure 5.14 to evaluate the effects of the curing temperature. For roof tile-based samples, no signs of compressive strength development up to 65 °C have been observed. After 65 °C curing temperature, compressive strength started to develop and followed a trend proportional to increased levels of temperature as in current studies in the literature. Geopolymers gain strength with thermal curing and this situation is mainly due to the conversion of 2D polymer bonds in the polymerization process into 3D polymer bonds as a result of increasing temperature (Nagral, 2014). In addition, polymerization reactions which are very slow at low temperatures are accelerated by increasing temperature (Rowles and O'Connor, 2003). It can therefore be stated that the inability to obtain strength at low curing temperatures is due to the slow progress of polymerization reactions and the lack of strong bonding. Thus it is okay to mention that the temperature acts as a catalyst for geopolymerization reactions. This relationship between the temperature and compressive strength values of the roof tile-based samples was corrupted after 115 °C for 24-hour-cured samples and the strength losses were observed. The compressive strength values between 85-115 °C showed a slow increase for the samples cured for 48 hours and decreased after 115 °C. Although the increase in compressive strength up to 85 °C for samples which were

cured 72 hours have been replaced by a loss of strength up to 105 °C, samples reached maximum compressive strength value at 115 °C as in other curing times and decreased after 115 °C.

The first evidence of compressive strength was obtained at 65 °C, which could be considered as the lower limit of required curing temperature for all three different curing times. Strength gain continued to increase until an optimum curing temperature and began to decrease at a temperature that could be considered as the upper limit of curing temperature. The presence of a threshold for the curing temperature in geopolymer samples can be related to the evaporation of the required water to maintain the polymerization reactions and the disruption of reactions due to lack of sufficient water (Al Bakri, 2011).

Different variations related with the effect of curing time on roof tile-based samples were observed. Up to 75 °C, at ambient temperature and 50 °C any compressive strength evidence could not be observed for three different curing periods. The compressive strength values for 65 °C curing temperature showed an increase of 44% and 53% after 48 and 72 hours compared to 24 hours curing time, respectively. The compressive strength values for 75 °C curing temperature showed an increase of 142% and 158% after 48 and 72 hours compared to the 24 hours, respectively. For 85 °C curing temperature, the increase in compressive strength was 130% for 48 hours and 180% for 72 hours. The samples which were cured at 95 °C showed a low rate of increase of compressive strength. Moreover for 48 and 72 hours, significant changes for compressive strength results were not observed. For 105 °C and above curing temperatures, changes in strength results were inconsiderable. The homogeneous and proper propagation of the reactions in the matrix can be mentioned as the results of the slower propagation of polymerization reactions at the lower curing temperature (Rowles and O'Connor, 2003), dissolution of SiO₂ and Al₂O₃ components and the prevention of rapid evaporation of the pore water which prepared the required medium for the actualization of alkaline activation reactions. For high temperatures, due to the rapid progress of the geopolymerization process, it can be mentioned that the formation of a heterogeneous and porous structure in the matrix causes the decreament of strength when the threshold of curing temperature is exceeded, even in cases of prolonged curing.

For red clay brick-based samples, maximum compressive strength value obtained at 105 °C for 24 hours and at 95 °C for 48 and 72 hours. For geopolymer production, it is possible to reach the desired strengths at higher temperatures with short term curing or lower

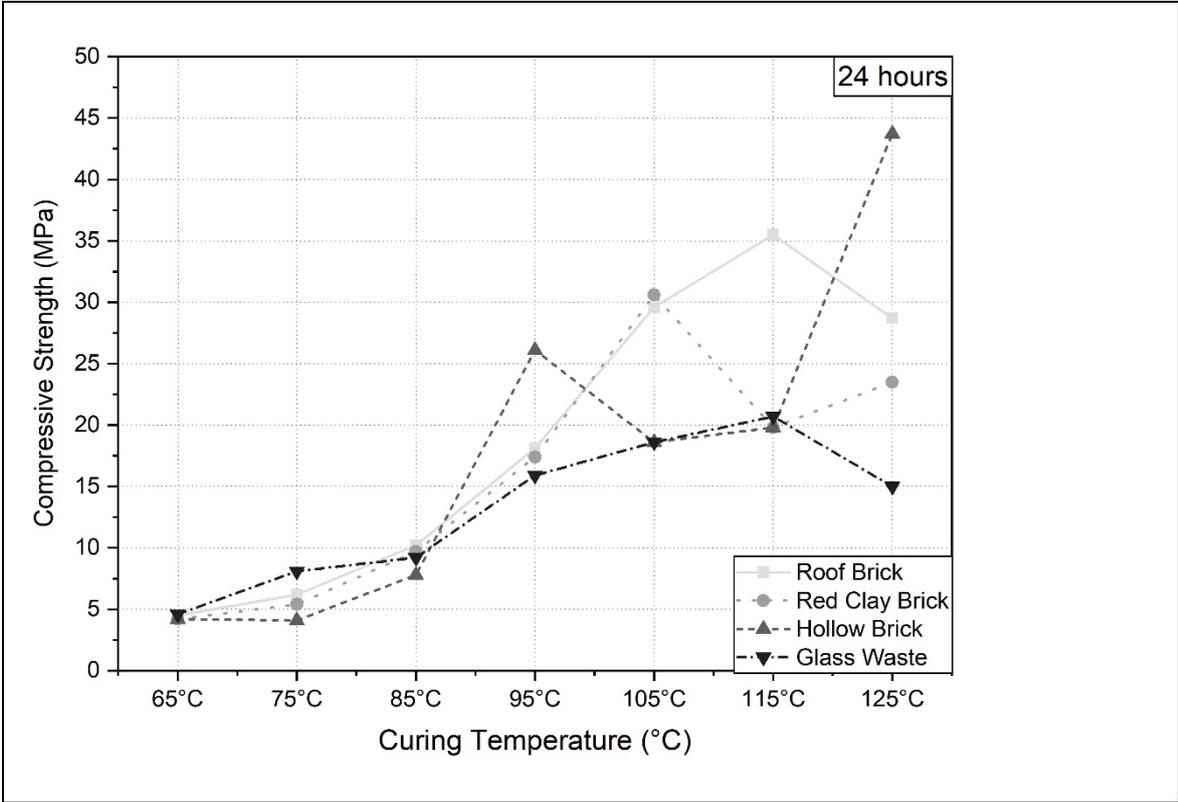
temperatures with prolonged curing. However, exceeding of thresholds for curing temperature causes the loss of strength due to non-homogenous matrix system and formation of thermal shrinkage cracks. Evaluation of curing time and compressive strength relationship shows that red clay brick-based samples exhibited similar behaviors as roof tile-based samples until 75°C. At 85°C, compared to 24-hour curing, compressive strength results increased by 132% and 264% for 48 and 72 hours, respectively. At 95°C, increments of compressive strength were noted as 140% for 48 hours and 131% for 72 hours. 42 MPa was obtained after 48 hours at 95 °C curing temperature and 35 MPa was obtained after 72 hours at 85 °C. Evaluation of compressive strength results indicated that it is possible to reach the desired compressive strength values at lower temperatures by increasing the curing time. Differences in particle size and SiO₂/Al₂O₃ ratios may be related to the higher ultimate strength of red clay brick-based samples among all other CDW-based samples.

Compressive strength results of hollow brick-based samples which were included in the brick group showed different characteristics despite the similar chemical contents with roof tile and red clay brick. Compressive strength values of red clay brick-based samples which were cured at 95 °C for 24 and 48 hours and at 85°C for 72 hours, showed an increase until these curing temperatures. Exceeding these curing temperatures led to a decrease in strength. Additionally, hollow brick-based samples obtained their maximum strength at 125 °C curing temperature different from the roof tile and red clay brick-based samples. This can be attributed to the fact that hollow brick-based samples contain high amounts of amorphous SiO₂ compared to other brick-based wastes and show more polymerization reactions at lower temperatures than other waste materials.

Examination of the curing time vs. strength relationship of the hollow brick-based geopolymers indicates that samples do not exhibit high strengths up to 95 °C at the end of 24-hour curing time. Maximum compressive strength value was 43.7 MPa for these samples and was obtained at 125°C curing temperature after 24 hours. For the curing temperature of 125 °C, compressive strength values which have decreased with small differences at the end of 48 and 72 hours showed that the desired strength values can be reached in shorter times through the optimization of temperature and curing time.

Compressive strength values of the waste glass-based samples increased with high rates at 95 °C for 24 hours, and 75 °C for 48 hours and 72 hours. For 24 hours of curing, maximum strength value obtained at 115 °C and strength values decreased at the higher temperature

levels. For 48 hours of curing, strength values of samples reached their maximum value and for higher temperatures they remained approximately stable. Evaluation of 72 hours of curing temperature showed that the samples reached maximum strength at 75 °C than until 105 °C which was considered as threshold of curing temperature, exhibited a stable behavior. Evaluation of 72 hours of curing temperature showed that the samples reached maximum strength at 75 °C. Until 105 °C which was considered as a threshold of curing temperature, samples exhibited a stable behavior and at above 105 °C, decrements in strength values were observed. It is a known fact that the Al content accelerates the kinetics of the polymerization reaction (Kovalchuk, 2007), the amount of Al₂O₃ in the waste glass powder-based samples is considerably lower than other waste materials. For this reason, glass waste-based samples reached maximum strength values at the end of 72 hours of curing. Examination of the strength results of glass waste-based samples shows that for curing temperatures of 75 °C and 85 °C, the compressive strength values increased with high ratios. At 75 °C, strength values increased by 112% and 342% for 48 and 72 hours, respectively. At 85 °C, compressive strength increased by 112% for 48 hours and 272% for 72 hours. At higher temperatures, strength results approximately remained stable. It has been determined that the samples based on glass waste which have been cured at a temperature of 75-85 °C can reach to the final strength.



