Valorisation Wastes from Sugar Mill Plant and Water Supply Treatment Process as Alternative Materials for Ecological Ceramic Floor Tiles

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Abstract. Wastes from many industries have an effect on environmental degradation and led problems to manufacturers for disposing them. Likewise, the sugar mill process also generates substantially wastes i.e., bagasse ash and calcium carbonate, which are difficult to eliminate. Furthermore, in water supply treatment process, it has generated the abundant of sediment soil, which are still unutilized and need budgeting for disposing. This research aims to utilize wastes from sugar mill process and water supply treatment process for developing eco-friendly floor tiles ceramics by implementing bagasse ash, calcium carbonate and sediment soil. Tri axial diagram is employed to construct the formula mixtures of three alternative materials with adding brown cullet glass. After dry mixing for all materials according to formulas mixtures, they are moulded by 100 bars of uniaxial pressing in dimension 50x100x7 mm. Then, they are fired at 1100\textdegree{} and 1150\textdegree{} C. Physical properties; bending strength, water absorption, bulk density, \% shrinkage, \% weight loss is examined. Bending strength and water absorption are compared with TIS 2508-2555. In addition, microstructure of fired specimens is analysed by Scanning Electron Microscope and X-ray Diffractometer.

1. Introduction
Thailand is the agricultural country cultivating many types of crops i.e., rice, sugarcane, oil palm, casava, etc. With the high production of sugarcane, in 2019 Thailand is ranked third for planting this crop after Brazil and India. [1]. Sugarcane is used as raw material source in the sugar mill manufacturing. When feeding into the extracting process, it is transformed to bagasse. This residue has been recycled as fuel material of boiler in the sugar mill plant. After the combustion process, huge amount of bagasse ash has been generated. In addition, in the process of producing sugar, milk of calcium oxide is exploited for purifying sugar and transformed to calcium carbonate (CaCO\textsubscript{3}) after used. These residues; bagasse ash and calcium carbonate (CaCO\textsubscript{3}) have led the problems to manufacturers for disposing and eliminating them. The alternative ways for reutilizing these wastes have been investigated. With the content of silica in bagasse ash and calcium in CaCO\textsubscript{3}, they have the potential to be exploited for developing ceramic bodies. However, soil and clay should be utilized in ceramic bodies for promoting the work pieces’ plasticity. Considering on water supply treatment process, Metropolitan Waterworks Authority (MWA) is one of the important state enterprises providing water supply to people in the metropolitan area [2]. In the treatment process, abundant of sediment soil has been generated at the clarification station, accounting for 0.1 million ton/year. Utilizing this sediment soil in ceramic items is should be carried out.
Considering on solid wastes which had been reported by the Pollution Control Department of Thailand, it found that 2.5 million tons of glass cullet were generated in 2017. The 73% of cullet had been recycled which 27% of wastes was remained [3]. Therefore, recycling glass cullet for promoting low sintering temperature of ceramic tiles should be performed. Brown glass cullet is derived from the glass manufacturing in Thailand. As mentioned above, this paper aims at utilizing the four residue materials; bagasse ash, CaCO₃, sediment soil, and brown glass cullet for developing ceramic tiles. However, the literature review about the relevant research has been investigated which will be described in the following section.

2. Literature review

There are many researchers studying on reutilizing agro-industrial residue for developing the eco-products and further conserving the environment. Likewise, the present paper focuses on utilizing wastes from the sugar mill plant; bagasse ash and calcium carbonate and wastes from the water supply treatment process; sediment soil. The relevant studies will be described as follows.

