

Enhancing the Thermal Conductivity of Clay Using Iron Phosphate as an Additive

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I. INTRODUCTION

Clay has been a close companion in human endeavor for millennia. Clay's highly porous nature, environmentally friendly extraction, and waste-free disposal have made it a promising material in the journey towards sustainability. Clay is already being used as carbon dioxide trappers as well as green catalysts for well-known organic reactions [1]. One of clay's most prominent applications is being used as heat transfer interfaces, in cookware, nuclear waste containers, and geothermal borehole heat exchangers, etc. [2], [3]. However, the low thermal conductivity of clay makes it a less efficient heat transfer material, which is addressed in this study by incorporating iron phosphate as an additive. Iron phosphate used in the study was obtained as a byproduct from Alpha titanium bis(hydrogenphosphate) monohydrate, $\alpha\text{-Ti}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$, $\alpha\text{-TiP}$ synthesis using alkaline roasting of ilmenite [4]. This process yields a phosphoric leachate that contains iron phosphate. Thus, this study valorizes a highly acidic byproduct while improving the heat transfer capabilities of a sustainable material; thereby further aligning the objectives of the study towards sustainability.

II. LITERATURE REVIEW

Effects of firing temperature, mineralogical composition, as well as bulk density, manipulated in means such as compaction pressure, have been intensively studied by research teams such as Gracia et al. [5], [6]. The effect of mineral composition has been further studied by Dondi et al., Chin C. et al., and Tanjung et al., whose studies reflect that increasing iron phases enhances the thermal conductivity of clay [7], [8]. Jobmann et al. have demonstrated a substantial increase in the thermal conductivity of clay when graphite is used as an additive [2]. Whereas Mgbemene et al. have added iron filings, which increase the thermal conductivity of clay [9]. However, no recorded attempt to use iron phosphate or a chemical byproduct as an additive was observed. Even though additives such as graphite and iron filings have shown thermal conductivity enhancements, each of them presents inherent challenges. Graphite is comparatively expensive, and in order to get the maximum enhancements, specific particle size and shape requirements should be fulfilled [3]. Whereas, in the other method, about 40% to 50% of the composition must be iron filings for the maximum enhancement, which must significantly deviate the clay from its original state.

III. MATERIALS AND METHODS

A kaolin clay sample was obtained from the clay deposit in Meetiyyagoda, Galle, and it was refined using the following

procedure. First, 500 g of clay was dispersed in water, filtered through a double muslin cloth twice, the sediment was collected, and sun-dried for 48 h, after which it was powdered using the ball mill. Then it was subjected to Thermogravimetric Analysis / Differential Thermal Analysis (TGA/DTA). Meanwhile, the iron Phosphate was obtained by neutralizing the phosphoric leachate, discarded from the $\alpha\text{-TiP}$ synthesis process. The obtained leachate was diluted 10-fold and neutralized to pH 7 using 25% Ammonia. Precipitate was isolated by centrifuging at 500 RPM for 5 min, and then it was washed with 5 mL of distilled water by centrifuging for an additional 5 min. Then iron phosphate was dried, and X-ray diffraction analysis (XRD) was carried out. Afterwards, 10% iron phosphate clay composite discs, as well as pure clay discs with a 35 mm diameter, were composed after compressing at 1 MPa uniaxial pressure. The discs were air-dried for 72 h and sintered in a muffle furnace from 25 °C to 900 °C, holding 5 min at every 50 °C increment, 10 min at 400 °C, and 1 h at 900 °C. Thermal conductivity, diffusivity, and volumetric heat capacity were then measured using the Transient Plane Source, TPS 500 S Hot Disk analyzer.

IV. RESULTS AND DISCUSSION

The XRD patterns of the iron phosphate precipitates obtained at pH 6 and pH 7 are shown in Fig. 1. At pH 7, distinct diffraction peaks corresponding to strengite ($\text{FePO}_4 \cdot 2\text{H}_2\text{O}$), (122) and (613) planes at $2\theta \approx 29.03^\circ$ and 67.13° , confirm the presence of crystalline iron phosphate. Nevertheless, the broad background signal indicates that an amorphous iron phosphate phase remains predominant.

Furthermore, Fig. 2 depicts the TGA/DTA curve for the pure clay sample. As evident from the TGA curve, the initial weight loss was observed up to 100 °C, which is due to the loss of unbound water. The substantial weight loss starting from 300 °C to 500 °C is assumed to be due to the organic matter degradation and dehydroxylation process of the material, respectively.

