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Calcinated Singapore marine clay as a form of cement substitute for concrete

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ABSTRACT

The rapid pursued for urban and economic development across the globe leads to an increase of construction activities. Concrete being one of the most common building material would continue to be in high demand. Unfortunately, the primary constituent of concrete, cement, is not only energy-intensive to produce but contributes significantly to the Earth's carbon footprint. Recent studies suggest that the use of calcined clay as a means of substituting cement in a concrete mix may offer a sustainable solution to cater to this growing demand. In addition, calcined clay when used as substitution to the concrete matrix may enhance engineering properties such as an increase in compressive strength, while contributing lowering CO_2 emissions as compared to conventional Ordinary Portland cement. The potential of this substitution is highly dependent on the minerals and composition of natural occurring clays. Since little or no investigation on the suitability of Singapore Marine Clay (SMC) has been carried out, this study aims to formulate an optimal technique of converting unwanted SMC as a form of cement substitute. Our results shows that calcined SMC can optimally replace cement by 20% while achieving strength greater than its pure cement mortar with lower energy requirement and carbon emission given that calcination requires only an activation temperature of *700°C* as compared to *1450°C* for cement.

Keywords: metakaolin, kaolin clay, supplementary cementitious materials

1 INTRODUCTION

The Building Construction Authority of Singapore recently announced that the projected construction demand for 2019-2022 are valued between \$28 billion and \$35 billion. The appeal for construction works in Singapore will cause an increase in demand for concrete, which will pose a huge challenge to our already resource scarce island. Amongst all other construction material, concrete emerges as the most suitable building material as it exhibits favourable properties such as high durability, high compressive strength and low maintenance. However, the production of a main constituent of concrete, cement, have been heavily criticized as not only energy-intensive but highly hazardous, accounting for up to 8% of total man-made CO_2 emissions (Scrivener and Nonat, 2011). Production of concrete involves a closely-controlled chemical combination of limestone, clay and other natural minerals heating at a high temperature of 1450°C in a kiln. Calcium carbonate (limestone) undergoes decomposition under high heat to form calcium oxide, as shown in Eq. 1.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \qquad (1)$$

Moreover, large amounts of fossil fuels are required to generate the heat required for this process, leading to another contribution of CO_2. It is estimated that 0.8-0.9 tonne of CO_2 is emitted in the production of 1 tonne of ordinary cement concrete (Damtoft et al.,2008).

In pursue of maximizing land, many construction projects also involves underground excavation works, resulting in unwanted excavated soil. In Singapore, enormously large amount of unwanted excavated soil are derived from islandwide underground subway network and basement construction that has to be disposed of. More underground construction activities are expected as revealed by the Masterplan of Singapore's Underground Space (Ng, 2018). These wastes have to either be disposed off at offshore containment sites or landfill sites. Both of which are undesirable. Hence, in order to support continual development plans, Singapore has to look into alternative means to address such influx of unwanted soils.

Studies elsewhere have shown that by heating naturally occurring clay 550-900°C allows calcination to occur (Tironi et al., 2013). However, little or no investigations have been made on the possibility of obtaining calcined clay from our native strata underground. Simply using an activation temperature from comparable studies will not yield accurate results as it is unique to the chemical composition of the naturally occurring clay, determined by climate, years of deposition and sedimentation. This paper thus aims to investigate the suitability of converting unwanted Singapore marine clay as a sustainable substitution of cement through thermal treatment called calcination. The temperature of this thermal treatment is at least 40% lower than conventional cement production (Tironi et al., 2013). As a result, it could serve as a greener technology given its lower CO_2 emissions.

2 POTENTIAL OF SINGAPORE MARINE CLAY AS CEMENTITIOUS SUBSTITUTE

Calcined clay is produced by heating clays containing kaolinite mineral in a kiln at high temperatures for dehydroxylation to occur. In order to affirm the abundance of kaolinite in our naturally occur clay, an X-ray Power Diffraction (XRD) test was conducted. The XRD result is shown in Figs 1 and 2.

The higher intensity implies a stronger diffraction of x-ray by the crystal at that direction of the sample. However, individual peak intensities do not reflect concentration or percentage by mass of a phase. Hence, matching of diffraction patterns to known crystalline structures was carried out to find out the presence of minerals in the sample.

It can be seen in Table 1 that in raw Singapore marine clay, kaolinite exists in the largest amount making up 78% by weight with illite making up 21%. When the same procedure was carried out with calcined SMC, the percentage by weight of kaolinite decreased significantly from 78.9% to 29.7% after thermal treatment. With that, we have reason to believe that the kaolinite mineral undergoes a breakdown of crystalline structure from stable kaolinite to amphorous metakaolin.

