The development of potential alternative binders to Portland cement is still becoming a global challenge in housing and infrastructure aspects. That is because cement and concrete becomes the major materials needed in building constructions. The Ordinary Portland cement can form a solid and hard mass when mixed with water with a certain ratio. This is due to the formation of ettringite and calcium silicate hydrate (CSH) phases that contribute to the strength of the hydrated products about 33–53 MPa. However, the manufacturing temperature of Portland cement can reach up to 1,500 °C in producing clinker. In order to lower the energy consumption and production cost, scientists were trying to utilize pozzolanic materials.

The research of pozzolanic materials as alkali-activated cement, such as soil cement or geopolymer cement, is also still conducted. Hence, a better understanding of pozzolanic reaction and its hydration products is needed. In this work, the hydration products of low-energy binders composed of Ca(OH)$_2$–SiO$_2$ and Ca(OH)$_2$–metakaolin–gypsum mixtures were studied.

The hydrated products of 41 wt. % Ca(OH)$_2$–41 wt. % metakaolin – 18 wt. % gypsum mixtures followed by water immersion curing at 50 °C for 28 days underwent a pozzolanic reaction. XRD characterization showed that the hydrated product is mainly composed of ettringite (60.0 %) and crystalline-CSH (23.4 %). The diffractograms obtained have shown a specific hump indicating the presence of amorphous phases besides the crystalline. To confirm the presence of the non-crystalline or amorphous phases of the hydrated products, a polarizing optical microscope (OM) using a crossed Nicols method was used. The characterization of the phases is the novelty of the present research. The ettringite, crystalline CSH and the amorphous phases act as a strong binder that consequently contribute to its average maximum compressive strength of 22.17 MPa.

Keywords: low-energy binder, alkaline activator, metakaolin, pozzolanic reaction, diffractogram hump, amorphous phase, polarised optical microscope

1. Introduction

Portland cement production with a firing process in a rotary kiln requires a clinkering temperature of up to 1,500 °C [1, 2]. It consumes a large amount of energy and produces highly carbon dioxide emissions [3]. In addition, the firing process also produces fine-powered silica dust that can cause respiratory disturbances of silicosis [4]. Thus, the focus of the present cement industry is to find an alternative method to reduce the energy consumption during the manufacturing process of cement powder in order to save the production costs and environment, while producing high-quality products [1, 5]. One such alternative is by utilizing alkali-activated cements through the role of pozzolanic materials. Pozzolanic materials generally consist of aluminosilicates, which have alkali-reactive properties, are eco-friendly, and require low energy consumptions [6, 7]. Among them are metakaolin, fly ash, silica fume, blast furnace slag, etc. The pozzolanic reaction occurs when the reactive pozzolanic materials are activated by using alkaline solutions, such as alkali hydroxides, i.e. sodium hydroxide (NaOH) or calcium hydroxide (Ca(OH)$_2$), and alkali sulphates [5]. The reaction between pozzolanic materials and alkaline solution with the presence of water will cause the formation of the hard, solid, and compact body, thus it is called a hydraulic binder.

Actually, viewed from the historical milestones, the principle of the hydraulic binder using alkali-activated aluminosilicate materials was firstly found by Glukhovsky in the late 1950s. He called that binder as “soil cements”. Later, Krivenko called it as “geocements”, while Davidovits termed it as “geopolymer” because it has a polymer-like structure [5]. Up to now, scientists are still developing the possibility of using alkali-activated cements as an alternative to Portland cement due to the low energy consumption and production costs. One of the potential candidates is by using fine-powered silica and metakaolin as the pozzolanic materials, with calcium hydroxides as the alkaline activator.

2. Literature review and problem statement

Portland cement is manufactured by calcining three main materials such as limestone (CaCO$_3$), silica sand (SiO$_2$), and...
clay (xAlOyZSiO2·xH2O) with suitable chemical compositions at about 1,500 °C in a rotary kiln machine. The materials are melted, mixed, and then cooled as clinkers. After that, the clinkers are mixed again with the gypsum chunks and ground in a ball mill machine to obtain the finely powdered cement [1, 2].