Exploiting bagasse ash is extensively interested and has been carried out by many researchers [4] [5]. Chusilp et al. [6] had utilized bagasse ash as pozzolanic material of concrete. They summarized that replacement 20% bagasse ash for Type I Portland cement of concrete had the highest compressive strength. Rukzon and Chindaprasirt [7] also studied the effect of replacement bagasse ash in Portland cement Type I on compressive strength of concrete. The result showed that 30% bagasse ash can improve the specimens’ strength. Setayesh et al. [8] examined the physical properties and resistance to sustained elevated temperatures of concrete by using bagasse ash as admixture. They reported that up to 10% bagasse ash content at room temperature, can increase the compressive strength of concrete. As mentioned earlier, most researches have focused on utilizing bagasse ash as alternative material in concrete. However, incorporation this residue in ceramic mixtures is also attempted in the other studies. Souza et al. [9] investigated the result of bagasse mixed in clayed raw material for producing roofing tile. They reported that 60% bagasse ash replacement in clayed material fired at 1100 °C can provide higher than 13 MPa flexural strength of ceramic bodies. The experimental result of Maza-Ignacio et al. [10] proposed that the mixture of 70% CLAY + 20% bagasse ash + 10% silica fume fired at 1100 °C can provide 8 MPa flexural strength of fired bricks.

Calcium carbonate, residue from industrial process, is also highly concerned to be recycled. Montero et al. [11] utilized calcium carbonate, residue from the stone industry for producing ceramic bodies. The increase of residue has decreased the bending strength of fired specimens. However, 15 and 20% of calcium carbonate replacing in clayed material fired at 1050 °C have 9 and 11 MPa bending strength of ceramic bodies. Wangrakdiskul et al. [12] used crushed limestone dust from stone mill plant for developing non-fire wall tile. The optimal content of calcium carbonate is 15% having 2.32 MPa of bending strength. Zanelli et al. [13] studied about utilizing Calcium Carbonate, waste from pulp and paper industry. They suggested that 15% CaCO₃ can replace material in wall tiles.

Clayey material is mainly used in ceramic manufacturing. Investigating the alternative material for substitution clay has been attempted. Sediment soil or sludge, residues from industrial process can be considered as clay material. Exploiting these wastes for ceramic manufacturing has been proposed by many efforts. Teixeira et al. [14] studied about utilizing sludge from water treatment plant for ceramic material. They concluded that higher 20% content of sludge fired at above 1000 °C can be incorporated in ceramic bodies. Martínez-García et al. [15] evaluated the effect of using sludge from waste water on ceramic manufacturing fired at 950 °C. They summarized up to 5% sludge can be substituted clay material of ceramic bodies. Wangrakdiskul et al. [16] developed the vitreous china ceramic by utilizing sediment soil which fired at 1250 °C. They concluded that 15% sediment soil is the optimal content. Wangrakdiskul and Neumrat [17] reported that exploiting 35% sediment soil for developing non-fired wall tiles can provide higher bending strength than that of wall tile fired at 850 °C.

In addition to recognition on utilizing residues from industrial process, reducing fossil energy-consumed in manufacturing process is also concerned. Especially, ceramic industry is also consuming high energy in the firing process. Solid waste, i.e., glass cullet can be considered as material for reducing temperature in ceramic manufacturing. Demir [18] proposed that a mixture with additive of waste glass up to 10%
in building brick production is feasible and a suitable firing temperature was 950 °C. Phonphuak et al. [19] proposed that used of 10 wt.% waste glass in clay brick fired at 900 °C had the similar strength compared with the normal clay brick fired at 1000 °C. Kazmi et al. [20] showed the results of utilizing 25% waste glass in clay brick and firing at 850 °C. It can yield the 12.1 MPa compressive strength and 2.1 MPa modulus of rupture. The experiment of [21] summarized that 60% green glass cullet mixing with local clay fired at 950 °C can produce Light Greenish Brown Color Wall Tile with the high bending strength. Wangrakdiskul [22] also studied the reutilizing of glass cullet and sediment soil for wall tile. The experiment showed that the formula contains 60% glass cullet and 30% sediment soil fired at 950 °C has the high bending strength and achieve TIS 2508-2550 standard of Thailand. All relevant studies as mentioned above, the combination the mixture of bagasse ash (BA), calcium carbonate (CC), sediment soil (SS), and brown glass cullet (BGC) is just not carried out. Therefore, this study aims at utilizing these wastes for producing ceramic floor tile and comparing with Thai Industrial Standard (TIS 2508-2555, type B1.b).

