A Comparative Study of Metakaolin/Slag-Based Geopolymer Mortars Incorporating Natural and Recycled Sands

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Abstract

Great efforts are being made to minimize the negative impact of the Portland cement industry on the environment by using industrial by-products during the manufacture of clinker or by the partial replacement of cement during the preparation of concrete. However, the carbon footprint remains relatively high in addition to the large consumption of natural resources such as sand and other aggregates. A solution to these problems is to completely replace Portland cement with a new generation of mineral binders, commonly known as geopolymers, which have properties similar to those of Portland cement. These binders can be obtained by the alkali-activation of siliceous or aluminosilicate materials. This study aims to develop pozzolanic type binders at room temperature (20°C) from the alkali-activation of aluminosilicate materials based on metakaolin and blast furnace slag at different percentages. Different activators were employed, including solid (NaOH) and liquid (Na2SiO3·nH2O). The optimal mixtures were used for making mortars based on natural sand (NS) and concrete recycled sand (CRS). A comparative experimental study of the physical, mechanical, and microstructural characteristics of the two types of mortars was conducted. Cement mixtures with a high amount of slag and an association of sodium hydroxide and sodium silicate gave the best physico-mechanical properties. A drop in the compressive strength of mortars prepared with CRS was observed after 365 days, but it was still higher than those with NS. The obtained results show the possibility of designing an eco-friendly CRS-based geopolymer mortar that is more resistant than NS-based mortar with a homogeneous and integrated microstructure.

Keywords: Geopolymer; Metakaolin; Slag; Alkali-activation; Recycled Sand; Mortar; Strength.

1. Introduction

Global concrete production stands at over six billion cubic meters per year, or nearly one cubic meter used by each inhabitant each year, making it the most consumed manufactured material globally. It is worth indicating that worldwide, the amount of carbon dioxide (CO2) released by the cement industry (half from calcination of CaCO3 and the other half from fuel) is estimated at one billion tonnes. In addition, according to the International Energy Agency and World Energy Outlook [1] report, cement pollutes more than all the trucks in the world. Indeed, its manufacture produces 7% of global carbon dioxide emissions. Cement production is considered the third-largest emitter of carbon dioxide on the planet. Other important environmental impacts should also be mentioned; those are linked to the production of cement...
and of concrete, where there is a daily significant consumption of natural resources and raw materials in addition to energy. It should also be noted that 50% of the materials extracted from the Earth's crust are intended for the production of construction materials, with a high production of waste [2].

This situation must be taken seriously because the need to build is becoming increasingly important and indispensable for the development of several human activities. Therefore, it is essential and urgent today to develop materials that emit little or very little carbon dioxide (CO₂) and at the same time consume fewer natural resources. For this, it was decided to use industrial waste as a binder and construction and demolition waste as aggregate in order to remedy this problem.

In 1988, Davidovits conducted a study to show that research carried out in the 1970s on organic polymers can be directed today towards new ranges of binders, commonly known as geopolymer cements. Moreover, other studies, carried out in 1994, indicated that, for the emission of the same quantity of CO₂, geopolymer technology would make it possible to produce five to ten times more cement than the Portland cement technology, for the same financial investment and lower energy consumption [3]. Therefore, it can be stated that geopolymers constitute an accurate and reliable alternative to Portland cement, which incorporates limestone, clay, and even some industrial wastes such as fly ash, blast furnace slag, and others [4]. On the other hand, using construction and demolition wastes, which generally include inert mineral materials (concrete, bricks, tiles, ceramics, etc.), as aggregates for the manufacturing of mortar and concrete, allows minimizing the already high enough consumption of natural resources. In this regard, Kurad et al. [5] reported that the increase in global demand for aggregates is estimated at an annual rate of around 5.2%.