Portland cement is also one of the hydraulic binders because it can harden and form a solid body after mixed with water at a room temperature with a certain water/cement ratio. The reaction is called a hydration reaction. Portland cement powder contains some important phases that contribute to the hydration reaction, namely alite (3CaO·SiO2), belite (2CaO·SiO2), aluminate (3CaO·Al2O3), ettringite (4CaO·Al2O3·3CaSO4·3H2O), and the additional gypsum (CaSO4·2H2O) powder as a set retarder and a strength accelerator [2, 8]. The products of hydration reaction mainly consist of calcium silicate hydrate (CSH), ettringite or calcium aluminosilicate hydrate (CASH), calcium aluminohydrate (CAH), and calcium hydroxide (CH or Ca(OH)2) [2, 6].

The issue of studying alkali-activated cements has remained relevant and important. Alkali-activated cements using pozzolanic materials and alkaline activators undergo hydration reaction, as well as the Portland cement. In addition, specifically, they also undergo a pozzolanic reaction. The papers [6, 9] state that the hydration products of the pozzolanic materials reacted with alkaline solution are CSH, ettringite, and CAH. From this standpoint, the alkali-activated cement using pozzolanic materials probably has similarity with Portland cement in terms of chemical reaction mechanism, reaction products, and mechanical properties of the hydrated products.

Based on the American Concrete Institute (ACI CT-13), pozzolanic materials are defined as a siliceous or silico-aluminous material, which in fine form can chemically react with calcium hydroxide and water at room temperature to form compounds having cementitious properties. The pozzolanic reaction produces a CSH phase that contributes to the long-term strength of the hydrated products [10].

Metakaolin (MK), xAl2O3·ySiO2, is one example of the pozzolanic materials that can be obtained from the calcination of kaolinite clay (xAl2O3·ySiO2·zH2O) at the elevated temperature of about 750–900 °C [4, 11]. It is usually added into blended Portland cements as supplementary cementitious materials (SCMs) due to its special properties. The paper [11] shows that metakaolin improves the workability of the cement paste, increases the setting time of the concrete by 10% addition, and also enhances the compressive strength of the concrete. The high reactivity of metakaolin may increase the heat of hydration and accelerates the hydration reaction of the cement paste, resulting in a faster setting time. The paper [6] states that the structure of penta-coordinated aluminum ions makes metakaolin very reactive, and in its fine form in the cement paste it consumes portlandite or calcium hydroxide (Ca(OH)2) producing CSH and CAH binding phases. While the reaction of the Al2O3 site with gypsum (CaSO4·2H2O) in aqueous solutions will produce an ettringite phase, which contributes to the initial strength of the concrete structure [8, 12]. The paper [13] also shows that the addition of 15% metakaolin to the cement composition possibly prevents destructive processes in concrete exposed in a high alkali content environment.

Geopolymer cement is one of the alkali-activated cements that use the reaction between metakaolin as pozzolanic material and NaOH as alkaline activator, resulting in the polymer-like binding structure of sodium aluminosilicate hydrate (NASH). Meanwhile, besides NaOH, the paper [14] suggests that Ca(OH)2 can also be used as another alkaline activator for metakaolin. Thus, Zemlicka et. al [6] presented the research of the hydration reaction products of metakaolin-Ca(OH)2 and metakaolin-Ca(OH)2-gypsum mixtures. X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) methods showed the presence of ettringite and CSH phases. But, there was an unresolved issue related to the characterization of the amorphous phase of the hydrated products. The reason for this may be the objective difficulty associated with the suitable method chosen, which makes relevant research impractical. However, in studying an alternative binder to Portland cement, it is also important to understand and distinguish the crystalline and amorphous structures that mainly contribute to the strength of the products. A way to overcome this difficulty can be through a conventional petrographic examination. The papers [15, 16] state that conventional petrographic examination using a polarising optical microscope (OM) is commonly used as a quick method in characterizing the amorphous phase of cementitious materials. Polarising OM is the simplest way to overcome this difficulty in observing the amorphous phase structure. The methods used are parallel nicols and crossed nicols by adjusting the analyzer and polarizer. The observed light will behave depending on the structure of the materials. By using both parallel nicols and crossed nicols, if the observed light passing through the specimen shows a variety of colors, then the materials can be classified as anisotropic, e.g. silica, portlandite, and kaolinite. While by using crossed nicols, if the observed light passing through the specimen shows only dark color, then the materials can be classified as isotropic, e.g. diamond, glass, and amorphous solids.