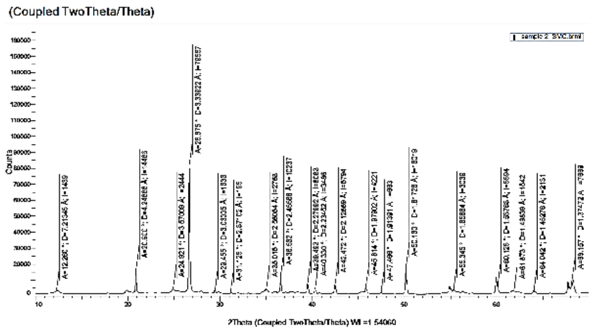


Fig. 1 XRD test results for Singapore Marine Clay

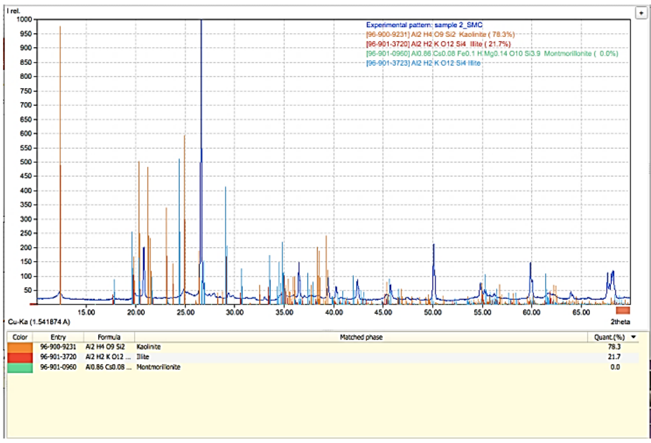
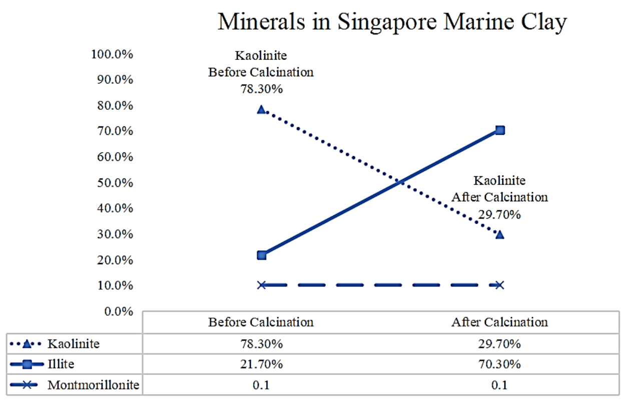


Fig. 2 Phase identification and % by weight of Singapore Marine Clay

Table 1 Percentage by weight of minerals from obtained from phase identification



Mineral (Excluding the impurity, Quartz)	% by weight of Mineral before calcination	% by weight of Mineral after calcination

3 OPTIMIZING CALCINATION TO OBTAIN ACTIVE METAKAOLIN

Dehydroxylation is the process of removing structural water or hydroxyl group (OH), leaving the kaolin clays thermally active in an amphorous state forming active metakaolin. It can be represented by the formation of H_2O and oxygen from two hydroxyl groups as shown in Eq 2.

$$2Al_2Si_2O_5(OH)_4 \rightleftharpoons 2Al_2Si_2O_7 + 4H_2O \quad (2)$$

The formation of active metakaolin highly influences the strength of the resulting concrete structure. In order to adapt this to local soils Singapore marine clay and construction purpose, our objectives are to:

1) Determine the optimal temperature to obtain the highest amount of metakaolin from Singapore marine clay.
2) Determine the suitable percentage of calcined clay to substitute cement in the concrete mix.

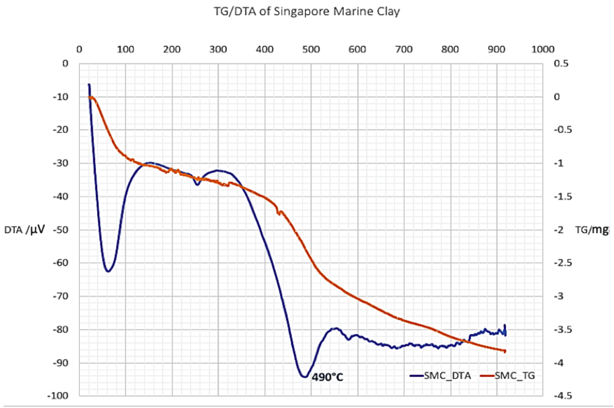


Fig. 3 TG and DTA of 30mg of dried Singapore Marine Clay

Since the optimal temperature is still unique to the compositions of the clay mineral, Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) test were done on a 30mg sample of oven-dried powdered Singapore marine clay. The output can the found in Fig. 3. TGA measures the changes in weight in relation to the increase in temperature and the resulting decomposition and chemisorption to the sample. On the other hand, DTA measures the change in mass of sample over a range of temperature. It allows the identification of any exothermic and endothermic reactions. The reaction of clay in response to the changes in thermal decomposition indicates how Singapore marine clay will react at these temperatures. From the test, we can conclude that the desired calcination temperature to optimize the calcination procedure will lie between 580°C and 950°C.