Furthermore, it would be interesting to know that geopolymers are aluminosilicate mineral materials made up of cross-linked chains of the Si-O-Al-O type. These materials are obtained by activating an aluminosilicate source using a strongly alkaline solution [6]. Their properties strongly depend on the synthesis parameters, such as those of the raw materials (aluminosilicate source, activators, etc.), as well as on the proportions of the mixture and on the curing conditions. It is worth indicating that, over the past few years, several geopolymer formulations entirely based on fly ash [7], slag [8] or metakaolin [9] have been proposed in the literature. However, it should be noted that the fly ash-based geopolymer requires a specific hardening temperature to achieve the desired final mechanical performance [7, 10, 11]. This makes their application in the construction field quite complicated and expensive from an energy point of view. In contrast, slag-based geopolymers have a quick setting time [8], which, in general, is rather disadvantageous. It is essential to add also that these last two formulations generally lead to an unstable structure where the cations are not chemically fixed. This would allow these cations to move freely and generate free alkalinity (NaOH or KOH), leading to concrete’s efflorescence problems [12, 13]. However, metakaolin-based geopolymers were found to have strong adhesion that affects the mixture's workability and compaction [14]. Furthermore, it was ascertained that a geopolymer made of two aluminosilicate materials, such as slag and metakaolin, seems to have a high efficiency that can overcome these problems [14].

Regarding Huseien et al. [15], they studied the effect of replacing metakaolin with granulated blast furnace slag on the properties of a geopolymer mortar. They then concluded that the inclusion of metakaolin up to the level of 15% would improve the mechanical strength of the manufactured mortar. Furthermore, strong alkali-activators in the mixture are essential for the geopolymerization reaction. It is worth mentioning that the main function of alkali-activators is to accelerate the dissolution of the aluminosilicate source, which should promote the formation of stable hydrates with low solubility and the emergence of a compact structure. Additionally, the physical and chemical properties of the activators play an essential role in the behaviour of the activated material.

The most commonly used activators are hydroxides or alkali salts. Also, the most widely employed and the most economically advantageous among these are NaOH, Na₂CO₃, Na₂O·nSiO₂ and Na₂SO₄. It should be noted that certain potassium compounds (KOH, K₂OnSiO₂, etc.) have been used in some laboratory studies; however, their industrial applications remain very limited due to the insufficient availability and costs of these compounds.

Sodium silicate solutions (Na₂O·nSiO₂), commonly known as water glass, are among the most widely used chemicals in the alkali-activation of minerals based on green low-CO₂ cement [16]. Sodium silicate solutions have a complex molecular structure and present a phase behaviour that is highly dependent on the pH [17]. Despite several years of hard research, some questions remain to be addressed concerning the configuration of the molecular species of these solutions. In this regard, researchers should tackle these questions to obtain enough clarification on the best conditions for the different applications of these solutions. In particular, for higher pH values, the structure and behaviour of these solutions are not well understood yet [17]. Additionally, the addition of sodium hydroxide (NaOH) to water glass (sodium silicate solution) decreases the (SiO₂/Na₂O) ratio (molar ratio or weight ratio). This ratio, known as the water glass (n) modulus, can be used to determine several physical and chemical properties, such as the pH and viscosity of the solution. An earlier study on water glass by Yang et al. [18], showed that the viscosity depends significantly on the
(n) modulus, and increases when the solution becomes either more siliceous or alkaline. Moreover, it was found that the alkali-activation of finely ground blast furnace slag is highly dependent on the modulus (n) of water glass [19-21].

It is worth recalling that the use of recycled concrete aggregates in geopolymer materials, in the form of aggregates, has been thoroughly investigated in the last years, and encouraging results have been recorded and reported [22, 23]. Also, geopolymers have demonstrated remarkable flexibility in using many types of waste and different industrial by-products [24, 25].

Furthermore, some authors have succeeded in developing alkali-activated mortars or concretes that contain high amounts of recycled aggregates that are used either as aggregates [26-28] or as binding powders [29-32]. Note that the compressive strength of the synthetic mixtures reached 40 MPa in both preceding cases. These same researchers found out that the compressive strength may be influenced by several parameters, such as the precursor ratio, the type and molarity of activator, and the cure temperature. On the other hand, Panizza et al. [28] conducted a study on geopolymers incorporating recycled aggregates and found that the strength gains increased as the curing temperature went up. However, curing temperature is generally not controlled when casting mortars and concretes for routine civil engineering projects, due to financial and technical constraints. Besides, rising temperature leads to a decrease in the open time, which is a disadvantage.

It was also revealed that recycled aggregates are characterized by high absorption, which affects the formulation and preparation of mixtures [33]. To overcome this problem, Mastali et al. [34] replaced the additional amount of water (absorbed by the aggregates during mixing) with an equivalent quantity of the alkali-activator, which resulted in a slight decrease in the fluidity of the mixture, with a limited aggregate segregation and a noticeable improvement in strength. For their part, Frankovic et al. [35] indicated that the adding short plastic fibres improves the behaviour of concrete towards shrinkage-induced cracks.