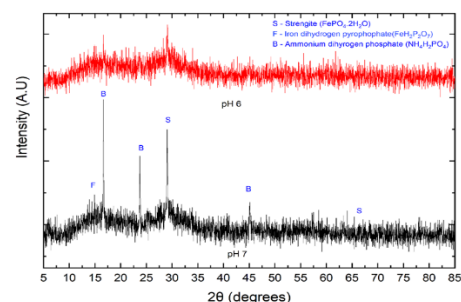


Fig. 1. XRD of the iron phosphate byproduct obtained

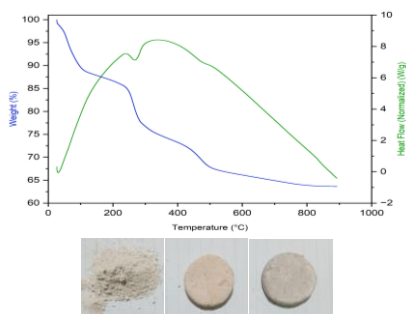


Fig. 2. TGA/DTA of the pure clay sample (Top), refined dry clay (Bottom left), Clay disc with 0% iron phosphate fired at 900 °C (Bottom middle), fired 10% iron phosphate clay composite (Bottom right).

TABLE I. PROPERTIES OF FIRED PURE CLAY AND IRON PHOSPHATE CLAY COMPOSITES

Parameter	0% Iron Phosphate Composition	10% Iron Phosphate Composition	Percentage Increase
Thermal Conductivity (W/m.K)	0.3092	0.5434	75.7%
Thermal Diffusivity (mm ² /s)	0.08208	0.09363	14.1%
Volumetric Heat Capacity (MJ/m ³ .K)	3.767	5.804	54.1%

Upon firing, the clay disc turned to porcelain white as expected. With the addition of iron phosphate, the discs became silvery in color, as is depicted in Fig. 2. And more importantly, the mechanical strength of the fired clay discs had increased upon the addition of iron phosphate. The thermal conductivity, thermal diffusivity, and the volumetric heat capacity of the pure clay disc were 0.3092 W/m.K, 0.08208 mm²/s, and 3.767 MJ/m³.K, respectively. Upon addition of 10% iron phosphate, values changed to 0.5434 W/m.K, 0.09363 mm²/s, and 5.804 MJ/m³.K, respectively, with percentage increases being 75.7%, 14.1%, and 54.1% as depicted in Table I.

The 75.7% increase in thermal conductivity is consistent with previous findings that iron-rich phases enhance heat transport in clays [7], [8]. Thermal property enhancement can be attributed to the following mechanisms.

Iron phosphate is a known fluxing agent that reduces the melting temperature of clay, leading to partial vitrification; thus, it could lessen the porosity and strengthen the grain bonding. Thus, increasing thermal conductivity by facilitating smooth phonon transfer as well as contributing to improved mechanical strength.

Iron Phosphate has a lower thermal resistance than clay. This additive in clay composites can be imagined to be a set of phases that are parallel to thermal pathways. Therefore, the thermal resistance (R) can be written as below.

$$\frac{1}{R_{total}} = \frac{1}{R_{clay}} + \frac{1}{R_{additive}} \quad (1)$$

Equation 1 above rationalizes how thermal conductivity increases with the addition of a higher conductive phase.

While the higher volumetric heat capacity enhances the material's ability to buffer thermal energy, which is important for high-temperature and cyclic applications, the moderately increased thermal diffusivity means that heat propagates

through the material more rapidly, resulting in quicker heating and cooling.

These findings demonstrate that, unlike graphite or iron filings, which require high loadings or strict size control [3], [9], iron phosphate achieves comparable enhancement at only 10%, while valorizing an industrial byproduct and maintaining the clay's structural integrity.

V. CONCLUSION

The addition of just 10% iron phosphate significantly enhanced all three measured thermal properties of clay, with thermal conductivity, thermal diffusivity, and volumetric heat capacity increasing by 75.7%, 14.1%, and 54.1%, respectively. The composite also exhibited improved mechanical strength and a more appealing appearance. Thus, the study demonstrates that a highly acidic byproduct from a synthesis process can be valorized as a functional additive to enhance the thermal properties of clay, an inherently sustainable material, while simultaneously reducing waste disposal and improving its energy efficiency.

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