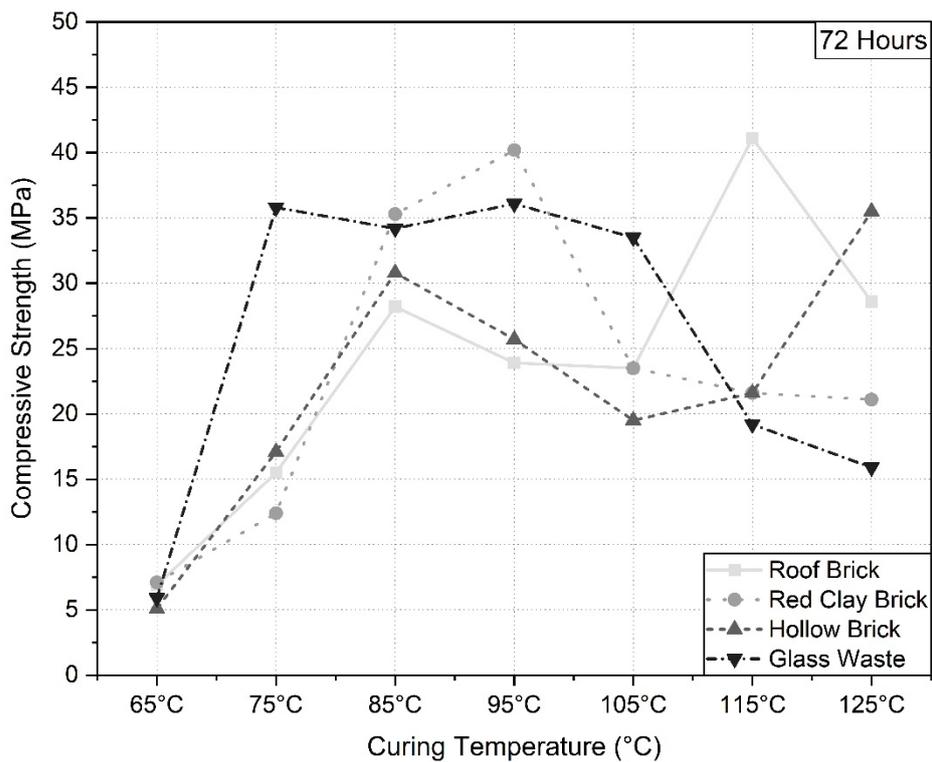
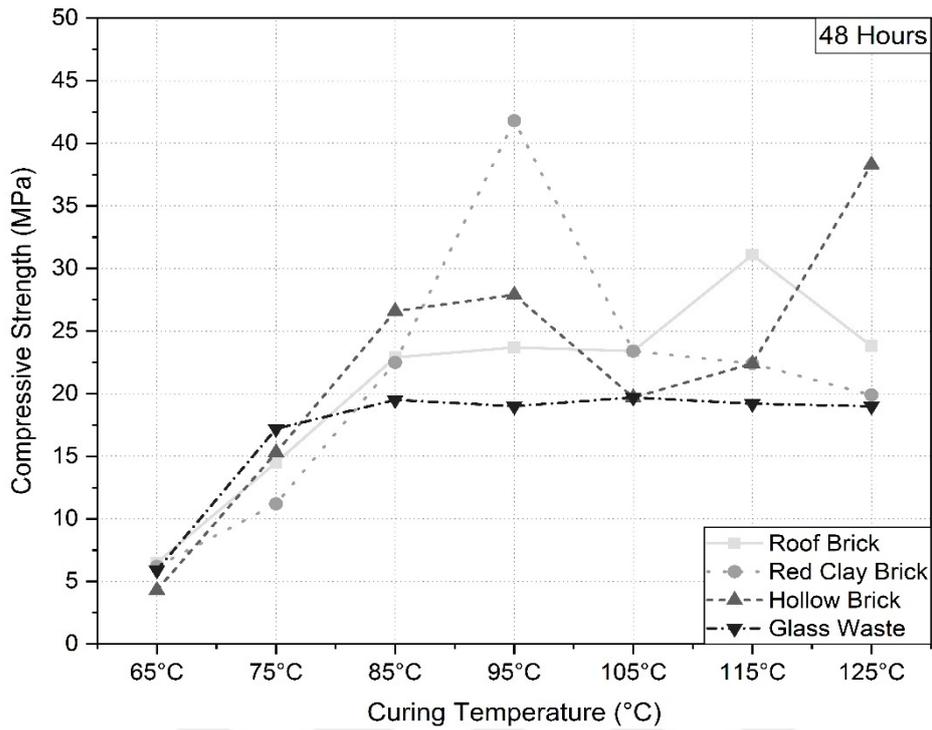


Figure 5.14 Effect of curing time on samples with 10% sodium concentration

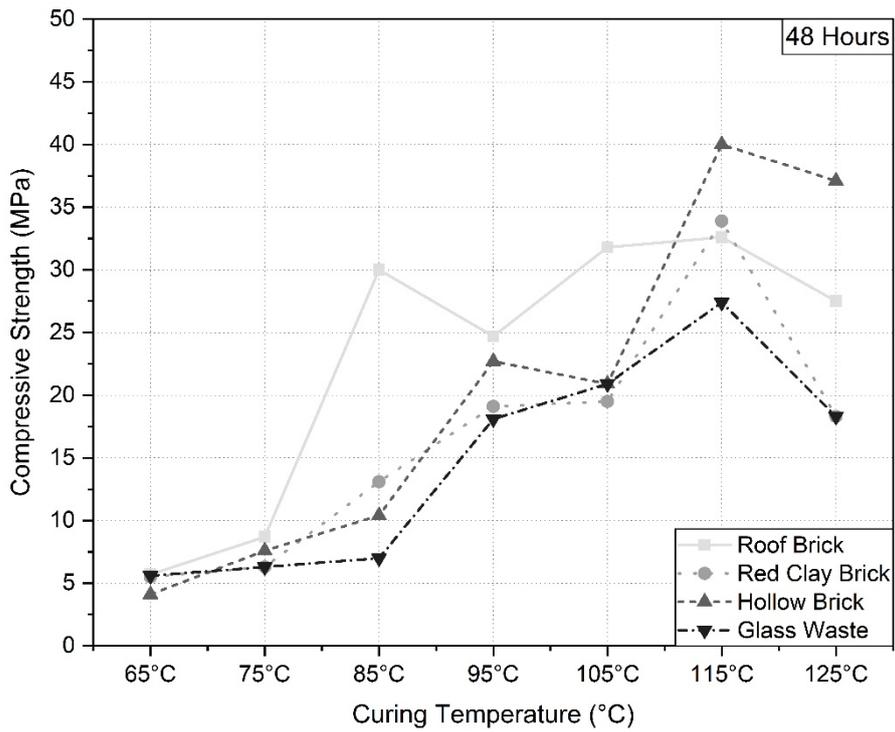
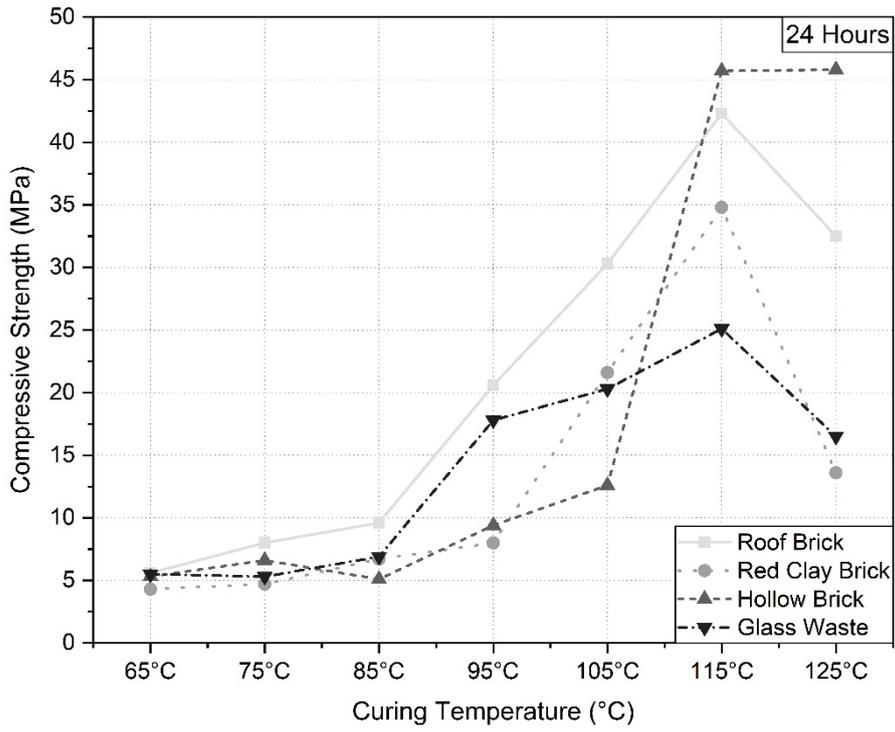
The compressive strengths results of the samples with a sodium concentration of 12% were indicated in Figure 5.15. For roof tile-based samples had no signs of compressive strength attainment up to 50 °C. For samples which were cured for 24 hours, strength results increased

until 115 °C and reached to maximum values at 115 °C. This value of 42.3 MPa was determined as the maximum compressive strength value reached after all different curing times and temperatures. 115 °C curing temperature for 24 hours can be accepted as the optimum curing conditions for roof tile-based samples. At 85 °C, an increase in compressive strength by 213% and 218% were determined for 48 and 72 hours, respectively. For the other curing temperatures, the samples have not shown significant changes, in general, have reached the limit strength values for every curing temperature for 24-hour curing time.

Assessment of the effect of curing time on red clay brick-based samples shows that 115 °C for 24 and 48 hours and 105 °C for 72 hours are the thresholds for curing temperatures. At temperatures up to 115 °C, an increase in the strength values with the prolongation of the curing time was determined. This case can be explained by the slow progress of polymerization reactions at low temperatures. For higher temperatures, non-homogeneity of matrix due to different propagation rate of reactions at different parts of the matrix and, the triggering of reactions when the unreacted particles are exposed to the temperature at which the reaction can proceed can be the reasons for this behavior.

Hollow brick-based samples showed lower strength results up to 105 °C for 24 hour curing time. At 115 °C, samples reached a compressive strength of 45.7 MPa with an increase of 262% and maintained this value at 125 °C. For the curing time of 48 hours, the temperature at which the samples obtained desired levels of strength decreased down to 95 °C, strength values showed a high increase at 85 °C for 72 hour curing time.

At the end of 72 hours, strength results of samples reached close to the maximum level at a temperature of 75 °C, and this situation is the evidence that the optimum strength is reached at low curing temperatures with prolongation of cure.



