# MARBLE BASED GREEN CEMENT BY USING GEOPOLYMER TECHNOLOGY

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## ABSTRACT

Greenhouse effect is an important topic since it has been responsible for global warming. Carbon dioxide also plays a part of role in the greenhouse effect. Therefore, human has the responsibility of reducing $CO_2$ emissions in their daily operations. Except iron making and power plants, another major $CO_2$ production industry is the cement industry. Estimation by EPA of Taiwan, production 1 ton of cement will produce 520.29 kg carbon dioxide. There are 7.8 million tons of $CO_2$ produced annually. Thus, to synthesize low $CO_2$ emission geopolymeric green cement is important and can reduce $CO_2$ emission problems in Taiwan.

The purpose of this study is trying to use marble wastes as the raw material to fabricate geopolymer green cement. Experiment results show that the setting time of green cement was exceed 4 hours. After curing 28 days, the compressive strength of marble based geopolymer green cement paste can reach 65 MPa, that is higher than traditional Portland Cement.This study is based on resource recovery and recycling. Its basic characteristics are low consumption, low emission and high efficiency that meet the Taiwan government's policy of "Circular Economy", and this is an international tendency. According to experimental results, the marble-based geopolymer green cement can be developed as a low $CO_2$ emission green cement. By comparing with Portland cement paste, production 1 ton of marble-based geopolymer green cement paste, it can be saved around 53.8% carbon dioxide emission. Production 1 ton of green cement paste will cost about 1350 NTD (~42 USD) that cheaper than traditional Portland cement paste. It is proved that the green cement has very good potential for further engineering development in the future.

## 1 INTRODUCTION

The greenhouse effect is an important topic since it has been responsible for global warming. Carbon dioxide also plays a part of role in the greenhouse effect. Therefore, human has the responsibility of reducing $CO_2$ emissions in their daily operations. According to International Energy Agency IEA/OECD statistics in 2015, energy related carbon dioxide emissions was over 248.7 million tonnes in Taiwan and ranked No. 22 in the world's [1]. It is well known that the production of OPC emits large quantity of carbon dioxide [2]. Cement manufacturing is one of the highest carbon dioxide emission industries. According to EPA of Taiwan statistics in 2015, production 1 tons of cement will produce 520.29kg $CO_2$( not including mining development stage). There are 15 million tonnes of cement will produced every year in Taiwan, it means 7.8 million tonnes of $CO_2$ produced annually in Taiwan by cement industries. Thus, to synthesize low $CO_2$ emission geopolymeric green cement is important and can reduce $CO_2$ emission problems in Taiwan.[3]

Geopolymer, similar to natural zeolite minerals, is a class of three-dimensionally networked alumino-silicate materials [2], and is an inorganic non-metallic material newly developed in recent years. Due to its superior mechanical and physical properties, such as non-combustible, heat-resistant, fire/acid resistant, easy to make it, and formed at low temperatures, geopolymer have been gradually attracting world attention as potentially revolutionary green materials. Previous studies have presented when using geopolymeric technology to make geopolymer could reduce over 70 % carbon dioxide emission [5].

In this study, marble and blast furnace slag (BFS) were used as raw materials to fabricate marble-based geopolymeric green cement under the activation of alkaline solutions of various molar ratios at ambient condition. The characteristics of marble-based geopolymeric green cement in workability (viscosity, setting time), compressive strength, specimen shrinkage and $^{29}Si$, $^{27}Al$ NMR analysis were presented in this study.

## 2 EXPERIMENTAL

The marble samples used in this study were collected from a marble mine in eastern Taiwan. The blast furnace slag (BFS) samples were produced from China Steel in southern Taiwan. The chemical composition of marble and BFS were analyzed by X-ray fluorescence (XRF), as listed in Table 1.The major composition in marble and blast furnace slag was calcium oxide, however, the blast furnace slag also contains 27.7 % of $SiO_2$. Alkali solution was prepared by mixing NaOH, sodium silicate and sodium aluminate, the $SiO_2/Na_2O$ molar ratio was controlled at 1.28 and 1.5, the $SiO_2/Al_2O_3$ molar ratio was controlled at 20, 50 and 100 . The experimental procedure and test parameters were shown in Figure 1 and Table 2.

The setting time test of green cement was followed CNS 786 and analysis by Vicat Needle. Compressive strength test of green cement was followed CNS 1232. Specimen shrinkage test was followed CNS 1258. According to CNS 3036, the specimen shrinkage should less than 0.8%.

