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Combined effect of high temperatures and crystalline slag on the mechanical behavior of geopolymers mortars

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ABSTRACT

As part of protecting the environment from carbon dioxide emissions, all research aims to reduce the use of cement in concrete with cheaper and energy efficient materials. Geopolymer mortar is an environmentally friendly mortar made from industrial solid waste and by-products such as crystalline slag (CS). This research aims to produce a geopolymer mortar from local materials available in Algeria which are not sufficiently valued at present. The aim of this study is to provide geopolymer mortar at high temperatures, operating with a constant hardening temperature of around 60° C. The alkaline activator used in this study was a combination of sodium silicate (Na_2SiO_3) and 10 M NaOH solution. In addition, crystalline geopolymer mortars (MCS) as the binder material at a curing temperature of 60 °C, ratios of two mixtures of binder were prepared by substituting the sand with 40% CS and 100% CS. For this purpose, the mortar sample with the highest compressive strength was subjected to temperatures of 200, 400, 600 and 800 °C for exposure times of 10 °C per minute and changes in temperature and changes in the physical and mechanical properties was analyzed. As a result of the experiments, the highest mechanicals values were obtained from the mortar samples with a 40% CS content. Following the high temperature tests, 400 °C and 600 °C were determined as critical temperatures for changes in mechanical properties and changes in physical properties, respectively. However, the geopolymer mortars lost around 60% of strength at 800 °C which is the final temperature.

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1. Introduction

Recycling industrial waste to obtain new materials such as concrete or mortar seems to be one of the best solutions to preserve the ecology. Researchers are looking for binders consisting mainly of post-process waste that would provide alternatives to cement, and are making efforts to efficiently use this type of waste, using it to produce new, safe building materials, which include geopolymers based on active alkali-activated aluminosilicates [1]. The types of solid aluminosilicate base materials could be divided into natural materials such as such as kaolin and metakaolin [2] or industrial by-products such as fly ash and slag [3].

Annual production of crude steel was estimated about 1.874 billion metric tonnes produced all over the world [4].Granulated blast furnace slag, a by-product of the raw iron production, is almost exclusively used as a main ingredient of standard cements in Algeria so far. Slag can be classified in two group which is coming from the ferrous (e.g. blast furnace slag, iron steel slag and ferroalloy slag) and non-ferrous metallurgy (e.g. lead, nickel, zinc, cadmium, tin, copper slag) [5]. However, the accumulation of this by-product of the steel production can leads to the environmental pollution plus the imbalanced reuse as a useful materials [6]. Therefore, in order to achieve sustainable development, the valorization of steel slag with appropriate physic-chemical, mechanical and thermal properties raise the interest to study further.

Research works have proven the use of crystalline slag (CS) with other binders, as mentioned below:

Senani et al. [7] has been study the using of crystallized sand slag of blast furnace in the production of ordinary concrete. The

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natural sand is substitute totally or partially by the crystallized sand slag in the composition of concrete. The characterization of these concretes was made based on their mechanical properties: compressive strength, tensile strength as well as durability: capillary, absorption of water and shrinkage. Results show that the percentages of crystallized sand slag on the composition of concrete have an important effect on the mechanical proprieties of concrete. The comparison of different characteristics of the study in this work shows the benefits of use of crystallized sand slag in the composition of concrete compared with ordinary concrete, which confirms the possibility to use the crystallized sand slag in the manufacturing of concrete. The crystallized slag was used as an aggregate in the composition of concrete core of rectangular thin welded steel tubes subjected to axial or eccentric load performed by Ferhoune and Zeghich [8]. The concrete sand slag has not fact object a comprehensive study to identify its different properties.