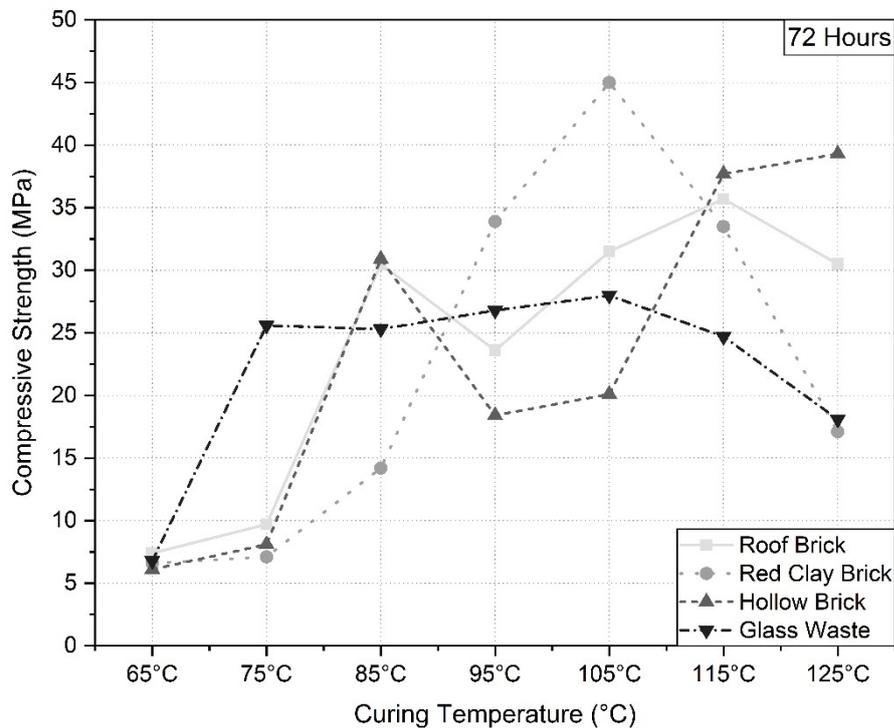
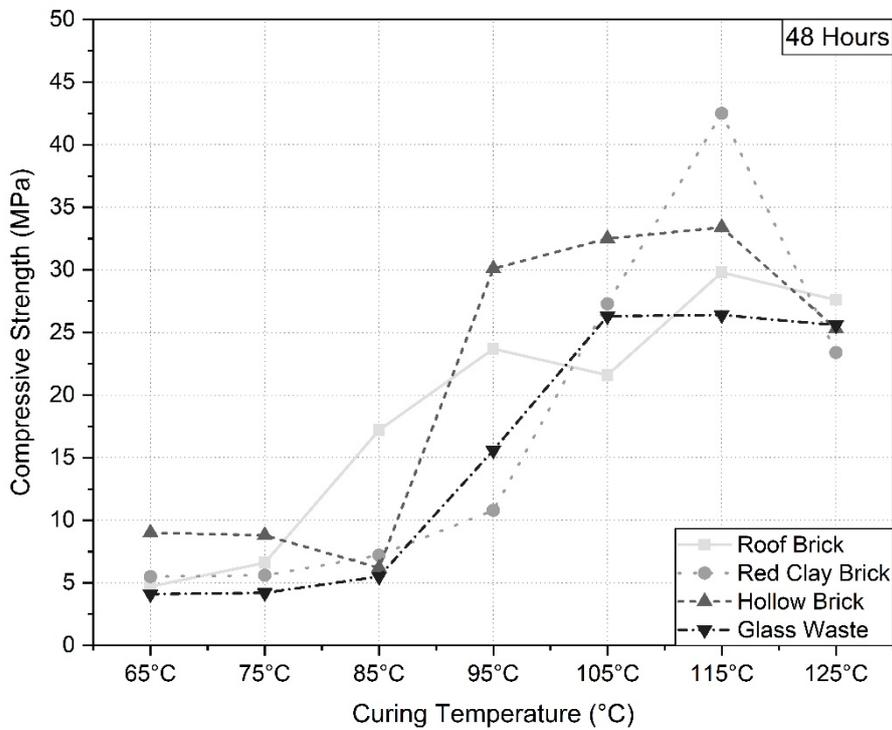
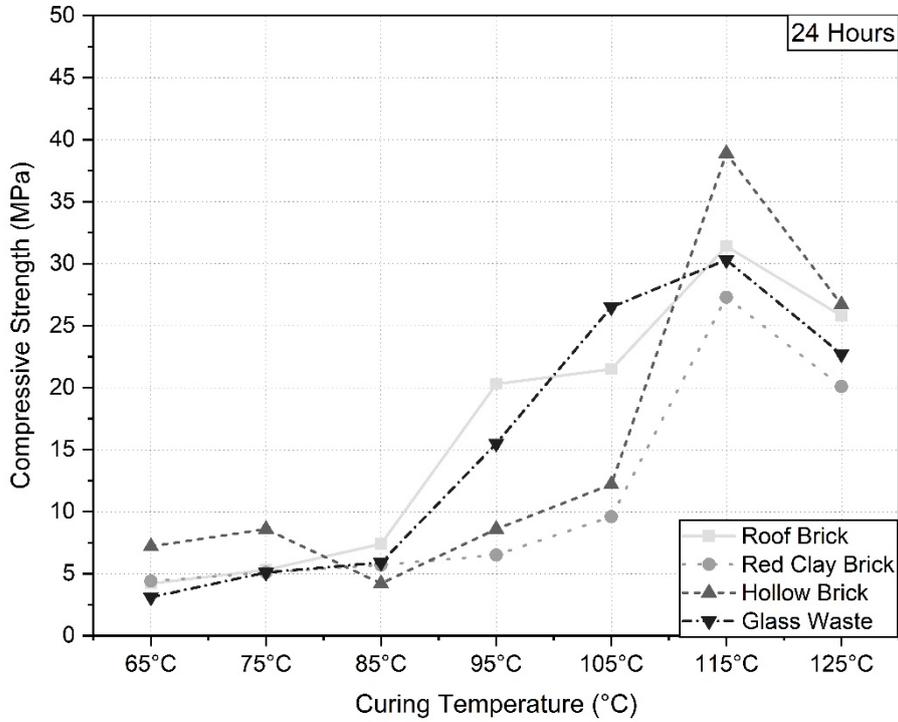


Figure 5.15 Effect of curing time on samples with 12% sodium concentration

The compressive strength results of samples with sodium concentration of 15% were given in Figure 5.16. Compressive strength results of roof brick-based samples showed an increase for curing conditions of 24 hours at 115 °C. The same trend observed for the curing time of 48 and 72 hours. However, the strength values of roof brick-based geopolymers did not show an increase due to prolongation of curing at 105 °C and above temperatures. Therefore, the strength values either conserved or showed reduced levels of strength. The increase in sodium concentration influenced the reaction process and caused remaining of unreacted particles and voids in the matrix. Therefore, strength losses and discontinuities have occurred.

Red clay brick-based samples showed almost the same characteristics as the samples with a sodium concentration of 12%. Increments in strength up to 115 °C for 24 and 48 hours of curing and up to 105 °C for 72 hours of curing were observed. Exceeding of these thresholds for curing temperatures caused strength losses. Similarly, hollow brick-based samples showed the same behavior for their limit temperatures. Glass waste-based samples also showed similar properties with samples having a sodium concentration of 12% in terms of changes in compressive strength. For the 24-hour-cured samples, 26.5 MPa at 105 °C and

30.6 MPa at 115 °C were obtained. This is due to the fact that the sodium concentration of 12% is not a limit for glass waste-based geopolymers, unlike other waste materials. However, the increase in curing time resulted in strength losses for the glass waste samples.



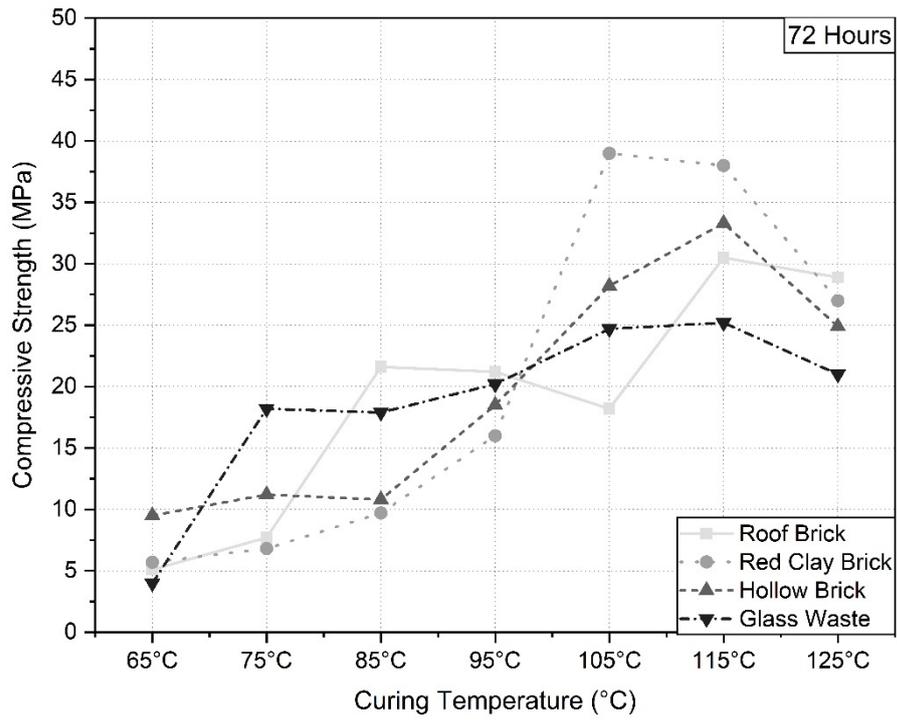


Figure 5.16 Effect of curing time on samples with 15% sodium concentration

6. CONCLUSION

In the context of this study, the utilization of construction demolition wastes as the binders was evaluated. The aluminosilicate precursors such as roof tile, red clay brick, hollow brick, concrete and glass wastes which are forming a large part of construction demolition wastes were used as raw materials. These waste materials were used as aluminosilicate precursors individually for alkali activation without inclusion of any type of mainstream pozzolanic materials. Sodium hydroxide, sodium silicate, potassium hydroxide were used individually or combined at different ratios as alkaline activator for polymerization reactions at different molarity and concentrations. As a result of the data obtained from experimental studies, significant compressive strength results were obtained from samples using sodium hydroxide. Thus, the study focused on using sodium hydroxide as an alkali activator due to better performance on polymerization compared to other activators.

Evaluation of usability of the CDWs in the production of geopolymer binders and polymerization performance of each raw material shows that it is possible to obtain the desirable strength grades from geopolymer pastes by alkali activation of brick-based construction demolition waste. However, it seems necessary to place more focus on the improved usability of waste concrete and glass in the production of geopolymer pastes.

As can be seen with the comparison of compressive strength results of geopolymer specimens which produced with roof tile, red clay brick, hollow brick, concrete and glass wastes, hollow brick-based geopolymer specimens showed best performance among all raw materials. Due to the fact that the brick group materials are similar in terms of chemical content and the same processes were applied while obtaining the waste brick powders, these binders have shown the same characteristics, the different results of compressive strength tests could be related with particle size of binders, the crystallographic structure and the variation of surface loads. Additionally, the lower compressive strength results of red clay brick-based geopolymers could be related with the finer particle size of material, compared to the other CDWs. Red clay brick was insufficient in terms of workability due to its finer particle size. For the glass waste-based geopolymers, the high amorphous SiO_2 content of the raw material supports the geopolymerization process, however, the low alumina (Al_2O_3) content limits the final strength achieved.

In terms of influence of sodium concentration on the geopolymerization process, brick-based geopolymers followed a trend. If the increase in the sodium concentration of the activator in

the bricks group is not exceeded the threshold, the positive effects on the strength can be clearly seen. In case of exceeding 12% sodium content, which is determined as a threshold according to the data obtained from the tests performed, the viscosity of the geopolymer paste increases, the mixing and casting processes become more difficult preventing the appropriate compaction of the geopolymer pastes. However, this is different for waste glass based samples. Although glass waste is a very suitable material for the production of geopolymer due to its amorphous structure and high SiO_2 content, low Al_2O_3 content constitutes an obstacle to the proper propagation of the polymerization process.

In terms of the influence of sodium concentration on the geopolymerization process, variations were observed. As mentioned previous, the temperature acts as a catalyst for geopolymerization reactions. The general trend is that development in compressive strength up to the threshold values of curing temperatures and decrease in compressive strength when the threshold value is exceeded. The first evidence of compressive strength was obtained at 65 °C for all type of CDWs, which could be considered as the lower limit of required curing temperature for all three different curing times. Strength gain continued to increase until an optimum curing temperature and began to decrease at a temperature that could be considered as the upper limit of curing temperature. The thresholds of curing temperature varying for all CDWs, according to sodium concentration, curing duration, and characteristics of CDW. For instance, the optimum curing temperatures are found as 105, 115 °C for brick group waste and glass waste geopolymers. However, for hollow brick-based geopolymers strength development continued up to 125 °C for 24 hours curing duration. For 48 hours curing, specimens almost reached their maximum strength values. For 72 hours, exceeding of 115 °C caused the decreasing of strength.

Different variations related with the effect of curing time on roof tile-based samples, which produced with 10 % sodium concentration, were observed. Up to 75 °C, at ambient temperature and 50 °C any compressive strength evidence could not be observed for three different curing periods. Up to 105 °C, development on compressive strength was observed for all curing times. For 105 °C and above curing temperatures, changes in strength results were inconsiderable. For high temperatures, due to the rapid progress of the geopolymerization process, it can be mentioned that the formation of a heterogeneous and porous structure in the matrix causes the decreament of strength when the threshold of curing temperature is exceeded, even in cases of prolonged curing.