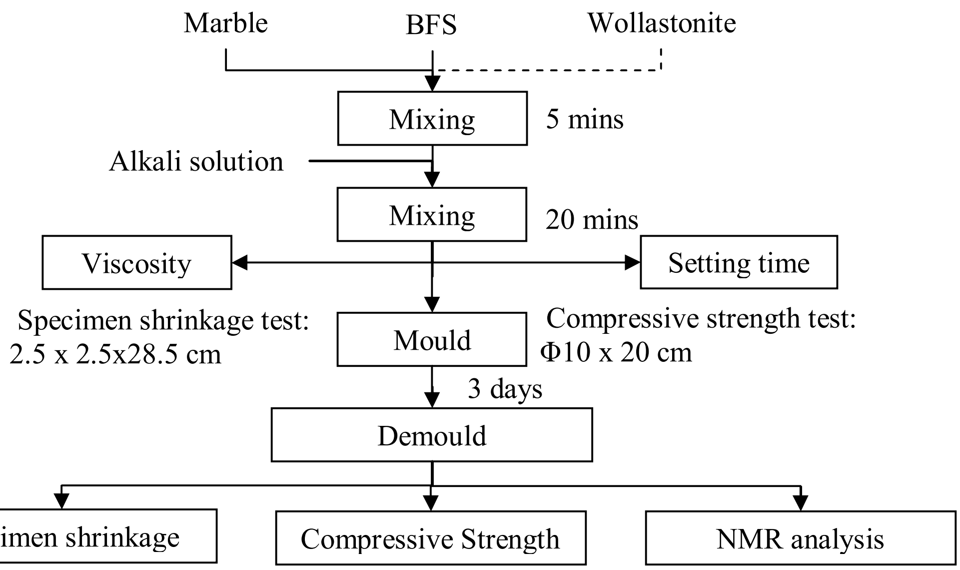


Figure 1: Overall experiment procedures

| Composition / wt. % | $SiO_2$ | CaO | $Al_2O_3$ | $Fe_2O_3$ | L.O.I. | Other |
|---|---|---|---|---|---|---|
| Marble | 1.0 | 60.9 | 1.3 | - | 35.6 | 1.2 |
| Blast furnace slag | 27.7 | 57.9 | 11.2 | 0.4 | - | 2.8 |

Table 1: Marble & Blast furnace slag Chemical Composition

| Experiment No. | Solid Materials wt.% | Alkali Solution | | | Liquid / Solid wt.% ratio |
|---|---|---|---|---|---|
| | Marble: BFS | NaOH | $SiO_2/Na_2O$ | $SiO_2/Al_2O_3$ | |
| MS01 | 80:20 | 6M | 1.28 | 20 | 0.55 |
| MS02 | | | 1.5 | 50 | |
| MS03 | | | 1.28 | 100 | |
| MS04 | | | 1.5 | 20 | |
| MS05 | | | 1.28 | 50 | |
| MS06 | | | 1.5 | 100 | |
| MS07 | 60:40 | 6M | 1.28 | 20 | |
| MS08 | | | 1.5 | 50 | |
| MS09 | | | 1.28 | 100 | |
| MS10 | | | 1.5 | 20 | |
| MS11 | | | 1.28 | 50 | |
| MS12 | | | 1.5 | 100 | |

Table 2: Experiment Parameters

## 3 RESULTS AND DISCUSSION

### 3.1 Workability of green cement (viscosity, setting time)

The effects of different parameters on workability of green cement are shown on Table 3. The viscosity of green cement paste can be decreased by increases the amount of sodium aluminate in alkali solution. The initial and final setting time increases as the amount of sodium aluminate in alkali solution increases. Because green cement was formed by geopolymerization, and the structure of geopolymerization usually was Si-O-Al, it means more Al involved in reaction, the structure of green cement will more complete. As the results shown, when geopolymerization more complete, more geopolymer gel will release, thus the viscosity of green cement paste will decrease and the setting time of green cement will increased.

However, when increased the amount of sodium aluminate in alkali solution will making alkali solution unstable, thus the $SiO_2/Al_2O_3$ =20 was the limitation of the adding amount of sodium aluminate.

According to the experiment results and the properties of portland cement, while using different parameters to form green cement, the viscosity of paste can be less than 5000 mPa • s, the initial setting can longer than 45 min, and the finial setting time can less than 360 min.

### 3.2 Compressive strength test

The effects of different parameters on compressive strength of green cement are shown on Figure 2 and Figure 3. As the results shown, the compressive strength of green cement was affected by the mixing ratio of marble and BFS. The compressive strength of green cement increases as the amount of BFS increase. Because BFS has higher reactivity than marble, and it leads the geopolymerization more complete.