Within this context, the following research aims to obtain more environmentally friendly materials than those based on Portland cement and natural aggregates by making geopolymeric binders. The optimal binder composition was obtained from the assessment of mixtures of metakaolin and slag cement pastes. These mixtures were activated using two alkali-activators: sodium hydroxide and sodium silicate (separately and mixed). The optimal geopolymer mixture obtained was then used to study the possibility of preparing mortars with concrete recycled sand at room temperature (20°C) while maintaining satisfying physomechanical properties. The methodology used in this work is summarized in the flowchart presented in Figure 1.

![Flowchart of research methodology](attachment:flowchart.png)
2. Used Materials

2.1. Metakaolin

Metakaolin (MK) is obtained after a heat treatment of two local kaolins, KT01 and KT03 (of El-Milia deposit SOALKA is located in the wilaya of Jijel in the North – East of Algeria, 17 km north of the Daira of El-Milia whose reserves of the deposit amount to more than 14,000,000 tons. Figure 2), at a temperature of 650 °C, for five hours. The chemical, mineralogical, and particle size characteristics were obtained using the X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) analytical techniques, in addition to a particle size analysis that was carried out at LAFAERGE cement plant in the Wilaya M’Sila (Algeria).

Figure 2. El-Milia deposit SOALKA

2.2. Granulated Blast Furnace Slag

The granulated blast furnace slag (GBFS) is a by-product of cast iron production. The slag used in this study was brought from the Steel Complex of El-Hadjar in the Wilaya of Annaba (Northeastern Algeria); it has a glassy structure and a low hydraulic power, with a vitrification rate of 97%. Its hydraulicity is mainly attributed to the water quench treatment. The slag is in the form of light grey spherical grains. Figure 3-a illustrates the X-ray diffractogram of the granulated slag. The slag, a predominantly glassy material, possesses a small amount of crystallized phases such as calcite and metallic iron. The diffractograms of the two metakaolins MK1 and MK3 and that of slag are shown in Figure 3. Their chemical, mineralogical, particle size and physical characteristics are summarized in Table 1.
Figure 3. X-Ray diffractograms of: (a) granulated slag, (b) MK01, (c) MK03

Table 1. Characteristics of used materials: MK01, MK03 and granulated blast furnace slag (GBFS)

| Chemical analysis | Percent (%) by weight | MK01 | MK03 | GBFS |
|-------------------|-----------------------|------|------|------|
| Al₂O₃              | 20.72                 | 37.52| 10.98|
| CaO               | 0.53                  | 0.33 | 41.07|
| Fe₂O₃             | 2.81                  | 3.68 | 1.14 |
| K₂O               | 3.30                  | 2.74 | 0.39 |
| MgO               | 0.11                  | 0.15 | 7.73 |
| Na₂O              | 0.27                  | 0.13 | 0.29 |
| SiO₂              | 70.83                 | 45.66| 33.6 |
| SO₃               | 0.03                  | 0.05 | 1.56 |
| Loss on ignition (LOI) | 1.50               | 3.24 | 1.48 |
Mineralogical composition

|          | Calcite | Dolomite | Quartz | Pyrite | Illite | Chlorite | Kaolinite | Alkali phase |
|----------|---------|----------|--------|--------|--------|----------|-----------|--------------|
| Mass %   | 1.91    | 0.55     | 59.12  | 0      | 27.6   | 0        | 1.63      | 96.3         |
|          | 4.11    | 0        | 23.13  | 0      | 54.38  | 0.44     | 9.56      |              |
|          |         |          | 0      |        |        |          | 8.38      |              |

Particle size analysis

|        | 32-45 μ | 45-92 μ | 92-212 μ | > 212 μ |
|--------|---------|---------|----------|---------|
| Passing (%) | 51.9    | 39.4    | 12.3     | 02.5    |
| Density g/cm³ | 1.515    | 1.90      | 1.90    | 1.90     |

Density g/cm³

|        | 2.57    | 1.90    | 2.54    |

Specific surface cm²/g

|        | 5721    | 9850    | 4300    |

2.3. Activators

Two alkaline products are used in this work, with different concentrations:

- Sodium hydroxide (NaOH) with a molarity of 12 mol/L for the preparation of the paste, and 10 and 14 mol/L for the preparation of mortar.
- Sodium silicate Na2SiO3 (WG); its characteristics are given in Table 2.