Evaluation of curing time and compressive strength relationship shows that red clay brick-based samples, which produced with 10% sodium concentration, exhibited similar behaviors as roof tile-based samples until 75 °C. For red clay brick-based samples, maximum compressive strength value obtained at 105 °C for 24 hours and at 95 °C for 48 and 72 hours. This can be the evidence that, it is possible obtained high strength values at higher temperatures with short term curing or lower temperatures with at least 72 hours curing.

Compressive strength results of hollow brick-based samples with 10% sodium concentration which were included in the brick group showed different characteristics despite the similar chemical contents with roof tile and red clay brick. Up to 95 °C for 24 and 48 hours and at 85 °C for 72 hours, compressive strength results showed an increase. Exceeding these curing temperatures led to a decrease in strength. This can be related to the fact that higher amounts of amorphous SiO₂ content of hollow brick-based samples compared to other brick-based wastes and show more polymerization reactions at lower temperatures than other waste materials. Maximum compressive strength value was 43.7 MPa for these samples and was obtained at 125°C curing temperature after 24 hours. For the curing temperature of 125 °C, compressive strength values which have decreased with small differences at the end of 48 and 72 hours showed that the desired strength values can be reached in shorter times through the optimization of temperature and curing time.

Compressive strength values of the waste glass-based samples which produced with 10% sodium concentration increased with high rates at 95 °C for 24 hours, and 75 °C for 48 hours and 72 hours. For 24 hours of curing, maximum strength value obtained at 115 °C and strength values decreased at the higher temperature levels. For 48 hours of curing, strength values of samples reached their maximum value and for higher temperatures they remained approximately stable. Evaluation of 72 hours of curing temperature showed that the samples reached maximum strength at 75 °C. Until 105 °C which was considered as a threshold of curing temperature, samples exhibited a stable behavior and at above 105 °C, decrements in strength values were observed. This can be related to the lower amount of Al₂O₃ in the waste glass powder-based sample.

For the CDW-based geopolymers which produced with 12% and 15% sodium concentration, influence of curing time exhibit almost the same results for all CDW-based specimens cured for 24 hours. For all type of CDWs, strength development up to 115 °C curing temperature was observed. However, for 48 and 72 hours, discontinuities has begun

due to influenced reaction process because of increased sodium concentration. The increase in sodium concentration influenced the reaction process and caused remaining of unreacted particles and voids in the matrix. Therefore, strength losses and discontinuities for CDW-based geopolymer have occurred. Additionally, for glass waste-based geopolymer the sodium concentration of 12% is not a limit for glass waste-based geopolymer, unlike other waste materials because of strength development for 15% sodium concentration. However, the increase in curing time resulted in strength losses for the glass waste samples.

As a result of the use of sodium hydroxide as the only alkaline activator, for all different types of CDW-based materials, best results (i.e. highest compressive strength results) were acquired. Moreover, this was valid for geopolymer mixtures incorporating mixtures of different types of CDW-based aluminosilicate sources. Among other mixture parameters tried throughout the experimental studies, highest compressive strength results were recorded for samples activated by sodium hydroxide solution having sodium concentration of 12%, water/binder ratio of 0.35 and heat cured at 105 °C. Moreover, increased curing periods further enhanced the results.

Consequently, it can be clearly stated that different types of CDW-based materials can safely be used as aluminosilicate sources in the production of geopolymer individually or in combination with specific ratios. Although it was possible to obtain the desired strength grades by means of alkaline activation of samples with brick-based construction demolition waste, it is also necessary to focus on and improve the utilization of waste glass and waste concrete in geopolymer production.

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APPENDIX

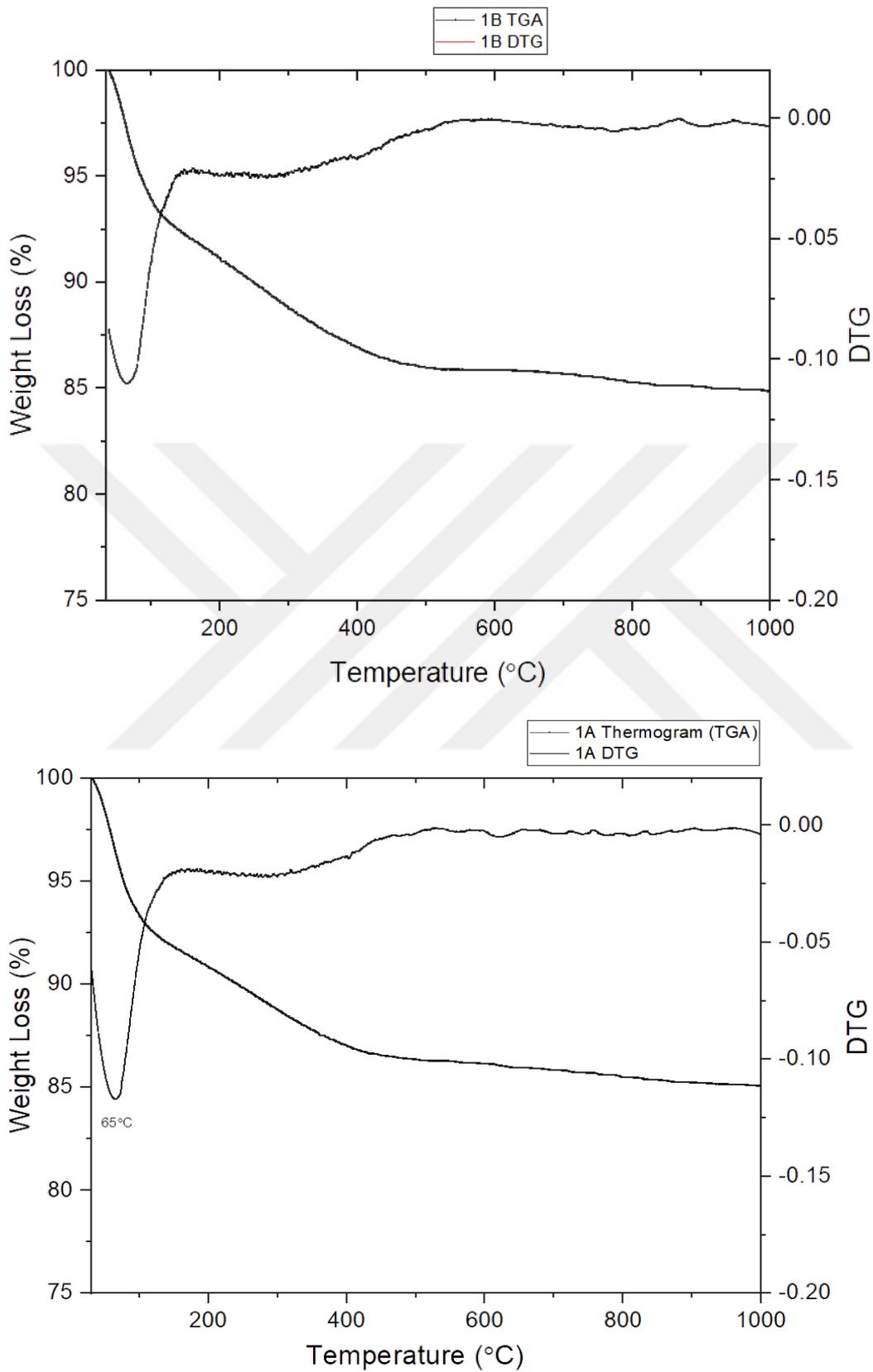


Figure A.1 TGA, DTG results of roof tile based specimens (12% Na Conc. 115 °C, 1A-24 h. cured, 1B-72 h. cured)

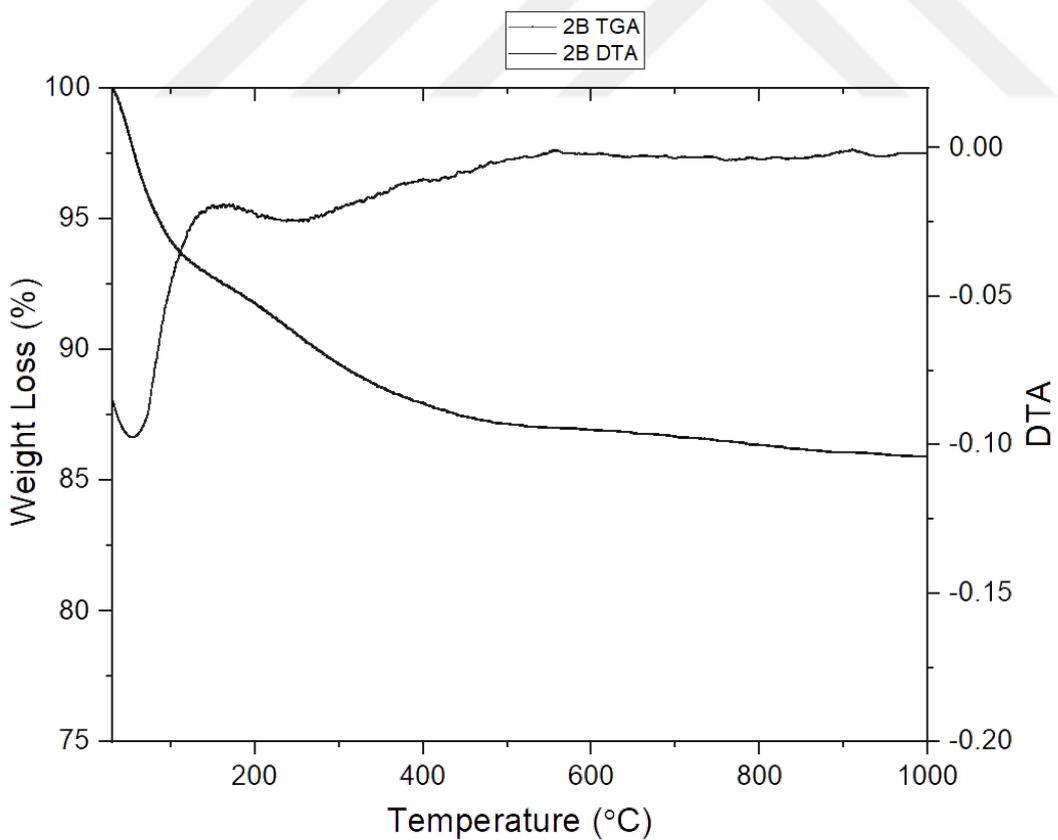
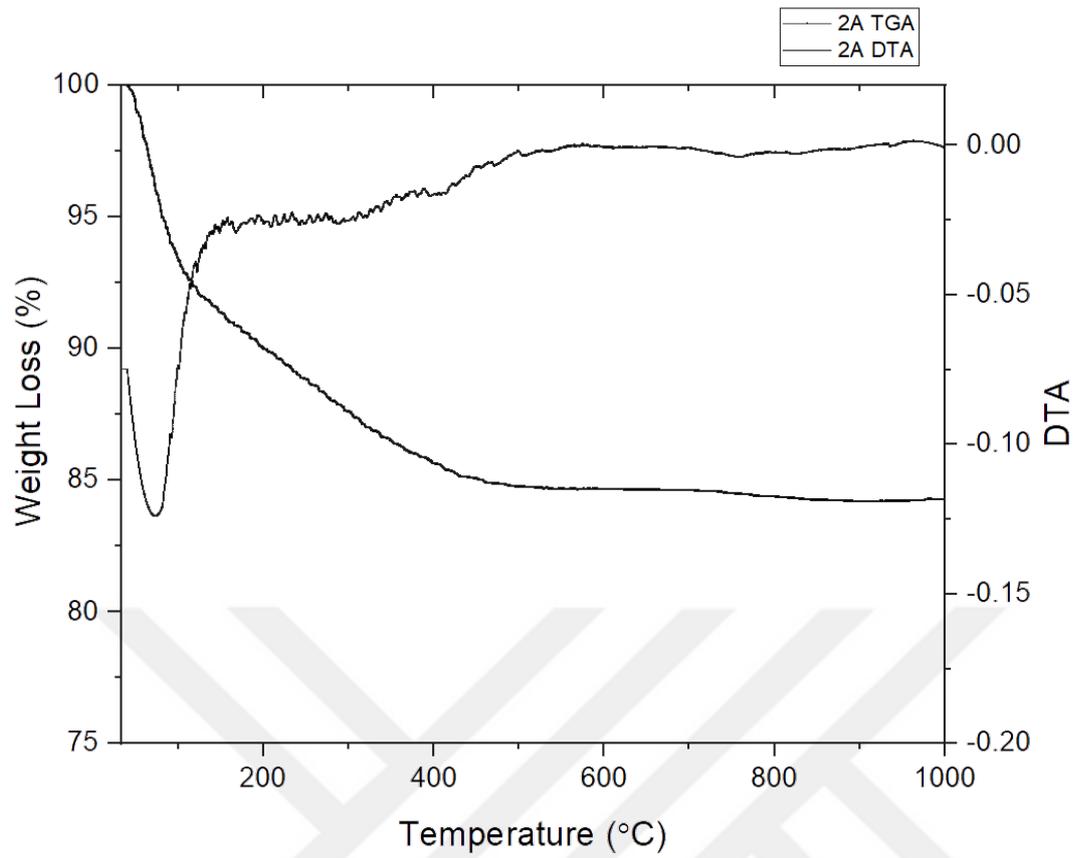