All this suggests that it is advisable to design alternative binder mixtures to Portland cement. In this work, the idea is taken from the secondary pozzolanic reaction on a high-strength concrete of which Ca(OH)2 as a product of the primary hydration process reacts usually with reactive SiO2 resulting in a secondary CSH phase or called as CSH2.

\[
\text{Calcium-silicates + H}_2\text{O} \rightarrow \text{CSH} + \text{Ca(OH)}_2, \\
\text{Ca(OH)}_2 + \text{reactive SiO}_2 + \text{H}_2\text{O} \rightarrow \text{CSH}_2. 
\]

The production of the CSH2 product from the secondary hydration or the pozzolanic reaction was an interesting phenomenon to observe.

### 3. The aim and objectives of the study

The aim of the study is the development of the low-energy binder composed of Ca(OH)2·SiO2 and Ca(OH)2-metakaolin-gypsum mixtures without the addition of Portland or any other conventional cement products. This will make it possible to obtain the hydrated products with the compressive strength not below 20 MPa at 28 days.

To achieve the aim, the following objectives have been set:
- to determine the compressive strength of hydrated products of Ca(OH)2·SiO2 and Ca(OH)2·SiO2 mixtures with CaO and metakaolin addition;
- to determine the compressive strength development of the hydrated products of Ca(OH)2-metakaolin-gypsum mixtures;
4. Materials and methods

The Ca(OH)$_2$-SiO$_2$ system was used as the initial experimental base, by using Ca(OH)$_2$ as an alkaline activator and fine-powdered silica as pozzolanic material. The materials used in this work are as follows. Limestone was obtained from Padalarang, Bandung, Indonesia. It was then burned at a temperature of 1100 °C for one hour. The burned limestone was left in the open air for a week in order to obtain Ca(OH)$_2$ powder. Silica powder, SiO$_2$ (SikaFume, Indonesia) with a grain size of about 0.75 microns or passed 200-mesh sieve. White kaolin powder (Bolus Alba, Bandung, Indonesia) and gypsum powder (Bratachem, Bandung, Indonesia). The white kaolin was burned at a temperature of 750 °C for two hours to convert the kaolin into a metakaolin phase [4].

There were two mixtures used in this work: Ca(OH)$_2$-SiO$_2$ and Ca(OH)$_2$-metakaolin-gypsum mixtures as shown in Table 1. Ca(OH)$_2$ and SiO$_2$ were mixed in a weight ratio Ca(OH)$_2$/SiO$_2$ of 0.2, 0.4, 0.6, and 1.0. They were mixed with water using a water/solid ratio of 0.3. After that, they were cast into a 5×5×5 cm cube mold to form specimens for compressive strength test after 14, 21, and 28 days of curing. The curing method used was atmospheric curing and the specimen demoulding process was done after 6–7 days of casting. We also applied some modification to Ca(OH)$_2$-SiO$_2$ mixtures. The CaO and metakaolin were added into the mixtures, as simply shown in Table 1. Ca(OH)$_2$, metakaolin, and gypsum were mixed with a composition of 41 wt. % Ca(OH)$_2$ – 41 wt. % metakaolin – 18 wt. % gypsum according to the work of Zemlicka et al. [6]. They were mixed with water using a water/solid ratio of 0.7. Then, they were cast into a 5×5×5.5 cm cube mold for compressive strength test specimens with ages of 3, 7, 14, and 28 days. After 2 days of casting, the specimens were demoulded for the curing process. The curing method used was immersed in water, and it was performed at a temperature of 50 °C and 20 °C. The water-immersed curing method was used to get the most effective result, i.e. the highest result in compressive strength.

Compressive tests of Ca(OH)$_2$-SiO$_2$ and Ca(OH)$_2$-metakaolin-gypsum specimens were performed by using a Tarnogrocki compression machine with a load cell of 50–200 kN and a load speed of 0.7 mm/min.