Table 2. Physical analysis and chemical composition of WG

| Physical analysis | Chemical composition |
|-------------------|----------------------|
| Appearance        | Odour                | Density at 20°C | Na2O % | SiO2 % | (SiO2/Na2O) Ratio | % Concentration | Fe |
| Slightly turbid and colourless | Odourless | 1.515 | 15.40 | 29.24 | 1.90 | 44.64 | < 40 ppm |

2.4. Aggregates

Two types of aggregate were used in this work: the first one is a local wadi natural sand (NS) which is the most used in construction sites, and is characterized by a series particle size (Figure 4), with a high cleanliness rate and a very low absorption capacity; and the second is a recycled sand (RS) obtained after grinding concrete wastes from residual cylindrical test pieces and the one-year-old concrete consisting of Portland cement CEM II/42.5N which has a compressive strength equal to 40 MPa at 28 days.

![Figure 4. Granulometric distribution of natural sand (NS), recycled sand (RS) and corrected recycled sand (CRS)](image)

According to the grain size curve, shown in Figure 4, and the physical characteristics of the used sands, presented in Table 3, the recycled sand (RS) has a low sand equivalent value and high water absorption.
Table 3. Physical characteristics of (NS), (RS) and (CRS)

|         | Sand equivalent (%) | Bulk density (g/cm³) | Specific density (g/cm³) | Fineness modulus (FM) | Absorption (%) |
|---------|----------------------|----------------------|--------------------------|-----------------------|----------------|
| NS      | 78.13                | 1.648                | 2.56                     | 1.22                  | 1.5            |
| RS      | 44.24                | 1.58                 | 2.538                    | 2.69                  | 13             |
| CRS     | 86.29                | 1.34                 | 2.47                     | 2.95                  | 12             |

Therefore, a grain size correction, using a 0.08mm sieve, is required in order to obtain the corrected recycled sand (CRS). The recycled sand (RS) and corrected recycled sand (CRS) sands are shown in Figure 5.

Figure 5. Waste before and after grinding and correction: (a) Recycled sand, (b) Corrected recycled sand

3. Optimization of Mortar Composition

3.1. Preparation of Mixture

To optimize the geopolymer binder used in the composition of the mortar, nine paste mixtures were prepared with different contents of metakaolin, slag and alkaline component, with a solution-to-powder (S/P) ratio equal to 0.40 for MK01 and 0.60 for MK03. These mixtures are reported in Table 4.

Table 4. Mixtures of geopolymer pastes

| Component | A | B | C | D | E | F | G | H | I |
|-----------|---|---|---|---|---|---|---|---|---|
| % MK      | 100| 100| 100| 80| 80| 80| 50| 50| 50|
| % GBFS    | -  | -  | -  | 20| 20| 20| 50| 50| 50|
| % WG      | 100| -  | 80 | 100| - | 80| 100| 80| 50|
| % NaOH    | -  | 100| 20 | - | 100| 20| - | 20| 50|

Afterwards, cubic test specimens of pure paste of dimensions (4x4x4) cm³ (Figure 6) were prepared with the mixtures discussed previously (Table 4), in accordance with the NF EN 196-1 standard. Note that mixing the different compositions was done with the alkaline component (NaOH) diluted in water until the desired molarity was obtained. Then the sodium silicate Na₂SiO₃ (WG) was added. It is worth pointing out that the solutions were prepared in advance, i.e. one day before use, to obtain thermal equilibrium. The specimens were kept moist under plastic wrap, with a cure period of 28 days in order to perform the compressive strength tests.

Figure 6. Cubic specimens of geopolymer paste with different MK contents
3.2. Analysis of the Compressive Strength Results

The compressive strength (Cs) was determined at 28 days, according to the NF EN 196-1 standard. The results are shown in Figures 7-a, and 7-b.