Figure A.2 TGA, DTG results of red clay brick based specimens (12% Na Conc. 115 °C, 2A-24 h. cured, 2B-72 h. cured)

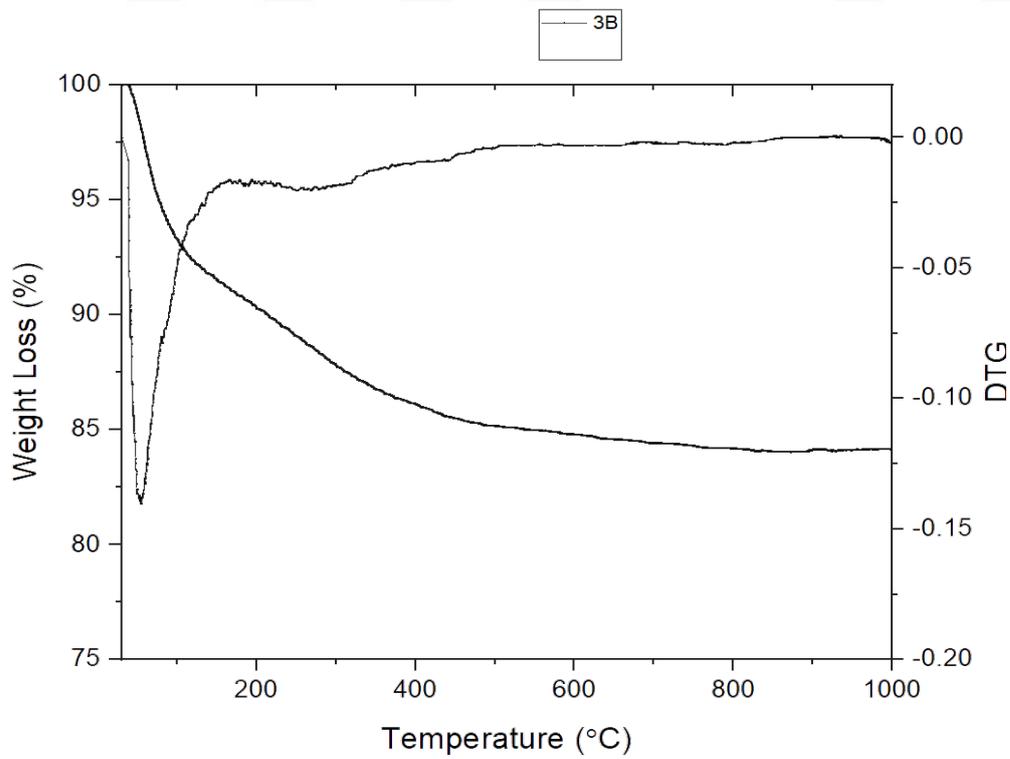
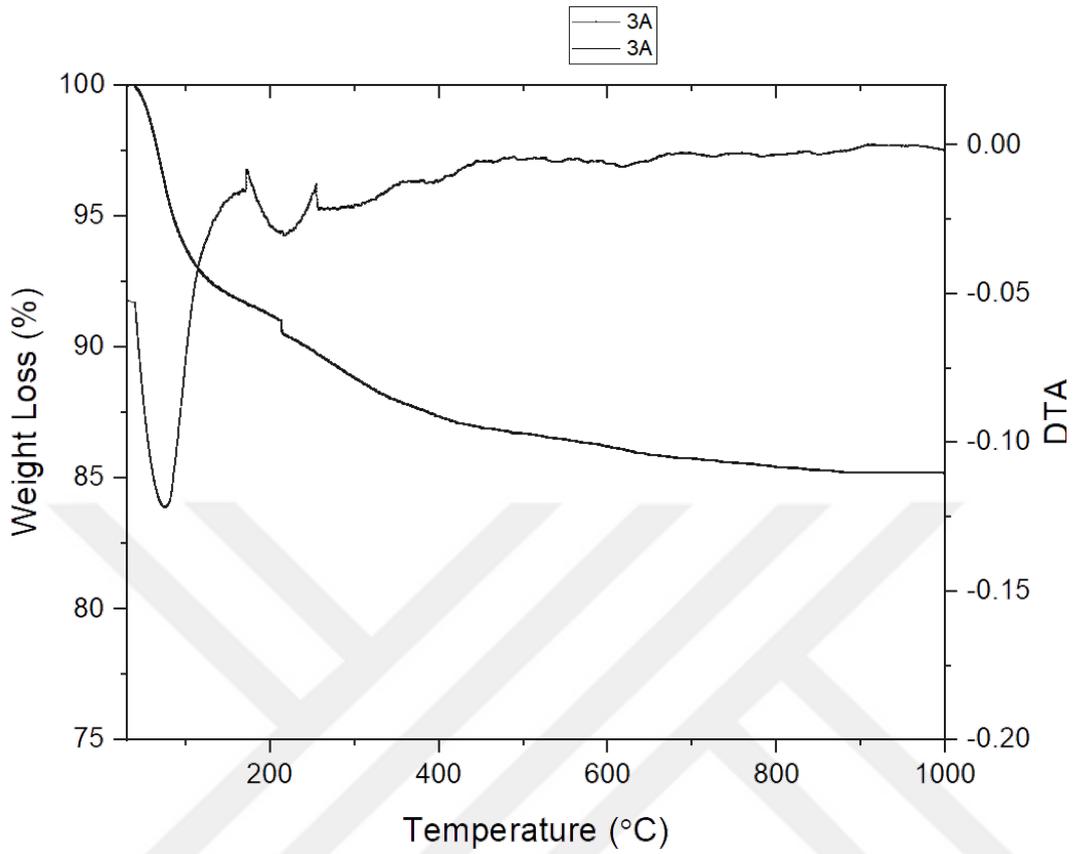


Figure A.3 TGA, DTG results of hollow brick based specimen (12% Na Conc. 115 °C, 3A-24 h. cured, 3B-72 h. cured)

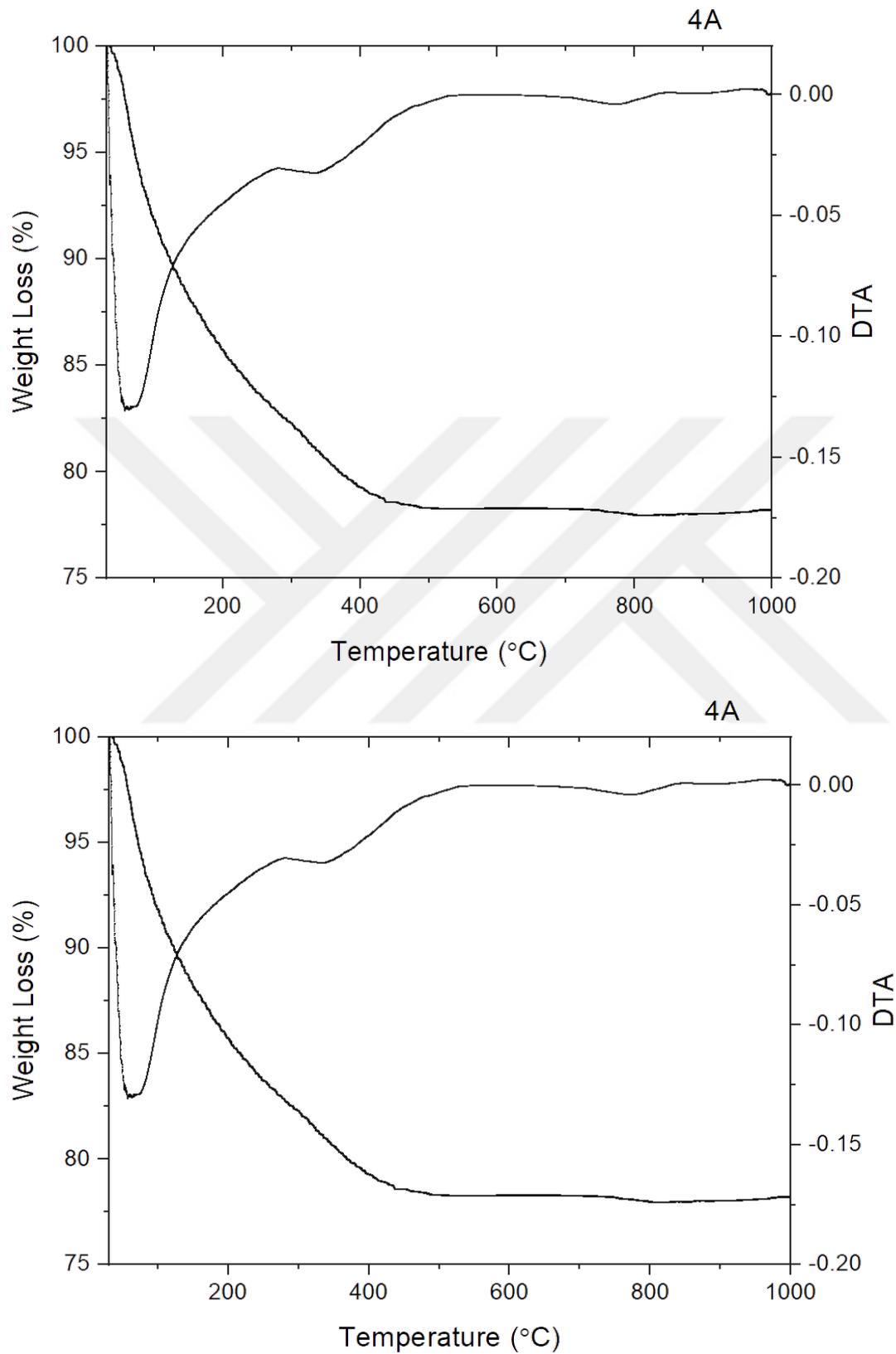


Figure A.4 TGA, DTG results of glass waste based specimens (*12% Na Conc. 115 °C, 4A-24 h. cured, 4B-72 h. cured*)