However, micro cracks on geopolymer specimen were observed if the amount of BFS is over 40 %, and thus, the amount of BFS can't be increased over than 40%. According to the experiment results, the compressive strength of green cement can be reached over 40MPa. Compare with portland cement, the compressive strength of green cement was higher than Portland cement.

| Experiment No. | Solid Materials wt.% | Alkali Solution | | | Viscosity (mPa·s) | Setting time (min) | |
|---|---|---|---|---|---|---|---|
| | Marble: BFS | NaOH | $SiO_2/Na_2O$ | $SiO_2/Al_2O_3$ | | Initial | Final |
| MS01 | 80:20 | 6M | 1.28 | 20 | 4100 | 125 | 225 |
| MS02 | | | 1.5 | 50 | 3900 | 95 | 170 |
| MS03 | | | 1.28 | 100 | 8250 | 45 | 65 |
| MS04 | | | 1.5 | 20 | 2500 | 135 | 180 |
| MS05 | | | 1.28 | 50 | 4150 | 75 | 110 |
| MS06 | | | 1.5 | 100 | 2400 | 85 | 140 |
| MS07 | 60:40 | 6M | 1.28 | 20 | 4100 | 100 | 145 |
| MS08 | | | 1.5 | 50 | 5700 | 30 | 60 |
| MS09 | | | 1.28 | 100 | 8500 | 35 | 60 |
| MS10 | | | 1.5 | 20 | 4200 | 40 | 80 |
| MS11 | | | 1.28 | 50 | 4150 | 60 | 85 |
| MS12 | | | 1.5 | 100 | 8300 | 30 | 55 |

Table 3: Workability of green cement ( viscosity and setting tim)

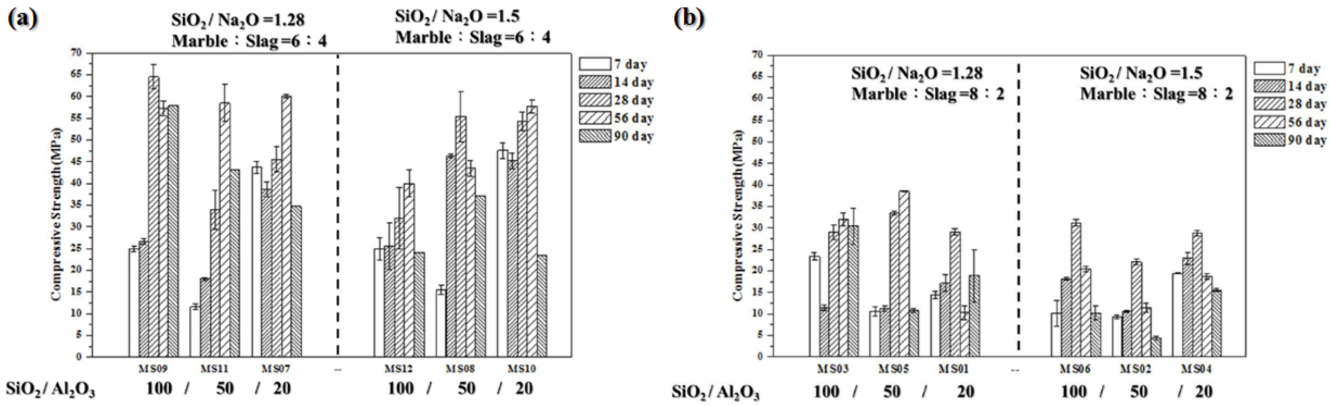


Figure 2: Effect of various alkali solution condition on green cement compressive strength (a) Marble / BFS wt.% ratio = 60:40 (b) Marble / BFS wt.% ratio = 80:20. Liquid / Solid wt.% ratio = 0.55.

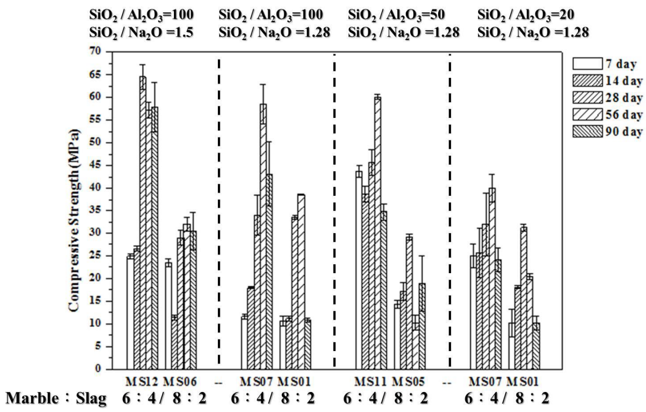


Figure 3: Effect of marble/BFS ratio on green cement compressive strength.
Liquid / Solid wt.% ratio = 0.55.