The obtained results show that the mixtures made up of metakaolin (MK01) exhibit higher compressive strengths than those of the mixtures containing metakaolin (MK03), which is mainly attributed to the reactivity of MK01. As for the mixtures containing WG, they showed a greater compressive strength than those containing NaOH. Indeed, the addition of 20% NaOH to the WG solution leads to higher strength (mixtures of pastes F and H) because sodium hydroxide increases the pH of the solution and makes the silicate species that contribute to the formation of the geopolymeric gel more reactive [36].

4. Formulation of Mortars

Nine mortar mixtures were prepared from the paste variants F and H, depending on the content of metakaolin MK01 and slag, and also on the type of sand (NS or CRS), density and pH of the alkali, with a solution-to-powder (S/P) ratio equal to 0.80. These mixtures are reported in Table 5. Furthermore, prismatic test specimens, with dimensions (4x4x16) cm³ of mortar were prepared according to the NF EN 196-1 standard. The mixing and storage conditions are identical to those used for the pastes.

Table 5. Mortar mixtures

| Identification | 1-1NS | 1-2NS | 1-3NS | 2-1NS | 2-2NS | 2-3NS | 3-1CRS | 3-2CRS | 3-3CRS |
|----------------|------|------|------|------|------|------|-------|-------|-------|
| % MK (01)      | 80   | 80   | 80   | 50   | 50   | 50   | 50    | 50    | 50    |
| % GBFS         | 20   | 20   | 20   | 50   | 50   | 50   | 50    | 50    | 50    |
| Type of sand   | NS   | NS   | NS   | NS   | NS   | NS   | CRS   | CRS   | CRS   |
| Molarity of NaOH within the solution (80%WG+20%NaOH) (Mol/L) | 10 | 12 | 14 | 10 | 12 | 14 | 10 | 12 | 14 |
| Density of the alkali | 1.43 | 1.44 | 1.45 | 1.43 | 1.44 | 1.45 | 1.43 | 1.44 | 1.45 |
| pH of the alkali | 11.97 | 12.16 | 12.26 | 11.97 | 12.16 | 12.26 | 11.97 | 12.16 | 12.26 |

5. Experimental Methods

Several tests were carried out on mortars in the fresh state (setting) and the hardened state to determine the porosity accessible to water, absorption, density, and mechanical strength, and perform a microstructural analysis, at 28 and 365 days.

5.1. Setting Time Test

The Vicat apparatus was used to determine the setting time of mortars, following the NF P 15-431 standard. The 1.13 mm needle penetrating the mortar was subjected to 1000g. The principle of this test consists of following the needle's penetration in mortar over time until it stops sinking under the effect of the applied load. The needle stops at a distance d from the bottom of the mould greater than 2.5 mm. This is known as the initial setting time. Then, to determine the end of setting, the mould must be turned over so that the end-of-setting test can be carried out on the face that was initially in contact with the base plate. Hence, the needle penetration, which must not exceed 2.5mm, is then estimated.
5.2. Porosity Accessible to Water

The method adopted to measure the porosity is very simple. This method allows measuring the quantity of water that can circulate within the network of interconnected pores inside the material. For this, a series of cubic test specimens of dimensions (4×4×4) cm³ were used. The operating mode followed is that recommended by Ollivier [37]. It requires three weighings:

- The mass of the saturated sample (m_sat).
- The hydrostatic mass (m_hyd) which corresponds to the sample’s mass while in water.
- The dry mass (m_dry) of the sample corresponding to its mass after stabilization inside the oven.

Afterwards, the porosity n of the sample is then calculated using the following formula:

\[ n = \frac{m_{sat} - m_{dry}}{m_{sat} - m_{hyd}} \] (1)

5.3. Absorption

Test pieces of dimensions (4×4×4) cm³ were prepared with all the mixtures and then dried at 105 °C until mass stabilization (m_dry) after immersion in water for 24 hours. Next, the mass of the saturated test pieces (m_sat) was estimated. Finally, the water absorption coefficient was determined using the following formula:

\[ Abs \ (\%) = \frac{m_{sat} - m_{dry}}{m_{dry}} \times 100 \] (2)

5.4. Density

The density of the test specimens of size (4×4×16) cm³, which were made with the different mixtures, was calculated after 28 and 365 days of hardening, using the following expression:

\[ \rho = \frac{m}{V} \] (3)

where \( \rho \) is the density, \( m \) is the mass of the specimen (g) and \( V \) is its volume (cm³).