3. Materials and method

3.1 Materials

Four main materials have been used in this study consisting of BA and CC are derived from the sugar mill plant, SS is derived from the water treatment process, and BGC is from the bottle glass manufacturing in Thailand. They are determined the composition by wavelength dispersive X-Ray fluorescence spectroscopy (WD-XRF) series Bruker S8 Tiger. The results are shown in table 1.

| Composition | BA   | CC   | SS   | BGC  |
|-------------|------|------|------|------|
| SiO₂        | 73.02| 3.03 | 60.95| 72.1 |
| Al₂O₃       | 10.91| 0.9  | 25.96| 1.6  |
| CaO         | 5.44 | 52.29| 0.91 | 2.4  |
| MgO         | 1.85 | 1    | 1.41 | 0.05 |
| K₂O         | 3.36 | 0.07 | 1.93 | 0.2  |
| Na₂O        | 0.22 | 0.25 | 0.33 | 12.9 |
| Fe₂O₃       | 2.53 | 0.38 | 6.22 | 0.1  |
| SO₃         | 0.54 | 0.66 | 0.57 | 0.15 |
| TiO₂        | 0.41 | 0.04 | 0.85 |      |
| P₂O₅        | 1.44 | 0.21 | 0.45 |      |
| Cl          | 0.1  | 0.09 |      |      |
| ZnO         | 0.01 | 0.01 | 0.02 |      |
| MnO         | 0.09 | 0.01 | 0.18 |      |
| SrO         | 0.01 | 0.01 | 0.01 |      |
| ZrO₂        | 0.04 | 0.03 |      |      |
| Rb₂O        | 0.02 | 0.02 |      |      |

Remark: Analysed by XRF technique

3.2 Methods

All materials have been prepared before mixing up the experimental formulas. First of all, they are dried in the oven at 200 °C for 2 h. Then, they are milled by the ball mill for 2 h and sizing by sieved no. 50 mesh (298 micrometre). The formulation mixtures are conducted as shown in table 2. The composition is determined that SS content is varying from 20, 30, 40, 50, and 60%, which at least 20% proportion of SS for facilitating the plasticity of mixture. Calcium carbonate (CC) content is varying from 10, 20, 30, 40, 50, and 60%. And BA content is varying from 10-70%. For BGC content, it is 20% used as the additional mixture, which for promoting low sintering temperature.
Table 2 Formulation mixture of the experiment

| Group | Formula no. | Raw materials (% wt.) | CC  | SS  | BA  | BGC |
|-------|-------------|-----------------------|-----|-----|-----|-----|
| A     | 1           |                       | 60  | 30  | 10  | 20  |
|       | 2           |                       | 60  | 20  | 30  | 20  |
| B     | 3           |                       | 50  | 50  | 10  | 20  |
|       | 4           |                       | 50  | 30  | 20  | 20  |
| C     | 5           |                       | 50  | 20  | 30  | 20  |
|       | 6           |                       | 40  | 50  | 10  | 20  |
|       | 7           |                       | 40  | 30  | 20  | 20  |
|       | 8           |                       | 40  | 30  | 20  | 20  |
|       | 9           |                       | 40  | 20  | 40  | 20  |
| D     | 10          |                       | 30  | 60  | 10  | 20  |
|       | 11          |                       | 30  | 50  | 20  | 20  |
|       | 12          |                       | 30  | 40  | 30  | 20  |
|       | 13          |                       | 30  | 30  | 40  | 20  |
|       | 14          |                       | 30  | 20  | 50  | 20  |
| E     | 15          |                       | 20  | 70  | 10  | 20  |
|       | 16          |                       | 20  | 60  | 20  | 20  |
|       | 17          |                       | 20  | 50  | 30  | 20  |
|       | 18          |                       | 20  | 40  | 40  | 20  |
|       | 19          |                       | 20  | 30  | 50  | 20  |
|       | 20          |                       | 20  | 20  | 60  | 20  |
| F     | 21          |                       | 10  | 80  | 10  | 20  |
|       | 22          |                       | 10  | 70  | 20  | 20  |
|       | 23          |                       | 10  | 60  | 30  | 20  |
|       | 24          |                       | 10  | 50  | 40  | 20  |
|       | 25          |                       | 10  | 40  | 50  | 20  |
|       | 26          |                       | 10  | 30  | 60  | 20  |
|       | 27          |                       | 10  | 20  | 70  | 20  |