Metakaolin and the specimens with the highest compressive strength were used for XRD characterization. Those three samples are CH-MK-G-50, CH-MK-G-20, and CH-15MK/S. Samples CH-MK-G-50 and CH-MK-G-20 were characterized by using Shimadzu XRD-7000 Maxima type diffractometer operating at 40 kV–30 mA and using CuKα radiation. While metakaolin and CH-15MK/S samples were characterized by using Philips XPert MPD type diffractometer operating at 40 kV–30 mA and using CuKα radiation. The diffractograms were analyzed qualitatively to identify the phases. While CH-MK-G-50 and CH-MK-G-20 were also analyzed semi-quantitatively to determine their phase compositions by using XPowder™ software with PDF2 database.

The petrographic examination of samples CH-MK-G-50 and CH-MK-G-20 was done using two kinds of polarizing OM. Both samples were in the form of thin sections with about 30 microns thickness. The presence of the amorphous phase was observed by using conventional polarizing OM supported by a LED lamp as a light source to obtain the best lighting. Samsung J7-6 rear camera was used to take about 5–8 images for each sample observed in the crossed nicols mode. While the other phases and aggregates were observed by using Nikon digital polarizing OM with both parallel nics and crossed nics methods. All the images were processed by using ImageJ software to adjust the image brightness and/or sharpness.

| No. | Sample code | Mixture Compositions | w/s ratio | Curing method | Curing time (days) |
|-----|-------------|----------------------|-----------|---------------|-------------------|
| 1   | CH/S-0.2    | Ca(OH)$_2$/SiO$_2$=0.2 | 0.3       | Atmospheric curing | 14, 21, 28       |
|     | CH/S-0.4    | Ca(OH)$_2$/SiO$_2$=0.4 | 0.3       | Atmospheric curing | 14              |
|     | CH/S-0.6    | Ca(OH)$_2$/SiO$_2$=0.6 | 0.3       | Atmospheric curing | 14              |
|     | CH/S-1.0    | Ca(OH)$_2$/SiO$_2$=1.0 | 0.3       | Atmospheric curing | 14              |
| 2   | CH-5C/S     | [Ca(OH)$_2$]+5 wt. % CaO/$\text{SiO}_2=1.0$ | 0.3       | Atmospheric curing | 14              |
|     | CH-10C/S    | [Ca(OH)$_2$]+10 wt. % CaO/$\text{SiO}_2=1.0$ | 0.3       | Atmospheric curing | 14              |
|     | CH-15C/S    | [Ca(OH)$_2$]+15 wt. % CaO/$\text{SiO}_2=1.0$ | 0.3       | Atmospheric curing | 14              |
|     | CH-5MK/S    | [Ca(OH)$_2$]+5 wt. % metakaolin/$\text{SiO}_2=1.0$ | 0.3       | Atmospheric curing | 14              |
|     | CH-10MK/S   | [Ca(OH)$_2$]+10 wt. % metakaolin/$\text{SiO}_2=1.0$ | 0.3       | Atmospheric curing | 14              |
| 3   | CH-MK-G-50  | 41 wt. % Ca(OH)$_2$ – 18 wt. % metakaolin – 41 wt. % gypsum | 0.7       | Immersed in water; T=50 °C | 3, 7, 14, 28 |
|     | CH-MK-G-20  | 41 wt. % Ca(OH)$_2$ – 18 wt. % gypsum | 0.7       | Immersed in water; T=20 °C | 3, 7, 14, 28 |

5. Research results of testing and characterization of alternative low-energy binders

5.1. Compressive strength of the Ca(OH)$_2$-SiO$_2$ hydrated products

Fig. 1 shows an increase in the compressive strength of the hydrated products along with the addition of Ca(OH)$_2$ (higher Ca(OH)$_2$/SiO$_2$ or CH/S) from 14 until 28 days of atmospheric curing. It means that the mixture has the ability to form a solid mass with low binding or cementing properties because the compressive strength of the materials is still less than 1 MPa. In this case, it should be noted that the mixture does not undergo a pozzolanic reaction. Ca(OH)$_2$ acts as a binder and SiO$_2$ acts as a filler or aggregate, and they exhibit only adhesion bonding. Thus, for CH/S=0.2 and
CH/S=0.6, as the CH/S ratio increases with the curing time, the more the cementing ability of the binder, the higher the compressive strength of the hydrated products. While for CH/S=0.4 and CH/S=1.0, there is an inconsistent trend which may be caused by some errors during the mixing and casting process, i.e., porosity, dimensional shrinkage, or non-homogeneous water content in the slurry.

