A Review of Carbonate Minerals as an Additive to Geopolymer Materials

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Abstract. In Malaysia, several geopolymer materials were mainly from fly ashes, kaolin, metakaolin, and boiler ash which were mainly used to prosper sustainable development especially in the building and construction sector. Geopolymers can be classified as inorganic materials that were formed with the reaction between aluminosilicate materials and alkaline solutions. This reaction causing a crystalline compounds mixture to form that toughen to become a novel compound through a process called geopolymerization process. These geopolymer materials have many admirable advantages, including high strength, small shrinkage, decent thermal resistance and good chemical resistance. Although they were used as a stand-alone material with great properties, combination with another material might be another way to improve their properties. A few studies had shown that the geopolymer material can achieve better properties with the addition of moderate amount of calcium-containing material to a geopolymer. The addition of carbonate materials can have insignificant effect on the geopolymer configuration and properties. Thus, this paper review the usage of carbonate materials for example Dolomite (CaMg(CO3)2) and Calcite (CaCO3) as an addition into these geopolymer material.

1. Introduction

Carbonate is a mineral that consists of CO3 component in its molecule structure. The molecular structure of CO3 consists of one carbon atom that is bonded with three oxygen atoms. It was built by the covalent bond between the atoms of carbon and oxygen [1]. One of the oxygen atoms shares two electrons with carbon, whereas the other one shares one electron for each oxygen atom. This structure leaves two negative charges for carbonate sub molecule. A carbonate molecule is built through ionic bond between this negative charge and the positive charge from certain metallic element [2].

Surrounded by all the carbonate minerals, calcite is categorized as the most mutual one that is often used conventionally. One of the usages is to make the composite for construction structures like roads and buildings when calcite is heated and assorted with additional materials [3]. Besides calcite, the carbonate mineral that frequently used for construction is dolomite. Dolomite is carbonate mineral that contains magnesium besides calcite. The existence of magnesium in dolomite make it is used as
magnesium foundation for human, animal and plants, since magnesium is one of vital elements wanted by breathing mortals [4].

Moreover, dolomite is commonly used in road and building construction for foundation bases and as an aggregate for cement and asphalt concrete. Other than can reduce the mechanical properties of the product, dolomite at the same time can improve the formation of better contact zone for cement paste aggregate for the carbonate aggregate [5].

The benefits of using carbonate minerals in road construction are improve structural quality, greater load bearing, reduced maintenance cost and extended life [6]. Besides that, calcium carbonate materials such as calcite and dolomite are abundant and generally inexpensive natural minerals. It will be a great interest to be using this bulk of calcium carbonate materials to improve the properties of a geopolymer [7].

2. Chemical Composition of Dolomite and Calcite

Table 1 display the chemical composition of dolomite and calcite as determined by XRF. Both of the materials are from Clayworks, Australia. Based on the table, dolomite contains high calcium oxide (CaO) and magnesium oxide (MgO) composition. Besides that, dolomite also contains silicon dioxide (SiO₂) and alumina oxide (Al₂O₃). The silica and alumina are the core ingredients to produce geopolymer binder. Thus, it is possible to make dolomite as a raw material for geopolymer. Comparison between dolomite and calcite shows that calcite has higher CaO content meanwhile dolomite has higher MgO content. Other than that, dolomite has a small composition of K₂O Na₂O meanwhile calcite had none.

|                | CaO  | SiO₂ | Al₂O₃ | Fe₂O₃ | MgO  | K₂O  | Na₂O | LOI  |
|----------------|------|------|-------|-------|------|------|------|------|
| Dolomite       | 33.4 | 2.5  | 0.7   | 0.3   | 17.1 | 0.07 | 0.02 | 42.9 |
| Calcite        | 53.5 | 1.5  | 0.3   | 0.2   | 1.7  | 0    | 0    | 42.8 |

LOI: Loss on ignition at 1000°C

However, different sources of carbonate materials compose different composition. Based on XRF analysis, the dolomite from Jawa Timur, Indonesia composed 61.83 %wt. of CaO content is and MgO content is 25.75 %wt. [8]. Compared from table 1, the composition have huge different of CaO content. The dolomite from Indonesia has more CaO content compared to dolomite from Australia [9]. Another comparison is the dolomite composition content from Sverdlovsk Oblast, Russia. The CaO content is 23.16 %wt. and the MgO content is 15.6 %wt. Other than that, the SiO content is very high with 21.7 %wt. Thus, it can be conclude that, different raw materials form different country had various compositions and those compositions are different to one and another. The different of compositions can lead to dissimilar properties and reactions.