5.5. Mechanical Strength

It is worth specifying that the mechanical performances of the different geopolymer mixtures were measured using compression and flexural tensile tests, following the EN 196-1 standard.

Furthermore, prismatic specimens of dimensions (4×4×16) cm³ were used to determine the flexural tensile strength (three points). Finally, the resulting half pieces were used to determine the compressive strength.

6. Results and Discussion

6.1. Setting Time

Table 6 summarizes the results obtained. It explicitly shows that the characteristic initial and final setting times of the mortars made with natural sand (NS) and recycled sand (RS) are different. One can also note that the initial setting time recorded for the mortar (2-3NS) is the longest. In contrast, the mortar (3-2CRS) shows the shortest setting time, which can be explained by the fact that the recycled sand possesses a specific capacity to quickly capture the alkaline solution contained in the paste, thus modifying the (S/P) ratio and the rheological properties of fresh mortar. Additionally, hydrated cement adhering to the recycled sand grains can accelerate the geopolymerization process. It should also be mentioned that the (S/P) ratio has a disadvantageous effect on the setting time of mortars containing natural sand.

| Mixtures  | 1-1NS | 1-2NS | 1-3NS | 2-1NS | 2-2NS | 2-3NS | 3-1CRS | 3-2CRS | 3-3CRS |
|-----------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Setting time (min) |       |       |       |       |       |       |       |       |       |
| Beginning | -     | -     | -     | 438   | 165   | 700   | 100   | 65    | 122   |
| End       | -     | -     | -     | 543   | 240   | 850   | 120   | 99    | 135   |

The initial setting time of the mortar under consideration is the fastest when a solution of pH equal to 12.16, with medium viscosity, is used. It becomes slower for pH values above and below that value. Increasing the pH value leads to reduced solubility of calcium ions, while the reverse occurs for silicates [38, 39], which affects the initial phase. This is known as the dissolution phase of the hydration process of green cementitious materials activated by alkalis. During
the dissolution phase, the bonds of the activated slag break out, and ions, such as calcium ions, migrate out of the slag into the liquid phase surrounding the activated slag particles [40]. A smaller size of the silicate structural units results in a shorter initial setting time.

The initial setting time becomes longer when the alkaline solution is either more siliceous or more alkaline, that is to say, for lower or higher pH values. At the same time, the solubility of calcium ions in slag decreased due to the increase in pH [38]. Therefore, only a few dissolved calcium ions will be available for the pozzolanic reaction. Additionally, the number of negatively charged sites becomes smaller, and, as expected, the initial setting time becomes longer, as shown in Table 6.

The sting time results of all the CRS-based mixtures are better than those obtained by Huseien et al. [15] and Panizza et al. [28]. In addition, the mortars (3-1CRS) and (3-3CRS) initial setting times are comparable to conventional Portland cement.

6.2. Porosity Accessible to Water and Absorption

Figure 8 shows that mortars made with recycled sand (CRS) have a higher porosity than those made with natural sand (NS). Additionally, it was shown that the more angular shape and the lower compactness of the recycled aggregate induce a low compactness of the granular mixture, which leads to a higher number of voids. This is not the case for natural sand, which has a rather rounded shape.

![Figure 8. Porosity and absorption of different mortar mixtures at 28 days](image)

On the other hand, the selected (S/P) ratio is relatively high, which contributes to forming an extensive network of interconnected pores inside the geopolymer matrix. Moreover, the polymerization process releases excess water during polycondensation. The evaporation of this water leaves some open channels. It is worth indicating that mixtures containing 80% of metakaolin exhibit lower porosity values than those containing only 50% of metakaolin. It should also be noted that the density and pH of the alkaline solution have little effect on the porosity. The average porosity obtained was estimated at 16.48%, with a 0.7% standard deviation. This value is close to that found by Panizza et al. (10-15%) [28].

Regarding the absorption, it is mainly influenced by the nature of sand and activator used, and the level of metakaolin employed. A maximum absorption value, of the order of 2.64%, was observed for the mixture (3-1CRS) because the absorption rate of recycled sand is greater than that of natural sand. The used CRS absorption is low, compared to that used by Hasnaoui et al. [52]. This may be explained by the difference in the nature of the original aggregates in the concrete wastes used in each study. Aggregates with a high (Ca/Si) ratio, such as limestone, are characterized with high water absorption [41].