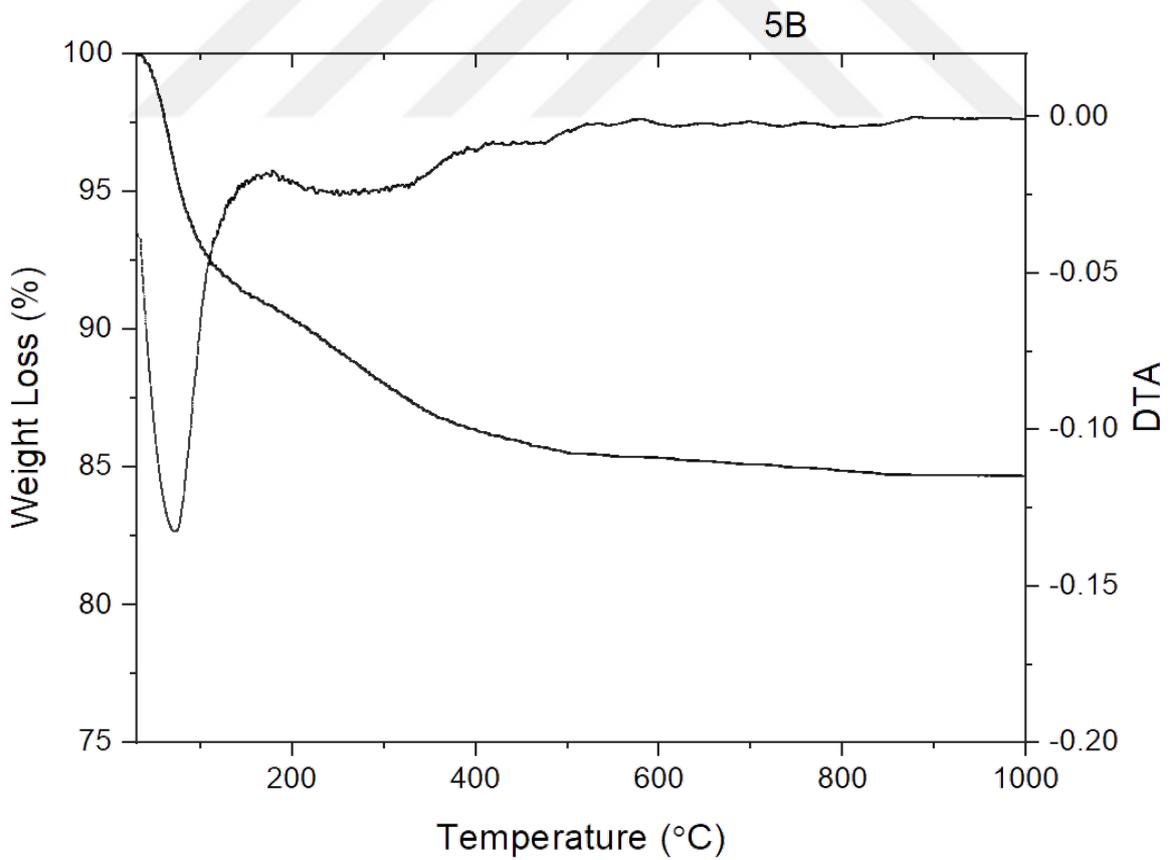
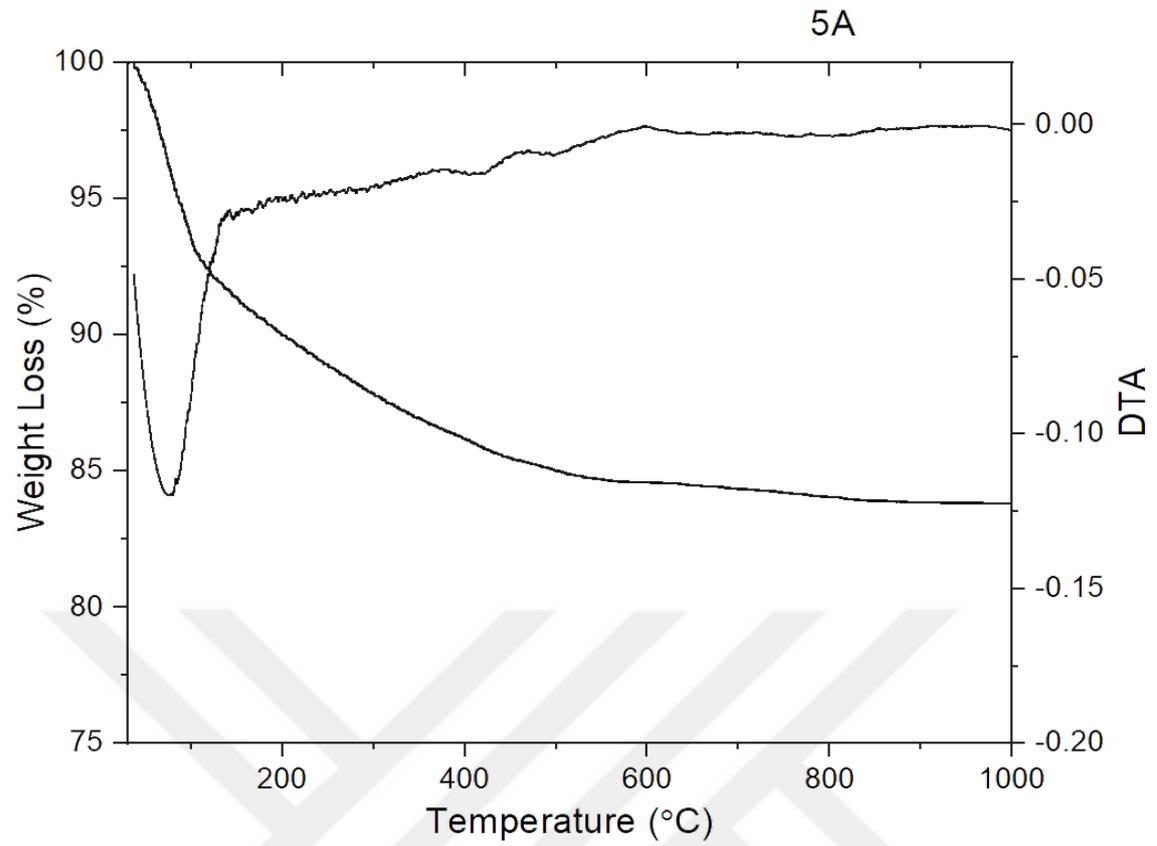


Figure A.5 TGA, DTG results of red clay brick based specimen (12% Na Conc. 105 °C, 5A-24 h. cured, 5B-72 h. cured)

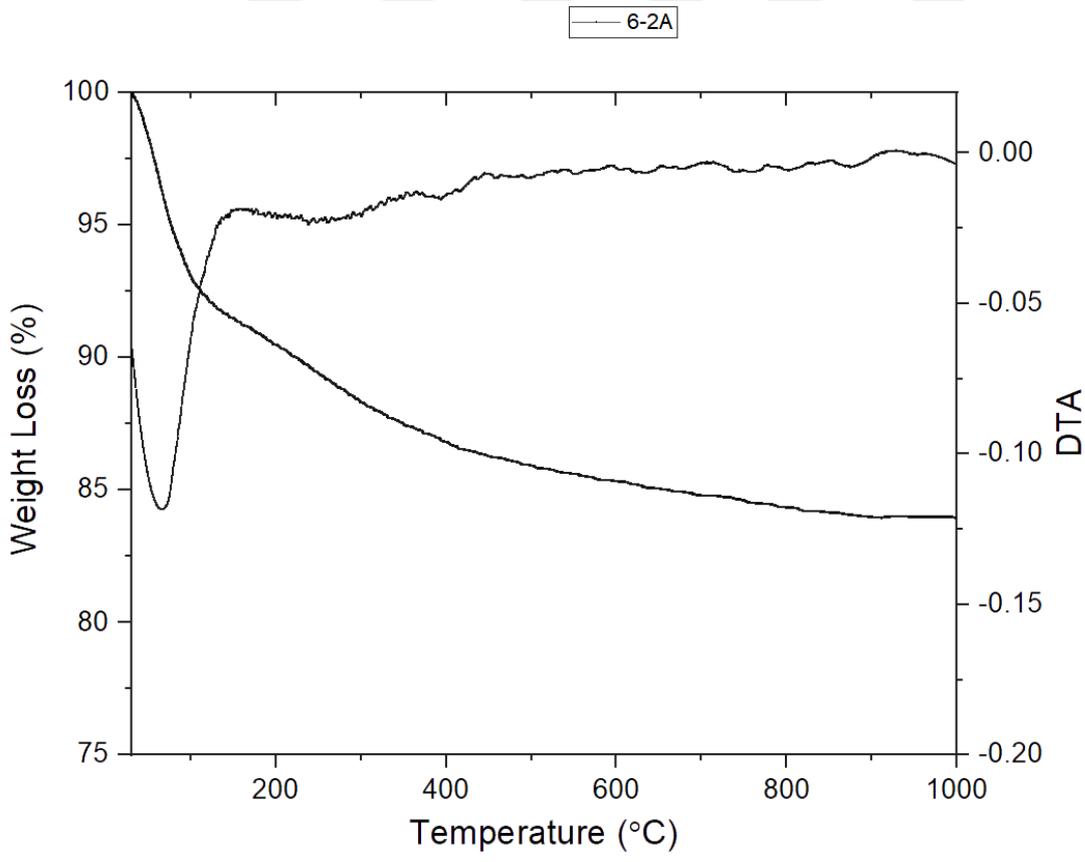
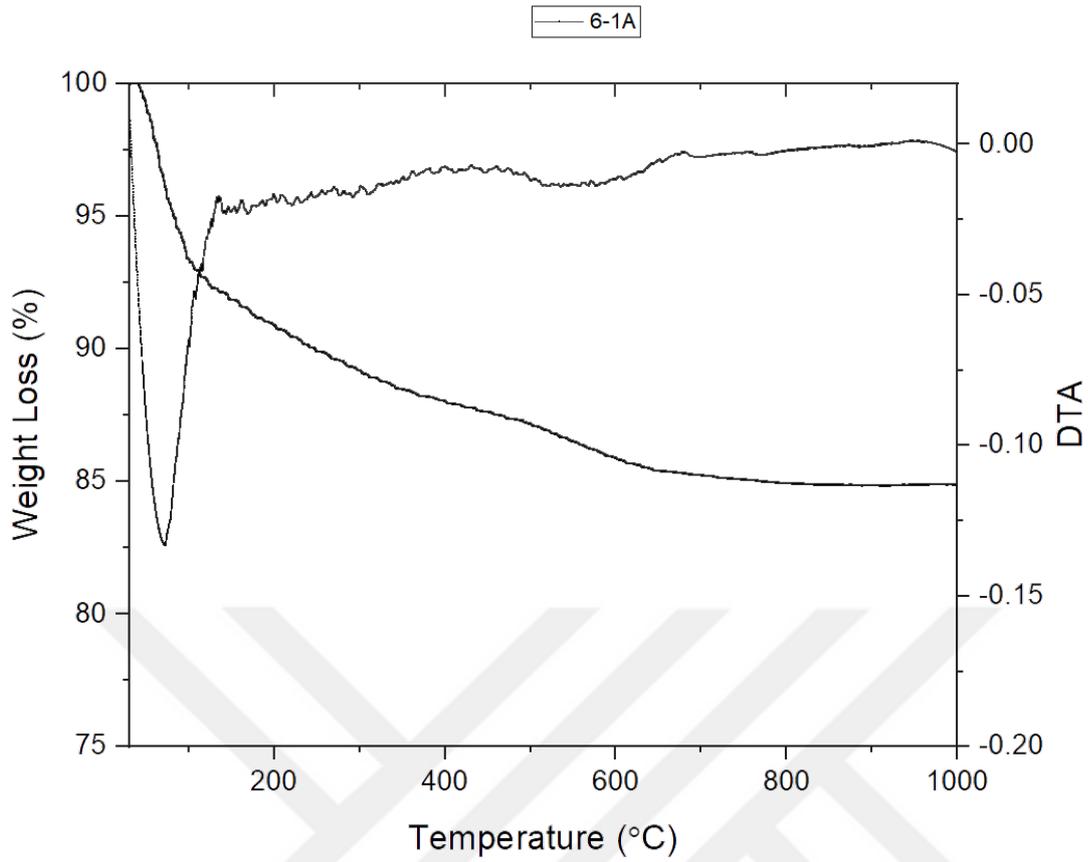