4 CALCINATION OF SINGAPORE MARINE CLAY

The calcination will be conducted using a well-insulated and ventilated furnace at 500 $°C$, 700 $°C$ and 900° C with a dwelling time of 1-hour at atmospheric pressure. This is done by placing the marine clay into crucibles and stacking them to maximize the space in the furnace as illustrated in Figure 5.3. The furnace is set to ramp up and down at a rate of $75\,°C/min$. However, we note that it took approximately 40 minutes for the furnace to ramp up to the desired temperature. After the 1 hour dwelling at the desired temperature, it takes an hour for it to cool down to 100-200$°C$. The calcined clay was then removed from the furnace. The total heating and cooling process is shown in Fig. 4.

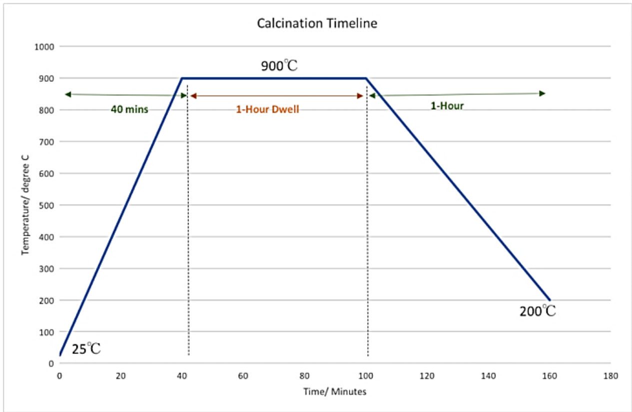


Fig. 4 Calcination timeline for thermal treatment

Fig. 5 Calcination procedure of Singapore Marine Clay

After which, the crucibles are removed from the furnace and cooled on a tray at ambient temperature for 30 minutes before the calcined clay is emptied from the crucibles and blended to powdered form.

5 COMPRESSIVE STRENGTH OF CEMENT WITH CALCINED CLAY

Now that we have obtained the blended calcined clay, we will prepare cement specimens substituted with calcined clay for compressive testing. The viability of using calcined clay as a substitute is assessed by changing two parameters. First, trial Mix A investigates the effect of calcined clay obtained from different temperatures namely $500\,°C$, $700\,°C$ and $900°C$. The mix proportion is displayed in Table 2. Secondly, Mix B examines how the different percentages of cement substitution by mass of calcined clay influences compressive strength of cement mortar. In both studies, the obtained strength was compared against pure Ordinary Portland cement (OPC).

Table 2 Mix Proportion of Cement Mix A

Name of Mix	Cement	Calcined clay	Water
OPC	1	0	0.5
$500°C$	1	0.1	0.5
$700°C$	1	0.1	0.5
$900°C$	1	0.1	0.5

Table 3 Mix Proportion of Cement Mix B

Name of Mix	Cement	Calcined clay obtained at $900°C$	Water
OPC	1	0	0.5
10% CC	0.9	0.1	0.5
20% CC	0.8	0.2	0.5
30% CC	0.7	0.3	0.5

Note: 10% CC – 10% of cement replaced with calcined clay

The mixing was facilitated with the use of a Hobart Mixer. Each mechanical mixing took 10mins to ensure consistency, following the Japanese Standard JGS 0821 (Japanese Geotechnical Society, 2009), in which 1 minute of manual mixing is required to remove soil attached to the walls of mixing bowl in between the 10mins of mechanical mixing. A uniform paste is obtained and transferred to a plastic cylindrical split mold of 50mm in diameter and 100mm in height. The specimen was compacted in 5 layers by manual tapping at a constant rate for 30 seconds for each layer. This was carried out to minimize any entrapped air voids in the concrete block when it hardens. Once the plastic molds were filled, their mass were checked for consistency before leaving them to cure in a water bath till the desired age for testing. The ambient temperature was set to around $23\,°C$. The specimen's compressive strengths were tested at 4 curing ages, namely: 1-day, 3-day, 7-day and 28-day. To obtain a smooth surface for testing, the specimens were trimmed or grinded (Fig 6).