Fig. 2 shows Ca(OH)$_2$-SiO$_2$ mixtures with the addition of metakaolin and CaO both perform increases in compressive strength as the wt. % of addition increases. However, there is a significant increase in compressive strength after the addition of metakaolin into Ca(OH)$_2$-SiO$_2$ mixtures. The mixture of Ca(OH)$_2$-SiO$_2$ with the addition of metakaolin can form a solid mass with higher cementing properties.

From these results, metakaolin is a reactive pozzolan that contains SiO$_2$ and Al$_2$O$_3$ sites, which can react with Ca(OH)$_2$ in the mixture, then it is suspected that the mixture may experience a pozzolanic reaction. This result should be further confirmed by using XRD characterization to identify the phases. Whereas, the addition of CaO into the mixture shows a slight increase in the compressive strength value along with the composition of CaO added. It has no significant effect at all due to CaO will react soon with H$_2$O, resulting in Ca(OH)$_2$, which has a low cementing ability.

5.2. Compressive strength of the Ca(OH)$_2$-metakaolin-gypsum hydrated products

The compressive strength of the specimens with 41 wt. % Ca(OH)$_2$ – 41 wt. % metakaolin – 18 wt. % gypsum at two different curing temperatures is shown in Fig. 3. It is shown that the mixture forms a solid mass and there is an increase in the compressive strength value of the hydrated products as the curing time increases.

The specimen shows a significant increase in compressive strength, indicating the formation of solid mass in the specimen due to the pozzolanic reaction. This result should be also further confirmed by using XRD characterization to identify the phases. Compared to the Ordinary Portland cement, its hydration product can have a compressive strength value of up to 33–53 MPa at 28 days of atmospheric curing. In addition, [18] also mentioned that the water immersed curing method also supports the hydration reaction of the mixture that improves the pore structure and decreases the porosity level of the products. Besides, specimens with a curing temperature of 50 °C have a more significant increase in compressive strength than with 20 °C. It is also shown in [18] that curing temperature plays a role in the kinetics of the hydration reaction of cementitious materials. Thus, the water immersed curing method with a temperature of 50 °C has a higher kinetics or reaction rate than with 20 °C, resulting in a faster reaction and more hydration products.

5.3. XRD characterization of the Ca(OH)$_2$-SiO$_2$ and Ca(OH)$_2$-metakaolin-gypsum hydrated products

The specimens with the highest compressive strength of CH-MK-G-50, CH-MK-G-20, and CH-15MK/S were characterized using the XRD method. The phase composition contained in samples CH-MK-G-50 and CH-MK-G-20 is shown in Table 2. Whereas the diffractograms are shown in Fig. 4.
Phase composition identified by XRD on samples CH-MK-G-50 and CH-MK-G-20

| Sample code | Compressive strength (28 days curing), MPa | Phase identified |
|-------------|------------------------------------------|------------------|
| CH-MK-G-50  | 22.17                                    | Crystaline CSH 60% | Ettringite 23.4% | Calcite 12% | Quartz 4.6% | Portlandite – |
| CH-MK-G-20  | 6.13                                     | Crystaline CSH 30.4% | Ettringite 40.2% | Calcite 19% | Quartz 2.9% | Portlandite 5.6% |

Ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O) and crystalline-CSH (sheet PDF-33-0306) [19] phases were only identified in both samples CH-MK-G-50 and CH-MK-G-20.

The presence of ettringite was caused by the reaction between Ca(OH)₂, Al₂O₃ sites of metakaolin, gypsum, and water. The formation of ettringite has a role to speed up the strength development at the earlier period of the specimens, like so in Portland cement hydration [6, 8]. So that, the specimens can maintain their shapes while they were immersed and cured in the water after the demoulding process.