Figure A.6 TGA, DTG results of hollow brick based specimen (*12% Na Conc., 6.1A-at 75 °C, 6.2A-at 105 °C*)

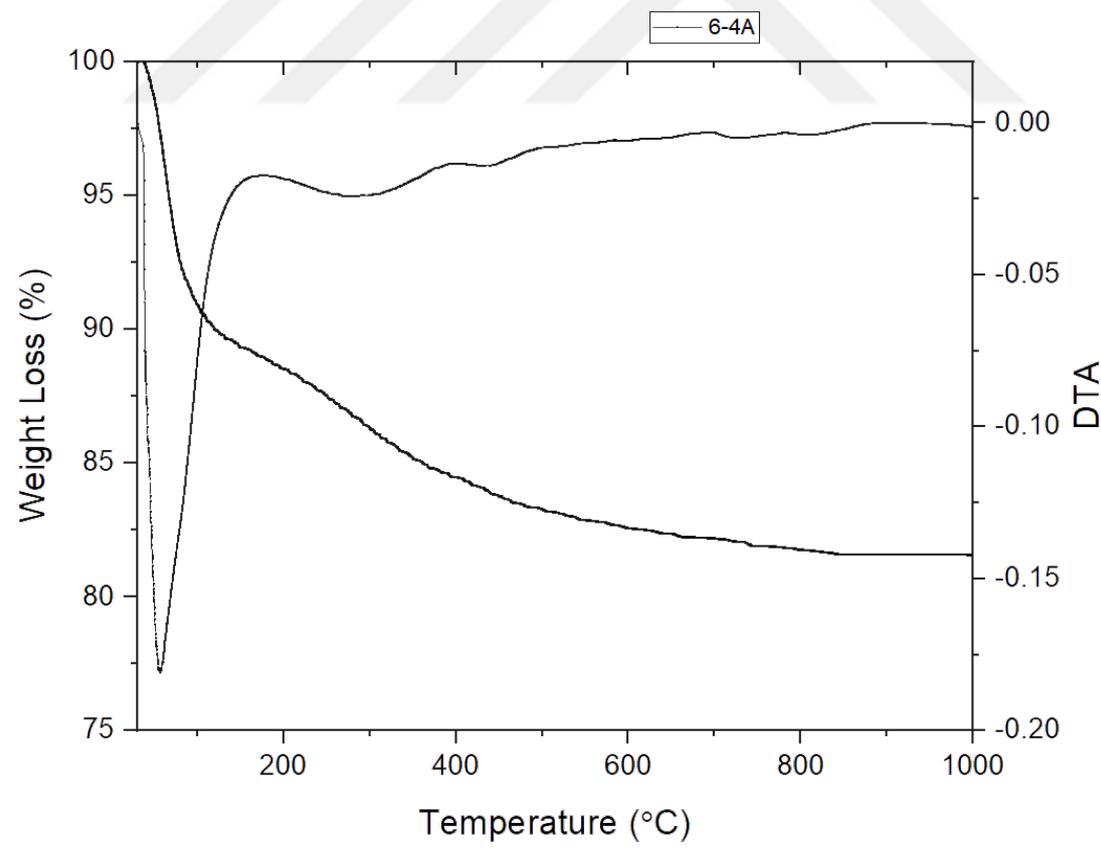
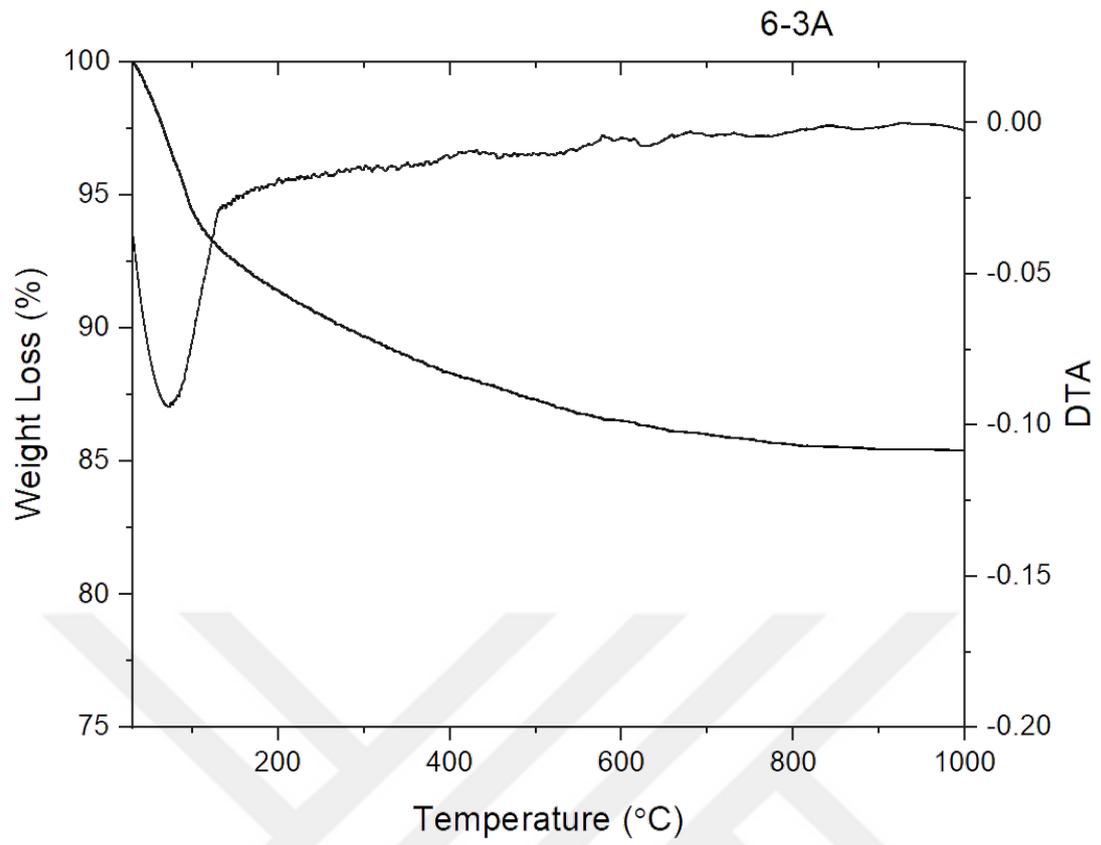


Figure A.7 TGA, DTG results of hollow brick based specimen (12% Na Conc., 6.3A-at 115 °C, 6.4A-at 125 °C)

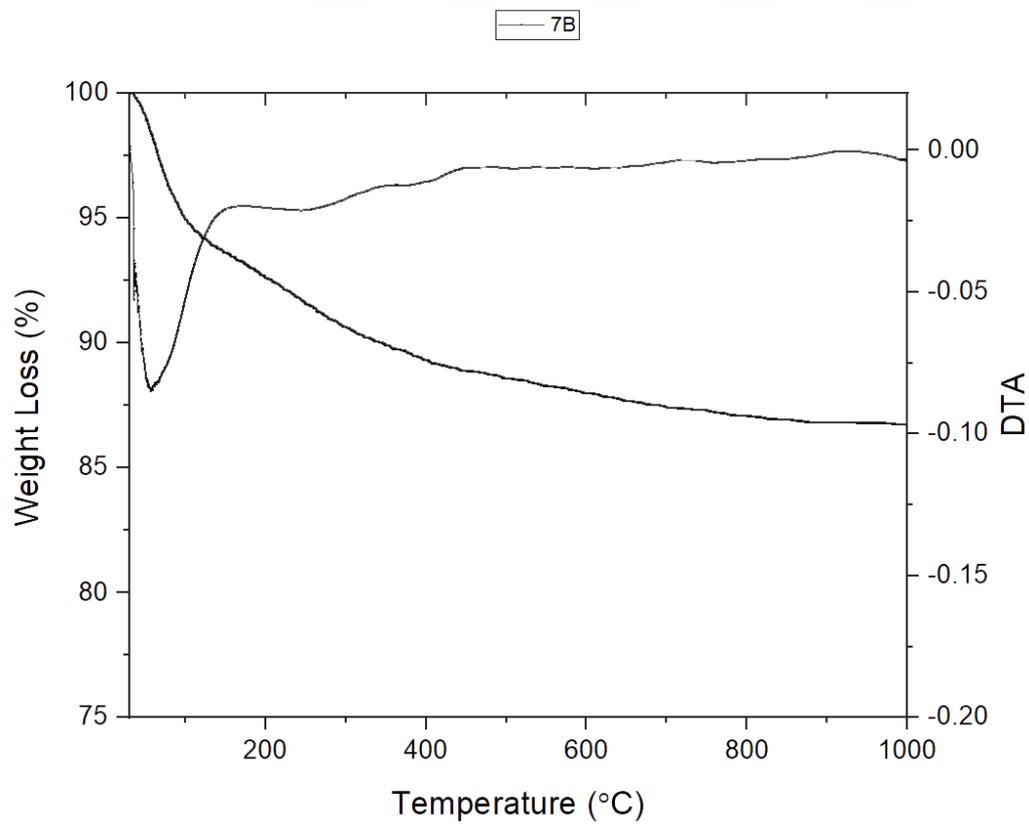
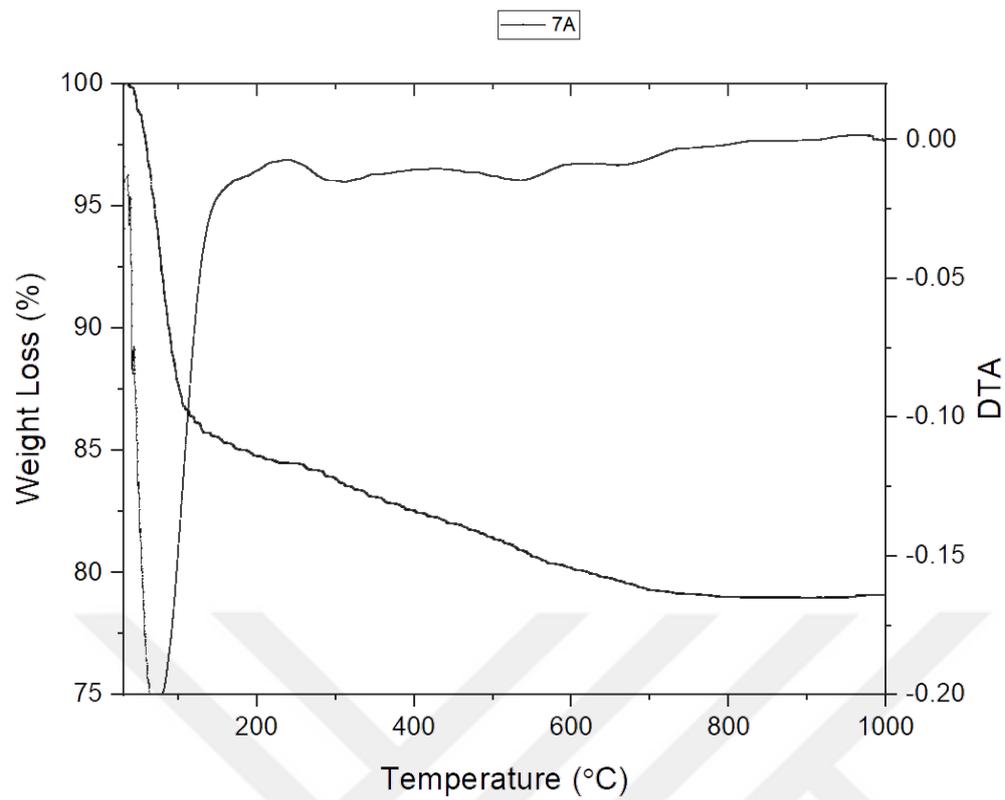