Ikmal Hakem Aziz et al. [9] characterized the analysis of alkali-activated steel slag. The combination of sodium hydroxide solution of 15 mol concentration and sodium silicate was used as an alkaline activator. The ratio between steel slag and alkaline liquid was fixed at 3.31 for all mixtures. Ambient curing (20 ℃ – 25 ℃) are used throughout the experiment. Compressive strength shows the alkali-activated steel slag presented high strength at 14 days curing which is 21.56 MPa. In comparison, the alkali activated steel slag had better strength than 50/50 Fe/SS alkali-activated slag which only achieved 16.75 MPa. Result obtained shows that alkali-activated steel slag had better water absorption than 50/50 Fe/SS alkali-activated slag at 7 days curing.

The fresh and rheological properties of alkali mortars activated by blast furnace slag (BFS) were investigated by Markssuel et al. [10]. The results obtained permitted understanding that mortars containing 2.5 to 7.5% sodium present a rheological behavior similar to cementitious mortars by the Bingham model. In turn, the activated alkali mortars containing 10 to 15% sodium showed a very significant change in the properties of dynamic viscosity, which is associated with a change in the type of model, starting to behave similar to the Herschel–Bulkley model. Evaluating the properties of incorporated air and water retention, it appears that mortars containing12.5% and 15% sodium do not have compatible properties, which is related to the occupation of sodium ions in the interstices of the material.

Recently, we have seen growing interest in geopolymer binders owing to their favourable mechanical properties and durability, low cost of manufacturing and high resistance to chemical agents as well as to high temperature [11]. Thanks to these properties, geopolymer materials may provide an interesting alternative to traditional cementitious binders.

During the heating of geopolymers, the volume of aggregate increases and the cementitious binder shrinks, which results in a significant loss in material strength. Differences in coefficients of thermal expansion between aggregate and cement paste cause damage to composites under elevated temperature conditions. The extent of damage depends on the coefficient of thermal expansion of the aggregate used and on the properties of the cement paste such as the amount of shrinkage and its ability to absorb the resulting strains [11,12].

Ren Junru et al. [13] provides experimental data of geopolymer concrete manufactured with granulated blast furnace slag (GBFS) and fly ash after high temperature exposures of 400 °C, 600 °C, 800 °C and 1 000 °C. Residual compressive strength and splitting strength, as well as the effects of standing time were examined and compared with equivalent OPC concrete findings. The results revealed that both kinds of strength improved about 14% and 9% after being exposed to 400 °C, and the reduction was less than OPC concrete. Additionally, the residual compressive strength after different exposures evolved variously with prolonging of standing time. Furthermore, researchers Wang et al. [14] studied the effect of elevated curing temperature on the compressive strength of high-volume slag cement, indicating that the activity of ground iron and steel slag is more sensitive to the increase in curing temperature than that of OPC. The effect of high-temperature exposure on the behavior of slag-blended cement materials has been investigated scientifically [15] It has been reported that, concrete comprising granulated blast-furnace slag (GGBFS) cement exhibits an earlier strength development under elevated curing temperature owing to the temperature-dependent properties of slag cement.

A Few studies have been made on the characterization of this geopolymer; for this, we conducted a comparative study between mortar containing crystallized sand slag (named in this paper mortar sand slag) and reference mortar. In this work, we have characterized the different mechanical proprieties and study the effect of high temperatures and crystalline slag on the mechanical behavior of geopolymers mortars, and compared theme to the performance of ordinary mortar.

2. Materials and methods

2.1. Materials

Geopolymer mixtures were prepared from granulated slag powder and crystalline slag (CS) sand as aluminosilicate precursors, and modified sodium water glass was used as an alkaline activator. The characteristics of all materials used are shown below:

Granulated Slag) GS): Fillers of granulated slag are obtained by milling the blast furnace slag of El-Hajar to a specific surface area of 5000 cm^2/g. This surface is larger than the specific surface of cement. The slag of El-Hadjar has the advantage of being rather acid (the CaO/SiO_2 report/ratio varies within the limits of 0.95 to 1.04); it is relatively stable.