Fig. 6 Unconfined compression strength test procedure

The specimens were subsequently tested for compressive strength via an unconfined compression apparatus. A loading rate of 1250 kN/min was applied until the specimen fails. The peak force was recorded for each specimen, and the unconfined compressive strength of the specimen obtained using Eq 3:

$$\sigma_C = \frac{F}{A} \tag{3}$$

where:

F= Peak compressive force at failure

A= Cross-sectional area of specimen

Results and Discussion

From Fig. 7, the trial mix with calcined clay obtained at $700°C$ yielded the highest compressive strength, even higher than that of pure OPC. This is attributed to several reasons. First, the finer calcined clay particles provides a filling effect that reduces the void spacing between the concrete mix which ultimately results in a higher compressive strength as denser and interlocking particles provide additional resistance against compressive loads.

Second, a heating temperature of $700°C$ appears to produce an optimal meta-state with more reactive $Al^{[V]}$

in the crystalline metakaolinite, causing the reaction to have a higher pozzolanic activity. This is where the unstable metakaolin in calcined clay react with calcium hydroxide from the hydration of cement. Whereas upon further heating to $900°C$, slight recrystallization occurs which forms a small amount of Spinel- a less reactive, more stable crystalline form of kaolinite. Calcined clay heated to $500°C$ on the other hand seem to result in a low strength mix which suggests that the kaolinite mineral in Singapore marine clay is not activated at this temperature. These are in agreement with the findings from the TGA test in Fig. 3.

Another possibility could be due amphorous metakaolinite reverts back to its stable kaolinite state at $500°C$ after reacting with water vapour in the atmosphere, preventing activation of its pozzolanic potential. Assuming $700°C$ proves to display the highest pozzolanic activity and eventual compressive strength, the unstable metakaolin in this calcined clay will react with calcium hydroxide from the hydration of cement, eventually forming a more strength enhancing calcium silicate hydrate (C-S-H) bond, leading to a higher strength compared to conventional concrete with a compressive strength of 47MPa.

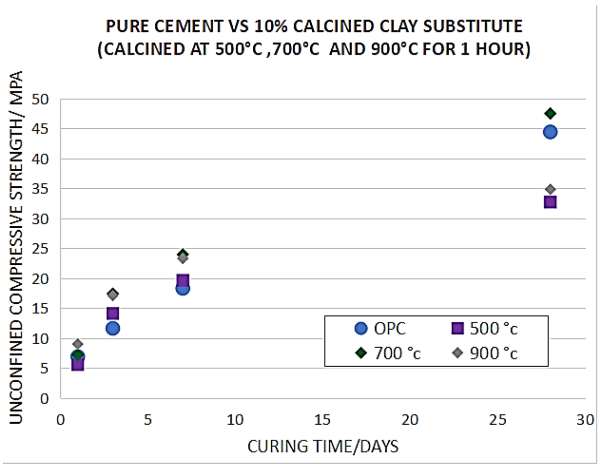


Fig. 7 Results from Mix A: Unconfined compressive strength versus curing time using 10% calcined clay obtained by heating at 500, 700 and 900°C

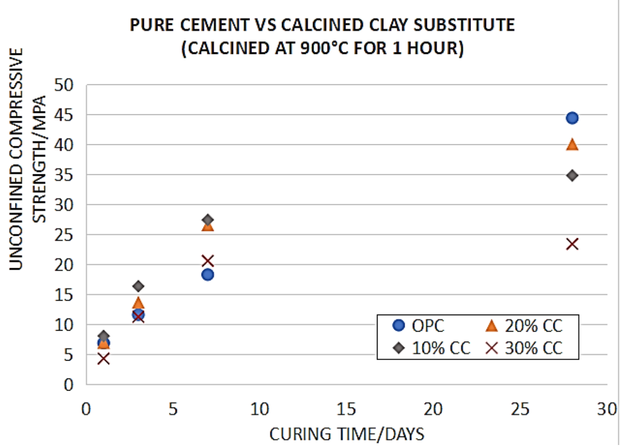


Fig. 8 Results from Mix B: Unconfined compressive strength versus curing time using calcined clay obtained by heating to $900°C$

The optimal percentage of substitution was simultaneously studied and the results indicate that replacement of cement by 20% yields the highest strength of 40 MPa. However, is it noteworthy that Mix B was cured using calcined clay treated at $900°C$ where unreactive layers have formed around the pozzolan. Further experiments using the affirmed optimal temperature of $700°C$ is required to verify the highest compressive strength that this technology can potentially attain.

CONCLUSION

This study has successfully proven that SMC, when calcined, is a viable partial substitute for concrete that offers a higher strength than conventional cement. A better strength performance, yet lower environmental impact, is relevant in land scare cities in the world for greater optimization of space and resources. Calcination of excessive unwanted Kaolinite rich clays would certainly pave a promising avenue to reduce waste, increase resources, lower environmental impact, and higher performance of our infrastructure to meet growing population demand.

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