The presence of crystalline-CSH was caused by the reaction between Ca(OH)₂, SiO₂ site of metakaolin, and water [6]. It has the main contribution to the long-term strength of the products. Meanwhile, in Portland cement hydration, CSH is obtained from the reaction between calcium-silicates (in the cement powder) with water. Actually, the formation of CSH in Portland cement occurs in two steps of hydration [10] as mentioned in equations (1) and (2). The first hydration is calcium silicates react with water, yielding CSH and Ca(OH)₂ as a side product. Then, the side product can continue to react with reactive silica compounds with the presence of the water yielding CSH₂, which is known as secondary hydration. The secondary hydration is also called as a pozzolanic reaction. However, some literature sources state that the product of the pozzolanic reaction is not limited only to CSH, but also ettringite or CASH (calcium-aluminate-silicate-hydrate), and CAH (calcium-aluminate-hydrate) [6, 9, 12]. Therefore, from this theory and presented results, samples CH-MK-G-50 and CH-MK-G-20 experienced pozzolanic reaction due to the presence of ettringite and crystalline-CSH. They give strong binding properties to the specimens. Associated with that, sample CH-15MK/S did not experience any pozzolanic reaction. This result confirms its compressive strength value that the low binding strength of the CH-15MK/S specimen comes from the only adhesion bonding.

Portlandite (Ca(OH)₂) was identified in both samples CH-MK-G-20 and CH-15MK/S. In sample CH-MK-G-20, the presence of portlandite was due to a pozzolanic reaction that did not completely occur yet. That is because according to the reaction (2), the pozzolanic reaction needs to consume portlandite to yield CSH. Whereas in sample CH-15MK/S that did not undergo pozzolanic reaction, portlandite was surely identified. However, it may undergo a carbonation reaction due to the presence of CO₂ in the solution, so that it also contributes to the formation of calcium carbonate or calcite (CaCO₃) in the specimens [9, 20].

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}. \tag{3}
\]
Calcite and quartz (SiO₂) were identified in all samples. The presence of calcite was mainly due to the carbonation reaction. While quartz was identified in sample CH-15MK/S due to the silica raw materials in the mixture, or as impurities for all samples.

From Table 2, both samples CH-MK-G-50 and CH-MK-G-20 have more dominant compositions of both ettringite and crystalline-CSH. Those phases act as binding or cementing agents that give strong and tight binding properties to the specimens, so that both samples have a high compressive strength value. While the calcite, quartz, and the unreacted portlandite act as fillers in the specimens [21]. The diffractograms showed that the amount of crystalline-CSH phase was 23.4\% (22.17 MPa) and 30.4\% (6.13 MPa). It seems that the increase in the amount of CSH phase was not linearly followed by the increase of their strength. Hence there is a possibility that the increase of strength could also be contributed by the non-crystalline or amorphous phases present in the hydrated product. It can be clearly seen that XRD patterns of samples CH-MK-G-50 and CH-MK-G-20 have a hump (at 2θ from 20° to 40°) as found in the XRD patterns of the MK (metakaolin) and the hydrated cement paste [22–24].

The smoothing or background subtraction process was not undertaken so that the diffractogram results showed more detailed information about the phases present. From the detected hump, it gives information that both samples contained an amorphous phase. Whereas the XRD patterns of sample CH-15MK/S have no hump at all and it can be ascertained that it contains entirely crystalline phases. As shown in Fig. 5, the work of Zemlicka et al [6] did not elaborate on the amorphous phases observed by the hump in the diffractograms. The hypothesis was that the amorphous phase was suspected to be CSH gels. According to the literature, the structure of CSH can range from crystalline to amorphous depending on several factors, such as the C/S/H ratio and w/c ratio [1, 2]. Hence, this led the examination by using a polarizing optical microscope to identify the presence of an amorphous phase.

5.4. Polarizing Optical Microscope examination of the Ca(OH)₂-Metakaolin-Gypsum hydrated products

In the examination of sample CH-MK-G-50, needle-like ettringite [15] was identified (Fig. 6, a). It is found in the area along the cracks of the sample. While the crossed Nicols (Fig. 6, b) identified the calcite grains as indicated by a yellowish-orange color [25]. The void observed was due to the air bubble trapped in the sample.