3. Geopolymer Concrete

Geopolymer concrete is a new eco green product synthesized from precursor and alkaline activator revealed as a promising construction material to reduce utilization of Portland cement [10]. Geopolymers is an inorganic material of cement where materials that are formed by reacting silica and alumina with a solution of alkaline solutions which consist of Na₂SiO₃ and NaOH resulting from a mixture of crystalline compounds that eventually harden into a new strong compound through a process called geopolymerization process [11]. The precursors for geopolymer are developed from various sources including the natural resource kaolin and industrial wastes or byproducts, such as fly ash and ground granulated blast furnace slag (GGBFS) [12].

Chemically, geopolymers contain of cross-linked units of AlO₄ and SiO₄ tetrahedra, where charge-balancing cations are provided by alkali metal cations such as Li⁺, Na⁺, K⁺, and Cs⁺. [13]. Duxson et.
 reported that the geopolymer have many advantages which are high compressive strength, low shrinkage, fire resistance, acid resistance, and low thermal conductivity depending on materials used [14-15]. Additionally, the environmental impacts can be reduced by using the building material that was mixed with green building material for example, geopolymer. The environmental impacts that can be reduced are the low manufacturing energy consumption, low CO2 emission [16], and removal of these construction industry basis resources [17].

Metakaolin, a material produced from kaolin calcinations which has similar content to fly ash was considering as alternative precursor material besides fly ash [18]. Study from Pelisser et al. [19] stated that metakaolin based geopolymers showed high flexural strength and an excellent relationship between the flexural and compressive strength, which indicated good resistance to cracking while under stress.

Other than that, material that contains high calcium (Ca) and magnesium (Mg) also can be used as geopolymer materials. Materials that contain Ca and Mg can have certain effect to geopolymer properties. W.K.W. Lee and J.S.J. van Deventer [20] studied that it was found that calcium (Ca) and magnesium (Mg) shortened the setting time by providing heterogeneous nucleation centers in the initial paste solution. The Ca and Mg accelerated the setting in a similar fashion as all the other no treated systems.

4. Dolomite Addition into Geopolymer

A study conducted by Christina K. Yip et. al. [21] demonstrated 20% of dolomite additions into metakaolin increase its compressive strength of all the samples done. The strength was significantly increased up to 100 days with more than 50MPa. More than 20% of dolomite addition in the metakaolin was found to be detrimental, which is likely to be caused by a low degree of geopolymeric gel formation and connectivity. They also conclude that it is possible that Mg2+ plays a similar role to Ca2+.

E. A. Aizat [22] studied the compressive strength of the dolomite geopolymer with different NaOH molarities. The usage of solid/liquid ratio prepared is 2.5 and the Na2SiO3/NaOH is also 2.5 to this dolomite geopolymer. After that, they were cured at the temperature 80°C for 24 hours. After 7 day the test for compressive strength was done and the compressive strength of dolomite geopolymer increased as the NaOH increased. NaOH molarity up to 20M gave the highest compressive strength of all molarities. The usage of dolomite as the core material results that high concentration of NaOH and high curing temperature needed to be used. This is due to the low composition of Al and Si in dolomite that causes the less reactivity between dolomite and alkaline activator. Thus, a high NaOH concentration is needed which is 20M to increase the dissolution process for ions Al3+ and SiO4+ as well as the development of geopolymer network systems.

The geopolymer material that had composition of high CaO will improve the geopolymer strength [23]. Although with the high content of CaO in the dolomite geopolymer, the compressive strength is still low compared to the fly ash geopolymer [24]. Thus, the dolomite geopolymer need a filler to increase its properties or it can be used as a filler to improve other properties.