6.3. Density

The results obtained indicate that the density of the studied mortars varies between 2.05 and 2.18 (g/cm³), after 28 days of hardening (Figure 9). However, after 365 days, it exhibits a decrease due to the water departure from the material. This density drop is more pronounced for mortars incorporating recycled sand (CRS); it is in the order of 4.2% for mortar (3-1CRS).

It is worth emphasizing that the pH of the solution seems to affect the density, for both types of mortar. Additionally, it was observed that the density increases as the pH goes up. In this case, the solution becomes denser. Furthermore, mortars based on recycled sand exhibit a slight density increase compared to those based on natural sand (NS), although the density of recycled sand is smaller than that of natural sand. This result can be explained by the fact that the pores of the recycled sand are replaced by the solid material (geopolymer paste), which leads to the increase of the density.
Figure 9. Density of the different mortar mixtures at 28 and 365 days

The porosity and absorption values obtained agree with the results found for the density. The highest porosity (19.44%) was recorded for the mortar (3-1CRS), which has the lowest density. These results are in agreement with those reported in the studies conducted on recycled sands by Nixon [33] and Hansen [42]. Note that the high porosity of geopolymer mortar prepared with recycled sand (RS) is mainly due to the quality of the used recycled aggregates and not to shrinkage cracking since all mixtures were kept under a plastic film to avoid shrinkage.

6.4. Mechanical Resistance to Compression and Traction

The compressive strength (Cs) and flexural tensile strength (Fs) of the various mortars was estimated after 7, 28 and 365 days of hardening under a plastic film. Figure 10 shows the results found.

Figure 10. Flexural strength and compressive strength for the different mixtures: (a) Flexion, (b) Compression, at 7, 28 and 365 days

The results shown in Figure 10 indicates that the strength is higher for mortars containing corrected recycled sand, with a percentage improvement of more than 60%, i.e. from 3.86 to 6.41 MPa, for the tensile strength at 7 days, and more than 200%, i.e. from 9.62 to 37.06 MPa, for the compressive strength at the same age. Furthermore, an increase in strength was observed between 7 and 28 days for mixtures based on natural sand (NS) and containing 20% of granulated blast furnace slag (GBFS). Note also that using higher percentages of slag (50%) improves the strength of mortars because the chemical composition of GBFS is close to that of ordinary Portland cement (PC). It is worth indicating that the main activator of blast furnace slag is calcium alumino-silicate hydrate (CASH) gel, that is similar to the gel produced during the ordinary hydration of Portland cement, but with a lower (Ca/Si) ratio, which is usually between 0.9 and 1.2 [43, 44]. When the activator used is hydrated sodium silicate (water glass), the silicon in the solution causes a drop in the (Ca/Si) ratio to 0.8, which promotes the formation of medium or long chains, and structures comparable to that of tobermorite, thus giving a final product with high strength [45].

On the other hand, increasing the pH of the solution makes the silicate species, which play an important role in the formation of the geopolymeric gel, more reactive. These findings are in good agreement with the observations of Shi et al [16]. According to Runzhang et al [46], only solutions with pH values above 12 can promote the solubility of the slag
constituents, and therefore can encourage the formation of hydrates, which increases in the mechanical strength. Several authors [33, 47-50] suggested that using fine recycled sand in the formulation of mortar or geopolymer concrete influences the strength of the material. It should also be noted that the increase in strength observed in this work is due to the presence of the corrected recycled sand, which renders its granulometry more suitable for this type of mortar. One can therefore say that the results obtained are acceptable compared with those reported in works where the authors used the pre-saturation technique of recycled sand to improve the rheological performance of concrete or that of ordinary mortar incorporating recycled sand [51]. Hasnaoui et al. [52] also adopted this technique in their study of a recycled sand-based geopolymer. Moreover, the decrease in strength of recycled sand mortars after one year of curing is attributed to durability problems resulting from the increase in the percentage of pores after the departure of a certain amount of water, which decreases the mechanical strength [53].