Crystalline slags sand (CS): (0/5 mm) from blast furnace of the El Hadjar steel complex, Algeria.

Dune Sable (DS): The sand used was dune sand with particles ranging from 0.08 mm to 5 mm in size. The natural sand was taken from Boussâada, Algeria. The granulometric study is performed according to the European standard NF EN 933-1 [16]. The mineralogical composition determined by X-ray diffraction shows that the siliceous sand dune is more than 95% of quartz and calcite traces. The results are shown in Fig. 1.

Binary sand mixtures: The natural and manufactured fine aggregates used in this study were DS (dune sand) and CS (crystalline slags sand). Eight series of binary fine aggregate mixtures and one reference control mixture (100% DS) were prepared. The characteristics of binary sand mixtures are given in Table 1 and designated as: Mix (0%CS + 100%DS), Mix (30%CS + 70%DS), Mix (40%CS

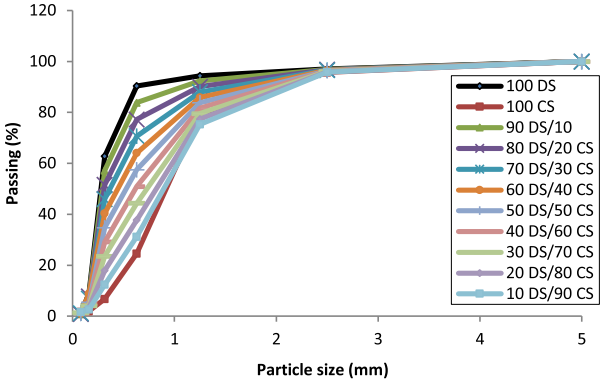

Fig 1. Particle size distribution curve of the crystalline and dune sands studied.

Table 1
Physical properties of the mixed crystalline slags and dune sands.

Physical properties	Absolute density (g/cm^3)	Apparent density (g/cm^3)	Porosity (%)	Compactness (%)
100 DS	2.53	1.43	43.48	57.52
100 CS	1.88	1.18	37.23	62.77
90DS/10CS	2.57	1.46	43.19	56.81
80DS/20 CS	2.40	1.44	40	60
70DS/30 CS	2.40	1.44	40	60
60DS/40 CS	2.31	1.41	38.96	61.04
50DS/50 CS	2.28	1.36	40.36	59.64
40DS/60 CS	2.35	1.35	42.98	57.02
30DS/70 CS	2.28	1.28	43.86	56.14
20DS/80 CS	2.22	1.24	44.14	55.86
10DS/90 CS	2.25	1.23	45.33	54.67

+ 60%DS), Mix (50%CS + 50%DS), Mix (60%CS + 40%DS) , Mix (70% CS + 30%DS), Mix (80%CS + 20%DS) and Mix(90%CS + 40%DS). The sieve analysis of binary sand mixtures is shown in Fig. 1 and their physical properties are summarized in Table 1.

In order to obtain a solid and resistant mortar, it is necessary to take care of its basic components by correcting the grain distribution, as well as reducing the porosity by replacing part of the SD with different percentages of CS (see the table 1).

The alkaline activator solution: The alkaline activator used in this study was a combination of sodium silicate (Na_2SiO_3) and NaOH. The NaOH was in pellet form with 100.5% purity and 10 M solution was fixed. NaOH solution was prepared by dissolving the pellets in one liter of distilled water in a volumetric flask and stirred it. The Na_2SiO_3 consisted of 10.6% Na_2O, 26.5% SiO_2, and 62.9% H_2O (with a SiO_2/Na_2O weight ratio of 3 and a specific gravity of 1.39 at 20 °C. The properties of the materials used are shown in Table 2.