Unfortunately, Study form Y. Zarina et al. [25] with the addition of dolomite into the boiler ash with up to 5% has decreased the strength of boiler ash based geopolymer. The NaOH molarity was fixed with 12M used for all the mix design. The solid/liquid ratio used is 1 and the Na2SiO3/NaOH used is 2.5 [26]. The boiler ash geopolymer without dolomite addition into it gave the highest compressive strength out of all compared to the dolomite addition into boiler ash. The compressive strength for boiler ash with no dolomite addition is 19.4 MPa. The comparison between the additions of dolomite showed that the addition of 4% dolomite has the best out of all addition compared to other composition with dolomite. The researchers also conclude that the addition of dolomite has disturbed the formation of three-dimensional geopolymeric aluminosilicate network which has influence the strength of geopolymer.

5. Calcite Addition into Geopolymer
C. K. Yip et al. also did the study on the calcite addition into metakaolin. Calcite content results also parallel to dolomite. Calcite addition tends to lead a stronger geopolymeric reaction compared to dolomite. It is due to simple a micro-aggregate effect which suggests that the minor quantity of dissolution of the carbonate minerals that is observed is enough to release enough Ca²⁺ or Mg²⁺ to have a noteworthy result on the geopolymer gel structure [21].

Another studies form C. K. Yip et al. which focuses on role of calcium in improving cement durability [27]. It is suggested that calcium provides a crucial link between the chemistries of geopolymerisation and the hydration of cement. Samples were synthesised using a metakaolin to calcite ratio of 0.8. The solid to liquid ratio was 0.69 for Ms = 2.3 and 0.61 for Ms = 1.5. These ratios were selected so as to maintain consistent water content in all synthesised material. Results showed that addition of calcite during Ms = 2.3 showed low strength at day 1 which was less than 5MPa. But, on day 90, the strength increased to 30.1MPa. Meanwhile for Ms = 1.5, the strength shows steady increased from day 1 to day 90 which was from 42.1MPa to 47.6MPa. It is also clear that the type of calcium source added and the alkaline conditions used have a significant impact on the resultant binder.

Other than that, Patrick N. Lemougna et al. [28] reports the development of inorganic polymers from laterite, for a potential use at least as non-load bearing building materials The effect of blending laterite with Ground Granulated Blast Furnace Slag (GGBS) and calcite (CaCO₃) was investigated. Laterite was substituted by calcite at 2 to 20% in mass. Sodium silicate solutions of modulus ranging from 1.6 to 2.2 were used to prepare inorganic polymers from laterite that had been thermally treated at 700 °C. The strength increased with the reduction of the modulus of the activating solution, achieving a 28 days maximum compressive strength of 36 MPa at 25 °C. The substitution of up to 20% laterite by calcite was found to have little effect on the compressive strength. At variance, slag/laterite combination presented better strength performance, mainly above 20% of slag, and achieved a 28 days compressive strength of 65 MPa with a composition made of 50% laterite and 50% slag.

Conclusions

Epoxidized vegetable oils have been researched by many researchers in this past years because of they are derived from renewable and sustainable resources that can be used to replace petrochemical raw material in the future. In this study, palm olein from palm oil has been epoxidized using in-situ formed peracetic acid in order to produce epoxidized oleic acid. The DHSA can be synthesised from the epoxidized palm olein by reacting with water that can decreasing the RCO% and producing hydroxyl fatty acid that can also be used as ramaterial for industries.

6. Conclusion

As conclusion, this paper summarized the usage of carbonate material which is dolomite and calcite in geopolymer. Carbonate material is a potential to become a precursor material for the replacement of used precursor material for geopolymer. Moreover, it was found that the CaO content in calcium sources had impact on the resultant compressive strength. On the contrary, the mineralogy of the calcium sources used and the concentration of sodium hydroxide present were found to have a significant influence on the resultant product. Besides, the use of dolomite which is abundant and potentially offer sustainable solution and environmental friendly for extending the service life of infrastructure and maintenance cost. Development of carbonate material geopolymer less been explored. It is hoped that future research in this field will drive a new era of greener materials in the geopolymer industry.

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