All mixture formulas are mixed up by dry process. After that all mixtures are sprayed with 10% water, then the specimens are pressed in dimension 50x100x7 millimetres by uniaxial pressing at 100 bars. All specimens are dried at 200 °C for 2 h in the oven. Then, they are fired at 1100 and 1150 °C with heating rate 100 °C/h, and soaking for 1 h. After the firing step, all specimens are tested the physical properties; bending strength, water absorption, linear firing shrinkage, weight loss, and bulk density. Samples of each formula consist of 12 pieces. The physical properties of tested samples in terms of bending strength and water absorption are compared with the Thai Industrial Standard (TIS 2508-2555, type BIa). Furthermore, the microstructure of test samples is carried out by Scanning Electron Microscopy (SEM) and X-ray Diffractometer (XRD). The results of the experiment are illustrated in the following section.

4. Results and discussion

4.1 Physical properties

The tested samples are examined the physical properties as mentioned in the earlier section. They are illustrated in table 3, which will be described in details as follows.

4.1.1 Bending strength (BD)

Three points bending has been employed for testing bending strength of specimens. The results are discussed below.

- For firing at 1100 °C, the results show that decreasing of CC has an effect of increasing bending strength. Similarly, trending of firing specimens at 1150 °C has increased the bending strength along with decreasing content of CC. However, the effect of CC that is lower than 20% in group F has led the lower bending strength of specimens.

- The trend of bending strength of each group mixture, it shows that the optimal contents are varying from 30-40% and 20-50% of SS and BA, respectively. This the same results of firing samples at 1100 and 1150 °C.
Higher firing temperature (1150 °C) can induce the higher BD. It is also the effect of sintering material viz BGC.

Table 3 Physical properties of tested specimens; bending strength (BD), water absorption (WA), weight loss (WL), linear firing shrinkage (Sh), and bulk density (Den) fired at 1100, and 1150 °C

4.1.2 Water absorption (WA)
Water absorption is tested to determine the porous body of specimens. All specimens are boiled at 100 °C for 2 h and leave them under water for 24 h. Then, calculating the different weight of specimens before and after boiling. The results of WA of fired specimens at 1100 and 1150 °C are expressed as follows.
- As firing samples at temperature 1100, and 1150 °C, it leads to decrease the WA of specimens as decreasing CC content. Note that, firing temperature at 1150 °C has the higher WA of specimens in group F, containing lower 20% of CC. It shows the inverse effect as comparing with the bending strength (BD).
- It can be stated that low WA of specimens have the high BD, due to highly dense of ceramic bodies.

4.1.3 Weight loss (WL)
After a firing process, ceramic bodies will be loss their weight as the combustion of carbonaceous matter of raw materials used. The different weight of specimens before and after firing process has been calculated.
- Weight loss (WL) of specimens firing at two temperatures; 1100, and 1150 °C, are slightly different. However, its trending shows decreasing of WL as decreasing of CC content. This phenomenon indicates that low CC proportion contribute to the low amount of CO₂ emissions.

4.1.4 Linear firing shrinkage (Sh)
In addition to loss of weight after firing, ceramic specimens are also decreased their bodies. This leads to shrinkage of their dimension. In this study, linear shrinkage is measured by calculating the different of before and after firing’s dimension of specimens. The results are expressed below.
The results of two firing temperature; 1100, and 1150 °C, indicate that reducing CC content has increased the linear firing shrinkage (Sh) of tested samples. It can be evaluated that effect of CC contribute to reduce specimens’ shrinkage. Particularly, 60% content of CC (mixture no. 1 and 2) makes the expansion of samples’ dimensions. It is also led to high porous bodies, and has high water absorption of test pieces (>54% WA of mixture no. 1 and 2). Furthermore, bending strength (BD) of specimens is low and led to zero.

4.1.5 Bulk density (Den)
Archimedes technique has been used for testing bulk density of fired specimens. The results in table 3 illustrates that all formulas have density varying from 2.1-2.38 g/cc. It is slightly difference which can be summarized that influence of varying materials composition and firing temperature have the low effect on specimens’ bulk density.