### 3.3 Specimen shrinkage test and improvement

Due to the micro cracks was observed on marble based green cement. These micro cracks were generated from shrinkage as shown on table 4. Thus, in this part of experimental is trying to add some filler to improve the shrinkage issue. As the results shown on table 4, the shrinkage issue of green cement can be improved when adding wollastonite into green cement. Because the particle shape of wollastonite is needle-like, when green cement dehydration, it can grabs different particles to prevent shrinkage. According to experiment results, when adding 1wt% of wollastonite into green cement, the specimen shrinkage can be controlled belows to 0.8%.

| Experiment No. | Specimen shrinkage (%) in different curing days | | | Curing method |
|---|---|---|---|---|
| | 7 days | 14 days | 28 days | |
| MS11 | -2.33 | -2.4 | -2.46 | Curing in ambient temperature |
| MS11 - 1wt% Wollastonite | -0.51 | -0.53 | -0.63 | Curing in ambient temperature |
| MS11- 3wt% Wollastonite | -0.23 | -0.35 | -0.42 | Curing in ambient temperature |
| MS11- 5wt% Wollastonite | -0.04 | -0.21 | -0.25 | Curing in ambient temperature |

Table 4: Shrinkage of green cement - Results of before and after improvement

### 3.4 NMR analysis

After 28 days curing, marble-based green cement sample was analyzed using Nuclear Magnetic Resonance Spectroscopy (NMR).

NMR analyze results as shown in Figure 4, it can be found that the $Q_4^4$ in marble based green cement, the $Q_4^4$ area was increased when increased the amount of slag. This is because slag have better reaction, after geopolymeric reaction, slag can dissolve large amount of Si for forming $Q_4^4$. In marble-based green cement system, the main Si sources is BFS or sodium silicate, therefore over 50% $Q_4^4$ was measured in the marble based green cement. According to the analyze results, the $^{27}$Al structure in green cement was major with Al(IV), it means most Al were bond with Al-O-Si.

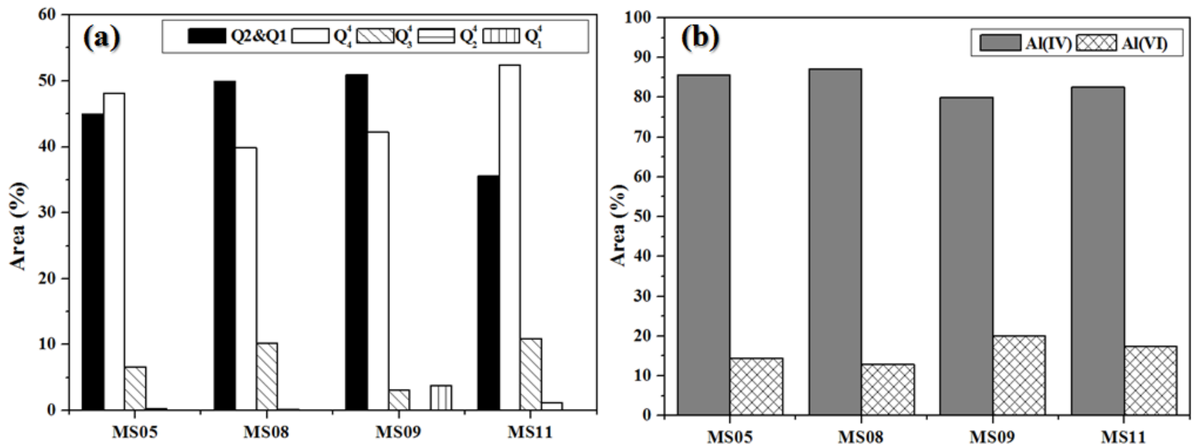


Figure 4: NMR analyze result (a) $^{29}$Si (b) $^{27}$Al

### 3.5 Green cement- $CO_2$ emission estimate

According to Taiwan EPA statistics in 2015, production 1 tons of portland cement will produce 520.29kg $CO_2$ ( not including mining development stage). The statistics of $CO_2$ emission on marble based green cement as shown on table 5. By comparing with Portland cement paste, production 1 ton of marble based green cement paste, it can be saved around 53.8% carbon dioxide emission.

| Item | Marble based green cement paste | Portland cement | Portland cement paste |
|---|---|---|---|
| $CO_2$ emission estimate | 0.17162 ton $CO_2$ /ton green cement | 0.52029 ton$CO_2$ /ton cement | 0.37200 ton $CO_2$ /ton cement paste |
| $CO_2$ emission reduction | - | 67.0% | 53.8% |

Table 5: $CO_2$ emission estimate of green cement paste (compare with Portland cement paste)

## 4 CONCLUSIONS

Marble and BFS based green cement was successfully developed in this study. After curing for 28 days, the compressive strength of marble-based green cement can reachs 42~60 MPa. The viscosity of geopolyme paste can be controlled between 2400 ~ 8250 mPa • s, and the final setting time can be controlled between 55~220 min. After adding needle-like filler into green cement system, the shrinkage issues can be improved. It is believed that the fabrication of marble-based green cement has great potential for engineering application.

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