Figure A.8 TGA, DTG results of hollow brick based specimen (10% Na Conc. 85 °C, 7A-24 h. cured, 7B-72 h. cured)

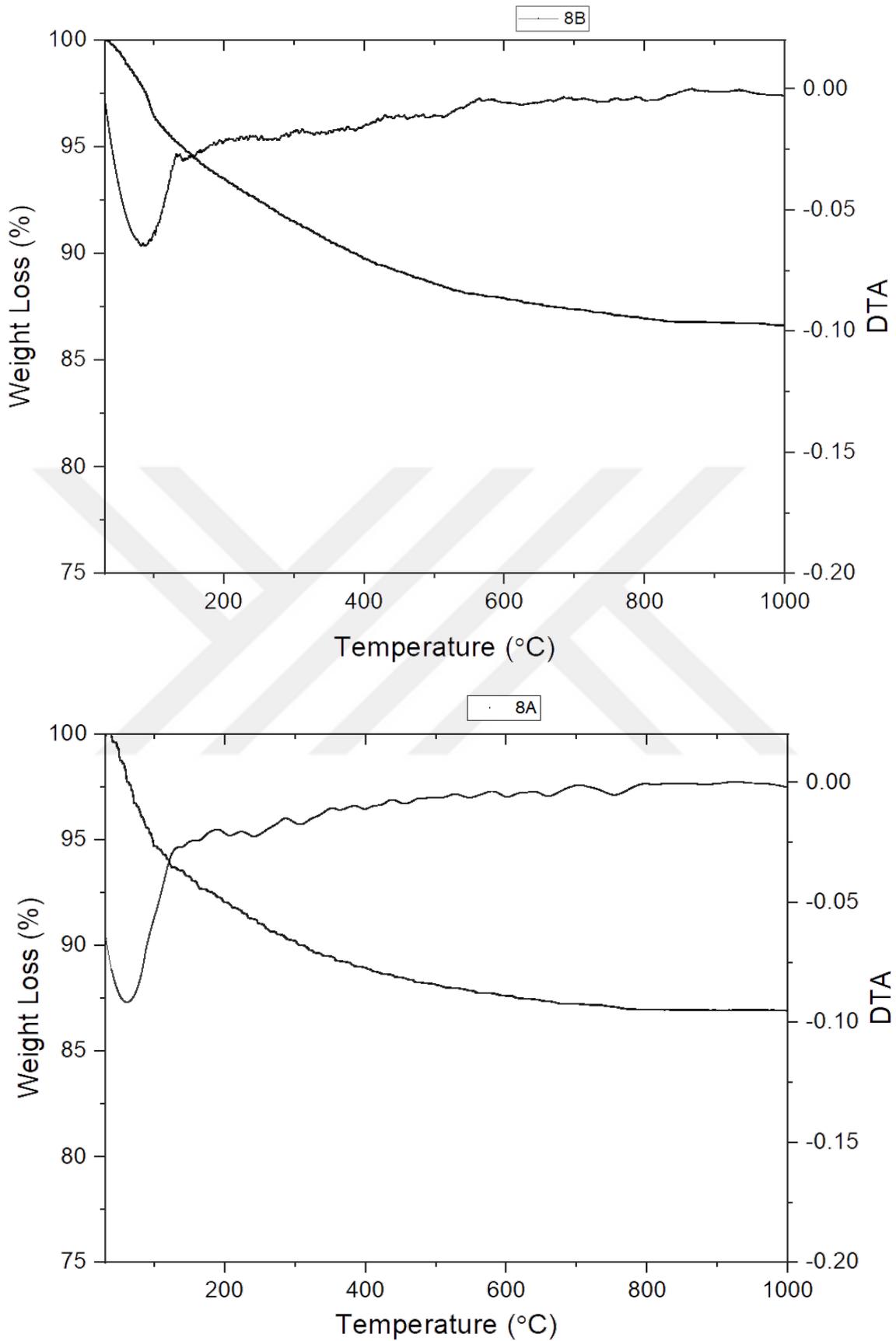


Figure A.9 TGA, DTG results of hollow brick based specimen (10% Na Conc. 115 °C, 8A-24 h. cured, 8B-72 h. cured)

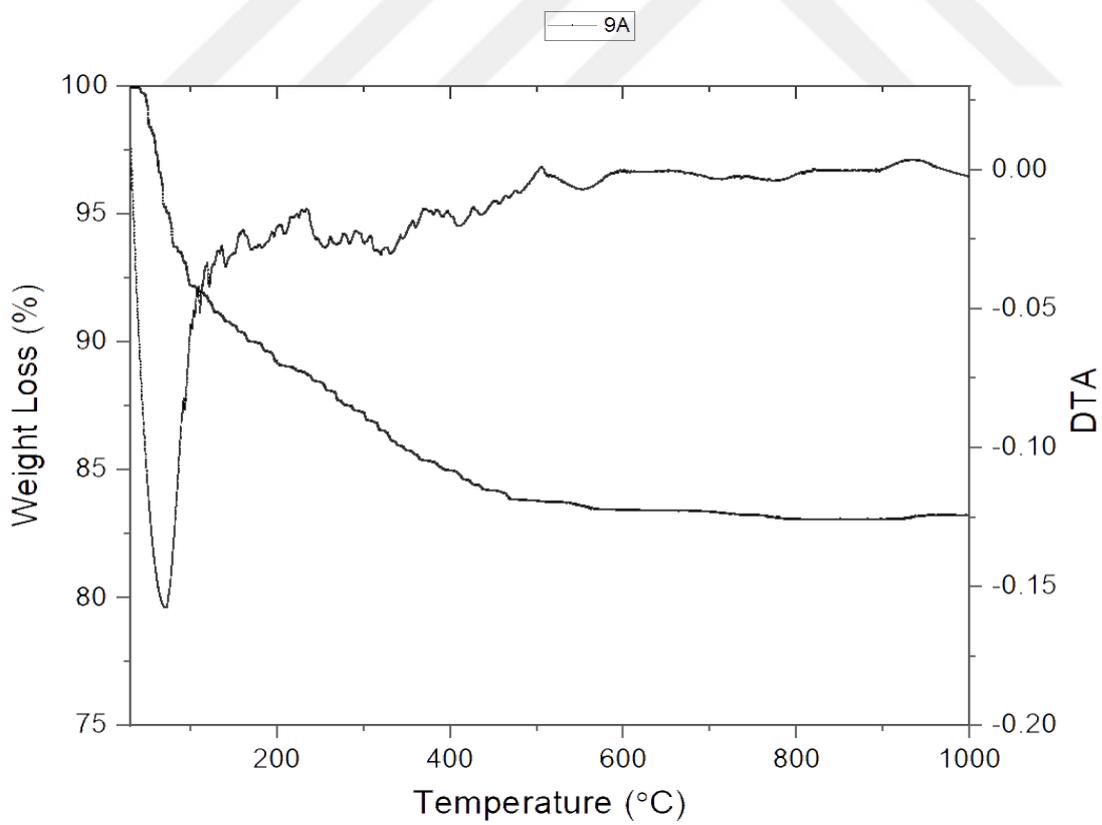
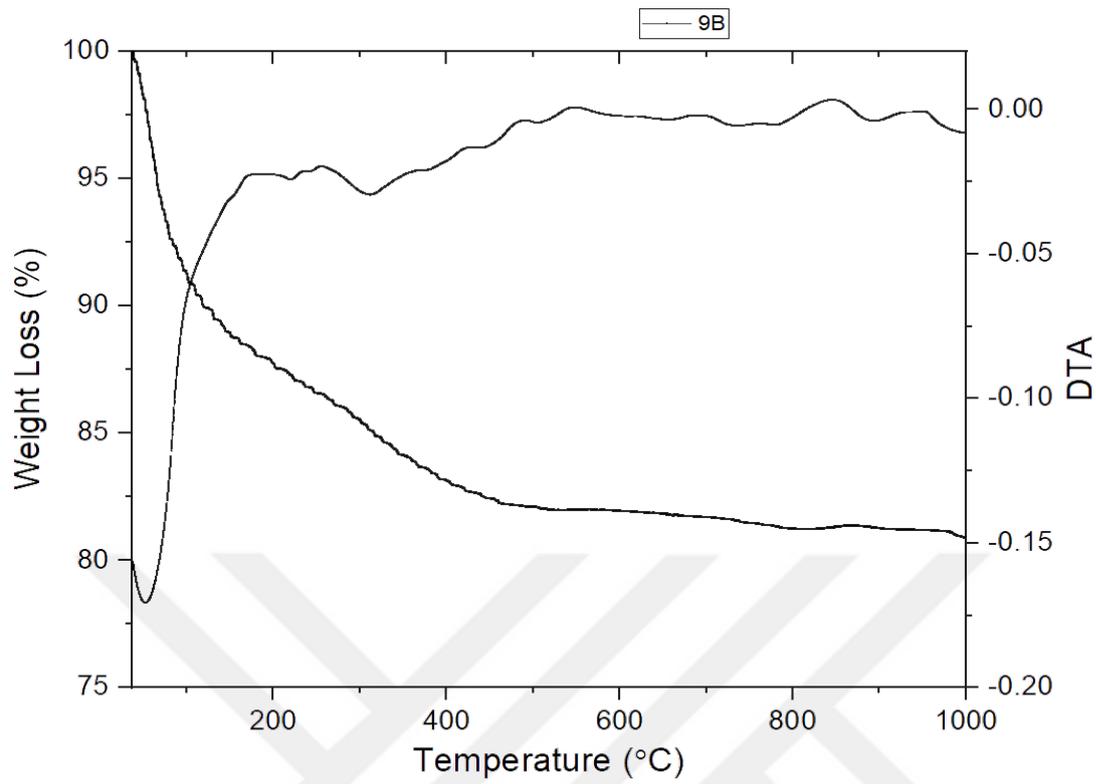


Figure A.10 TGA, DTG results of hollow brick based specimen (15% Na Conc. 115 °C, 9A-24 h. cured, 9B-72 h. cured)



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