In sample CH-MK-G-20, the quartz grain (Fig. 6, c, d) also showed up and was easily recognized by its color and its irregular fracture properties [26]. The granular aggregate with opaque properties was presented in the sample (Fig. 6, e, f), and it may come from the limestone impurities. Portlandite grains were also identified (Fig. 7). The quartz, aggregate, and portlandite are all surrounded by the binder or matrix.

Fig. 8 shows the visual comparison of the black color of both samples in crossed nicols. It can be seen that both samples have the black (or thin black) color area, indicating the existence of amorphous phases. Those amorphous phases act as a strong matrix or binder in the samples.

Theoretically, in petrographic analysis, minerals with the isotropic system have uniform properties and the same refractive index in all directions. This means that the minerals will only show dark or black color when the polarized light passes through it (in crossed nicols). Moreover, the crossed Nicols examination of the thin section of the hydrated cement paste also shows that CSH gels have a black (or grey) color [15, 26]. Meanwhile, the humps in the XRD pattern have revealed the presence of an amorphous phase in samples CH-MK-G-50 and CH-MK-G-20. Due to its irregular structure and low crystallinity, the amorphous phase is classified as isotropic materials. Whereas the observed black globular, elongated, or irregular forms are aggregate-like structures, which have opaque properties.

It can be seen that the black color portion in sample CH-MK-G-50 is darker, denser and more concentrated compared to sample CH-MK-G-20. This means that the isotropic portion of sample CH-MK-G-50 is much more than that of sample CH-MK-G-20. Therefore, sample CH-MK-G-50 has more amorphous portions than sample CH-MK-G-20. Viewed from the curing process, the curing temperature plays role in the formation of the amorphous structure, thus affecting the black color portions in the samples. Sample CH-MK-G-50 with the curing temperature of 50°C allows the faster formation of the CSH structure due to the high rate of pozzolanic reaction [18], resulting in more CSH products obtained. Also in that condition, it makes sense that the CSH structure does not have enough time to self-assemble; it means that CSH is randomly formed and thus resulting in the amorphous structure.

Sample No. 12 has similar compositions with the present work. It is thought that the characterization of the amorphous phase of the XRD hump was important in understanding the reaction products of the pozzolanic reaction. The present research diffractograms (Fig. 4) are different from the work [6] as shown in Fig. 5. In [6], the smoothing or background subtraction process of the diffractograms can lead to a miss information, such as the elimination of the XRD hump. While in this work, smoothing or background subtraction processes were not performed. Hence the observed hump at 2θ from 20° to 40° shows information about the presence of the amorphous phase, which is not explained by the work [6]. The result is interesting from the theoretical point of view and led us to the examination of the amorphous phase by using polarizing optical microscopy. This became the scientific novelty in this work.
Fig. 6. Polarizing optical microscope examination of samples by using: \( a \) – parallel nicols (sample CH-MK-G-50); \( b \) – crossed nicols (sample CH-MK-G-50); \( c, e \) – parallel nicols (sample CH-MK-G-20); \( d, f \) – crossed nicols (sample CH-MK-G-20); 
\[E\text{ – ettringite; } C\text{ – calcite; } Q\text{ – quartz}\]

Fig. 7. Portlandite grains in sample CH-MK-G-20 identified by: \( a \) – parallel nicol; \( b \) – crossed nicols with different location. The binder dissolves the surface of the portlandite grains indicating that the reaction occurs in that area.