With regard to the interaction between the geopolymer paste and recycled sand (RS), Koushkbaghi et al [48] studied the interfacial zone between the recycled sand and paste for the RS-based geopolymer; they found out that the interfacial area was relatively small, which was attributed to the old mortar that was attached to the corrected recycled sand. Nevertheless, the hydration products, which can be formed from old mortar, overlap and intertwine to form a good geopolymer paste around the recycled aggregate particles [48, 54]. Furthermore, the mechanical strengths of mortars made with natural sand are smaller than those of mortars with recycled sand for different curing ages. This can certainly be assigned to the rate of quartz fines contained in natural sand and also to the relatively high (S/P) ratio. It should be emphasized that in the geopolymerization process, quartz is generally chemically inert.

According to Panizza et al. [28], curing CRS-based mortars at room temperature decreases their Cs compared to higher curing temperatures. However, the obtained strength values are satisfying for regular concrete use, despite the drop in strength in the long term (after 365 days). A further study of the chemical and physical phenomena that occurred during hydration and the curing of mortars would better explain the causes of this drop in mechanical strength.

6.5. Microstructure Analysis by Scanning Electron Microscope

Mortar samples of different compositions were analyzed under a scanning electron microscope (SEM) to study their microstructure and the interface area between the two types of sand and the new geopolymer cement paste. Figure 11 shows the SEM analysis results of the mortar with the highest strength (3-2CRS) and the one with the lowest strength (1-3NS). This same figure shows that the matrix of mortar (3-2CRS) is more compact and presents fewer cracks, hence becoming more homogeneous and integrated. However, the matrix of mortar (1-3NS) exhibits cracks besides some lightly stacked aluminosilicate particles and unreacted material. The presence of residual unreacted particles prevents the development of the network of a uniform geopolymer network [55]. Additionally, the blast furnace slag and corrected recycled sand in the mixture facilitated the formation of an increased amount of C-A-S-H gels [43, 44]. Figure 11 clearly indicates that the compactness of the gel in (a) is higher than that in (c). In addition, Figure 12 shows that the ratios (Na/Al) and (Na/Si) are greater in the mortar (3-2CRS) in comparison with those observed in the mortar (1-3NS). This increase leads to the formation of stronger and more stable crystal structures [56]. Furthermore, it was found that using recycled sand can lead to internal hardening, which improves the microstructure of the interfacial transition zone between the recycled sand particles and the Portland cement paste [57].

![SEM Images](a) (b)
Figure 11. Results of SEM analysis for mortars: (a) and (b): mortar (3-2CRS), (c) and (d): mortar (1-3NS)

Figure 12. Results of energy dispersive spectroscopy (EDS) analysis of mortars: (a): mortar (1-3NS), (b): mortar (3-2CRS)
7. Conclusions

The present study developed an alkali-activated geopolymer binder based on metakaolin and slag. A comparative experimental investigation was then carried out to study the feasibility of CRS as fine aggregate for mortar made using the optimal obtained cement mixture. The study provided encouraging results on the possibility of making CRS-based mortars cured at room temperature (20°C) with acceptable properties for regular use. The following are the main conclusions and recommendations:

- The addition of metakaolin slows the binder hydration kinetics and delays the initial setting time, making it comparable to that of Portland cement. Besides, the setting time is significantly influenced by the CRS and the pH of the alkaline solution;
- The CRS-Based mortars' density is related to the porosity of the used recycled aggregates. The drop in density in the long term is then due to water departure from the material;
- The association of the two alkali-activators (80%WG + 20%NaOH) gives higher strength due to the increase in the pH of the solution, favouring the binder's hydration. The influence of the alkaline solution pH on the mechanical strength is more pronounced for the CRS-based mortars containing 50% slag (37.06 MPa at 28 days);
- The SEM analysis shows that mortar including CRS has a more homogeneous and integrated matrix than mortar incorporating fine NS;
- The energy dispersive spectroscopy (EDS) analysis shows an increase in the (Na/Al) and (Na/Si) ratios in CRS-based mortar compared to NS-based mortar. This increase leads to more robust and more stable crystal structures.

Further studies would better explain the designed mortars' behaviour and durability in the long term.

8. Declarations

8.1. Author Contributions

Conceptualization, B.S., and Z.L.; writing original draft preparation, B.S., and Z.L.; writing review and editing, B.S., Z.L., and B.Z. All authors have read and agreed to the published version of the manuscript.

8.2. Data Availability Statement

The data presented in this study are available in article.

8.3. Funding

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8.5. Conflicts of Interest

The authors declare no conflict of interest.

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