2.2. Preparation of mortar samples

To develop the alkali-activated binders, granulated Slags powder and crystalline slags materials were mixed with an alkaline solution. The activating solution was prepared by dissolving sodium hydroxide pellets with water and a sodium silicate solution. A crystalline slag (CS) was used at proportions of sand dune CS: DS of 0:100 and 40:60 by weight. Therefore, these mortars were designed as M (100SD) and M (60 CS /40 DS).

Geopolymer mortar mixes were prepared after replacing cement totally by the same amount of granulated slags powder and activating it by alkaline solutions of sodium hydroxide and sodium silicate. This process has repeated itself for mixtures with 100 DS [M (100 DS)] and for mixture 40% CS + 60% DS [M (60DS/40CS)].

Geopolymer mortars were prepared using 1: 3 proportions of sand. For the mixing procedure, NaOH solution, base water and binder of filler were first mixed for 5 min in a pan mixer. Sand was then added and mixed for 5 min. Finally, sodium silicate solution was included and mixed for another 5 min. This mixing procedure was test and found to produce high strength geopolymer. Subsequent to mixing, were molded in $2.5 \times 2.5 \times 10\ cm^3$ prismatic, which were then subjected to a precured treatment that consisted of subjecting them to a relative humidity of 100% , with a temperature of 40 °C and for a period of 24 h, in order to accelerate the activation process of mortar. After curing at an elevated temperature, the mortars were put in laboratory to cool down and demoulded the next day and kept in 25 °C room until testing age. The specimens were tested at the age of 28 days. The reported results were the average of three samples.

Strengt test: The mortar compressive strengths test were determined using prismatic specimens of square section $2.5 \times 2.5\ cm^2$ and length 10 cm in accordance with EN 196-1 [17]. The purpose of the conducted research was to compare the strength characteristics of mortar based on geopolymer binder after heating specimens in a furnace at a rate of 1 °C/min to 200, 400, 600 and 800 °C and then cooling them down to room temperature. All tests were conducted after 28 days of curing. Three specimens were tested for each heating temperature.

Table 2
Chemical composition of Granulated Slag) GS), Crystalline Slag (GS) and Dune Sand (SD).

Compositions (%)	Granulated Slags) GS)	Crystalline Slags) CS)	Dune sand (DS)
SiO_2	36.03	34.99	88.25
CaO	41.97	45.78	2.94
Al_2O_3	11.35	9.79	00.71
Fe_2O_3	0.76	0.67	00.96
MgO	7.32	3.92	00.17
SO_3	1.89	0.38	0.08
MnO	–	2.47	–
Na_2O	0.16	0.29	00.01
K_2O	0.45	0.86	00.30
TiO_2	–	0.34	–
PAF	–	0.50	–

3. Results and discussion

3.1. Mass loss test

Based on the visual inspection of specimens, the geopolymer mortar exhibited significantly better thermal resistance. On the fig. 2, changes in the color of mortars based on geopolymer as a result of heat-ing are shown. As a result of these color changes, it can be absolutely appraised the range of temperature values. It can be seen that color changes happened much more in the concrete samples exposed to 800 °C than the ones to 200 °C and 400° C.

The surface of specimens has been observed after exposed to different temperature levels and cooled to ambient temperature. Mortar 100DS and 60DS/40CS did not detect any visible cracking at higher exposure temperature of 600 °C.

The mass losses of exposed concrete, mortar and paste specimens were tested before the mechanical test. The mass loss was determined by weighting the exposed specimens before and after heating. At least three specimens were tested for each exposure condition.

Fig. 3 shows the evolution of mass loss during the heating cycle of the studied specimens.

The mass of mortars decreases with increasing temperature due to loss of moisture. The preservation in mass of mortar at elevated temperatures is highly influenced by the type of aggregate [18]. Here are some facts for this.

