Physical and chemical characterization of Lopburi clay before and after calcination

P Chomyen¹,², S Sinthupinyo³, B Chamnankid³, W Hanpongpun¹ and A Chaipanich¹,⁴*

¹ Advanced Cement-based Materials Laboratory, Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
² Master Degree’s Program in Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
³ Research and Innovation Center SCG Cement Co., Ltd., Kaeng Khoi, Saraburi 18260, Thailand
⁴ Center of Excellent in Materials Science and Technology, Chiang Mai University, Chiang Mai 50200, Thailand

*Corresponding author’s E-mail address: arnon.chaipanich@cmu.ac.th

Abstract. Supplementary cementitious materials (SCMs) may be used as a substitution of Portland cement to reduce CO₂ emissions in the cement industry. One of promising Supplementary cementitious materials for practical use in the construction industry is calcined clay. Clay must be calcined to form high reactivity pozzolanic materials from mineral addition known as amorphous metakaolin (AS₂). Calcined clay may be used to improve mechanical properties, durability and some characteristic. This research aimed to study clay mineralogy and chemical composition of Lopburi clay in Thailand. Physical and chemical characterizations of Lopburi clay before and after calcination were investigated using X-Ray Diffraction, Qualitative X-Ray Diffraction (QXRD), Scanning Electron Microscopy (SEM) and X-Ray Fluorescence. The results showed that Lopburi clay main major oxides are silicon dioxide (SiO₂), alumina oxide (Al₂O₃) and iron oxide (Fe₂O₃) furthermore, Lopburi clay is kaolinite clay.

1. Introduction
Pozzolanic material are silica or silica and alumina materials when some moisture and presence of water react with calcium hydroxide (Ca(OH)_2) to form compounds possessing cementitious properties [1]. Calcined clay has benefit for use as a supplementary cementitious material as mortar and concrete, including lower shrinkage, compressive strength enhancement, improve durability properties and calcined clay limestone cement application. Moreover, calcined clay may have good pozzolanic activity depend on calcinating temperature, crystal structure and kaolinite content of clay [2-3]. Clay composes of many mineral and specific crystal structure. In order to identify clay type for crystalline, amorphous phase and chemical composition technical methods are used such as thermal analysis, X-ray diffraction analysis, X-ray fluorescence analysis, scanning electron microscopy and other chemical analysis [4-5]. Transformation of kaolinite mineral to metakaolin (pozzolanic) occurred at 730 °C as reported by Murat [6] and 750 °C as reported by Ambroise [7] would lead to metakaolin to be the most reactive. This research investigated the characterizations of the Lopburi clay structures before and after calcination.
2. Materials and methods

2.1. Materials
Raw clay was obtained from Lopburi in the center of Thailand. Lopburi clay was calcined in a static furnace at 750 °C for 30 minutes to form Lopburi calcined clay product by Siam Research and Innovation Co., Ltd.

2.2. Chemical technical methods
X-ray fluorescence (XRF) was used to investigate the chemical composition of the Lopburi clay and calcined clay in this project by D4 ENDEAVOR (Bruker AXS). The mineralogical phase analysis of raw clay and calcined clay were determined with quantitative X-ray diffraction (QXRD). X-ray diffraction pattern were scanned between 5°-65° 2θ. In steps of 0.01° and speed is 10 degree per minute by Rigaku SmartLab diffractometer (CuKα at room temperature).

2.3. Physical technical methods
Microstructure of Lopburi calcined clay was investigated by scanning electron microscope JSM-IT300 series with energy dispersive spectrometry (EDS). Particle size and distribution of clay and calcined clay were measured using Mastersizer 2000 Malvern laser diffraction particle size analyzer.

3. Results and discussion

3.1. Chemical composition of Lopburi clay and Lopburi calcined clay
The chemical and phase compositions of Lopburi clay and Lopburi calcined clay were investigated with XRF and the results are given in the table 1. It should be noted that Lopburi clay before thermal transformation with the combination of main oxide such as silicon oxide (SiO₂), Alumina oxide (Al₂O₃) and iron oxide (Fe₂O₃) are 82.11% and loss on ignition value (LOI) is 15.4% due to loss of water in kaolinite layer transformation to amorphous phase (metakaolinite) [8-9]. Lopburi clay may be classed as pozzolan Class N. In order to qualitative information about the Lopburi clay and Lopburi calcined clay was quantified using QXRD analysis shown in the table 2. Lopburi clay can be classified as kaolinite clay since kaolinite content is 53.42%. Lopburi clay was heated at 750 °C Moreover, it shows that goethite conversion to hematite [10]. XRD pattern of Lopburi calcined clay is shown in figure 1. It shows the presence of quartz (JCPDs no. 46-1045) as the main peak and minor peaks are anatase (JCPDs no.21-1272), hematite (JCPDs no.33-0664), calcite (JCPDs no.05-0586) and muscovite (JCPDs no.07-0042).