Fig. 8. Visual comparison of the images of both samples: \( a, b, c \) – CH-MK-G-50; \( d, e, f \) – CH-MK-G-20. The black granular aggregates are observed in sample CH-MK-G-20.
6. Discussion of the results of the testing and characterization of the alternative low-energy binders

The compressive strength of the hydrated products of Ca(OH)$_2$-SiO$_2$ with or without the addition of CaO was around 0.55 MPa (Fig. 1), whereas the compressive strength of Ca(OH)$_2$-SiO$_2$ with the addition of metakaolin was about 2.66 MPa (Fig. 2). The hydrated products that consist of 41 wt. % of Ca(OH)$_2$ – 41 wt. % of metakaolin and 18 wt. % of gypsum mixtures prevents them from being broken when they were immersed in water for curing. During the initial strength development of the hydrated products, ettringite, crystalline-CSH and amorphous phase act as a strong binder. Whereas calcite, quartz, and portlandite act as fillers. All of them together contributed to the compressive strength of the mixture that was water-cured at 50 °C for 28 days. Both diffractograms exhibit a hump at the 20° to 40°, indicating the presence of amorphous phases. [27] shows fly ash-based geopolymer concrete with certain molarity of NaOH can obtain compressive strength of 29.34 MPa in 28 days of atmospheric curing method. [28] presents that by determining the hydraulic activity of SCMs, it can influence the technological, mechanical, and chemical properties of the low-emission multi-component cement. It is shown that combining super-zolite (SZ) and separated fly ash (SFA) can reduce power consumption for the preparation of highly active SCMs up to 31 kWh/tonne. Another idea comes from [29] on designing an alternative alkali-activated Portland cement by using a mineral additive of granulated blast furnace slag and fly ash. The aim of the research is to accomplish the blended cement composition, in which the hydrated products can reach a higher strength than 40 MPa.

This study still uses the water immersion curing method at a certain temperature to obtain the highest compressive strength value. Whereas the study [6] used acetone to stop the hydration reaction after the curing process. Future development should be undertaken for atmospheric curing related to technical and practical applications. The hydration product of Ordinary Portland cement has a compressive strength value of about 33–53 MPa in 28 days of atmospheric curing.

It should be noted that XRD characterization provides qualitative and semi-quantitative analysis for the crystalline phase. Indeed, quantitative XRD analysis for the amorphous phase in cementitious materials also has also been developed [23, 30, 31]. Hence, for further development, it can roughly estimate the comparison between crystalline and amorphous phases that dominantly contribute to the strength of the hydrated binders.

Some development should be further undertaken in this research scope of alkali-activated cements. For example, by varying binder compositions, or developing quaternary mixtures consisting of Ca(OH)$_2$-metakaolin-gypsum combined with other elements such as blast furnace slag, fly ash and silica fume.

7. Conclusions

1. The mixtures of Ca(OH)$_2$–SiO and Ca(OH)$_2$–SiO$_2$ with the addition of CaO and metakaolin did not undergo a pozzolanic reaction. The compressive strength of Ca(OH)$_2$–SiO$_2$ with or without the addition of CaO was around 0.55 MPa. While Ca(OH)$_2$–SiO$_2$ with the addition of metakaolin showed a value of about 2.66 MPa and as confirmed by XRD this mixture did not undergo pozzolanic reaction as no CSH or ettringite phases were identified.

2. The mixtures of 41 wt. % Ca(OH)$_2$ – 41 wt. % metakaolin – 18 wt. % gypsum with 28-days water immersion curing at temperatures of 50 °C and 20 °C have an average compressive strength value of 22.17 MPa and 6.13 MPa, respectively. The compressive strength showed a significant increase for the mixture that was water-cured at 50 °C for 28 days. Both treatments underwent pozzolanic reaction as shown by the presence of CSH and ettringite phases as confirmed by XRD.

3. From XRD characterization, CH-MK-G-50 mainly contains ettringite and crystalline CSH. While CH-MK-G-20 mainly contains ettringite, crystalline – CSH, with some portions of portlandite. Both diffractograms exhibit a hump at the 20° of 20° to 40°, indicating the presence of amorphous phases.

4. The examination using a polarizing optical microscope confirmed the presence of amorphous phases indicated by a darker color feature of the microstructure. Sample CH-MK-G-50 has a denser and darker color in visual observation compared to sample CH-MK-G-20, indicating that it has more portions of the amorphous phase. The amorphous phase is suspected to be CSH gels. Other phases such as ettringite, calcite, quartz, and portlandite were also observed. It is concluded that ettringite, crystalline-CSH, and the amorphous phases act as a strong binder, while calcite, quartz, and portlandite act as fillers. All of them together contributed to the compressive strength of the mixture.

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