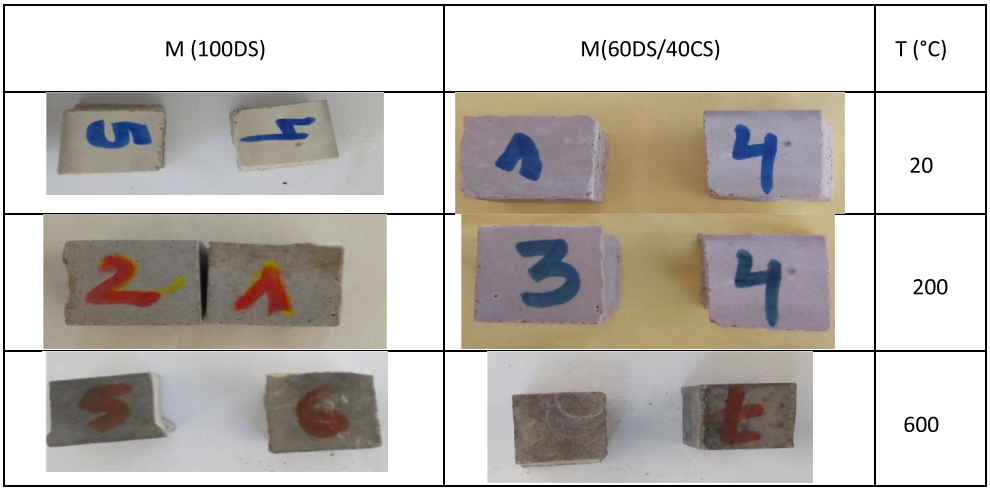

Fig 2. Colour change of heated mortars.

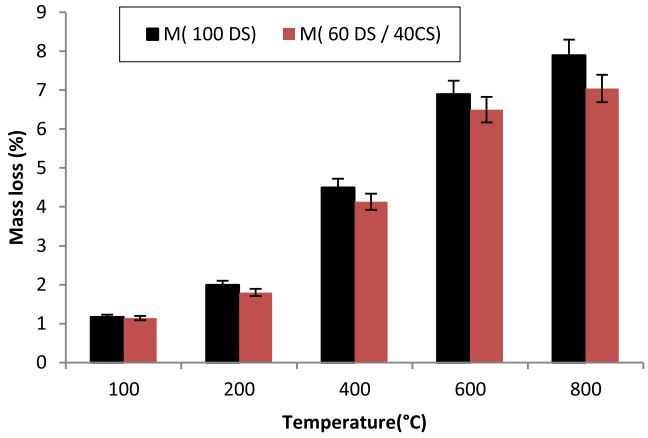

Fig 3. Evolution of mass loss related to temperature.

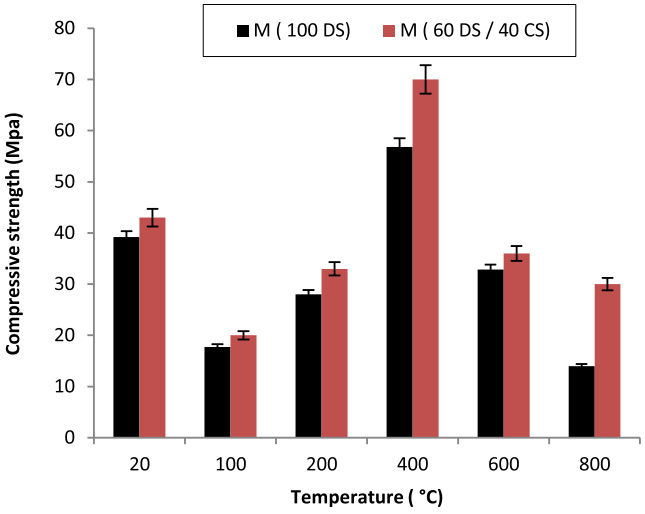

Fig 4. Compressive strength after cooling relative to the initial strength.

Before 200 °C, the mass change is very low. The weight loss in this temperature range is generally the leaking water pores of the mortar geopolymer [19].