| Chemical composition | Lopburi clay | Calcined clay |
|----------------------|--------------|---------------|
| SiO₂                 | 36.65%       | 47.72%        |
| Al₂O₃                | 32.38%       | 30.82%        |
| Fe₂O₃                | 13.08%       | 14.4%         |
| CaO                  | 0.32%        | 1.30%         |
| LOI                  | 15.4%        | 1.00%         |
| SO₃                  | 0.11%        | 0.01%         |
| Other oxide          | 0.00%        | 3.73%         |

Table 1. Chemical composition of Lopburi clay and calcined clay by XRF.
Table 2. Phase composition of Lopburi clay and calcined clay by QXRD.

| Qualitative X-ray diffraction | Composition phase of Lopburi clay | %  | Composition phase of calcined clay | %  |
|-------------------------------|----------------------------------|----|-----------------------------------|----|
| Kaolinite                     | 53.42                            |    | Kaolinite                         | -  |
| Quartz                        | 2.255                            |    | Quartz                            | 3.425|
| Albite                        | -                                |    | Albite                            | 2.085|
| Anatase                       | 2.635                            |    | Anatase                           | 0.790|
| Goethite                      | 2.810                            |    | Goethite                          | -  |
| Hematite                      | 3.115                            |    | Hematite                          | 10.17|
| Magnesiochloritoid            | 6.245                            |    | Magnesiochloritoid                | 1.280|
| Gibbsite                      | 2.890                            |    | Gibbsite                          | -  |
| Anorthoclase                  | -                                |    | Anorthoclase                      | 0.705|
| Calcite                       | -                                |    | Calcite                           | 0.505|
| Lime                          | -                                |    | Lime                              | 0.080|
| Amorphous                     | 26.63                            |    | Amorphous                         | 80.96|
| Sum                           | 100                              |    | Sum                               | 100 |

Figure 1. XRD result of Lopburi calcined clay.

3.2. Physical composition of Lopburi calcined clay
SEM micrographs and EDS spectrum of Lopburi calcined clay are shown in figure 2. The microstructure of particle is of irregular shape (figure 2(a-b)) likewise, the results show that the elements of Lopburi calcined clay are consist of Al, Si, Fe, C and O in spectrum 1-2. The particle size distribution of Lopburi calcined clay results are found to have a specific surface area (SSA) of 6.49 m²/g and D-values (diameter of the sphere which divides the sample's mass into a specified percentage) are 0.25, 12.05, 48.45 and 18.99 µm for D10 (v,0.1), D50 (v,0.5), D90 (v,0.9) and D[4,3] (mean) respectively.
Figure 2. SEM micrographs of Lopburi calcined clay (a) 1500× and (b) 5,000× (with EDS spectrum).

4. Conclusions
This investigation showed that Lopburi clay composed of kaolinite as the main phase. Kaolin transformed to metakaolin which is a pozzolanic material. Metakaolin is important and is considered as very active pozzolanic admixture according to ASTM C618. From the results, it is found that the Lopburi clay after calcination can be pozzolanic material corresponding with the increase in the amorphous metakaolin phase content increased (26.63% to 80.96%) in XRD analysis. Therefore, calcined clay is a supplementary cementitious material that can be used in the cement industry. Lopburi calcined clay can be used to help reduce the environmental impact of Portland cement and concrete.

Acknowledgements
The authors are thankful to staff members at the Research and Innovation Center SCG Cement Co., Ltd. for Master Research Grant, Research and Researcher for Industry (RRI) (Contract No. MSD60I0033) and Thailand Science Research and Innovation (TSRI). The authors are also grateful to the Thailand Science Research and Innovation for the funding of Research Scholar Award given to Associate Professor Dr. Arnon Chaipanich. This research work was partially supported by Chiang Mai University.

References
[1] ASTM C618-19 2019 Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete 100 (West Conshochen, PA: American Society for Testing and Materials)
[2] Sabir B B, Wild S and Bai J 2001 Cem. Concr. Compos. 23 441
[3] Scrivener K, Martirena F, Bishnoi S and Maity S 2018 Cem. Concr. Res. 114 49
[4] Schulze E S and Rickert J 2019 Cem. Concr. Compos. 95 92
[5] Fernandez R, Martirena F and Scrivener K 2011 Cem. Concr. Res. 41 113
[6] Murat M 1983 Cem. Concr. Res. 13 259
[7] Ambroise J, Murat M and Pera J 1985 Cem. Concr. Res. 15 261
[8] Souza Santos S H, Campos W T, Santos S P and Kiyohara K P 2005 Ceram. Int. 31 1077
[9] Tironi A, Trezza M A, Scian N A and Irassa E F 2014 J. Therm. Anal. Calorim. 117 547
[10] Liu H, Chen T, Zou X, Qing C and Frost R L 2013 Thermochim. Acta. 568 115