4.1.6 Comparison bending strength and water absorption of specimens with TIS 2508-2555
The optimal mixture has been proposed. Mixture no. 18 has utilized 20%CC, 40%SS, 40%BA and adding 20% BGC and fired at 1150 °C. It has 36.72 MPa of bending strength and 0.41% of water absorption which can achieve TIS 2508-2555 Type BI as depicted in table 4. Note that, all materials used in this formula are industrial waste.

| Raw materials (% wt.) | TIS 2508-2555 (MPa) |
|-----------------------|---------------------|
| Group Mixture CC SS BA BGC Bending strength >30 MPa Water absorption <1 % |
| E 18 20 40 40 20 | 36.72 0.41 |

4.2 Analysing the microstructure of selected mixtures

4.2.1 Scanning Electron Microscope (SEM)
Although physical properties of samples are examined, the microstructure of samples should be investigated. This is for proving the results of physical properties. Scanning Electron Microscope (SEM) series Hitachi SU3500 at an acceleration voltage of 10 kV with 100x and 5000x magnification has been employed. Mixture no. 1 and 18 fired at 1150 °C are selected to be analyzed by SEM. The results are shown in fig. 1. Fig 1 (a) and 1 (b) illustrates the microstructure of mixture no.1 with magnification 100x and 1000x, respectively. They represented the high porous bodies which leads to low bending strength (0 MPa). In contrast, fig 1(c) and 1(d) expresses the microstructure of mixture no. 18 with magnification 100x and 1000x, respectively. They represented that high dens bodies have been developed. It related with the high bending strength of ceramic bodies (36.72 MPa).

4.2.2 X-Ray Diffractometer (XRD)
For analysing the crystallographic of test samples, X-ray diffraction (XRD) is carried out with the series; Bruker D8 diffractometer (Cu Kα radiation) with a step size of 0.01° and step time of 1s over an angular range of 5–80°. Mixture no. 1 and 18 fired at 1150 °C are examined the crystallographic phase by XRD as expressed in fig 2. Fig 2 (a) and 2 (b) represented the pattern of mixture no. 1 and 18. Their phases are represented in table 5. Main phase of mixture no.1 is Gehlenite (2CaO.Al2O3.SiO2). This phase is porous [23] which yield the low bending strength of mixture no. 1 (0 MPa). Furthermore, Anorthite (CaO.Al2O3.2SiO2) is the main phase of mixture no. 18. This phase has led the high bending strength to this formula (36.72 MPa).
Fig 1. SEM micrograph of specimens containing a) mixture no.1 (100X); b) mixture no.1 (1000X) c) mixture no.18 (100X); d) mixture no.18 (1000X)

Fig 2. XRD pattern of (a) mixture no.1 (b) mixture no.18

Table 5 Crystallographic phases found in tested mixture no. 1 and 18

| Mixture no. | Mixture No. | Gehlenite | Anorthite | Quartz | Calcite | Wollastonite | C2S alpha | Cristobalite |
|-------------|-------------|-----------|-----------|--------|---------|-------------|-----------|-------------|
| 1           | 2CaO.Al2O3.SiO2 | 45.60%    | 12.57%    | 22.88% | 7.81%   | 1.87%       |           |             |
| 18          | CaO.Al2O3.2SiO2 | 0.17%     | 49.60%    | 13.78% | 25.56%  | 9.90%       |           |             |

5. Conclusion
This present study has provided the evident of utilizing industrial wastes as alternative material in ceramic floor tile. The experiment expresses that manufacturing ceramic floor tile is feasible which complied with TIS 2508-2555. Optimal content consists of 20% CC, 40% SS, 40% BA, and adding 20% BGC which fired at 1150 °C. Obviously, all materials used are industrial wastes. The benefit of this
study can alleviate the burden of manufacturers for disposing their wastes and prevent degradation of the environment. Furthermore, the developed product is the ecological items that can respond the consumer who prefer the eco-products. For further investigation, adding boric acid, adding BGC higher than 20%. should be done for reducing firing temperature.

6. References
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