Between 200 and 600 °C, a high loss of mass for all geopolymer mortars tested. The two mortars lost almost 4% to 5% of its original mass. Maximum of water in each mortar evaporated during heating between 200 and 400 °C.

The increase is almost linear up to a temperature of 600 °C. This is due to the evaporation of water and the progressive dehydration of CSH gel.

On the other hand, after the material had been heated to 800 °C, an increase in mass loss was observed again, probably resulting from the sintering of mineral ingredients.

The mass loss is minimal for M(60ds/40CS) mortar up to about 600 °C. However, the type of aggregate has significant influence on mass loss in concretes beyond 800 °C. In the case of crystalline slags mortars M (60ds/40CS), mass loss is little significant above 600 °C compared with the dune sand M(100DS). This higher percentage of mass loss in mortar is attributed to dissociation of dolomite in carbonate aggregate at around 600 °C [18].

3.2. Compressive strength

Compressive strength of the slag mortars with the four different under high temperature conditions at 28 days are shown in Fig. 4.

At temperature room, the compressive strength of the geopolymer mortar was found to increase with the increase in the amount of CS in the mixes. This increase can be explained by:

The compressive strength is strongly affected by the amount of CS in the mixes. Since CS contains a high amount of calcium, C-S-H gel was formed and thus contributed to the strength development of geopolymer specimens [20,21].

Another factor that contributes to the strength development is the concentration of the alkali solution [22]. According to other research, when molarity increases the compressive strength also increases [21].

Between 100 and 400 °C, it can be seen that the compressive strength of the geopolymer mortar increases after exposure to elevated temperatures of 100–400 °C. The M(60DS/40CS) exposed to elevated temperatures of 100, 200 and 400 °C attained compressive strengths of 13%, 18% and 23%, respectively, as compared to the compressive strength of the unexposed M (100DS) (Fig. 4). The strength-gaining of the exposed GS-based geopolymers to elevated temperatures of 100 – 400 °C has been already reported in previous investigations [14,15].

After 400 °C, the compressive strength of the M (100DS) is observed to decrease gradually after being exposed to an elevated temperature of 400 °C, and further up to 800 °C (Fig. 4). The

strength losses of 11% and 50% respectively, are reported for the M (60DS/40CS) exposed to 600 and 800 °C which is the result of the visible cracking of the specimen, the dehydration of binder paste and the decomposition of portlandite. The compressive strength of 100 DS mortar as a result of heating exhibited a quasi-linear decrease within the entire tested temperature range, which was the result of the C-S-H phase dehydration process, portlandite decomposition and the cracking, which was clearly visible on the surface of the specimens heated to 600 °C and 800 °C. In the case of the geopolymer mortar (M (60DS/40CS), an increase in compressive strength was observed at 200 °C. This increase is most probably caused by the progressive geopolymerisation process, which results in the strength increase of the material. Further geopolymer heating to 400 °C and 600 °C caused a progressive decrease in strength compared to the initial value recorded at 20 °C.

4. Conclusion

From this study, one can conclude, the resistance of mineral composites to high temperature depends on many factors. In geopolymer mortars, the paste becomes dehydrated and shrinks while aggregate volume increases.

- The compressive strength of geopolymer mortars increases after heating to 200 °C, reaching 40% of the initial value, which is most probably the result of the continued polymerisation process;
- Heating to 600 °C and 800 °C results in compressive strength decreasing by 11% and 50%, respectively, relative to the initial values recorded at 20 °C;
- As concerns the appearance of mortar after heating, geopolymer materials with crystalline slag exhibit greater resistance to high temperature.
- The geopolymer mortars tested formulated with 40SC /60 DS showed greater absolute strength after being heated to 400 °C and 800 °C compared to mortars formulated by 100DS.
- This research one demonstrated that geopolymers with crystalline slag activated exhibit better thermal resistance than geopolymer base- dune sand, which loses its mechanical properties when heated to a temperature higher than 800 °C.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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